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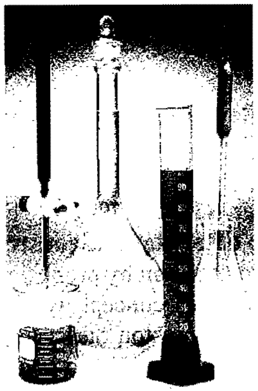
SPONTANEOUS ASSESSMENT SECTION



CHAPTER 1

BASIC PRINCIPLES

1.1 CHEMISTRY AND ITS SCOPE

Chemistry is a branch of physical science which deals with the study of matter, its physical and chemical properties, its chemical composition, the physical and chemical changes which it undergoes and the energy changes that accompany these processes.

All objects in this universe are composed of matter. Most of these objects are visible (solids and liquids) but some are invisible. Chemistry is termed as a material science because it is concerned with all material substances such as air, water, rocks, minerals, plants, animals including man, the earth on which we all live, and other planets. According to one of the famous scientists of twentieth century, **Linus Pauling,** *Chemistry is the science of substances, their properties, their structure and their transformations*.

Chemistry is a very interesting subject which touches almost every aspect of our lives, our culture and our environment. It has changed our civilization to a great extent. The present day chemistry,has provided man with more comforts for a healthier and happier life. A large number of materials which we use these days were unknown at the turn of the century. A few decades back, our clothes and footwears were exclusively of natural origin such as vegetable fibres, wool, hair, skin of animals, etc., but, now the synthetic fibres produced in chemical factories have largely replaced them. Modern chemistry has given man new plastics, fuels, metal alloys, fertilizers, building materials, drugs, energy sources, etc.

During the last few decades, the expansion of chemistry has been tremendous. The field has become wide and complex. For convenience and better understanding of the subject, it has been divided into various branches. The four main branches of chemistry are:

(1) Organic chemistry; (2) Inorganic chemistry;
(3) Physical chemistry; (4) Analytical chemistry.

(1) Organic chemistry: It is concerned with the study of compounds of carbon except carbonates, bicarbonates, cyanides, isocyanides, carbides and oxides of carbon. It is actually the study of hydrocarbons and their derivatives.

(2) Inorganic chemistry: It deals with the study of all known elements and their compounds except organic compounds. It is concerned with the materials obtained from minerals, air, sea and soil.

(3) Physical chemistry: It is concerned with the physical properties and constitution of matter, the laws of chemical combination and theories governing reactions. The effect of temperature, pressure, light, concentration, etc., on reactions come under the scope of physical chemistry.

(4) Analytical chemistry: It deals with various methods of analysis of chemical substances both qualitative and quantitative. It includes chemical and physical methods of analysis.

A number of specialised branches have been introduced as to cope with the extraordinary expansion in the subject of chemistry. Some of the specialised branches are:

(i) Biochemistry: It comprises the studies of the substances related to living organisms and life processes.

(ii) Medicinal chemistry: It deals with the application of chemical substances for the prevention and cure of various diseases in living beings.

(iii) Soil and agriculture chemistry: It deals with the analysis and treatment of soils so as to increase its fertility for the better yields of crops. It is concerned with the chemicals used as fertilizers, insecticides, germicides, herbicides, etc.

(iv) Geochemistry: It includes the study of natural substances like ores and minerals, coal, petroleum, etc.

(v) Industrial chemistry: It deals with the study of chemical processes for the production of useful chemicals on a large scale at relatively low costs.

(vi) Nuclear chemistry: It is the most recent branch. It includes the study of nuclear reactions, the production of radioactive isotopes and their applications in various fields.

(vii) Structural chemistry: It deals with various techniques used for elucidation of the structure of chemical substances. It is concerned with the properties of substances in terms of their structure.

(viii) Polymer chemistry: It includes the study of chemical substances of very high molecular masses of the order of 100,000 or greater, called polymers—natural or artificial. This branch is gaining popularity as the use of plastics, rubber, synthetic fibres, silicones, etc., is on the increase these days.

(ix) Limnochemistry: It deals with the study of chemistry involved in the river water or water reservoirs.

(x) Phytochemistry: It includes the study of chemistry of plants.

Thus, it can be said that there is no other branch of science which is so wide in its scope as chemistry.

1.2 BRIEF HISTORY OF CHEMISTRY

It is difficult to specify the date when science of chemistry came into existence; however, its growth must have gone side by side with the growth of civilization. Broadly, the history of chemistry can be studied under five periods of its development.

(i) Ancient period up to 350 A.D.: In ancient times, many chemical operations such as souring of milk, conversion of sweet juices into wines, the conversion of wines into vinegar, etc., were known. Around 3000 B.C., techniques of making glass, pottery, pigments, dyes, perfumes and extraction of metals especially gold* and silver were known in China, India, Egypt and Greece. The beginning of chemistry as a science could probably be set about 400 B.C., when the theory was proposed that everything is composed of four elements: earth, air, fire and water. The first book of chemistry was written in Egypt around 300 A.D. The term chemistry meant the Egyptian art.

(ii) The alchemical period (350–1500): During this period, scientists called alchemists tried to discover two things: an elixir of life which could make man eternally young and a philospher's stone which could transmute base metals like zinc, copper, iron, etc., into gold. The alchemists failed in their efforts because no philospher's stone and elixir of life actually existed but we are indebted to them for designing new types of apparatus and for discovering new chemical operations such as distillation, sublimation, extraction of gold by amalgamation process and preparation of caustic alkalies from ashes of plants.

(iii) †Iatro chemistry period (1500–1650): During this era, chemists paid their attention towards medico-chemical problems. They believed that the primary object of chemistry was to prepare medicines and not to make gold from base metals. During this period, the study of gases was begun and quantitative experiments were undertaken for the first time. **Robert Boyle** (1627–1691) found that when a metal is heated in air, the mass increases. He also established the relationship between volume and pressure of a gas. In 1661, Boyle wrote the book 'The Skeptical Chymist' in which he criticised the basic ideas of alchemy.

(iv) The phlogiston period (1650–1774): The phlogiston theory was proposed by **Ernst Stahl** (1660–1734). Phlogiston was described as a substance in a combustible material which is given off when the material burns. This theory persisted for about 100 years and was a centre of much controversy. During the end of the eighteenth century, much work was done with gases, especially by **Joseph Black, Henry Cavendish, Josepth Priestley** and **Carl Scheele. Priestley** was a very conservative scientist. Even after his discovery of oxygen, he still believed in phlogiston theory.

(v) Modern period: Lavoisier (1743–1793), a French chemist, is regarded as the **father of modern chemistry.** He presented the exact explanation of combustion by proposing that oxygen is necessary for combustion. This concept was largely responsible for the overthrow of the phlogiston theory. Among his other contributions, he showed that water is composed of hydrogen and oxygen, proposed the theory of indestructibility of matter, presented a clear definition of an element and proposed a system of chemical nomenclature.

Another major step towards modern chemistry was taken in the first decade of the nineteenth century when the English chemist, **John Dalton,** postulated that all elements are made up of atoms. He pictured atoms as tiny, indestructible units that could combine to form **compound atoms** or **molecules.** Dalton proposed that each element has its own kind of atoms and the atoms of different elements differ in essentially nothing but their masses. He determined the relative masses of atoms of many elements. Thus, a new era had begun. The other important chemists of this period are:

(a) **Richter**—Law of Reciprocal Proportions (1794)
(b) **Proust**—Law of Definite Proportions (1799)
(c) **Gay-Lussac**—Law of Combining Volumes of Gases (1808)
(d) **Avogadro**—Avogadro Hypothesis (1811)
(e) **Berzelius**—Introduced the Modern Symbols for Elements (1813)
(f) **Faraday**—Laws of Electrolysis (1833)
(g) **Thomas Graham**—Law of Gaseous Diffusion (1861)
(h) **Mendeleev**—Periodic Law and Periodic Table (1869)
(i) **Arrhenius**—Theory of Ionization (1887)
(j) **Henry Becquerel**—Discovery of Radioactivity (1896)
(k) **Madam Curie**—Discovered Radium and Polonium (1898)

The twentieth century is regarded as an active era of chemistry. During this period, chemistry has made many contributions to human knowledge and civilization. Now, we live in a world of synthetic materials. Chemistry of today is actually helping in solving major problems of our present day civilization such as population explosion, food and diseases, depletion of sources of energy, depletion of natural sources and environmental pollution.

1.3 MATTER AND ENERGY

Besides life, matter and energy are regarded the two fundamental entities with which whole of the universe is composed of. **Matter is anything that has mass and occupies space.** All bodies in the universe conform to this definition. Mass is the quantity of matter in a particular sample of matter. Mass of a body is constant and does not change regardless of where it is measured. The mass of a

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*Gold was probably the first metal to be used because it occurred as a free metal in the earth.

†*Iatro* is a Greek word meaning a physician.

body would be the same on the moon as it is on the earth. Our senses of sight and touch usually tell us that an object occupies space except in the case of colourless, odourless and tasteless gases where some other evidence is required to satisfy the definition of matter.

The term **weight** should not be used in place of mass as it has a different meaning. The term **weight** refers to the force with which an object is attracted towards earth. An object resting on earth experiences a force called its weight, W, that is equal to its mass m, multiplied by the acceleration due to gravity g, that is,

$$W = mg$$

The weight of an object thus depends on the value of 'g' which varies from place to place. However, the mass of an object is determined by comparing the weights of two objects, one of known mass, the other of unknown mass in the same location on earth as both experience the same gravitational acceleration.

Matter is indestructible, *i.e.*, it can neither be created, nor destroyed, but it can change its form; thus, the total quantity of matter of the universe is constant.

Energy is defined as the capacity of doing work. Anything which has the capacity to push the matter from one place to another possesses energy. There are various forms of energy such as heat, light, etc. Energy is neither created, nor destroyed, but can only be transformed from one form of energy to another.

The world became aware of the fact that matter can be converted into energy with the discovery of nuclear reactions, especially nuclear fission and nuclear fusion. The relationship between mass and energy was given by **Einstein.** The famous relation is:

$$E = mc^2$$

where, E = energy, m = mass and c = velocity of light.

On account of this equation, the above two laws are amalgamated into a single statement:

"The total amount of matter and energy available in the universe is fixed."

Example 1. *Calculate the amount of energy released in ergs, calories and in joules when 0.001 kg of mass disappears.*
[*Given, Velocity of light* $= 3 \times 10^8\ ms^{-1}$]

Solution: According to Einstein equation, $E = mc^2$

$$m = 0.001\,\text{kg} = 1 \times 10^{-3}\ \text{kg};\ c = 3 \times 10^8\ \text{ms}^{-1}$$

$$E = (1 \times 10^{-3})(3 \times 10^8)^2 = 9 \times 10^{13}\ \text{J}$$

$$1\,\text{J} = 10^7\ \text{erg} = 0.24\,\text{cal}$$

$$9 \times 10^{13}\ \text{J} = 9 \times 10^{13} \times 10^7\ \text{erg} = 9 \times 10^{13} \times 0.24\ \text{cal}$$

$$= 9 \times 10^{20}\ \text{erg} = 2.16 \times 10^{13}\ \text{cal}$$

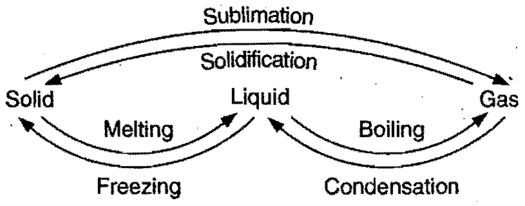
Classification of Matter

(i) Physical classification: Matter can exist in any one of three forms, (a) solid, (b) liquid and (c) gas.

In the solid state, substances are rigid. They have a definite shape and fixed volume. There is negligible effect of changes in pressure and temperature on their volumes. The individual particles that make up a solid occupy definite positions in the structure and are very near to one another. This form of matter is associated with minimum amount of energy.

In liquid state, substances have no definite shape but possess a fixed volume. There is slight effect of pressure and temperature on their volumes. They have the property of flowing. The particles are nearer to one another than in a gas and this form of matter is associated with energy more than solids.

In a gaseous state, substances have no definite shape and volume. Gases fill completely any vessel in which they are confined and thus occupy the whole space available to them. There is a large effect of pressure and temperature on their volumes. The particles are far apart from one another and move with very high speeds in all possible directions. This form of matter is associated with maximum amount of energy.

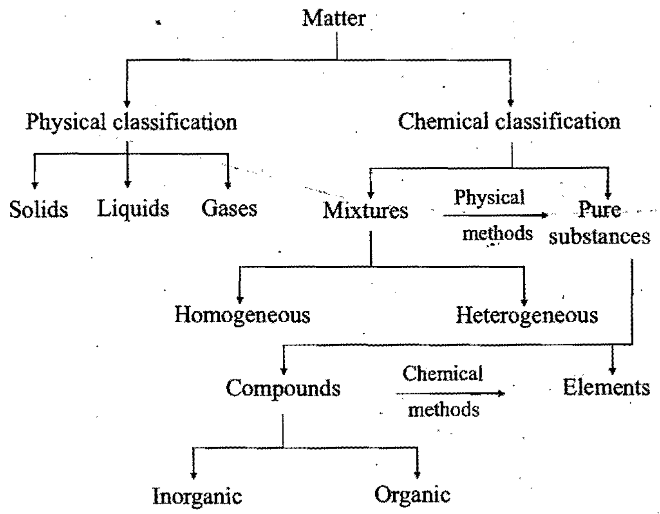


$$\text{Solid} \underset{-\text{energy}}{\overset{+\text{energy}}{\rightleftharpoons}} \text{Liquid} \underset{-\text{energy}}{\overset{+\text{energy}}{\rightleftharpoons}} \text{Gas}$$

$$\xrightarrow{\text{Absorption of energy}}$$
$$\xleftarrow[\text{Release of energy}]{}$$

Depending on temperature and pressure, a substance can exist in any one of the three forms of matter.

(ii) Chemical classification: Matter exists in nature in the form of chemical substances. **A pure substance is defined as a variety of matter, all samples of which have same composition and properties.** Pure substances are divided into elements and compounds. Most of the materials found in nature are in the form of mixtures consisting of two or more substances. There are two types of mixtures—Homogeneous and Heterogeneous. Both types of mixtures can be separated into their components (pure substances) by mechanical and physical methods. The classification can be summarized in the following way:



Properties of Matter: Properties are the characteristic qualities with the help of which different kinds of matter can be commonly recognised. In chemistry, substances are distinguished by two types of properties, *viz* (i) Chemical properties and (ii) Physical properties.

The chemical properties of substances are those in which they undergo change in composition either alone or by interactions with other substances, *i.e.*, to form new substances having different compositions from the substances which undergo change.

The properties of substances which are observed in absence of any change in composition under specific physical state are termed physical properties. Colour, density, melting point, boiling point, hardness, refractive index, thermal conductivity, electrical conductivity, malleability, ductility, etc., are some examples of the physical properties. The properties of matter can be further classified into two: (i) Intensive properties and (ii) Extensive properties. The **intensive properties** are those which do not depend upon the quantity of matter, *e.g.*, colour, density, melting point, boiling point, refractive index, etc. These properties are same irrespective of the quantity of the substance. Chemical properties are also intensive properties. The **extensive properties** of matter depend on the quantity of matter. Volume, mass, weight, energy, etc., are the extensive properties.

1.4 ELEMENTS AND COMPOUNDS

Elements are pure substances that cannot be decomposed into simpler substances by chemical changes. The smallest particles of an element possess the same properties as the bigger particles. An element can also be defined as **a pure substance which consists of only one type of atoms.** Due to discovery of isotopes, this definition does not seem to be correct. The modern definition of an element is that it is a simple individual which has a definite atomic number (see atomic structure) and has a definite position in the periodic table. It cannot be decomposed in a chemical change. In chemistry, the elements are the chemical alphabet and compounds are the words, *i.e.*, combinations of elements.

There are presently 117 different elements known. Every element has been given a definite name and for convenience a nick name which in chemical language is called a **symbol.** *Symbol is a small abbreviation to represent a full and lengthy name of the element.* Symbols have been derived:

(i) either by taking the first letter of the name of the element which is capitalized:

O—Oxygen
C—Carbon
P—Phosphorus
N—Nitrogen
H—Hydrogen
S—Sulphur
F— Fluorine
U— Uranium
I— Iodine

(ii) or by taking the first letter and one more letter from the name of the element. The first letter is always capitalized.

Ca—Calcium
Mg—Magnesium
Cl—Chlorine
Ni—Nickel
Co—Cobalt
Br—Bromine
Al—Aluminium
Bi—Bismuth
Ba—Barium

(iii) or from names of the elements in other languages such as Latin, German, etc.

Na—Sodium (Latin name Natrium)
Cu—Copper (Latin name Cuprum)
Fe—Iron (Latin name Ferrum)
Ag—Silver (Latin name Argentum)
Pb—Lead (Latin name Plumbum)
Au—Gold (Latin name Aurum)
K—Potassium (Latin name Kalium)
Hg—Mercury (Latin name Hydragyrum)
W—Tungsten (German name Wolfram)

Out of 117 elements known, 88 have been isolated from natural sources and the remaining have been prepared by artificial means. The man made elements are:

S.No.	Name	Symbol	S.No.	Name	Symbol
1.	Neptunium	Np	**16.**	Hassium or Unniloctium	Hs or Uno
2.	Plutonium	Pu	**17.**	Meitnerium or Unnilennium	Mt or Une
3.	Americium	Am	**18.**	Ununnilium	Uun
4.	Curium	Cm	**19.**	Unununium	Uuu
5.	Berkelium	Bk	**20.**	Ununbium	Uub
6.	Californium	Cf	**21.**	Ununtrium	Uut
7.	Einsteinium	Es	**22.**	Ununquadium	Uuq
8.	Fermium	Fm	**23.**	Ununpentium	Uup
9.	Mendelevium	Md	**24.**	Ununhexium	Uuh
10.	Nobelium	No	**25.**	Ununoctium	Uuo
11.	Lawrencium	Lr	**26.**	Technetium	Tc
12.	Kurchatovium	Ku	**27.**	Promethium	Pm
13.	Hahnium	Ha	**28.**	Astatine	At
14.	Seaborgium or Unnilhexium	Sg or Unh	**29.**	Francium	Fr
15.	Nielsbohrium or Unnilseptium	Bh or Uns			

The elements from S. No. 1 to 25 are called transuranic elements. The credit for the discovery of most of the transuranic elements goes to the scientist **G.T. Seaborg.** The first artificially produced element was technetium. It was synthesised in 1937 by scientists at the University of California at Berkley.

Most of the earth's crust is made up of a small number of elements. Only ten of the naturally occurring elements make up 99% mass of the earth's crust, oceans and atmosphere. The following table shows the abundance of highly abundant elements in nature:

Note : Among the naturally occurring elements, $^{1}_{1}H$ is lightest and $^{238}_{92}U$ is the heaviest atom.

Abundance of Elements (Earth's Crust, Oceans and Atmosphere)

Oxygen	49.5%	99.2%	Chlorine	0.19%	0.7%
Silicon	25.7%		Phosphorus	0.12%	
Aluminium	7.5%		Manganese	0.09%	
Iron	4.7%		Carbon	0.08%	
Calcium	3.4%		Sulpur	0.06%	
Sodium	2.6%		Barium	0.04%	
Potassium	2.4%		Chromium	0.033%	
Magnesium	1.9%		Nitrogen	0.030%	
Hydrogen	0.87%		Fluorine	0.027%	
Titanium	0.58%		Zirconium	0.023%	

If the entire universe is considered, then 90% of matter is hydrogen. Helium is the second most abundant element amounting to 9% and the remaining elements make up only 1% of the universe with oxygen, neon, carbon and nitrogen next in order of decreasing abundance.

The commercial use of an element depends not only upon its abundance but also upon its accessibility. Some of the common elements such as copper, zinc, tin and lead are not abundant but are found in nature in rich deposits from which these can be easily extracted. On the other hand, the elements such as titanium and zirconium which are found in abundance in nature are not widely used because their ores are not rich and their extraction is difficult and expensive.

Metals, Non-metals and Metalloids

All the elements may be classified into two groups, **metals** and **non-metals.** The division is based on both physical and chemical properties.

Metals are regarded as those elements which possess the following properties:

(i) They are generally solids at ordinary conditions. Mercury is an exception which is in liquid state.
(ii) They are lustrous in nature.
(iii) They possess high density.
(iv) They are good conductors of electricity and heat.
(v) They are malleable and ductile.
(vi) They possess generally high melting and boiling points.
(vii) They react with mineral acids liberating hydrogen.
(viii) They form basic oxides.
(ix) They form non-volatile hydrides if combine with hydrogen.
(x) They have molecules usually mono-atomic in the vapour state.

Sodium, calcium, aluminium, copper, silver, zinc, iron, nickel, gold, mercury, etc., are the examples of metals.

The non-metals do not show the above properties. Six of the non-metals, carbon, boron, phosphorus, sulphur, selenium and iodine, are solids. Bromine is the only liquid non-metal at room temperature and normal pressure. The remaining non-metals; nitrogen, oxygen, fluorine, chlorine, hydrogen, helium, argon, neon, krypton, xenon and radon are gases. Non-metals are generally (i) brittle, (ii) non-lustrous, (iii) having low melting and boiling points, (iv) non-conductors of heat, (v) capable of forming acidic oxides or neutral oxides, (vi) not capable of evolving hydrogen from acids, and (vii) capable of forming volatile hydrides.

There are some elements which do not fit completely into either the metal or non-metal class. Elements which have some properties of both metals and non-metals are called semi-metals or metalloids. The semi-metals are silicon, germanium, arsenic, antimony and tellurium.

The above classification of elements is a rough one as certain metals like lithium, sodium, potassium possess low density; certain non-metals like hydrogen and graphite (a form of carbon) are good conductors of electricity. Metals rarely combine with one another while non-metals combine with one another to form compounds. Metals and non-metals commonly combine with each other to form compounds.

Compounds

Compounds are also pure substances that are composed of two or more different elements in a fixed proportion by mass. Compounds containing more than four elements are rare. The properties of a compound are altogether different from the properties of the elements from which it has been constituted. The compound **water** has a definite composition, *i.e.*, 11.2% hydrogen and 88.8% oxygen, Thus, the two are present in the ratio of 1 : 8 by mass. The properties of water are totally different from the properties of hydrogen and oxygen both. Hydrogen and oxygen are in gaseous state while water is in liquid state under ordinary atmospheric conditions. Oxygen supports combustion while hydrogen is combustible but water is normally used for extinguishing fire. Component elements in compounds can be separated only by chemical means and not by physical methods.

Compounds are classified into two types:

(i) Organic compounds: The compounds obtained from living sources are termed organic compounds. The term organic is now applied to hydrocarbons (compounds of carbon and hydrogen) and their derivatives.

(ii) Inorganic compounds: The compounds obtained from non-living sources such as rocks and minerals are termed inorganic compounds. The compounds of all elements except hydrocarbons and their derivatives are included in this category. The number of organic compounds is very large in comparison to inorganic compounds.

Some Specific Properties of Substances: Some specific properties of substances are given below:

(i) Deliquescence: The property of certain compounds of taking up the moisture present in atmosphere and becoming wet when exposed, is known as deliquescence. These compounds are known as deliquescent. Sodium hydroxide, potassium hydroxide, anhydrous calcium chloride, anhydrous magnesium chloride, anhydrous ferric chloride, etc., are the examples of deliquescent compounds. Sodium chloride is not deliquescent but when common salt is placed in atmosphere it becomes wet due to presence of an impurity of magnesium chloride.

(ii) Hygroscopicity: Certain compounds combine with the moisture of atmosphere and are converted into hydroxides or hydrates. Such substances are called hygroscopic. Anhydrous copper sulphate, quick lime (CaO), anhydrous sodium carbonate, etc., are of hygroscopic nature.

(iii) Efflorescence: The property of some crystalline substances of losing their water of crystallisation on exposure and becoming powdery on the surface is called efflorescence. Such salts are known as efflorescent. The examples are:

Ferrous sulphate ($FeSO_4 \cdot 7H_2O$), sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), sodium sulphate ($Na_2SO_4 \cdot 10H_2O$), potash alum $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$, etc.

(iv) Malleability: This property is shown by metals. When the solid is beaten and does not break but is converted into a thin sheet, it is said to possess the property of malleability. Copper, gold, silver, aluminium, lead, etc., can be easily hammered into sheets. Gold is the most malleable metal.

(v) Ductility: The property of a metal to be drawn into wires is termed ductility. Copper, silver, gold, aluminium, iron, etc., are ductile in nature. Platinum is the most ductile metal.

(vi) Elasticity: When the stress is small, the solid completely regains its original shape, size or volume after the deforming force is removed. The solid is then said to be elastic. Steel, glass, ivory, etc., are elastic bodies.

(vii) Plasticity: When stress is increased on a metal, a limit is reached beyond which, if the stress is removed, the solid does not come back to its original shape or size. It acquires a permanent deformation. Such materials can be given any shape without any difficulty.

(viii) Brittleness: The solid materials which break into small pieces on hammering are called brittle. The solids of non-metals are generally brittle in nature.

(ix) Hardness: A material is said to be harder than the other if it can scratch it. The hardness is measured on Mho's scale. For this purpose, ten minerals have been selected which have been assigned hardness from 1 to 10.

Hardness	Mineral	Hardness	Mineral
1	Talc	6	Orthoclase
2	Gypsum	7	Quartz
3	Calcite	8	Topaz
4	Fluorite	9	Corundum
5	Apatite	10	Diamond

On Mho's scale, hardness of diamond is maximum and that of talc is minimum. If a material can scratch topaz but cannot scratch corundum it possesses hardness equal to 8.

1.5 MIXTURES

A **mixture** is a material containing two or more substances either elements or compounds or both in any proportion. Substances which form a mixture are called **components.** Components are present in the mixture without loss of their identity. There are two types of mixtures—**homogeneous** and **heterogeneous.** In a homogeneous mixture, the components are mixed uniformly to microscopic level. The components cannot be seen by naked eye or with the help of a microscope. The mixture is uniform throughout having a single **phase***. The homogeneous mixture is **isotropic** in nature, *i.e.*, every portion of it has the same composition and properties.

Alloys such as brass, steel, 22-carat gold; solutions such as common salt dissolved in water, sugar dissolved in water, iodine dissolved in carbon tetrachloride, benzene in toluene, methyl alcohol in water; gasoline (a mixture of hydrocarbons), air, etc., are some of the examples of homogeneous mixtures.

A heterogeneous mixture is not uniform. It can have two or more phases. The components can be seen by naked eye or with the help of a microscope. It has **anisotropic** properties, *i.e.*, properties are not uniform throughout the mixture. Soil, a mixture of sulphur and sand, a mixture of iron filings and sand, smoke, etc., are the examples of heterogeneous mixtures.

The components of a mixture differ in many of their physical and chemical properties. The advantage of this difference is taken in the separation of a mixture. The method of separation employed should not bring about the destruction of any one of the components. Some preliminary techniques based on physical properties are described here in brief.

(i) Filtration: This method is useful when one of the components is an insoluble solid in a solvent. The insoluble solid is obtained by filtration of the suspension through filter-paper. For example, common salt containing sand is separated by filtration. The mixture is mixed with water. It is shaken so as to dissolve common salt. The sand remains insoluble. The suspension is put to filtration. The sand collects on the filter-paper. It is taken in a basin and dried by heating. The filtrate is taken in evaporating dish and heated till whole of the water is evaporated. Solid common salt is thus obtained in the dish.

Sugar containing charcoal, potassium nitrate containing saw dust or mixtures having insoluble components can be separated by filtration.

(ii) Sublimation: It is a process in which a solid substance is directly converted into its vapours by application of heat and vapour is reconverted into solid by subsequent cooling. The method is used when one of the components undergoes sublimation and other components are not decomposed by heating. For example, naphthalene can be separated from common salt by sublimation. Similarly, a mixture of ammonium chloride and potassium chloride can be separated by sublimation as ammonium chloride sublimes on heating.

(iii) Distillation: It is a process of converting a liquid into its vapour by heating and then condensing the vapours again into the same liquid by cooling. Thus, distillation involves vaporisation and condensation both.

Distillation = Vaporisation + Condensation

This method is employed to separate liquids which have different boiling points or a liquid from non-volatile solid or solids either in solution or suspension. The mixture of copper sulphate and water or mixture of water (b.p. 100°C) and methyl alcohol (b.p. 45°C) can be separated by this method.

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* Phase is defined as part of a system which has uniform properties and composition. A solution or mixture of sugar and water is a one phase system. Every drop of the solution has same properties and same composition.

(iv) Magnetic separation: If one of the components of a mixture has magnetic properties, it can be separated by using a magnet. Iron is separated from a mixture of iron filings and sulphur by moving a magnet through the mixture.

(v) Solvent extraction: This method is based on the preferential solubility of one of the components of the mixture in a particular solvent (usually a low-boiling organic solvent) which forms a distinctly separate layer with the other liquid if present in the mixture. For example, iodine present in water can be recovered with the help of ether or carbon disulphide. For this method, a separating funnel is utilized. The aqueous solution of iodine is taken in separating funnel to which ether is added. The funnel is shaken. Two layers are formed. The upper layer which is dark brown consists of ether and iodine and the colourless lower layer consists of only water. The lower layer is taken out. The coloured layer is then poured out and ether is removed cautiously by distillation when iodine is left behind.

Two immiscible liquids such as water and oil can also be separated by the use of a separating funnel.

Example 2. *How will you separate the following mixtures?*

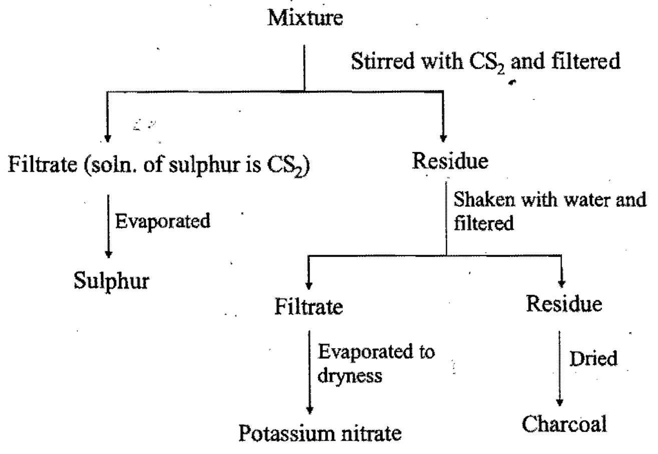
(*a*) *Sulphur, potassium nitrate and charcoal,*

(*b*) *Sand, common salt, iron filings and naphthalene,*

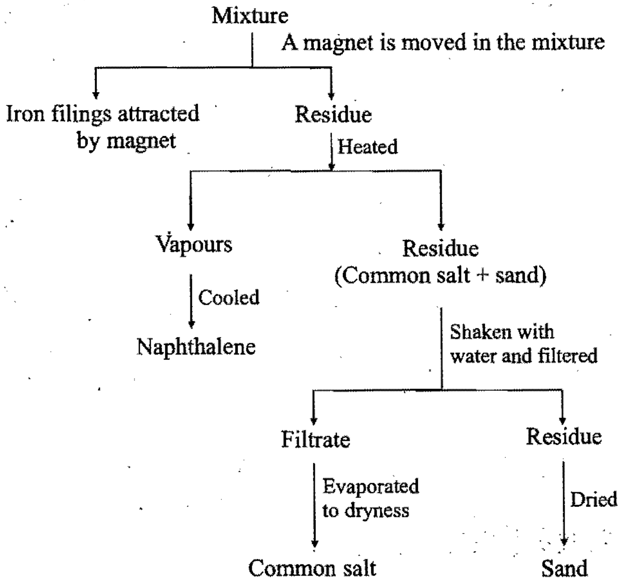
(*c*) *Powdered glass, ammonium chloride and potassium chloride.*

Solution:

(a) (i) Sulphur is soluble in carbon disulphide,
(ii) Potassium nitrate is soluble in water,
(iii) Charcoal is insoluble in carbon disulphide as well as in water.



(b) (i) Iron filings are separated by a magnet,
(ii) Naphthalene sublimes on heating,
(iii) Sand is insoluble in water.



(c) (i) Ammonium chloride sublimes on heating,
(ii) Potassium chloride is soluble in water,
(iii) Powdered glass is insoluble in water.

1.6 ALLOYS

When two or more elements are melted together and resulting liquid is allowed to solidify, the product so obtained is called an alloy if it possesses metallic properties. An alloy may consist of a mixture of a metal with another metal, a metal with a non-metal or a metal with both metal and non-metal.

Alloys are prepared because they have properties more suitable for certain applications than do the simple metals. Alloys are used because they are harder and stronger, have desirable casting properties, special physical properties such as magnetic properties and resistance to corrosion in certain environments. Melting point of an alloy is normally lower than the melting point of either of the pure components. Thermal and electrical conductivities are normally reduced in alloys.

An alloy containing one component mercury is called amalgam. Most of the metals form amalgams. Iron, platinum, tungsten, etc., are few metals which do not form amalgams.

Alloys are mainly classified into two distinct types, namely ferrous and non-ferrous. Ferrous alloys always contain iron, carbon and one or two of the other elements such as manganese, nickel, chromium, copper, vanadium, molybdenum, tungsten, etc. When the percentage of carbon in the alloy is below 0.1, the alloy is termed the iron alloy and if it is above 0.1, the alloys are called steels. When iron is not present in the alloy, it is termed a non-ferrous alloy. Some of the important alloys have been listed below:

Alloy	**Composition**	**Main uses**
1. Brass	Cu 60–80%, Zn 20–40%	Utensils, condenser tubes, electrical goods, cartridge shell
2. Bronze	Cu 75–90%, Sn 10–25%	Coins, statues, utensils.

3. German silver	Cu 56%, Zn 24%, Ni 20%	Utensils, resistance coils
4. Gun metal	Cu 87%, Sn 10%, Zn 3%	Machine parts, guns
5. Rolled gold	Cu 95%, Al 5%	Artificial jewellery
6. Magnalium	Al 94%, Mg 6%	Balance beams, light instruments
7. Electron	Mg 95%, Zn 5%	Construction of aircraft
8. Duralumin	Al 95%, Cu 4%, Mn 0.5%, Mg 0.5%	Making aeroplanes
9. Type metal	Pb 82%, Sb 15%, Sn 3%	Making printing types
10. Solder	Pb 50–70%, Sn 30–50%	Soldering
11. Britannia	Sn 93%, Sb 5%, Cu 2%	Tableware
12. Wood's metal	Bi 50%, Pb 25%, Sn 12.5%, Cd 12.5%	Electric fuses and other safety devices
13. Nichrome	Ni 60%, Cr 15%, Fe 25%	Electrical resistances
14. Constantan	Ni 40%, Cu 60%	Electrical resistances
15. Monel metal	Ni 70%, Cu 30%	Chemical plants
16. Invar	Ni 35%, Steel 65%	Surveying instruments, pendulums, chronometers
17. Stainless steel	Fe 89.4%, Cr 10%, Mn 0.35%, C 0.25%	Utensils, ornamental pieces.

1.7 PHYSICAL AND CHEMICAL CHANGES

Matter undergoes two types of changes; physical and chemical. A physical change is one in which a substance changes its physical state but keeps its chemical identity. In physical change, a new substance does not come into existence. Mass remains the same. Physical properties are altered. This is a temporary change. For example, water shows all of its chemical properties whether it is in the form of ice or water or steam. Ice melts to form water and water can be converted again into ice by placing it in a freezer. When 10 g of ice melts, 10 g of water is obtained. Melting, evaporation, condensation, freezing, sublimation, distillation, passing of electric current through metallic conductor, making of magnet from an iron piece, are some examples of physical changes.

In a chemical change, a new substance or substances come into existence. The starting materials called reactants, are used up and new substances called products, are formed. The composition of the new substances is different from that of the starting materials. It is a permanent change as it is not easy to obtain the starting materials again from the products.

Energy is always released or absorbed when chemical or physical changes occur. Energy is required to melt ice and energy is required to boil water. Conversely, the condensation of steam to form liquid water always liberates energy, as does the freezing of liquid water to form ice. Chemical changes either release energy (exothermic) or adsorb energy (endothermic).

Chemical changes are of various types. The important ones are:

(i) Combination: Two or more substances react to form one product. When a compound is obtained by the direct reaction between elements, it is termed direct union or synthesis.

$$H_2 + Cl_2 = 2HCl \quad ; \quad C + O_2 = CO_2$$

$$2Mg + O_2 = 2MgO \quad ; \quad SO_2 + H_2O = H_2SO_3$$

(ii) Decomposition: When a compound is broken down into two or more simple constituents, the change is called decomposition. Often heat is utilised for the decomposition. Such decomposition is termed **thermal decomposition.**

$$2HgO = 2Hg + O_2 ; \quad 2KClO_3 = 2KCl + 3O_2$$

$$CaCO_3 = CaO + CO_2 ; 2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

(iii) Substitution: When one element enters into a compound by the replacement of the other element, the change is termed substitution.

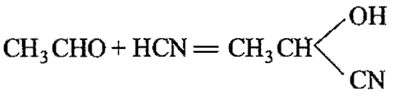
$$CuSO_4 + Zn = Cu + ZnSO_4 ; \; C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

$$2KI + Cl_2 = 2KCl + I_2 \quad ; \quad Zn + 2HCl = ZnCl_2 + H_2$$

(iv) Addition: Something is added to a chemical substance without elimination.

$$KI + I_2 = KI_3$$

$$C_2H_4 + HBr = C_2H_5Br$$

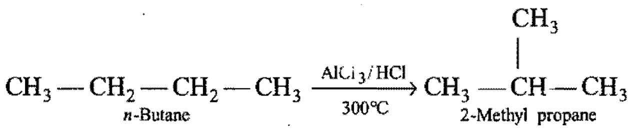


$$CH_3CHO + HCN = CH_3CH\begin{matrix} OH \\ CN \end{matrix}$$

(v) Internal rearrangement: When nothing is added or nothing is eliminated from a chemical substance but due to rearrangement of the various atoms present in a molecule, a new compound comes into existence. When ammonium cyanate is heated, a new substance urea is formed.

$$NH_4CNO = NH_2CONH_2$$

The chemical change is termed isomerisation, when one isomer is converted into another.



$$\underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[300^\circ C]{AlCl_3/HCl} \underset{\text{2-Methyl propane}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3}$$

(vi) Polymerization: Two or more molecules of a substance combine to form a giant molecule,

$$\underset{\text{Acetylene}}{3C_2H_2} = \underset{\text{Benzene}}{C_6H_6}$$

$$\underset{\text{Formaldehyde}}{nHCHO} = \underset{\text{Para formaldehyde}}{(HCHO)_n}$$

(vii) Double decomposition: An exchange of partners occurs between two compounds.

$$AB + CD = AD + CB$$

$$BaCl_2 + Na_2SO_4 = BaSO_4 + 2NaCl$$

$$KOH + HCl = KCl + H_2O$$

The reaction is also termed neutralisation, *i.e.*, a reaction between an acid and a base to form a salt and water molecule.

$$\mathrm{Fe\overbrace{\underbrace{Cl_3 + 3}_{\text{Water}}H}OH = Fe(OH)_3 + 3HCl}$$

Reaction of above type is termed hydrolysis.

1.8 LAWS OF CHEMICAL COMBINATION

In order to understand the composition of various compounds, it is necessary to have a theory which accounts for both qualitative and quantitative observations during chemical changes. Observations of chemical reactions were most significant in the development of a satisfactory theory of the nature of matter. These observations of chemical reactions are summarised in certain statements known as laws of chemical combination.

(i) Law of conservation of mass: The law was first stated by **Lavoisier** in 1774. It is also known as the law of indestructibility of matter. According to this law, **in all chemical changes, the total mass of a system remains constant or in a chemical change, mass is neither created nor destroyed.** This law was tested by **Landolt.** All chemical reactions follow this law. Thus, this law is the basis of all quantitative work in chemistry.

Example: *1.70 g of silver nitrate dissolved in 100 g of water is taken. 0.585 g of sodium chloride dissolved in 100 g of water is added to it and chemical reaction occurs. 1.435 g of silver chloride and 0.85 g of sodium nitrate are formed.*

Solution: Total masses before chemical change

$$= \text{Mass of } \mathrm{AgNO_3} + \text{Mass of NaCl} + \text{Mass of water}$$

$$= 1.70\,\mathrm{g} + 0.585\,\mathrm{g} + 200.0\,\mathrm{g}$$

$$= 202.285\ \mathrm{g}$$

Total masses after the chemical reaction,

$$= \text{Mass of AgCl} + \text{Mass of } \mathrm{NaNO_3} + \text{Mass of water}$$

$$= 1.435\,\mathrm{g} + 0.85\,\mathrm{g} + 200.0\,\mathrm{g}$$

$$= 202.285\,\mathrm{g}$$

Thus, in this chemical change,

Total masses of reactants = Total masses of products

This relationship holds good when reactants are completely converted into products.

In case, the reacting materials are not completely consumed, the relationship will be

Total masses of reactants = Total masses of products
+ Masses of unreacted reactants

(ii) Law of definite or constant proportions: This law was presented by **Proust** in 1799 and may be stated as follows:

A chemical compound always contains the same element combined together in fixed proportion by mass, *i.e.*, a chemical compound has a fixed composition and it does not depend on the method of its preparation or the source from which it has been obtained.

For example, carbon dioxide can be obtained by using any one of the following methods:

(a) by heating calcium carbonate,
(b) by heating sodium bicarbonate,
(c) by burning carbon in oxygen,
(d) by reacting calcium carbonate with hydrochloric acid.

Whatever sample of carbon dioxide is taken, it is observed that carbon and oxygen are always combined in the ratio of 12 : 32 or 3 : 8.

The converse of this law that when same elements combine in the same proportion, the same compound will be formed, is not always true. For example, carbon, hydrogen and oxygen when combine in the ratio of 12 : 3 : 8 may form either ethyl alcohol (C_2H_5OH) or dimethyl ether (CH_3OCH_3) under different experimental conditions.

(iii) Law of multiple proportions: This law was put forward by **Dalton** in 1808. According to this law, **if two elements combine to form more than one compound, then the different masses of one element which combine with a fixed mass of the other element, bear a simple ratio to one another.**

Hydrogen and oxygen combine to form two compounds H_2O (water) and H_2O_2 (hydrogen peroxide).

In water,	Hydrogen 2 parts	Oxygen 16 parts
In hydrogen peroxide,	Hydrogen 2 parts	Oxygen 32 parts

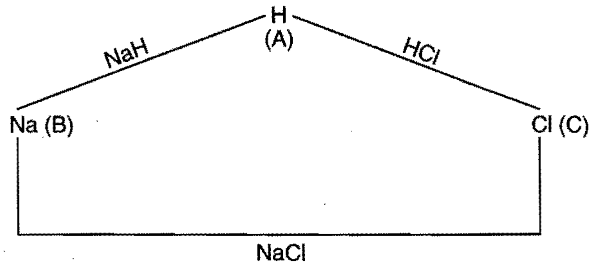
The masses of oxygen which combine with same mass of hydrogen in these two compounds bear a simple ratio 1 : 2.

Nitrogen forms five stable oxides.

N_2O	Nitrogen 28 parts	Oxygen 16 parts
N_2O_2	Nitrogen 28 parts	Oxygen 32 parts
N_2O_3	Nitrogen 28 parts	Oxygen 48 parts
N_2O_4	Nitrogen 28 parts	Oxygen 64 parts
N_2O_5	Nitrogen 28 parts	Oxygen 80 parts

The masses of oxygen which combine with same mass of nitrogen in the five compounds bear a ratio 16 : 32 : 48 : 64 : 80 or 1 : 2 : 3 : 4 : 5.

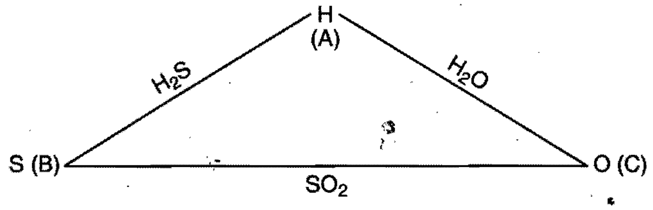
(iv) Law of reciprocal proportions: This law was given by **Richter** in 1794. The law states that **when definite mass of an element *A* combines with two other elements *B* and *C* to form two compounds and if *B* and *C* also combine to form a compound, their combining masses are in same proportion or bear a simple ratio to the masses of *B* and *C* which combine with a constant mass of *A*.**



For example, hydrogen combines with sodium and chlorine to form compounds NaH and HCl respectively.

In NaH,	Sodium 23 parts	Hydrogen one part
In HCl,	Chlorine 35.5 parts	Hydrogen one part

Sodium and chlorine also combine to form NaCl in which 23 parts of sodium and 35.5 parts of chlorine are present. These are the same parts which combine with one part of hydrogen in NaH and HCl respectively.



Hydrogen combines with sulphur and oxygen to form compounds H_2S and H_2O respectively.

In H_2S,	Hydrogen 2 parts	Sulphur 32 parts
In H_2O,	Hydrogen 2 parts	Oxygen 16 parts

Thus, according to this law, sulphur should combine with oxygen in the ratio of 32 : 16 or a simple multiple of it. Actually, both combine to form SO_2 in the ratio of 32 : 32 or 1 : 1.

The law of reciprocal proportions is a special case of a more general law, the law of equivalent masses, which can be stated as under :

"In all chemical reactions, substances always react in the ratio of their equivalent masses."

(v) Law of gaseous volumes: This law was enunciated by **Gay-Lussac** in 1808. According to this law, gases react with each other in the simple ratio of their volumes and if the product is also in gaseous state, the volume of the product also bears a simple ratio with the volumes of gaseous reactants when all volumes are measured under similar conditions of temperature and pressure.

$$\underset{1\text{ vol}}{H_2} + \underset{1\text{ vol}}{Cl_2} = \underset{2\text{ vol}}{2HCl} \qquad \text{ratio} \qquad 1:1:2$$

$$\underset{2\text{ vol}}{2H_2} + \underset{1\text{ vol}}{O_2} = \underset{2\text{ vol}}{2H_2O} \qquad \text{ratio} \qquad 2:1:2$$

$$\underset{2\text{ vol}}{2CO} + \underset{1\text{ vol}}{O_2} = \underset{2\text{ vol}}{2CO_2} \qquad \text{ratio} \qquad 2:1:2$$

$$\underset{1\text{ vol}}{N_2} + \underset{3\text{ vol}}{3H_2} = \underset{2\text{ vol}}{2NH_3} \qquad \text{ratio} \qquad 1:3:2$$

SOME SOLVED EXAMPLES

Example 3. *What mass of sodium chloride would be decomposed by 9.8 g of sulphuric acid, if 12 g of sodium bisulphate and 2.75 g of hydrogen chloride were produced in a reaction assuming that the law of conservation of mass is true?*

Solution: $NaCl + H_2SO_4 = NaHSO_4 + HCl$

According to law of conservation of mass,

Total masses of reactants = Total masses of products

Let the mass of NaCl decomposed be x g, so

$$x + 9.8 = 12.0 + 2.75$$
$$= 14.75$$
$$x = 4.95\text{ g}$$

Example 4. *In an experiment, 2.4 g of iron oxide on reduction with hydrogen yield 1.68 g of iron. In another experiment, 2.9 g of iron oxide give 2.03 g of iron on reduction with hydrogen. Show that the above data illustrate the law of constant proportions.*

Solution:

In the first experiment

The mass of iron oxide = 2.4 g

The mass of iron after reduction = 1.68 g

The mass of oxygen = Mass of iron oxide – Mass of iron

$$= (2.4 - 1.68) = 0.72\text{ g}$$

Ratio of oxygen and iron = 0.72 : 1.68 = 1 : 2.33

In the second experiment

The mass of iron oxide = 2.9 g

The mass of iron after reduction = 2.03 g

The mass of oxygen = (2.9 – 2.03) = 0.87 g

Ratio of oxygen and iron = 0.87 : 2.03 = 1 : 2.33

Thus, the data illustrate the law of constant proportions, as in both the experiments the ratio of oxygen and iron is the same.

Example 5. *Carbon combines with hydrogen to form three compounds A, B and C. The percentages of hydrogen in A, B and C are 25, 14.3 and 7.7 respectively. Which law of chemical combination is illustrated?*

Solution:

Compound	% of Hydrogen	% of Carbon
A	25.0	(100 – 25.0) = 75.0
B	14.3	(100 – 14.3) = 85.7
C	7.7	(100 – 7.7) = 92.3

In Compound *A*

25 parts of hydrogen combine with 75 parts of carbon

1 part of hydrogen combines with 75/25

= 3 parts of carbon

In Compound *B*

14.3 parts of hydrogen combine with 85.7 parts of carbon

1 part of hydrogen combines with 85.7/14.3

= 6.0 parts of carbon

In Compound *C*

7.7 parts of hydrogen combine with 92.3 parts of carbon

1 part of hydrogen combines with 92.3/7.7

= 12.0 parts of carbon

Thus, the masses of carbon in three compounds A, B and C, which combine with a fixed mass of hydrogen are in the ratio of 3 : 6 : 12 or 1 : 2 : 4. This is a simple ratio. Hence, the data illustrate the law of multiple proportions.

Example 6. *Two compounds each containing only tin and oxygen had the following composition:*

	Mass % of tin	*Mass % of oxygen*
Compound A	78.77	21.23
Compound B	88.12	11.88

Show how this data illustrate the law of multiple proportions?

Solution:

In Compound A

21.23 parts of oxygen combine with 78.77 parts of tin

1 part of oxygen combines with 78.77/21.23

= 3.7 parts of tin

In Compound B

11.88 parts of oxygen combine with 88.12 parts of tin

1 part of oxygen combines with 88.12/11.88

= 7.4 parts of tin

Thus, the mass of tin in compounds A and B which combine with a fixed mass of oxygen are in the ratio of 3.7 : 7.4 or 1 : 2. This is a simple ratio. Hence, the data illustrate the law of multiple proportions.

Example 7. *Illustrate the law of reciprocal proportions from the following data: KCl contains 52.0% potassium, KI contains 23.6% potassium and ICl contains 78.2% iodine.*

Solution: **In KCl:** Potassium 52.0%,

Chlorine (100 − 52) = 48%

In KI: Potassium 23.6%;

Iodine (100 − 23.6) = 76.4%

23.6 parts of potassium combine with 76.4 parts of iodine

52.0 parts of potassium will combine with

(76.4/23.6) × 52.0 = 168.3 parts of iodine.

The ratio of masses of chlorine and iodine which combines with same mass of potassium = 48 : 168.3 or 1 : 3.5

In ICl: Iodine = 78.2% and chlorine

= (100 − 78.2) = 21.8%

The ratio of chlorine and iodine in ICl = 21.8 : 78.2 = 1 : 3.5. Hence, the data illustrate the law of reciprocal proportions.

Example 8. *Zinc sulphate crystals contain 22.6% of zinc and 43.9% of water. Assuming the law of constant proportions to be true, how much zinc should be used to produce 13.7 g of zinc sulphate and how much water will they contain?*

Solution: 100 g of zinc sulphate crystals are obtained from

= 22.6 g zinc

1 g of zinc sulphate crystals will be obtained from

= 22.6 / 100 g zinc

13.7 g of zinc sulphate crystals will be obtained from

$$= \frac{22.6}{100} \times 13.7$$

= 3.0962 g of zinc

100 g of zinc sulphate crystals contain water

= 43.9 g

1 g of zinc sulphate crystals contain water

= 43.9 / 100 g

13.7 g of zinc sulphate crystals shall contain water

$$= \frac{43.9}{100} \times 13.7 = 6.0143\text{ g}$$

Example 9. *Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation,* $2CO + O_2 = 2CO_2$. *In an experiment, 400 mL of carbon monoxide and 180 mL of oxygen were allowed to react, when 80% of carbon monoxide was transformed to carbon dioxide.*

All the volumes were measured under the same conditions of temperature and pressure. Find out the composition of the final mixture.

Solution:

$$\underset{2\text{ vol}}{2CO} + \underset{1\text{ vol}}{O_2} = \underset{2\text{ vol}}{2CO_2}$$

From the above equation, it is observed that volume of oxygen required for the transformation of carbon monoxide into carbon dioxide is half the volume of carbon monoxide and the volume of carbon dioxide produced is same as that of carbon monoxide.

Volume of carbon monoxide transformed

$$= \frac{80 \times 400}{100} = 320\text{ mL}$$

Hence, volume of oxygen required for transformation

$$= \frac{1}{2} \times 320 = 160\text{ mL}$$

Volume of carbon dioxide produced

= 320 mL

So, the composition of final mixture is

Carbon monoxide = (400 − 320)

= 80 mL

Carbon dioxide = 320 mL

Oxygen = 180 − 160 = 20 mL

Example 10. *How much volume of oxygen will be required for complete combustion of 40 mL of acetylene* (C_2H_2) *and how much volume of carbon dioxide will be formed? All volumes are measured at NTP.*

Solution:

$$\begin{array}{ccccccc} 2C_2H_2 & + & 5O_2 & = & 4CO_2 & + & 2H_2O \\ 2\text{ vol} & & 5\text{ vol} & & 4\text{ vol} & & \\ 40\text{ mL} & & \frac{5}{2}\times 40\text{ mL} & & \frac{4}{2}\times 40\text{ mL} & & \\ 40\text{ mL} & & 100\text{ mL} & & 80\text{ mL} & & \end{array}$$

So, for complete combustion of 40 mL of acetylene, 100 mL of oxygen are required and 80 mL of carbon dioxide is formed.

1.9 DALTON'S ATOMIC THEORY

The concept that matter is composed of very small particles was given by Indian and Greek philosophers. As early as 400 to 500 B.C. the Greek philosopher **Democritus** suggested that matter cannot be forever divided into smaller and smaller parts. The ultimate particles were considered as indivisible. These particles were called atoms. The word atom has been derived from the Greek word '*atomos*' meaning 'indivisible'. These early ideas, however, were not based on experiments but were mere speculations. The existence of atoms was accepted by Boyle in his book '*The Sceptical Chymist*' (1661) and by **Newton** in his books '*Principia*' and '*Opticks*' (1704). The old ideas were put on a scientific scale by **John Dalton** in the years 1803 to 1808 in the form of a theory known as **Dalton's Atomic Theory** which is a landmark in the history of chemistry. The main points of Dalton's atomic theory are:

(i) Elements consist of minute, indivisible, indestructible particles called atoms.
(ii) Atoms of an element are identical to each other. They have the same mass and size.
(iii) Atoms of different elements differ in properties and have different masses and sizes.
(iv) Compounds are formed when atoms of different elements combine with each other in simple numerical ratios such as one-to-one, one-to-two, two-to-three and so on.
(v) Atoms cannot be created, destroyed or transformed into atoms of other elements.
(vi) The relative numbers and kind of atoms are always the same in a given compound.

The theory convincingly explained the various laws of chemical combination, but the theory has undergone a complete shake up with the modern concept of structure of atom. However, the Daltonian atom still retains its significance as the unit participating in chemical reactions. The following are the modified views regarding Dalton's atomic theory:

(i) The atom is no longer supposed to be indivisible. The atom is not a simple particle but a complex one.
(ii) Atoms of the element may not necessarily possess the same mass but possess the same atomic number and show similar chemical properties **(Discovery of isotopes).**
(iii) Atoms of the different elements may possess the same mass but they always have different atomic numbers and differ in chemical properties **(Discovery of isobars).**
(iv) Atoms of one element can be transmuted into atoms of other element. **(Discovery of artificial transmutation).**
(v) In certain organic compounds, like proteins, starch, cellulose, etc., the ratio in which atoms of different elements combine cannot be regarded as simple. There are a number of compounds which do not follow the law of constant proportions. Such compounds are called **non-stoichiometric compounds.**

1.10 ATOMS, MOLECULES AND FORMULAE

An atom is the smallest particle of an element. The atom of hydrogen is the smallest and the lightest. Atoms take part in chemical combination and remain as indivisible. All atoms do not occur free in nature. **Avogadro** introduced the idea of another kind of particles called the molecules. **A molecule is the smallest particle of an element or compound that can have a stable and independent existence.** A molecule of an element consists of one or more atoms of the same element. Certain elements are capable of existence as single atoms and their atoms can be regarded as molecules. A molecule of an element that consists of one atom only is called monoatomic molecule as in the case of inert gases. Oxygen is not stable in atomic form but is stable in molecular form. A molecule of oxygen is diatomic in nature, *i.e.*, its molecule consists of two oxygen atoms. Hydrogen, nitrogen, fluorine, chlorine, bromine, iodine are also diatomic like oxygen. Some elements exist in more complex molecular forms. The molecule of phosphorus consists of four phosphorus atoms and the molecule of sulphur consists of eight sulphur atoms. Such molecules having more than two atoms are said to be polyatomic. A representation of the molecule of an element involves use of a subscript to the right of the elemental symbol. The diatomic molecule of chlorine is represented as Cl_2, whereas molecules of phosphorus and sulphur are represented as P_4 and S_8, respectively.

The molecule is the smallest possible unit of a compound which shows the properties of the compound. The molecules of all compounds contain two or more different types of atoms. These differ from the molecules of elements which contain only one type of atoms.

Thus, it becomes clear that atoms are the components of molecules and the molecules are components of elements or compounds.

The formula is a group of symbols of elements which represents one molecule of a substance. The formula of a substance represents its chemical composition. Water consists of molecules containing two hydrogen atoms and one oxygen atom which are represented as H_2O. The subscript to the right of the symbol for hydrogen indicates the number of hydrogen atoms contained in a molecule. No subscript follows the symbol for oxygen which means, by convention, that only one atom of oxygen is contained in the molecule.

The subscripts representing the number of atoms contained in a molecule of a compound are in no way related to the number of atoms present in the molecule of a free element. Although both hydrogen and oxygen are composed of diatomic molecules, a water molecule contains only one atom of oxygen and two atoms of hydrogen. The two hydrogen atoms present in H_2O are not molecular hydrogen but rather two hydrogen atoms that have chemically combined with an oxygen atom.

For a chemical formula to be correct, it must contain two pieces of information: (i) it must indicate the elements in the make up of the compound, and (ii) it must indicate the combining ratio of atoms of these elements in the particular compound. The first information is provided by including in the formula correct chemical symbols for all the elements in the compound. The second piece of information is provided by subscripts, *i.e.*, numbers written to the right slightly below the chemical symbols of the elements.

Nitric acid is a combination of hydrogen, nitrogen and oxygen giving a base formula HNO. These elements combine in the ratio 1 : 1 : 3. Therefore, the correct formula for nitric acid is HNO_3.

Some compounds are composed of ions rather than of molecules. Ions differ from atoms and molecules by being electrically charged particles of matter. The charges may be positive or negative and generally vary in magnitude. The positively charged ions are called cations and negatively charged ions are called anions. Simple cations and anions come into existence by loss and acceptance of an electron or electrons by neutral atoms respectively. Ions that consist of several atoms held together by chemical bonds similar to those involved in the molecules are called polyatomic ions or complex ions. These complex ions differ from molecules in the sense that they bear a charge. Some of the common complex ions are:

NO_3^-	Nitrate	PO_4^{3-}	Phosphate	NH_4^+	Ammonium
SO_4^{2-}	Sulphate	ClO_4^-	Perchlorate	PH_4^+	Phosphonium
SO_3^{2-}	Sulphite	CO_3^{2-}	Carbonate	MnO_4^-	Permanganate

When ions are present in a compound, the number of positive charges on a cation must balance with the negative charges on an anion to produce electrically neutral matter. Since, the charge on the anion may not always be equal to that on the cation, the number of anions will not always be equal to the number of cations.

Calcium nitrate consists of calcium and nitrate ions. Each calcium ion carries 2 units positive charge while each nitrate ion carries 1 unit negative charge. Thus, to make net charge zero, two nitrate ions will link with one calcium ion and the formula will be $Ca(NO_3)_2, [Ca^{2+} + 2NO_3^-]$. Names and formulae of some common chemical compounds are listed below :

Common Name	Chemical Name	Chemical Formula
Alum	Ammonium aluminium sulphate	$(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Aspirin	Acetyl salicylic acid	$C_9H_8O_4$
Battery acid or oil of vitriol	Sulphuric acid	H_2SO_4
Blue vitriol	Copper sulphate	$CuSO_4 \cdot 5H_2O$
Baking soda	Sodium bicarbonate	$NaHCO_3$
Bleaching powder	Calcium chlorohypochlorite	$CaOCl_2$
Borax	Sodium tetraborate	$Na_2B_4O_7 \cdot 10H_2O$
Butter of tin	Stannic chloride	$SnCl_4 \cdot 5H_2O$
Caustic soda	Sodium hydroxide	$NaOH$
Caustic potash	Potassium hydroxide	KOH
Carbolic acid	Phenol	C_6H_5OH
Chile saltpetre	Sodium nitrate	$NaNO_3$
Carborundum	Silicon carbide	SiC
Corrosive sublimate	Mercuric chloride	$HgCl_2$
Calomel	Mercurous chloride	Hg_2Cl_2
Dry ice	Carbon dioxide (solid)	CO_2
Formalin	Formaldehyde (40% solution)	$HCHO$
Grain alcohol (Spirit)	Ethyl alcohol	C_2H_5OH
Green vitriol	Ferrous sulphate	$FeSO_4 \cdot 7H_2O$
Gypsum	Calcium sulphate	$CaSO_4 \cdot 2H_2O$
Gammexane (BHC)	Benzene hexachloride	$C_6H_6Cl_6$
Hydrolith	Calcium hydride	CaH_2
Hypo (Antichlor)	Sodium thiosulphate	$Na_2S_2O_3 \cdot 5H_2O$
Indian nitre	Potassium nitrate	KNO_3
Limestone	Calcium carbonate	$CaCO_3$
Lunar caustic	Silver nitrate	$AgNO_3$
Laughing gas	Nitrous oxide	N_2O
Litharge	Lead monoxide	PbO
Muratic acid	Hydrochloric acid	HCl
Mohr's salt	Ferrous ammonium sulphate	$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
Milk of magnesia	Magnesium hydroxide	$Mg(OH)_2$
Microcosmic salt	Sodium ammonium hydrogen ortho-phosphate	$Na(NH_4)HPO_4$
Marsh gas (Damp fire)	Methane	CH_4
Oleum	Sulphuric acid (Fuming)	$H_2S_2O_7$
Oxone	Sodium peroxide	Na_2O_2
Plaster of Paris	Calcium sulphate hemihydrate	$CaSO_4 \cdot \frac{1}{2}H_2O$
Philosphers's wool	Zinc oxide	ZnO
Phosgene	Carbonyl chloride	$COCl_2$
Pearl ash	Potassium carbonate	K_2CO_3
Pyrene	Carbon tetrachloride	CCl_4
Picric acid	2,4,6-Trinitrophenol	$C_6H_2(OH)(NO_2)_3$
Quick lime	Calcium oxide	CaO
Red lead (Minium)	Lead tetroxide	Pb_3O_4
Sugar	Sucrose	$C_{12}H_{22}O_{11}$
Slaked lime (Milk of lime)	Calcium hydroxide	$Ca(OH)_2$
Sal ammoniac	Ammonium chloride	NH_4Cl
Sugar of lead	Lead acetate	$(CH_3COO)_2Pb$
Sand	Silicon dioxide	SiO_2
Table salt (Common salt)	Sodium chloride	$NaCl$
TEL	Tetra-ethyl lead	$Pb(C_2H_5)_4$
Tear gas	Chloropicrin	CCl_3NO_2
Washing soda	Sodium carbonate	$Na_2CO_3 \cdot 10H_2O$
Water glass	Sodium silicate	Na_2SiO_3
White vitriol	Zinc sulphate	$ZnSO_4 \cdot 7H_2O$

1.11 ATOMIC AND MOLECULAR MASS

One of the most important concepts derived from Dalton's atomic theory is that of atomic mass, *i.e.*, each element has a characteristic atomic mass. As atoms are very tiny particles, their absolute masses are difficult to measure. However, it is possible to determine the relative masses of different atoms if a small unit of mass is taken as a standard. For this purpose, mass of one atom of hydrogen was assumed as unity and was accepted as standard. **The atomic mass of an element can be defined as the number which indicates how many times the mass of one atom of the element is heavier in comparison to the mass of one atom of hydrogen.**

$$A = \text{Atomic mass of an element}$$
$$= \frac{\text{Mass of one atom of the element}}{\text{Mass of one atom of hydrogen}}$$

In 1858, oxygen atom was adopted as a standard on account of the following reasons:

(i) It is much easier to obtain compounds of elements with oxygen than with hydrogen as oxygen is more reactive than hydrogen.

(ii) The atomic masses of most of the elements become approximately whole numbers but with hydrogen as standard the atomic masses of most of the elements are fractional.

The mass of one atom of natural oxygen was taken to be 16.0.

Thus, atomic mass of an element

$$= \frac{\text{Mass of one atom of the element}}{\frac{1}{16}\text{ th part of the mass of one atom of oxygen}}$$
$$= \frac{\text{Mass of one atom of the element}}{\text{Mass of one atom of oxygen}} \times 16$$

By accepting oxygen as a standard, the atomic mass of hydrogen comes as 1.008, sodium 22.991 and sulphur 32.066.

In 1961, the International Union of Chemists selected a new unit for expressing the atomic masses. They accepted the stable isotope of carbon (^{12}C) with mass number of 12 as the standard. **Atomic mass of an element can be defined as the number which indicates how many times the mass of one atom of the element is heavier in comparison to $\frac{1}{12}$ th part of the mass of one atom of carbon-12 (^{12}C).**

$$A = \text{Atomic mass of an element}$$
$$= \frac{\text{Mass of one atom of the element}}{\frac{1}{12}\text{ th part of the mass of one atom of carbon-12}}$$
$$= \frac{\text{Mass of one atom of the element}}{\text{Mass of one atom of carbon-12}} \times 12$$

[The quantity 'A' was formerly known as atomic weight. However, this term is no longer used as the word 'weight' means gravitational force.]

Atomic mass unit: The quantity $\frac{1}{12}$ mass of an atom of carbon-12 (^{12}C) is known as the atomic mass unit and is abbreviated as amu. The actual mass of one atom of carbon-12 is 1.9924×10^{-23} g or 1.9924×10^{-26} kg.

Thus,

$$1\,\text{amu}^{*} = \frac{1.9924 \times 10^{-23}}{12} = 1.66 \times 10^{-24}\text{ g or }1.66 \times 10^{-27}\text{ kg}$$

$$A = \text{Atomic mass of an element}$$
$$= \frac{\text{Mass of one atom of the element}}{1\,\text{amu}}$$

The atomic masses of some elements on the basis of carbon-12 are given below:

Hydrogen	1.008 amu	Iron	55.847 amu
Oxygen	16.00 amu	Sodium	22.989 amu
Chlorine	35.453 amu	Zinc	65.38 amu
Magnesium	24.305 amu	Silver	107.868 amu
Copper	63.546 amu		

The actual mass of an atom of an element

= The atomic mass of an element in amu $\times 1.66 \times 10^{-24}$ g

So, the actual mass of hydrogen atom

$$= 1.008 \times 1.66 \times 10^{-24} = 1.6736 \times 10^{-24}\text{ g}$$

Similarly, the actual mass of oxygen atom

$$= 16 \times 1.66 \times 10^{-24} = 2.656 \times 10^{-23}\text{ g}$$

It is clear from the above list of atomic masses that atomic masses of a number of elements are not nearly whole numbers. Actually, the above values are average relative masses. Most of the elements occur in nature as a mixture of isotopes. (Isotopes—the atoms of the same element having different atomic masses). With very few exceptions, however, elements have constant mixtures of isotopes. Chlorine is found in nature as a mixture containing two isotopes Cl-35 (34.969 amu) and Cl-37 (36.966 amu). These are found in the ratio of 75.53% (Cl-35) and 24.47% (Cl-37). Therefore, the average relative mass of chlorine is calculated as:

$$(34.969 \times 0.7553) + (36.966 \times 0.2447) = 35.46\text{ amu}$$

Based on the average mass, the atomic mass of chlorine is 35.46 or 35.5 amu but it is never possible to have an atom having a relative mass 35.5 amu. It can have relative mass of about 35.0 or 37.0 amu depending on the particular isotope. Thus, average relative mass of any naturally occurring sample of chlorine is 35.46 or 35.5 amu as it is a mixture of two isotopes present in definite proportion. The same reasoning applies to all other elements.

The average atomic masses of various elements are determined by multiplying the atomic mass of each isotope by its fractional abundance and adding the values thus obtained. The fractional abundance is determined by dividing percentage abundance by hundred.

$$\text{Average isotopic mass} = \frac{m \times a + n \times b}{m + n}$$

here, a, b are atomic masses of isotopes in the ratio $m : n$.

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*The term Dalton is used for one atomic mass unit, 1 Dalton = 1 amu.

$$\text{Average isotopic mass} = \frac{x}{100} \times a + \frac{y}{100} \times b$$

here, x, y are percentage abundance of the two isotopes $(y = 100 - x)$.

Example 11. *Boron has two isotopes boron-*10 *and boron-*11 *whose percentage abundances are* 19.6% *and* 80.4% *respectively. What is the average atomic mass of boron?*

Solution:

$$\text{Contribution of boron-10} = 10.0 \times 0.196 = 1.96\,\text{amu}$$

$$\text{Contribution of boron-11} = 11.0 \times 0.804 = 8.844\,\text{amu}$$

$$\text{Adding both} = 1.96 + 8.844 = 10.804\,\text{amu}$$

Thus, the average atomic mass of boron is 10.804 amu.

Example 12. *Carbon occurs in nature as a mixture of carbon-*12 *and carbon-*13. *The average atomic mass of carbon is* 12.011. *What is the percentage abundance of carbon-*12 *in nature?*

Solution: Let x be the percentage abundance of carbon-12; then $(100 - x)$ will be the percentage abundance of carbon-13.

$$\text{Therefore,} \quad \frac{12x}{100} + \frac{13(100 - x)}{100} = 12.011$$

$$\text{or} \quad 12x + 1300 - 13x = 1201.1$$

$$\text{or} \quad x = 98.9$$

Abundance of carbon-12 is 98.9%.

Gram-atomic Mass or Gram Atom

When numerical value of atomic mass of an element is expressed in grams, the value becomes gram-atomic mass or gram atom. The atomic mass of oxygen is 16 while gram-atomic mass or gram atom of oxygen is 16 g. Similarly, the gram-atomic masses of hydrogen, chlorine and nitrogen are 1.008 g, 35.5 g and 14.0 g respectively. **Gram-atomic mass or gram atom of every element consists of same number of atoms.** This number is called **Avogadro's number.** The value of Avogadro's number is 6.02×10^{23}.

Absolute mass of one oxygen atom

$$= 16\,\text{amu} = 16 \times 1.66 \times 10^{-24}\,\text{g}$$

Therefore, the mass of 6.02×10^{23} atoms of oxygen will be

$$= 16 \times 1.66 \times 10^{-24} \times 6.02 \times 10^{23}$$

$$= 16\,\text{g (gram-atomic mass)}$$

Thus, gram-atomic mass can be defined as the absolute mass in grams of 6.02×10^{23} atoms of any element.

Number of gram atoms of any element can be calculated with the help of the following formula:

$$\text{No. of gram atoms} = \frac{\text{Mass of the element in grams}}{\text{Atomic mass of the element in grams}}$$

Molecular Mass

Like an atom, a molecule of a substance is also a very small particle possessing a mass of the order of 10^{-24} to 10^{-22} g. Similar to atomic mass, molecular mass is also expressed as a relative mass with respect to the mass of the standard substance which is an atom of hydrogen or an atom of oxygen or an atom of carbon-12. The molecular mass of a substance may be defined as the mass of a molecule of a substance relative to the mass of an atom of hydrogen as 1.008 or of oxygen taken as 16.00 or the mass of one atom of carbon taken as 12. **Molecular mass is a number which indicates how many times one molecule of a substance is heavier in comparison to $\frac{1}{16}$th of the mass of oxygen atom or $\frac{1}{12}$th of the mass of one atom of carbon-12.**

$$M = \text{Molecular mass}$$

$$= \frac{\text{Mass of one molecule of the substance}}{\frac{1}{12}\text{th mass of one atom of carbon-12}}$$

The mass of a molecule is equal to sum of the masses of the atoms present in a molecule. One molecule of water consists of 2 atoms of hydrogen and one atom of oxygen. Thus, molecular mass of water $= (2 \times 1.008) + 16.00 = 18.016\,\text{amu}$. One molecule of H_2SO_4 (sulphuric acid) consists of 2 atoms of hydrogen, one atom of sulphur and four atoms of oxygen. Thus, the molecular mass of sulphuric acid is

$$= (2 \times 1.008) + 32.00 + (4 \times 16.00)$$

$$= 98.016 \text{ or } 98.016\,\text{amu}$$

Gram-molecular Mass or Gram Molecule

A quantity of substance whose mass in grams is numerically equal to its molecular mass is called gram-molecular mass. In other words, molecular mass of a substance expressed in grams is called gram-molecular mass or gram molecule. For example, the molecular mass of chlorine is 71 and, therefore, its gram-molecular mass or gram molecule is 71 g.

Similarly, molecular mass of oxygen (O_2) is 32, *i.e.*, $2 \times 16 = 32\,\text{amu}$.

$$\text{Gram-molecular mass of oxygen} = 32\,\text{g}$$

Molecular mass of nitric acid (HNO_3) is 63, *i.e.*,

$$= 1 + 14 + 3 \times 16 = 63\,\text{amu}$$

$$\text{Gram-molecular mass of nitric acid} = 63\,\text{g}$$

Gram-molecular mass should not be confused with the mass of one molecule of the substance in grams. The mass of one molecule of a substance is known as its **actual mass.** For example, the actual mass of one molecule of oxygen is equal to $32 \times 1.66 \times 10^{-24}$ g, *i.e.*, 5.32×10^{-23} g.

The number of gram molecules of a substance present in a given mass of a substance can be determined by the application of following formula:

No. of gram molecules

$$= \frac{\text{Mass of a substance in grams}}{\text{Molecular mass of the substance in grams}}$$

$$\text{Mass of single molecule} = \frac{\text{Molar mass in grams}}{6.023 \times 10^{23}}$$

$$= \text{Molar mass in amu} \times 1.66 \times 10^{-24}\,\text{grams}$$

Example 13. *Calculate the mass of* 2.5 *gram atoms of oxygen.*

Solution: We know that,

$$\text{No. of gram atoms} = \frac{\text{Mass of the element in grams}}{\text{Atomic mass of the element in grams}}$$

So, Mass of oxygen $= 2.5 \times 32 = 80.0\,\text{g}$

Example 14. *Calculate the gram atoms in 2.3 g of sodium.*

Solution: No. of gram atoms $\frac{2.3}{23} = 0.1$

[Atomic mass of sodium = 23 g]

Example 15. *Calculate the mass of 1.5 gram molecule of sulphuric acid.*

Solution: Molecular mass of

$$H_2SO_4 = 2 \times 1 + 32 + 4 \times 16 = 98.0\,\text{amu}$$

$$\text{Gram-molecular mass of } H_2SO_4 = 98.0\,\text{g}$$

$$\text{Mass of 1.5 gram molecule of } H_2SO_4 = 98.0 \times 1.5 = 147.0\,\text{g}$$

Example 16. *Calculate the actual mass of one molecule of carbon dioxide (CO_2).*

Solution: Molecular mass of CO_2 = 44 amu

$$1\,\text{amu} = 1.66 \times 10^{-24}\,\text{g}$$

So, The actual mass of $CO_2 = 44 \times 1.66 \times 10^{-24}$

$$= 7.304 \times 10^{-23}\,\text{g}$$

1.12 AVOGADRO'S HYPOTHESIS

According to Dalton's atomic theory, elements react with each other in the simple ratio of their atoms. Gay-Lussac proposed that gases combine in simple ratio of their volumes. In an attempt to correlate Dalton's atomic theory with Gay-Lussac law of gaseous volumes, **Berzelius** stated that **under similar conditions of temperature and pressure, equal volume of all gases contain the same number of atoms.** This hypothesis was subsequently found to be incorrect as it failed to interpret the experimental results and contradicted the very basic assumption of Dalton's atomic theory, *i.e.*, an atom is indivisible. For example, the formation of hydrogen chloride from hydrogen and chlorine could not be explained on the basis of Berzelius hypothesis.

Hydrogen +	Chlorine =	Hydrogen chloride
1 vol	1 vol	2 vol
n atoms	*n* atoms	2*n* compound atoms
1 atom	1 atom	2 compound atoms
½ atom	½ atom	1 compound atom

i.e., for the formation of 1 compound atom of hydrogen chloride, ½ atom of hydrogen and ½ atom of chlorine are needed. In other words, each atom of hydrogen and chlorine has been divided which is against Dalton's atomic theory. Thus, the hypothesis of Berzelius was discarded.

The Italian scientist, **Amedeo Avogadro,** in 1811, solved the above problem by proposing two types of particles from which whole of the matter is composed of.

(i) Atom: The smallest particle of an element that can take part in chemical change but generally cannot exist freely as such.

(ii) Molecule: The smallest particle of a substance (element or compound) which has free or independent existence and possesses all characteristic properties of the substance. A molecule of an element is composed of like atoms while a molecule of a compound contains fixed number of atoms of two or more different elements. A molecule may be broken down into its constituent atoms but the atom is indivisible during a chemical change.

Avogadro after making the above differentiation, presented a hypothesis known as **Avogadro hypothesis** which can be stated as follows:

"Under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules."

Avogadro hypothesis explains successfully the formation of hydrogen chloride.

Hydrogen +	Chlorine =	Hydrogen chloride
1 vol	1 vol	2 vol
n molecules	*n* molecules	2*n* molecules
1 molecule	1 molecule	2 molecules
$\frac{1}{2}$ molecule	$\frac{1}{2}$ molecule	1 molecule
1 atom	1 atom	1 molecule

(Both hydrogen and chlorine are diatomic in nature.)

Thus, the hypothesis explains that the molecules of reacting gases break up into constituent atoms during chemical change which then combine to form new molecules of the product or products.

Applications of Avogadro's hypothesis

(i) Atomicity*: Atomicity means number of atoms present in one molecule of an elementary gas. Hydrogen, oxygen, nitrogen, chlorine, etc., are diatomic in nature. Noble gases are monoatomic while ozone is triatomic in nature. Avogadro's hypothesis helps in determining the atomicity of elements.

(ii) Relationship between molecular mass and vapour density: The vapour density of any gas is the ratio of the densities of the gas and hydrogen under similar conditions of temperature and pressure.

$$\text{Vapour Density (V.D.)} = \frac{\text{Density of gas}}{\text{Density of hydrogen}}$$

$$= \frac{\text{Mass of a certain volume of the gas}}{\text{Mass of same volume of hydrogen at the same temp. and pressure}}$$

If *n* molecules are present in the given volume of a gas and hydrogen under similar conditions of temperature and pressure,

$$\text{V.D.} = \frac{\text{Mass of } n \text{ molecules of gas}}{\text{Mass of } n \text{ molecules of hydrogen}}$$

$$= \frac{\text{Mass of 1 molecule of gas}}{\text{Mass of 1 molecule of hydrogen}}$$

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*Atomicity can be ascertained with the values of ratio of two specific heats of gases $\left(\frac{C_P}{C_V}\right)$

$\frac{C_P}{C_V} = 1.66$ (Monoatomic), $\frac{C_P}{C_V} = 1.40$ (Diatomic), $\frac{C_P}{C_V} = 1.33$ (Polyatomic)

$$= \frac{\text{Molecular mass of gas}}{\text{Molecular mass of hydrogen}}$$

$$= \frac{\text{Mol. mass}}{2}$$

(since, mol. mass of hydrogen = 2)

Hence, $2 \times \text{V.D.} = \text{Mol. mass}$

This formula can be used for the determination of molecular masses of volatile substances from vapour density. Vapour density is measured mainly by two methods:

(a) Victor Meyer and (b) Duma's methods.

(iii) Gram-molecular volume: 1 g mole of any gas occupies 22.4 litres or 22400 mL of volume at NTP or STP conditions.*

The density of hydrogen at NTP is 0.00009 g mL^{-1}. Thus, 0.00009 g of hydrogen will occupy volume at NTP = 1 mL

$$\text{1 g of hydrogen occupies volume at NTP} = \frac{1}{0.00009}\ \text{mL}$$

1g mole of hydrogen (2.016 g) occupies volume at NTP

$$= \frac{2.016}{0.00009} = 22400\ \text{mL} = 22.4\ \text{litre}$$

According to Avogadro's hypothesis, equal volumes of different gases contain same number of molecules under similar conditions of temperature and pressure. Thus, 22.4 litre or 22400 mL of any gas at NTP will contain one gram mole or its molecular mass in grams.

Loschmidt number : Number of molecules in 1 cm^3 or 1 mL of a gas at S.T.P. is known as Loschmidt number.

$$\text{Loschmidt number} = \frac{6.023 \times 10^{23}}{22400}$$

$$= 2.68 \times 10^{18}\ \text{molecules mL}^{-1}$$

(iv) Molecular formula: Avogadro's hypothesis helps in finding the molecular formulae of gases. Under similar conditions of temperature and pressure, 2 volumes of ozone after decomposition give 3 volumes of oxygen.

$$\underset{2\text{ vol}}{\text{Ozone}} \xrightarrow{\text{Decomposition}} \underset{3\text{ vol}}{\text{Oxygen}}$$

2 molecules	3 molecules
1 molecule	3/2 molecules
1 molecule	3 atoms

Thus, the formula of ozone is O_3.

1.13 MOLE CONCEPT

For the counting of articles, the unit **dozen** or unit **gross** is commonly used irrespective of their nature. For example, one dozen pencils means 12 pencils or one dozen apples means 12 apples or one gross books means 144 books or one gross oranges means 144 oranges. In a similar way, for counting of atoms, molecules, ions, etc., chemists use the unit mole. The term mole was introduced by **Ostwald** in 1896. This is the Latin word 'moles' meaning heap or pile. **A mole (mol) is defined as the number of atoms in 12.00 g of carbon-12.** The number of atoms in 12 g of carbon-12 has been found experimentally to be 6.02×10^{23}. This number is also known as Avogadro's number named in honour of **Amedeo Avogadro** (1776 – 1856).

Thus, a mole contains 6.02×10^{23} units. These units can be atoms, molecules, ions, electrons or anything else.

1 mole of hydrogen atoms means 6.02×10^{23} hydrogen atoms.

1 mole of hydrogen molecules means 6.02×10^{23} hydrogen molecules.

1 mole of potassium ions means 6.02×10^{23} potassium ions.

1 mole of electrons means 6.02×10^{23} electrons.

The type of entity must be specified when the mole designation is used. A mole of oxygen atoms contains 6.02×10^{23} oxygen atoms and a mole of oxygen molecules contains 6.02×10^{23} oxygen molecules. Therefore, a mole of oxygen molecules is equal to two moles of oxygen atoms, *i.e.*, $2 \times 6.02 \times 10^{23}$ oxygen atoms.

How much does one mole weigh? That depends on the nature of particles (units). **The mass of one mole atoms of any element is exactly equal to the atomic mass in grams (gram-atomic mass or gram atom) of that element.**

For example, the atomic mass of aluminium is 27 amu. One amu is equal to 1.66×10^{-24} g. One mole of aluminium contains 6.02×10^{23} aluminium atoms.

$$\text{Mass of one atom aluminium} = 27 \times 1.66 \times 10^{-24}\ \text{g}$$

$$\text{Mass of one mole aluminium} = 27 \times 1.66 \times 10^{-24} \times 6.02 \times 10^{23}$$

$$= 27\,\text{g}$$

This is the atomic mass of aluminium in grams or it is one gram atomic mass or one gram atom of aluminium.

Similarly, **the mass of 6.02×10^{23} molecules (1 mole) of a substance is equal to its molecular mass in grams or gram-molecular mass or gram molecule.** For example, molecular mass of water is 18 amu. Thus, mass of one mole of water will be $18 \times 1.66 \times 10^{-24} \times 6.02 \times 10^{23}$, *i.e.*, 18 g. This is the molecular mass of water in grams or one gram-molecular mass or one gram molecule.

Mole concept is also applicable to ionic compounds which do not contain molecules. In such cases, the formula of an ionic compound represents the ratio between constituent ions. The mass of 6.02×10^{23} formula units represents one mole of an ionic compound.

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* 0°C or 273 K temperature and one atmosphere or 760 mm of Hg or 76 cm of Hg pressure are known as the standard conditions of temperature and pressure (STP) or normal conditions of temperature and pressure (NTP).

One mole of $BaCl_2 = 6.02 \times 10^{23}$ $BaCl_2$ units

$= 208.2$ g $BaCl_2$

= Molecular mass (formula mass) of $BaCl_2$

$= 6.02 \times 10^{23}$ Ba^{2+} ions $+ 2 \times 6.02 \times 10^{23}$ Cl^- ions

$= 137.2 + 71.0 = 208.2$ g

One mole of a substance will have mass equal to formula mass of that substance expressed in grams.

It has been established by Avogadro's hypothesis that one gram-molecular mass of any gaseous substance occupies a volume of 22.4 litres at NTP. One gram-molecular mass is nothing but one mole of substance. Thus, one mole, *i.e.*, 6.02×10^{23} molecules of any gaseous substance occupies 22.4 litres as volume at NTP.

The following formulae satisfy the above discussion.

1 mole of a substance $= 6.02 \times 10^{23}$ particles of the substance

Number of moles of a substance

$$= \frac{\text{Mass of substance in gram}}{\text{Mass of one mole of the substance in gram}}$$

Further, $$\text{Number of moles} = \frac{\text{No. of particles}}{6.02 \times 10^{23}}$$

Thus,

$$\frac{\text{No. of particles}}{6.02 \times 10^{23}} = \frac{\text{Mass of substance in gram}}{\text{Mass of one mole of the substance in gram}}$$

Mass of one atom of an element

$$= \frac{\text{Gram atom of an element}}{6.02 \times 10^{23}}$$

Mass of one molecule of a substance

$$= \frac{\text{Gram-molecular mass of the substance}}{6.02 \times 10^{23}}$$

Number of molecules

$$= \frac{\text{Volume of gas in litres at NTP}}{22.4} \times 6.02 \times 10^{23}$$

SOME SOLVED EXAMPLES

Example 17. *A piece of copper weighs* 0.635 g. *How many atoms of copper does it contain?* **[CEE (Bihar) 1992]**

Solution: Gram-atomic mass of copper = 63.5 g

Number of moles in 0.635 g of copper $= \frac{0.635}{63.5} = 0.01$

Number of copper atoms in one mole $= 6.02 \times 10^{23}$

Number of copper atoms in 0.01 moles $= 0.01 \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{21}$

Example 18. *How many molecules of water and oxygen atoms are present in* 0.9 *g of water?*

Solution: Gram-molecular mass of water = 18 g

Number of moles in 0.9 g of water $= \frac{0.9}{18} = 0.05$

Number of water molecules in one mole of water

$= 6.02 \times 10^{23}$

Number of molecules of water in 0.05 moles

$= 0.05 \times 6.02 \times 10^{23}$

$= 3.010 \times 10^{22}$

As one molecule of water contains one oxygen atom,

So, number of oxygen atoms in 3.010×10^{22} molecule of water $= 3.010 \times 10^{22}$

Example 19. *Calculate the mass of a single atom of sulphur and a single molecule of carbon dioxide.*

Solution:

Gram-atomic mass of sulphur = 32 g

$$\text{Mass of one sulphur atom} = \frac{\text{Gram-atomic mass}}{6.02 \times 10^{23}}$$

$$= \frac{32}{6.02 \times 10^{23}} = 5.33 \times 10^{-23} \text{ g}$$

Formula of carbon dioxide $= CO_2$

Molecular mass of $CO_2 = 12 + 2 \times 16 = 44$

Gram-molecular mass of $CO_2 = 44$ g

$$\text{Mass of one molecule of } CO_2 = \frac{\text{Gram-molecular mass}}{6.02 \times 10^{23}}$$

$$= \frac{44}{6.02 \times 10^{23}} = 7.308 \times 10^{-23} \text{ g}$$

Example 20. *What is the mass of* 3.01×10^{22} *molecules of ammonia?*

Solution: Gram-molecular mass of ammonia = 17 g

Number of molecules in 17 g (one mole) of $NH_3 = 6.02 \times 10^{23}$

Let the mass of 3.01×10^{22} molecules of NH_3 be $= x$ g

So, $$\frac{3.01 \times 10^{22}}{6.02 \times 10^{23}} = \frac{x}{17}$$

or $$x = \frac{17 \times 3.01 \times 10^{22}}{6.02 \times 10^{23}} = 0.85 \text{ g}$$

Example 21. *From* 200 *mg of* CO_2, 10^{21} *molecules are removed. How many moles of* CO_2 *are left?*

Solution:

Gram-molecular mass of $CO_2 = 44$ g

$$\text{Mass of } 10^{21} \text{ molecules of } CO_2 = \frac{44}{6.02 \times 10^{23}} \times 10^{21} = 0.073 \text{ g}$$

Mass of CO_2 left $= (0.2 - 0.073) = 0.127$ g

$$\text{Number of moles of } CO_2 \text{ left} = \frac{0.127}{44} = 2.88 \times 10^{-3}$$

Example 22. *How many molecules and atoms of oxygen are present in 5.6 litres of oxygen (O_2) at NTP?*

Solution: We know that, 22.4 litres of oxygen at NTP contain 6.02×10^{23} molecules of oxygen.

So, 5.6 litres of oxygen at NTP contain

$$= \frac{5.6}{22.4} \times 6.02 \times 10^{23} \text{ molecules}$$

$$= 1.505 \times 10^{23} \text{ molecules}$$

1 molecule of oxygen contains = 2 atoms of oxygen

So, 1.505×10^{23} molecules of oxygen contain

$$= 2 \times 1.505 \times 10^{23} \text{ atoms}$$

$$= 3.01 \times 10^{23} \text{ atoms}$$

Example 23. *How many electrons are present in 1.6 g of methane?*

Solution: Gram-molecular mass of methane,

$$(CH_4) = 12 + 4 = 16 \text{g}$$

Number of moles in 1.6 g of methane

$$= \frac{1.6}{16} = 0.1$$

Number of molecules of methane in 0.1 mole

$$= 0.1 \times 6.02 \times 10^{23}$$

$$= 6.02 \times 10^{22}$$

One molecule of methane has = 6 + 4 = 10 electrons

So, 6.02×10^{22} molecules of methane have

$$= 10 \times 6.02 \times 10^{22} \text{ electrons}$$

$$= 6.02 \times 10^{23} \text{ electrons}$$

Example 24. *The electric charge on the electron is 1.602×10^{-19} coulomb. How much charge is present on 0.1 mole of Cu^{2+} ions?*

Solution: Charge on one mole of electrons

$$= 6.02 \times 10^{23} \times 1.602 \times 10^{-19} \text{ coulomb}$$

$$= 96500 \text{ coulomb} = 1 \text{ faraday}$$

Charge on one mole of Cu^{2+} ions

$$= 2 \times 96500 \text{ coulomb} = 2 \text{ faraday}$$

Charge on 0.1 mole of Cu^{2+} ions

$$= 0.1 \times 2 = 0.2 \text{ faraday}$$

Example 25. *How many years it would take to spend one Avogadro's number of rupees at a rate of 10 lakh of rupees in one second?* **(MLNR 1990)**

Solution: Number of rupees spent in one second = 10^6

Number of rupees spent in one year

$$= 10^6 \times 60 \times 60 \times 24 \times 365$$

Avogadro's number of rupees will be spent

$$= \frac{6.02 \times 10^{23}}{10^6 \times 60 \times 60 \times 24 \times 365}$$

$$= 19.089 \times 10^9 \text{ years} = 1.9089 \times 10^{10} \text{ years}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 116 mg of a compound on vaporisation in Victor Meyer's apparatus displaces 44.8 mL of air measured at STP. The molecular mass of the compound is: **[CEE (Kerala) 2004]**
(a) 116 (b) 232 (c) 58 (d) 44.8 (e) 46.4
[Ans. (c)]
[Hint: Molar mass of compound

$$= \text{Mass of 22400 mL vapour at STP}$$

$$= \frac{0.116 \times 22400}{44.8} = 58]$$

2. A gas has a vapour density 11.2. The volume occupied by 1 g of the gas at NTP is: **(JCECE 2004)**
(a) 1 L (b) 11.2 L (c) 22.4 L (d) 4 L
[Ans. (a)]
[Hint: Molar mass = 2 × 11.2 = 22.4 g

$$\text{Volume of 1 g compound at STP} = \frac{22.4}{22.4} = 1 \text{ L}]$$

3. 3 g of hydrocarbon on combustion with 11.2 g of oxygen produce 8.8 g of CO_2 and 5.4 g of H_2O. The data illustrate the law of:
(a) conservation of mass (b) multiple proportions
(c) constant proportions (d) reciprocal proportions
[Ans. (a)]
[Hint: Σ Masses of reactants = Σ Masses of products
(3 + 11.2) g (8.8 + 5.4) g
Hence, law of conservation of mass is verified.]

4. The maximum number of molecules is present in: **[CBSE (PMT) 2004; Manipal (Medical) 2007]**
(a) 15 L of H_2 gas at STP (b) 5 L of N_2 gas at STP
(c) 0.5 g of H_2 gas (d) 10 g of O_2 gas
[Ans. (a)]
[Hint:

$$\text{Number of molecules in 15 L } H_2 = \frac{15}{22.4} \times N = 0.669\,N$$

$$\text{Number of molecules in 5 L } N_2 = \frac{5}{22.4} \times N = 0.223\,N$$

$$\text{Number of molecules in 0.5 g } H_2 = \frac{0.5}{2} \times N = 0.25\,N$$

$$\text{Number of molecules in 10 g } O_2 = \frac{10}{32} \times N = 0.312\,N\,]$$

5. Insulin contains 3.4% sulphur. Then, the minimum molecular mass of the insulin is about:
(a) 940 amu (b) 9400 amu
(c) 3600 amu (d) 970 amu
[Ans. (a)]
[Hint: ∵ 3.4 g sulphur is present in 100 g insulin

$$\therefore \text{32 g sulphur will be present in } \frac{100}{3.4} \times 32 \text{ g insulin} = 940$$

∴ Molar mass of insulin is about 940 amu]

6. 25 g of MCl_4 contains 0.5 mol chlorine then its molecular mass is: **(DPMT 2007)**
(a) $100 g\ mol^{-1}$ (b) $200 g\ mol^{-1}$
(c) $150 g\ mol^{-1}$ (d) $400 g\ mol^{-1}$
[Ans. (b)]
[Hint: 1 mol of MCl_4 contains 4 mol of chlorine
$\because$ 0.5 mol chlorine is present in 25 g of MCl_4
$\therefore$ 4 mol chlorine will be present in $\frac{25}{0.5} \times 4$, *i.e.*, 200 g of MCl_4.]

1.14 EQUIVALENT MASSES OR CHEMICAL EQUIVALENTS

Equivalent mass of a substance (element or compound) is defined as **the number of parts by mass of the substance which combine or displace directly or indirectly 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine or 108 parts by mass of silver.**

The equivalent mass is a pure number. When the equivalent mass of a substance is expressed in grams, it is called gram equivalent mass. For example, equivalent mass of sodium is 23, hence, its gram equivalent mass is 23 g.

The equivalent mass of a substance may have different values under different conditions. The equivalent mass of an element may vary with change of valency. For example, copper forms two oxides CuO and Cu_2O. In CuO, 63.5 parts of copper combine with 16 parts of oxygen. Thus, equivalent mass of copper in this oxide is $\frac{63.5}{2} = 31.75$. In Cu_2O, 2×63.5 parts of copper combine with 16 parts of oxygen; thus, the equivalent mass of copper in this oxide is:

$$\frac{2 \times 63.5}{2} = 63.5$$

Relation between atomic mass, equivalent mass and valency: Suppose an element X combines with hydrogen to form a compound, XH_n, where n is the valency of the element X.

n parts by mass of hydrogen combine with atomic mass of element X.

1 part by mass of hydrogen combines with

$$\frac{\text{Atomic mass of element}}{n}$$

By above definition, $\frac{\text{Atomic mass of element}}{n}$ is the equivalent mass of the element.

Thus, $$\text{Equivalent mass} = \frac{\text{Atomic mass}}{n}$$

or $$\text{Atomic mass} = \text{Equivalent mass} \times \text{Valency}$$

Note: Detailed discussion on equivalent masses of compounds (acids, bases, salts, oxidising agents, reducing agents, etc.,) will be taken in chapter on volumetric analysis.

The following methods are used for the determination of equivalent mass of elements.

(i) Hydrogen displacement method: This method is used for those elements which can evolve hydrogen from acids, *i.e.*, active metals. A known mass of the active metal is reacted with dilute mineral acid. Hydrogen gas thus evolved is measured under experimental conditions. The volume of hydrogen is then reduced to NTP conditions. The mass of liberated hydrogen is determined using density of hydrogen (0.00009 at NTP).

$$\text{Equivalent mass} = \frac{\text{Mass of element}}{\text{Mass of hydrogen}} \times 1.008$$

$$= \frac{\text{Mass of element} \times 1.008}{\text{Volume in mL of hydrogen displaced at NTP} \times 0.00009}$$

$$= \frac{\text{Mass of element} \times 11200}{\text{Volume in mL of hydrogen displaced at NTP}}$$

(ii) Oxide formation method: A known mass of the element is changed into oxide directly or indirectly. The mass of oxide is noted.

$$\text{Mass of oxygen} = (\text{Mass of oxide} - \text{Mass of element})$$

Thus, the equivalent mass of the element

$$= \frac{\text{Mass of element}}{(\text{Mass of oxide} - \text{Mass of element})} \times 8$$

$$= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$$

(iii) Chloride formation method: A known mass of the element is changed into chloride directly or indirectly. The mass of the chloride is determined.

$$\text{Mass of chlorine} = (\text{Mass of chloride} - \text{Mass of element})$$

Thus, the equivalent mass of the element

$$= \frac{\text{Mass of element} \times 35.5}{(\text{Mass of chloride} - \text{Mass of element})}$$

$$= \frac{\text{Mass of element} \times 35.5}{\text{Mass of chlorine}}$$

(iv) Metal to metal displacement method: A more active metal can displace less active metal from its salt's solution. For example, when zinc is added to copper sulphate, copper is precipitated. A known mass of active metal is added to the salt's solution of less active metal. The precipitated metal after drying is accurately weighed. The masses of the displacing metal and the displaced metal bear the same ratio as their equivalent masses. If E_1 and E_2 are the equivalent masses of two elements and m_1 and m_2 their respective masses, then,

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated.

(v) Double decomposition method: This method is based on the following points:

(a) The mass of the compound reacted and the mass of product formed are in the ratio of their equivalent masses.

(b) The equivalent mass of the compound (electrovalent) is the sum of equivalent masses of its radicals.

(c) The equivalent mass of a radical is equal to the formula mass of the radical divided by its charge.

$$AB + CD \longrightarrow \underset{\text{ppt.}}{AD} + CB$$

$$\frac{\text{Mass of } AB}{\text{Mass of } AD} = \frac{\text{Equivalent mass of } AB}{\text{Equivalent mass of } AD}$$

$$= \frac{\text{Eq. mass of } A + \text{Eq. mass of } B}{\text{Eq. mass of } A + \text{Eq. mass of } D}$$

Knowing the equivalent masses of B and D, equivalent mass of A can be calculated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. An unknown element forms an oxide. What will be the equivalent mass of the element if the oxygen content is 20% by mass: **[JEE (WB) 2008]**

(a) 16 (b) 32 (c) 8 (d) 64

[Ans. (b)]

[Hint: Equivalent mass of element $= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$

$$= \frac{80}{20} \times 8 = 32]$$

8. A metal M of equivalent mass E forms an oxide of molecular formula M_xO_y. The atomic mass of the metal is given by the correct equation: **[PMT (Kerala) 2008]**

(a) $2E(y/x)$ (b) xyE

(c) E/y (d) y/E

(e) $\frac{E}{2} \times \frac{x}{y}$

[Ans. (a)]

[Hint: Let atomic mass of metal M is 'a'.

Mass of metal $= a \times x$

Mass of oxygen $= 16 \times y$

Equivalent mass of element $= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$

$$E = \frac{ax}{16y} \times 8$$

$$a = 2E\left(\frac{y}{x}\right)]$$

9. The percentage of an element M is 53 in its oxide of molecular formula M_2O_3. Its atomic mass is about: **[PET (Kerala) 2008]**

(a) 45 (b) 9 (c) 18 (d) 38

(e) 27

[Ans. (e)]

[Hint: Equivalent mass of element $= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$

$$= \frac{53}{47} \times 8 \simeq 9$$

Atomic mass = Equivalent mass × Valency

$= 9 \times 3 = 27$ amu.]

10. The equivalent weight of a metal is double than that of oxygen. How many times is the weight of its oxide greater than the weight of metal?

(a) 4 (b) 2 (c) 3 (d) 1.5

[Ans. (d)]

[Hint: Equivalent mass of metal $= 16 = \frac{x}{n}$

Where x = atomic mass of metal

n = valency of metal

Molecular formula of metal oxide $= M_2O_n$

$$\frac{\text{Mass of metal oxide}}{\text{Mass of metal}} = \frac{2(16n) + 16(n)}{2(16n)} = 1.5]$$

1.15 METHODS FOR THE DETERMINATION OF ATOMIC MASS

(i) Dulong and Petit's Law: According to this law, the product of atomic mass and specific heat of a solid element is approximately equal to 6.4. The product of atomic mass and specific heat is called atomic heat. Thus,

$$\text{Atomic mass} \times \text{Specific heat} = 6.4$$

or

$$\text{Atomic mass (approximate)} = \frac{6.4}{\text{Specific heat}}$$

In above formula, the specific heat must be in cal/g unit.

The equivalent mass of the element is determined experimentally and the valency, which is always a whole number, can be obtained by dividing approximate atomic mass with the equivalent mass and changing the value so obtained to the nearest whole number. In this way, exact atomic mass can be determined by multiplying equivalent mass with valency.

Example 26. *A chloride of an element contains 49.5% chlorine. The specific heat of the element is 0.056. Calculate the equivalent mass, valency and atomic mass of the element.*

Solution: Mass of chlorine in the metal chloride = 49.5%

$$\text{Mass of metal} = (100 - 49.5) = 50.5$$

$$\text{Equivalent mass of the metal} = \frac{\text{Mass of metal}}{\text{Mass of chlorine}} \times 35.5$$

$$= \frac{50.5}{49.5} \times 35.5 = 36.21$$

According to Dulong and Petit's law,

$$\text{Approximate atomic mass of the metal} = \frac{6.4}{\text{Specific heat}}$$

$$= \frac{6.4}{0.056} = 114.3$$

$$\text{Valency} = \frac{\text{Approximate atomic mass}}{\text{Equivalent mass}} = \frac{114.3}{36.21} = 3.1 \approx 3$$

Hence, exact atomic mass $= 36.21 \times 3 = 108.63$

Example 27. *On dissolving* 2.0 g *of metal in sulphuric acid,* 4.51g *of the metal sulphate was formed. The specific heat of the metal is* 0.057 cal g^{-1}. *What is the valency of the metal and exact atomic mass?*

Solution: Equivalent mass of SO_4^{2-} radical

$$= \frac{\text{Ionic mass}}{\text{Valency}} = \frac{96}{2} = 48$$

$$\text{Mass of metal sulphate} = 4.51\,\text{g}$$
$$\text{Mass of metal} = 2.0\,\text{g}$$
$$\text{Mass of sulphate radical} = (4.51 - 2.0) = 2.51\,\text{g}$$

2.51 g of sulphate combine with 2.0 g of metal.

So, 48 g of sulphate will combine with

$$= \frac{2}{2.51} \times 48 = 38.24\,\text{g metal}$$

$$\text{Equivalent mass of metal} = 38.24$$

According to Dulong and Petit's law,

$$\text{Approximate atomic mass} = \frac{6.4}{\text{Specific heat}} = \frac{6.4}{0.057} = 112.5$$

$$\text{Valency} = \frac{\text{Approximate atomic mass}}{\text{Equivalent mass}}$$
$$= \frac{112.5}{38.24} = 2.9 \approx 3$$

$$\text{Exact atomic mass} = 38.24 \times 3 = 114.72$$

(ii) Cannizzaro's method: Atomic mass of an element may be defined as the smallest mass of the element present in the molecular mass of any one of its compounds. For this purpose, the following steps are followed:

(a) Molecular masses of a number of compounds in which the element is present are determined.

(b) Each compound is analysed. Mass of the element is determined in the molecular mass of each compound.

(c) The lowest mass of the element is taken its atomic mass.

The following table shows the application of this method:

Compound	Vapour density (V.D.)	Molecular mass = 2 V.D.	% of carbon by mass in compound	Mass of carbon in one molecular mass of the compound
Methane	8	16	75.0	$\frac{75.0 \times 16}{100} = 12\,\text{g}$
Ethane	15	30	80.0	$\frac{80.0 \times 30}{100} = 24\,\text{g}$
Carbon monoxide	14	28	42.9	$\frac{42.9 \times 28}{100} = 12\,\text{g}$
Carbon dioxide	22	44	27.3	$\frac{27.3 \times 44}{100} = 12\,\text{g}$
Propane	22	44	81.8	$\frac{81.8 \times 44}{100} = 36\,\text{g}$

Least mass of carbon is 12 g.

Thus, the atomic mass of carbon is 12.

(iii) The law of isomorphism: Isomorphous substances form crystals which have same shape and size and can grow in the saturated solution of each other. They have a property of forming mixed crystals. Isomorphous substances have same composition, *i.e.*, they have same number of atoms arranged similarly.

Examples of isomorphous compounds are:

(a) K_2SO_4 and K_2CrO_4 (potassium sulphate and potassium chromate)

(b) $ZnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$ (zinc sulphate and ferrous sulphate)

(c) $KClO_4$ and $KMnO_4$ (potassium perchlorate and potassium permanganate)

(d) $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ (potash alum and chrome alum).

The following conclusions have been deduced from the phenomenon of isomorphism:

(i) Masses of two elements that combine with same mass of other elements in their respective compounds are in the ratio of their atomic masses.

$$\frac{\begin{array}{c}\text{Mass of one element } (A) \text{ that combines}\\ \text{with a certain mass of other elements}\end{array}}{\begin{array}{c}\text{Mass of other element } (B) \text{ that combines}\\ \text{with the same mass of other elements}\end{array}} = \frac{\text{Atomic mass of } A}{\text{Atomic mass of } B}$$

(ii) The valencies of the elements forming isomorphous compounds are the same.

Example 28. *Potassium chromate is isomorphous to potassium sulphate* (K_2SO_4) *and is found to contain* 26.78% *chromium. Calculate the atomic mass of chromium* ($K = 39.10$).

Solution: Since, the formula of potassium sulphate is K_2SO_4, so the formula of potassium chromate should be K_2CrO_4 as it is isomorphous to K_2SO_4.

If the atomic mass of chromium is A, then

formula mass of potassium chromate should be

$$= 2 \times 39.1 + A + 64 = (142.2 + A)$$

$$\%\text{ of chromium} = \frac{A}{(142.2 + A)} \times 100$$

So, $$\frac{100A}{(142.2 + A)} = 26.78$$

$$100A = 26.78\,(142.2 + A)$$

or $$A = \frac{26.78 \times 142.2}{73.22} = 52.00$$

(iv) Atomic mass from vapour density of a chloride: The following steps are involved in this method:

(a) Vapour density of the chloride of the element is determined.

(b) Equivalent mass of the element is determined.

Let the valency of the element be x. The formula of its chloride will be MCl_x.

$$\text{Molecular mass} = \text{Atomic mass of } M + 35.5x$$
$$= A + 35.5x$$
$$\text{Atomic mass} = \text{Equivalent mass} \times \text{Valency}$$
$$A = E \times x$$
$$\text{Molecular mass} = E \times x + 35.5x$$

$$2\,\text{V.D.} = x(E + 35.5)$$

$$x = \frac{2\,\text{V.D.}}{E + 35.5}$$

Knowing the value of valency, the atomic mass can be determined.

Example 29. *One gram of a chloride was found to contain* 0.835 *g of chlorine. Its vapour density is* 85. *Calculate its molecular formula.*

Solution: Mass of metal chloride = 1g

$$\text{Mass of chlorine} = 0.835\,\text{g}$$

$$\text{Mass of metal} = (1 - 0.835) = 0.165\ \text{g}$$

$$\text{Equivalent mass of metal} = \frac{0.165 \times 35.5}{0.835}$$

$$= 7.01$$

$$\text{Valency of the metal} = \frac{2\,\text{V.D.}}{E + 35.5}$$

$$= \frac{2 \times 85}{7.01 + 35.5}$$

$$= 4$$

$$\text{Formula of the chloride} = MCl_4$$

Example 30. *The oxide of an element contains* 32.33 *per cent of the element and the vapour density of its chloride is* 79. *Calculate the atomic mass of the element.*

Solution: Mass of the element = 32.33 parts

$$\text{Mass of oxygen} = (100 - 32.33) = 67.67\ \text{parts}$$

$$\text{Equivalent mass of the element} = \frac{32.33}{67.67} \times 8 = 3.82$$

$$\text{Valency of the element} = \frac{2\,\text{V.D.}}{E + 35.5} = \frac{2 \times 79}{3.82 + 35.5} = 4$$

$$\text{Hence, the atomic mass of the element} = 3.82 \times 4$$

$$= 15.28$$

1.16 TYPES OF FORMULAE

As already stated in section 1.10, a formula is a group of symbols of the elements which represents one molecule of the substance. Formula represents chemical composition of the substance. There are three kinds of formulae in the case of compounds.

(i) Empirical formula: It represents the simplest relative whole number ratio of atoms of each element present in the molecule of the substance. For example, CH is the empirical formula of benzene in which ratio of the atoms of carbon and hydrogen is 1 : 1. It also indicates that the ratio of carbon and hydrogen is 12 : 1 by mass.

(ii) Molecular formula: Molecular formula of a compound is one which expresses as the actual number of atoms of each element present in one molecule. C_6H_6 is the molecular formula of benzene indicating that six carbon atoms and six hydrogen atoms are present in a molecule of benzene. Thus,

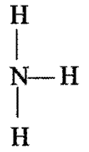
$$\text{Molecular formula} = n \times \text{Empirical formula}$$

where, $$n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}}$$

Molecular formula gives the following informations:

(i) Various elements present in the molecule.
(ii) Number of atoms of various elements in the molecule.
(iii) Mass ratio of the elements present in the molecule. The mass ratio of carbon and oxygen in CO_2 molecule is 12 : 32 or 3 : 8.
(iv) Molecular mass of the substance.
(v) The number written before the formula indicates the number of molecules, *e.g.*, $2CO_2$ means 2 molecules of carbon dioxide.

(iii) Structural formula: It represents the way in which atoms of various elements present in the molecule are linked with one another. For example, ammonia is represented as:



The formula indicates that three hydrogen atoms are linked to one nitrogen atom by three single covalent bonds.

1.17 PERCENTAGE COMPOSITION OF A COMPOUND

Percentage composition of a compound is the relative mass of the each of the constituent element in 100 parts of it. It is readily calculated from the formula of the compound. Molecular mass of a compound is obtained from its formula by adding up the masses of all the atoms of the constituent elements present in the molecule.

Let the molecular mass of a compound be M and X be the mass of an element in the molecule.

$$\text{Percentage of element} = \frac{\text{Mass of element}}{M} \times 100$$

$$= \frac{X}{M} \times 100$$

Example 31. *Calculate the percentage composition of calcium nitrate.*

Solution: The formula of calcium nitrate is $Ca(NO_3)_2$.

Thus, the formula mass or molecular mass

= At. mass of Ca + 2 × At. mass of N + 6 × At. mass of oxygen

$= 40 + 2 \times 14 + 6 \times 16$

$= 164$

$$\%\text{ of Ca} = \frac{40}{164} \times 100 = 24$$

$$\%\text{ of N} = \frac{28}{164} \times 100 = 17$$

$$\%\text{ of O} = 100 - (24 + 17) = 59$$

Example 32. *Determine the percentage of water of crystallisation, iron, sulphur and oxygen in pure ferrous sulphate* ($FeSO_4 \cdot 7H_2O$).

Solution: The formula mass of ferrous sulphate

$$= \text{At. mass of Fe} + \text{At. mass of S} + 4 \times \text{At. mass of oxygen} + 7 \times \text{Mol. mass of } H_2O$$

$$= 56.0 + 32.0 + 4 \times 16.0 + 7 \times 18.0$$

$$= 278.0$$

So, $\% \text{ of water of crystallisation} = \frac{126}{278} \times 100 = 45.32$

$$\% \text{ of iron} = \frac{56}{278} \times 100 = 20.14$$

$$\% \text{ of sulphur} = \frac{32}{278} \times 100 = 11.51$$

$$\% \text{ of oxygen} = \frac{64}{278} \times 100 = 23.02$$

(Oxygen present in water molecules is not taken into account.)

Example 33. *It is found that* 16.5 g *of metal combine with oxygen to form* 35.60 g *of metal oxide. Calculate the percentage of metal and oxygen in the compound.*

Solution:

$$\text{Mass of oxygen in oxide} = (35.60 - 16.50) = 19.10 \text{ g}$$

$$\% \text{ of metal} = \frac{16.50}{35.60} \times 100 = 46.3$$

$$\% \text{ of oxygen} = \frac{19.10}{35.60} \times 100 = 53.7$$

Example 34. *Hydrogen and oxygen are combined in the ratio* 1 : 16 *by mass in hydrogen peroxide. Calculate the percentage of hydrogen and oxygen in hydrogen peroxide.*

Solution: 17 parts of hydrogen peroxide contain hydrogen = 1 part

100 parts of hydrogen peroxide contain hydrogen

$$= \frac{1}{17} \times 100 = 5.88$$

$$\% \text{ of oxygen} = (100 - 5.88) = 94.12$$

Example 35. *On analysis of an impure sample of sodium chloride, the percentage of chlorine was found to be* 45.5. *What is the percentage of pure sodium chloride in the given sample?*

Solution: The molecular mass of pure sodium chloride (NaCl)

$$= \text{At. mass of Na} + \text{At. mass of chlorine}$$

$$= (23 + 35.5) = 58.5$$

% of chlorine in pure NaCl

$$= \frac{35.5}{58.4} \times 100 = 60.6$$

Thus,

% of purity of NaCl in the sample

$$= \frac{45.5}{60.6} \times 100 = 75$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

11. A gas mixture contains 50% helium and 50% methane by volume. What is the percentage by mass of methane in the mixture? [CEE (Kerala) 2004]

(a) 19.97% (b) 20.05% (c) 50% (d) 75%
(e) 80.03%

[Ans. (e)]

[Hint: Molar and volume ratio will be same, *i.e.*, 1 : 1.

∴ Mass of 1 mole CH_4 and He will be 16 and 4 g respectively.

$$\text{Percentage by mass of } CH_4 = \frac{\text{Mass of } CH_4}{\text{Total mass}} \times 100 = \frac{16}{20} \times 100 \approx 80\%]$$

12. The atomic composition of the entire universe is approximately given in the table below:

Atom	% of total no. of atoms
H	93
He	7

Hydrogen atoms constitute what percentage of the universe by mass?

(a) 77% (b) 23% (c) 37% (d) 73%

[Ans. (a)]

[Hint: Mass of 93 'H' atoms = 93 amu

Mass of 7 'He' atoms = 28 amu

$$\% \text{ Hydrogen by mass} = \frac{93}{(93 + 28)} \times 100 = 77\%]$$

13. Which pair of species has same percentage of carbon?

(a) CH_3COOH and $C_6H_{12}O_6$
(b) CH_3COOH and C_2H_5OH
(c) $HCOOCH_3$ and $C_{12}H_{22}O_{11}$
(d) $C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$

[Ans. (a)]

[Hint: Percentage of carbon in acetic acid $= \frac{24}{60} \times 100 = 40\%$

Percentage of carbon in $C_6H_{12}O_6 = \frac{72}{180} \times 100 = 40\%$]

14. Which of the following alkanes has 75% of carbon?

(a) C_2H_6 (b) CH_4 (c) C_3H_8 (d) C_4H_{10}

[Ans. (b)]

[Hint: Percentage of carbon in methane $= \frac{12}{16} \times 100 = 75\%$]

15. Which of the following two oxides of nitrogen have 30.5% nitrogen?

(a) NO (b) NO_2 (c) N_2O_4 (d) N_2O_5

[Ans. (b) and (c)]

[Hint: Percentage of nitrogen in $NO_2 = \frac{14}{46} \times 100 = 30.5\%$

Percentage of nitrogen in $N_2O_4 = \frac{28}{92} \times 100 = 30.5\%$]

1.18 DETERMINATION OF EMPIRICAL AND MOLECULAR FORMULAE

The following steps are followed to determine the empirical formula of the compound :

(i) The percentage composition of the compound is determined by quantitative analysis.

(ii) The percentage of each element is divided by its atomic mass. It gives atomic ratio of the elements present in the compound.

(iii) The atomic ratio of each element is the divided by the minimum value of atomic ratio as to get the simplest ratio of the atoms of elements present in the compound.

(iv) If the simplest ratio is fractional, then values of simplest ratio of each element is multiplied by a smallest integer to get a simplest whole number for each of the element.

(y) To get the empirical formula, symbols of various elements present are written side by side with their respective whole number ratio as a subscript to the lower right hand corner of the symbol.

The molecular formula of a substance may be determined from the empirical formula if the molecular mass of the substance is known. The molecular formula is always a simple multiple of empirical formula and the value of simple multiple is obtained by dividing molecular mass with empirical formula mass.

Example 36. *Calculate the empirical formula for a compound that contains* 26.6% *potassium,* 35.4% *chromium and* 38.1% *oxygen.*

[*Given* $K = 39.1; Cr = 52; O = 16$]

Solution:

Element	Percentage	Atomic mass	Relative number of atoms	Simplest ratio	Simplest whole number ratio
Potassium	26.6	39.1	$\frac{26.6}{39.1} = 0.68$	$\frac{0.68}{0.68} = 1$	$1 \times 2 = 2$
Chromium	35.4	52.0	$\frac{35.4}{52} = 0.68$	$\frac{0.68}{0.68} = 1$	$1 \times 2 = 2$
Oxygen	38.1	16.0	$\frac{38.1}{16} = 2.38$	$\frac{2.38}{0.68} = 3.5$	$3.5 \times 2 = 7$

Therefore, empirical formula is $K_2Cr_2O_7$.

Example 37. *A compound contains* 34.8% *oxygen,* 52.2% *carbon and* 13.0% *hydrogen. What is the empirical formula mass of the compound?*

Solution:

Element	Percentage	Atomic mass	Relative number of atoms	Simplest ratio
Oxygen	34.8	16	$\frac{34.8}{16} = 2.175$	$\frac{2.175}{2.175} = 1$
Carbon	52.2	12	$\frac{52.2}{12} = 4.35$	$\frac{4.35}{2.175} = 2$
Hydrogen	13.0	1	$\frac{13.0}{1} = 13.0$	$\frac{13.0}{2.175} = 6$

The empirical formula is C_2H_6O.

Empirical formula mass $= (2 \times 12) + (6 \times 1) + 16 = 46$

Example 38. *A compound of carbon, hydrogen and nitrogen contains these elements in the ratio* 9 : 1 : 3.5. *Calculate the empirical formula. If its molecular mass is* 108, *what is the molecular formula?*

Solution:

Element	Element ratio	Atomic mass	Relative number of atoms	Simplest ratio
Carbon	9	12	$\frac{9}{12} = 0.75$	$\frac{0.75}{0.25} = 3$
Hydrogen	1	1	$\frac{1}{1} = 1$	$\frac{1}{0.25} = 4$
Nitrogen	3.5	14	$\frac{3.5}{14} = 0.25$	$\frac{0.25}{0.25} = 1$

The empirical formula $= C_3H_4N$

Empirical formula mass $= (3 \times 12) + (4 \times 1) + 14 = 54$

$$n = \frac{\text{Mol. mass}}{\text{Emp. mass}} = \frac{108}{54} = 2$$

Thus, molecular formula of the compound

$$= 2 \times \text{Empirical formula}$$

$$= 2 \times C_3H_4N = C_6H_8N_2$$

Example 39. *A carbon compound containing only carbon and oxygen has an approximate molecular mass of* 290. *On analysis, it is found to contain* 50% *by mass of each element. What is the molecular formula of the compound?*

Solution:

Element percentage	Atomic mass	Relative number of atoms	Simplest ratio	Simplest whole number ratio
Carbon 50.0	12	4.166	$\frac{4.166}{3.125} = 1.33$	4
Oxygen 50.0	16	3.125	$\frac{3.125}{3.125} = 1$	3

The empirical formula $= C_4O_3$

Empirical formula mass $= (4 \times 12) + (3 \times 16) = 96$

Molecular mass $= 290$

$$n = \frac{\text{Mol. mass}}{\text{Emp. mass}} = \frac{290}{96} = 3 \text{ approximately}$$

Molecular formula $= n \times$ Empirical formula

$$= 3 \times C_4O_3 = C_{12}O_9$$

Example 40. *A compound on analysis, was found to have the following composition: (i) Sodium* $= 14.31\%$, *(ii) Sulphur* $= 9.97\%$, *(iii) Oxygen* $= 69.50\%$, *(iv) Hydrogen* $= 6.22\%$. *Calculate the molecular formula of the compound assuming that whole of hydrogen in the compound is present as water of crystallisation. Molecular mass of the compound is* 322.

Solution:

Element	Percentage	Atomic mass	Relative number of atoms	Simplest ratio
Sodium	14.31	23	0.622	$\frac{0.622}{0.311} = 2$
Sulphur	9.97	32	0.311	$\frac{0.311}{0.311} = 1$
Hydrogen	6.22	1	6.22	$\frac{6.22}{0.311} = 20$
Oxygen	69.50	16	4.34	$\frac{4.34}{0.311} = 14$

The empirical formula $= Na_2SH_{20}O_{14}$

Empirical formula mass $= (2 \times 23) + 32 + (20 \times 1) + (14 \times 16)$
$= 322$

Molecular mass $= 322$

Molecular formula $= Na_2SH_{20}O_{14}$

Whole of the hydrogen is present in the form of water. Thus, 10 water molecules are present in the molecule.

So, molecular formula $= Na_2SO_4 \cdot 10H_2O$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

16. An organic compound contains 49.30% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is: **[CET (Kerala) 2004]**

(a) $C_3H_8O_2$ (b) $C_3H_{10}O_2$ (c) C_6H_9O (d) $C_4H_{10}O_2$
(e) $C_6H_{10}O_4$

[Ans. (e)]

[Hint: Molecular mass $= 2 \times 73 = 146$

$$C = \frac{\%}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass}} = \frac{49.30}{100} \times \frac{146}{12} = 6$$

$$H = \frac{\%}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass}} = \frac{6.84}{100} \times \frac{146}{1} = 10$$

$$O = \frac{\%}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass}} = \frac{43.86}{100} \times \frac{146}{16} = 4$$

Molecular formula $= C_6H_{10}O_4$

Molecular mass$= 12 \times 6 + 10 \times 1 + 16 \times 4 = 146$

'Or'

Element	Percentage	Atomic mass	Relative number of atoms	Simplest ratio
Carbon	49.30	12	4.10	$1.5 \times 2 = 3$
Hydrogen	6.84	1	6.84	$2.5 \times 2 = 5$
Oxygen	43.86	16	2.74	$1 \times 2 = 2$

The empirical formula $= C_3H_5O_2$

$$n = \frac{2 \times 73}{73} = 2$$

Molecular formula $= 2 \times C_3H_5O_2 = C_6H_{10}O_4$]

17. A compound has an empirical formula C_2H_4O. An independent analysis gave a value of 132.16 for its molecular mass. What is the correct molecular formula? **[CET (Kerala) 2004]**

(a) $C_4H_4O_5$ (b) $C_{10}H_{12}$
(c) C_7O_3 (d) $C_6H_{12}O_3$
(e) $C_4H_8O_5$

[Ans. (d)]

[Hint: Molecular formula $= (C_2H_4O)_n$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{132.16}{44} = 3$$

Molecular formula $= (C_2H_4O)_3 = C_6H_{12}O_3$]

18. An organic compound containing C and H has 92.30% carbon. Its empirical formula is:

(a) CH (b) CH_3
(c) CH_2 (d) CH_4

[Ans. (a)]

[Hint: Percentage of carbon $= \frac{12}{13} \times 100 = 92.30\%$

'Or'

Element	Percentage	Atomic mass	Relative number of atoms	Simplest ratio
Carbon	92.30	12	7.69	1
Hydrogen	7.70	1	7.70	1

Empirical formula = CH]

19. Two oxides of a metal contain 50% and 40% of metal *M* respectively. If the formula of first oxide is *M*O, the formula of 2nd oxide will be:

(a) MO_2 (b) M_2O_3
(c) M_2O (d) M_2O_5

[Ans. (b)]

[Hint:

Compound 1		Compound 2	
M	O	*M*	O
50%	50%	40%	60%
50 g	50 g	40 g	60 g
1 g	$\frac{50}{50} = 1$ g	1 g	$\frac{60}{40} = 1.5$ g
2 g	2 g	2 g	3 g

Formula: MO M_2O_3]

20. Two elements *X* and *Y* have atomic mass 75 and 16 respectively. They combine to give a compound having 75.8% *X*. The formula of the compound is:

(a) XY (b) X_2Y
(c) X_2Y_2 (d) X_2Y_3

[Ans. (d)]

[Hint: Molecular mass of $X_2Y_3 = 2 \times 75 + 3 \times 16 = 198$

$$\text{Percentage of } X = \frac{150}{198} \times 100 = 75.80\%$$

'Or'

Element	Percentage	Atomic mass	Relative number of atoms	Simplest ratio
X	75.80	75	1.01	$1 \times 2 = 2$
Y	24.20	16	1.51	$1.5 \times 2 = 3$

Formula = X_2Y_3]

21. The crystalline salt $Na_2SO_4 \cdot xH_2O$ on heating loses 55.9% of its mass. The formula of crystalline salt is:

(a) $Na_2SO_4 \cdot 5H_2O$ (b) $Na_2SO_4 \cdot 7H_2O$
(c) $Na_2SO_4 \cdot 2H_2O$ (d) $Na_2SO_4 \cdot 10H_2O$
(e) $Na_2SO_4 \cdot 6H_2O$ **[PMT (Kerala) 2007]**

[Ans. (d)]

[Hint: Molecular mass of $Na_2SO_4 \cdot 10H_2O$

$$= 46 + 96 + 180 = 322 \text{ amu}$$

$$\% \text{ by mass of } H_2O = \frac{180}{322} \times 100 = 55.9\%]$$

1.19 CHEMICAL EQUATION

A chemical equation is a symbolic representation of a chemical change.

The substances, in which the chemical change is brought, are called reactants and the substances which come into existence as the result of chemical change are called products. The relationship between reactants and products is represented in the form of a chemical equation. The symbols or formulae of the reactants are written on left hand side of equality (=) or → sign and the symbols or formulae of products on right hand side. The symbols or formulae on both the sides are added by + sign. Such an equation is known as skeleton equation. The equation becomes balanced when total number of atoms of various elements are made equal on both the sides. Gases are always written in molecular form.

$$KClO_3 \longrightarrow KCl + O_2$$

This is the skeleton equation as it only represents reactant and products involved in the chemical change but the following equation is a balanced equation as the number of atoms of various elements is equal on both sides.

$$\underset{\text{Reactant}}{2KClO_3} = \underbrace{2KCl + 3O_2}_{\text{Products}}$$

The following notations are also used in chemical equations as to provide more information about chemical change:

(i) Upper arrow (↑) is written immediately after the gaseous product.
(ii) Lower arrow (↓) is written immediately after the insoluble substance (solid) which deposits from a solution.
(iii) Symbols, (*s*) for solid, (*l*) for liquid and (*g*) for gas are also written to represent the physical state of the reactants and products.
(iv) Symbol (*aq.*) is written for substances dissolved in water.
(v) Symbol (Δ) is written over an arrow or over an equality sign to represent heating.

Information Obtained from Chemical Equation

A balanced chemical equation provides the following informations:

(i) What are the reactants and products involved in the chemical change?
(ii) The relative number of molecules of reactants and products.
(iii) The relative number by parts of mass of reactants and products.
(iv) Relative volumes of gaseous reactants and products.

For example, consider the following reaction:

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g)$$

This equation tells us that methane and oxygen are reactants and carbon dioxide and water are products. One molecule of methane reacts with two molecules of oxygen to produce one molecule of CO_2 and two molecules of water or one mole of methane reacts with two moles of oxygen to produce one mole of carbon dioxide and two moles of water or 16 g of methane reacts with 64 g of oxygen to produce 44 g of CO_2 and 36 g of water. This equation also tells that 1 vol. of methane reacts with 2 vol. of oxygen to produce 1 vol. of CO_2 and 2 vol. of steam under similar conditions of temperature and pressure.

Limitations of Chemical Equation

A chemical equation fails to provide the following informations:

(i) Actual concentration of the reactants taken and the actual concentration of the products obtained.
(ii) Time taken for the completion of the chemical change.
(iii) Conditions applied for bringing the chemical change.
(iv) Whether the reaction is reversible or irreversible.

The following efforts have been made to make the chemical equations more informative by introducing:

(i) Experimental conditions: If a particular chemical change occurs under certain temperature and pressure conditions, these are mentioned above and below the (→) or (=) sign.

$$N_2 + 3H_2 \xrightarrow[450°C]{200 \text{ atm}} 2NH_3$$

If the reaction occurs in presence of a catalyst, it is written above the (→) or (=) sign.

$$2SO_2 + O_2 \xrightarrow{Pt} 2SO_3$$

(ii) Heat evolved or absorbed: Heat evolved or absorbed in a chemical change can be represented by adding or subtracting the amount of heat on right hand side.

$$N_2 + O_2 \longrightarrow 2NO - 43.2 \text{ kcals}$$
$$C + O_2 \longrightarrow CO_2 + 94.3 \text{ kcals}$$

(iii) Reversible or irreversible nature: Reversible reactions are shown by changing the sign of equality (=) or arrow (→) with sign of double arrow ($\rightleftharpoons$).

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Types of Chemical Equations

Chemical equations are of two types:

(i) Molecular equations
(ii) Ionic equations.

Molecular equations are those in which reactants and products are represented in the form of molecules.

$$BaCl_2 + Na_2SO_4 = BaSO_4 \downarrow + 2NaCl$$
$$2NaOH + H_2SO_4 = Na_2SO_4 \downarrow + 2H_2O$$

Ionic equations are those in which reactants and products are written in ionic form. The molecular equation

$$BaCl_2 + Na_2SO_4 = BaSO_4 \downarrow + 2NaCl$$

can be written in ionic form as:

$$Ba^{2+} + 2Cl^- + 2Na^+ + SO_4^{2-} = BaSO_4 \downarrow + 2Na^+ + 2Cl^-$$
$$Ba^{2+} + SO_4^{2-} = BaSO_4 \downarrow$$

Note: Calculations based on chemical equations have been dealt in the chapter 'Stoichiometry' in 'Inorganic Chemistry'.

1.20 MEASUREMENT IN CHEMISTRY: FUNDAMENTAL AND DERIVED UNITS

Chemistry is an experimental science. An experiment always involves observation of a phenomenon under certain set of conditions. The quantitative scientific observation generally requires the measurement of one or more physical quantities such as mass, length, density, volume, pressure, temperature, etc.

A physical quantity is expressed in terms of a number and a unit. Without mentioning the unit, the number has no meaning. For example, the distance between two points is "four" has no meaning unless a specific unit (inch, centimetre, metre, etc.,) is associated with the number. The units of physical quantities depend on three basic units, *i.e.*, units of mass, length and time. Since, these are independent units and cannot be derived from any other units, they are called **fundamental units.** It was soon realised that the three fundamental units cannot describe all the physical quantities such as temperature, intensity of luminosity, electric current and the amount of the substance. Thus, seven units of measurement, namely mass, length, time, temperature, electric current, luminous intensity and amount of substance are taken as **basic units.** All other units can be derived from them and are, therefore, called **derived units.** The units of area, volume, force, work, density, velocity, energy, etc., are all derived units.

SI Units of Measurement

Various systems of units were in use prior to 1960. The common ones are the following:

(i) The English or FPS system: The system uses the **foot,** the **pound** and the **second** for length, mass and time measurements respectively. It is not used now-a-days.

(ii) MKS system: Here M stands for **metre** (a unit of length), K for **kilogram** (a unit of mass) and S for **second** (a unit of time). This is a decimal system.

(iii) CGS system: Here the unit of length is **centimetre,** the unit of mass is **gram** and the unit of time is **second.** It is also a decimal system.

MKS system often known as metric system was very popular throughout the world, but the drawback with this system was that a number of different metric units for the same quantity were used in different parts of the world. In 1964, the National Bureau of Standards adopted a slightly modified version of the metric system, which had been officially recommended in 1960 by an international body, **General Conference of Weights and Measures.** This revised set of units is known as the **International System of Units** (abbreviated SI). Now the SI units have been accepted by the scientists all over the world in all branches of science, engineering and technology.

The SI system have seven basic units. The various fundamental quantities that are expressed by these units along with their symbols are tabulated below:

Basic physical quantity	Unit	Symbol
Length	Metre	m
Mass	Kilogram	kg
Time	Second	s
Temperature	Kelvin	K
Electric current	Ampere	amp or A
Luminous intensity	Candela	cd
Amount of substance	Mole	mol

Sometimes, submultiples and multiples are used to reduce or enlarge the size of the different units. The names and symbols of sub-multiples and multiples are listed in the table given below.

The name for the base unit for mass, the kilogram, already contains a prefix. The names of other units of mass are obtained by substituting other prefixes for prefix kilo. The names of no other base units contain prefixes.

The use of SI system is slowly growing, however, older systems are still in use. Furthermore, the existence of older units in scientific literature demands that one must be familiar with both old and new systems.

Submultiples			Multiples		
Prefix	**Symbol**	**Sub-multiple**	**Prefix**	**Symbol**	**Multiple**
deci	d	10^{-1}	deca	da	10
centi	c	10^{-2}	hecto	h	10^2
milli	m	10^{-3}	kilo	k	10^3
micro	μ	10^{-6}	mega	M	10^6
nano	n	10^{-9}	giga	G	10^9
pico	p	10^{-12}	tera	T	10^{12}
femto	f	10^{-15}	peta	P	10^{15}
atto	a	10^{-18}	exa	E	10^{18}
zepto	z	10^{-21}	zeta	Z	10^{21}
yocto	y	10^{-24}	yotta	Y	10^{24}

Greek Alphabets

Alpha	A	α	Nu	N	ν
Beta	B	β	Xi	Ξ	ξ
Gamma	Γ	γ	Omicron	O	o
Delta	Δ	δ	Pi	Π	π
Epsilon	E	ε	Rho	P	ρ
Zeta	Z	ζ	Sigma	Σ	σ
Eta	H	η	Tau	τ	τ

Theta	Θ	θ	Upsilon	ϒ	υ
Iota	Ι	ι	Phi	Φ	ϕ
Kappa	Κ	κ	Chi	Χ	χ
Lambda	Λ	λ	Psi	Ψ	ψ
Mu	Μ	μ	Omega	Ω	ω

Numerical Prefix

Prefix	Value	Prefix	Value
Hemi	(1/2)	Deca	10
Mono	1	Undeca	11
Sesqui	$1\frac{1}{2}$	Dodeca	12
Di or Bi	2	Trideca	13
Tri	3	Tetradeca	14
Tetra	4	Pentadeca	15
Penta	5	Hexadeca	16
Hexa	6	Heptadeca	17
Hepta	7	Octadeca	18
Octa	8	Nonadeca	19
Nona	9	Eicosa	20

SI Units for Some Common Derived Quantities

(a) $$\text{Area} = \text{length} \times \text{breadth}$$
$$= \text{m} \times \text{m} = \text{m}^2 \text{ [square metre]}$$

(b) $$\text{Volume} = \text{length} \times \text{breadth} \times \text{height}$$
$$= \text{m} \times \text{m} \times \text{m} = \text{m}^3 \text{ [cubic metre]}$$

(c) $$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{\text{kg}}{\text{m}^3} = \text{kg m}^{-3}$$

(d) $$\text{Speed} = \frac{\text{distance covered}}{\text{time}} = \frac{\text{metre}}{\text{time}} = \text{m s}^{-1}$$

(e) $$\text{Acceleration} = \frac{\text{change in velocity}}{\text{time taken}} = \frac{\text{m s}^{-1}}{\text{s}} = \text{m s}^{-2}$$

(f) $$\text{Force} = \text{mass} \times \text{acceleration}$$
$$= \text{kg} \times \text{m s}^{-2}$$
$$= \text{kg m s}^{-2} \text{ (Newton, abbreviated as N)}$$

(g) $$\text{Pressure} = \text{force per unit area}$$
$$= \frac{\text{kg m s}^{-2}}{\text{m}^2} = \text{kg m}^{-1}\text{ s}^{-2} \text{ or Nm}^{-2}$$
(Pascal—Pa)

(h) $$\text{Energy} = \text{force} \times \text{distance travelled}$$
$$= \text{kg m s}^{-2} \times \text{m}$$
$$= \text{kg m}^2 \text{ s}^{-2}$$
(joule — J)

Some Old Units Still in Use

The use of some of the old units is still permitted. The 'litre', for example, which is defined as 1 cubic decimetre is used frequently by chemists. Certain other units which are not a part of SI units are still retained for a limited period of time. The term atmosphere (atm), the unit of pressure, falls into this category. Few of the old units along with conversion factors are given below:

Length: The interatomic distances are reported in units of angstrom (Å), nanometre (nm) or picometre (pm).

$$1\,\text{Å} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$$
$$1\,\text{nm} = 10^{-7} \text{ cm} = 10^{-9} \text{ m} = 10\,\text{Å}$$
$$1\,\text{pm} = 10^{-10} \text{ cm} = 10^{-12} \text{ m} = 10^{-2}\,\text{Å}$$
$$1\,\text{nm} = 10^{3} \text{ pm}$$

Mass: The basic unit of mass is generally taken as gram (g). The gram is 10^{-3} kg.

$$1 \text{ kilogram (kg)} = 10^{3} \text{ g}$$
$$1 \text{ milligram (mg)} = 10^{-3} \text{ g}$$
$$1 \text{ microgram } (\mu\text{g}) = 10^{-6} \text{ g}$$

While dealing with atoms and molecules, the term atomic mass unit (amu) is used. One amu is taken exactly as $\frac{1}{12}$ of the mass of an atom of the carbon isotope, C^{12}.

$$1 \text{ amu} = 1.6605 \times 10^{-24} \text{ g} = 1.6605 \times 10^{-27} \text{ kg}$$

Volume: The units of volume are reported as cubic centimetre (cm^3) and cubic decimetre (dm^3). Cubic decimetre is termed **litre** while cubic centimetre is termed **millilitre.**

$$1 \text{ litre (lit or L)} = (10\,\text{cm})^3 = 1000\,\text{cm}^3 = 10^{-3} \text{ m}^3$$
$$1 \text{ millilitre (mL)} = (1\,\text{cm})^3 = 1\,\text{cm}^3 \text{ (cc)} = 10^{-6} \text{ m}^3$$

So, $1 \text{ litre} = 1000 \text{ mL}$

Temperature: The **celsius temperature scale** which is not a part of SI system, is employed in scientific studies. This scale is based on the assignment of 0°C to the normal freezing point of water and 100°C to the normal boiling point of water. The celsius scale was formerly called the **centigrade scale.**

The unit of temperature in SI system is **Kelvin.** A degree on the kelvin scale has the same magnitude as the degree on the celsius scale but zero on the kelvin scale is equal to –273.15°C. The temperature (0 K) is often referred to as **absolute zero.**

So, $$\text{K} = (°\text{C} + 273.15)$$
or $$°\text{C} = (\text{K} - 273.15)$$

There is another important temperature scale known as **fahrenheit scale.** In this scale, the normal freezing point of water is 32°F and normal boiling point is 212°F. Thus, 100°C equals 180°F. Both the scales are related by the following equations:

$$°\text{C} = \frac{5}{9} \times (°\text{F} - 32)$$ [since, 100 parts on celsius scale = 180 parts on fahrenheit scale]

$$°\text{F} = \frac{9}{5} \times (°\text{C}) + 32$$

Pressure: There are three non-SI units for pressure which are commonly used.

(a) Atmosphere (atm) is defined as the pressure exerted by a column of mercury of 760 mm or 76 cm height at 0°C.

(b) Torr is defined as the pressure exerted by a 1 mm column of mercury at 0°C.

(c) Millimetre of mercury (mm Hg).

These three units are related as:

$$1\,\text{atm} = 760\,\text{torr} = 760\,\text{mm Hg} = 76\,\text{cm Hg} = 1.013 \times 10^5\ \textbf{Pa}$$

Energy: Calorie has been used in the past as a unit of energy measurement. The calorie was defined as the amount of heat required to raise the temperature of one gram of water from 14.5°C to 15.5 °C. One calorie is defined as exactly equal to 4.184 joules.

$$1\,\text{cal} = 4.184\,\text{J} \qquad \text{or} \qquad 1\,\text{J} = 0.2390\,\text{cal}$$

$$1\,\text{kcal} = 1000\,\text{cal} = 4.184\,\text{kJ}$$

Conversion factors

$$1\,\text{angstrom (Å)} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm} = 10^{2}\ \text{pm}$$

$$1\,\text{inch} = 2.54\,\text{cm} \qquad \text{or} \qquad 1\,\text{cm} = 0.394\,\text{inch}$$

$$39.37\,\text{inch} = 1\,\text{metre} \qquad 1\,\text{km} = 0.621\,\text{mile}$$

$$1\,\text{kg} = 2.20\,\text{pounds (lb)} \qquad 1\,\text{g} = 0.0353\,\text{ounce (o)}$$

$$1\,\text{pound (lb)} = 453.6\,\text{g}$$

$$\begin{aligned}1\,\text{atomic mass unit (amu)} &= 1.6605 \times 10^{-24}\,\text{g}\\ &= 1.6605 \times 10^{-27}\,\text{kg}\\ &= 1.492 \times 10^{-3}\ \text{erg} = 1.492 \times 10^{-10}\ \text{J}\\ &= 3.564 \times 10^{11}\ \text{cal} = 9.310 \times 10^{8}\ \text{eV}\\ &= 931.48\,\text{MeV}\end{aligned}$$

$$\begin{aligned}1\,\text{atmosphere (atm)} &= 760\,\text{torr} = 760\,\text{mm Hg} = 76\,\text{cm Hg}\\ &= 1.01325 \times 10^{5}\ \text{Pa}\end{aligned}$$

$$\begin{aligned}1\,\text{calorie (cal)} &= 4.1840 \times 10^{7}\ \text{erg} = 4.184\ \text{J}\\ &= 2.613 \times 10^{19}\ \text{eV}\end{aligned}$$

$$1\,\text{coulomb (coul)} = 2.9979 \times 10^{9}\ \text{esu}$$

$$1\,\text{curie (Ci)} = 3.7 \times 10^{10}\ \text{disintegrations sec}^{-1}$$

$$\begin{aligned}1\,\text{electron volt (eV)} &= 1.6021 \times 10^{-12}\text{erg} = 1.6021 \times 10^{-19}\,\text{J}\\ &= 3.827 \times 10^{-20}\,\text{cal}\\ &= 23.06\,\text{kcal mol}^{-1}\end{aligned}$$

$$1\,\text{erg} = 10^{-7}\,\text{J} = 2.389 \times 10^{-8}\,\text{cal} = 6.242 \times 10^{11}\,\text{eV}$$

$$1\,\text{electrostatic unit (esu)} = 3.33564 \times 10^{-10}\ \text{coul}$$

$$1\,\text{faraday}\ (F) = 9.6487 \times 10^{4}\ \text{coul}$$

$$1\,\text{dyne (dyne)} = 10^{-5}\ \text{N}$$

$$1\,\text{joule} = 10^{7}\ \text{erg} = 0.2390\,\text{cal}$$

$$\begin{aligned}1\,\text{litre} &= 1000\,\text{cc} = 1000\,\text{mL} = 1\,\text{dm}^{3}\\ &= 10^{-3}\ \text{m}^{3}\end{aligned}$$

Values of Some Useful Constants

Fundamental constant	Value in old units	Value in SI units
Avogadro's number (N)	6.023×10^{23} mol^{-1}	6.023×10^{23} mol^{-1}
Atomic mass unit (amu)	1.6605×10^{-24} g	1.6605×10^{-27} g
Bohr radius (a_0)	0.52918 Å = 0.52918 $\times 10^{-8}$ cm	5.2918×10^{-11} m
Boltzmann constant (k)	1.3807×10^{-16}erg deg^{-1}	1.3807×10^{-23} JK^{-1}
Charge on electron (e)	(–) 4.8029×10^{-10} esu	(–) 1.6021×10^{-19} coul
Charge to mass ratio e/m of electron	1.7588×10^{8} coul g^{-1}	1.7588×10^{11}coul kg^{-1}
Electron rest mass (m_e)	9.1091×10^{-28} g	9.1091×10^{-31} kg
Gas constant (R)	0.0821 lit atm deg^{-1}mol^{-1} 8.314×10^{7}erg deg^{-1}mol^{-1} $1.987 \simeq 2.0$ cal deg^{-1}mol^{-1}	8.314 J K^{-1} mol^{-1}
Molar volume at NTP (V_m)	22.4 L mol^{-1}	22.4×10^{-3} m^3 mol^{-1}
Planck's constant (h)	6.6252×10^{-27} erg sec	6.6252×10^{-34} J sec
Proton mass (m_p)	1.6726×10^{-24} g	1.6726×10^{-27} kg
Neutron mass (m_n)	1.67495×10^{-24} g	1.67495×10^{-27} kg
Rydberg constant (R_z)	109678 cm^{-1}	1.09678×10^{7} m^{-1}
Velocity of light (c) in vacuum	2.9979×10^{10} cm sec^{-1} or 186281 miles sec^{-1}	2.9979×10^{8} m sec^{-1}
Faraday (F)	9.6487×10^{4} C / equiv. or 96500 C/equiv.	9.6487×10^{4}C / equiv.
$\dfrac{1}{4\pi\varepsilon_0}$	1	0.8988×10^{10} N m^{2}C^{-2} or 9×10^{9} N m^{2}C^{-2}

Derived SI Units

Quantity with Symbol	Unit (SI)	Symbol
Velocity (v)	metre per sec	m s^{-1}
Area (A)	square metre	m^2
Volume (V)	cubic metre	m^3
Density (ρ)	kilogram m^{-3}	kg m^{-3}
Acceleration (a)	metre per sec^2	m s^{-2}
Energy (E)	joule (J)	kg m^2 s^{-2}
Force (F)	newton (N)	kg m s^{-2}

Power (W)	watt (W)	$J\ s^{-1}$; $kg\ m^2\ s^{-3}$
Pressure (P)	pascal (Pa)	$N\ m^{-2}$
Resistance (R)	ohm (Ω)	$V\ A^{-1}$
Conduction (C)	ohm^{-1}, mho, siemens	$m^{-2}\ kg^{-1}\ s^3\ A^2$ or Ω^{-1}
Potential difference	volt (V)	$kg\ m^2\ s^{-3}\ A^{-1}$
Electrical charge	coulomb (C)	A-s (ampere-second)
Frequency (ν)	hertz (Hz)	cycle per sec
Magnetic flux × density	tesla (T)	$kg\ s^{-2}\ A^{-1} = N\ A^{-1}\ m^{-1}$

Popular Units and their SI Equivalents

Physical quantity	Unit with symbol	Equivalent in SI unit
Mass	1 amu	1 amu = 1.6605×10^{-27} kg
Energy	1 electron volt (eV)	1.602×10^{-19} joule
Length	1 Å	10^{-10} m (10^{-1} nm)
Volume	litre	$10^{-3}\ m^3 = dm^3$
Force	dyne	10^{-5} N
Pressure	1 atmosphere	760 torr (760 mm Hg) 101325 pa or 10^5 pa
	1 bar	101325 pa or 10^5 pa
	1 torr	133.322 $N\ m^{-2}$
Dipole moment	debye, 10^{-18} esu-cm	3.324×10^{-30} cm
Magnetic flux density	gauss (G)	10^{-4} T
Area of nuclear cross section	1 barn	$10^{-28}\ m^2$
Nuclear Diameter	1 fermi (1 femto)	10^{-15} m

Significant Figures

There is always some degree of uncertainty in every scientific measurement except in counting. The uncertainty in measurement mainly depends upon two factors:

(i) Skill and accuracy of the observer,

(ii) Limitation of the measuring scale.

To indicate the precision of a measurement, scientists use the term **significant figures.** The significant figures in a number are all certain digits plus one doubtful digit. The number of significant figures gives the information that except the digit at extreme right, all other digits are precise or reproducible. For example, mass of an object is 11.24 g. This value indicates that actual mass of the object lies between 11.23 g and 11.25 g. Thus, one is sure of first three figures (1, 1 and 2) but the fourth figure is somewhat inexact. The total significant figures in this number are four.

The following rules are observed in counting the number of significant figures in a given measured quantity:

(i) All non-zero digits are significant. For example,

42.3 has three significant figures.

243.4 has four significant figures.

24.123 has five significant figures.

(ii) A zero becomes significant figure if it appears between two non-zero digits. For example,

5.03 has three significant figures.

5.604 has four significant figures.

4.004 has four significant figures.

(iii) Leading zeros or the zeros placed to the left of the number are never significant. For example,

0.543 has three significant figures.

0.045 has two significant figures.

0.006 has one significant figure.

(iv) Trailing zeros or the zeros placed to the right of the number are significant. For example,

433.0 has four significant figures.

433.00 has five significant figures.

343.000 has six significant figures.

(v) In exponential notation, the numerical portion gives the number of significant figures. For example,

1.32×10^{-2} has three significant figures.

1.32×10^{4} has three significant figures.

(vi) The non-significant figures in the measurements are rounded off.

(a) If the figure following the last number to be retained is less than 5, all the unwanted figures are discarded and the last number is left unchanged, *e.g.*,

5.6724 is 5.67 to three significant figures.

(b) If the figure following the last number to be retained is greater than 5, the last figure to be retained is increased by 1 unit and the unwanted figures are discarded, *e.g.*,

8.6526 is 8.653 to four significant figures.

(c) If the figure following the last number to be retained is 5, the last figure is increased by 1 only in case it happens to be odd. In case of even number the last figure remains unchanged.

2.3524 is 2.4 to two significant figures.

7.4511 is 7.4 to two significant figures.

Calculations Involving Significant Figures

In most of the experiments, the observations of various measurements are to be combined mathematically, *i.e.*, added, subtracted, multiplied or divided as to achieve the final result. Since, all the observations in measurements do not have the same precision, it is natural that the final result cannot be more precise than the least precise measurement. The following two rules should be followed to obtain the proper number of significant figures in any calculation.

Rule 1: The result of an addition or subtraction in the numbers having different precisions should be reported to the same number of decimal places as are present in the number having the least number of decimal places. The rule is illustrated by the following examples:

(a) 33.3 ← (has only one decimal place)
3.11
0.313
Sum 36.723 ← (answer should be reported to one decimal place)

Correct answer = 36.7

(b) 3.1421
0.241
0.09 ← (has 2 decimal places)
Sum 3.4731 ← (answer should be reported to 2 decimal places)

Correct answer = 3.47

(c) 62.831 ← (has 3 decimal places)
− 24.5492
Difference 38.2818 ← (answer should be reported to 3 decimal places after rounding off)

Correct answer = 38.282

Rule 2: The answer to a multiplication or division is rounded off to the same number of significant figures as is possessed by the least precise term used in the calculation. Examples are:

(a) 142.06
× 0.23 ← (two significant figures)
32.6738 ← (answer should have two significant figures)

Correct answer = 33

(b) 51.028
× 1.31 ← (three significant figures)
66.84668

Correct answer = 66.8

(c) $\frac{0.90}{4.26} = 0.2112676$

Correct answer = 0.21

Note: (i) Same procedure is followed if an expression involves multiplication as well as division.
(ii) The presence of exact numbers in an expression does not affect the number of significant figures in the answer.

Examples are:

(a) $\frac{3.24 \times 0.0866}{5.046} = 0.055643$ (b) $\frac{4.28 \times 0.146 \times 3}{0.0418} = 44.84784$

Correct answer = 0.0556 Correct answer = 44.8

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *0.44 g of a hydrocarbon on complete combustion with oxygen gave 1.8 g water and 0.88 g carbon dioxide. Show that these results are in accordance with the law of conservation of mass.*

Solution: A hydrocarbon is a compound which consists of carbon and hydrogen only. It undergoes combustion forming carbon dioxide and water as products.

Formula of carbon dioxide = CO_2;
Molecular mass = 12 + 32 = 44 g
Formula of water = H_2O;
Molecular mass = 2 + 16 = 18 g

$$\text{Mass of carbon in 0.88 g of } CO_2 = \frac{12}{44} \times 0.88 = 0.24 \text{ g}$$

$$\text{Mass of hydrogen in 1.8 g of } H_2O = \frac{2}{18} \times 1.8 = 0.20 \text{ g}$$

Total masses of carbon and hydrogen in the products
= 0.24 + 0.20 = 0.44 g

This is equal to the mass of hydrocarbon before combustion.

Thus, the results are in accordance with the law of conservation of mass.

Example 2. *Calcium carbonate decomposes completely, on heating, into lime (CaO) and carbon dioxide (CO_2). 1 kg of calcium carbonate is completely decomposed by heat, when 560 g of lime are obtained. How much quantity of carbon dioxide in grams, moles and litres at NTP is produced in the process?*

Solution: According to law of conservation of mass,

Mass of lime + Mass of carbon dioxide = Mass of calcium carbonate

$$560 \text{ g} + \text{Mass of } CO_2 = 1000 \text{ g}$$

$$\text{Mass of } CO_2 = 1000 - 560 = 440 \text{ g}$$

$$\text{Molecular mass of } CO_2 = 12 + 32 = 44 \text{ g (1 mole)}$$

$$\text{No. of moles in 440 g of } CO_2 = \frac{440}{44} = 10$$

1 mole of CO_2 occupies volume at NTP = 22.4 litre

10 moles of CO_2 will occupy volume at NTP
= 22.4 × 10 = 224 litre

Example 3. *10 mL of hydrogen combine with 5 mL of oxygen to yield water. When 200 mL of hydrogen at NTP are passed over heated CuO, the CuO loses 0.144 g of its mass. Do these results correspond to the law of constant proportions?*

Solution: 1st Case:

$$\text{Mass of 10 mL hydrogen at NTP} = \frac{2}{22400} \times 10 = 0.00089 \text{ g}$$

$$\text{Mass of 5 mL of oxygen at NTP} = \frac{32}{22400} \times 5 = 0.00714 \text{ g}$$

$$\text{Mass of 22400 mL of Hg vapour at NTP} = \frac{8.923}{1000} \times 22400$$
$$= 199.87 \text{ g}$$

Hence, molecular mass of Hg = 199.87 g

(c) $\text{Approximate atomic mass} = \frac{6.4}{\text{Sp. heat}} = \frac{6.4}{0.033} \doteq 193.93 \text{ g}$

$$\text{Valency of Hg} = \frac{193.93}{100} \simeq 2 \text{ (nearest whole number)}$$

So, accurate atomic mass = Eq. mass × Valency

$$= 100 \times 2 = 200 \text{ g}$$

$$\text{Atomicity} = \frac{\text{Mol. mass}}{\text{At. mass}} = \frac{199.88}{200} \simeq 1$$

Hence, mercury molecules are monoatomic.

Example 23. *How many grams of CaO are required to neutralise 852 g of P_4O_{10}?* **(IIT 2005)**

Solution: The reaction will be:

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2$$
$$852 \text{ g } P_4O_{10} \equiv 3 \text{ mol } P_4O_{10}$$

1 mole of P_4O_{10} neutralises 6 moles of CaO.

∴ 3 moles of P_4O_{10} will neutralise 18 moles of CaO.

∴ Mass of CaO = 18 × 56 = 1008 g

Example 24. *If 1 grain is equal to 64.8 mg, how many moles of aspirin (mol. wt. = 169) are present in a 5 grain aspirin tablet?*

Solution: Mass of aspirin in the tablet = 64.8 × 5 = 324 mg

$$= 0.324 \text{ g}$$

$$\text{Number of moles} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{0.324}{169}$$
$$= 1.92 \times 10^{-3}$$

Example 25. *If the volume occupied in a crystal by a molecule of NaCl is 47×10^{-24} mL, calculate the volume of the crystal weighing 1 g.*

Solution: Number of molecules of NaCl

$$= \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23}$$
$$= \frac{1}{58.5} \times 6.023 \times 10^{23} = 1.03 \times 10^{22}$$

$$\text{Volume of crystal} = 1.03 \times 10^{22} \times 47 \times 10^{-24} = 0.484 \text{ mL}$$

Example 26. *A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm³/g. If the virus is considered to be a single particle, find its molecular mass.* **(IIT 1999)**

Solution: Volume of cylindrical virus = $\pi r^2 l$

$$= 3.14 \times \left(\frac{150}{2} \times 10^{-8}\right)^2 \times 5000 \times 10^{-8}$$
$$= 0.884 \times 10^{-16} \text{ cm}^3$$

$$\text{Mass of virus} = \frac{\text{Volume}}{\text{Specific volume}} = \frac{0.884 \times 10^{-16}}{0.75}$$
$$= 1.178 \times 10^{-16} \text{ g}$$

$$\text{Molar mass of virus} = \text{Mass of single virus} \times 6.023 \times 10^{23}$$
$$= 1.178 \times 10^{-16} \times 6.023 \times 10^{23}$$
$$= 7.095 \times 10^{7}$$

Example 27. *Weighing 3104 carats (1 carat = 200 mg), the Cullinan diamond was the largest natural diamond ever found. How many carbon atoms were present in the stone?*

Solution: Mass of the stone

$$= 3104 \times 200 = 620800 \text{ mg} = 620.8 \text{ g}$$

Number of atoms of carbon

$$= \frac{\text{Mass in gram}}{\text{Gram-atomic mass}} \times 6.023 \times 10^{23}$$
$$= \frac{620.8}{12} \times 6.023 \times 10^{23} = 3.12 \times 10^{25}$$

Example 28. *A cylinder of compressed gas contains nitrogen and oxygen in the ratio 3 : 1 by mole. If the cylinder is known to contain 2.5×10^4 g of oxygen, what is the total mass of the gas mixture?*

Solution: Number of moles of oxygen in the cylinder

$$= \frac{\text{Mass in gram}}{\text{Molecular mass in gram}} = \frac{2.5 \times 10^4}{32}$$
$$= 781.25$$

∴ Number of moles of N_2 = 3 × 781.25 = 2343.75

$$\text{Mass of nitrogen in the cylinder} = 2343.75 \times 28$$
$$= 65625 \text{ g}$$
$$= 6.5625 \times 10^4 \text{ g}$$

Total mass of the gas in the cylinder

$$= 2.5 \times 10^4 + 6.5625 \times 10^4 = 9.0625 \times 10^4 \text{ g}$$

Example 29. *Atmospheric air has 78% N_2; 21% O_2; 0.9 % Ar and 0.1 % CO_2 by volume. What is the molecular mass of air in the atmosphere?*

Solution: Molecular mass of mixture

$$= \frac{\Sigma \text{ \% of each}}{100} \times \text{Molar mass}$$
$$= \frac{78}{100} \times 28 + \frac{21}{100} \times 32 + \frac{0.9}{100} \times 40 + \frac{0.1}{100} \times 44 = 28.964$$

Example 30. *The famous toothpaste Forhans contains 0.76 g of sodium per gram of sodium monofluoroorthophosphate (Na_3PO_4F) in 100 mL.*

(*a*) *How many fluorine atoms are present?*

(*b*) *How much fluorine in milligrams is present?*

Solution:

Molar mass of $Na_3PO_4F = 3 \times 23 + 31 + 16 \times 4 + 19 = 183$

183 g Na_3PO_4F contains = 19 g fluorine

$$\therefore \quad 0.76\,g\ Na_3PO_4F \text{ contains} = \frac{19}{183} \times 0.76\,g \text{ fluorine}$$

$$= 0.0789\ g = 78.9\ mg \text{ fluorine}$$

Number of fluorine atoms

$$= \frac{\text{Mass in gram}}{\text{Gram-atomic mass}} \times 6.023 \times 10^{23}$$

$$= \frac{0.0789}{19} \times 6.023 \times 10^{23}$$

$$= 2.5 \times 10^{21} \text{ atoms}$$

Example 31. *An alloy of iron* (54.7%), *nickel* (45%) *and manganese* (0.3%) *has a density of* 8.17 g/cm^3. *How many iron atoms are there in a block of alloy measuring* $10\,cm \times 20\,cm \times 15\,cm$?

Solution:

$$\text{Volume of the block of alloy} = 10 \times 20 \times 15\,cm^3$$

$$= 3000\,cm^3$$

$$\text{Mass of the block} = 3000 \times 8.17\,g = 24510\,g$$

$$\text{Mass of iron in the block} = \frac{54.7}{100} \times 24510 = 13406.97\ g$$

$$\text{Number of iron atoms in the block} = \frac{\text{Mass}}{\text{Atomic mass}} \times 6.023 \times 10^{23}$$

$$= \frac{13406.97}{56} \times 6.023 \times 10^{23}$$

$$= 1.442 \times 10^{26}$$

Example 32. *An analysis of pyrex glass showed* 12.9% B_2O_3, 2.2% Al_2O_3, 3.8% Na_2O, 0.4% K_2O *and remaining is* SiO_2. *What is the ratio of silicon to boron atoms in the glass ?* **(BCECE 2007)**

Solution:

Percentage composition of $B_2O_3 = 12.9\%$

Percentage composition of

$$SiO_2 = 100 - [12.9 + 2.2 + 3.8 + 0.4]$$

$$= 80.7\%$$

$$\text{Number of moles of } B_2O_3 = \frac{\text{Mass}}{\text{Molar mass}} = \frac{12.9}{70} = 0.184$$

Number of moles of boron atoms $= 2 \times 0.184$

$$\text{Number of moles of } SiO_2 = \frac{\text{Mass}}{\text{Molar mass}} = \frac{80.7}{60} = 1.345$$

Number of moles of silicon atoms = 1.345

$$\frac{\text{Number of atoms of silicon}}{\text{Number of atoms of boron}} = \frac{N_A \times 1.345}{N_A \times 0.184} = \frac{7.3}{1}$$

Where, N_A = Avogadro's number

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

22. *x* gram of $CaCO_3$ was completely burnt in air. The mass of the solid residue formed is 28 g. What is the value of '*x*' in gram? **(EAMCET 2005)**

(a) 44 (b) 200 (c) 150 (d) 50

[Ans. (d)]

[Hint: $\underset{100\,g}{CaCO_3(s)} \longrightarrow \underset{56\,g}{CaO(s)} + CO_2(g)$

56 g residue ≡ 100 g $CaCO_3$

$\therefore$ 28 g residue ≡ 50 g $CaCO_3$]

23. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of Al metal from bauxite by Hall process is:

(a) 270 kg (b) 540 kg (c) 90 kg (d) 180 kg

[Ans. (c)]

[Hint: $\underset{3 \times 12\,g}{3C} + 2Al_2O_3 \longrightarrow \underset{4 \times 27\,=\,108\,g}{4Al} + 3CO_2$

$\because$ 108 g Al is produced by consuming = 36 g carbon

$\therefore$ 270×10^3 g Al will be produced by consuming

$$= \frac{36}{108} \times 270 \times 10^3 \text{ g carbon}$$

$$= 90 \times 10^3\ g = 90 \text{ kg carbon}\,]$$

24. The equivalent mass of an element is 4. Its chloride has vapour density 59.25. Then the valency of the element is:

(a) 4 (b) 3 (c) 2 (d) 1

[Ans. (b)]

[Hint: Molecular mass of $MCl_n = 59.25 \times 2 = 118.5$

$$a + 35.5 \times n = 118.5 \qquad \ldots\text{(i)}$$

$$\text{Equivalent mass} \times n + 35.5 \times n = 118.5$$

$$4n + 35.5n = 118.5 \qquad \ldots\text{(ii)}$$

$$\therefore \qquad n = 3\,]$$

25. Sulphur trioxide is prepared by the following two reactions:

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

How many grams of SO_3 are produced from 1 mole S_8?

(a) 1280 (b) 640

(c) 960 (d) 320

[Ans. (b)]

[Hint: From the given reaction, it is clear that, 1 mole S_8 will give 8 moles of SO_3.

$\therefore$ Mass of SO_3 formed will be $= 80 \times 8 = 640\,g$.]

26. Calculate the number of millilitres at STP of H_2S gas needed to precipitate cupric sulphide completely from 100 mL of a solution containing 0.75 g of $CuCl_2$ in 1 L.

(a) 21.4 (b) 14.2

(c) 41.2 (d) 124

[Ans. (d)]

[**Hint:** $CuCl_2 + H_2S \longrightarrow CuS + 2HCl$

Number of moles of H_2S = Number of moles of $CuCl_2$

$$= \frac{0.75}{134.5} = 0.00557$$

Volume of $H_2S = 0.00557 \times 22400 = 124.8$ mL]

27. In the reaction,

$$As_2S_5 + xHNO_3 \longrightarrow 5H_2SO_4 + yNO_2 + 2H_3AsO_4 + 12H_2O$$

the values of x and y are: **[JEE (Orissa) 2006]**

(a) 40, 40
(b) 10, 10
(c) 30, 30
(d) 20, 20

[**Ans.** (a)]

[**Hint:** In RHS, there are 40 hydrogen atoms, hence only option (a) will be suitable.]

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. **Chemistry:** Branch of physical science which deals with the properties, composition and changes of matter. It has several branches. Main branches are (i) organic (ii) inorganic (iii) physical and (iv) analytical. It is wide in its scope and touches almost every aspect of our lives.
2. **Matter:** It is anything which has mass and occupies space. Matter exists in three physical states (i) solid (ii) liquid and (iii) gas. It is chemically classified into (a) elements (b) compounds and (c) mixtures.
3. **Energy:** The capacity of doing work. It is of various forms. One form can be converted into another but cannot be created or destroyed. The total amount of matter and energy available in the universe is constant. The relationship between mass and energy is given by Einstein equation, $E = mc^2$ (where, E = energy, m = mass, c = velocity of light).
4. **Intensive properties:** Do not depend on the quantity of matter, *e.g.*, colour, density, melting point, boiling point, etc.
5. **Extensive properties:** Depend on the quantity of matter, *e.g.*, volume, mass, weight, etc.
6. **Substance:** A variety of matter, all samples of which have the same composition and properties. Pure substances are divided into (i) elements and (ii) compounds.
7. **Element:** A substance which cannot be decomposed into anything more simpler by ordinary physical or chemical means. 117 elements are known. 88 elements have been isolated from natural sources and remaining 29 have been prepared by artificial means. Every element is represented by a **symbol** which is a small abbreviation of its full and lengthy name. Oxygen is the most abundant element. Silicon, aluminium, iron are second, third and fourth most abundant elements. Elements are classified as (i) metals (ii) non-metals and (iii) metalloids.
8. **Metals:** Generally solids (Hg—exception). They have properties such as lustre, hardness, malleable, ductile, good conductors of heat and electricity. Copper, zinc, iron, aluminium are metals.
9. **Non-metals:** Usually non-lustrous, brittle and poor conductors of electricity. Oxygen, carbon, nitrogen, chlorine, helium, etc., are non-metals.
10. **Metalloids:** Possess mixed properties of metals and non-metals both (*e.g.*, As, Sb, Sn).
11. **Compound:** Pure substance composed of two or more different elements in a fixed proportion of mass. The properties of a compound are altogether different from the properties of elements from which it has been constituted.
12. **Mixture:** A material containing two or more substances (elements or compounds) in any proportion, in which components do not lose their identity. Homogeneous mixture has a single phase while heterogeneous has more than one phase. Mixture can be separated into components by physical methods.
13. **Alloy:** A homogeneous mixture of two or more elements—metal and metal, metal and non-metal or non-metal and non-metal. They have unique properties.
14. **Physical change:** A temporary change, no change in chemical composition and mass. Physical properties alter. It can be reversed easily.
15. **Chemical change:** A permanent change, new substance is formed which possesses different composition and properties. It cannot be reversed easily. Chemical changes are of various types. The important ones are decomposition, synthesis, substitution, addition, internal rearrangement, polymerisation, double decomposition, etc.
16. **Law of conservation of mass:** (Lavoisier—1774) In a chemical change, mass is neither created nor destroyed. In chemical reactions:

    Total masses of reactants = Total masses of products.
17. **Law of constant proportions:** (Proust—1799) A chemical compound always contains the same element combined together in fixed proportion by mass.
18. **Law of multiple proportions:** (Dalton—1808) When two elements combine to form two or more compounds, the different masses of one element which combine with a fixed mass of the other element, bear a simple ratio to one another.
19. **Law of reciprocal proportions:** (Richter—1794) When two different elements combine with the same mass of a third element, the ratio in which they do so will be the same or simple multiple if both directly combine with each other. In all chemical reactions, substances react in the ratio of their equivalent masses.
20. **Law of gaseous volumes:** (Gay-Lussac—1808) Gases react with each other in simple ratio of their volumes and if product is also in gaseous state, its volume also bears a simple ratio with the volumes of gaseous reactants under similar conditions of temperature and pressure.

21. **Dalton's atomic theory:** Every element is composed of small indivisible, indestructible particles called atoms. Atoms of the same element are identical but differ in properties, mass and size of atoms of other elements. Atoms of different elements combine in simple ratio to form compounds. The relative number and kind of atoms are always the same in a given compound. Atoms cannot be created or destroyed.

22. **Atom:** The smallest particle of an element that takes part in a chemical reaction.

23. **Molecule:** The smallest particle of an element or compound that can have a stable existence.

24. **Formula:** Group of symbols of elements which represents one molecule of a substance. It represents also the chemical composition.

25. **Atomic mass:** Atomic mass of an element is the ratio of mass of one atom of an element to $\frac{1}{12}$th part of the mass of carbon-12.

Atomic mass of an element

$$= \frac{\text{Mass of one atom of the element}}{\text{Mass of one atom of carbon-12}} \times 12$$

26. **Atomic mass unit (amu):** $\frac{1}{12}$th mass of carbon-12. It is equal to 1.66×10^{-24} g.

Atomic mass of an element

$$= \frac{\text{Mass of one atom of the element}}{1\,\text{amu}}$$

The actual mass of an atom of element = Atomic mass in amu $\times 1.66 \times 10^{-24}$ g.

The atomic masses of elements are actually average relative masses because elements occur as mixture of isotopes.

27. **Gram-atomic mass or Gram atom:** Atomic mass expressed in grams. It is the absolute mass in grams of 6.02×10^{23} atoms of any element.

$$\text{No. of gram atoms} = \frac{\text{Mass of element in grams}}{\text{Atomic mass of the element in grams}}$$

28. **Molecular mass:** It indicates how many times one molecule of a substance is heavier in comparison to $\frac{1}{12}$th of mass of one atom of carbon-12. Mass of a molecule is equal to sum of masses of the atoms present in a molecule.

29. **Gram-molecular mass or Gram molecule:** Molecular mass expressed in gram. It is the absolute mass in gram of 6.02×10^{23} molecules of any substance.

No. of gram molecules

$$= \frac{\text{Mass of a substance in gram}}{\text{Molecular mass of the substance in gram}}$$

30. **Avogadro's hypothesis:** Under similar conditions of temperature and pressure, equal volumes of all gases contain same number of molecules.

31. **Gram molar volume:** The volume occupied by one gram-molecular mass of any gas at NTP (0°C or 273 K and one atm or 76 cm of Hg as pressure). Its value is 22.4 litre.

32. **Vapour density:**

$$\text{V.D.} = \frac{\text{Density of a gas}}{\text{Density of hydrogen}}$$

$$= \frac{\text{Mass of a certain volume of a gas}}{\text{Mass of same volume of hydrogen under same temperature and pressure}}$$

$$2\,\text{V.D.} = \text{Molecular mass}$$

33. **Mole:** A mole (mol) is defined as the number of atoms in 12.0 g of carbon-12. The number of atoms is 6.02×10^{23}. This number is called Avogadro's number.

$$\text{No. of moles} = \frac{\text{Mass of substance in gram}}{\text{Mass of one mole of the substance in gram}}$$

$$= \frac{\text{No. of particles}}{6.02 \times 10^{23}}$$

$$= \frac{\text{Volume of gas in litres at NTP}}{22.4}$$

Mass of one atom of an element

$$= \frac{\text{Gram atom of an element}}{6.02 \times 10^{23}}$$

Mass of one molecule of a substance

$$= \frac{\text{Gram-molecular mass of a substance}}{6.02 \times 10^{23}}$$

34. **Equivalent mass:** The number of parts by mass of the substance which combine or displace directly or indirectly 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine or 108 parts by mass of silver.

The equivalent mass of an element may vary with change of valency.

Eq. mass of an element

$$= \frac{\text{Mass of element}}{\text{Mass of hydrogen}} \times 1.008$$

$$= \frac{\text{Mass of element} \times 11200}{\text{Volume in mL of hydrogen displaced at NTP}}$$

$$= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$$

$$= \frac{\text{Mass of element}}{\text{Mass of chlorine}} \times 35.5$$

35. **Metal to metal displacement:** $\frac{m_1}{m_2} = \frac{E_1}{E_2}$

36. **Double decomposition:** $AB + CD \rightarrow \underset{\text{ppt.}}{AD} + CB$

$$\frac{\text{Mass of } AB}{\text{Mass of } AD} = \frac{\text{Eq. mass of } A + \text{Eq. mass of } B}{\text{Eq. mass of } A + \text{Eq. mass of } D}$$

Atomic mass of an element

= Eq. mass of the element × Valency

37. **Dulong and Petit's law:**

$$\text{Atomic mass (approximate)} = \frac{6.4}{\text{Specific heat}}$$

38. **Cannizzaro's method:** Atomic mass of an element is the smallest mass of the element present in the molecular mass of any one of its compounds.

39. **Law of isomorphism:** Isomorphous compounds form crystals which have same size and shape and can grow in the saturated solution of each other.

    Masses of two elements that combine with same mass of other elements in their respective compounds are in the ratio of their atomic masses.

40. **Atomic mass from vapour density of a chloride:**

$$\text{Valency of an element} = \frac{2\,\text{V.D. of a volatile chloride}}{\text{Eq. mass} + 35.5}$$

41. **Types of formulae:**
    - (i) **Empirical:** It represents the simplest relative whole number ratio of atoms of each element present in the molecule of a substance.
    - (ii) **Molecular:** It represents the actual number of atoms of each element present in one molecule of a substance.

      Molecular formula = $n \times$ Empirical formula

$$n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}}$$

    - (iii) **Structural:** It represents the way in which atoms of various elements are linked with each other.

42. **Percentage of element:**

$$\text{Percentage of element} = \frac{\text{Mass of element}}{\text{Molecular mass}} \times 100$$

43. **Chemical equation:** It is a symbolic representation of a chemical change. The equation becomes balanced when total number of atoms of various elements are made equal on both the sides of equation. Chemical equations are of two types (i) molecular and (ii) ionic. Chemical equation is based on law of conservation of mass.

44. **Unit:** It is the primary standard chosen to measure any physical quantity.

    The seven units of measurement, namely mass, length, time, temperature, electric current, luminous intensity and amount of substance are taken as basic units. All other units can be derived from them and are, therefore, called derived units. SI units are used these days in all branches of science.

45. **Significant figure:** It is the total number of certain digits plus one doubtful digit.

Questions

1. Match the following, choosing one item from Column-X and the appropriate related item from Column-Y.

[A]

Column-X	**Column-Y**
(a) Efflorescence	(i) Homogeneous mixture
(b) Malleability	(ii) Heterogeneous mixture
(c) Alloy	(iii) Mole
(d) 1 amu	(iv) (1/12)th mass of carbon-12
(e) Sulphur and sand	(v) Tendency to lose water of crystallisation
(f) Amount of substance	(vi) Property of metal being hammered into thin sheets

[B]

Column-X	**Column-Y**
(a) Equal volumes of all gases contain equal number of molecules at NTP.	(i) Dalton's atomic theory
(b) The atom is indestructible.	(ii) Law of conservation of mass
(c) All pure samples of the same compound contain the same elements combined in the same proportion by mass.	(iii) Avogadro's law
(d) Total mass before and after the chemical reaction is same.	(iv) Dulong and Petit's law
(e) Atomic mass $= \dfrac{6.4}{\text{Specific heat}}$	(v) Gay-Lussac's law
(f) Gases react in simple ratio of their volumes.	(vi) Law of constant proportions

[C]

Column-X	**Column-Y**
(a) Most abundant element	(i) Platinum
(b) Most abundant metal	(ii) Diamond
(c) Liquid at room temp.	(iii) Aluminium
(d) Hardest substance	(iv) Plutonium
(e) Most ductile metal	(v) Mercury
(f) Transuranic element	(vi) Oxygen

2. **Matrix Matching Problems:**
(According to the new pattern of IIT Screening)

[A] Match the Column-X and Column-Y:

Column-X	**Column-Y**
(a) Vapour density	(i) Unitless
(b) Mole	(ii) 1 mol electrons
(c) 12 g carbon	(iii) Collection of 6.023×10^{23} atoms
(d) 96500 C	(iv) Molecular mass $\times \frac{1}{2}$

[B] Match the Column-X and Column-Y:

Column-X	**Column-Y**
(a) 1.6 g CH_4	(i) 0.1 mol
(b) 1.7 g NH_3	(ii) 6.023×10^{23} electrons
(c) HCHO	(iii) 40% carbon
(d) $C_6H_{12}O_6$	(iv) Vapour density = 15

[C] Match the Column-X and Column-Y:

Column-X	**Column-Y**
(a) 1 amu	(i) Heaviest particle of atom
(b) Proton	(ii) 1.66×10^{-27} kg
(c) Neutron	(iii) 931.5 MeV
(d) α-particle	(iv) Positively charged

[D] Match the Column-X with Column-Y for the reaction:

$$A + B_2 \rightarrow AB_2$$

Column-X	**Column-Y**
(a) 300 atoms of A + 200 molecules of B_2	(p) B_2 is limiting reagent
(b) 100 atoms of A + 100 molecules of B_2	(q) A is limiting reagent
(c) 5 mol of A + 2.5 mol of B_2	(r) None of the reactant is in excess
(d) 2.5 mol of A + 5 mol of B_2	(s) 200 molecules of AB_2 will be formed

Answers

1. [A] (a–v); (b–vi); (c–i); (d–iv); (e–ii); (f–iii)
   [B] (a–iii); (b–i); (c–vi); (d–ii); (e–iv); (f–v)
   [C] (a–vi); (b–iii); (c–v); (d–ii); (e–i); (f–iv).

2. [A] (a–i, iv); (b–iii); (c–iii); (d–ii)
   [B] (a–i, ii); (b–i, ii); (c–iii, iv); (d–iii)
   [C] (a–ii, iii); (b–ii, iv); (c–i); (d–iv)
   [D] (a–p, s); (b–r); (c–p); (d-q).

• PRACTICE PROBLEMS •

1. The density of mercury is 13.6 g/mL. Calculate the diameter of an atom of mercury assuming that each atom of mercury is occupying a cube of edge-length equal to the diameter of mercury atom.
(Atomic mass of mercury = 200)
[**Ans.** 2.9×10^{-8} cm]

2. A metal *M* of atomic mass 54.94 has a density of 7.42 g/cc. Calculate the apparent volume occupied by one atom of the metal.
[**Ans.** 1.23×10^{-23} cc]

3. Find the charge of 1 g ion of N^{3-} in coulomb.
[**Ans.** 2.894×10^{5} coulomb]

4. Calculate the volume at NTP occupied by 6.25 g of nitrogen.
[**Ans.** 5.0 litre]

5. 10 mL of hydrogen contains 2×10^{3} molecules of hydrogen at certain pressure and temperature. Calculate the number of molecules of oxygen whose volume is 200 mL at the same temperature and pressure.
[**Ans.** 4×10^{4} molecules]

6. The masses of equal volumes of a gas and hydrogen are 25.6 g and 0.8 g respectively under same conditions of temperature and pressure. Find the molecular mass of the gas.
[**Hint:** V.D. of the gas $= \dfrac{25.6}{0.8} = 32.0$

Molecular mass = 2 V.D. = 2 × 32.0 = 64.0]

7. One litre of a gas at NTP weighs 1.97 g. Find the molecular mass of gas.
[**Ans.** 44.128]

8. How many moles of water are present in one litre of water?
[**Ans.** 55.5 moles]

9. Calculate the mass of 6.02×10^{21} molecules of nitrogen.
[**Ans.** 0.28 g]

10. 1.5276 g of $CdCl_2$ was found to contain 0.9367 g of cadmium. Calculate the atomic mass of cadmium.
[**Ans.** 112.54]

[**Hint:** Equivalent mass of cadmium $= \dfrac{\text{Mass of Cd}}{\text{Mass of Cl}} \times 35.5$

$$= \frac{0.9367}{0.5909} \times 35.5 = 56.27$$

Atomic mass = Equivalent mass × Valency]

11. Calculate how many methane molecules and how many hydrogen and carbon atoms are there in 25.0 g of methane? **(MLNR 1990; Dhanbad 1992)**
[**Ans.** 9.41×10^{23} CH_4 molecules, 9.41×10^{23} carbon atoms and 37.64×10^{23} hydrogen atoms.]

[**Hint:** No. of moles of methane $= \dfrac{25.0}{16.0}$

One molecule of methane contains one carbon atom and four hydrogen atoms.]

12. How much sugar ($C_{12}H_{22}O_{11}$) will be required if each person on the earth is given 100 molecules of sugar? The population of the earth is 3×10^{10}.
[**Ans.** 170.43×10^{-11} g]

13. A mixture of hydrogen and oxygen contains 20% by mass of hydrogen. What is the total number of molecules present per gram of the mixture?
[**Ans.** 7.528×10^{22}]

[**Hint:** In 1 gram of the mixture, 0.2 g of hydrogen and 0.8 g of oxygen are present. Moles of $H_2 = \dfrac{0.2}{2} = 0.1$, moles of oxygen $= \dfrac{0.8}{32} = 0.025$. Calculate the number of molecules of hydrogen and oxygen and then add.]

14. How many electrons are present in 18 mL of water? **(MLNR 1995)**
[**Hint:** 18 mL water = 18 g water = 1 mole water $= 6.02 \times 10^{23}$ molecules, each molecule consists 10 electrons (8 electrons per oxygen atom, 2 electrons for two hydrogen atoms). Total electrons $= 10 \times 6.02 \times 10^{23} = 6.02 \times 10^{24}$]

15. Sulphur molecule is known to be composed of 8 atoms of the element. In a sample of 192 g of pure sulphur, calculate (i) number of g-atoms of sulphur; (ii) number of atoms of sulphur; (iii) number of moles of sulphur; (iv) number of molecules of sulphur.
[**Ans.** g-atoms = 6; No. of atoms $= 6 \times 6.02 \times 10^{23}$; No. of moles = 0.75; No. of molecules $= 4.52 \times 10^{23}$]

[**Hint:** The atomic mass of sulphur is 32.]

16. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the moles of NO_2 in 100 g of the mixture. **(MLNR 1993)**
[**Hint:** Mol. mass of mixture = 2 × 38.3 = 76.6

No. of moles in 100 g of mixture $= \dfrac{100}{76.6}$

Let *a* g of NO_2 is present in mixture.

Moles of NO_2 + Moles of N_2O_4 = Moles of mixture

$$\frac{a}{46} + \frac{100-a}{92} = \frac{100}{76.6} \quad \text{or} \quad a = 20.10 \text{ g}$$

Moles of NO_2 in mixture $= \frac{20.10}{46} = 0.437$]

17. Calculate the number of oxygen atoms in 88 g CO_2. What would be the mass of CO having the same number of oxygen atoms? **(BITS 1990)**

[Hint: 88 g CO_2 = 2 moles of CO_2. One molecule consists of 2 oxygen atoms.

No. of oxygen atoms $= 2 \times 2 \times 6.02 \times 10^{23} = 24.08 \times 10^{23}$

CO molecule has one oxygen atom.
Mass of CO containing 24.08×10^{23} oxygen atoms

$$= \frac{28}{6.02 \times 10^{23}} \times 24.08 \times 10^{23} = 112 \text{ g }]$$

18. Density of water at room temperature is 1.0 g cm^{-3}. How many molecules are there in one drop of water if its volume is 0.1 cm^3?

[Ans. 3.34×10^{21} molecules]

[Hint: Mass of one drop = Vol. × $d = 0.1 \times 1 = 0.1$ g

No. of moles $= \frac{0.1}{18}$; No. of molecules $= 6.02 \times 10^{23} \times \frac{0.1}{18}$]

19. Naturally occurring boron consists of two isotopes, whose atomic masses are 10.01 and 11.01. The atomic mass of natural boron is 10.81. Calculate the percentage of each isotope in natural boron. **(MLNR 1994)**

[Ans. % of isotope with atomic mass 10.01 = 20; % of isotope with atomic mass 11.01 = 80]

[Hint: Let x be the percentage of the isotope with atomic mass 10.01.

$$\frac{10.01 \times x}{100} + \frac{11.01(100-x)}{100} = 10.81 \quad \text{or} \quad x = 20]$$

20. Chlorine has isotopes ^{35}Cl and ^{37}Cl. There are three ^{35}Cl isotopes for every ^{37}Cl isotope in a sample of chlorine. Calculate the atomic mass of chlorine.

[Ans. $A = \frac{3 \times 35 + 37 \times 1}{4} = 35.5$]

21. Natural hydrogen gas is a mixture of ^1H and ^2H in the ratio of 5000 : 1. Calculate the atomic mass of the hydrogen.

[Ans. 1.000199]

22. Chromium has the following isotopic composition:

Mass number	Isotopic mass	Fractional abundance
50	49.9461	x
52	51.9405	0.8379
53	52.9407	0.0950
54	53.9389	0.0236

Calculate the value of x.

[Ans. 0.0435]

23. Use the data given in the following table to calculate the molar mass of naturally occurring argon:

Isotope	Isotopic molar mass	Abundance
^{36}Ar	35.96755 g mol^{-1}	0.337%
^{38}Ar	37.96272 g mol^{-1}	0.063%
^{40}Ar	39.9624 g mol^{-1}	99.6%

[Ans. 39.947]

24. Density of oxygen at NTP is 1.429 g/litre. Calculate the standard molar volume of the gas.

[Ans. 22.39 litre mol^{-1}]

25. How many iron atoms are present in a stainless steel ball bearing having a radius of 0.254 cm? The stainless steel contains 85.6% Fe by weight and has density of 7.75 g/cm^3.

[Ans. 4.91×10^{21}]

26. The nucleus of an atom X is supposed to be a sphere with a radius of 5×10^{-13} cm. Find the density of the matter in the atomic nucleus if the atomic weight of X is 19.

[Ans. 6.02×10^{13} g/mL]

27. Calculate the number of atoms of each element present in 122.5 g of $KClO_3$.

[Ans. Number of atoms of 'K' $= 1 \times 6.023 \times 10^{23}$
Number of atoms of 'Cl' $= 1 \times 6.023 \times 10^{23}$
Number of atoms of 'O' $= 3 \times 6.023 \times 10^{23}$]

28. In an experiment, 1.0 g $CaCO_3$ on heating evolved 224 mL of CO_2 at NTP. What mass of CaO (calcium oxide) is formed?

[Ans. Mass of CaO = 0.56 g]

[Hint: Mass of 224 mL of $CO_2 = \frac{44}{22400} \times 224 = 0.44$ g]

29. What mass of potassium chlorate ($KClO_3$) on heating gives 1.491 g of potassium chloride (KCl) and 0.672 litres of oxygen at NTP?

[Ans. Mass of $KClO_3$ = 2.451 g]

[Hint: Mass of 22.4 litre of oxygen at NTP = 32 g]

30. A compound AB completely decomposes into A and B on heating. 50 g of AB, on strong heating, gave 40 g of A. How much quantity of AB should be decomposed by heating to obtain 2.5 g of B? How much quantity of A will be produced in the process?

[Ans. 12.5 g AB is to be decomposed, 10.0 g of A will be produced.]

[Hint: $\underset{50\text{ g}}{AB} \longrightarrow \underset{40\text{ g}}{A} + \underset{10\text{ g}}{B}$]

31. If 12.6 g of $NaHCO_3$ is added to 20.0 g of HCl solution, the residue solution is found to weigh 24.0 g. What is the mass and volume of CO_2 released at NTP in the reaction?

[Ans. 8.6 g CO_2 released. Volume at NTP $= \frac{22.4}{44} \times 8.6 = 4.378$ litre]

32. (i) 5.06 g of pure cupric oxide (CuO), on complete reduction by heating in a current of hydrogen, gave 4.04 g of metallic copper.

(ii) 1.3 g of pure metallic copper was completely dissolved in nitric acid and the resultant solution was carefully dried and ignited. 1.63 g CuO was produced in the process. Show that these results illustrate the law of constant proportions.

[**Ans.** In both cases, the ratio of copper and oxygen is 1 : 0.25. Hence, the law of constant proportions is illustrated.]

33. Metal M and chlorine combine in different proportions to form two compounds A and B. The mass ratio M : Cl is 0.895 : 1 in A and 1.791 : 1 in B. What law of chemical combination is illustrated?

[**Ans.** Masses of metal which combine with 1 part of chlorine are in the ratio of 1 : 2, which is a simple ratio. Hence, law of multiple proportions is illustrated.]

34. 2.8 g of calcium oxide (CaO) prepared by heating limestone were found to contain 0.8 g of oxygen. When one gram of oxygen was treated with calcium, 3.5 g of calcium oxide was obtained. Show that the results illustrate the law of definite proportions.

35. By means of the given analytical results show that law of multiple proportions is true:

Mercurous chloride	**Mercuric chloride**
Mercury = 84.92 %	Mercury = 73.80%
Chlorine = 15.08 %	Chlorine = 26.20%

[**Ans.** The masses of mercury which combine with 1 part of chlorine are in the ratio of 2 : 1, which is a simple ratio. Hence, law of multiple proportions is illustrated.]

36. 1 g of a metal, having no variable valency, produces 1.67 g of its oxide when heated in air. Its carbonate contains 28.57% of the metal. How much oxide will be obtained by heating 1 g of the carbonate?

[**Ans.** 0.477 g]

[**Hint:** $\dfrac{\text{Mass of metal}}{\text{Mass of oxygen}} = \dfrac{\text{Mass of metal in 1g of carbonate}}{x}$

i.e., $x = 0.1914$ g of oxygen

Mass of oxide = 0.2857 + 0.1914 = 0.4771 g]

37. 0.36 g of Mg combines with chlorine to produce 1.425 g of magnesium chloride. 9.50 g of another sample of anhydrous magnesium chloride gave, on electrolysis 2.24 litre of chlorine at NTP. Show that these data agree with the law of constant proportions.

[**Hint:** Mass of 2.24 litre of chlorine at NTP $= \dfrac{71}{22.4} \times 2.24$ = 7.1 g. In both cases, the ratio of masses of Mg and Cl is 1 : 3. Hence, law of constant proportions is followed.]

38. Carbon dioxide contains 27.27% carbon, carbon disulphide contains 15.97% carbon and sulphur dioxide contains 50% sulphur. Show that these figures illustrate the law of reciprocal proportions.

[**Hint:** The masses of oxygen and sulphur which combine with 1 part of carbon are in the ratio of 2.667 : 5.25, *i.e.*, 1 : 2. In sulphur dioxide, the masses of sulphur and oxygen are in the ratio of 1 : 1 which is a simple multiple of first. Hence, law of reciprocal proportions is illustrated.]

39. Phosphorus and chlorine form two compounds. The first contains 22.54% by mass of phosphorus and the second 14.88% of phosphorus. Show that these data are consistent with law of multiple proportions.

[**Hint:** The ratio of the masses of chlorine which combines with a fixed mass of phosphorus in two compounds is 3 : 5 which is a simple whole number ratio. Thus, the data illustrate law of multiple proportions.]

40. A and B are two hydrocarbons. A and B are heated separately in excess of oxygen when 0.028 g of A gave 44.8 mL CO_2 and 0.044 g of B gave 67.2 mL CO_2 at NTP. Show that the results are in agreement with law of multiple proportions.

[**Hint:** Determine the masses of CO_2 at NTP and then masses of carbon.

(A) Mass of $CO_2 = \dfrac{44}{22400} \times 44.8 = 0.088$ g,

Mass of carbon = 0.024 g, mass of hydrogen = 0.004 g.

(B) Mass of $CO_2 = \dfrac{44}{22400} \times 67.2 = 0.132$ g,

Mass of carbon = 0.036 g, mass of hydrogen = 0.008 g.

Thus, the masses of carbon combining with same mass of hydrogen are in the ratio of 4 : 3 which is a simple ratio. Hence, law of multiple proportions is followed.]

41. Aluminium oxide contains 52.9% aluminium and carbon dioxide contains 27.27% carbon. Assuming the validity of the law of reciprocal proportions, calculate the percentage of aluminium in aluminium carbide.

[**Hint:** From the data, it is observed that the ratio of masses of aluminium and carbon in aluminium carbide should be 3 : 1 or its simple multiple. Hence, percentage of aluminium in aluminium carbide $= \dfrac{3}{4} \times 100 = 75.0$]

42. Two volumes of ammonia, on dissociation gave one volume of nitrogen and three volumes of hydrogen. How much hydrogen will be obtained from dissociation of 40 mL of NH_3?

[**Ans.** 60 mL]

43. The following results were obtained by heating different oxides of lead in a current of hydrogen:

(a) 1.393 g of litharge gave 1.293 g of lead.
(b) 2.173 g of lead peroxide gave 1.882 g of lead.
(c) 1.721 g of red lead gave 1.552 g of lead.

Show that these results are in accordance with the law of multiple proportions.

[**Ans.** Masses of lead that combine with same mass of oxygen are in the ratio of 4 : 2 : 3 which is a simple ratio. So, the results are in accordance with the law of multiple proportions.]

44. Calculate the number of g-moles of CaO that could be obtained from 42.54 g of $CaCO_3$ and convert the number of g-moles to grams.

[No. of g-moles $= \dfrac{42.54}{100} = 0.4254$,

Mass of CaO = 0.4254 × 56 = 23.8 g]

45. 1 g of a metal M which has specific heat of 0.06 combines with oxygen to form 1.08 g of oxide. What is the atomic mass of M?

[Hint: Approximate atomic mass $= \frac{6.4}{0.06} = 106.6$

$$\text{Equivalent mass of } M = \frac{1}{0.08} \times 8 = 100$$

$$\text{Valency} = \frac{106.6}{100} \approx 1$$

$$\text{Exact atomic mass} = 100 \times 1 = 100]$$

46. A compound contains 28% of nitrogen and 72% metal by mass. 3 atoms of the metal combine with 2 atoms of the nitrogen. Find the atomic mass of the metal.

[Hint: Valency of metal = 2 and valency of nitrogen = 3

Equivalent mass of nitrogen $= \frac{14}{3}$; $\frac{\text{Eq. mass of metal}}{14/3} = \frac{72}{28}$

Equivalent mass of metal = 12

Atomic mass of metal $= 12 \times 2 = 24$]

47. The chloride of a solid metallic element contains 57.89% by mass of the element. The specific heat of the element is 0.0324 cal deg^{-1} g^{-1}. Calculate the exact atomic mass of the element.

[Hint: Equivalent mass of the element $= \frac{57.89}{42.11} \times 35.5 = 48.8$

$$\text{Approximate atomic mass} = \frac{6.4}{0.0324} = 200$$

$$\text{Valency} = \frac{200}{48.8} \approx 4$$

$$\text{Exact atomic mass} = 48.8 \times 4 = 195.2\ ]$$

48. Two oxides of a metal contain 63.2% and 69.62% of the metal. The specific heat of the metal is 0.117. What are the formulae of the two oxides?

[Ans. MO_2 and M_2O_3]

49. White vitriol (hydrated zinc sulphate) is isomorphous with $MgSO_4 \cdot 7H_2O$. White vitriol contains 22.95% zinc and 43.9% of water of crystallisation. Find the atomic mass of zinc.

[Hint: The formula of white vitriol should be $ZnSO_4 \cdot 7H_2O$ as it is isomorphous to $MgSO_4 \cdot 7H_2O$, *i.e.*, 7 water molecules are associated with one zinc atom. $7H_2O = 7 \times 18 = 126$. Mass of Zn with which 126 parts of water by mass are associated $= \frac{22.95}{43.90} \times 126 = 65.87$. Atomic mass of zinc.]

50. A solid element burns in oxygen without any change in volume (of gas) under similar conditions of temperature and pressure. If the vapour density of pure gaseous product is 32, what is the equivalent mass of the element?

[Hint: One vol. of oxide contains 1 vol. of O_2.

One mole of oxide contains one mole of O_2.

$$\text{Mol. mass of oxide} = A + 32 = 2\ \text{V.D.} = 64$$

So, $A = 32$

32 parts of element combine with 32 parts of oxygen.

So, Equivalent mass of element $= \frac{32}{32} \times 8 = 8$]

51. If the equivalent mass of a metal (M) is x and the formula of its oxide is $M_m\ O_n$, then show that the atomic mass of M is $\frac{2xn}{m}$.

[Hint: m atoms of M combine with n atoms of oxygen.

1 atom of M combines with $\frac{n}{m}$ atoms of oxygen.

Hence, $\text{Valency} = \frac{2n}{m}$

$$\text{Atomic mass} = \text{Equivalent mass} \times \text{Valency}$$
$$= x \times \frac{2n}{m} = \frac{2nx}{m}\ ]$$

52. Two oxides of metals A and B are isomorphous. The metal A whose atomic mass is 52, forms a chloride whose vapour density is 79. The oxide of the metal B contains 47.1% oxygen. Calculate the atomic mass of B.

[Hint: Let the valency of A be x. The formula of chloride $= ACl_x$

$$2\ \text{V.D.} = A + x \times 35.5 \qquad \text{or} \qquad x \approx 3$$

As the two oxides are isomorphous, the valency of B is also 3. Equivalent mass of $B = \frac{52.9}{47.1} \times 8 = 8.99$, atomic mass of $B = 8.99 \times 3 = 26.97$]

53. A mixture of 1.65×10^{21} molecules of X and 1.85×10^{21} molecules of Y weighs 0.688 g. If molecular mass of Y is 187, what is the molecular mass of X?

[Hint: $\frac{A \times 1.65 \times 10^{21}}{6.02 \times 10^{23}} + \frac{187 \times 1.85 \times 10^{21}}{6.02 \times 10^{23}} = 0.688, A = 41.35$]

54. The equivalent mass of a metal is 29.73 and the vapour density of its chloride is 130.4. Find out the atomic mass of the metal.

[Ans. Atomic mass = 118.92]

[Hint: $\text{Valency} = \frac{2 \times \text{V.D.}}{\text{Eq. mass} + 35.5} = \frac{2 \times (130.4)}{(29.73 + 35.5)} \approx 4$]

55. Calculate the percentage of aluminium, sulphate radical and water in potash alum.

[Ans. Al = 5.69%; $SO_4^{2-} = 40.51\%$; Water = 45.57%]

56. Carbohydrates are represented by the general formula $C_m(H_2O)_n$. On heating, in absence of air, they decompose into steam (H_2O) and carbon. 3.1 g of a carbohydrate, on complete decomposition by heating in absence of air, leave a residue of 1.24 g of carbon. If the molecular mass of the carbohydrate be 180, find its molecular formula.

[Hint: Determine % of carbon in carbohydrate. It is 40%. Water is 60%. Empirical formula $= CH_2O$. Molecular formula $= 6 \times CH_2O = C_6H_{12}O_6$.]

57. A gaseous hydrocarbon contains 85.7% carbon and 14.3% hydrogen. 1 litre of the hydrocarbon weighs 1.26 g at NTP. Determine the molecular formula of the hydrocarbon.

[Ans. C_2H_4]

58. Equal masses of oxygen, hydrogen and methane are taken in a container under identical conditions. Find the ratio of their volumes.

[Ans. 1 : 16 : 2]

59. How many moles are there in 1 m^3 of any gas at NTP?
[**Ans.** 44.6 moles]

60. A hydrated chloride of metal contains 18.26% metal and 32.42% chloride ion by mass. The specific heat of metal is 0.16. What is hydrated chloride?
[**Ans.** $CaCl_2 \cdot 6H_2O$]

61. 1.878 g of MBr_x when heated in a stream of HCl gas was completely converted to chloride MCl_x which weighed 1.0 g. The specific heat of metal is 0.14 cal g^{-1}. Calculate the molecular masses of metal bromide and metal chloride.
[**Ans.** Mol. mass of metal bromide = 285.54;
Mol. mass of metal chloride = 152.2]

62. An automobile antifreeze consists of 38.7% C; 9.7% H and remaining oxygen by weight. When 0.93 g of it are vaporised at 200°C and 1 atm pressure, 582 mL of vapour are formed. Find the molecular formula of the antifreeze.
[**Ans.** $C_2H_6O_2$]

63. A mineral contained MgO = 31.88%; SiO_2 = 63.37% and H_2O = 4.75%. Show that the simplest formula for the mineral is $H_2Mg_3Si_4O_{12}$.
(H = 1; Mg = 24; Si = 28; O = 16)

64. How many moles of NH_3 are there in 250 cm^3 of a 30% solution, the specific gravity of which is 0.90?
[**Ans.** 3.97 moles]

65. Haemoglobin contains 0.25% iron by mass. The molecular mass of haemoglobin is 89600. Calculate the number of iron atoms per molecule of haemoglobin.
[Atomic mass of Fe = 56]
[**Ans.** 4 atoms]

66. A sample of potato-starch was ground to give a starch like molecule. The product analysed 0.086% phosphorus. If each molecule is assumed to contain one atom of phosphorus, what is the average molecular mass of the material?
[**Ans.** 36000 amu]

67. Insulin contains 3.4% sulphur. Calculate minimum molecular mass of the insulin.
[**Ans.** 941.176 amu]
[**Hint:** For minimum molecular mass, one molecule of insulin must have atleast one sulphur atom.]

68. Calculate the number of carbon, hydrogen and oxygen atoms in 18 g of glucose.
[**Ans.** 3.61×10^{23} carbon atoms, 7.22×10^{23} hydrogen atoms, 3.61×10^{23} oxygen atoms]

69. Hydrated sulphate of a divalent metal of atomic weight 65.4 loses 43.85% of its weight on dehydration. Find the number of molecules of water of crystallisation in the formula of hydrated salt. **[JEE (West Bengal) 2005]**

[**Hint:** Formula of divalent hydrated metal sulphate will be

$$MSO_4 \cdot xH_2O$$

Molecular mass of salt = 65.4 + 96 + 18x

$$= (161.4 + 18x)$$

$$\% \text{ of water} = \frac{18x}{161.4 + 18x} \times 100 = 43.85$$

On solving, $x = 7$

∴ Molecular formula of hydrated salt = $MSO_4 \cdot 7H_2O$]

70. A person with fever has a temperature of 102.5°F. What is the temperature in degree celsius?
[**Hint:** Use $C = \frac{5(F-32)}{9}$]

71. An ornamental ring contains 275 carats of diamond. How many grams diamond does it have?
[**Hint:** 1 carat = 200 mg
∴ Mass of diamond = $275 \times 200 \times 10^{-3}$ g]

72. 1 volume of a gaseous compound consisting C, H, O on complete combustion in presence of 2.5 volume of O_2 gives 2 vol. of steam and 2 vol. of CO_2. What is the formula of the compound if all measurements are made at NTP?
[**Ans.** C_2H_4O]

73. 60 mL of a mixture of nitrous oxide and nitric oxide was exploded with excess of hydrogen. If 38 mL of N_2 was formed, calculate the volume of each gas in the mixture.
[**Ans.** NO = 44 mL and N_2O = 16 mL]

74. For a precious stone, 'carat' is used for specifying its mass. If 1 carat = 3.168 grains (a unit of mass) and 1 gram = 15.4 grains, find the total mass in kilogram of the ring that contains 0.5 carat diamond and 7 gram gold.
[**Ans.** 7.1×10^{-3} kg]

75. The density of a gaseous element is 5 times that of oxygen under similar conditions. If the molecule of the element is triatomic, what will be its atomic mass?
[**Ans.** 53.33]

76. Calculate the number of electrons, protons and neutrons in 1 mole of $^{18}O^{2-}$ ions.
[**Ans.** Electrons = $10 \times 6.023 \times 10^{23}$

Protons = $8 \times 6.023 \times 10^{23}$

Neutrons = $8 \times 6.023 \times 10^{23}$]

77. 600 mL of a mixture of O_2 and O_3 weighs 1 gm at NTP. Calculate the volume of ozone in the mixture.
[**Ans.** 200 mL]

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. The father of modern chemistry is:
(a) Priestley (b) Lavoisier
(c) Dalton (d) Mendeleev

2. A pure substance can only be:
(a) a compound
(b) an element
(c) an element or a compound
(d) a heterogeneous mixture

3. A pure substance which contains only one type of atoms is called:
(a) an element (b) a compound
(c) a solid (d) a liquid

4. Which one of the phrases would be incorrect to use?
(a) A mole of an element (b) A mole of a compound
(c) An atom of an element (d) An atom of a compound

5. A symbol not only represents the name of the element but also its:
(a) atomic mass (b) atomic number
(c) atomicity (d) atomic volume

6. The credit for the discovery of transuranic elements goes to:
(a) Hahn (b) Rutherford
(c) Seaborg (d) Curie

7. The most abundant metal in earth's crust is:
(a) iron (b) magnesium
(c) calcium (d) aluminium

8. The most abundant element in earth's crust is:
(a) hydrogen (b) oxygen (c) nitrogen (d) silicon

9. Which one of the elements is not found in nature?
(a) Radium (b) Technetium
(c) Polonium (d) Helium

10. Which one of the following is not a compound?
(a) Marble (b) Ozone
(c) Carborundum (d) Quicklime

11. Which one of the following is not an element?
(a) Diamond (b) Ozone (c) Silica (d) Graphite

12. The direct change from solid to gaseous state is referred to as:
(a) dissociation (b) decomposition
(c) sublimation (d) deliquescence

13. Sulphur burns in oxygen to form sulphur dioxide. The properties of sulphur dioxide are:
(a) totally different from sulphur and oxygen
(b) similar to sulphur
(c) similar to oxygen
(d) more similar to sulphur than oxygen

14. Which one of the following statements is incorrect?
(a) All elements are homogeneous
(b) Compounds always contain two or more different elements
(c) A mixture is not always heterogeneous
(d) Air is a heterogeneous mixture

15. One sample of air is found to have 0.03% carbon dioxide and another sample 0.02%. This illustrates that:
(a) air is a compound
(b) air is an element
(c) air does not follow the law of constant proportions
(d) air is a mixture

16. Which one of the following is not a mixture?
(a) Distilled water
(b) Sugar dissolved in water
(c) Liquefied Petroleum Gas (LPG)
(d) Gasoline

17. Which of the following is a characteristic property of both mixtures and compounds?
(a) Their properties are same as those of their components
(b) Energy is released when they are formed
(c) Their masses are equal to the sum of the masses of their components
(d) They contain the components in fixed proportions

18. Name the scientist who stated that matter can be converted into energy:
(a) Boyle (b) Lavoisier (c) Avogadro (d) Einstein

19. Which one of the following is not an intensive property?
(a) Weight (b) Density
(c) Refractive index (d) Melting point

20. The metalloid among the following group of elements is: **(CPMT 1993)**
(a) P (b) As (c) Al (d) Po

21. Which of the following alloys does contain Cu and Zn? **(IIT 1993)**
(a) Bronze (b) Brass
(c) Type metal (d) Rolled gold

22. Which metal is present in german silver?
(a) Copper (b) Iron (c) Silver (d) Zinc

23. Which of the following processes results in the formation of a new compound?
(a) Dissolving common salt in water
(b) Heating water
(c) Heating platinum rod
(d) Heating iron rod

24. Which one of the following is not a chemical change?
(a) Sublimation (b) Combustion
(c) Electrolysis (d) Rusting

25. The law of multiple proportions is illustrated by the pair of compounds:
(a) sodium chloride and sodium bromide
(b) water and heavy water
(c) sulphur dioxide and sulphur trioxide
(d) magnesium hydroxide and magnesium oxide

26. In compound *A*, 1.0 g nitrogen combines with 0.57 g oxygen. In compound *B*, 2.0 g nitrogen unite with 2.24 g oxygen and in compound *C*, 3.0 g nitrogen combine with 5.11 g oxygen. These results obey the law of:

(a) multiple proportions (b) constant proportions
(c) reciprocal proportions (d) none of these

27. Which one is the best example of law of conservation of mass?
(a) 6 g of carbon is heated in vacuum, there is no change in mass
(b) 6 g of carbon combines with 16 g of oxygen to form 22 g of CO_2
(c) 6 g water is completely converted into steam
(d) A sample of air is heated at constant pressure when its volume increases but there is no change in mass

28. A chemical equation is balanced according to the law of:
(a) multiple proportions (b) constant proportions
(c) reciprocal proportions (d) conservation of mass

29. SO_2 gas was prepared by (i) burning sulphur in oxygen, (ii) reacting sodium sulphite with dilute H_2SO_4 and (iii) heating copper with conc. H_2SO_4. It was found that in each case sulphur and oxygen combined in the ratio of 1 : 1. The data illustrates the law of:
(a) conservation of mass (b) multiple proportions
(c) constant proportions (d) reciprocal proportions

30. A sample of $CaCO_3$ has Ca = 40%, C = 12% and O = 48%. If the law of constant proportions is true, then the mass of Ca in 5 g of $CaCO_3$ from another source will be:
(a) 2.0 g (b) 0.2 g (c) 0.02 g (d) 20.0 g

31. Potassium combines with two isotopes of chlorine (^{35}Cl and ^{37}Cl) respectively to form two samples of KCl. Their formation follows the law of:
(a) constant proportions (b) multiple proportions
(c) reciprocal proportions (d) none of these

32. Different proportions of oxygen in the various oxides of nitrogen, prove the law of:
(a) reciprocal proportions (b) multiple proportions
(c) constant proportions (d) conservation of mass

33. One part of an element *A* combines with two parts of *B* (another element). Six parts of element *C* combine with four parts of element *B*. If *A* and *C* combine together, the ratio of their masses will be governed by:
(a) law of definite proportions
(b) law of multiple proportions
(c) law of reciprocal proportions
(d) law of conservation of mass

34. H_2S contains 5.88% hydrogen, H_2O contains 11.11% hydrogen while SO_2 contains 50% sulphur. These figures illustrate the law of:
(a) conservation of mass (b) constant proportions
(c) multiple proportions (d) reciprocal proportions

35. Number of atoms in 4.25 g of NH_3 is: **(AFMC 2010)**
(a) 6.023×10^{23} (b) $4 \times 6.023 \times 10^{23}$
(c) 1.7×10^{24} (d) $4.5 \times 6.023 \times 10^{23}$

[**Hint:** Number of molecules of $NH_3 = \frac{w}{M} \times 6.023 \times 10^{23}$

$$= \frac{4.25}{17} \times 6.023 \times 10^{23}$$

$$\text{Number of atom} = 4 \times \frac{4.25}{17} \times 6.023 \times 10^{23}$$

$$= 6.023 \times 10^{23}]$$

36. Hydrogen combines with chlorine to form HCl. It also combines with sodium to form NaH. If sodium and chlorine also combine with each other, they will do so in the ratio of their masses as:
(a) 23 : 35.5 (b) 35.5 : 23
(c) 1 : 1 (d) 23 : 1

37. Zinc sulphate contains 22.65% Zn and 43.9% H_2O. If the law of constant proportions is true, then the mass of zinc required to give 40 g crystals will be:
(a) 90.6 g (b) 9.06 g (c) 0.906 g (d) 906 g

38. 3 g of a hydrocarbon on combustion in excess of oxygen produces 8.8 g of CO_2 and 5.4 g of H_2O. The data illustrates the law of:
(a) conservation of mass (b) multiple proportions
(c) constant proportions (d) reciprocal proportions

[**Hint:** Mass of carbon in 8.8 g $CO_2 = \frac{12}{44} \times 8.8 = 2.4$ g;

$$\text{Mass of hydrogen in 5.4 g } H_2O = \frac{2}{18} \times 5.4 = 0.6 \text{ g}$$

$$\text{Total mass of } (C + H) = 2.4 + 0.6 = 3.0 \text{ g}]$$

39. In the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, the ratio of volumes of nitrogen, hydrogen and ammonia is 1 : 3 : 2. These figures illustrate the law of:
(a) constant proportions (b) Gay-Lussac
(c) multiple proportions (d) reciprocal proportions

40. Two volumes of ammonia, on dissociation gave one volume of nitrogen and three volumes of hydrogen. How much hydrogen will be obtained from the dissociation of 10 litre of NH_3?
(a) 30 litre (b) 10 litre (c) 15 litre (d) 20 litre

41. If 6 litre of H_2 and 5.6 litre of Cl_2 are mixed and exploded in an eudiometer, the volume of HCl formed is:
(a) 6.0 litre (b) 5.6 litre (c) 11.2 litre (d) 11.6 litre

42. The law of constant proportions was enunciated by:
(a) Dalton (b) Berthelot (c) Avogadro (d) Proust

43. An important postulate of Dalton's atomic theory is:
(a) an atom contains electrons, protons and neutrons
(b) atom can neither be created nor destroyed nor divisible
(c) all the atoms of an element are not identical
(d) all the elements are available in nature in the form of atoms

44. The atomic masses of the elements are usually fractional because:
(a) elements consist of impurities
(b) these are mixtures of allotropes
(c) these are mixtures of isobars
(d) these are mixtures of isotopes

45. The chemical formula of a particular compound represents:
(a) the size of its molecule
(b) the shape of its molecule
(c) the total number of atoms in a molecule
(d) the number of different types of atoms in a molecule

46. Which one of the following properties of an element is not variable?
(a) Valency (b) Atomic mass
(c) Equivalent mass (d) All of these

47. 1 amu is equal to:
(a) 1.00758 g (b) 0.000549 g
(c) 1.66×10^{-24} g (d) 6.02×10^{-23} g

48. Which one of the following relationships is correct?
(a) At. mass = 6.4 × Sp. heat.
(b) At. mass × Sp. heat = 6.4
(c) At. mass × 6.4 = Sp. heat
(d) At. mass × Sp. heat × 6.4 = 1

49. A_1 g of an element gives A_2 g of its oxide. The equivalent mass of the element is:
(a) $\frac{A_2 - A_1}{A_1} \times 8$ (b) $\frac{A_2 - A_1}{A_2} \times 8$
(c) $\frac{A_1}{A_2 - A_1} \times 8$ (d) $(A_2 - A_1) \times 8$

50. A_1 g of an element gives A_2 g of its chloride; the equivalent mass of the element is:
(a) $\frac{A_1}{A_2 - A_1} \times 35.5$ (b) $\frac{A_2}{A_2 - A_1} \times 35.5$
(c) $\frac{A_2 - A_1}{A_1} \times 35.5$ (d) $\frac{A_2 - A_1}{A_2} \times 35.5$

51. Which one of the relationship is wrong?
(a) 2 V.D. = Mol. mass
(b) At. mass = Eq. mass × Valency
(c) At. mass = $\frac{6.4}{\text{Sp. heat}}$
(d) Valency = $\frac{\text{Mol. mass}}{\text{Eq. mass}}$

52. In m_1 g of a metal A displaces m_2 g of another metal B from its salt solution and if their equivalent masses are E_1 and E_2 respectively, then the equivalent mass of A can be expressed as:
(a) $E_1 = \frac{m_2 \times E_2}{m_1}$ (b) $E_1 = \frac{m_1}{m_2} \times E_2$
(c) $E_1 = \frac{m_1 \times m_2}{E_2}$ (d) $E_1 = \sqrt{\frac{m_1}{m_2} \times E_2}$

53. When the specific heat of a metallic element is 0.214 cal g^{-1}, the atomic mass will be closest to which one of the following?
(a) 1 (b) 12 (c) 30 (d) 66

54. Approximate atomic mass of an element is 26.89. If its equivalent mass is 8.9, the exact atomic mass of the element is:
(a) 26.89 (b) 8.9 (c) 17.8 (d) 26.7

55. When an element forms an oxide in which oxygen is 20% of the oxide by mass, the equivalent mass of the element will be:
(a) 32 (b) 40 (c) 60 (d) 128

56. 0.32 g of a metal gave on treatment with an acid 112 mL of hydrogen at NTP. Calculate equivalent mass of the metal:
[AMU (Engg.) 2010]
(a) 58 (b 32 (c) 11.2 (d) 24

[**Hint:** Mass of metal that displaces 11200 mL hydrogen at STP will be its equivalent mass.

∴ Equivalent mass of metal = $\frac{0.32}{112} \times 11200 = 32$]

57. 74.5 g of a metallic chloride contains 35.5 g of chlorine. The equivalent mass of the metal is:
(a) 19.5 (b) 35.5 (c) 39.0 (d) 78.0

58. The product of atomic mass and specific heat of any element is a constant, approximately 6.4. This is known as:
(a) Dalton's law (b) Avogadro's law
(c) Gay-Lussac law (d) Dulong Petit's law

59. The molecular mass of chloride, MCl, is 74.5. The equivalent mass of the metal M will be:
(a) 39.0 (b) 74.5
(c) 110.0 (d) 35.5

[**Hint:** Mol. mass = At. mass + 35.5 = Eq. mass × valency + 35.5, Valency of M from the formula MCl is 1]

60. 1 g of hydrogen is found to combine with 80 g of bromine. 1 g of calcium combines with 4 g of bromine. The equivalent mass of calcium is:
(a) 10 (b) 20 (c) 40 (d) 80

61. 2.8 g of iron displaces 3.2 g of copper from a solution of copper sulphate. If the equivalent mass of iron is 28, the equivalent mass of copper will be:
(a) 16 (b) 32 (c) 48 (d) 64

62. The specific heat of a metal of atomic mass 32 is likely to be:
(a) 0.25 (b) 0.24 (c) 0.20 (d) 0.15

63. The equivalent mass of an element is 4. Its chloride has a vapour density 59.25. The valency of the element will be:
(a) 4 (b) 3 (c) 2 (d) 1

64. The equivalent mass of iron in the reaction,
$3Fe + 4H_2O = Fe_3O_4 + 4H_2$ would be:
(a) 21 (b) 56 (c) 42 (d) 10

65. The specific heat of a bivalent metal is 0.16. The approximate equivalent mass of the metal will be:
(a) 40 (b) 20 (c) 80 (d) 10

66. A sample of pure calcium weighing 1.35 g was quantitatively converted to 1.88 g of pure calcium oxide. Atomic mass of calcium would be:
(a) 20 (b) 40 (c) 16 (d) 35.5

67. A metal oxide is reduced by heating it in a stream of hydrogen. It is found that after complete reduction, 3.15 g of the oxide have yielded 1.05 g of the metal. We may conclude that:
(MLNR 1991)
(a) atomic mass of the metal is 4
(b) atomic mass of the metal is 8
(c) equivalent mass of the metal is 4
(d) equivalent mass of the metal is 8

68. Compounds with identical crystal structure and analogous chemical formula are called:
(a) isomers (b) isotones
(c) allotropes (d) isomorphous

69. Which pair of the following substances is said to be isomorphous?
(a) White vitriol and blue vitriol
(b) Epsom salt and Glauber's salt
(c) Blue vitriol and Glauber's salt
(d) White vitriol and epsom salt

c mass of chlorine is 35.5. It has two isotopes of atomic 5 and 37. The percentage of heavier isotope is:

(b) 15 (c) 20 (d) 25

c mass of boron is 10.81. It has two isotopes with 80% 0% abundance respectively. The atomic mass of the e having 80% abundance is 11.01. The atomic mass of ier isotope is:

.81 (b) 11.01 (c) 10.01 (d) 21.82

of chlorine combines with a metal giving 111 g of its le. The chloride is isomorphous with $MgCl_2 \cdot 6H_2O$. The mass of the metal is:

(b) 30 (c) 40 (d) 69

apour density of a volatile chloride of a metal is 59.5 and uivalent mass of the metal is 24. The atomic mass of the nt will be:

(b) 48 (c) 24 (d) 12

xide of an element possesses the molecular formula, . If the equivalent mass of the metal is 9, the atomic of the metal will be:

(b) 18 (c) 9 (d) 4.5

olecular mass of a compound having formula *MO* and lent mass 20 is:

(b) 40 (c) 28 (d) 20

ensity of air is 0.001293 g mL^{-1}. Its vapour density is:

3 (b) 14.3 (c) 1.43 (d) 0.143

Divide with the density of hydrogen, *i.e.*, 0.00009 g

of a substance when vaporised occupy a volume of 5.6 NTP. The molecular mass of the substance will be:

(b) $2M$ (c) $3M$ (d) $4M$

apour densities of two gases are in the ratio of 1 : 3. molecular masses are in the ratio of:

3 (b) 1 : 2 (c) 2 : 3 (d) 3 : 1

ganic compound on analysis was found to contain % of sulphur. The molecular mass of the compound, if its ule contains two sulphur atoms, is:

0 (b) 2000

000 (d) 200000

tomic mass of an element is 27. If valency is 3, the r density of the volatile chloride will be:

.75 (b) 6.675 (c) 667.5 (d) 81

ensity of a gas '*A*' is three times that of a gas '*B*'. If the ular mass of *A* is *M*, the molecular mass of *B* is:

(b) $M/3$ (c) $\sqrt{3}M$ (d) $\frac{M}{\sqrt{3}}$

r density of a volatile substance is 4 in comparison to ne ($CH_4 = 1$). Its molecular mass will be:

(b) 2 (c) 64 (d) 128

e the wrong statement:

nole means 6.02×10^{23} particles

olar mass is mass of one molecule

olar mass is mass of one mole of a substance

olar mass is molecular mass expressed in grams

le of CO_2 contains: **(MLNR 1990; CBSE 1993)**

2×10^{23} atoms of C

(c) 18.1×10^{23} molecules of CO_2

(d) 3 g-atoms of CO_2

85. Which among the following is the heaviest? **[PMT (Kerala) 2006]**

(a) One mole of oxygen
(b) One molecule of sulphur trioxide
(c) 100 amu of uranium
(d) 10 moles of hydrogen
(e) 44 g of carbon dioxide

86. The largest number of molecules is in:

(a) 28 g of CO (b) 46 g of C_2H_5OH
(c) 36 g of H_2O (d) 54 g of N_2O_5

87. Which of the following has the smallest number of molecules?

(a) 22.4×10^3 mL of CO_2 gas
(b) 22 g of CO_2 gas
(c) 11.2 litre of CO_2 gas
(d) 0.1 mole of CO_2 gas

88. The number of grams of H_2SO_4 present in 0.25 mole of H_2SO_4 is:

(a) 0.245 (b) 2.45 (c) 24.5 (d) 49.0

89. Number of molecules in 1 litre of oxygen at NTP is:

(a) $\frac{6.02 \times 10^{23}}{32}$ (b) $\frac{6.02 \times 10^{23}}{22.4}$
(c) 32×22.4 (d) $\frac{32}{22.4}$

90. 4.6×10^{22} atoms of an element weigh 13.8 g. The atomic mass of the element is:

(a) 290 (b) 180 (c) 34.4 (d) 10.4

91. The number of molecules in 89.6 litre of a gas at NTP are: **(BHU 1992)**

(a) 6.02×10^{23} (b) $2 \times 6.02 \times 10^{23}$
(c) $3 \times 6.02 \times 10^{23}$ (d) $4 \times 6.02 \times 10^{23}$

92. The total number of protons in 10 g of calcium carbonate is: **(CPMT 1992)**

(a) 3.0115×10^{24} (b) 1.5057×10^{24}
(c) 2.0478×10^{24} (d) 4.0956×10^{24}

93. 19.7 kg of gold was recovered from a smuggler. The atoms of gold recovered are: (Au = 197)

(a) 100 (b) 6.02×10^{23}
(c) 6.02×10^{24} (d) 6.02×10^{25}

94. The molecular mass of CO_2 is 44 amu and Avogadro's number is 6.02×10^{23}. Therefore, the mass of one molecule of CO_2 is:

(a) 7.31×10^{-23} (b) 3.65×10^{-23}
(c) 1.01×10^{-23} (d) 2.01×10^{-23}

95. Equal volumes of different gases at any definite temperature and pressure have:

(a) equal weights (b) equal masses
(c) equal densities (d) equal number of moles

96. A gaseous mixture contains oxygen and nitrogen in the ratio of 1 : 4 by mass. Therefore, the ratio of their number of molecules is:

m will react with ethyl alcohol to give:
of hydrogen (b) one mole of oxygen
of NaOH (d) 1/2 mole of hydrogen
an atom of carbon is:
(b) 1.99×10^{-23} g
(d) 1.99×10^{23} g
of moles of H_2 in 0.224 litre of hydrogen gas at
(MLNR 1994)
(b) 0.1 (c) 0.01 (d) 0.001
of 1 g helium at NTP in litres is:
(b) 0.56 (c) 2.8 (d) 0.28
s to contain 1.0×10^{24} particles, the mass of one
gen is:
(b) 5.32 g
(d) 16.0 g
of 1 litre capacity each are separately filled with
le, O_2 and O_3. At the same temperature and
ratio of the number of atoms of these gases
fferent flasks would be:
1 (b) 2 : 1 : 2 : 3
3 (d) 3 : 2 : 2 : 1
mperature and pressure, two flasks of equal
filled with H_2 and SO_2 separately. Particles which
umber, in the two flaskes are:
(b) electrons
es (d) neutrons
a mixture of 6.02×10^{23} oxygen atoms and
ydrogen molecules at NTP is:
(b) 33.6 litre
(d) 22.4 litre
of molecules present in a drop of water, if its
)5 mL, are:
^{21} (b) 1.66×10^{22}
^{23} (d) 1.66×10^{24}
was found to contain nitrogen and oxygen in the
n 28 g and oxygen 80 g. The formula of the
:
(b) N_2O_3
(d) N_2O_4
t formula of a compound containing 50% of
At. mass = 10) and 50% of the element *Y* (At.
;: **(IIT 1994)**
(b) X_2Y
(d) X_2Y_3
ts *X* (At. mass = 75) and *Y* (At. mass = 16)
ive a compound having 75.8% of *X*. The formula
und is: **(MLNR 1991)**
(b) X_2Y
(d) X_2Y_3
a certain compound was found to contain iodine
in the ratio of 254 : 80. The formula of the
: (At. mass of I = 127, O = 16)
(b) I_2O
(d) I_2O_5

110. A compound of aluminium and chlorine is composed of 9.0 g Al for every 35.5 g of chlorine. The empirical formula of the compound is:
(a) AlCl (b) $AlCl_3$ (c) $AlCl_2$ (d) $AlCl_4$

111. The haemoglobin from red corpuscles of most mammels contain approximately 0.33% of iron by mass. The molecular mass of haemoglobin is 67200. The number of iron atoms in each molecule of haemoglobin is:
(a) 4 (b) 3 (c) 2 (d) 1

112. The percentage of P_2O_5 in diammonium hydrogen phosphate, $[(NH_4)_2HPO_4]$ is: **(CPMT 1992)**
(a) 23.48 (b) 46.96
(c) 53.78 (d) 71.00

113. The percentage of nitrogen in urea (NH_2CONH_2), is:
(a) 38.4 (b) 46.6 (c) 59.1 (d) 61.3

114. The chloride of a metal has the formula MCl_3. The formula of its phosphate is:
(a) M_2PO_4 (b) MPO_4 (c) M_3PO_4 (d) $M(PO_4)_2$

115. 10 g of hydrofluoric acid gas occupies 5.6 litre of volume at NTP. If the empirical formula of the gas is HF, then its molecular formula will be: (At. mass of F = 19)
(a) HF (b) H_3F_3
(c) H_2F_2 (d) H_4F_4
[**Hint:** Molecular mass $=\frac{10}{5.6}\times 22.4=40$]

116. Calcium pyrophosphate is represented by the formula $Ca_2P_2O_7$. The molecular formula of ferric pyrophosphate is:
(a) $Fe_2P_2O_7$ (b) FeP_2O_7
(c) $Fe(P_2O_7)_3$ (d) $Fe_4(P_2O_7)_3$

117. The percentage of available chlorine in a sample of bleaching powder, $CaOCl_2\cdot 2H_2O$, is:
(a) 30 (b) 50 (c) 43.5 (d) 59.9

118. SI unit of energy is:
(a) kg $m^2\ s^{-2}$ (b) kg $m^{-1}\ s^2$
(c) kg $m^2\ s^{-1}$ (d) kg $m^2\ s^2$

119. One micro gram is equal to:
(a) 10^{-3} g (b) 10^3 g (c) 10^6 g (d) 10^{-6} g

120. Significant figures in 0.00051 are:
(a) 5 (b) 3 (c) 2 (d) 4

121. The number of significant figures in 6.02×10^{23} is:
(a) 23 (b) 3 (c) 4 (d) 26

122. Express 0.006006 into scientific notation in three significant digits:
(a) 6.01×10^{-3} (b) 6.006×10^{-3}
(c) 6.00×10^{-3} (d) 6.0×10^{-3}

123. The proper value of significant figures in 38.0 + 0.0035 + 0.00003 is:
(a) 38 (b) 38.0035
(c) 38.00353 (d) 38.0

124. Which of the following is the correct unit for measuring nuclear radii?
(a) Micron (b) Millimetre

er to prepare 1 litre normal solution of $KMnO_4$, how grams of $KMnO_4$ are required if the solution is to be acid medium for oxidation? **[PET (MP) 2002]**

8 g (b) 31.6 g (c) 62 g (d) 790 g

an oxide of a metal is converted to chloride completely yields 5 g chloride. The equivalent weight of metal is: **(KCET 2002)**

.25 (b) 3.325 (c) 12 (d) 20

er of atoms 558.5 g Fe (At. wt. of Fe = 55.85 g mol^{-1}) is: **(AIEEE 2002)**

ice that in 60 g carbon (b) 6.023×10^{23}

lf that of 8 g He (d) $558.5 \times 6.023 \times 10^{23}$

efix 10^{18} is: **[MEE (Kerala) 2002]**

ga (b) exa (c) kilo (d) nano

ega

ence in density is the basis of: **[MEE (Kerala) 2002]**

ra filtration (b) molecular sieving

avity separation (d) molecular attraction

omic absorption

yields

ective of the source, pure sample of water algen. This is % mass of oxygen and 11.11% mass of h(Kerala) 2002]

ned by the law of:

tant composition

nservation of mass (b) constant volume

ltiple proportion

y-Lussac's l of electron weigh one kilogram?

nany **[IIT (Screening) 2002]**

3×10^{23} (b) $\frac{1}{9.108} \times 10^{31}$

$\frac{3 \times 10^{54}}{9.108}$ (d) $\frac{1}{9.108 \times 6.023} \times 10^{8}$

he numbers: 161 cm; 0.161 cm; 0.0161 cm. The of significant figure for three numbers is: **[AFMC (Pune) 2002]**

, 5 (b) 3, 3, 3 (c) 3, 3, 4 (d) 3, 4, 4

one of the following laws directly explains the law of ation of mass? **(AFMC 2002)**

d's rule (b) Dalton's law

gadro's law (d) Berzelius hypothesis

as maximum number of atoms? **[IIT (Screening) 2003]**

C(12) (b) 56 g Fe(56)

Al(27) (d) 108 g Ag(108)

ich of sulphur is present in an organic compound, if ompound gave 1.158 g of $BaSO_4$ on analysis? **[PET (Kerala) 2005]**

(b) 15% (c) 20% (d) 25%

of H_2 and 20 mL of O_2 react to form water, what is e end of the reaction? **(AFMC 2005)**

137. The density of a liquid is 1.2 g/mL. There are 35 drops in 2 mL. The number of molecules in one drop (molar mass of liquid = 70) is:

(a) $\left(\frac{1.2}{35}\right) N_A$ (b) $\left(\frac{1}{35}\right)^2 N_A$

(c) $\frac{1.2}{(35)^2} N_A$ (d) $1.2N_A$

138. A sample of PCl_3 contains 1.4 mole the substance. How many atoms are there in the sample? **[CEE (Kerala) 2004]**

(a) 4 (b) 5.

(c) 8.431×10^{23} (d) 72×10^{24}

(e) 2.409×10^{24}

139. The equivalent weight of phosphoric acid H_3PO_4 in the reaction, $NaOH + H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$ is: **[BHU (Pre.) 2005]**

(a) 50 (b) 49 (c) 25 (d) 98

nt: Only one hydrogen of H_3PO_4 is replaced, *i.e.*, its basicity = 1

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{1} = 98]$$

140. 5.6 g of an organic compound on burning with excess of oxygen gave 17.6 g of CO_2 and 7.2 g H_2O. The organic compound is: **[PET (Kerala) 2006]**

(a) C_6H_6 (b) C_4H_8 (c) C_3H_8 (d) CH_3COOH

(e) CH_3CHO

141. The decomposition of a certain mass of $CaCO_3$ gave 11.2 dm^3 of CO_2 gas at STP. The mass of KOH required to completely neutralise the gas is: **(KCET 2006)**

(a) 56 g (b) 28 g (c) 42 g (d) 20 g

[**Hint:** 11.2 dm^3 of CO_2 at STP = $\frac{1}{2}$ mole CO_2

$$KOH + CO_2 \longrightarrow KHCO_3$$

$\frac{1}{2}$ mole CO_2 will be neutralised by $\frac{1}{2}$ mole KOH, *i.e.*, 28 g KOH.]

142. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$, will contain 0.25 mole of oxygen atoms? **(AIEEE 2006)**

(a) 0.02 (b) 3.125×10^{-2}

(c) 1.25×10^{-2} (d) 2.5×10^{-2}

[**Hint:**

$\because$ 8 mole oxygen atoms are present in 1 mole $Mg_3(PO_4)_2$

$\therefore$ 0.25 mole oxygen atoms will be present in $\frac{1}{8} \times 0.25$ mole

$Mg_3(PO_4)_2$, *i.e.*, 3.125×10^{-2} mole $Mg_3(PO_4)_2$]

143. An element, X has the following isotopic composition,

$^{200}X : 90\%$

$^{199}X : 8\%$

$^{202}X : 2\%$

the weighted average atomic mass of the naturally- occurring element 'X' is closest to : **[CBSE (Med.) 2007]**

(a) 201 amu (b) 202 amu (c) 199 amu (d) 200 amu age atomic mass of

$$\times 200 \Big] + \Big[\frac{8}{100} \times 199\Big] + \Big[\frac{2}{100} \times 202\Big]$$

6 amu ≈ 200 amu]

statement for 14 g CO is : **(VMMC 2007)**

s 2.24 L at NTP

pods to $\frac{1}{2}$ mole of CO

pond to same mole of CO and N_2

ponds 3.01×10^{23} molecules of CO

r of hydrogen atoms present in 25.6 g of sucrose
) which has molar mass of 342.3 g, is: **(VITEEE 2008)**

3 (b) 9.91×10^{23}

3 (d) 44 [illegible]

mber of moles of sucrose

$$= \frac{\text{Mass}}{\text{Molar mass}} = \frac{\text{[illegible]}}{342.3}$$

$$= 0.075$$

noles of hydrogen atom $= 0.075 \times 22$

toms of hydrogen $= 0.075 \times 22 \times 6.023 \times 10^{23}$

$$= 9.9 \times 10^{23}]$$

upied by one molecule of water (density = 1 g/cm^3) **[CBSE-PMT (Pre.) 2008]**

3 cm^3 (b) 5.5×10^{-23} cm^3

3 cm^3 (d) 6.023×10^{-23} cm^3

ass of one molecule $= \dfrac{18}{6.023 \times 10^{23}}$ g

$$= 2.98 \times 10^{-23}\ \text{g}$$

ne molecule $= \dfrac{M}{\text{Density}} = \dfrac{2.98 \times 10^{-23}}{1}$ cm^3

$$\approx 3 \times 10^{-23}\ \text{cm}^3\ ]$$

gen contains as many atoms as in: **(KCET 2008)**

ydrogen (b) 5 g of hydrogen

ydrogen (d) 1 g of hydrogen

s consists of uniform cylindrical particles of 150Å and 5000Å long. The specific volume of virus is If the virus is considered to be a single particle, its ass is:

)^7 g mol^{-1} (b) 7.90×10^7 g mol^{-1}

)^7 g mol^{-1} (d) 9.70×10^7 g mol^{-1}

ume of single virus $= \pi r^2 h$

$$= 3.14 \times (75 \times 10^{-8})^2 \times (5000 \times 10^{-8})$$

$$= 8.836 \times 10^{-17}\ \text{cm}^3$$

ingle virus $= \dfrac{\text{Volume}}{\text{Specific volume}} = \dfrac{8.836 \times 10^{-17}\ \text{cm}^3}{0.75\ \text{cm}^3/\text{g}}$

$$= 1.178 \times 10^{-16}\ \text{g}$$

ss of virus $= 1.178 \times 10^{-16} \times 6.023 \times 10^{23}$

$$= 7.09 \times 10^7\ \text{g mol}^{-1}\ ]$$

149. Common salt obtained from sea-water contains 95% NaCl by mass. The approximate number of molecules present in 10 g salt is: **(DPMT 2009)**

(a) 10^{21} (b) 10^{22}

(c) 10^{23} (d) 10^{24}

[**Hint :** Mass of NaCl in 10 g salt $= 10 \times \dfrac{95}{100} = 9.5$ g

Number of molecules of NaCl $= \dfrac{9.5}{58.5} \times 6.023 \times 10^{23}$

$$= 9.78 \times 10^{22} \approx 10^{23}]$$

150. 10 g hydrogen and 64 g oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be: **[CBSE (PMT) 2009]**

(a) 3 mol (b) 4 mol

(c) 1 mol (d) 2 mol

[**Hint :** $n_{H_2} = \dfrac{10}{2} = 5$ $\quad n_{O_2} = \dfrac{64}{32} = 2$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Case I : If H_2 is completely consumed then :

$$n_{H_2O} = 5\,\text{mol}$$

Case II : If O_2 is completely consumed then

$$n_{H_2O} = \frac{2}{1} \times 2 = 4\ \text{mol}$$

Since, O_2 gives le
hence, it is limiting amount of product on complete consumption
equal to 4.] ber of moles of water formed will be

151. An organic compound made of and N contains 20% nitrogen. What will be its molecular ma [it contains only one nitrogen atom in it? B) 2009]

(a) 70 (b) 140

(c) 100 (d) 65

[**Hint :** % N $= \dfrac{\text{Mass of nitrogen}}{\text{Molecular mass}} \times 100$

$$20 = \frac{14}{m} \times 100$$

$$m = 70\ ]$$

152. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5% respectively, the atomic mass of Fe is: **(IIT 2009)**

(a) 55.85 u (b) 55.95 u

(c) 55.75 u (d) 56.05 u

[**Hint :** Atomic mass of Fe $= \dfrac{5}{100} \times 54 + \dfrac{90}{100} \times 56 + \dfrac{5}{100} \times 57$

$$= 55.95\ \text{amu}]$$

153. The number of atoms in 0.1 mol triatomic gas is: ($N_A = 6.02 \times 10^{23}$ mol^{-1}) **[CBSE (PMT) 2010]**

(a) 6.026×10^{22} (b) 1.806×10^{23}

(c) 3.6×10^{23} (d) 1.8×10^{22}

[**Hint :** No. of atoms $= 0.1 \times 3 \times 6.02 \times 10^{23}$

$$= 1.806 \times 10^{23}]$$

questions given below may have more than one correct answers

the following relationships are wrong?

≈ 0.1 bar (b) 1 litre = 1 dm^3

0.239 cal (d) 1 eV = 9.11 × 10^{-4} J

of the following numbers have same significant

(b) 0.60 (c) 6.0 (d) 60

f the following have the same mass?

nole of O_2 gas

nole of SO_2 gas

3 × 10^{22} molecules of SO_2 gas

4 × 10^{23} molecules of O_2 gas

4. Select the numbers with same significant figures:
   (a) 6.02×10^{23} (b) 0.25
   (c) 6.60×10^{-34} (d) 1.50
5. Which are isomorphic to each other?
   (a) $CuSO_4 \cdot 5H_2O$ (b) $ZnSO_4 \cdot 7H_2O$
   (c) $FeSO_4 \cdot 7H_2O$ (d) $FeSO_4 \cdot 8H_2O$
6. 11.2 L of a gas at STP weighs 14 g. The gas could be:
   (a) N_2 (b) CO
   (c) NO_2 (d) N_2O
7. 8 g O_2 has same number of molecules as that in:
   (a) 14 g CO (b) 7 g CO
   (c) 11 g CO_2 (d) 22 g CO_2

Assertion-Reason TYPE QUESTIONS

e following questions, two statements are given as
A) and **'Reason' (R)**. Answer the questions by
er codes given below:

oth (A) and (R) are correct and (R) is the correct
anation of (A).

oth (A) and (R) are correct but (R) is not the correct
anation of (A).

) is correct and (R) is wrong.

) is wrong but (R) is correct.

oth (A) and (R) are wrong.

O_2 and 1 g O_3 have equal number of atoms.

ss of 1 mole atom is equal to its gram-atomic mass.

our density of sulphur vapour relative to oxygen is 2
ause sulphur atom is twice as heavy as that of oxygen
n.

our density depends upon the molecular state of the
stance in vapour state.

vogram is equal to 1 amu.

gram is reciprocal of Avogadro's number.

ole H_2SO_4 contains same mass of oxygen and sulphur.

ole H_2SO_4 represents 98 g mass.

nole oxygen and N_2 have same volume at same
perature and pressure.

ole gas at NTP occupies 22.4 litre volume at STP.

6. (A) Empirical formula of glucose is HCHO.
   (R) Molecular formula of glucose will also be equal to HCHO.
7. (A) The volume of 1 mole of an ideal gas at 1 bar pressure at 25°C is 24.78 litre.
   (R) 1 bar = 0.987 atm.
8. (A) Atomic weight = Specific heat (cal/mol) × 6.4
   (R) The formula is valid for metals only.
9. (A) Number of moles of H_2 in 0.224 L of H_2 is 0.01 mol.
   (R) 22.4 litres of H_2 at STP contains 6.023×10^{23} mol. **(AIIMS 1996)**
10. (A) The equivalent weight of an element is variable.
    (R) The valency of an element is variable. **(AIIMS 1995)**
11. (A) The number of significant figures in 507000 is three.
    (R) In 507000, all the zeros are significant.
12. (A) Law of conservation of mass is invalid for nuclear fission, fusion and disintegration.
    (R) The law proposes that mass is neither created nor destroyed in a reaction.
13. (A) Mass spectrometer is used for determination of atomic mass of isotopes.
    (R) Isotopes are the atoms of same element having same atomic number but different mass numbers.

E QUESTIONS

3. (a) 4. (d) 5. (a) 6. (c) 7. (d) 8. (b)
1. (c) 12. (c) 13. (a) 14. (d) 15. (d) 16. (a)
9. (a) 20. (b) 21. (b) 22. (a) 23. (d) 24. (a)
7. (b) 28. (d) 29. (c) 30. (a) 31. (d) 32. (b)
5. (a) 36. (a) 37. (b) 38. (a) 39. (b) 40. (c)
3. (b) 44. (d) 45. (d) 46. (b) 47. (c) 48. (b)
1. (d) 52. (b) 53. (c) 54. (d) 55. (a) 56. (b)
9. (a) 60. (b) 61. (b) 62. (c) 63. (b) 64. (a)
7. (c) 68. (d) 69. (d) 70. (d) 71. (c) 72. (c)
5. (a) 76. (b) 77. (d) 78. (a) 79. (d) 80. (a)
3. (b) 84. (a) 85. (e) 86. (c) 87. (d) 88. (c)
1. (d) 92. (a) 93. (d) 94. (a) 95. (d) 96. (c)
9. (c) 100. (a) 101. (a) 102. (b) 103. (c) 104. (d)
7. (b) 108. (d) 109. (d) 110. (b) 111. (a) 112. (c)
5. (c) 116. (d) 117. (c) 118. (a) 119. (d) 120. (c)
3. (d) 124. (d) 125. (b) 126. (a) 127. (a) 128. (b)
1. (d) 132. (b) 133. (c) 134. (a) 135. (e) 136. (d)
. (d) 140. (b) 141. (b) 142. (b) 143. (d) 144. (a)
. (b) 148. (a) 149. (c) 150. (b) 151. (a) 152. (b)

3. (b, c) 4. (a, c, d) 5. (b, c) 6. (a, b) 7. (b, c)

I-REASON TYPE QUESTIONS

(c) 4. (d) 5. (b) 6. (c) 7. (b) 8. (b)
(e) 12. (b) 13. (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

ng questions contain single correct option:

the following table:

npound l. mass)	**Mass of the compound (in grams) taken**
CO_2 (44)	4.4
NO_2 (46)	2.3
H_2O_2 (34)	6.8
SO_2 (64)	1.6

two compounds have least mass of oxygen?
cular masses of compounds are given in brackets.)

(EAMCET 2004)

nd IV (b) I and III (c) I and II (d) III and IV

I. Mass of oxygen present $= \frac{4.4}{44} \times 32 = 3.2$ g

II. Mass of oxygen present $= \frac{2.3}{46} \times 32 = 1.6$ g

II. Mass of oxygen present $= \frac{6.8}{34} \times 32 = 6.4$ g

V. Mass of oxygen present $= \frac{1.6}{64} \times 32 = 0.8$ g

l IV have least mass of oxygen.]

osphate of a certain metal M is $M_3(PO_4)_2$. The correct a of metal sulphate would be:

$(SO_4)_3$ (b) MSO_4

$(SO_4)_2$ (d) M_2SO_4

rcentage of Se in peroxidase enzyme is 0.5% by mass mass of Se = 78.4 amu). Then, the minimum ılar mass of enzyme which contains not more than one n is:

8×10^4 amu (b) 1.568×10^7 amu

8×10^3 amu (d) 1.568×10^6 amu

$\because$ 0.5 g Se is present in 100 g enzyme.

Se will be present in $\frac{100}{0.5} \times 78.4$ g enzyme

$= 15680$ amu

$= 1.568 \times 10^4$ amu]

mber of moles of a gas in 1 m^3 of volume at NTP is:

(b) 0.446 (c) 1.464 (d) 44.6

1 m^3 = 1000 L

nber of moles $= \frac{1000}{22.4} = 44.6$]

al number of electrons present in 18 mL water (density) is:

3×10^{23} (b) 6.023×10^{24}

3×10^{25} (d) 6.023×10^{21}

[Hint: Mass = 18 g

Number of molecules of H_2O in 18 g mass $= 6.023 \times 10^{23}$

Number of electrons in 18 g water $= 6.023 \times 10^{23} \times 10$

$= 6.023 \times 10^{24}$

$\because$ Each molecule of water contains 10 electrons.]

6. What is the empirical formula of vanadium oxide if 2.74 g of metal oxide contains 1.53 g of metal?

(a) V_2O_3 (b) VO (c) V_2O_5 (d) V_2O_7

[Hint: % of V $= \frac{1.53}{2.74} \times 100 = 55.83$

$\therefore$ % of O = 44.17

Element	**%**	**Atomic ratio**	**Simplest ratio**
V	55.83	$\frac{55.83}{52} = 1.1$	$\frac{1.1}{1.1} = 1$
O	44.17	$\frac{44.17}{16} = 2.76$	$\frac{2.76}{1.1} = 2.5$

V : O = 2 : 5

Thus, empirical formula = V_2O_5]

7. Number of moles of electrons in 4.2 g of N^{3-} ion (nitride ion) is:

(a) 3 (b) 2 (c) 1.5 (d) 4.2

8. The ratio of volumes occupied by 1 mole O_2 and 1 mole CO_2 under identical conditions of temperature and pressure is:

(a) 1 : 1 (b) 1 : 2 (c) 1 : 3 (d) 2 : 1

9. The maximum amount of $BaSO_4$ that can be obtained on mixing 0.5 mole $BaCl_2$ with 1 mole H_2SO_4 is:

(a) 0.5 mol (b) 0.1 mol (c) 0.15 mol (d) 0.2 mol

[Hint: $H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$

0.5 mole $BaCl_2$ will react with 0.5 mole H_2SO_4 to give 0.5 mole $BaSO_4$]

10. If 10^{21} molecules are removed from 100 mg CO_2, then number of moles of CO_2 left are:

(a) 6.10×10^{-4} (b) 2.8×10^{-3}

(c) 2.28×10^{-3} (d) 1.36×10^{-2}

[Hint: Number of molecules in 100 mg CO_2

$$= \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23}$$

$$= \frac{0.1}{44} \times 6.023 \times 10^{23}$$

$$= 1.368 \times 10^{21}$$

Molecules remaining $= 1.368 \times 10^{21} - 10^{21} = 0.368 \times 10^{21}$

Number of moles remaining $= \frac{0.368 \times 10^{21}}{6.023 \times 10^{23}} = 6.1 \times 10^{-4}$]

on one gram ion of Al^{3+} ion is:

: e coulomb (b) $\frac{1}{3} \times N_A \times e$ coulomb

e coulomb (d) $3 \times N_A \times e$ coulomb

: gram ion of Al^{3+} means one mole ion of Al^{3+}.
mole $Al^{3+} = 3 \times e \times N_A$ coulomb.]

ıass of N_2O as well as CO_2 is 44 g mol^{-1}. At 25°C
:essure, 1 L N_2O contains n molecules of gas. The
O_2 molecules in 2 L under same conditions will

(b) $2n$ (c) $\frac{n}{2}$ (d) $\frac{n}{4}$

is dissolved in 1 L water. The number of ions of
$^-$ in 1 mL of this solution will be:
^{19} (b) 1.2×10^{22} (c) 1.2×10^{20} (d) 6.02×10^{20}

nber of moles of NaCl

$$= \frac{\text{Mass}}{\text{Molar mass}} = \frac{5.85}{58.5} = 0.1$$

ons ($Na^+ + Cl^-$) in 1 L

$$= 2 \times 0.1 \times 6.023 \times 10^{23}$$

$$= 12.046 \times 10^{22}$$

ons in 1 mL $= \frac{12.046 \times 10^{22}}{1000} = 1.2 \times 10^{20}$]

de has the formula X_2O_3. It can be reduced by
give free metal and water. 0.1596 g of metal oxide
g of hydrogen for complete reduction. The atomic
al in amu is:

(b) 155.8 (c) 5.58 (d) 55.8

$$\underset{\substack{\text{mol} \\ 48)\text{ g}}}{{}_2O_3} + \underset{\substack{3\text{ mol} \\ 6\text{g}}}{3H_2} \longrightarrow 2X + 3H_2O$$

H_2 is required by 0.1596 g oxide
ill be required by 159.6 g oxide

$$2a + 48 = 159.6$$

$$a = 55.8$$

tomic mass of metal M.]

(PH_3) decomposes to produce vapours of
and H_2 gas. What will be the change in volume
L of phosphine is decomposed?

(b) 500 mL

(d) – 500 mL

$PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$

4 mL $\longrightarrow$ 1 mL 6 mL

0 mL $\longrightarrow \frac{100}{4}$ $\frac{6}{4} \times 100$

0 mL $\longrightarrow$ 25 mL 150 mL

eases by 75 mL.]

neutron is assumed to half of its original value,
t of proton is assumed to be twice of its original
he atomic mass of $^{14}_{6}C$ will be:

[**Hint:** In the isotope $^{14}_{6}C$: Number of protons = 6

Number of neutrons = 8

New atomic mass will be $= 2 \times 6 + \frac{1}{2} \times 8 = 16$

% Increase in mass $= \frac{16 - 14}{14} \times 100 = 14.28\%$]

17. The mass and charge of 1 mole electrons will be:
(a) 1 kg; 96500 C (b) 0.55 mg; 96500 C
(c) 1.55 mg; 96500 C (d) 5.5 mg; 96500 C

18. The simplest formula of the compound containing 50% X (atomic mass 10 amu) and 50% Y (atomic mass 20 amu) is:
(a) XY_2 (b) X_2Y (c) X_2Y_3 (d) XY

[**Hint:**

Element	**%**	**Atomic ratio**	**Simplest ratio**
X	50	$\frac{50}{10} = 5$	$\frac{5}{2.5} = 2$
Y	50	$\frac{50}{20} = 2.5$	$\frac{2.5}{2.5} = 1$

Formula = X_2Y]

19. Rest mass of 1 mole neutrons ($m_n = 1.675 \times 10^{-27}$ kg) is:
(a) 1.8×10^{-3} kg (b) 1.008×10^{-4} kg
(c) 1.08×10^{-3} kg (d) 1.008×10^{-3} kg

[**Hint:** Mass of 1 mole neutrons

$$= 1.675 \times 10^{-27} \times 6.023 \times 10^{23}$$

$$= 1.008 \times 10^{-3} \text{ kg}]$$

20. Loschmidt number is the number of:
(a) molecules present in 1 mL of a gas at STP
(b) molecules present in 1 gram mole of a gas at STP
(c) atoms present in 1 mL of a gas at STP
(d) atoms present in 1 gram mole of a gas at STP

21. Which of the following statements is incorrect?
(a) One gram mole of silver equals $\frac{108}{6.023} \times 10^{-23}$ g
(b) One mole of CH_4 and 17 g of NH_3 at NTP occupy same volume
(c) One mole Ag weighs more than that of two moles of Ca
(d) One gram mole of CO_2 is 6.023×10^{23} times heavier than one molecule of CO_2

22. One atom of an element 'X' weighs 6.664×10^{-23} gm. The number of gram atoms in 40 kg of it is:
(a) 10 (b) 100 (c) 10000 (d) 1000

23. The density of a liquid is 1.2 g/mL. There are 35 drops in 2 mL. The number of molecules in 1 drop is (molecular weight of liquid = 70):
(a) $\frac{1.2}{35} N_A$ (b) $\left(\frac{1}{35}\right)^2 N_A$
(c) $\frac{1.2}{(35)^2} N_A$ (d) $1.2 N_A$

[**Hint:** Volume of one drop $= \frac{2}{35}$ mL

Number of moles in one drop $= \frac{2 \times 1.2}{35 \times 70} = \frac{1.2}{(35)^2}$

nolecules in one drop $= \frac{1.2}{(35)^2} \times N_A$]

ne of a liquid will contain 4 mole? Molar mass of
0 and its density is 1.4 g/mL:
(b) 1.6 L (c) 0.8 L (d) 4.8×10^{23} L

t x L liquid contain 4 mole of it.

$$\text{ber of moles} = \frac{\text{Mass}}{\text{Molar mass}}$$

$$4 = \frac{x \times 1000 \times 1.4}{280}$$

$$x = \frac{4 \times 280}{1.4 \times 1000} = 0.8 \text{ L}]$$

ratio of Fe^{2+} to Fe^{3+} in a mixture of $FeSO_4$ and having equal number of sulphate ions in both
l ferric sulphates is:
(b) 3 : 2
(d) none of these

$SO_4 \longrightarrow Fe^{2+} + SO_4^{2-}$

$O_4)_3 \longrightarrow 2Fe^{3+} + 3SO_4^{2-}$

mole SO_4^{2-} ions are furnished by both $FeSO_4$ and

moles of $Fe^{2+} = x$

moles of $Fe^{3+} = \frac{2}{3}x$

$$Fe^{2+} : Fe^{3+} :: x : \frac{2}{3}x$$

$$= 3 : 2]$$

f electrons present in 3.6 mg of NH_4^+ are:
0^{21} (b) 1.2×10^{20} (c) 1.2×10^{22} (d) 2×10^{-3}

umber of electrons in one ion of $NH_4^+ = 10$

ions in 3.6 mg NH_4^+

$$= \frac{3.6 \times 10^{-3}}{18} \times 6.023 \times 10^{23} = 1.2 \times 10^{20}$$

ber of electrons in 3.6 mg $NH_4^+ = 1.2 \times 10^{20} \times 10$

$$= 1.2 \times 10^{21}]$$

ction $4A + 2B + 3C \longrightarrow A_4B_2C_3$, what will be the
moles of product formed, starting from one mole of
le of B and 0.72 mole of C?
(b) 0.3 (c) 0.24 (d) 2.32

$$\underset{\text{nol}}{A} + \underset{0.6\text{ mol}}{2B} + \underset{0.72\text{ mol}}{3C} \longrightarrow A_4B_2C_3$$

sent case, reactant 'C' will be the limiting reactant
will give least amount of product on being completely

gives 1 mol product,

'C' will give 0.24 mol of product.]

f $Na_2SO_4 \cdot nH_2O$ contains 12.6 gm of water. The
' is:

[**Hint:** $Na_2SO_4 \cdot nH_2O$

Molar mass = (142 + 18n)

$$\text{Mass of water} = \frac{12.6}{26.8} \times (142 + 18n)$$

$$18n = \frac{12.6}{26.8} \times (142 + 18n)$$

$$n = 7]$$

29. Consider the following data:

Element	Atomic weight
A	12.01
B	35.5

A and B combine to form a new substance X. If 4 moles of B combine with 1 mole of A to give 1 mole of X, then the weight of 1 mole of X is:
(a) 154 g (b) 74 g (c) 47.5 g (d) 160 g

30. How many moles of Na^+ ions are in 20 mL of 0.4 M Na_3PO_4?
(a) 0.008 (b) 0.024 (c) 0.05 (d) 0.20

[**Hint:** No. of moles of $Na_3PO_4 = \frac{MV}{1000} = \frac{0.4 \times 20}{1000}$

$= 0.008$

Number of moles of Na^+ = 3 × Number of moles of Na_3PO_4

$= 3 \times 0.008 = 0.024$]

31. The element whose one atom has mass of 10.86×10^{-26} kg is:
(a) boron (b) calcium (c) silver (d) zinc

32. An electric discharge is passed through a mixture containing 50 cc of O_2 and 50 cc of H_2. The volume of the gases formed (i) at room temperature, (ii) at 110°C will be:
(a) (i) 25 cc (ii) 50 cc (b) (i) 50 cc (ii) 75 cc
(c) (i) 25 cc (ii) 75 cc (d) (i) 75 cc (ii) 75 cc

[**Hint:** $2H_2(g) + O_2(g) \longrightarrow 2H_2O$

50 cc H_2 will combine with 25 cc O_2 to form 50 cc H_2O

∴ O_2 left = 25 cc

At room temperature, H_2O will be in liquid state but at 110°C, it will be gaseous. Thus, volume of gases at 25°C and 110°C will be 25 cc and 75 cc respectively.]

33. The mass of carbon present in 0.5 mole of $K_4[Fe(CN)_6]$ is:
(a) 1.8 g (b) 18 g (c) 3.6 g (d) 36 g

[**Hint:** 1 mole of $K_4[Fe(CN)_6]$ contains 6 mole carbon, *i.e.*, 72 g carbon.]

34. Caffeine has a molecular weight of 194. If it contains 28.9% by mass of nitrogen, number of atoms of nitrogen in one molecule of caffeine is:
(a) 4 (b) 6 (c) 2 (d) 3

[**Hint:** Mass of nitrogen in 194 amu caffeine $= \frac{28.9}{100} \times 194$

$= 56$ amu

∴ One molecule of caffeine will contain 4 atoms of nitrogen.]

35. Chlorine can be prepared by reacting HCl with MnO_2. The reaction is represented by the equation,

$$MnO_2(s) + 4HCl(aq.) \longrightarrow Cl_2(g) + MnCl_2(aq.) + 2H_2O(l)$$

Assuming that the reaction goes to completion, what mass of conc. HCl solution (36% HCl by mass) is needed to produce 2.5 g

36. What is the mass per cent of oxygen in $Al_2(SO_4)_3 \cdot 18H_2O$? The molar mass of this substance is 666.43 g/mol :
(a) 9.60 (b) 28.8 (c) 43.2 (d) 72

37. 0.25 g of an element 'M' reacts with excess fluorine to produce 0.547 g of the hexafluoride MF_6. What is the element?
(a) Cr (b) Mo (c) S (d) Te

38. How many electrons are present in 2×10^{-3} moles of ${}^{18}_{8}O^{2-}$?
(a) 1.2×10^{21} (b) 9.6×10^{21} (c) 1.2×10^{22} (d) 1.9×10^{22}

39. Fluorine reacts with uranium to form UF_6.

$$U(s) + 3F_2(g) \longrightarrow UF_6(g)$$

How many fluorine molecules are required to produce 2 mg of UF_6 from an excess of uranium? The molar mass of UF_6 is 352 g mol^{-1}.
(a) 3.4×10^{18} (b) 1×10^{19} (c) 2×10^{19} (d) 3.4×10^{21}

40. What is the formula of a substance with mass percentages of 35.79% for S, 62.92% for O and 1.13% for H?
(a) H_2SO_3 (b) H_2SO_4 (c) $H_2S_2O_7$ (d) $H_2S_2O_8$

41. In 1811, Avogadro calculated the formula of camphor by means of elemental chemical analysis and by measuring the density of its vapour. Avogadro found the density to be 3.84 g/L when he made the measurement at 210°C at 1 atm pressure. Which of the following is the correct formula of camphor?
(a) $C_{10}H_{14}O$ (b) $C_{10}H_{16}O$ (c) $C_{10}H_{16}O_2$ (d) $C_{10}H_{18}O$
(e) None of these

[**Hint:** $Pm = dRT$

$$m = \frac{dRT}{P} = \frac{3.84 \times 0.0821 \times 483}{1} = 152.27$$

$\therefore C_{10}H_{16}O$ will be the correct formula.]

42. A quantity of aluminium has a mass of 54 g. What is the mass of same number of magnesium atoms?
(a) 12.1 g (b) 24.3 g (c) 48.6 g (d) 97.2 g

43. When 1 L of CO_2 is heated with graphite, the volume of the gases collected is 1.5 L. Calculate the number of moles of CO produced at STP:
(a) $\frac{1}{11.2}$ (b) $\frac{28}{22.4}$ (c) $\frac{1}{22.4}$ (d) $\frac{14}{22.4}$

[**Hint:** $\underset{1-x}{CO_2(g)} + C(s) \longrightarrow \underset{2x}{2CO(g)}$

$$\text{Total volume} = 1 - x + 2x = 1 + x = 1.5$$
$$x = 0.5 \text{ L}$$
$$\therefore \text{ Volume of CO} = 2 \times 0.5 = 1 \text{ L}$$

Number of moles of CO $= \frac{1}{22.4}$]

44. Which of the following has greatest number of atoms?
(a) 1 g of butane (C_4H_{10}) (b) 1 g of nitrogen (N_2)
(c) 1 g of silver (Ag) (d) 1 g of water (H_2O)

45. A metal oxide has the formula M_2O_3. It can be reduced by H_2 to give free metal and water. 0.1596 g of M_2O_3 required 6 mg of H_2 for complete reduction. The atomic mass of the metal is:
(a) 27.9 (b) 79.8
(c) 55.8 (d) 159.8

[**Hint:** $\underset{(2x+48)\text{ g}}{M_2O_3} + \underset{6\text{ g}}{3H_2} \longrightarrow 2M + 3H_2O$

x = Atomic mass of metal

$\because$ 0.006 g H_2 reduces 0.1596 g M_2O_3

$\therefore$ 6 g H_2 will reduce $\frac{0.1596}{0.006} \times 6 \text{ g } M_2O_3 = 159.6 \, M_2O_3$

$$2x + 48 = 159.6$$
$$2x = 111.6$$
$$x = 55.8]$$

46. In a compound of molecular formula A_mB_n:
(a) number of equivalents of A, B and A_mB_n are same
(b) number of moles of A, B and A_mB_n are same
(c) $m \times$ moles of $A = n \times$ moles of $B = (m+n) \times$ moles of A_mB_n
(d) $n \times$ moles of $A = m \times$ moles of $B = (m+n) \times$ moles of A_mB_n

47. 4.4 g of CO_2 and 2.24 litre of H_2 at STP are mixed in a container. The total number of molecules present in the container will be:
(a) 6.022×10^{23} (b) 1.2044×10^{23}
(c) 6.023×10^{26} (d) 6.023×10^{24}

48. A partially dried clay mineral contains 8% water. The original sample contained 12% water and 45% silica. The % of silica in the partially dried sample is nearly:
(a) 50% (b) 49%
(c) 55% (d) 47%

[**Hint:**

	Clay	**Silica**	**Water**
Initial stage:	43%	45%	12%
Final stage:	$(92 - x)$	x	8%

Ratio of silica and clay will remain constant, before and after drying.

$$\therefore \quad \frac{45}{43} = \frac{x}{92 - x}$$
$$x = 47\%]$$

49. Which of the following is isomorphous with $MgSO_4 \cdot 7H_2O$?
(a) Green vitriol (b) Blue vitriol
(c) Red vitriol (d) Vitriol of mass

50. In the reaction;

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2; \quad N_2 + O_2 \longrightarrow 2NO$$

10 mL of mixture containing carbon monoxide and nitrogen required 7 mL oxygen to form CO_2 and NO, on combustion. The volume of N_2 in the mixture will be:
(a) 7/2 mL (b) 17/2 mL (c) 4 mL (d) 7 mL

[**Hint:** $\underset{x}{CO(g)} + \underset{x/2}{\frac{1}{2}O_2(g)} \longrightarrow CO_2(g)$

$$\underset{y}{N_2(g)} + \underset{y}{O_2(g)} \longrightarrow 2NO(g)$$

$$x + y = 10 \quad \ldots (i)$$
$$\frac{x}{2} + y = 7 \quad \ldots (ii)$$

Solving eqs. (i) and (ii),

$$x = 6 \text{ and } y = 4]$$

51. 1.44 g of titanium (Ti) reacted with excess of O_2 and produced x gm of a nonstoichiometric compound $Ti_{1.44}O_1$. The value of x is:

(b) 1.77
(d) None of these

he reaction:

$$Ti + O_2 \longrightarrow Ti_{1.44}O_1$$

noles of titanium = Number of moles of $Ti_{1.44}O_1$

$$\frac{1.44}{48} = \frac{x}{48 \times 1.44 + 16}$$

$x = 1.77$ g]

e of 75% alcohol by mass ($d = 0.8$ g/cm^3) must be pare 150 cc of 30% alcohol by mass ($d = 0.9$

L (b) 56.25 mL
 (d) 33.56 mL

V mL of alcohol was used.

$$\frac{75}{100} \times V \times 0.8 = \frac{30}{100} \times 150 \times 0.9$$

$V = 67.5$ mL]

Following questions may have more than one correct options:

1. 11.2 L of a gas at STP weighs 14 g. The gas could be:
   (a) N_2O (b) NO_2 (c) N_2 (d) CO
2. In which of the following pairs do 1 g of each have an equal number of molecules?
   (a) N_2O and CO (b) N_2 and C_3O_2
   (c) N_2 and CO (d) N_2O and CO_2
3. 8 g of oxygen has the same number of molecules as in:
   (a) 11 g CO_2 (b) 22 g CO_2 (c) 7 g CO (d) 14 g CO
4. Which of the following has three significant figures?
   (a) 6.02×10^{23} (b) 0.25
   (c) 6.60×10^{-34} (d) 1.50
5. 1 mole of ${}^{14}_{7}N^{3-}$ ions contains:
   (a) $7 \times 6.023 \times 10^{23}$ electrons (b) $7 \times 6.023 \times 10^{23}$ protons
   (c) $7 \times 6.023 \times 10^{23}$ neutrons (d) $14 \times 6.023 \times 10^{23}$ protons
6. 1 g atom of nitrogen represents:
   (a) 14 g nitrogen
   (b) 11.2 litre of N_2 at NTP
   (c) 22.4 litre of N_2 at NTP
   (d) 6.023×10^{23} molecules of N_2

vers

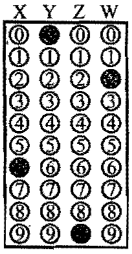
ect option

2. (b) 3. (a) 4. (d) 5. (b) 6. (c) 7. (a) 8. (a)
10. (a) 11. (d) 12. (b) 13. (c) 14. (d) 15. (c) 16. (b)
18. (b) 19. (d) 20. (a) 21. (a) 22. (d) 23. (c) 24. (c)
26. (a) 27. (c) 28. (d) 29. (a) 30. (b) 31. (d) 32. (c)
34. (a) 35. (b) 36. (d) 37. (b) 38. (c) 39. (b) 40. (c)
42. (c) 43. (c) 44. (a) 45. (c) 46. (a) 47. (b) 48. (d)
50. (c) 51. (b) 52. (c)

e than one correct options

2. (c, d) 3. (a, c) 4. (a, c, d) 5. (b, c) 6. (a)

Integer Answer TYPE QUESTIONS



o each of the following questions is a teger, ranging from 0 to 9. If the correct estion numbers X, Y, Z and W (say) are respectively, then the correct darkening ll look like the given figure.

ous alkane (C_nH_{2n+2}) is exploded with oxygen. The of O_2 used and CO_2 formed are in the ratio of 7 : 4. the value of *n*.

$$C_nH_{2n+2}+\left[n+\frac{n+1}{2}\right]O_2 \longrightarrow nCO_2+(n+1)\,H_2O$$

$$\frac{n+\frac{(n+1)}{2}}{n}=\frac{7}{4}$$

$$n=2\,]$$

nany atoms do a mercury vapour molecule consist of, if pour density of mercury vapour relative to air is 6.92? ic mass of mercury is 200). The average molar mass of 29 g/mol.

$$\frac{\text{Vapour density of Hg vapour}}{\text{Vapour density of air}}=\frac{\text{Molar mass of Hg}}{\text{Molar mass of Air}}$$

$$\frac{6.92}{1}=\frac{m}{29}$$

$$m=200\text{ g/mol}$$

mass is same as that of atomic mass hence mercury vapour ns monoatomic mercury.]

nole of an element contains 4.2×10^{24} electrons. What is omic number of the element?

romolecule of iron has molar mass 2800 amu, it contains on by mass. The number of iron atom in one formula unit macromolecule is:

Number of iron atoms in one formula unit of compound

$$=\frac{\%}{100}\times\frac{\text{Molecular mass}}{\text{Atomic mass}}=\frac{8}{100}\times\frac{2800}{56}=4\,]$$

es of '*A*' and 10 moles of '*B*' are mixed and allowed to ccording to the equation :

$$A+3B\longrightarrow 2C$$

nany moles of *C* are present when there are 4 moles of *A* container?

nany water molecules will be there in 3×10^{-23} g sample er?

7. 5 g H_2 is allowed to react with 14 g N_2 for the following reaction:

$$N_2(g)+3H_2(g)\longrightarrow 2NH_3(g)$$

What mass of H_2 will be left unreacted at the end of reaction?

[**Hint :** N_2 is limiting reactant, thus 14 g N_2 will give 17 g NH_3 and *x*g H_2 remains unreacted.

Mass before reaction = Mass after reaction

$$(5+14)\quad=\quad(17+x)$$

$$x=2\text{g}\,]$$

8. Calculate the number of moles of water in 976 g $BaCl_2\cdot2H_2O$.

9. If Avogadro's number be 3.01×10^{23} then the atomic mass of carbon will be:

10. How many moles of *R* will be produced when 8 mol of *P* and 5 mol of *Q* are allowed to react according to the equation :

$$2P+Q\longrightarrow R$$

11. The mass of 1×10^{22} molecules of blue vitriol ($CuSO_4\cdot xH_2O$) is 4.144 g. The value of '*x*' will be:

12. What will be the mass (in kg) of 7.298×10^{6} mol electrons?

13. Silver (Atomic weight = 108 g mol^{-1}) has a density of 10.5 g cm^{-3}. The number of silver atoms on a surface area of $10^{-12}m^2$ can be expressed in scientific notation as $y\times10^x$. The value of *x* is: **(IIT 2010)**

[**Hint :** Mass of 1 cm^3 Ag = 1 × 10.5 g

$$\text{Number of atoms}=\frac{10.5}{108}\times6.023\times10^{23}$$

$$\text{Number of atoms in 1 cm}=\left[\frac{10.5}{108}\times6.023\times10^{23}\right]^{1/3}$$

$$\text{Number of atoms in 1 cm}^2=\left[\frac{10.5}{108}\times6.023\times10^{23}\right]^{2/3}$$

Number of atoms in $10^{-2}m^2$ or $10^{-8}\,cm^2$

$$=\left[\frac{10.5}{108}\times6.023\times10^{23}\right]^{2/3}\times10^{-8}=1.5\times10^{7}]$$

14. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL and 25.0 mL. The number of significant figures in average titre value is: **(IIT 2010)**

[**Hint :** Average titre value $=\dfrac{25.2+25.25+25.0}{3}$

$$=\frac{75.45}{3}=\frac{75.4}{3}=25.1$$

(In addition, result is reported upto least place of decimal)]

swers

2. (1) **3.** (7) **4.** (4) **5.** (4) **6.** (1) **7.** (2) **8.** (8)
10. (4) **11.** (5) **12.** (4) **13.** (7) **14.** (3)

LINKED COMPREHENSION TYPE QUESTIONS

1

y, 'mole' is an essential tool for the chemical t is a basic SI unit adopted by the 14th general weights and measurements in 1971. A mole contains ıtary particles as the number of atoms present in 12 g of a gas at STP occupies 22.4 litre volume. Molar ids and liquids is not definite. Molar mass of a o called gram-atomic mass or gram molar mass. The g of mole is plenty, heap or the collection of large le of a substance contains 6.023×10^{23} elementary om or molecule. Atomic mass unit (amu) is the unit of g., atomic mass of single carbon is 12 amu.

lowing questions:

s of one amu is approximately:
(b) 0.5 g
10^{-24} g (d) 3.2×10^{-24} g

of a gas at STP are found to have a mass of 22 g. The r mass of the gas is:
(b) 44 (c) 88 (d) 33

s of one molecule of water is approximately:
(b) 0.5 g
10^{-24} g (d) 3.2×10^{-23} g

ıy atoms are present in 49 g of H_2SO_4?
023×10^{23} (b) $5 \times 6.023 \times 10^{23}$
023×10^{23} (d) $7 \times 3.02 \times 10^{23}$

s at STP contains 3×10^{22} molecules. The number of s in x L ozone at STP will be:
^{22} (b) 4×10^{23} (c) 6.02×10^{23} (d) 3×10^{24}

lro's number is 1×10^{23} mol^{-1} then the mass of one xygen would be:
nu (b) 16×6.02 amu
ı (d) 16×10^{-23} amu

the Avogadro's number then number of valence n 4.8 g of O^{2-} is:
(b) 4.2 N_A (c) 1.6 N_A (d) 3.2 N_A

2

he atoms of same element; they have same atomic rent mass numbers. Isotopes have different number ieir nucleus. If an element exists in two isotopes asses 'a' and 'b' in the ratio m : n, then average be $\frac{m \times a + n \times b}{m + n}$.

opes of same element have same position in the he elements which have single isotope are called nents. Greater is the percentage composition of an

Answer the following questions:

1. The isotopes of chlorine with mass number 35 and 37 exist in the ratio of..... Its average atomic mass is 35.5.
(a) 1 : 1 (b) 2 : 1 (c) 3 : 1 (d) 3 : 2
2. Which of the following isotopes is/are used to decide the scale of atomic mass?
(a) $^{12}_{6}C$ (b) $^{14}_{6}C$ (c) $^{16}_{8}O$ (d) $^{14}_{7}N$
3. Atomic mass of boron is 10.81. It has two isotopes namely $^{11}_{5}B$ and $^{x}_{5}B$ with their relative abundance of 80% and 20% respectively. The value of x is:
(a) 10.05 (b) 10 (c) 10.01 (d) 10.02
4. The ratio of the mass of ^{12}C atom to that of an atom of element X (whose atomicity is four) is 1 : 9. The moleculaı mass of element X is:
(a) 480 g mol^{-1} (b) 432 g mol^{-1}
(c) 36 g mol^{-1} (d) 84 g mol^{-1}
5. ^{12}C and ^{14}C isotopes are found as 98% and 2% respectively in any sample. Then, the number of ^{14}C atoms in 12 g of the sample will be:
(a) 1.5 mole atoms (b) 1.032×10^{22} atoms
(c) 2.06×10^{21} atoms (d) 2 g atoms

Passage 3

Empirical formula is the simplest formula of the compound which gives the atomic ratio of various elements present in one molecule of the compound. However, the molecular formula of the compound gives the number of atoms of various elements present in one molecule of the compound.

$$\text{Molecular formula} = (\text{Empirical formula}) \times n$$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

A compound may have same empirical and molecular formulae. Both these formulae are calculated by using percentage composition of constituent elements.

Answer the following questions:

1. Two metallic oxides contain 27.6% and 30% oxygen respectively. If the formula of first oxide is M_3O_4, that of second will be:
(a) MO (b) MO_2 (c) M_2O_5 (d) M_2O_3
2. Which of the following compounds have same empirical formula?
(a) Formaldehyde (b) Glucose
(c) Sucrose (d) Acetic acid
3. Which of the following represents the formula of a substance which contains 50% oxygen?
(a) N_2O (b) CO_2
(c) NO_2 (d) CH_3OH
4. An oxide of iodine (I = 127) contains 25.4 g of iodine and 8 g of oxygen. Its formula could be:
(a) I_2O_3 (b) I_2O
(c) I_2O_5 (d) I_2O_7

lrofluoric acid gas occupies 5.6 litres of volume at
e empirical formula of the gas is HF, then its
formula in the gaseous state will be:

(b) H_2F_2 (c) H_3F_3 (d) H_4F_4

species having different percentage composition of
:

)OH and $C_6H_{12}O_6$ (b) CH_3COOH and C_2H_5OH
CH_3 and HCOOH (d) C_2H_5OH and CH_3OCH_3

nd of Na, C and O contains 0.0887 mol Na, 0.132
2.65×10^{22} atoms of carbon. The empirical formula
ıpound is:

(b) $Na_3C_5O_2$
)$_3$ (d) $Na_{0.0887}C_{2.65 \times 10^{22}}O_{0.132}$

4

*loids are extracted from the extracts of the plants
na. Marijuana owes its activity to tetrahydro
ıich contains 70% as many as carbon atoms as
s and 15 times as many hydrogen atoms as oxygen
m of tetrahydro cannabinol is* 0.00318.

lowing questions:

ır mass of the compound is:

mu (b) 314 amu (c) 143 amu (d) 341 amu

ar formula of the compound is:

$_{30}O_2$ (b) $C_{21}H_{14}O_3$
$_{46}O$ (d) none of these

of oxygen atoms in 1 mol of the tetrahydro
ıol is:

(b) N_A (c) $3\ N_A$ (d) $4\ N_A$

$_A = 6.023 \times 10^{23}$

ge composition of carbon in the compound is:

% (b) 70.85% (c) 80.25% (d) 59.64%

5

*sity of a compound is defined as the ratio of mass of a
of gas to the mass of the same volume of hydrogen
tical conditions of temperature and pressure.*

$$= \frac{\text{Mass of certain volume of gas (22.4 L) at STP}}{\text{Mass of same volume of } H_2 \text{ gas (22.4 L) at STP}}$$

$$= \frac{Mw}{2}$$

lecular mass of gas = Vapour density × 2

*is a unitless quantity; it is unaffected by variation of
ıd pressure.*

llowing questions:

density of a metal chloride is 66. Its oxide contains
tal. The atomic mass of the metal is:

(b) 54 (c) 27.06 (d) 2.086

Number of equivalents of metal = Number of equivalents of oxygen

$$\frac{53}{E} = \frac{47}{8}$$

$$E = 9.02$$

Molecular formula of metal chloride = MCl_n

Molecular mass = $[n \times 9.02 + n \times 35.5] = 132$

$\therefore \quad n = 3$

$\therefore$ Atomic mass of metal = $3 \times 9.02 = 27.06$]

2. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. The moles of NO_2 in 100 moles of mixture are:
   (a) 33.48 (b) 53.52 (c) 38.3 (d) 76.6
3. At STP, 5.6 litre of a gas weighs 60 g. The vapour density of gas is:
   (a) 60 (b) 120 (c) 30 (d) 240
4. Which of the following two substances have same vapour density?
   (a) Glucose (b) Fructose (c) Sucrose (d) Starch
5. Let $NH_4HS(s)$ is heated in a closed vessel to decompose.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

The vapour density of the mixture will be:

(a) equal to that of NH_4HS
(b) lesser than that of NH_4HS
(c) greater than that of NH_4HS
(d) cannot be predicted

• Passage 6

Precision refers to the closeness of a set of values obtained for identical measurement of a quantity. Precision depends on the limitations of measuring devices and the skills with which it is used. However, accuracy refers to the closeness of a single measurement to its true value.

The digits in a properly recorded measurement are known as significant figures. These are meaningful digits in a measured or calculated quantity. The greater the number of significant figures in a reported result, smaller is the uncertainty and greater is the precision. The zeros at the beginning are not counted. The zeros to the right of a decimal point are counted. In the numbers that do not contain a decimal point, "trailing" zeros may or may not be significant. The purpose of zeros at the end of a number is to convey the correct range of uncertainty.

Answer the following questions:

1. If repeated measurements give values close to one another, the number is:
   (a) surely precise (b) surely accurate
   (c) surely precise and accurate (d) all of these are correct
2. The number of significant figures in a measured number contains how many uncertain number of digits?
   (a) Zero (b) 1
   (c) 2 (d) Cannot be predicted
3. In the number 2.4560, there are 5 significant digits. Which one is the least significant digit?
   (a) 2 (b) 4 (c) 0 (d) 6
4. If we add 296.2 and 2.256, we get the answer as 298.456 g. The number of significant figures in the result are:
   (a) 6 (b) 5 (c) 4 (d) 3
5. In which of the following numbers, all the zeros are not significant?
   (a) 0.0010 (b) 0.00100 (c) 0.001000 (d) 0.001

Answers

Passage 1.	**1.** (c)	**2.** (c)	**3.** (d)	**4.** (d)	**5.** (a)	**6.** (c)	**7.** (a)
Passage 2.	**1.** (c)	**2.** (a, c)	**3.** (b)	**4.** (b)	**5.** (b)		
Passage 3.	**1.** (d)	**2.** (a, b)	**3.** (d)	**4.** (c)	**5.** (b)	**6.** (b, c)	**7.** (a)
Passage 4.	**1.** (b)	**2.** (a)	**3.** (a)	**4.** (c)			
Passage 5.	**1.** (c)	**2.** (c)	**3.** (b)	**4.** (a, b)	**5.** (b)		
Passage 6.	**1.** (a)	**2.** (b)	**3.** (c)	**4.** (c)	**5.** (d)		

SELF ASSESSMENT

ASSIGNMENT NO. 1

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Cartisone is a molecular substance containing 21 atoms of carbon per molecule. The mass percentage of carbon in cartisone is 69.98%. What is the molecular mass of cartisone?
(a) 360.4 (b) 176.5 (c) 287.6 (d) 312.8

2. Total number of atoms present in 25 mg of camphor, $C_{10}H_{16}O$ is:
(a) 2.57×10^{21} (b) 9.89×10^{19}
(c) 2.67×10^{21} (d) 6.02×10^{20}

3. The oxide of a metal contains 60% of the metal. What will be the percentage of bromine in the bromide of the metal, if the valency of the metal is the same in both, the oxide and the bromide?
(a) 93% (b) 87% (c) 70% (d) 77%

4. The radius of water molecule having density 1 g mL^{-1} is:
(a) 1.925 Å (b) 73.46 Å (c) 19.25 Å (d) 7.346 Å

5. 3 g of an oxide of a metal is converted completely to 5 g chloride. Equivalent mass of metal is:
(a) 33.25 (b) 3.325 (c) 12 (d) 20

6. Quantitative analysis of a compound shows that it contains 0.110 mole of 'C', 0.055 mole of 'N' and 0.165 mole of 'O'. Its molecular mass is about 270. How many atoms of carbon are there in empirical and molecular formulae of the compound respectively?

	Empirical formula	Molecular formula
(a)	1	3
(b)	2	2
(c)	2	6
(d)	3	2

7. Total number of electrons present in 11.2 L of NH_3 at STP is:
(a) 6.02×10^{23} (b) 3.01×10^{23}
(c) 3.01×10^{24} (d) 5.1×10^{24}

8. Which one of the following is not a unit of length?
(a) Angstrom (b) Light-year
(c) Micron (d) Radian

9. Unit of J pa^{-1} is equivalent to:
(a) m^3 (b) cm^3
(c) dm^3 (d) none of these

10. The relative abundance of two isotopes of atomic masses 85 and 87 are 75% and 25% respectively. The average atomic mass of element is:
(a) 86 (b) 40 (c) 85.5 (d) 75.5

SECTION-II

Multiple Answers Type Objective Questions

11. Mass of one atom of oxygen is/are:
(a) 16 amu (b) 32 amu
(c) 16 gm (d) 2.656×10^{-23} gm

12. Which of the following compounds have same percentage composition of carbon?
(a) $C_6H_{12}O_6$ (b) CH_3COOH
(c) $HCOOCH_3$ (d) $C_{12}H_{22}O_{11}$

13. Which of the following is/are correct about 1 mole electrons?
(a) 6.023×10^{23} electrons (b) 5.48×10^{-7} kg
(c) 96500 coulomb charge (d) None of these

14. In which of the following numbers, all zeros are significant?
(a) 5.0005 (b) 0.0030 (c) 30.000 (d) 0.5200

15. Which of the following are correct SI units?
(a) Amount of substance in mol L^{-1}
(b) Pressure of gas in pascal
(c) Density of a solid in kg m^{-3}
(d) Force in newton

SECTION-III

Assertion-Reason Type Questions

This section contains 4 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Avogadro's number is a dimensionless quantity.

Because

Statement-2: It is a number of atoms or molecules in one gram mole.

17. **Statement-1:** An element has variable equivalent mass.

Because

Statement-2: The valency of element is variable.

18. **Statement-1:** Vapour density of CH_4 is half of O_2.

Because

Statement-2: 1.6 g of CH_4 contains same number of electrons as 3.2 g of O_2.

19. **Statement-1:** Specific gravity is dimensionless quantity.

Because

Statement-2: Specific gravity is relative density of a substance, measured with respect to density of water at 4°C.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then the correctly bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

20. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) N_2	(p) 40% carbon by mass
(b) CO	(q) Empirical formula CH_2O
(c) $C_6H_{12}O_6$	(r) Vapour density = 14
(d) CH_3COOH	(s) $14N_A$ ($N_A = 6.023 \times 10^{23}$) electrons in a mole

21. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) 1 L	(p) 10^{-5} N
(b) 1 J	(q) 0.2389 cal
(c) 9.9×10^6 erg	(r) 10^{-3} m^3
(d) 1 Dyne	(s) 6.25×10^{18} eV

22. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) 1 g mole of $O_2(g)$	(p) mass, 32 g
(b) 0.5 mole of $SO_2(g)$	(q) mass, 24 g
(c) 1 g of $H_2(g)$	(r) volume, 11.2 L at STP
(d) 0.5 mole of $O_3(g)$	(s) $1.5 \times 6.023 \times 10^{23}$ atoms

Answers

1. (a) **2.** (c) **3.** (b) **4.** (a) **5.** (a) **6.** (c) **7.** (c) **8.** (d)
9. (a) **10.** (c) **11.** (a, d) **12.** (a, b, c) **13.** (a, b, c) **14.** (a, c) **15.** (b, c, d) **16.** (a)
17. (b) **18.** (c) **19.** (a) **20.** (a-r, s) (b-r, s) (c-p, q) (d-p, q) **21.** (a-r) (b-q, s) (c-q) (d-p)
22. (a-p) (b-p, r, s) (c-r) (d-q, s)

CHAPTER 2

ATOMIC STRUCTURE

2.1 INTRODUCTION

The word **atom** is a Greek word meaning indivisible, *i.e.*, an ultimate particle which cannot be further subdivided. The idea that all matter ultimately consists of extremely small particles was conceived by ancient Indian and Greek philosophers. The old concept was put on firm footing by **John Dalton** in the form of **atomic theory** which he developed in the years 1803–1808. This theory was a landmark in the history of chemistry. According to this theory, atom is the smallest indivisible part of matter which takes part in chemical reactions. Atom is neither created nor destroyed. Atoms of the same element are similar in size, mass and characteristics; however, atoms of different elements have different size, mass and characteristics.

In 1833, Michael Faraday showed that there is a relationship between matter and electricity. This was the first major breakthrough to suggest that atom was not a simple indivisible particle of all matter but was made up of smaller particles. Discovery of **electrons, protons** and **neutrons** discarded the indivisible nature of the atom proposed by John Dalton.

The complexity of the atom was further revealed when the following discoveries were made in subsequent years:

(i) Discovery of cathode rays.
(ii) Discovery of positive rays.
(iii) Discovery of X-rays.
(iv) Discovery of radioactivity.
(v) Discovery of isotopes and isobars.
(vi) Discovery of quarks and the new atomic model.

During the past 100 years, scientists have made contributions which helped in the development of modern theory of atomic structure. The works of **J.J. Thomson** and **Ernest Rutherford** actually laid the foundation of the modern picture of the atom. It is now believed that the atom consists of several particles called **subatomic particles** like electron, proton, neutron, positron, neutrino, meson, etc. Out of these particles, the electron, the proton and the neutron are called **fundamental particles** and are the building blocks of the atoms.

2.2 CATHODE RAYS—DISCOVERY OF ELECTRON

The nature and existence of electron was established by experiments on conduction of electricity through gases. In 1859, **Julius Plucker** started the study of conduction of electricity through gases at low pressure in a discharge tube. [A common discharge tube consists of a hard glass cylindrical tube (about 50 cm long) with two metal electrodes sealed on both the ends. It is connected to a side tube through which it can be evacuated to any desired pressure with the help of a vacuum pump.] Air was almost completely removed from the discharge tube (pressure about 10^{-4} atmosphere). When a high voltage of the order of 10,000 volts or more was impressed across the electrodes, some sort of invisible rays moved from the negative electrode to the positive electrode (Fig. 2.1). Since, the negative electrode is referred to as cathode, these rays were called **cathode rays.**

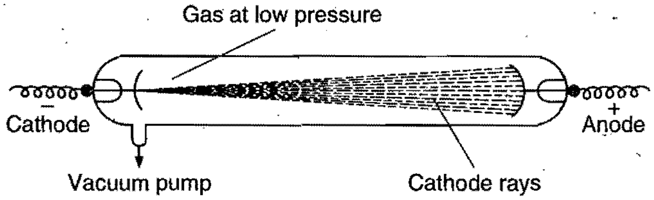


Fig. 2.1 Production of cathode rays

Further investigations were made by W. Crookes, J. Perrin, J.J. Thomson and others. Cathode rays possess the following properties:

(i) They travel in straight lines away from the cathode with very high velocities ranging from $10^9 - 10^{11}$ cm per second. A shadow of metallic object placed in the path is cast on the wall opposite to the cathode.

(ii) They produce a green glow when strike the glass wall beyond the anode. Light is emitted when they strike the zinc sulphide screen.

(iii) They produce heat energy when they collide with the matter. It shows that cathode rays possess kinetic energy which is converted into heat energy when stopped by matter.

(iv) They are deflected by the electric and magnetic fields. When the rays are passed between two electrically charged plates, these are deflected towards the positively charged plate. They discharge a positively charged gold leaf electroscope. It shows that **cathode rays carry negative charge.**

(v) They possess kinetic energy. It is shown by the experiment that when a small pin wheel is placed in their path, the blades of the wheel are set in motion. Thus, the **cathode rays consist of material particles which have mass and velocity.**

These particles carrying negative charge were called **negatrons** by Thomson.

The name 'negatron' was changed to 'electron' by **Stoney.**

(vi) Cathode rays produce X-rays. When these rays fall on a material having high atomic mass, new type of penetrating rays of very small wavelength are emitted which are called X-rays.

(vii) These rays affect the photographic plate.

(viii) These rays can penetrate through thin foils of solid materials and cause ionisation in gases through which they pass.

(ix) The nature of the cathode rays is independent of:

(a) the nature of the cathode and

(b) the gas in the discharge tube.

In 1897, **J. J. Thomson** determined the e/m value (charge/mass) of the electron by studying the deflections of cathode rays in electric and magnetic fields. The value of e/m has been found to be -1.7588×10^8 coulomb/g.

[The path of an electron in an electric field is parabolic, given as:

$$y = \frac{eE}{2mv^2} x^2$$

where, y = deflection in the path of electron in y-direction
e = charge on electron
E = intensity of applied electric field
m = mass of electron
v = velocity of electron
x = distance between two parallel electric plates within which electron is moving.

The path of an electron in a magnetic field is circular with radius 'r' given as:

$$r = \frac{mv}{eB}$$

where, m = mass of electron
v = velocity of electron
e = charge on electron
B = intensity of applied magnetic field

The radius of the path is proportional to momentum.]

By performing a series of experiments, **Thomson** proved that **whatever be the gas taken in the discharge tube and whatever be the material of the electrodes, the value of e/m is always the same.** Electrons are thus common universal constituents of all atoms.

J.J. Thomson gave following relation to calculate charge/mass ratio:

$$\frac{e}{m} = \frac{E}{rB^2}$$

where the terms have usual significance given before

$$= -1.7588 \times 10^{11} \text{ C kg}^{-1}$$

Electrons are also produced by the action of ultraviolet light or X-rays on a metal and from heated filaments. β-particles emitted by radioactive materials are also electrons.

The first precise measurement of the charge on an electron was made by **Robert A. Millikan** in 1909 by oil drop experiment. The charge on the electron was found to be -1.6022×10^{-19} coulomb. **Since, an electron has the smallest charge known, it was, thus,** designated as unit negative charge.

Mass of the electron: The mass of the electron can be calculated from the value of e/m and the value of e.

$$m = \frac{e}{e/m} = \frac{-1.6022 \times 10^{-19}}{-1.7588 \times 10^{8}}$$

$$= 9.1096 \times 10^{-28} \text{ g or } 9.1096 \times 10^{-31} \text{ kg}$$

This is termed as the rest mass of the electron, *i.e.*, mass of the electron when moving with low speed. The mass of a moving electron may be calculated by applying the following formula:

$$\text{Mass of moving electron} = \frac{\text{rest mass of electron}}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

where v is the velocity of the electron and c is the velocity of light. When v becomes equal to c, mass of the moving electron becomes infinity and when the velocity of the electron becomes greater than c, mass of the electron becomes imaginary.

Mass of the electron relative to that of hydrogen atom:

Mass of hydrogen atom = 1.008 amu

$$= 1.008 \times 1.66 \times 10^{-24} \text{ g} \quad (\text{since } 1 \text{ amu} = 1.66 \times 10^{-24} \text{ g})$$

$$= 1.673 \times 10^{-24} \text{ g}$$

$$\frac{\text{Mass of hydrogen atom}}{\text{Mass of the electron}} = \frac{1.673 \times 10^{-24}}{9.1096 \times 10^{-28}}$$

$$= 1837$$

$$\text{Thus, Mass of an electron} = \frac{1}{1837} \times \text{mass of hydrogen atom}$$

$$= \frac{1.008}{1837}$$

$$= 0.000549 \text{ amu}$$

An electron can, thus, be defined as a subatomic particle which carries charge -1.60×10^{-19} coulomb, *i.e.*, one unit negative charge and has mass 9.1×10^{-28} g, *i.e.*, $\frac{1}{1837}$th mass of the hydrogen atom (0.000549 amu).

[Millikan's oil drop method is used to determine the charge on an electron by measuring the terminal velocity of a charged spherical oil drop which is made stationary between two electrodes on which a very high potential is applied.

$$\text{Charge on an electron '}q\text{'} = \frac{6\pi\eta r}{E}(v_1 + v_2)$$

where, η = coefficient of viscosity of the gas medium
v_1, v_2 = terminal velocities
E = field strength

$$r = \text{radius of the oil drop} = \sqrt{\frac{9\eta v_1}{2(f-\sigma)g}}$$

(f = density of oil; σ = density of gas; g = gravitational force)]

2.3 POSITIVE RAYS—DISCOVERY OF PROTON

With the discovery of electrons, scientists started looking for positively charged particles which were naturally expected because matter is electrically neutral under ordinary conditions. The first experiment that led to the discovery of the positive particle was conducted by **Goldstein** in 1886. He used a perforated cathode in the modified cathode ray tube (Fig. 2.2). It was observed that when a high potential difference was applied between the electrodes, not only cathode rays were produced but also a new type of rays were produced simultaneously from anode moving towards cathode and passed through the holes or canals of the cathode. These rays were termed **canal rays** since these passed through the canals of the cathode. These were also named **anode rays** as these originated from anode. When the properties of these rays were studied by Thomson, he observed that these rays consisted of positively charged particles and named them as **positive rays.**

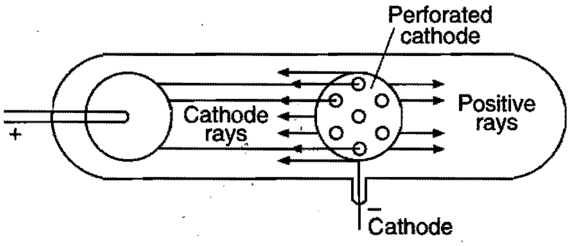


Fig. 2.2

The following characteristics of the positive rays were recognised:

(i) The rays travel in straight lines and cast a shadow of the object placed in their path.

(ii) Like cathode rays, these rays also rotate the wheel placed in their path and also have heating effect. Thus, the rays possess kinetic energy, *i.e.*, mass particles are present.

(iii) The rays produce flashes of light on zinc sulphide screen.

(iv) The rays are deflected by electric and magnetic fields in a direction opposite to that of cathode rays. These rays are attracted towards the negatively charged plate showing thereby that **these rays carry positive charge.**

(v) These rays can pass through thin metal foils.

(vi) These rays can produce ionisation in gases.

(vii) These rays are capable of producing physical and chemical changes.

(viii) Positive particles in these rays have e/m values much smaller than that of electron. This means either m is high or the value of charge is small in comparison to electron. Since, positive particle is formed by the loss of electron or electrons, the charge on the positive particle must be an integral multiple of the charge present on the electron. Hence, for a smaller value of e/m, it is definite that positive particles possess high mass.

(ix) e/m value is dependent on the nature of the gas taken in the discharge tube, *i.e.*, positive particles are different in different gases.

Accurate measurements of the charge and the mass of the particles obtained in the discharge tube containing hydrogen, the lightest of all gases, were made by J.J. Thomson in 1906. These particles were found to have the e/m value as $+9.579 \times 10^4$ coulomb/g. This was the maximum value of e/m observed for any positive particle. It was thus assumed that the positive particle given by hydrogen represents a fundamental particle of positive charge. This particle was named **proton** by **Rutherford** in 1911. Its charge was found to be equal in magnitude but opposite in sign to that of electron.

Thus, **proton carries a charge $+1.602 \times 10^{-19}$ coulomb, *i.e.*, one unit positive charge.**

The mass of the proton, thus, can be calculated.

$$\text{Mass of the proton} = \frac{e}{e/m} = \frac{1.602 \times 10^{-19}}{9.579 \times 10^4}$$

$$= 1.672 \times 10^{-24} \text{ g}$$

$$\text{or} \qquad = 1.672 \times 10^{-27} \text{ kg}$$

$$\text{Mass of the proton in amu} = \frac{1.672 \times 10^{-24}}{1.66 \times 10^{-24}} = 1.0072 \text{ amu}$$

A proton is defined as a subatomic particle which has a mass nearly 1 amu and a charge of +1 unit ($+1.602 \times 10^{-19}$ coulomb).

Protons are produced in a number of nuclear reactions. On the basis of such reactions, proton has been recognised as a fundamental building unit of the atom.

2.4 RUTHERFORD EXPERIMENT—DISCOVERY OF NUCLEUS

After the discovery of electron and proton, the question arose how these charged particles are distributed in an atom. The answer was given by J.J. Thomson in the form of first model of the atom.

He proposed that the positive charge is spread over a sphere in which the electrons are embedded to make the atom as a whole neutral. This model was much like raisins in a pudding and is also known as *Thomson's plum pudding model.* This model was discarded as it was not consistent with the results of further investigations such as scattering of α-particles by thin metal foils.

In 1911, Ernest Rutherford and his co-workers carried out a series of experiments using α-particles* (Fig. 2.3 and 2.4). A beam of α-particles was directed against a thin foil of about 0.0004 cm thickness of gold, platinum, silver or copper

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*The radiations emitted by radioactive substances consist of α-particles. These particles are positively charged. These particles are actually helium atoms from which electrons have been removed. Each α-particle consists of a mass equal to about 4 times that of hydrogen atom and carries a positive charge of two units. It is represented by the symbol α or ${}^4_2\text{He}$.

$$\underset{\text{Helium atom}}{\text{He}} \longrightarrow \underset{\alpha\text{-particle}}{\text{He}^{2+}} + \underset{\text{Electron}}{2e}$$

α-particles are usually obtained from a natural isotope of polonium-214.

respectively. The foil was surrounded by a circular fluorescent zinc sulphide screen. Whenever an α-particle struck the screen, it produced a flash of light.

The following observations were made:

(i) Most of the α-particles (nearly 99%) went straight without suffering any deflection.

(ii) A few of them got deflected through small angles.

(iii) A very few (about one in 20,000) did not pass through the foil at all but suffered large deflections (more than 90°) or even came back in more or less the direction from which they have come, *i.e.*, a deflection of 180°.

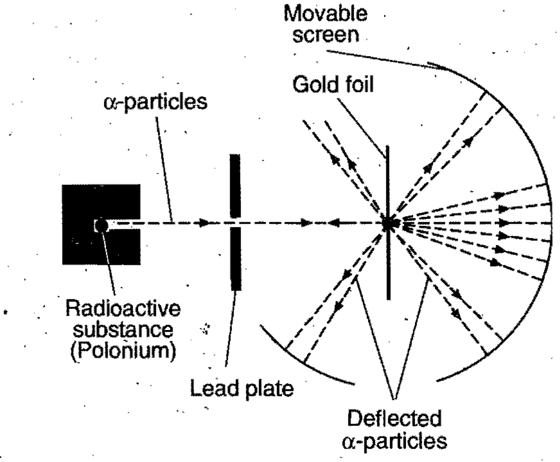

Fig. 2.3

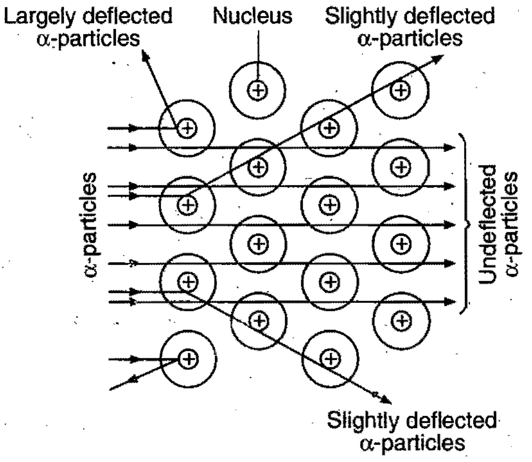

Fig. 2.4 (a)

Consider an α-particle of mass '*m*' moving directly towards a nucleus with velocity '*v*' at any given time. As this α-particle approaches the nucleus, its velocity and hence kinetic energy continues to decrease. At a certain distance r_0 from the nucleus, the α-particle will stop and then start retracing its depicted path. This distance is called the distance of closest approach. At this distance, the kinetic energy of the α-particle is transformed into electrostatic potential energy. If Z be the atomic number of the nucleus, then

$$\frac{1}{2}mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Z_e \times 2e}{r_0}$$

$$\because \text{ Electrostatic PE} = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r}$$

$$r_0 = \frac{1}{4\pi\varepsilon_0}\frac{4Ze^2}{mv^2}$$

$$r_0 = \frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{E_K}$$

where, E_K is the original kinetic energy of the α-particles.

Here, $$\frac{1}{4\pi\varepsilon_0} = 9\times10^9 \text{ Nm}^2\text{C}^{-2} \text{ (MKS)}$$

$$= 1 \text{(CGS)}$$

The distance of closest approach is of the order of 10^{-14} m. So, the radius of the nucleus should be less than 10^{-14} m.

Following conclusions were drawn from the above observations:

(i) Since, most of the α-particles went straight through the metal foil undeflected, it means that **there must be very large empty space within the atom** or **the atom is extraordinarily hollow.**

(ii) A few of the α-particles were deflected from their original paths through moderate angles; it was concluded that whole of the positive charge is concentrated and the space occupied by this positive charge is very small in the atom. When α-particles come closer to this point, they suffer a force of repulsion and deviate from their paths.

The positively charged heavy mass which occupies only a small volume in an atom is called **nucleus.** It is supposed to be present at the centre of the atom.

(iii) A very few of the α-particles suffered strong deflections or even returned on their path indicating that the nucleus is rigid and α-particles recoil due to direct collision with the heavy positively charged mass.

The graph between angle of scattering and the number of α-particles scattering in the corresponding direction is as shown in Fig. 2.4 (b).

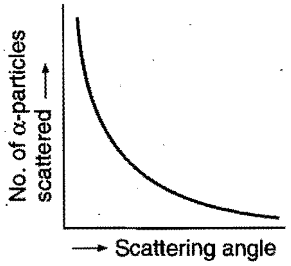

Fig. 2.4 (b)

Information of Rutherford's scattering equation can be memorised by the following relations:

(a) Kinetic energy of α-particles:

$$N = K_1/[(1/2)mv^2]^2$$

(b) Scattering angle 'θ':

$$N = K_2/[\sin^4(\theta/2)]$$

(c) Nuclear charge:

$$N = K_3(Ze)^2$$

Here, N = Number of α-particles striking the screen and K_1, K_2 and K_3 are the constants.

2.5 MOSELEY EXPERIMENT—ATOMIC NUMBER

Roentgen, in 1895, discovered that when high energy electrons in a discharge tube collide with the anode, penetrating radiations are produced which he named X-rays (Fig. 2.5).

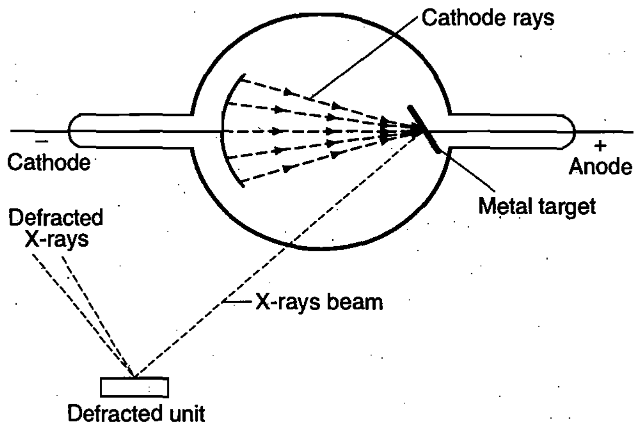

Fig. 2.5

X-rays are electromagnetic radiations of very small wavelengths (0.1–20 Å). X-rays are diffracted by diffraction gratings like ordinary light rays and X-ray spectra are, thus, produced. Each such spectrum is a characteristic property of the element used as anode.

Moseley (1912–1913), investigated the X-ray spectra of 38 different elements, starting from aluminium and ending in gold. He measured the frequency of principal lines of a particular series (the α-lines in the *K* series) of the spectra. It was observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But, it was soon realised that the frequency of the particular spectral line was more precisely related with the serial number of the element in the periodic table which he termed as atomic number (Z). He presented the following relationship:

$$\sqrt{\nu} = a(Z - b)$$

where, ν = frequency of X-rays, Z = atomic number, a and b are constants. When the values of square root of the frequency were plotted against atomic numbers of the elements producing X-rays, a straight line was obtained (Fig. 2.6).

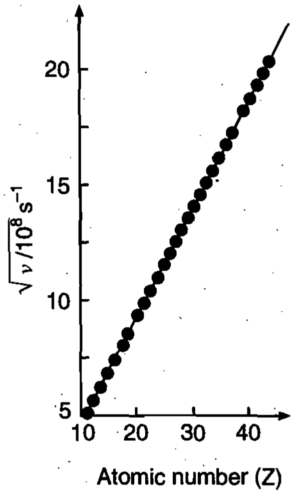

Fig. 2.6

van den Broek (1913) pointed out that the atomic number of an element is equal to the total positive charge contained in the nucleus of its atom. Rutherford was also having the same opinion that the atomic number of an element represents the number of protons in the nucleus of its atom. Thus,

Atomic number of the element
= Serial number of the element in periodic table
= Charge on the nucleus of the atom of the element
= Number of protons present in the nucleus of the atom of the element
= Number of extranuclear electrons present in the atom of the element

2.6 DISCOVERY OF NEUTRON

The discovery of neutron was actually made about 20 years after the structure of atom was elucidated by Rutherford. Atomic masses of different atoms could not be explained if it was accepted that atoms consisted only of protons and electrons. Thus, Rutherford (1920) suggested that in an atom, there must be present at least a third type of fundamental particles which should be electrically neutral and possess mass nearly equal to that of proton. He proposed the name for such fundamental particle as **neutron.** In 1932, **Chadwick** bombarded beryllium with a stream of α-particles. He observed that penetrating radiations were produced which were not affected by electric and magnetic fields. These radiations consisted of neutral particles, which were called neutrons. The nuclear reaction can be shown as:

$$\underset{\text{Beryllium}}{{}^{9}_{4}\text{Be}} + \underset{\alpha\text{-particle}}{{}^{4}_{2}\text{He}} \longrightarrow \underset{\text{Carbon}}{{}^{12}_{6}\text{C}} + \underset{\text{Neutron}}{{}^{1}_{0}n}$$

The mass of the neutron was determined. It was 1.675×10^{-24} g, *i.e.*, nearly equal to the mass of proton.

Thus, **a neutron is a subatomic particle which has a mass 1.675×10^{-24} g, approximately 1 amu, or nearly equal to the mass of proton or hydrogen atom and carrying no electrical charge.** The e/m value of a neutron is thus zero.

2.7 RUTHERFORD MODEL

On the basis of scattering experiments, Rutherford proposed a model of the atom which is known as nuclear atomic model. According to this model:

(i) An atom consists of a heavy positively charged nucleus where all the protons and neutrons are present. Protons and neutrons are collectively referred to as **nucleons.** Almost whole of the mass of the atom is contributed by these nucleons. The magnitude of the positive charge on the nucleus is different for different atoms.

(ii) The volume of the nucleus is very small and is only a minute fraction of the total volume of the atom. Nucleus has a diameter of the order of 10^{-12} to 10^{-13} cm and the atom has a diameter of the order of 10^{-8} cm.

$$\frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^{5}$$

Thus, diameter (size) of an atom is 100,000 times the diameter of the nucleus.*

The radius of a nucleus is proportional to the cube root of the number of nucleons within it.

$$R = R_0 A^{1/3} \text{ cm}$$

where, $R_0 = 1.33 \times 10^{-13}$ cm; A = mass number; R = Radius of the nucleus.

Rutherford and **Marsden** calculated the density of the hydrogen nucleus containing only one proton.

$$d = \frac{\text{Mass}}{\text{Volume}} = \frac{[A \times 1.66 \times 10^{-24} \text{ g}]}{\frac{4}{3} \times \pi R^3 \text{ cm}^3}$$

$$= \frac{A \times 1.66 \times 10^{-24}}{\frac{4}{3} \times 3.14 \times (1.33 \times 10^{-13})^3 \times A}$$

$$= 1.685 \times 10^{14} \text{ g/cm}^3$$

(iii) There is an empty space around the nucleus called extranuclear part. In this part, electrons are present. The number of electrons in an atom is always equal to number of protons present in the nucleus. As the nucleus part of the atom is responsible for the mass of the atom, the extranuclear part is responsible for its volume. The volume of an atom is about 10^{15} times the volume of the nucleus.

$$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{(10^{-8})^3}{(10^{-13})^3} = \frac{10^{-24}}{10^{-39}} = 10^{15}$$

(iv) Electrons revolve round the nucleus in closed orbits with high speed. The centrifugal force acting on the revolving electrons is being counterbalanced by the force of attraction between the electrons and the nucleus.

This model was similar to the solar system, the nucleus representing the sun and revolving electrons as planets. The electrons are, therefore, generally referred to as **planetary electrons.**

Dissimilarities between Nuclear Atomic Model and Solar System

(i) The sun and the planets are very big bodies and uncharged while the nucleus and electrons are very small objects and charged.

(ii) The revolution of the planets in the solar system is governed by gravitational forces, while the revolution of electrons around the nucleus is governed by electrostatic forces.

(iii) In the solar system, there is only one planet which revolves in any particular orbit, but in the nuclear atomic model more than one electron may rotate in any particular orbit.

Drawbacks of Rutherford Model

(i) According to classical electromagnetic theory, when a charged particle moves under the influence of attractive force, it loses energy continuously in the form of electromagnetic radiations. Thus, when the electron (a charged particle) moves in an attractive field (created by protons present in the nucleus), it must emit radiations. As a result of this, the electron should lose energy at every turn and move closer and closer to the nucleus following a spiral path (Fig. 2.7). The ultimate result will be that it will fall into the nucleus, thereby making the atom unstable. Bohr made calculations and pointed out that an atom would collapse in 10^{-8} seconds. Since, the atom is quite stable, it means the electrons do not fall into the nucleus, thereby this model does not explain the stability of the atom.

(ii) If the electrons lose energy continuously, the observed spectrum should be continuous but the actual observed spectrum consists of well defined lines of definite frequencies. Hence, the loss of energy by the electrons is not continuous in an atom.

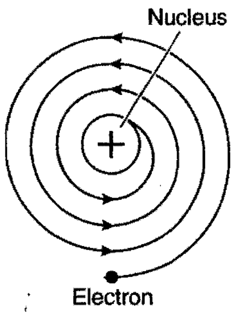

Fig. 2.7

2.8 ELECTROMAGNETIC RADIATIONS

These are energy radiations which do not need any medium for propagation, *e.g.*, visible, ultraviolet, infrared, X-rays, γ-rays, etc. An electromagnetic radiation is generated by oscillations of a charged body in a magnetic field or a magnet in an electrical field. The frequency of a wave is the frequency of oscillation of the oscillating charged particle. These radiations or waves have electrical and magnetic fields associated with them and travel at right angle to these fields. The following are thus the important characteristics of electromagnetic radiations:

- All electromagnetic radiations travel with the velocity of light.
- These consist of electric and magnetic fields that oscillate in directions perpendicular to each other and perpendicular to the direction in which the wave is travelling.

S. No.	Name	Wavelength (Å)	Frequency (Hz)	Source
1.	Radio wave	$3 \times 10^{14} - 3 \times 10^7$	$1 \times 10^5 - 1 \times 10^9$	Alternating current of high frequency
2.	Micro wave	$3 \times 10^7 - 6 \times 10^6$	$1 \times 10^9 - 5 \times 10^{11}$	Klystron tube
3.	Infrared (IR)	$6 \times 10^6 - 7600$	$5 \times 10^{11} - 3.95 \times 10^{16}$	Incandescent objects
4.	Visible	7600–3800	$3.95 \times 10^{16} - 7.9 \times 10^{14}$	Electric bulbs, sun rays
5.	Ultraviolet (UV)	3800–150	$7.9 \times 10^{14} - 2 \times 10^{16}$	Sun rays, arc lamps with mercury vapours
6.	X-Rays	150–0.1	$2 \times 10^{16} - 3 \times 10^{19}$	Cathode rays striking metal plate
7.	γ-Rays	0.1–0.01	$3 \times 10^{19} - 3 \times 10^{20}$	Secondary effect of radioactive decay
8.	Cosmic rays	0.01–Zero	3×10^{20}–Infinity	Outer space

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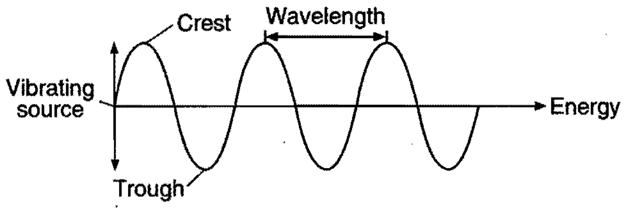
*The diameter of various atoms lies in the range of 0.74 to 4.70 Å (1 Å = 10^{-8} cm).

A wave is always characterized by the following six characteristics:

(i) Wavelength: The distance between two nearest crests or nearest troughs is called the wavelength. It is denoted by λ (lambda) and is measured in terms of centimetre (cm), angstrom (Å), micrometre (μm) or nanometre (nm).



$$1\,\text{Å} = 10^{-8}\ \text{cm} = 10^{-10}\ \text{m}$$
$$1\ \mu\text{m} = 10^{-4}\ \text{cm} = 10^{-6}\ \text{m}$$
$$1\ \text{nm} = 10^{-7}\ \text{cm} = 10^{-9}\ \text{m}$$
$$1\ \text{cm} = 10^{8}\ \text{Å} = 10^{4}\ \mu\text{m} = 10^{7}\ \text{nm}$$

(ii) Frequency: It is defined as the number of waves which pass through a point in one second. It is denoted by the symbol ν (nu) and is measured in terms of cycles (or waves) per second (cps) or hertz (Hz).

$$\lambda\nu = \text{distance travelled in one second} = \text{velocity} = c$$

or $$\nu = \frac{c}{\lambda}$$

(iii) Velocity: It is defined as the distance covered in one second by the wave. It is denoted by the letter 'c'. All electromagnetic waves travel with the same velocity, *i.e.*, 3×10^{10} cm/sec.

$$\lambda\nu = 3 \times 10^{10}$$

Thus, a wave of higher frequency has a shorter wavelength while a wave of lower frequency has a longer wavelength.

(iv) Wave number: This is the reciprocal of wavelength, *i.e.*, the number of wavelengths per centimetre. It is denoted by the symbol $\bar{\nu}$ (nu bar).

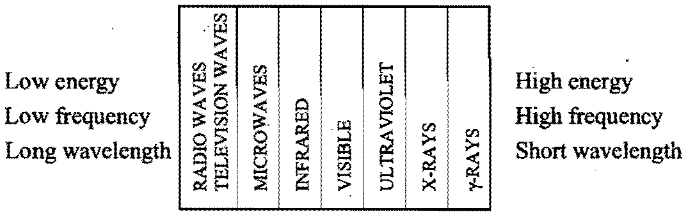
$$\bar{\nu} = \frac{1}{\lambda}$$

It is expressed in cm^{-1} or m^{-1}.

(v) Amplitude: It is defined as the height of the crest or depth of the trough of a wave. It is denoted by the letter 'a'. It determines the intensity of the radiation.

The arrangement of various types of electromagnetic radiations in the order of their increasing or decreasing wavelengths or frequencies is known as electromagnetic spectrum.

$$\nu = 3 \times 10^{7}\ (\text{cycle/sec}) \xrightarrow{\text{Frequency}} 3 \times 10^{21}$$
$$\lambda\ (\text{cm}) = 10^{3} \xleftarrow{\text{Wavelength}} 10^{-11}$$



(vi) Time period: Time taken by the wave for one complete cycle or vibration is called time period. It is denoted by T.

$$T = \frac{1}{\nu}$$

Unit: Second per cycle.

2.9 EMISSION SPECTRA—HYDROGEN SPECTRUM

Spectrum is the impression produced on a screen when radiations of particular wavelengths are analysed through a prism or diffraction grating. It is broadly of two types:

(i) Emission spectra (ii) Absorption spectra.

Difference between Emission and Absorption Spectrum

Emission spectrum	Absorption spectrum
1. It gives bright lines (coloured) on the dark background.	It gives dark lines on the bright background.
2. Radiations from emitting source are analysed by the spectroscope.	It is observed when the white light is passed through the substance and the transmitted radiations are analysed by the spectroscope.
3. It may be continuous (if source emits white light) and may be discontinuous (if the source emits coloured light).	These are always discontinuous.

Emission spectra: It is obtained from the substances which emit light on excitation, *i.e.*, either by heating the substances on a flame or by passing electric discharge through gases at low pressure or by passing electric current discharge through a thin filament of a high melting point metal. Emission spectra are of two types:

(a) Continuous spectra and (b) Discontinuous spectra.

(a) Continuous spectra: When white light is allowed to pass through a prism, it gets resolved into several colours (Fig. 2.8). The spectrum is a rainbow of colours, *i.e.*, violet merges into blue, blue into green, and so on. This is a continuous spectrum.

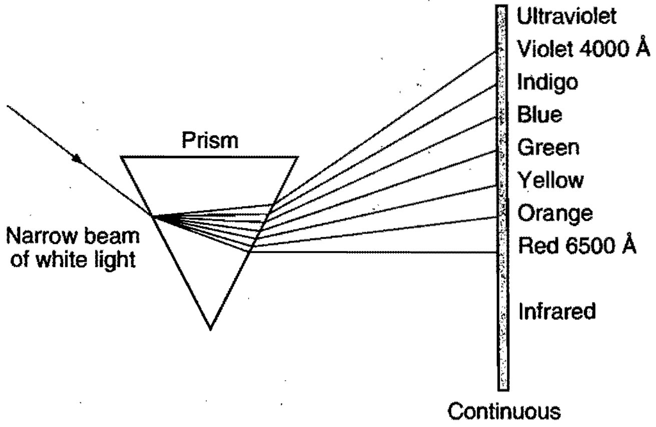


Fig. 2.8 Continuous spectrum of white light

(b) Discontinuous spectra: When gases or vapours of a chemical substance are heated in an electric arc or in a Bunsen flame, light is emitted. If a ray of this light is passed through a prism, a line spectrum is produced. This spectrum consists of a limited number of lines, each of which corresponds to a different wavelength of light. The line spectrum of each element is unique. Hydrogen spectrum is an example of line emission spectrum or atomic emission spectrum.

When an electric discharge is passed through hydrogen gas at low pressure, a bluish light is emitted. When a ray of this light is passed through a prism, a discontinuous line spectrum of several isolated sharp lines is obtained. The wavelengths of various lines show that these lines lie in visible, ultraviolet and infrared regions. All these lines observed in the hydrogen spectrum can be classified into six series.

Spectral series	Discovered by	Appearing in
Lyman series	Lyman	Ultraviolet region
Balmer series	Balmer	Visible region
Paschen series	Paschen	Infrared region
Brackett series	Brackett	Infrared region
Pfund series	Pfund	Infrared region
Humphrey series	Humphrey	Far infrared region

Ritz presented a mathematical formula to find the wavelengths of various hydrogen lines.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Where, R is a universal constant, known as Rydberg constant. Its value is 109,678 cm^{-1}, n_1 and n_2 are integers (such that $n_2 > n_1$). For a given spectral series, n_1 remains constant while n_2 varies from line to line in the same series.

The value of $n_1 = 1, 2, 3, 4$ and 5 for the Lyman, Balmer, Paschen, Brackett and Pfund series respectively. n_2 is greater than n_1 by at least 1.

Values of n_1 and n_2 for various series

Spectral series	Value of n_1	Value of n_2
Lyman series	1	2, 3, 4, 5, . . .
Balmer series	2	3, 4, 5, 6, . . .
Paschen series	3	4, 5, 6, 7, . . .
Brackett series	4	5, 6, 7, 8, . . .
Pfund series	5	6, 7, 8, 9, . . .

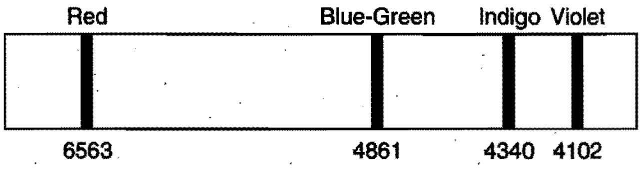


Fig. 2.9 (a) Balmer series in the hydrogen spectrum

Lyman series: $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$

$n_2 = 2, 3, 4, 5, \ldots$

Obtained in emission as well as in absorption spectrum ratio of m^{th} to n^{th} wavelength of Lyman series.

$$\frac{\lambda_m}{\lambda_n} = \left(\frac{m+1}{n+1}\right)^2 \cdot \left\{\frac{(n+1)^2 - 1}{(m+1)^2 - 1}\right\}$$

Balmer series: $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{2^2} - \frac{1}{n_2^2}\right]$

$n_2 = 3, 4, 5, 6, \ldots$

Obtained only in emission spectrum.

Paschen series: $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{3^2} - \frac{1}{n_2^2}\right]$

$n_2 = 4, 5, 6, 7, \ldots$

Brackett series: $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{4^2} - \frac{1}{n_2^2}\right]$

$n_2 = 5, 6, 7, 8, \ldots$

Pfund series: $\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{5^2} - \frac{1}{n_2^2}\right]$

$n_2 = 6, 7, 8, 9, \ldots$

Note : (i) Atoms give line spectra while molecules give band spectra.
(ii) Balmer, Paschen, Brackett, Pfund series are found in emission spectrum.

Electronic transition	Name of line	Wave no.	Wavelength and colour
$n_2 = \underset{(M)}{3} \longrightarrow n_1 = \underset{(L)}{2}$	H_α (First line)	$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5R}{36}$	$\lambda = 6563$ Å (Red)
$n_2 = \underset{(N)}{4} \longrightarrow n_1 = \underset{(L)}{2}$	H_β (Second line)	$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \frac{3R}{16}$	$\lambda = 4861$ Å (Blue-Green)
$n_2 = \underset{(O)}{5} \longrightarrow n_1 = \underset{(L)}{2}$	H_γ (Third line)	$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{5^2}\right] = \frac{21R}{100}$	$\lambda = 4340$ Å (Indigo)
$n_2 = \underset{(P)}{6} \longrightarrow n_1 = \underset{(L)}{2}$	H_δ (Fourth line)	$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{6^2}\right] = \frac{8R}{36}$	$\lambda = 4102$ Å (Violet)

(Above four lines were viewed in Balmer series by naked eye.)

Absorption Spectrum : Suppose the radiations from a continuous source like a hot body (sun light) containing the quanta of all wavelengths passes through a sample of hydrogen gas, then the wavelengths missing in the emergent light give dark lines on the bright background. This type of spectrum that contains lesser number of wavelengths in the emergent light than in incident light is called absorption spectrum.

Let the radiations of wavelengths $\lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5$ are passed through the sample of hydrogen gas such that λ_1 and λ_4 are absorbed then the absorption spectrum may be represented as:

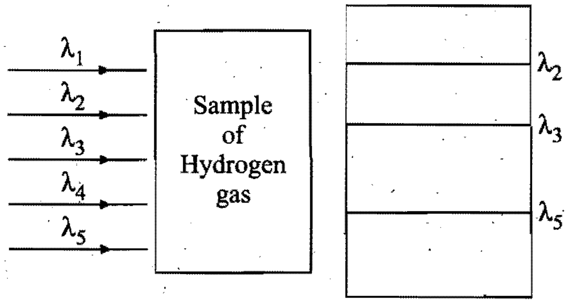


Fig. 2.9 (b) Absorption Spectrum

2.10 QUANTUM THEORY OF RADIATION

The wave theory successfully explains many properties of electromagnetic radiations such as reflection, refraction, diffraction, interference, polarisation, etc., but fails to explain some phenomena like black body radiation, photoelectric effect, etc.

In order to explain black body radiation and photoelectric effect, Max Planck in 1901 presented a new theory which is known as **quantum theory of radiation.** According to this theory, a hot body emits radiant energy not continuously but discontinuously in the form of small packets of energy called **quantum** (in plural quanta). The energy associated with each quantum of a given radiation is proportional to the frequency of the emitted radiation.

$$E \propto \nu$$

Or $E = h\nu$ where, h is a constant known as Planck's constant. Its numerical value is 6.624×10^{-27} erg-sec. The energy emitted or absorbed by a body can be either one quantum or any whole number multiple of $h\nu$, *i.e.*, $2h\nu, 3h\nu, 4h\nu, \ldots, nh\nu$ quanta of energy.

Thus, energy emitted or absorbed = $nh\nu$, where n can have values 1, 2, 3, 4, ... Thus, the energy emitted or absorbed is quantised.

In 1905, Einstein pointed out that light can be supposed to consist of a stream of particles, called **photons.** The energy of each photon of light depends on the frequency of the light, *i.e.*, $E = h\nu$. Energy is also related according to Einstein, as $E = mc^2$ where m is the mass of photon. Thus, it was pointed out that light has wave as well as particle characteristics (dual nature).

SOME SOLVED EXAMPLES

Example 1. *How many protons, electrons and neutrons are present in* 0.18 g $^{30}_{15}P$?

Solution: No. of protons in one atom of P

= No. of electrons in one atom of P = 15

No. of neutrons in one atom of P = $(A - Z) = (30 - 15) = 15$

$$0.18\text{ g } ^{30}_{15}\text{P} = \frac{0.18}{30} = 0.006 \text{ mol}$$

No. of atoms in 0.006 mol = $0.006 \times 6.02 \times 10^{23}$

No. of protons in 0.006 mol $^{30}_{15}$P = $15 \times 0.006 \times 6.02 \times 10^{23}$

$= 5.418 \times 10^{22}$

So, No. of electrons = 5.418×10^{22}

and No. of neutrons = 5.418×10^{22}

Example 2. *Calculate the frequency and wave number of radiation with wavelength* 480 *nm.*

Solution: Given,

$$\lambda = 480 \text{ nm} = 480 \times 10^{-9} \text{ m} \qquad [\because 1 \text{ nm} = 10^{-9} \text{ m}]$$

$$c = 3 \times 10^8 \text{ m/sec}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ ms}^{-1}}{480 \times 10^{-9} \text{ m}} = 6.25 \times 10^{14} \text{ s}^{-1}$$

$$= 6.25 \times 10^{14} \text{ Hz}$$

Example 3. *Calculate the energy associated with photon of light having a wavelength* 6000 *Å*. [$h = 6.624 \times 10^{-27}$ *erg-sec.*]

Solution: We know that, $E = h\nu = h \cdot \dfrac{c}{\lambda}$

$h = 6.624 \times 10^{-27}$ erg-sec; $c = 3 \times 10^{10}$ cm/sec;

$\lambda = 6000 \text{ Å} = 6000 \times 10^{-8}$ cm

$$\text{So, } E = \frac{(6.624 \times 10^{-27}) \times (3 \times 10^{10})}{6 \times 10^{-5}} = 3.312 \times 10^{-12} \text{ erg.}$$

Example 4. *Which has a higher energy, a photon of violet light with wavelength* 4000 *Å or a photon of red light with wavelength* 7000 *Å*? [$h = 6.62 \times 10^{-34}$ *Js*]

Solution: We know that, $E = h\nu = h \cdot \dfrac{c}{\lambda}$

Given, $h = 6.62 \times 10^{-34}$ Js, $c = 3 \times 10^8 \text{ ms}^{-1}$

For a photon of violet light,

$$\lambda = 4000 \text{ Å} = 4000 \times 10^{-10} \text{ m}$$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{4 \times 10^{-7}} = 4.96 \times 10^{-19} \text{ J}$$

For a photon of red light,

$$\lambda = 7000 \text{ Å} = 7000 \times 10^{-10} \text{ m}$$

$$E = 6.62 \times 10^{-34} \times \frac{3 \times 10^8}{7000 \times 10^{-10}} = 2.83 \times 10^{-19} \text{ J}$$

Hence, photon of violet light has higher energy than the photon of red light.

Example 5. *What is the ratio between the energies of two radiations one with a wavelength of* 6000 *Å and other with* 2000 *Å*?

Solution: $\lambda_1 = 6000 \text{ Å}$ and $\lambda_2 = 2000 \text{ Å}$

$$E_1 = h \cdot \frac{c}{\lambda_1} \text{ and } E_2 = h \cdot \frac{c}{\lambda_2}$$

$$\text{Ratio, } \quad \frac{E_1}{E_2} = \frac{h \cdot c}{\lambda_1} \times \frac{\lambda_2}{h \cdot c} = \frac{\lambda_2}{\lambda_1} = \frac{2000}{6000} = \frac{1}{3}$$

$$\text{or} \quad E_2 = 3E_1$$

Example 6. *Calculate the wavelength, wave number and frequency of photon having an energy equal to three electron volt.* ($h = 6.62 \times 10^{-27}$ *erg-sec.*)

Solution: We know that,

$$E = h\cdot\nu$$

$$\nu = \frac{E}{h} \qquad (1\,\text{eV} = 1.602\times10^{-12}\text{ erg})$$

$$= \frac{3\times(1.602\times10^{-12})}{6.62\times10^{-27}} = 7.26\times10^{14}\text{ s}^{-1} = 7.26\times10^{14}\text{ Hz}$$

$$\lambda = \frac{c}{\nu} = \frac{3\times10^{10}}{7.26\times10^{14}} = 4.132\times10^{-5}\text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{4.132\times10^{-5}} = 2.42\times10^{4}\text{ cm}^{-1}$$

Example 7. *Calculate the energy in kilocalorie per mol of the photons of an electromagnetic radiation of wavelength 7600 Å.*

Solution: $\lambda = 7600\,\text{Å} = 7600\times10^{-8}$ cm

$$c = 3\times10^{10}\text{ cm s}^{-1}$$

$$\text{Frequency, } \nu = \frac{c}{\lambda} = \frac{3\times10^{10}}{7600\times10^{-8}} = 3.947\times10^{14}\text{ s}^{-1}$$

$$\text{Energy of one photon} = h\nu = 6.62\times10^{-27}\times3.947\times10^{14}$$
$$= 2.61\times10^{-12}\text{ erg}$$

$$\text{Energy of one mole of photons} = 2.61\times10^{-12}\times6.02\times10^{23}$$
$$= 15.71\times10^{11}\text{ erg}$$

Energy of one mole of photons in kilocalorie

$$= \frac{15.71\times10^{11}}{4.185\times10^{10}}\left[1\text{ kcal} = 4.185\times10^{10}\text{ erg}\right]$$
$$= 37.538\text{ kcal per mol}$$

Example 8. *Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy in kJ mol^{-1}, $h = 6.6256\times10^{-34}$ Js.* **(IIT 1992)**

Solution: $\lambda = 242\text{ nm} = 242\times10^{-9}$ m

$$c = 3\times10^{8}\text{ ms}^{-1}$$

$$E = h\nu = h\cdot\frac{c}{\lambda} = 6.6256\times10^{-34}\times\frac{3\times10^{8}}{242\times10^{-9}}$$
$$= 0.082\times10^{-17}\text{ J} = 0.082\times10^{-20}\text{ kJ}$$

$$\text{Energy per mole for ionisation} = 0.082\times10^{-20}\times6.02\times10^{23}$$
$$= 493.6\text{ kJ mol}^{-1}$$

Example 9. *How many photons of light having a wavelength 4000 Å are necessary to provide 1.00 J of energy?*

Solution: Energy of one photon

$$= h\nu = h\cdot\frac{c}{\lambda}$$
$$= \frac{(6.62\times10^{-34})(3.0\times10^{8})}{4000\times10^{-10}}$$
$$= 4.965\times10^{-19}\text{ J}$$

$$\text{Number of photons} = \frac{1.00}{4.965\times10^{-19}} = 2.01\times10^{18}$$

Example 10. *Find the number of quanta of radiations of frequency 4.67×10^{13} s^{-1}, that must be absorbed in order to melt 5 g of ice. The energy required to melt 1 g of ice is 333 J.*

Solution: Energy required to melt 5 g of ice

$$= 5\times333 = 1665\text{ J}$$

Energy associated with one quantum

$$= h\nu = (6.62\times10^{-34})\times(4.67\times10^{13})$$
$$= 30.91\times10^{-21}\text{ J}$$

Number of quanta required to melt 5 g of ice

$$= \frac{1665}{30.91\times10^{-21}} = 53.8\times10^{21}$$
$$= 5.38\times10^{22}$$

Example 11. *Calculate the wavelength of the spectral line, when the electron in the hydrogen atom undergoes a transition from the energy level 4 to energy level 2.*

Solution: According to Rydberg equation,

$$\frac{1}{\lambda} = R\left(\frac{1}{x^2} - \frac{1}{y^2}\right)$$

$R = 109678\text{ cm}^{-1}$; $x = 2$; $y = 4$

$$\frac{1}{\lambda} = 109678\left[\frac{1}{4} - \frac{1}{16}\right]$$
$$= 109678\times\frac{3}{16}$$

On solving, $\lambda = 486$ nm

Example 12. *A bulb emits light of wavelength $\lambda = 4500$ Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second?* **(IIT 1995)**

Solution: Energy emitted per second by the bulb

$$= 150\times\frac{8}{100}\text{ J}$$

$$\text{Energy of 1 photon} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\times3\times10^{8}}{4500\times10^{-10}}$$
$$= 4.42\times10^{-19}\text{ joule}$$

Let n photons be evolved per second.

$$\therefore\quad n\times4.42\times10^{-19} = 150\times\frac{8}{100}$$
$$n = 27.2\times10^{18}$$

Example 13. *A near ultraviolet photon of 300 nm is absorbed by a gas and then remitted as two photons. One photon is red with wavelength of 760 nm. What would be the wave number of the second photon?*

Solution:

Energy absorbed = Sum of energy of two quanta

$$\frac{hc}{300\times10^{-9}} = \frac{hc}{760\times10^{-9}} + \frac{hc}{\lambda\times10^{-9}}$$

On solving, we get,

$$\bar{\nu}\,(\text{wave number}) = \frac{1}{\lambda} = 2.02 \times 10^{-3}\ \text{m}^{-1}$$

Example 14. *Calculate the wavelength of the radiation which would cause the photodissociation of chlorine molecule if the Cl—Cl bond energy is 243 kJ mol* $^{-1}$.

Solution: Energy required to break one Cl—Cl bond

$$= \frac{\text{Bond energy per mole}}{\text{Avogadro's number}}$$

$$= \frac{243}{6.023 \times 10^{23}}\ \text{kJ} = \frac{243 \times 10^{3}}{6.023 \times 10^{23}}\ \text{J}$$

Let the wavelength of the photon to cause rupture of one Cl—Cl bond be λ.

We know that,

$$\lambda = \frac{hc}{E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^{8} \times 6.023 \times 10^{23}}{243 \times 10^{3}}$$

$$= 4.90 \times 10^{-7}\ \text{m} = 490\ \text{nm}$$

Example 15. *How many moles of photon would contain sufficient energy to raise the temperature of 225 g of water 21°C to 96°C? Specific heat of water is 4.18 J g* $^{-1}$ *K* $^{-1}$ *and frequency of light radiation used is* $2.45 \times 10^{9}\ s^{-1}$.

Solution: Energy associated with one mole of photons

$$= N_0 \times h \times \nu$$

$$= 6.02 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.45 \times 10^{9}$$

$$= 97.727 \times 10^{-2}\ \text{J mol}^{-1}$$

Energy required to raise the temperature of 225 g of water by 75°C $= m \times s \times t$

$$= 225 \times 4.18 \times 75 = 70537.5\ \text{J}$$

Hence, number of moles of photons required

$$= \frac{mst}{N_0 h\nu} = \frac{70537.5}{97.727 \times 10^{-2}} = 7.22 \times 10^{4}\ \text{mol}$$

Example 16. *During photosynthesis, chlorophyll-a absorbs light of wavelength 440 nm and emits light of wavelength 670 nm. What is the energy available for photosynthesis from the absorption-emission of a mole of photons?*

Solution: $\Delta E = \left[\frac{Nhc}{\lambda}\right]_{\text{absorbed}} - \left[\frac{Nhc}{\lambda}\right]_{\text{evolved}}$

$$= Nhc\left[\frac{1}{\lambda_{\text{absorbed}}} - \frac{1}{\lambda_{\text{evolved}}}\right]$$

$$= 6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^{8}\left[\frac{1}{440 \times 10^{-9}} - \frac{1}{670 \times 10^{-9}}\right]$$

$$= 0.1197[2.272 \times 10^{6} - 1.492 \times 10^{6}]$$

$$= 0.0933 \times 10^{6}\ \text{J/mol} = 93.3\ \text{kJ/mol}$$

Example 17. *Photochromic sunglasses, which darken when exposed to light, contain a small amount of colourless AgCl (s) embedded in the glass. When irradiated with light, metallic silver atoms are produced and the glass darkens.*

$$AgCl(s) \longrightarrow Ag(s) + Cl$$

Escape of chlorine atoms is prevented by the rigid structure of the glass and the reaction therefore, reverses as soon as the light is removed. If 310 kJ / mol of energy is required to make the reaction proceed, what wavelength of light is necessary?

Solution: Energy per mole = Energy of one Einstein

i.e., energy of one mole quanta

$$= \frac{Nhc}{\lambda}$$

$$\therefore\quad 310 \times 1000 = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3 \times 10^{8}}{\lambda}$$

$$\lambda = 3.862 \times 10^{-7}\ \text{m} = 3862 \times 10^{-10}\ \text{m} = 3862\ \text{Å}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. The frequency of the radiation having wave number 10 m^{-1} is:

(a) 10 s^{-1} (b) 3×10^{7} s^{-1}

(c) 3×10^{11} s^{-1} (d) 3×10^{9} s^{-1}

[**Ans.** (d)]

[**Hint:** $\bar{\nu} = \frac{1}{\lambda}$

$$\nu = c\bar{\nu} = \frac{c}{\lambda} = 3 \times 10^{8} \times 10 = 3 \times 10^{9}\ \text{s}^{-1}]$$

2. The energy of a photon of radiation having wavelength 300 nm is:

(a) 6.63×10^{-29} J (b) 6.63×10^{-19} J

(c) 6.63×10^{-28} J (d) 6.63×10^{-17} J

[**Ans.** (b)]

[**Hint:** $E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{300 \times 10^{-9}} = 6.63 \times 10^{-19}$ J]

3. The maximum kinetic energy of the photoelectrons is found to be 6.63×10^{-19} J, when the metal is irradiated with a radiation of frequency 2×10^{15} Hz. The threshold frequency of the metal is about:

(a) 1×10^{15} s^{-1} (b) 2×10^{15} s^{-1}

(c) 3×10^{15} s^{-1} (d) 1.5×10^{15} s^{-1}

[**Ans.** (a)]

[**Hint:** $\text{KE} = h(\nu - \nu_0)$

$$\nu_0 = \nu - \frac{\text{KE}}{h}$$

$$= 2 \times 10^{15} - \frac{6.63 \times 10^{-19}}{6.63 \times 10^{-34}} = 1 \times 10^{15}\ \text{s}^{-1}]$$

4. The number of photons of light having wavelength 100 nm which can provide 1 J energy is nearly:

(a) 10^{7} photons (b) 5×10^{18} photons

(c) 5×10^{17} photons (d) 5×10^{7} photons

[**Ans.** (c)]

[**Hint:** $E = \frac{nhc}{\lambda}$

$$n = \frac{E\lambda}{hc} = \frac{1 \times 100 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 5 \times 10^{17}\ ]$$

5. The atomic transition gives rise to the radiation of frequency (10^4 MHz). The change in energy per mole of atoms taking place would be:

(a) 3.99×10^{-6} J (b) 3.99 J

(c) 6.62×10^{-24} J (d) 6.62×10^{-30} J

[**Ans.** (b)]

[**Hint:** $E = Nh\nu$

$= 6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 10^4 \times 10^6$

$= 3.99$ J]

2.11 BOHR'S ATOMIC MODEL

To overcome the objections of Rutherford's model and to explain the hydrogen spectrum, **Bohr** proposed a **quantum mechanical model** of the atom. This model was based on the quantum theory of radiation and the classical laws of physics. The important postulates on which Bohr's model is based are the following:

(i) The atom has a nucleus where all the protons and neutrons are present. The size of the nucleus is very small. It is present at the centre of the atom.

(ii) Negatively charged electrons are revolving around the nucleus in the same way as the planets are revolving around the sun. The path of the electron is circular. The force of attraction between the nucleus and the electron is equal to centrifugal force of the moving electron.

Force of attraction towards nucleus = centrifugal force

(iii) Out of infinite number of possible circular orbits around the nucleus, the electron can revolve only on those orbits whose angular momentum* is an integral multiple of $\frac{h}{2\pi}$, *i.e.*, $mvr = n\frac{h}{2\pi}$ where m = mass of the electron, v = velocity of electron, r = radius of the orbit and $n = 1, 2, 3, \ldots$ number of the orbit. The angular momentum can have values such as, $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$, etc., but it cannot have a fractional value. Thus, the angular momentum is quantized. The specified or circular orbits (quantized) are called **stationary orbits.**

(iv) By the time, the electron remains in any one of the stationary orbits, it does not lose energy. Such a state is called **ground** or **normal state.**

In the ground state, potential energy of electron will be minimum, hence it will be the most stable state.

(v) Each stationary orbit is associated with a definite amount of energy. The greater is the distance of the orbit from the nucleus, more shall be the energy associated with it. These orbits are also called energy levels and are numbered as 1, 2, 3, 4, ... or K, L, M, N, ... from nucleus outwards.

i.e., $E_1 < E_2 < E_3 < E_4 \ldots$

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) \ldots$$

(vi) The emission or absorption of energy in the form of radiation can only occur when an electron jumps from one stationary orbit to another.

$$\Delta E = E_{\text{high}} - E_{\text{low}} = h\nu$$

Energy is absorbed when the electron jumps from inner to outer orbit and is emitted when it moves from outer to an inner orbit.

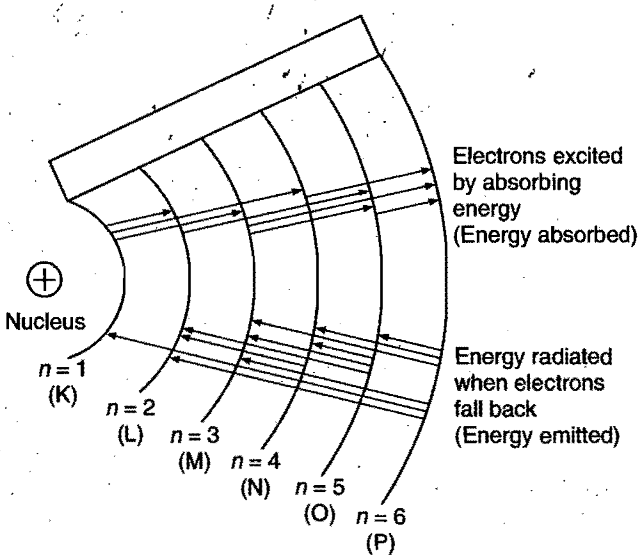


Fig. 2.10

When the electron moves from inner to outer orbit by absorbing definite amount of energy, the new state of the electron is said to be **excited state** (Fig. 2.10).

Using the above postulates, Bohr calculated the radii of various stationary orbits, the energy associated with each orbit and explained the spectrum of hydrogen atom.

Radii of various orbits: Consider an electron of mass 'm' and charge 'e' revolving around the nucleus of charge Ze (Z = atomic number). Let 'v' be the tangential velocity of the revolving electron and 'r' the radius of the orbit (Fig. 2.11). The electrostatic force of attraction between the nucleus and electron (applying Coulomb's law) $= \frac{kZe \times e}{r^2} = \frac{kZe^2}{r^2}$

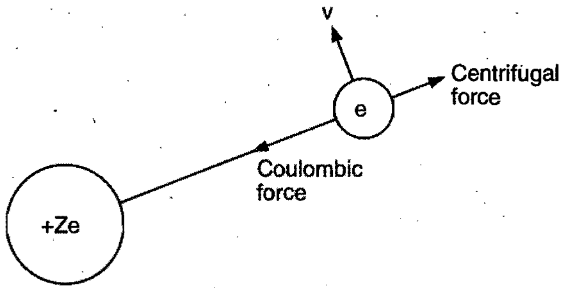


Fig. 2.11

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*Angular momentum = $I\omega$, where, I = moment of inertia and ω = angular velocity;
$\omega = \frac{v}{r}$, where, v = linear velocity and r = radius; and $I = mr^2$. So angular momentum $= mr^2 \cdot \frac{v}{r} = mvr$.

where, k is a constant. It is equal to $\frac{1}{4\pi\varepsilon_0}$, ε_0 being absolute permittivity of medium. In SI units, the numerical value of $\frac{1}{4\pi\varepsilon_0}$ is equal to $9\times10^9\ \text{Nm}^2/\text{C}^2$.

[**Note:** In CGS units, value of k is equal to 1.]

As force of attraction = centrifugal force

So, $\frac{kZe^2}{r^2} = \frac{mv^2}{r}$ or $v^2 = \frac{kZe^2}{rm}$

$$v^2 = \frac{1}{4\pi\varepsilon_0}\cdot\frac{Ze^2}{rm} \quad \text{. . . (i)}$$

According to one of the postulates,

Angular momentum $= mvr = n\frac{h}{2\pi}$

or $$v = \frac{nh}{2\pi mr} \quad \text{. . . (ii)}$$

Putting the value of 'v' in eq. (i),

$$\frac{n^2h^2}{4\pi^2m^2r^2} = \frac{kZe^2}{mr} \quad \text{or} \quad \frac{n^2h^2}{4\pi^2mr} = kZe^2$$

or $$r = \frac{n^2h^2}{4\pi^2mkZe^2} \quad \text{. . . (iii)}$$

Greater is the value of 'n', larger is the size of atom. On the other hand, greater is the value of 'Z', smaller is the size of the atom. Across a period from left to right, atomic number 'Z' increases with constant value of 'n' hence atomic radius decreases towards right. On moving down the group, both 'Z' and 'n' increase but due to shielding, Z^* (effective nuclear charge) remains same. Hence, on moving downwards, atomic radius increases due to increase in 'n'.

For hydrogen atom, $Z = 1$; so $r = \frac{n^2h^2}{4\pi^2mke^2}$

Now putting the values of h, π, m, e and k,

$$r = \frac{n^2\times(6.625\times10^{-34})^2}{4\times(3.14)^2\times(9.1\times10^{-31})\times(1.6\times10^{-19})^2\times(9\times10^9)}$$

$$= 0.529\times n^2\times10^{-10}\ \text{m} = 0.529\times n^2\ \text{Å}$$

$$= 0.529\times10^{-8}\times n^2\ \text{cm}$$

where $h = 6.625\times10^{-34}$ J-sec, $\pi = 3.14$

$m = 9.1\times10^{-31}$ kg, $e = 1.6\times10^{-19}$ coulomb

$k = 9\times10^9\ \text{Nm}^2/\text{C}^2$

Thus, radius of 1st orbit

$= 0.529\times10^{-8}\times1^2 = 0.529\times10^{-8}\ \text{cm} = 0.529\times10^{-10}\ \text{m}$

Radius of 2nd orbit

$= 0.529\times10^{-8}\times2^2 = 2.11\times10^{-8}\ \text{cm} = 2.11\times10^{-10}\ \text{m}$

Radius of 3rd orbit

$= 0.529\times10^{-8}\times3^2 = 4.76\times10^{-8}\ \text{cm} = 4.76\times10^{-10}\ \text{m}$

and so on.

$$r_n = r_1\times n^2 \text{ for hydrogen atom}$$

and $$r_n = 0.529\times\frac{n^2}{Z}\ \text{Å} \quad \text{(for hydrogen like species)}$$

Energy of an electron: Let the total energy of the electron be E. It is the sum of kinetic energy and potential energy.

$$E = \text{kinetic energy} + \text{potential energy}$$

$$= \frac{1}{2}mv^2 - \frac{kZe^2}{r}$$

Putting the value of mv^2 from eq. (i),

$$E = \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$$

Putting the value of r from eq. (iii),

$$E = -\frac{kZe^2}{2}\times\frac{4\pi^2mkZe^2}{n^2h^2} = -\frac{2\pi^2Z^2k^2me^4}{n^2h^2} \quad \text{...(iv)}$$

For hydrogen atom, $Z = 1$

So, $$E = -\frac{2\pi^2k^2me^4}{n^2h^2}$$

Putting the values of π, k, m, e and h,

$$E = -\frac{2\times(3.14)^2\times(9\times10^9)^2\times(9.1\times10^{-31})\times(1.6\times10^{-19})^4}{n^2\times(6.625\times10^{-34})^2}$$

$$= -\frac{21.79\times10^{-19}}{n^2}\ \text{J per atom}$$

$$E = -\frac{R_H}{n^2} \quad \text{(where, } R_H = 2.18\times10^{-18}\ \text{J)}$$

$$= -\frac{13.6}{n^2}\ \text{eV per atom} \quad (1\ \text{J} = 6.2419\times10^{18}\ \text{eV})$$

$$= -\frac{313.6}{n^2}\ \text{kcal/mol} \quad (1\ \text{eV} = 23.06\ \text{kcal/mol})$$

$$= -\frac{1312}{n^2}\ \text{kJ/mol}$$

$$\text{Kinetic energy in } n\text{ th shell} = \frac{13.6\times Z^2}{n^2}\ \text{eV}$$

$$\text{Potential energy in } n\text{ th shell} = \frac{-27.2\times Z^2}{n^2}\ \text{eV}$$

Substituting the values of $n = 1, 2, 3, 4, \ldots$, etc., the energy of electron in various energy shells in hydrogen atom can be calculated.

Energy shell	E (Joule per atom)	E (eV per atom)	E (kcal /mol)
1	-21.79×10^{-19}	−13.6	− 313.6
2	-5.44×10^{-19}	−3.4	−78.4
3	-2.42×10^{-19}	−1.51	−34.84
4	-1.36×10^{-19}	− 0.85	−19.6
—	—	—	—
—	—	—	—
∞	0	0	0

$$E_n = \frac{E_1}{n^2} \quad \text{(for hydrogen atom)}$$

and $$E_n = E_1\times\frac{Z^2}{n^2} \quad \text{(for hydrogen like species)}$$

where, E_1 = energy of hydrogen first orbit.

Since, n can have only integral values, it follows that total energy of the electron is quantised. The negative sign indicates that the electron is under attraction towards nucleus, *i.e.*, it is bound to the nucleus. The electron has minimum energy in the first orbit and its energy increases as n increases, *i.e.*, it becomes less negative. The electron can have a maximum energy value of zero when $n = \infty$. The zero energy means that the electron is no longer bound to the nucleus, *i.e.*, it is not under attraction towards nucleus.

For hydrogen like species such as He^+, Li^{2+}, etc., $E_n = Z^2 \times E_n$ for hydrogen atom.

Velocity of an electron: We know that,

Centrifugal force on electron

= force of attraction between nucleus and electron

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad \text{(in CGS units)} \qquad \ldots \text{(i)}$$

The angular momentum of an electron is given as:

$$mvr = nh/2\pi \qquad \ldots \text{(ii)}$$

From eqs. (i) and (ii), we have

$$v\left(\frac{nh}{2\pi}\right) = Ze^2$$

$$v = \frac{Z}{n}\left(\frac{2\pi e^2}{h}\right)$$

$$v = \frac{Z}{n} \times 2.188 \times 10^8 \text{ cm/sec} \qquad \ldots \text{(iii)}$$

$$v = \frac{2.188 \times 10^8}{n} \text{ cm/sec} \quad \text{(For hydrogen, } Z = 1\text{)}$$

$$v_1 = 2.188 \times 10^8 \text{ cm/sec}$$

$$v_2 = \frac{1}{2} \times 2.188 \times 10^8 \text{ cm/sec}$$

$$v_3 = \frac{1}{3} \times 2.188 \times 10^8 \text{ cm/sec}$$

Here, v_1, v_2 and v_3 are the velocities of electron in first, second and third Bohr orbits in hydrogen.

From equation (iii),

$$\frac{v_1}{v_2} = \frac{2}{1} \quad \text{and} \quad \frac{v_3}{v_1} = \frac{1}{3} \text{ and so on.}$$

Orbital frequency: Number of revolutions per second by an electron in a shell is called **orbital frequency**; it may be calculated as,

Number of revolutions per second by an electron in a shell

$$= \frac{\text{Velocity}}{\text{Circumference}} = \frac{v}{2\pi r} = -\frac{E_1}{h}\left(\frac{2}{n^3}\right)$$

$$= \frac{Z^2}{n^3} \times 6.66 \times 10^{15}$$

where, E_1 = Energy of first shell.

Time period of revolution of electron in nth orbit (T_n):

$$T_n = \frac{2\pi r}{v_n} = \frac{n^3}{Z^2} \times 1.5 \times 10^{-16} \text{ sec}$$

Interpretation of hydrogen spectrum: The only electron in the hydrogen atom resides under ordinary conditions on the first orbit. When energy is supplied, the electron moves to higher energy shells depending on the amount of energy absorbed. When this electron returns to any of the lower energy shells, it emits energy. Lyman series is formed when the electron returns to the lowest energy state while Balmer series is formed when the electron returns to second energy shell. Similarly, Paschen, Brackett and Pfund series are formed when electron returns to the third, fourth and fifth energy shells from higher energy shells respectively (Fig. 2.12).

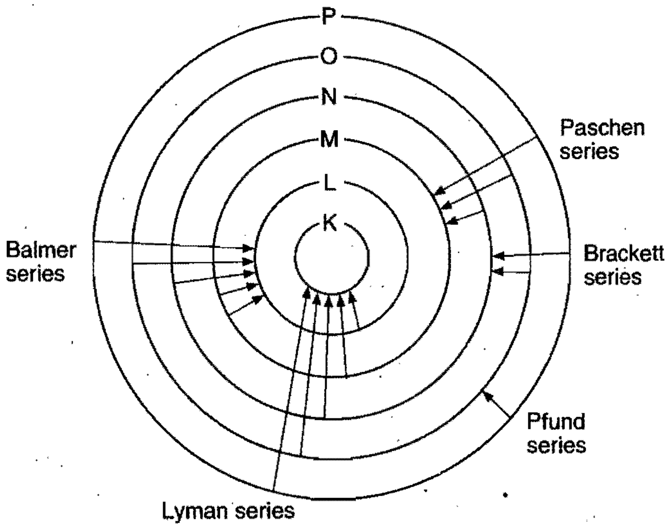


Fig. 2.12

Maximum number of lines produced when an electron jumps from nth level to ground level is equal to $\frac{n(n-1)}{2}$. For example, in the case of $n = 4$, number of lines produced is 6. ($4 \to 3, 4 \to 2, 4 \to 1, 3 \to 2, 3 \to 1, 2 \to 1$). When an electron returns from n_2 to n_1 state, the number of lines in the spectrum will be equal to.

$$\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

If the electron comes back from energy level having energy E_2 to energy level having energy E_1, then the difference may be expressed in terms of energy of photon as:

$$E_2 - E_1 = \Delta E = h\nu$$

or the frequency of the emitted radiation is given by

$$\nu = \frac{\Delta E}{h}$$

Since, ΔE can have only definite values depending on the definite energies of E_2 and E_1, ν will have only fixed values in an atom,

or
$$\nu = \frac{c}{\lambda} = \frac{\Delta E}{h}$$

or
$$\lambda = \frac{hc}{\Delta E}$$

Since, h and c are constants, ΔE corresponds to definite energy; thus, each transition from one energy level to another will produce a light of definite wavelength. This is actually observed as a line in the spectrum of hydrogen atom.

Thus, the different spectral lines in the spectra of atoms correspond to different transitions of electrons from higher energy levels to lower energy levels.

Derivation of Rydberg Equation

Let an excited electron from n_2 shell come to the n_1 shell with the release of radiant energy. The wave number $\bar{\nu}$ of the corresponding spectral line may be calculated in the following manner:

$$\Delta E = E_2 - E_1 = (-)\frac{2\pi^2 mZ^2 e^4}{n_2^2 h^2} - (-)\frac{2\pi^2 mZ^2 e^4}{n_1^2 h^2}$$

$$\frac{hc}{\lambda} = \frac{2\pi^2 mZ^2 e^4}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where, $\Delta E = h\nu = \frac{hc}{\lambda}$

$$\therefore \quad \bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 mZ^2 e^4}{ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $\quad \bar{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

where, $\quad R = \frac{2\pi^2 me^4}{ch^3}$ = Rydberg constant = 109743 cm^{-1}

This value of R is in agreement with experimentally determined value 109677.76 cm^{-1}. Rydberg equation for hydrogen may be given as,

$$\bar{\nu} = \frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Modification of Rydberg Equation

According to the Rydberg equation:

$$\underset{\text{wave number}}{\bar{\nu}} = \frac{2\pi^2 mZ^2 e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

It can be considered that the electron and the nucleus revolve around their common centre of mass. Therefore, instead of the mass of the electron, the reduced mass of the system was introduced and the equation becomes:

$$\bar{\nu} = \frac{2\pi^2 \mu Z^2 e^4}{ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

Reduced mass 'μ' can be calculated as,

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$$

where, $\quad m$ = mass of electron

and $\quad M$ = mass of nucleus

$$\therefore \quad \mu = \frac{mM}{m+M}$$

(i) *First line of a series:* It is called 'line of longest wavelength' or 'line of shortest energy'.

For first line,

$$n_2 = (n_1 + 1)$$

$$\therefore \quad \bar{\nu}_{\text{first}} = \frac{1}{\lambda_{\text{first}}} = R\left[\frac{1}{n_1^2} - \frac{1}{(n_1+1)^2}\right]$$

Similarly for second, third and fourth lines,

$n_2 = n_1 + 2$; $n_2 = n_1 + 3$ and $n_2 = n_1 + 4$ respectively

∴ Rydberg equation may be written as,

$$\bar{\nu} = \frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{(n_1+x)^2}\right]$$

where, x = number of line in the spectrum.

e.g., $x = 1, 2, 3, 4, \ldots$ for first, second, third and fourth lines in the spectrum respectively.

(ii) *Series limit or last line of a series:* It is the line of shortest wavelength or line of highest energy.

For last line, $\quad n_2 = \infty$

$$\bar{\nu}_{\text{last}} = \frac{1}{\lambda_{\text{last}}} = \frac{R}{n_1^2}$$

Lyman limit $= \frac{R}{1^2}$; $\quad$ Balmer limit $= \frac{R}{2^2}$

Paschen limit $= \frac{R}{3^2}$; $\quad$ Brackett limit $= \frac{R}{4^2}$

Pfund limit $= \frac{R}{5^2}$; $\quad$ Humphrey limit $= \frac{R}{6^2}$

(iii) *Intensities of spectral lines:* The intensities of spectral lines in a particular series decrease with increase in the value of n_2, *i.e.*, higher state.

e.g.,

Lyman series $\underset{(n_2 \to n_1)}{}$ $(2 \to 1) > (3 \to 1) > (4 \to 1) > (5 \to 1)$

Balmer series $\underset{(n_2 \to n_1)}{}$ $(3 \to 2) > (4 \to 2) > (5 \to 2) > (6 \to 2)$

$$\xrightarrow{\hspace{6cm}}$$

Decreasing intensity of the spectral lines

Ionization Energy and Excitation Energy

$$\text{Excitation potential for } n_1 \to n_2 = \frac{E_{n_2} - E_{n_1}}{\text{Electronic charge}}$$

$$\text{Ionization potential for } n_1 \to \infty = \frac{E_{n_1}}{\text{Electronic charge}}$$

The energy required to remove an electron from the ground state to form cation, *i.e.*, to take the electron to infinity, is called **ionization energy.**

$$\text{IE} = E_\infty - E_{\text{ground}}$$

$$\text{IE} = 0 - E_1(\text{H}) = 13.6\,\text{eV atom}^{-1}$$

$$= 2.17 \times 10^{-18}\ \text{J atom}^{-1}$$

$$\text{IE} = \frac{Z^2}{n^2} \times 13.6\,\text{eV}$$

$$\frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}$$

$$(\text{IE})_Z = \frac{(\text{IE})_H \times Z^2}{n^2}$$

If an electron is already present in the excited state, then the energy required to remove that electron is called **separation energy.**

$$E_{\text{separation}} = E_{\infty} - E_{\text{excited}}$$

The following points support Bohr theory:

(i) The frequencies of the spectral lines calculated from Bohr equation are in close agreement with the frequencies observed experimentally in hydrogen spectrum.

(ii) The value of Rydberg constant for hydrogen calculated from Bohr equation tallies with that determined experimentally.

(iii) The emission and absorption spectra of hydrogen like species such as He^+, Li^{2+} and Be^{3+} can be explained with the help of Bohr theory.

Limitations of Bohr Theory

(i) It does not explain the spectra of multi-electron atoms.

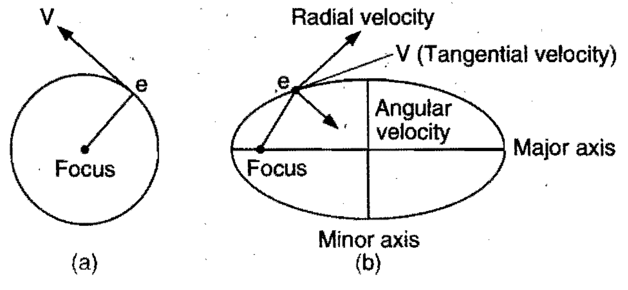
(ii) When a high resolving power spectroscope is used, it is observed that a spectral line in the hydrogen spectrum is not a simple line but a collection of several lines which are very close to one another. This is known as fine spectrum. Bohr theory does not explain the fine spectra of even the hydrogen atom.

(iii) It does not explain the splitting of spectral lines into a group of finer lines under the influence of magnetic field (Zeeman effect) and electric field (Stark effect).

(iv) Bohr theory is not in agreement with Heisenberg's uncertainty principle.

2.12 SOMMERFELD'S EXTENSION OF BOHR THEORY

To account for the fine spectrum of hydrogen atom, **Sommerfeld,** in 1915, proposed that the moving electron might describe elliptical orbits in addition to circular orbits and the nucleus is situated at one of the foci. During motion on a circle, only the angle of revolution changes while the distance from the nucleus remains the same but in elliptical motion both the angles of revolution and the distance of the electron from the nucleus change. The distance from the nucleus is termed as **radius vector** and the angle of revolution is known as **azimuthal angle.** The tangential velocity of the electron at a particular instant can be resolved into two components: one along the radius vector called **radial velocity** and the other perpendicular to the radius vector called **transverse** or **angular velocity.** These two velocities give rise to radial momentum and angular or azimuthal momentum. **Sommerfeld** proposed that both the momenta must be integral multiples of $\frac{h}{2\pi}$ [Fig. 2.13 (b)].



(a) (b)

Fig. 2.13

$$\text{Radial momentum} = n_r \frac{h}{2\pi}$$

$$\text{Azimuthal momentum} = n_\phi \frac{h}{2\pi}$$

n_r and n_ϕ are related to the main orbit 'n' as:

$$n = n_r + n_\phi$$

or
$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{Length of major axis}}{\text{Length of minor axis}}$$

(i) 'n_ϕ' cannot be zero because under this condition, the ellipse shall take the shape of a straight line.

(ii) 'n_ϕ' cannot be more than 'n' because minor axis is always smaller than major axis.

(iii) 'n_ϕ' can be equal to 'n'. Under this condition, the major axis becomes equal to minor axis and the ellipse takes the shape of a circle. Thus, n_ϕ can have all integral values up to 'n' but not zero. When the values are less than 'n', orbits are elliptical and when it becomes equal to 'n', the orbit is circular in nature.

For $n = 1$, n_ϕ can have only one value, *i.e.*, 1. Therefore, the first orbit is circular in nature.

For $n = 2$, n_ϕ can have two values 1 and 2, *i.e.*, the second orbit has two sub-orbits, one is elliptical and the other is circular in nature.

For $n = 3$, n_ϕ can have three values 1, 2 and 3, *i.e.*, third orbit has three sub-orbits, two are elliptical and one is circular in nature.

For $n = 4$, n_ϕ can have four values 1, 2, 3 and 4, *i.e.*, fourth orbit has four sub-orbits, three are elliptical and fourth one is circular in nature (Fig. 2.14).

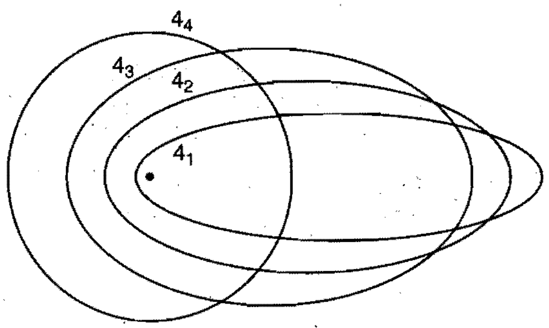


Fig. 2.14

Sommerfeld thus introduced the concept of subenergy shells. In a main energy shell, the energies of subshells differ slightly from one another. Hence, the jumping of an electron from one energy shell to another energy shell will involve slightly different amount of energy as it will depend on subshell also. This explains to some extent the fine spectrum of hydrogen atom. However, Sommerfeld extension fails to explain the spectra of multielectron atoms.

SOME SOLVED EXAMPLES

Example 18. *Calculate the wavelength and energy of radiation emitted for the electronic transition from infinite to stationary state of hydrogen atom. (Given, $R = 1.09678 \times 10^7\ m^{-1}$, $h = 6.6256 \times 10^{-34}$ J-s and $c = 2.9979 \times 10^8\ ms^{-1}$)*

Solution:
$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$n_1 = 1 \text{ and } n_2 = \infty$$
$$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{(\infty)^2}\right] = R$$

or
$$\lambda = \frac{1}{R} = \frac{1}{1.09678 \times 10^7} = 9.11 \times 10^{-8}\ \text{m}$$

We know that,
$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.6256 \times 10^{-34} \times \frac{2.9979 \times 10^8}{9.11 \times 10^{-8}}$$
$$= 2.17 \times 10^{-18}\ \text{J}$$

Example 19. *Calculate the velocity (cm/sec) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electron makes around the nucleus.*

Solution: Radius of 3rd orbit
$$= 3^2 \times 0.529 \times 10^{-8} = 4.761 \times 10^{-8}\ \text{cm}$$

We know that,
$$mvr = \frac{nh}{2\pi} \quad \text{or} \quad v = \frac{nh}{2\pi mr}$$
$$= \frac{3 \times 6.624 \times 10^{-27}}{2 \times 3.14 \times (9.108 \times 10^{-28}) \times (4.761 \times 10^{-8})}$$
$$= 0.729 \times 10^8\ \text{cm/sec}$$

Time taken for one revolution $= \dfrac{2\pi r}{v}$

Number of revolutions per second
$$= \frac{1}{\dfrac{2\pi r}{v}} = \frac{v}{2\pi r}$$
$$= \frac{0.729 \times 10^8}{2 \times 3.14 \times 4.761 \times 10^{-8}}$$
$$= 2.4 \times 10^{14}\ \text{revolutions/sec}$$

Example 20. *The electron energy in hydrogen atom is given by $E = -\dfrac{21.7 \times 10^{-12}}{n^2}$ erg. Calculate the energy required to remove an electron completely from $n = 2$ orbit. What is the longest wavelength (in cm) of light that be used to cause this transition?*

Solution: $E = -\dfrac{21.7 \times 10^{-12}}{n^2}$ erg

Electron energy in the 2nd orbit, *i.e.*, $n = 2$,
$$E_2 = -\frac{21.7 \times 10^{-12}}{2^2}\ \text{erg} = -5.425 \times 10^{-12}\ \text{erg}$$

and $E_\infty = 0$

ΔE = Change in energy $= E_\infty - E_2 = 5.425 \times 10^{-12}$ erg

Thus, energy required to remove an electron from 2nd orbit
$$= 5.425 \times 10^{-12}\ \text{erg}$$

According to quantum equation,
$$\Delta E = h \cdot \frac{c}{\lambda}$$

or
$$\lambda = \frac{hc}{\Delta E}$$
$$(h = 6.625 \times 10^{-27}\ \text{erg-sec}; c = 3 \times 10^{10}\ \text{cm/sec})$$

and $\Delta E = 5.425 \times 10^{-12}$ erg

So,
$$\lambda = \frac{(6.625 \times 10^{-27}) \times (3 \times 10^{10})}{5.425 \times 10^{-12}}$$
$$= 3.7 \times 10^{-5}\ \text{cm}$$

Thus, the longest wavelength of light that can cause this transition is 3.7×10^{-5} cm.

Example 21. *Calculate the shortest and longest wavelengths in hydrogen spectrum of Lyman series.*

Or

Calculate the wavelengths of the first line and the series limit for the Lyman series for hydrogen. ($R_H = 109678\ cm^{-1}$)

Solution: For Lyman series, $n_1 = 1$.

For shortest wavelength in Lyman series (*i.e.*, series limit), the energy difference in two states showing transition should be maximum, *i.e.*, $n_2 = \infty$.

So,
$$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = R_H$$
$$\lambda = \frac{1}{109678} = 9.117 \times 10^{-6}\ \text{cm}$$
$$= 911.7\ \text{Å}$$

For longest wavelength in Lyman series (*i.e.*, first line), the energy difference in two states showing transition should be minimum, *i.e.*, $n_2 = 2$.

So,
$$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3}{4}R_H$$

or
$$\lambda = \frac{4}{3} \times \frac{1}{R_H} = \frac{4}{3 \times 109678} = 1215.7 \times 10^{-8}\ \text{cm}$$
$$= 1215.7\ \text{Å}$$

Example 22. *Show that the Balmer series occurs between 3647 Å and 6563 Å. ($R = 1.0968 \times 10^7\ m^{-1}$)*

Solution: For Balmer series,
$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

where, $n = 3, 4, 5, \ldots \infty$

To obtain the limits for Balmer series $n = 3$ and $n = \infty$ respectively.

$$\lambda_{\max}\ (n = 3) = \frac{1}{R\left[\frac{1}{2^2} - \frac{1}{3^2}\right]} = \frac{36}{5R}$$

$$= \frac{36}{5 \times 1.0968 \times 10^7}\ \text{m}$$

$$= 6563\ \text{Å}$$

$$\lambda_{\min}\ (n = \infty) = \frac{1}{R\left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]} = \frac{4}{R}$$

$$= \frac{4}{1.0968 \times 10^7}\ \text{m}$$

$$= 3647\ \text{Å}$$

Example 23. *Light of wavelength 12818 Å is emitted when the electron of a hydrogen atom drops from 5th to 3rd orbit. Find the wavelength of the photon emitted when the electron falls from 3rd to 2nd orbit.*

Solution: We know that,

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

When, $n_1 = 3$ and $n_2 = 5$,

$$\frac{1}{12818} = R\left[\frac{1}{9} - \frac{1}{25}\right] = \frac{16R}{9 \times 25}$$

or $$12818 = \frac{9 \times 25}{16 \times R} \qquad \ldots\text{(i)}$$

When, $n_1 = 2$ and $n_2 = 3$,

$$\frac{1}{\lambda} = R\left[\frac{1}{4} - \frac{1}{9}\right] = \frac{5R}{36}$$

$$\lambda = \frac{36}{5R} \qquad \ldots\text{(ii)}$$

Dividing eqn. (ii) by eqn. (i),

$$\frac{\lambda}{12818} = \frac{36}{5R} \times \frac{16R}{9 \times 25} = \frac{64}{125}$$

$$\lambda = \frac{64}{125} \times 12818 = 6562.8\ \text{Å}$$

Example 24. *The ionisation energy of hydrogen atom is 13.6 eV. What will be the ionisation energy of He^+ and Li^{2+} ions?*

Solution: Ionisation energy = – (energy of the 1st orbit)

Energy of the 1st orbit of hydrogen = – 13.6 eV

Energy of the 1st orbit of $He^+ = -13.6 \times Z^2$ (Z for $He^+ = 2$)

$= -13.6 \times 4\ \text{eV} = -54.4\ \text{eV}$

So, Ionisation energy of $He^+ = -(-54.4) = 54.4$ eV

Energy of 1st orbit of $Li^{2+} = -13.6 \times 9$ (Z for $Li^{2+} = 3$)

$= -122.4$ eV

Ionisation energy of $Li^{2+} = -(-122.4) = 122.4$ eV

Example 25. *If the energy difference between two electronic states is 46.12 kcal mol^{-1}, what will be the frequency of the light emitted when the electrons drop from higher to lower states? ($Nh = 9.52 \times 10^{-14}$ kcal sec mol^{-1}, where, N is the Avogadro's number and h is the Planck's constant)*

Solution: $\Delta E = 46.12\ \text{kcal mol}^{-1}$

According to Bohr theory, $\Delta E = Nh\nu$

or $$\nu = \frac{\Delta E}{Nh} = \frac{46.12}{9.52 \times 10^{-14}}$$

$$= 4.84 \times 10^{14}\ \text{cycle sec}^{-1}$$

Example 26. *According to Bohr theory, the electronic energy of the hydrogen atom in the nth Bohr orbit is given by*

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2}\ J$$

Calculate the longest wavelength of light that will be needed to remove an electron from the 3rd orbit of the He^+ ion.

(IIT 1990)

Solution: The electronic energy of He^+ ion in the nth Bohr orbit

$$= -\frac{21.76 \times 10^{-19}}{n^2} \times Z^2\ \text{J}$$

where, $Z = 2$

Thus, energy of He^+ in the 3rd Bohr orbit

$$= -\frac{21.76 \times 10^{-19}}{9} \times 4\ \text{J}$$

$$\Delta E = E_\infty - E_3$$

$$= 0 - \left[-\frac{21.76 \times 10^{-19} \times 4}{9}\right]$$

$$= \frac{21.76 \times 10^{-19} \times 4}{9}$$

We know that, $$\lambda = \frac{hc}{\Delta E} = \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4}$$

$$= 2.055 \times 10^{-7}\ \text{m}$$

Example 27. *Calculate the ratio of the velocity of light and the velocity of electron in the first orbit of a hydrogen atom. (Given, $h = 6.624 \times 10^{-27}$ erg-sec; $m = 9.108 \times 10^{-28}$ g, $r = 0.529 \times 10^{-8}$ cm)*

Solution: $$v = \frac{h}{2\pi mr}$$

$$= \frac{6.624 \times 10^{-27}}{2 \times 3.14 \times 9.108 \times 10^{-28} \times 0.529 \times 10^{-8}}$$

$$= 2.189 \times 10^8\ \text{cm/sec}$$

$$\frac{c}{v} = \frac{3 \times 10^{10}}{2.189 \times 10^8} = 137$$

Example 28. *The wavelength of a certain line in Balmer series is observed to be 4341 Å. To what value of 'n' does this correspond?* ($R_H = 109678\ cm^{-1}$)

Solution:
$$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$
$$\frac{1}{n^2} = \frac{1}{4} - \frac{1}{\lambda \times R_H}$$
$$= \frac{1}{4} - \frac{1}{4341 \times 10^{-8} \times 109678}$$
$$= 0.04$$
$$n^2 = \frac{1}{0.04} = 25$$
or
$$n = 5$$

Example 29. *Estimate the difference in energy between the first and second Bohr orbit for hydrogen atom. At what minimum atomic number would a transition from n = 2 to n = 1 energy level result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m ? Which hydrogen-like species does this atomic number correspond to?* **(IIT 1993)**

Solution: $\Delta E = h\nu = \dfrac{h \cdot c}{\lambda}$

and
$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\Delta E = R \cdot h \cdot c\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\Delta E = h \cdot c \cdot \frac{3}{4} R$$
$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 1.09678 \times 10^7 \times 3}{4}$$
$$= 1.635 \times 10^{-18}\ \text{J}$$

For hydrogen-like species,
$$\Delta E = Z^2\ Rhc\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\frac{1}{\lambda} = Z^2 R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$\frac{1}{3.0 \times 10^{-8}} = Z^2 \times 1.09678 \times 10^7 \times \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$
$$Z^2 = \frac{4}{3 \times 10^{-8} \times 1.09678 \times 10^7 \times 3} \approx 4$$
or
$$Z = 2$$

The species is He^+.

Example 30. *What transition in the hydrogen spectrum have the same wavelength as Balmer transition n = 4 to n = 2 of He^+ spectrum?* **(IIT 1993)**

Solution: For He^+ ion,
$$\frac{1}{\lambda} = Z^2 R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
$$= (2)^2\ R\left[\frac{1}{2^2} - \frac{1}{4^2}\right] = \frac{3R}{4}$$

For hydrogen atom,
$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
So,
$$\frac{3R}{4} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$
or
$$\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$$
i.e., $n_1 = 1$ and $n_2 = 2$

Example 31. *Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum.* ($R_H = 1.1 \times 10^7\ m^{-1}; c = 3 \times 10^8\ m\,s^{-1}; h = 6.62 \times 10^{-34}$ *J-s*) **(IIT 1993)**

Solution: The transition occurs like Balmer series as spectral line is observed in visible region.

Thus, the line of lowest energy will be observed when transition occurs from 3rd orbit to 2nd orbit, *i.e.*, $n_1 = 2$ and $n_2 = 3$.
$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5}{36} R$$
$$E = h\nu = h \cdot \frac{c}{\lambda} = 6.62 \times 10^{-34} \times 3 \times 10^8 \times \frac{5}{36} \times 1.1 \times 10^7$$
$$= 3.03 \times 10^{-19}\ \text{J per atom}$$

Energy corresponding to 1.0 g atom of hydrogen
$$= 3.03 \times 10^{-19} \times \text{Avogadro's number}$$
$$= 3.03 \times 10^{-19} \times 6.023 \times 10^{23}\ \text{J}$$
$$= 18.25 \times 10^4\ \text{J}$$

Example 32. *How many times does the electron go around the first Bohr's orbit of hydrogen in one second?*

Solution: Number of revolutions per second $= \dfrac{v}{2\pi r}$ ... (i)
$$v = \frac{2.188 \times 10^8}{n}\ \text{cm/sec}$$
$$v = \frac{2.188 \times 10^8}{1} = 2.188 \times 10^8\ \text{cm/sec}$$
$$r = \frac{n^2}{Z} \times 0.529\ \text{Å}$$
$$= \frac{1^2}{1} \times 0.529 \times 10^{-8}\ \text{cm}$$
$$= 0.529 \times 10^{-8}\ \text{cm}$$

$\therefore$ Number of revolutions per sec $= \dfrac{2.188 \times 10^8}{2 \times 3.14 \times 0.529 \times 10^{-8}}$
$$= 6.59 \times 10^{15}$$

Example 33. *Calculate the wavelength of radiations emitted, produced in a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom.* ($R_H = 1.1 \times 10^7 \ m^{-1}$) **(IIT 1995)**

Solution: $\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$= 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2}\right)$$

$$= 969.6 \times 10^{-10} \text{ metre}$$

$$\therefore \quad \lambda = 969.6 \text{ Å}$$

Example 34. *What is the degeneracy of the level of the hydrogen atom that has the energy* $\left(-\frac{R_H}{9}\right)$*?*

Solution: $E_n = -\frac{R_H}{n^2} = -\frac{R_H}{9}$

$$\therefore \quad n = 3$$

Thus, $l = 0$ and $m = 0$ (one 3*s*-orbital)

$l = 1$ and $m = -1, 0, +1$ (three 3*p*-orbitals)

$l = 2$ and $m = -2, -1, 0, +1, +2$ (five 3*d*-orbitals)

Thus, degeneracy is nine $(1 + 3 + 5 = 9 \text{ states})$.

Example 35. *Calculate the angular frequency of an electron occupying the second Bohr orbit of He$^+$ ion.*

Solution: Velocity of electron $(v) = \frac{2\pi Ze^2}{nh}$ . . . (i)

Radius of He$^+$ ion in an orbit $(r_n) = \frac{n^2h^2}{4\pi^2 mZe^2}$ . . . (ii)

Angular frequency or angular velocity (ω)

$$= \frac{v}{r_n} = \frac{2\pi Ze^2}{nh} \times \frac{4\pi^2 mZe^2}{n^2h^2} = \frac{8\pi^3 mZ^2e^4}{n^3h^3}$$

Given, $n = 2, m = 9.1 \times 10^{-28}$ g, $Z = 2, e = 4.8 \times 10^{-10}$ esu

$h = 6.626 \times 10^{-27}$ erg-sec

$$\therefore \quad \omega = \frac{8 \times \left(\frac{22}{7}\right)^3 \times 2^2 \times 9.1 \times 10^{-28} \times (4.8 \times 10^{-10})^4}{(2)^3 \times (6.626 \times 10^{-27})^3}$$

$$= 2.067 \times 10^{16} \text{ sec}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. If the speed of electron in first Bohr orbit of hydrogen be '*x*', then speed of the electron in second orbit of He$^+$ is:

(a) $x/2$ (b) $2x$ (c) x (d) $4x$

[Ans. (c)]

[Hint: $v_n = \frac{v_1 \times Z}{n} = \frac{x \times 2}{2} = x$]

7. If first ionisation energy of hydrogen is E, then the ionisation energy of He$^+$ would be:

(a) E (b) $2E$ (c) $0.5E$ (d) $4E$

[Ans. (d)]

[Hint: $I_2(\text{He}^+) = Z^2 I_1(\text{H})$

$= 2^2 \times E = 4E$]

8. The number of spectral lines that are possible when electrons in 7th shell in different hydrogen atoms return to the 2nd shell is:

(a) 12 (b) 15 (c) 14 (d) 10

[Ans. (b)]

[Hint: Number of spectral lines $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

$= \frac{(7-2)(7-2+1)}{2} = 15$]

9. The ratio of radii of first orbits of H, He$^+$ and Li^{2+} is:

(a) 1 : 2 : 3 (b) 6 : 3 : 2 (c) 1 : 4 : 9 (d) 9 : 4 : 1

[Ans. (b)]

[Hint: $r = \frac{n^2}{Z} \times 0.529$ Å

$r_H : r_{He^+} : r_{Li^{2+}}$

$1 : \frac{1}{2} : \frac{1}{3}$

$6 : 3 : 2$]

10. The energy of second orbit of hydrogen is equal to the energy of:

(a) fourth orbit of He$^+$ (b) fourth orbit of Li^{2+}

(c) second orbit of He$^+$ (d) second orbit of Li^{2+}

[Ans. (a)]

[Hint: $E = -\frac{Z^2}{n^2} \times 13.6$ eV

$E_2 = -\frac{13.6}{4}$ for 'H'

$E = -\frac{Z^2}{n^2} \times 13.6$ eV

$-\frac{13.6}{4} = -\frac{Z^2}{n^2} \times 13.6$

$\frac{Z^2}{n^2} = \frac{1}{4} \ (Z = 1, n = 2)$]

11. What is the energy in eV required to excite the electron from $n = 1$ to $n = 2$ state in hydrogen atom? (n = principal quantum number) **[CET (J&K) 2006]**

(a) 13.6 (b) 3.4 (c) 17 (d) 10.2

[Ans. (d)]

[Hint: $\Delta E = E_2 - E_1$

$= \left(-\frac{13.6}{2^2}\right) - \left(-\frac{13.6}{1^2}\right)$

$= 13.6\left(1 - \frac{1}{4}\right) = \frac{3}{4} \times 13.6 = 10.2$ eV]

12. An electron in an atom undergoes transition in such a way that its kinetic energy changes from x to $\frac{x}{4}$, the change in potential energy will be :

(a) $+\frac{3}{2}x$ (b) $-\frac{3}{8}x$ (c) $+\frac{3}{4}x$ (d) $-\frac{3}{4}x$

[Ans. (a)]

[**Hint** : PE = − 2KE

$\therefore$ PE will change from $-2x$ to $-\frac{2x}{4}$

Change in potential energy $= \left(-\frac{2x}{4}\right) - (-2x)$

$= -\frac{x}{2} + 2x = \frac{3x}{2}$]

2.13 PARTICLE AND WAVE NATURE OF ELECTRON

In 1924, **de Broglie** proposed that an **electron,** like light, behaves both as a material particle and as a wave. This proposal gave birth to a new theory known as **wave mechanical theory of matter.** According to this theory, the electrons, protons and even atoms, when in motion, possess wave properties.

de Broglie derived an expression for calculating the wavelength of the wave associated with the electron.

According to Planck's equation,

$$E = h\nu = h\cdot\frac{c}{\lambda} \qquad \ldots \text{(i)}$$

The energy of a photon on the basis of Einstein's mass- energy relationship is

$$E = mc^2 \qquad \ldots \text{(ii)}$$

where, c is the velocity of the electron.

Equating both the equations, we get

$$h\frac{c}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} = \frac{h}{p}$$

Momentum of the moving electron is inversely proportional to its wavelength.

Let kinetic energy of the particle of mass 'm' is E.

$$E = \frac{1}{2}mv^2$$

$$2Em = m^2v^2$$

$$\sqrt{2Em} = mv = p(\text{momentum})$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2Em}}$$

Davisson and **Germer** made the following modification in de Broglie equation:

Let a charged particle, say an electron be accelerated with a potential of V; then the kinetic energy may be given as:

$$\frac{1}{2}mv^2 = eV$$

$$m^2v^2 = 2eVm$$

$$mv = \sqrt{2eVm} = p$$

$$\lambda = \frac{h}{\sqrt{2eVm}}$$

$$\lambda = \frac{h}{\sqrt{2qVm}} \text{ for charged particles of charge } q$$

de Broglie waves are not radiated into space, *i.e.*, they are always associated with electron. The wavelength decreases if the value of mass (m) increases, *i.e.*, in the case of heavier particles, the wavelength is too small to be measured. de Broglie equation is applicable in the case of smaller particles like electron and has no significance for larger particles.

(A) de Broglie wavelength associated with charged particles

(i) For electron:

$$\lambda = \frac{12.27}{\sqrt{V}} \text{Å}$$

(ii) For proton:

$$\lambda = \frac{0.286}{\sqrt{V}} \text{Å}$$

(iii) For α-particles:

$$\lambda = \frac{0.101}{\sqrt{V}} \text{Å}$$

where, V = accelerating potential of these particles.

(B) de Broglie wavelength associated with uncharged particles

(i) For neutrons:

$$\lambda = \frac{h}{\sqrt{2Em}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times E}}$$

$$= \frac{0.286}{\sqrt{E\,(\text{eV})}} \text{Å}$$

(ii) For gas molecules:

$$\lambda = \frac{h}{m \times v_{\text{rms}}}$$

$$= \frac{h}{\sqrt{3mkT}}$$

where, k = Boltzmann constant

Bohr theory versus de Broglie equation: One of the postulates of Bohr theory is that angular momentum of an electron is an integral multiple of $\frac{h}{2\pi}$. This postulate can be derived with the help of de Broglie concept of wave nature of electron.

Consider an electron moving in a circular orbit around nucleus. The wave train would be associated with the circular orbit as shown in Fig. 2.15. If the two ends of an electron wave meet to give a regular series of crests and troughs, the electron wave is said to be in phase, *i.e.*, the circumference of Bohr orbit is equal to whole number multiple of the wavelength of the electron wave.

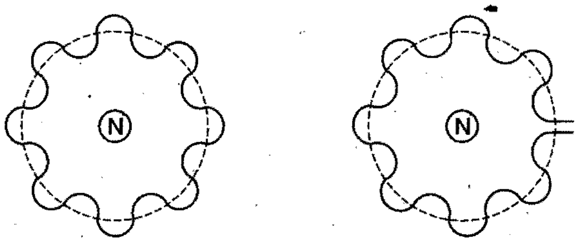


Fig. 2.15

So, $$2\pi r = n\lambda$$

or $$\lambda = \frac{2\pi r}{n} \qquad \ldots \text{(i)}$$

From de Broglie equation,

$$\lambda = \frac{h}{mv} \qquad \ldots \text{(ii)}$$

Thus, $$\frac{h}{mv} = \frac{2\pi r}{n}$$

or $$mvr = n \cdot \frac{h}{2\pi} \quad (v = \text{velocity of electron and } r = \text{radii of the orbit})$$

i.e., $$\text{Angular momentum} = n \cdot \frac{h}{2\pi} \qquad \ldots \text{(iii)}$$

This proves that the de Broglie and Bohr concepts are in perfect agreement with each other.

2.14 HEISENBERG UNCERTAINTY PRINCIPLE

Bohr theory considers an electron as a material particle. Its position and momentum can be determined with accuracy. But, when an electron is considered in the form of wave as suggested by de Broglie, it is not possible to ascertain simultaneously the exact position and velocity of the electron more precisely at a given instant since the wave is extending throughout a region of space. To locate the electron, radiation with extremely short wavelength is required. Radiation that has short wavelength is very energetic in nature. When it strikes the electron, the impact causes a change in the velocity of the electron. Thus, the attempt to locate the electron changes ultimately the momentum of the electron. Photons with longer wavelengths are less energetic and cause less effect on the momentum of the electron. Because of larger wavelength, such photons are not able to locate the position of an electron precisely.

In 1927, **Werner Heisenberg** presented a principle known as **Heisenberg uncertainty principle** which states: **"It is impossible to measure simultaneously the exact position and exact momentum of a body as small as an electron."**

The uncertainty of measurement of position, Δx and the uncertainty of momentum, Δp or Δmv are related by Heisenberg's relationship as:

$$\Delta x \cdot \Delta p \geq h / 4\pi$$

or $$\Delta x \cdot \Delta mv \geq h / 4\pi$$

where, h is Planck's constant.

For an electron of mass $m\,(9.10 \times 10^{-28}$ g), the product of uncertainty is quite large.

$$\Delta x \cdot \Delta v \geq \frac{6.626 \times 10^{-27}}{4\pi m}$$

$$\geq \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 9.10 \times 10^{-28}}$$

$$\approx 0.57 \text{ erg-sec per gram approximately}$$

$\Delta x \cdot \Delta v$ = uncertainty product

When $\Delta x = 0, \Delta v = \infty$ and *vice-versa*.

In the case of bigger particles (having considerable mass), the value of uncertainty product is negligible. If the position is known quite accurately, *i.e.*, Δx is very small, Δv becomes large and *vice-versa*. Thus, uncertainty principle is important only in the case of smaller moving particles like electrons.

For other canonical conjugates of motion, the equation for Heisenberg uncertainty principle may be given as:

$$\text{momentum} = \text{mass} \times \text{velocity}$$

$$= \text{mass} \times \frac{\text{velocity}}{\text{time}} \times \text{time}$$

$$= \text{force} \times \text{time}$$

$$\text{momentum} \times \text{distance} = \text{force} \times \text{distance} \times \text{time}$$

$$= \text{energy} \times \text{time}$$

$$\Delta p\, \Delta x = \Delta E\, \Delta t$$

$$\Delta E\, \Delta t \geq \frac{h}{4\pi} \qquad \text{(for energy and time)}$$

Similarly, $$\Delta \phi\, \Delta \theta \geq \frac{h}{4\pi} \qquad \text{(for angular motion)}$$

On the basis of this principle, therefore, Bohr picture of an electron in an atom, which gives a fixed position in a fixed orbit and definite velocity to an electron, is no longer tenable. The best we can think of in terms of probability of locating an electron with a probable velocity in a given region of space at a given time. The space or a three dimensional region round the nucleus where there is maximum probability of finding an electron of a specific energy is called an **atomic orbital**.

SOME SOLVED EXAMPLES

Example 36. *Calculate the wavelength associated with an electron moving with a velocity of* 10^{10} *cm per sec.*

Solution: Mass of the electron $= 9.10 \times 10^{-28}$ g

Velocity of electron $= 10^{10}$ cm per sec

$h = 6.62 \times 10^{-27}$ erg-sec

According to de Broglie equation,

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-27}}{9.10 \times 10^{-28} \times 10^{10}}$$

$$= 7.72 \times 10^{-10} \text{ cm}$$

$$= 0.0772 \text{ Å}$$

Example 37. *Calculate the uncertainty in the position of a particle when the uncertainty in momentum is:*
(a) 1×10^{-3} *g cm* sec^{-1} *(b) zero.*

Solution: (a) Given,

$\Delta P = 1 \times 10^{-3}$ g cm sec^{-1}

$h = 6.62 \times 10^{-27}$ erg-sec

$\pi = 3.142$

According to uncertainty principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

So, $$\Delta x \geq \frac{h}{4\pi} \cdot \frac{1}{\Delta p} \geq \frac{6.62 \times 10^{-27}}{4 \times 3.142} \times \frac{1}{10^{-3}}$$

$$= 0.527 \times 10^{-24} \text{ cm}$$

(b) When the value of $\Delta p = 0$, the value of Δx will be infinity.

Example 38. *Calculate the momentum of a particle which has a de Broglie wavelength of* 2.5×10^{-10} *m.*
$(h = 6.6\times10^{-34}\ kg\ m^2\ s^{-1})$

Solution: $$\text{Momentum} = \frac{h}{\lambda} \text{ (using de Broglie equation)}$$
$$= \frac{6.6\times10^{-34}}{2.5\times10^{-10}}$$
$$= 2.64\times10^{-24} \text{ kg m sec}^{-1}$$

Example 39. *What is the mass of a photon of sodium light with a wavelength of* $5890\ \mathring{A}$*?*
$(h = 6.63\times10^{-27}\ erg\text{-}sec, c = 3\times10^{10}\ cm/sec)$

Solution: $$\lambda = \frac{h}{mc}$$

or $$m = \frac{h}{\lambda c}$$

So, $$m = \frac{6.63\times10^{-27}}{5890\times10^{-8}\times3\times10^{10}}$$
$$= 3.752\times10^{-33} \text{ g}$$

Example 40. *The uncertainty in position and velocity of a particle are* 10^{-10} *m and* $5.27\times10^{-24}\ m\,s^{-1}$ *respectively. Calculate the mass of the particle.* $(h = 6.625\times10^{-34}\ J\text{-}s)$

Solution: According to Heisenberg's uncertainty principle,
$$\Delta x\cdot m\,\Delta v = \frac{h}{4\pi}$$

or $$m = \frac{h}{4\pi\,\Delta x\cdot\Delta v}$$
$$= \frac{6.625\times10^{-34}}{4\times3.143\times10^{-10}\times5.27\times10^{-24}}$$
$$= 0.099 \text{ kg}$$

Example 41. *Calculate the uncertainty in velocity of a cricket ball of mass* 150 g *if the uncertainty in its position is of the order of* $1\ \mathring{A}$ $(h = 6.6\times10^{-34}\ kg\ m^2\ s^{-1})$.

Solution: $$\Delta x\cdot m\,\Delta v = \frac{h}{4\pi}$$
$$\Delta v = \frac{h}{4\pi\,\Delta x\cdot m}$$
$$= \frac{6.6\times10^{-34}}{4\times3.143\times10^{-10}\times0.150}$$
$$= 3.499\times10^{-24} \text{ ms}^{-1}$$

Example 42. *Find the number of waves made by a Bohr electron in one complete revolution in the* 3rd *orbit.* **(IIT 1994)**

Solution: Velocity of the electron in 3rd orbit $= \dfrac{3h}{2\pi mr}$

where, m = mass of electron and r = radius of 3rd orbit.

Applying de Broglie equation,
$$\lambda = \frac{h}{mv} = \frac{h}{m}\times\frac{2\pi mr}{3h} = \frac{2\pi r}{3}$$
$$\text{No. of waves} = \frac{2\pi r}{\lambda} = \frac{2\pi r}{2\pi r}\times3 = 3$$

Example 43. *The kinetic energy of an electron is* 4.55×10^{-25} *J. Calculate the wavelength,* $(h = 6.6\times10^{-34}$ *J-sec, mass of electron* $= 9.1\times10^{-31}$ *kg).*

Solution: $$\text{KE} = \frac{1}{2}mv^2 = 4.55\times10^{-25}$$

or $$\frac{1}{2}\times9.1\times10^{-31}\times v^2 = 4.55\times10^{-25}$$

or $$v^2 = \frac{2\times4.55\times10^{-25}}{9.1\times10^{-31}}$$
$$v = 10^3 \text{ ms}^{-1}$$

Applying de Broglie equation,
$$\lambda = \frac{h}{mv} = \frac{6.6\times10^{-34}}{9.1\times10^{-31}\times10^3} = 0.72\times10^{-6} \text{ m}$$

Example 44. *The speeds of the Fiat and Ferrari racing cars are recorded to* $\pm4.5\times10^{-4}\ m\,sec^{-1}$. *Assuming the track distance to be known within* $\pm16\,m$, *is the uncertainty principle violated for a* 3500 *kg car?*

Solution: $$\Delta x\,\Delta v = 4.5\times10^{-4}\times16$$
$$= 7.2\times10^{-3} \text{ m}^2 \text{ sec}^{-1} \qquad \ldots(i)$$
$$\frac{h}{4\pi m} = \frac{6.626\times10^{-34}}{4\times3.14\times3500} \qquad \ldots(ii)$$
$$= 1.507\times10^{-38}$$

Since, $\Delta x\,\Delta v \geq h/4\pi m$

Hence, Heisenberg uncertainty principle is not violated.

Example 45. *Alveoli are tiny sacs in the lungs whose average diameter is* 5×10^{-5} *m. Consider an oxygen molecule* $(5.3\times10^{-26}\ kg)$ *trapped within a sac. Calculate uncertainty in the velocity of oxygen molecule.*

Solution: Uncertainty in position Δx = Diameter of Alveoli
$$= 5\times10^{-10} \text{ m}$$
$$\Delta x\,\Delta v \geq \frac{h}{4\pi m}$$
$$\Delta v \geq \frac{6.626\times10^{-34}}{4\times3.14\times5.3\times10^{-26}\times5\times10^{-10}}$$
$$\Delta v \approx 1.99 \text{ m/sec}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

13. If the kinetic energy of an electron is increased 4 times, the wavelength of the de Broglie wave associated with it would become:

(a) 4 times	(b) 2 times
(c) $\frac{1}{2}$ times	(d) $\frac{1}{4}$ times

[Ans. (c)]

[Hint: $\lambda = \dfrac{h}{\sqrt{2Em}}$, where, E = kinetic energy

When, the kinetic energy of electron becomes 4 times, the de Broglie wavelength will become half.]

14. The mass of photon having wavelength 1 nm is:

(a) 2.21×10^{-35} kg (b) 2.21×10^{-33} g

(c) 2.21×10^{-33} kg (d) 2.21×10^{-26} kg

[Ans. (c)]

[Hint: $\lambda=\frac{h}{mc}$

$$m=\frac{h}{\lambda c}=\frac{6.626\times10^{-34}}{1\times10^{-9}\times3\times10^{8}}$$

$$=2.21\times10^{-33}\text{ kg}]$$

15. The de Broglie wavelength of 1 mg grain of sand blown by a 20 ms^{-1} wind is:

(a) 3.3×10^{-29} m (b) 3.3×10^{-21} m

(c) 3.3×10^{-49} m (d) 3.3×10^{-42} m

[Ans. (a)]

[Hint: $\lambda=\frac{h}{mv}=\frac{6.626\times10^{-34}}{1\times10^{-6}\times20}=3.313\times10^{-29}\text{ m}]$

16. In an atom, an electron is moving with a speed of 600 m sec^{-1} with an accuracy of 0.005%. Certainty with which the position of the electron can be located is:
($h=6.6\times10^{-34}\text{ kg m}^2\text{ s}^{-1}$, mass of electron $=9.1\times10^{-31}$ kg) **(AIEEE 2009)**

(a) 1.52×10^{-4} m (b) 5.1×10^{-3} m

(c) 1.92×10^{-3} m (d) 3.84×10^{-3} m

[Ans. (c)]

[Hint: Accuracy in velocity = 0.005%

$$\Delta v=\frac{600\times0.005}{100}=0.03$$

According to Heisenberg's uncertainty principle,

$$\Delta x\, m\Delta v\geq\frac{h}{4\pi}$$

$$\Delta x=\frac{6.6\times10^{-34}}{4\times3.14\times9.1\times10^{-31}\times0.03}$$

$$=1.92\times10^{-3}\text{ m}]$$

17. Velocity of de Broglie wave is given by:

(a) $\frac{c^2}{\nu}$ (b) $\frac{h\nu}{mc}$ (c) $\frac{mc^2}{h}$ (d) $\nu\lambda$

[Ans. (b)]

[Hint: $\lambda=\frac{h}{mv}=\frac{h}{p}$

$$p=\frac{h}{\lambda}$$

$$mv=\frac{h\nu}{c}$$

$$v=\frac{h\nu}{mc}\;]$$

2.15 WAVE MECHANICAL MODEL OF ATOM

The atomic model which is based on the particle and wave nature of the electron is known as **wave mechanical model of the atom.** This was developed by **Erwin Schrödinger** in 1926. This model describes the electron as a three-dimensional wave in the electronic field of positively charged nucleus. Schrödinger derived an equation which describes wave motion of an electron. The differential equation is:

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}+\frac{8\pi^2m}{h^2}(E-V)\psi=0$$

where, x, y and z are cartesian coordinates of the electron; m = mass of the electron; E = total energy of the electron; V = potential energy of the electron; h = Planck's constant and ψ(psi) = wave function of the electron.

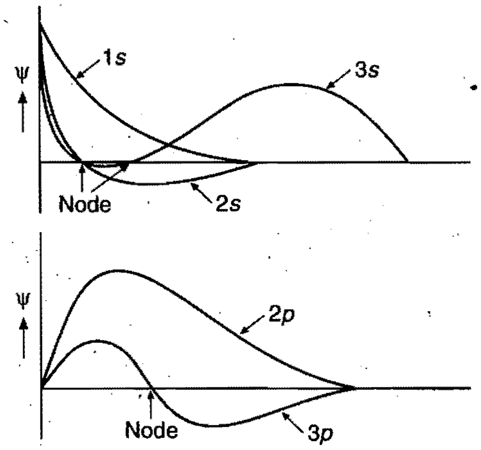
Significance of ψ: The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z. The wave function may have positive or negative values depending upon the values of coordinates.

The main aim of Schrödinger equation is to give a solution for the probability approach. When the equation is solved, it is observed that for some regions of space the value of ψ is positive and for other regions the value of ψ is negative. But the probability must be always positive and cannot be negative. It is, thus, proper to use ψ^2 in favour of ψ.

Significance of ψ^2: ψ^2 is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital.

The solution of the wave equation is beyond the scope of this book. The important point of the solution of this equation is that it provides a set of numbers, called **quantum numbers,** which describe energies of the electrons in atoms, information about the shapes and orientations of the most probable distribution of electrons around the nucleus.

Wave function ψ can be plotted against distance 'r' from nucleus as,



For hydrogen wave function, number of nodes can be calculated as,

(i) Number of radial nodes = $(n - l - 1)$

(ii) Number of angular nodes = l

(iii) Total number of nodes = $(n - 1)$

(iv) Number of nodal planes = l

Note: If the node at $r = \infty$ is also considered then no. of nodes will be 'n' (not $n - 1$).

Examples: *(i) For 1s-orbital $n = 1$, $l = 0$, it will have no radial or angular node.*

(ii) For 2s-orbital, $n = 2$, $l = 0$, it will have only one radial node.

(iii) For 3s-orbital, $n = 3$, $l = 0$, it will have two radial nodes.

(iv) For 2p-orbital, $n = 2$, $l = 1$, it will have no radial node but it has only one angular node.

(v) For 3p-orbital, $n = 3$, $l = 1$, it will have one radial and one angular node.

For *s*-orbitals:

$(n - 1)$ radial nodes + 0 angular node = $(n - 1)$ total nodes.

For *p*-orbitals:

$(n - 2)$ radial nodes + 1 angular node = $(n - 1)$ total nodes.

For *d*-orbitals:

$(n - 3)$ radial nodes + 2 angular nodes = $(n - 1)$ total nodes.

d_{z^2} like all *d*-orbitals has two angular nodes. The difference is that the angular nodes are cones in a d_{z^2} orbital, not planes.

Operator form Schrödinger Wave Equation

$$\hat{H}\Psi = E\Psi \qquad \text{(Operator form)}$$

where $\hat{H} = \left[-\frac{h^2}{8\pi^2 m}\nabla^2 + \hat{V}\right]$ = Hamiltonian operator

$$= \hat{T} + \hat{V}$$

Here, $\hat{T}$ = Kinetic energy operator

$\hat{V}$ = Potential energy operator

Complete wave function can be given as

$$\Psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{Radial part}} \quad \underbrace{\Theta(\theta)\Phi(\phi)}_{\text{Angular part}}$$

Dependence of the wave function on quantum number can be given as,

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\ \Theta_{lm}(\theta)\Phi_m(\phi)$$

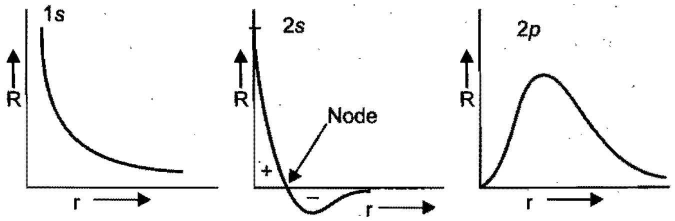
The function R depend only on r, therefore they describe the distribution of the electron as a function of r from the nucleus. These functions depend upon two quantum numbers, n and l. The two functions Θ and Φ taken together give the angular distribution of the electron.

The radial part of the wave function for some orbitals may be given as,

	n	l	R_{nl}
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2s	2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2p	2	1	$\frac{1}{\sqrt{3}}\left(\frac{Zr}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$

where, Z = atomic number, a_0 = radius of first Bohr orbit of hydrogen.

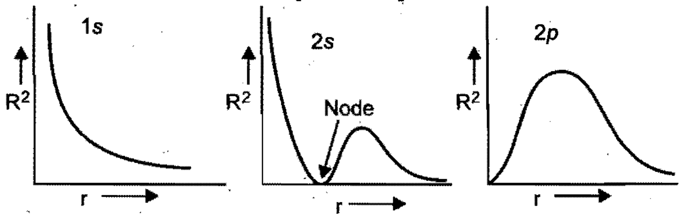
Plot of Radial Wave Function '*R*':



Number of radial nodes = $(n - l - 1)$.

At node, the value of 'R' changes from positive to negative.

Plot of Radial Probability Density 'R^2':



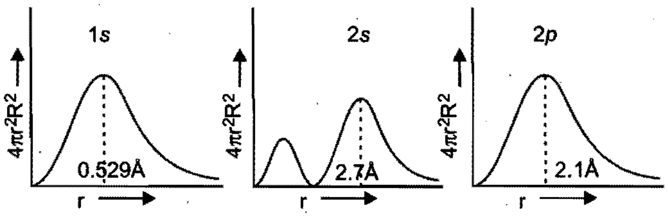
The plots of probability, *i.e.*, R^2 or Ψ^2 are more meaningful than the plots of functions themselves. It can be seen that for both 1*s* and 2*s* orbitals, the probability has a maximum value at $r = 0$, *i.e.*, in the nucleus. In case of 2*s* orbital, one more maximum in the probability plot is observed.

Plot of Radial Probability Function ($4\pi r^2 R^2$):

In order to visualize the electron cloud within a spherical shell is placed at radii 'r' and '$r + dr$' from the nucleus. Thus radial probability function describes the total probability of finding the electron in a spherical shell of thickness 'dr' located at the distance r from the nucleus.

R.P.F. = (Volume of spherical shell) × Probability density

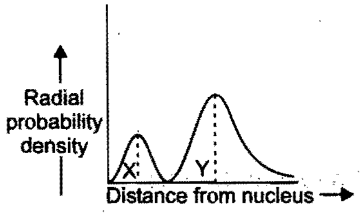
$$= (4\pi r^2 dr) \times R^2$$



In the plot of radial probability against 'r', number peaks, *i.e.*, region of maximum probability = $n - l$.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

18.



If the above radial probability curve indicates '2s' orbital, the distance between the peak points X, Y is :

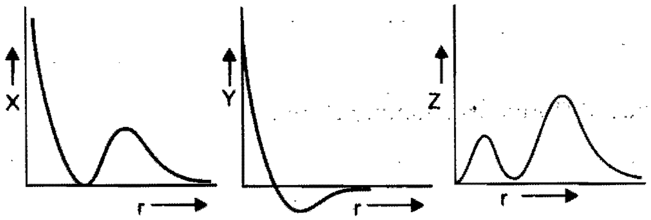
(a) 2.07Å (b) 1.59Å (c) 0.53Å (d) 2.12Å

[**Ans.** (a)]

[**Hint :** $X = 0.53\text{Å}, \ Y = 2.6\text{Å}$

$Y - X = 2.6 - 0.53 = 2.07\text{Å}$]

19. Plots for 2s orbital are :



X, Y and Z are respectively

(a) R, R^2 and $4\pi r^2R^2$ (b) R^2, R and $4\pi r^2R^2$

(c) $4\pi r^2R^2, R^2$ and R (d) $R^2, 4\pi r^2R^2$ and R

[**Ans.** (b)]

[**Hint :** Y will be definitely 'R' because value of R cannot be negative, thus X will be R^2 and Z will be $4\pi r^2R$. Z represents radial probability function; its value will be zero at origin]

20. The wave function (Ψ) of 2s is given by :

$$\Psi_{2s} = \frac{1}{2\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{1/2}\left\{2 - \frac{r}{a_0}\right\}e^{-r/2a_0}$$

At $r = r_0$, radial node is formed. Thus for 2s, r_0 in terms of a_0 is :

(a) $r_0 = a_0$ (b) $r_0 = 2a_0$ (c) $r_0 = a_0/2$ (d) $r_0 = 4a_0$

[**Ans.** (b)]

[**Hint :** When $r = r_0$, $\psi_{2s} = 0$, then from the given equation:

$$2 - \frac{r}{a_0} = 0$$

$$r = 2a_0\text{]}$$

21. The wave function for 1s orbital of hydrogen atom is given by :

$$\Psi_{1s} = \frac{\pi}{\sqrt{2}}e^{-r/a_0}$$

where, a_0 = Radius of first Bohr orbit

r = Distance from the nucleus (Probability of finding the electron varies with respect to it)

What will be the ratio of probabilities of finding the electrons at the nucleus to first Bohr's orbit a_0?

(a) e (b) e^2 (c) $1/e^2$ (d) zero

[**Ans.** (d)]

[**Hint :** For 1s orbital, probability of finding the electron at the nucleus is zero.]

22. The radial wave equation for hydrogen atom is :

$$\Psi = \frac{1}{16\sqrt{4}}\left(\frac{1}{a_0}\right)^{3/2}[(x-1)(x^2 - 8x + 12)]e^{-x/2}$$

where, $x = 2r/a_0$; a_0 = radius of first Bohr orbit.

The minimum and maximum position of radial nodes from nucleus are :

(a) $a_0, 3a_0$ (b) $\frac{a_0}{2}, 3a_0$ (c) $\frac{a_0}{2}, a_0$ (d) $\frac{a_0}{2}, 4a_0$

[**Ans.** (b)]

[**Hint :** At radial node, $\Psi = 0$

∴ From given equation,

$$x - 1 = 0 \text{ and } x^2 - 8x + 12 = 0$$

$$x - 1 = 0 \Rightarrow x = 1$$

i.e., $\frac{2r}{a_0} = 1; r = \frac{a_0}{2}$ (Minimum)

$$x^2 - 8x + 12 = 0$$

$$(x-6)(x-2) = 0$$

when $x - 2 = 0$

$$x = 2$$

$\frac{2r}{a_0} = 2$, i.e., $r = a_0$ (Middle value)

when $x - 6 = 0$

$$x = 6$$

$$\frac{2r}{a_0} = 6$$

$r = 3a_0$ (Maximum)]

2.16 QUANTUM NUMBERS

As we know, to search a particular person in this world, four things are needed:

(i) The country to which the person belongs
(ii) The city in that country to which the person belongs
(iii) The street in that city where the person is residing
(iv) The house number

Similarly, four identification numbers are required to locate a particular electron in an atom. These identification numbers are called **quantum numbers.** The four quantum numbers are discussed below.

Principal Quantum Number

It was given by **Bohr;** it is denoted by 'n'. It represents the name, size and energy of the shell to which the electron belongs.

The value of 'n' lies between 1 to ∞.

$$n = 1, 2, 3, 4, \ldots \infty$$

Value of n	=	1	2	3	4	5	6	7
Designation of shell	=	K	L	M	N	O	P	Q

(i) Higher is the value of 'n', greater is the distance of the shell from the nucleus.

$$r_1 < r_2 < r_3 < r_4 < r_5 < \ldots$$

$$r = \frac{n^2}{Z} \times 0.529 \text{ Å}$$

(ii) Higher is the value of 'n', greater is the magnitude of energy.

$$E_1 < E_2 < E_3 < E_4 < E_5 \ldots$$

$$E = -\frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J / atom}$$

$$= -\frac{Z^2}{n^2} \times 313.3 \text{ kcal per mol}$$

Energy separation between two shells decreases on moving away from nucleus.

$$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3) > (E_5 - E_4)$$

(iii) Maximum number of electrons in a shell* $= 2n^2$

(iv) Angular momentum can also be calculated using principal quantum number

$$mvr = \frac{nh}{2\pi}$$

Azimuthal Quantum Number

It was given by **Sommerfeld;** it is also called **angular quantum number, subsidiary quantum number** or **secondary quantum number.** It is denoted by 'l'; its value lies between 0, 1, 2, . . . $(n - 1)$.

It describes the spatial distribution of electron cloud and angular momentum. It gives the name of the subshell associated with the main shell

$l = 0$ s-subshell; $l = 1$ p-subshell;
$l = 2$ d-subshell; $l = 3$ f-subshell;
$l = 4$ g-subshell.

s, p, d, f and g are spectral terms and signify *sharp, principal, diffused, fundamental* and *generalised* respectively.

The energies of the various subshells in the same shell are in the order of $s < p < d < f < g$ (increasing order). Subshells having equal l values but with different n values have similar shapes but their sizes increase as the value of 'n' increases. 2s-subshell is greater in size than 1s-subshell. Similarly $2p, 3p, 4p$-subshells have similar shapes but their sizes increase in the order $2p < 3p < 4p$.

Orbital angular momentum of an electron is calculated using the expression

$$\mu_l = \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$$

here, $\hbar = \dfrac{h}{2\pi}$

The magnitude of magnetic moment μ_L may be given as:

$$\mu_L = \sqrt{l(l+1)} \text{ BM}$$

where, BM = Bohr Magneton

$$1 \text{ BM} = \frac{eh}{4\pi mc} = 9.2732 \times 10^{-14} \text{ J}$$

Maximum electrons present in a subshell $= 2(2l + 1)$

s-subshell → 2 electrons
d-subshell → 10 electrons
p-subshell → 6 electrons
f-subshell → 14 electrons
g-subshell → 18 electrons

Magnetic Quantum Number

This quantum number is designated by the symbol 'm'. To explain splitting of a single spectral line into a number of closely spaced lines in the presence of magnetic field **(Zeeman effect),** Linde proposed that electron producing a single line has several possible space orientations for the same angular momentum vector in a magnetic field, *i.e.*, under the influence of magnetic field each subshell is further sub-divided into orbitals. Magnetic quantum number describes the orientation or distribution of electron cloud. For each value of 'l', the magnetic quantum number 'm' may assume all integral values from $-l$ to $+l$ including zero, *i.e.*, total $(2l + 1)$ values.

Thus, when $l = 0, m = 0$ (only one value)
when $l = 1, m = -1, 0, +1$ (three values)
i.e., three orientations.

One orientation corresponds to one orbital. Three orientations (orbitals) are designated as p_x, p_y and p_z.

When $l = 2, m = -2, -1, 0, +1, +2$ (five values), *i.e.*, five orientations.

The five orbitals are designated as:

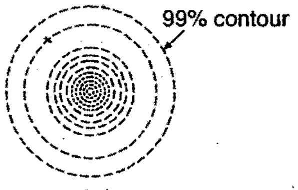
$$d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2} \text{ and } d_{z^2}.$$

When $l = 3, m = -3, -2, -1, 0, +1, +2, +3$ (seven values), *i.e.*, seven orientations.

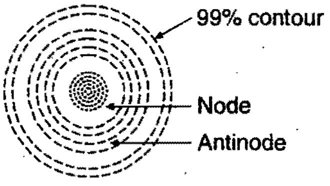
Different values of 'm' for a given value of 'l' provide the total number of ways in which a given s, p, d and f subshells in presence of magnetic field can be arranged in space along x, y and z axes or total number of orbitals into which a given subshell can be divided.

When $l = 0, m = 0$, *i.e.*, one value implies that 's' subshell has only one space orientation and hence it can be arranged in space only in one way along x, y or z axes. Thus, 's' orbital has a symmetrical spherical shape and is usually represented as in Fig. 2.16.

In case of 1s-orbital, the electron cloud is maximum at the nucleus and decreases with the distance. The electron density at a particular distance is uniform in all directions. The region of maximum electron density is called **antinode.** In case of '2s'-orbital, the electron density is again maximum at the nucleus and decreases with increase in distance. The '2s'-orbital differs in detail from a 1s-orbital. The electron in a '2s'-orbital is likely to be found in two regions, one near the nucleus and other in a spherical shell about the nucleus. Electron density is zero in nodal region.



1s



2s-orbital

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*No energy shell in atoms of known elements possesses more than 32 electrons.

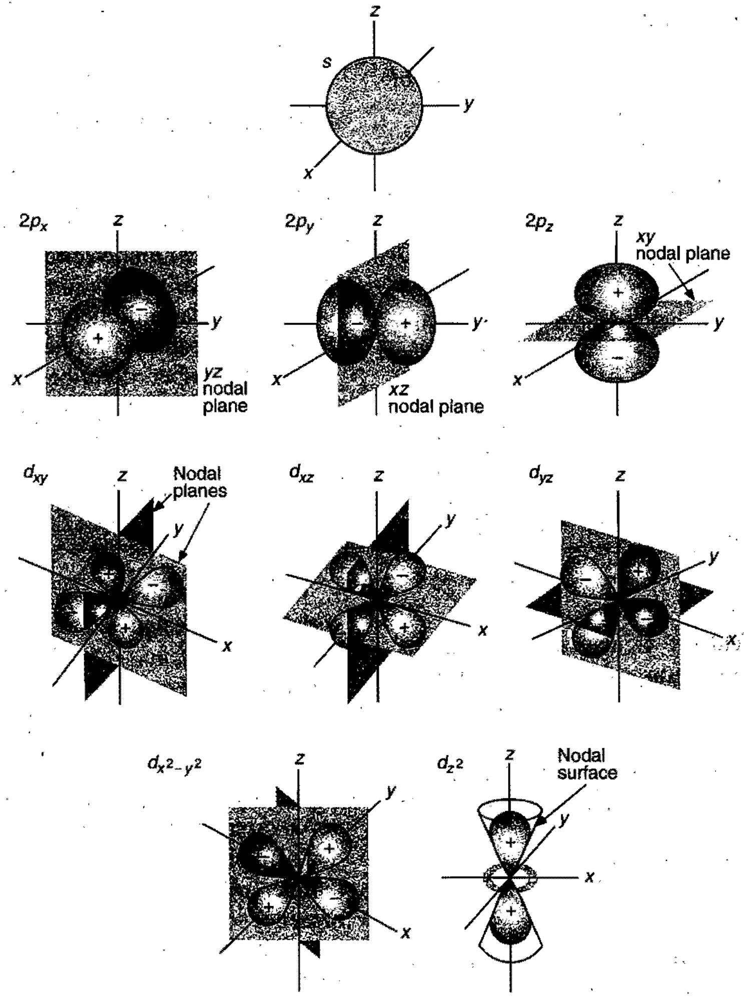


Fig. 2.16

When $l = 1$, 'm' has three values −1, 0, +1. It implies that 'p' subshell of any energy shell has three space orientations, *i.e.*, three orbitals. Each p-orbital has **dumb-bell** shape. Each one is disposed symmetrically along one of the three axes as shown in Fig. 2.16. p-orbitals have directional character.

Orbital	p_z	p_x	p_y
m	0	± 1	± 1
Nodal plane	xy	yz	zx

When $l = 2$, 'm' has five values −2, −1, 0, + 1, + 2. It implies that d-subshell of any energy shell has five orientations, *i.e.*, five orbitals. All the five orbitals are not identical in shape. Four of the d-orbitals $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ contain four lobes while fifth orbital d_{z^2} consists of only two lobes. The lobes of d_{xy} orbital lie between x and y-axes. Similar is the case for d_{yz} and d_{zx}. Four lobes of $d_{x^2-y^2}$ orbital are lying along x and y-axes while the two lobes of d_{z^2} orbital are lying along z-axis and contain a ring of negative charge surrounding the nucleus in xy-plane (Fig. 2.16).

Orbital	d_{xy}	d_{yz}	d_{zx}	$d_{x^2-y^2}$	d_{z^2}
m	± 2	± 1	± 1	± 2	0

Nodal planes :

Orbital	Nodal planes
d_{xy}	xz, yz
d_{yz}	xy, zx
d_{zx}	xy, yz
$d_{x^2-y^2}$	$x - y = 0, x + y = 0$
d_{z^2}	No nodal plane, it has a ring around the lobe

There are seven f-orbitals designated as $f_{x(x^2-y^2)}, f_{y(x^2-y^2)}, f_{z(x^2-y^2)}, f_{xyz}, f_{z^3}, f_{yz^2}$ and f_{xz^2}. Their shapes are complicated ones.

Positive values of m_l describes the orbital angular momentum component in the direction of applied magnetic field while the negative values of m_l are for the components in opposite direction to the applied magnetic field.

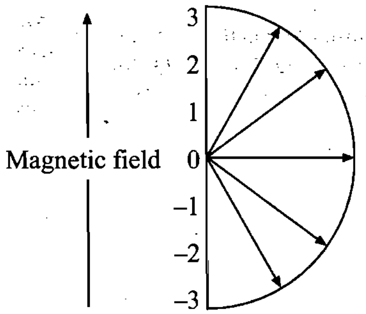


Fig. 21.6 (a) Space quantization in magnetic field

Characteristics of Orbitals

(i) All orbitals of the same shell in the absence of magnetic field possess same energy, *i.e.*, they are **degenerate.**

(ii) All orbitals of the same subshell differ in the direction of their space orientation.

(iii) Total number of orbitals in a main energy shell is equal to n^2 (but not more than 16 in any of the main shells of the known elements).

$n = 1$ No. of orbitals $= (1)^2 = 1\,(1s)$

$n = 2$ No. of orbitals $= (2)^2 = 4\,(2s, 2p_x, 2p_y, 2p_z)$

$n = 3$ No. of orbitals $= (3)^2 = 9\,(3s, 3p_x, 3p_y, 3p_z, 3d_{xy}, 3d_{yz}, 3d_{zx}, 3d_{x^2-y^2}, 3d_{z^2})$

$n = 4$ No. of orbitals $= (4)^2 = 16$

The division of main shells into subshells and that of subshell into orbitals has been shown below:

Note: Magnetic quantum number also represents quantized value of z-component of angular momentum of the electron in an orbital through the expression

$$Lz = m\left(\frac{h}{2\pi}\right)$$

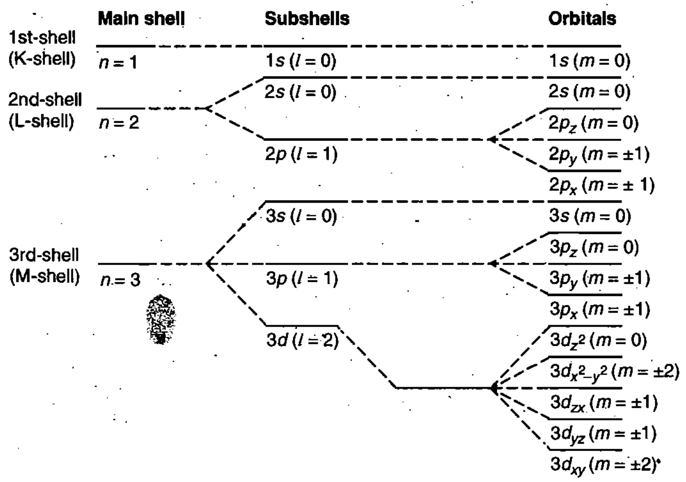
If θ is the angle between z-axis and angular momentum vector,

$$Lz = L\cos\theta$$

$$m\left(\frac{h}{2\pi}\right) = \sqrt{l(l+1)}\,\frac{h}{2\pi}\cos\theta$$

or

$$m = \sqrt{l(l+1)}\cos\theta$$



Degenerate Orbitals

Orbitals which are located at the same energy level on the energy level diagram are called degenerate orbitals. Thus, electrons have equal probability to occupy any of the degenerate orbitals.

p_x, p_y and $p_z \longrightarrow$ 3-fold degenerate

d-orbitals $\longrightarrow$ 5-fold degenerate

f-orbitals $\longrightarrow$ 7-fold degenerate

Degeneracy of p-orbitals remains unaffected in presence of external uniform magnetic field but degeneracy of d and f-orbitals is affected by external magnetic field.

Spin Quantum Number

It is denoted by 's' and it was given by **Goldschmidt.**

Spin quantum number represents the direction of electron spin around its own axis.

(i) For clockwise spin, $s = +\frac{1}{2}$ (↑ arrow representation).

(ii) For anticlockwise spin, $s = -\frac{1}{2}$ (↓ arrow representation).

Spin electron produces angular momentum equal to μ_s given by

$$\mu_s = \sqrt{s(s+1)}\,\frac{h}{2\pi}, \text{ where, } s = +\frac{1}{2}$$

Total spin of an atom $= n \times \frac{1}{2}$ (n = number of unpaired electrons)

Spin magnetic moment (μ_s) is given by

$$\mu_s = \sqrt{s(s+1)}\,\frac{eh}{2\pi mc}$$

Each orbital can accommodate two electrons with opposite spin or spin paired; paired electrons cancel the magnetic moment and develop mutual magnetic attraction as shown in the following Fig. 2.17.

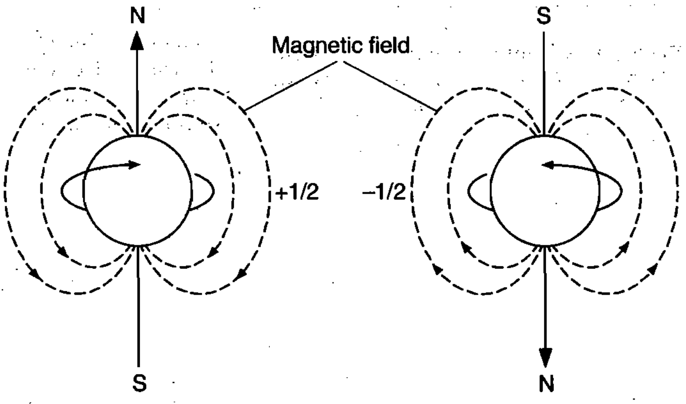


Fig. 2.17

Electrons having same spin are called spin parallel and those having opposite spin are called spin paired.

Spin paired $\longrightarrow \boxed{\uparrow\downarrow}$

Spin parallel $\longrightarrow \boxed{\uparrow\uparrow}$

Spin multiplicity:

Spin multiplicity $= [2\Sigma s + 1]$

where, s = spin quantum number

e.g., carbon	=	$1s^2$	$2s^2$	$2p^2$		
Normal state	=	↑↓	↑↓	↑	↑	
Excited state	=	↑↓	↑	↑	↑	↑

$$\text{Spin multiplicity} = 2\left[\left(+\frac{1}{2}\right)5+\left(-\frac{1}{2}\right)\right]+1=5$$

2.17 PAULI'S EXCLUSION PRINCIPLE

Each electron in an atom is designated by a set of four quantum numbers. In 1925, Pauli proposed that *no two electrons in an atom can have same values of all the four quantum numbers.*

An orbital accommodates two electrons with opposite spin; these two electrons have same values of principal, azimuthal and magnetic quantum number but the fourth, *i.e.*, spin quantum number will be different.

This principle can be illustrated by taking example of nitrogen.

$$N_7 = 1s^2 \; ; \; 2s^2 \; ; \; 2p^3$$

$$= 1s^2 \; ; \; 2s^2 \; ; \; 2p_x^1 \; 2p_y^1 \; 2p_z^1$$

$$= \boxed{\uparrow\downarrow} \; ; \; \boxed{\uparrow\downarrow} \; ; \; \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

Principal quantum number (n)	1	2	2	2	2
Azimuthal quantum number (l)	0	0	1	1	1
Magnetic quantum number (m)	0	0	+1	−1	0
Spin quantum number (s)	$+\frac{1}{2}-\frac{1}{2}$;	$+\frac{1}{2}-\frac{1}{2}$;	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$

Out of seven electrons no two have same values of all four quantum numbers. With the help of this principle, it is possible to calculate the maximum number of electrons which can be accommodated on main energy shells and subshells.

Principal Q. No. 'n'	Azimuthal Q. No. 'l'	Magnetic Q. No. 'm'	Spin Q. No. 's'	No. of electrons on a subshell	No. of electrons on a main shell
1	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
	1(p)	−1	$+\frac{1}{2}, -\frac{1}{2}$	6	
		0	$+\frac{1}{2}, -\frac{1}{2}$		
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
3	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
	1(p)	−1	$+\frac{1}{2}, -\frac{1}{2}$	6	
		0	$+\frac{1}{2}, -\frac{1}{2}$		
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
	2(d)	−2	$+\frac{1}{2}, -\frac{1}{2}$	10	
		−1	$+\frac{1}{2}, -\frac{1}{2}$		
		0	$+\frac{1}{2}, -\frac{1}{2}$		
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
		+2	$+\frac{1}{2}, -\frac{1}{2}$		
4	0(s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
	1(p)			6	
	2(d)			10	
	3(f)	−3	$+\frac{1}{2}, -\frac{1}{2}$	14	
		−2	$+\frac{1}{2}, -\frac{1}{2}$		
		−1	$+\frac{1}{2}, -\frac{1}{2}$		
		0	$+\frac{1}{2}, -\frac{1}{2}$		
		+1	$+\frac{1}{2}, -\frac{1}{2}$		
		+2	$+\frac{1}{2}, -\frac{1}{2}$		
		+3	$+\frac{1}{2}, -\frac{1}{2}$		

Conclusions:

(i) The maximum capacity of a main energy shell is equal to $2n^2$ electrons.

(ii) The maximum capacity of a subshell is equal to $2(2l+1)$ electrons.

Subenergy shell	Azimuthal Q. No. 'l'	Maximum capacity of electrons $2(2l+1)$
s	0	$2(2\times0+1)=2$
p	1	$2(2\times1+1)=6$
d	2	$2(2\times2+1)=10$
f	3	$2(2\times3+1)=14$

(iii) Number of subshells in a main energy shell is equal to the value of n.

Value of n	No. of subenergy shells	Designated as
1	1	$1s$
2	2	$2s, 2p$
3	3	$3s, 3p, 3d$
4	4	$4s, 4p, 4d, 4f$

(iv) Number of orbitals in a main energy shell is equal to n^2.

n	No. of orbitals	
1	$(1)^2=1$	s
2	$(2)^2=4$	s, p_x, p_y, p_z
3	$(3)^2=9$	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{z^2}$

(v) One orbital cannot have more than two electrons. If two electrons are present, their spins should be in opposite directions.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

23. The orbital angular momentum of an electron in a d-orbital is: **(DCE 2007)**

(a) $\sqrt{6}\,\frac{h}{2\pi}$ (b) $\sqrt{2}\,\frac{h}{2\pi}$ (c) $\frac{h}{2\pi}$ (d) $\frac{2h}{2\pi}$

[Ans. (a)]

[Hint: Orbital angular momentum $= \sqrt{l(l+1)}\,\dfrac{h}{2\pi}$

$$= \sqrt{2(2+1)}\,\frac{h}{2\pi} = \sqrt{6}\,\frac{h}{2\pi}$$

(Here, $l = 2$, for *d*-orbitals)]

24. Which of the following sets of quantum numbers is correct for an electron in $4f$-orbital?

(Jamia Millia Islamia Engg. Ent. 2007)

(a) $n = 4, l = 3, m = +4, s = +\frac{1}{2}$
(b) $n = 4, l = 4, m = -4, s = -\frac{1}{2}$
(c) $n = 4, l = 3, m = +1, s = +\frac{1}{2}$
(d) $n = 3, l = 2, m = -2, s = +\frac{1}{2}$
[Ans. (c)]

[Hint: For $4f$, $n = 4, l = 3, m = -3, -2, -1, 0, +1, +2, +3$
$s = -\frac{1}{2}$ or $+\frac{1}{2}$]

25. Match the List-I with List-II and select the correct set from the following sets given below:

	List-I		**List-II**
(A)	The number of sub-energy levels in an energy level	(1)	n^2
(B)	The number of orbitals in a sub-energy level	(2)	$3d$
(C)	The number of orbitals in an energy level	(3)	$2l + 1$
(D)	$n = 3, l = 2, m = 0$	(4)	n

[PET (Raj.) 2005]

Sets	**(A)**	**(B)**	**(C)**	**(D)**
(a)	4	3	1	2
(b)	3	1	2	4
(c)	1	2	3	4
(d)	3	4	1	2

[Ans. (a)]

[Hint: Number of orbitals in a shell $= n^2$

Number of subshells in a shell $= n$

Number of orbitals in a subshell $= (2l + 1)$

$n = 3, l = 2, m = 0$ represents $3d$]

26. Which of the following is not possible?

[BCECE (Medical) 2007]

(a) $n = 2, l = 1, m = 0$ (b) $n = 2, l = 0, m = -1$
(c) $n = 3, l = 0, m = 0$ (d) $n = 3, l = 1, m = -1$
[Ans. (b)]

[Hint: When $l = 0$, 'm' will also be equal to zero.]

27. What is the maximum number of electrons in an atom that can have the quantum numbers $n = 4$, $m_e = +1$?

[PMT (Kerala) 2007]

(a) 4 (b) 15 (c) 3 (d) 1 (e) 6
[Ans. (e)]
[Hint: $n = 4$; $l = 0$; $m_e = 0$
$l = 1$; $m_e = -1, 0, +1$
$l = 2$; $m_e = -2, -1, 0, +1, +2$
$l = 3$; $m_e = -3, -2, -1, 0, +1, +2, +3$

There are three orbitals having $m_e = +1$, thus maximum number of electrons in them will be 6.]

2.18 AUFBAU PRINCIPLE

Aufbau is a German word meaning 'building up'. This gives us a sequence in which various subshells are filled up depending on the relative order of the energy of the subshells. **The subshell with minimum energy is filled up first and when this obtains maximum quota of electrons, then the next subshell of higher energy starts filling.**

The sequence in which the various subshells are filled is the following:

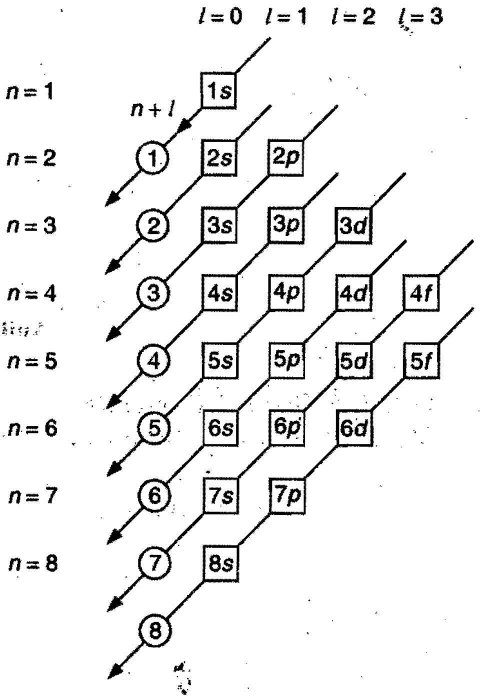


Fig. 2.18 Order of filling of various subshells

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p$.

The sequence in which various subshells are filled up can also be determined with the help of $(n + l)$ value for a given subshell. **The subshell with lowest $(n + l)$ value is filled up first. When two or more subshells have same $(n + l)$ value, the subshell with lowest value of 'n' is filled up first.**

Subshell	***n***	***l***	**$(n + l)$**	
1s	1	0	1	
2s	2	0	2	
2p	2	1	3	Lowest value of *n*
3s	3	0	3	
3p	3	1	4	Lowest value of *n*
4s	4	0	4	
3d	3	2	5	Lowest value of *n*
4p	4	1	5	
5s	5	0	5	

Subshell	n	l	$(n+l)$	
$4d$	4	2	6	Lowest value of n
$5p$	5	1	6	
$6s$	6	0	6	
$4f$	4	3	7	Lowest value of n
$5d$	5	2	7	
$6p$	6	1	7	
$7s$	7	0	7	
$5f$	5	3	8	Lowest value of n
$6d$	6	2	8	
$7p$	7	1	8	

The energy of electron in a hydrogen atom and other single electron species like He^+, Li^{2+} and Be^{3+} is determined solely by the principal quantum number. The energy of orbitals in hydrogen and hydrogen like species increases as follows:

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \ldots$$

The complete electronic configuration of all the known elements have been given in the table on next page. It is observed that few of the elements possess slightly different electronic configurations than expected on the basis of **Aufbau Principle.** These elements have been marked with asterisk (*) sign.

2.19 HUND'S RULE OF MAXIMUM MULTIPLICITY (Orbital Diagrams)

There is one more method of representing the electronic configuration which is usually called as **orbital diagram.** In this method, the electron is shown by an arrow: upward direction $\uparrow$ (clockwise spin) and downward direction $\downarrow$ (anti-clockwise spin).

To indicate the distribution of electrons among the orbitals of an atom, arrows are placed over bars that symbolise orbitals.

Hydrogen, for example, is represented as $\underset{1s}{\underline{\uparrow}}$. The next element with atomic number 2 is helium. It is represented as $\underset{1s}{\underline{\uparrow\downarrow}}$, *i.e.*, both the electrons are present on the same orbital 1s and are paired (spins are in opposite directions). The next two elements are Li and Be with three and four electrons, respectively. These are represented by orbital diagrams as:

Li $\underset{1s}{\underline{\uparrow\downarrow}}\ \underset{2s}{\underline{\uparrow}}$

Be $\underset{1s}{\underline{\uparrow\downarrow}}\ \underset{2s}{\underline{\uparrow\downarrow}}$

These can also be written as:

Li $[\text{He}]\underset{2s}{\underline{\uparrow}}$

Be $[\text{He}]\underset{2s}{\underline{\uparrow\downarrow}}$

In Be, 2s-orbital has been completed. The fifth electron in the case of boron enters the next available subshell which is $2p$. Thus, the electronic configuration of boron is $1s^2 2s^2 2p^1$. In the orbital diagram $[\text{He}]\underset{2s}{\underline{\uparrow\downarrow}} - \underset{2p}{\underline{\uparrow}} -$, the $2p$ subshell has three orbitals p_x, p_y and p_z. All the three have same energy. The electron can be accommodated on any one of the 2p-orbitals. In the case of carbon, sixth electron is also accommodated on $2p$ subshell and its electronic configuration is represented as $1s^2 2s^2 2p^2$ but three orbital diagrams can be expected.

(i) $[\text{He}]\underset{2s}{\underline{\uparrow\downarrow}}\ \underbrace{\underline{\uparrow}\ \underline{\uparrow}\ \underline{\ \ }}_{2p}$ Electrons are present on two different orbitals with parallel spins.

(ii) $[\text{He}]\underset{2s}{\underline{\uparrow\downarrow}}\ \underbrace{\underline{\uparrow}\ \underline{\downarrow}\ \underline{\ \ }}_{2p}$ Electrons are present on two different orbitals with opposite spins.

(iii) $[\text{He}]\underline{\uparrow\downarrow}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\ \ }\ \underline{\ \ }}_{2p}$ Both the electrons are present on one orbital with opposite spins.

Experiments show that (i) orbital diagram is correct while (ii) and (iii) are not correct. This has given birth to a new rule known as **Hund's rule of maximum multiplicity.** It states that **electrons are distributed among the orbitals of a subshell in such a way as to give the maximum number of unpaired electrons with parallel spins.** Thus, the orbitals available in a subshell are first filled singly before they begin to pair. This means that pairing of electrons occurs with the introduction of second electron in s-orbitals, the fourth electron in p-orbitals, sixth electron in d-orbitals and eighth electron in f-orbitals. The orbital diagrams of nitrogen, oxygen, fluorine and neon are as given below:

Nitrogen	(7)	[He]	$\underset{2s}{\underline{\uparrow\downarrow}}\ \underbrace{\underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{2p}$
Oxygen	(8)	[He]	$\underset{2s}{\underline{\uparrow\downarrow}}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{2p}$
Fluorine	(9)	[He]	$\underset{2s}{\underline{\uparrow\downarrow}}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}}_{2p}$
Neon	(10)	[He]	$\underset{2s}{\underline{\uparrow\downarrow}}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}_{2p}$

The orbital diagrams of elements from atomic number 21 to 30 can be represented on similar lines as below:

Sc	$[\text{Ar}]\,3d^1 4s^2$	[Ar]	$\uparrow$	—	—	—	—	$\uparrow\downarrow$
Ti	$[\text{Ar}]\,3d^2 4s^2$		$\uparrow$	$\uparrow$	—	—	—	$\uparrow\downarrow$
V	$[\text{Ar}]\,3d^3 4s^2$		$\uparrow$	$\uparrow$	$\uparrow$	—	—	$\uparrow\downarrow$
Cr	$[\text{Ar}]\,3d^5 4s^1$		$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
Mn	$[\text{Ar}]\,3d^5 4s^2$		$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Fe	$[\text{Ar}]\,3d^6 4s^2$		$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Co	$[\text{Ar}]\,3d^7 4s^2$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Ni	$[\text{Ar}]\,3d^8 4s^2$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow\downarrow$
Cu	$[\text{Ar}]\,3d^{10} 4s^1$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$
Zn	$[\text{Ar}]\,3d^{10} 4s^2$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
			3d					4s

ELECTRONIC CONFIGURATION OF ELEMENTS

Element	At. No.	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s* 5*p* 5*d* 5*f*
H	1	1										
He	2	2										(1*s* completed)
Li	3	2	1									
Be	4	2	2									(2*s* completed)
B	5	2	2	1								
C	6	2	2	2								
N	7	2	2	3								
O	8	2	2	4								
F	9	2	2	5								
Ne	10	2	2	6								(2*p* completed)
Na	11	2	2	6	1							
Mg	12	2	2	6	2							(3*s* completed)
Al	13	2	2	6	2	1						
Si	14	2	2	6	2	2						
P	15	2	2	6	2	3						
S	16	2	2	6	2	4						
Cl	17	2	2	6	2	5						
Ar	18	2	2	6	2	6						(3*p* completed)
K	19	2	2	6	2	6		1				
Ca	20	2	2	6	2	6		2				(4*s* completed)
Sc	21	2	2	6	2	6	1	2				
Ti	22	2	2	6	2	6	2	2				
V	23	2	2	6	2	6	3	2				
*Cr	24	2	2	6	2	6	5	1				
Mn	25	2	2	6	2	6	5	2				
Fe	26	2	2	6	2	6	6	2				
Co	27	2	2	6	2	6	7	2				
Ni	28	2	2	6	2	6	8	2				
*Cu	29	2	2	6	2	6	10	1				
Zn	30	2	2	6	2	6	10	2				(3*d* completed)
Ga	31	2	2	6	2	6	10	2	1			
Ge	32	2	2	6	2	6	10	2	2			
As	33	2	2	6	2	6	10	2	3			
Se	34	2	2	6	2	6	10	2	4			
Br	35	2	2	6	2	6	10	2	5			
Kr	36	2	2	6	2	6	10	2	6			(4*p* completed)
Rb	37	2	2	6	2	6	10	2	6			1
Sr	38	2	2	6	2	6	10	2	6			2 (5*s* completed)
Y	39	2	2	6	2	6	10	2	6	1		2
Zr	40	2	2	6	2	6	10	2	6	2		2
*Nb	41	2	2	6	2	6	10	2	6	4		1
*Mo	42	2	2	6	2	6	10	2	6	5		1
Tc	43	2	2	6	2	6	10	2	6	5		2
*Ru	44	2	2	6	2	6	10	2	6	7		1
*Rh	45	2	2	6	2	6	10	2	6	8		1
*Pd	46	2	2	6	2	6	10	2	6	10		
*Ag	47	2	2	6	2	6	10	2	6	10		1
Cd	48	2	2	6	2	6	10	2	6	10		2 (4*d* completed)
In	49	2	2	6	2	6	10	2	6	10		2 1
Sn	50	2	2	6	2	6	10	2	6	10		2 2
Sb	51	2	2	6	2	6	10	2	6	10		2 3
Te	52	2	2	6	2	6	10	2	6	10		2 4
I	53	2	2	6	2	6	10	2	6	10		2 5
Xe	54	2	2	6	2	6	10	2	6	10		2 6 (5*p* completed)

ELECTRONIC CONFIGURATION OF ELEMENTS

Element	At. No.	K	L	M	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s
Cs	55	2	8	18	2	6	10		2	6			1				
Ba	56	2	8	18	2	6	10		2	6			2	(6s completed)			
*La	57	2	8	18	2	6	10		2	6	1		2				
*Ce	58	2	8	18	2	6	10	1	2	6	1		2				
Pr	59	2	8	18	2	6	10	3	2	6			2				
Nd	60	2	8	18	2	6	10	4	2	6			2				
*Pm	61	2	8	18	2	6	10	5	2	6			2				
Sm	62	2	8	18	2	6	10	6	2	6			2				
Eu	63	2	8	18	2	6	10	7	2	6			2				
*Gd	64	2	8	18	2	6	10	7	2	6	1		2				
Tb	65	2	8	18	2	6	10	9	2	6			2				
Dy	66	2	8	18	2	6	10	10	2	6			2				
Ho	67	2	8	18	2	6	10	11	2	6			2				
Er	68	2	8	18	2	6	10	12	2	6			2				
Tm	69	2	8	18	2	6	10	13	2	6			2				
Yb	70	2	8	18	2	6	10	14	2	6			2				
Lu	71	2	8	18	2	6	10	14	2	6	1		2	(4*f* completed)			
Hf	72	2	8	18	32				2	6	2		2				
Ta	73	2	8	18	32				2	6	3		2				
W	74	2	8	18	32				2	6	4		2				
Re	75	2	8	18	32				2	6	5		2				
Os	76	2	8	18	32				2	6	6		2				
Ir	77	2	8	18	32				2	6	7		2				
*Pt	78	2	8	18	32				2	6	9		1				
*Au	79	2	8	18	32				2	6	10		1				
Hg	80	2	8	18	32				2	6	10		2	(5*d* completed)			
Tl	81	2	8	18	32				2	6	10		2	1			
Pb	82	2	8	18	32				2	6	10		2	2			
Bi	83	2	8	18	32				2	6	10		2	3			
Po	84	2	8	18	32				2	6	10		2	4			
At	85	2	8	18	32				2	6	10		2	5			
Rn	86	2	8	18	32				2	6	10		2	6(6*p* completed)			
Fr	87	2	8	18	32				2	6	10		2	6			1
Ra	88	2	8	18	32				2	6	10		2	6			2 (7*s* completed)
*Ac	89	2	8	18	32				2	6	10		2	6	1		2
*Th	90	2	8	18	32				2	6	10	0	2	6	2		2
*Pa	91	2	8	18	32				2	6	10	2	2	6	1		2
*U	92	2	8	18	32				2	6	10	3	2	6	1		2
*Np	93	2	8	18	32				2	6	10	4	2	6	1		2
Pu	94	2	8	18	32				2	6	10	6	2	6			2
Am	95	2	8	18	32				2	6	10	7	2	6			2
*Cm	96	2	8	18	32				2	6	10	7	2	6	1		2
*Bk	97	2	8	18	32				2	6	10	8	2	6	1		2
Cf	98	2	8	18	32				2	6	10	10	2	6			2
Es	99	2	8	18	32				2	6	10	11	2	6			2
Fm	100	2	8	18	32				2	6	10	12	2	6			2
Md	101	2	8	18	32				2	6	10	13	2	6			2
No	102	2	8	18	32				2	6	10	14	2	6			2
*Lr	103	2	8	18	32				2	6	10	14	2	6	1		2 (5*f* completed)
Ku or Rf	104	2	8	18	32				2	6	10	14	2	6	2		2 Predicted electronic configurations
Ha or Db	105	2	8	18	32				2	6	10	14	2	6	3		2
Sg	106	2	8	18	32				2	6	10	14	2	6	4		2
Bh	107	2	8	18	32				2	6	10	14	2	6	5		2
Hs	108	2	8	18	32				2	6	10	14	2	6	6		2
Mt	109	2	8	18	32				2	6	10	14	2	6	7		2
*Uun or Ds	110	2	8	18	32				2	6	10	14	2	6	9		1
*Uuu or Rg	111	2	8	18	32				2	6	10	14	2	6	10		1
Uub	112	2	8	18	32				2	6	10	14	2	6	10		2 (6*d* completed)

All those atoms which consist of at least one of the orbitals singly occupied behave as **paramagnetic** materials because these are weakly attracted to a magnetic field, while all those atoms in which all the orbitals are doubly occupied behave as **diamagnetic** materials because they have no attraction for magnetic field. However, these are slightly repelled by magnetic field due to induction.

Magnetic moment may be calculated as,

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

$$1\ \text{BM (Bohr Magneton)} = \frac{eh}{4\pi mc}$$

where, n = no. of unpaired electron

Exceptions to Aufbau Principle

In some cases, it is seen that actual electronic arrangement is slightly different from arrangement given by aufbau principle. A simple reason behind this is that half-filled and full-filled subshells have got extra stability.

$Cr_{24} \longrightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^4, 4s^2$ (wrong)

$\longrightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$ (right)

$Cu_{29} \longrightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^9, 4s^2$ (wrong)

$\longrightarrow 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$ (right)

Similarly the following elements have slightly different configurations than expected:

$$Nb_{41} \longrightarrow [Kr]4d^4 5s^1$$
$$Mo_{42} \longrightarrow [Kr]4d^5 5s^1$$
$$Ru_{44} \longrightarrow [Kr]4d^7 5s^1$$
$$Rh_{45} \longrightarrow [Kr]4d^8 5s^1$$
$$Pd_{46} \longrightarrow [Kr]4d^{10} 5s^0$$
$$Ag_{47} \longrightarrow [Kr]4d^{10} 5s^1$$
$$Pt_{78} \longrightarrow [Xe]4f^{14} 5d^9 6s^1$$
$$Au_{79} \longrightarrow [Xe]4f^{14} 5d^{10} 6s^1$$
$$La_{57} \longrightarrow [Kr]\,4d^{10} 5s^2 5p^6 5d^1 6s^2$$
$$Ce_{58} \longrightarrow [Kr]\,4d^{10} 4f^2 5s^2 5p^6 5d^0 6s^2$$
$$Gd_{64} \longrightarrow [Kr]\,4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$$

2.20 PHOTOELECTRIC EFFECT

Emission of electrons from a metal surface when exposed to light radiations of appropriate wavelength is called **photoelectric effect**. The emitted electrons are called **photoelectrons**.

Work function or threshold energy may be defined as the minimum amount of energy required to eject electrons from a metal surface.

According to Einstein,

Maximum kinetic energy of the ejected electron

= absorbed energy − work function

$$\frac{1}{2} mv^2_{\max} = h\nu - h\nu_0$$

$$= hc\left[\frac{1}{\lambda} - \frac{1}{\lambda_0}\right]$$

where, ν_0 and λ_0 are threshold frequency and threshold wavelength respectively.

Stopping potential: The minimum potential at which the plate photoelectric current becomes zero is called **stopping potential.**

If V_0 is the stopping potential, then

$$eV_0 = h(\nu - \nu_0)$$

Laws of Photoelectric Effect

(i) Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.

(ii) The maximum kinetic energy of photoelectrons is directly proportional to the frequency of incident radiation; moreover, it is independent of the intensity of light used.

(iii) There is no time lag between incidence of light and emission of photoelectrons.

(iv) For emission of photoelectrons, the frequency of incident light must be equal to or greater than the threshold frequency.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

28. The maximum kinetic energy of photoelectrons ejected from a metal, when it is irradiated with radiation of frequency $2 \times 10^{14}\ s^{-1}$ is 6.63×10^{-20} J. The threshold frequency of the metal is: [PMT (Kerala) 2008]

(a) $2 \times 10^{14}\ s^{-1}$ (b) $3 \times 10^{14}\ s^{-1}$

(c) $2 \times 10^{-14}\ s^{-1}$ (d) $1 \times 10^{-14}\ s^{-1}$

(e) $1 \times 10^{14}\ s^{-1}$

[Ans. (e)]

[**Hint :** Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$h\nu = h\nu_0 + \text{KE}$$
$$h\nu_0 = h\nu - \text{KE}$$
$$6.626 \times 10^{-34} \times \nu_0 = 6.626 \times 10^{-34} \times 2 \times 10^{14} - 6.63 \times 10^{-20}$$
$$\nu_0 = \frac{1.3252 \times 10^{-19} - 6.63 \times 10^{-20}}{6.626 \times 10^{-34}}$$
$$\nu_0 = 9.99 \times 10^{13} = 10^{14}\ s^{-1}\ ]$$

29. If λ_0 and λ be the threshold wavelength and the wavelength of incident light, the velocity of photoelectrons ejected will be:

(a) $\sqrt{\frac{2h}{m}(\lambda_0 - \lambda)}$ (b) $\sqrt{\frac{2hc}{m}(\lambda_0 - \lambda)}$

(c) $\sqrt{\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)}$ (d) $\sqrt{\frac{2h}{m}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)}$

[Ans. (c)]

[**Hint :** Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \frac{1}{2}mv^2$$

$$v = \sqrt{\frac{2hc}{m}\frac{(\lambda_0 - \lambda)}{\lambda\lambda_0}}\,]$$

30. A radiation of wavelength λ illuminates a metal and ejects photoelectrons of maximum kinetic energy of 1eV. Another radiation of wavelength $\frac{\lambda}{3}$, ejects photoelectrons of maximum kinetic energy of 4 eV. What will be the work function of metal?

(a) 1eV (b) 2eV (3) 0.5eV (d) 3eV

[Ans. (c)]

[Hint : Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$h\frac{c}{\lambda} = E_0 + 1\text{ eV} \qquad \text{...(i)}$$

$$3h\frac{c}{\lambda} = E_0 + 4\text{eV} \qquad \text{...(ii)}$$

$$3(E_0 + 1\text{ eV}) = E_0 + 4\text{eV}$$

$$E_0 = 0.5\text{eV}\,]$$

31. The ratio of slopes of maximum kinetic energy *versus* frequency and stopping potential (V_0) *versus* frequency, in photoelectric effect gives:

(a) charge of electron (b) planck's constant

(c) work function (d) threshold frequency

[Ans. (a)]

[Hint :
$$h\nu = h\nu_0 + eV_0$$

$$eV_0 = h\nu - h\nu_0$$

$$V_0 = \frac{h}{e}\nu - \frac{h}{e}\nu_0 \qquad \text{...(i)}$$

$$(\text{Slope})_1 = h/e$$

$$(\text{KE})_{\text{max}} = h\nu - h\nu_0 \qquad \text{...(ii)}$$

$$(\text{Slope})_2 = h$$

$$(\text{Slope})_2/(\text{Slope})_1 = \frac{h}{h/e} = e\,]$$

32. Ground state energy of H-atom is $(-E_1)$, the velocity of photoelectrons emitted when photon of energy E_2 strikes stationary Li^{2+} ion in ground state will be:

(a) $v = \sqrt{\frac{2(E_2 - E_1)}{m}}$ (b) $v = \sqrt{\frac{2(E_2 + 9E_1)}{m}}$

(c) $v = \sqrt{\frac{2(E_2 - 9E_1)}{m}}$ (d) $v = \sqrt{\frac{2(E_2 - 3E_1)}{m}}$

[Ans. (c)]

[Hint: Threshold energy of $Li^{2+} = 9E_1$

Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$E_2 = 9E_1 + \frac{1}{2}mv^2$$

$$mv^2 = 2(E_2 - 9E_1)$$

$$v = \sqrt{\frac{2(E_2 - 9E_1)}{m}}\,]$$

2.21 SOME OTHER FUNDAMENTAL PARTICLES

Besides protons, neutrons and electrons, many more elementary particles have been discovered. These particles are also called **Fundamental particles.** Some of these particles are stable while the others are unstable. Out of stable particles, the electron, the proton, the antiproton and the positron are four mass particles while neutrino, photon and graviton are three energy particles. Among these, unstable particles are neutron, meson and ν-particles. The main characteristics of the particles are given in table 2.1 below.

Table 2.1

Particle	Symbol	Nature	Charge esu × 10^{-10}	Mass (amu)	Discovered by
Positron	e^+, $1e^0$, β^+	+	+ 4.8029	0.0005486	Anderson (1932)
Neutrino	ν	0	0	< 0.00002	Pauli
Antiproton	p^-	–	– 4.8029	1.00787	Chamberlain Sugri and Weighland (1955)
Photon	$h\nu$	0	0	0	Planck
Graviton	G	0	0	0	
Positive mu meson	μ^+	+	+ 4.8029	0.1152	Yukawa (1935)
Negative mu meson	μ^-	–	– 4.8029	0.1152	Anderson (1937)
Positive pi meson	π^+	+	+ 4.8029	0.1514	Powell (1947)
Negative pi meson	π^-	–	– 4.8029	0.1514	
Neutral pi meson	π^0	0	0	0.1454	

2.22 ISOTOPES

Isotopes are the atoms of the same element having different atomic masses (see determination of isotopic mass). The term 'isotope' was introduced by **Soddy**. This is a Greek word meaning same position (*Isos* = same, *topes* = position), since all the isotopes of an element occupy the same position in the periodic table. Isotopes of an element possess identical chemical properties but differ slightly in physical properties which depend on atomic mass. Isotopes were first identified in radioactive elements by **Soddy**. In 1919, Thomson established the existence of isotopes in a non-radioactive element, neon. Until now, more than 1000 isotopes have been identified (natural as well as artificial). Out of these about 320 occur in nature, approximately 280 of these are stable and the remaining 40 are radioactive.

Conclusions

(i) Number of neutrons present in the nuclei of various isotopes of an element is always different. The number of neutrons is determined by applying the formula $N = A - Z$ where A is mass number and Z is atomic number.
Hydrogen has three isotopes, ${}_1^1\text{H}$, ${}_1^2\text{H}$ and ${}_1^3\text{H}$.

	A (Mass number)	**Z**	**No. of neutrons**
${}_1^1\text{H}$	1	1	0
${}_1^2\text{H}$	2	1	1
${}_1^3\text{H}$	3	1	2

Oxygen has three isotopes, ${}^{16}\text{O}$, ${}^{17}\text{O}$ and ${}^{18}\text{O}$.

	A	**Z**	**No. of neutrons**
${}_8^{16}\text{O}$	16	8	8
${}_8^{17}\text{O}$	17	8	9
${}_8^{18}\text{O}$	18	8	10

(ii) In a neutral atom, the number of protons and the number of electrons are always the same, *i.e.*, the electronic configuration of all the isotopes of an element is the same. Thus, all the isotopes of an element show the same chemical properties. However, the rates of reactions may be different for different isotopes of an element.

(iii) All the isotopes of an element occupy the same position in the periodic table.

(iv) The isotopes of an element differ slightly in physical properties. The compounds formed by these isotopes will also have different physical properties.

Determination of Isotopic Mass

Chlorine has two isotopes ${}_{17}\text{Cl}^{35}$ and ${}_{17}\text{Cl}^{37}$; these are found in nature in 3 : 1 ratio or 75% : 25% respectively. Isotopic mass may be calculated as:

Isotopic mass of chlorine

$$= \frac{\%\text{ of Cl}^{35}}{100} \times \text{mass of Cl}^{35} + \frac{\%\text{ of Cl}^{37}}{100} \times \text{mass of Cl}^{37}$$

$$= \frac{75}{100} \times 35 + \frac{25}{100} \times 37 = 35.5$$

OR

Isotopic mass of chlorine

$$= \frac{\text{Ratio of Cl}^{35} \times \text{mass of Cl}^{35} + \text{Ratio of Cl}^{37} \times \text{mass of Cl}^{37}}{\text{Sum of ratio}}$$

$$= \frac{3 \times 35 + 1 \times 37}{4} = 35.5$$

2.23 THEORIES OF NUCLEAR STABILITY

Since, a nucleus contains positively charged protons, there must exist a strong repulsive force between them. It has been calculated that there exists an electrostatic repulsion of approximately six tons between two protons situated at a nuclear distance but at the same time the forces which bind the nucleus are very high. It has been found that nuclear forces attracting the same two particles (*i.e.*, protons) are at least forty times greater than the repulsive forces. Thus, two major forces exist in the nucleus. These are electrostatic and nuclear. The nuclear forces are stronger and the range of these forces is extremely small. The forces which operate between nucleons are referred to as exchange forces. In order to account for the stability of the nucleus, a theory known as **meson theory** was put forward by **Yukawa,** in 1935. Yukawa pointed out that neutrons and protons are held together by very rapid exchange of nuclear particles called **pi mesons.** These mesons may be electrically neutral, positive or negative (designated as π^0, π^+ and π^-) and possess a mass 275 times the mass of an electron. Nuclear forces arise from a constant exchange of mesons between nucleons with very high velocity (practically the velocity of light).

Let a neutron be converted into a proton by the emission of a negative meson. The emitted meson is accepted by another proton and converted into a neutron.

$$n_A \rightarrow p_A^+ + \pi^-$$

$$\pi^- + p_B^+ \rightarrow n_B$$

Similarly, a proton after emitting a positive meson is converted into a neutron and *vice-versa.*

$$p_A^+ \rightarrow n_A + \pi^+$$

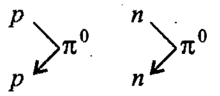
$$\pi^+ + n_B \rightarrow p_B^+$$

or simply

$$p \rightleftharpoons \pi^+ + n$$

$$n \rightleftharpoons \pi^- + p$$

There may be two more types of exchange, *i.e.*, between neutron-neutron and proton-proton, involving neutral pi mesons.



or simply $p \underset{\pi^0}{\overset{\pi^0}{\rightleftharpoons}} p$ and $n \underset{\pi^0}{\overset{\pi^0}{\rightleftharpoons}} n$

Mass Defect—Binding Energy

It is observed that the atomic mass of all nuclei (except hydrogen) is different from the sum of the masses of protons and neutrons. For example, the helium nucleus consists of 2 protons and 2 neutrons. The combined mass of 2 protons and 2 neutrons should be

$$= 2 \times 1.00758 + 2 \times 1.00893$$
$$= 4.03302 \text{ amu}$$

The actual observed mass of helium nuclei is 4.0028 amu. A difference of 0.0302 amu is observed between these two values. This difference is termed as **mass defect.**

Mass defect = Total mass of nucleons − Observed atomic mass

This decrease in mass (*i.e.*, mass defect) is converted into energy according to Einstein equation $E = mc^2$. The energy released when a nucleus is formed from protons and neutrons is called the **binding energy.** This is the force which holds all the nucleons together in the nucleus. Binding energy can be defined in other ways also, *i.e.*, the energy required to break the nucleus into constituent protons and neutrons. Binding energy is measured in MeV (Million Electron-Volts), *i.e.*, 1 amu = 931 MeV.

Binding energy = Mass defect × 931 MeV

Binding energy can also be calculated in erg. This is

$$= \text{Mass defect (amu)} \times 1.66 \times 10^{-24} \times (3 \times 10^{10})^2 \text{ erg}$$

$$(1\,\text{MeV} = 1.60 \times 10^{6}\text{ erg})$$

The binding energy increases with the increase in atomic number of the element. This indicates that heavier nuclei should be more stable than lighter nuclei. But, it is not so because heavier nuclei above atomic number 82 are unstable. It is thus clear that total binding energy of a nucleus does not explain the stability of the nucleus.

The total binding energy of a nucleus when divided by the number of nucleons gives the average or mean binding energy per nucleon. The binding energy per nucleon is actually the measure of the stability of the nucleus. The greater the binding energy per nucleon, more stable is the nucleus.

$$\text{Binding energy per nucleon} = \frac{\text{Total binding energy}}{\text{Total number of nucleons}}$$

When binding energy per nucleon of a number of nuclei is plotted against the corresponding mass number, a graph is obtained (Fig. 2.19) whose characteristics are as follows:

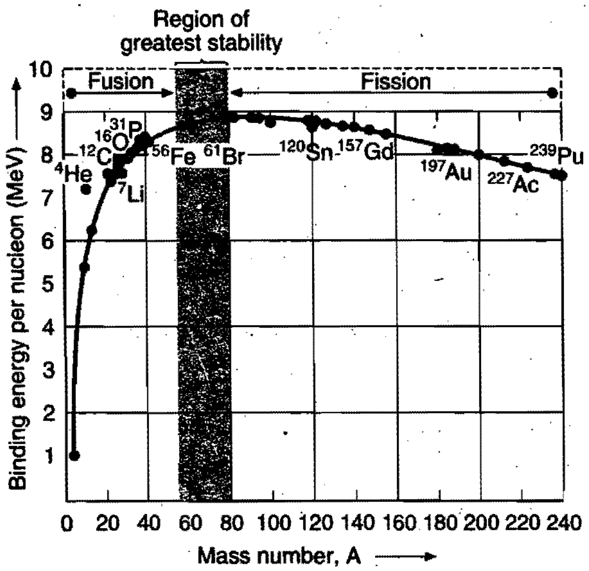


Fig. 2.19

(i) Binding energy per nucleon increases from 1.1 to 8.0 MeV from mass number 2 to 20.

(ii) Binding energy per nucleon increases from 8 to 8.6 MeV from mass number 20 to 40.

(iii) Binding energy per nucleon remains 8.6 – 8.7 MeV from mass number 40 to 90. Iron (56) has the maximum value of 8.7 MeV per nucleon.

(iv) The value of binding energy per nucleon decreases from 8.6 to 7.5 MeV from mass number 90 to 240.

(v) Points for helium, carbon, oxygen lie quite high in the graph showing that these nuclei are highly stable.

The binding energy per nucleon can be increased in two ways:

(i) Either by breaking heavy nucleus to those of intermediate mass numbers (process of fission) or

(ii) By fusing lighter nuclei to form heavier nuclei (process of fusion).

2.24 THE WHOLE NUMBER RULE AND PACKING FRACTION

Aston believed that mass number values (sum of protons and neutrons) of isotopes should be whole numbers on the scale of oxygen ($^{16}O = 16$) but actually it was observed that these were not integers. The difference in the atomic mass of an isotope and mass number was expressed by **Aston** (1927) as **packing fraction** by the following expression:

$$\text{Packing fraction} = \frac{\text{Isotopic atomic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Thus, the packing fraction of $^1H = \frac{1.0078 - 1}{1} \times 10^4 = 78$ and the packing fraction of $^{35}Cl = \frac{34.980 - 35.0}{35.0} \times 10^4 = -5.7$. The packing fraction of oxygen is zero.

It is clear that the value of packing fraction varies from one atom to other. This is sometime positive or zero but more often negative.

A negative packing fraction means that atomic mass is less than nearest whole number and this suggests that some mass has been converted into energy when the particular isotope has been constituted. This energy is responsible for nuclear stability. All those having negative values of packing fraction are stable nuclei.

A positive packing fraction generally indicates instability of the nucleus. However, this statement is not correct for lighter nuclei.

In general, lower the value of packing fraction, the greater is the stability of the nucleus. The lowest values of packing fractions are observed for transition elements or iron family indicating thereby maximum stability of their nuclei.

2.25 THE MAGIC NUMBERS

It has been observed that atoms with an even number of nucleons in their nuclei are more plentiful than those with odd number. This indicates that a nucleus made up of even number of nucleons is more stable than a nuclei which consists of odd number of nucleons. It has also been observed that a stable nuclei results when either the number of neutrons or that of protons is equal to one of the numbers 2, 8, 20, 50, 82, 126. These numbers are called **magic numbers.** It is thought that the magic numbers form closed nuclear shells in the same way as the atomic numbers of inert gases form stable electronic configuration. In general, elements that have nuclei with magic number of protons as well as magic number of neutrons such as ^4_2He, $^{16}_8O$, $^{40}_{20}Ca$, $^{208}_{82}Pb$ are highly stable and found in abundance in nature.

A survey of stable nuclei found in nature shows the following trend:

Protons	Even	Even	Odd	Odd
Neutrons	Even	Odd	Even	Odd
No. of stable nuclei	157	52	50	5

Only five stable odd-odd nuclides are known; these nuclides are ^2_1H, ^6_3Li, $^{10}_5B$, $^{14}_7N$ and $^{180}_{73}Ta$.

SOME SOLVED EXAMPLES

Example 46. *The minimum energy required to overcome the attractive forces between an electron and the surface of Ag metal is 5.52×10^{-19} J. What will be the maximum kinetic energy of electrons ejected out from Ag which is being exposed to UV light of $\lambda = 360$ Å?*

Solution: Energy of the photon absorbed

$$= \frac{h \cdot c}{\lambda} = \frac{6.625 \times 10^{-27} \times 3 \times 10^{10}}{360 \times 10^{-8}}$$

$$= 5.52 \times 10^{-11} \text{ erg}$$

$$= 5.52 \times 10^{-18} \text{ J}$$

E(photon) = work function + KE

$$\text{KE} = 5.52 \times 10^{-18} - 7.52 \times 10^{-19}$$

$$= 47.68 \times 10^{-19} \text{ J}$$

Example 47. *Let a light of wavelength λ and intensity 'I' strikes a metal surface to emit x electrons per second. Average energy of each electron is 'y' unit. What will happen to 'x' and 'y' when (a) λ is halved (b) intensity I is doubled?*

Solution: (a) Rate of emission of electron is independent of wavelength. Hence, 'x' will be unaffected.

Kinetic energy of photoelectron = Absorbed energy − Threshold energy

$$y = \frac{hc}{\lambda} - w_0$$

when, λ is halved, average energy will increase but it will not become double.

(b) Rate of emission of electron per second 'x' will become double when intensity I is doubled. Average energy of ejected electron, *i.e.*, 'y' will be unaffected by increase in the intensity of light.

Example 48. *How many orbits, orbitals and electrons are there in an atom having atomic mass 24 and atomic number 12?*

Solution:

Atomic number = No. of protons = No. of electrons = 12

Electronic configuration = 2, 8, 2

No. of orbits = (K, L and M)

No. of orbitals on which electrons are present

= (one 1s + one 2s + three 2p + one 3s)

Example 49. *A neutral atom has 2K electrons, 8L electrons and 6 M electrons. Predict from this:*

(a) its atomic number, (b) total number of s-electrons, (c) total number of p-electrons, (d) total number of d-electrons.

Solution: (a) Total number of electrons

$$= (2 + 8 + 6) = 16$$

So, Atomic number = 16

Electronic configuration = $1s^2, 2s^2 2p^6, 3s^2 3p^4$

(b) Total number of s-electrons = $(1s^2 + 2s^2 + 3s^2) = 6$

(c) Total number of p-electrons = $(2p^6 + 3p^4) = 10$

(d) Total number of d-electrons = 0

Example 50. *Write down the values of quantum numbers of all the electrons present in the outermost orbit of argon (At. No. 18).*

Solution: The electronic configuration of argon is

$$1s^2, 2s^2 2p^6, 3s^2 3p_x^2 3p_y^2 3p_z^2$$

Values of quantum numbers are:

	n	l	m	s
$3s^2$	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$
$3p_x^2$	3	1	±1	$+\frac{1}{2}, -\frac{1}{2}$
$3p_y^2$	3	1	±1	$+\frac{1}{2}, -\frac{1}{2}$
$3p_z^2$	3	1	0	$+\frac{1}{2}, -\frac{1}{2}$

Example 51. (*a*) *An electron is in 5f-orbital. What possible values of quantum numbers n, l, m and s can it have?*

(*b*) *What designation is given to an orbital having*

(*i*) $n = 2, l = 1$ *and* (*ii*) $n = 3, l = 0$?

Solution: (a) For an electron in 5f-orbital, quantum numbers are:

$$n = 5; \; l = 3; \qquad m = -3, -2, -1, 0, +1, +2, +3$$

and $s = $ either $+\frac{1}{2}$ or $-\frac{1}{2}$

(b) (i) 2p, (ii) 3s

Example 52. *Atomic number of sodium is 11. Write down the four quantum numbers of the electron having highest energy.*

Solution: The electronic configuration of sodium is:

$$1s^2, 2s^2 2p^6, 3s^1$$

3s-electron has the highest energy. Its quantum numbers are:

$$n = 3, l = 0, m = 0, s = +\frac{1}{2} \text{ or } -\frac{1}{2}$$

Example 53. *An element has 8 electrons in 4d-subshell. Show the distribution of 8 electrons in the d-orbitals of the element within small rectangles.*

Solution: 4d-subshell has five d-orbitals. These are first occupied singly and then pairing occurs. The distribution can be shown in the following manner:

4d

↑↓	↑↓	↑↓	↑	↑

Example 54. *How many elements would be in the third period of the periodic table if the spin quantum number m_s could have the value $-\frac{1}{2}$, 0 and $+\frac{1}{2}$?*

Solution:

$$n = 3, l = 0, m = 0 \qquad m_s = -\tfrac{1}{2}, 0, +\tfrac{1}{2}$$

$$l = 1; m = -1, 0, +1 \begin{array}{l} \nearrow m_s = -\tfrac{1}{2}, 0, +\tfrac{1}{2} \\ \rightarrow m_s = -\tfrac{1}{2}, 0, +\tfrac{1}{2} \\ \searrow m_s = -\tfrac{1}{2}, 0, +\tfrac{1}{2} \end{array}$$

$$l = 2; \quad m = -2, -1, 0, +1, +2 \left\{ \begin{array}{c} m_s = -\tfrac{1}{2}, 0, +\tfrac{1}{2} \\ \text{for each value of} \\ \text{magnetic} \\ \text{quantum no.} \end{array} \right\}$$

Number of elements = $3s$ ($3e$)

$3p$ ($9e$)

$3d$ ($15e$)

$\therefore$ 27 elements will be there in third period of periodic table.

Example 55. *The binding energy of ^4_2He is 28.57 MeV. What shall be the binding energy per nucleon of this element?*

Solution: The nucleus of $^4_2$He consists of 4 nucleons.

$$\text{So, Binding energy per nucleon} = \frac{\text{Total binding energy}}{\text{No. of nucleons}}$$

$$= \frac{28.57}{4} = 7.14 \text{ MeV}$$

Example 56. *Calculate the binding energy of the oxygen isotope $^{16}_8O$. The mass of the isotope is 16.0 amu. (Given $e = 0.0005486$ amu, $p = 1.00757$ amu and $n = 1.00893$ amu.)*

Solution: The isotope $^{16}_8$O contains 8 protons, 8 neutrons and 8 electrons.

Actual mass of the nucleus of $^{16}_8$O

$$= 16 - \text{mass of 8 electrons}$$

$$= 16 - 8 \times 0.0005486 = 15.9956 \text{ amu}$$

Mass of the nucleus of $^{16}_8$O

$$= \text{mass of 8 protons} + \text{mass of 8 neutrons}$$

$$= 8 \times 1.00757 + 8 \times 1.00893 = 16.132 \text{ amu}$$

$$\text{Mass defect} = (16.132 - 15.9956) = 0.1364 \text{ amu}$$

$$\text{Binding energy} = 0.1364 \times 931 = 127 \text{ MeV}$$

Example 57. *There are four atoms which have mass numbers 9, 10, 11 and 12 respectively. Their binding energies are 54, 70, 66 and 78 MeV respectively. Which one of the atoms is most stable?*

Solution: Stability depends on the value of binding energy per nucleon.

	A	*B*	*C*	*D*
Binding energy (MeV)	54	70	66	78
No. of nucleons	9	10	11	12
Binding energy per nucleon (MeV)	6	7	6	6.5

Thus, *B* is most stable.

MISCELLANEOUS NUMERICAL EXAMPLES

These examples will give the sharp edge to the aspirants for IIT and various other entrance examinations.

Example 1. *The Schrödinger wave equation for hydrogen atom is*

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[2 - \frac{r_0}{a_0}\right]e^{-r/a_0}$$

where a_0 is Bohr radius. If the radial node in 2s be at r_0, then find r in terms of a_0. **(IIT 2004)**

Solution: Given,

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[2 - \frac{r_0}{a_0}\right]e^{-r/a_0}$$

$$\psi^2_{2s} = 0 \text{ at node}$$

$$\therefore \quad 2 - \frac{r_0}{a_0} = 0$$

$$r_0 = 2a_0$$

Example 2. *Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr radius) whose charge is neutralized by the addition of an electron to the cavity in vacuum infinitely slowly. Estimate the average total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also, if the magnitude of average KE is half the magnitude of average potential energy, find the average potential energy.* **(IIT 1996)**

Solution:

Coulombic force of attraction = Centrifugal force

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze \times e}{a_0^2} = \frac{mv^2}{a_0}$$

where, v = velocity of electron

a_0 = distance between electron and nucleus

$$\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a_0} = mv^2$$

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{2a_0}$$

$$\text{PE} = -2 \times \text{KE}$$

$$= -2 \times \frac{1}{4\pi\varepsilon_0} \times \frac{Ze^2}{2a_0} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{a_0}$$

Example 3. *Hydrogen atoms are excited from ground state. Its spectrum contains wavelength 486 nm. Find, what transition does the line corresponds to. Also find from this information what other wavelengths will be present in the spectrum?*

Solution: Wavelength 486 nm, *i.e.*, 4860 Å indicates that the spectrum is in visible region, *i.e.*, Balmer series.

$$\frac{1}{\lambda} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{4860\times10^{-8}}=109677.76\times1^{2}\left[\frac{1}{2^{2}}-\frac{1}{n_{2}^{2}}\right]$$

On solving, we get

$$n_2^2=16$$

$$n_2=4$$

Thus, transition is from, $4\rightarrow2$

Other transitions in the spectrum are

$$4\rightarrow3\rightarrow2$$

$$\frac{1}{\lambda}=109677.76\times1^{2}\times\left[\frac{1}{3^{2}}-\frac{1}{4^{2}}\right]$$

$$\lambda=1875\times10^{-7}\text{ cm}$$

Example 4. *If uncertainties in the measurement of position and momentum of an electron are equal, calculate uncertainty in the measurement of velocity.*

Solution: According to Heisenberg's uncertainty principle,

$$\Delta x.\Delta p\geq\frac{h}{4\pi}$$

$$\text{Given, }\Delta x=\Delta p=\sqrt{\frac{h}{4\pi}}=0.726\times10^{-17}$$

$$\Delta p=m\,\Delta V$$

or
$$\Delta V=\frac{\Delta p}{m}=\frac{0.726\times10^{-17}}{9.1\times10^{-31}}=7.98\times10^{12}\text{ ms}^{-1}$$

Example 5. *How much energy will be released when a sodium ion and a chloride ion, originally at infinite distance are brought together to a distance of* $2.76\,\text{Å}$ *(the shortest distance of approach in a sodium chloride crystal)? Assume that ions act as point charges, each with a magnitude of* 1.6×10^{-19} *C. Permittivity constant of the medium is* $9\times10^{9}\ Nm^{2}C^{-2}$.

Solution: Energy released

$$=-K\frac{q_1\,q_2}{r}=-\frac{9\times10^{9}\times(1.6\times10^{-19})^{2}}{2.76\times10^{-10}}=-8.35\times10^{-19}\text{ J}$$

Example 6. *The angular momentum of an electron in a Bohr orbit of H-atom is* 4.2178×10^{-34} *kg* m^2*/sec. Calculate the spectral line emitted when an electron falls from this level to the next lower level.*

Solution: We know, $mvr=n\dfrac{h}{2\pi}$

$$4.2178\times10^{-34}=n\times\frac{6.626\times10^{-34}}{2\times3.14}$$

$$\therefore\quad n=4$$

$$\frac{1}{\lambda}=R_{\text{H}}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$=109678\left[\frac{1}{3^2}-\frac{1}{4^2}\right]$$

$$\lambda=1.8\times10^{-4}\text{ cm}$$

Example 7. *A negatively charged particle called Negatron was discovered. In the Millikan's oil-drop experiment, the charges of the oil-drops in five experiments are reported as* 3.2×10^{-19} *coulomb;* 4.8×10^{-19} *coulomb;* 6.4×10^{-19} *coulomb;* 8×10^{-19} *coulomb and* 9.6×10^{-19} *coulomb. Calculate the charge on the negatron.*

Solution: In Millikan's oil-drop experiment; the charges on the oil-drops are integral multiples of the charge of the particle. Dividing the charges of droplets by the lowest charge:

(i) $\dfrac{3.2\times10^{-19}}{3.2\times10^{-19}}=1$ (ii) $\dfrac{4.8\times10^{-19}}{3.2\times10^{-19}}=1.5$

(iii) $\dfrac{6.4\times10^{-19}}{3.2\times10^{-19}}=2$ (iv) $\dfrac{8\times10^{-19}}{3.2\times10^{-19}}=2.5$

(v) $\dfrac{9.6\times10^{-19}}{3.2\times10^{-19}}=3$

All the values are not integral; they can be converted to integers on multiplying by 2.

∴ Charge of the negatron will be

$$\frac{3.2\times10^{-19}}{2}=1.6\times10^{-19}\text{ C}$$

Example 8. *When a certain metal was irradiated with light of frequency* 3.2×10^{16} *Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency* 2.0×10^{16} *Hz. Calculate* ν_0 *for the metal.*

Solution: Applying photoelectric equation,

$$\text{KE}=h\nu-h\nu_0$$

or
$$(\nu-\nu_0)=\frac{\text{KE}}{h}$$

Given,
$$\text{KE}_2=2\text{KE}_1$$

$$\nu_2-\nu_0=\frac{\text{KE}_2}{h}\qquad\ldots\text{(i)}$$

and
$$\nu_1-\nu_0=\frac{\text{KE}_1}{h}\qquad\ldots\text{(ii)}$$

Dividing equation (i) by equation (ii),

$$\frac{\nu_2-\nu_0}{\nu_1-\nu_0}=\frac{\text{KE}_2}{\text{KE}_1}=\frac{2\text{KE}_1}{\text{KE}_1}=2$$

or
$$\nu_2-\nu_0=2\nu_1-2\nu_0$$

or
$$\nu_0=2\nu_1-\nu_2=2\,(2.0\times10^{16})-(3.2\times10^{16})$$

$$=8.0\times10^{15}\text{ Hz}$$

Example 9. *An electron moves in an electric field with a kinetic energy of 2.5 eV. What is the associated de Broglie wavelength?*

Solution: Kinetic energy

$$= \frac{1}{2} mv^2 \quad \left(v = \frac{h}{m\lambda}\right)$$

$$= \frac{1}{2} m \left(\frac{h}{m\lambda}\right)^2$$

$$= \frac{1}{2} \frac{h^2}{m\lambda^2}$$

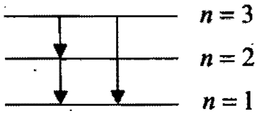
or
$$\lambda^2 = \frac{1}{2} \frac{h^2}{m \times \text{KE}}$$

$$\lambda = \frac{h}{\sqrt{2m \times \text{KE}}} \quad \left(\begin{array}{l} m = 9.108 \times 10^{-28} \text{ g} \\ h = 6.626 \times 10^{-27} \text{ erg -sec} \\ 1\text{eV} = 1.602 \times 10^{-12} \text{ erg} \end{array}\right)$$

$$= \frac{6.626 \times 10^{-27}}{\sqrt{2 \times 9.108 \times 10^{-28} \times 2.5 \times 1.602 \times 10^{-12}}}$$

$$= 7.7 \times 10^{-8} \text{ cm}$$

Example 10. *Consider the following two electronic transition possibilities in a hydrogen atom as pictured below:*



(*a*) *The electron drops from third Bohr orbit to second Bohr orbit followed with the next transition from second to first Bohr orbit.*

(*b*) *The electron drops from third Bohr orbit to first Bohr orbit directly. Show that the sum of energies for the transitions* $n = 3$ *to* $n = 2$ *and* $n = 2$ *to* $n = 1$ *is equal to the energy of transition for* $n = 3$ *to* $n = 1$.

Solution: Applying, $\Delta E = R_{\text{H}} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

For $n = 3$ to $n = 2$;

$$\Delta E_{3 \to 2} = R_{\text{H}} \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = R_{\text{H}} \times \frac{5}{36} \qquad \text{. . . (i)}$$

For $n = 2$ to $n = 1$;

$$\Delta E_{2 \to 1} = R_{\text{H}} \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = R_{\text{H}} \times \frac{3}{4} \qquad \text{. . . (ii)}$$

For $n = 3$ to $n = 1$;

$$\Delta E_{3 \to 1} = R_{\text{H}} \left[\frac{1}{1^2} - \frac{1}{3^2}\right] = R_{\text{H}} \times \frac{8}{9} \qquad \text{. . . (iii)}$$

Adding equations (i) and (ii),

$$R_{\text{H}} \left(\frac{5}{36} + \frac{3}{4}\right) = R_{\text{H}} \left(\frac{5 + 27}{36}\right) = R_{\text{H}} \times \frac{8}{9}$$

Thus, $\Delta E_{3 \to 1} = \Delta E_{3 \to 2} + \Delta E_{2 \to 1}$

Example 11. *If an electron is moving with velocity* $500 \, ms^{-1}$, *which is accurate up to 0.005% then calculate uncertainty in its position.* [$h = 6.63 \times 10^{-34}$ *Js, mass of electron* $= 9.1 \times 10^{-31}$ *kg*] **[AIPMT (Mains) 2008]**

Solution : Uncertainty in velocity

$$\Delta v = \frac{600 \times 0.005}{100} = 3 \times 10^{-2} \text{ms}^{-1}$$

According to Heisenberg's uncertainty principle

$$\Delta x \, \Delta v \geq \frac{h}{4\pi m}$$

$$\Delta x \geq \frac{h}{4\pi m \Delta v}$$

$$\geq \frac{6.63 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 3 \times 10^{-2}}$$

$$= 1.9 \times 10^{-3} \text{m}$$

Example 12. *Applying Bohr's model when H atom comes from* $n = 4$ *to* $n = 2$, *calculate its wavelength. In this process, write whether energy is released or absorbed? Also write the range of radiation.* $R_H = 2.18 \times 10^{-18}$ *J*, $h = 6.63 \times 10^{-34}$ *Js*.

(AIPMT 2008)

Solution : Energy is released in this process; and the radiation will belong to visible region (Balmer series)

$$E = \frac{hc}{\lambda} = R_{\text{H}} Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\frac{1}{\lambda} = \frac{R_{\text{H}} Z^2}{hc} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= \frac{2.18 \times 10^{-18} \times 1^2}{6.63 \times 10^{-34} \times 3 \times 10^8} \left[\frac{1}{4} - \frac{1}{16}\right]$$

$$= \frac{2.18 \times 10^{-18} \times 1^2}{6.63 \times 10^{-34} \times 3 \times 10^8} \left[\frac{3}{16}\right]$$

$$\lambda = \frac{6.63 \times 10^{-34} \times 3 \times 10^8 \times 16}{3 \times 2.18 \times 10^{-18}} = 4866 \times 10^{-10} \text{m}$$

$$= 4866 \text{ Å}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Atom is the smallest indivisible particle of matter (proposed by John Dalton in 1808).

2. All atoms except hydrogen atom are composed of three fundamental particles, namely, electron, proton and neutron. Hydrogen atom has one electron and one proton but no neutron.

(a) Electron: The nature and existence of electron was established by experiments on conduction of electricity through gases, *i.e.*, discovery of cathode rays. In 1897, **J.J. Thomson** determined e/m value (-1.7588×10^8 coulomb/g) and proved that whatever gas be taken in the discharge tube and whatever be the material of the electrodes, the value of e/m is always the same. Electrons are, thus, common universal constituents of all atoms.

Electron is a subatomic particle which carries charge -1.60×10^{-19} coulomb, *i.e.*, one unit negative charge and has mass 9.1×10^{-28} g (or 9.1×10^{-31} kg), *i.e.*, $\frac{1}{1837}$th mass of hydrogen atom (0.000549 amu). The name electron was given by **Stoney.**

(b) Proton: The nature and existence of proton was established by the discovery of positive rays (**Goldstein** 1886). Proton is a subatomic particle which carries $+1.6 \times 10^{-19}$ coulomb or one unit positive charge and has mass 1.672×10^{-24} g (or 1.672×10^{-27} kg), *i.e.*, 1.0072 amu. The e/m was determined by **Thomson** in 1906 and the value is $+9.579 \times 10^4$ coulomb/g. It was named as proton by **Rutherford.**

(c) Neutron: It is a subatomic particle which carries no charge. Its mass is 1.675×10^{-24} g (1.675×10^{-27} kg) or 1.0086 amu. It is slightly heavier than proton. It was discovered by **Chadwick** in 1932 by bombarding beryllium with α-particles.

$$^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$$

The e/m value of neutron is zero.

3. According to the Rutherford's model of atom, (i) it consists of **nucleus** of very small size and high density (ii) electrons revolve round the nucleus in a circular path.

$$\text{Radius of nucleus} = 10^{-15}\ \text{m}$$

$$\text{Density of nucleus} = 10^{8}\ \text{tonnes/cc}$$

4. Atomic number (Z) = Number of protons in the nucleus

5. Mass number (A) = Number of protons + Number of neutrons

6. **Isotopes:** These are atoms of same element having same atomic number but different mass numbers, *e.g.*,

$$({}^{1}_{1}\text{H}, {}^{2}_{1}\text{H}, {}^{3}_{1}\text{H}) : ({}^{35}_{17}\text{Cl}, {}^{37}_{17}\text{Cl})$$

7. **Isobars:** These are atoms of different elements having same mass number but different atomic numbers, *e.g.*,

$${}^{40}_{18}\text{Ar}, {}^{40}_{19}\text{K}, {}^{40}_{20}\text{Ca}$$

8. **Isotones:** These are atoms of different elements having same number of neutrons in the nucleus, *e.g.*,

$${}^{14}_{6}\text{C} : {}^{15}_{7}\text{N}, {}^{16}_{8}\text{O}$$

9. Electromagnetic radiations are energy waves containing both electric and magnetic vector perpendicular to each other.

(i) These are transverse waves.

(ii) They do not need any medium for their propagation. They travel with the velocity of light.

(iii) $\nu = \frac{c}{\lambda}$, ν = frequency, c = velocity of light,

λ = wavelength

$\bar{\nu} = \frac{1}{\lambda}$ = wave number, $T = \frac{1}{\nu}$ = time period.

(iv) According to Planck's quantum theory, the energy is emitted or absorbed in the form of energy packets called **quanta.** Quantum of visible light is called **photon.**

$$\text{Energy of one quantum} = h\nu = h\frac{c}{\lambda}$$

$$h = \text{Planck's constant} = 6.626 \times 10^{-34}\ \text{J sec}$$

10. **Hydrogen spectrum:** Hydrogen spectrum is a line spectrum. The lines lie in visible, ultraviolet and infrared regions. All the lines can be classified into five series. Ritz presented a mathematical formula to find the wavelengths of various lines,

$$\frac{1}{\lambda} = \bar{\nu} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

where, R is Rydberg constant ($R = 109678\ \text{cm}^{-1}$).

		n_1	n_2
Lyman series	(UV region)	1	2, 3, 4, 5, ...
Balmer series	(Visible region)	2	3, 4, 5, 6, ...
Paschen series	(IR region)	3	4, 5, 6, 7, ...
Brackett series		4	5, 6, 7, 8, ...
Pfund series		5	6, 7, 8, 9, ...

Balmer series consists of four prominent lines H_α, H_β, H_γ and H_δ having wavelength 6563 Å, 4861 Å, 4340 Å and 4102 Å respectively.

Balmer equation is,

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$

where, $n = 3, 4, 5, 6, \ldots$

The Rydberg formula is used to calculate the wavelength of any line of the spectrum

$$\frac{1}{\lambda}=RZ^2\left[\frac{1}{n_1^2}-\frac{1}{(n_1+x)^2}\right]$$

where, x = number of lines in the spectrum; $x=\infty$ for series limit or last line. Let, transition of electrons takes place from n_2 to n_1 shell; then the number of lines can be calculated as:

$$\text{Number of lines}=\frac{(n_2-n_1)(n_2-n_1+1)}{2}$$

11. Bohr's atomic model: It is based on Planck's quantum theory. Its main postulates are summarised as:

(i) Electrons revolve round the nucleus in circular path of fixed energy called **stationary states.**

(ii) Angular momentum of electrons are quantised, *i.e.*,

$$mvr=n\left(\frac{h}{2\pi}\right)$$

(iii) The energy as well as angular momentum both are quantised for electrons. It means they can have only certain values of energy and angular momenta.

12. Important formulations obtained from Bohr's atomic model which are valid for single electron species like H, He^+, Li^{2+}, Be^{3+}, etc.:

(i) $E_1<E_2<E_3<E_4$

(ii) $(E_2-E_1)>(E_3-E_2)>(E_4-E_3)\ldots$

where, $E_1, E_2, E_3, \ldots$ are energies of corresponding shells.

(iii) $r_n=\dfrac{n^2h^2}{4\pi^2Ke^2mZ}$

$$K=\frac{1}{4\pi\varepsilon_0}=9\times10^9\ \text{Nm}^2/\text{C}^2$$

$r=\dfrac{n^2}{Z}\times0.529$ Å (where, r is the radius of Bohr orbit of electrons.)

(iv) Energy of electrons in a particular shell can be calculated as:

$$E=-\frac{Z^2}{n^2}\frac{2\pi^2mK^2e^4}{h^2}$$

$$E=-\frac{Z^2}{n^2}\times21.79\times10^{-19}\ \text{J/atom}$$

$$=-\frac{Z^2}{n^2}\times13.6\text{eV}$$

$$=-\frac{Z^2}{n^2}\times1312\ \text{kJ/mol}$$

$$E_n=\frac{Z^2R_E}{n^2}$$

$R_E=-13.6$ eV (Rydberg energy)

(v) $E_n=E_1/n^2$; $E_n=E_1\times\dfrac{Z^2}{n^2}$ for hydrogen-like species.

(vi) Velocity of electrons in a particular shell or orbit can be calculated as:

$$v=\sqrt{\frac{Ke^2}{mr}}$$

where, $K=\dfrac{1}{4\pi\varepsilon_0}=9\times10^9\ \text{Nm}^2/\text{C}^2$

$$v=\frac{Z}{n}\times2.188\times10^8\ \text{cm/sec}$$

(vii) Potential energy of electrons in a particular shell:

$$\text{PE}=\frac{-KZe^2}{r}=-\frac{27.2}{n^2}\times Z^2\ \text{eV}$$

(viii) Kinetic energy of electrons in a particular shell:

$$\text{KE}=\frac{1}{2}\frac{KZe^2}{r}=+\frac{13.6}{n^2}Z^2\ \text{eV}$$

$$\text{Total Energy, TE}=-\frac{1}{2}\frac{KZe^2}{r}$$

$$\text{TE}=\frac{1}{2}\text{PE}$$

$$\text{TE}=-\text{KE}$$

(ix) Number of revolutions per second by an electron in a shell:

$$=\frac{\text{Velocity}}{\text{Circumference}}=\frac{v}{2\pi r}=-\frac{E_1}{h}\times\frac{2}{n^3}$$

(x) Frequency of electrons in nth orbit:

$$=\frac{v}{2\pi r}$$

$$=\frac{6.62\times10^{15}Z^2}{n^3}$$

(xi) Period of revolution of electrons in nth orbit (T_n),

$$T_n=\frac{2\pi r}{V_n}=\frac{1.5\times10^{-16}n^3}{Z^2}\ \text{sec}$$

$$T\propto\frac{n^3}{Z^2}$$

(xii) Ionization energy $=E_\infty-E_n$

$$=0-\left(-\frac{Z^2}{n^2}\times13.6\text{eV}\right)$$

$$=\frac{Z^2}{n^2}\times13.6\text{eV}$$

$$=\frac{Z^2}{n^2}\times21.79\times10^{-19}\ \text{J/atom}$$

(xiii) $\dfrac{I_1}{I_2}=\dfrac{Z_1^2}{Z_2^2}\times\dfrac{n_2^2}{n_1^2}$

I_1 and I_2 are ionization energies of two elements 1 and 2.

(xiv) ΔE (Energy of transition) $=R_E\left(\dfrac{1}{n_1^2}-\dfrac{1}{n_2^2}\right)$

$$R_E=-13.6\ \text{eV}$$

R_H = Rydberg constant $= \frac{R_E}{hc} = 109677\ \text{cm}^{-1}$

Defects of Bohr theory: (i) It fails to explain the spectra of multi-electron atoms. (ii) It fails to explain fine spectrum of hydrogen. (iii) It does not provide an explanation why angular momentum should always be an integral multiple of $h/2\pi$. (iv) It does not explain splitting of spectral lines under the influence of magnetic field (Zeeman effect) and electric field (Stark effect).

13. Sommerfeld's extension: Sommerfeld (1915) introduced the idea of elliptical orbits. Except first orbit which is only circular, the other orbits are elliptical. The second orbit has one elliptical and one circular suborbit. The third orbit has two elliptical and one circular suborbit.

14. Dual nature: Light has dual character, *i.e.*, it behaves sometimes like particles and sometimes like waves. de Broglie (1924) predicted that small particles such as electrons should show wave-like properties along with particle character. The wavelength (λ) associated with a particle of mass m and moving with velocity v is given by the relationship $\lambda = \frac{h}{mv}$; where, h is Planck's constant.

The wave nature was confirmed by Davisson and Germer's experiment.

Davisson and Germer gave some modified equations for calculation of de Broglie wavelength:

$\lambda = \frac{h}{\sqrt{2Em}}$; where, E = kinetic energy of the particle.

$\lambda = \frac{h}{\sqrt{2qVm}}$; where, q = charge of the particle accelerated by the potential of V volt.

15. Heisenberg uncertainty principle: It is impossible to measure simultaneously both the position and momentum of any microscopic particle with accuracy. Mathematically, $\Delta x\, \Delta p \approx \frac{h}{4\pi}$; where, Δx = uncertainty in position and Δp = uncertainty in momentum. It introduces the concept of probability of locating the electron in space around the nucleus.

16. de Broglie concept as well as uncertainty principle have no significance in everyday life because they are significant for only microscopic systems.

17. When radiations of a certain minimum frequency (ν_0), called threshold frequency, strike the surface of a metal, electrons called photoelectrons are ejected from the surface. The minimum energy required to eject the electrons from the metal surface is called threshold energy or work function.

Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

$$E = E_0 + \text{KE}$$

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

$$\frac{hc}{\lambda} = \frac{hc}{\lambda_0} + \frac{1}{2}mv^2$$

ν_0 and λ_0 are called threshold frequency and threshold wavelength respectively.

18. Quantum numbers: The set of four integers required to define an electron completely in an atom are called quantum numbers. The first three have been derived from Schrödinger's wave equation.

(i) Principal quantum number: It describes the name, size and energy of the shell to which the electron belongs.

$n = 1, 2, 3, 4, \ldots$ represent K, L, M, N, ... shells respectively.

Formulae for radius, energy and angular momentum of electrons are given earlier.

(ii) Azimuthal quantum number: It is denoted by 'l'. It describes the shape of electron cloud and number of subshells in a shell.

$$l = 0, 1, 2, 3, \ldots, (n-1)$$

$l = 0$ (s-subshell); $l = 1$ (p-subshell); $l = 2$ (d-subshell); $l = 3$ (f-subshell).

Orbital angular momentum of electron

$$= \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$$

when $l = 0$, electrons revolve in a circular orbit and when $l \neq 0$, the electrons revolve round the nucleus in an elliptical path.

(iii) Magnetic quantum number: It is denoted by 'm'. It describes the orientations of the subshells. It can have values from $-l$ to $+l$ including zero, *i.e.*, total $(2l+1)$ values. Each value corresponds to an orbital. s-subshell has one orbital, p-subshell has three orbitals (p_x, p_y and p_z), d-subshell has five orbitals (d_{xy}, d_{yz}, $d_{zx}, d_{x^2-y^2}$ and d_{z^2}) and f-subshell has seven orbitals. One orbital can accommodate either one or two electrons but not more than two. s-orbital is spherically symmetrical and non-directional. p-orbitals have dumb-bell shape and are directional in nature. Four d-orbitals have double dumb-bell shape but d_{z^2} has a baby soother shape. The total number of orbitals present in a main energy level is 'n^2'.

(iv) Spin quantum number (s): It describes the spin of the electron. It has values +1/2 and −1/2. (+) signifies clockwise spinning and (−) signifies anticlockwise spinning.

$$\text{Spin angular momentum} = \sqrt{s(s+1)}\,\frac{h}{2\pi}$$

$$= \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar \quad \left(\text{where, } s = \frac{1}{2}\right)$$

Total spin of an atom or an ion $= n \times \frac{1}{2}$; where, 'n' is the number of unpaired electrons.

Spin multiplicity of an atom $= (2\Sigma s + 1)$

Singlet state (Normal)

$\underline{\uparrow\downarrow}$

Spin multiplicity

$= 2\Sigma s + 1$

$= 2 \times 0 + 1 = 1$

Singlet excited

$\underline{\downarrow}$

$\underline{\uparrow}$

Spin multiplicity = 1

Triplet excited state

$\underline{\uparrow}$

$\underline{\uparrow}$

Spin multiplicity

$$= 2 \times \left(\frac{1}{2} + \frac{1}{2}\right) + 1 = 3$$

19. (i) Number of subshells in a shell = n

(ii) Number of maximum orbitals in a shell = n^2

(iii) Number of maximum orbitals in a subshell = $2l + 1$

(iv) Maximum number of electrons in a shell = $2n^2$

(v) Maximum number of electrons in a subshell $= 2(2l + 1)$

(vi) Z-component of the angular momentum depends upon magnetic quantum number and is given as:

$$L_Z = m\left(\frac{h}{2\pi}\right)$$

(vii) Number of radial/spherical nodes in any orbital $= (n - l - 1)$

1s orbital has no node; 2s orbital has one spherical node; $2p$ orbital has no spherical node; $3p$ orbital has one spherical node.

(viii) Schrödinger wave equation does not give spin quantum number.

(ix) A plane passing through the nucleus at which the probability of finding the electron is zero, is called nodal plane.

The number of nodal plane in an orbital = l

s-orbitals have no nodal plane; p-orbitals have one nodal plane, d-orbitals have two nodal planes and so on.

20. Pauli's exclusion principle: No two electrons in an atom can have the same set of all the four quantum numbers, *i.e.*, an orbital cannot have more than 2 electrons because three quantum numbers (principal, azimuthal and magnetic) at the most may be same but the fourth must be different, *i.e.*, spins must be in opposite directions. It is possible to calculate the maximum number of electrons which can be accommodated on a main energy shell or subenergy shell on the basis of this principle.

21. **Electronic configuration:** The arrangement of electrons in various shells, subshells and orbitals in an atom is termed electronic configuration. It is written in terms of nl^x where n indicates the order of shell, l indicates the subshell and x the number of electrons present in the subshell.

22. Aufbau principle: Aufbau is a German word meaning building up. The electrons are filled in various orbitals in an order of their increasing energies. An orbital of lowest energy is filled first. The sequence of orbitals in the order of their increasing energy is:

1s, 2s, $2p$, 3s, $3p$, 4s, $3d$, $4p$, 5s, $4d$, $5p$, 6s, $4f$, $5d$, $6p$, 7s, $5f$, $6d$, ...

The energy of the orbitals is governed by $(n + l)$ rule.

(i) Subshell with lower of $(n + l)$ has lower energy, hence filled first, *e.g.*,

$$3p(n + l = 4) \text{ will be filled before } 3d(n + l = 5).$$

(ii) When $(n + l)$ values are same, then the subshell with lower value of 'n' is filled first, *e.g.*,

$3p(n + l = 4)$ will be filled before $4s\,(n + l = 4)$ because $3p$ has lower value of n.

23. Hund's rule: No electron pairing takes place in the orbitals in a subenergy shell until each orbital is occupied by one electron with parallel spin. Exactly half-filled and fully-filled orbitals make the atoms more stable, *i.e.*, p^3, p^6, d^5, d^{10}, f^7 and f^{14} configurations are most stable.

All those atoms which consist of at least one orbital singly occupied behave as **paramagnetic** while all those atoms in which all the orbitals are doubly occupied are **diamagnetic** in nature.

Magnetic moment $= \sqrt{n(n + 2)}$ BM

n = number of unpaired electrons

24. Half-filled and fully-filled subshells have extra stability due to **greater exchange energy** and **spherical symmetry** around the nucleus.

25. It is only dz^2 orbitals which do not have four lobes like other d-orbitals.

26. The d-orbital whose lobes lie along the axes is $d_{x^2 - y^2}$.

27. Wave mechanical model of atom: It was Schrödinger who developed a new model known as wave mechanical model of atom by incorporating the conclusions of de Broglie and Heisenberg uncertainty principles. He derived an equation, known as Schrödinger equation.

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

The solution of the equation provides data which enables us to calculate the probability of finding an electron of specific energy. It is possible to determine the regions of space around the nucleus where there is maximum probability of locating an electron of specific energy. This region of space is termed orbital.

ψ is the amplitude of the wave at a point with coordinates x, y and z. 'E' is total energy called eigen value and V denotes the potential energy of the electron.

ψ^2 gives the probability of finding the electron at (x, y and z).

Operator form of the equation can be given as:

$$\hat{H}\psi = E\psi$$

$\hat{H} = \left[-\frac{h^2}{8\pi^2 m}\Delta^2 + \hat{V}\right]$ called Hamiltonian operator

$= \hat{T} + \hat{V}$

$\hat{T}$ = Kinetic energy operator

$\hat{V}$ = Potential energy operator

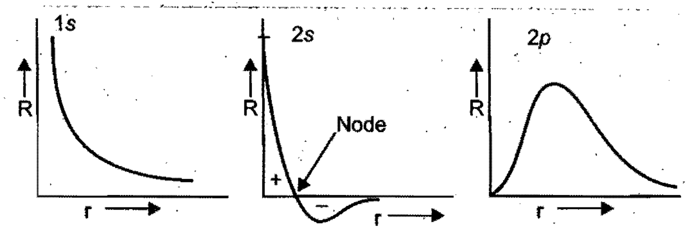
28. Complete wave function can be given as:

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{Radial part}}\ ;\underbrace{\Theta(\theta)\,\Phi(\phi)}_{\text{Angular part}}$$

Dependence of the wave function on quantum number can be given as:

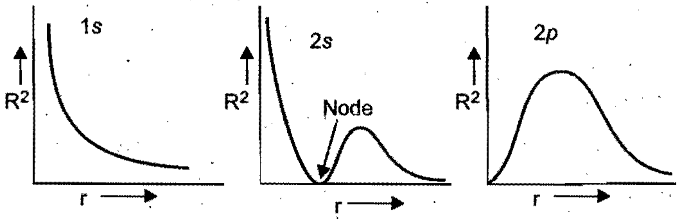
$$\psi_{nlm}(r,\theta,\phi) = R_{n,\,l}\,(r)\,\Theta_{lm}(\theta)\,\Phi_m(\phi)$$

29. Graph of radial wave function '*R*': At node, the value of '*R*' changes from positive to negative.

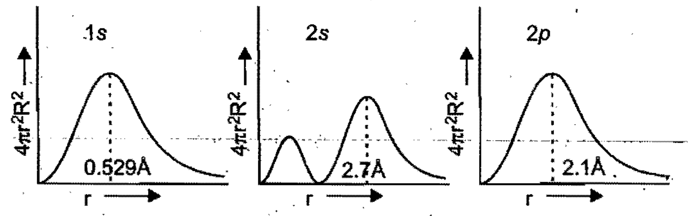


Number of radial nodes = $(n - l - 1)$.

30. Plot of radial probability density 'R^2':



31. Plot of radial probability function ($4\pi r^2 R^2$):



In the plot of radial probability against '*r*', number peaks, *i.e.*, region of maximum probability = *n* − *l*.

Questions

1. Match the following:

[A]

(i) Aufbau principle	(a) Line spectrum in visible region
(ii) de Broglie	(b) Orientation of an electron in an orbital
(iii) Angular momentum	(c) Photon
(iv) Hund's rule	(d) $\lambda = h/(mv)$
(v) Balmer series	(e) Electronic configuration
(vi) Planck's law	(f) mvr

[B]

(i) Thomson	(a) Exclusion principle
(ii) Pauli	(b) Radioactivity
(iii) Becquerel	(c) Atomic model
(iv) Soddy	(d) Cathode rays
(v) Bohr	(e) Neutron
(vi) Chadwick	(f) Isotopes

[C]

(i) Cathode rays	(a) Helium nuclei
(ii) Dumb-bell	(b) Uncertainty principle
(iii) Alpha particles	(c) Electromagnetic radiation
(iv) Moseley	(d) p-orbital
(v) Heisenberg	(e) Atomic number
(vi) X-rays	(f) Electrons

2. **Matrix Matching Problems (For IIT Aspirants):**

[A] Match the Column-I and Column-II:

Column-I	**Column-II**
(a) X-rays	(p) Davisson and Germer experiment
(b) Atomic number determination	(q) Crystal structure determination
(c) Dual nature of matter	(r) Moseley's law
(d) Dual nature of radiation	(s) Bragg's law

[B] Match the Column-I and Column-II:

Column-I	**Column-II**
(a) Lyman series	(p) Visible region
(b) Balmer series	(q) UV region
(c) Pfund series	(r) IR region
(d) Light emitted by sodium lamp	(s) Line emission spectrum

[C] Match the List-I with List-II in hydrogen atom spectrum:

List-I	**List-II**
(a) Lyman series	(p) Visible region
(b) Balmer series	(q) Infrared region
(c) Paschen series	(r) Absorption spectrum
(d) Brackett series	(s) Ultraviolet region

[D] Match the List-I with List-II:

List-I	**List-II**
(a) K-shell	(p) Electrons in elliptical orbit
(b) L-shell	(q) Electrons in circular orbit
(c) Hydrogen atom	(r) Shell of lowest energy
(d) Boron atom in ground state	(s) Bohr's atomic model

[E] Match the ions of List-I with the properties of List-II:

List-I	**List-II**
(a) Mn^{2+}	(p) Diamagnetic
(b) V^{2+}	(q) Paramagnetic
(c) Zn^{2+}	(r) Coloured compounds
(d) Ti^{4+}	(s) Magnetic moment = 2.82 BM

[F] Match the List-I with List-II:

List-I	**List-II**
(a) Mg^{2+}	(p) Zero spin multiplicity
(b) Fe^{2+}	(q) Spin multiplicity = 3
(c) Co^{3+}	(r) Total spin = 0
(d) Ca^{2+}	(s) Total spin = 2

[G] Match the properties of List-I with the formulae in List-II:

List-I	**List-II**
(a) Angular momentum of electron	(p) $\sqrt{l(l+1)}\dfrac{h}{2\pi}$
(b) Orbital angular momentum	(q) $I\omega$
(c) Wavelength of matter wave	(r) $nh/2\pi$
(d) Quantised value(s)	(s) h/p

[H] Match the orbitals of List-I with the nodal properties of List-II:

List-I	**List-II**
(a) $2s$	(p) Angular node = 1
(b) $1s$	(q) Radial node = 0
(c) $2p$	(r) Radial node = 1
(d) $3p$	(s) Angular node = 0

[I] Match the electronic transitions of List-I with spectral properties of List-II:

List-I	List-II
(a) $n = 6 \longrightarrow n = 3$	(p) 10 lines in the spectrum
(b) $n = 7 \longrightarrow n = 3$	(q) Spectral lines in visible region
(c) $n = 5 \longrightarrow n = 2$	(r) 6 lines in the spectrum
(d) $n = 6 \longrightarrow n = 2$	(s) Spectral lines in infrared region

[J] Match the List-I with List-II:

List-I	List-II
(a) Radius of electron orbit	(p) Principal quantum number
(b) Energy of electron	(q) Azimuthal quantum number
(c) Energy of subshell	(r) Magnetic quantum number
(d) Orientation of the atomic orbitals	(s) Spin quantum number

[K] Match the List-I with List-II:

List-I	List-II
(a) Electron cannot exist in the nucleus	(p) de Broglie wave
(b) Microscopic particles in motion are associated with	(q) Electromagnetic wave
(c) No medium is required for propagation	(r) Uncertainty principle
(d) Concept of orbit was replaced by orbital	(s) Transverse wave

[L] According to Bohr theory: **(IIT 2006)**

E_n = Total energy
K_n = Kinetic energy
V_n = Potential energy
r_n = Radius of nth orbit

Match the following:

Column-I	Column-II
(a) $V_n / K_n = ?$	(p) 0
(b) If radius of nth orbit $\propto En^x$; $x = ?$	(q) -1
(c) Angular momentum in lowest orbital	(r) -2
(d) $\frac{1}{r^n} \propto Z^y$; $y = ?$	(s) 1

[M] Match the List-I with List-II:

List-I	List-II
(a) Radius of nth orbital	(p) Inversely proportional to Z
(b) Energy of nth shell	(q) Integral multiple of $h/2\pi$
(c) Angular momentum of electron	(r) Proportional to n^2
(d) Velocity of electron in nth orbit	(s) Inversely proportional to 'n'

[N] Match the entries in Column-I with the correctly related quantum number(s) in Column-II:

Column-I	Column-II
(a) Orbital angular momentum of the electron in a hydrogen-like atomic orbital	(p) Principal quantum number
(b) A hydrogen-like one electron wave function obeying Pauli principle	(q) Azimuthal quantum number
(c) Shape, size and orientation of hydrogen-like atomic orbitals	(r) Magnetic quantum number
(d) Probability density of electron at the nucleus in hydrogen-like atom	(s) Electron spin quantum number

[O] Match the List-I with List-II: **(IIT 2006)**

List-I	List-II
(a) Wave nature of radiation	(p) Photoelectric effect
(b) Photon nature of radiation	(q) Compton effect
(c) Interaction of a photon with an electron, such that quantum energy is slightly equal to or greater than the binding energy of electron, is more likely to result in:	(r) Diffraction
(d) Interaction of a photon with an electron, such that photon energy is much greater than the binding energy of electron, is more likely to result in:	(s) Interference

[P] Match the Column-I with Column-II:

Column-I	Column-II
(a) Orbital angular momentum of an electron	(p) $\sqrt{s(s+1)}\, h/2\pi$
(b) Angular momentum of electron	(q) $\sqrt{n(n+2)}$ BM
(c) Spin angular momentum of electron	(r) $nh/2\pi$
(d) Magnetic moment of atom	(s) $\sqrt{l(l+1)}\, h/2\pi$

[Q] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Scintillation	(p) Wave nature
(b) Photoelectric effect	(q) Particle nature
(c) Diffraction	(r) Particle nature dominates over wave nature
(d) Principle of electron microscope	(s) Wave nature dominates over particle nature

[R] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Radial function R	(p) Principal quantum number 'n'
(b) Angular function Θ	(q) Azimuthal quantum number 'l'
(c) Angular function Φ	(r) Magnetic quantum number 'm'
(d) Quantized angular momentum	(s) Spin quantum number 's'

Answers

1. [A] (i—e); (ii—d); (iii—f); (iv—b); (v—a); (vi—c)
   [B] (i—d); (ii—a); (iii—b); (iv—f); (v—c); (vi—e)
   [C] (i—f); (ii—d); (iii—a); (iv—e); (v—b); (vi—c)
2. [A] (a—q, r, s) (b—r) (c—p) (d—does not match)
   [B] (a—q, s) (b—p, s) (c—r, s) (d—p, s)
   [C] (a—r, s) (b—p) (c—q) (d—q)
   [D] (a—q, r) (b—p, q) (c—s) (d—p, q)
   [E] (a—q, r) (b—q, r, s) (c—p) (d—p)
   [F] (a—p, r) (b—q, s) (c—q, s) (d—p, r)
   [G] (a—q, r) (b—p) (c—s) (d—q, r)
   [H] (a—r, s) (b—q, s) (c—q, p) (d—p, r)
   [I] (a—r, s) (b—p, s) (c—q, r) (d—p, q)
   [J] (a—p) (b—p) (c—p, r) (d—r)
   [K] (a—r) (b—p) (c—q, s) (d—r)
   [L] (a—r) (b—q) (c—p) (d—s)
   [M] (a—r, p) (b—r) (c—q) (d—s)
   [N] (a—p) (b—s) (c—p, q, r) (d—p, q)
   [O] (a—r, s) (b—p, q) (c—p) (d—q)
   [P] (a—s) (b—r) (c—p) (d—q)
   [Q] (a—q) (b—r) (c—p) (d—p, s)
   [R] (a—p, q) (b—q, r) (c—r) (d—q, s)

• PRACTICE PROBLEMS •

1. An atom of an element contains 13 electrons. Its nucleus has 14 neutrons. Find out its atomic number and approximate atomic mass. An isotope has atomic mass 2 units higher. What will be the number of protons, neutrons and electrons in the isotope?

[**Ans.** At. No. = 13, atomic mass = 27; the isotope will have same number of protons and electrons = 13 but neutrons will be 14 + 2 = 16]

2. From the following find out groups of isotopes, isobars and isotones:

$$^{16}_{8}O,\ ^{39}_{19}K,\ ^{14}_{6}C,\ ^{239}_{92}U,\ ^{14}_{7}N,\ ^{40}_{20}Ca,\ ^{238}_{92}U,\ ^{77}_{32}Ge,$$
$$^{77}_{33}As,\ ^{18}_{8}O,\ ^{76}_{32}Ge,\ ^{78}_{34}Se$$

[**Ans.** Isotopes—same at. no. but different at. masses.

$$^{16}_{8}O,\ ^{18}_{8}O;\ ^{239}_{92}U,\ ^{238}_{92}U;\ ^{77}_{32}Ge,\ ^{76}_{32}Ge$$

Isobars—same atomic masses but different at. numbers

$$^{14}_{6}C,\ ^{14}_{7}N;\ ^{77}_{32}Ge,\ ^{77}_{33}As$$

Isotones—same number of neutrons.

$$^{16}_{8}O,\ ^{14}_{6}C;\ ^{39}_{19}K,\ ^{40}_{20}Ca;\ ^{77}_{33}As,\ ^{78}_{34}Se]$$

3. An element has atomic number 30. Its cation has 2 units positive charge. How many protons and electrons are present in the cation?

[**Ans.** Protons = 30, Electrons = 28]

4. Calculate the number of neutrons in 18 mL of water. (Density of water = 1)

[**Ans.** 48.16×10^{23}]

[**Hint:** One molecule of water contains = 8 neutrons]

5. Find (i) the total number of neutrons and (ii) the total mass of neutrons in 7 mg of ^{14}C (assuming that mass of neutron = mass of hydrogen atom).

[**Ans.** (i) 24.08×10^{20} and (ii) 4 mg]

6. Calculate the wavelength of a photon in Angstroms having an energy of 1 electron volt.

[**Hint:** $1\text{ eV} = 1.602 \times 10^{-19}$ joule;

$$h = 6.62 \times 10^{-34}\text{ J-s},\ c = 3 \times 10^{8}\text{ ms}^{-1}$$

$$\lambda = \frac{h \cdot c}{E} = 12.42 \times 10^{-7}\text{ m} = 12.42 \times 10^{3}\text{ Å}]$$

7. A photon of light with wavelength 6000 Å has an energy E. Calculate the wavelength of photon of a light which corresponds to an energy equal to $2E$.

[**Ans.** 3000 Å]

8. Calculate the energy in kilocalorie per mol of the photons of an electromagnetic radiation of wavelength 5700 Å.

[**Ans.** 56.3 kcal per mol]

9. Light of what frequency and wavelength is needed to ionise sodium atom. The ionisation potential of sodium is 8.2×10^{-19} J.

[Ans. $\nu = 1.238 \times 10^{15}$ Hz; $\lambda = 242$ nm]

10. Determine the energy of 1 mole photons of radiations whose frequency is $5 \times 10^{10}\ \text{s}^{-1}$. ($h = 6.62 \times 10^{-34}$ J - s)

[Ans. 19.9 J]

11. Find e/m for He^{2+} ion and compare with that for electron.

[Ans. 4.87×10^{7} coulomb kg^{-1}]

12. A ball of mass 100 g is moving with a velocity of 100 m sec^{-1}. Find its wavelength.

[Hint: $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{0.1 \times 100} = 6.626 \times 10^{-35}$ m]

13. Calculate the wavelength of radiation and energy per mol necessary to ionize a hydrogen atom in the ground state.

[Ans. $\lambda = 9.12 \times 10^{-8}$ m; 1313 kJ / mol]

14. Bond energy of F_2 is 150 kJ mol^{-1}. Calculate the minimum frequency of photon to break this bond.

[Ans. $3.759 \times 10^{14}\ \text{s}^{-1}$]

15. If an Einstein (E) is the total energy absorbed by 1 mole of a substance and each molecule absorbs one quantum of energy, then calculate the value of 'E' in terms of λ in cm.

[Ans. $\frac{1.198 \times 10^{8}}{\lambda}$ erg mol^{-1}]

16. How many chlorine atoms can you ionize in the process? $Cl \rightarrow Cl^{+} + e$ by the energy liberated from the following process:

$Cl + e \rightarrow Cl^{-}$ for 6×10^{23} atoms

given that electron affinity of chlorine is 3.61 eV and ionization energy of chlorine is 17.422 eV.

[Ans. 1.24×10^{23} atoms]

17. Find the velocity (ms^{-1}) of electron in first Bohr orbit of radius a_0. Also find the de Broglie wavelength (in 'm'). Find the orbital angular momentum of $2p$ orbital of hydrogen atom in units of $h/2\pi$.

[Hint: $v = \frac{2.188 \times 10^{6}}{n}$ m sec^{-1}

$$v = \frac{2.188 \times 10^{6}}{1} = 2.188 \times 10^{6} \text{ m sec}^{-1}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.188 \times 10^{6}}$$

$$= 3.3 \times 10^{-10} \text{ m}$$

$$\text{Orbital angular momentum} = \sqrt{l(l+1)}\,\frac{h}{2\pi}$$

$$= \sqrt{1(1+1)}\,\frac{h}{2\pi} \qquad (\because l = 1 \text{ for } 2p)$$

$$= \sqrt{2}\,\frac{h}{2\pi}\ ]$$

18. The energy of an α-particle is 6.8×10^{-18} J. What will be the wavelength associated with it? **[CBSE-PMT (Mains) 2005]**

[Hint: $\lambda = \frac{h}{\sqrt{2Em}} = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 6.8 \times 10^{-18} \times 4 \times 1.66 \times 10^{-27}}}$

$= 2.2 \times 10^{-12}$ m]

19. Determine the number of revolutions made by an electron in one second in the 2nd Bohr orbit of H-atom.

[Ans. $n = \frac{2\pi r}{v}$]

20. What is the speed of an electron whose de Broglie wavelength is 0.1 nm? By what potential difference, must have such an electron accelerated from an initial speed zero?

[Ans. 7.28×10^{6} m/sec; 150 V]

21. A green ball weighs 75 g; it is travelling towards observer at a speed of 400 cm/sec. The ball emits light of wavelength 5×10^{-5} cm. Assuming that the error in the position of ball is the same as wavelength of itself, calculate error in the momentum of the green ball.

[Hint: $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$$\Delta p \geq \frac{h}{4\pi\,\Delta x}$$

$$\Delta p \geq \frac{h}{4\pi\lambda}$$

$$\Delta p \approx \frac{6.626 \times 10^{-27}}{4 \times 3.14 \times 5 \times 10^{-5}} \approx 1.055 \times 10^{-23}\ ]$$

22. What is the relationship between the eV and the wavelength in metre of the energetically equivalent photons?

[Ans. $\lambda = 12.4237 \times 10^{-7}$ metre]

23. What is the velocity of an electron ($m = 9.11 \times 10^{-31}$ kg) in the innermost orbit of the hydrogen atom? (Bohr radius $= 0.529 \times 10^{-10}$ m)

[Ans. 2.187×10^{6} m/sec]

24. In a hydrogen atom, an electron jumps from the third orbit to the first orbit. Find out the frequency and wavelength of the spectral line. ($R_H = 1.09678 \times 10^{7}\ \text{m}^{-1}$)

[Ans. 2.925×10^{15} Hz, 1025.6 Å]

25. The energy of the electron in the second and third Bohr orbits of hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.

[Ans. 6.6×10^{3} Å]

26. Calculate the wavelength in angstroms of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionisation potential of the ground state of hydrogen atom is 2.17×10^{-11} erg per atom.

[Hint: Energy of the electron in the 1st orbit = − (ionisation potential), $\Delta E = (3/4) \times 2.17 \times 10^{-11}$ erg per atom]

[Ans. $\lambda = 1220$ Å]

27. Calculate the wave number for the shortest wavelength transition in Balmer series of atomic hydrogen. **(IIT 1996)**

[Ans. 27419.25 cm^{-1}]

28. The wavelength of the first member of the Balmer series of hydrogen is 6563×10^{-10} m. Calculate the wavelength of its second member.

[**Hint:** $\frac{1}{\lambda_1} = R_H \left[\frac{1}{2^2} - \frac{1}{3^2}\right]$ and $\frac{1}{\lambda_2} = R_H \left[\frac{1}{2^2} - \frac{1}{4^2}\right]$

$$\frac{\lambda_2}{\lambda_1} = \frac{5}{36} \times \frac{16}{3} = \frac{20}{27}$$

$$\lambda_2 = \frac{20}{27} \times 6563 \times 10^{-10} = 4861 \times 10^{-10} \text{ m}]$$

29. According to Bohr theory, the electronic energy of hydrogen atom in the *n*th Bohr orbit is given by,

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2} \text{ J}$$

Calculate the longest wavelength of light that will be needed to remove an electron from the 2nd orbit of Li^{2+} ion.

[**Ans.** 4.059×10^{-8} m]

30. Calculate the frequency, energy and wavelength of the radiation corresponding to spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also calculate the energy of the corresponding line in the spectra of Li^{2+}.

(IIT 1991)

[**Ans.** $\lambda = 1.216 \times 10^{-7}$ m, $\nu = 2.47 \times 10^{15}$ cycle sec^{-1}, $E = 16.36 \times 10^{-19}$ J, $E_{Li^{2+}} = Z^2 \times E_H = 9 \times 16.36 \times 10^{-19}$ J $= 147.27 \times 10^{-19}$ J]

31. Calculate the ratio of the velocity of light and the velocity of electron in the 2nd orbit of a hydrogen atom. (Given $h = 6.624 \times 10^{-27}$ erg-sec; $m = 9.108 \times 10^{-28}$ g; $r = 2.11 \times 10^{-8}$ cm)

[**Ans.** 273.2]

32. What hydrogen-like ion has the wavelength difference between the first lines of Balmer and Lyman series equal to 59.3 nm ($R_H = 109678 \text{ cm}^{-1}$)?

[**Hint:** Wavelength of 1st line in Balmer series,

$$\frac{1}{\lambda_B} = Z^2 R_H \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = \frac{5}{36} R_H Z^2$$

or $$\lambda_B = \frac{36}{5 R_H Z^2}$$

Wavelength of 1st line in Lyman series is,

$$\frac{1}{\lambda_L} = Z^2 R_B \left[\frac{1}{1^2} - \frac{1}{2^2}\right]$$

or $$\lambda_L = \frac{4}{3 \times R_H Z^2}$$

$$\text{Difference } \lambda_B - \lambda_L = 59.3 \times 10^{-7} = \frac{36}{5 R_H Z^2} - \frac{4}{3 R_H Z^2}$$

$$= \frac{1}{R_H Z^2}\left[\frac{36}{5} - \frac{4}{3}\right]$$

$$Z^2 = \frac{88}{59.3 \times 10^{-7} \times 109678 \times 15} = 9.0$$

or $Z = 3$

Hydrogen-like species is Li^{2+}.]

33. The velocity of an electron in certain Bohr orbit of H-atom bears the ratio 1 : 275 to the velocity of light. (a) What is the quantum number '*n*' of the orbit? (b) Calculate the wave number of the radiation when the electron jumps from $(n + 1)$ state to ground state.

[**Ans.** $\bar{\nu} = 9.75 \times 10^4 \text{ cm}^{-1}$]

[**Hint:** (a) $\frac{v}{c} = \frac{1}{275}$ or $v = \frac{3 \times 10^{10}}{275} = 1.09 \times 10^8$ cm sec^{-1}

$$v = \frac{nh}{2\pi mr} = \frac{nh}{2\pi m \times 0.529 \times 10^{-8} \times n^2}$$

or $$n = \frac{h}{2\pi m \times 0.529 \times 10^{-8} \times v}$$

$$= \frac{6.625 \times 10^{-27}}{2 \times 3.14 \times 9.1 \times 10^{-28} \times 0.529 \times 10^{-8} \times 1.09 \times 10^8}$$

$$= 2$$

(b) Thus, $n + 1 = 2 + 1 = 3$. The electron jumps from 3rd orbit to 1st orbit.]

34. Find out the wavelength of the next line in the series having lines of spectrum of H-atom of wavelengths 6565 Å, 4863 Å, 4342 Å and 4103 Å.

[**Ans.** 3972 Å]

[**Hint:** All these lines are in visible region and thus, belong to Balmer series. Next line is, therefore, from 7th orbit.]

35. Which jump is responsible for the wave number of emitted radiations equal to $9.7490 \times 10^6 \text{ m}^{-1}$ in Lyman series of hydrogen spectrum? ($R = 1.09678 \times 10^7 \text{ m}^{-1}$)

[**Ans.** 3]

36. Calculate the ionisation energy of the hydrogen atom. How much energy will be required to ionise 1 mole of hydrogen atoms? Given, that the Rydberg constant is $1.0974 \times 10^7 \text{ m}^{-1}$.

[**Ans.** IE per hydrogen atom = 2.182×10^{-18} J
IE per mole = 1314 kJ mol^{-1}]

37. Calculate the ionisation energy of (a) one Li^{2+} ion and (b) one mole of Li^{2+} ion. (Given, $R = 1.0974 \times 10^{-7} \text{ m}^{-1}$)

[**Ans.** (a) 19.638×10^{-18} J (b) 1.118×10^4 kJ mol^{-1}]

38. A series of lines in the spectrum of atomic hydrogen lies at 656.46 nm, 486.27 nm, 439.17 nm and 410.29 nm. What is the wavelength of the next line in this series? What is the ionisation energy of the atom when it is in the lower state of transition?

[**Ans.** $\lambda_{next} = 397.15$ nm; IE = 3.40 eV]

39. A certain line of the Lyman series of hydrogen and a certain line of the Balmer series of He^+ ion have nearly the same wavelength. To what transition do they belong? Small differences between their Rydberg constant may be neglected.

[**Ans.**

Hydrogen	Helium
2 → 1	4 → 2
3 → 1	6 → 2
4 → 1	8 → 2]

40. What element has a hydrogen-like spectrum whose lines have wavelengths four times shorter than those of atomic hydrogen?

[**Ans.** He^+]

41. What lines of atomic hydrogen absorption spectrum fall within the wavelength ranges from 94.5 to 130 nm?
[**Ans.** 97.3; 102.6; 121.6 nm]

42. The binding energy of an electron in the ground state of an atom is equal to 24.6 eV. Find the energy required to remove both the electrons from the atom.
[**Ans.** 79 eV]

43. What is the ratio of the speeds of an electron in the first and second orbits of a hydrogen atom?
[**Ans.** 2 : 1]

44. Find out the number of waves made by a Bohr electron in one complete revolution in its third orbit. **(IIT 1994)**
[**Ans.** 3]

45. The wave number of first line in Balmer series of hydrogen is 15200 cm^{-1}. What is the wave number of first line in Balmer series of Be^{3+}?
[**Ans.** 2.43×10^5 cm^{-1}]

46. Calculate the speed of an electron in the ground state of hydrogen atom. What fraction of the speed of light is this value? How long does it take for the electron to complete one revolution around the nucleus? How many times does the electron travel around the nucleus in one second?
[**Ans.** 2.186×10^6 ms^{-1}; 7.29×10^{-3}]

47. An electron, in a hydrogen atom, in its ground state absorbs 1.5 times as much energy as the minimum required for its escape (*i.e.*, 13.6 eV) from the atom. Calculate the value of λ for the emitted electron.
[**Ans.** 4.69 Å]

48. The radius of the fourth orbit of hydrogen is 0.85 nm. Calculate the velocity of an electron in this orbit ($m_e = 9.1 \times 10^{-31}$ kg).
[**Ans.** 5.44×10^5 m sec^{-1}]

49. A beam of electrons accelerated with 4.64 V was passed through a tube having mercury vapours. As a result of absorption, electronic changes occurred with mercury atoms and light was emitted. If the full energy of single electron was converted into light, what was the wave number of emitted light?
[**Ans.** 3.75×10^4 cm^{-1}]

50. An electron jumps from an outer orbit to an inner orbit with the energy difference of 3.0 eV. What will be the wavelength of the line and in what region does the emission take place?
[**Ans.** λ = 4140 Å ; visible region]
[**Hint:** 1 eV = 1.6×10^{-12} erg]

51. The first ionisation energy of a certain atom took place with an absorption of radiation of frequency 1.5×10^{18} cycle per second. Calculate its ionisation energy in calorie per gram atom.
[**Ans.** 1.43×10^8 cal]
[**Hint:** 1 calorie = 4.18×10^7 erg
Apply $E = h \times \nu \times$ Avogadro's number]

52. Find the wavelength associated with an electron which has mass 9.1×10^{-28} g and is moving with a velocity of 10^5 cm sec^{-1}. (Given $h = 6.625 \times 10^{-27}$ erg-sec)
[**Ans.** $\lambda = 7.28 \times 10^{-5}$ cm]

53. Calculate the momentum of the particle which has de Broglie wavelength 1 Å (10^{-10} m) and $h = 6.6 \times 10^{-34}$ J-sec.
[**Ans.** 6.6×10^{-24} kg m sec^{-1}]

54. The uncertainty of a particle in momentum is 3.3×10^{-2} kg ms^{-1}. Calculate the uncertainty in its position. ($h = 6.6 \times 10^{-34}$ J-sec)
[**Ans.** 3.1×10^{-14} m]

55. Calculate the product of uncertainties of displacement and velocity of a moving electron having a mass 9.1×10^{-28} g.
[**Ans.** 5.77×10^{-5} m^2 s^{-1}]
[**Hint:** $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$]

56. (a) A transition metal cation x^{3+} has magnetic moment $\sqrt{35}$ BM. What is the atomic number of x^{3+}?
(b) Select the coloured ion and the ion having maximum magnetic moment (i) Fe^{2+}, (ii) Cu^+, (iii) Sc^{3+} and (iv) Mn^{2+}

$\boxed{1}\boxed{1}\boxed{1}\boxed{1}\boxed{1}\quad\boxed{}$

(b) $Fe^{2+} \rightarrow \boxed{1\!\downharpoonleft}\boxed{1}\boxed{1}\boxed{1}\boxed{1}$

$Mn^{2+} \rightarrow \boxed{1}\boxed{1}\boxed{1}\boxed{}\boxed{}$

[**Hint:** (a) 26, $_{26}Fe \rightarrow 3d^6 4s^2$

$$Fe^{3+} \rightarrow 3d^5 4s^0$$

$$\mu = \sqrt{n(n+2)} = \sqrt{5 \times 7} = \sqrt{35}$$

Both these ions will be coloured and magnetic moment of Fe^{2+} will be greater.]

57. A photon of wavelength 4000 Å strikes a metal surface, the work function of the metal being 2.13 eV. Calculate (i) energy of the photon in eV; (ii) kinetic energy of the emitted photoelectron and (iii) velocity of the photoelectron.
[**Ans.** E = 3.10 eV; KE = 0.97 eV; Velocity = 5.85×10^5 ms^{-1}]
[**Hint:** 1 eV = 1.602×10^{-19} J]

58. Calculate the ratio between the wavelengths of an electron and a proton, if the proton is moving at half the velocity of the electron (mass of the proton = 1.67×10^{-27} kg; mass of the electron = 9.11×10^{-28} g).
[**Ans.** 9.2455×10^{-2} m]
[**Hint:** Apply de Broglie equation, $\lambda = \frac{h}{mv}$

$$\text{Wavelength of electron} = \frac{6.625 \times 10^{-34}}{9.11 \times 10^{-31} v}$$

$$\text{Wavelength of proton} = \frac{6.625 \times 10^{-34}}{1.67 \times 10^{-27} \times 0.5v}$$]

59. A moving electron has 2.8×10^{-25} J of kinetic energy. Calculate its wavelength.
(Mass of electron = 9.1×10^{-31} kg)
[**Ans.** 9.2455×10^{-7} m]

[**Hint:** $v = \sqrt{\frac{2 \times \text{KE}}{m}} = 784.46\ \text{ms}^{-1}$; $\lambda = \frac{h}{mv}$]

60. Helium has mass number 4 and atomic number 2. Calculate the nuclear binding energy per nucleon (mass of neutron = 1.00893 amu and proton = 1.00814 amu, He = 4.0039 amu and mass of electron is negligible).

[**Ans.** 7.038 MeV]

61. Calculate the mass defect and binding energy per nucleon of $^{16}_{8}O$ which has a mass 15.99491 amu.

Mass of neutron = 1.008655 amu
Mass of proton = 1.007277 amu
Mass of electron = 0.0005486 amu
1 amu = 931.5 MeV

[**Ans.** 7.976 MeV/nucleon]

62. The circumference of the second Bohr orbit of electron in the hydrogen atom is 600 nm. Calculate the potential difference to which the electron has to be subjected so that the electron stops. The electron had the de Broglie wavelength corresponding to the circumference.

[**Hint:** Number of waves 'n' = $\frac{\text{Circumference}}{\text{Wavelength}}$

$$n\lambda = 2\pi r$$
$$2\lambda = 600$$
$$\lambda = 300\ \text{nm}$$

Let stopping potential is V_0.

$$eV_0 = \frac{1}{2}mv^2 \quad \ldots \text{(i)}$$
$$\lambda = \frac{h}{mv}$$
$$v = \frac{h}{\lambda m} \quad \ldots \text{(ii)}$$

From equations (i) and (ii),

$$eV_0 = \frac{1}{2}m\left(\frac{h}{\lambda m}\right)^2$$
$$V_0 = \frac{h^2}{2m\lambda^2 e}$$
$$= \frac{(6.626 \times 10^{-34})^2}{2 \times (9.1 \times 10^{-31}) \times (300 \times 10^{-9})^2 \times 1.6 \times 10^{-19}}$$
$$= 1.675 \times 10^{-5}\ \text{V}$$]

63. The velocity of an electron of mass 9.1×10^{-31} kg moving round the nucleus in the Bohr orbit (diameter of the orbit is 1.058 Å) is 2.2×10^{-6} m sec^{-1}. If momentum can be measured within the accuracy of 1%, then calculate uncertainty in position (Δx) of the electron.

[**Ans.** 2.64×10^3 metre]

64. An electron wave has wavelength 1 Å. Calculate the potential with which the electron is accelerated.

[**Ans.** 0.0826 volt]

65. Calculate the de Broglie wavelength associated with an α-particle having an energy of 7.7×10^{-13} J and a mass of 6.6×10^{-24} g. ($h = 6.6 \times 10^{-34}$ J-s)

[**Ans.** 6.56×10^{-13} cm]

66. An electron has mass 9.1×10^{-28} g and is moving with a velocity of 10^5 cm/sec. Calculate its kinetic energy and wavelength when $h = 6.626 \times 10^{-27}$ erg-sec.

[**Ans.** 4.55×10^{-8} erg; $\lambda = 7.28 \times 10^{-5}$ cm]

67. Calculate the de Broglie wavelengths of an electron and a proton having same kinetic energy of 100 eV.

[**Ans.** $\lambda_e = 123$ pm; $\lambda_p = 2.86$ pm]

68. Work function of sodium is 2.5 eV. Predict whether the wavelength 6500 Å is suitable for a photoelectron or not?

[**Ans.** No ejection]

69. Calculate the de Broglie wavelength associated with a helium atom in a helium gas sample at 27°C and 1 atm pressure.

[**Ans.** 7.3×10^{-11} metre]

70. The threshold frequency for a certain metal is 3.3×10^{14} cycle/sec. If incident light on the metal has a cut-off frequency 8.2×10^{14} cycle/sec, calculate the cut-off potential for the photoelectron.

[**Ans.** 2 volt]

71. Can you locate the electron within 0.005 nm?

[**Ans.** No.]

[**Hint:** Use uncertainty principle to determine uncertainty in velocity.

$$\Delta v \geq \frac{h}{4\pi m\,\Delta x}$$

On substitution, you will get,

$$\Delta v \geq 1.16 \times 10^7\ \text{ms}^{-1}$$

Velocity of electron is therefore expected to be as high as velocity of light. We may say that the velocity of electron is uncertain within 0.005 nm.]

72. The photoelectric cut-off voltage in a certain experiment is 1.5 volt. What is the maximum kinetic energy of the photoelectrons emitted?

[**Ans.** 2.4×10^{-19} joule]

73. A proton is accelerated to one-tenth the velocity of light. If its velocity can be measured with a precision of ±1%, what must be its uncertainty in position?
($h = 6.6 \times 10^{-34}$ J-s; mass of proton = 1.66×10^{-27} kg)

[**Ans.** 1.05×10^{-14} m]

74. In a photoelectric effect experiment, irradiation of a metal with light of frequency 5.2×10^{14} sec^{-1} yields electrons with maximum kinetic energy 1.3×10^{-19} J. Calculate the ν_0 of the metal.

[**Ans.** 3.2×10^{14} sec^{-1}]

75. Calculate the wavelength of a CO_2 molecule moving with a velocity of 440 m sec^{-1}.

[**Ans.** 2.06×10^{-11} metre]

76. The predominant yellow line in the spectrum of a sodium vapour lamp has a wavelength of 590 nm. What minimum accelerating potential is needed to excite this line in an electron tube having sodium vapours?

[**Ans.** 2.11 volt]

77. Find out the wavelength of a track star running a 100 metre dash in 10.1 sec, if its weight is 75 kg.

[Ans. 8.92×10^{-37} m]

78. At what velocity ratio are the wavelengths of an electron and a proton equal?

($m_e = 9.1 \times 10^{-28}$ g and $m_p = 1.6725 \times 10^{-24}$ g)

[Ans. $\frac{v_e}{v_p} = 1.8 \times 10^3$]

79. Through what potential difference must an electron pass to have a wavelength of 500 Å?

[Ans. 6.03×10^{-4} eV]

[Hint: Use $\lambda = \frac{h}{\sqrt{2\,eV\,m}}$]

80. Calculate the velocity of an α-particle which begins to reverse its direction at a distance of 2×10^{-14} m from a scattering gold nucleus ($Z = 79$).

[Ans. 2.346×10^7 m / sec]

81. Two hydrogen atoms collide head-on and end up with zero kinetic energy. Each then emits a photon with a wavelength 121.6 nm. Which transition leads to this wavelength? How fast were the hydrogen atoms travelling before the collision? (Given, $R_H = 1.097 \times 10^7\ \text{m}^{-1}$ and $m_H = 1.67 \times 10^{-27}$ kg)

[Ans. $n_1 = 1$; $n_2 = 2$; 4.43×10^4 m sec^{-1}]

[Hint: Wavelength is in UV region; thus n_1 will be 1.

$$\frac{1}{121.6 \times 10^{-9}} = 1.097 \times 10^7 \times 1^2 \times \left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

$$n_2 = 2$$

$$\frac{1}{2} mv^2 = \frac{hc}{\lambda}$$

$$\frac{1}{2} \times 1.67 \times 10^{-27} \times v^2 = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{121.6 \times 10^{-9}}$$

$$v = 4.43 \times 10^4 \text{ m sec}^{-1}\,]$$

82. Show that the wavelength of electrons moving at a velocity very small compared to that of light and with a kinetic energy of V electron volt can be written as,

$$\lambda = \frac{12.268}{\sqrt{V}} \times 10^{-8} \text{ cm}$$

[Hint: Use the relation, $\lambda = \frac{h}{\sqrt{2Em}}$

Here, h = Planck's constant

$m = 9.1 \times 10^{-28}$ g (mass of e^-)

E = Kinetic energy of electron

$= V$ eV $= V \times 1.6 \times 10^{-12}$ erg]

83. What is the distance of closest approach to the nucleus of an α-particle which undergoes scattering by 180° in Geiger-Marsden experiment?

[Ans. $r_0 = 4.13$ fm]

[Hint: For closest approach,

$$\frac{1}{2} mv^2 = K \frac{Ze \times e}{r_0}$$

For Rutherford experiment,

$$\frac{1}{2} mv^2 = 5.5 \text{ MeV} = 5.5 \times 10^6 \times 1.6 \times 10^{-19} \text{ J} = 8.8 \times 10^{-13} \text{ J}$$

$$8.8 \times 10^{-13} = \frac{9 \times 10^9 \times 2 \times 79 \times (1.6 \times 10^{-19})^2}{r_0}$$

$$r_0 = 4.136 \times 10^{-15} \text{ m}$$

$$r_0 = 4.13 \text{ fm}\,]$$

84. Photoelectrons are liberated by ultraviolet light of wavelength 3000 Å from a metallic surface for which the photoelectric threshold is 4000 Å. Calculate de Broglie wavelength of electrons emitted with maximum kinetic energy.

[Ans. $\lambda = 1.2 \times 10^{-9}$ m]

[Hint:

$$\text{KE} = \text{Quantum energy} - \text{Threshold energy}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{3000 \times 10^{-10}} - \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4000 \times 10^{-10}}$$

$$= 6.626 \times 10^{-19} - 4.9695 \times 10^{-19}$$

$$= 1.6565 \times 10^{-19} \text{ joule}$$

$$\frac{1}{2} mv^2 = 1.6565 \times 10^{-19}$$

$$m^2v^2 = 2 \times 1.6565 \times 10^{-19} \times 9.1 \times 10^{-31}$$

$$mv = 5.49 \times 10^{-25}$$

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}}{5.49 \times 10^{-25}} = 1.2 \times 10^{-9} \text{ m}\,]$$

85. Show that de Broglie wavelength of electrons accelerated V volt is very nearly given by:

$$\lambda \text{ (in Å)} = \left(\frac{150}{V}\right)^{1/2}$$

[Hint: $\lambda = \frac{h}{\sqrt{2eVm}}$

$$\lambda = \left[\frac{h^2}{2eVm} \times 10^{20}\right]^{1/2} \text{Å}$$

$$= \left[\frac{(6.626 \times 10^{-34})^2 \times 10^{20}}{2 \times 1.6 \times 10^{-19} \times V \times 9.1 \times 10^{-31}}\right]^{1/2} = \left[\frac{150}{V}\right]^{1/2}\,]$$

86. A 1 MeV proton is sent against a gold leaf ($Z = 79$). Calculate the distance of closest approach for head-on collision.

[Ans. 1.137×10^{-13} m]

[Hint: $d = \frac{Ze^2}{4\pi\varepsilon_0(\frac{1}{2}mv^2)}$. Do like Q.No. 83]

87. What is the energy, momentum and wavelength of the photon emitted by a hydrogen atom when an electron makes a transition from $n = 2$ to $n = 1$? Given that ionization potential is 13.6 eV.

[**Ans.** 16.32×10^{-19} J, 5.44×10^{-27} kg m / sec, 1218 Å]

[**Hint:** $E_1 = -13.6$ eV

$$E_2 = \frac{-13.6}{4} \text{ eV}$$

$$\Delta E = \frac{3}{4} \times 13.6 \text{ eV}$$

$$= 0.75 \times 13.6 \times 1.6 \times 10^{-19} \text{ J} = 1.632 \times 10^{-18} \text{ J}$$

$$\frac{hc}{\lambda} = 1.632 \times 10^{-18}$$

$$\lambda = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{1.632 \times 10^{-18}} = 1218 \times 10^{-10} \text{ m} = 1218 \text{ Å}$$

$$\lambda = \frac{h}{p}$$

$$\therefore \quad p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}}{1218 \times 10^{-10}} = 5.44 \times 10^{-27} \text{ kg-m/sec}]$$

88. Calculate the orbital angular momentum of the following orbitals:

(a) $3p$ (b) $3d$ (c) $3s$

[**Ans.** (a) $\sqrt{2}\hbar$ (b) $\sqrt{6}\hbar$ (c) 0]

[**Hint:** (a) $\mu_l = \sqrt{l(l+1)}\,\frac{h}{2\pi}$ for $3p$, $l = 1 = \sqrt{2}\,\hbar$

(b) $\mu_l = \sqrt{6}\hbar$ for $3d$, $l = 2$

(c) $\mu_l = 0$ for $3s$, $l = 0$]

89. A single electron system has ionization energy 11180 kJ mol^{-1}. Find the number of protons in the nucleus of the system.

[**Ans.** $Z = 3$]

[**Hint:** $$\text{IE} = \frac{Z^2}{n^2} \times 21.69 \times 10^{-19} \text{ J}$$

$$\frac{11180 \times 10^3}{6.023 \times 10^{23}} = \frac{Z^2}{1^2} \times 21.69 \times 10^{-19}$$

$$Z \approx 3]$$

90. Suppose 10^{-17} J of light energy is needed by the interior of the human eye to see an object. How many photons of green light ($\lambda = 550$ nm) are needed to generate this minimum amount of energy?

[**Ans.** 28]

91. How many hydrogen atoms in the ground state are excited by means of monochromatic radiation of wavelength 970.6 Å. How many different lines are possible in the resulting emission spectrum? Find the longest wavelength among these.

[**Ans.** Six different lines, $\lambda = 1215.6$ Å]

[**Hint:** $$E_n - E_1 = \frac{hc}{\lambda}$$

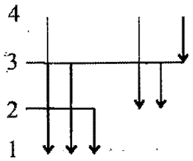
$$\frac{-21.69 \times 10^{-19}}{n^2} + \frac{21.69 \times 10^{-19}}{1} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{970.6 \times 10^{-10}}$$

$$n \approx 4$$

$$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{1}{\lambda} = 109677.77 \times 1^2\left(\frac{1}{1^2} - \frac{1}{4}\right)$$

$$\lambda = 1215.68 \text{ Å}]$$



six different lines

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. The ratio of e/m for a cathode ray:
   (a) varies with a gas in a discharge tube
   (b) is fixed
   (c) varies with different electrodes
   (d) is maximum if hydrogen is taken
2. Which of the following statements is wrong about cathode rays?
   (a) They travel in straight lines towards cathode
   (b) They produce heating effect
   (c) They carry negative charge
   (d) They produce X-rays when strike with material having high atomic masses
3. Cathode rays are:
   (a) electromagnetic waves (b) stream of α-particles
   (c) stream of electrons (d) radiations
4. Cathode rays have:
   (a) mass only (b) charge only
   (c) no mass and no charge (d) mass and charge both
5. Which is the correct statement about proton?
   (a) It is a nucleus of deuterium
   (b) It is an ionised hydrogen molecule
   (c) It is an ionised hydrogen atom
   (d) It is an α-particle
6. Neutron was discovered by:
   (a) J.J. Thomson (b) Chadwick
   (c) Rutherford (d) Priestley
7. The discovery of neutron came very late because:
   (a) it is present in nucleus
   (b) it is a fundamental particle
   (c) it does not move
   (d) it does not carry any charge
8. The fundamental particles present in equal numbers in neutral atoms (atomic number 71) are:
   (a) protons and electrons (b) neutrons and electrons
   (c) protons and neutrons (d) protons and positrons
9. The nucleus of the atom consists of:
   (a) protons and neutrons
   (b) protons and electrons
   (c) neutrons and electrons
   (d) protons, neutrons and electrons
10. The absolute value of charge on the electron was determined by:
    (a) J.J. Thomson (b) R.A. Millikan
    (c) Rutherford (d) Chadwick
11. Atomic number of an element represents: **(CBSE 1990)**
    (a) number of neutrons in the nucleus
    (b) atomic mass of an element
    (c) valency of an element
    (d) number of protons in the nucleus
12. Rutherford's experiment on scattering of α-particles showed for the first time that the atom has: **[CMC (Vellore) 1991]**
    (a) electrons (b) protons (c) neutrons (d) nucleus
13. Rutherford's scattering experiment is related to the size of the:
    (a) nucleus (b) atom (c) electron (d) neutron
14. When alpha particles are sent through a thin metal foil, most of them go straight through the foil because:
    (a) alpha particles are much heavier than electrons
    (b) alpha particles are positively charged
    (c) most part of the atom is empty space
    (d) alpha particles move with very high velocity
15. The radius of an atomic nucleus is of the order of: **[PMT (MP) 1991]**
    (a) 10^{-10} cm (b) 10^{-13} cm
    (c) 10^{-15} cm (d) 10^{-8} cm
16. Atomic size is of the order of:
    (a) 10^{-8} cm (b) 10^{-10} cm (c) 10^{-13} cm (d) 10^{-6} cm
17. Atoms may be regarded as comprising of protons, neutrons and electrons. If the mass attributed by electrons was doubled and that attributed by neutrons was halved, the atomic mass of ^{12}C would be:
    (a) approximately the same (b) doubled
    (c) reduced approx. 25% (d) approx. halved
18. Positive ions are formed from neutral atoms by the loss of:
    (a) neutrons (b) protons
    (c) nuclear charge (d) electrons
19. The nitrogen atom has 7 protons and 7 electrons. The nitride ion will have:
    (a) 10 protons and 7 electrons
    (b) 7 protons and 10 electrons
    (c) 4 protons and 7 electrons
    (d) 4 protons and 10 electrons
20. A light whose frequency is equal to 6×10^{14} Hz is incident on a metal whose work function is 2eV ($h = 6.63 \times 10^{-34}$ Js, $1\text{eV} = 1.6 \times 10^{-19}$ J). The maximum energy of electrons emitted will be: **(VITEEE 2008)**
    (a) 2.49 eV (b) 4.49 eV (c) 0.49 eV (d) 5.49 eV
    [**Hint :** Absorbed energy = Threshold energy + Kinetic energy of photoelectrons

    $$\begin{aligned}\text{Absorbed energy} &= h\nu \\ &= 6.626 \times 10^{-34} \times 6 \times 10^{14} \\ &= 3.9756 \times 10^{-19}\ \text{J} \\ &= \frac{3.9756 \times 10^{-19}}{1.6 \times 10^{-19}} = 2.49\ \text{eV}\end{aligned}$$

    $$2.49 = 2\ \text{eV} + \text{Kinetic energy of photoelectron}$$

    Kinetic energy of photoelectron = 0.49 eV]
21. The size of the nucleus is measured in:
    (a) amu (b) angstrom
    (c) cm (d) fermi
22. The highest value of e/m of anode rays has been observed when the discharge tube is filled with:
    (a) nitrogen (b) oxygen (c) hydrogen (d) helium

23. The particle with 13 protons and 10 electrons is:
(a) Al atom (b) Al^{3+} ion
(c) nitrogen isotope (d) none of these

24. Which of the following atoms contains the least number of neutrons?
(a) ${}^{235}_{92}U$ (b) ${}^{238}_{92}U$
(c) ${}^{239}_{93}Np$ (d) ${}^{240}_{93}Np$

25. The number of neutrons in dipositive zinc ion (Zn^{2+}, with mass number 70) is:
(a) 34 (b) 36 (c) 38 (d) 40

26. Which of the properties of the elements is a whole number?
(a) Atomic mass (b) Atomic number
(c) Atomic radius (d) Atomic volume

27. Increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and α-particle (α) is:
(a) e, p, n, α (b) n, p, e, α
(c) n, p, α, e (d) n, α, p, e

28. The mass of neutron is of the order of:
(a) 10^{-27} kg (b) 10^{-26} kg
(c) 10^{-25} kg (d) 10^{-24} kg

29. The atoms of various isotopes of a particular element differ from each other in the number of:
(a) electrons in the outer shell only
(b) protons in the nucleus
(c) electrons in the inner shell only
(d) neutrons in the nucleus

30. Isotopes of the same element have:
(a) same number of neutrons
(b) same number of protons
(c) same atomic mass
(d) different chemical properties

31. Which of the following conditions is incorrect for a well behaved wave function (ψ)? **[EAMCET (Engg.) 2010]**
(a) ψ must be finite (b) ψ must be single valued
(c) ψ must be infinite (d) ψ must be continuous

32. Atomic mass of an element is not a whole number because:
(a) it contains electrons, protons and neutrons
(b) it contains isotopes
(c) it contains allotropes
(d) all of the above

33. Nucleons are:
(a) protons and neutrons
(b) neutrons and electrons
(c) protons and electrons
(d) protons, neutrons and electrons

34. Isotopes of an element have:
(a) different chemical and physical properties
(b) similar chemical and physical properties
(c) similar chemical but different physical properties
(d) similar physical and different chemical properties

35. Isotopes are identified by:
(a) positive ray analysis
(b) Astons' mass spectrograph
(c) Dempster's mass spectrograph
(d) all of the above

36. Mass spectrograph helps in the detection of isotopes because they:
(a) have different atomic masses
(b) have same number of electrons
(c) have same atomic number
(d) have same atomic masses

37. Which of the following statements is incorrect?
(a) The charge on an electron and proton are equal and opposite
(b) Neutrons have no charge
(c) Electrons and protons have the same mass
(d) The mass of a proton and a neutron are nearly the same

38. The charge on positron is equal to the charge on:
(a) proton (b) electron
(c) α-particle (d) neutron

39. Discovery of the nucleus of an atom was due to the experiment carried out by:
(a) Bohr (b) Rutherford
(c) Moseley (d) Thomson

40. Isobars are the atoms of: **(CBSE 1991)**
(a) same elements having same atomic number
(b) same elements having same atomic mass
(c) different elements having same atomic mass
(d) none of the above

41. Which of the following pairs represents isobars?
(a) ${}^{3}_{2}He$ and ${}^{4}_{2}He$ (b) ${}^{24}_{12}Mg$ and ${}^{25}_{12}Mg$
(c) ${}^{40}_{19}K$ and ${}^{40}_{20}Ca$ (d) ${}^{40}_{19}K$ and ${}^{39}_{19}K$

42. Na^+ ion is isoelectronic with: **(CPMT 1990)**
(a) Li^+ (b) Mg^{2+} (c) Ca^{2+} (d) Ba^{2+}

43. The triad of nuclei that is isotonic is:
(a) ${}^{14}_{6}C$, ${}^{14}_{7}N$, ${}^{19}_{9}F$ (b) ${}^{12}_{6}C$, ${}^{14}_{7}N$, ${}^{19}_{9}F$
(c) ${}^{14}_{6}C$, ${}^{14}_{7}N$, ${}^{17}_{9}F$ (d) ${}^{14}_{6}C$, ${}^{15}_{7}N$, ${}^{17}_{9}F$

44. Sodium atoms and sodium ions:
(a) are chemically similar
(b) both react vigorously with water
(c) have same number of electrons
(d) have same number of protons

45. In ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$, which of the following is false?
(a) Both have 17 protons
(b) Both have 17 electrons
(c) Both have 18 neutrons
(d) Both show same chemical properties

46. Which of the following is isoelectronic with neon?
(a) O^{2-} (b) F^+ (c) Mg (d) Na

47. Neutrino has:
(a) charge +1, mass 1 (b) charge 0, mass 0
(c) charge −1, mass 1 (d) charge 0, mass 1

48. Positronium is the name given to an atom-like combination formed between: **(JIPMER 1991)**
(a) a positron and a proton
(b) a positron and a neutron

(c) a positron and an α-particle
(d) a positron and an electron

49. An isotone of ${}^{76}_{32}Ge$ is:
(a) ${}^{77}_{32}Ge$ (b) ${}^{78}_{33}As$ (c) ${}^{77}_{34}Se$ (d) ${}^{78}_{34}Se$

50. Which of the following does not characterise X-rays? **(IIT 1992)**
(a) The radiations can ionise gases
(b) It causes ZnS to fluorescence
(c) Deflected by electric and magnetic fields
(d) Have wavelengths shorter than ultraviolet rays

51. X-rays are produced when a stream of electrons in an X-ray tube:
(a) hits the glass wall of the tube
(b) strikes the metal target
(c) passes through a strong magnetic field
(d) none of the above

52. Radius of a nucleus is proportional to:
(a) A (b) $A^{1/3}$ (c) A^2 (d) $A^{2/3}$

53. The nature of positive rays produced in a vacuum discharge tube depends upon:
(a) the nature of the gas filled
(b) nature of the material of cathode
(c) nature of the material of anode
(d) the potential applied across the electrodes

54. Electromagnetic radiation with maximum wavelength is: **(MLNR 1991)**
(a) ultraviolet (b) radiowaves
(c) X-rays (d) infrared

55. The ratio of energy of radiations of wavelengths 2000 Å and 4000 Å is: **(CBSE 1994)**
(a) 2 (b) 4 (c) $1/2$ (d) $1/4$

56. The ratio of the diameter of the atom and the diameter of the nucleus is:
(a) 10^5 (b) 10^3 (c) 10 (d) 10^{-1}

57. The ratio of the volume of the atom and the volume of the nucleus is:
(a) 10^{10} (b) 10^{12} (c) 10^{15} (d) 10^{20}

58. Which of the following statements is incorrect?
(a) The frequency of radiation is inversely proportional to its wavelength
(b) Energy of radiation increases with increase in frequency
(c) Energy of radiation decreases with increase in wavelength
(d) The frequency of radiation is directly proportional to its wavelength

59. Visible light consists of rays with wavelengths in the approximate range of:
(a) 4000 Å to 7500 Å
(b) 4×10^{-3} cm to 7.5×10^{-4} cm
(c) 4000 nm to 7500 nm
(d) 4×10^{-5} m to 7.5×10^{-6} m

60. Which of the following statements concerning light is false?
(a) It is a part of the electromagnetic spectrum
(b) It travels with same velocity, *i.e.*, 3×10^{10} cm/s
(c) It cannot be deflected by a magnet
(d) It consists of photons of same energy

61. A 600 W mercury lamp emits monochromatic radiation of wavelength 331.3 nm. How many photons are emitted from the lamp per second ? **[PET (Kerala) 2010]**
($h = 6.626 \times 10^{-34}$ Js, velocity of light $= 3 \times 10^8$ ms^{-1})
(a) 1×10^{19} (b) 1×10^{20}
(c) 1×10^{21} (d) 1×10^{23}
(e) 1×10^{22}

[**Hint :** Power $= \dfrac{\text{Energy}}{\text{Time}}$

$$600 = \frac{nhc}{\lambda \times 1\text{ sec}}$$

$$600 = \frac{n \times 6.626 \times 10^{-34} \times 3 \times 10^8}{331.3 \times 10^{-9}}$$

$$n = 1 \times 10^{21}]$$

62. Out of X-rays, visible, ultraviolet, radiowaves, the largest frequency is of:
(a) X-rays (b) visible
(c) ultraviolet (d) radiowaves

63. The wave number which corresponds to electromagnetic radiations of 600 nm is equal to:
(a) 1.6×10^4 cm^{-1} (b) 0.16×10^4 cm^{-1}
(c) 16×10^4 cm^{-1} (d) 160×10^4 cm^{-1}

64. Line spectrum is characteristic of:
(a) molecules (b) atoms
(c) radicals (d) none of these

65. Which one of the following is not the characteristic of Planck's quantum theory of radiation? **(AIIMS 1991)**
(a) The energy is not absorbed or emitted in whole number multiple of quantum
(b) Radiation is associated with energy
(c) Radiation energy is not emitted or absorbed continuously but in the form of small packets called quanta
(d) This magnitude of energy associated with a quantum is proportional to the frequency

66. Which of the following among the visible colours has the minimum wavelength?
(a) Red (b) Blue
(c) Green (d) Violet

67. The spectrum of helium is expected to be similar to that of:
(a) H (b) Na (c) He^+ (d) Li^+

68. According to classical theory if an electron is moving in a circular orbit around the nucleus:
(a) it will continue to do so for sometime
(b) its orbit will continuously shrink
(c) its orbit will continuously enlarge
(d) it will continue to do so for all the time

69. Bohr advanced the idea of:
(a) stationary electrons (b) stationary nucleus
(c) stationary orbits (d) elliptical orbits

70. On Bohr stationary orbits:
(a) electrons do not move
(b) electrons move emitting radiations
(c) energy of the electron remains constant
(d) angular momentum of the electron is $\dfrac{h}{2\pi}$

71. Energy of Bohr orbit: **(DPMT 1991)**
(a) increases as we move away from the nucleus
(b) decreases as we move away from the nucleus
(c) remains the same as we move away from the nucleus
(d) none of the above

72. Which of the following statements does not form part of Bohr's model of the hydrogen atom?
(a) Energy of the electron in the orbit is quantized
(b) The electron in the orbit nearest to the nucleus has the lowest energy
(c) Electrons revolve in different orbit nucleus
(d) The position and velocity of the electron in the orbit cannot be determined simultaneously

73. Which of the following statements does not form a part of Bohr's model of hydrogen atom? **(DCE 2005)**
(a) Energy of the electrons in the orbit is quantised
(b) The electron in the orbit nearest to the nucleus has the lowest energy
(c) Electrons revolve in different orbits around the nucleus
(d) The position and velocity of the electrons in the orbit cannot be determined simultaneously

74. The radius of the first orbit of H-atom is r. Then the radius of the first orbit of Li^{2+} will be: **[AMU-PMT 2009]**
(a) $\frac{r}{9}$ (b) $\frac{r}{3}$ (c) $3r$ (d) $9r$

[Hint : $r = \frac{n^2}{z} \times 0.529 \text{Å}$**]**

75. The energy liberated when an excited electron returns to its ground state can have:
(a) any value from zero to infinity
(b) only negative values
(c) only specified positive values
(d) none of the above

76. On the basis of Bohr's model, the radius of the 3rd orbit is:
(a) equal to the radius of first orbit
(b) three times the radius of first orbit
(c) five times the radius of first orbit
(d) nine times the radius of first orbit

77. The ratio of 2nd, 4th and 6th orbits of hydrogen atom is:
(a) 2 : 4 : 6 (b) 1 : 4 : 9
(c) 1 : 4 : 6 (d) 1 : 2 : 3

78. Which point does not pertain to Bohr's model of atom?
(a) Angular momentum is an integral multiple of $h/(2\pi)$
(b) The path of the electron is circular
(c) Force of attraction towards nucleus = centrifugal force
(d) The energy changes are taking place continuously

79. The distance between 3rd and 2nd orbits in the hydrogen atom is:
(a) 2.646×10^{-8} cm (b) 2.116×10^{-8} cm
(c) 1.058×10^{-8} cm (d) 0.529×10^{-8} cm

80. The correct expression derived for the energy of an electron in the nth energy level in hydrogen atom is:
(a) $E_n = \frac{2\pi^2 me^4}{n^2h^2}$ (b) $E_n = -\frac{2\pi^2 me^4}{nh^2}$
(c) $E_n = -\frac{2\pi me^2}{n^2h^2}$ (d) $E_n = -\frac{2\pi^2 me^4}{n^2h^2}$

81. According to Bohr theory, the angular momentum for an electron of 5th orbit is:
(a) $5h/\pi$ (b) $2.5h/\pi$ (c) $5\pi/h$ (d) $25h/\pi$

82. The value of Bohr radius of hydrogen atom is: **(CBSE 1991)**
(a) 0.529×10^{-7} cm (b) 0.529×10^{-8} cm
(c) 0.529×10^{-9} cm (d) 0.529×10^{-10} cm

83. The energy of an electron in the nth Bohr orbit of hydrogen atom is: **(CBSE 1992)**
(a) $-\frac{13.6}{n^4}$ eV (b) $-\frac{13.6}{n^3}$ eV (c) $-\frac{13.6}{n^2}$ eV (d) $-\frac{13.6}{n}$ eV

84. Which of the following electron transitions in hydrogen atom will require largest amount of energy? **(MLNR 1992)**
(a) from $n = 1$ to $n = 2$ (b) from $n = 2$ to $n = 3$
(c) from $n = \infty$ to $n = 1$ (d) from $n = 3$ to $n = 5$

85. For a hydrogen atom, the energies that an electron can have are given by the expression, $E = -13.58/n^2$ eV, where n is an integer. The smallest amount of energy that a hydrogen atom in the ground state can absorb is:
(a) 1.00 eV (b) 3.39 eV (c) 6.79 eV (d) 10.19 eV

86. The energy of hydrogen atom in its ground state is −13.6 eV. The energy of the level corresponding to $n = 5$ is: **(CBSE 1990)**
(a) − 0.54 eV (b) − 5.40 eV (c) − 0.85 eV (d) − 2.72 eV

87. $E_n = -313.6/n^2$ kcal/mol. If the value of $E = -34.84$ kcal/mol, to which value does 'n' correspond?
(a) 4 (b) 3 (c) 2 (d) 1

88. The ratio of the difference between 1st and 2nd Bohr orbits energy to that between 2nd and 3rd orbits energy is:
(a) 1/2 (b) 1/3 (c) 27/5 (d) 5/27

89. Bohr's model can explain:
(a) spectrum of hydrogen atom only
(b) spectrum of any atom or ion having one electron only
(c) spectrum of hydrogen molecule
(d) solar spectrum

90. The energy difference between two electronic states is 43.56 kcal/mol. The frequency of light emitted when the electron drops from higher orbit to lower orbit, is:
(Planck's constant = 9.52×10^{-14} kcal/mol)
(a) 9.14×10^{14} cycle/sec (b) 45.7×10^{14} cycle/sec
(c) 91.4×10^{14} cycle/sec (d) 4.57×10^{14} cycle/sec

91. Which of the following transitions of an electron in hydrogen atom emits radiation of the lowest wavelength? **[EAMCET (Engg.) 2010]**
(a) $n_2 = \infty$ to $n_1 = 2$ (b) $n_2 = 4$ to $n_1 = 3$
(c) $n_2 = 2$ to $n_1 = 1$ (d) $n_2 = 5$ to $n_1 = 3$

92. The wavelength of a spectral line for an electronic transition is inversely related to:
(a) number of electrons undergoing transition
(b) the nuclear charge of the atom
(c) the velocity of an electron undergoing transition
(d) the difference in the energy levels involved in the transition

93. The ionisation energy of the electron in the 1*s*-orbital of the hydrogen atom is 13.6 eV. The energy of the electron after promotion to 2*s*-orbital is: **[ISC (Bihar) 1993]**
(a) −3.4 eV (b) −13.6 eV
(c) −27.2 eV (d) 0.0 eV

94. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit it?
(a) 1*s* (b) 2*s* (c) 3*s* (d) 4*s*

95. The spectral lines corresponding to the radiation emitted by an electron jumping from 6th, 5th and 4th orbits to second orbit belong to:
(a) Lyman series (b) Balmer series
(c) Paschen series (d) Pfund series

96. The spectral lines corresponding to the radiation emitted by an electron jumping from higher orbits to first orbit belong to:
(a) Paschen series (b) Balmer series
(c) Lyman series (d) None of these

97. In a hydrogen atom, the transition takes place from $n = 3$ to $n = 2$. If Rydberg constant is $1.097 \times 10^7\ \text{m}^{-1}$, the wavelength of the emitted radiation is:
(a) 6564 Å (b) 6064 Å
(c) 6664 Å (d) 5664 Å

[**Hint:** Apply $\frac{1}{\lambda} = R\left[\frac{1}{x^2} - \frac{1}{y^2}\right]$]

98. The speed of the electron in the 1st orbit of the hydrogen atom in the ground state is (c is the velocity of light):
(a) $\frac{c}{1.37}$ (b) $\frac{c}{1370}$ (c) $\frac{c}{13.7}$ (d) $\frac{c}{137}$

[**Hint:** Velocity of electron in the 1st orbit, $v = h/(2\pi mr)$ $= 2.189 \times 10^8$ cm/sec.; velocity of light, $c = 3 \times 10^{10}$ cm/sec. Ratio $c/v = 137$]

99. Find the value of wave number $\bar{\nu}$ in terms of Rydberg's constant, when transition of electron takes place between two levels of He^+ ion whose sum is 4 and difference is 2.
(a) $\frac{8R}{9}$ (b) $\frac{32R}{9}$
(c) $\frac{3R}{4}$ (d) None of these

[**Hint :** $n_1 + n_2 = 4, \quad n_2 - n_1 = 2 \quad \therefore \quad n_1 = 1, n_2 = 3$

$$\bar{\nu} = RZ^2\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$= R \times 2^2\left[\frac{1}{1} - \frac{1}{3^2}\right] = \frac{32R}{9}$$]

100. With the increasing principal quantum number, the energy difference between adjacent energy levels in hydrogen atom:
(a) increases (b) decreases
(c) is the same (d) none of these

101. An electron in an atom: **[CEET (Bihar) 1992]**
(a) moves randomly around the nucleus
(b) has fixed space around the nucleus
(c) is stationary in various energy levels
(d) moves around its nucleus in definite energy levels

102. The wave number of first line of Balmer series of hydrogen is 15200 cm^{-1}. The wave number of the first Balmer line of Li^{2+} ion is: **[IIT (Screening) 1992]**
(a) 15,200 cm^{-1} (b) 60,800 cm^{-1}
(c) 76,000 cm^{-1} (d) 1,36,800 cm^{-1}

103. "The position and the velocity of a small particle like electron cannot be simultaneously determined." This statement is:
(a) Heisenberg uncertainty principle
(b) Pauli's exclusion principle
(c) aufbau's principle
(d) de Broglie's wave nature of the electron

104. de Broglie equation describes the relationship of wavelength associated with the motion of an electron and its:
(a) mass (b) energy (c) momentum (d) charge

105. If the magnetic quantum number of a given atom is represented by −3, then what will be its principal quantum number? **[BHU (Pre.) 2005]**
(a) 2 (b) 3 (c) 4 (d) 5

106. Which of the following relates to photons both as wave motion and as a stream of particles? **(IIT 1992)**
(a) Interference (b) Diffraction
(c) $E = h\nu$ (d) $E = mc^2$

107. If uncertainty in the position of an electron is zero, the uncertainty in its momentum would be:
(a) zero (b) $< h/(4\pi)$
(c) $> h/(4\pi)$ (d) infinite

108. Which one of the following explains light both as a stream of particles and as wave motion?
(a) Diffraction (b) $\lambda = h/p$
(c) Interference (d) Photoelectric effect

109. A body of mass x kg is moving with velocity of 100 m sec^{-1}. Its de Broglie wavelength is 6.62×10^{-35} m. Hence x is:
($h = 6.62 \times 10^{-34}$ J sec) **[CET (Karnataka) 2009]**
(a) 0.25 kg (b) 0.15 kg
(c) 0.2 kg (d) 0.1 kg

110. A 200 g cricket ball is thrown with a speed of 3.0×10^3 cm sec^{-1}. What will be its de Broglie's wavelength?
($h = 6.6 \times 10^{-27}$ g cm^2 sec^{-1}) **[CET (Gujarat) 2008]**
(a) 1.1×10^{-32} cm (b) 2.2×10^{-32} cm
(c) 0.55×10^{-32} cm (d) 11.0×10^{-32} cm

111. The electronic configuration of a dipositive ion M^{2+} is 2, 8, 14 and its atomic mass is 56. The number of neutrons in the nucleus would be:
(a) 30 (b) 32 (c) 34 (d) 42

112. An element with atomic number 20 will be placed in which period of the periodic table?
(a) 5th (b) 4th (c) 3rd (d) 2nd

113. The frequency of radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionisation energy of $H = 2.18 \times 10^{-18}$ J atom^{-1} and $h = 6.626 \times 10^{-34}$ Js): **[Manipal (Med.) 2007]**
(a) 1.54×10^{15} s^{-1} (b) 1.03×10^{15} s^{-1}
(c) 3.08×10^{15} s^{-1} (d) 2×10^{15} s^{-1}

114. In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields? **(AIEEE 2005)**
(i) $n = 1, l = 0, m = 0$ (ii) $n = 2, l = 0, m = 0$

(iii) $n = 2, l = 1, m = 1$ (iv) $n = 3, l = 2, m = 1$
(v) $n = 3, l = 2, m = 0$
(a) (i) and (ii) (b) (ii) and (iii)
(c) (iii) and (iv) (d) (iv) and (v)

115. Which of the ions is not having the configuration of Ne?
(a) Cl^- (b) F^- (c) Na^+ (d) Mg^{2+}

116. Which of the following has the maximum number of unpaired *d*-electrons? **(KCET 2008)**
(a) Ni^{3+} (b) Cu^+ (c) Zn^{2+} (d) Fe^{2+}

117. Which of the following expressions gives the de Broglie relationship? **[JEE (WB) 2008]**
(a) $p = \frac{h}{mv}$ (b) $\lambda = \frac{h}{mv}$
(c) $\lambda = \frac{h}{mp}$ (d) $\lambda m = \frac{h}{p}$

118. The principal quantum number of an atom is related to the: **(MLNR 1990)**
(a) size of the orbital
(b) orbital angular momentum
(c) spin angular momentum
(d) orientation of the orbital in space

119. The magnetic quantum is a number related to:
(a) size (b) shape
(c) orientation (d) spin

120. The principal quantum number represents: **(CPMT 1991)**
(a) shape of an orbital
(b) number of electrons in an orbit
(c) distance of electron from nucleus
(d) number of orbitals in an orbit

121. The quantum number not obtained from the Schrödinger's wave equation is: **(IIT 1990)**
(a) n (b) l (c) m (d) s

122. In a given atom, no two electrons can have the same values for all the four quantum numbers. This is called: **(CPMT 1990)**
(a) Hund's rule (b) Pauli's exclusion principle
(c) Uncertainty principle (d) aufbau principle

123. The atomic orbital is:
(a) the circular path of the electron
(b) elliptical shaped orbit
(c) three-dimensional field around nucleus
(d) the region in which there is maximum probability of finding an electron

124. If the ionization energy for hydrogen atom is 13.6 eV, then the ionization energy for He^+ ion should be: **[PMT (Haryana) 2004]**
(a) 13.6 eV (b) 6.8 eV
(c) 54.4 eV (d) 72.2 eV

125. Principal, azimuthal and magnetic quantum numbers are respectively related to:
(a) size, shape and orientation
(b) shape, size and orientation
(c) size, orientation and shape
(d) none of the above

126. Energy of electron in the H-atom is determined by :
(a) only n (b) both n and l
(c) n, l and m (d) all the four quantum numbers

127. Any *p*-orbital can accommodate up to: **(MLNR 1990)**
(a) 4 electrons
(b) 2 electrons with parallel spins
(c) 6 electrons
(d) 2 electrons with opposite spins

128. How many electrons can fit into the orbitals that comprise the 3rd quantum shell $n = 3$?
(a) 2 (b) 8 (c) 18 (d) 32

129. The total number of orbitals in a principal shell is:
(a) n (b) n^2 (c) $2n^2$ (d) $3n^2$

130. Two electrons in K-shell will differ in:
(a) principal quantum number
(b) spin quantum number
(c) azimuthal quantum number
(d) magnetic quantum number

131. Which one of the following orbitals has the shape of a baby-boother ?
(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (d) p_y

132. Which one of the following represents an impossible arrangement? **(AIEEE 2009)**

	n	l	m	s		n	l	m	s
(a)	3	2	−2	1/2	(b)	4	0	0	1/2
(c)	3	2	−3	1/2	(d)	5	3	0	1/2

133. Which of the following sets of quantum numbers is correct for an electron in 4*f*-orbital? **(AIEEE 2004)**
(a) $n = 4, l = 3, m = +4, s = +1/2$
(b) $n = 4, l = 4, m = -4, s = -1/2$
(c) $n = 4, l = 3, m = +1, s = +1/2$
(d) $n = 3, l = 2, m = -2, s = +1/2$

134. The correct quantum numbers of 3*p*-electrons are: **[PMT (Raj.) 2004]**
(a) $n = 3, l = 2, m = +2, s = +1/2$
(b) $n = 3, l = 1, m = -1, s = -1/2$
(c) $n = 3, l = -2, m = -2, s = +1/2$
(d) none of the above

135. In any subshell, the maximum number of electrons having same values of spin quantum number is :
(a) $\sqrt{l(l+1)}$ (b) $l + 2$
(c) $2l + 1$ (d) $4l + 2$

[**Hint :** Number of electrons with same spin

$$= \frac{1}{2} \times \text{Total no. of electrons}$$
$$= \frac{1}{2} \times 2(2l + 1) = (2l + 1)]$$

136. Which of the following represents the correct set of four quantum numbers of a 4*d*-electron? **(MLNR 1992)**
(a) $4, 3, 2, +1/2$ (b) $4, 2, 1, 0$
(c) $4, 3, -2, +1/2$ (d) $4, 2, 1, -1/2$

137. Values of magnetic orbital quantum number for an electron of M-shell can be : **[PET (Raj.) 2008]**
(a) 0, 1, 2 (b) −2, −1, 0, +1, +2
(c) 0, 1, 2, 3 (d) −1, 0, +1

138. Correct set of four quantum numbers for the outermost electron of rubidium ($Z = 37$) is:

(a) 5, 0, 0, 1/2 (b) 5, 1, 0, 1/2
(c) 5, 1, 1, 1/2 (d) 6, 0, 0, 1/2

139. Which one of the following subshells is spherical in shape?
(a) 4*s* (b) 4*p* (c) 4*d* (d) 4*f*

140. In hydrogen atom, the electron is at a distance of 4.768 Å from the nucleus. The angular momentum of the electron is : **[EAMCET (Med.) 2010]**
(a) $\frac{3h}{2\pi}$ (b) $\frac{h}{2\pi}$
(c) $\frac{h}{\pi}$ (d) $\frac{3h}{\pi}$

[**Hint :** $r = \frac{n^2}{z} \times 0.529$ Å

$4.768 = \frac{n^2}{1} \times 0.529$

$n = 3$

$\therefore$ Angular momentum $(mvr) = \frac{nh}{2\pi} = \frac{3h}{2\pi}$]

141. Total number of *m* values for $n = 4$ is:
(a) 8 (b) 16 (c) 12 (d) 20

142. What is the total number of orbitals in the shell to which the *g*-subshell first arise?
(a) 9 (b) 16 (c) 25 (d) 36

[**Hint :** For *g*-subshell, $l = 4$

$\therefore$ It will arise in 5th shell.

Total number of orbitals in 5th shell = $n^2 = 25$]

143. In Bohr's model, if the atomic radius of the first orbit r_1, then radius of fourth orbit will be : **[BHU (Screening) 2010]**
(a) $4r_1$ (b) $6r_1$ (c) $16r_1$ (d) $\frac{r_1}{16}$

144. Which of the following statements is not correct for an electron that has quantum numbers $n = 4$ and $m = 2$? **(MLNR 1993)**
(a) The electron may have the q. no. $l = +1/2$
(b) The electron may have the q. no. $l = 2$
(c) The electron may have the q. no. $l = 3$
(d) The electron may have the q. no. $l = 0, 1, 2, 3$

145. The angular momentum of an electron depends on:
(a) principal quantum number
(b) azimuthal quantum number
(c) magnetic quantum number
(d) all of the above

146. The correct set of quantum numbers for the unpaired electron of a chlorine atom is: **(DPMT 2009)**
(a) $2, 0, 0, +\frac{1}{2}$ (b) $2, 1, -1, +\frac{1}{2}$
(c) $3, 1, -1, \pm\frac{1}{2}$ (d) $3, 0, 0, \pm\frac{1}{2}$

147. The magnetic quantum number for valency electron of sodium atom is:
(a) 3 (b) 2 (c) 1 (d) zero

148. The shape of the orbital is given by: **[PET (Raj.) 2008]**
(a) spin quantum number
(b) magnetic quantum number
(c) azimuthal quantum number
(d) principal quantum number

149. The energy of an electron of $2p_y$ orbital is:
(a) greater than $2p_x$ orbital
(b) less than $2p_z$ orbital
(c) equal to 2*s* orbital
(d) same as that of $2p_x$ and $2p_z$ orbitals

150. The two electrons occupying the same orbital are distinguished by:
(a) principal quantum number
(b) azimuthal quantum number
(c) magnetic quantum number
(d) spin quantum number

151. The maximum number of electrons in a subshell is given by the expression: **(AIEEE 2009)**
(a) $4l + 2$ (b) $4l - 2$
(c) $2l + 1$ (d) $2n^2$

152. The electronic configuration of an atom/ion can be defined by which of the following?
(a) Aufbau principle
(b) Pauli's exclusion principle
(c) Hund's rule of maximum multiplicity
(d) All of the above

153. An electron has a spin quantum number +1/2 and a magnetic quantum number − 1. It cannot be present in:
(a) *d*-orbital (b) *f*-orbital (c) *s*-orbital (d) *p*-orbital

154. The value of azimuthal quantum number for electrons present in 4*p*-orbitals is:
(a) 1
(b) 2
(c) any value between 0 and 3 except 1
(d) zero

155. For the energy levels in an atom which one of the following statements is correct?
(a) The 4*s* sub-energy level is at a higher energy than the 3*d* sub-energy level
(b) The *M*-energy level can have maximum of 32 electrons
(c) The second principal energy level can have four orbitals and contain a maximum of 8 electrons
(d) The 5th main energy level can have maximum of 50 electrons

156. A new electron enters the orbital when:
(a) $(n + l)$ is minimum (b) $(n + l)$ is maximum
(c) $(n + m)$ is minimum (d) $(n + m)$ is maximum

157. For a given value of *n* (principal quantum number), the energy of different subshells can be arranged in the order of:
(a) $f > d > p > s$ (b) $s > p > d > f$
(c) $f > p > d > s$ (d) $s > f > p > d$

158. After filling the 4*d*-orbitals, an electron will enter in:
(a) 4*p* (b) 4*s* (c) 5*p* (d) 4*f*

159. According to Aufbau principle, the correct order of energy of 3*d*, 4*s* and 4*p*-orbitals is: **[CET (J&K) 2006]**
(a) $4p < 3d < 4s$ (b) $4s < 4p < 3d$
(c) $4s < 3d < 4p$ (d) $3d < 4s < 4p$

160. Number of *p*-electrons in bromine atom is: **[PMT (Haryana) 2004]**
(a) 12 (b) 15
(c) 7 (d) 17

161. [Ar] $3d^{10}4s^1$ electronic configuration belongs to: **[PET (MP) 2008]**

(a) Ti (b) Tl (c) Cu (d) V

162. How many unpaired electrons are there in Ni^{2+} ? ($Z = 28$)

(a) Zero (b) 8 (c) 2 (d) 4

163. The electronic configuration of chromium ($Z = 24$) is: **[PMT (MP) 1993; BHU (Pre.) 2005]**

(a) [Ne] $3s^2 3p^6 3d^4 4s^2$ (b) [Ne] $3s^2 3p^6 3d^5 4s^1$

(c) [Ne] $3s^2 3p^6 3d^1 4s^2$ (d) [Ne] $3s^2 3p^6 4s^2 4p^4$

164. The number of d-electrons in Fe^{2+} (At. No. 26) is not equal to that of the: **(MLNR 1993)**

(a) p-electrons in Ne (At. No. 10)

(b) s-electrons in Mg (At. No. 12)

(c) d-electrons in Fe atom

(d) p-electrons in Cl^- ion (At. No. 17)

165. If the electronic structure of oxygen atom is written as

$1s^2, 2s^2 \overset{\longleftarrow 2p \longrightarrow}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{}}$; it would violate: **[ISC (Bihar) 1993]**

(a) Hund's rule

(b) Pauli's exclusion principle

(c) both Hund's and Pauli's principles

(d) none of the above

166. The orbital diagram in which 'aufbau principle' is violated, is:

$2s$ $\longleftarrow 2p \longrightarrow$

(a) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}$

(b) $\boxed{\uparrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

(c) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

(d) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

167. The manganese ($Z = 25$) has the outer configuration:

$4s$ $\longleftarrow 3p \longrightarrow$

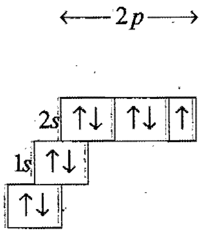
(a) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

(b) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

(c) $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}\boxed{}$

(d) $\boxed{}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$

168. Which of the following elements is represented by the electronic configuration?



(a) Nitrogen (b) Fluorine

(c) Oxygen (d) Neon

169. The radial probability distribution curve obtained for an orbital wave function (ψ) has 3 peaks and 2 radial nodes. The valence electron of which one of the following metals does this wave function (ψ) correspond to ? **[EAMCET (Med.) 2010]**

(a) Co (b) Li (c) K (d) Na

[**Hint :** $Na_{11} \longrightarrow 1s^2, 2s^2 2p^6, \underbrace{3s^1}_{\text{Valence electron}}$

Number of radial node $= n - l - 1$ ($n = 3$)

$= 3 - 0 - 1 = 2$]

170. Krypton (At. No. 36) has the electronic configuration [A] $4s^2 3d^{10} 4p^6$. The 37th electron will go into which one of the following sub-levels?

(a) $4f$ (b) $4d$

(c) $3p$ (d) $5s$

171. An ion which has 18 electrons in the outermost shell is: **(CBSE 1990)**

(a) K^+ (b) Cu^+ (c) Cs^+ (d) Th^{4+}

172. Which of the following has non-spherical shell of electrons? **(IIT 1993)**

(a) He (b) B (c) Be (d) Li

173. Which one of the following sets of quantum numbers is not possible for an electron in the ground state of an atom with atomic number 19? **[PET (Kerala) 2006; CET (Karnataka) 2009]**

(a) $n = 2, l = 0, m = 0$ (b) $n = 2, l = 1, m = 0$

(c) $n = 3, l = 1, m = -1$ (d) $n = 3, l = 2, m = \pm 2$

(e) $n = 4, l = 0, m = 0$

174. Helium nucleus is composed of two protons and two neutrons. If the atomic mass is 4.00388, how much energy is released when the nucleus is constituted?

(Mass of proton = 1.00757, Mass of neutron = 1.00893)

(a) 283 MeV (b) 28.3 MeV

(c) 2830 MeV (d) 2.83 MeV

175. Binding energy per nucleon of three nuclei A, B and C are 5.5, 8.5 and 7.5 respectively. Which one of the following nuclei is most stable?

(a) A (b) C

(c) B (d) Cannot be predicted

176. The mass of ${}^7_3Li$ is 0.042 less than the mass of 3 protons and 4 neutrons. The binding energy per nucleon in ${}^7_3Li$ is: **(BHU 1992)**

(a) 5.6 MeV (b) 56 MeV (c) 0.56 MeV (d) 560 MeV

177. Meson was discovered by:

(a) Powell (b) Seaborg

(c) Anderson (d) Yukawa

178. In most stable elements, the number of protons and neutrons are:

(a) odd-odd (b) even-even

(c) odd-even (d) even-odd

179. Nuclear particles responsible for holding all nucleons together are:

(a) electrons (b) neutrons

(c) positrons (d) mesons

180. The introduction of a neutron into the nuclear composition of an atom would lead to a change in: **(MLNR 1995)**

(a) its atomic mass
(b) its atomic number
(c) the chemical nature of the atom
(d) number of the electron also

181. Which of the following has highest orbital angular momentum?
(a) $4s$ (b) $4p$ (c) $4d$ (d) $4f$

182. Which of the following has maximum number of unpaired electrons? **[PMT (Raj.) 2004; BHU (Pre.) 2005]**
(a) Fe^{3+} (b) Fe^{2+} (c) Co^{2+} (d) Co^{3+}

183. An electron is not deflected on passing through a certain region, because:
(a) there is no magnetic field in that region
(b) there is a magnetic field but velocity of the electron is parallel to the direction of magnetic field
(c) the electron is a chargeless particle
(d) none of the above

184. In Millikan's oil drop experiment, we make use of:
(a) Ohm's law (b) Ampère's law
(c) Stoke's law (d) Faraday's law

185. A strong argument for the particle nature of cathode rays is:
(a) they can propagate in vacuum
(b) they produce fluorescence
(c) they cast shadows
(d) they are deflected by electric and magnetic fields

186. As the speed of the electrons increases, the measured value of charge to mass ratio (in the relativistic units):
(a) increases
(b) remains unchanged
(c) decreases
(d) first increases and then decreases

187. Which of the following are true for cathode rays?
(a) It travels along a straight line
(b) It emits X-rays when strikes a metal
(c) It is an electromagnetic wave
(d) It is not deflected by magnetic field

188. Three isotopes of an element have mass numbers, M, $(M+1)$ and $(M+2)$. If the mean mass number is $(M+0.5)$ then which of the following ratios may be accepted for $M, (M+1), (M+2)$ in that order?
(a) 1 : 1 : 1 (b) 4 : 1 : 1
(c) 3 : 2 : 1 (d) 2 : 1 : 1

189. The radii of two of the first four Bohr orbits of the hydrogen atom are in the ratio 1 : 4. The energy difference between them may be:
(a) either 12.09 eV or 3.4 eV (b) either 2.55 eV or 10.2 eV
(c) either 13.6 eV or 3.4 eV (d) either 3.4 eV or 0.85 eV

190. Photoelectric emission is observed from a surface for frequencies ν_1 and ν_2 of the incident radiation $(\nu_1 > \nu_2)$. If the maximum kinetic energies of the photoelectrons in the two cases are in the ratio $1 : k$ then the threshold frequency ν_0 is given by:
(a) $\frac{\nu_2 - \nu_1}{k-1}$ (b) $\frac{k\nu_1 - \nu_2}{k-1}$ (c) $\frac{k\nu_2 - \nu_1}{k-1}$ (d) $\frac{\nu_2 - \nu_1}{k}$

191. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number +2 is:
(a) 3 (b) 4 (c) 2 (d) 1

192. A certain negative ion X^{2-} has in its nucleus 18 neutrons and 18 electrons in its extranuclear structure. What is the mass number of the most abundant isotope of X?
(a) 36 (b) 35.46 (c) 32 (d) 39

193. Which of the following statements is not correct?
(a) The shape of an atomic orbital depends on the azimuthal quantum number
(b) The orientation of an atomic orbital depends on the magnetic quantum number
(c) The energy of an electron in an atomic orbital of multielectron atom depends on the principal quantum number
(d) The number of degenerate atomic orbitals of one type depends on the values of azimuthal and magnetic quantum numbers

194. Gases begin to conduct electricity at low pressure because: **(CBSE 1994)**
(a) at low pressures gases turn to plasma
(b) colliding electrons can acquire higher kinetic energy due to increased mean free path leading to ionisation of atoms
(c) atoms break up into electrons and protons
(d) the electrons in atoms can move freely at low pressure

195. An electron of mass m and charge e, is accelerated from rest through a potential difference V in vacuum. Its final speed will be: **(CBSE 1994)**
(a) $\sqrt{(eV/m)}$ (b) $2eV/m$
(c) $\sqrt{(eV/2m)}$ (d) $\sqrt{(2eV/m)}$

196. The difference in angular momentum associated with the electron in the two successive orbits of hydrogen atom is:
(a) h/π (b) $h/2\pi$ (c) $h/2$ (d) $(n-1)h/2\pi$

197. Photoelectric effect can be explained by assuming that light:
(a) is a form of transverse waves
(b) is a form of longitudinal waves
(c) can be polarised
(d) consists of quanta

198. The photoelectric effect supports quantum nature of light because:
(a) there is a minimum frequency of light below which no photoelectrons are emitted
(b) the maximum kinetic energy of photoelectrons depends only on the frequency of light and not on its intensity
(c) even when metal surface is faintly illuminated the photoelectrons leave the surface immediately
(d) electric charge of photoelectrons is quantised

199. The mass of a proton at rest is: **(CBSE 1991)**
(a) zero (b) 1.67×10^{-35} kg
(c) one amu (d) 9×10^{-31} kg

200. Momentum of a photon of wavelength λ is: **(CBSE 1993)**
(a) h/λ (b) zero (c) $h\lambda/c^2$ (d) $h\lambda/c$

201. When X-rays pass through air they:
(a) produce light track in the air
(b) ionise the gas

(c) produce fumes in the air
(d) accelerate gas atoms

202. X-rays: **(CPMT 1991)**
(a) are deflected in a magnetic field
(b) are deflected in an electric field
(c) remain undeflected by both the fields
(d) are deflected in both the fields

203. Find the frequency of light that corresponds to photons of energy 5.0×10^{-5} erg: **(AIIMS 2010)**
(a) $7.5 \times 10^{-21} \text{sec}^{-1}$ (b) 7.5×10^{-21} sec
(c) 7.5×10^{21} sec^{-1} (d) 7.5×10^{21} sec

[**Hint :** $\nu = \dfrac{E}{h} = \dfrac{5 \times 10^{-5} \text{ erg}}{6.63 \times 10^{-27} \text{ erg sec}}$
$= 7.54 \times 10^{21} \text{ sec}^{-1}$]

204. The energy of an electron in the first Bohr orbit of H-atom is -13.6 eV. The possible energy value(s) of the excited state(s) for electrons in Bohr orbits of hydrogen is/are: **(IIT 1998)**
(a) -3.4 eV (b) -4.2 eV
(c) -6.8 eV (d) $+6.8$ eV

205. The electrons identified by quantum numbers n and l, (i) $n = 4$, $l = 1$ (ii) $n = 4, l = 0$ (iii) $n = 3, l = 2$ (iv) $n = 3, l = 1$ can be placed in order of increasing energy, from the lowest to highest as: **(IIT 1999)**
(a) (iv) < (ii) < (iii) < (i) (b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv) (d) (iii) < (i) < (iv) < (ii)

206. The wavelength of the radiation emitted when an electron falls from Bohr orbit 4 to 2 in hydrogen atom is: **(IIT 1999)**
(a) 243 nm (b) 972 nm
(c) 486 nm (d) 182 nm

207. The energy of the electron in the first orbit of He^+ is -871.6×10^{-20} J. The energy of the electron in the first orbit of hydrogen would be: **(IIT 1998)**
(a) -871.6×10^{-20} J (b) -435×10^{-20} J
(c) -217.9×10^{-20} J (d) -108.9×10^{-20} J

208. The wavelength associated with a golf ball weighing 200 g and moving with a speed of 5 m/h is of the order of: **(IIT 2000)**
(a) 10^{-10} m (b) 10^{-20} m (c) 10^{-30} m (d) 10^{-40} m

209. Who modified Bohr theory by introducing elliptical orbits for electron path? **(CBSE 1999)**
(a) Hund (b) Thomson
(c) Rutherford (d) Sommerfeld

210. The uncertainty in momentum of an electron is 1×10^{-5} kg ms^{-1}. The uncertainty in its position will be:
($h = 6.62 \times 10^{-34}$ kg-m^2-s) **(CBSE 1999; BHU 2010)**
(a) 1.05×10^{-28} m (b) 1.05×10^{-26} m
(c) 5.27×10^{-30} m (d) 5.25×10^{-28} m

211. The Bohr orbit radius for the hydrogen atom ($n = 1$) is approximately 0.530 Å. The radius for the first excited state ($n = 2$) orbits is: **(CBSE 1998)**
(a) 0.13 Å (b) 1.06 Å (c) 4.77 Å (d) 2.12 Å

212. The number of nodal planes in p_x-orbital is: **(IIT 2000)**
(a) one (b) two (c) three (d) zero

213. The angular momentum (L) of an electron in a Bohr orbit is given as: **(IIT 1997)**
(a) $L = \dfrac{nh}{2\pi}$ (b) $L = \sqrt{l(l+1)}\dfrac{h}{2\pi}$
(c) $L = \dfrac{mg}{2\pi}$ (d) $L = \dfrac{h}{4\pi}$

214. Ground state electronic configuration of nitrogen atom can be represented by: **(IIT 1999)**

1. $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$ 2. $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\,|\,\downarrow\,|\,\uparrow}$
3. $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\uparrow\,|\,\downarrow\,|\,\downarrow}$ 4. $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\ \boxed{\downarrow\,|\,\downarrow\,|\,\downarrow}$

(a) 1 only (b) 1,2 only (c) 1,4 only (d) 2,3 only

215. Which of the following statement(s) are correct?
1. Electronic configuration of Cr is [Ar] $3d^5 4s^1$ (At. No. of Cr = 24)
2. The magnetic quantum number may have negative value
3. In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (At. No. of Ag = 47)
4. The oxidation state of nitrogen in HN_3 is -3 **(IIT 1998)**

(a) 1,2,3 (b) 2,3,4 (c) 3,4 (d) 1,2,4

216. The electronic configuration of an element is $1s^2 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$. This represents: **(IIT 2000)**
(a) excited state (b) ground state
(c) cationic state (d) anionic state

217. The quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ for the electron spin represents: **(IIT 2000)**
(a) rotation of the electron in clockwise and anticlockwise directions respectively
(b) rotation of the electron in anticlockwise and clockwise directions respectively
(c) magnetic moment of electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogues

218. Rutherford's experiment, which established the nuclear model of the atom, used a beam of: **(IIT 2002)**
(a) β-particles, which impinged on a metal foil and got absorbed
(b) γ-rays, which impinged on a metal foil and ejected electrons
(c) helium atoms, which impinged on a metal foil and got scattered
(d) helium nuclei, which impinged on a metal foil and got scattered

219. How many moles of electrons weigh one kilogram?
(Mass of electron = 9.108×10^{-31} kg, Avogadro's number = 6.023×10^{23}) **(IIT 2002)**
(a) 6.023×10^{23} (b) $\dfrac{1}{9.108} \times 10^{31}$
(c) $\dfrac{6.023}{9.108} \times 10^{54}$ (d) $\dfrac{1}{9.108 \times 6.023} \times 10^{8}$

220. If the electronic configuration of nitrogen had $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$ because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates: **(IIT 2002)**

(a) Heisenberg uncertainty principle
(b) Hund's rule
(c) Pauli's exclusion principle
(d) Bohr postulates of stationary orbits

221. The orbital angular momentum of an electron in 2*s*-orbital is: **[IIT 1996; AIEEE 2003; PMT (MP) 2004]**

(a) $+\frac{1}{2}\frac{h}{2\pi}$ (b) zero
(c) $\frac{h}{2\pi}$ (d) $\sqrt{2}\frac{h}{2\pi}$

222. Calculate the wavelength (in nanometre) associated with a proton moving at 1×10^3 m sec^{-1}.
(mass of proton = 1.67×10^{-27} kg, $h = 6.63\times10^{-34}$ J sec) **(AIEEE 2009)**

(a) 0.032 nm (b) 0.40 nm
(c) 2.5 nm (d) 14 nm

[**Hint :** $\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34}}{1.67\times10^{-27}\times10^3}$

$= 0.397\times10^{-9}$ m $= 0.4$ nm]

223. The value of Planck's constant is 6.63×10^{-34} J-s. The velocity of light is 3×10^8 m/sec. Which value is closest to the wavelength in nanometer of a quantum of light with frequency of 8×10^{15} sec^{-1}? **[CBSE (PMT) 2003]**

(a) 5×10^{-18} (b) 4×10^1
(c) 3×10^7 (d) 2×10^{-25}

224. Which of the following statements in relation to the hydrogen atom is correct? **(AIEEE 2005)**

(a) 3*s*-orbital is lower in energy than 3*p*-orbital
(b) 3*p*-orbital is lower in energy than 3*d*-orbital
(c) 3*s*-and 3*p*-orbitals are of lower energy than 3*d*-orbital
(d) 3*s*, 3*p*-and 3*d*-orbitals all have the same energy

225. The number of *d*-electrons in Ni (At. No. = 28) is equal to that of the: **[CPMT (UP) 2004]**

(a) *s* and *p*-electrons in F^-
(b) *p*-electrons in Ar (At. No. = 18)
(c) *d*-electrons in Ni^{2+}
(d) total number of electrons in N (At. No. = 7)

226. The number of radial nodes of 3*s*- and 2*p*-orbitals are respectively: **[IIT (Screening) 2005]**

(a) 2, 0 (b) 0, 2 (c) 1, 2 (d) 2, 1

227. Which of the following is not permissible? **(DCE 2005)**

(a) $n = 4, l = 3, m = 0$ (b) $n = 4, l = 2, m = 1$
(c) $n = 4, l = 4, m = 1$ (d) $n = 4, l = 0, m = 0$

228. According to Bohr theory, the angular momentum of electron in 5th orbit is: **(AIEEE 2006)**

(a) $25\frac{h}{\pi}$ (b) $1\frac{h}{\pi}$ (c) $10\frac{h}{\pi}$ (d) $2.5\frac{h}{\pi}$

229. Which of the following sets of quantum numbers represents the highest energy of an atom? **(AIEEE 2007)**

(a) $n = 3, l = 0, m = 0, s = +\frac{1}{2}$
(b) $n = 3, l = 1, m = 1, s = +\frac{1}{2}$
(c) $n = 3, l = 2, m = 1, s = +\frac{1}{2}$
(d) $n = 4, l = 0, m = 0, s = +\frac{1}{2}$

230. In ground state, the radius of hydrogen atom is 0.53 Å. The radius of Li^{2+} ion ($Z = 3$) in the same state is: **[PET (Raj.) 2007]**

(a) 0.17 Å (b) 1.06 Å (c) 0.53 Å (d) 0.265 Å

231. How many *d*-electrons in Cu^+ (At. No. = 29) can have the spin quantum number $(-\frac{1}{2})$? **(SCRA 2007)**

(a) 3 (b) 7 (c) 5 (d) 9

232. Which of the following electronic configurations, an atom has the lowest ionisation enthalpy? **[CBSE (Med.) 2007]**

(a) $1s^2 2s^2 2p^3$ (b) $1s^2 2s^2 2p^6 3s^1$
(c) $1s^2 2s^2 2p^6$ (d) $1s^2 2s^2 2p^5$

233. The measurement of the electron position is associated with an uncertainty in momentum, which is equal to 1×10^{-18} g cm s^{-1}. The uncertainty in electron velocity is: (mass of an electron is 9×10^{-28} g) **[CBSE-PMT (Pre.) 2008]**

(a) 1×10^5 cm s^{-1} (b) 1×10^{11} cm s^{-1}
(c) 1×10^9 cm s^{-1} (d) 1×10^6 cm s^{-1}

234. The ionization enthalpy of hydrogen atom is 1.312×10^6 J mol^{-1}. The energy required to excite the electron in the atom from $n = 1$ to $n = 2$ is : **(AIEEE 2008)**

(a) 9.84×10^5 J mol^{-1} (b) 8.51×10^5 J mol^{-1}
(c) 6.56×10^5 J mol^{-1} (d) 7.56×10^5 J mol^{-1}

[**Hint :** $E_1 = -1.312\times10^6$ J mol^{-1}

$$E_2 = \frac{E_1}{2^2} = -\frac{1.312\times10^6}{4} \text{ J mol}^{-1}$$

$$\Delta E = (E_2 - E_1) = 1.312\times10^6\left(1-\frac{1}{4}\right)$$

$$= \frac{3}{4}\times1.312\times10^6 = 9.84\times10^5 \text{ J mol}^{-1}]$$

235. The wavelengths of electron waves in two orbits is 3 : 5. The ratio of kinetic energy of electrons will be: **(EAMCET 2009)**

(a) 25 : 9 (b) 5 : 3
(c) 9 : 25 (d) 3 : 5

[**Hint :** We know, $\lambda = \frac{h}{\sqrt{2Em}}$

$$\frac{\lambda_1}{\lambda_2} = \sqrt{\frac{E_2}{E_1}}$$

$$\frac{3}{5} = \sqrt{\frac{E_2}{E_1}}$$

$\therefore$ $E_1 : E_2 = 25 : 9$]

236. Electrons with a kinetic energy of 6.023×10^4 J/mol are evolved from the surface of a metal, when it is exposed to radiation of wavelength of 600 nm. The minimum amount of energy required to remove an electron from the metal atom is : **(EAMCET 2009)**

(a) 2.3125×10^{-19} J (b) 3×10^{-19} J
(c) 6.02×10^{-19} J (d) 6.62×10^{-34} J

[**Hint :** Absorbed energy = Threshold energy + kinetic energy of photoelectron

$$\frac{hc}{\lambda} = E_0 + KE$$

$$\frac{6.62\times10^{-34}\times3\times10^8}{600\times10^{-9}} = E_0 + \frac{6.023\times10^4}{6.023\times10^{23}} \text{ J/atom}$$

$$3.31\times10^{-19} = E_0 + 1\times10^{-19}$$

$$E_0 = 2.31\times10^{-19}\text{ J}]$$

237. For the Paschen series the value of n_1 and n_2 in the expression $\Delta E = R_H \times c\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$ is: **[JEE (WB) 2009]**

(a) $n_1 = 1, n_2 = 2, 3, 4 \ldots$

(b) $n_1 = 2, n_2 = 3, 4, 5 \ldots$

(c) $n_1 = 3, n_2 = 4, 5, 6 \ldots$

(d) $n_1 = 4, n_2 = 5, 6, 7 \ldots$

238. Ionization energy of He^+ is 19.6×10^{-18} J atom^{-1}. The energy of the first stationary state ($n = 1$) of Li^{2+} is: **(AIEEE 2010)**

(a) -2.2×10^{-15} J atom^{-1} (b) 8.82×10^{-17} J atom^{-1}

(c) 4.41×10^{-16} J atom^{-1} (d) -4.41×10^{-17} J atom^{-1}

[**Hint :** $\frac{I_{He^+}}{I_{Li^{2+}}} = \frac{Z_1^2}{Z_2^2}$

$$\frac{19.6\times10^{-18}}{I_{Li^{2+}}} = \frac{4}{9}$$

$$I_{Li^{2+}} = \frac{9}{4}\times19.6\times10^{-18}$$

$$= 44.1\times10^{-18}$$

$$= 4.41\times10^{-17}\text{ J atom}^{-1}$$

$$E_{Li^{2+}} = -4.41\times10^{-17}\text{ J atom}^{-1}]$$

239. The energy required to break one mole of Cl—Cl bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking single Cl—Cl bond is: **(AIEEE 2010)**

($c = 3\times10^8$ m sec^{-1}, $N_A = 6.023\times10^{23}$ mol^{-1})

(a) 700 nm (b) 494 nm (c) 594 nm (d) 640 nm

[**Hint :** Bond energy of single bond $= \frac{242}{6.023\times10^{23}}$

$$= 4.017\times10^{-22}\text{ kJ}$$

$$= 4.017\times10^{-19}\text{ J}$$

$$E = \frac{hc}{\lambda}$$

$$4.017\times10^{-19} = \frac{6.626\times10^{-34}\times3\times10^8}{\lambda}$$

$$\lambda = 4.94\times10^{-7}\text{ m} = 494\text{ nm}]$$

240. In Sommerfeld's modification of Bohr's theory, the trajectory of an electron in a hydrogen atom is: **[JEE (WB) 2010]**

(a) perfect ellipse

(b) a closed ellipse like curve, narrower at the perihelion position and flatter at the aphelion position

(c) a closed loop on spherical surface

(d) a rosette

Set-2: The questions given below may have more than one correct answers

1. Correct order of radius of the 1st orbit of H, He^+, Li^{2+} and Be^{3+} is:

(a) H $> He^+ > Li^{2+} > Be^{3+}$

(b) $Be^{3+} > Li^{2+} > He^+ >$ H

(c) $He^+ > Be^{3+} > Li^{2+} >$ H

(d) $He^+ >$ H $> Li^{2+} > Be^{3+}$

2. Which is the correct relationship?

(a) E_1 of H = 1/2 E_2 of He^+ = 1/3 E_3 of Li^{2+} = 1/4 E_4 of Be^{3+}

(b) $E_1(H) = E_2(He^+) = E_3(Li^{2+}) = E_4(Be^{3+})$

(c) $E_1(H) = 2E_2(He^+) = 3E_3(Li^{2+}) = 4E_4(Be^{3+})$

(d) No relation

3. Which is correct for any kind of species?

(a) $(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$

(b) $(E_2 - E_1) < (E_3 - E_2) < (E_4 - E_3)$

(c) $(E_2 - E_1) = (E_3 - E_2) = (E_4 - E_3)$

(d) $(E_2 - E_1) = 1/4(E_3 - E_2) = 1/9(E_4 - E_3)$

4. No. of visible lines when an electron returns from 5th orbit to ground state in H spectrum is:

(a) 5 (b) 4 (c) 3 (d) 10

5. Quantum numbers $l = 2$ and $m = 0$ represent which orbital?

(a) d_{xy} (b) $d_{x^2-y^2}$ (c) d_{z^2} (d) d_{zx}

6. If n and l are principal and azimuthal quantum numbers respectively, then the expression for calculating the total numbers of electrons in any energy level is:

(a) $\sum_{l=0}^{l=n} 2(2l+1)$ (b) $\sum_{l=1}^{l=n-1} 2(2l+1)$

(c) $\sum_{l=0}^{l=n+1} 2(2l+1)$ (d) $\sum_{l=0}^{l=n-1} 2(2l+1)$

7. Order of no. of revolution/sec $\gamma_1, \gamma_2, \gamma_3$ and γ_4 for I, II, III and IV orbits is:

(a) $\gamma_1 > \gamma_2 > \gamma_3 > \gamma_4$ (b) $\gamma_4 > \gamma_3 > \gamma_2 > \gamma_1$

(c) $\gamma_1 > \gamma_2 > \gamma_4 > \gamma_3$ (d) $\gamma_2 > \gamma_3 > \gamma_4 > \gamma_1$

8. Consider the following statements:

(A) Electron density in the xy-plane in $3d_{x^2-y^2}$ orbital is zero

(B) Electron density in the xy-plane in $3d_{z^2}$ orbital is zero

(C) $2s$-orbital has one nodal surface

(D) For $2p_z$-orbital yz is the nodal plane,

Which are the correct statements?

(a) (A) and (C) (b) (B) and (C)

(c) Only (B) (d) (A), (B), (C) and (D)

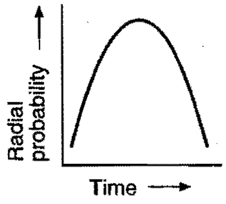
9. The first emission line in the H-atom spectrum in the Balmer series appears at:

(a) $\frac{5R}{36}$ cm^{-1} (b) $\frac{3R}{4}$ cm^{-1} (c) $\frac{7R}{144}$ cm^{-1} (d) $\frac{9R}{400}$ m^{-1}

10. 1 BM is equal to:

(a) $\frac{hc}{m\pi e^4}$ (b) $\frac{hc}{4\pi m}$ (c) $\frac{e^2hc}{4m}$ (d) $\frac{ehc}{\pi m}$

11. Radial probability distribution curve is shown for s-orbital. The curve is:



(a) $1s$

(b) $2s$

(c) $3s$

(d) $4s$

12. dz^2 orbital has:

(a) a lobe along z-axis and a ring along xy-plane

(b) a lobe along z-axis and a lobe along xy-plane

(c) a lobe along z-axis and a ring along yz-plane

(d) a lobe and ring along z-axis

13. When a light of frequency ν_1 is incident on a metal surface the photoelectrons emitted have twice the kinetic energy as did the photoelectron emitted when the same metal has irradiated with light of frequency ν_2. What will be the value of threshold frequency?
(a) $\nu_0 = \nu_1 - \nu_2$ (b) $\nu_0 = \nu_1 - 2\nu_2$
(c) $\nu_0 = 2\nu_1 - \nu_2$ (d) $\nu_0 = \nu_1 + \nu_2$

14. Heisenberg's uncertainty principle is not valid for:
(a) moving electrons (b) motor car
(c) stationary particles (d) all of these

15. Consider these electronic configurations for neutral atoms;
(i) $1s^2 2s^2 2p^6 3s^1$ (ii) $1s^2 2s^2 2p^6 4s^1$
Which of the following statements is/are false?
(a) Energy is required to change (i) to (ii)
(b) (i) represents 'Na' atom
(c) (i) and (ii) represent different elements
(d) More energy is required to remove one electron from (i) than (ii)

16. For the energy levels in an atom which one of the following statements is/are correct?
(a) There are seven principal electron energy levels
(b) The second principal energy level can have 4 subenergy levels and contain a maximum of 8 electrons
(c) The M energy level can have a maximum of 32 electrons
(d) The 4s subenergy level is at a lower energy than the 3d subenergy level

17. Which of the following statements are correct for an electron that has $n = 4$ and $m = -2$?
(a) The electron may be in a d-orbital
(b) The electron is in the fourth principal electronic shell
(c) The electron may be in a p-orbital
(d) The electron must have the spin quantum number = + 1/2

18. The angular momentum of electron can have the value(s):
(a) $\frac{h}{2\pi}$ (b) $\frac{h}{\pi}$
(c) $\frac{2h}{\pi}$ (d) $\frac{5}{2}\frac{h}{2\pi}$

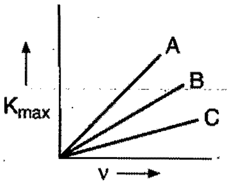
19. Which of the following statements is/are wrong?
(a) If the value of $l = 0$, the electron distribution is spherical
(b) The shape of the orbital is given by magnetic quantum no.
(c) Angular moment of 1s, 2s, 3s electrons are equal
(d) In an atom, all electrons travel with the same velocity

20. Consider the following sets of quantum numbers:

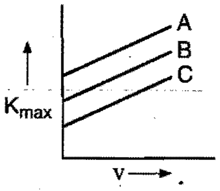
	n	l	m	s
(A)	3	0	0	$+\frac{1}{2}$
(B)	2	2	1	$+\frac{1}{2}$
(C)	4	3	-2	$-\frac{1}{2}$
(D)	1	0	-1	$-\frac{1}{2}$
(E)	3	2	3	$+\frac{1}{2}$

Which of the following sets of quantum numbers is not possible? **[CBSE (Med.) 2007]**
(a) (A), (B), (C) and (D) (b) (B), (D) and (E)
(c) (A) and (C) (d) (B), (C) and (D)

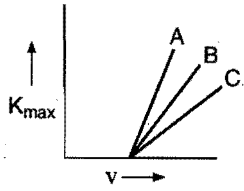
21. For three different metals A, B, C photo-emission is observed one by one. The graph of maximum kinetic energy versus frequency of incident radiation are sketched as : **[BHU (Screening) 2010]**



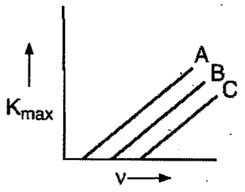
(a)



(b)



(c)



(d)

22. For which of the following species, the expression for the energy of electron in the n^{th} $\left[E_n = -\frac{13.6 Z^2}{n^2} \text{eV atom}^{-1}\right]$ has the validity? **[BHU (Mains) 2010]**
(a) Tritium (b) Li^{2+}
(c) Deuterium (d) He^{2+}

Assertion-Reason TYPE QUESTIONS

Set–1

The questions given below consist of an **'Assertion' (A)** and the **'Reason' (R).** Use the following keys for the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct reason for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

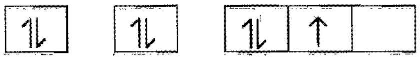
1. (A) F-atom has less electron affinity than Cl^- atom.
(R) Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F-atom.

2. (A) Nuclide $^{30}_{13}Al$ is less stable than $^{40}_{20}Ca$.
(R) Nuclide having odd number of protons and neutrons are generally unstable. **(IIT 1998)**

3. (A) The first IE of Be is greater than that of B.
(R) $2p$-orbital is lower in energy than $2s$.

4. (A) The electronic configuration of nitrogen atom is represented as:

and not as:



(R) The electronic configuration of the ground state of an atom is the one which has the greatest multiplicity.

5. (A) The atomic radii of the elements of oxygen family are smaller than the atomic radii of corresponding elements of the nitrogen family.
(R) The members of oxygen family are all more electronegative and thus have lower value of nuclear charge than those of the nitrogen family.

6. (A) For $n = 3$, l may be 0, 1 and 2 and may be 0, ±1 and 0, ±1 and ±2.
(R) For each value of n, there are 0 to $(n - 1)$ possible values of l; for each value of l, there are 0 to $\pm l$ values of m.

7. (A) An orbital cannot have more than two electrons.
(R) The two electrons in an orbital create opposite magnetic field.

8. (A) The configuration of B-atom cannot be $1s^2 2s^2$.
(R) Hund's rule demands that the configuration should display maximum multiplicity.

9. (A) The ionization energy of N is more than that of O.
(R) Electronic configuration of N is more stable due to half-filled $2p$-orbitals.

10. (A) p-orbital is dumb-bell shaped.
(R) Electron present in p-orbital can have any one of the three values of magnetic quantum number, *i.e.*, 0, +1 or –1.

Set–2

The questions given below consist of two statements as **'Assertion' (A)** and **'Reason' (R);** while answering these choose any one of them:

(a) If (A) and (R) are both correct and (R) is the correct reason for (A).
(b) If (A) and (R) are both correct but (R) is not the correct reason for (A).
(c) If (A) is true but (R) is false.
(d) If both (A) and (R) are false.

11. (A) A special line will be seen for $2p_x - 2p_y$ transition.
(R) Energy is released in the form of wave of light when the electron drops from $2p_x$ to $-2p_y$ orbital. **(AIIMS 1996)**

12. (A) Ionization potential of Be (At. No. = 4) is less than B (At. No. = 5).
(R) The first electron released from Be is of p-orbital but that from B is of s-orbital. **(AIIMS 1997)**

13. (A) In Rutherford's gold foil experiment, very few α-particles are deflected back.
(R) Nucleus present inside the atom is heavy.

14. (A) Limiting line in the Balmer series has a wavelength of 364.4 mm.
(R) Limiting line is obtained for a jump of electron from $n = \infty$.

15. (A) Each electron in an atom has two spin quantum numbers.
(R) Spin quantum numbers are obtained by solving Schrödinger wave equation.

16. (A) There are two spherical nodes in $3s$-orbital.
(R) There is no planar node in $3s$-orbital.

17. (A) In an atom, the velocity of electron in the higher orbits keeps on decreasing.
(R) Velocity of electrons is inversely proportional to radius of the orbit.

18. (A) If the potential difference applied to an electron is made 4 times, the de Broglie wavelength associated is halved.
(R) On making potential difference 4 times, velocity is doubled and hence λ is halved.

19. (A) Angular momentum of $1s$, $2s$, $3s$, etc., all have spherical shape.
(R) $1s$, $2s$, $3s$, etc., all have spherical shape.

20. (A) The radial probability of $1s$ electron first increases, till it is maximum at 53 Å and then decreases to zero.
(R) Bohr radius for the first orbit is 53 Å.

21. (A) On increasing the intensity of incident radiation, the number of photoelectrons ejected and their KE increases.
(R) Greater the intensity means greater the energy which in turn means greater the frequency of the radiation.

22. (A) A spectral line will be seen for a $2p_x - 2p_y$ transition.
(R) Energy is released in the form of wave of light when the electron drops from $2p_x$ to $2p_y$ orbital. **(VMMC 2007)**

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (b) **2.** (a) **3.** (c) **4.** (d) **5.** (c) **6.** (b) **7.** (d) **8.** (a)
9. (a) **10.** (b) **11.** (d) **12.** (d) **13.** (a) **14.** (c) **15.** (b) **16.** (a)
17. (c) **18.** (d) **19.** (b) **20.** (c) **21.** (d) **22.** (c) **23.** (b) **24.** (a)
25. (d) **26.** (b) **27.** (d) **28.** (a) **29.** (d) **30.** (b) **31.** (c) **32.** (b)
33. (a) **34.** (c) **35.** (d) **36.** (a) **37.** (c) **38.** (a) **39.** (b) **40.** (c)
41. (c) **42.** (b) **43.** (d) **44.** (d) **45.** (c) **46.** (a) **47.** (b) **48.** (d)
49. (d) **50.** (c) **51.** (b) **52.** (b) **53.** (a) **54.** (b) **55.** (a) **56.** (a)
57. (c) **58.** (d) **59.** (a) **60.** (d) **61.** (c) **62.** (a) **63.** (a) **64.** (b)
65. (a) **66.** (d) **67.** (d) **68.** (b) **69.** (c) **70.** (c) **71.** (a) **72.** (d)
73. (d) **74.** (b) **75.** (c) **76.** (d) **77.** (b) **78.** (d) **79.** (a) **80.** (d)
81. (b) **82.** (b) **83.** (c) **84.** (a) **85.** (b) **86.** (a) **87.** (b) **88.** (c)
89. (b) **90.** (d) **91.** (a) **92.** (d) **93.** (a) **94.** (a) **95.** (b) **96.** (c)
97. (a) **98.** (d) **99.** (b) **100.** (b) **101.** (d) **102.** (d) **103.** (a) **104.** (c)
105. (c) **106.** (c) **107.** (d) **108.** (b) **109.** (d) **110.** (a) **111.** (a) **112.** (b)
113. (c) **114.** (d) **115.** (a) **116.** (d) **117.** (b) **118.** (a) **119.** (c) **120.** (c)
121. (d) **122.** (b) **123.** (d) **124.** (c) **125.** (a) **126.** (a) **127.** (c) **128.** (c)
129. (b) **130.** (b) **131.** (c) **132.** (c) **133.** (c) **134.** (b) **135.** (c) **136.** (d)
137. (b) **138.** (a) **139.** (a) **140.** (a) **141.** (b) **142.** (c) **143.** (c) **144.** (a)
145. (b) **146.** (c) **147.** (d) **148.** (c) **149.** (d) **150.** (d) **151.** (a) **152.** (d)
153. (c) **154.** (a) **155.** (c) **156.** (a) **157.** (a) **158.** (c) **159.** (c) **160.** (d)
161. (c) **162.** (c) **163.** (b) **164.** (b) **165.** (a) **166.** (b) **167.** (b) **168.** (b)
169. (d) **170.** (d) **171.** (b) **172.** (b) **173.** (d) **174.** (b) **175.** (c) **176.** (a)
177. (d) **178.** (b) **179.** (d) **180.** (a) **181.** (d) **182.** (a) **183.** (a, b) **184.** (c)
185. (a) **186.** (a) **187.** (b) **188.** (b) **189.** (b) **190.** (b) **191.** (a) **192.** (c)
193. (c) **194.** (b) **195.** (a) **196.** (a) **197.** (d) **198.** (a) **199.** (c) **200.** (a)
201. (a) **202.** (c) **203.** (c) **204.** (a) **205.** (a) **206.** (b) **207.** (c) **208.** (c)
209. (d) **210.** (c) **211.** (d) **212.** (a) **213.** (a) **214.** (c) **215.** (a) **216.** (b)
217. (d) **218.** (d) **219.** (d) **220.** (c) **221.** (b) **222.** (b) **223.** (b) **224.** (d)
225. (c) **226.** (a) **227.** (c) **228.** (d) **229.** (c) **230.** (a) **231.** (c) **232.** (b)
233. (c) **234.** (a) **235.** (a) **236.** (a) **237.** (c) **238.** (d) **239.** (b) **240.** (c)

- **Set–2**

1. (a) **2.** (b) **3.** (a) **4.** (c) **5.** (c) **6.** (d) **7.** (a) **8.** (a)
9. (a) **10.** (a) **11.** (a) **12.** (a) **13.** (c) **14.** (b, c) **15.** (c, d) **16.** (a, d)
17. (b, c) **18.** (a, b, c) **19.** (c) **20.** (b) **21.** (d) **22.** (a, b, c)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c) **2.** (a) **3.** (c) **4.** (a) **5.** (c) **6.** (a) **7.** (b) **8.** (c)
9. (c) **10.** (a) **11.** (d) **12.** (d) **13.** (b) **14.** (a) **15.** (d) **16.** (b)
17. (c) **18.** (a) **19.** (b) **20.** (b) **21.** (d) **22.** (d)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain a single correct option:

1. The configuration of Cr atom is $3d^5 4s^1$ but not $3d^4 4s^2$ due to reason R_1 and the configuration of Cu atom is $3d^{10} 4s^1$ but not $3d^9 4s^2$ due to reason R_2, R_1 and R_2 are:

(a) R_1: The exchange energy of $3d^5 4s^1$ is greater than that of $3d^4 4s^2$.
R_2: The exchange energy of $3d^{10} 4s^1$ is greater than that of $3d^9 4s^2$.

(b) R_1: $3d^5 4s^1$ and $3d^4 4s^2$ have same exchange energy but $3d^5 4s^1$ is spherically symmetrical.
R_2: $3d^{10} 4s^1$ is also spherically symmetrical.

(c) R_1: $3d^5 4s^1$ has greater exchange energy than $3d^4 4s^2$.
R_2: $3d^{10} 4s^1$ has spherical symmetry.

(d) R_1: $3d^5 4s^1$ has greater energy than $3d^4 4s^2$.
R_2: $3d^{10} 4s^1$ has greater energy than $3d^9 4s^2$.

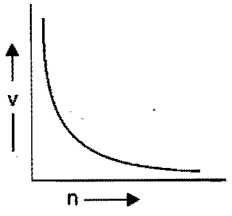
[**Hint:** $3d^5 4s^1$ is correct because it has greater exchange possibilities of unpaired electrons.

1	1	1	1	1
1	2	3	4	5

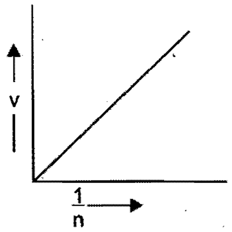
Exchange possibilities: (10)
1–2, 1–3, 1–4, 1–5
2–3, 2–4, 2–5
3–4, 3–5
4–5

$3d^{10} 4s^1$ is correct because $3d^{10}$-orbitals are spherically symmetrical.]

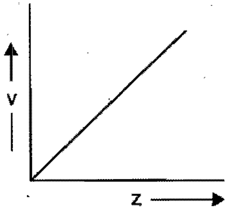
2. Which of the following graphs is incorrect ?



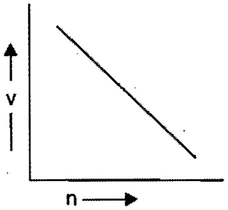
(a)



(b)



(c)



(d)

3. Which among the following is correct of $_5$B in normal state?

	2s	2p			
(a)	↑↑		↑		: Against Hund's rule
(b)	↑	↑	↑		: Against aufbau principle as well as Hund's rule
(c)	↑↑	↑			: Violation of Pauli's exclusion principle and not Hund's rule
(d)	↑↓	↑			: Against aufbau principle

4. Maximum value $(n + l + m)$ for unpaired electrons in second excited state of chlorine $_{17}$Cl is:

(a) 28 (b) 25
(c) 20 (d) none of these

[**Hint:** Configuration in second excited state may be given as:

	3p			3d				
	1	1	1	1	1			
n	3	3	3	3	3			
l	1	1	1	2	2			
m	−1	0	+1	+2	+1			

Total $n + l + m = 25$]

5. Which of the following is correctly matched?

(a) Momentum of H-atom when electrons return from $n = 2$ to $n = 1$: $\frac{3Rh}{4}$

(b) Momentum of photon : Independent of wavelength of light

(c) e/m ratio of anode rays : Independent of gas in the discharge tube

(d) Radius of nucleus : $(\text{Mass no.})^{1/2}$

[**Hint:**
$$\frac{1}{\lambda} = R\left[\frac{1}{1^2} - \frac{1}{2^2}\right] = \frac{3R}{4}$$
$$\lambda = \frac{h}{p}$$
$$p = \frac{h}{\lambda} = h \times \frac{3R}{4} = \frac{3Rh}{4}$$
]

6. In hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electrons from Bohr orbit of hydrogen?

(a) $4 \rightarrow 1$ (b) $2 \rightarrow 5$ (c) $3 \rightarrow 2$ (d) $5 \rightarrow 2$

7. In which of the following pairs is the probability of finding the electron in xy-plane zero for both orbitals?

(a) $3d_{yz}, 4d_{x^2-y^2}$ (b) $2p_z, d_{z^2}$
(c) $4d_{zx}, 3p_z$ (d) None of these

8. In which of the following orbital diagrams are both Pauli's exclusion principle and Hund's rule violated?

(a) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$ (b) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow}\boxed{\uparrow\downarrow}\boxed{}$

(c) $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\boxed{\uparrow\uparrow}\boxed{\downarrow}$ (d) $\boxed{\downarrow\downarrow}\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}$

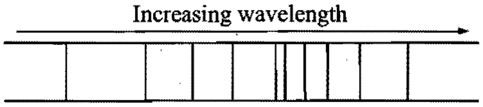
9. The distance between 3rd and 2nd Bohr orbits of hydrogen atom is:

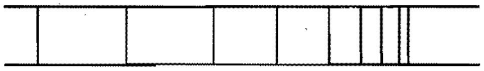
(a) 0.529×10^{-8} cm (b) 2.645×10^{-8} cm
(c) 2.116×10^{-8} cm (d) 1.058×10^{-8} cm

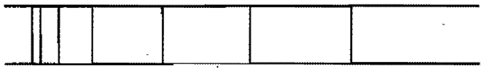
[**Hint:** $r_3 - r_2 = (3^2 - 2^2) \times 0.529 \times 10^{-8}$ cm]

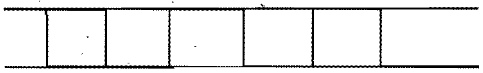
10. Which diagram represents the best appearance of the line spectrum of atomic hydrogen in the visible region?

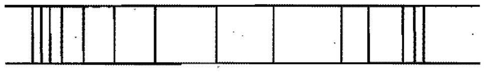
[PET (Kerala) 2007]

(a)


(b)


(c)


(d)


(e)


11. The 'm' value for an electron in an atom is equal to the number of m values for $l = 1$. The electron may be present in:

(a) $3d_{x^2-y^2}$ (b) $5f_{x(x^2-y^2)}$

(c) $4f_{x^3/z}$ (d) none of these

[**Hint:** Total values of $m = (2l + 1) = 3$ for $l = 1$

$m = 3$ is for f-subshell orbitals.]

12. If m = magnetic quantum number, l = azimuthal quantum number, then:

(a) $m = l + 2$ (b) $m = 2l^2 + 1$

(c) $l = \frac{m-1}{2}$ (d) $l = 2m + 1$

[**Hint:** Magnetic quantum number 'm' lies between $(-l, 0, +l)$; thus total possible values of 'm' will be $(2l + 1)$.

$m = 2l + 1$, *i.e.*, $l = \frac{m-1}{2}$]

13. What are the values of the orbital angular momentum of an electron in the orbitals $1s$, $3s$, $3d$ and $2p$?

(a) $0, 0, \sqrt{6}\,\hbar, \sqrt{2}\,\hbar$ (b) $1, 1, \sqrt{4}\,\hbar, \sqrt{2}\,\hbar$

(c) $0, 1, \sqrt{6}\,\hbar, \sqrt{3}\,\hbar$ (d) $0, 0, \sqrt{20}\,\hbar, \sqrt{6}\,\hbar$

[**Hint:** Orbital angular momentum $= \sqrt{l(l+1)}\,\frac{h}{2\pi} = \sqrt{l(l+1)}\,\hbar$]

14. After np-orbitals are filled, the next orbital filled will be:

(a) $(n+1)s$ (b) $(n+2)p$ (c) $(n+1)d$ (d) $(n+2)s$

15. The ratio of $(E_2 - E_1)$ to $(E_4 - E_3)$ for the hydrogen atom is approximately equal to:

(a) 10 (b) 15 (c) 17 (d) 12

[**Hint:**

$$\frac{E_4-E_3}{E_2-E_1}=\frac{\left(-\frac{1}{16}\right)-\left(-\frac{1}{9}\right)}{\left(-\frac{1}{4}\right)-(-1)}=\frac{\frac{1}{9}-\frac{1}{16}}{\frac{3}{4}}=\frac{7}{144}\times\frac{4}{3}=\frac{7}{108}\approx\frac{1}{15}$$]

16. Which of the following electronic configurations has zero spin multiplicity?

(a) | ↑ | ↑ | ↑ | (b) | ↑ | ↑ | ↓ |

(c) | ↑ | ↓ | ↓ | (d) | ↓ | ↓ | ↓ |

[**Hint:** Spin multiplicity $= (2\Sigma s + 1)$]

17. A photosensitive material would emit electrons if excited by photons beyond a threshold. To overcome the threshold, one would increase: **(VITEEE 2007)**

(a) the voltage applied to the light source

(b) the intensity of light

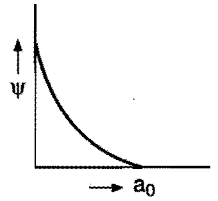
(c) the wavelength of light

(d) the frequency of light

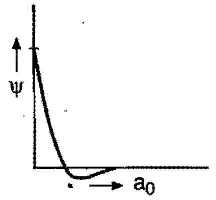
18. Which of the following electronic configurations have the highest exchange energy?

	3d					4s
(a)	↑	↑	↑			↑
(b)	↑	↑	↑	↑	↑	↑
(c)	↑↓	↑↓	↑↓	↑↓	↑	↑
(d)	↑↓	↑↓	↑↓	↑↓	↑↓	↑

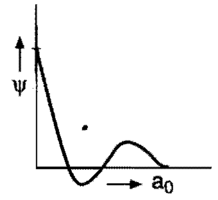
19. Which of the following graphs correspond to one node?



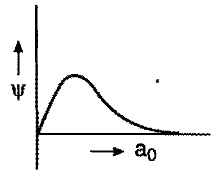
(a)



(b)



(c)



(d)

20. Angular distribution functions of all orbitals have:

(a) l nodal surfaces (b) $(l - 1)$ nodal surfaces

(c) $(n + l)$ nodal surfaces (d) $(n - l - 1)$ nodal surfaces

21. If uncertainty in position and momentum are equal then uncertainty in velocity is: **[CBSE-PMT (Pre.) 2008]**

(a) $\sqrt{\frac{h}{\pi}}$ (b) $\sqrt{\frac{h}{2\pi}}$ (c) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (d) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$

[**Hint:** $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$

$\Delta p \geq \sqrt{\frac{h}{4\pi}}$ when $\Delta x = \Delta p$

$m\Delta v \geq \sqrt{\frac{h}{4\pi}}$

$\Delta v \geq \frac{1}{2m}\sqrt{\frac{h}{\pi}}$]

22. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number 3 is:

(a) 3 (b) 4 (c) 2 (d) 1

[**Hint:** $m = 3, l = 3, n = 4$

For, $n = 4$, number of waves will be 4.]

23. The number of elliptical orbits excluding circular orbits in the N-shell of an atom is:

(a) 3 (b) 4 (c) 2 (d) 1

[**Hint:** For, N-shell, $n = 4$. This shell will have one circular and three elliptical orbits.]

24. From the electronic configuration of the given elements K, L, M and N, which one has the highest ionization potential?

(a) $M = [Ne]\,3s^2 3p^2$ (b) $L = [Ne]\,3s^2 3p^3$

(c) $K = [Ne]\,3s^2 3p^1$ (d) $N = [Ar]\,3d^{10}, 4s^2 4p^3$

[**Hint:** L has half-filled p-subshell and it is smaller than N, hence, L will have the highest ionization potential.]

25. Which of the following pairs of electrons is excluded from an atom?

(a) $n = 2, l = 0, m = 0, s = +\frac{1}{2}$ and $n = 2, l = 0, m = 0, s = +\frac{1}{2}$

(b) $n = 2, l = 1, m = +1, s = +\frac{1}{2}$ and $n = 2, l = 1, m = -1, s = +\frac{1}{2}$

(c) $n = 1, l = 0, m = 0, s = +\frac{1}{2}$ and $n = 1, l = 0, m = 0, s = -\frac{1}{2}$

(d) $n = 3, l = 2, m = -2, s = +\frac{1}{2}$ and $n = 3, l = 0, m = 0, s = +\frac{1}{2}$

[**Hint:** Both $2s$ electrons have same spin, hence excluded from the atom.]

26. Given set of quantum numbers for a multielectron atom is:

n	l	m	s
2	0	0	+1/2
2	0	0	−1/2

What is the next higher allowed set of 'n' and 'l' quantum numbers for this atom in the ground state?

(a) $n = 2, l = 0$ (b) $n = 2, l = 1$

(c) $n = 3, l = 0$ (d) $n = 3, l = 1$

27. In how many elements does the last electron have the quantum numbers of $n = 4$ and $l = 1$?

(a) 4 (b) 6 (c) 8 (d) 10

[**Hint:** $n = 4, l = 1$ represent $4p$-subshell containing six electrons. Thus, there will be six elements having $4p^1$ to $4p^6$ electronic configuration.]

28. If there are three possible values $(-1/2, 0, +1/2)$ for the spin quantum, then electronic configuration of K (19) will be:

(a) $1s^3, 2s^3 2p^9, 3s^3 3p^1$ (b) $1s^2, 2s^2 2p^6, 3s^2 3p^6, 4s^1$

(c) $1s^2, 2s^2 2p^9, 3s^2 3p^4$ (d) none of these

29. If the radius of first Bohr orbit of hydrogen atom is 'x' then de Broglie wavelength of electron in 3rd orbit is nearly:

(a) $2\pi x$ (b) $6\pi x$ (c) $9x$ (d) $\frac{x}{3}$

[**Hint:**
$$r_n = n^2 r_1$$
$$r_3 = 9r_1 = 9x$$
$$mvr = n\frac{h}{2\pi}$$
$$mv9x = 3\frac{h}{2\pi}$$
$$\frac{h}{mv} = 6\pi x$$
$$\lambda = 6\pi x]$$

30. How many times does light travel faster in vacuum than an electron in Bohr first orbit of hydrogen atom?

(a) 13.7 times (b) 67 times (c) 137 times (d) 97 times

[**Hint:**
$$v = \frac{Z}{n} \times 2.188 \times 10^8 \text{ cm/sec}$$
$$v_1 = \frac{1}{1} \times 2.188 \times 10^8 \text{ cm/sec}$$
$$\frac{\text{Velocity of light}}{\text{Velocity of electron}} = \frac{3 \times 10^{10}}{2.188 \times 10^8} = 137 \text{ times}]$$

31. A compound of vanadium has a magnetic moment of 1.73 BM. The electronic configuration of vanadium ion in the compound is:

(a) $[Ar]\,3d^2$ (b) $[Ar]3d^1 4s^0$ (c) $[Ar]\,3d^3$ (d) $[Ar]\,3d^0 4s^1$

[**Hint:** Magnetic moment $= \sqrt{n(n+2)}$ BM
$$1.73 = \sqrt{n(n+2)}$$
$$\sqrt{3} = \sqrt{n(n+2)}$$
$$n = 1 \quad \text{(number of unpaired electrons)}$$
$$V_{22} \rightarrow 3d^2 4s^2$$
$$V^{3+} \rightarrow 3d^1 4s^0 \quad \text{(has one unpaired electron)}]$$

32. The orbital angular momentum of an electron in p-orbital is: **[PET (Kerala) 2006]**

(a) zero (b) $\frac{h}{\sqrt{2}\pi}$ (c) $\frac{h}{2\pi}$ (d) $\frac{1}{2}\frac{h}{2\pi}$

(e) $\frac{h}{2\sqrt{2}\pi}$

33. When a hydrogen atom emits a photon of energy 12.1 eV, the orbital angular momentum changes by:

(a) 1.05×10^{-34} J sec (b) 2.11×10^{-34} J sec

(c) 3.16×10^{-34} J sec (d) 4.22×10^{-34} J sec

[**Hint:** Emission of photon of 12.1 eV corresponds to the transition from $n = 3$ to $n = 1$.

∴ Change in angular momentum
$$= (n_2 - n_1)\frac{h}{2\pi}$$
$$= (3 - 1)\frac{h}{2\pi} = \frac{h}{\pi}$$
$$= \frac{6.626 \times 10^{-34}}{3.14}$$
$$= 2.11 \times 10^{-34} \text{ J sec}]$$

34. The total energy of the electron of H-atom in the second quantum state is $-E_2$. The total energy of the He^+ atom in the third quantum state is:

(a) $-\left(\frac{3}{2}\right)E_2$ (b) $-\left(\frac{2}{3}\right)E_2$ (c) $-\left(\frac{4}{9}\right)E_2$ (d) $-\left(\frac{16}{9}\right)E_2$

[**Hint:** Energy of electrons in nth state
$$= -\frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

$$E_2(\text{H}) = -\frac{13.6}{1}\text{ eV}$$

$$E_3\ (\text{He}^+) = -\frac{13.6 \times 4}{9}\text{ eV}$$

$$\frac{E_2}{E_3} = \frac{9}{4} \quad \text{or} \quad E_3 = \frac{4}{9}E_2$$

For negative value of E_2, E_3 will also be negative.]

35. What is the ratio of the Rydberg constant for helium to hydrogen atom?

(a) 1/2 (b) 1/4 (c) 1/8 (d) 1/16

[Hint: $R = \frac{-2\pi^2 mZ^2 e^4}{ch^3}$

$$\frac{R_{\text{He}}}{R_{\text{H}}} = \frac{2 \times 2^2}{1 \times 1^2} = 8$$

$$\therefore \quad \frac{R_{\text{H}}}{R_{\text{He}}} = \frac{1}{8}\ ]$$

36. If the kinetic energy of a particle is doubled, de Broglie wavelength becomes:

(a) 2 times (b) 4 times (c) $\sqrt{2}$ times (d) $\frac{1}{\sqrt{2}}$ times

[Hint: $\lambda = \frac{h}{\sqrt{2Em}}$, where, E = Kinetic energy of the particle

$$\therefore \quad \lambda_1 = \frac{h}{\sqrt{2Em}}; \quad \lambda_2 = \frac{h}{\sqrt{2 \times 2Em}}$$

$$\therefore \quad \frac{\lambda_1}{\lambda_2} = \sqrt{2}, \quad i.e., \ \lambda_2 = \frac{\lambda_1}{\sqrt{2}}\ ]$$

37. Imagine an atom made up of a proton and a hypothetical particle of double the mass of the electron but having the same charge as the electron. Apply the Bohr's atomic model and consider all possible transitions of this hypothetical particle to the first excited level. The largest wavelength photon that will be emitted has wavelength λ (given in terms of the Rydberg constant R for the hydrogen atom) equal to:

(a) $\frac{9}{5R}$ (b) $\frac{36}{5R}$ (c) $\frac{18}{5R}$ (d) $\frac{4}{R}$

[Hint: Energy is related to mass:

$$E_n \propto m$$

The longest wavelength $\lambda_{\max}$ photon will correspond to the transition of particle from $n = 3$ to $n = 2$

$$\frac{1}{\lambda_{\max}} = 2R\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\lambda_{\max} = \frac{18}{5R}\ ]$$

38. What is ratio of time periods (T_1 / T_2) in second orbit of hydrogen atom to third orbit of He$^+$ ion?

(a) $\frac{8}{27}$ (b) $\frac{32}{27}$ (c) $\frac{27}{32}$ (d) $\frac{27}{8}$

[Hint : $T \propto \frac{n^3}{Z^2}$

$$\frac{T_1}{T_2} = \frac{n_1^3 \times Z_2^2}{Z_1^2 \times n_2^3} = \frac{2^3 \times 2^2}{1^2 \times 3^3} = \frac{32}{27}\ ]$$

39. The de Broglie wavelength of an electron accelerated by an electric field of V volt is given by :

(a) $\lambda = \frac{1.23}{\sqrt{m}}$ (b) $\lambda = \frac{1.23m}{\sqrt{h}}$ (c) $\frac{1.23}{\sqrt{V}}\,nm$ (d) $\lambda = \frac{1.23}{V}$

40. An excited electron of H-atoms emits of photon of wavelength λ and returns in the ground state, the principal quantum number of excited state is given by :

(a) $\sqrt{\lambda R\ (\lambda R - 1)}$ (b) $\sqrt{\frac{\lambda R}{(\lambda R - 1)}}$

(c) $\frac{1}{\sqrt{\lambda R\ (\lambda R - 1)}}$ (d) $\sqrt{\frac{(\lambda R - 1)}{\lambda R}}$

[Hint : $\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = R\left[\frac{1}{1} - \frac{1}{n_2^2}\right]$

$$n_2 = \sqrt{\frac{\lambda R}{\lambda R - 1}}\ ]$$

41. A dye absorbs a photon of wavelength λ and re-emits the same energy into two photons of wavelength λ_1 and λ_2 respectively. The wavelength λ is related to λ_1 and λ_2 as :

(a) $\lambda = \frac{\lambda_1\lambda_2}{(\lambda_1 + \lambda_2)^2}$ (b) $\lambda = \frac{\lambda_1 + \lambda_2}{\lambda_1\lambda_2}$

(c) $\lambda = \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}$ (d) $\frac{\lambda_1^2\lambda_2^2}{\lambda_1 + \lambda_2}$

42. The radii of maximum probability for $3s$, $3p$ and $3d$-electrons are in the order :

(a) $(r_{\max})_{3s} > (r_{\max})_{3p} > (r_{\max})_{3d}$

(b) $(r_{\max})_{3s} = (r_{\max})_{3p} = (r_{\max})_{3d}$

(c) $(r_{\max})_{3d} > (r_{\max})_{3p} > (r_{\max})_{3s}$

(d) $(r_{\max})_{3d} > (r_{\max})_{3s} > (r_{\max})_{3p}$

Following questions may have more than one correct options:

1. Select the correct relations on the basis of Bohr theory:

(a) velocity of electron $\propto \frac{1}{n}$ (b) frequency of revolution $\propto \frac{1}{n^3}$

(c) radius of orbit $\propto n^2Z$ (d) force on electron $\propto \frac{1}{n^4}$

2. To which of the following species, the Bohr theory is not applicable?

(a) He (b) Li^{2+} (c) He^{2+} (d) H-atom

3. The magnitude of spin angular momentum of an electron is given by:

(a) $S = \sqrt{s(s+1)}\,\frac{h}{2\pi}$ (b) $S = s\frac{h}{2\pi}$

(c) $S = \frac{\sqrt{3}}{2} \times \frac{h}{2\pi}$ (d) $S = \pm\frac{1}{2} \times \frac{h}{2\pi}$

[Hint: Spin angular momentum $= \sqrt{s(s+1)}\,\frac{h}{2\pi}$

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)}\,\frac{h}{2\pi} = \frac{\sqrt{3}}{2} \times \frac{h}{2\pi}\ ]$$

4. Select the correct configurations among the following:

(a) Cr $(Z = 24)$: [Ar] $3d^5, 4s^1$

(b) Cu $(Z = 29)$: [Ar] $3d^{10}, 4s^1$

(c) Pd $(Z = 46)$: [Kr] $4d^{10}, 5s^0$

(d) Pt $(Z = 78)$: [Xe] $4d^{10}\ 4s^2$

5. Which among the following statements is/are correct?
(a) ψ^2 represents the atomic orbitals
(b) The number of peaks in radial distribution is $(n - l)$
(c) Radial probability density $\rho_{nl}(r) = 4\pi r^2 R_{nl}^2(r)$
(d) A node is a point in space where the wave function (ψ) has zero amplitude

6. Select the correct statement(s) among the following:
(i) Total number of orbitals in a shell with principal quantum number 'n' is n^2
(ii) Total number of subshells in the n th energy level is n
(iii) The maximum number of electrons in a subshell is given by the expression $(4l + 2)$
(iv) $m = l + 2$, where l and m are azimuthal and magnetic quantum numbers
(a) (i), (iii) and (iv) are correct
(b) (i), (ii) and (iii) are correct
(c) (ii), (iii) and (iv) are correct
(d) (i), (ii) and (iv) are correct

7. Which among the following are correct about angular momentum of electron?
(a) $2\hbar$ (b) $1.5\frac{h}{\pi}$ (c) $2.5\hbar$ (d) $0.5\frac{h}{\pi}$

8. Which of the following is/are incorrect for Humphrey lines of hydrogen spectrum?
(a) $n_2 = 7 \rightarrow n_1 = 2$ (b) $n_2 = 10 \rightarrow n_1 = 6$
(c) $n_2 = 5 \rightarrow n_1 = 1$ (d) $n_2 = 11 \rightarrow n_1 = 3$

9. In the Bohr's model of the atom:
(a) the radius of n th orbit is proportional to n^2
(b) the total energy of the electron in the n th orbit is inversely proportional to 'n'
(c) the angular momentum of the electron is integral multiple of $h/2\pi$
(d) the magnitude of potential energy of an electron in an orbit is greater than kinetic energy

10. Which among the following series is obtained in both absorption and emission spectrums?
(a) Lyman series (b) Balmer series
(c) Paschen series (d) Brackett series

11. The maximum kinetic energy of photoelectrons is directly proportional to . . . of the incident radiation. The missing word can be:
(a) intensity (b) wavelength
(c) wave number (d) frequency

12. Rutherford's experiment established that:
(a) inside the atom there is a heavy positive centre
(b) nucleus contains protons and neutrons
(c) most of the space in an atom is empty
(d) size of nucleus is very small

13. Which of the following orbital(s) lie in the xy-plane?
(a) $d_{x^2-y^2}$ (b) d_{xy} (c) d_{xz} (d) d_{yz}

14. In which of the following sets of orbitals, electrons have equal orbital angular momentum?
(a) 1s and 2s (b) 2s and 2p (c) 2p and 3p (d) 3p and 3d

15. Which of the following orbitals have no spherical nodes?
(a) 1s (b) 2s (c) 2p (d) 3p

16. For a shell of principal quantum number $n = 4$, there are:
(a) 16 orbitals (b) 4 subshells
(c) 32 electrons (maximum) (d) 4 electrons with $l = 3$

17. The isotopes contain the same number of:
(a) neutrons (b) protons
(c) protons + neutrons (d) electrons

18. Which of the following species has less number of protons than the number of neutrons?
(a) $^{12}_{6}C$ (b) $^{19}_{9}F$ (c) $^{23}_{11}Na$ (d) $^{24}_{12}Mg$

19. The angular part of the wave function depends on the quantum numbers are:
(a) n (b) l (c) m (d) s

20. Which of the following species are expected to have spectrum similar to hydrogen?
(a) He^+ (b) He^{2+} (c) Li^{2+} (d) Li^+

21. Which of the following statements is/are correct regarding a hydrogen atom?
(a) Kinetic energy of the electron is maximum in the first orbit
(b) Potential energy of the electron is maximum in the first orbit
(c) Radius of the second orbit is four times the radius of the first orbit
(d) Various energy levels are equally spaced

Answers

Single correct option

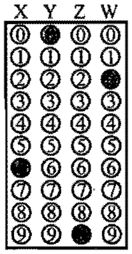
1. (c) 2. (d) 3. (c) 4. (b) 5. (a) 6. (d) 7. (d) 8. (d)
9. (b) 10. (c) 11. (b) 12. (c) 13. (a) 14. (a) 15. (b) 16. (c)
17. (d) 18. (b) 19. (b) 20. (a) 21. (c) 22. (b) 23. (a) 24. (b)
25. (a) 26. (b) 27. (b) 28. (a) 29. (b) 30. (c) 31. (b) 32. (b)
33. (b) 34. (c) 35. (c) 36. (d) 37. (c) 38. (b) 39. (c) 40. (b)
41. (c) 42. (a)

One or more than one correct options

1. (a, b, d) 2. (a, c) 3. (a, c) 4. (a, b, c) 5. (a, b, c, d) 6. (b) 7. (a, b, d) 8. (a, c, d)
9. (a, c, d) 10. (a) 11. (c, d) 12. (a, c, d) 13. (a, b) 14. (a, c) 15. (a, c) 16. (a, b, c)
17. (b, d) 18. (b, c) 19. (b, c) 20. (a, c) 21. (a, c)

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the figure :



1. For Li^{2+}, when an electron falls from a higher orbit to nth orbit, all the three types of lines, *i.e.*, Lyman, Balmer and Paschen was found in the spectrum. Here, the value of 'n' will be:
2. The emission lines of hydrogen contains ten lines. The highest orbit in which the electron is expected to be found is :

   [**Hint :** Number of lines $= \frac{n(n-1)}{2} = 10$

   $\therefore \qquad n = 5$]
3. Total number of nodes present in $4d$ orbitals will be :
4. Spin multiplicity of nitrogen in ground state will be :
5. Orbital frequency of electron in nth orbit of hydrogen is twice that of 2nd orbit. The value of n is :
6. If kinetic energy of an electron is reduce by (1/9) then how many times its de Broglie wavelength will increase.
7. If electrons in hydrogen sample return from 7th shell to 4th shell then how many maximum number of lines can be observed in the spectrum of hydrogen.
8. An electron in Li^{2+} ion is in excited state (n_2) . The wavelength corresponding to a transition to second orbit is 48.24 nm. From the same orbit, wavelength corresponding to a transition to third orbit is 142.46 nm. The value of n_2 is :
9. The energy corresponding to one of the lines in the Paschen series for H-atom is 18.16×10^{-20} J. Find the quantum numbers for the transition which produce this line.

   [**Hint :** $\Delta E = 2.18 \times 10^{-18}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

   $18.16 \times 10^{-20} = 2.18 \times 10^{-18}\left[\frac{1}{9} - \frac{1}{n^2}\right]$

   On solving, $n = 6$]
10. The angular momentum of electron in the shell in which the g-subshell first appears is $x \times \frac{h}{2\pi}$. The value of x will be :

    [**Hint :** $l = 4$ for g-subshell

    Thus, the subshell will first appear in $(n = l + 1 = 5)$ 5th shell.

    Angular momentum $(mvr) = n\frac{h}{2\pi}$

    $= 5\frac{h}{2\pi}$

    $\therefore \qquad n = 5$]

Answers

1. (1) **2.** (5) **3.** (3) **4.** (4) **5.** (1) **6.** (3) **7.** (6) **8.** (5)
9. (6) **10.** (5)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

The observed wavelengths in the line spectrum of hydrogen atom were first expressed in terms of a series by Johann Jakob Balmer, a Swiss teacher.

Balmer's empirical formula is:

$$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right] n = 3, 4, 5, \ldots$$

$R_H = 109678 \text{ cm}^{-1}$ *is the Rydberg constant.*

Niels Bohr derived this expression theoretically in 1913. *The formula is generalised to any one electron atom/ion.*

Answer the following questions:

1. Calculate the longest wavelength in Å (1 Å = 10^{-10} m) in the Balmer series of singly ionized helium He^+. Select the correct answer. Ignore the nuclear motion in your calculation.

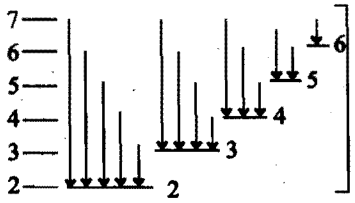
   (a) 2651 Å (b) 1641.1 Å
   (c) 6569 Å (d) 3249 Å

   [Hint: $$\frac{1}{\lambda_{He^+}} = R_H Z^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$
   $$= 109678 \times 4\left[\frac{5}{36}\right]$$
   $$\lambda_{He^+} = 1641.1 \text{ Å}]$$

2. How many lines in the spectrum will be observed when electrons return from 7th shell to 2nd shell?

   (a) 13 (b) 14 (c) 15 (d) 16

   [Hint: Number of lines in the spectrum
   $$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$
   $$= \frac{(7-2)(7-2+1)}{2} = 15$$



15 lines in the spectrum.]

3. The wavelength of first line of Balmer spectrum of hydrogen will be:

   (a) 4340 Å (b) 4101 Å (c) 6569 Å (d) 4861 Å

   [Hint: $$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$$
   for first line $n = 3$,
   $$\therefore \quad \frac{1}{\lambda} = 109678\left[\frac{1}{2^2} - \frac{1}{3^2}\right]$$
   $$\lambda = 6569 \text{ Å}]$$

4. In which region of electromagnetic spectrum does the Balmer series lie?

   (a) UV (b) Visible
   (c) Infrared (d) Far infrared

5. Which of the following is not correctly matched?

   (a) H_α— 6569 Å (Red) (b) H_β — 4861 Å (Blue)
   (c) H_γ— 4340 Å (Orange) (d) H_δ — 4101 Å (Violet)

• Passage 2

A formula analogous to the Rydberg formula applies to the series of spectral lines which arise from transitions from higher energy level to the lower energy level of hydrogen atom.

A muonic hydrogen atom is like a hydrogen atom in which the electron is replaced by a heavier particle, the 'muon'. The mass of the muon is about 207 *times the mass of an electron, while the charge remains same as that of the electron. Rydberg formula for hydrogen atom is:*

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] (R_H = 109678 \text{ cm}^{-1})$$

Answer the following questions:

1. Radius of first Bohr orbit of muonic hydrogen atom is:

   (a) $\frac{0.259}{207}$ Å (b) $\frac{0.529}{207}$ Å
   (c) 0.529×207 Å (d) 0.259×207 Å

2. Energy of first Bohr orbit of muonic hydrogen atom is:

   (a) $-\frac{13.6}{207}$ eV (b) -13.6×207 eV
   (c) $+\frac{13.6}{207}$ eV (d) $+13.6 \times 207$ eV

3. Ionization energy of muonic hydrogen atom is:

   (a) $+\frac{13.6}{207}$ eV (b) $+13.6 \times 207$ eV
   (c) $-\frac{13.6}{207}$ eV (d) -13.6×207 eV

4. Angular momentum of 'muon' in muonic hydrogen atom may be given as:

   (a) $\frac{h}{\pi}$ (b) $\frac{h}{2\pi}$ (c) $\frac{h}{4\pi}$ (d) $\frac{h}{6\pi}$

5. Distance between first and third Bohr orbits of muonic hydrogen atom will be:

   (a) $\frac{0.529}{207} \times 2$ Å (b) $\frac{0.529}{207} \times 7$ Å
   (c) $\frac{0.529}{207} \times 8$ Å (d) $\frac{0.529}{207}$ Å

• Passage 3

Nuclei that have 2, 8, 20, 28, 50, 82 *and* 126 *neutrons or protons are more abundant and more stable than other nuclei of similar mass. It is suggested that in the nuclear structure of the numbers* 2, 8, 20, 28, 50, 82 *and* 126, *which have become known as magic numbers, the nuclei possessing magic numbers are spherical and have zero quadruple moment and hence they are highly stable. Nuclear shells are filled when there are* 2, 8, 20, 28, 50, 82 *and* 126 *neutrons or protons in a nucleus. In even-even nuclei all the neutrons and protons are paired and cancel out spin and orbital angular momenta.*

Answer the following questions regarding the stability of nucleus:

1. Which of the following element(s) is/are stable though having odd number of neutrons and protons?
   (a) $^{6}_{3}Li$ (b) $^{11}_{5}B$ (c) $^{4}_{2}He$ (d) $^{14}_{7}N$
2. Stable nuclei having number of neutrons less than number of protons are:
   (a) $^{1}_{1}H$ (b) $^{3}_{2}He$ (c) $^{11}_{5}B$ (d) $^{11}_{6}C$
3. Doubly magic nucleus is . . . .
   (a) $^{207}_{82}Pb$ (b) $^{206}_{82}Pb$ (c) $^{208}_{82}Pb$ (d) $^{209}_{83}Bi$
4. Which among the following has unstable nucleus?
   (a) $^{14}_{7}N$ (b) $^{15}_{7}N$ (c) $^{13}_{7}N$ (d) $^{16}_{8}O$
5. Which of the following has zero spin and angular momentum?
   (a) $^{40}_{20}Ca$ (b) $^{3}_{1}H$ (c) $^{14}_{6}C$ (d) $^{37}_{17}Cl$

• Passage 4

The substances which contain species with unpaired electrons in their orbitals behave as paramagnetic substances. Such substances are weakly attracted by the magnetic field. The paramagnetism is expressed in terms of magnetic moment. The magnetic moment is related to the number of unpaired electrons according to the following relation:

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)}\ BM$$

where, n = number of unpaired electrons.

BM stands for Bohr magneton, a unit of magnetic moment.

$$1\,BM = \frac{eh}{4\pi mc} = 9.27 \times 10^{-24}\ Am^2 \text{ or } J\,T^{-1}$$

Answer the following questions:

1. Which of the following ions has the highest magnetic moment?
   (a) Fe^{2+} (b) Mn^{2+} (c) Cr^{3+} (d) V^{3+}
2. Which of the following ions has magnetic moment equal to that of Ti^{3+}:
   (a) Cu^{2+} (b) Ni^{2+} (c) Co^{2+} (d) Fe^{2+}
3. An ion of a *d*-block element has magnetic moment 5.92 BM Select the ion among the following:
   (a) Zn^{2+} (b) Sc^{3+} (c) Mn^{2+} (d) Cr^{3+}
4. In which of these options do both constituents of the pair have the same magnetic moment?
   (a) Zn^{2+} and Cu^{+} (b) Co^{2+} and Ni^{2+}
   (c) Mn^{4+} and Co^{2+} (d) Mg^{2+} and Sc^{+}
5. Which of the following ions are diamagnetic?
   (a) He^{2+} (b) Sc^{3+} (c) Mg^{2+} (d) O^{2-}

• Passage 5

At the suggestion of Ernest Rutherford, Hans Geiger and Ernest Marsden bombarded a thin gold foil by α-particles from a polonium source. It was expected that α-particles would go right through the foil with hardly any deflection. Although, most of the alpha particles indeed were not deviated by much, a few were scattered through very large angles. Some were even scattered in the backward direction. The only way to explain the results, Rutherford found, was to picture an atom as being composed of a tiny nucleus in which its positive charge and nearly all its mass are concentrated. Scattering of α-particles is proportional to target thickness and is inversely proportional to the fourth power of sin $\frac{\theta}{2}$, where, θ is scattering angle. Distance of closest approach may be calculated as:

$$r_{min} = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 K}$$

where, K = kinetic energy of α-particles.

Answer the following questions:

1. Rutherford's α-particle scattering experiment led to the conclusion that:
   (a) mass and energy are related
   (b) mass and positive charge of an atom are concentrated in the nucleus
   (c) neutrons are present in the nucleus
   (d) atoms are electrically neutral
2. From the α-particle scattering experiment, Rutherford concluded that:
   (a) α-particles can approach within a distance of the order of 10^{-14} m of the nucleus
   (b) the radius of the nucleus is less than 10^{-14} m
   (c) scattering follows Coulomb's law
   (d) the positively charged parts of the atom move with extremely high velocities
3. Rutherford's scattering formula fails for very small scattering angles because:
   (a) the gold foil is very thin
   (b) the kinetic energy of α-particles is very high
   (c) the full nuclear charge of the target atom is partially screened by its electron
   (d) there is strong repulsive force between the α-particles and nucleus of the target
4. Alpha particles that come closer to the nuclei:
   (a) are deflected more (b) are deflected less
   (c) make more collision (d) are slowed down more
5. Which of the following quantities will be zero for alpha particles at the point of closest approach to the gold atom, in Rutherford's scattering of alpha particles?
   (a) Acceleration (b) Kinetic energy
   (c) Potential energy (d) Electrical energy

• Passage 6

The splitting of spectral lines by a magnetic field is called the Zeeman effect after the Dutch physicist Pieter Zeeman. The Zeeman effect is a vivid confirmation of space quantization. Magnetic quantum number 'm' was introduced during the study of Zeeman effect. 'm' can have the $(2l+1)$ values $(-l, 0, +l)$. Magnetic quantum number represents the orientation of atomic orbitals in three-dimensional space. The normal Zeeman effect consists of the splitting of a spectral line of frequency ν_0 into three components, i.e.,

$$\nu_1 = \nu_0 - \frac{e}{4\pi m}B;\ \nu_2 = \nu_0;\ \nu_3 = \nu_0 + \frac{e}{4\pi m}B$$

Here, B is magnetic field.

Answer the following questions:

1. Which of the following statements is incorrect with reference to the Zeeman effect?
   (a) In a magnetic field, the energy of a particular atomic state depends on the values of 'm' and 'n'
   (b) Zeeman effect is used to calculate the e/m ratio for an electron
   (c) Individual spectral lines split into separate lines. The distance between them is independent of the magnitude of the magnetic field
   (d) The Zeeman effect involves splitting of a spectral line of frequency v_0 into three components
2. A d-subshell in an atom in the presence and absence of magnetic field is:
   (a) five-fold degenerate, non-degenerate
   (b) seven-fold degenerate, non-degenerate
   (c) five-fold degenerate, five-fold degenerate
   (d) non-degenerate, five-fold degenerate
3. Which among the following is/are correct about the orientation of atomic orbitals in space?
   (a) s-orbitals has single orientation
   (b) d-subshell orbitals have three orientations along x, y and z directions
   (c) f-subshell have seven orientations in their orbitals
   (d) None of the above
4. Zeeman effect explains splitting of spectral lines in:
   (a) magnetic field (b) electric field
   (c) both (a) and (b) (d) none of these
5. In presence of magnetic field, d-suborbit is:
   (a) five-fold degenerate (b) three-fold degenerate
   (c) seven-fold degenerate (d) non-degenerate

Passage 7

Spin angular momentum of an electron has no analogue in classical mechanics. However, it turns out that the treatment of spin angular momentum is closely analogous to the treatment of orbital angular momentum.

$$\text{Spin angular momentum} = \sqrt{s(s+1)}\,\hbar$$

$$\text{Orbital angular momentum} = \sqrt{l(l+1)}\,\hbar$$

Total spin of an atom or ion is a multiple of $\frac{1}{2}$. Spin multiplicity is a factor to confirm the electronic configuration of an atom or ion.

$$\text{Spin multiplicity} = (2\Sigma s + 1)$$

Answer the following questions:

1. Total spin of Mn^{2+} ($Z = 25$) ion will be:
   (a) $\frac{3}{2}$ (b) $\frac{1}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$
2. Which of the following electronic configurations have four spin multiplicity?
   (a) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ (b) $\boxed{\uparrow}\boxed{\uparrow}\boxed{\downarrow}$
   (c) $\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}$ (d) $\boxed{\downarrow}\boxed{\downarrow}\boxed{\downarrow}$
3. Which of the following quantum numbers is not derived from Schrödinger wave equation?
   (a) Principal (b) Azimuthal
   (c) Magnetic (d) Spin
4. In any subshell, the maximum number of electrons having same value of spin quantum number is:
   (a) $\sqrt{l(l+1)}$ (b) $l+2$ (c) $2l+1$ (d) $4l+2$
5. The orbital angular momentum for a $2p$-electron is:
   (a) $\sqrt{3}\,\hbar$ (b) $\sqrt{6}\,\hbar$ (c) zero (d) $\sqrt{2}\,\frac{h}{2\pi}$

• Passage 8

Dual nature of matter was proposed by de Broglie in 1923, it was experimentally verified by Davisson and Germer by diffraction experiment. Wave character of matter has significance only for microscopic particles. de Broglie wavelength or wavelength of matter wave can be calculated using the following relation:

$$\lambda = \frac{h}{mv}$$

where, 'm' and 'v' are the mass and velocity of the particle.

de Broglie hypothesis suggested that electron waves were being diffracted by the target, much as X-rays are diffracted by planes of atoms in the crystals.

Answer the following questions:

1. Planck's constant has same dimension as that of:
   (a) work (b) energy
   (c) power (d) angular momentum
2. Wave nature of electrons is shown by:
   (a) photoelectric effect (b) Compton effect
   (c) diffraction experiment (d) Stark effect
3. de Broglie equation is obtained by combination of which of the following theories?
   (a) Planck's quantum theory
   (b) Einstein's theory of mass-energy equivalence
   (c) Theory of interference
   (d) Theory of diffraction
4. Which among the following is not used to calculate the de Broglie wavelength?
   (a) $\lambda = \frac{c}{v}$ (b) $\lambda = \frac{h}{mv}$
   (c) $\lambda = \frac{h}{\sqrt{2Em}}$ (d) $\lambda = \frac{h}{\sqrt{2qVm}}$
5. The wavelength of matter waves associated with a body of mass 1000 g moving with a velocity of 100 m/sec is:
   (a) 6.62×10^{-39} cm (b) 6.62×10^{-36} cm
   (c) 6.626×10^{-36} m (d) 3.31×10^{-32} m
6. An electron microscope is used to probe the atomic arrangements to a resolution of 5 Å. What should be the electric potential to which the electrons need to be accelerated ? **(VITEEE 2008)**
   (a) 2.5 V (b) 6 V
   (c) 2.5 kV (d) 5 kV

Passage 9

Orbital is the region in an atom where the probability of finding the electron is maximum. It represents three-dimensional motion of an electron around the nucleus. Orbitals do not specify a definite path according to the uncertainty principle. An orbital is described with the help of wave function ψ. Whenever an electron is described by a wave function, we say that an electron occupies that orbital. Since, many wave functions are possible for an electron, there are many atomic orbitals in an atom. Orbitals have different shapes; except s-orbitals, all other orbitals have directional character. Number of spherical nodes in an orbital is equal to $(n - l - 1)$. *Orbital angular momentum of an electron is* $\sqrt{l(l+1)}\,\hbar$.

Answer the following questions:

1. Which of the following orbitals is not cylindrically symmetrical about z-axis?
   (a) $3d_{z^2}$ (b) $4p_z$ (c) $6s$ (d) $3d_{yz}$
2. The nodes present in $5p$-orbital are:
   (a) one planar, five spherical (b) one planar, four spherical
   (c) one planar, three spherical (d) four spherical
3. When an atom is placed in a magnetic field, the possible number of orientations for an orbital of azimuthal quantum number 3 is:
   (a) three (b) one (c) five (d) seven
4. Orbital angular momentum of f-electrons is:
   (a) $\sqrt{2}\,\hbar$ (b) $\sqrt{3}\,\hbar$ (c) $\sqrt{12}\,\hbar$ (d) $2\,\hbar$
5. Which of the following orbitals has/have two nodal planes?
   (a) d_{xy} (b) d_{yz} (c) $d_{x^2-y^2}$ (d) All of these

Passage 10

The hydrogen-like species Li^{2+} *is in a spherically symmetric state* S_1 *with one radial node. Upon absorbing light the ion undergoes transition to a state* S_2. *The state* S_2 *has one radial node and its energy is equal to the ground state energy of the hydrogen atom.*

(IIT 2010)

Answer the following questions:

1. The state S_1 is :
   (a) $1s$ (b) $2s$ (c) $2p$ (d) $3s$
   [**Hint:** $2s$ is symmetrical having one radial node.]
2. Energy of the state S_1 in units of the hydrogen atom ground state energy is:
   (a) 0.75 (b) 1.50 (c) 2.25 (d) 4.50
   [**Hint:** $\dfrac{E_{Li^{2+}}(2s)}{E_H} = \dfrac{-\frac{9}{4}\times 13.6}{-13.6} = 2.25$]
3. The orbital angular momentum quantum number of the state S_2 is:
   (a) 0 (b) 1 (c) 2 (d) 3
   [**Hint:** Orbital angular momentum quantum number of $3p$ subshell, *i.e.*, $l = 1$
   $$\underset{2s}{S_1} \xrightarrow{\text{Transition}} \underset{3p}{S_2}$$]

Answers

Passage 1.	1. (b)	2. (c)	3. (c)	4. (b)	5. (c)	
Passage 2.	1. (b)	2. (b)	3. (b)	4. (b)	5. (c)	
Passage 3.	1. (a, d)	2. (a, b)	3. (c)	4. (c)	5. (a)	
Passage 4.	1. (b)	2. (a)	3. (c)	4. (a, c)	5. (b, c, d)	
Passage 5.	1. (b)	2. (a, b, c)	3. (c, d)	4. (a)	5. (b)	
Passage 6.	1. (b)	2. (d)	3. (a, c)	4. (a)	5. (d)	
Passage 7.	1. (c)	2. (a)	3. (d)	4. (c)	5. (d)	
Passage 8.	1. (d)	2. (c)	3. (a, b)	4. (a)	5. (c)	6. (b)
Passage 9.	1. (d)	2. (c)	3. (d)	4. (c)	5. (d)	
Passage 10.	1. (b)	2. (c)	3. (b)			

SELF ASSESSMENT

ASSIGNMENT NO. 2

SECTION-I

Straight Objective Type Questions

This section contains 11 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Which one of the following leads to third line of Balmer spectrum from red end (For hydrogen atom)?
(a) $2 \longrightarrow 5$ (b) $5 \longrightarrow 2$ (c) $3 \longrightarrow 2$ (d) $4 \longrightarrow 1$

2. The orbital angular momentum and angular momentum (classical analogue) for the electron of 4*s*-orbital are respectively, equal to:
(a) $\sqrt{12}\,\frac{h}{2\pi}$ and $\frac{h}{2\pi}$ (b) zero and $\frac{2h}{\pi}$
(c) $\sqrt{6}h$ and $\frac{2h}{\pi}$ (d) $\sqrt{2}\,\frac{h}{2\pi}$ and $\frac{3h}{2\pi}$

3. A sample of hydrogen atom is excited to $n = 4$ state. In the spectrum of emitted radiation, the number of lines in the ultraviolet and visible regions are respectively:
(a) 3 : 2 (b) 2 : 3 (c) 1 : 3 (d) 3 : 1

4. Number of de Broglie waves made by a Bohr electron in an orbit of maximum magnetic quantum number + 2 is:
(a) 1 (b) 2 (c) 3 (d) 4

5. First line of Lyman series of hydrogen atom occurs at $\lambda = x$ Å. The corresponding line of He^+ will occur at:
(a) $4x$ (b) $3x$ (c) $x/3$ (d) $x/4$

6. Electronic transition in He^+ ion takes from n_2 to n_1 shell such that;

$$2n_2 + 3n_1 = 18 \quad \text{...(i)}$$
$$2n_2 - 3n_1 = 6 \quad \text{...(ii)}$$

then what will be the total number of photons emitted when electrons transit to n_1 shell?
(a) 21 (b) 15 (c) 20 (d) 10

7. Which of the following sets of quantum numbers is not possible for an electron ? **[PET (Raj.) 2008]**
(a) $n = 1, l = 0, m_l = 0, m_s = -1/2$
(b) $n = 2, l = 1, m_l = 0, m_s = -1/2$
(c) $n = 1, l = 1, m_l = 0, m_s = +1/2$
(d) $n = 2, l = 1, m_l = 0, m_s = +1/2$

8. The average life of an excited state of hydrogen atom is of the order of 10^{-8} sec. The number of revolutions made by an electron when it returns from $n = 2$ to $n = 1$ is:
(a) 2.28×10^6 (b) 22.8×10^6 (c) 8.23×10^6 (d) 2.82×10^6

9. The wave number of a particular spectral line in the atomic spectrum of a hydrogen like species increases 9/4 times when deuterium nucleus is introduced into its nucleus, then which of the following will be the initial hydrogen like species?
(a) Li^{2+} (b) Li^+ (c) He^+ (d) Be^{3+}

10. Energy of electron in the first Bohr orbit of H-atom is -313.6 kcal mol^{-1}; then the energy in second Bohr orbit will be:
(a) $+313.6$ kcal mol^{-1} (b) -78.4 kcal mol^{-1}
(c) -34.84 kcal mol^{-1} (d) -12.5 kcal mol^{-1}

11. Which phenomenon best supports the theory that matter has a wave nature ? **(VITEEE 2008)**
(a) Electron momentum (b) Electron diffraction
(c) Photon momentum (d) Photon diffraction

SECTION-II

Multiple Answers Type Objective Questions

12. Which of the following is/are correct?
(a) An electron in excited state cannot absorb a photon
(b) Energy of electrons depends only on the principal quantum numbers
(c) Energy of electrons depends only on the principal quantum number for hydrogen atom
(d) Difference in potential energy of two shells is equal to the difference in kinetic energy of these shells

13. Which of the following statements is/are correct?
(a) Energy of 4*s*, 4*p*, 4*d* and 4*f* are same for hydrogen
(b) Angular momentum of electron = $I\omega$
(c) For all values of '*n*', the *p*-orbitals have the same shape
(d) Orbital angular momentum = $nh/2\pi$

14. Which of the following orbitals are associated with angular nodes?
(a) *f* (b) *d* (c) *p* (d) *s*

15. The correct statement(s) among the following is/are:
(a) All *d*-orbitals except d_{z^2} have two angular nodes
(b) $d_{x^2-y^2}, d_{z^2}$ lie on the axes
(c) The degeneracy of *p*-orbitals remains unaffected in the presence of external magnetic field
(d) *d*-orbitals have 3-fold degeneracy

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Kinetic energy of photoelectrons increases with increase in the frequency of incident radiation.

Because

Statement-2: The number of photoelectrons ejected increases with increase in intensity of incident radiation.

17. **Statement-1:** Photoelectric effect is easily pronounced by caesium metal.

Because

Statement-2: Photoelectric effect is easily pronounced by the metals having high ionization energy.

18. **Statement-1:** Electrons in K-shell revolve in circular orbit.

Because

Statement-2: Principal quantum number 'n' is equal to 1 for the electrons in K-shell.

19. **Statement-1:** Orbit and orbital are synonymous.

Because

Statement-2: Orbit is the path around the nucleus in which electron revolves.

20. **Statement-1:** $C_6 = 1s^2, 2s^1, 2p^3$ is the electronic configuration in first excited state.

Because

Statement-2: Maximum energy by an electron is possessed in its ground state.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then the correctly bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

21. Match the Column-I with Column-II:

	Column-I	Column-II
(a)	$4s$	(p) Circular orbit around nucleus
(b)	$4p$	(q) Non-direction orbitals
(c)	$1s$	(r) Angular momentum = $\frac{2h}{\pi}$
(d)	$3d$	(s) Number of radial node = 0

22. Match the properties of Column-I with the formulae in Column-II:

Column-I	Column-II
(a) Angular momentum of electron	(p) $\sqrt{l(l+1)}\frac{h}{2\pi}$
(b) Orbital angular momentum	(q) $I\omega$
(c) Wavelength of matter wave	(r) $\frac{nh}{2\pi}$
(d) Quantised value(s)	(s) h/p

23. Match the Column-I with Column-II:

	Column-I		Column-II
(a)	Electrons cannot exist in the nucleus	(p)	de Broglie wave
(b)	Microscopic particles in motion are associated with	(q)	Electromagnetic wave
(c)	No medium is required for propagation	(r)	Uncertainty principle
(d)	Concept of orbit was replaced by orbital	(s)	Transverse wave

SECTION-V

Linked Comprehension Type Questions

A chemist was performing an experiment to study the effect of varying voltage on the velocity and de Broglie wavelength of the electrons. In first experiment, the electron was accelerated through a potential difference of 1 kV and in second experiment, it was accelerated through a potential difference of 2 kV.

The wavelength of de Broglie waves associated with electron is given by:

$$\lambda = \frac{h}{\sqrt{2qVm}}$$

where, V is the voltage through which an electron is accelerated.

Putting the values of h, m and q we get:

$$\lambda = \frac{12.3}{\sqrt{V}} \text{ Å}$$

Answer the following questions:

24. The wavelength of electron will be:

(a) 1.4 times in first case than in second case

(b) 1.4 times in second case than in first case

(c) double in second case than in first case

(d) double in first case than in second case

25. In order to get half velocity of electrons in second case, the applied potential will be:

(a) 0.25 kV (b) 2 kV (c) 0.5 kV (d) 0.75 kV

26. The velocity of electron will be:

(a) same in both cases

(b) 1.4 times in second experiment than in first experiment

(c) double in second experiment than in first experiment

(d) four times in the second case than in first case

Answers

1. (b) **2.** (b) **3.** (a) **4.** (c) **5.** (d) **6.** (d) **7.** (c) **8.** (c)
9. (d) **10.** (b) **11.** (b) **12.** (a, c, d) **13.** (a, b, c) **14.** (a, b, c) **15.** (a, b, c) **16.** (b)
17. (c) **18.** (b) **19.** (d) **20.** (c) **21.** (a-p, q,r) (b-r) (c-p,q) (d-s)
22. (a-q,r) (b-p) (c-s) (d-q,r) **23.** (a-r) (b-p) (c-q,s) (d-r) **24.** (a) **25.** (a) **26.** (b)

CHAPTER 3

RADIOACTIVITY AND NUCLEAR TRANSFORMATION

3.1 RADIOACTIVITY

Radioactivity is a process in which nuclei of certain elements undergo spontaneous disintegration without excitation by any external means.

All heavy elements from bismuth through uranium and a few of lighter elements have naturally occurring isotopes which possess the property of radioactivity. These isotopes have unstable nuclei and attain stability through the phenomenon of radioactivity. The activity results in the emission of a complex type of powerful radiations known as alpha, beta and gamma rays. **All those substances which have the tendency to emit these radiations are termed radioactive materials.** The property of disintegration of a radioactive material is independent of temperature, pressure and other external conditions. **Radioactivity is a nuclear phenomenon,** *i.e.*, the kind of intensity of the radiation emitted by any radioactive substance is absolutely the same whether the element is present as such or in any one of its compounds. $^{226}_{88}$Ra isotope is radioactive. When this isotope is dissolved in sulphuric acid, it is converted into radium sulphate ($RaSO_4$). The property of radioactivity in radium sulphate and free radium isotope is the same, no doubt that the radium ion in radium sulphate has different number of electrons than free neutral radium isotope.

	Radium atom (Ra)	Radium ion (Ra^{2+})
No. of protons	88	88
No. of electrons	88	86
Atomic mass	226	226

This example clearly shows that the phenomenon of radioactivity does not depend on the orbital electrons but depends only on the composition of nucleus.

In the universe, there are only 81 stable elements having one or more non-radioactive isotopes. No stable isotope exists for the elements above $^{209}_{83}$Bi. Thus, **bismuth** is the heaviest stable nuclide. Two earlier elements **technetium** and **promethium** exist only as radioactive isotopes (see table at the bottom).

3.2 CHARACTERISTICS OF RADIOACTIVE RADIATIONS

The following are the main characteristics of radiations emitted by radioactive materials:

(i) Photographic effect: Radiations affect the photographic plate in a similar manner to that of light. The effect is even observed in dark. The portions of the photographic plate where radiations fall, become blackened after treatment with a developer.

This property is used for the detection of radioactivity.

(ii) Scintillations: When radiations fall on the zinc sulphide (ZnS) screen, flashes of light are produced. This is known as scintillations. The number of particles emitted in unit time can be counted by noting the scintillations produced in the apparatus having a zinc sulphide screen.

The apparatus is called spinthariscope.

(iii) Emission of heat: Radioactive materials continuously emit energy in the form of kinetic energy. Heat energy is

								H									He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Shaded elements are radioactive

produced when the radiation particles collide with matter. Radium produces 134.7 cals of heat per gram per hour.

(iv) Physiological effect: Radioactive radiations have serious physiological effects, which may be cumulative over a period of time. Even a short exposure to intense source of radiations is sufficient to cause painful inflammation. **Gamma rays are most effective.** In general, abnormal cells are more affected than the healthy cells. On account of this property radiations are used to destroy cancerous tumours.

(v) Ionisation of gases: This is the most important effect observed in the case of radioactive radiations. Radiations produce ionisation in the gases through which they are passed. **This effect is used for quantitative measurement of radioactivity.** The radiations cause a number of molecules of the gas to lose electrons and pass into positive ions. The electrons immediately become attached to the neutral molecules, thus making them negative ions. **The total ions of one sign are equal to the total ions of the other type. The rate of production of these ions is proportional to the intensity of radiation.** The extent, to which a definite quantity of a gas is rendered a conductor by a radioactive substance, is a measure of the radioactive power of a radioactive substance. The apparatus used for this purpose is called **electroscope** (Fig. 3.1).

Geiger-Muller counter is based on this effect. The ionisation chamber consists of 90% argon and 10% ethyl alcohol vapour at 10 mm pressure. Due to ionisation, a flow of current occurs, which is measured after amplification.

3.3 HISTORY OF THE DISCOVERY OF RADIOACTIVITY

In 1895, **Henri Becquerel** was studying the effect of sunlight on various phosphorescent minerals, among them a uranium ore. During a period of several cloudy days, he left the uranium sample in a drawer along with some photographic paper wrapped in black paper. Much to his surprise, he discovered that the photographic paper had been fogged by exposure to some invisible radiation from uranium. He called this mysterious property of the ore 'radioactivity'. **Radioactivity means ray-emitting activity.** He further observed that the radioactive mineral emitted these mysterious radiations day after day and month after month and the emission seemed to be endless. The emission was completely unaffected by physical and chemical conditions. A year later, in 1896, **Marie Curie** found that besides uranium and its compounds, thorium was another element which possessed the property of radioactivity. In 1898, **Marie Curie** and her husband **P. Curie** observed that the uranium ore '*pitchblende*', contained more activity than was expected from the uranium which it contained. It must be obviously due to the presence of some other radioactive elements which were far more radioactive than uranium. Finally, they isolated two new radioactive elements **polonium** and **radium.**

Almost in the same period, **G. C. Schmidt** reported that thorium compounds possessed radioactivity. In 1901, **A. Debierne and F.S. Giesel** discovered another new radioactive element actinium in uranium minerals. Further systematic researches led to the discovery of many more radioactive elements. At present over forty such materials are known to exist in nature.

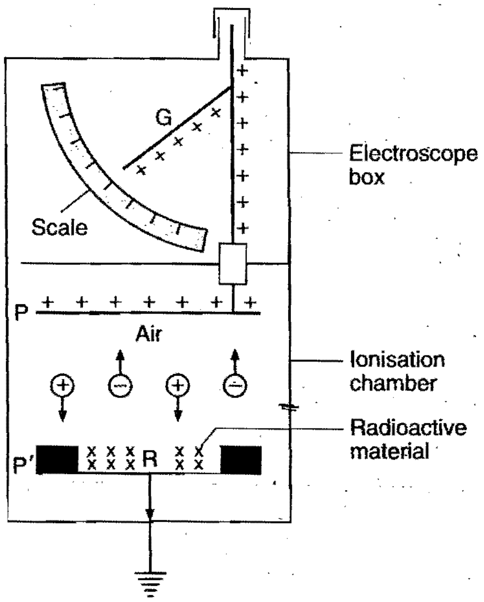
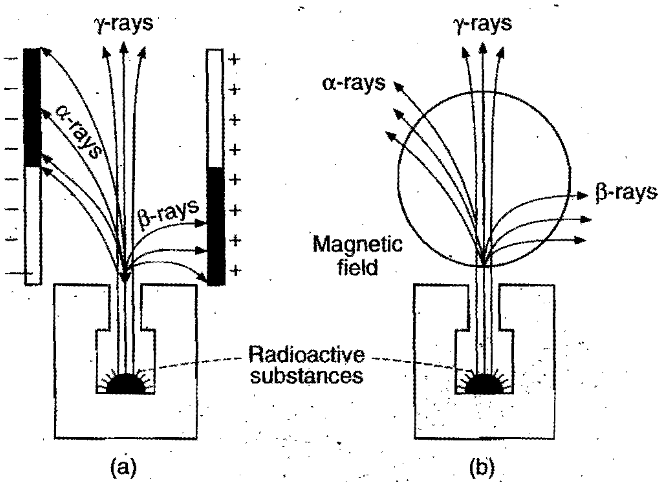


Fig. 3.1 Electroscope for measurement of radioactivity

3.4 ANALYSIS OF RADIOACTIVE RADIATIONS

In 1904, **Rutherford and his co-workers** observed that when radioactive radiations were subjected to a magnetic field or a strong electric field, these were split into three types, as shown in Fig. 3.2. The rays which are attracted towards the negative plate are positively charged and are called **alpha (α) rays.** The rays which are deflected towards the positive plate are negatively charged and are called **beta (β) rays.** The third type of rays which are not deflected on any side but move straight are known as **gamma (γ) rays.** The important properties of these radiations are tabulated on next page:



(a) (b)

Fig. 3.2 (a) Deflection of radioactive rays in electric field and (b) Emission of radioactive rays and their deflection in a magnetic field.

Property	α-rays	β-rays	γ-rays
1. Nature	These consist of small positively charged particles which are merely nuclei of helium atoms, each consisting of 2 protons and 2 neutrons. These are represented as $^{4}_{2}$He.	These consist of negatively charged particles which have the same e/m value as the cathode rays. β-rays are merely electrons. The β-rays are represented as $_{-1}^{0}\beta$ or $_{-1}^{0}e$.	γ-rays are similar to X-rays. These are neutral in nature. They have very small wavelengths of the order of 10^{-10} to 10^{-13} m.
2. Velocity	The α-rays are ejected with high velocities ranging from 1.4×10^9 to 1.7×10^9 cm/sec. The velocity of α-rays depends upon the kind of nucleus from which they are emitted.	The β-rays are much faster than α-rays. They have generally different velocities sometimes approaching the velocity of light.	They travel with the velocity of light.
3. Penetrating power	α-particles have small penetrating power due to relatively larger size. They are stopped by a piece of aluminium foil of 0.1 mm thickness.	β-rays are more penetrating than α-particles. This is due to small size and high velocity. These are stopped by a 1 cm thick sheet of aluminium.	Due to high velocity and non-material character, γ-rays are 10^{10} times more penetrating than α-rays.
4. Ionising power	α-particles produce intense ionisation in gases. Ionising power is 100 times greater than β-rays and 10,000 times greater than γ-rays. This is due to high kinetic energy.	Due to low value of kinetic energy ionising power is less than α-particles but 100 times greater than γ-rays.	γ-rays produce minimum ionisation or no ionisation.
5. Photographic effect	α-particles affect the photographic plate.	β-rays effect on a photographic plate is greater than α-particles. Like cathode rays, β-rays produce X-rays.	γ-rays have little effect on photographic plate.
6. Effect on zinc sulphide screen	α-particles produce luminosity on ZnS screen due to high kinetic energy.	β-particles have little effect on ZnS screen due to low kinetic energy.	γ-rays have very little effect on ZnS screen.

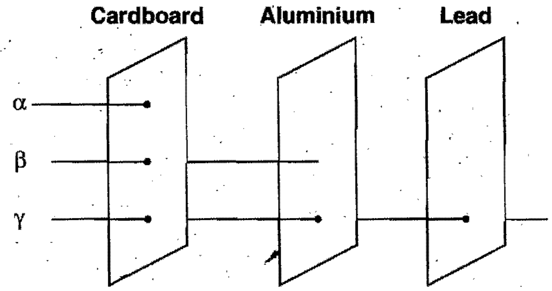


Fig. 3.2 (c) Comparison of penetrating power of α, β and γ-rays

Note :

(i) The quantum energy of γ-rays emitted by a radioactive substance can have unique and discrete values.

(ii) The energy of α-particles emitted by a radioactive substance (α-emitter) has unique value.

(iii) The energy of β-particles emitted by a radioactive substance, (β-emitter) can have any value between zero and end point energy.

3.5 CAUSE OF RADIOACTIVITY

Except in the case of ordinary hydrogen, all other nuclei contain both neutrons and protons. A look at the stable nuclei shows that the ratio n/p (neutrons/protons) in them is either equal to 1 or more than 1. The ratio is ≈ 1 in all the light-stable nuclei up to calcium ($^{40}_{20}\text{Ca}$) and thereafter the ratio is greater than 1 and increases up to 1.6 for heavy stable nuclei as shown in the following table:

Neutron-proton ratio in some stable nuclei

Isotope	$^{12}_{6}\text{C}$	$^{14}_{7}\text{N}$	$^{16}_{8}\text{O}$	$^{20}_{10}\text{Ne}$	$^{40}_{20}\text{Ca}$	$^{64}_{30}\text{Zn}$	$^{90}_{40}\text{Zr}$	$^{120}_{50}\text{Sn}$	$^{150}_{60}\text{Nd}$	$^{202}_{80}\text{Hg}$
n	6	7	8	10	20	34	50	70	90	122
p	6	7	8	10	20	30	40	50	60	80
n/p	1	1	1	1	1	1.13	1.25	1.40	1.50	1.53

The variation of n *versus* p for some nuclei is shown in Fig. 3.3.

The stable nuclei lie within the shaded area which is called the **region** or **zone of stability.** All the nuclei falling outside this zone are invariably radioactive and unstable in nature. **Nuclei that fall above the stability zone have an excess of neutrons while those lying below have more protons.** Both of these cause instability. These nuclei attain stability by making adjustment in the n/p ratio.

Two cases thus arise:

(i) n/p ratio is higher than required for stability. Such nuclei have a tendency to emit β-rays, *i.e.*, transforming a neutron into proton.

$$^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}e \text{ (β-particle)}$$

Thus, in β-emission n/p ratio decreases. For example, in the change of $^{14}_{6}\text{C}$ to $^{14}_{7}\text{N}$, n/p ratio decreases from 1.33 to 1.

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$$

Similarly, in the following examples, the n/p ratio decreases during β-emission:

$$^{32}_{15}P \longrightarrow ^{32}_{16}S + ^{0}_{-1}e$$

n/p ratio 17/15 16/16

$$^{87}_{36}Kr \longrightarrow ^{87}_{37}Rb + ^{0}_{-1}e$$

n/p ratio 51/36 50/37

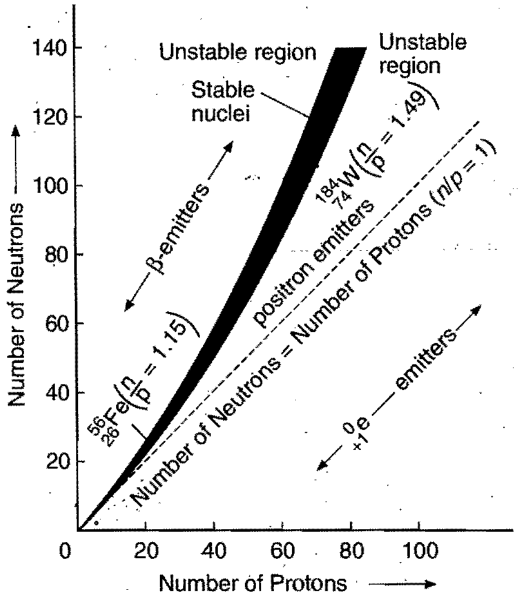


Fig. 3.3 Variation of number of neutrons with number of protons in stable non-radioactive nuclei

(ii) n/p ratio is lower than required for stability. Such nuclei can increase n/p ratio by adopting any one of the following three ways:

(a) By emission of an alpha particle (Natural radioactivity):

$$^{238}_{92}U \longrightarrow ^{234}_{90}Th + ^{4}_{2}He \ (\alpha\text{-particle})$$

n/p ratio 146/92 = 1.58 144/90 = 1.60

(b) By emission of a positron (Artificial emission):

$$^{13}_{7}N \longrightarrow ^{13}_{6}C + ^{0}_{+1}e$$

n/p ratio 6/7 7/6

(c) By *K*-electron capture:

$$^{194}_{79}Au + ^{0}_{-1}e \longrightarrow ^{194}_{78}Pt$$

n/p ratio 115/79 116/78

Alpha emission is usually observed in natural radioactive isotopes while emission of positron or *K*-electron capture is observed in artificial radioactive isotopes. The unstable nuclei continue to emit alpha or beta particles until a stable nucleus comes into existence.

Conclusion: (i) For the elements (mass number $A \leq 40$), nature prefers the number of protons and neutrons in the nucleus to be same or perhaps one more neutron than protons. *e.g.*, $^{7}_{3}Li$, $^{12}_{6}C$, $^{16}_{8}O$, $^{32}_{16}S$, etc.

(ii) For the elements (mass number $A \geq 40$), there is preference for the number of neutrons to be greater than the number of protons ($n > Z$), *e.g.*, $^{11}_{5}B$ is stable but $^{11}_{6}C$ is not. There are two stable elements $^{1}_{1}H$ and $^{3}_{2}He$, in which number of neutrons is less than that of protons.

(iii) Beyond Bi ($Z = 83$), all isotopes are unstable and radioactive. These elements do not have a strong nuclear **"superglue"** to hold nucleons together.

Illustration :

Nuclide	$\frac{n}{p}$ Ratio	Nature of Emission
$^{35}_{16}S$	$\frac{19}{16} = 1.2$	β-emission $^{35}_{16}S \longrightarrow ^{35}_{17}Cl + ^{0}_{-1}e$
$^{17}_{9}F$	$\frac{8}{9}\left(\frac{n}{p} < 1\right)$	Positron emission $^{17}_{9}F \longrightarrow ^{17}_{8}O + ^{0}_{+1}e$
$^{105}_{47}Ag$	$\frac{n}{p} = \frac{58}{47} = 1.23$	Lies below stability belt, it has a heavy nucleus and it decays by K-electron capture. $^{105}_{47}Ag + ^{0}_{-1}e \longrightarrow ^{105}_{46}Pd + h\nu$
$^{238}_{92}U$	$\frac{n}{p} = \frac{146}{92} = 1.59$	It is a neutron rich species. It undergoes decay by α-emission. $^{238}_{92}U \longrightarrow ^{234}_{90}Th + ^{4}_{2}He$

Some other examples : $^{60}_{29}Cu$ (positron emission), $^{140}_{54}Xe$ (α or β-decay), $^{240}_{93}N_p$ (α-decay), $^{33}_{15}P$ (β-decay), $^{125}_{53}I$ (K-electron capture).

3.6 THEORY OF RADIOACTIVE DISINTEGRATION

Rutherford and **Soddy**, in 1903, postulated that radioactivity is a nuclear phenomenon and all the radioactive changes are taking place in the nucleus of the atom. They presented an interpretation of the radioactive processes and the origin of radiations in the form of a theory known as **theory of radioactive disintegration.** The main points of the theory are:

(i) The atomic nuclei of the radioactive elements are unstable and liable to disintegrate any moment.

(ii) The disintegration is spontaneous, *i.e.*, constantly breaking. The rate of breaking is not affected by external factors like temperature, pressure, chemical combination, etc.

(iii) During disintegration, atoms of new elements called daughter elements having different physical and chemical properties than the parent element come into existence.

(iv) During disintegration, either alpha or beta particles are emitted from the nucleus.

The disintegration process may proceed in one of the following two ways:

(a) α-particle emission: When an α-particle [$^{4}_{2}He$] is emitted from the nucleus of an atom of the parent element, the nucleus of the new element, called daughter element, possesses atomic mass or atomic mass number less by four units and nuclear charge or atomic number less by 2 units because α-particle has mass of 4 units and nuclear charge of two units.

The daughter element after α-emission is called an isodiaphere of parent element.

Parent element $\xrightarrow{-\alpha}$ Daughter element

Atomic mass	W	$W-4$
Atomic number	Z	$Z-2$

For example, in the following transformations, each α-particle emission is accompanied by decrease of atomic mass by 4 and of atomic number by 2.

$$\underset{\text{(Radium)}}{{}^{226}_{88}\text{Ra}} \longrightarrow \underset{\text{(Radon)}}{{}^{222}_{86}\text{Rn}} + {}^{4}_{2}\text{He}$$

$$\underset{\text{(Uranium)}}{{}^{238}_{92}\text{U}} \longrightarrow \underset{\text{(Thorium)}}{{}^{234}_{90}\text{Th}} + {}^{4}_{2}\text{He}$$

$$\underset{\text{(Bismuth)}}{{}^{213}_{83}\text{Bi}} \longrightarrow \underset{\text{(Thallium)}}{{}^{209}_{81}\text{Tl}} + {}^{4}_{2}\text{He}$$

$$\underset{\text{(Polonium)}}{{}^{215}_{84}\text{Po}} \longrightarrow \underset{\text{(Lead)}}{{}^{211}_{82}\text{Pb}} + {}^{4}_{2}\text{He}$$

(b) β-particle emission: β-particle is merely an electron which has negligible mass. Whenever a beta particle is emitted from the nucleus of a radioactive atom, the nucleus of the new element formed possesses the same atomic mass but nuclear charge or atomic number is increased by 1 unit over the parent element. Beta particle emission is due to the result of decay of neutron into proton and electron.

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}p + {}^{0}_{-1}e$$

The electron produced escapes as a beta particle leaving proton in the nucleus.

Parent element $\xrightarrow{-\beta}$ Daughter element

Atomic mass	W	W
Atomic number	Z	$Z+1$

For example, in the following transformations, beta particle emission results in increase of atomic number by one without any change in atomic mass, *i.e.*, **daughter element is an isobar of parent element.** (See table 3.1)

Table 3.1 Isotopes, Isobars, Isotones, Isomers, Isoters and Isodiapheres

	Characteristics Z = at. no., A = mass no., N = neutrons, P = protons	Examples
Isotopes	Z = same, A = different	${}^{1}_{1}\text{H}, {}^{2}_{1}\text{H}, {}^{3}_{1}\text{H}, {}^{235}_{92}\text{U}, {}^{238}_{92}\text{U}$
Isobars	Z = different, A = same	${}^{228}_{88}\text{Ra}, {}^{228}_{89}\text{Ac}, {}^{228}_{90}\text{Th}$
Isotones	N = same, nucleons = different, Z = different	${}^{39}_{18}\text{Ar}, {}^{40}_{19}\text{K}$
Isomers	N = same, P = same, Z = same, A = same Nuclear energy levels = different	U - X_2, U - Z
Isoters	No. of atoms = same, No. of electrons = same, physical properties = same.	CO_2, N_2O
Isodiapheres	Isotopic excess mass (N—P) = same.	${}_{92}\text{U}^{235}$, ${}_{90}\text{Th}^{231}$

$$\underset{\text{(Lead)}}{{}^{214}_{82}\text{Pb}} \longrightarrow \underset{\text{(Bismuth)}}{{}^{214}_{83}\text{Bi}} + {}^{0}_{-1}e$$

$$\underset{\text{(Thorium)}}{{}^{234}_{90}\text{Th}} \longrightarrow \underset{\text{(Protoactinium)}}{{}^{234}_{91}\text{Pa}} + {}^{0}_{-1}e$$

$$\underset{\text{(Bismuth)}}{{}^{213}_{83}\text{Bi}} \longrightarrow \underset{\text{(Polonium)}}{{}^{213}_{84}\text{Po}} + {}^{0}_{-1}e$$

Special case: If in a radioactive transformation, 1 alpha and 2 beta particles are emitted, the resulting nucleus possesses the same atomic number but atomic mass is less by 4 units. A radioactive transformation of this type always produces an isotope of the parent element.

$${}^{W}_{Z}A \xrightarrow{-\alpha} {}^{W-4}_{Z-2}B \xrightarrow{-\beta} {}^{W-4}_{Z-1}C \xrightarrow{-\beta} {}^{W-4}_{Z}D$$

A and D are isotopes.

(v) Gamma rays are emitted due to secondary effects. After the emission of an alpha particle or a beta particle, the nucleus is left behind in excited state due to recoil. The excess of energy is released in the form of gamma rays. **Thus, γ-rays arise from energy rearrangements in the nucleus.** As γ-rays are short wavelength electromagnetic radiations with no charge and no mass, **their emission from a radioactive element does not produce a new element.**

On passing through an absorbing material, the intensity of γ-radiation decreases exponentially with the thickness traversed and is given by :

$$I = I_0 e^{-\mu x}$$

where μ = Absorption coefficient,

x = Thickness

I_0 = Initial intensity

I = Transmitted intensity

All radioactive nuclei have the same probability of disintegration. However, a radioactive nucleus may undergo decay next moment while some other may have to wait for billions of years to decay one cannot predict, when a particular atom will decay.

(vi) Internal conversion: An excited nucleus, in some cases, may return to its ground state by giving up its excitation energy to one of the orbital electrons around it. The emitted electron has a kinetic energy equal to the lost nuclear excitation energy minus the binding energy of the electron in the atom.

Kinetic energy of the ejected electron

= Available excitation energy

− Binding energy of the ejected electron

This process is called *internal conversion* and emitted electron is called conversion electron.

(vii) Brems strahlung (German word meaning 'Breaking Radiation'): Continuous γ-radiations emitted when β-particles are slowed down by interaction with atomic nucleus.

Note: Counting of the number of α and β-particles in a radioactive transformation:

$$\text{Parent element} \longrightarrow \text{Daughter element}$$

$$_{Z_1}A^{M_1} \longrightarrow {}_{Z_2}B^{M_2}$$

$$\text{Number of } \alpha\text{-particles} = \frac{\text{Change in mass number}}{4} = \frac{M_1 - M_2}{4}$$

Let 'x' α and 'y' β-particles be emitted.

Atomic number of parent element $- 2x + y$ = Atomic number of daughter element

$$Z_1 - 2x + y = Z_2$$

3.7 GROUP DISPLACEMENT LAW

This law was presented by **Fajan, Soddy** and **Russel** in 1913 to explain the changes which occur when an alpha particle or a beta particle is emitted from a radioactive element. According to this law, **"when an α-particle is emitted, the daughter element has atomic number 2 units less than that of the parent element. It is consequently displaced two places (groups) to the left in the periodic table. When a β-particle is emitted, the daughter element has an atomic number 1 unit higher than that of the parent element. It is consequently displaced one place (group) to the right in the periodic table."**

Examples

(i) Polonium ($^{214}_{84}$Po) belongs to group 16 (VIA) of the periodic table. On losing an alpha particle, it is transformed into lead ($^{210}_{82}$Pb) which belongs to group 14 (IVA), *i.e.*, two places to the left of the parent element, polonium.

$$\begin{array}{ccc} ^{214}_{84}\text{Po} & \longrightarrow & ^{210}_{82}\text{Pb} \\ 16 & & 14 \\ (\text{VI A}) & & (\text{IV A}) \end{array}$$

(ii) Bismuth ($^{213}_{83}$Bi) belongs to group 15 (VA) of the periodic table. It emits an alpha particle resulting in the formation of thallium which belongs to group 13 (IIIA), *i.e.*, two places to the left of the parent element, bismuth.

$$\begin{array}{ccc} ^{213}_{83}\text{Bi} & \longrightarrow & ^{209}_{81}\text{Tl} \\ 15 & & 13 \\ (\text{V A}) & & (\text{III A}) \end{array}$$

(iii) Carbon ($^{14}_{6}$C) belongs to group 14 (IV A) and emits a β-particle forming nitrogen ($^{14}_{7}$N) which belongs to group 15 (V A), *i.e.*, one place to the right of the parent element.

$$\begin{array}{ccc} ^{14}_{6}\text{C} & \longrightarrow & ^{14}_{7}\text{N} + {}^{0}_{-1}e \\ (\text{IV A}) & & (\text{V A}) \end{array}$$

(iv) Phosphorus ($^{32}_{15}$P) belongs to group 15 (VA) and emits a β-particle forming sulphur ($^{32}_{16}$S) which belongs to group 16 (VIA), *i.e.*, one place right to the parent element.

$$\begin{array}{ccc} ^{32}_{15}\text{P} & \longrightarrow & ^{32}_{16}\text{S} + {}^{0}_{-1}e \\ (\text{V A}) & & (\text{VI A}) \end{array}$$

The above examples follow group displacement law rigidly in accordance with the statement. However, there are a number of examples where confusion arises regarding the position of the element in the periodic table if the above statement is followed rigidly.

$^{27}_{12}$Mg is β-radioactive. It belongs to group 2 (IIA) of the periodic table. On losing a beta particle, it is transformed to aluminium ($^{27}_{13}$Al) which belongs to group 13 (IIIA), *i.e.*, 11 places right to the parent element.

$$^{27}_{12}\text{Mg} \longrightarrow {}^{27}_{13}\text{Al} + {}^{0}_{-1}e$$

$^{234}_{90}$Th is a member of actinide series. All the fourteen members of the actinide series have been placed along with actinium in the III B group, *i.e.*, group 3. It emits a beta particle and is transformed to protactinium ($^{234}_{91}$Pa) which also belongs to actinide series, *i.e.*, group 3 of the periodic table.

$$^{234}_{90}\text{Th} \longrightarrow {}^{234}_{91}\text{Pa} + {}^{0}_{-1}e$$

Hence, group displacement law should be applied with great care especially in the case of elements of lanthanide series (57 to 71), actinide series (89 to 103), VIII group (26 to 28; 44 to 46; 76 to 78), IA and IIA groups. It is always beneficial to keep in mind the setup and skeleton of the extended form of periodic table.

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII		
1	2	3	4	5	6	7	8	9	10

IB	IIB	IIIA	IVA	VA	VIA	VIIA	Zero
11	12	13	14	15	16	17	18

SOME SOLVED EXAMPLES

Example 1. *Calculate the number of neutrons in the remaining atom after emission of an alpha particle from $^{238}_{92}U$ atom.*

Solution: On account of emission of an alpha particle, the atomic mass is decreased by 4 units and atomic number by 2 units.

So, Atomic mass of daughter element = 234

Atomic number of daughter element = 90

Number of neutrons = atomic mass − atomic number

= 234 − 90 = 144

Example 2. *Radioactive disintegration of $^{226}_{88}Ra$ takes place in the following manner into RaC,*

$$Ra \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} RaA \xrightarrow{-\alpha} RaB \xrightarrow{-\beta} RaC$$

Determine mass number and atomic number of RaC.

Solution: Parent element is $^{226}_{88}$Ra.

Atomic mass = 226

Atomic number = 88

Ra*C* is formed after the emission of 3 alpha particles. Mass of 3 alpha particles = 3 × 4 = 12

So, Atomic mass of RaC = (226 − 12) = 214

With emission of one α-particle, atomic number is decreased by 2 and with the emission of one β-particle, atomic number is increased by 1.

So, Atomic number of Ra$C = 88 - (3 \times 2) + 1 = 83$

Example 3. *A radioactive element A disintegrates in the following manner,*

$$A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$$

which ones of the elements A, B, C and D are isotopes and which ones are isobars?

Solution: Let the mass number and atomic number of element A be M and Z, respectively. The following changes shall occur during disintegration:

$$^{M}_{Z}A \xrightarrow{-\alpha} {}^{M-4}_{Z-2}B \xrightarrow{-\beta} {}^{M-4}_{Z-1}C \xrightarrow{-\beta} {}^{M-4}_{Z}D$$

A and D are isotopes as both have same value of Z.

B, C and D are isobars as these have same values of atomic mass.

Example 4. *${}^{234}_{90}Th$ disintegrates to give ${}^{206}_{82}Pb$ as the final product. How many alpha and beta particles are emitted in this process?*

Solution:

$$\underset{\text{Parent}}{{}^{234}_{90}\text{Th}} \longrightarrow \underset{\text{End product}}{{}^{206}_{82}\text{Pb}}$$

Decrease in mass $= (234 - 206) = 28$

Mass of α-particle $= 4$

So, Number of α-particles emitted $= \dfrac{28}{4} = 7$

No. of β-particles emitted = 2 × No. of α-particles–(At. No. of parent – At. No. of end product)

$= 2 \times 7 - (90 - 82) = 6$

Example 5. *The atomic mass of thorium is 232 and its atomic number is 90. During the course of its radioactive disintegration 6α and 4β-particles are emitted. What is the atomic mass and atomic number of the final atom?*

Solution: Decrease in mass due to emission of 6α-particles $= 6 \times 4 = 24$.

So, Atomic mass of the product atom $= (232 - 24) = 208$

No. of β-particles emitted = 2 × No. of α-particles $- (Z_{\text{Thorium}} - Z_{\text{Final atom}})$

$$4 = 2 \times 6 - (90 - Z_{\text{Final atom}})$$

or $Z_{\text{Final atom}} = 82$

Example 6. *An atom has atomic mass 232 and atomic number 90. During the course of disintegration, it emits 2β-particles and few α-particles. The resultant atom has atomic mass 212 and atomic number 82. How many α-particles are emitted during this process?*

Solution: The decrease in atomic mass

$= (232 - 212) = 20$

Decrease in mass occurs due to emission of α-particles. Let x be the number of alpha particles emitted.

Mass of 'x' α-particles $= 4x$

So, $4x = 20$

or $x = \dfrac{20}{4} = 5$

Alternative method: This can also be determined by the application of the following equation:

No. of β-particles emitted = 2 × No. of α-particles emitted $-(Z_{\text{Parent}} - Z_{\text{End product}})$

$$2 = 2 \times x - (90 - 82)$$

or $x = 5$

Example 7. *How many moles of helium are produced when one mole of ${}^{238}_{92}U$ disintegrates into ${}^{206}_{82}Pb$?*

Solution: Radioactive change is

$${}^{238}_{92}\text{U} \longrightarrow {}^{206}_{82}\text{Pb}$$

Decrease in mass $= (238 - 206) = 32$

Let the number of α-particles emitted be x.

$$4x = 32$$

$$x = 8$$

Thus, 8 moles of helium are produced when one mole of ${}^{238}_{92}$U disintegrates into ${}^{206}_{82}$Pb.

Example 8. *How many 'α' and 'β'-particles will be emitted when ${}_{90}Th^{234}$ changes into ${}_{84}Po^{218}$?*

Solution: The change is;

$$\underset{\text{Parent}}{{}_{90}\text{Th}^{234}} \longrightarrow \underset{\text{End product}}{{}_{84}\text{Po}^{218}}$$

Decrease in mass $= (234 - 218) = 16$ amu

Mass of 1 α-particle = 4 amu

Therefore, number of α-particles emitted $= \dfrac{16}{4} = 4.$

Number of β-particles emitted

= 2 × No. of α-particles emitted – (At. No. of parent – At. No. of end product)

$= 2 \times 4 - (90 - 84) = (8 - 6) = 2$

Hence, number of α-particles emitted = 4

and number of β-particles emitted = 2

Example 9. *${}^{238}_{92}U$ is a natural an α-emitter. After α-emission, the residual nucleus U_{X_1} in turns emits a β-particle to produce another nucleus U_{X_2}. Find out the atomic number and mass number of U_{X_1} and U_{X_2}. Also if uranium belongs to IIIrd group to which group U_{X_1} and U_{X_2} belong.*

Solution:

$${}^{238}_{92}\text{U} - {}^{4}_{2}\text{He} \longrightarrow {}^{234}_{90}\text{U}_{X_1}$$

$${}^{234}_{90}\text{U}_{X_1} - ({}^{0}_{-1}e) \longrightarrow {}^{234}_{91}\text{U}_{X_2}$$

Both U_{X_1} and U_{X_2} will belong to IIIrd group because both lie in actinide series.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. During the transformation of ${}^{a}_{c}X$ to ${}^{b}_{d}Y$, the number of β-particles emitted are: **[PET (Kerala) 2006, 08]**

(a) $\frac{a-b}{4}$ (b) $d+\frac{a-b}{2}+c$

(c) $d+\left(\frac{a-b}{2}\right)-c$ (d) $2c-d+a-b$

[**Ans.** (c)]

[**Hint:** No. of α-particles $=\left(\frac{a-b}{4}\right)$

$$Z_1-2\alpha+\beta=Z_2$$

$$\beta=Z_2-Z_1+2\alpha$$

$$=d-c+2\frac{(a-b)}{4}$$

$$=d+\frac{(a-b)}{2}-c]$$

2. A radioactive nuclide emits γ-rays due to:
   (a) K-electron capture
   (b) nuclear transition from higher to lower energy state
   (c) presence of greater number of neutrons than protons
   (d) presence of greater number of protons than neutrons
   [**Ans.** (b)]
   [**Hint:** After α, β-emission, nucleus goes to excited state; when it returns to normal state, emission of γ-radiations takes place.]

3. In which of the following transformations, the β-particles are emitted?
   (a) Proton to neutron (b) Neutron to proton
   (c) Proton to proton (d) Neutron to neutron
   [**Ans.** (b)]
   [**Hint:** ${}_0^1n \longrightarrow {}_1^1\text{H} + {}_{-1}^{0}e$ + antineutrino]

4. In the radioactive decay:

$${}_Z^AX \longrightarrow {}_{Z+1}^{\;\;A}Y \longrightarrow {}_{Z-1}^{A-4}Z \longrightarrow {}_{Z-1}^{A-4}Z^*$$

   the sequence of emission is:
   (a) α, β, γ (b) β, α, γ (c) γ, α, β (d) β, γ, α
   [**Ans.** (b)]
   [**Hint:** ${}_Z^AX - {}_{-1}^{0}e \longrightarrow {}_{Z+1}^{\;\;A}Y$; ${}_{Z+1}^{\;\;A}Y - {}_2^4\text{He} \longrightarrow {}_{Z-1}^{A-4}Z$;
   ${}_{Z-1}^{A-4}Z - \gamma \longrightarrow {}_{Z-1}^{A-4}Z^*$]

5. Which of the following elements is an isodiaphere of ${}_{92}^{235}\text{U}$?
   (a) ${}_{83}^{209}\text{Bi}$ (b) ${}_{82}^{212}\text{Pb}$ (c) ${}_{90}^{231}\text{Th}$ (d) ${}_{91}^{231}\text{Pa}$
   [**Ans.** (c)]
   [**Hint:** Isodiapheres are formed by α-emission.
   ${}_{92}^{235}\text{U} - {}_2^4\text{He} \longrightarrow {}_{90}^{231}\text{Th}$ (Isodiaphere)]

6. A certain radioactive material ${}_Z^AX$ starts emitting α and β particles successively such that the end product is ${}_{Z-3}^{A-8}Y$. The number of α and β particles emitted are : **(VITEEE 2008)**
   (a) 4 and 3 respectively (b) 2 and 1 respectively
   (c) 3 and 4 respectively (d) 3 and 8 respectively
   [**Ans.** (b)]
   [**Hint:** ${}_Z^AX \longrightarrow {}_{Z-3}^{A-8}Y$

$$\text{Number of α-particles} = \frac{\text{Change in mass number}}{4} = \frac{8}{4} = 2$$

$Z - 2 \times$ Number of α-particles + Number of β-particles $= Z - 3$

$Z - 2 \times 2 +$ Number of β-particles $= Z - 3$

Number of β- particles = 1]

3.8 RADIOACTIVE DISINTEGRATION SERIES

Elements beyond bismuth are all radioactive in nature. Most of them have several radioactive isotopes. These radioactive elements disintegrate to give new elements which again disintegrate to form other elements and so on. The process continues till a non-radioactive end product is reached.

"The whole chain of such elements starting from the parent element (radioactive) to the end element (non-radioactive) is called a radioactive series or a family".

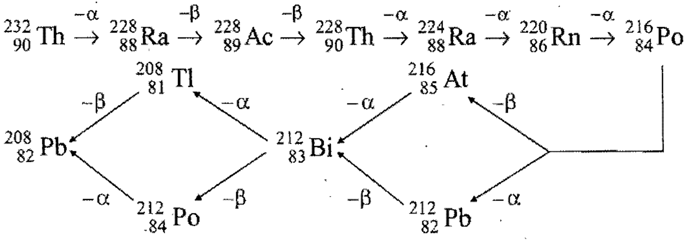
All the naturally occurring radioactive elements above atomic number 82 belong to one of the three radioactive series. These are known as:

(i) Thorium series (ii) Uranium series
(iii) Actinium series

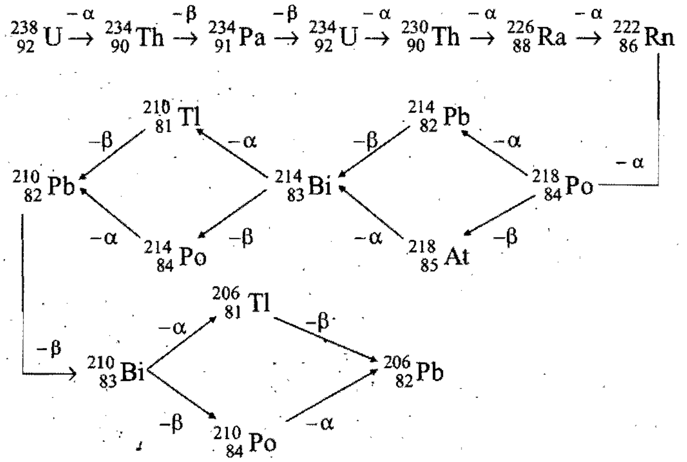
Uranium and thorium series have been named on the basis of long lived isotopes of ${}^{238}\text{U}$ and ${}^{232}\text{Th}$. The parent element of **actinium** series is ${}^{235}\text{U}$ but originally it was thought to be an isotope of actinium, ${}^{227}\text{Ac}$. The three series are also referred to $4n$ (thorium), $4n+2$ (uranium) and $4n+3$ (actinium) series as when the mass numbers of various members belonging to these series when divided by four, either there is no remainder (as in thorium series) or the remainder is 2 (as in uranium series) or 3 (as in actinium series). The end product in all the three series is an isotope of lead which is stable and non-radioactive in nature. The following table shows the main characteristics of three radioactive series:

Series	First member	Half life of first member in years	Last member	Atomic masses when divided by 4, the remainder	No. of α-particles emitted	No. of β-particles emitted
Thorium ($4n$)	${}_{90}^{232}\text{Th}$	1.4×10^{10}	${}_{82}^{208}\text{Pb}$	0	6	4
Uranium ($4n+2$)	${}_{92}^{238}\text{U}$	4.51×10^{9}	${}_{82}^{206}\text{Pb}$	2	8	6
Actinium ($4n+3$)	${}_{92}^{235}\text{U}$	7.07×10^{8}	${}_{82}^{207}\text{Pb}$	3	7	4

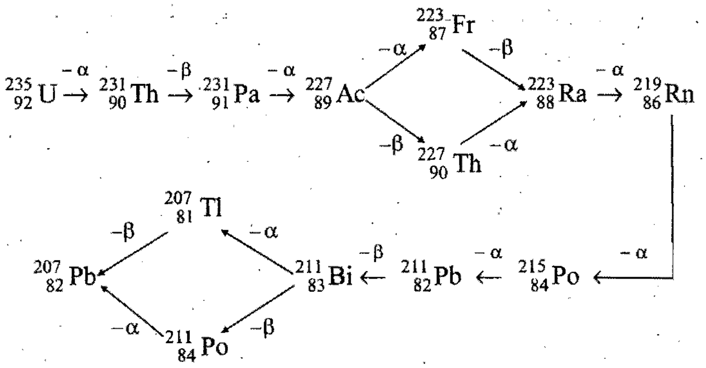
(i) Thorium series ($4n$ series):



(ii) Uranium series [(4*n* + 2) series]:



(iii) Actinium series [(4*n* + 3) series]:



Only 18 radioactive isotopes with atomic number 82 or less are found in nature. ^{14}C is the exception because it is continuously synthesized in our atmosphere. All these natural radioactive elements have half-life longer than 10^9 yrs (age of earth). Another 45 radioactive isotopes having atomic number greater than 82 are also found in nature and fall in above three natural decay series.

Similarities between Radioactive Series

(i) In all the series, there is an element of zero group with atomic number 86. This element comes in the gaseous state and is called emanation. Different names are given to three isotopes. These are **radon** in uranium series, **thoron** in thorium series and **actinon** in actinium series.

(ii) In all the series, the last product is an isotope of lead (atomic number 82), ^{206}Pb in uranium series, ^{207}Pb in actinium series while ^{208}Pb in thorium series. Due to this reason, lead is found in nature as a mixture of these three isotopes.

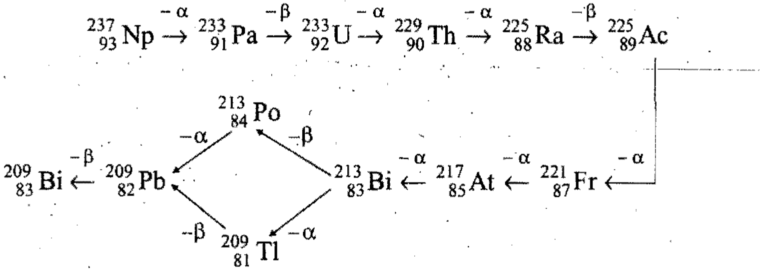
(iii) In all the series, there are certain elements which disintegrate in a branching process by emitting either α or β-particles. The species thus formed are then disintegrated in such a way as to give a common product.

Neptunium series [(4*n* + 1) series]: For many years scientists speculated upon the failure to find a disintegration series in nature whose isotopic masses carry a numerical relationship of 4*n* + 1. The most reasonable explanation for the absence of this series in nature was that no member of this series was sufficiently long lived to have survived over the years since the series might have been formed. Except the last member, all other members of this series have been obtained by artificial means. The name of this series is given on the long lived isotope of neptunium (Half life $^{237}_{93}Np = 2.25 \times 10^6$ years). This family differs from the other three naturally occurring series in the following respects:

(a) The last member of this series is an isotope of bismuth ($^{209}_{83}Bi$) and not an isotope of lead.

(b) The only member of this series which is found in nature is the last member.

(c) The series does not contain gaseous emanation.



In this series, seven alpha and four beta particles are emitted.

3.9 RATE OF DISINTEGRATION AND HALF LIFE PERIOD

The radioactive decay of the different radioactive substances differ widely. The rate of disintegration of a given substance depends upon the **nature of disintegrating substance and its total amount. The law of radioactive disintegration may be defined as "the quantity of radioactive substance which disappears in unit time is directly proportional to the amount* of radioactive substance present or yet not decayed."** The quantity of the radioactive substance which disintegrates or disappears in unit time is called rate of disintegration.

The rate of disintegration decreases with time as the amount of radioactive substance decreases with time. One of the most important characteristics of the radioactive disintegration is that a certain definite fraction of a radioactive sample undergoes disintegration in a definite period of time. This time period does not depend upon the initial amount of the radioactive substance.

For example, whatever be the amount (initial) of ^{131}I taken, it becomes half within 8 days. This has been shown in Fig. 3.4 (a).

Initial amount of ^{131}I	**The amount of ^{131}I after 8 days**
20 grams	10 grams
10 grams	5 grams
5 grams	2.5 grams, etc.

Rutherford introduced a constant known as **half life period.** It is defined **"as the time during which half the amount of a given sample of the radioactive substance disintegrates".**

Amount of a radioactive substance can be taken in terms of number of atoms or moles or grams, milligrams, etc.

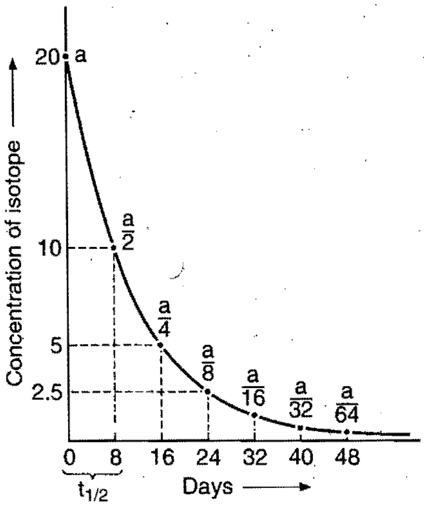


Fig. 3.4 (a)

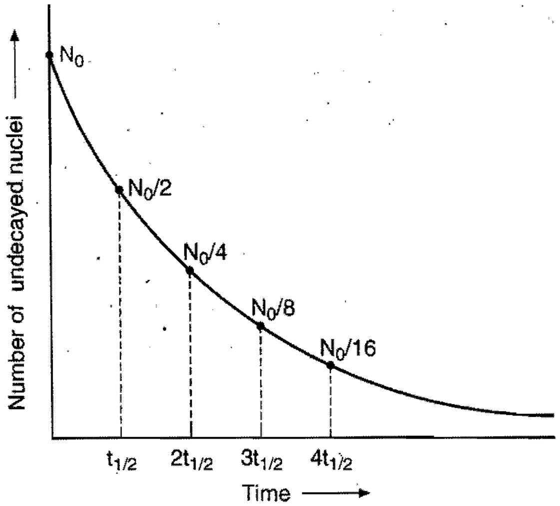


Fig. 3.4 (b)

Every radioactive element is characterised by a definite constant value of half life period. Half life period of an element is also a measure of its radioactivity, since shorter the half life period, the greater is the number of disintegrations and hence greater its radioactivity. Half life periods vary from billions of years for some radioisotopes to a fraction of a second.

Half life period is represented as $t_{1/2}$.

Let the initial amount of a radioactive substance be N_0.

After one half life period ($t_{1/2}$), it becomes $= N_0/2$

After two half life periods ($2t_{1/2}$), it becomes $= N_0/4$

After three half life periods ($3t_{1/2}$), it becomes $= N_0/8$

and After n half life periods ($nt_{1/2}$), it shall become $= \left(\frac{1}{2}\right)^n N_0$

Thus, for the total disintegration of a radioactive substance an infinite time will be required.

Time (T)	Amount of radioactive substance (N)	Amount of radioactive substance decomposed ($N_0 - N$)
0	N_0	0
$t_{1/2}$	$\frac{1}{2}N_0 = \left(\frac{1}{2}\right)^1 N_0$	$\frac{1}{2}N_0 = \left[1-\frac{1}{2}\right]N_0$
$2t_{1/2}$	$\frac{1}{4}N_0 = \left(\frac{1}{2}\right)^2 N_0$	$\frac{3}{4}N_0 = \left[1-\frac{1}{4}\right]N_0$
$3t_{1/2}$	$\frac{1}{8}N_0 = \left(\frac{1}{2}\right)^3 N_0$	$\frac{7}{8}N_0 = \left[1-\frac{1}{8}\right]N_0$
$4t_{1/2}$	$\frac{1}{16}N_0 = \left(\frac{1}{2}\right)^4 N_0$	$\frac{15}{16}N_0 = \left[1-\frac{1}{16}\right]N_0$
$nt_{1/2}$	$\left(\frac{1}{2}\right)^n N_0$	$[1-\left(\frac{1}{2}\right)^n]N_0$

Amount of radioactive substance left after n half life periods

$$N = \left(\frac{1}{2}\right)^n N_0$$

and total time $T = n \times t_{1/2}$

where, n is a whole number.

SOME SOLVED EXAMPLES

Example 10. *The half life period of radium is 1580 years. How do you interpret this statement?*

Solution: Whatever quantity of radium is taken, it shall become half after the expiry of 1580 years. The following table explains the statement:

Quantity of radium at present	Quantity of radium after 1580 years
100 atoms	50 atoms
50 gram	25 gram
5 mole	2.5 mole

Example 11. *The radioactive isotope ^{137}Cs has a half life period of 30 years. Starting with 1 mg of ^{137}Cs, how much would remain after 120 years?*

Solution: At this time, we have 1.0 mg of ^{137}Cs; after 30 years, we shall have one half of the original, or 0.50 mg; after 60 years, we shall have 0.25 mg; after 90 years, we shall have 0.125 mg and, finally, after 120 years, we shall have 0.0625 mg.

After	30 years	—	0.50 mg
	60 years	—	0.25 mg
	90 years	—	0.125 mg
	120 years	—	0.0625 mg

Alternative solution: Total time = 120 years

We know that, total time $= n \times t_{1/2}$

So, $120 = n \times 30$

$n = 4$

Thus, the quantity of the isotope left after

four half life periods $= \left(\frac{1}{2}\right)^4 N_0 = \left(\frac{1}{2}\right)^4 \times 1$

$= \frac{1}{16} = 0.0625$ mg

Example 12. *A radioactive element has half life period of 30 days. How much of it will be left after 90 days?*

Solution: Total time = 90 days

Half life $(t_{1/2}) = 30$ days

We know that, total time $= n \times t_{1/2}$

So, $90 = n \times 30$

$n = 3$

Thus, quantity left after three half life periods

$$= \left(\frac{1}{2}\right)^3 N_0 \quad [N_0 = \text{original amount}]$$

$$= \frac{1}{8} \times N_0 = \frac{1}{8} N_0$$

Example 13. *The half life period of* $^{210}_{84}Po$ *is 140 days. In how many days 1 g of this isotope is reduced to 0.25 g?*

Solution: Original quantity of the isotope $(N_0) = 1$ g

Final quantity of the isotope $N = 0.25$ g

We know that, $N = \left(\frac{1}{2}\right)^n N_0$

So, $\frac{1}{4} = \left(\frac{1}{2}\right)^n \times 1$

or $\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$

or $n = 2$

Time taken $T = n \times t_{1/2} = 2 \times 140 = 280$ days

Example 14. *The half life period of* ^{234}U *is* 2.5×10^5 *years. In how much time is the quantity of an isotope reduced to 25% of the original amount?*

Solution: Initial amount of this isotope $N_0 = 100$

Final amount of the isotope $N = 25$

We know that, $N = \left(\frac{1}{2}\right)^n N_0$

So, $25 = \left(\frac{1}{2}\right)^n \times 100$

or $\frac{25}{100} = \left(\frac{1}{2}\right)^n$

or $\frac{1}{4} = \left(\frac{1}{2}\right)^n$

or $\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$

or $n = 2$

Time taken $T = n \times t_{1/2}$

$= 2 \times 2.5 \times 10^5 = 5 \times 10^5$ years

$$\log\frac{N_0}{N} = \lambda t \text{ or } \log\frac{N}{N_0} = -\lambda t \text{ or } \frac{N}{N_0} = e^{-\lambda t} \text{ or } N = N_0 e^{-\lambda t}$$

Example 15. *A radioisotope has* $t_{1/2} = 5$ *years. After a given amount decays for 15 years, what fraction of the original isotope remains?*

Solution: Half life $(t_{1/2}) = 5$ years

Time for decay $(T) = 15$ years

We know that, $T = n \times t_{1/2}$

So, $15 = n \times 5$

or $n = 3$

Let the original amount be $= N_0$

Let the amount left after three half life periods be $= N$

fraction $= N / N_0$

We know that, $N = \left(\frac{1}{2}\right)^n N_0$

or $\frac{N}{N_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^3 = \frac{1}{8}$

Thus, after 15 years $\frac{1}{8}$th of the original amount remains.

Example 16. *If in 3160 years, a radioactive substance becomes one-fourth of the original amount, find its half life period.*

Solution: $\frac{N}{N_0} = \frac{1}{4}$

So, $\frac{1}{4} = \left(\frac{1}{2}\right)^n$

or $\left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^n$

or $n = 2$

We know that, total time 'T' $= n \times t_{1/2}$

So, $3160 = 2 \times t_{1/2}$

or $t_{1/2} = \frac{3160}{2} = 1580$ years

The half life period of the radioactive substance is 1580 years.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. Half life of a radioactive sample is $2x$ years. What fraction of this sample will remain undecayed after x years?

(a) $\frac{1}{2}$ (b) $\frac{1}{\sqrt{2}}$ (c) $\frac{1}{\sqrt{3}}$ (d) 2

[Ans. (b)]

[Hint: $\lambda = \frac{2.303}{t} \log\left(\frac{N_0}{N}\right)$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{2x} = \frac{2.303}{x} \log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{1}{2}\log_{10} 2 = \log\left(\frac{N_0}{N}\right)$$

$$\frac{N}{N_0} = \frac{1}{\sqrt{2}}$$

Fraction undecayed $= \frac{1}{\sqrt{2}}$]

8. Half life of a radioactive element is 10 days. What percentage of the element will remain undecayed after 100 days?
   (a) 10% (b) 0.1%
   (c) 0% (d) 99%
   [**Ans.** (b)]
   [**Hint:** In ten times of half life 99.9%, the element undergoes decay; then percentage of undecayed radioactive element will be 0.1%.]
9. Which among the following relations is correct?
   (a) $t_{1/2} = 2t_{3/4}$ (b) $t_{1/2} = 3t_{3/4}$
   (c) $t_{3/4} = 2t_{1/2}$ (d) $t_{3/4} = 3t_{1/2}$
   [**Ans.** (c)]
   [**Hint:** $\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log\left(\frac{N_0}{N}\right)$

   $$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{3/4}} \log \frac{100}{75}$$

   $t_{3/4} = 2t_{1/2}$]
10. Select the correct statement:
    (a) Same amount will decay in every half life
    (b) Amount decayed in first half life is maximum
    (c) Amount decayed in first half life is minimum
    (d) Amount decayed in a half life depends on the nature of element
    [**Ans.** (b)]
    [**Hint:** Amount decayed in first half life is maximum. Half of the initial amount is decayed in first half life.]
11. The half life period of a radioactive mineral is 15 min. What percent of radioactivity of that mineral will remain after 45 min? [UGET (Manipal Medical) 2006]
    (a) 17.5% (b) 15% (c) 12.5% (d) 10%
    [**Ans.** (c)]
    [**Hint:** $n = \frac{45}{15} = 3$ = No. of half lives

    $$N = N_0\left(\frac{1}{2}\right)^n = 100 \times \left(\frac{1}{2}\right)^3 = 12.5\%]$$
12. Half life of a radioactive element is 16 hrs. What time will it take for 75% disintegration? (DCE 2006)
    (a) 32 days (b) 32 hrs (c) 48 hrs (d) 16 hrs
    [**Ans.** (b)]
    [**Hint:** 75% decay takes place in $t_{3/4}$ (3 / 4th life)

    $$t_{3/4} = 2t_{1/2} = 2 \times 16 = 32 \text{ hrs}]$$

Disintegration constant: A chemical reaction whose rate of reaction varies directly as the concentration of one molecular species only, is termed a first order reaction. Radioactive disintegration is similar to such a chemical reaction as one radioactive species changes into other. This change can be represented by the equation:

$$A \longrightarrow B$$

Suppose the number of atoms of a radioactive substance present at the start of observation, *i.e.*, when $t = 0$, is N_0 and after time t, the number of atoms remaining unchanged is N. At this instant a very small number of atoms dN disintegrate in a small time dt; the rate of change of A into B is given by $-\frac{dN}{dt}$. The negative sign indicates that number of atoms decreases as time increases. Since, rate of disintegration or change is proportional to the total number of atoms present at that time, the relation becomes

$$-\frac{dN}{dt} = \lambda \cdot N \quad \text{... (i)}$$

'λ' is called the **disintegration constant** or **decay constant.**

Evidently $$-\frac{dN}{N} = \lambda \cdot dt \quad \text{... (ii)}$$

If $dt = 1$ second, $$\lambda = -\frac{dN}{N} \quad \text{... (iii)}$$

Thus, λ may be defined as **the fraction of the total number of atoms which disintegrate per second at any time.** This is constant for a given radioactive isotope.

Integrating eq. (ii), $-\int \frac{dN}{N} = \lambda \int dt$

$$-\log N = \lambda t + C \quad \text{... (iv)}$$

C is the integration constant.

When $t = 0$, $N = N_0$

Putting the values in eq. (iv),

$$-\log N_0 = C \quad \text{... (v)}$$

Putting the value of C in eq. (iv)

$$-\log N = \lambda t - \log N_0 \quad \text{or} \quad \log N_0 - \log N = \lambda t$$

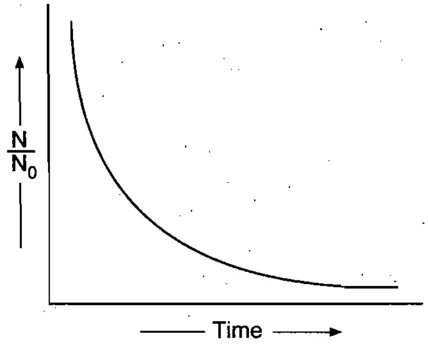


Fig. 3.5 Fraction of radioisotope remaining versus time

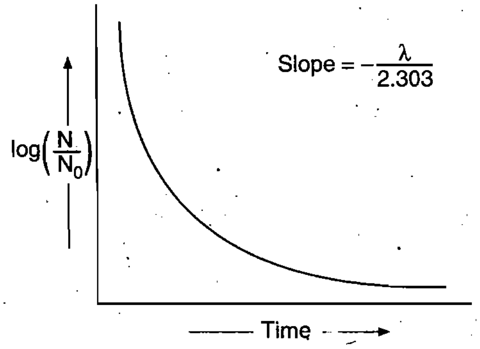


Fig. 3.6 Log of fraction remaining versus time

or $\log \frac{N_0}{N} = \lambda t$ or $2.303 \log_{10} \frac{N_0}{N} = \lambda t$

or $$\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N} \quad \text{... (vi)}$$

This equation is called kinetic equation and is obeyed by first order reactions.

Relationship between half life period and radioactive disintegration constant.

When $t = t_{1/2}$, $N = \frac{N_0}{2}$

Putting the values in eq. (vi)

$$\lambda = \frac{2.303}{t_{1/2}} \log_{10} \frac{N_0}{N_0/2} = \frac{2.303}{t_{1/2}} \log_{10} 2$$

The value of $\log_{10} 2$ is 0.3010.

So, $\lambda = \frac{0.693}{t_{1/2}}$ or $t_{1/2} = \frac{0.693}{\lambda}$

Thus, half life period of a given radioactive substance does not depend on the initial amount of a radioactive substance but depends only on the disintegration constant of the radioactive element.

3.10 AVERAGE LIFE

It is the sum of the periods of existence of all the atoms divided by the total number of atoms of the radioactive substance.

$$\text{Average life} = \frac{\text{Total life time of all the atoms}}{\text{Total number of atoms}}$$

$$= \frac{\int_0^\infty t\,dN}{N_0} = \frac{1}{\lambda}$$

Thus, **average life** of a radioactive element is the inverse of its disintegration or decay constant.

$$\text{Average life} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

The **average life** of a radioactive substance is 1.44 times of its half life period.

Alternatively:

We know that, $$\lambda = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$$

or $$\lambda t = \log_e \left(\frac{N_0}{N}\right)$$

$$e^{\lambda t} = \frac{N_0}{N}$$

or $$\frac{N}{N_0} = e^{-\lambda t}$$

Let $t = \frac{1}{\lambda}$; then $$\frac{N}{N_0} = e^{-1} = \frac{1}{e}$$

$$\frac{N}{N_0} = \frac{1}{2.718} = 0.3679$$

$$\% \text{ remaining amount} = \frac{N}{N_0} \times 100 = 36.79$$

$$\% \text{ decayed amount} = 100 - 36.79 = 63.21$$

Time during which 63.21% substance undergoes decay is called average life.

Relation between rate of decay and mass of given element

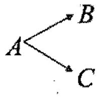
$$\text{Rate}\left(-\frac{dN}{dt}\right) = \lambda \times N$$

$$= \lambda \times \text{No. of atoms of element undergoing decay}$$

$$= \frac{0.693}{t_{1/2}} \times \frac{\text{mass}}{\text{atomic mass}} \times \text{Avogadro's number}$$

Parallel Path Decay

Let a radioactive element 'A' decays to 'B' and 'C' in two parallel paths:



Decay constant of

'A' = Decay constant of 'B' + Decay constant of 'C'

$$\lambda_A = \lambda_B + \lambda_C \quad \text{... (i)}$$

Here, $\lambda_B = [\text{fractional yield of } B] \times \lambda_A$

$\lambda_C = [\text{fractional yield of } C] \times \lambda_A$

Maximum Yield of Daughter Element

Let a radioactive element 'A' decays to daughter element 'B'.

$$A \longrightarrow B$$

λ_A and λ_B are decay constants of 'A' and 'B'. Maximum activity time of daughter element can be calculated as:

$$t_{\max} = \frac{2.303}{(\lambda_B - \lambda_A)} \log_{10}\left[\frac{\lambda_B}{\lambda_A}\right]$$

3.11 RADIOACTIVE EQUILIBRIUM

Let us consider that a radioactive element A disintegrates to give B which is also radioactive and disintegrates into C.

$$A \longrightarrow B \longrightarrow C$$

The element B is said to be in radioactive equilibrium with A if its rate of formation from A is equal to its rate of decay into C. If λ_1 and λ_2 are the disintegration constants of A and B, N_1 and N_2 are the number of atoms of each radioactive element present at equilibrium, then we have

Rate of formation of B = Rate of decay of $A = \lambda_1 N_1$

and Rate of decay of $B = \lambda_2 N_2$

At radioactive equilibrium,

$$\lambda_1 N_1 = \lambda_2 N_2$$

or $$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{1/\lambda_1}{1/\lambda_2} = \frac{\text{Average life of A}}{\text{Average life of B}} = \frac{Z_A}{Z_B}$$

Thus, the number of atoms of A and B are in the ratio of their average life periods.

$$\frac{N_1}{N_2} = \frac{\lambda_2}{\lambda_1} = \frac{0.693/(t_{1/2})_2}{0.693/(t_{1/2})_1}$$

$$\frac{N_1}{N_2} = \frac{(t_{1/2})_1}{(t_{1/2})_2}$$

When λ_A of parent element is less than λ_B of daughter element, but both are not very small then a *transient equilibrium* is reached, when

$$\frac{N_B}{N_A} = \frac{\lambda_A}{\lambda_B - \lambda_A}$$

in fact it is steady state.

3.12 UNITS OF RADIOACTIVITY

In radioactivity, the number of atoms which disintegrate in unit time is of real importance rather than the total amount of the radioactive substance expressed by mass or number of atoms, *i.e.*, the activity of a radioactive substance is the rate of decay or number of disintegrations per second.

The unit of radioactivity called **Curie (Ci) is defined as that quantity of any radioactive substance which has a decay rate of 3.7×10^{10} disintegrations per second.**

This unit is a large one and hence smaller units like **millicurie** (mCi) and **microcurie** (μCi) are used.

$$1 \text{ millicurie} = 3.7 \times 10^7 \text{ disintegrations per sec}$$

$$1 \text{ microcurie} = 3.7 \times 10^4 \text{ disintegrations per sec}$$

There is another unit Rutherford (Rd) which is also used these days. **It is defined as the amount of a radioactive substance which undergoes 10^6 disintegrations per second.** Smaller units like milli-Rutherford and micro-Rutherford are also used.

$$1 \text{ milli-Rutherford} = 10^3 \text{ disintegrations per sec (dps)}$$

$$1 \text{ micro-Rutherford} = 1 \text{ disintegration per sec}$$

The SI unit of radioactivity is proposed as Becquerel which refers to one dps.

$$1 \text{ curie} = 3.7 \times 10^4 \text{ Rutherford} = 3.7 \times 10^{10} \text{ Becquerel}$$

$$1 \text{ curie} = 37 \text{ GBq}$$

Here, G stands for 10^9, *i.e.*, giga

Gray (Gy) = 1 kg tissue receiving 1 J of energy

Sievert (Sv) = gray × quality number of radiation

Quality number of 1α-particle = 20

Quality number of 1β-particle = 1

Specific activity of a radionuclide is its activity per kilogram (or dm^3) of the radioactive material.

(In some cases, specific activity is taken as the activity per gram.)

Radiation counter: There are two main radiation counters in practice.

1. Geiger-Muller counter: It is used to count charged particles, *e.g.*, α and β-particles, emitted by a radioactive nucleus. This counter is simply a metal tube filled with a gas like argon.

In order to count and detect neutrons, boron trifluoride (BF_3) is added along with a gas in the G.M. counter. Neutron strikes $^{10}_{5}B$ nuclei to produce α-particle, which is then detected and counted in Geiger counter.

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{7}_{3}Li + ^{4}_{2}He$$

2. Scintillation counter: γ-radiations are detected by Scintillation counter. A phosphor is used in this counter which produces flash of light when it is struck by electromagnetic radiation like γ-rays, for detection of γ-rays. Sodium iodide (NaI) and thallium iodide (TlI) are used as phosphor. Rutherford first of all used zinc sulphide (ZnS) as phosphor in detection of α-particles.

SOME SOLVED EXAMPLES

Example 17. *The half life period of radium is 1600 years. Calculate the disintegration constant of radium. Mention its unit.*

Solution: Disintegration constant $\lambda = \dfrac{0.693}{t_{1/2}}$

Since, $t_{1/2} = 1600$ years

So, $\lambda = \dfrac{0.693}{1600}$

or $\lambda = 4.33 \times 10^{-4} \text{ year}^{-1}$

Example 18. *The disintegration constant of ^{238}U is 1.54×10^{-10} year^{-1}. Calculate the half life period of ^{238}U.*

Solution: Half life period, $t_{1/2} = \dfrac{0.693}{\lambda}$

Since, $\lambda = 1.54 \times 10^{-10} \text{ year}^{-1}$

So, $t_{1/2} = \dfrac{0.693}{1.54 \times 10^{-10}} = 4.5 \times 10^9$ years

Example 19. *The half life period of radon is 3.8 days. After how many days will only one-twentieth of radon sample be left over?*

Solution: We know that, $\lambda = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{3.8} = 0.182 \text{ day}^{-1}$

Let the initial amount of radon be N_0 and the amount left after t days be N which is equal to $\dfrac{N_0}{20}$.

Applying the equation,

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$= \frac{2.303}{0.182} \log_{10} \frac{N_0}{N_0/20} = \frac{2.303}{0.182} \log_{10} 20$$

$$= 16.54 \text{ days}$$

Example 20. *A counter rate meter is used to measure the activity of a radioactive sample. At a certain instant, the count rate was recorded as 475 counters per minute. Five minutes later, the count rate recorded was 270 counts per minute. Calculate the decay constant and half life period of the sample.*

Solution: Let N_0 and N be the number of atoms of the radioactive substance present at the start and after 5 minutes respectively.

Rate of disintegration at the start $= \lambda N_0 = 475$

and rate of disintegration after 5 minutes $= \lambda N = 270$

Dividing both, $\dfrac{\lambda N_0}{\lambda N} = \dfrac{475}{270}$

or $\dfrac{N_0}{N} = 1.76$

We know that, $\lambda = \frac{2.303}{t}\log_{10}\frac{N_0}{N}$

$$\lambda = \frac{2.303}{5}\log_{10} 1.76 = 0.113\ \text{minute}^{-1}$$

$$\text{Half life period} = \frac{0.693}{\lambda} = \frac{0.693}{0.113} = 6.1\ \text{minutes}$$

Example 21. *You have* $0.1\,g$ *atom of a radioactive isotope* $^{A}_{Z}X$ *(half life = 5 days). How many atoms will decay during the 11th day?*

Solution: Amount of radioactive substance = 0.1 g atom

So, $N_0 = 0.1 \times$ Avogadro's number

$$= 0.1 \times 6.02 \times 10^{23}$$

$$= 6.02 \times 10^{22}\ \text{atoms}$$

$$\text{Number of atoms after 5 days} = \frac{6.02 \times 10^{22}}{2} = 3.01 \times 10^{22}$$

$$\text{Number of atoms after 10 days} = \frac{3.01 \times 10^{22}}{2} = 1.505 \times 10^{22}$$

Let the number of atoms left after 11 days be N.

We know that,

$$t = \frac{2.303}{\lambda}\log_{10}\frac{N_0}{N}$$

Given, $t = 11$, $\lambda = \frac{0.693}{5}$, $N_0 = 6.02 \times 10^{22}$

So, $$11 = \frac{2.303 \times 5}{0.693}\log_{10}\frac{6.02 \times 10^{22}}{N}$$

or $$\log_{10}\frac{6.02 \times 10^{22}}{N} = \frac{11 \times 0.693}{2.303 \times 5} = 0.6620$$

$$\frac{6.02 \times 10^{22}}{N} = \text{Antilog } 0.6620 = 4.592$$

So, $$N = \frac{6.02}{4.592} \times 10^{22} = 1.3109 \times 10^{22}$$

Atoms decayed during 11th day

$$= [1.5050 \times 10^{22} - 1.3109 \times 10^{22}]$$

$$= 0.1941 \times 10^{22}$$

$$= 1.941 \times 10^{21}$$

Example 22. $10\,g$ *atoms of an* α*-active radioisotope are disintegrating in a sealed container. In one hour, the helium gas collected at STP is* $11.2\,cm^3$*. Calculate the half life of the radio isotope.*

Solution: Amount of radioactive isotope = 10 g atoms

or $$N_0 = 10 \times 6.023 \times 10^{23}\ \text{atoms}$$

$$= 6.023 \times 10^{24}\ \text{atoms}$$

$$22400\ \text{cm}^3 \text{ of helium contains} = 6.023 \times 10^{23}\ \text{atoms}$$

$$11.2\ \text{cm}^3 \text{ of helium will contain} = \frac{6.023 \times 10^{23}}{22400} \times 11.2\ \text{atoms}$$

$$= 3.01 \times 10^{20}\ \text{atoms}$$

As one helium atom is obtained by disintegration of one atom of radioisotope, the total number of atoms of the radioactive isotope which have disintegrated in one hour

$$= 3.01 \times 10^{20} \quad \text{or} \quad 0.0003 \times 10^{24}$$

The number of atoms of the radioactive isotope left after one hour,

$$N = (6.023 \times 10^{24} - 0.000301 \times 10^{24})$$

$$= 6.0227 \times 10^{24}$$

Using, $$\lambda = \frac{2.303}{t}\log\frac{N_0}{N}$$

$$\lambda = \frac{2.303}{t}\log\frac{6.023 \times 10^{24}}{6.0227 \times 10^{24}}$$

$$= 2.303 \times 2.1632 \times 10^{-5} = 4.982 \times 10^{-5}\ \text{hr}^{-1}$$

$$t_{1/2} = 0.693/(4.982 \times 10^{-5} \times 24 \times 365) = 1.58\ \text{years}$$

Example 23. *Calculate the average life of a radioactive substance whose half life period is* 1650 *years.*

Solution: Average life $= 1.44 \times t_{1/2}$

$$= 1.44 \times 1650 = 2376\ \text{years}$$

Example 24. ^{90}Sr *shows* β*-activity and its half life period is* 28 *years. What is the activity of a sample containing* 1 *g of* ^{90}Sr*?*

Solution: Activity = No. of atoms disintegrating per second

= $\lambda \times$ total number of atoms

$$\lambda = \frac{0.693}{28 \times 365 \times 24 \times 60 \times 60}$$

$$\text{Total number of atoms in 1 g of } ^{90}\text{Sr} = \frac{6.023 \times 10^{23}}{90}$$

$$\text{Activity} = \frac{0.693}{28 \times 365 \times 24 \times 60 \times 60} \times \frac{6.023 \times 10^{23}}{90}$$

$$= 5.25 \times 10^{12}\ \text{disintegrations per second}$$

$$= \frac{5.25 \times 10^{12}}{3.7 \times 10^{10}} = 141.89\ \text{curie}$$

Example 25. *A chemist prepares* $1.00\,g$ *of pure* $^{11}_{6}C$*. This isotope has half life of* 21 *minutes, decaying by the equation:*

$$^{11}_{6}C \rightarrow {}^{11}_{5}B + {}^{0}_{1}e$$

(*a*) *What is the rate of disintegration per second (dps) at start?*

(*b*) *What are the activity and specific activity of* $^{11}_{6}C$ *at start?*

(*c*) *How much of this isotope* ($^{11}_{6}C$) *is left after 24 hours of its preparation?*

Solution: (a) Applying, $-\frac{dN}{dt} = \lambda N_0$

$$= \frac{0.693}{21 \times 60} \times \frac{1 \times 6.02 \times 10^{23}}{11}$$

$$= 3 \times 10^{19}\ \text{dps}$$

(b) $\text{Activity} = \dfrac{3\times 10^{19}}{3.7\times 10^{10}}$ (1 curie = 3.7×10^{10} dps)

$= 8.108\times 10^{8}$ curie

$\text{Sp. activity} = 3\times 10^{19}\times 10^{3} = 3\times 10^{22}$ dis/kg s

$= 8.108\times 10^{11}$ curie

(c) Applying, $N = N_0\left(\dfrac{1}{2}\right)^n \quad \left[n = \dfrac{t}{t_{1/2}} = \dfrac{24\times 60}{21} = 68.57\right]$

$$N = 1\times\left(\frac{1}{2}\right)^{68.57} = 2.29\times 10^{-21}\ \text{g}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

13. The time of decay for the nuclear reaction is given by $t = 5t_{1/2}$. The relation between mean life τ and time of decay 't' is given by:

(a) $2\tau \ln 2$ (b) $5\tau \ln 2$ (c) $2\tau^4 \ln 2$ (d) $\dfrac{1}{\tau^4}\ln 2$

[Ans. (b)]

[Hint: $t = 5t_{1/2}$

$t = 5\times\dfrac{\ln 2}{\lambda}$

$t = 5\tau \ln 2$]

14. The activity of a sample of radioactive element ^{100}A is 6.02 curie. Its decay constant is $3.7\times 10^{4}\ \text{s}^{-1}$. The initial mass of the sample will be:

(a) 10^{-14} g (b) 10^{-6} g (c) 10^{-15} g (d) 10^{-3} g

[Ans. (c)]

[Hint: $\text{Activity} = \lambda\times\dfrac{w}{\text{At. wt.}}\times 6.023\times 10^{23}$

$6.02\times 3.7\times 10^{10} = 3.7\times 10^{4}\times\dfrac{w}{100}\times 6.023\times 10^{23}$

$w = 10^{-15}$ g]

15. A freshly prepared radio medicine has half life 2 hours. Its activity is 64 times the permissible safe value. The minimum time after which it would be possible to treat the patients with the medicine is:

(a) 3 hrs (b) 9 hrs (c) 24 hrs (d) 12 hrs

[Ans. (d)]

[Hint: $N = N_0\left(\dfrac{1}{2}\right)^n$

$\dfrac{N}{N_0} = \left(\dfrac{1}{2}\right)^n$

$\dfrac{1}{64} = \left(\dfrac{1}{2}\right)^n$; $n = 6$ half lives

$\therefore$ time $= 2\times 6 = 12$ hrs]

16. One gram of ^{226}Ra has an activity of nearly 1 Ci. The half life of ^{226}Ra is:

(a) 1582 yrs (b) 12.5 hrs

(c) 140 days (d) 4.5×10^{9} yrs

[Ans. (a)]

[Hint: Use the following relation for calculation of activity:

$$\text{Activity} = \frac{0.693}{t_{1/2}}\times\frac{w}{\text{At. wt.}}\times 6.023\times 10^{23}$$

$$3.7\times 10^{10} = \frac{0.693}{t_{1/2}}\times\frac{1}{226}\times 6.023\times 10^{23}$$

It will give the half life in seconds.]

17. Assuming that ^{226}Ra ($t_{1/2} = 1.6\times 10^{3}$ yrs) is in secular equilibrium with ^{238}U ($t_{1/2} = 4.5\times 10^{9}$ yrs) in a certain mineral, how many grams of radium will be present in for every gram of ^{238}U in this mineral?

(a) 3.7×10^{-7} (b) 3.4×10^{7}

(c) 3.4×10^{-7} (d) 3.7×10^{7}

[Ans. (c)]

[Hint: $\dfrac{N_1\ ^{226}\text{Ra}}{N_2\ ^{238}\text{U}} = \dfrac{t_{1/2}\ ^{226}\text{Ra}}{t_{1/2}\ ^{238}\text{U}}$

$\dfrac{w/226}{1/238} = \dfrac{1.6\times 10^{3}}{4.5\times 10^{9}}$; $w = 3.4\times 10^{-7}$ g]

18. A certain radioactive isotope decay has α-emission,

$$^{A_1}_{Z_1}X \longrightarrow {}^{A_1-4}_{Z_1-2}Y$$

half life of X is 10 days. If 1 mol of X is taken initially in a sealed container, then what volume of helium will be collected at STP after 20 days?

(a) 22.4 L (b) 11.2 L (c) 16.8 L (d) 33.6 L

[Ans. (c)]

[Hint: After 20 days 0.75 mol helium will be formed.

$\therefore$ Volume of helium at STP $= 0.75\times 22.4$

$= 16.8$ L]

3.13 ARTIFICIAL TRANSMUTATION

Transmutation is defined as the conversion of one element into another or one type of atom into another. When this conversion is achieved by artificial means, it is termed as artificial transmutation.

The conversion of elements into one another has been the dream of the human race for many centuries. In the middle ages, it was popular under the name of '*Alchemy*'. Alchemists were unsuccessful in this attempt as they were having very little knowledge about the structure of atom. With the background of the clear picture of the structure of the atom, modern scientists have realised that to convert one element into another, the nucleus should be attacked and altered.

The first indication that a stable nucleus could be disrupted was given by Rutherford in 1919. He observed that when nitrogen was bombarded with high speed α-particles from ^{214}Po, protons were emitted. Thus, nitrogen was changed into an isotope of oxygen.

$$^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

Later on, Rutherford and Chadwick showed that many other elements from boron to potassium with the exception of carbon and oxygen could be transmuted by bombardment with α-particles. However with heavier elements, there was only scattering of α-particles as these suffered a force of repulsion. It was, thus, concluded that to bring transmutation in heavier elements, the projectiles must have higher energies than α-particles obtained from natural sources. It was suggested by Gamow in 1928 that a proton (${}^{1}_{1}\text{H}$) would be a much more effective projectile than an α-particle, but it was not available as a high speed particle.

The charged particles, like alpha particles, protons, deuterons can be made much more effective projectiles if they have high velocity. Out of all the instruments which have been devised for accelerating projectiles, the one which has attracted the widest interest is the cyclotron of E.O. Lawrence. The projectile can be accelerated to the speed of 25,000 miles per second.

The discovery of neutron by Chadwick, in 1932, added another projectile for transmutation. The neutron being electrically neutral can penetrate easily into the atomic nucleus. Although neutrons are the most effective and versatile of projectiles, yet they suffer the objection that they must be produced by transmutation at the time of use. High speed neutrons are obtained when beryllium-9 is bombarded with α-particles,

$${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$$

and slow neutrons are obtained by bombarding lithium-7 with protons.

$${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \longrightarrow {}^{7}_{4}\text{Be} + {}^{1}_{0}n$$

In general, for the transmutation of lighter elements, charged particles like alpha particles, protons, deuterons are used while for heavier elements, neutrons are used.

Nuclear Reactions

The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as alpha particle, proton, deuteron, neutron, etc., resulting in the formation of a new nucleus and one or more elementary particles are called nuclear reactions. Nuclear reactions are expressed in the same fashion as chemical reactions, *i.e.*, reactants on left hand side and the products on right hand side of the sign of (=) or (→). **In all nuclear reactions, the total number of protons and neutrons are conserved as in chemical reactions, the number of atoms of each element are conserved.** The symbols ${}^{1}_{0}n$, ${}^{1}_{1}\text{H}$, ${}^{4}_{2}\text{He}$, ${}^{2}_{1}\text{H}$, ${}^{0}_{-1}e$, ${}^{0}_{+1}e$ and γ are used to represent neutron, proton, α-particle, deuteron, electron, positron, γ-rays respectively. A short hand notation is often used for the representation of nuclear reactions. As for example, the nuclear reaction

$${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$$

is represented as ${}^{14}_{7}\text{N}(\alpha, p)\,{}^{17}_{8}\text{O}$. Some of the characteristics that differentiate between nuclear reactions and ordinary chemical reactions are summarised below:

Nuclear reactions	**Chemical reactions**
1. Elements may be converted from one to another.	No new element can be produced.
2. Particles within the nucleus are involved.	Only outermost electrons participate.
3. Often accompanied by release or absorption of tremendous amount of energy.	Accompanied by release or absorption of relatively small amount of energy.
4. Rate of reaction is independent of external factors such as temperature, pressure and catalyst.	Rate of reaction is influenced by external factors.

Example 26. *Calculate the energy in the reaction*

$$2\,{}^{1}_{1}H + 2\,{}^{1}_{0}n \rightarrow {}^{4}_{2}He$$

Given, $H = 1.00813$ *amu,* $n = 1.00897$ *amu and*
$He = 4.00388$ *amu*

Solution: Loss of mass in the given nuclear reaction

$$= 2(1.00813 + 1.00897) - 4.00388$$

$$= 0.03032 \text{ amu}$$

$$\text{Energy released} = 0.03032 \times 931 = 28.3 \text{ MeV}$$

Types of Nuclear Reactions

(a) Projectile capture reactions: The bombarding particle is absorbed with or without the emission of γ-radiations.

$${}^{238}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}\text{U} + \gamma$$

$${}^{27}_{13}\text{Al} + {}^{1}_{0}n \longrightarrow {}^{28}_{13}\text{Al} + \gamma$$

(b) Particle-particle reactions: Majority of nuclear reactions come under this category. In addition to the product nucleus, an elementary particle is also emitted.

$${}^{23}_{11}\text{Na} + {}^{1}_{1}\text{H} \longrightarrow {}^{23}_{12}\text{Mg} + {}^{1}_{0}n$$

$${}^{23}_{11}\text{Na} + {}^{2}_{1}\text{H} \longrightarrow {}^{24}_{11}\text{Na} + {}^{1}_{1}\text{H}$$

$${}^{23}_{11}\text{Na} + {}^{4}_{2}\text{He} \longrightarrow {}^{26}_{12}\text{Mg} + {}^{1}_{1}\text{H}$$

$${}^{14}_{7}\text{N} + {}^{1}_{0}n \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$$

(c) Spallation reactions: High speed projectiles with energies approximately 40 MeV may chip fragments from a heavy nucleus, leaving a smaller nucleus.

$${}^{63}_{29}\text{Cu} + {}^{4}_{2}\text{He} + 400\text{ MeV} \longrightarrow {}^{37}_{17}\text{Cl} + 14\,{}^{1}_{1}\text{H} + 16\,{}^{1}_{0}n$$

$${}^{75}_{33}\text{As} + {}^{2}_{1}\text{H} \longrightarrow {}^{56}_{25}\text{Mn} + 9\,{}^{1}_{1}\text{H} + 12\,{}^{1}_{0}n$$

$${}^{238}_{92}\text{U} + {}^{4}_{2}\text{He} \longrightarrow {}^{187}_{74}\text{W} + 20\,{}^{1}_{1}\text{H} + 35\,{}^{1}_{0}n$$

(d) Fission reactions: A reaction in which a heavy nucleus is broken down into two or more medium heavy fragments. The process is usually accompanied with emission of neutrons and large amount of energy.

$${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3\,{}^{1}_{0}n + 200\text{ MeV}$$

(e) Fusion reactions: Light nuclei fuse together to reproduce comparatively heavier nuclei.

$${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n + 17.6\text{ MeV}$$

A fusion reaction is the source of tremendous amount of energy.

Pair production : Pair production is the most striking example of mass-energy equivalence.

We can write pair production symbolically as :

$$\text{Photon} + \text{Photon} \longrightarrow \text{Particle} + \text{Antiparticle}$$

$$\text{Particle} + \text{Antiparticle} \longrightarrow \text{Photon} + \text{Photon}$$

A particle and antiparticle can collide and annihilate each other, producing two high-energy gamma ray photons. Pair production must obey the law of conservation of energy and momentum.

The following are the important contributions of artificial transmutation:

(i) Discovery of neutron
(ii) Artificial radioactivity
(iii) Nuclear fission
(iv) Nuclear fusion

3.14 ARTIFICIAL RADIOACTIVITY

In 1934, Irene Curie and F. Joliot observed that when boron and aluminium were bombarded by α-particles, neutrons, protons and positrons were emitted. When bombardment was stopped, the emission of protons and neutrons ceased but that of positrons did not. The emission of positrons continued with time but decreased exponentially in a manner similar to natural radioactivity. Curie and Joliot explained this observation by saying that during bombardment, a metastable isotope is formed which behaves as a radioactive element. This process was termed as **artificial radioactivity.**

"The process in which a stable isotope is converted into a radioactive element by artificial transmutation is called artificial radioactivity."

When $^{27}_{13}\text{Al}$ is bombarded by α-particles, radioactive isotope $^{30}_{15}\text{P}$ is formed.

$$^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow ^{30}_{14}\text{Si} + ^{1}_{1}\text{H} \text{ (95\% of total conversion)}$$

$$\longrightarrow ^{30}_{15}\text{P}^{*} + ^{1}_{0}n \text{ (5\% of total conversion)}$$

$$\longrightarrow ^{30}_{14}\text{Si} + ^{0}_{+1}e$$

Positron

In a similar manner, the artificial radioactivity was observed when $^{10}_{5}\text{B}$ was bombarded by α-particles.

$$^{10}_{5}\text{B} + ^{4}_{2}\text{He} \longrightarrow ^{13}_{6}\text{C} + ^{1}_{1}\text{H}$$

$$\longrightarrow ^{13}_{7}\text{N}^{*} + ^{1}_{0}n$$

$$\longrightarrow ^{13}_{6}\text{C} + ^{0}_{+1}e$$

The following are some of the nuclear reactions in which radioactive isotopes are formed.

$$^{23}_{11}\text{Na} + ^{2}_{1}\text{H} \longrightarrow ^{24}_{11}\text{Na}^{*} + ^{1}_{1}\text{H} \quad [^{24}_{11}\text{Na} — \beta \text{ radioactive}]$$

$$^{238}_{92}\text{U} + ^{1}_{0}n \longrightarrow ^{239}_{92}\text{U}^{*} + \gamma \quad [^{239}_{92}\text{U} — \beta \text{ radioactive}]$$

$$^{12}_{6}\text{C} + ^{1}_{1}\text{H} \longrightarrow ^{13}_{7}\text{N}^{*} + \gamma \, [^{13}_{7}\text{N} — \text{positron radioactive}]$$

$$^{25}_{12}\text{Mg} + ^{4}_{2}\text{He} \longrightarrow ^{28}_{13}\text{Al}^{*} + ^{1}_{1}\text{H} \quad [^{28}_{13}\text{Al} — \beta \text{ radioactive}]$$

3.15 NUCLEAR FISSION

"The process of artificial transmutation in which heavy nucleus is broken down into two lighter nuclei of nearly comparable masses with release of large amount of energy is termed nuclear fission." The word fission is derived from its resemblance to the biological process called fission in which a living cell breaks up into two cells of roughly same size.

After the discovery of neutron, **Fermi,** in 1934, made an attempt to synthesise transuranic elements from uranium by bombarding with neutrons. This experiment was repeated in Germany by **Hahn** and **Strassmann.** In one of the chemical tests, they found that one of the products was an isotope of barium along with the formation of an isotope of the element with atomic number 93 (neptunium). In 1939, they proposed that uranium after capturing neutron undergoes two types of reactions—one with ^{238}U isotope and the other with ^{235}U isotope.

(a) $^{238}_{92}\text{U}$ is converted into $^{239}_{93}\text{Np}$ and $^{239}_{94}\text{Pu}$.

$$^{238}_{92}\text{U} + ^{1}_{0}n \longrightarrow ^{239}_{92}\text{U} \xrightarrow{-\beta} ^{239}_{93}\text{Np} \xrightarrow{-\beta} \underset{\text{(Plutonium)}}{^{239}_{94}\text{Pu}}$$

(b) $^{235}_{92}\text{U}$ captures slow neutron and splits up into fragments.

$$^{235}_{92}\text{U} + ^{1}_{0}n \longrightarrow ^{236}_{92}\text{U} \longrightarrow ^{144}_{56}\text{Ba} + ^{90}_{36}\text{Kr} + 2\, ^{1}_{0}n$$

It has been observed that during fission of $^{235}_{92}\text{U}$ not only isotopes of Ba and Kr are formed but isotopes of various other elements come into existence. These isotopes fall under two groups. First type—isotopes having atomic masses from 80 to 110 and atomic numbers from 35 to 43 and second type—isotopes having atomic masses from 120 to 150 and atomic numbers 51 to 57. It is believed that only two isotopes are first formed as primary fission products which then give rise to secondary products by successive disintegration.

$$\left.\begin{aligned} ^{235}_{92}\text{U} + ^{1}_{0}n &\longrightarrow ^{141}_{56}\text{Ba} + ^{92}_{36}\text{Kr} + 3\, ^{1}_{0}n \\ &\longrightarrow ^{139}_{54}\text{Xe} + ^{95}_{38}\text{Sr} + 2\, ^{1}_{0}n \\ &\longrightarrow ^{140}_{54}\text{Xe} + ^{95}_{38}\text{Sr} + ^{1}_{0}n \end{aligned}\right\} \text{Primary products}$$

$$\underbrace{^{140}_{54}\text{Xe} \xrightarrow{-\beta} ^{140}_{55}\text{Cs} \xrightarrow{-\beta} ^{140}_{56}\text{Ba} \xrightarrow{-\beta} ^{140}_{57}\text{La} \xrightarrow{-\beta} ^{140}_{58}\text{Ce}}_{\text{Secondary products}}$$

During fission, there is always loss of mass which is converted into energy according to Einstein equation $E = mc^2$. There is a loss of about 0.215 amu mass during one fission. Thus, energy released in one fission is equal to 0.215×931, *i.e.*, 200 MeV.

Chain reaction: Whatever are the primary products of fission of uranium, it is certain that neutrons are always set free. If the conditions are so arranged that each of these neutrons can, in turn, bring about the fission, the number of neutrons will increase at a continuously accelerating rate until whole of the material is exhausted. Such type of reaction is called **chain reaction.** It takes very small time and is uncontrolled. It ends in a

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* Half life period of $^{30}_{15}\text{P}$ is 3.2 minutes.

terrible explosion due to release of enormous amount of energy. The chain reaction is shown in Fig. 3.7.

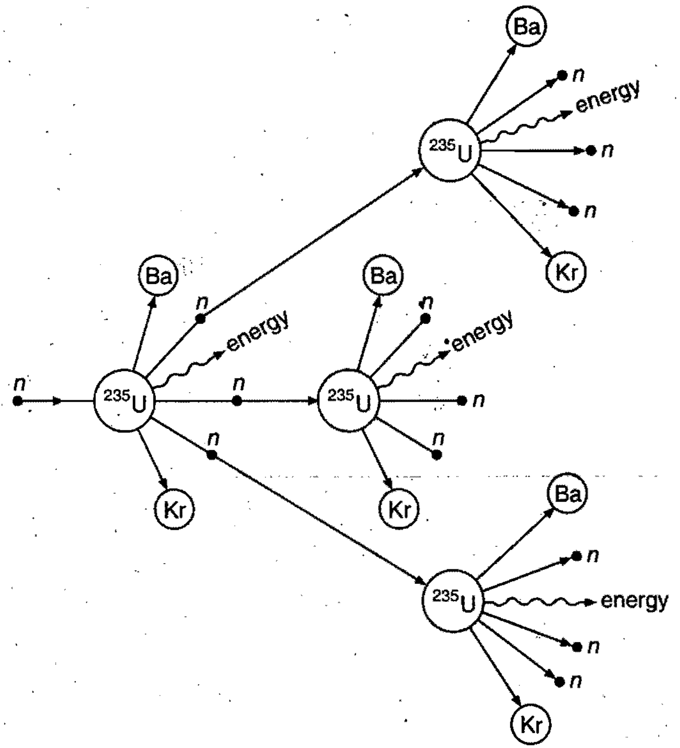


Fig. 3.7 Chain reaction in uranium-235

The chain reaction is self-propagating if the value of multiplication factor is more than 1.

Multiplication factor,

$$K = \frac{\text{No. of neutrons produced in one step}}{\text{No. of neutrons produced in preceding step}}$$

The value of K is 2.5 for ^{235}U and 0.5 for ^{238}U. This shows that if all other factors are ignored, natural uranium which is a mixture of three isotopes ($^{238}U = 99.29\%$, $^{235}U = 0.7\%$, $^{234}U = 0.0006\%$) is not suitable for a chain reaction. The following two factors hinder the self-propagation of a chain reaction:

(i) Leakage of neutrons from the system.

(ii) Presence of non-fissionable material.

If the system is such that loss of neutrons is more than their production, it is a subcritical stage. When the loss of neutrons is equal to their production, it is said to be the critical stage and when loss of neutrons is less than their production, it is the over-critical stage. Over-critical stage is required for self-propagation of chain reaction. The leakage of neutrons from the system can be reduced by suitable choice of size and shape of the fissionable material. The second source of loss of neutrons is due to absorption of neutrons by non-fissionable material. It may be reduced by careful purification of natural uranium, *i. e.*, natural uranium is submitted to the process of enrichment by which the percentage of ^{235}U in the sample is increased. The chain reaction can be carried out under two conditions: (a) uncontrolled (atom bomb) and (b) controlled (nuclear reactors).

Nuclear fuels: Nuclear fuels are of two types:

(i) Fissile materials: These, on bombardment with slow neutrons, directly produce a chain reaction leading to release of energy. Three fissile materials are in use at present. These are ^{235}U, ^{239}Pu and ^{233}U. ^{235}U is obtained from natural sources while ^{239}Pu and ^{233}U are obtained by artificial transmutation.

(ii) Fertile materials: A fertile material is one which by itself is non-fissile in nature, can be converted into a fissile material by reaction with neutrons. ^{238}U and ^{232}Th are fertile materials. ^{238}U is converted into ^{239}Pu by the following nuclear reaction:

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U^{*} \xrightarrow[(23\text{ min})]{-\beta} ^{239}_{93}Np^{*} \xrightarrow[(2.3\text{ days})]{-\beta} ^{239}_{94}Pu$$

Similarly ^{232}Th is converted into ^{233}U.

$$^{232}_{90}Th + ^{1}_{0}n \longrightarrow ^{233}_{90}Th^{*} \xrightarrow[(23\text{ min})]{-\beta} ^{233}_{91}Pa^{*} \xrightarrow[(27\text{ days})]{-\beta} ^{233}_{92}U$$

Applications of nuclear fission: Three practical applications of nuclear fission are:

(a) Atomic bomb, (b) Nuclear reactor and (c) Power plant.

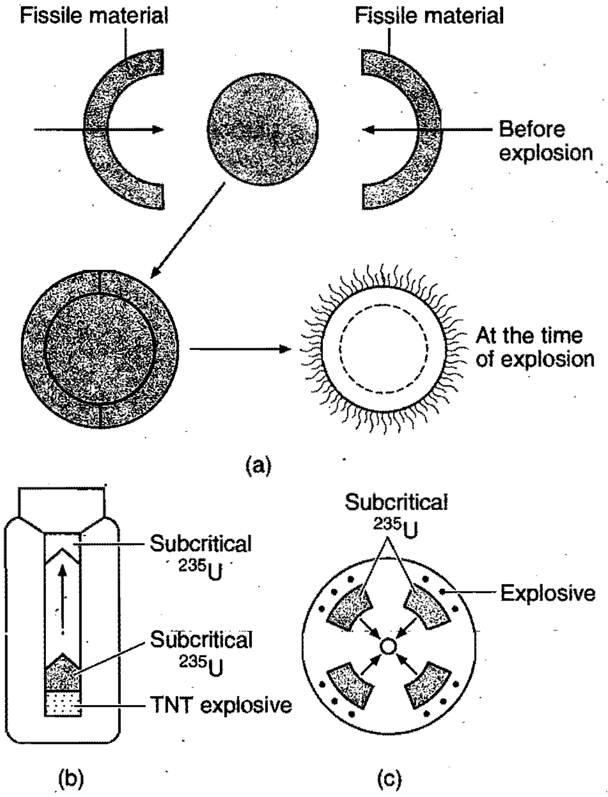


Fig. 3.8 (a), (b) and (c) various designs used in the assembly of atom bomb. (The atom bomb is made in two or more pieces of the fissile material each smaller than the critical size. The moment these pieces are forced together, the bomb explodes with terrific violence).

(a) Atomic bomb: It is based on uncontrolled chain reaction. The shape and size of the fissionable material is so adjusted at the time of explosion that it reaches the over-critical stage. In the atom bomb, a few pounds of fissionable material (^{235}U or ^{239}Pu) is taken in the form of a number of separate pieces; each piece is in subcritical stage (surface area is very large, *i.e.*, loss of neutrons is high.) At the time of explosion, these pieces are driven together rapidly by using explosives like TNT (trinitro toluene) lying behind each of ^{235}U pieces as to make one large piece of fissionable material. At this instant, the over-critical stage is achieved and a fast chain reaction is set- up. This results in a violent explosion with the release of tremendous amount of energy. Fig. 3.8 shows some of the designs of atomic bomb.

On account of explosion, the fragments fly apart with tremendous speeds. These collide with each other and kinetic energy is changed to heat energy. The amount of energy liberated in an atomic explosion is of the order of the detonation of about 20,000 or 30,000 tons of TNT raising the temperature to about 10^7°C. Air expands suddenly and a shock wave of great destructive impulse travels across. The explosion also produces a violent and intense blast of highly penetrating γ-rays which are exceedingly dangerous. The radioactive dust (fallout) scatters over wide areas causing contamination.

The first atomic bomb dropped over Hiroshima city during the second World War in 1945 utilised ^{235}U and the second atomic bomb dropped on Nagasaki made use of ^{239}Pu. India exploded their first atomic bomb at **Pokhran** in **Rajasthan** in May 1974, and used ^{239}Pu as the fissionable material.

Nuclear Power and India (Recent Developments)

Indian scientists recently repeated the history of 11th May 1974. Our great scientists successfully conducted five underground nuclear tests at **Pokhran** range in **Rajasthan,** 24 years after the nation had conducted the first such test. Three tests were conducted at 3.45 p.m. on 11th May 1998 and the two tests were made later on 13th May. These tests were up to the mark and as per our expectations.

(b) Nuclear reactor or atomic reactor or atomic pile: The reactor is the furnace of the atomic age, the place where fissionable material is burnt for useful purposes. **It is essentially an instrument designed to allow a nuclear chain to develop, under control.** All the neutrons produced are not allowed to carry out the chain reaction. A fission reactor has five main components: (i) fuel, (ii) moderator, (iii) control rods, (iv) cooling system and (v) shielding.

(i) Fuel: Either enriched uranium or natural uranium is usually used as fuel. Heterogeneous reactors employ the fuel in the form of rods, plates or hollow cylinders. Homogeneous reactors employ solution of the fuel prepared in the moderator.

(ii) Moderator: The most efficient fission reactions occur with slow neutrons. Thus, the fast neutrons ejected during fission must be slowed down by collisions with atoms of comparable mass that do not absorb them. Such materials are called **moderators.** The most commonly used moderators are ordinary water and graphite. The most efficient moderator is helium. The next most efficient one is heavy water (D_2O) but this is so expensive that it has been used only in research reactors.

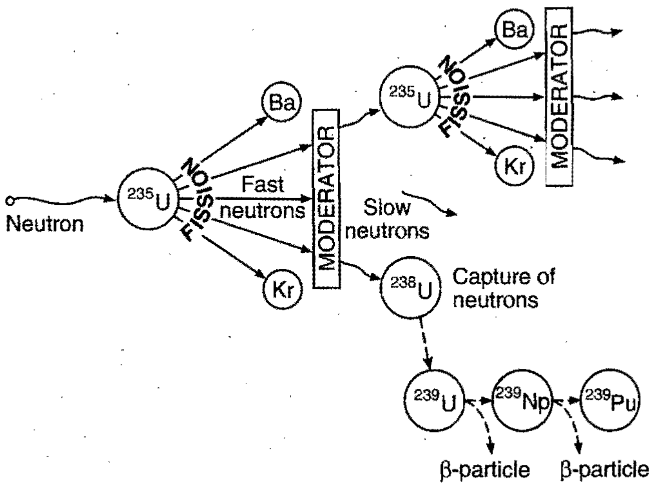


Fig. 3.9 Nuclear fission in a nuclear reactor using enriched uranium

(iii) Control rods: Boron or cadmium steel rods are used as control rods. These rods absorb neutrons and thereby control the rate of fission, *e.g.*,

$$_5B^{10} + {}_0n^1 \longrightarrow {}_3Li^7 + {}_2He^4$$

(iv) Cooling system: Liquid alloy of sodium and potassium is used as coolant; it takes away the heat to the exchanger. Heavy water, polyphenyls and carbon dioxide have also been used as coolants.

(v) Shielding: The reactor is enclosed in a steel containment vessel, which is housed in a thick-walled concrete building. Operating people are protected by a shield of compressed wood fibres.

Nuclear reactors are used:

1. To produce ^{239}Pu and ^{233}U: It is predicted that our limited supply of ^{235}U will last only another 50 years. However, non-fissionable ^{238}U and ^{232}Th are plentiful and can be converted into ^{239}Pu and ^{233}U. This conversion can be done in special type of reactors called **breeder reactors.** These reactors not only produce large quantities of heat from fission but also generate more fuel than they use because neutrons are absorbed in a thorium or uranium blanket to form ^{233}U and ^{239}Pu. This type of reactor requires the use of fast neutrons; no moderator is needed, but control is more difficult. Heat must be transferred very efficiently because ^{239}Pu melts at a relatively low temperature of 640°C. The process in which non fissile Nuclei $^{238}_{92}$U and $^{232}_{90}$Th are converted to fissile nuclei in breeder reactors is given below:

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \xrightarrow{-\beta^-} {}^{239}_{93}Np \xrightarrow{-\beta^-} {}^{239}_{94}Pu$$

$$^{232}_{90}Th + {}^{1}_{0}n \longrightarrow {}^{232}_{90}Th \xrightarrow{-\beta^-} {}^{233}_{91}Pa \xrightarrow{-\beta^-} {}^{233}_{92}U$$

2. To produce a strong beam of neutrons: These neutrons are used for making various isotopes which do not occur in nature. For example, $^{32}_{15}P$ and $^{60}_{27}Co$ are produced from the following nuclear reactions:

$$^{130}_{52}Te + ^{1}_{0}n \longrightarrow ^{131}_{53}I + ^{0}_{-1}e$$

$$^{31}_{15}P + ^{1}_{0}n \longrightarrow ^{32}_{15}P$$

$$^{32}_{16}S + ^{1}_{0}n \longrightarrow ^{32}_{15}P + ^{1}_{1}H$$

$$^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{60}_{27}Co$$

The non-radioactive isotope is taken in aluminium capsule which is placed inside the aluminium ball. The ball is rolled into the reactor where it is bombarded by neutrons slowed down by paraffin wax. The bombardment is continued for required period, which varies from element to element.

(c) Power plant (to generate electricity): The heat produced is utilised in generating steam which runs the steam turbines. The electric generator is connected to the turbine. The electric power is obtained from the generator. The atomic reactor when used for production of electricity is termed **power plant.**

The first nuclear reactor was assembled by **Fermi** and his co-workers at the University of Chicago in the United States of America, in 1942. In India, the first nuclear reactor was put into operation at Trombay (Mumbai), in 1956.

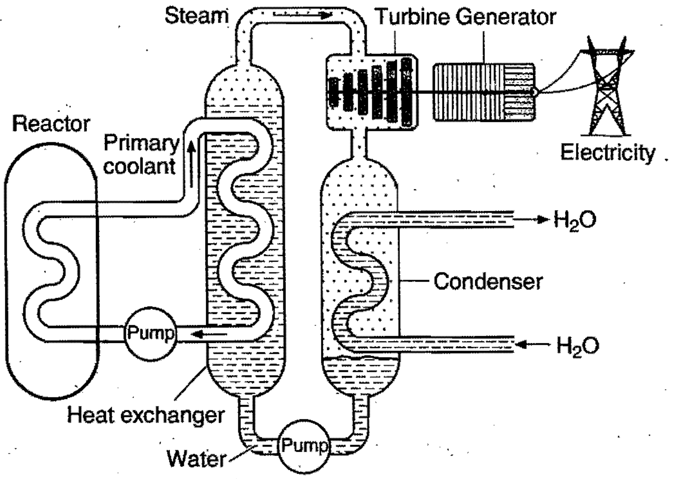


Fig. 3.10 Power plant : Application of nuclear fission for the production of electricity

3.16 NUCLEAR FUSION

A nuclear reaction in which two lighter nuclei are fused together to form a heavier nuclei is called nuclear fusion. In such a process, more stable nuclei come into existence as binding energy per nucleon increases (see sec. 2.23). A fusion reaction is difficult to occur because positively charged nuclei repel each other. At very high temperatures of the order of 10^6 to 10^7 K, the nuclei may have sufficient energy to overcome the repulsive forces and fuse. It is for this reason, fusion reactions are also called **thermonuclear reactions.** Fusion reactions are highly exothermic in nature because loss of mass occurs when heavier nuclei is formed from the two lighter nuclei. To initiate a fusion reaction is difficult, but once it is started, its continuity is maintained due to huge release of energy. Some examples of the fusion reactions are given below:

$$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{4}_{2}He + 24.9\ MeV$$

$$^{3}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + 2\,^{1}_{0}n + 11.0\ MeV$$

$$^{1}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + 20.0\ MeV$$

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n + 17.8\ MeV$$

$$^{7}_{3}Li + ^{1}_{1}H \longrightarrow 2\,^{4}_{2}He + 17.7\ MeV$$

Hydrogen bomb is based on fusion reactions. Energy released is so enormous that it is about 1000 times that of an atomic bomb. In hydrogen bomb, a mixture of deuterium oxide (D_2O) and tritium oxide (T_2O) is enclosed in a space surrounding an ordinary atomic bomb. The temperature produced by the explosion of the atomic bomb initiates the fusion reaction between $^{3}_{1}H$ and $^{2}_{1}H$ releasing huge amount of energy. The first hydrogen bomb was exploded in 1952. So far, it has not been possible to bring about fusion under controlled conditions.

It is believed that the high temperature of stars including the sun is due to fusion reactions. **Bethe** and **Weizsaeker,** in 1939, proposed that a carbon-nitrogen cycle is responsible for the production of solar energy in which hydrogen is converted into helium. The cycle is:

$$\begin{aligned}
^{12}_{6}C + ^{1}_{1}H &\longrightarrow ^{13}_{7}N + \gamma\\
^{13}_{7}N &\longrightarrow ^{13}_{6}C + ^{0}_{+1}e\\
^{13}_{6}C + ^{1}_{1}H &\longrightarrow ^{14}_{7}N + \gamma\\
^{14}_{7}N + ^{1}_{1}H &\longrightarrow ^{15}_{8}O + \gamma\\
^{15}_{8}O &\longrightarrow ^{15}_{7}N + ^{0}_{+1}e\\
^{15}_{7}N + ^{1}_{1}H &\longrightarrow ^{12}_{6}C + ^{4}_{2}He + \gamma\\
\hline
\text{or} \quad 4\,^{1}_{1}H &\longrightarrow ^{4}_{2}He + 2\,^{0}_{+1}e + 24.7\ MeV
\end{aligned}$$

$^{12}_{6}C$ acts as a kind of nuclear catalyst.

E. Saltpeter, in 1953, proposed a proton-proton chain reaction:

$$\begin{aligned}
^{1}_{1}H + ^{1}_{1}H &\longrightarrow ^{2}_{1}H + ^{0}_{+1}e + \gamma\\
^{2}_{1}H + ^{1}_{1}H &\longrightarrow ^{3}_{2}He + \gamma\\
^{3}_{2}He + ^{1}_{1}H &\longrightarrow ^{4}_{2}He + ^{0}_{+1}e + \gamma\\
\hline
4\,^{1}_{1}H &\longrightarrow ^{4}_{2}He + 2\,^{0}_{+1}e + 24.7\ MeV
\end{aligned}$$

As a potential source of commercial electrical power, the fusion process has several advantages over the fission reaction. (i) The quantity of energy liberated in the fusion is much greater than in fission. (ii) The products of fusion are non-radioactive. Fission produces many unstable radioactive products. Fission reactors, therefore, pose a waste-disposal problem.

Difference between Nuclear Fission and Nuclear Fusion

Nuclear Fission	Nuclear Fusion
(i) This process occurs in heavy nuclei.	This process occurs in lighter nuclei.
(ii) The heavy nucleus splits into lighter nuclei of comparable masses.	The lighter nuclei fuse together to form a heavy nucleus.
(iii) The binding energy per nucleon increases.	The binding energy per nucleon increases.
(iv) This reaction occurs at ordinary temperature.	This occurs at a very high temperature.
(v) The energy liberated in one fission is about 200 MeV.	The energy liberated in one fusion is about 24 MeV.
(vi) This can be controlled.	This cannot be controlled.
(vii) Products of fission are usually unstable radioactive in nature.	Products of fusion are usually stable and non-radioactive in nature.
(viii) Percentage efficiency is less. % efficiency $= \frac{200}{236 \times 931} \times 100 = 0.09$	Percentage efficiency is high. % efficiency $= \frac{17.8}{5 \times 931} \times 100 = 0.38$ $[{}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n$ $+ 17.8 \text{ MeV}]$
(ix) The links of fission reactions are neutrons.	The links of fusion reactions are protons.

3.17 SYNTHETIC ELEMENTS INCLUDING TRANSACTINIDES

Elements 43 (technetium), 61 (promethium), 85 (astatine) and all elements with $Z > 92$ do not exist naturally on the earth, because no isotopes of these elements are stable. The elements coming after uranium ($Z = 92$) are named **transuranic** or **transuranium** elements. The actinide series which starts with the element thorium ($Z = 90$) is complete at the element lawrencium ($Z = 103$). The elements with $Z = 104 - 112$ have been reported recently and are transition (*d*-block-fourth series) elements. These are called **transactinides** or **super heavy elements.** After the discovery of nuclear reactions early in the twentieth century, scientists between 1937 and 1945, set out to make the missing elements, *i.e.*, technetium, promethium and astatine and three members of the actinide series, neptunium ($Z = 93$), plutonium ($Z = 94$) and americium ($Z = 95$). The missing elements and all the elements above atomic number 92 are called **synthetic elements** as these have been synthesised by artificial transmutation, *i.e.*, by nuclear reactions. The credit for the discovery of most of the transuranic elements goes to **Seaborg.**

Much less is known about synthetic elements as these are radioactive and short-lived. This is also due to their limited availability. The production of synthetic elements requires binuclear reactions between two positive nuclei that must be fused together against the force of electrical repulsion. Nuclear accelerators were used for this purpose. High energy deuterons were used to increase the atomic number of target nuclei by one unit.

$${}^{98}_{42}\text{Mo} + {}^{2}_{1}\text{H} \longrightarrow {}^{99}_{43}\text{Tc} + {}^{1}_{0}n$$

$${}^{238}_{92}\text{U} + {}^{2}_{1}\text{H} \longrightarrow {}^{238}_{93}\text{Np} + 2{}^{1}_{0}n$$

Elements 93 and 94 were produced using neutrons (obtained during fission) instead of accelerated positive nuclei. Neutron capture by ${}^{238}\text{U}$ followed by β-emission gives isotopes with mass number 239.

$${}^{238}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}\text{U} \xrightarrow{-\beta} {}^{239}_{93}\text{Np} \xrightarrow{-\beta} {}^{239}_{94}\text{Pu}$$

${}^{239}_{94}\text{Pu}$ is an α-emitter with half life of 2.4×10^{4} years.

Americium is formed in a similar way.

$${}^{239}_{94}\text{Pu} \xrightarrow{(n,\gamma)} {}^{240}_{94}\text{Pu} \xrightarrow{(n,\gamma)} {}^{241}_{94}\text{Pu} \xrightarrow{-\beta} {}^{241}_{95}\text{Am}$$

As Z increases, the efficiency of nuclear reactions with neutron bombardment falls sharply. Instead, nuclides in the $Z = 95$ to 99 range are bombarded with beams of helium nuclei accelerated in the cyclotron to form nuclides with atomic numbers 96 to 101.

$${}^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}n$$

$${}^{241}_{95}\text{Am} + {}^{4}_{2}\text{He} \longrightarrow {}^{243}_{97}\text{Bk} + 2{}^{1}_{0}n$$

$${}^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^{1}_{0}n$$

$${}^{249}_{98}\text{Cf} + {}^{4}_{2}\text{He} \longrightarrow {}^{251}_{100}\text{Fm} + 2{}^{1}_{0}n$$

$${}^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}n$$

Beyond element with $Z = 101$, increasingly heavier nuclei are used as projectiles. These projectiles are accelerated by linear rather than circular accelerators. Examples of nuclear reactions of this type are the following:

$${}^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4{}^{1}_{0}n$$

$${}^{252}_{98}\text{Cf} + {}^{11}_{5}\text{B} \longrightarrow {}^{257}_{103}\text{Lr} + 6{}^{1}_{0}n$$

$${}^{238}_{92}\text{U} + {}^{14}_{7}\text{N} \longrightarrow {}^{249}_{99}\text{Es} + 3{}^{1}_{0}n$$

$${}^{238}_{92}\text{U} + {}^{16}_{8}\text{O} \longrightarrow {}^{250}_{100}\text{Fm} + 4{}^{1}_{0}n$$

The superheavy elements have been discovered by bombardment with medium weight nuclei. For example, the elements with $Z = 107$ and $Z = 109$ have been obtained by bombardment of ${}^{209}_{83}\text{Bi}$ with accelerated ${}^{54}_{24}\text{Cr}$ and ${}^{58}_{26}\text{Fe}$ respectively.

$${}^{209}_{83}\text{Bi} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{261}_{107}\text{Uns} + 2{}^{1}_{0}n$$

$${}^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Une} + {}^{1}_{0}n$$

The elements with $Z = 104$, 105, 106 and 108 have also been reported by the applications of the following reactions:

$${}^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Unq} + 4{}^{1}_{0}n$$

$${}^{249}_{98}\text{Cf} + {}^{15}_{7}\text{N} \longrightarrow {}^{260}_{105}\text{Unp} + 4{}^{1}_{0}n$$

$$^{249}_{98}\text{Cf} + ^{18}_{8}\text{O} \longrightarrow ^{263}_{106}\text{Unh} + 4^{1}_{0}n$$

$$^{208}_{82}\text{Pb} + ^{58}_{26}\text{Fe} \longrightarrow ^{265}_{108}\text{Uno} + ^{1}_{0}n$$

The elements up to 100 (fermium) undergo radioactive decay mainly by emitting α-particles or β-particles. The elements become increasingly unstable as the atomic number increases and nobelium has a half life of only three seconds. With these heavy elements, spontaneous nuclear fission becomes the most important method of decay. ^{252}Cf could become a valuable neutron source.

The IUPAC names for the elements $Z > 100$ have been given below:

101 Unnilunium	Unu	107 Unnilseptium	Uns
102 Unnilbium	Unb	108 Unniloctium	Uno
103 Unniltrium	Unt	109 Unnilennium	Une
104 Unnilquadium	Unq	110 Ununnilium	Uun
105 Unnilpentium	Unp	111 Unununium	Uuu
106 Unnilhexium	Unh	112 Ununbium	Uub

Elements with an even number of protons in the nucleus are usually more stable than their neighbours with odd atomic numbers, *i.e.*, they are less likely to decay. Also nuclei with both an even number of protons and an even number of neutrons are more likely to be stable. A nucleus is more stable than average if the numbers of neutrons or protons are 2, 8, 20, 28, 50, 82 or 126. These are called 'magic numbers' and can be explained by the shell structure of the nucleus. This theory also requires the inclusion of numbers 114, 164 and 184 in the series of magic numbers. The stability is particularly high if number of protons and the number of neutrons are magic numbers. Thus, $^{208}_{82}\text{Pb}$ is very stable with 82 protons and (208 – 82) 126 neutrons. This suggests that nuclides as Uuq ($Z = 114$, $A = 278$), Uuq ($Z = 114$, $A = 298$) and Ubh ($Z = 126$, $A = 310$) might be stable enough to exist. Considerable efforts are being made to produce elements 114 and 126 but the present techniques have so far only succeeded in producing unstable isotopes. The elements up to $Z = 112$ have been reported so far.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The radioactive isotope $^{60}_{27}\text{Co}$ which is used in the treatment of cancer can be made by (n, p) reaction. For this reaction, the target nucleus is:

(a) $^{59}_{28}\text{Ni}$ (b) $^{59}_{27}\text{Co}$ (c) $^{60}_{28}\text{Ni}$ (d) $^{60}_{27}\text{Co}$

[Manipal (Med.) 2007]

[**Ans.** (c)]

[**Hint:** $^{60}_{28}\text{Ni} + ^{1}_{0}n \longrightarrow ^{60}_{27}\text{Co} + ^{1}_{1}\text{H}$]

20. $^{14}_{7}\text{N}$ is attacked by doubly charged helium ion, it emits a proton and:

(a) $^{18}_{9}\text{F}$ (b) $^{17}_{8}\text{O}$ (c) $^{18}_{8}\text{O}$ (d) $^{19}_{9}\text{F}$

[JEE (Orissa) 2007]

[**Ans.** (b)]

[**Hint:** $^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$]

21. A nuclear reaction of $^{235}_{92}\text{U}$ with a neutron produces $^{90}_{36}\text{Kr}$ and two neutrons. Other element produced in this reaction is:

(a) $^{137}_{52}\text{Te}$ (b) $^{144}_{55}\text{Cs}$ (c) $^{137}_{56}\text{Ba}$ (d) $^{144}_{56}\text{Ba}$

(VITEEE 2007)

[**Ans.** (d)]

[**Hint:** $^{235}_{92}\text{U} + ^{1}_{0}n \longrightarrow ^{90}_{36}\text{Kr} + ^{144}_{56}\text{Ba} + 2\,^{1}_{0}n$]

22. The product P of the nuclear reaction $^{235}_{92}\text{U} + ^{1}_{0}n \longrightarrow P + ^{92}_{36}\text{Kr} + 3(^{1}_{0}n)$ is :

(a) $^{141}_{56}\text{Sr}$ (b) $^{141}_{56}\text{La}$ (c) $^{141}_{56}\text{Ba}$ (d) $^{141}_{56}\text{Cs}$

[JEE (WB) 2008]

[**Ans.** (c)]

[**Hint:** Let symbol of element is $^{M}_{Z}P$.

$92 = Z + 36$

$\therefore \quad Z = 56$

$235 + 1 = M + 92 + 3$

$M = 141$

Thus, the element P will be $^{141}_{56}\text{Ba}$]

3.18 APPLICATIONS OF RADIOACTIVITY

(a) Use of γ-rays: γ-rays are used for disinfecting food grains and for preserving foodstuffs. Onions, potatoes, fruits and fish, etc., when irradiated with γ-rays, can be preserved for long periods. High yielding disease resistant varieties of wheat, rice, groundnut, jute, etc., can be developed by the application of nuclear radiations. The γ-radiations are used in the treatment of cancer. The γ-radiations emitted by cobalt-60 can burn cancerous cells. γ-radiations are used to sterilize medical instruments like syringes, blood transfusion sets, etc. These radiations make the rubber and plastics objects heat resistant.

(b) The age of the earth: The age of the earth has been estimated by uranium dating technique. The uranium ore (rock) which is found in nature is associated with non-radioactive lead which is believed to be the end product of radioactive disintegration of uranium. A sample of uranium rock is analysed for ^{238}U and ^{206}Pb contents. From this analysis, let the quantities in mole be $N = {}^{238}\text{U}$ mole, $N_0 = {}^{238}\text{U}$ mole + ^{206}Pb mole.

Applying disintegration equation,

$$\lambda t = 2.303 \log_{10} \frac{N_0}{N}$$

$$= 2.303 \log_{10} \frac{^{238}\text{U} + ^{206}\text{Pb}}{^{238}\text{U}}$$

$$= 2.303 \log_{10} \left[1 + \frac{^{206}\text{Pb}}{^{238}\text{U}}\right]$$

The value of 't' can be calculated by putting the value of λ which is equal to $\dfrac{0.693}{t_{1/2}}$.

So, $$t = \frac{2.303 \times t_{1/2}}{0.693} \log_{10}\left[1 + \frac{^{206}\text{Pb}}{^{238}\text{U}}\right]$$

Here 't' corresponds to the age of earth which has been found to be 4.5 billion years.

Example 27. *A sample of uranium mineral was found to contain ^{206}Pb and ^{238}U in the ratio of 0.008 : 1. Estimate the age of the mineral. (Half life of ^{238}U is 4.51×10^9 years)*

Solution: We know that, $t = \frac{2.303 t_{1/2}}{0.693} \log\left[1 + \frac{^{206}\text{Pb}}{^{238}\text{U}}\right]$

Given, $t_{1/2} = 4.51 \times 10^9$ years

Ratio by mass of $^{206}\text{Pb} : {}^{238}\text{U} = 0.008 : 1$

Ratio by moles of $^{206}\text{Pb} : {}^{238}\text{U} = \frac{0.008}{206} : \frac{1}{238} = 0.0092$

So, $t = \frac{2.303 \times 4.51 \times 10^9}{0.693} \log[1 + 0.0092]$

$= \frac{2.303 \times 4.51 \times 10^9}{0.693} \times 0.00397$

$= \frac{0.0412}{0.693} \times 10^9 = 0.05945 \times 10^9$ years

Hence, age of the mineral is 5.945×10^7 years.

(c) Radio carbon dating: By using the half life period of ^{14}C, it is possible to determine the age of various objects. In living material the ratio of ^{14}C to ^{12}C remains relatively constant. When a tissue in an animal or plant dies, ^{14}C decreases because the intake and utilization of ^{14}C do not occur. Therefore, in the dead tissue the ratio of ^{14}C to ^{12}C would decrease, depending on the age of the tissue. The age of the dead tissue is determined in the following way. A sample of dead tissue is burnt to carbon dioxide and the carbon dioxide is analysed for the ratio of ^{14}C to ^{12}C. From this data, the age of the dead tissue can be determined. Thus:

$$\lambda = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{t_{1/2} \text{ of } C^{14}} = \frac{2.303}{t} \log_{10}\left(\frac{N_0}{N}\right)$$

N_0 = Ratio of C^{14} / C^{12} in green plant or atmosphere

N = Ratio of C^{14} / C^{12} in wood

or

N_0 = Activity of green plant per unit mass

N = Activity of wood per unit mass

Although, the method is suitable to a variety of organic materials, accuracy depends on the half life to be used, variations in levels of atmospheric carbon-14 and contamination. (The half life radio carbon was redefined from 5570 ± 30 years to 5730 ± 40 years by IUPAC). The rapid disintegration of carbon-14 generally limits the dating period to approximately 50,000 years.

Example 28. *The amount of $^{14}_{6}C$ isotope in a piece of wood is found to be one-fifth of that present in a fresh piece of wood. Calculate the age of wood. (Half life of ^{14}C = 5577 years)*

Solution: We know that, $t = \frac{2.303 \times t_{1/2}}{0.693} \log\left(\frac{N_0}{N}\right)$

Given, $N = \frac{N_0}{5}$

So, $t = \frac{2.303 \times 5577}{0.693} \log 5$

or $t = \frac{2.303 \times 5577}{0.693} \times 0.6989 = 12953$ years

Example 29. *A piece of wood was found to have $^{14}C/^{12}C$ ratio 0.6 times that in a living plant. Calculate the period when the plant died. (Half life of ^{14}C = 5760 years)*

Solution: We know that, $t = \frac{2.303 \times t_{1/2}}{0.693} \log\left(\frac{N_0}{N}\right)$

So, $t = \frac{2.303 \times 5760}{0.693} \log\left(\frac{1}{0.6}\right)$

$= \frac{2.303 \times 5760}{0.693} \times 0.2201$

$= 4213$ years

(d) Potassium-Argon method: The decay of radioactive potassium isotope to argon is widely used for dating rocks. The geologists are able to date entire rock samples in this way, because potassium-40 is abundant in micas, feldspars and hornblendes. Leakage of Argon is however problem if the rock has been exposed to temperature above 125° C.

(e) Rubidium-Strontium method: This method of dating is used to date ancient igneous and metamorphic terrestrial rocks as well as lunar samples. It is based on disintegration by beta decay of ^{87}Rb to ^{87}Sr. This method is frequently used to check potassium-argon dates, because the strontium daughter element is not diffused by mild heating like argon.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

23. A wooden artifact sample gave activity of 32 β-particles per second while the freshly cut wood gave activity of 64 β-particles per second in G. M. counter. Calculate the age of the wooden artifact ($t_{1/2}$ of ^{14}C = 5760 yrs):

(a) 11520 yrs (b) 5760 yrs
(c) 2880 yrs (d) 1440 yrs

[Ans. (b)]

[Hint: $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{age}} \log_{10}\left(\frac{N_0}{N}\right)$

$\frac{0.693}{5760} = \frac{2.303}{t_{age}} \log_{10}\left(\frac{64}{32}\right)$

$t_{age} = 5760$ yrs]

24. The analysis of a rock shows that the relative number of ^{206}Pb and ^{238}U atoms is Pb/U = 0.25. If $t_{1/2}$ of ^{238}U is 4.5×10^9 yrs, then the age of the rock will be:

(a) $\frac{2.303}{0.693}(4.5 \times 10^9) \log\left(\frac{5}{4}\right)$

(b) $\frac{2.303}{0.693}(4.5\times 10^9)\log\left(\frac{1}{4}\right)$

(c) $\frac{2.303}{0.693}(4.5\times 10^9)\log(4)$

(d) $\frac{2.303}{0.693}(4.5\times 10^9)\log\left(\frac{4}{5}\right)$

[Ans. (a)]

[Hint: $\frac{\text{Pb}}{\text{U}} = 0.25;\quad \therefore\ 1+\frac{\text{Pb}}{\text{U}} = 1.25$

$$\frac{\text{U}+\text{Pb}}{\text{U}} = 1.25$$

$$\frac{N_0}{N} = 1.25 = \frac{5}{4}$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{4.5\times 10^9} = \frac{2.303}{t_{\text{age}}}\log\left(\frac{5}{4}\right)$$

$$t_{\text{age}} = \frac{2.303}{0.693}(4.5\times 10^9)\log\left(\frac{5}{4}\right)]$$

25. Assuming that about 200 MeV of energy is released per fission of $^{235}_{92}\text{U}$ nuclei, then the mass of ^{235}U consumed per day in a fission reactor of power 1 megawatt will be approximately:

(a) 10^{-2} g (b) 1 g (c) 100 g (d) 1000 g

[Ans. (b)]

[Hint: 1 MW = $10^6 \times 24 \times 60 \times 60$ J

$$\text{Number of fissions} = \frac{24\times 6\times 6\times 10^8}{200\times 10^6\times 1.6\times 10^{-19}} = 2.7\times 10^{21}$$

$$\text{Mass of uranium} = 2.7\times 10^{21}\times 235\times 1.66\times 10^{-24} \approx 1.05 \text{ g}]$$

26. What is the binding energy of the hydrogen nucleus?

(a) Zero (b) 13.6 eV

(c) More than 13.6 eV (d) Infinite

[Ans. (a)]

[Hint: Nucleus of hydrogen has only one proton; hence its binding energy will be zero.]

27. Which of the following is not the inverse square law force?

(a) Electric force (b) Gravitational force

(c) Nuclear force

(d) Magnetic force between two poles

[Ans. (c)]

[Hint: Nuclear forces are short range forces which do not obey inverse square law.]

28. Lead is the final product formed by a series of changes in which the rate determining stage is the radioactive decay of uranium-238. This radioactive decay is first order with half life of 4.5×10^9 years. What would be the age of a rock sample originally leadfree, in which the molar proportion of uranium to lead is now 1 : 3? [PET (Kerala) 2006]

(a) 1.5×10^9 years (b) 2.25×10^9 years

(c) 4.5×10^9 years (d) 9×10^9 years

(e) 13.5×10^9 years

[Ans. (d)]

[Hint: $\frac{0.693}{t_{1/2}\text{U}^{238}} = \frac{2.303}{t_{\text{age}}}\log\left(\frac{N_0}{N}\right)$

$$\frac{0.693}{4.5\times 10^9} = \frac{2.303}{t_{\text{age}}}\log_{10}\left(\frac{4}{1}\right)$$

$$t_{\text{age}} = 9\times 10^9 \text{ years}]$$

(f) Use of radioisotopes (tracers): Tracers have been used in the following fields:

(i) **In medicine:** Radioisotopes are used to diagnose many diseases. For example, arsenic-74 tracer is used to detect the presence of tumours; sodium-24 tracer is used to detect the presence of blood clots and iodine-131 tracer is used to study the activity of the thyroid gland. It should be noted that the radioactive isotopes used in medicine have very short half life periods.

^{90}Y : This isotope is used in the treatment of joint effusion and arthritis.

^{59}Fe : Used in the detection of anaemia.

^{32}P : This isotope is used in the treatment of polycythaemia, thrombocythaemia, skeletal metastasis, prostate SR and breast SR.

Nuclear Medicine Scan: It is an advanced nuclear technology used in diagnosis of diseases. **Magnetic Resonance Imaging** (MRI), a diagnostic medical imaging technique utilizes the principle of nuclear magnetic resonance. The first images using magnetic resonance were published in early 1970s, and medical applications have accelerated in the world during the decade of 1983 to 1993. MRI is now a most versatile, powerful and sensitive diagnostic imaging modality available. Its medical importance can be summarised briefly as having the ability to non-invasively generate thin section, functional images of any part of the body at any angle and direction in a relatively short period of time. MRI also visualizes the heart with exquisite anatomical detail at any angle and direction.

The principle of MRI is applicable in human body because we are all filled with small biological magnets, the most abundant and responsive of which is the nucleus of hydrogen atom, the proton.

Computerized Axial Tomography: Computerized Axial Tomography (CT or CAT), non-invasive diagnostic technique uses a type of X-ray device that provides a clear view of soft internal organ tissues in the body. CT is used to diagnose various conditions, in particular cancer. A CT scan is the computer analysis of a sharply limited, thin X-ray beam passed circumferentially through an area of the body, producing a cross-sectional image, or slice.

The modern CT scanner comprises five major parts. A high-speed X-ray tube cooled by oil, air and water forms the X-ray source. Its X-ray detector, normally a bank of about 1,000 solid state-crystal microprocessors coated with caesium iodide, receives the attenuated X-ray signal as it passes through the various tissues and bones of the patient being examined. The signal is electronically converted to binary data, which is read by the computer—the heart of the CT imaging system. The CT has a gantry, a framework that is mounted in such a way that it surrounds the patient in a vertical plane, and contains a rotating sub-frame onto which the X-ray source and detectors are mounted. A patient table (or couch) is positioned perpendicular and axial to the gantry so that it is able to travel along that axis.

Topographic images are produced by using an X-ray source and a detector moving in a coupled way relative to the patient. In CT a thin fan beam of radiation rotates in a circular or spiral motion around the patient. Thousands of projected X-ray signals are reconstructed by computer algorithms to produce digital CT images, displayed by a high-resolution monitor. In this way the whole body can be imaged from head to toe.

Radiation Dosage in the Radiotherapy of Cancer

Radiations and the particles emitted by radioactive nuclei are harmful for living organisms. These radiations cause genetic disorders by affecting DNA.

Effect of biological radiations can be measured in terms of the unit called RAD.

RAD = Radiation absorbed dose

1 RAD = The radiation which deposits 1×10^{-2} J of energy per kilogram of tissue.

In order to measure biological destruction by radiation, an other unit REM was introduced.

REM = RAD × RBE

RBE = Relative biological effectiveness

RBE for α-particle = 10 unit

RBE for β and γ radiation = 1 unit

RBE for neutron = 5 unit

(ii) In agriculture: The use of radioactive phosphorus ^{32}P in fertilizers has revealed how phosphorus is absorbed by plants. This study has led to an improvement in the preparation of fertilizers. ^{14}C is used to study the kinetics of photosynthesis.

(iii) In industry: Radioisotopes are used in industry to detect the leakage in underground oil pipelines, gas pipelines and water pipes. Radioactive isotopes are used to measure the thickness of materials, to test the wear and tear inside a car engine and the effectiveness of various lubricants. Radioactive carbon has been used as a tracer in studying mechanisms involved in many reactions of industrial importance such as alkylation, polymerisation, catalytic synthesis, etc.

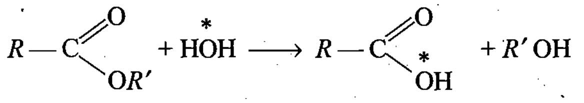
(iv) Analytical studies: Several analytical procedures can be used employing radioisotopes as tracers.

1. Adsorption and occlusion studies: A small amount of radioactive isotope is mixed with an inactive substance and the activity is studied before and after adsorption. Fall in activity gives the amount of substance adsorbed.

2. Solubility of sparingly soluble salts: The solubility of lead sulphate in water may be estimated by mixing a known amount of radioactive lead with ordinary lead. This is dissolved in nitric acid and precipitated as lead sulphate by adding sulphuric acid. Insoluble lead sulphate is filtered and the activity of the water is measured. From this, the amount of $PbSO_4$ still present in water can be estimated.

3. Ion-exchange technique: Ion exchange process of separation is readily followed by measuring activity of successive fractions eluted from the column.

4. Reaction mechanism: By labelling oxygen of the water, mechanism of ester hydrolysis has been studied.



5. Study of efficiency of analytical separations: The efficiency of analytical procedures may be measured by adding a known amount of radioisotope to the sample before analysis begins. After the completion, the activity is again determined. The comparison of activity tells about the efficiency of separation.

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *One mole of A present in a closed vessel undergoes decay as:*

$${}^{m}_{Z}A \longrightarrow {}^{m-8}_{Z-4}B + 2({}^{4}_{2}He)$$

What will be the volume of helium gas collected at STP after 20 *days* ($t_{1/2}$ *of* $A = 10\,days$)?

Solution: We know that,

$$N = N_0\left(\frac{1}{2}\right)^n \text{ where, } N = \text{remaining mole of } A$$

$$N = 1\left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

Number of decayed moles $= 1 - \frac{1}{4} = \frac{3}{4}$

Number of moles of helium formed

$= 2 \times$ number of decayed moles of $A = 2 \times \frac{3}{4} = \frac{3}{2}$

Volume of helium at STP $= \frac{3}{2} \times 22.4 = 33.6$ litre

Example 2. ^{131}I *has half life period* 13.3 *hour. After* 79.8 *hour, what fraction of* ^{131}I *will remain?* [CBSE (PMT) 2005]

Solution: $N = N_0\left(\frac{1}{2}\right)^n$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^6 = \frac{1}{64}$$

Example 3. *A sample of* $^{14}CO_2$ *was to be mixed with ordinary* CO_2 *for a biological tracer experiment. In order that* 10^3 cm^3 *of the diluted gas at NTP should have* 10^4 *dis/min, how many* μCi *of radiocarbon-*14 *are needed to prepare* 60 *L of the diluted gas?*

Solution: 10 cm^3 of the diluted gas at NTP

$$= 10^4 \text{ dis/min} = \frac{10^4}{60} \text{ dps}$$

$\therefore$ 60 L (60,000 cm^3) of the dilute gas at NTP

$$= \frac{10^4 \times 60{,}000}{60 \times 10} \text{ dps}$$

Thus, no. of μCi of $^{14}CO_2$ needed

$$= \frac{10^4 \times 60{,}000}{60 \times 10 \times 3.7 \times 10^4} \quad (1\,\mu\text{Ci} = 3.7 \times 10^4 \text{ dps})$$

$$= 27.03\,\mu\text{Ci}$$

Example 4. *A radioactive nuclide is produced at a constant rate of 'α' per second. Its decay constant is λ. If N_0 be the number of nuclei at time $t = 0$, then what will be the maximum number of possible nuclei?*

(a) $\frac{\alpha}{\lambda}$ (b) $N_0 + \frac{\alpha}{\lambda}$ (c) N_0 (d) $\frac{\lambda}{\alpha} + N_0$

Solution: Maximum number of nuclei will be present when

Rate of decay = Rate of formation

$$\lambda N = \alpha$$

or

$$N = \frac{\alpha}{\lambda}$$

Example 5. *The half life of ^{212}Pb is 10.6 hour. It undergoes decay to its daughter (unstable) element ^{212}Bi of half life 60.5 minute. Calculate the time at which the daughter element will have maximum activity.*

Solution: $\lambda_{Pb} = \frac{0.693}{10.6 \times 60} = 1.0896 \times 10^{-3} \text{ min}^{-1}$

$$\lambda_{Bi} = \frac{0.693}{60.5} = 11.45 \times 10^{-3} \text{ min}^{-1}$$

$$t_{max} = \frac{2.303}{\lambda_{Bi} - \lambda_{Pb}} - \log \frac{\lambda_{Bi}}{\lambda_{Pb}}$$

$$= \frac{2.303}{(11.45 \times 10^{-3} - 1.0896 \times 10^{-3})} \times \log \frac{11.45 \times 10^{-3}}{1.0896 \times 10^{-3}}$$

$$= 227.1 \text{ min}$$

Example 6. *A radioactive isotope is being produced at a constant rate x. Half life of the radioactive substance is 'y'. After sometime, the number of radioactive nuclei becomes constant, the value of this constant is ......*

Solution: At the stage of radioactive equilibrium,

Rate of formation of nuclide = Rate of decay of nuclide

$$x = \lambda N$$

$$N = \frac{x}{\lambda} = \frac{x}{(\ln 2)/y} = \frac{xy}{\ln 2}$$

Example 7. *$^{238}_{92}U$ by successive radioactive decay changes to $^{206}_{82}Pb$. A sample of uranium ore was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb. Assuming that all ^{206}Pb has accumulated due to decay of ^{238}U, find the age of the ore (half life of $^{238}U = 4.5 \times 10^9$ yrs).*

Solution: Number of moles of $^{238}U = \frac{1}{238}$

Number of moles of $^{206}Pb = \frac{0.1}{206}$

Applying the relationship,

$$t = \frac{2.303}{\lambda} \log \left[1 + \frac{^{206}Pb}{^{238}U}\right]$$

$$= \frac{2.303}{0.693} \times 4.5 \times 10^9 \log \left[1 + \frac{\frac{0.1}{206}}{\frac{1}{238}}\right]$$

$$= 7.098 \times 10^8 \text{ years}$$

Example 8. *Calculate the mass of C^{14} (half life = 5720 years) atoms which give 3.7×10^7 disintegrations per second.*

Solution: Let the mass of ^{14}C atoms be m g.

Number of atoms in m g of $^{14}C = \frac{m}{14} \times 6.02 \times 10^{23}$

$$\lambda = \frac{0.693}{\text{half life}} = \frac{0.693}{5720 \times 365 \times 24 \times 60 \times 60} = 3.84 \times 10^{-12} \text{ sec}^{-1}$$

We know that, $-\frac{dN}{dt} = \lambda \cdot N$

i.e., Rate of disintegration = λ × no. of atoms

$$3.7 \times 10^7 = \frac{0.693}{5720 \times 365 \times 24 \times 60 \times 60} \times \frac{m}{14} \times 6.02 \times 10^{23}$$

$$= \frac{3.84 \times 10^{-12} \times m \times 6.02 \times 10^{23}}{14}$$

So, $m = 2.24 \times 10^{-4}$ g

Example 9. *Prove that time required for 99.9% decay of a radioactive species is almost ten times its half life period.*

Solution: We know that, $t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$

$$N_0 = 100, \quad N = (100 - 99.9) = 0.1$$

So, Time required for 99.9% decay, $t = \frac{2.303}{\lambda} \log \frac{100}{0.1}$

$$= \frac{2.303}{\lambda} \times 3$$

$$\text{Half life period} = \frac{0.693}{\lambda}$$

So, $\frac{\text{Time required for 99.9\% decay}}{\text{Half life period}} = \frac{2.303 \times 3}{\lambda} \times \frac{\lambda}{0.693}$

$$\approx 10$$

Example 10. *Half life of a radioactive substance A is two times the half life of another radioactive substance B. Initially the number of nuclei of A and B are N_A and N_B respectively. After three half lives of 'A', number of nuclei of both become equal. The ratio of $\frac{N_A}{N_B}$ will be:*

(*a*) $\frac{1}{2}$ (*b*) $\frac{1}{8}$ (*c*) $\frac{1}{3}$ (*d*) $\frac{1}{6}$

Solution: We know that, the amount remaining after *n* half lives can be calculated as:

$$N = N_0\left(\frac{1}{2}\right)^n$$

$$\text{Remaining amount of } A = N_A\left(\frac{1}{2}\right)^3$$

$$\text{Remaining amount of } B = N_B\left(\frac{1}{2}\right)^6$$

$$N_A\left(\frac{1}{2}\right)^3 = N_B\left(\frac{1}{2}\right)^6$$

$$\frac{N_A}{N_B} = \frac{8}{64} = \frac{1}{8}$$

Example 11. *1.0 g of $^{198}_{79}Au$ ($t_{1/2}$ = 65 hours) decays by β-emission to produce mercury.*

(*a*) *Write the nuclear reaction for the process.*

(*b*) *How much mercury will be present after 260 hours?*

Solution: (a) $^{198}_{79}\text{Au} \longrightarrow {}^{198}_{80}\text{Hg} + {}^{0}_{-1}e$

(b) $\text{No. of half lives in 260 hours} = \frac{260}{65} = 4$

$$\text{Amount of gold left after 4 half lives} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}\text{g}$$

$$\text{Amount of gold disintegrated} = 1 - \frac{1}{16} = \frac{15}{16}\text{ g}$$

$$\text{Amount of mercury formed} = \frac{15}{16} = 0.9375\text{ g}$$

Example 12. *Calculate the probability (P) of survival of a radioactive nucleus for one mean life.*

Solution: $\text{Probability for survival} = \frac{N}{N_0} = e^{-\lambda t}$

$$t = \text{mean life} = \frac{1}{\lambda}$$

$$\therefore \quad \text{Probability} = e^{-\lambda \times 1/\lambda} = \frac{1}{e}$$

Example 13. *1 milligram radium has 2.68×10^{18} atoms. Its half life period is 1620 years. How many radium atoms will disintegrate from 1 milligram of pure radium in 3240 years?*

Solution: $\text{No. of half lives in 3240 years} = \frac{3240}{1620} = 2$

$$\text{Amount of radium left after two half lives} = 1 \times \left(\frac{1}{2}\right)^2$$

$$= 0.25\text{ mg}$$

$$\text{Amount of radium disintegrated} = (1 - 0.25) = 0.75\text{ mg}$$

$$\text{No. of atoms which have disintegrated} = 0.75 \times 2.68 \times 10^{18}$$

$$= 2.01 \times 10^{18}$$

Example 14. *A certain radioisotope $^{A}_{Z}X$ (Half life = 10 days) decays to $^{A-4}_{Z-2}Y$. If 1 g atom of $^{A}_{Z}X$ is kept in sealed vessel, how much helium will accumulate in 20 days?*

Solution: $^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}\text{He}$

In two half lives, $\frac{3}{4}$ of the isotope $^{A}_{Z}X$ has disintegrated, *i.e.*, $\frac{3}{4}$ g atom of helium has been formed from $\frac{3}{4}$ g atom of $^{A}_{Z}X$.

Volume of 1 g atom of helium = 22400 mL

$$\text{So, Volume of } \frac{3}{4} \text{ g atom of helium} = \frac{3}{4} \times 22400\text{ mL}$$

$$= 16800\text{ mL}$$

Example 15. *Binding energy per nucleon of $^{2}_{1}H$ and $^{4}_{2}He$ are 1.1 MeV and 7 MeV respectively. Calculate the amount of energy released in the following process:*

$$^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He$$

Solution: Amount of energy released

= Σ Binding energy of products

− Σ Binding energy of reactants

= [4 × 7] − [4 × 1.1]

= 23.6 MeV

Example 16. *Calculate the energy associated with the following nuclear reaction:*

$$\underset{26.9815\ amu}{^{27}_{13}Al} + \underset{2.0141\ amu}{^{2}_{1}H} \longrightarrow \underset{24.9858\ amu}{^{25}_{12}Mg} + \underset{4.0026\ amu}{^{4}_{2}He}$$

Solution: Mass defect = (26.9815 + 2.0141) − (24.9858 + 4.0026)

= 0.0072 amu

Energy of the reaction = 0.0072 × 931 MeV

= 6.70 MeV

Example 17. *A radioactive isotope $_{Z}A^{m}$ ($t_{1/2}$ = 10 days) decays to give $_{Z-6}B^{m-12}$ stable atom alongwith α-particles. If m g of 'A' are taken and kept in a sealed tube, how much 'He' will accumulate in 20 days at STP?*

Solution: $_{Z}A^{m} \longrightarrow {}_{Z-6}B^{m-12} + 3[{}_{2}\text{He}^{4}]$

$$\text{Mole of } A = \frac{m}{m} = 1$$

Number of half lives = 20/10 = 2

$$N = N_0\left(\frac{1}{2}\right)^n$$

$$=1\left(\frac{1}{2}\right)^2=\frac{1}{4}$$

$$\text{Decayed moles} = 1-1/4=3/4$$

$$\text{Moles of 'He' formed} = 3\times 3/4 = 9/4$$

$$\text{Volume of 'He' at STP} = 22.4\times\frac{9}{4}$$

$$= 50.4 \text{ litre}$$

Example 18. *A sample of pitchblende is found to contain 50% uranium and 2.425% of lead. Of this lead only 93% was Pb^{206} isotope. If the disintegration constant is $1.52\times10^{-10}\ yr^{-1}$, how old could be the pitchblende deposits?*

Solution: $\text{Moles of } U^{238} = \frac{50}{100\times238} = 2.1\times10^{-3}$

$$\text{Moles of } Pb^{206} = \frac{2.425}{100}\times\frac{93}{100\times206} = 0.109\times10^{-3}$$

$$N_0=(x+y)=2.1\times10^{-3}+0.109\times10^{-3}=2.209\times10^{-3}$$

$$N=x=2.1\times10^{-3}$$

$$\lambda=\frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$$

$$1.52\times10^{-10}=\frac{2.303}{t}\log\frac{2.209\times10^{-3}}{2.1\times10^{-3}}$$

$$t=3.3\times10^8 \text{ years}$$

Example 19. *On analysis, a sample of uranium ore was found to contain 0.277 g of $_{82}Pb^{206}$ and 1.667 g of $_{92}U^{238}$. The half life period of U^{238} is 4.51×10^9 yrs. If all the lead were assumed to have come from decay of $_{92}U^{238}$, what is the age of the earth?*

Solution: $\text{Moles of } U^{238}=\frac{1.667}{238}$

$$\text{Moles of } Pb^{206}=\frac{0.277}{206}$$

$$N_0=\frac{1.667}{238}+\frac{0.277}{206}$$

and $N=\frac{1.667}{238}$

$$t=\frac{2.303}{\lambda}\log\frac{N_0}{N}$$

$$=\frac{2.303\times4.51\times10^9}{0.693}\log_{10}\frac{\frac{1.667}{238}+\frac{0.277}{206}}{\frac{1.667}{238}}$$

$$=1.143\times10^9 \text{ years}$$

Example 20. *$_{19}K^{40}$ consists of 0.012% potassium in nature. The human body contains 0.35% potassium by weight. Calculate the total radioactivity resulting from $_{19}K^{40}$ decay in a 75 kg human body. Half life of $_{19}K^{40}$ is 1.3×10^9 years.*

Solution:

$$\text{Weight of radioactive potassium}=\frac{75000\times0.012}{100}\times\frac{0.35}{100}$$

$$=0.0315 \text{ g}$$

$$\text{Activity}=\frac{0.693}{t_{1/2}}\times\frac{\text{Weight}}{\text{Atomic weight}}\times\text{Avogadro's number}$$

$$\text{Activity}=\frac{0.693}{1.3\times10^9\times365\times24\times60}\times\frac{0.0315}{40}\times6.023\times10^{23}$$

$$=4.81\times10^5 \text{ dpm}$$

Example 21. *The sun radiates energy at the rate of $4\times10^{26}\ \text{J sec}^{-1}$. If the energy of fusion process is 27 MeV, calculate the amount of hydrogen that would be consumed per day for the given process.*

$$4\,{}_1^1H\longrightarrow{}_2^4He+2\,{}_1^0e.$$

Solution: $27\text{ MeV}=27\times10^6\times1.6\times10^{-19}$

$$=43.2\times10^{-13}\text{ J}$$

Energy radiated by the sun per day

$$=4\times10^{26}\times3600\times24\text{ J day}^{-1}$$

$$=34.56\times10^{30}\text{ J day}^{-1}$$

43.2×10^{-13} J of energy is obtained from

$$=4\text{ amu of H}$$

$$=4\times1.66\times10^{-24}\text{ g of H}$$

34.56×10^{30} J of energy is obtained from

$$=\frac{4\times1.66\times10^{-24}}{43.2\times10^{-13}}\times34.56\times10^{30}$$

$$=5.31\times10^{19}\text{ g}$$

Example 22. *A radioactive isotope X with half life of 1.37×10^9 years decays to Y, which is stable. A sample of rock from moon was found to contain both the elements X and Y in the ratio 1 : 7. What is the age of the rock?*

Solution: We know that,

$$\frac{0.693}{t_{1/2}}=\frac{2.303}{t_{\text{age}}}\log\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{1.37\times10^9}=\frac{2.303}{t_{\text{age}}}\log_{10}\left(\frac{1+7}{1}\right)$$

$$\therefore\quad t_{\text{age}}=4.11\times10^9\text{ years}$$

Example 23. *A sample of radioactive substance shows an intensity of 2.3 millicurie at a time 't' and an intensity of 1.62 millicurie, 600 seconds later. What is the half life period of the radioactive material?*

Solution: $\lambda=\frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{600}\log\left(\frac{2.3}{1.62}\right)$$

$$\therefore \quad t_{1/2} = 1187 \text{ seconds}$$

Example 24. *What mass of* ^{226}Ra*, whose* $t_{1/2} = 1620\, yrs$ *will give the activity of* 1 *millicurie?*

Solution:

$$\text{Activity} = \frac{0.693}{t_{1/2}} \times \frac{w}{\text{At. wt.}} \times 6.023 \times 10^{23}$$

$$3.7 \times 10^7 = \frac{0.693}{1620 \times 365 \times 24 \times 3600} \times \frac{w}{226} \times 6.023 \times 10^{23}$$

so $w = 10^{-3}$ g

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Radius of nucleus is calculated as:

$$R = R_0 A^{1/3},$$

where, $R_0 = 1.1 \times 10^{-15}$ m, A = Mass number of nucleus

Area of cross-section of a nucleus is expressed in barns ($1 \text{ barn} = 10^{-24} \text{ cm}^2$).

2. Nucleus density $\rho = \frac{3 \times \text{Mass}}{4\pi R_0^3}$

Density of all nuclei is constant, nuclear density is very large ($\approx 10^{17}$ kg/m^3) compared to atomic density ($\approx 10^3$ kg/m^3).

3. $1 \text{ amu} = 1.66 \times 10^{-27}$ kg

In terms of energy, $1 \text{ amu} \approx 931.5 \text{ MeV}$

4. Rate of radioactive decay is given as:

$$\text{Rate} = \lambda \times \frac{\text{Mass}}{\text{Atomic mass}} \times 6.023 \times 10^{23}$$
$$= \frac{0.693}{t_{1/2}} \times \frac{w}{\text{At. wt.}} \times 6.023 \times 10^{23}$$

(i) Radioactivity is the phenomenon of spontaneous emission of certain radiations. It was discovered by Henri Becquerel in 1895.

(ii) Marie Curie and her husband Piere Curie isolated two radioactive elements **polonium** and **radium.** Radium is 2 million times more reactive than uranium, it is the most radioactive element.

(iii) Radium and polonium were isolated from pitchblende (U_3O_8).

(iv) Francium is a liquid radioactive element in natural state.

(v) Radon is a gaseous radioactive element in natural state.

(vi) $^{238}_{92}U$ is the heaviest known natural element and it is radioactive.

(vii) α-particles evolved from radioactive elements possess energy up to about 10 MeV. They can penetrate an aluminium sheet of 0.02 cm thickness.

(viii) β-rays can penetrate an aluminium sheet up to 0.2 cm thickness.

(ix) γ-rays are high energy electromagnetic radiations of short wavelength of the order of 10 pm. These are highly penetrating rays; they can penetrate up to 100 cm thick aluminium sheet.

(x) After γ-decay, the daughter nuclide is the nuclear isomer of parent nuclide which differs in half life.

(xi) Potassium uranyl sulphate $K(UO_2)(SO_4)_2$ was the first compound found to be radioactive.

(xii) Tritium ^3_1H is the lightest radioactive element.

5. Units of rate of decay:

1 curie (Ci) = 3.7×10^{10} dis sec^{-1}

1 millicurie (mCi) = 3.7×10^7 dis sec^{-1}

1 microcurie (μCi) = 3.7×10^4 dis sec^{-1}

1 rutherford (Rd) = 10^6 dis sec^{-1}

1 millicurie (mCi) = 37 rutherford

1 becquerel (Bq) = 1 dis sec^{-1}

6. Kinetic equation of radioactive decay:

$$N = N_0 e^{-\lambda t} \qquad \text{(Exponential form)}$$

$$\lambda = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right) \qquad \text{(logarithmic form)}$$

λ = Decay constant

N_0 = Initial amount of radioactive element

N = Amount remaining after time 't'

7. Half life $t_{1/2} = \frac{0.693}{\lambda}$

$$\text{Average life } \tau = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693}$$

$$\tau = 1.44 \times t_{1/2}$$

8. Amount remaining after 'n' half lives can be calculated as:

$$N = N_0\left(\frac{1}{2}\right)^n$$

$$n = \frac{\text{Total time}}{\text{Half life}}$$

(i) A radioactive element undergoes 50% decay in one half life.

(ii) The time in which 63.2% radioactive element undergoes decay is called average life τ.

(iii) The radioactive element undergoes 99.9% decay in 10 times of half life.

(iv) An element undergoes 75% decay in twice of the half life.

(v) Total life span of a radioactive element is infinite.

9. Some radioactive elements undergo α and β-decay in parallel path.

$$\begin{tikzcd} & {}^{223}_{87}\mathrm{Fr} + {}^{4}_{2}\mathrm{He} \\ {}^{227}_{89}\mathrm{Ac} \arrow[ur, "K_1"] \arrow[dr, "K_2"'] & \\ & {}^{227}_{90}\mathrm{Th} + {}^{0}_{-1}e \end{tikzcd}$$

Overall decay constant $K = K_1 + K_2$

Fractional yield of Fr $= \dfrac{K_1}{K}$

Fractional yield of Th $= \dfrac{K_2}{K}$

10. At equilibrium,

$$A \longrightarrow B \longrightarrow C \ldots$$

$$\frac{\text{Amount of } `A'}{\text{Amount of } `B'} = \frac{\lambda_A}{\lambda_B} = \frac{t_{1/2}B}{t_{1/2}A}$$

11. If an element undergoes simultaneous α and β-decay, then

$$\lambda = \lambda_\alpha + \lambda_\beta; \quad \tau = \frac{\tau_\alpha \tau_\beta}{\tau_\alpha + \tau_\beta}$$

12. α-particles and γ-rays have line spectra, but β-particles have a continuous spectrum.

13. **Geiger-Muller counter** is used for detecting α and β-particles, **cloud chamber** is used for detecting radioactive radiations and for determining their **paths, range** and **energy.** In **scintillation counter,** the particles of radiations are detected by the flashes of light produced in the scintillator.

14. In every nuclear reaction representing transformation of one nucleus to other, the conservation of charge number, nucleons, energy and linear momentum is followed.

15. α-emission takes place when n/p ratio is lower than required for nuclear stability.

$$4\,{}^{1}_{1}\mathrm{H} \longrightarrow {}^{4}_{2}\mathrm{He} + 2[{}^{0}_{+1}e] + \text{energy}$$

α-particle emission shifts the daughter element two positions left in the periodic table.

$${}^{M}_{Z}A - {}^{4}_{2}\mathrm{He} \longrightarrow {}^{M-4}_{Z-2}B$$

(Here, A and B are **isodiapheres** to each other.)

16. β-emission takes place when n/p ratio is higher than the required value for nuclear stability.

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}\mathrm{H} + {}^{0}_{-1}e + \text{antineutrino} + \text{energy}$$

Emission of β-particles increases the atomic number by one hence, the daughter element occupies one position right to the parent element.

$${}^{M}_{Z}A - ({}^{0}_{-1}e) \longrightarrow {}_{Z+1}^{M}B$$

Here, A and B are **isobars;** thus β-emission is **isobaric** transformation.

17. In artificial radioactive elements, **positrons** are evolved when n/p ratio is lower than the required value for nuclear stability.

$${}^{1}_{1}\mathrm{H} \longrightarrow {}^{1}_{0}n + {}^{0}_{+1}e + \text{neutrino} + \text{energy}$$

Positron emission and K-electron capture are similar because both processes lower the number of proton by one unit.

18.
$${}^{M_1}_{Z_1}A \xrightarrow{(x\alpha,\, y\beta)} {}^{M_2}_{Z_2}B$$

Number of α-particles 'x' $= \dfrac{M_1 - M_2}{4}$ ... (i)

Number of β-particles can be calculated using the following relation:

$$Z_1 - 2x + y = Z_2 \qquad \text{... (ii)}$$

19. There are three natural and one artificial decay series:

$${}^{238}_{92}\mathrm{U} \xrightarrow[(8\alpha,\, 6\beta)]{\text{Uranium series } (4n+2)} {}^{206}_{82}\mathrm{Pb}$$

$${}^{232}_{90}\mathrm{Th} \xrightarrow[(6\alpha,\, 4\beta)]{\text{Thorium series } (4n)} {}^{208}_{82}\mathrm{Pb}$$

$${}^{235}_{92}\mathrm{U} \xrightarrow[(7\alpha,\, 4\beta)]{\text{Actinium series } (4n+3)} {}^{207}_{82}\mathrm{Pb}$$

Artificial series is also called neptunium series:

$${}^{237}_{93}\mathrm{Np} \xrightarrow[(7\alpha,\, 4\beta)]{(4n+1)} {}^{209}_{83}\mathrm{Bi}$$

20. If both parent and daughter elements belong to actinide series (89–103) then they will belong to same group, *i.e.*, third group.

$$\underset{\text{3rd group}}{{}^{238}_{92}\mathrm{U}} - {}^{4}_{2}\mathrm{He} \longrightarrow \underset{\text{3rd group}}{{}^{234}_{90}\mathrm{Th}}$$

21.
$$\xrightarrow{\alpha < \beta < \gamma} \text{Increasing penetrating power}$$

$$\xrightarrow{\alpha > \beta > \gamma} \text{Decreasing ionising power}$$

$$\xrightarrow{\alpha > \beta > \gamma} \text{Decreasing luminosity on ZnS screen}$$

22. Emission of one 'α' and two 'β' particles form an isotope of the parent element :

$${}^{M}_{Z}A - {}^{4}_{2}\mathrm{He} - 2[{}^{0}_{-1}e] \longrightarrow {}^{M-4}_{Z}A$$

23. There are only 81 stable elements having one or more non-radioactive isotopes.

24. No stable isotope exists for the elements above ${}^{209}_{83}\mathrm{Bi}$. Thus, bismuth is the heaviest stable element.

25. Two elements earlier than bismuth (Tc and Pm) are radioactive.

26.

Isotope	Use
$^{60}\mathrm{Co}$	Cancerous tumour detection and treatment.
$^{131}\mathrm{I}$	Detection and treatment of thyroid disorders.
$^{59}\mathrm{Fe}$	Anaemia.
$^{32}\mathrm{P}$	Leucaemia and agriculture research.
$^{24}\mathrm{Na}$	Location of blood clots and circulatory disorders.
$^{74}\mathrm{As}$	Detection of presence of tumours.
$^{90}\mathrm{Y}$	Treatment of joint effusion and arthritis.

^{18}O	Used in the study of mechanism of photosynthesis.
Radioactive technetium	Brain scan.

Note: Radioactive isotopes of carbon, chlorine and nitrogen are also used in the study of various reactions.

27. **Radiocarbon dating:** This method is used to determine age of wood.

$$\lambda = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{t_{1/2}\ {}^{14}C} = \frac{2.303}{t_{age}}\log_{10}\left(\frac{N_0}{N}\right)$$

$N_0 = {}^{14}C/{}^{12}C$ in freshly cut wood or in the atmosphere or activity of freshly cut wood.

$N = {}^{14}C/{}^{12}C$ in the given sample of wood or activity of given sample of wood.

28. **Uranium dating or rock dating:** It is used to calculate the age of a sample of rock and mineral, *i.e.*, before how many years it was separated from the fire ball of earth.

$$\lambda = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{t_{1/2}\ {}^{238}U} = \frac{2.303}{t_{age}}\log_{10}\left(\frac{N_0}{N}\right)$$

$$N_0 = \left(\frac{W}{238} + \frac{w}{206}\right)$$

$$N = \frac{W}{238}$$

where, W = amount of uranium in the sample
w = amount of ^{206}Pb in the sample

29. The force which binds the nucleons together in the nucleus is called nuclear force. These forces are short range forces operating over very small distances (1 fermi, 10^{-15} m). Nuclear forces are 10^{21} times stronger than electrostatic forces.

30. Hideki Yukawa of Japan discovered **mesons** in 1935. Protons and neutrons are held together by their fast mutual exchange.

$${}^1_1H + {}^{0}_{-1}\pi \longrightarrow {}^1_0n$$

$${}^1_0n + {}^{0}_{+1}\pi \longrightarrow {}^1_1H$$

$${}^1_1H + {}^0_0\pi \longrightarrow {}^1_1H$$

$${}^1_0n + {}^0_0\mu \longrightarrow {}^1_0n$$

31. **Artificial nuclear transmutation:** Conversion of one element to other by bombardment of a stable element with high speed subatomic particles. The first artificial transmutation was achieved by Rutherford in 1915 when he bombarded ${}^{14}_{7}N$ with α-particles emitted by ${}^{214}_{84}Po$.

$${}^{14}_{7}N + {}^4_2He \longrightarrow {}^{17}_{8}O + {}^1_1H$$

$${}^{27}_{13}Al + {}^1_0n \longrightarrow {}^{27}_{12}Mg + {}^1_1H$$

The nucleus bombarded is called **target;** the particles used for bombarding are called **projectiles** and the particles emitted are called **subsidiary particles.**

32. **Particle accelerator:** Various particle accelerators are used to give projectiles like protons, deuterons, α-particles and other cationic projectiles having sufficiently high kinetic energy to overcome the electrostatic repulsions of the target nuclei. Commonly used particle accelerators are linear accelerators, cyclotron and synchrotron. Synchrotron is used as proton accelerator.

33. Reactions of nuclear transformation are represented as:

$${}^9_4Be + {}^4_2He \longrightarrow {}^{12}_{6}C + {}^1_0n \quad \text{or} \quad {}^9_4Be\,(\alpha n)\,{}^{12}_{6}C$$

$${}^{23}_{11}Na + {}^1_1H \longrightarrow {}^{23}_{12}Mg + {}^1_0n \quad \text{or} \quad {}^{23}_{11}Na\,(pn)\,{}^{23}_{12}Mg$$

$${}^{27}_{13}Al + {}^1_0n \longrightarrow {}^{24}_{11}Na + {}^4_2He \quad \text{or} \quad {}^{27}_{13}Al\,(n\alpha)\,{}^{24}_{11}Na$$

34. **Artificial radioactivity** was first studied by Irene Curie. In this process, a stable nucleus is converted to radioactive isotope on bombardment of suitable particle. Radioactive isotope produced undergoes artificial decay.

$$\underset{\text{Stable}}{{}^{27}_{13}Al} + {}^4_2He \longrightarrow \underset{\text{Unstable}}{{}^{30}_{15}P} + {}^1_0n$$

$${}^{30}_{15}P \longrightarrow {}^{30}_{14}Si + {}^{0}_{+1}e \quad (t_{1/2} = 2.55 \text{ min})$$

35. **Nuclear fission** is the process in which a heavy nucleus breaks up into two smaller nuclei on bombardment with neutrons. Energy is released in the process of fission along with freshly prepared neutrons.

$${}^{235}_{92}U + {}^1_0n \longrightarrow {}^{236}_{92}U \begin{array}{l} \nearrow {}^{140}_{56}Ba + {}^{93}_{36}Kr + 3\,{}^1_0n \\ \longrightarrow {}^{144}_{54}Xe + {}^{90}_{38}Sr + 2\,{}^1_0n \\ \searrow {}^{144}_{55}Cs + {}^{90}_{37}Rb + 2\,{}^1_0n \end{array}$$

Mass defect of the reaction is converted to huge amount of energy.

Δm (Mass defect) = Σ Masses of reactants – Σ Masses of products

Energy released = Δmc^2

If mass defect is 1 amu then 931.5 MeV energy is released.

36. **Critical mass:** It is the minimum mass of fissionable material required that will lead to a self-sustaining chain fission reaction. For ${}^{235}_{92}U$, the critical mass is between 1 to 100 kg.

37. The material which directly undergoes fission is termed as fissile material such as ^{235}U, ^{239}Pu and ^{233}U. The material which can be converted to fissile material is termed fertile material such as ${}^{238}_{92}U$ and ${}^{232}_{90}Th$.

38. Breeder reactors not only involve the fission of ${}^{235}_{92}U$ but also converts fertile material into fissile material, *e.g.*, ^{238}U is converted to ^{239}Pu:

$${}^{238}_{92}U + {}^1_0n \longrightarrow {}^{239}_{92}U \xrightarrow{{}^{0}_{-1}e} {}^{239}_{93}Np \xrightarrow{-\beta} {}^{239}_{94}Pu$$

39. Nuclear fission is a chain reaction. If it is uncontrolled, explosion occurs as in the atom bomb. Two or more pieces of fissile material (^{235}U or ^{239}Pu) having subcritical mass are brought together rapidly by means of conventional explosion. The subcritical masses combine to be supercritical and then chain fission starts, releasing large amount of energy.

40. The controlled chain fission reaction takes place in nuclear reactors. In these reactors the energy is used for peaceful purposes. The heat energy produced in the nuclear reactors can be used to generate electricity. A reactor consists of:
    (i) enriched fuel $^{235}_{92}U$ (2–3%).
    (ii) heavy water (D_2O) or graphite moderator. It slows down the speed of fast moving neutrons.
    (iii) control rods made of boron and cadmium. These rods absorb some neutrons and thereby control the rate of nuclear fission.
    (iv) liquid alloy of sodium and potassium is used as a coolant.

41. Nuclear fusion is the process in which two nuclei of light atoms fuse to form heavy nuclei with the liberation large amount of energy.

$$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{4}_{2}He + 23 \times 10^{8} \text{ kJ/mol}$$

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n + 17.2 \times 10^{8} \text{ kJ/mol}$$

42. Fusion reactions are thermonuclear reactions which require very high temperature (10^6 K or more).

43. Hydrogen bomb involves nuclear fusion.

44. Energy of a star (sun) is due to nuclear fusion; this energy is called stellar energy.

45. Hydrogen bomb is much more powerful than atom bomb and there is no restriction of critical mass in this bomb.

46. Neutron activation analysis is a technique of finding the trace amount of an element present with the other. The trace element is activated by bombarding with neutrons. It is a non-destructive method, *e.g.*, traces of silver present in lead paintings can be detected by neutron activation analysis.

47. **Spallation reactions:** It is similar to fission but differ in the fact that they are brought about by high energy bombarding particles or photons. A number of smaller particles are released along with the product, *e.g.*,

$$^{238}_{92}U + ^{4}_{2}He \longrightarrow 6\ ^{1}_{1}H + 13\ ^{1}_{0}n + ^{223}_{88}Ra$$

48. The isotope $^{1}_{1}H$ has $n/p = 0$ and $^{3}_{1}H$ has $n/p = 2$ which is maximum.

49. Only $^{12}_{6}C$ has zero packing fraction. Packing fraction is maximum for hydrogen and minimum for iron.

$$\text{Packing fraction} = \frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

Elements with negative packing fraction are stable because some of their mass is converted to binding energy.

50. $^{14}_{6}C$ is produced in upper atmosphere due to bombardment of cosmic ray neutrons on atmospheric nitrogen.

Questions

1. Match the List-I and List-II and pick the correct answer from the codes given below: [PMT (Kerala) 2006]

List-I (Atomic/Molecular species)	List-II (Corresponding pairs)
(A) Isotopes	1. $^{228}_{88}Ra$ and $^{228}_{89}Ac$
(B) Isobars	2. $^{39}_{18}Ar$ and $^{40}_{19}K$
(C) Isotones	3. $^{2}_{1}H$ and $^{3}_{1}H$
(D) Isosters	4. $^{235}_{92}U$ and $^{231}_{90}Th$
(E) Isodiapheres	5. CO_2 and N_2O

(a) A—2, B—1, C—4, D—5, E—3
(b) A—2, B—5, C—1, D—4, E—3
(c) A—3, B—1, C—2, D—5, E—4
(d) A—5, B—4, C—1, D—2, E—3
(e) A—5, B—3, C—1, D—2, E—4

2. **Matrix Matching Problems (For IIT aspirants):**

[A] Match the Column-I with Column-II:

Column-I	Column-II
(a) Stability of nucleus	(p) Depends on mass number
(b) Density of nucleus	(q) Packing fraction
(c) Spin angular momentum of proton	(r) Binding energy per nucleon
(d) Dimensionless quantity	(s) Independent of mass number

[B] Match the Column-I with Column-II:

Column-I	Column-II
(a) 2/3rd life	(p) 63.2% decay
(b) Average life	(q) 75% decay
(c) $1/\lambda$	(r) $2 \times t_{1/2}$
(d) Ten times of half life	(s) 99.9% decay

[C] Match the nuclear transformations of Column-I with the particles emitted of Column-II:

Column-I	Column-II
(a) $^{209}_{83}Bi + ^{4}_{2}He \longrightarrow ^{211}_{85}At + ...$	(p) $^{1}_{1}H$
(b) $^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ...$	(q) $^{4}_{2}He$
(c) $^{24}_{12}Mg(^{1}_{0}n ...)\, ^{24}_{11}Na$	(r) $^{2}_{1}H$
(d) $^{23}_{11}Na(^{2}_{1}H ...)\, ^{21}_{10}Ne$	(s) $^{1}_{0}n$

[D] Match the Column-I with Column-II:

Column-I	Column-II
(a) Binding energy per nucleon increases	(p) β-decay
(b) Mass number is conserved	(q) α-decay
(c) Charge number is conserved	(r) Nuclear fusion
(d) Mass of products formed is less than the mass of reactants	(s) Nuclear fission

[E] Match the Column-I with Column-II:

Column-I	Column-II
(a) α-rays	(p) Radiations, undeviated in electric field
(b) β-rays	(q) Produced when electrons strike metal surface
(c) γ-rays	(r) Highest deflection in electromagnetic field
(d) X-rays	(s) Nucleus of helium

[F] Match the Column-I with Column-II:

Column-I	Column-II
(a) α-emission	(p) Mass number changes
(b) β-emission	(q) Atomic number and mass number are affected
(c) γ-emission	(r) Atomic number decreases
(d) β^+-emission	(s) Atomic number increases

3. Write the complete nuclear reactions:

(a) $^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ...$
(b) $^{3}_{1}H \longrightarrow ^{3}_{2}He + ...$
(c) $^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ...$
(d) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{92}_{38}Sr + Xe + 3\, ^{1}_{0}n$
(e) $^{7}_{3}Li + ^{1}_{0}n \longrightarrow 2\, ^{4}_{2}He + ...$
(f) $^{238}_{92}U + ... \longrightarrow ^{239}_{92}U \longrightarrow ^{239}_{93}Np + ...$
(g) $^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{3}_{1}H + ...$
(h) $^{7}_{3}Li + ... \longrightarrow ^{8}_{4}Be + \gamma$ - radiations
(i) $^{2}_{1}H + ... \longrightarrow ^{4}_{2}He + ^{1}_{0}n$
(j) $^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{24}_{11}Na + ...$
(k) $^{27}_{13}Al + ^{4}_{2}He \longrightarrow .... + ^{1}_{1}H$
(l) $^{235}_{92}U + ^{1}_{0}n \longrightarrow .... + ^{137}_{52}Te + ^{97}_{40}Zr$ (IIT 2005)
(m) $^{86}_{34}Se \longrightarrow .... + 2\, ^{0}_{-1}e$ (IIT 2005)

4. Write the particles emitted from each nuclide in the following reactions:

(a) $^{231}_{90}Th \xrightarrow[(i)]{} ^{231}_{91}Pa \xrightarrow[(ii)]{} ^{227}_{89}Ac$
(b) $^{217}_{85}At \xrightarrow[(i)]{} ^{213}_{83}Bi \xrightarrow[(ii)]{} ^{209}_{81}Tl$
(c) $^{239}_{92}U \xrightarrow[(i)]{} ^{239}_{93}Np \xrightarrow[(ii)]{} ^{239}_{94}Pu$
(d) $^{30}_{15}P \xrightarrow[(i)]{} ^{30}_{14}Si$

5. Find the atomic number and mass number of the last member in the following series:

(a) ${}^{226}_{188}\text{Ra} \xrightarrow{-\alpha} \text{Rn} \xrightarrow{-\alpha} \text{Ra}A \xrightarrow{-\alpha} \text{Ra}B \xrightarrow{-\beta} \text{Ra}C$

(b) ${}^{M}_{Z}A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D \xrightarrow{-\alpha} E$

6. Complete the following:

(a) ${}^{238}X \xrightarrow{-\alpha} Y \xrightarrow{-\beta} {}_{91}Z$

(b) ${}^{214}A \xrightarrow{-\beta} B \xrightarrow{-\beta} {}_{84}C$

7. Write the equations for the following transformations:

(a) ${}^{39}_{19}\text{K}\,(p, d)$ (b) ${}^{14}_{7}\text{N}\,(n, p)$ (c) ${}^{23}_{11}\text{Na}\,(\alpha, p)$

(d) ${}^{9}_{4}\text{Be}\,(\alpha, n)$.

8. To which radioactive families do the following nuclides belong?

${}^{222}\text{Rn}$, ${}^{228}\text{Ra}$, ${}^{207}\text{Pb}$, ${}^{209}\text{Bi}$, ${}^{233}\text{Pa}$.

9. To which group of the periodic table does the last member of the following series belong?

(a) ${}^{239}_{92}\text{U} \xrightarrow{-\beta} {}^{239}_{93}\text{Np} \xrightarrow{-\beta} {}^{239}_{94}\text{Pu}$

III Group

(b) ${}^{140}_{55}\text{Cs} \xrightarrow{-\beta} {}^{140}_{56}\text{Ba} \xrightarrow{-\beta} {}^{140}_{57}\text{La} \xrightarrow{-\beta} {}^{140}_{58}\text{Ce}$

I Group

(c) ${}^{226}_{88}\text{Ra} \xrightarrow{-\alpha} {}^{222}_{86}\text{Rn} \xrightarrow{-\alpha} {}^{218}_{84}\text{Po}$

II Group

10. Name the process represented below:

(a) ${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{141}_{56}\text{Ba} + {}^{92}_{36}\text{Kr} + 3\,{}^{1}_{0}n + 200\text{ MeV}$

(b) ${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n + 17.6\text{ MeV}$

(c) ${}^{63}_{29}\text{Cu} + {}^{4}_{2}\text{He} + 400\text{ MeV} \longrightarrow {}^{37}_{17}\text{Cl} + 14\,{}^{1}_{1}\text{H} + 16\,{}^{1}_{0}n$

(d) ${}^{10}_{5}\text{B} + {}^{4}_{2}\text{He} \longrightarrow {}^{13}_{7}\text{N} + {}^{1}_{0}n$

$\hookrightarrow {}^{13}_{6}\text{C} + {}^{0}_{+1}e$

Answers

1. (c) A–3, B–1, C–2, D–5, E–4

2. [A] (a — p, q, r); (b — s); (c — s); (d — q)
[B] (a — q, r); (b — p); (c — p); (d — s)
[C] (a — s); (b — s); (c — p); (d — q)
[D] (a–p, q, r, s); (b–p, q, r, s); (c–p, q, r, s); (d–p, q, r, s)
[E] (a — s); (b — r); (c — p); (d — p, q)
[F] (a — p, r) (b — s) (c — q) (d — q)

3. (a) ${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$;
(b) ${}^{3}_{1}\text{H} \longrightarrow {}^{3}_{2}\text{He} + {}^{0}_{-1}e$;
(c) ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$;
(d) ${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{92}_{38}\text{Sr} + {}^{141}_{54}\text{Xe} + 3\,{}^{1}_{0}n$;
(e) ${}^{7}_{3}\text{Li} + {}^{1}_{0}n \longrightarrow 2\,{}^{4}_{2}\text{He} + {}^{0}_{-1}e$;
(f) ${}^{238}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}\text{U} \longrightarrow {}^{239}_{93}\text{Np} + {}^{0}_{-1}e$;
(g) ${}^{14}_{7}\text{N} + {}^{1}_{0}n \longrightarrow {}^{12}_{6}\text{C} + {}^{3}_{1}\text{H}$;
(h) ${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \longrightarrow {}^{8}_{4}\text{Be} + \gamma$-radiations;
(i) ${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n$;
(j) ${}^{27}_{13}\text{Al} + {}^{1}_{0}n \longrightarrow {}^{24}_{11}\text{Na} + {}^{4}_{2}\text{He}$;
(k) ${}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{14}\text{Si} + {}^{1}_{1}\text{H}$;
(l) ${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow 2\,{}^{1}_{0}n + {}^{137}_{52}\text{Te} + {}^{97}_{40}\text{Zr}$;
(m) ${}^{86}_{34}\text{Se} \longrightarrow {}^{86}_{36}\text{Kr} + 2\,{}^{0}_{-1}e$

4. (a) (i) β (ii) α (b) (i) α (ii) α (c) (i) β (ii) β (d) (i) ${}^{0}_{+1}e$

5. (a) Atomic mass = 214, Atomic number = 83
(b) Atomic mass = $M - 8$, Atomic number = $Z - 2$

6. (a) ${}^{238}_{92}X \xrightarrow{-\alpha} {}^{234}_{90}Y \xrightarrow{-\beta} {}^{234}_{91}Z$
(b) ${}^{214}_{82}A \xrightarrow{-\beta} {}^{214}_{83}B \xrightarrow{-\beta} {}^{214}_{84}C$

7. (a) ${}^{39}_{19}\text{K} + {}^{1}_{1}\text{H} \longrightarrow {}^{38}_{19}\text{K} + {}^{2}_{1}\text{H}$ (b) ${}^{14}_{7}\text{N} + {}^{1}_{0}n \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$
(c) ${}^{23}_{11}\text{Na} + {}^{4}_{2}\text{He} \rightarrow {}^{26}_{12}\text{Mg} + {}^{1}_{1}\text{H}$ (d) ${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$

8. ${}^{222}\text{Rn}$ belongs to $(4n + 2)$ family, *i.e.*, uranium family.
${}^{228}\text{Ra}$ belongs to $(4n)$ family, *i.e.*, thorium family.
${}^{207}\text{Pb}$ belongs to $(4n + 3)$ family, *i.e.*, actinium family.
${}^{209}\text{Bi}$ belongs to $(4n + 1)$ family, *i.e.*, neptunium series.
${}^{233}\text{Pa}$ belongs to $(4n + 1)$ family, *i.e.*, neptunium series.

9. (a) ${}^{239}_{94}\text{Pu}$ belongs to actinide series, hence it is present in III group.
(b) ${}^{140}_{58}\text{Ce}$ belongs to lanthanide series, hence it is present in III group.
(c) ${}^{218}_{84}\text{Po}$ belongs to VI group.

10. (a) Nuclear fission (b) nuclear fusion (c) spallation reaction (d) artificial radioactivity.

• PRACTICE PROBLEMS •

1. Half life of ^{24}Na is 14.8 hours. In what period of time will a sample of this element lose 90% of its activity?
   [**Ans.** 49.17 hour]
2. A β-particle emitter has a half life of 60.6 min. At any instant of time, a sample of this element registers 2408 counts per second. Calculate the counting rate after 1.5 hours.
   [**Ans.** 860 counts per sec]
3. A radio-isotope $^{32}_{15}$P has half life of 15 days. Calculate the time in which the radioactivity of 1 mg quantity will fall to 10% of the initial value.
   [**Ans.** 49.85 days]
4. Consider an α-particle just in contact with $^{238}_{92}$U nucleus. Calculate the coulombic repulsion energy assuming that the distance between them is equal to the sum of their radii.
   [**Ans.** 24.2 MeV]
5. The activity of a certain sample of radioactive element '*A*' decreases to $1/\sqrt{2}$ of its value in 4 days. What is its half life? Assuming that,

$$^{M}_{Z}A - {}^{4}_{2}\text{He} \longrightarrow {}^{M-4}_{Z-2}B$$

   what mass of the sample will be left over after 24 days if we start with one gram of '*A*'? Calculate this in terms of *M*.

   [**Ans.** $t_{1/2} = 8$ days; mass of sample left over $= \left(1 - \frac{3-5}{M}\right)$ g]

   [**Hint:** $\lambda = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{4}\log_{10}(\sqrt{2}) \quad \because \quad N = \frac{N_0}{\sqrt{2}}$$

$$t_{1/2} = 8 \text{ days}$$

   Use $N = N_0\left(\frac{1}{2}\right)^n$ for next part.]
6. The half life of $^{238}_{92}$U is 4.5×10^9 years. Uranium emits an α-particle to give thorium. Calculate the time required to get the product which contains equal masses of thorium and uranium.
   [**Ans.** 4.55×10^9 yrs]

   [**Hint:** $N_0 = \frac{1}{238} + \frac{1}{234}$; $N = \frac{1}{238}$

   Use, $\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$]
7. 32 mg of pure $^{238}_{94}\text{PuO}_2$ has an activity of 6.4×10^7 sec^{-1}.

   (i) What will be the half life of $^{238}_{94}$Pu in years?

   (ii) What amount of PuO_2 will remain if 100 mg PuO_2 is kept for 5000 years?

   [**Ans.** (i) 2.45×10^4 years (ii) 86.7 mg]

   [**Hint:** (i) Mass of ^{238}Pu $= \frac{238}{270} \times 32 = 28.207$ mg

$$\text{Rate} = \frac{0.693}{t_{1/2}} \times \frac{w}{\text{At. wt.}} \times N$$

$$6.4 \times 10^7 = \frac{0.693}{t_{1/2}} \times \frac{28.207 \times 10^{-3}}{238} \times 6.023 \times 10^{23}$$

$$t_{1/2} = 7.729 \times 10^{11} \text{ sec} = 2.45 \times 10^4 \text{ years}$$

   (ii) Use, $\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$

$$\frac{0.693}{2.45 \times 10^4} = \frac{2.303}{5000}\log_{10}\left(\frac{100}{N}\right)$$

$$N = 86.7 \text{ mg}$$]
8. A radioactive isotope decays as:

$$^{M}_{Z}A \longrightarrow {}^{M-4}_{Z-2}B \longrightarrow {}^{M-4}_{Z-1}C$$

   The half lives of *A* and *B* are 6 and 10 months respectively. Assuming that initially only *A* was present, will it be possible to achieve the radioactive equilibrium for *B*? If so, what would be the ratio of *A* and *B* at equilibrium? What would happen if the half lives of *A* and *B* were 10 and 6 months respectively?

   [**Hint:** At equilibrium, ratio of amounts of *A* and *B* will be

$$\frac{N_A}{N_B} = \frac{t_{1/2}A}{t_{1/2}B} = \frac{6}{10} = 0.6$$

   If the half lives of *A* and *B* are 10 and 6 months respectively, then *B* will decay faster than '*A*', hence equilibrium will not be achieved.]
9. Lowest level of ^{14}C activity for experimental detection is 0.03 dis per min per gram. What is the maximum age of an object that can be determined by ^{14}C method? The activity of ^{14}C in the atmosphere is 15 dis per min per gram of ^{14}C ($t_{1/2}$ for ^{14}C = 5730 yrs).
   [**Ans.** 51379.28 yrs]
10. An analysis of a rock shows that relative number of ^{87}Sr and ^{87}Rb atoms is 0.052, *i.e.*, ($^{87}\text{Sr}/^{87}\text{Rb} = 0.052$). Determine the age of the rock. Given that half life period for β-decay of Rb to Sr is 4.7×10^{10} years.
    [**Ans.** 3.43×10^9 years]

    [**Hint:**

$$\frac{^{87}\text{Rb}}{^{87}\text{Sr}} = \frac{x}{y} = \frac{1}{0.052}$$

$$\frac{x}{x+y} = \frac{1}{1.052}$$

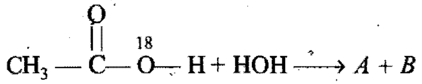
$$\frac{N}{N_0} = \frac{1}{1.052}$$

$$\lambda = \frac{2.303}{t}\log_{10}\frac{N_0}{N}$$

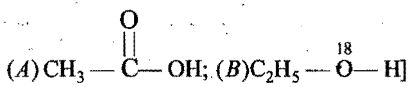
$$\frac{0.693}{4.7 \times 10^{10}} = \frac{2.303}{t}\log_{10}1.052$$

$$t = 3.43 \times 10^9 \text{ years}$$]

11. Hydrolysis of ester was studied by isotopic labelling method. Write down the structures of products A and B in the given reaction: **(IIT 2000)**



$$CH_3-\overset{\overset{O}{||}}{C}-\overset{18}{O}-H+HOH\longrightarrow A+B$$



[Ans. $(A)\,CH_3-\overset{\overset{O}{||}}{C}-OH;\ (B)\,C_2H_5-\overset{18}{O}-H$]

12. Arrange the following species in decreasing order of chemical reactivity and radioactivity:

$${}^1_1H,\ {}^2_1H,\ {}^3_1H$$

[Ans. Reactivity ${}^1_1H > {}^2_1H > {}^3_1H$

Radioactivity ${}^3_1H > {}^2_1H > {}^1_1H$]

13. The half life of ${}^{212}Pb$ is 10.6 hours and that of its daughter element ${}^{212}Bi$ is 60.5 minutes. After how much time will the daughter element have maximum activity?

[Ans. 3.78 hours]

[Hint: $\lambda_p = \dfrac{0.693}{10.6\times 60}$; $\lambda_d = \dfrac{0.693}{60.5} = 0.01145\ \text{min}^{-1}$

$= 0.001089\ \text{min}^{-1}$

$$t_{\max} = \frac{2.303}{(\lambda_d-\lambda_p)}\log_{10}\frac{\lambda_d}{\lambda_p}$$

$$= \frac{2.303}{0.01145-0.001089}\log_{10}\left[\frac{0.01145}{0.001089}\right]$$

$$= 222.2758\log_{10}\frac{0.01145}{0.001089}$$

$$= 227.1\ \text{min}$$

$$= 3.785\ \text{hours}]$$

14. Radioactive element is spread over a room, its half life is 30 days. Its activity is 50 times the permissible value. After how many days will it be safe?

[Ans. 169.30 days]

[Hint: $N_0 = 50N$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{30} = \frac{2.303}{t}\log_{10}\left(\frac{50N}{N}\right)$$

$t = 169.3$ days]

15. Calculate the energy released in joules and MeV in the following nuclear reaction:

$${}^2_1H + {}^2_1H \longrightarrow {}^3_2He + {}^1_0n$$

Assume that the masses of ${}^2_1H$, ${}^3_2He$ and neutron respectively are 2.0141, 3.0160 and 1.0087 amu.

[Ans. 5.223×10^{-13} J; 3.260 MeV]

16. A radioactive element due to an accident in research laboratory gets embedded in its floor and walls. The initial rate of decay is 64 times the safe limit. The half life of the element is 32 days. Calculate the time after which the laboratory will be safe for use.

[Ans. 192 days]

[Hint: $N_0 = 64N$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log_{10}\frac{N_0}{N}$$

$$\frac{0.693}{32} = \frac{2.303}{t}\log_{10}\left[\frac{64N}{N}\right]$$

$t = 192$ days]

17. Radium has a half life 1600 years and its daughter element radon has a half life 3.82 days. In an enclosure, the volume of radon was found constant for a week. Explain and calculate the ratio of the number of radium and radon nuclei. Will the ratio be constant after 400 years?

[Ans. 1.528×10^5]

[Hint: $\dfrac{N_1(\text{Ra})}{N_2(\text{Rn})} = \dfrac{t_{1/2}(\text{Rn})}{t_{1/2}(\text{Ra})}$

$$\frac{N_1}{N_2} = \frac{1600}{3.82}\times 365$$

$$= 1.528\times 10^5]$$

18. Calculate the radius and density of ${}^{235}_{92}U$.

[Ans. $R = 6.8\times 10^{-13}$ cm; $d = 2.979\times 10^{14}$ g / cc]

[Hint: $R = R_0 A^{1/3} = 1.1\times 10^{-15}\,(235)^{1/3} = 6.788\times 10^{-15}$ m

$= 6.788\times 10^{-13}$ cm

$$d = W/V = \frac{235\times 1.66\times 10^{-24}}{\frac{4}{3}\times \pi\times (6.788\times 10^{-13})^3}\ \text{g / cc}$$

$$= 2.979\times 10^{14}\ \text{g / cc}]$$

19. ${}^{235}_{92}U$ decays with emission of α and β-particles to form ultimately ${}^{207}_{82}Pb$. How many α and β-particles are emitted per atom of Pb produced?

[Ans. 7 α and 4 β]

20. The half life of radium is 1600 years. After how much time, $\frac{1}{16}$th part of radium will remain undisintegrated in a sample?

[Ans. 6400 years]

21. The half life of polonium is 140 days. In what time will 15 g of polonium be disintegrated out of its initial mass of 16 g?

[Ans. 560 days]

[Hint: Polonium left is $\frac{1}{16}$th of the initial, *i.e.*, 4 half lives.]

22. The activity of a radioactive isotope falls to 12.5% in 90 days. Calculate the half life and decay constant of the radioactive isotope.

[Ans. 30 days, 0.0231 day^{-1}]

23. The radioactivity of an element was found to be one millicurie. What will be its radioactivity after 42 days if it has half life of 14 days?

[Ans. 0.125 millicurie]

24. There are 10^6 radioactive nuclei in a given radioactive element. Its half life is 20 seconds. How many nuclei will remain after 10 seconds? (Given, $\sqrt{2} = 1.41$)

[Ans. 7×10^5 (approximately)]

[Hint: $N = N_0\left(\frac{1}{2}\right)^n = 10^6 \times \left(\frac{1}{2}\right)^{1/2}$ as $n = \frac{10}{20} = \frac{1}{2} = \frac{10^6}{1.41}$]

25. A radioactive element decays at such a rate that after 68 minutes only one-fourth of its original amount remains. Calculate its decay constant and half life period.

[Ans. $\lambda = 0.0204\ \text{min}^{-1}$, $t_{1/2} = 34$ min.]

26. One gram of a radioactive element decays by β-emission to 0.125 in 200 hours. How much more time will elapse until only 0.10 g of it is left?

[Ans. 21.46 hours]

27. A wooden article found in a cave has only 40% as much ^{14}C activity as a fresh piece of wood. How old is the article? ($t_{1/2}$ for $^{14}C = 5760$ years)

[Ans. 7617 years]

28. A sample of carbon derived from one of dead sea scrolls is found to be decaying at the rate of 12.0 disintegrations per minute per gram of carbon. Estimate the age of dead sea scrolls when carbon from living plants disintegrates at the rate of 15.3 disintegrations per minute per gram. ($t_{1/2}$ for $^{14}C = 5760$ years)

[Ans. 2020 years]

29. One μg of a radioactive iodine contained in thyroxine is injected into the blood of a patient. How long will it take for radioactivity to fall to 50%, 25% and 10% of the initial value? ($t_{1/2}$ for $^{131}_{53}I = 8.05$ days)

[Ans. 8.05 days, 16.1 days, 26.75 days]

30. 1 g radium is reduced by 2.1 mg in 5 years by alpha decay, calculate the half life period.

[Ans. Half life = 1672 years]

[Hint: Mass of radium left after 5 years = (1.0 − 0.0021) g

= 0.9979 g

Apply $\lambda = \frac{2.303}{t} \log_{10} \frac{N_0}{N} = \frac{2.303}{5} \log_{10} \frac{1}{0.9979}$]

31. The activity of a radioactive substance falls to 87.5% of the initial value in 5 years. What is the half life of the element? Calculate the time in which the activity will fall by 87.5%.

[Ans. Half life = 9.52 years, $t = 28.58$ years]

32. Starting with 1.0 g of a radioactive sample, 0.25 g of it is left after 5 days. Calculate the amount which was left after one day.

[Ans. 0.758 g]

33. A sample of wooden artifact is found to undergo 9 disintegrations per minute per gram of carbon. What is the approximate age of the artifact? The half life of $^{14}_{6}C$ is 5730 years and radioactivity of wood recently cut is 15 disintegrations per minute per gram of carbon.

34. Xenon-127 has a half life of 36.4 days. How much of a sample of xenon that originally weighed 1.0 g remains after 20 days? **(Dhanbad 1992)**

[Ans. 0.6835 g]

35. Calculate the ratio of $\frac{N}{N_0}$ after an hour has passed for a radioactive material of half life 47.2 seconds.

[Ans. $\frac{N}{N_0} = 1.12 \times 10^{-23}$]

[Hint: $\lambda t = 2.303 \log_{10} \frac{N_0}{N}$

$\frac{0.693}{47.2} \times \frac{60 \times 60}{2.303} = \log_{10} \frac{N_0}{N}$]

36. The activity of the hair of an Egyptian mummy is 7 disintegrations minute^{-1} of ^{14}C. Find the age of the mummy. Given, $t_{1/2}$ of ^{14}C is 5770 years and disintegration rate of fresh sample of ^{14}C is 14 disintegrations minute^{-1}.

[Ans. 5770 years]

37. On analysis a sample of ^{238}U ore was found to contain 20.6 g of $^{206}_{82}Pb$ and 23.8 g of $^{238}_{92}U$. The half life period of ^{238}U is 4.50×10^9 years. If all the lead were assumed to have come from decay of $^{238}_{92}U$, what is the age of the ore? **(IIT 1996)**

[Ans. 4.49×10^9 years]

38. It is known that 1 g of ^{226}Ra emits 11.6×10^{17} atoms of α per year. Given, the half life of ^{226}Ra to be 1600 years, compute the value of Avogadro's number.

[Ans. 6.052×10^{23}]

[Hint: Rate = λ × number of atoms in one gram

$= \lambda \times \frac{\text{Avogadro's number}}{226}$]

39. A uranium mineral contains ^{238}U and ^{206}Pb in the ratio of 4 : 1 by weight. Calculate the age of the mineral $t_{1/2}$ ^{238}U $= 4.5 \times 10^9$ years. Assume that all the lead present in the mineral is formed from disintegration of ^{238}U.

[Ans. 1.648×10^9 years]

40. In a sample of pitchblende, the atomic ratio of $^{206}Pb : ^{238}U$ is 0.23 : 1. Calculate the age of the mineral if half life of uranium is 4.5×10^9 years. Assume that all lead has originated from uranium.

[Ans. 1.34×10^9 years]

41. The ratio of the atoms of two elements *A* and *B* at radioactive equilibrium is $5.0 \times 10^5 : 1$ respectively. Calculate half life of *B* if half life of *A* is 245 days.

[Ans. 4.9×10^{-4} days]

42. Calculate the energy released in MeV during the reaction $^{7}_{3}Li + ^{1}_{1}H \rightarrow 2[^{4}_{2}He]$ if the masses of $^{7}_{3}Li$, $^{1}_{1}H$ and $^{4}_{2}He$ are 7.018, 1.008 and 4.004 amu respectively.

[Ans. 16.76 MeV]

43. 1.0 g of $^{226}_{88}Ra$ is placed in a sealed vessel. How much helium will be collected in the vessel in 100 days? ($t_{1/2}$ of radium = 1600 years)

[Ans. 2.12×10^{-6} g]

44. The half life period of $^{141}_{58}Ce$ is 13.11 days. It is a β-particle emitter and the average energy of the β-particle emitted is 0.442 MeV. What is the total energy emitted per second in watts by 10 mg of $^{141}_{58}Ce$?

[**Ans.** 1.84 watt]

[**Hint:** Rate of disintegrations per sec = λ × No. of atoms

$$= \frac{0.693}{13.11 \times 24 \times 60 \times 60} \times \frac{6.023 \times 10^{23}}{141} \times 0.01$$

Total β-particles emitted = 2.61×10^{13}

Total energy emitted = $2.61 \times 10^{13} \times 0.442 = 1.1536 \times 10^{13}$ MeV

$$\text{Energy in erg} = (1.1536 \times 10^{13})(1.6 \times 10^{-6})$$

$$\text{Energy in watt} = \frac{1.1536 \times 10^{13} \times 1.6 \times 10^{-6}}{10^{7}} = 1.84 \text{ watt}]$$

45. A sample of $^{90}_{38}Sr$ has an activity of 0.5 mCi. What is its specific activity? ($t_{1/2}$ of $^{90}_{38}Sr$ = 19.9 years)

[**Ans.** 7.4×10^{12} dis g^{-1} s^{-1}]

[**Hint:** Rate of disintegrations = λ × No. of atoms

So, No. of atoms

$$= \frac{0.5 \times 3.7 \times 10^{7}}{0.693} \times 19.9 \times 365 \times 24 \times 60 \times 60$$

$$= 1.675 \times 10^{16}$$

$$\text{Mass} = \frac{90 \times 1.675 \times 10^{16}}{6.023 \times 10^{23}} = 2.50 \times 10^{-6} \text{ g}$$

$$\text{Specific activity} = \frac{0.5 \times 3.7 \times 10^{7}}{2.5 \times 10^{-6}} = 7.4 \times 10^{12} \text{ dis g}^{-1} \text{ s}^{-1}]$$

46. Calculate the Q-value of the reaction;

$$^{6}_{3}Li + ^{1}_{0}n \longrightarrow ^{4}_{2}He + ^{3}_{1}H$$

Given, $^{6}_{3}Li = 6.015126$ amu, $^{4}_{2}He = 4.002604$ amu

$^{3}_{1}H = 3.016049$ amu, $^{1}_{0}n = 1.008665$ amu

[**Ans.** +4.7835 MeV]

47. The disintegration rate of a certain radioactive sample at any instant is 4750 dpm. Five minutes later, the rate becomes 2700 dpm. Calculate half life of sample.

[**Ans.** $t_{1/2} = 6.13$ minute]

48. One of the hazards of nuclear explosion is the generation of ^{90}Sr and its subsequent incorporation in bones. This nuclide has a half life of 28.1 years. Suppose one microgram was absorbed by a new-born child, how much ^{90}Sr will remain in his bones after 20 years? (IIT 1995)

[**Ans.** 0.61 μg]

[**Hint:** $t = \frac{2.303}{\lambda} \log \frac{\text{initial}}{\text{remaining}}$

$\lambda = \frac{2.303}{28.1} y^{-1}$ $t = 20y$, initial = 1 μg, remaining = x μg

$$20 = \frac{2.303}{0.693} \times 28.1 \log \frac{1}{x}$$

$$x = 0.61\,\mu g]$$

49. It has been estimated that the carbon-14 in the atmosphere is responsible for producing 60 atoms of nitrogen-14 and 60 electrons every hour for each gram of carbon. We can quote this disintegration rate as 60 counts hour^{-1} g^{-1}. A sample of sea shell found near a sea shore was found to have a count of 4 counts hour^{-1} g^{-1}. Estimate the age of the shell. ($t_{1/2}$ for ^{14}C = 5730 years).

[**Ans.** 21000 years (approximately)]

50. Upon irradiating californium with neutrons, a scientist discovered a new nuclide having mass number of 250 and half life of 0.5 hours. Three hours after the irradiation, the observed radioactivity due to the nuclide was 10 dis/min. How many atoms of the nuclide were prepared initially?

[**Ans.** 2.8×10^{4}]

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Natural radioactivity was discovered by:
   (a) Rutherford (b) Becquerel
   (c) Curie (d) Schmidt
2. Radioactivity is due to:
   (a) stable electronic configuration
   (b) unstable electronic configuration
   (c) stable nucleus
   (d) unstable nucleus
3. Radioactivity is essentially:
   (a) a chemical activity (b) a physical property
   (c) a nuclear property (d) a property of non-metals
4. Radioactivity is generally found in:
   (a) light nuclei (b) stable nuclei
   (c) heavy nuclei (d) nuclei of intermediate mass
5. The activity of radioisotope changes with:
   (a) temperature (b) pressure
   (c) chemical environment (d) none of these
6. The rays are given off by a radioactive element from:
   (a) nucleus (b) valence electrons
   (c) all the orbits (d) outer orbit
7. The alpha particles are:
   (a) high energy electrons
   (b) positively charged hydrogen ions
   (c) high energy X-ray radiations
   (d) double positively charged helium nuclei
8. The emission of beta particles is from: (CBSE 1999)
   (a) the valence shell of an atom
   (b) the inner shell of an atom
   (c) the nucleus due to the nuclear conversion proton → neutron + electron
   (d) the nucleus due to the nuclear conversion neutron → proton + electron
9. Identify the nuclear reaction that differs from the rest:
   (a) Positron emission (b) *K*-capture
   (c) β-decay (d) α-decay
   (e) γ-decay [PET(Kerala) 2008]
   [**Hint :** Only γ-emission does not change the n/p (Neutron/Proton, ratio) of the parent element.]
10. Gamma rays are: (MLNR 1990)
    (a) high energy electrons
    (b) low energy electrons
    (c) high energy electromagnetic waves
    (d) high energy positrons
11. Radium is a radioactive substance. It dissolves in dilute H_2SO_4 and forms a compound radium sulphate. The compound is:
    (a) no longer radioactive
    (b) half as radioactive as the radium content
    (c) as radioactive as the radium content
    (d) twice as radioactive as the radium content
12. The velocity of α-rays is approximately:
    (a) equal to that of the velocity of light
    (b) $\frac{1}{10}$th of the velocity of light
    (c) 10 times more than the velocity of light
    (d) uncomparable to the velocity of light
13. α-rays have ionisation power because they possess:
    (a) lesser kinetic energy
    (b) higher kinetic energy
    (c) lesser penetration power
    (d) higher penetration power
14. The radiations from a naturally occurring radioactive substance as seen after deflection by a magnetic field in one direction are:
    (a) definitely α-rays (b) definitely β-rays
    (c) both α and β-rays (d) either α or β-rays
15. Which of the following statements about radioactivity is wrong?
    (a) It involves outer electrons activity
    (b) It is not affected by temperature or pressure
    (c) It is an exothermic process
    (d) The radioactivity of an element is not affected by any other element compounded by it
16. The radioactivity of uranium minerals is usually more in comparison to pure uranium. This is due to presence of . . . in the mineral.
    (a) actinium (b) thorium
    (c) radium (d) plutonium
17. Radioactive disintegration differs from a chemical change in being: (MLNR 1991)
    (a) an exothermic change
    (b) a spontaneous process
    (c) a nuclear process
    (d) an unimolecular first order reaction
18. The ionising power of α, β and γ-rays is in the decreasing order:
    (a) $\alpha > \beta > \gamma$ (b) $\beta > \alpha > \gamma$
    (c) $\gamma > \alpha > \beta$ (d) $\beta > \gamma > \alpha$
19. Which of the following radiations have least effect on both the photographic plate and zinc sulphide screen?
    (a) α-rays (b) β-rays
    (c) γ-rays (d) All have equal effect
20. γ-rays are emitted from a nucleus due to:
    (a) high n/p ratio
    (b) excess energy possessed by nucleus after emission of α or β-particles
    (c) fission reaction
    (d) fusion reaction
21. If a radioactive substance is placed in vacuum at 100°C, its rate of disintegration in comparison to one atmospheric pressure:

(a) is not affected
(b) increases
(c) decreases
(d) increases when the product is gas

22. In α-decay, n/p ratio:
(a) may increase or decrease
(b) remains constant
(c) decreases
(d) increases

23. In β-decay, n/p ratio:
(a) remains unchanged (b) may increase or decrease
(c) increases (d) decreases

24. A device used for the measurement of radioactivity is:
(a) mass spectrometer (b) cyclotron
(c) nuclear reactor (d) G.M. counter

25. Which of the following does not contain material particles? [CET (Pb.) 1991]
(a) α-rays (b) β-rays (c) γ-rays (d) Anode rays

26. If by mistake some radioactive substance gets into human body, then from the point of view of radiation damage, the most harmful will be one that emits:
(a) γ-rays (b) neutrons (c) β-rays (d) α-rays

27. Radioactive decay is a reaction of:
(a) zero order (b) first order
(c) second order (d) third order

28. If n/p ratio is high, the nucleus tends to stabilise by:
(a) the emission of a β-particle
(b) neutron capture
(c) losing a positron
(d) any one of the above

29. Emission of β-particles by an atom of an element results in the formations of:
(a) isobar (b) isomer (c) isotope (d) isotone

30. Which of the following process will cause the emission of X-ray?
(a) α-emission (b) β-emission
(c) *K*-electron capture (d) γ-emission

31. When a β-particle is emitted by the atom of a radioactive element, the new species formed possesses: [PET (MP) 1990]
(a) same atomic mass and atomic number less by one unit
(b) same atomic mass and atomic number less by two units
(c) same atomic mass and atomic number higher by one unit
(d) same atomic mass and atomic number higher by two units

32. Successive emission of an α-particle and two β-particles by an atom of a radioactive element results in the formation of its: [IIT (Screening) 1993]
(a) isobar (b) isomer (c) isotone (d) isotope

33. The isotope $^{235}_{92}U$ decays in a number of steps to an isotope of $^{207}_{82}Pb$. The groups of particles emitted in this process will be:
(a) $4\alpha, 7\beta$ (b) $6\alpha, 4\beta$ (c) $7\alpha, 4\beta$ (d) $10\alpha, 8\beta$

34. The number of α and β-particles emitted in the nuclear reaction $^{228}_{90}Th \longrightarrow {}^{212}_{83}Bi$ are: [MLNR 1992; JEE (Orissa) 2010]
(a) $8\alpha, 1\beta$ (b) $4\alpha, 7\beta$ (c) $3\alpha, 7\beta$ (d) $4\alpha, 1\beta$

35. $^{210}_{84}Po \longrightarrow {}^{206}_{82}Pb + {}^{4}_{2}He$
In above reaction, predict the position of Po in the periodic table when lead belongs to IVB group:
(a) IIA (b) VIB (c) IVB (d) VB

36. When $^{226}_{88}Ra$ emits an α-particle, the new element formed belongs to:
(a) third group (b) zero group
(c) fourth group (d) second group

37. The radius of nucleus is: (VITEEE 2007)
(a) proportional to its mass number
(b) inversely proportional to its mass number
(c) proportional to the cube root of its mass number
(d) not related to its mass number

38. The last product of $4n$ series is:
(a) $^{208}_{82}Pb$ (b) $^{207}_{82}Pb$ (c) $^{209}_{82}Pb$ (d) $^{210}_{83}Bi$

39. $4n+2$ series is known as:
(a) actinium series (b) thorium series
(c) uranium series (d) neptunium series

40. A radioactive element *A* on disintegration gives two elements *B* and *C*. If *B* is helium and *C* is the element of atomic number 90 and atomic mass 234, the element *A* is:
(a) $^{238}_{92}U$ (b) $^{234}_{88}Ra$ (c) $^{234}_{90}Th$ (d) $^{234}_{91}Pa$

41. Group displacement law was given by:
(a) Becquerel (b) Rutherford
(c) Mendeleeff (d) Soddy and Fajan

42. ^{234}U has 92 protons and 234 nucleons total in its nucleus. It decays by emitting an alpha particle. After the decay it becomes: (VITEEE 2008; DUMET 2010)
(a) ^{232}U (b) ^{232}Pa (c) ^{230}Th (d) ^{230}Ra

43. Starting from radium, the radioactive disintegration process terminates when the following is obtained:
(a) lead (b) radon (c) radium *A* (d) radium *B*

44. The only, most stable nucleus formed by bombarding either $^{27}_{13}Al$ by neutrons or $^{23}_{11}Na$ by deutrons is: [CET (J&K) 2007]
(a) $^{30}_{15}P$ (b) $^{30}_{14}Si$ (c) $^{24}_{12}Mg$ (d) $^{137}_{56}Ba$

45. Quantity of radioactive material which undergoes 10^6 disintegrations per second is called:
(a) Becquerel (b) Rutherford
(c) Curie (d) Faraday

46. The number of α-particles emitted per second by 1 g of ^{226}Ra is 3.7×10^{10}. The decay constant is:
(a) 1.39×10^{-11} sec^{-1} (b) 13.9×10^{-11} sec^{-1}
(c) 139×10^{-10} sec^{-1} (d) 13.9×10^{-10} sec^{-1}

[**Hint:** $\dfrac{\text{No. of atoms disintegrating per second}}{\text{Total number of atoms present}} = \lambda$

or $$\frac{3.7 \times 10^{10}}{\dfrac{6.02 \times 10^{23}}{226}} = \frac{226 \times 3.7 \times 10^{10}}{6.02 \times 10^{23}} = \lambda]$$

47. The decay constant of ^{226}Ra is 1.37×10^{-11} sec^{-1}. A sample of ^{226}Ra having an activity of 1.5 millicurie will contain ...... atoms:
(a) 4.05×10^{18} (b) 3.7×10^{17} (c) 2.05×10^{15} (d) 4.7×10^{10}

[Hint: 1 millicurie = 3.7×10^7 disintegrations per sec

1.5 millicurie = 5.55×10^7 disintegrations per sec

$$\frac{5.55 \times 10^7}{N_0} = \lambda = 1.37 \times 10^{-11}]$$

48. One curie of activity is equivalent to:
(a) 3.7×10^{17} disintegrations per sec
(b) 3.7×10^{10} disintegrations per sec
(c) 3.7×10^{14} disintegrations per sec
(d) 3.7×10^{3} disintegrations per sec

49. A sample of $^{40}_{19}K$ contains invariably $^{40}_{18}Ar$. This is because $^{40}_{19}K$ has tendency to undergo: **[JEE (Orissa) 2006]**
(a) α-decay (b) positronium decay
(c) β-decay (d) γ-decay

50. The value of disintegration constant of a radioactive isotope:
(a) decreases with increasing temperature
(b) decreases with increasing pressure
(c) increases with increasing concentration
(d) is independent of temperature, pressure and concentration

51. If the amount of a radioactive substance is increased three times, the number of atoms disintegrating per unit time would:
(a) be double
(b) not be change
(c) be triple
(d) be $\frac{1}{3}$rd of the original number of atoms

52. The half life of a radioactive element depends upon:
(a) the amount of the element
(b) the temperature
(c) the pressure
(d) none of these

53. The decay constant of a radioactive sample is λ. The half life and mean life of the sample are respectively: **(MLNR 1990)**
(a) $1/\lambda, \ln 2/\lambda$ (b) $\ln 2/\lambda, 1/\lambda$
(c) $\lambda \ln 2, 1/\lambda$ (d) $\lambda / Pn_2, 1/\lambda$

54. Average life of a radioactive substance is:
(a) 0.44 times of half life (b) 2.44 times of half life
(c) 1.44 times of half life (d) 0.693 times of half life

55. Radium has atomic mass 226 and half life of 1600 years. The number of disintegrations per second per gram are: **(BHU 1990)**
(a) 4.8×10^{10} (b) 3.7×10^{8}
(c) 9.2×10^{6} (d) 3.7×10^{10}

[Hint:
$$\frac{\text{No. of disintegrations per sec}}{\text{Total no. of atoms in one gram of Ra}} = \lambda$$
$$= \frac{0.693}{1600 \times 365 \times 24 \times 60 \times 60}$$

or No. of disintegrations per sec
$$= \frac{0.693 \times 6.023 \times 10^{23}}{1600 \times 365 \times 24 \times 60 \times 60 \times 226}]$$

56. A radioactive sample has a half life 1500 years. A sealed tube containing 1 g of the sample will contain after 3000 years: **(MLNR 1994)**
(a) 1 g of the sample (b) 0.5 g of the sample
(c) 0.25 g of the sample (d) 0.01 g of the sample

57. ^{14}C has a half life of 5760 years. 100 mg of the sample containing ^{14}C is reduced to 25 mg in: **[PET (Raj.) 2006]**
(a) 11520 years (b) 2880 years
(c) 1440 years (d) 17280 years

58. If 3/4 quantity of radioactive substance disintegrates in 2 hours, its half life period will be: **(BHU 2006)**
(a) 15 minutes (b) 30 minutes
(c) 60 minutes (d) 90 minutes

59. Initial mass of a radioactive element is 40 g. How many grams of it would be left after 24 years if its half life period is of 8 years?
(a) 2 (b) 5 (c) 10 (d) 20

60. Half life of radium is 1580 years. It remains 1/16 after the years.......: **(VMMC 2007)**
(a) 1580 yrs (b) 3160 yrs (c) 4740 yrs (d) 6320 yrs

61. If half life period of radium is 1600 years, its average life period will be:
(a) 2304 years (b) 4608 years
(c) 230.4 years (d) 23040 years

62. A radioactive isotope having a half life of 3 days was received after 12 days. It was found that there were 3 g of the isotope in the container. The initial mass of the isotope when packed was:
(a) 48 g (b) 36 g (c) 24 g (d) 12 g

63. Radioactivity of a radioactive element remains 1/10 of the original radioactivity after 2.303 seconds. The half life period is:
(a) 2.303 (b) 0.2303 (c) 0.693 (d) 0.0693

[Hint:
$$\lambda = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

or
$$\lambda = \frac{2.303}{2.303} \log_{10} \frac{1}{1/10} = 1, T = \frac{0.693}{\lambda} = 0.693]$$

64. A freshly prepared radioactive source of half life period 2 hours emits radiations of intensity which is 64 times the permissible safe level. The minimum time after which it would be possible to work with this source is:
(a) 6 hours (b) 12 hours
(c) 24 hours (d) 48 hours

65. A radio isotope has a half life of 10 days. If today there is 125 g of it left, what was its mass 40 days earlier? **(EAMCET 1991)**
(a) 600 g (b) 1000 g (c) 1250 g (d) 2000 g

66. The half life period of four isotopes is given below:
(i) 7.6 years (ii) 4000 years
(iii) 6000 years (iv) 3.2×10^5 years
Which of the above isotopes is most stable?
(a) (iv) (b) (iii) (c) (ii) (d) (i)

67. The first indication that a stable nucleus can be broken down was afforded by:
(a) Rutherford (b) Madam Curie
(c) Soddy (d) Schmidt

68. The first stable isotope which was transmuted by artificial means was:
(a) $^{16}_{8}O$ (b) $^{14}_{7}N$ (c) $^{12}_{6}C$ (d) $^{9}_{4}Be$

69. The instability of a nucleus is due to: **(AIIMS 1999)**
(a) high, proton : electron ratio
(b) high, proton : neutron ratio
(c) low, proton : electron ratio
(d) low, proton : neutron ratio

70. When ${}^{27}_{13}\text{Al}$ is bombarded with α-particles, a radioactive isotope of phosphorus ${}^{30}_{15}\text{P}$ with the emission of . . . is formed. **[CET (Gujarat) 2006]**
(a) neutrons (b) protons
(c) positrons (d) electrons

71. Nuclear reaction accompanied with emission of neutron(s) is: **[PMT (MP) 1991]**
(a) ${}^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{30}_{15}\text{P} + {}^{1}_{0}n$
(b) ${}^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \longrightarrow {}^{13}_{7}\text{N}$
(c) ${}^{30}_{15}\text{P} \longrightarrow {}^{30}_{14}\text{Si} + {}^{0}_{1}e$
(d) ${}^{240}_{96}\text{Am} + {}^{4}_{2}\text{He} \longrightarrow {}^{244}_{97}\text{Bk} + {}^{0}_{1}e$

72. Which of the following transformations is not correct?
(a) ${}^{75}_{33}\text{As} + {}^{4}_{2}\text{He} \longrightarrow {}^{78}_{35}\text{Br} + {}^{1}_{0}n$
(b) ${}^{7}_{3}\text{Li} + {}^{1}_{1}\text{H} \longrightarrow {}^{7}_{4}\text{Be} + {}^{1}_{0}n$
(c) ${}^{45}_{21}\text{Sc} + {}^{1}_{0}n \longrightarrow {}^{45}_{20}\text{Ca} + {}^{1}_{0}n$
(d) ${}^{209}_{83}\text{Bi} + {}^{2}_{1}\text{H} \longrightarrow {}^{210}_{84}\text{Po} + {}^{1}_{0}n$

73. The reaction, ${}^{235}_{92}\text{U} + {}^{1}_{0}n \longrightarrow {}^{140}_{56}\text{Ba} + {}^{93}_{36}\text{Kr} + 3\,{}^{1}_{0}n$ represents:
(a) artificial radioactivity
(b) nuclear fission
(c) nuclear fusion
(d) none of these

74. ${}^{14}_{6}\text{C}$ in upper atmosphere is generated by the nuclear reaction: **[PET (MP) 1993]**
(a) ${}^{14}_{7}\text{N} + {}^{1}_{1}\text{H} \longrightarrow {}^{14}_{6}\text{C} + {}^{0}_{+1}e + {}^{1}_{1}\text{H}$
(b) ${}^{14}_{7}\text{N} \longrightarrow {}^{14}_{6}\text{C} + {}^{0}_{+1}e$
(c) ${}^{14}_{7}\text{N} + {}^{1}_{0}n \longrightarrow {}^{14}_{6}\text{C} + {}^{1}_{1}\text{H}$
(d) ${}^{14}_{7}\text{N} + {}^{1}_{1}\text{H} \longrightarrow {}^{11}_{6}\text{C} + {}^{4}_{2}\text{He}$

75. In the transformation of ${}^{238}_{92}\text{U}$ to ${}^{234}_{92}\text{U}$, if one emission is an α-particle, what should be the other emission(s)? **(AIEEE 2006)**
(a) two β^- (b) two β^- and one β^+
(c) one β^- and one γ (d) one β^+ and one β^-
[**Hint:** ${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{92}\text{U} + {}^{4}_{2}\text{He} + 2\,{}^{0}_{-1}e$]

76. The reaction, ${}^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \longrightarrow {}^{3}_{2}\text{He} + {}^{1}_{0}n$ is called: **(CPMT 1990)**
(a) fusion (b) fission
(c) endothermic reaction (d) spontaneous reaction

77. When the nucleus of uranium is bombarded with neutrons, it breaks up into two nuclei of nearly equal mass. This process is called:
(a) nuclear fission (b) nuclear fusion
(c) physical change (d) artificial radioactivity

78. Which one of the following is an artificial fuel for nuclear reactors?
(a) ${}^{238}\text{U}$ (b) ${}^{239}\text{Pu}$ (c) ${}^{235}\text{U}$ (d) ${}^{232}\text{Th}$

79. A positron is emitted from ${}^{23}_{11}\text{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is: **(IIT 2007)**
(a) 22/10 (b) 22/11 (c) 23/10 (d) 23/12
[**Hint:** $${}^{1}_{1}\text{H} \longrightarrow {}^{1}_{0}n + \underset{\text{Positron}}{{}^{0}_{+1}e}$$

On positron emission, proton is converted to neutron, therefore, atomic number decreases by one unit but atomic mass remains constant.

$$\therefore \frac{n}{p}\text{ ratio} = \frac{23}{10}$$]

80. Hydrogen bomb is based on the principle of: **(AIEEE 2005)**
(a) nuclear fission (b) natural radioactivity
(c) nuclear fusion (d) artificial radioactivity

81. In nuclear reactors, the speed of neutrons is slowed down by:
(a) heavy water (b) ordinary water
(c) zinc rods (d) molten caustic soda

82. Which of the following is not a fissile material?
(a) ${}^{235}\text{U}$ (b) ${}^{238}\text{U}$
(c) ${}^{233}\text{U}$ (d) ${}^{239}\text{Pu}$

83. Which one of the following statements is wrong?
(a) An atom bomb is based on nuclear fission
(b) In atomic reactor, the chain reaction is carried out under control
(c) Fission reactions are the sources of sun's energy
(d) Hydrogen bomb is always associated with atomic bomb

84. The fuel in atomic pile is:
(a) carbon (b) sodium
(c) petroleum (d) uranium

85. Large energy released in atomic bomb explosion is mainly due to:
(a) conversion of heavier to lighter atoms
(b) products having lesser mass than initial substance
(c) release of neutrons
(d) release of electrons

86. One gram of mass is equal to:
(a) 5×10^{10} erg (b) 9×10^{20} erg
(c) 7×10^{5} erg (d) 11×10^{12} erg

87. If the energy released by burning 1 g of carbon is 3×10^{11} erg, then the amount of energy released by converting 1 g of carbon completely to nuclear energy would be equivalent to energy produced by burning ...... g of carbon.
(a) 10^{6} (b) 10^{8}
(c) 9×10^{20} (d) 3×10^{10}

88. Liquid sodium is used in nuclear reactors. Its function is:
(a) to collect the reaction products
(b) to act as heat exchanger
(c) to absorb the neutrons in order to control the chain reaction
(d) to act as moderator to slow down the neutrons

89. A sample of rock from moon contains equal number of atoms of uranium and lead ($t_{1/2}$ for U = 4.5×10^{9} years). The age of the rock would be: **[UGET Manipal (Medical) 2006]**
(a) 9.0×10^{9} years (b) 4.5×10^{9} years
(c) 13.5×10^{9} years (d) 2.25×10^{9} years

[Hint: $t = \frac{2.303}{\lambda}\log_{10}\left[1 + \frac{\text{No. of Pb atoms}}{\text{No. of U atoms}}\right]$

$= \frac{2.303 \times 4.5 \times 10^9}{0.693}\log_{10}(1+1)$]

90. In treatment of cancer, which of the following is used?
(a) $^{131}_{53}I$ (b) $^{32}_{15}P$ (c) $^{60}_{27}Co$ (d) $^{2}_{1}H$

91. In nuclear reactor, chain reaction is controlled by introducing: (AIIMS 1991)
(a) cadmium rod (b) iron rod
(c) platinum rod (d) graphite rod

92. Wooden artifact and freshly cut tree are 7.6 and 15.2 $\min^{-1}\,g^{-1}$ of carbon ($t_{1/2}$ = 5760 years) respectively. The age of the artifact is:
(a) 5760 years (b) $5760 \times \frac{15.2}{7.6}$ years
(c) $5760 \times \frac{7.6}{15.2}$ years (d) $5760 \times (15.2 - 7.6)$ years

[Hint: $t = \frac{2.303}{\lambda}\cdot\log\frac{15.2}{7.6}$ or $t = \frac{2.303 \times 5760}{0.693}\log 2$]

93. The isotope used for dating archaeological finding is:
(a) $^{1}_{1}H$ (b) $^{18}_{8}O$ (c) $^{14}_{6}C$ (d) $^{235}_{92}U$

94. Which one of the following statements is wrong?
(a) Neutron was discovered by Chadwick
(b) Nuclear fission was discovered by Hahn and Strassmann
(c) Polonium was discovered by Madam Curie
(d) Nuclear fusion was discovered by Fermi

95. Neutrons are more effective projectiles than protons because they:
(a) are attracted by nuclei (b) are not repelled by nuclei
(c) travel with high speed (d) none of these

96. The source of enormous energy of sun is:
(a) fusion of hydrogen to form helium
(b) fission of uranium
(c) fusion of deuterium and tritium
(d) fusion of tritium to form helium

97. In the neutron-induced fission of $^{235}_{92}U$; one of the products is $^{90}_{37}Rb$. In this mode, another nuclide and two neutrons are also produced. The other nuclide is: |PMT (HP) 2006|
(a) $^{144}_{54}Xe$ (b) $^{144}_{55}Co$ (c) $^{145}_{55}Co$ (d) $^{143}_{54}Xe$

98. $^{228}_{88}X - 3\alpha - \beta \longrightarrow Y$. The element Y is : |JEE (Orissa) 2008|
(a) $^{216}_{82}Pb$ (b) $^{217}_{82}Pb$
(c) $^{218}_{83}Bi$ (d) $^{216}_{83}Bi$

99. Which radioactive isotope is used to detect tumours?
(a) ^{74}As (b) ^{24}Na (c) ^{131}I (d) ^{60}Co

100. Natural uranium consists of ^{235}U:
(a) 99% (b) 50%
(c) 10% (d) 0.7%

101. In the nuclear reaction, $^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{p}_{q}X + ^{1}_{1}H$ the nucleus X is: (MLNR 1995)
(a) nitrogen of mass 16 (b) nitrogen of mass 17
(c) oxygen of mass 16 (d) oxygen of mass 17

102. The radioactive decay of $^{88}_{35}X$ by a beta emission produces an unstable nucleus which spontaneously emits a neutron. The final product is: (MLNR 1995)
(a) $^{88}_{37}X$ (b) $^{89}_{35}Y$
(c) $^{88}_{34}Z$ (d) $^{87}_{36}W$

103. $^{27}_{13}Al$ is a stable isotope. $^{29}_{13}Al$ is expected to disintegrate by: (IIT 1996)
(a) α-emission (b) β-emission
(c) positron emission (d) proton emission

104. The mass defect of the nuclear reaction $^{8}_{5}B \rightarrow ^{8}_{4}Be + ^{0}_{1}e$ is: (JIPMER 1999)
(a) Δm = atomic mass of $(^{8}_{4}Be - ^{8}_{5}B)$
(b) Δm = atomic mass of $(^{8}_{4}Be - ^{8}_{5}B)$ + mass of one electron
(c) Δm = atomic mass of $(^{8}_{4}Be - ^{8}_{5}B)$ + mass of the positron
(d) Δm = atomic mass of $(^{8}_{4}Be - ^{8}_{5}B)$ + mass of two electrons

105. Which of the following is the man-made radioactive disintegration series?
(a) Thorium series (b) Neptunium series
(c) Uranium series (d) Actinium series

106. The density of nucleus is of the order of:
(a) 10^5 kg m^{-3} (b) 10^{10} kg m^{-3}
(c) 10^{17} kg m^{-3} (d) 10^{25} kg m^{-3}

107. A radioactive isotope having a half life of 3 days was received after 12 days. It was found that there were 3 g of the isotope in the container. The initial weight of the isotope when packed was:
(a) 12 g (b) 24 g
(c) 36 g (d) 48 g

108. A radioactive substance is decaying with $t_{1/2}$ = 30 days. On being separated into two fractions, one of the fractions, immediately after separation, decays with $t_{1/2}$ = 2 days. The other fraction, immediately after separation would show:
(a) constant activity (b) increasing activity
(c) decay with $t_{1/2}$ = 30 days (d) decay with $t_{1/2}$ = 28 days

109. A radioactive substance has a constant activity of 2000 disintegrations per minute. The material is separated into two fractions, one of which has an initial activity of 1000 disintegrations per second while the other fraction decays with $t_{1/2}$ = 24 hours. To the total activity in both samples after 48 hours of separation is:
(a) 1500 (b) 1000 (c) 1250 (d) 2000

110. A radioactive element X has an atomic number of 100. It decays directly into an element Y which decays directly into the element Z. In both processes a charged particle is emitted. Which of the following statements would be true?
(a) Y has an atomic number of 102
(b) Y has an atomic number of 101
(c) Z has an atomic number of 100
(d) Z has an atomic number of 99

111. Three isotopes of an element have mass numbers M, $(M + 1)$ and $(M + 2)$. If the mean mass number is $(M + - 0.5)$, then which of the following ratios may be accepted for M, $(M + 1)$, $(M + 2)$ in that order?
(a) 1 : 1 : 1 (b) 4 : 1 : 1 (c) 3 : 2 : 1 (d) 2 : 1 : 1

112. Enrichment of uranium is made by:
(a) distillation (b) diffusion
(c) evaporation (d) bleaching

113. Let us consider emission of α-particle from uranium nucleus:

$${}_{92}U^{235} - {}_{2}He^{4} \rightarrow {}_{90}Th^{231}$$

$e = 92$ $e = 0$ $e = 90$
$p = 92$ $p = 2$ $p = 90$
$n = 143$ $n = 2$ $n = 141$

Shortage of two electrons in thorium is due to:
(a) conversion of electron to positron
(b) combination with positron to evolve energy
(c) annihilation
(d) absorption in the nucleus

114. Artificial radioactive elements are present in:
(a) *s*-block (b) *p*-block (c) *d*-block (d) *f*-block

115. Half life of ${}_{6}C^{14}$, if its λ is 2.13×10^{-4} yrs, is: (CBSE 1999)
(a) 3.5×10^{4} years (b) 3×10^{3} years
(c) 2×10^{2} years (d) 4×10^{3} years

116. The ${}^{60}Co$ isotope decays with a half life of 5.3 years. How long would it take for 7/8 of a sample of 500 mg of ${}^{60}Co$ to disintegrate? (SCRA 2007)
(a) 21.2 years (b) 15.9 years
(c) 10.6 years (d) 5.3 years

117. Isotope of uranium used in atomic bomb is : [PET (MP) 2008]
(a) ${}^{237}_{92}U$ (b) ${}^{238}_{92}U$ (c) ${}^{239}_{92}U$ (d) ${}^{235}_{92}U$

118. Which among the following is wrong about isodiapheres?
(a) They have the same difference of neutrons and protons or same isotopic number
(b) Nuclide and its decay product after α-emission are isodiapheres
(c) ${}_{Z}A^{M} \longrightarrow {}_{Z-2}B^{M-4} + {}_{2}He^{4}$
'*A*' and '*B*' are isodiapheres
(d) All are correct

119. At radioactive equilibrium, the ratio of two atoms *A* and *B* are $3.1 \times 10^{9} : 1$. If half life of '*A*' is 2×10^{10} yrs, what is half life of '*B*'?
(a) 6.45 yrs (b) 4.65 yrs (c) 5.46 yrs (d) 5.64 yrs

120. The decay constant for an α-decay of Th^{232} is $1.58 \times 10^{-10}\ s^{-1}$. How many α-decays occur from 1 g sample in 365 days?
(a) 2.89×10^{19} (b) 1.298×10^{19}
(c) 8.219×10^{19} (d) None of these

121. What percentage of decay takes place in the average life of a substance?
(a) 63.21% (b) 36.79% (c) 90% (d) 99%

122. SI unit of radioactive decay is: [PMT (MP) 2006]
(a) curie (b) rutherford
(c) becquerel (d) all of these

123. The number of neutrons accompanying the formation of ${}^{139}_{54}Xe$ and ${}^{94}_{38}Sr$ from the absorption of a slow neutron by ${}^{235}_{92}U$, followed by nuclear fission is: (IIT 1999)
(a) 0 (b) 2 (c) 1 (d) 3

124. Thiosulphate ion ($S_2O_3^{2-}$) on acidification changes to SO_2 along with precipitation of sulphur,

$${}^{35}S^{32}SO_3^{2-} + 2H^{+} \longrightarrow H_2O + SO_2 + S$$

which is the correct statement?
(a) S^{35} is in sulphur (b) S^{35} is in SO_2
(c) S^{35} is in both (d) S^{35} is in none

125. A radioactive element decays as,

$$X \xrightarrow[t_{1/2} = 30\text{ min}]{\alpha \text{ decay}} Y \xrightarrow[t_{1/2} = 2\text{ days}]{(-2\beta)\beta \text{ decay}} Z$$

which of the following statements about this decay process is incorrect?
(a) After two hours, less than 10% of the initial *X* is left
(b) Maximum amount of *Y* present at any time before 30 min is less than 50% of the initial amount of *X*
(c) Atomic number of *X* and *Z* are same
(d) The mass number of *Y* is greater than *X*

126. Among the following nuclides, the highest tendency to decay by (β^{+}) emission is:
(a) ${}^{59}Cu$ (b) ${}^{63}Cu$ (c) ${}^{67}Cu$ (d) ${}^{68}Cu$

127. Identify [*A*] and [*B*] in the following:

$${}^{227}_{89}Ac \xrightarrow{-\beta} [A] \xrightarrow{-\alpha} [B] \xrightarrow{-\alpha} Rn$$ [JEE (WB) 2010]

(a) Po, Rn (b) Th, Po (c) Ra, Th (d) Th, Ra

[**Hint:** ${}^{227}_{89}Ac \xrightarrow{-\beta} {}^{227}_{90}Th \xrightarrow{-\alpha} {}^{223}_{88}Ra$]

128. β-particle is emitted in radioactivity by: (AIEEE 2002)
(a) conversion of proton to neutron
(b) from outermost orbit
(c) conversion of neutron to proton
(d) β-particle is not emitted

129. The nuclear reaction,

$${}^{63}_{29}Cu + {}^{4}_{2}He \longrightarrow {}^{37}_{17}Cl + 14\ {}^{1}_{1}H + 16\ {}^{1}_{0}n$$

is referred to as: [PET (MP) 2002]
(a) spallation reaction (b) fusion reaction
(c) fission reaction (d) chain reaction

130. ${}^{226}Ra$ disintegrates at such a rate that after 3160 yrs only one fourth of its original amount remains. Half life of ${}^{226}Ra$ will be: [PET (MP) 2002]
(a) 790 years (b) 3160 years
(c) 1580 years (d) 6230 years

131. ${}^{235}_{92}U$ nucleus absorbs a neutron and disintegrates into ${}^{139}_{54}Xe$, ${}^{94}_{38}Sr$ and '*x*'. What will be the product *x*? [CBSE (PMT) 2002]
(a) 3-neutrons (b) 2-neutrons
(c) α-particles (d) β-particles

132. A radioisotope, tritium (${}^{3}_{1}H$) has half life of 12.3 years. If the initial amount of tritium is 32 mg, how many milligrams of it would remain after 49.2 years? [CBSE (PMT) 2003]
(a) 1 mg (b) 2 mg
(c) 4 mg (d) 8 mg

133. The radio nuclide ${}^{234}_{90}Th$ undergoes two successive β-decays followed by one α-decay. The atomic number and mass number of the resulting radio nuclide are: (AIEEE 2003)

(a) 92, 234 (b) 94, 230 (c) 90, 230 (d) 92, 230

134. The half life of a radioactive isotope is three hours. If the initial mass of isotope were 256 g, the mass of it remaining undecayed after 18 hours would be: (AIEEE 2003)

(a) 4 g (b) 8 g (c) 12 g (d) 16 g

135. Consider the following nuclear reactions:

$${}^{238}_{92}M \rightarrow {}^{X}_{Y}N + 2\,{}^{4}_{2}\text{He};\quad {}^{X}_{Y}N \longrightarrow {}^{A}_{B}L + 2\beta^{+}$$

The number of neutrons in the element L is: (AIEEE 2004)

(a) 142 (b) 144 (c) 140 (d) 146

136. A radioactive element gets spilled over the floor of a room. Its half life period is 30 days. If initial rate is ten times the permissible value, after how many days will it be safe to enter the room? (AIEEE 2007)

(a) 100 days (b) 1000 days
(c) 300 days (d) 10 days

137. A photon of hard gamma radiation knocks a proton out of ${}^{24}_{12}\text{Mg}$ nucleus to form: (AIEEE 2005)

(a) the isotope of parent nucleus
(b) the isobar of parent nucleus
(c) the nuclide of ${}^{23}_{11}\text{Na}$
(d) the isobar of ${}^{23}_{11}\text{Na}$

138. The element ${}^{232}_{90}\text{Th}$ belongs to thorium series. Which of the following will act as the end product of the series? [BHU (Pre.) 2005]

(a) ${}^{208}_{82}\text{Pb}$ (b) ${}^{209}_{82}\text{Bi}$ (c) ${}^{206}_{82}\text{Pb}$ (d) ${}^{207}_{82}\text{Pb}$

139. ${}^{238}_{92}\text{U}$ emits 8α-particles and 6β-particles. The neutron/proton ratio in the product nucleus is: (AIIMS 2005)

(a) 60/41 (b) 61/40 (c) 62/41 (d) 61/42

140. Calculate the mass loss in the following:

$${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n$$

Given the masses: ${}^{2}_{1}\text{H} = 2.014$ amu, ${}^{3}_{1}\text{H} = 3.016$ amu; ${}^{4}_{2}\text{He} = 4.004$ amu, ${}^{1}_{0}n = 1.008$ amu. [PET (Kerala) 2005]

(a) 0.018 amu (b) 0.18 amu
(c) 0.0018 amu (d) 1.8 amu
(e) 18 amu

141. A nuclide of an alkaline earth metal undergoes radioactive decay by emission of the α-particles in succession. The group of the periodic table to which the resulting daughter element would belong is: [CBSE (PMT) 2005]

(a) 4th group (b) 6th group (c) 14th group (d) 16th group

142. In the reaction ${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \longrightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n$, if the binding energies of ${}^{2}_{1}\text{H}$, ${}^{3}_{1}\text{H}$ and ${}^{4}_{2}\text{He}$ are a, b and c (in MeV) respectively, then energy (in MeV) released in this reaction is: [CBSE-PMT (Physics) 2005]

(a) $a + b - c$ (b) $c + a - b$
(c) $c - a - b$ (d) $a + b + c$

143. Two radioactive elements X and Y have half lives 6 min and 15 min respectively. An experiment starts with 8 times as many atoms of X as Y. How long it takes for the number of atoms of X left to equal the number of atoms of Y left? [PET (Kerala) 2008]

(a) 6 min (b) 12 min (c) 48 min (d) 30 min
(e) 24 min

144. Which of the following has the highest value of radioactivity? (DPMT 2009)

(a) 1 g of Ra (b) 1 g of RaSO_4
(c) 1 g of RaBr_2 (d) 1 g of $\text{Ra(HPO}_4\text{)}$

145. An artificial transmutation was carried out on ${}^{14}_{7}\text{N}$ by an α-particle which resulted in an unstable nuclide and a proton. What is the ratio of the atomic mass to the atomic number of the unstable nuclide? (SCRA 2009)

(a) $\frac{17}{8}$ (b) $\frac{15}{7}$ (c) $\frac{17}{9}$ (d) $\frac{15}{8}$

[**Hint :** ${}^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \longrightarrow {}^{17}_{8}\text{O} + {}^{1}_{1}\text{H}$

$$\frac{\text{Mass Number}}{\text{Atomic Number}} = \frac{17}{8}]$$

146. If 0.4 curie be the activity of 1 gram of a radioactive sample whose atomic mass is 226, then what is the half-life period of the sample? (1 curie $= 3.7 \times 10^{10}$ dis sec^{-1}) (SCRA 2009)

(a) 1.2×10^{11} sec (b) 1.8×10^{11} sec
(c) 1.2×10^{10} sec (d) 1.8×10^{10} sec

[**Hint :** Rate of decay $= \frac{0.693}{t_{1/2}} \times \frac{w}{A_w} \times 6.023 \times 10^{23}$

$$0.4 \times 3.7 \times 10^{10} = \frac{0.693}{t_{1/2}} \times \frac{1}{226} \times 6.023 \times 10^{23}$$

$$t_{1/2} = 1.2 \times 10^{11}\ \text{sec}]$$

147. The half-life period of uranium is 4.5 billion years. After 9.0 billion years, the number of moles of helium liberated from the following nuclear reaction will be :

$${}^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

Initially there was 1 mole uranium. [PET (MP) 2010]

(a) 0.75 mol (b) 1.0 mol (c) 11.2 mol (d) 22.4 mol

Set-2: The questions given below may have more than one correct answers

1. Match the following radioactive series:

(A) $4n$ (i) Uranium series
(B) $4n + 1$ (ii) Neptunium series
(C) $4n + 2$ (iii) Actinium series
(D) $4n + 3$ (iv) Thorium series

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(ii)	(i)	(iii)
(c)	(iii)	(i)	(iv)	(ii)
(d)	(ii)	(iii)	(i)	(iv)

2. Match the following reactions:

(A) ${}_{4}\text{Be}^{9} + {}_{2}\text{He}^{4} \rightarrow {}_{6}\text{C}^{12} + \ldots$ (i) ${}_{2}\text{He}^{4}$
(B) ${}_{6}\text{C}^{12} + \ldots \rightarrow {}_{5}\text{B}^{10} + {}_{2}\text{He}^{4}$ (ii) ${}_{0}n^{1}$
(C) ${}_{7}\text{N}^{14} + \ldots \rightarrow {}_{8}\text{O}^{17} + {}_{1}\text{H}^{1}$ (iii) ${}_{1}\text{D}^{2}$
(D) ${}_{20}\text{Ca}^{40} + \ldots \rightarrow {}_{19}\text{K}^{37} + {}_{2}\text{He}^{4}$ (iv) ${}_{1}\text{H}^{1}$

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(ii)	(iii)	(i)	(iv)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(iii)	(ii)	(i)	(iv)

3. A radioactive element is present in VIII group of the periodic table. If it emits one α-particle, the new position of the nuclide will be:

(a) VI B (b) VIII
(c) VII B (d) I B

4. Which statement is true about n/p ratio?
(a) It increases by β-emission
(b) It increases by α-emission
(c) It increases by γ-emission
(d) None of the above

5. How many α and β-particles should be eliminated so that an isodiaphere is formed?
(a) $n\alpha, n\beta$ (b) $n\alpha, (n+1)\beta$
(c) $n\alpha$ (d) $n\beta$

6. Match the following:

Series	Particles emitted
(a) Thorium	(i) $8\alpha, 5\beta$
(b) Neptunium	(ii) $8\alpha, 6\beta$
(c) Actinium	(iii) $6\alpha, 4\beta$
(d) Uranium	(iv) $7\alpha, 4\beta$

	A	B	C	D
(a)	(iv)	(iii)	(ii)	(i)
(b)	(ii)	(i)	(iv)	(iii)
(c)	(iii)	(i)	(iv)	(ii)
(d)	(i)	(ii)	(iii)	(iv)

7. Which of the following are used as control rods in a nuclear reactor?
(a) Cadmium rods (b) Graphite rods
(c) Steel rods (d) All of these

8. Which of the following notations shows the product incorrectly?
(a) $_{96}\text{Cm}^{242}(\alpha, 2n)\,_{97}\text{Bk}^{243}$ (b) $_{5}\text{B}^{10}(\alpha, n)\,_{7}\text{N}^{13}$
(c) $_{7}\text{N}^{14}(n, p)\,_{6}\text{C}^{14}$ (d) $_{14}\text{Si}^{28}(d, n)\,_{15}\text{P}^{29}$

9. Which is true about decay constant (λ)?
(a) Unit is time^{-1}
(b) Value of λ is always less than 1
(c) λ is independent of temperature
(d) λ is defined as the ratio of no. of atoms disintegrating per unit time to the total no. of atoms present at that time

10. Which of the following is not correct? (EAMCET 2006)
(a) Nuclei of atoms participate in nuclear reactions
(b) $^{40}_{20}\text{Ca}$ and $^{40}_{18}\text{Ar}$ are isotones
(c) 1 amu of mass defect is approximately equal to 931.5 MeV
(d) Uranium (U^{238}) series is known as $(4n+2)$ series

11. Correct order of radioactivity is:
(a) $_1\text{H}^1 > {}_1\text{H}^2 > {}_1\text{H}^3$ (b) $_1\text{H}^3 > {}_1\text{H}^2 > {}_1\text{H}^1$
(c) $_1\text{H}^3 > {}_1\text{He}^1 > {}_1\text{H}^2$ (d) $_1\text{H}^3 > {}_1\text{H}^1 = {}_1\text{H}^2$

12. At radioactive equilibrium, the ratio between 2 atoms of radioactive elements A and B is $3 \times 10^9 : 1$. If $t_{1/2}$ of A is 10^{10} yrs what is $t_{1/2}$ of B?
(a) 30 yrs (b) 3 yrs
(c) 3.3 yrs (d) None of these

13. In the sequence of the following nuclear reaction,

$$X_{98}^{238} \xrightarrow{-\alpha} Y \xrightarrow{-\beta} Z \xrightarrow{-\beta} L \xrightarrow{n\alpha} {}_{90}M^{218}$$

what is the value of n?
(a) 3 (b) 4
(c) 5 (d) 6

14. ^{60}Co has $t_{1/2} = 5.3$ years. The time taken for 7/8 of the original sample to disintegrate will be:
(a) 4.6 yrs (b) 9.2 yrs
(c) 10.6 yrs (d) 15.9 yrs

15. Which of the following is/are correct?
(a) α-rays are more penetrating than β-rays
(b) α-rays have greater ionizing power than β-rays
(c) β-particles are not present in the nucleus, yet they are emitted from the nucleus
(d) γ-rays are not emitted simultaneously with α and β-rays

16. Select the wrong statement:
(a) Nuclear isomers contain the same number of protons and neutrons
(b) The decay constant is independent of the amount of the substance taken
(c) One curie = 3.7×10^{10} dis/minute
(d) Actinium series starts with U^{238}

17. In a nuclear reactor, heavy water is used to:
(a) provide high speed to neutrons
(b) reduce the speed of neutrons
(c) capture neutrons produced by nuclear fission
(d) transfer the heat from the nuclear reactor

18. The correct starting material and product of different disintegration series are:
(a) $^{232}\text{Th}, {}^{208}\text{Pb}$ (b) $^{235}\text{U}, {}^{206}\text{Pb}$
(c) $^{238}\text{U}, {}^{207}\text{Pb}$ (d) $^{237}\text{Np}, {}^{209}\text{Bi}$

19. Which of the following is/are not true?
(a) The most radioactive element present in pitchblende is uranium
(b) ^{32}P is used for the treatment of leukaemia
(c) CO_2 present in the air contains ^{12}C only
(d) Omission of γ-rays changes the mass number but not atomic number

20. Which of the following is/are correct?
(a) 1 Curie = 3.7×10^{10} d/s
(b) 1 Rutherford = 10^6 d/s
(c) 1 Becquerel = 1 d/s
(d) 1 Fermi = 10^3 d/s

21. Match the List-I and List-II and select the correct answer using the codes given below the lists:

List-I **Nuclear reactor component**	**List-II** **Substance used**
1. Moderator	A. Uranium
2. Control rods	B. Graphite
3. Fuel rods	C. Boron
4. Coolant	D. Lead
	E. Sodium

[PET (Kerala) 2005]

Codes:

(a) 1—B, 2—A, 3—C, 4—E
(b) 1—B, 2—C, 3—A, 4—E
(c) 1—C, 2—B, 3—A, 4—E
(d) 1—C, 2—D, 3—A, 4—B
(e) 1—D, 2—C, 3—B, 4—A

22. Match the List-I and List-II and select the correct answer using the codes given below the lists:

List-I Isotope	**List-II Characteristics**
A. $^{40}_{20}Ca$	1. Unstable, α-emitter
B. $^{133}_{53}I$	2. Unstable, β-emitter
C. $^{121}_{53}I$	3. Unstable, positron emitter
D. $^{232}_{90}Th$	4. Stable

Codes:	A	B	C	D
(a)	1	2	3	4
(b)	1	3	2	4
(c)	4	3	2	1
(d)	4	2	3	1

23. Match the List-I with List-II and select the correct answer using the codes given below the lists:

List-I Isotope	**List-II Characteristics**
A. ^{32}P	1. Location of tumour in brain
B. ^{24}Na	2. Location of blood clot and circulatory disorders
C. ^{60}Co	3. Radiotherapy
D. ^{131}I	4. Agriculture research

Codes:	A	B	C	D
(a)	4	1	2	3
(b)	4	3	2	1
(c)	4	2	3	1
(d)	3	1	2	4

24. Consider the following nuclear reactions:

1. $^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H$
2. $^{9}_{4}Be + ^{1}_{1}H \longrightarrow ^{9}_{3}Li + ^{4}_{2}He$
3. $^{24}_{12}Mg + ^{4}_{2}He \longrightarrow ^{27}_{14}Si + ^{1}_{0}n$
4. $^{10}_{5}B + ^{4}_{2}He \longrightarrow ^{13}_{7}N + ^{1}_{0}n$

Examples of induced radioactivity would include the reactions:

(a) 3 and 4 (b) 1 and 2 (c) 1, 3 and 4 (d) 1, 2, 3 and 4

25. Match the Column-I Radio-isotope with Column-II Medicinal use and select correct matching:

Column-I	**Column-II**
(I) ^{60}Co	(a) Leucaemia
(II) ^{131}I	(b) Anaemia
(III) ^{59}Fe	(c) Cancerous tumours
(IV) ^{32}P	(d) Disorders of thyroid gland

(a) I—c; II—d; III—a; IV—b
(b) I—a; II—b; III—c, IV—d
(c) I—c; II—d; III—b; IV—a
(d) I—d; II—c; III—b; IV—a

26.

Column-I	**Column-II**
(I) $^{14}_{6}C$	(a) Unstable and β-emitter
(II) $^{24}_{11}Na$	(b) Stable
(III) $^{13}_{7}N$	(c) Unstable, positron emitter
(IV) $^{13}_{6}C$	(d) Unstable, α-emitter

Correct matching is/are:

(a) I only (b) III only
(c) II and IV (d) I and III

27. Which of the following statements is/are correct?

1. A nucleus in an excited state may give up its excitation energy and return to the ground state by emission of electromagnetic γ-radiation.
2. γ-radiations are emitted as secondary effect of α and β-emission.
3. The nuclear isomers produced by γ-ray bombardment have the same atomic and mass number but differ in their life-times (whatever their ground state may be).
4. X-ray and γ-ray are both electromagnetic.

(a) 1 and 2 (b) 1, 2 and 3 (c) 2 and 3 (d) 1, 2, 3 and 4

28. Which of the following statements is/are correct?

1. When an electron is emitted by an atom and its nucleus gets de-excited as a result, the process is called internal conversion.
2. Electron capture and positron emission are identical.
3. Neutrons are emitted in the electron capture process.
4. Pair production is a process which involves the creation of positron-electron pair by a photon of energy 1.02 MeV.

(a) 1 and 2 (b) 1, 2 and 4
(c) 2, 3 and 4 (d) All are wrong

29. A nuclide has mass number (A) and atomic number (Z). During a radioactive process if:

1. both A and Z decrease, the process is called α-decay.
2. A remains unchanged and Z decreases by one, the process is called β^+ or positron decay or K-electron capture.
3. both A and Z remain unchanged, the process is called γ-decay.
4. both A and Z increase, the process is called nuclear isomerism.

The correct answer is:

(a) 1, 2 and 3 (b) 2, 3 and 4
(c) 1, 3 and 4 (d) 1, 2 and 4

30. In the decay process:

$$A \xrightarrow{-\alpha} B \xrightarrow{-\alpha} C \xrightarrow{-\beta} D$$

1. A and B are isobars
2. A and D are isotopes
3. C and D are isobars
4. A and C are isotones

The correct answer is:

(a) 1 and 2 (b) 2 and 3
(c) 3 and 4 (d) 1 and 4

31. The nuclide X undergoes α-decay and another nuclide Y, β^--decay. Which of the following statements are correct?

1. The β^--particles emitted by Y may have widely different speeds.
2. The α-particles emitted by X may have widely different speeds.
3. The α-particles emitted by X will have almost same speed.
4. The β-particles emitted by Y will have the same speed.

(a) 1 and 3 are correct (b) 2 and 3 are correct
(c) 3 and 4 are correct (d) 1 and 4 are correct

32. Fill in the blank space with a suitable answer selected from the list below. Write only the letter (A, B, C, ..., etc) of the correct answer in the blanks.

	Answer
(i) $^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N$	......
(ii) $^{27}_{13}Al + ^{1}_{1}H \longrightarrow ^{24}_{12}Mg + ^{4}_{2}He$	......
(iii) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{140}_{56}Ba + ^{93}_{36}Kr + 3\,^{1}_{0}n$	......
(iv) $^{75}_{33}As + ^{2}_{1}H \longrightarrow ^{56}_{25}Mn + 9\,^{1}_{1}H + 12\,^{1}_{0}n$	......
(v) $^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$	......

Answers:

A: Projectile capture
B: Spallation
C: Fusion
D: Projectile capture and particle emission
E: Fission

Select the correct answers according to the given codes:

Codes:	(i)	(ii)	(iii)	(iv)	(v)
(a)	A	D	E	B	C
(b)	D	C	A	E	B
(c)	A	B	C	D	E
(d)	E	D	C	B	A

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as **Assertion (A)** and **Reason (R)**. While answering these questions you are required to choose any one of the following four:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct and (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If both (A) and (R) are incorrect.
(e) If (A) is incorrect but (R) is correct.

1. (A) Mass numbers of most of the elements are fractional.
(R) Mass numbers are obtained by comparing with the mass number of carbon taken as 12.

2. (A) The activity of 1 g pure uranium-235 will be greater than the same amount present in U_3O_6.
(R) In the combined state, the activity of the radioactive element decreases.

3. (A) α-rays have greater ionising power than β.
(R) α-particles carry 2^+ charge while β-particles carry only 1^- charge.

4. (A) β-particles have greater penetrating power than α-rays but less than γ-rays.
(R) β-particles are lighter than α but heavier than γ.

5. (A) During β-decay, a new element with atomic number greater than one is obtained.
(R) Protons and neutrons keep on changing into one another through meson.

6. (A) The average life of a radioactive element is infinity.
(R) As a radioactive element disintegrates, more of it is formed in nature by itself.

7. (A) Hydrogen bomb is more powerful than atomic bomb.
(R) In hydrogen bomb, reaction is initiated.

8. (A) The archaeological studies are based on the radioactive decay of carbon-14 isotope.
(R) The ratio of C-14 to C-12 in the animals or plants is the same as that in the atmosphere.

9. (A) The reactions taking place in the sun are nuclear fusion reactions.
(R) The main reason for nuclear fusion reactions in the sun is that H_2 is present in the sun's atmosphere so that hydrogen nuclei can fuse to form helium.

10. (A) In a radioactive disintegration, an electron is emitted by the nucleus.
(R) Electrons are always present inside the nucleus.

11. (A) In radioactive disintegrations, $_2He^4$ nuclei can come out of the nucleus but lighter $_2He^3$ can't.
(R) Binding energy of $_2He^3$ is more than that of $_2He^4$.

12. (A) Protons are better projectiles than neutrons.
(R) The neutrons being neutral do not experience repulsion from positively charged nucleus.

13. (A) Enrichment of U^{235} from a mixture containing more abundant U^{238} is based on diffusion of UF_6.
(R) UF_6 is a gaseous compound under ordinary conditions.

14. (A) The nucleus emits β-particles though it doesn't contain any electron in it.
(R) The nucleus shows the transformation $_0n^1 \rightarrow p + \beta +$ anti-neutrino for β-emission.

15. (A) Any kind of exchange force helps the nucleus to be more destabilised.
(R) π-mesons are exchanged between nucleons incessantly.

16. (A) Nuclide $_{13}Al^{30}$ is less stable than $_{20}Ca^{40}$. (IIT 1998)
(R) Nuclides having odd number of protons and neutrons are generally unstable.

17. (A) During β-decay, a new element with atomic number greater than one is obtained.
(R) Protons and neutrons keep on changing into one another with the help of meson.

18. (A) The position of an element in periodic table after emission of one α and two β-particles remains unchanged.
(R) Emission of one α and two β-particles gives isotope of the parent element which acquires same position in the periodic table.

19. (A) Nuclear isomers have same atomic number and same mass number but with different radioactive properties.
(R) $U_{(A)}$ and $U_{(Z)}$ are nuclear isomers.

20. (A) The emission of α-particles results in the formation of isodiapheres of parent element.
(R) Isodiapheres have same isotopic number.

21. (A) $^{238}_{92}\text{U}\,(\text{IIIB}) \xrightarrow{-\alpha} A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C$
(R) Element B will be of IIA group.

22. (A) β-particles are deflected more than α-particles in a given electric field.
(R) Charge on α-particles is larger than on β-particles.

23. (A) The nucleus of gold is stable even though there is a very strong coulombic repulsion among the protons.
(R) The inverse square coulomb force is exactly balanced by another inverse square force which is very powerful, *i.e.*, nuclear force.

24. (A) K-shell electron capture is detected by analysing the wavelength of X-ray emitted.
(R) The wavelength of the X-ray is characteristic of the daughter element and not the parent element.

25. (A) Half life of a radioactive isotope is the time required to decrease its mass number by half.
(R) Half life of radioactive isotopes is independent of initial amount of the isotope.

26. (A) In a nuclear fission process, the total mass of fragments is always greater than the mass of the original nucleus.
(R) Difference in the mass due to the fission of a heavy nucleus is converted into energy according to mass-energy conversion. (SCRA 2007)

Answers : OBJECTIVE QUESTIONS

• Set–1

1. (b) **2.** (d) **3.** (c) **4.** (c) **5.** (d) **6.** (a) **7.** (d) **8.** (d)
9. (e) **10.** (c) **11.** (c) **12.** (b) **13.** (b) **14.** (d) **15.** (a) **16.** (c)
17. (c) **18.** (a) **19.** (c) **20.** (b) **21.** (a) **22.** (d) **23.** (d) **24.** (d)
25. (c) **26.** (a) **27.** (b) **28.** (a) **29.** (a) **30.** (c) **31.** (c) **32.** (d)
33. (c) **34.** (d) **35.** (b) **36.** (b) **37.** (c) **38.** (a) **39.** (c) **40.** (a)
41. (d) **42.** (c) **43.** (a) **44.** (d) **45.** (b) **46.** (a) **47.** (a) **48.** (b)
49. (b) **50.** (d) **51.** (c) **52.** (d) **53.** (b) **54.** (c) **55.** (d) **56.** (c)
57. (a) **58.** (c) **59.** (b) **60.** (d) **61.** (a) **62.** (a) **63.** (c) **64.** (b)
65. (d) **66.** (a) **67.** (a) **68.** (b) **69.** (b) **70.** (a) **71.** (a) **72.** (c)
73. (b) **74.** (c) **75.** (a) **76.** (a) **77.** (a) **78.** (b) **79.** (c) **80.** (d)
81. (a) **82.** (b) **83.** (c) **84.** (d) **85.** (b) **86.** (b) **87.** (d) **88.** (b)
89. (b) **90.** (c) **91.** (a) **92.** (a) **93.** (c) **94.** (d) **95.** (b) **96.** (a)
97. (b) **98.** (b) **99.** (a) **100.** (d) **101.** (d) **102.** (d) **103.** (b) **104.** (d)
105. (b) **106.** (c) **107.** (d) **108.** (b) **109.** (d) **110.** (b,d) **111.** (b) **112.** (b)
113. (b,c) **114.** (d) **115.** (c) **116.** (b) **117.** (d) **118.** (d) **119.** (a) **120.** (b)
121. (a) **122.** (c) **123.** (d) **124.** (a) **125.** (d) **126.** (c) **127.** (d) **128.** (c)
129. (a) **130.** (c) **131.** (b) **132.** (b) **133.** (c) **134.** (a) **135.** (b) **136.** (a)
137. (c) **138.** (a) **139.** (c) **140.** (a) **141.** (c) **142.** (c) **143.** (d) **144.** (a)
145. (a) **146.** (a) **147.** (a)

• Set–2

1. (b) **2.** (b) **3.** (a, b, c) **4.** (b) **5.** (c) **6.** (c) **7.** (a) **8.** (a)
9. (c) **10.** (b) **11.** (b) **12.** (c) **13.** (b) **14.** (d) **15.** (b, c, d) **16.** (c, d)
17. (b, d) **18.** (a, d) **19.** (a, d) **20.** (a, b, c) **21.** (b) **22.** (d) **23.** (c) **24.** (d)
25. (c) **26.** (d) **27.** (d) **28.** (b) **29.** (a) **30.** (b) **31.** (a) **32.** (a)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (d) **2.** (d) **3.** (b) **4.** (a) **5.** (b) **6.** (c) **7.** (b) **8.** (a)
9. (c) **10.** (c) **11.** (c) **12.** (d) **13.** (a) **14.** (a) **15.** (d) **16.** (a)
17. (b) **18.** (a) **19.** (a) **20.** (c) **21.** (b) **22.** (a) **23.** (c) **24.** (b)
25. (d) **26.** (e)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option:

1. The average life of a W gm sample of ${}^{200}\text{Ra}E$ is T seconds and average energy of the β-particles emitted is E MeV. At what rate in watts does the sample emit energy?

(a) $\frac{8WN_0E}{T}\times 10^{-16}$ (b) $\frac{8(\ln 2)WN_0E}{T}\times 10^{-13}$

(c) $\frac{8WN_0E}{T}\times 10^{-13}$ (d) None is correct

[**Hint:** Rate of β-particles emitted per second

$$=\lambda\times\frac{W}{\text{At. wt.}}\times N_0=\frac{1}{T}\times\frac{W}{200}\times N_0$$

Energy evolved per second

$$=\frac{1}{T}\times\frac{W}{200}\times N_0\times E\times 1.6\times 10^{-19}\times 10^6\ \text{J sec}^{-1}$$

$$=\frac{8WN_0E}{T}\times 10^{-16}\ \text{watt per second}]$$

2. In nuclear fission, 0.01% mass is converted into energy. The energy released by the fission of 100 kg mass will be:

(a) 9×10^{15} J (b) 9×10^{11} kJ (c) 9×10^{17} J (d) 9×10^{13} kJ

[**Hint:** $\Delta m = 100\times\frac{0.01}{100}=0.01$ kg

$$E=\Delta mc^2=0.01\times(3\times 10^8)^2\ \text{J}$$

$$=9\times 10^{14}\ \text{J}=9\times 10^{11}\ \text{kJ}]$$

3. The activity of a radioactive substance is R_1 at time t_1 and R_2 at time $t_2\ (>t_1)$. Its decay constant is λ. Then:

(a) $R_1t_1=R_2t_2$ (b) $R_2=R_1e^{\lambda(t_2-t_1)}$

(c) $R_2=R_1e^{\lambda(t_1-t_2)}$ (d) $\frac{R_1-R_2}{t_2-t_1}=\text{constant}$

[**Hint:** $\frac{R_2}{R_1}=\frac{R_0\,e^{-\lambda t_2}}{R_0\,e^{-\lambda t_1}}$, $R_2=R_1e^{\lambda(t_1-t_2)}$]

4. The age of a specimen 't' is related to the daughter/parent ratio by the equation:

(a) $t=\frac{1}{\lambda}\ln\left(\frac{D}{P}\right)$ (b) $t=\frac{1}{\lambda}\ln\left(1+\frac{P}{D}\right)$

(c) $t=\frac{1}{\lambda}\ln\left(1+\frac{D}{P}\right)$ (d) $t=\frac{1}{\lambda}\ln\left(2+\frac{D}{P}\right)$

5. A radioactive substance is being produced at a constant rate of 200 nuclei/sec. The decay constant of the substance is 1 sec^{-1}. After what time will the number of radioactive nuclei become 100? Initially, there are no nuclei present.

(a) 1 sec (b) 2 sec (c) ln (2) sec (d) $\frac{1}{\ln(2)}$ sec

[**Hint:** $N=N_0\,e^{-\lambda t}$

$$100=200e^{-1\times t}$$

$$\frac{1}{2}=e^{-t}$$

$$t=\ln(2)\ \text{sec}]$$

6. The rate of decay of a radioactive sample is given by R_1 at time t_1 and R_2 at a later time t_2. The mean life of this radioactive sample is:

(a) $T=\frac{R_1}{R_2}\times\frac{t_2}{t_1}$ (b) $T=\frac{t_1-t_2}{\ln(R_2/R_1)}$

(c) $T=\frac{t_2-t_1}{\ln(R_2/R_1)}$ (d) $T=\frac{\ln(R_2/R_1)}{t_1-t_2}$

[**Hint:** $R_2=R_0e^{-\lambda t_2}$

$$R_1=R_0\,e^{-\lambda t_1}$$

On dividing the above equations, we get

$$\frac{R_2}{R_1}=e^{\lambda(t_1-t_2)}$$

$$\ln\left(\frac{R_2}{R_1}\right)=\lambda(t_1-t_2)$$

$$\frac{1}{\lambda}=\frac{(t_1-t_2)}{\ln(R_2/R_1)}$$

$$T=\frac{(t_1-t_2)}{\ln(R_2/R_1)}\ ]$$

7. Isodiapheres are the atoms of two elements having same values of:

(a) p/n (b) $(p-n)$ (c) $(n-p)$ (d) $n\times p$

[**Hint:** Isodiapheres are formed by α-decay

$${}^M_ZA-{}^4_2\text{He}\longrightarrow{}^{M-4}_{Z-2}B$$

$(n-p)$ in ${}^M_ZA=(M-Z)-Z=(M-2Z)$

$(n-p)$ in ${}^{M-4}_{Z-2}B=\{(M-4)-(Z-2)\}-(Z-2)$

$$=\{M-Z-2\}-Z+2$$

$$=(M-2Z)$$

$\therefore (n-p)$ of isodiapheres are same.]

8. In a sample of radioactive material, what fraction of the initial number of active nuclei will remain undisintegrated after half of a half life of the sample?

(a) $\frac{1}{4}$ (b) $\frac{1}{2\sqrt{2}}$ (c) $\frac{1}{\sqrt{2}}$, (d) $\sqrt{2}-1$

[**Hint:** $\frac{0.693}{t_{1/2}}=\frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$

$$\frac{2.303\times\log 2}{t_{1/2}}=\frac{2.303}{(t_{1/2}/2)}\log_{10}\left(\frac{N_0}{N}\right)$$

$$\log_{10}(2^{1/2})=\log_{10}\left(\frac{N_0}{N}\right)$$

$$\left(\frac{N}{N_0}\right)=\frac{1}{\sqrt{2}}]$$

9. Let T be the mean life of a radioactive sample. 75% of the active nuclei present in the sample initially will decay in time:

(a) $2T$ (b) $\frac{1}{2}(\log_e 2)T$ (c) $4T$ (d) $2(\log_e 2)T$

10. $^{218}_{84}\text{Po}$ ($t_{1/2} = 183$ sec) decays to $^{214}_{82}\text{Pb}$ ($t_{1/2} = 161$ sec) by α-emission, while $^{214}_{82}\text{Pb}$ decays by β-emission. In how much time the number of nuclei of $^{214}_{82}\text{Pb}$ will reach to the maximum?

(a) 182 sec (b) 247.5 sec (c) 308 sec (d) 194.8 sec

[Hint: $^{218}_{84}\text{Po} \xrightarrow{\lambda_1 = \frac{0.693}{183} = (3.786 \times 10^{-3}\ \text{sec}^{-1})}$

$^{214}_{82}\text{Pb} \xrightarrow{\lambda_2 = \frac{0.693}{161} = 4304 \times 10^{-3}\ \text{sec}^{-1}}$

$$t_{\max} = \frac{2.303}{\lambda_1 - \lambda_2} \log \frac{\lambda_1}{\lambda_2}$$

$$= \frac{2.303}{3.786 \times 10^{-3} - 4.304 \times 10^{-3}} \log \frac{3.786 \times 10^{-3}}{4.304 \times 10^{-3}}$$

$$= -\frac{2.303}{5.183 \times 10^{-4}}[-0.05569]$$

$= 247.5$ sec]

11. Fusion reaction takes place at high temperature because:

(a) atoms are ionised at high temperature

(b) molecules break up at high temperature

(c) nuclei break up at high temperature

(d) kinetic energy is high enough to overcome repulsion between nuclei

12. In the radioactive change,

$$^{A}_{Z}P \longrightarrow {}^{A}_{Z+1}Q \longrightarrow {}^{A-4}_{Z-1}R \longrightarrow {}^{A-4}_{Z-1}S$$

the radiations emitted in sequence are:

(a) α, β, γ (b) β, α, γ (c) γ, α, β (d) β, γ, α

13. The half life of a radioactive isotope is 3 hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be:

(a) 12 g (b) 16 g (c) 4 g (d) 8 g

[Hint: $N = N_0\left(\frac{1}{2}\right)^n$ n = number of half lives $= \frac{18}{3} = 6$

$$= 256\left(\frac{1}{2}\right)^6 = 4 \text{ g}]$$

14. In an old rock, the mass ratio of $^{238}_{92}\text{U}$ to $^{206}_{82}\text{Pb}$ is found to be 595 : 103. The age of the rock is (Mean life of $^{238}_{92}\text{U}$ is T_0):

(a) $T_0 \ln 1.2$ (b) $T_0 \ln \frac{698}{595}$ (c) $T_0 \frac{\ln 1.2}{\ln 2}$ (d) $T_0 \frac{\ln \frac{698}{595}}{\ln 2}$

[Hint: $\lambda = \frac{2.303}{t} \log\left(\frac{N_0}{N}\right)$

$$\frac{1}{T_0} = \frac{1}{t} \ln\left(\frac{595 + 103}{595}\right)$$

$$t = T_0 \ln\left(\frac{698}{595}\right)\ ]$$

15. 80% of the radioactive nuclei present in a sample are found to remain undecayed after one day. The percentage of undecayed nuclei left after two days will be:

(a) 64 (b) 20 (c) 46 (d) 80

[Hint: $\lambda = \frac{2.303}{t} \log\left(\frac{N_0}{N}\right)$

$$= \frac{2.303}{1} \log\left(\frac{100}{80}\right) \quad \text{...(i)}$$

$$\lambda = \frac{2.303}{2} \log\left(\frac{100}{N}\right) \quad \text{...(ii)}$$

$$\frac{2.303}{1} \log\left(\frac{100}{80}\right) = \frac{2.303}{2} \log\left(\frac{100}{N}\right)$$

$$\left(\frac{5}{4}\right)^2 = \frac{100}{N}$$

$N = 64$]

16. A sample of radioactive material has mass 'm', decay constant λ and molecular mass 'M'. If N_A is Avogadro's number, the initial activity of the sample is:

(a) λm (b) $\lambda \frac{m}{M}$ (c) $\frac{\lambda m N_A}{M}$ (d) mMe^{λ}

17. A radioactive nucleus can decay by two different processes. The mean value period for the first process is Z_1 and that for the second process is Z_2. The effective mean value period for the two processes is:

(a) $\frac{Z_1 + Z_2}{2}$ (b) $Z_1 + Z_2$ (c) $\sqrt{Z_1 Z_2}$ (d) $\frac{Z_1 Z_2}{Z_1 + Z_2}$

18. The radioactivity of a sample is R_1 at time T_1 and R_2 at time T_2. If the half life of specimen is T, the number of atoms that have disintegrated in time $(T_2 - T_1)$ is proportional to:

(a) $(R_1 T_1 - R_2 T_2)$ (b) $R_1 - R_2$

(c) $\frac{(R_1 - R_2)}{T}$ (d) $(R_2 - R_1)T$

[Hint: Rate = λ × Number of atoms of element yet not decayed.

$R_1 = \lambda \times N_1$

$R_2 = \lambda \times N_2$

Number of atoms decayed in time $(T_2 - T_1)$

$$= \frac{R_2}{\lambda} - \frac{R_1}{\lambda} = \frac{(R_2 - R_1)}{\lambda} = \frac{T(R_2 - R_1)}{0.693}$$

$\therefore$ Number of atoms decayed in time $(T_2 - T_1) \propto T(R_2 - R_1)$]

19. Half life period of lead is:

(a) zero (b) infinite (c) 1590 years (d) 1590 days

20. A freshly prepared radioactive sample of half life 2 hours emits radiation of intensity which is 64 times the permissible safe level. The minimum time after which it would be possible to work safely with this source is:

(a) 6 hrs (b) 12 hrs (c) 24 hrs (d) 128 hrs

[Hint: $N = N_0\left(\frac{1}{2}\right)^n$

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$$

$$\frac{1}{64} = \left(\frac{1}{2}\right)^n$$

$n = 6$

$\therefore$ $t = 2 \times 6 = 12$ hours]

21. Which of the following is the best nuclear fuel?

(a) ^{238}U (b) ^{236}Th (c) ^{239}Pu (d) ^{239}Np

22. A radioactive element decays by parallel path as given below:

$$A \xrightarrow{\lambda_1} B \qquad \lambda_1 = 1.8 \times 10^{-2}\ sec^{-1}$$

$$2A \xrightarrow{\lambda_2} B \qquad \lambda_2 = 10^{-3}\ sec^{-1}$$

Average life of radio-nuclide A will be:

(a) 52.63 sec (b) 500 sec (c) 50 sec (d) 120 sec

[**Hint :**
$$\lambda = \lambda_1 + 2\lambda_2$$
$$= 1.8 \times 10^{-2} + 2 \times 10^{-3}$$
$$= 2 \times 10^{-2}\ sec^{-1}$$
$$\tau = \frac{1}{\lambda} = \frac{1}{2 \times 10^{-2}} = 50\ sec]$$

23. Among the following, which has the longest half life?

(a) $^{232}_{90}Th$ (b) $^{237}_{93}Np$ (c) $^{238}_{92}U$ (d) $^{235}_{92}U$

24. Which of the following is likely to be least stable?

(SCRA 2007)

(a) $^{40}_{20}Ca$ (b) $^{55}_{25}Mn$ (c) $^{119}_{50}Sn$ (d) $^{30}_{13}Al$

[**Hint:**	$^{40}_{20}Ca$	$^{55}_{25}Mn$	$^{119}_{50}Sn$	$^{30}_{13}Al$
$\frac{n}{p}$	$\frac{20}{20} = 1$	$\frac{30}{25} = 1.2$	$\frac{69}{50} = 1.38$	$\frac{17}{13} = 1.31$

All are stable according to n/p rule but experimental observations confirm that $^{30}_{13}Al$ is radioactive with half life of 3.7 sec]

25. $^{27}_{13}Al$ is a stable isotope. $^{29}_{13}Al$ is expected to disintegrate by:

(a) α-emission (b) β-emission

(c) positron emission (d) proton emission

[**Hint:** Number of neutrons will be reduced by β-decay.

$$^1_0n \longrightarrow {}^1_1H + {}_{-1}^{0}e + \text{Antineutrino} + \text{Energy}]$$

26. For a radioactive element, a graph of log N against time has a slope equal to:

(a) $+2.303\lambda$ (b) $+\frac{\lambda}{2.303}$ (c) $-\frac{\lambda}{2.303}$ (d) -2.303λ

[**Hint:**
$$\log N_0 - \log N = \frac{\lambda t}{2.303}$$
$$\log N = \left(\frac{-\lambda}{2.303}\right) t + \log N_0$$
$$Y = Mx + C$$
$$\therefore \quad \text{Slope } (M) = \frac{-\lambda}{2.303}\ ]$$

27. Two elements P and Q have half lives of 10 and 15 minutes respectively. Freshly prepared samples of each isotope initially contain the same number of atoms as each other. After 30 minutes, the ratio $\frac{\text{number of } P \text{ atoms}}{\text{number of } Q \text{ atoms}}$ will be:

(a) 0.5 (b) 2 (c) 1 (d) 3

[**Hint:** In 30 minutes, there will be 3 half lives of P and 2 half lives of Q.

∴ Number of P atoms will be 1/8 th and number of Q atoms will be 1/4th of original atoms.

Then, $\frac{\text{Number of atoms of } P}{\text{Number of atoms of } Q} = \frac{1/8}{1/4} = \frac{1}{2}$, *i.e.*, 0.5]

28. Select the wrong statement among the following:

(a) Antineutrino can be detected during β-emission

(b) Neutrino was predicted to conserve the spin of a nuclear reaction

(c) Synchrotron can accelerate neutrons

(d) Area of cross-section of nucleus is about 1 barn (1 barn $= 10^{-24}$ cm^2)

[**Hint:** Synchrotron can accelerate only charged particles, not the neutral particles like neutron.]

29. A radioactive atom 'X' emits a β-particle to produce an atom 'Y' which then emits an α-particle to give an atom 'Z':

(1) The atomic number of 'X' is less than that of 'Z'

(2) The atomic number of 'Y' is less than that of 'Z'

(3) The mass number of 'X' is same as that of 'Y'

(a) 1, 2 and 3 are correct

(b) 1 and 2 are correct

(c) 2 and 3 are correct

(d) 3 is correct

30. Which one of the following is an exact example of artificial radioactivity?

(a) $^{23}_{11}Na + {}^1_0n \longrightarrow {}^{24}_{11}Na + \gamma$

$^{24}_{11}Na + {}^1_1H \longrightarrow {}^{24}_{12}Mg + {}^1_0n$

(b) $^4_2He + {}^{14}_7N \longrightarrow {}^{17}_8O + {}^1_1H$

$^{17}_8O + {}^1_0n \longrightarrow {}^{18}_7O + \gamma$

(c) $^4_2He + {}^{27}_{13}Al \longrightarrow {}^{30}_{15}P + {}^1_0n$

$^{30}_{15}P \longrightarrow {}^{30}_{14}Si + {}^{0}_{+1}e$

(d) $^{228}_{89}Ac \longrightarrow {}^{228}_{90}Th + \beta$

$^{228}_{90}Th \longrightarrow {}^{224}_{88}Ra + \alpha$

31. Consider the following decay series:

$$A \longrightarrow B \longrightarrow C \longrightarrow D$$

Where, A, B and C are radioactive elements with half lives of 4.5 sec, 15 days and 1 sec respectively and D is non-radioactive element. Starting with 1 mole of A, the number of moles of A, B, C and D left after 30 days are:

(a) one mole of D and none of A, B or C

(b) 3/4 mol of B, 1/4 mol of D and none of A or C

(c) 1/4 mol of B, 3/4 mol of D and none of A or C

(d) 1/2 mol of B, 1/4 mol of C, 1/4 mol of D and none of A

(e) 1/4 mol of each A, B, C and D

32. Consider the following nuclear reactions:

$$^{238}_{92}M \longrightarrow {}^x_yN + 2\,{}^4_2He$$
$$^x_yN \longrightarrow {}^A_BL + 2\beta^+$$

the number of neutrons present in the element 'L' is:

(a) 142 (b) 144

(c) 140 (d) 146

33. If n_t is the number of radio-atoms present at time 't', the following expression will be a constant:

[JEE (West Bengal) 2009]

(a) $\frac{n_t}{t}$ (b) $\frac{\ln n_t}{t}$

(c) $\frac{d \ln n_t}{dt}$ (d) $t\,n_t$

[Hint : $-\dfrac{dn_t}{dt} = \lambda n_t$

$$-\frac{1}{n_t}\frac{dn_t}{dt} = \lambda$$

$$\frac{d}{dt}(l_n n_t) = -\lambda \text{ (constant)}]$$

34. $^{214}_{83}\text{Bi} \xrightarrow{\alpha\text{-emission}} A \xrightarrow{\beta\text{-emission}} B \xrightarrow{\beta\text{-emission}} C$

$$\xrightarrow{\beta\text{-emission}} D \xrightarrow{\alpha\text{-emission}} E$$

'*E*' is an element of stable nucleus. What is the element '*E*'?

(a) $^{207}_{81}\text{Tl}$ (b) $^{206}_{82}\text{Pb}$ (c) $^{206}_{80}\text{Hg}$ (d) $^{206}_{79}\text{Au}$

35. A radioactive element decays to one third of its initial amount in time '*t*'. What fraction of the element would be left after 0.5 *t* time ?

(a) $\dfrac{1}{\sqrt{3}}$ (b) $\dfrac{1}{2}$ (c) $\dfrac{1}{3}$ (d) $\sqrt{\dfrac{2}{3}}$

[Hint : $\lambda = \dfrac{2.303}{t}\log\left(\dfrac{N_0}{N}\right)$

$$\frac{N}{N_0} = \frac{1}{3} \text{ in time '}t\text{'}$$

$$\therefore \quad \lambda = \frac{2.303}{t}\log_{10} 3 \qquad \text{...(i)}$$

After 0.5 *t* time :

$$\lambda = \frac{2.303}{0.5t}\log\left(\frac{N_0}{N}\right) \qquad \text{...(ii)}$$

Equating (i) and (ii) we get

$$\frac{N}{N_0} = \frac{1}{\sqrt{3}}]$$

36. Two radioactive isotopes *A* and *B* of atomic mass *X* and *Y* are mixed in equal amount by mass. After 20 days, their mass ratio is found to be 1 : 4. Half life of '*A*' is 1 day. What will be the half life of *B* ?

(a) 1.11 day (b) 0.6237 day

(c) $0.11\dfrac{X}{Y}$ day (d) $1.11\dfrac{Y}{X}$ day

[Hint : Let 1 g of both *A* and *B* are taken initially. W_A and W_B are the amounts left after 20 days.

$$\lambda_A = \frac{2.303}{20}\log\frac{1}{W_A}$$

$$\lambda_B = \frac{2.303}{20}\log\frac{1}{W_B}$$

$$\lambda_A - \lambda_B = \frac{2.303}{20}\log\frac{W_B}{W_A}$$

$$= \frac{2.303}{20}\log 4 = 0.0693$$

$$\lambda_B = \lambda_A - 0.0693 = \frac{0.693}{t_{1/2}} - 0.0693$$

$$= \frac{0.693}{1} - 0.0693 = 0.6237$$

$$t_{1/2}B = \frac{0.693}{0.6237} = 1.11 \text{ day}]$$

37. A sample of rock from the moon was found to contain the elements *X* and *Y* in 1:7 ratio by mole. Element *X* is radioactive, it decays to *Y* with half life of 6.93×10^9 years

$$X \longrightarrow Y$$

$$t_{1/2} = 6.93 \times 10^9 \text{ yrs}]$$

What is the age of the rock?

(a) 2.079×10^{10} years (b) 1.33×10^9 years

(c) 1.94×10^{10} years (d) 10^{10} years

[Hint : $N_0 = 1 + 7 = 8$ (Initial moles of *X*)

$N = 1$ (Remaining moles of *X*)

We know,

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{6.93 \times 10^9} = \frac{2.303}{t}\log\frac{8}{1}$$

$$t = 2.079 \times 10^{10} \text{ years}]$$

38. If the relation between time of decay (*t*) and half life period ($t_{1/2}$) is ($t = 4\,t_{1/2}$); the relation between *t* and mean life (*T*) is:

(a) $\dfrac{\ln 2}{T^2}$ (b) $2T^4 \ln 2$ (c) $4T \ln 2$ (d) $2T \ln 2$

Following questions may have more than one correct options:

1. Which of the following nuclei are doubly magic?

   (a) $^{4}_{2}\text{He}$ (b) $^{16}_{8}\text{O}$ (c) $^{208}_{82}\text{Pb}$ (d) $^{238}_{92}\text{U}$

2. Which of the following make up an isotonic triad?

   (a) $^{14}_{6}\text{C}, ^{16}_{8}\text{O}, ^{15}_{7}\text{N}$ (b) $^{76}_{32}\text{Ge}, ^{77}_{33}\text{As}, ^{75}_{31}\text{Ga}$

   (c) $^{40}_{18}\text{Ar}, ^{40}_{19}\text{K}, ^{40}_{20}\text{Ca}$ (d) $^{233}_{92}\text{U}, ^{232}_{90}\text{Th}, ^{239}_{94}\text{Pu}$

3. In the decay process:

   $$A \xrightarrow{-\alpha} B \xrightarrow{-\beta} C \xrightarrow{-\beta} D$$ MU (Med.) 2010]

   (a) *A* and *B* are isodiapheres (b) *A* and *D* are isotopes

   (c) *B*, *C* and *D* are isobars (d) *A* and *C* are isotones

4. A nuclide *X* undergoes α-decay and another nuclide *Y* undergoes β-decay. Which of the following statements are correct?

   (a) The β-particles emitted by *Y* may have widely different speeds

   (b) The α-particles emitted by *X* may have widely different speeds

   (c) The α-particles emitted by *X* will have almost the same speed

   (d) The β-particles emitted by *Y* will have the same speed

5. Which among the following nuclides is/are likely to be stable?

   (a) $^{30}_{15}\text{P}$ (b) $^{24}_{12}\text{Mg}$ (c) $^{114}_{49}\text{In}$ (d) $^{114}_{48}\text{Cd}$

6. Which among the following is/are fissile?

   (a) $^{235}_{92}\text{U}$ (b) $^{238}_{92}\text{U}$ (c) $^{239}_{94}\text{Pu}$ (d) $^{238}_{94}\text{Pu}$

7. Select the correct statements among the following:

   (a) The decay of mass during nuclear fusion and nuclear fission are 0.1% and 0.231% respectively

   (b) Lesser is the half life, more dangerous is the radioactive element

   (c) *K*-electron capture emits γ-rays

   (d) Nuclear forces are about 10^{21} times stronger than coulombic forces

8. A radioactive element has atomic number '*Z*' and mass number '*A*'. Select the correct statements among the following:
(a) Both '*A*' and '*Z*' decrease in α-decay
(b) Both '*A*' and '*Z*' remain unchanged in γ-decay
(c) '*A*' remains unchanged and '*Z*' decreases by one; the process is called β^+ (positron) decay or *K*-electron capture
(d) Both '*A*' and '*Z*' increase in the nuclear isomerism

9. When nucleus of an electrically neutral atom undergoes a radioactive decay process, it will remain neutral after the decay if the process is:
(a) an α-decay (b) a β-decay
(c) a γ-decay (d) a *K*-capture process

10. Which of the following is/are characteristics of nuclear forces?
(a) These forces operate within small distances of 2×10^{-13} cm
(b) These forces drop to zero rapidly at a distance greater than 1.4×10^2 fermi
(c) They follow inverse square law
(d) They are stronger than electrostatic forces of attraction

11. The correct starting material and end product of different disintegration series are:
(a) $^{232}Th, ^{208}Pb$ (b) $^{235}U, ^{206}Pb$
(c) $^{238}U, ^{207}Pb$ (d) $^{237}Np, ^{209}Bi$

12. Select the wrong statement(s):
(a) Nuclear isomers contain the same number of protons and neutrons
(b) The decay constant is independent of the amount of the substance taken
(c) 1 curie = 3.7×10^{10} dis
(d) Actinium series starts with ^{238}U

13. Which of the following are synthetic elements?
(a) Tc (b) Pu (c) Np (d) U

14. Which of the following nuclides belong to actinium (U^{235}) series?
(a) ^{213}Po (b) ^{215}Po (c) ^{222}Rn (d) ^{207}Pb

15. In a nuclear reactor, heavy water is used to:
(a) transfer the heat from the reactor
(b) provide high speed neutrons for the fission reaction
(c) reduce the speed of fast moving neutrons
(d) increase the speed of neutrons

Answers

• Single correct option

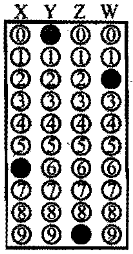
1. (a)	2. (b)	3. (c)	4. (c)	5. (b)	6. (b)	7. (c)	8. (c)
9. (d)	10. (b)	11. (d)	12. (b)	13. (c)	14. (b)	15. (a)	16. (c)
17. (d)	18. (d)	19. (b)	20. (b)	21. (c)	22. (c)	23. (a)	24. (d)
25. (b)	26. (c)	27. (a)	28. (c)	29. (d)	30. (c)	31. (d)	32. (b)
33. (c)	34. (b)	35. (a)	36. (a)	37. (a)	38. (c)		

• One or more than one correct options

1. (a, b, c)	2. (a, b)	3. (a, b, c)	4. (a, c)	5. (b, d)	6. (a, c)	7. (a, b, d)	8. (a, b, c)
9. (c, d)	10. (a, b, d)	11. (a, d)	12. (a, b)	13. (a, b, c)	14. (b, d)	15. (a, c)	

Integer Answer TYPE QUESTIONS

This section contains 7 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. The total number of α and β particles emitted in the nuclear reaction : $^{238}_{92}U \longrightarrow ^{214}_{82}Pb$ is : (IIT 2009)
2. The $t_{1/2}$ of a radionuclide is 8 hours. Starting with 40 g of the isotope, the amount in gm remaining after one day will be:
3. If $\frac{3}{4}$ quantity of a radioactive nuclide disintegrates in two hours, its half-life (in hour) will be:
4. $^{7}_{4}Be$ captures a *K*-electron into its nucleus. What will be the mass number of resulting nuclide?
   [**Hint** : In *K*-electron capture, a proton of nucleus changes into neutron.
   $$^{1}_{1}H + ^{0}_{-1}e \longrightarrow ^{1}_{0}n$$
   $$^{7}_{4}Be + ^{0}_{-1}e \longrightarrow ^{7}_{3}Li$$
5. $^{232}_{90}Th$ disintegrates to $^{208}_{82}Pb$. How many of β-particles are evolved?
6. What mass in milligram of ^{226}Ra, whose ($t_{1/2} = 1620$ yr), will be required to yield 1 millicurie of radiation?
7. The number of neutrons emitted when $^{235}_{92}U$ undergoes controlled nuclear fission to $^{142}_{54}Xe$ and $^{90}_{38}Sr$ is: (IIT 2010)
   [**Hint** : $^{235}_{92}U \longrightarrow ^{142}_{54}Xe + ^{90}_{38}Sr + 3\,[^{1}_{0}n]$]

Answers

1. (8) 2. (5) 3. (1) 4. (7) 5. (4) 6. (1) 7. (3)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

There are four radioactive decay series called thorium (4n); uranium (4n + 2); actinium (4n + 3) and neptunium (4n + 1) series. Neptunium series is artificial while other three series are natural. End products of each radioactive decay series have stable nuclei. All natural decay series terminate at lead but neptunium or artificial series terminates at bismuth.

Answer the following questions:

1. The end product formed in the disintegration of $^{222}_{88}Ra$ is:
(a) $^{204}_{81}Tl$ (b) $^{206}_{82}Pb$ (c) $^{222}_{86}Rn$ (d) $^{207}_{83}Bi$

2. Actinium series begins with an isotope of:
(a) actinium (b) radium (c) uranium (d) polonium

3. $^{219}_{86}Rn$ is a member of actinium series. Another member of same series is:
(a) $^{235}_{92}U$ (b) $^{222}_{89}Ac$ (c) $^{212}_{90}Th$ (d) $^{212}_{84}Po$

4. The end products of uranium and actinium series are respectively:
(a) ^{206}Pb, ^{207}Pb (b) ^{206}Pb, ^{208}Pb
(c) ^{207}Pb, ^{208}Pb (d) ^{206}Pb, ^{208}Bi

5. The starting isotope and the end product isotope of actinium series are:
(a) $^{227}_{88}Ac$ and $^{208}_{82}Pb$ (b) $^{235}_{92}U$ and $^{207}_{82}Pb$
(c) $^{238}_{92}U$ and $^{207}_{82}Pb$ (d) $^{235}_{92}U$ and $^{208}_{82}Pb$

• Passage 2

Initially the earth was a fire-ball; slowly it has cooled to form earth crust and its different layers. At the beginning $^{238}_{92}U$ was present and no $^{206}_{82}Pb$ was there. With the passage of time, uranium decayed to $^{206}_{82}Pb$. The decay process is:

$$^{238}_{92}U \xrightarrow[(x\alpha,\ y\beta)]{} {}^{206}_{82}Pb; \quad t_{1/2} \text{ of } {}^{238}U = 4.5\times10^{9} \ yrs$$

Answer the following questions:

1. x and y in above decay series are:
(a) 6, 8 (b) 8, 6 (c) 8, 8 (d) 6, 6

2. A sample of rock from South America contains equal number of atoms of ^{238}U and ^{206}Pb. The age of the rock will be:
(a) 4.5×10^{9} years (b) 9×10^{9} years
(c) 13.5×10^{9} years (d) 2.25×10^{9} years

[**Hint:** $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{age}}\log\left(\frac{N_0}{N}\right)$

$\frac{0.693}{4.5\times10^{9}} = \frac{2.303}{t_{age}}\log\left(\frac{2}{1}\right)$

$t_{age} = 4.5\times10^{9}$ yrs.

$N_0 = 1 + 1 = 2, \quad N = 1$]

3. Atomic mass of ^{238}U is 238.125 amu. Its packing fraction will be:
(a) 5.25 (b) 0.125 (c) 12.5 (d) 1.25

4. The analysis of a rock shows the relative number of ^{238}U and ^{206}Pb atoms (Pb/U = 0.25). The age of rock will be:
(a) $\frac{2.303}{0.693}\times4.5\times10^{9}\log1.25$ (b) $\frac{2.303}{0.693}\times4.5\times10^{9}\log0.25$
(c) $\frac{2.303}{0.693}\times4.5\times10^{9}\log4$ (d) $\frac{2.303}{4.5\times10^{9}}\times0.693\log4$

Nathan Thomson, one of the first inhabitants of Lord Howe Island, decided to plant some European deciduous trees in his garden. Unfortunately the exact timing of planting the seeds is not known. Over the years, pollen produced by the trees accumulated at the bottom of the lake near Nathan's house. Very small quantities of radioactive ^{210}Pb ($t_{1/2}$ = 22.3 years) were deposited at the same time. Note that European deciduous trees pollinate in their first year of growth.

In 1995, a team of researchers sampled a sediment core from the bottom of the lake. The examination of sediment core found that:

(a) Pollen of trees first occurs at the depth of 50 cm.

(b) The activity of ^{210}Pb at the top of sediment core is 356 Bq / kg and at 50 cm depth 1.40 Bq / kg.

Answer the following questions:

5. In what year did Nathan Thomson plant the seeds?
(a) 1719 ± 2 (b) 1819 ± 2 (c) 1519 ± 2 (d) 1919 ± 2

[**Hint:** $\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{age}}\log\left(\frac{N_0}{N}\right)$

$\frac{0.693}{22.3} = \frac{2.303}{t_{age}}\log\left(\frac{356}{1.40}\right)$

$t_{age} = 176$ yrs]

6. Which step in the decay scheme explains how ^{210}Pb ends up in rain water while its parent ^{238}U is only present in earth's crust?
(a) ^{238}U — ^{234}U (b) ^{234}U — ^{230}Th
(c) ^{230}Th — ^{226}Ra (d) ^{226}Ra — ^{222}Rn

• Passage 3

In the atmosphere, carbon dioxide is found in two forms, i.e., $^{12}CO_2$ and $^{14}CO_2$. Plants absorb CO_2 during photosynthesis. In presence of chlorophyll, plants synthesise glucose.

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2\uparrow$$

Half life of ^{14}C is 5760 years. The analysis of wooden artifacts for ^{14}C and ^{12}C gives useful information for determination of its age.

All living organisms; because of their constant exchange of CO_2 with the surroundings have the same ratio of ^{14}C to ^{12}C, i.e., 1.3×10^{-12}. When an organism dies, the ^{14}C in it keeps on decaying as follows:

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e + Energy$$

*Thus, the ratio $^{14}C/^{12}C$ decreases with the passage of time. We can measure the proportion of ^{14}C in the remains of a dead organism and determine how long ago it died. The method of **carbon dating** can be used to date anything made of organic matter, e.g., bone,* *skeleton, wood, etc. Using carbon dating, materials have been dated to about 50,000 years with accuracy.*

Answer the following questions:

1. ${}^{14}C$ exists in atmosphere due to:
   (a) conversion of ${}^{12}C$ to ${}^{14}C$
   (b) combustion of fossil fuel
   (c) bombardment of atmospheric nitrogen by cosmic ray neutrons
   (d) none of the above
2. A wooden piece is 11520 yrs old. What is the fraction of ${}^{14}C$ activity left in the piece?
   (a) 0.12 (b) 0.25 (c) 0.50 (d) 0.75
   [**Hint:** $\frac{0.693}{t_{1/2}\ {}^{14}C} = \frac{2.303}{t_{age}} \log\left(\frac{N_0}{N}\right)$
   $\frac{0.693}{5760} = \frac{2.303}{11520} \log\left(\frac{N_0}{N}\right)$
   $\frac{N}{N_0} = 0.25$]
3. In the process of photosynthesis, O_2 gas is released from:
   (a) CO_2 (b) H_2O
   (c) both H_2O and CO_2 (d) mechanism is not confirmed
4. A piece of wood from an archeological source shows a ${}^{14}C$ activity which is 60% of the activity found in fresh wood today. The age of archeological sample will be:
   (a) 4246 yrs (b) 4624 yrs (c) 4628 yrs (d) 6248 yrs
5. A sample of ancient wooden boat is found to undergo $9\,\text{dpm}\,g^{-1}$ of ${}^{14}C$. What is the approximate age of the boat? The rate of disintegration of wood recently cut down is $15\,\text{dpm}\,g^{-1}$ of ${}^{14}C$.
   (a) 4246.5 yrs (b) 5384 yrs (c) 4628 yrs (d) 2684 yrs

• Passage 4

The mineral monazite is a rich source of thorium, available in large quantity in Kerala. A typical monazite sample contains 9% ThO_2 and 0.35% U_3O_8. ${}^{208}Pb$ and ${}^{206}Pb$ are the stable end products in the radioactive decay series of ${}^{232}Th$ and ${}^{238}U$ respectively. All the lead in monazite is of radiogenic origin.

The isotopic ratio of ${}^{208}Pb/{}^{232}Th$ was found to be 0.104. The half lives of Th and U are 1.41×10^{10} years and 4.47×10^9 years respectively.

Answer the following questions:

1. The time elapsed since the formation of monazite sample will be:
   (a) 1.34×10^9 years (b) 2.01×10^9 years
   (c) 1.41×10^{10} years (d) 4.47×10^9 years
   [**Hint:** $\frac{0.693}{t_{1/2}\ Th} = \frac{2.303}{t_{age}} \log\left(\frac{N_0}{N}\right)$
   $\frac{0.693}{1.41 \times 10^{10}} = \frac{2.303}{t_{age}} \log(1.104)$
   $t_{age} = 2.01 \times 10^9$ years]
2. Estimated isotopic ratio of ${}^{206}Pb/{}^{238}U$ in the monazite sample will be:
   (a) 0.166 (b) 0.266 (c) 0.366 (d) 0.466
3. Select the incorrect information about ${}^{232}Th$:
   (a) It belongs to third group of actinide series
   (b) ${}^{232}Th$ is fissile material
   (c) It is a fertile material
   (d) It belongs to $4n$ series

• Passage 5

Geiger-Nuttal proposed that the activity of a nucleus is inversely proportional to its half or average life. Thus, shorter the half life of an element, greater is its radioactivity, i.e., greater the number of atoms disintegrating per second. Half life and average life are related with each other.

$$t_{1/2} = \frac{0.693}{\lambda} = \tau \times 0.693 \qquad or \qquad \tau = 1.44 t_{1/2}$$

Answer the following questions:

1. The half life periods of four isotopes are given:
   I = 6.7 years; II = 8000 years; III = 5760 years; IV = 2.35×10^5 years.
   Which of these is most stable?
   (a) I (b) II (c) III (d) IV
2. Mark the incorrect relation:
   (a) $N_0 = Ne^{\lambda t}$ (b) $\tau = 1.44 t_{0.5}$
   (c) $N = N_0 \left(\frac{1}{2}\right)^n$ (d) $t_{1/2} = \lambda \ln 2$
3. Half life of a radioactive element is 10 years. What percentage of it will decay in 100 years?
   (a) 0.1% (b) 100% (c) 99.9% (d) 10%

• Passage 6

It has been estimated that the total energy radiated by the sun is 3.8×10^{26} J per second. The source of energy of stars is a thermonuclear reaction called nuclear fusion. Fusion reactions are not controlled. It is presumed that the energy of stars is due to two processes called proton-proton cycle and carbon-nitrogen cycle. Fusion cannot take place at ordinary temperature. Thus, hydrogen bomb uses a small fission bomb, which on explosion causes the temperature to rise very high, about 10^7 K. We have yet to see how a hydrogen bomb can be used for peaceful life-sustaining purpose. Energy released in the process of fusion is due to mass defect. It is also called Q-value.

$$Q = \Delta mc^2, \quad \Delta m = \text{mass defect}$$

Answer the following questions:

1. The binding energy per nucleon of ${}^2_1H$ and ${}^4_2He$ are 1.1 MeV and 7 MeV respectively. If two deuteron nuclei react to form a single helium nucleus, then the energy released is:
   (a) 13.9 MeV (b) 26.9 MeV (c) 23.6 MeV (d) 19.2 MeV
2. Mass equivalent to the energy 931 MeV is:
   (a) 6.02×10^{-27} kg (b) 1.662×10^{-27} kg
   (c) 16.66×10^{-27} kg (d) 16.02×10^{-27} kg
3. Fusion reaction takes place at about:
   (a) 3×10^2 K (b) 3×10^3 K
   (c) 3×10^4 K (d) 3×10^6 K

4. A star has 10^{40} deuterons. It produces energy via the process:

$$^2_1H + ^2_1H \longrightarrow ^3_1H + ^1_1H$$
$$^2_1H + ^3_1H \longrightarrow ^4_2He + ^1_0n$$

If the average power radiated by the star is 10^{16} W, then the deuteron supply of the star is exhausted in a time of the order of:

(a) 10^6 sec (b) 10^8 sec (c) 10^{12} sec (d) 10^{16} sec

5. In a nuclear reaction,

$$^2_1H + ^2_1H \longrightarrow ^3_2He + ^1_0n$$

if the masses of ^2_1H and ^3_2He are 2.014741 amu and 3.016977 amu respectively, then the Q-value of the reaction is nearly:

(a) 0.00352 MeV (b) 3.27 MeV
(c) 0.82 MeV (d) 2.45 MeV

• Passage 7

Moderator is a material which is used to slow down the neutrons produced during nuclear fission. The neutrons from the source are of high speed and energy. Heavy water or graphite moderators slow down the speed of the neutrons. The energy of fast moving neutrons decreases from 2 MeV to 0.02535 eV; it corresponds to the velocity of 220 m sec^{-1}. At this velocity, the neutrons are in thermal equilibrium with the moderator. Such neutrons are called 'thermal neutrons'. Thermal neutrons cause further fission reaction. The essential characteristics of moderators are:

(*i*) *its molar mass must be low,*
(*ii*) *it should not absorb neutrons,*
(*iii*) *it should undergo elastic collisions with neutrons.*

Answer the following questions:

1. The moderator in a reactor:
   (a) absorbs neutrons
   (b) accelerates neutrons
   (c) slows down neutrons
   (d) absorbs thermal energy produced in the reactors
2. A good moderator should:
   (a) not be a gas only
   (b) not have appetite for neutrons only
   (c) be light in mass number only
   (d) be all the above three
3. Which of the following is not used as a moderator?
   (a) Heavy water (b) Graphite
   (c) Beryllium (d) Sodium
4. Moderator in the reactor yields:
   (a) fast moving neutrons
   (b) thermal neutrons
   (c) magnetic neutrons
   (d) electric neutrons
5. Which among the following characters make graphite a good moderator?
   (a) Cross-sectional area of graphite is very high
   (b) Graphite is a good conductor of electricity
   (c) There is elastic collision between graphite and neutron
   (d) Graphite has weak van der Waals' force between two layers

• Passage 8

Radioactive decay follows first order kinetics. The disintegration of radioactive elements does not depend on the temperature. Unlike chemical first order reactions, the nuclear reactions are also independent of catalyst. Mean life and half life of nuclear decay process are $\tau = \frac{1}{\lambda}$ *and* $t_{1/2} = \frac{0.693}{\lambda}$. *There are a number of radioactive elements in nature; their abundance is directly proportional to half life. Amount remaining after n half lives of radioactive elements can be calculated using the relation:*

$$N = N_0\left(\frac{1}{2}\right)^n$$

Answer the following questions:

1. Which is/are true about the decay constant?
   (a) Unit of λ is time^{-1}
   (b) λ is independent of temperature
   (c) λ depends on initial amount of element taken
   (d) λ depends on the nature of radioactive element
2. Amount of radioactive element (activity) decreases with passage of time as:
   (a) linearly (b) exponentially
   (c) parabolically (d) all of these
3. Half life of ^{60}Co is 5.3 yrs, the time taken for 99.9% decay will be:
   (a) 0.53 yrs (b) 53 yrs
   (c) 530 yrs (d) 5300 yrs
4. Rate of radioactive decay is:
   (a) independent of time
   (b) independent of temperature
   (c) dependent on catalyst
   (d) dependent on the amount of element not yet decayed
5. Select the correct relations:
   (a) $t_{1/2} = \frac{0.693}{\lambda}$ (b) $\tau = \frac{1}{\lambda}$
   (c) $\tau = 1.44 \times t_{1/2}$ (d) $\tau = \frac{t_{1/2}}{0.693}$

• Passage 9

In the disintegration of a radioactive element, α and β-particles are evolved from the nucleus.

$$^1_0n \longrightarrow ^1_1H + ^0_{-1}e + \text{Antineutrino} + \text{Energy}$$
$$4\,^1_1H \longrightarrow ^4_2He + 2\,^0_{+1}e + \text{Energy}$$

Then, emission of these particles changes the nuclear configuration and results into a daughter nuclide. Emission of an α-particle results into a daughter element having atomic number lowered by 2 and mass number by 4; on the other hand, emission of a β-particle yields an element having atomic number raised by one. Soddy and Fajan proposed that the daughter nuclide may occupy different positions in the periodic table.

Answer the following questions:

1. Which of the following combinations give finally an isotope of the parent element?
   (a) α, α, β (b) α, γ, α (c) α, β, β (d) β, γ, α
2. A radioactive element belongs to IIIB group; it emits one 'α' and one β-particle to form a daughter nuclide. The position of daughter nuclide will be in:
   (a) IIA (b) IA (c) IIB (d) IVB
3. During β-decay, the mass of atomic nucleus:
   (a) decreases by 1 unit (b) increases by 1 unit
   (c) decreases by 2 units (d) remains unaffected
4. How many α and β-particles should be emitted from a radioactive nuclide so that an isobar is formed?
   (a) $1\alpha, 1\beta$ (b) $1\alpha, 2\beta$ (c) $2\alpha, 2\beta$ (d) $n\beta$
5. Select the correct statements among the following:
   (a) Emission of a β-particle results into isobar of parent element
   (b) Emission of a β-particle results into isodiaphere of parent element
   (c) Emission of one α and two β-particles results into isotope of the parent element
   (d) Emission of γ-radiations may yield nuclear isomer

Answers

Passage 1.	1. (b)	2. (c)	3. (a)	4. (a)	5. (b)	
Passage 2.	1. (b)	2. (a)	3. (a)	4. (a)	5. (b)	6. (d)
Passage 3.	1. (c)	2. (b)	3. (b)	4. (a)	5. (a)	
Passage 4.	1. (b)	2. (c)	3. (b)			
Passage 5.	1. (d)	2. (d)	3. (c)			
Passage 6.	1. (c)	2. (b)	3. (d)	4. (c)	5. (b)	
Passage 7.	1. (c, d)	2. (d)	3. (d)	4. (b)	5. (a, c)	
Passage 8.	1. (a, d)	2. (b)	3. (b)	4. (b, d)	5. (a, b, c, d)	
Passage 9.	1. (c)	2. (a)	3. (d)	4. (d)	5. (a, b, c, d)	

SELF ASSESSMENT

ASSIGNMENT NO. 3

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. If $\frac{3}{4}$ quantity of a radioactive substance decays in 2 hrs, its half life would be:
(a) 1 hour (b) 45 minutes
(c) 30 minutes (d) 15 minutes

2. Radio carbon dating is done by estimating in a specimen: **(VITEEE 2007)**
(a) the amount of ordinary carbon still present
(b) the amount of radio carbon still present
(c) the ratio of amount of $^{14}_{6}C$ to $^{12}_{6}C$ still present
(d) the ratio of amount of $^{12}_{6}C$ to $^{14}_{6}C$ still present

3. Which of the following are correct with respect to the unit of radioactivity?
(i) The SI unit of radioactivity is curie (Ci)
(ii) $1\,Ci = 3.7 \times 10^{-10}$ dis s^{-1}
(iii) $1\,Bq = 3.7 \times 10^{-10}$ Ci
(iv) The SI unit of radioactivity is becquerel (Bq)
(v) $1\,Ci = 3.7 \times 10^{10}$ Bq
(a) (i) and (iii) (b) (iv) and (v)
(c) (i) and (ii) (d) (ii) and (iv)
(e) (i) and (v)

4. A freshly cut tree and a wooden artifact have 30.4 and 15.2 counts g^{-1} min^{-1} of C^{14} of half life of 5700 years. The age of the artifact in years would be:
(a) 2850 (b) 5700 (c) 570 (d) 6930
(e) 11400

5. The radioactive isotope of cerium-137 of weight 8g was collected on 1st Feb. 2006 and kept in a sealed tube. On 1st July, 2006, it was found that only 0.25 g of it remained. The half life period of the isotope is: **[PET (Kerala) 2007]**
(a) 37.5 days (b) 30 days
(c) 25 days (d) 50 days
(e) 60 days

6. The number of α and β-particles emitted in the nuclear reaction
$$^{228}_{90}Th \longrightarrow {}^{212}_{83}Bi$$ are: **(DCE 2007)**
(a) 4α and 1β (b) 3α and 7β
(c) 8α and 1β (d) 4α and 7β

7. A cyclotron cannot accelerate:
(a) protons (b) deutrons
(c) neutrons (d) electrons

8. Isotope I^{128} has no medicinal importance because:
(a) it is non-radioactive (b) it is poisonous
(c) it is radioactive (d) none of these

9. The decay of mass during nuclear fission and fusion are:
(a) 0.1% and 0.231% (b) 0.231% and 0.1%
(c) 0.4% and 0.2% (d) 0.3% and 0.3%
[**Hint:** Greater mass is converted to energy in nuclear fusion as compared to that of fission.]

10. On large scale, tritium is produced by which of the following nuclear reactions? **(SCRA 2009)**
(a) $^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}He + {}^{3}_{1}T$
(b) $^{2}_{1}D + {}^{2}_{1}D \rightarrow {}^{3}_{1}T + {}^{1}_{1}H$
(c) $^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{12}_{6}C + {}^{3}_{1}T$
(d) $^{14}_{7}N + {}^{1}_{1}H \rightarrow {}^{3}_{1}T$ + Other fragments

SECTION-II

Multiple Answers Type Objective Questions

11. Which of the following will emit positron?
(a) $^{30}_{15}P$ (b) $^{13}_{7}N$ (c) $^{3}_{1}H$ (d) $^{14}_{6}C$

[**Hint:** $^{30}_{15}P\left(\frac{n}{p} = 1\right)$ and $^{13}_{7}N\left(\frac{n}{p} < 1\right)$; these nuclei emit positron.

$$^{30}_{15}P \longrightarrow {}^{30}_{14}Si + {}^{0}_{+1}e$$
$$^{13}_{7}N \longrightarrow {}^{13}_{6}C + {}^{0}_{+1}e$$]

12. If $\frac{n}{p}$ ratio is less than 1, the nuclide can:
(a) *K*-capture (b) emit positron
(c) emit β-particle (d) emit α-particle

13. For radioactive decay:
(a) $t_{3/4} = 2\,t_{1/2}$ (b) $t_{7/8} = 3\,t_{1/2}$
(c) $t_{99\%} = 2\,t_{90\%}$ (d) $t_{90\%} = \frac{10}{3}\,t_{50\%}$

14. Which of the following statements is/are correct?
(a) Nuclear fusion produces more energy than nuclear fission
(b) Nuclear fusion takes place at very high temperature (10^6 K)
(c) Nuclear fusion yields radioactive product
(d) Nuclear fusion involves chain reaction

15. Decrease in atomic number is observed during:
(a) α-emission (b) β-emission
(c) positron emission (d) *K*-capture

SECTION-III

Assertion-Reason Type Questions

This section contains 4 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.

(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** β-particles are emitted by nucleus.

Because

Statement-2: Following transformation takes place in β-emission.

$$^{1}_{0}n \longrightarrow {}^{1}_{1}H + {}^{0}_{-1}e$$

17. **Statement-1:** Nuclide $^{40}_{20}Ca$ is less stable than $^{40}_{20}Ca$.

Because

Statement-2: Nuclides having even number of nucleons are stable.

18. **Statement-1:** Energy is released in the nuclear fusion of hydrogen nuclei to form helium nuclei.

Because

Statement-2: Binding energy per nucleon of helium is greater than hydrogen.

19. **Statement-1:** $^{133}_{56}Ba + e^- \longrightarrow {}^{133}_{55}Cs$ + X-ray

It is an example of K-electron capture.

Because

Statement-2: Atomic number of daughter nuclide decreases by one unit in K-electron capture.

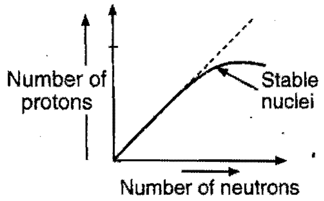
[**Hint:** Nucleus may capture electron from K-shell and the vacancy is filled by electrons from higher shells; X-ray is released in this process.]

20. **Statement-1:** The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of 45° slope as atomic number is increased.

Because

Statement-2: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides. **(IIT 2008)**

[**Hint:**



In heavier nuclei, attractive forces between proton-neutron overcome proton-proton electrostatic repulsion.]

SECTION-IV

Matrix-Matching Type Questions

This section contains 2 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p, s), (b-q, r), (c-p, q) and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

21. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $^{2}_{1}D + {}^{3}_{1}T \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$ + Energy	(p) β-emission
(b) $^{9}_{4}Be + {}^{4}_{2}He \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$	(q) Artificial transmutation
(c) $^{24}_{12}Mg + {}^{4}_{2}He \longrightarrow {}^{27}_{14}Si + {}^{1}_{0}n$	(r) Discovery of neutrons
(d) $^{1}_{0}n \longrightarrow {}^{1}_{1}H + {}^{0}_{-1}e$	(s) Hydrogen bomb

22. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $n \longrightarrow p^+ + ...$	(p) Positron emission
(b) $p^+ \longrightarrow n + ...$	(q) β-emission
(c) X-ray emission	(r) K-electron capture
(d) $4\,[^{1}_{1}H] \longrightarrow ..... + 2\beta^+$ + Energy	(s) α-emission

SECTION-V

Linked Comprehension Type Questions

Nucleus of an atom resembles with a drop of liquid. Density of nucleus is very high, *i.e.*, 10^8 tonne/cc or 130 trillion tonnes m^{-3}. This density is about a trillion times greater than that of water. Density of nuclei of all elements are same, it is independent of atomic number or atomic mass. However, the radius of nucleus depends on the mass number. Surface tension of nucleus is also very high, *i.e.*, about 1.24×10^{18} times, the surface tension of water.

Answer the following questions:

23. The radius of $^{12}_{6}C$ nucleus is:

(a) 5×10^{-15} m (b) 1.4×10^{-15} m
(c) 3.5×10^{-15} m (d) 6×10^{-15} m

[**Hint:** $r = r_0 \times A^{1/3}$ where A = Mass number
$r_0 = 1.4 \times 10^{-15}$ m]

24. Ratio of volume of atom and nucleus is:

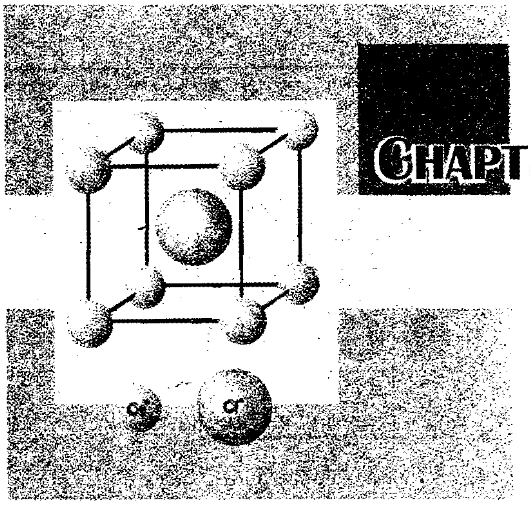
(a) $10^8 : 1$ (b) $10^{15} : 1$ (c) $10^{13} : 1$ (d) $10^{12} : 1$

25. Radius of nucleus is directly proportional to:

(a) A^2 (b) $A^{1/3}$ (c) $[A]^3$ (d) A

Answers

1. (c) **2.** (c) **3.** (b) **4.** (b) **5.** (b) **6.** (a) **7.** (c) **8.** (a)
9. (a) **10.** (b) **11.** (a, b) **12.** (a, b) **13.** (a, b, c, d) **14.** (a, b, c) **15.** (a, c, d) **16.** (a)
17. (d) **18.** (a) **19.** (b) **20.** (c) **21.** (a - s) (b - q, r) (c - q) (d - p)
22. (a - q) (b - p) (c - r) (d - s) **23.** (c) **24.** (b) **25.** (c)



CHAPTER 4

STATES OF MATTER

4.1 INTRODUCTION

Matter is capable of existing in three physical states: solid, liquid and gas. Matter is anything which has mass and occupies space. Any substance can exist in either of three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

The three states of a substance are interconvertible by variation of temperature and pressure. A liquid state is intermediate between the gaseous state (complete molecular randomness) and the solid state (orderly arrangement of molecules).

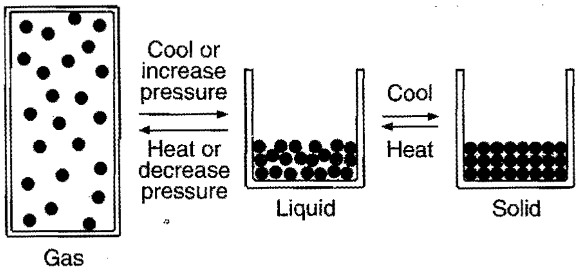


Fig. 4.1 Schematic representation of states of matter

Some common characteristics of three forms of matter are summarised below:

S.No.	Gases	Liquids	Solids
1.	No definite shape; can fill uniformly any volume available; have indefinite volume.	No definite shape, *i.e.,* assume the shape of the container; have definite volume.	Have definite shape and definite volume.
2.	Extremely disordered particles; much empty space; particles have random motion; intermolecular attraction very small but high kinetic energies (particles are free to move in all directions).	Disordered clusters of particles; quite close to each other; random motion; considerable intermolecular attraction; kinetic energy is less (particles free to move but always remain in contact with each other).	Ordered arrangement of particles; distances between the particles are very small and fixed. Intermolecular forces are high; vibrational motion only.
3.	Low density.	Intermediate density.	High density.
4.	Compressible.	Slightly compressible.	Nearly incompressible.
5.	Fluid, diffuse rapidly.	Fluid; diffuse through other liquids.	Not fluid; diffuse very slowly only through solids.

SECTION 1 : GASEOUS STATE

4.2 THE GASEOUS STATE

Of the three states of matter, the gaseous state is the simplest and shows greatest uniformity in behaviour. Gases have the following general characteristics:

(i) Gases are highly compressible. These can be compressed into smaller volumes, *i.e.*, increasing their densities by applying increased pressure.

(ii) Gases expand without limit. A gas sample can occupy completely and uniformly the volume of any container.

(iii) Gases exert pressure on the walls of the container uniformly in all directions.

(iv) Gases diffuse rapidly through each other to form a homogeneous mixture. Conversely, different gases in a mixture like air do not separate on standing.

(v) The characteristics of gases are described fully in terms of **four parameters** (measurable properties):

(a) the volume, V, of the gas
(b) its pressure, P
(c) its temperature, T
(d) the amount of the gas (*i.e.*, mass or number of moles).

(a) The volume of the container is the volume of the gas sample. Volume is expressed in litre (L), millilitre (mL) or cubic centimetre (cm^3) or cubic metre (m^3).

$$1\text{ L} = 1000\text{ mL};\ 1\text{ mL} = 10^{-3}\text{ L}$$

$$1\text{ L} = 1\text{ dm}^3;\quad 1\text{ dm}^3 = 10^3\text{ cm}^3$$

$$1\text{ m}^3 = 10^3\text{ dm}^3 = 10^6\text{ cm}^3 = 10^6\text{ mL} = 10^3\text{ L}$$

(b) The pressure of the gas is the force exerted by the gas per unit area of the walls of the container. The pressure of gases is measured by a device known as manometer. Two types of manometers, open-end manometer and closed-end manometer, are commonly used to measure gaseous pressure.

Pressure of one atmosphere (1 atm) is defined as the pressure that can support a column of mercury of 76 cm height at 0°C (density of mercury = 13.5951 g cm^{-3}) and at standard gravity = 980.665 cm s^{-2}. One atmosphere is also referred to as 760 torr.

$$1\text{ atm} = 76.0\text{ cm of mercury} = 760\text{ mm of mercury}$$
$$= 760\text{ torr}$$

SI unit of pressure is pascal (Pa) which is defined as the pressure exerted when a force of 1 newton acts on a 1 m^2 area.

$$1\text{ atm} = 101.325 \times 10^3\text{ N m}^{-2} = 101.325\text{ kPa}$$

An older unit of pressure is 'bar' which is equal to 10^5 Pa.

(c) The temperature of the gas is measured in centigrade degree (°C) or celsius degree with the help of thermometers.

SI unit of temperature is **Kelvin** (K) or **absolute degree.**

$$K = °C + 273$$

(d) Mass of gas is expressed in gram or kilogram.

$$1\text{ kg} = 10^3\text{ g}$$

The mass of the gas is also expressed in number of moles.

$$\text{moles of gas } (n) = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$$

(vi) All gases obey certain laws called **gas laws.**

4.3 GAS LAWS

(i) Boyle's law: It relates the volume and the pressure of a given mass of a gas at constant temperature.

The relationship between the volume and the pressure of a gas was studied by **Robert Boyle** in 1662. He found that increasing the pressure at constant temperature on a sample of a gas causes the volume of the gas to decrease proportionately, *i.e.*, if the pressure is doubled, the volume becomes half and so on. Boyle's law states that **at constant temperature, the volume of a sample of a gas varies inversely with the pressure.**

$$V \propto \frac{1}{P} \quad \text{(when temperature is kept constant)}$$

The proportionality can be changed into an equality by introducing a constant, k, *i.e.*,

$$V = \frac{k}{P} \quad \text{or} \quad PV = k$$

Alternatively, Boyle's law can also be stated as follows:

Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant.

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1V_1 = P_2V_2 = P_3V_3 = \ldots$$

Boyle's law can be verified by any one of the following three ways graphically (Fig. 4.2):

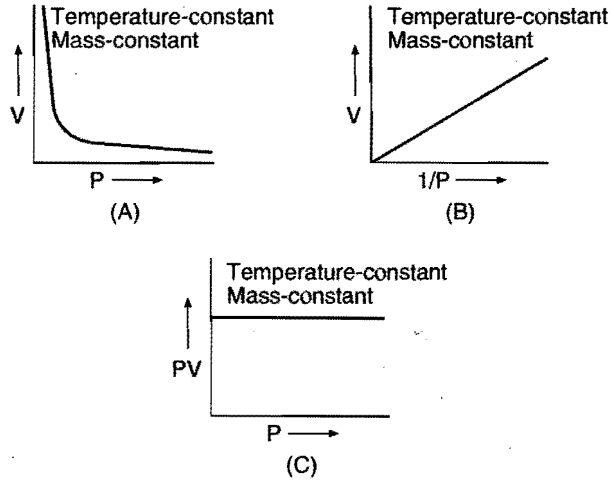


Fig. 4.2

The first curve shows the variation of volume of a given mass of gas with pressure at constant temperature. The shape of the curve is rectangular hyperbola. This curve is also called **isotherm.**

The second curve showing the relationship between volume and reciprocal of pressure is a straight line. It confirms the statement that at constant temperature, volume of a given mass of gas is inversely proportional to the pressure. The third curve shows a straight line parallel to pressure-axis. This confirms that the product of pressure and volume of a given mass of a gas at constant temperature is constant.

Location of straight line and curve changes with temperature in the isotherm.

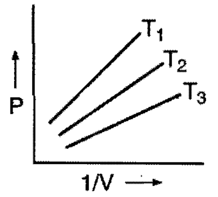


Fig. 4.2(D)

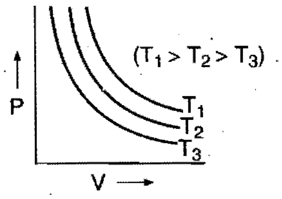


Fig. 4.2(E)

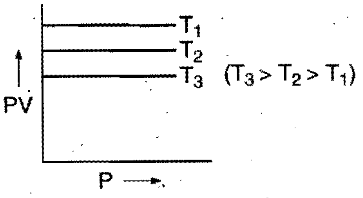


Fig. 4.2(F)

According to Boyle's law, $PV = \text{constant}$ at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V + \text{constant}$$

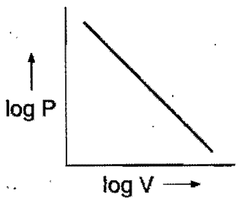


Fig. 4.2(G)

(ii) Charles' law: It relates the volume and temperature of a given mass of a gas at constant pressure.

Experiments have shown that when 273 mL sample of a gas at 0°C is heated to 1°C, its volume increases by 1 mL, *i.e.*, it becomes 274 mL. At 10°C, the volume increases to 283 mL if the pressure remains constant in both cases. Similarly, when 273 mL sample of gas at 0°C is cooled to −1°C, its volume decreases to 272 mL while at −10°C, the volume decreases to 263 mL if the pressure remains constant.

Thus, all gases expand or contract by the same fraction of their volumes at 0°C per degree change of temperature, *i.e.*, for each degree change of temperature, the volume of a sample of a gas changes by the fraction $\frac{1}{273}$ of its volume at 0°C.

Let the volume of a given amount of a gas be V_0 at 0°C. The temperature is increased by $t°$ C and the new volume becomes V_t.

Thus, $$V_t = V_0 + \frac{V_0}{273} \times t = V_0\left(1 + \frac{t}{273}\right)$$

or $$V_t = V_0\left(\frac{273 + t}{273}\right) \qquad \dots \text{(i)}$$

A new temperature scale was introduced known as **Kelvin scale** or **absolute scale** named after the British physicist and mathematician **Lord Kelvin.** The lower limit of the scale is called absolute zero which corresponds to −273°C. At absolute zero or −273°C, all molecular motions would stop and the volume of the gas would become zero. The gas would become a liquid or solid. Thus, **absolute zero is that temperature at which no substance exists in the gaseous state.** The temperature in absolute is always obtained by adding 273 to the temperature expressed in °C.

$$K = (°C + 273)$$

This new temperature scale may be used for deducing Charles' law.

By substituting T for $273 + t$ and T_0 for 273 in Eq. (i),

$$V_t = \frac{V_0 \times T}{T_0}$$

or $$\frac{V_t}{T} = \frac{V_0}{T_0}$$

or $$\frac{V}{T} = \text{constant (if pressure is kept constant)}$$

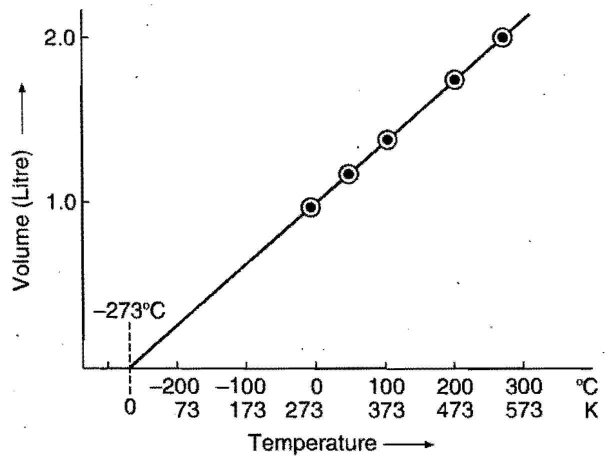


Fig. 4.3

This is Charles' law. It can be stated as follows:

The volume of a given amount of a gas at constant pressure varies directly as its absolute temperature.

$$V \propto T \quad \text{(if pressure is kept constant)}$$

Charles' law can be verified experimentally by plotting the values of volumes of a given amount of a gas under respective absolute temperatures at constant pressure. The straight line confirms the above statement.

(iii) Pressure-temperature law: It relates the pressure and absolute temperature of a given mass of a gas at constant volume.

Volume remaining constant, the pressure of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its pressure at 0°C per degree change of temperature.

$$P_t = P_0 + \frac{P_0 \times t}{273}$$

or $$P_t = P_0\left(1 + \frac{t}{273}\right)$$

or $$P_t = P_0\left(\frac{273+t}{273}\right) = P_0\frac{T}{T_0}$$

or $$\frac{P_t}{T} = \frac{P_0}{T_0}$$

or $$P \propto T \text{ (if volume is kept constant)}$$

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

4.4 IDEAL GAS EQUATION

This equation is obtained by combining Boyle's and Charles' laws.

$V \propto \frac{1}{P}$ ... (i) (at constant temperature and definite mass)

$V \propto T$ ... (ii) (at constant pressure and definite mass)

Combining eqs. (i) and (ii), we get

$$V \propto \frac{T}{P} \quad \text{(for definite mass)}$$

$$\frac{PV}{T} = \text{constant} \quad \text{... (iii)}$$

From the above relation, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{... (iv)}$$

From eq. (iii),

$$\frac{PV}{T} = R$$

or $$PV = RT \text{ for 1 mole gas}$$

$$PV = nRT \text{ for } n \text{ mole gas} \quad \text{... (v)}$$

When mass of the gas is taken in grams, the value of n will be given by:

$$n = \frac{\text{Mass of the gas in gram}}{\text{Mol. mass of the gas in gram}}$$

Let w and M be the mass and molecular mass of a gas; then

$$n = \frac{w}{M}$$

Hence, eq. (v) becomes

$$PV = \frac{w}{M}RT \quad \text{... (vi)}$$

or $$P = \frac{w}{M}\cdot\frac{RT}{V} \quad \left[\frac{w}{V} = \frac{\text{Mass}}{\text{Volume}} = \text{Density } (d)\right]$$

or $$P = \frac{d}{M}RT \quad \text{... (vii)}$$

Eqs. (vi) and (vii) are modified forms of gas equation. The above equations are strictly followed by ideal gases.

Nature of Molar Gas Constant R

Gas equation for one gram mole,

$$PV = RT$$

or $$R = \frac{P \times V}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$$

$$\text{Volume} = (\text{Length})^3$$

So, $$R = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}} = \frac{\text{Work}}{\text{Temperature}}$$

Thus, the value of R should always be expressed in units of work per degree kelvin per mole.

Numerical Values of R

$$R = \frac{PV}{T}$$

One gram mole of a gas at one atmospheric pressure and 0°C (273 K) occupies a volume 22.4 litre.

P = 1 atmosphere, T = 273 K, V = 22.4 litre

So, $$R = \frac{1 \times 22.4}{273} = 0.0821 \text{ litre-atm K}^{-1}\text{ mol}^{-1}$$

If pressure is taken in dyne/cm^2 and volume in mL,

$P = 76 \times 13.67 \times 981 \text{ dyne/cm}^2, V = 22400 \text{ mL}$ for 1 mole, $T = 273$ K

So, $$R = \frac{76 \times 13.67 \times 981 \times 22400}{273} = 8.314 \times 10^7 \text{ erg K}^{-1}\text{ mol}^{-1}$$

Since, 1 joule = 10^7 erg, so

$$R = 8.314 \text{ joule K}^{-1}\text{ mol}^{-1}$$

Since, 1 calorie = 4.184×10^7 erg, so

$$R = \frac{8.314 \times 10^7}{4.184 \times 10^7} = 1.987 \approx 2 \text{ calorie K}^{-1}\text{ mol}^{-1}$$

Note: Although, R can be expressed in different units, but for pressure-volume calculations, R must be taken in the same units of pressure and volume.

Barometric Distribution

In the case of ordinary gases, pressure in the container is unaffected by the gravitational field. But in high molecular mass polymeric gases, pressure varies with height.

Let P_0 be the pressure at ground level and P be the pressure at height 'h'; then

$$2.303 \log_{10}\left(\frac{P}{P_0}\right) = -\left\{\frac{Mgh}{R}\right\}$$

Similarly for density and number of moles the equation may be given as:

$$2.303 \log_{10}\left(\frac{d}{d_0}\right) = -\left\{\frac{Mgh}{R}\right\}$$

$$2.303 \log_{10}\left(\frac{n}{n_0}\right) = -\left\{\frac{Mgh}{R}\right\}$$

These relations are valid under isothermal conditions for density, pressure and number of moles.

If temperature is not constant then the relations of barometric distribution may be given as,

$$2.303 \log_{10}\left(\frac{P}{P_0}\right) = -\frac{Mgh}{RT}$$

$$2.303 \log_{10}\left(\frac{n}{n_0}\right) = -\frac{Mgh}{RT}$$

Open vessel concept: In open vessel of a gas, pressure and volume are always constant.

$$\therefore \qquad PV = n_1RT_1 \qquad \ldots (1)$$

$$PV = n_2RT_2 \qquad \ldots (2)$$

Here, n_1 and n_2 are number of moles at temperatures T_1 and T_2.

Dividing eq. (1) by (2), we get

$$n_1T_1 = n_2T_2$$

Dry and moist gas: If volume under moist condition is given then volume of dry gas can be determined.

$$P_{\text{moist}}V_{\text{moist}} = P_{\text{dry}}V_{\text{dry}}$$

$$P_{\text{dry}} = P_{\text{moist}} - \text{Aqueous tension or vapour pressure of water}$$

$$\text{Relative humidity} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

Payload (Lifting Capacity of Balloon)

When a balloon is filled with lighter gas like H_2 and He (lighter than air) then it rises up due to the difference in the density of air and the gas. Payload or lifting capacity of balloon may be calculated as:

$$\text{Pay Load} = \begin{bmatrix}\text{Mass of air filled}\\ \text{in the balloon}\end{bmatrix} - \begin{bmatrix}\text{Mass of gas filled in the}\\ \text{balloon at same tempera -}\\ \text{ture and pressure}\end{bmatrix} - \begin{bmatrix}\text{Mass of}\\ \text{balloon}\end{bmatrix}$$

SOME SOLVED EXAMPLES

Example 1. *A sample of a gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmosphere? Assume that the temperature of the gas sample does not change.*

Solution: $V_1 = 10$ litre $V_2 = ?$

$P_1 = 1$ atm $P_2 = 2$ atm

Applying Boyle's law,

$$P_1V_1 = P_2V_2$$

So, $$V_2 = \frac{P_1V_1}{P_2} = \frac{1 \times 10}{2} = 5 \text{ litre}$$

Example 2. *A sample of a gas occupies 600 mL at 27°C and 1 atm. What will be the volume at 127°C if the pressure is kept constant?*

Solution: $V_1 = 600$ mL $T_1 = 27 + 273 = 300$ K

$V_2 = ?$ $T_2 = 127 + 273 = 400$ K

Applying Charles' law, $$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1}{T_1} \times T_2$$

$$= \frac{600 \times 400}{300}$$

$$= 800 \text{ mL}$$

Example 3. *A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C. Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode?*

Solution: Since, the gas is confined in a cylinder, its volume will remain constant.

Initial conditions	Final conditions
$P_1 = 12$ atm	$P_2 = 14.9$ atm
$T_1 = 27 + 273 = 300$ K	$T_2 = ?$

Applying pressure-temperature law,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

So, $$T_2 = \frac{P_2 \times T_1}{P_1}$$

$$= \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

Temperature in °C = (372.5 − 273) = 99.5° C

Example 4. *A 1000 mL sample of a gas at −73°C and 2 atmosphere is heated to 123°C and the pressure is reduced to 0.5 atmosphere. What will be the final volume?*

Solution:

Initial conditions	Final conditions
$P_1 = 2$ atm	$P_2 = 0.5$ atm
$V_1 = 1000$ mL	$V_2 = ?$
$T_1 = -73°\text{ C} = (-73 + 273)$ $= 200$ K	$T_2 = 123°\text{ C} = (123 + 273)$ $= 400$ K

We know that,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

So,

$$\frac{2 \times 1000}{200} = \frac{0.5 \times V_2}{400}$$

or

$$V_2 = \frac{2 \times 1000 \times 400}{200 \times 0.5}$$

$$= 8000 \text{ mL}$$

Example 5. *A sample of a gas occupies a volume of* 512 *mL at* 20°C *and* 74 *cm of Hg as pressure. What volume would this gas occupy at STP?*

Solution:

Initial conditions	Final conditions (STP)
$P_1 = 74$ cm	$P_2 = 76$ cm
$T_1 = 20°\text{C} = (20 + 273) = 293$ K,	$T_2 = 0°\text{C} = 273$ K
$V_1 = 512$ mL	$V_2 = ?$

We know that,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{74 \times 512}{293} = \frac{76 \times V_2}{273}$$

So,

$$V_2 = \frac{74 \times 512 \times 273}{293 \times 76}$$

$$= 464.5 \text{ mL}$$

Example 6. 3.7 *g of a gas at* 25°C *occupied the same volume as* 0.184 *g of hydrogen at* 17°C *and at the same pressure. What is the molecular mass of the gas?*

Solution: For hydrogen,

$w = 0.184$ g ; $T = 17 + 273 = 290$ K; $M = 2$

We know that, $PV = \frac{w}{M}RT$

$$= \frac{0.184}{2} \times R \times 290 \quad \text{... (i)}$$

For unknown gas,

$w = 3.7$ g; $T = 25 + 273 = 298$ K; $M = ?$

$$PV = \frac{3.7}{M} \times R \times 298 \quad \text{... (ii)}$$

Equating both the equations,

$$\frac{3.7}{M} \times R \times 298 = \frac{0.184}{2} \times R \times 290$$

or

$$M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33$$

Example 7. *What is the pressure of HCl gas at* –40°C *if its density is* 8.0 *kg* m^{-3}? ($R = 8.314\ J\ K^{-1}\ mol^{-1}$)

Solution: Equation for ideal gas,

$$PV = \frac{w}{M}RT$$

or

$$P = \frac{w}{V} \times \frac{RT}{M}$$

$$= d \times \frac{RT}{M} \qquad \left(\frac{w}{V} = \text{density} = d\right)$$

Given, $d = 8.0 \text{ kg m}^{-3}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$;

$T = -40 + 273 = 233$ K

and $M = 36.5 \text{ g mol}^{-1} = 36.5 \times 10^{-3} \text{ kg mol}^{-1}$

Substituting the values in the above equation,

$$P = \frac{8.0 \times 8.314 \times 233}{36.5 \times 10^{-3}} = 424.58 \times 10^3 \text{ Pa}$$

Example 8. *A certain quantity of a gas occupies* 100 *mL when collected over water at* 15°C *and* 750 *mm pressure. It occupies* 91.9 *mL in dry state at NTP. Find the aqueous vapour pressure at* 15°C.

Solution: Let the aqueous vapour pressure be p mm.

Initial conditions	NTP conditions
P_1 (dry gas) $= (750 - p)$ mm	$P_2 = 760$ mm
$V_1 = 100$ mL	$V_2 = 91.9$ mL
$T_1 = 15 + 273 = 288$ K	$T_2 = 273$ K

Applying gas equation,

$$\frac{(750 - p) \times 100}{288} = \frac{760 \times 91.9}{273}$$

or

$$750 - p = \frac{760 \times 91.9 \times 288}{100 \times 273}$$

$$= 736.8 \text{ mm}$$

$$p = 750 - 736.8$$

$$= 13.2 \text{ mm}$$

Example 9. *A balloon of diameter* 20 *m weighs* 100 *kg. Calculate its payload if it is filled with helium at* 1.0 *atm and* 27°C. *Density of air is* 1.2 *kg* m^{-3}.
($R = 0.082\ dm^3\ atm\ K^{-1}\ mol^{-1}$) **(IIT 1994)**

Solution:

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.47 \text{ m}^3$$

Mass of the air displaced $= 4190.47 \times 1.2 = 5028.56$ kg

$$\text{No. of moles of helium in the balloon} = \frac{PV}{RT}$$

$$= \frac{1 \times 4190.47 \times 10^3}{0.082 \times 300} = 170344$$

Mass of helium $= 4 \times 170.344 \times 10^3$ g $= 681.376$ kg

Mass of filled balloon $= 681.376 + 100 = 781.376$ kg

Payload = Mass of air displaced – Mass of filled balloon

$= 5028.56 - 781.376 = 4247.184$ kg

Example 10. *The density of a gas is 0.259 gL^{-1} at 400 K and 190 torr. Find its molar mass.*

Solution: 760 torr = 1 atm

So, $$190 \text{ torr} = \frac{190}{760} \text{ atm}$$

We know that, $$P = \frac{d}{M} RT$$

or $$M = \frac{d}{P} RT$$

Given, $d = 0.259 \text{ gL}^{-1}$; $P = \frac{190}{760}$ atm;

$R = 0.0821 \text{ L-atm K}^{-1} \text{ mol}^{-1}$; $T = 400$ K

$$M = \frac{0.259 \times 0.0821 \times 400 \times 760}{190} = 34.02 \text{ g mol}^{-1}$$

Example 11. *The density of phosphorus vapour at 310°C and 775 torr is 2.64 g dm^{-3}. What is the molecular formula of phosphorus?*

Solution: We know that, $P = \frac{d}{M} RT$ or $M = \frac{d}{P} RT$

Given, $d = 2.64 \text{ g dm}^{-3}$; $P = \frac{775}{760}$ atm;

$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

and $T = 310 + 273 = 583$ K

So, $$M = \frac{2.64 \times 0.0821 \times 583 \times 760}{775} = 123.9 \text{ g mol}^{-1}$$

Atomic mass of P = 31 g mol^{-1}

No. of P atoms in a molecule $= \frac{123.9}{31} = 3.997 \approx 4$

Hence, molecular formula of phosphorus = P_4

Example 12. *What percentage of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are changed from 220°C, 3.0 atm and 1.65 L to 110° C, 0.7 atm and 1.0 L respectively?*

Solution: Applying the formula, m (mass of the gas) $= \frac{PV \times M}{RT}$, under both the conditions,

$$\text{Mass of gas before escaping} = \frac{3.0 \times 1.65 \times 28}{0.0821 \times 493} = 3.42 \text{ g}$$

$$\text{Mass of gas after escaping} = \frac{0.7 \times 1.0 \times 28}{0.0821 \times 383} = 0.62 \text{ g}$$

Percentage of nitrogen allowed to escape

$$= \frac{(3.42 - 0.62)}{3.42} \times 100 = 81.87$$

Example 13. *The density of oxygen is 1.43 g L^{-1} at STP. Determine the density of oxygen at 17°C and 800 torr.*

Solution: Applying the formula $d = \frac{MP}{RT}$

At STP, $$d_1 = \frac{MP_1}{RT_1}$$

$[P_1 = 760 \text{ torr}; T_1 = 273 \text{ K}; d_1 = 1.43 \text{ g L}^{-1}]$

At given conditions, $$d_2 = \frac{MP_2}{RT_2}$$

$[P_2 = 800 \text{ torr}; T_2 = 290 \text{ K}; d_2 = ?]$

So, $$\frac{d_2}{d_1} = \frac{P_2}{T_2} \times \frac{T_1}{P_1}$$

or $$d_2 = \frac{P_2}{P_1} \times \frac{T_1}{T_2} \times d_1$$

$$= \frac{800}{760} \times \frac{273}{290} \times 1.43$$

$$= 1.417 \text{ g L}^{-1}$$

Example 14. *A car tyre has a volume of 10 litre when inflated. The tyre is inflated to a pressure of 3 atm at 17°C with air. Due to driving the temperature of the tyre increases to 47°C. (a) What would be the pressure at this temperature? (b) How many litres of air measured at 47°C and pressure of 1 atm should be let out to restore the tyre to 3 atm at 47°C?*

Solution: (a) At constant volume,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

or $$\frac{3}{290} = \frac{P_2}{320}$$

or $$P_2 = \frac{320 \times 3}{290} = 3.31 \text{ atm}$$

(b) Pressure to be decreased in tyre

$$= 3.31 - 3.0 = 0.31 \text{ atm}$$

Let the volume of the gas to be taken out at 1 atmospheric pressure be V. As the temperature remains constant, *i.e.*, 47°C, Boyle's law can be applied to determine V.

$$1 \times V = 0.31 \times 10$$

or $$V = 3.1 \text{ litre}$$

Example 15. *Oxygen is present in a one litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate the number of oxygen molecules in the flask at 0°C.*

Solution: $$n = \frac{PV}{RT} \quad \text{... (i)}$$

$$P = \frac{7.6 \times 10^{-10}}{760} = 10^{-12} \text{ atm}$$

$V = 1 \text{ L}, T = 273 \text{ K}, R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

From eq. (i) $n = \dfrac{10^{-12} \times 1}{0.0821 \times 273}$

$$\text{Number of molecules} = n \times 6.023 \times 10^{23}$$

$$= \frac{10^{-12}}{0.0821 \times 273} \times 6.023 \times 10^{23}$$

$$= 2.68 \times 10^{10}$$

Example 16. *An open flask contains air at 27°C. Calculate the temperature at which it should be heated so that 1/3 rd of air measured at 27°C escapes out.*

Solution: Let the initial number of moles of air at 27°C (300 K) be $= n$

Number of moles of air left when the air is heated to the temperature $T \text{ K} = n - \dfrac{n}{3} = \dfrac{2n}{3}$

At constant pressure and constant volume,

$$n_1 T_1 = n_2 T_2$$

or
$$n \times 300 = \frac{2n}{3} \times T$$

or
$$T = 450 \text{ K} = (450 - 273) = 177° \text{ C}$$

Example 17. *A mixture of CO and CO_2 is found to have a density of $1.5\ gL^{-1}$ at 30°C and 730 torr. What is the composition of the mixture?*

Solution: Let the average molecular mass be M.

$$M = \frac{dRT}{P} = \frac{1.5 \times 0.0821 \times 303 \times 760}{730} = 38.85$$

Let x mole of CO and $(1 - x)$ mole of CO_2 be present.

$$x \times 28 + (1 - x) \times 44 = 38.85$$

$$x = 0.3218$$

$$\text{mole \% of CO} = 32.18 \text{ and mole \% of } CO_2 = 67.82$$

Example 18. *Calculate the value of molar gas constant, 'R' in (i) cc atm K^{-1} mol^{-1} (ii) torr cc K^{-1} mol^{-1} (iii) kPa litre K^{-1} mol^{-1}.*

Solution: (i) When the pressure is expressed in atmosphere and volume in cc.

$$P = 1 \text{ atm}; \quad V = 22400 \text{ cc}$$

$$R = \frac{PV}{nT} = \frac{1 \times 22400}{1 \times 273} = 82.1 \text{ cc atm K}^{-1} \text{ mol}^{-1}$$

(ii) When the pressure is expressed in torr and volume in cc.

$$P = 760 \text{ torr}; \quad V = 22400 \text{ cc}$$

$$R = \frac{760 \times 22400}{1 \times 273} = 62360 \text{ torr cc K}^{-1} \text{ mol}^{-1}$$

(iii) When the pressure is expressed in k Pascal and volume in litre.

$$P = 101.3 \text{ kPa}; V = 22.4 \text{ litre}$$

$$R = \frac{PV}{nT} = \frac{101.3 \times 22.4}{1 \times 273} = 8.31 \text{ kPa litre K}^{-1} \text{ mol}^{-1}$$

Example 19. *The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of V litre is one atmosphere. When the temperature is increased by 10°C at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V (Molecular mass of the gas = 120).* **(IIT 1999)**

Solution: As the volume is constant, pressure law can be applied, *i.e.*,

$$\frac{P_1}{P_2} = \frac{T_1}{T_2}$$

or
$$\frac{1}{1.1} = \frac{t + 273}{t + 283}$$

or
$$t = -173° \text{ C} = 100 \text{ K}$$

Now, applying gas equation,

$$PV = nRT$$

or
$$V = \frac{n}{P} RT = \frac{12 \times 0.082 \times 100}{120 \times 1} = 0.82 \text{ litre}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 2.5 L of a sample of a gas at 27°C and 1 bar pressure is compressed to a volume of 500 mL keeping the temperature constant, the percentage increase in the pressure is:

(a) 100% (b) 400% (c) 500% (d) 80%

[Ans. (b)]

[Hint: $P_1V_1 = P_2V_2$

$$1 \times 2.5 = P_2 \times \frac{1}{2}$$

$$P_2 = 5 \text{ bar}$$

$$\% \text{ Increase} = \frac{\text{Increase in pressure}}{\text{Initial pressure}} \times 100$$

$$= \frac{4}{1} \times 100 = 400\%]$$

2. Which of the following gases will have density of 1.8 g L^{-1} at 760 torr pressure and 27°C ?

(a) O_2 (b) CO_2 (c) NH_3 (d) SO_2

[Ans. (b)] .

[Hint: $Pm = dRT$

$$m = \frac{dRT}{P} = \frac{1.8 \times 0.0821 \times 300}{1} = 44$$

∴ The gas will be CO_2.]

3. 10 g C_2H_6 is filled in a bulb of 1 litre capacity which can withstand a maximum pressure of 10 atm. At what temperature will the pressure of gas reach the bursting limit?

(a) 76°C (b) 361.4°C (c) 92.4°C (d) 120°C

[Ans. (c)]

[Hint: $T = \dfrac{PV}{nR} = \dfrac{10 \times 1}{(10/30) \times 0.0821} = 365.4 \text{ K} = 92.4° \text{C}]$

4. The vapour of phosphine gas at 27°C and 3 bar pressure has density:

(a) 4.09 g mL^{-1} (b) 4.14 g L^{-1}

(c) 2.04 kg L^{-1} (d) 2.04 g L^{-1}

[Ans. (b)]

[**Hint:** $d = \frac{Pm}{RT} = \frac{3 \times 34}{0.0821 \times 300} = 4.14 \text{ g L}^{-1}$]

5. Coefficient of volume expansion of a gas is:

(a) $\frac{1}{273}$ (b) $\frac{2}{273}$

(c) $\frac{3}{273}$ (d) $\frac{4}{273}$

[**Ans.** (a)]

[**Hint:** According to Charles' law,

$$V_t = V_0\left(1 + \frac{t}{273}\right)$$

$$V_t = V_0 (1 + \alpha t)$$

$$\alpha = \frac{1}{273} = \text{Coefficient of volume expansion}$$

Here, V_0 = Volume at 0°C and V_t = Volume at t °C]

6. A gas has a vapour density 11.2. The volume occupied by 1 gram of the gas at STP will be:

(a) 11.2 L (b) 22.4 L (c) 1 L (d) 10 L

[**Ans.** (c)]

[**Hint:** Number of moles $= \frac{\text{Mass}}{\text{Molar mass}}$

$$= \frac{\text{Mass}}{2 \times \text{Vapour density}}$$

$$= \frac{1}{2 \times 11.2} = \frac{1}{22.4}$$

Volume of gas $= n \times 22.4$ L

$$= \frac{1}{22.4} \times 22.4 \text{ L} = 1 \text{ L}]$$

7. When a gas is heated from 25°C to 50°C at constant pressure of 1 bar, its volume:

(a) increases from V to $2V$

(b) increases from V to $1.5V$

(c) increases from V to $1.084V$

(d) increases from V to $1.8V$

[**Ans.** (c)]

[**Hint:** $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{V}{298} = \frac{V_2}{323}$$

$$V_2 = V \times \frac{323}{298} = 1.084\ V\ ]$$

8. The molecular weights of two ideal gases A and B are respectively 100 and 200. One gram of A occupies V litre of volume at STP. What is the volume (in litre) occupied by one gram of B at STP? **(EAMCET 2006)**

(a) $\frac{V}{2}$ (b) V (c) V^2 (d) $2V$

[**Ans.** (a)]

[**Hint:** Under identical conditions of temperature and pressure:

$$\frac{V_A}{V_B} = \frac{n_A}{n_B}$$

$$\frac{V}{V_B} = \frac{1/100}{1/200}$$

$$V_B = \frac{V}{2}\ ]$$

9. A bubble of volume V_1 is at the bottom of a pond at 15°C and 1.5 atm pressure. When it comes at the surface, it observes a pressure of 1 atm at 25°C and has volume V_2; give $\left(\frac{V_2}{V_1}\right)$: **(DCE 2006)**

(a) 15.5 (b) 0.155 (c) 155.0 (d) 1.55

[**Ans.** (d)]

[**Hint:** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$$

$$= \frac{1.5 \times 288}{1 \times 298} = 1.5]$$

4.5 DALTON'S LAW OF PARTIAL PRESSURES

When different gases that do not react chemically with each other are enclosed in the same container, they intermix rapidly and exert a definite pressure. Again, each of the gas in the mixture exerts its own individual pressure if it is present only in the same container at the same temperature. **John Dalton,** in 1801, established the relation between the pressure of the mixture of gases and individual pressures of the constituent gases. This relationship is known as **Dalton's law of partial pressures.** It states that,

At a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases. Mathematically,

$$P = p_A + p_B + p_C + \dots$$

when P is the total pressure and $p_A, p_B, p_C, \dots$ are the partial pressures of the component gases $A, B, C, \dots$ respectively. *The pressure that a component gas of the gaseous mixture would exert if it were only present in the volume under consideration at a given temperature, is the partial pressure of the component.*

Derivation of Dalton's Law

Let n_1 and n_2 be the no. of moles of two non-reacting gases 'A' and 'B' filled in a vessel of volume 'V' at temperature T.

Total pressure in the vessel 'P' may be calculated as,

$$PV = (n_1 + n_2)RT \quad \dots \text{(i)}$$

Individual or partial pressure may be calculated as,

$$p_AV = n_1RT \quad \dots \text{(ii)}$$

$$p_BV = n_2RT \quad \dots \text{(iii)}$$

Adding eqs. (ii) and (iii), we get

$$(p_A + p_B)V = (n_1 + n_2)RT \quad \dots \text{(iv)}$$

Comparing equations (i) and (iv), we get

$$P = p_A + p_B \quad \text{(Dalton's expression)}$$

Dividing eq. (ii) by (i), we get

$$\frac{p_A}{P} = \frac{n_1}{n_1 + n_2} = x_A$$

$$p_A = x_A \times P$$

where, x_A = mole fraction of 'A'.

Similarly, dividing eq. (iii) by (i), we get

$$p_B = x_B \times P$$

i.e., Partial pressure of a component

= Mole fraction × Total pressure

Relationship between Total Pressure and Individual Pressure (before Mixing) of the Constituent Gases at Constant Temperature

At constant temperature, let V_1 volume of a gas A at a pressure p_1 be mixed with V_2 volume of gas B at a pressure p_2. Both these gases do not react chemically.

$$\text{Total volume} = V_1 + V_2$$

Let the total pressure be P and partial pressures of A and B be p_A and p_B respectively. Applying Boyle's law,

$$p_A(V_1 + V_2) = p_1V_1 \qquad \ldots \text{(i)}$$

and

$$p_B(V_1 + V_2) = p_2V_2 \qquad \ldots \text{(ii)}$$

Adding eqs. (i) and (ii),

$$p_A + p_B = \frac{p_1V_1}{V_1 + V_2} + \frac{p_2V_2}{V_1 + V_2} = \frac{p_1V_1 + p_2V_2}{V_1 + V_2}$$

or

$$P = \frac{p_1V_1 + p_2V_2}{V_1 + V_2}$$

In the laboratory, it is often convenient to collect a gas over water. When a gas is collected over water, the observed pressure of the gas is equal to the sum of the pressure of dry gas and the pressure of water vapour.

Therefore, the pressure of dry gas

= pressure of moist gas − pressure of water vapour

= pressure of moist gas − aqueous tension

Amagat Law of Partial Volume

Total volume of a mixture of gases which does not react at constant temperature and pressure is equal to sum of individual volumes (partial volumes) of constituent gases.

$$V = \Sigma V_i = V_1 + V_2 + V_3 + \ldots + V_n$$

4.6 DIFFUSION OF GASES AND GRAHAM'S LAW OF DIFFUSION

When two or more non-reacting gases are kept side by side, they have the tendency to mix with one another spontaneously and form a homogeneous mixture. This can occur also if two gases have different densities. The heavier gas moves up and the lighter one comes down even against the action of gravity. Such a phenomenon is due to the fact that gas particles are moving at random with very high velocities and there is much intermolecular empty space in the volume of any gas. When two gases are brought together, they mix with each other in no time. **This ability of a gas to mix spontaneously and to form a homogeneous mixture is known as diffusion.** It is due to this phenomenon that we can readily detect the fragrance of a flower or a perfume or bad smell of hydrogen sulphide, sulphur dioxide, chlorine, etc., when these are evolved or used in any work in laboratory or in industry.

Effusion

It is a process in which a gas is allowed to escape under pressure through a fine orifice or a small aperture made in the wall of a closed container. The difference between diffusion and effusion is that in the former case, the gas spontaneously streams through a porous partition while in the case of effusion, the gas is forced out through a small hole by applying some external pressure. However, both the processes are essentially the same.

Instantaneous rate of effusion is directly proportional to the instantaneous gas pressure and inversely proportional to the square root of molar mass.

$$-\frac{dP}{dt} = \frac{KP}{\sqrt{M}}$$

$$-\int_{P_1}^{P_2} \frac{dP}{P} = \frac{K}{\sqrt{M}} \int_0^t dt$$

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{Kt}{\sqrt{M}}$$

$$\ln P_2 = \ln P_1 - \frac{Kt}{\sqrt{M}}$$

$$P_2 = P_1 e^{-Kt/\sqrt{M}}$$

Hence, partial pressure decreases exponentially with time as

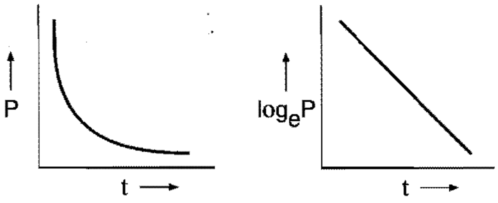


Fig. 4.4 Variation of partial pressure of gas with time, in the process of effusion.

Graham's Law of Diffusion or Effusion

This law was presented by **Thomas Graham** in 1833. The law states that **"At constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density."**

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}}$$

If r_1 and r_2 represent the rates of diffusion of two gases and d_1 and d_2 are their respective densities, then

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

This equation can be written as:

$$\frac{r_1}{r_2} = \sqrt{\frac{\dfrac{\text{density of gas II}}{\text{density of hydrogen}}}{\dfrac{\text{density of gas I}}{\text{density of hydrogen}}}} = \sqrt{\frac{\text{VD gas II}}{\text{VD gas I}}}$$

$$= \sqrt{\frac{2\,\text{VD gas II}}{2\,\text{VD gas I}}} = \sqrt{\frac{\text{Mol. mass gas II}}{\text{Mol. mass gas I}}} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

i.e., the volume which diffuses in unit time.

(i) Comparison of times taken for the same volume of two gases: Let the times of diffusion for the same volume of two gases be t_1 and t_2 respectively; then

$$\frac{r_1}{r_2} = \frac{\dfrac{V}{t_1}}{\dfrac{V}{t_2}} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

or
$$\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(ii) Comparison of the volumes of the gases that diffuse in same time: Let V_1 and V_2 be the volumes of two gases that diffuse in the same time t. Then

$$\frac{r_1}{r_2} = \frac{\dfrac{V_1}{t}}{\dfrac{V_2}{t}} = \frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(iii) Effect of pressure on rate of diffusion: When pressure is not constant then rate of effusion may be taken proportional to pressure.

$$r \propto \frac{1}{\sqrt{M}} \qquad r \propto P$$

Combination of these equations gives:

$$r \propto \frac{P}{\sqrt{M}}$$

or
$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

How to Determine Rate of Diffusion?

(a) Rate of diffusion is equal to distance travelled by gas per unit time through a tube of uniform cross-section.

(b) Number of moles effusing per unit time is also called rate of diffusion.

(c) Decrease in pressure of a cylinder per unit time is called rate of effusion of gas.

Application of Graham's Law of Diffusion

According to Graham's law of diffusion, the ratio of rate of diffusion of two gases may be given as:

$$\frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{1/2}$$

where, M_1 and M_2 are respective molar masses of the gases.

The factor $\left(\dfrac{M_2}{M_1}\right)^{1/2}$ is called enrichment factor; this tells about the preferential effusion of lighter species relative to the heavier ones. This enrichment can be applied to separate isotopes. For example, the isotope U^{235}, the active component in atomic weapons and in nuclear power generation, has a natural abundance of only 0.7% while U^{238} is far more abundant. By reaction of the isotopic mixture with fluorine, gaseous UF_6 is produced and can be enriched by passing it through a porous barrier. The process of diffusion through the porous barrier is repeated many times to achieve sufficient enrichment.

$$\text{Separation factor '}f\text{'} = \frac{n_1'/n_2'}{n_1/n_2}$$

where, $n_1 n_2$ and $n_1' n_2'$ are the concentration of two isotopes before and after diffusion.

$$\text{Theoretical separation factor for single step } f' = \sqrt{\frac{M_2}{M_1}}$$

Let enrichment of species '1' is achieved after 'n' times then

$$(f')^n = \frac{n_1'/n_2'}{n_1/n_2} = f$$

$$n \log f' = \log\left(\frac{n_1'/n_2'}{n_1/n_2}\right)$$

$$n \log\sqrt{\frac{M_2}{M_1}} = \log\left(\frac{n_1'/n_2'}{n_1/n_2}\right)$$

$$\frac{n}{2}\log\left(\frac{M_2}{M_1}\right) = \log\left(\frac{n_1'/n_2'}{n_1/n_2}\right)$$

$$n = \frac{2\log\left(\dfrac{n_1'/n_2'}{n_1/n_2}\right)}{\log(M_2/M_1)} = \frac{2\log(f)}{\log\left(\dfrac{M_2}{M_1}\right)}$$

SOME SOLVED EXAMPLES

Example 20. *A 10 litre flask contains 0.2 mole of methane, 0.3 mole of hydrogen and 0.4 mole of nitrogen at 25°C. What is the partial pressure of each component and what is the pressure inside the flask?*

Solution:
$$P = \frac{nRT}{V}$$

$$\text{Partial pressure of methane} = \frac{0.2 \times 0.0821 \times 298}{10} = 0.489 \text{ atm}$$

$$\text{Partial pressure of hydrogen} = \frac{0.3 \times 0.0821 \times 298}{10} = 0.734 \text{ atm}$$

$$\text{Partial pressure of nitrogen} = \frac{0.4 \times 0.0821 \times 298}{10} = 0.979 \text{ atm}$$

$$\text{Total pressure} = (0.489 + 0.734 + 0.979)\ \text{atm} = 2.202\ \text{atm}$$

Alternative solution: Total number of moles

$$= 0.2 + 0.3 + 0.4 = 0.9$$

Let the total pressure be P.

We know that,

$$P = \frac{\text{total number of moles}}{V} \cdot RT$$

$$V = 10\ \text{litre},\ R = 0.0821\ \text{L atm K}^{-1},\ T = (25 + 273) = 298\ \text{K}$$

$$P = \frac{0.9}{10} \times 0.0821 \times 298 = 2.20\ \text{atm}$$

$$\text{Partial pressure of } CH_4 = \text{Mole fraction of methane} \times \text{total pressure}$$

$$= \frac{0.2}{0.9} \times 2.20 = 0.489\ \text{atm}$$

$$\text{Partial pressure of } H_2 = \text{Mole fraction of } H_2 \times \text{total pressure}$$

$$= \frac{0.3}{0.9} \times 2.20 = 0.733\ \text{atm}$$

$$\text{Partial pressure of } N_2 = \text{Mole fraction of } N_2 \times \text{total pressure}$$

$$= \frac{0.4}{0.9} \times 2.20 = 0.978\ \text{atm}$$

Example 21. *If 200 mL of N_2 at 25°C and a pressure of 250 mm are mixed with 350 mL of O_2 at 25°C and a pressure of 300 mm so that, the volume of resulting mixture is 300 mL, what would be the final pressure of the mixture at 25°C?*

Solution: In the case of nitrogen, volume increases, its pressure must decrease. Let the new pressure be P_{N_2}.

$$P_{N_2} = \frac{250 \times 200}{300} = 166.6\ \text{mm} \qquad \text{(Applying Boyle's law)}$$

In the case of oxygen, volume decreases, its pressure must increase. Let the new pressure be P_{O_2}.

$$P_{O_2} = \frac{300 \times 350}{300} = 350\ \text{mm} \qquad \text{(Applying Boyle's law)}$$

$$\text{Total pressure} = P_{N_2} + P_{O_2} = (166.6 + 350) = 516.6\ \text{mm}$$

Example 22. *1.22 g of a gas measured over water at 15°C and a pressure of 775 mm of mercury occupied 900 mL. Calculate the volume of dry gas at NTP. Vapour pressure of water at 15°C is 14 mm.*

Solution: Pressure of dry gas = Pressure of moist gas − Aqueous tension

$$= 775 - 14$$

$$= 761\ \text{mm}$$

Initial conditions	NTP conditions
$V_1 = 900\ \text{mL}$	$V_2 = ?$
$P_1 = 761\ \text{mm}$	$P_2 = 760\ \text{mm}$
$T_1 = (273 + 15) = 288\ \text{K}$	$T_2 = 273\ \text{K}$

Since,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

So,

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$= \frac{761 \times 900 \times 273}{288 \times 760}$$

$$= 854.2\ \text{mL}$$

Example 23. *When 2 g of a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1-atmosphere. 3 g of another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atmosphere. Calculate the ratio of molecular masses of A and B assuming ideal gas behaviour.*

Solution: Let the molecular masses of A and B be M_A and M_B respectively.

Pressure exerted by the gas $B = (1.5 - 1.0) = 0.5$ atm. Volume and temperature are same in both the gases.

For gas A: $P = 1$ atm, $w = 2$ g, $M = M_A$

We know that,

$$PV = \frac{w}{M} RT$$

$$1 \times V = \frac{2}{M_A} \cdot RT \quad \text{or} \quad M_A = \frac{2RT}{V} \qquad \text{... (i)}$$

For gas B: $P = 0.5$ atm, $w = 3$ g, $M = M_B$

$$0.5 \times V = \frac{3}{M_B} \cdot RT \quad \text{or} \quad M_B = \frac{3RT}{0.5 \times V} \qquad \text{... (ii)}$$

Dividing Eq. (i) by Eq. (ii),

$$\frac{M_A}{M_B} = \frac{2RT}{V} \times \frac{0.5 \times V}{3RT}$$

$$= \frac{2 \times 0.5}{3} = \frac{1}{3}$$

Thus, $M_A : M_B = 1 : 3$

Example 24. *Find the total pressure exerted by 1.6 g methane and 2.2 g CO_2 contained in a four litre flask at 27°C.*

Solution:

$$PV = (n_1 + n_2)RT$$

$$P \times 4 = \left(\frac{1.6}{16} + \frac{2.2}{44}\right) \times 0.0821 \times 300$$

$$P = 0.9236\ \text{atm}$$

Example 25. *1500 mL flask contains 400 mg O_2 and 60 mg H_2 at 100°C.*

(a) What is the total pressure in the flask?

(b) If the mixture is permitted to react to form water vapour at 100°C, what will be left and what will be their partial pressures?

Solution: (a) No. of moles of $O_2 = \frac{400}{1000 \times 32} = 0.0125$

$$\text{No. of moles of } H_2 = \frac{60}{1000 \times 2} = 0.03$$

$$\text{Partial pressure of } O_2 = \frac{0.0125 \times 0.0821 \times 373}{1.5} = 0.255\ \text{atm}$$

$$\text{Partial pressure of } H_2 = \frac{0.03 \times 0.0821 \times 373}{1.5} = 0.612\ \text{atm}$$

$$\text{Total pressure} = 0.255 + 0.612 = 0.867\ \text{atm}$$

(b)

	$2H_2$	+ O_2	$= 2H_2O$
Initial	0.03	0.0125	0
After reaction	0.005	0	0.025

$$\text{Partial pressure of } H_2 = \frac{0.005 \times 0.0821 \times 373}{1.5} = 0.102 \text{ atm}$$

$$\text{Partial pressure of } H_2O = \frac{0.025 \times 0.0821 \times 373}{1.5} = 0.51 \text{ atm}$$

Example 26. *20 dm^3 of SO_2 diffuse through a porous partition in 60 s. What volume of O_2 will diffuse under similar conditions in 30 s?* **(IIT 1996)**

Solution: Rate of diffusion of $SO_2 = \frac{20}{60}$ dm^3 s^{-1}

Rate of diffusion of $O_2 = \frac{V}{30}$ dm^3 s^{-1}

According to Graham's law of diffusion,

$$\frac{(V/30)}{(20/60)} = \sqrt{\frac{M_{SO_2}}{M_{O_2}}} = \sqrt{\frac{64}{32}}$$

$$V = 14.1 \text{ dm}^3$$

Example 27. *50 volume of hydrogen take 20 minute to diffuse out of a vessel. How long will 40 volume of oxygen take to diffuse out from the same vessel under the same conditions?*

Solution: Rate of diffusion for hydrogen, $r_1 = \frac{50}{20}$

Rate of diffusion for oxygen, $r_2 = \frac{40}{t}$

Mol. mass of hydrogen = 2

Mol. mass of oxygen = 32

So $$\frac{50/20}{40/t} = \sqrt{\frac{32}{2}}$$

or $$\frac{50}{20} \times \frac{t}{40} = 4$$

$$t = 64 \text{ minute}$$

Example 28. *Calculate the relative rates of diffusion of $^{235}UF_6$ and $^{238}UF_6$ in the gaseous state (At. mass of F = 19).*

Solution: Mol. mass $^{235}UF_6 = 235 + 6 \times 19 = 349$

Mol. mass $^{238}UF_6 = 238 + 6 \times 19 = 352$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{352}{349}} = 1.0043$$

$$r_1 : r_2 :: 1.0043 : 1.0000$$

Example 29. *180 mL of a hydrocarbon diffuses through a porous membrane in 15 minutes while 120 mL of SO_2 under identical conditions diffuses in 20 minutes. What is the molecular mass of the hydrocarbon?*

Solution:

r_1 = rate of diffusion of hydrocarbon $= \frac{180}{15}$ mL min^{-1}

r_2 = rate of diffusion of $SO_2 = \frac{120}{20}$ mL min^{-1}

$$\frac{r_1}{r_2} = \frac{M_{SO_2}}{M}$$

Thus, $$\frac{180/15}{120/20} = \sqrt{\frac{64}{M}}$$

$$2 = \sqrt{\frac{64}{M}}$$

So, $$M = 16$$

Example 30. *The reaction between gaseous NH_3 and HBr produces a white solid NH_4Br. Suppose a small quantity of gaseous NH_3 and gaseous HBr are introduced simultaneously into opposite ends of an open tube which is one metre long. Calculate the distance of white solid formed from the end which was used to introduce NH_3.*

Solution: Let the distance of white solid from NH_3 end = x cm.

The distance of white solid from HBr end = $(100 - x)$ cm.

Rates of diffusion shall be proportional to these distances.

$$\frac{r_1}{r_2} = \frac{x}{(100 - x)} = \sqrt{\frac{M_{HBr}}{M_{NH_3}}}$$

Mol. mass of HBr = 1 + 80 = 81

Mol. mass of NH_3 = 14 + 3 = 17

So, $$\frac{x}{(100 - x)} = \sqrt{\frac{81}{17}}$$

or, $$\frac{x}{(100 - x)} = 2.18$$

So, $$x = 100 \times 2.18 - 2.18x$$

or, $$3.18x = 100 \times 2.18$$

So, $$x = \frac{100 \times 2.18}{3.18}$$

$$= 68.55 \text{ cm}$$

Example 31. *At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minute. Another unknown gas at the same temperature and pressure as that of hydrogen leaked through the same hole for 20 minute. After the effusion of the gases the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litre, what is the molecular mass of the unknown gas?* **(IIT 1992)**

Solution: Let p_{H_2} and p_{un} be the partial pressures of hydrogen and unknown gas respectively and w be the number of moles of unknown gas.

$$p_{H_2} = \frac{0.7}{3} \times 0.0821 \times 300$$

$$p_{un} = \frac{w}{3} \times 0.0821 \times 300$$

Adding both,

$$p_{H_2} + p_{un} = 6 = (1/3) \times 0.0821 \times 300(0.7 + w)$$

$$w = 0.0308 \text{ mole}$$

Applying law of diffusion,

$$\frac{0.7/20}{0.0308/20}=\sqrt{\frac{M}{2}} \text{ or } M=1033$$

Example 32. *The ratio of velocities of diffusion of gases A and B is* $1:4$. *If the ratio of their masses present in the mixture is* $2:3$, *calculate the ratio of their mole fractions.* **[CEE (Bihar) 1990]**

Solution:

$$\frac{r_A}{r_B}=\sqrt{\frac{M_B}{M_A}}=\frac{1}{4}$$

or

$$\frac{M_B}{M_A}=\frac{1}{16}$$

Let masses W_A and W_B of A and B be present respective.

$$\text{Mole fraction of } A=\frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A}+\frac{W_B}{M_B}}$$

$$\text{Mole fraction of } B=\frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}+\frac{W_B}{M_B}}$$

$$\text{Ratio}=\frac{W_A}{M_A}\times\frac{M_B}{W_B}$$

or

$$\frac{W_A}{W_B}\times\frac{M_B}{M_A}=\frac{2}{3}\times\frac{1}{16}=\frac{1}{24}$$

Example 33. *A space capsule is filled with neon gas at* 1.00 *atm and* 290 *K. The gas effuses through a pin hole into outer space at such a rate that pressure drops by* 0.30 *torr per second.*

(*a*) *If the capsule is filled with ammonia at the same temperature and pressure, what would be rate of pressure drop?*

(*b*) *If the capsule is filled with* 30.0 *mol % helium,* 20.0 *mol % oxygen and* 50.0 *mol % nitrogen at a total pressure of* 1.0 *atm and a temperature of* 290 *K, what would be the corresponding rate of pressure drop?*

Solution: (a) The rate of pressure drop is directly proportional to rate of effusion.

$$\frac{r_{Ne}}{r_{NH_3}}=\sqrt{\frac{M_{NH_3}}{M_{Ne}}}=\sqrt{\frac{17.0}{20}}=0.92$$

$$r_{NH_3}=\frac{r_{Ne}}{0.92}=\frac{0.30}{0.92}=0.326 \text{ torr / second}$$

(b) The average molecular mass of the gaseous mixture is

$$0.3\times4+0.2\times32+0.5\times28=21.6$$

$$\text{Rate of drop of pressure}=\sqrt{\frac{20}{21.6}}\times0.30$$

$$=0.29 \text{ torr / second}$$

Example 34. *One mole of nitrogen gas at* 0.8 *atm takes* 38 *second to diffuse through a pin hole whereas one mole of an unknown compound of xenon with fluorine at* 1.6 *atm takes* 57 *second to diffuse through the same hole. Calculate the molecular formula of the compound.* **(IIT 1999)**

Solution:

$$\frac{r_{N_2}}{r_{XeF_n}}=\frac{P_{N_2}}{P_{XeF_n}}\sqrt{\frac{M_{XeF_n}}{M_{N_2}}}$$

$$\frac{r_{N_2}}{r_{XeF_n}}=\frac{\frac{\text{Molar volume}}{t_{N_2}}}{\frac{\text{Molar volume}}{t_{XeF_n}}}=\frac{t_{XeF_n}}{t_{N_2}}=\frac{57}{38}$$

$\therefore$

$$\frac{57}{38}=\frac{0.8}{1.6}\sqrt{\frac{M_{XeF_n}}{28}}$$

$$M_{XeF_n}=\left(\frac{57}{38}\right)^2\times\left(\frac{1.6}{0.8}\right)^2\times28$$

$$=252$$

$$Xe+nF=252$$

$$131+n\times19=252$$

$$n=6$$

Molecular formula $=XeF_6$

Example 35. $100\,cm^3$ *of* NH_3 *diffuses through a pin hole in* 32.5 *second. How much time will* 60 *cc of* N_2 *take to diffuse under the same conditions?*

Solution:

$$\frac{r_{NH_3}}{r_{N_2}}=\sqrt{\frac{M_{N_2}}{M_{NH_3}}}$$

$$\frac{100/32.5}{60/t}=\sqrt{\frac{28}{17}}$$

$$\frac{100\times t}{60\times32.5}=\sqrt{\frac{28}{17}}$$

$$t=25 \text{ second}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

10. A gas with molecular formula C_nH_{2n+2} diffuses through a porous plug at a rate 1/6th of the rate of diffusion of hydrogen gas under similar conditions. The formula of the gas is:

(a) C_2H_6 (b) $C_{10}H_{22}$ (c) C_5H_{12} (d) C_6H_{14}

[Ans. (c)]

[Hint: $\frac{r_1}{r_2}=\sqrt{\frac{M_2}{M_1}}$

$$\frac{r_1}{r_1/6}=\sqrt{\frac{M_2}{2}}$$

$$M_2=72$$

$\therefore$ The formula of gas will be C_5H_{12}.]

11. Under similar conditions which of the following gases will diffuse four times as quickly as oxygen?

(a) He (b) H_2 (c) N_2 (d) D_2

[Ans. (b)]

[Hint: $\frac{r_{gas}}{r_{O_2}}=\sqrt{\frac{M_{O_2}}{M_{gas}}}$

$$4 = \sqrt{\frac{32}{M_{\text{gas}}}} \quad \text{or} \quad 16 = \frac{32}{M_{\text{gas}}}$$

$$\text{or} \quad M_{\text{gas}} = \frac{32}{16} = 2, \ i.e., \ H_2]$$

12. The rates of diffusion of hydrogen and deuterium are in the ratio:

(a) 1 : 1 (b) $\sqrt{2} : 1$ (c) 4 : 1 (d) 1 : 4

[Ans. (b)]

[Hint: $\frac{r_{H_2}}{r_{D_2}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}}$

$$\frac{r_{H_2}}{r_{D_2}} = \sqrt{\frac{4}{2}}$$

$$r_{H_2} = \sqrt{2} r_{D_2} \ ]$$

13. The time taken for effusion of 64 mL of oxygen will be same as the time taken for the effusion of which of the following gases under identical conditions?

(a) 64 mL of H_2 (b) 100 mL of N_2

(c) 64 mL of CO_2 (d) 45.24 mL of SO_2

[Ans. (d)]

[Hint: $\frac{r_{O_2}}{r_{\text{gas}}} = \sqrt{\frac{M_{\text{gas}}}{M_{O_2}}}$

$$\frac{64}{V} = \sqrt{\frac{64}{32}} \quad \text{or} \quad V = \frac{64}{\sqrt{2}} = 45.25 \text{ mL}]$$

14. Which of the following pairs of gases will have identical rate of effusion under similar conditions?

(a) Diprotium and dideuterium

(b) Carbon dioxide and ethane

(c) Dideuterium and helium

(d) Ethene and ethane

[Ans. (c)]

[Hint: Dideuterium and helium have same molar mass, hence they will diffuse with identical rate under identical conditions.]

15. Two gas bulbs *A* and *B* are connected by a tube having a stopcock. Bulb *A* has a volume of 100 mL and contains hydrogen. After opening the gas from *A* to the evacuated bulb *B*, the pressure falls down to 40%. The volume (mL) of *B* must be: **[PET (Kerala) 2006]**

(a) 75 (b) 150 (c) 125 (d) 200

(e) 250

[**Ans.** (b)]

[Hint: $P_1V_1(A) + P_2V_2(B) = P_R(V_1 + V_2)$

$$100 \times 100 + 0 \times V_2 = 40(100 + V_2)$$

$$V_2 = 250 - 100 = 150 \text{ mL}]$$

4.7 KINETIC THEORY OF GASES

This theory was a generalization for about ideal gases. It was presented by **Bernoulli** in 1738 and developed in 1860 by Clausius, Maxwell, Kroning and Boltzmann. Postulates of kinetic theory of gases are:

(1) Gases are made up of small structural units called atoms or molecules. Volume of individual atom or molecule is considered negligible.

(2) Gas molecules are always in rapid random motion colliding with each other and with the wall of container.

(3) Collision among gas molecules is perfectly elastic, *i.e.*, there is no loss in kinetic energy and moment during such collision.

(4) Gas molecules neither attract nor repel each other.

(5) Pressure exerted by gas is due to collisions of gas molecules with the wall of the container.

Pressure ∝ Number of collisions per unit time per unit area by the molecules on the wall of the container

(6) Kinetic energy of gas molecules depends only on absolute temperature.

Kinetic energy ∝ absolute temperature

(7) The force of gravity has no effect on the speed of gas molecules.

Derivation of Kinetic Gas Equation

On the basis of the postulates of kinetic theory of gases, it is possible to derive the mathematical expression, commonly known as kinetic gas equation, *i.e.*,

$$PV = \frac{1}{3} mnc^2$$

where, P = pressure of the gas, V = volume of the gas, m = mass of a molecule, n = number of molecules present in the given amount of a gas and c = root mean square speed.

The root mean square speed (rms speed) may be defined as the square root of the mean of squares of the individual speed of all the molecules.

$$\text{rms speed} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots + c_n^2}{n}}$$

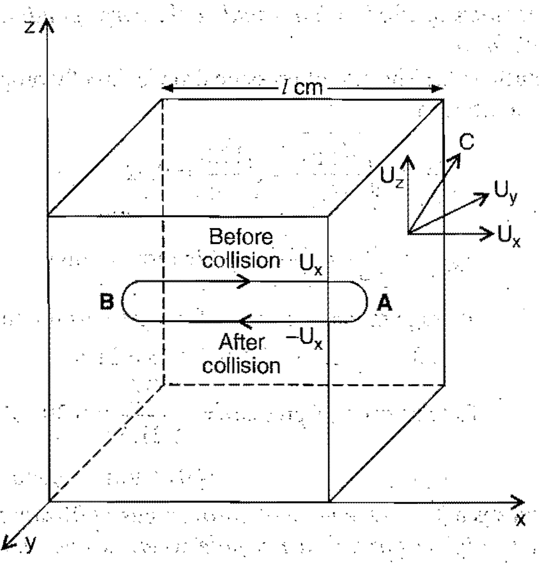


Fig. 4.5

Consider a certain mass of a gas enclosed in a cubical vessel of side 'l' cm. Let the total number of gas molecules be 'n' and mass of each molecule be 'm'. Let c be the root mean square speed. Speed can be resolved into three components, *i.e.*, U_x, U_y and U_z parallel to the edges of the container (*i.e.*, parallel to three axes x, y and z).

$$c^2 = U_x^2 + U_y^2 + U_z^2$$

Consider the movement of a single molecule between opposite faces A and B parallel to x-axis. When the molecule strikes with one wall of the container, it bounces back with the same speed and subsequently strikes the opposite wall.

The momentum of the molecule before collision with face $A = mU_x$.

The momentum of the molecule after collision $= -mU_x$

The change in momentum in one collision $= mU_x - (-mU_x)$

$$= 2mU_x$$

After collision, the molecule must move a distance $2l$ cm along x-axis before making another impact on this wall. Since the velocity 'U_x' remains unchanged, the time taken to travel a distance $2l$ cm $= \frac{2l}{U_x}$ second.

So, the number of collisions by the gas molecule in one second $= \frac{1}{\frac{2l}{U_x}} = \frac{U_x}{2l}$.

$$\text{Change of momentum per second} = 2mU_x \times \frac{U_x}{2l} = m\frac{U_x^2}{l}$$

The change of momentum on both the opposite faces A and B along x-axis per second would be double, *i.e.*, $\frac{2mU_x^2}{l}$.

Similarly,

$$\text{Change in momentum per second along } y\text{-axis} = \frac{2mU_y^2}{l}$$

and change in momentum per second along z-axis $= \frac{2mU_z^2}{l}$.

Hence, total change of momentum per second on all faces will be

$$= \frac{2mU_x^2}{l} + \frac{2mU_y^2}{l} + \frac{2mU_z^2}{l}$$

$$= \frac{2m}{l}(U_x^2 + U_y^2 + U_z^2)$$

$$= \frac{2m}{l}c^2$$

Change of momentum per second = Force

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$\text{Pressure created by one molecule} = \frac{2m}{l}\frac{c^2}{6l^2}$$

$$\text{Pressure created by } n \text{ molecules} = \frac{2mnc^2}{6l^3}$$

$$P = \frac{1}{3}\frac{mnc^2}{V} \qquad [l^3 = V]$$

or $$PV = \frac{1}{3}mnc^2$$

This equation is called kinetic gas equation.

For one gram mole of the gas,

$$n = N \qquad \text{(Avogadro's number)}$$
$$= 6.02 \times 10^{23}$$

$m \times N = M$ = molecular mass of the gas.

The above kinetic equation can be written as:

$$PV = \frac{1}{3}Mc^2$$

or $$c^2 = \frac{3PV}{M}$$

$$c = \sqrt{\frac{3PV}{M}}$$

$$= \sqrt{\frac{3P}{d}} \qquad [d = \text{density}]$$

$$= \sqrt{\frac{3RT}{M}}$$

Thus, $$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

The value of R should be taken in erg K^{-1} mol^{-1}, *e.g.*,

$R = 8.314 \times 10^7$ erg K^{-1} mol^{-1}

$$c = \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{M}} = 1.58\sqrt{\frac{T}{M}} \times 10^4 \text{ cm/sec}$$

Calculation of Kinetic Energy

$$PV = \frac{1}{3}mnc^2$$

For one gram mole of the gas,

$$PV = RT \quad \text{and} \quad n = N$$

$$\frac{1}{3}mNc^2 = RT$$

or $$\frac{2}{3}\cdot\frac{1}{2}mNc^2 = RT \quad \left(\frac{1}{2}mNc^2 = \text{KE per mol}\right)$$

$$\frac{2}{3}\cdot\text{KE} = RT$$

or $$\text{KE} = \frac{3}{2}RT$$

Average kinetic energy per mol does not depend on the nature of the gas but depends only on temperature. Thus, when two gases are mixed at the same temperature, there will be no rise or decrease in temperature unless both react chemically.

$$\text{Average kinetic energy per molecule} = \frac{\text{Average KE per mole}}{N}$$

$$= \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$$

k = Boltzmann constant

The ratio R/N is constant and is known as Boltzmann constant. Its numerical value is 1.38×10^{-16} erg K^{-1} molecule^{-1}.

4.8 MAXWELL-BOLTZMANN DISTRIBUTION OF MOLECULAR SPEEDS

The gas molecules are moving in all possible directions. They collide with one another and also with the walls of the container. As a result of collisions, the speed and direction of the gas molecules are ever changing, *i.e.*, all the molecules in a given sample of gas do not have the same speed.

The distribution of gas molecules among different possible speeds was studied by **Maxwell** and **Boltzmann** using the theory of probability. The results are mathematically expressed as,

$$dNu = 4\pi N\left[\frac{M}{2\pi RT}\right]^{3/2} e^{-\frac{Mu^2}{2RT}} u^2\, du$$

$$= 4\pi N\left[\frac{m}{2\pi kT}\right]^{3/2} e^{-\frac{mu^2}{2RT}} u^2 du$$

Here, N = Total number of molecules, M = molar mass of gas

This expression gives the number of molecules (dNu) having speed between u and $(u+du)$ at temperature (T).

A plot of fraction of molecules in the speed range $(u+du)$, $\frac{1}{N}\left(\frac{dNu}{du}\right)$ against speed u is:

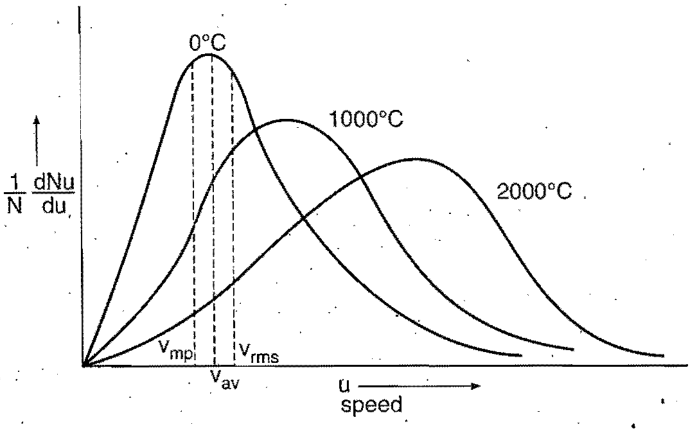


Fig. 4.6

v_{mp} = most probable speed
v_{av} = average speed
v_{rms} = root mean square speed

Kinds of Molecular Speeds

Molecular speeds are of three types:

(i) The rms speed,
(ii) The average speed and
(iii) The most probable speed

(i) The root mean square speed: The speed in kinetic gas equation, $PV = \frac{1}{3}mnc^2$, is the hypothetical speed possessed by all the gas molecules when the total kinetic energy is equally distributed amongst them. The total kinetic energy of the n molecules of the gas is sum of the kinetic energies of the individual molecules.

Total kinetic energy

$$= \frac{1}{2}mc_1^2 + \frac{1}{2}mc_2^2 + \frac{1}{2}mc_3^2 + \ldots + \frac{1}{2}mc_n^2 \qquad \ldots \text{(i)}$$

Let c be the velocity possessed by each of the n molecules; then,

$$\text{total kinetic energy} = n \times \frac{1}{2}mc^2 \qquad \ldots \text{(ii)}$$

Equating both the equations,

$$n \times \frac{1}{2}mc^2 = \frac{1}{2}mc_1^2 + \frac{1}{2}mc_2^2 + \frac{1}{2}mc_3^2 + \ldots + \frac{1}{2}mc_n^2$$

or
$$c^2 = \frac{c_1^2 + c_2^2 + c_3^2 + c_4^2 + \ldots + c_n^2}{n}$$

or
$$c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots + c_n^2}{n}}$$

Thus, rms speed is defined as the square root of the mean of the squares of the speed of all the molecules present in the given sample of the gas. The value of c is determined by using the following expressions:

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

In SI units, the values of R, P, V, M and d used are given below:

(i) $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$ or $R = 8.314\ \text{kPa dm}^3\ \text{K}^{-1}\ \text{mol}^{-1}$
(ii) V of the gas always in litre
(iii) P of the gas in kilopascal (kPa). 1 atm = 101.3 kPa and 1 torr = 0.133 kPa
(iv) M in kg mol^{-1}
(v) d in kg m^{-3}

(ii) Average speed: It is the arithmetic mean of the various speeds of the molecules.

$$\text{Average speed} = \frac{c_1 + c_2 + c_3 + \ldots + c_n}{n}$$

It is equal to $\sqrt{\frac{8RT}{\pi M}}$.

It is related to rms speed by the following relationship:

Average speed = 0.9213 × rms speed
rms speed = 1.085 × average speed

(iii) Most probable speed: This is defined as the speed possessed by maximum number of molecules of a gas at a given temperature.

Note: Root mean square speed explained the non-existence of gases in the atmosphere of moon. Root mean square speed of gases exceeds the escape velocity of moon and hence gases escape from atmosphere of moon against the gravitational barrier of moon.

It is equal to $\sqrt{\frac{2RT}{M}}$.

This is related to rms speed by the following relationship:

$$\text{Most probable speed} = \left\{\sqrt{\frac{2}{3}}\right\} \text{rms} = 0.816 \text{ rms}$$

or $$\text{rms} = 1.224 \text{ most probable speed}$$

The three kinds of molecular speeds are related to each other as:

Most probable speed : Average speed : rms speed

$$= \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1 : 1.128 : 1.224$$

rms speed at any temperature t° C may be related to its value at STP as:

$$c_t = c_0 \sqrt{\frac{(273+t)}{273}} \quad \text{... (i)}$$

$$c_0 = \sqrt{\frac{3P}{d}} \quad \text{... (ii)}$$

From eqs. (i) and (ii), we get

$$c_t = \sqrt{\frac{3P}{d}} \sqrt{\frac{(273+t)}{273}}$$

$$= \sqrt{\frac{3P(273+t)}{273d}}$$

Some Essential Points for Distribution of Molecular Speed

(i) The fraction of molecules with very low or very high speeds is very small. Maximum fraction of molecules have speed near to the most probable speed v_{mp}.

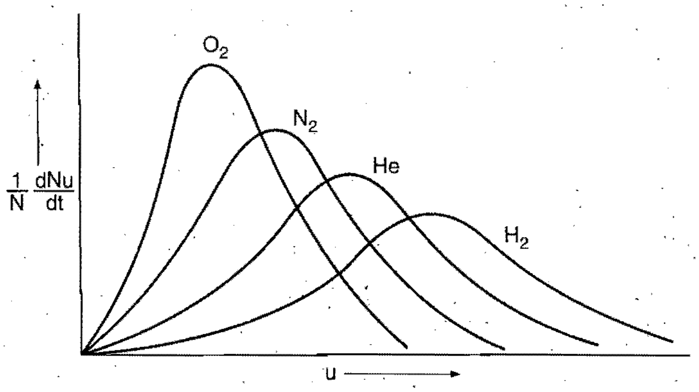


Fig. 4.7 Distribution of molecular speeds of various gases at a constant temperature

(ii) Total area under the curve is a measure of total number of molecules in the collection. Thus, area under the curve remains constant at different temperature.

(iii) Distribution of molecular speed also depends upon the molecular mass of the gas. At similar temperature a heavier gas molecule has a narrow distribution of speed than those of lighter gas molecules.

(iv) The fraction of molecules having speeds greater than minimum goes on increasing with increase in speed. It reaches to a maximum value and then begins to decrease.

(v) As long as temperature of the gas is constant, the fraction having a particular speed remains the same inspite of the fact that the molecules change their speeds due to collisions.

The increase in the temperature of the gas increases the molecular speed. As a result, the most probable speed increases with the increase of temperature and the distribution curve shifts towards right. The general shape of the curve remains the same but the maxima of the curve becomes somewhat flat at a higher temperature, *i.e.*, there is a wider distribution of molecular speeds and the fraction of the molecules having high speeds increases. However, the fraction of molecules possessing most probable speeds decreases with increase in temperature.

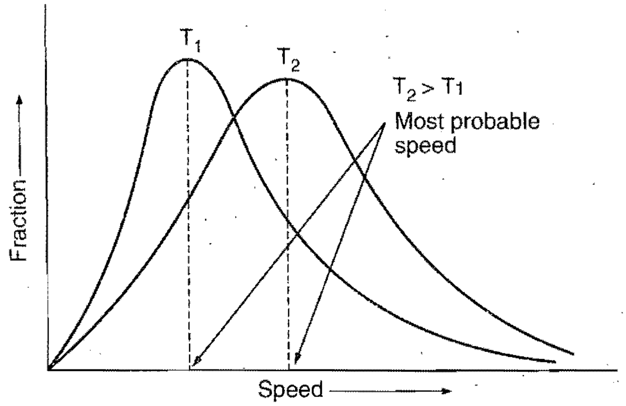


Fig. 4.8

SOME SOLVED EXAMPLES

Example 36. *Calculate the kinetic energy in joule of 8.00 g of methane at 27°C.*

Solution: Number of gram moles of methane $= \frac{8}{16} = \frac{1}{2}$

$$T = (27 + 273) = 300 \text{ K}$$

$$R = 8.32 \text{ J K}^{-1} \text{ mol}^{-1}$$

Kinetic energy for one gram mole $= \frac{3}{2} RT$

$$= \frac{3}{2} \times 8.32 \times 300 \text{ J}$$

Thus,

kinetic energy for $\frac{1}{2}$ gram mole $= \frac{1}{2} \times \frac{3}{2} \times 8.32 \times 300 = 1872$ J

Example 37. *Calculate the average and total kinetic energy of 0.5 mole of an ideal gas at 0°C.*

Solution: Average kinetic energy per molecule of the gas

$$= \frac{3}{2}\frac{R}{N}T$$

$$= \frac{3}{2} \times \frac{8.314 \times 10^7}{6.023 \times 10^{23}} \times 273$$

$$= 5.65 \times 10^{-14} \text{ erg} = 5.65 \times 10^{-21} \text{ J}$$

Total kinetic energy of 0.5 mole of the gas

$$= \frac{3}{2} RT \times 0.5$$

$$= \frac{3}{2} \times 8.314 \times 10^7 \times 273 \times 0.5$$

$$= 1.702 \times 10^{10} \text{ erg} = 1.702 \text{ kJ}$$

Example 38. *Calculate the pressure exerted by 10^{23} gas molecules each of mass 10^{-22} g in a container of volume 1 litre, the rms speed is 10^5 cm s^{-1}.*

Solution: Using kinetic gas equation,

$$P = \frac{1}{3}\frac{mnc^2}{V}$$

Given, $V = 1$ litre $= 1000$ mL $= 1000$ cm^3; $n = 10^{23}$; $m = 10^{-22}$ g and $c = 10^5$ cm s^{-1}.

Substituting the values in the above equation,

$$P = \frac{1}{3} \times \frac{10^{-22} \times 10^{23} \times 10^{10}}{1000} = 3.33 \times 10^7 \text{ dyne cm}^{-2}$$

Example 39. *Calculate the root mean square speed of an oxygen molecule at 288 K in SI units.*

Solution: $c = \sqrt{\frac{3RT}{M}}$

$R = 8.314$ kPa dm^3 K^{-1} mol^{-1}, $T = 288$ K

and $M = 0.032$ kg mol^{-1}

Substituting the values in above equation

$$c = \sqrt{\frac{3 \times 8.314 \times 288}{0.032}} = 473.79 \text{ ms}^{-1}$$

Example 40. *Calculate the root mean square speed of hydrogen molecule at STP.*

Solution: $c = \sqrt{\frac{3PV}{M}}$

$P = 1$ atm $= 101.3$ kPa

$V = 22.4$ dm^3

$M = 2$ g mol^{-1} $= 0.002$ kg mol^{-1}

Substituting the values,

$$c = \sqrt{\frac{3 \times 101.3 \times 22.4}{0.002}} = 1844.91 \text{ ms}^{-1}$$

Alternative method:

$$c = \sqrt{\frac{3RT}{M}}$$

$R = 8.314$ kPa dm^3 K^{-1} mol^{-1}; $T = 273$ K;

$M = 0.002$ kg mol^{-1}

Substituting the values,

$$c = \sqrt{\frac{3 \times 8.314 \times 273}{0.002}} = 1845.15 \text{ ms}^{-1}$$

Example 41. *Oxygen at 1 atmosphere and 0°C has a density of 1.4290 g L^{-1}. Find the rms speed of oxygen molecule.*

Solution: $P = 1$ atm $= 101.3 \times 10^3$ Pa

$d = 1.4290$ g L^{-1} $= 1.4290$ kg m^{-3}

We know that,

$$c = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 101.3 \times 10^3}{1.4290}} = 461.15 \text{ ms}^{-1}$$

Example 42. *At what temperature will hydrogen molecules have the same root mean square speed as nitrogen molecules at 27°C?*

Solution :

$$\sqrt{\frac{3RT}{M_H}} = \sqrt{\frac{3R \times 300}{M_N}}$$

or

$$\frac{T}{M_H} = \frac{300}{M_N} \text{ or } T = \frac{300}{28} \times 2 = 21.43 \text{ K}$$

Example 43. *Calculate the root mean square, average and most probable speed of oxygen at 27°C.*

Solution: 27°C = 300 K

$$\text{Root mean square speed} = \sqrt{\frac{3RT}{M}}$$

$R = 8.314 \times 10^7$ erg K^{-1} mol^{-1}; $M = 32$ g mol^{-1}; $T = 300$ K

Substituting the values,

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}}$$

$= 48356$ cm/sec

$= 483.56$ m/sec

$$\text{Average speed} = \sqrt{\frac{8RT}{\pi M}}$$

$$= \sqrt{\frac{8 \times 8.314 \times 10^7 \times 300 \times 7}{22 \times 32}}$$

$= 44542$ cm/sec

$= 445.42$ m/sec

$$\text{Most probable speed} = \sqrt{\frac{2 \times R \times T}{M}}$$

$$= \sqrt{\frac{2 \times 8.314 \times 10^7 \times 300}{32}}$$

$= 39483$ cm/sec

$= 394.83$ m/sec

Example 44. *Calculate the average kinetic energy per mole of CO_2 gas at 27°C in different units.*

Solution: $\text{KE} = \frac{3}{2} nRT$

$$= \frac{3}{2} \times 1 \times 1.987 \times 300 = 894.15 \text{ cal}$$

$$\text{KE} = \frac{3}{2} nRT$$

$$= \frac{3}{2} \times 1 \times 8.314 \times 300$$

$$= 3741 \text{ J}$$

$$= 3.741 \times 10^{10} \text{ erg}$$

Example 45. *A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 N m^{-2}. Calculate the root mean square speed and temperature of the gas molecules. If the ratio of most probable speed to the root mean square speed is 0.82, calculate the most probable speed of these molecules at this temperature.* **(IIT 1993)**

Solution: Amount of the gas $= \frac{2.0 \times 10^{21}}{6.023 \times 10^{23}}$ mole

Given, $V = 1$ litre $= 10^{-3}$ m^3; $P = 7.57 \times 10^3$ Nm^{-2}, $R = 8.314$ J K^{-1} mol^{-1}.

Applying $PV = nRT$ or $T = \frac{PV}{nR}$

$$T = \frac{10^{-3} \times 7.57 \times 10^3}{\frac{2.0 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314} = 274.2 \text{ K}$$

$$\text{rms speed} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}} = 494.22 \text{ ms}^{-1}$$

Most probable speed $= 0.8 \times$ rms

$$= 0.8 \times 494.22 \text{ ms}^{-1} = 395.376 \text{ ms}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

16. At what temperature is the root mean square speed of N_2 gas equal to that of propane gas at STP?
(a) 173.7°C (b) 173.7 K (c) 273 K (d) –40°C
[Ans. (b)]
[Hint: $v_{\text{rms}}(N_2) = v_{\text{rms}}(C_3H_8)$

$$\sqrt{\frac{3RT}{28}} = \sqrt{\frac{3R\ 273}{44}}$$

$$T = 173.7 \text{ K}]$$

17. At what temperature is the kinetic energy of a gas molecule half of its value at 327°C?
(a) 13.5°C (b) 150°C (c) 27°C (d) –123°C
[Ans. (c)]
[Hint: $\text{KE} = \frac{3}{2} RT$

$$\frac{E_1}{E_2} = \frac{\frac{3}{2} RT_1}{\frac{3}{2} RT_2}$$

$$\frac{1}{1/2} = \frac{600}{T_2}$$

$$T_2 = 300 \text{ K}$$

$$t = 27° \text{C}]$$

18. The root mean square speed of molecules of nitrogen gas is v at a certain temperature. When the temperature is doubled, the molecules dissociate into individual atoms. The new rms speed of the atom is:
(a) $\sqrt{2}v$ (b) $2v$ (c) v (d) $4v$
[Ans. (b)]
[Hint: $v_1 = \sqrt{\frac{3RT}{M}}$

$$T_2 = 2T, \ M_2 = M/2$$

$$v_2 = \sqrt{\frac{3R \times 2T}{M/2}} = 2v_1]$$

19. The translational kinetic energy of an ideal gas depends only on its:
(a) pressure (b) force
(c) temperature (d) molar mass
[Ans. (c)]
[Hint: $\text{KE} = \frac{3}{2} RT$ ∴ Kinetic energy depends on temperature.]

20. At what temperature is the rms speed of H_2 molecules the same as that of oxygen molecules at 1327°C?
(a) 173 K (b) 100 K (c) 400 K (d) 523 K
[Ans. (b)]
[Hint: $\left(\sqrt{\frac{3RT_1}{M_1}}\right)_{H_2} = \left(\sqrt{\frac{3RT_2}{M_2}}\right)_{O_2}$

$$\sqrt{\frac{T_1}{2}} = \sqrt{\frac{1600}{32}}$$

$$T_1 = 100 \text{ K}]$$

21. If the temperature of 1 mole of a gas is increased by 50°C, calculate the change in kinetic energy of the system: **(DCE 2006)**
(a) 62.32 J (b) 6.235 J (c) 623.5 J (d) 6235.0 J
[Ans: (c)]
[Hint: $E = \frac{3}{2} RT$ (Kinetic energy of 1 mole gas)

$$\Delta E = \frac{3}{2} R(T + 50) - \frac{3}{2} RT$$

$$= \frac{3}{2} R \times 50 = \frac{3}{2} \times 8.314 \times 50$$

$$= 623.55 \text{ J}]$$

22. At same temperature, calculate the ratio of average velocity of SO_2 to CH_4: **(DCE 2006)**
(a) 2 : 3 (b) 3 : 4 (c) 1 : 2 (d) 1 : 6
[Ans. (c)]
[Hint: $v_{\text{av}} = \sqrt{\frac{8RT}{\pi m}}$

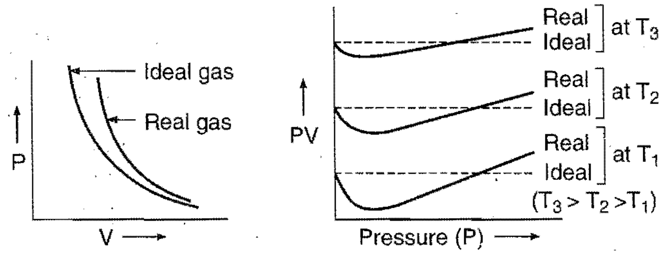
$$\frac{v_{SO_2}}{v_{CH_4}} = \sqrt{\frac{m_{CH_4}}{m_{SO_2}}}$$

$$= \sqrt{\frac{16}{64}} = \frac{1}{2} \;]$$

4.9 VAN DER WAALS' EQUATION

The gas which conforms to all of the postulates of kinetic theory or which obeys Boyle's law and Charles' law rigidly for all values of temperature and pressure or which strictly follows the general gas equation ($PV = nRT$) is called **ideal** or **perfect gas.** Actually no gas is ideal or perfect in nature. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc.

At low pressure and moderately high temperature, the real gases approach ideal behaviour (see fig.).



(a) (b)

Fig. 4.9 (a) Ideal and real gas, (b) Ideal and real gas (real gas is approaching ideal behaviour with rise in temperature)

It is observed that deviations from gas laws are high under high pressure and low temperature. van der Waals suggested that these deviations are due to the following two faulty assumptions in the kinetic theory of gases:

(i) Actual volume of the gas molecules is negligible as compared to the total volume of the gas.

(ii) Intermolecular attractions are not present in gases.

van der Waals pointed out that in the case of real gases, molecules do have a volume and also exert intermolecular attractions especially when the pressure is high and temperature is low. He applied two corrections:

(a) Volume correction: van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume. Thus, the volume of a real gas, *i.e.*, volume available for compression or movement is, therefore, actual volume minus the volume occupied by gas molecules. If b is the effective volume of the molecules per mol of the gas, the ideal volume for the gas equation is $(V - b)$ and not V, *i.e.*,

corrected volume 'V_i' $= V - b$ for one mole of the gas

and for n mole of the gas, 'V_i' $= V - nb$.

b is termed the excluded volume which is constant and characteristic for each gas. The excluded volume 'b' is actually four times the actual volume of the gas molecules.

$$b = \left[\frac{4}{3}\pi r^3\right] \times 4N$$

where 'r' = radius of gas molecule

N = Avogadro's number

(b) Pressure correction: A molecule in the interior of the gas is attracted by other molecules on all sides. These forces, thus, are not effective, as equal and opposite forces cancel each other. However, a gas molecule which is just going to strike the wall of the vessel experiences an inward pull due to unbalanced attractive forces. Therefore, it strikes the wall with less momentum and the observed pressure will be less than the ideal pressure.

$$P_{\text{ideal}} = P_{\text{obs}} + P'$$

where P' is the pressure correction.

Pressure Correction Depends upon Two Factors

(i) The attractive force exerted on a single molecule about to strike the wall is proportional to the number of molecules per unit volume in the bulk of the gas.

(ii) The number of molecules striking the wall which is also proportional to the number of molecules per unit volume of the gas.

Both these factors are proportional to the density of the gas. Therefore, the attractive force is proportional to the square of the density of the gas.

$$P' \propto \text{total attractive force}$$

$$\propto d^2$$

$$\propto \frac{1}{V^2}$$

or $$P' = \frac{a}{V^2}$$

where 'a' is a constant depending upon the nature of the gas and V is the volume of 1 mole of the gas.

Thus, corrected pressure, $P_{\text{ideal}} = P_{\text{obs}} + \frac{a}{V^2}$

Making both the corrections, the general gas equation $PV = RT$ may be written as:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

The equation is called van der Waals' equation. van der Waals' equation for n moles of the gas is:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

van der Waals' equation is obeyed by real gases over a wide range of temperature and pressure and hence this equation is called equation of state for the real gases. The constants 'a' and 'b' are called van der Waals' constants and they are characteristic of each gas.

Unit of van der Waals' Constants

a and b are expressed in terms of the units of P and V.

$$\text{Pressure correction } P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P'V^2}{n^2} = \frac{\text{Pressure correction} \times (\text{Volume})^2}{(\text{Mole})^2}$$

Thus, if pressure and volume are expressed in atmosphere and litre respectively, the units of constant 'a' will be atmosphere litre^2 mol^{-2}.

$$\text{SI unit, } 'a' = \text{N m}^4 \text{ mol}^{-2}$$

'b' is the effective volume of the gas molecules in one gram mole of the gas. Thus, the unit of 'b' is the same as for the volume, *i.e.*, litre mol^{-1}.

$$\text{SI unit, } 'b' = \text{m}^3 \text{ mol}^{-1}$$

Boyle temperature: The temperature at which real gas behaves like ideal gas and obeys the gas laws over a wide range of pressure is called Boyle temperature 'T_b'. At this temperature, PV remains constant for an appreciable range of pressure

$$T_b = \frac{a}{Rb} = \frac{1}{2T_i}$$

where, T_i = inversion temperature

a, b = van der Waals' constants

At Boyle temperature, $\frac{\partial PV}{\partial P} \approx 0$ when P approaches zero.

4.10 CRITICAL PHENOMENON AND LIQUEFACTION OF GASES

During the early part of nineteenth century, a number of gases such as carbon dioxide, sulphur dioxide, ammonia, etc. were liquefied by subjecting the gas to low temperature and high pressure. On cooling, the kinetic energy of the gas molecules decreases. The slow moving molecules come nearer to each other due to forces of attraction and, thus, aggregate and are converted into liquid. The increase of pressure can also bring the gas molecules closer to each other and, thus, is helpful in converting a gas into liquid. The effect of temperature is rather more important than that of pressure. The essential conditions for liquefaction of gases were discovered by **Andrews** in 1869 as a result of his study of Pressure-Volume-Temperature (P-V-T) relationship for carbon dioxide. It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. **The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature** (T_c). The pressure required to liquefy a gas at this temperature is called the **critical pressure** (P_c). The volume occupied by one mole of the substance at the critical temperature and pressure is called **critical volume** (V_c).

The results of Andrews experiments are shown in the following Figure. 4.10(a) in which the pressure is plotted against volume at various temperatures for carbon dioxide. Each pressure-volume plot is called isotherm.

Let us consider an isotherm at 13.1°C. At low pressure, carbon dioxide is entirely gaseous and is represented by the point (A) in the isotherm. On increasing pressure, volume decreases as shown by the portion AX of the isotherm, approximately in accordance with Boyle's law. At X, deviations from Boyle's law begin to appear and the volume decreases rapidly as the gas is converted into liquid. At point Y, carbon dioxide has been completely liquefied. Between X and Y, pressure remains constant and both the gas and liquid phases are in equilibrium. The pressure corresponding to the horizontal portion XY of the isotherm is the vapour pressure of the liquid at the temperature of the isotherm.

The isotherm at 21.5°C shows a similar behaviour except that liquefaction starts at higher pressure and the horizontal portion MN is shorter. As the temperature is raised, the horizontal portion of the isotherm becomes smaller and smaller until at 31.1°C at which it reduces to a point P. Point P is called **critical point;** at this point the boundary between liquid and gas phase (meniscus) disappears indicating that both the phases have identical characteristics. Above 31.1°C, there is no indication of liquefaction. The isotherm at critical temperature 31.1°C is called **critical isotherm.** The tangent at critical point P is horizontal, so that, $\frac{dP}{dV}$ at critical point will be zero. Thus, the point 'P' is also called the **point of inflection.**

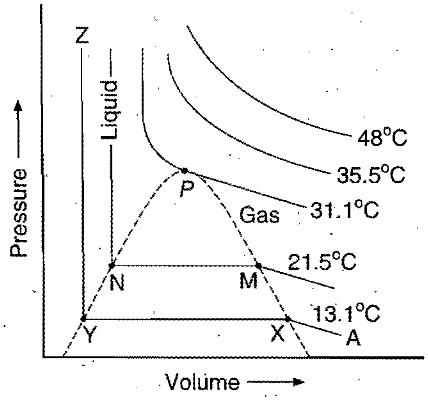


Fig. 4.10 (a) Isotherms of carbon dioxide showing critical region

It may be concluded from this explanation that in the area to the left of the dotted line below the critical isotherm, only liquid carbon dioxide exists. To the right of the dotted line, only gaseous carbon dioxide exists. The horizontal portion, within the dotted line shows the equilibrium between gas and liquid phase.

The van der Waals' Equation and the Critical Constants

The van der Waals' equation for 1 mole of a gas is given by:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This equation may be written as,

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

or
$$PV^3 + aV - PbV^2 - ab - RTV^2 = 0$$

Dividing above equation by 'P', we get
$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0$$

Arranging in descending powers of V, we get
$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \qquad \text{... (i)}$$

Equation (i) is a cubic equation in 'V' and therefore for any value of P and T, it will have three values of V, all of which may be real or one may be real and the other two imaginary. When pressure *versus* volume plots are constructed using equation (i) we get the curves as shown in Fig. 4.10(b).

It is evident from the Fig. 4.10 (b) that the curves at and above the critical temperature are similar to those in Fig. 4.10 (a). However, below critical temperature, the horizontal portion determining the coexistence of gas and liquid is replaced by a (~) shaped curve ABC in Fig. 4.10(b). Thus, this curve predicts that there are three values of V corresponding to the points A, B and C. At the critical point 'P', the three roots of van der Waals' equation are not only real and positive but also identical and equal to the critical value V_c. This condition may be expressed as,

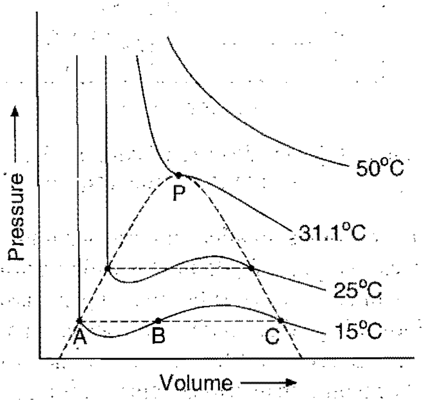


Fig. 4.10 (b) Isotherms of carbon dioxide according to van der Waals' equation

$$V = V_c$$
or
$$V - V_c = 0$$
$$(V - V_c)^3 = 0$$
$$\therefore \quad V^3 - 3V_cV^2 + 3VV_c^2 - V_c^3 = 0 \qquad \text{... (ii)}$$

At critical point, equations (i) and (ii) must be identical. Comparing and equating the coefficients of like powers of V gives:
$$3V_c = b + \frac{RT_c}{P_c} \qquad \text{... (iii)}$$
$$3V_c^2 = \frac{a}{P_c} \qquad \text{... (iv)}$$
$$V_c^3 = \frac{ab}{P_c} \qquad \text{... (v)}$$

In above equations, $T = T_c$, $P = P_c$ at critical state.

Dividing equation (v) by (iv), we get,
$$\frac{V_c}{3} = b$$
i.e.,
$$V_c = 3b \qquad \text{... (vi)}$$

Substituting the value of V_c from eq. (vi) in (v), we get
$$(3b)^3 = \frac{ab}{P_c}$$
$$\therefore \quad P_c = \frac{a}{27b^2} \qquad \text{... (vii)}$$

Finally, substituting the values of P_c and V_c in eq. (iii), we get
$$T_c = \frac{8a}{27Rb} \qquad \text{... (viii)}$$

We can express the constants a, b and R in terms of critical constants as:
$$b = \frac{V_c}{3}$$
$$a = 3P_cV_c^2$$
$$R = \frac{8P_cV_c}{3T_c}$$
$$P_cV_c = \frac{3}{8}RT_c \qquad \text{...(ix)}$$

Equation (ix) is called equation of critical state. Critical compressibility factor of a gas may be calculated as,
$$Z_c = \frac{P_cV_c}{RT_c} = \frac{\left(\frac{a}{27b^2}\right)(3b)}{R\left(\frac{8a}{27Rb}\right)} = 0.375$$

Critical constants of gases :

Gas	P_c (atm)	V_c (cm^3 mol^{-1})	T_c (K)
He	2.3	57.8	5.3
H_2	12.8	65	33.2
Ne	26.9	41.7	44.4
N_2	33.6	90.1	126.1
O_2	50.3	74.4	154.5
CO_2	72.7	95.0	304.2
H_2O	218.0	55.6	647.3
NH_3	112.0	72.0	405.5
CH_4	45.8	99.0	191.0
C_2H_6	48.2	139.0	305.5
C_2H_4	50.5	124.0	417.2

4.10.1 EXPERIMENTAL METHODS FOR LIQUEFACTION OF GASES

Discovery of critical phenomenon by Andrews in 1869 showed that gases cannot be liquefied by the application of pressure alone; they must first be cooled below their critical temperatures and then subjected to adequate pressure to cause liquefaction.

Principles involved in liquefaction are:

(1) A gas must be at or below its critical temperature. Lower the temperature below the critical value, easier would be the liquefaction.

(2) The gas is cooled either by doing external work or by expanding against the internal forces of molecular attraction.

Low temperature for liquefaction of gases can be achieved by the following techniques:

(a) Cooling by rapid evaporation of a volatile liquid.

(b) Cooling by Joule-Thomson effect.

(c) Cooling by adiabatic expansion involving mechanical work.

(a) Cooling by Rapid Evaporation of a Volatile Liquid

This method was first employed by **Pictet** and **Cailletet.** An easily volatile liquid is rapidly evaporated to cool and liquefy a less volatile liquid. This is the principle underlying the cascade process [Fig. 4.11(a)] for liquefaction of O_2.

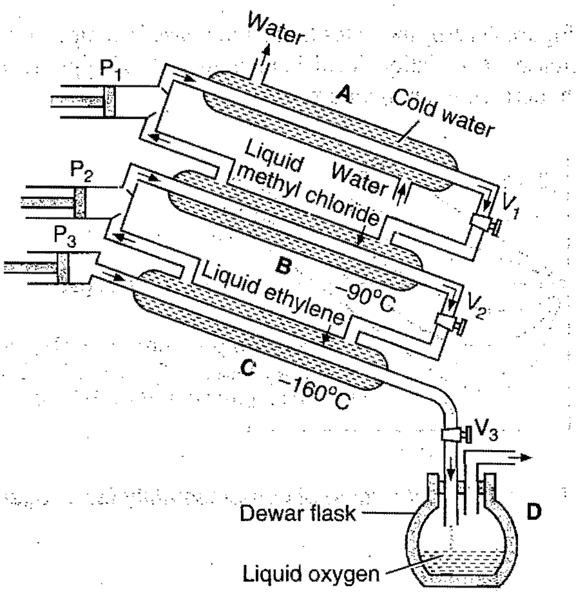


Fig. 4.11 (a) Cascade process for the liquefaction of oxygen

The apparatus consists of three compression pumps P_1, P_2 and P_3 and three compression chambers A, B and C. The compression pumps are joined in series. The pump P_1 compresses methyl chloride gas which is cooled by cold water circulating in outer jacket of A. As the critical temperature of methyl chloride is 143°C, it is liquefied at room temperature. The liquid methyl chloride passes through valve V_1 into the outer jacket of B which is connected to the suction side of P_1. As a result of reduced pressure, the liquid methyl chloride evaporates and the temperature in B reaches –90°C.

The inner tube of B is filled with ethylene gas which is cooled to –90°C. As the critical temperature of ethylene is 10°C, it gets liquefied and passes through valve V_2 into the outer jacket of C. Ethylene liquid is allowed to evaporate under reduced pressure with the help of pump P_2 resulting in a sharp fall in the temperature of oxygen (–118°C) which is filled in the inner tube of C. Oxygen gets liquefied during the compression stroke of pumps P_3 and is collected in the Dewar flask D.

(b) Cooling by Joule-Thomson Effect
(Linde's process for liquefaction of air)

When a compressed gas is allowed to expand into a low pressure or vacuum under adiabatic conditions, a lowering of temperature is observed. This is known as Joule-Thomson effect. In the expansion, molecules of the gas move far apart from one another. Work is done by the gas molecules to overcome intermolecular forces. Work is done at the cost of the kinetic energy of gas molecules. Consequently a cooling effect is observed. For each gas, there is a characteristic temperature above which a gas on expansion shows a heating effect while below it the gas cools on expansion. This temperature is known as **inversion temperature** of the gas. This temperature is related to van der Waals' constant a and b by the expression:

$$T_i = \frac{2a}{Rb}$$

where, T_i is the inversion temperature of the gas.

Gases like H_2 and He have low inversion temperatures ($T_{i\,H_2}$ = 193 K and $T_{i\,He}$ = 33 K) and they show heating effects in Joule-Thomson expansion under ordinary temperature. If these gases are cooled below their inversion temperatures, they also show cooling effects.

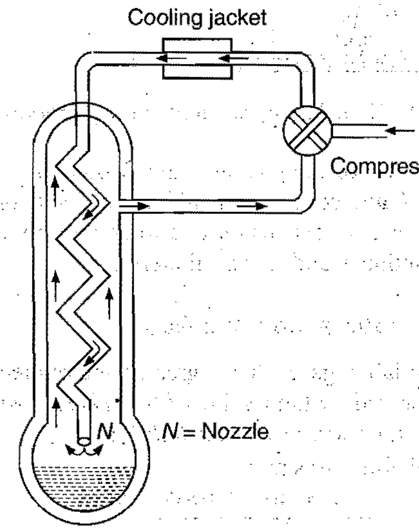


Fig. 4.11 (b) Linde's process for liquefaction of air

Joule-Thomson effect is the basis for liquefaction of air by Linde's process. The apparatus is shown in Fig. 4.11 (b).

Pure and dry air is compressed to a pressure of about 200 atm. Any heat produced during the compression is removed by passing the gas through a cooling jacket. Compressed air is allowed to expand suddenly through a nozzle (N) to a large chamber, where it gets cooled and the pressure reduced to about 1 atmosphere. The cooled air is made to pass through the outer tube and is sent back to the compressor. The incoming air further cools on expansion. The process is continued until air liquefies and is collected at the bottom.

(c) Cooling by Adiabatic Expansion Involving Mechanical Work

When a gas is allowed to expand adiabatically against a pressure, it does some external work at the cost of its kinetic energy, due to which its temperature falls. This principle is used in Claude's process for liquefaction of air. The apparatus is shown in Fig. 4.11 (c).

Pure and dry air is compressed to about 200 atmospheric pressure and then passed through the tube T. Compressed air divides itself into two parts at 'A' and a portion enters through 'C' fitted with an airtight piston. There, it expands, pushing the piston outward and performs some external work.

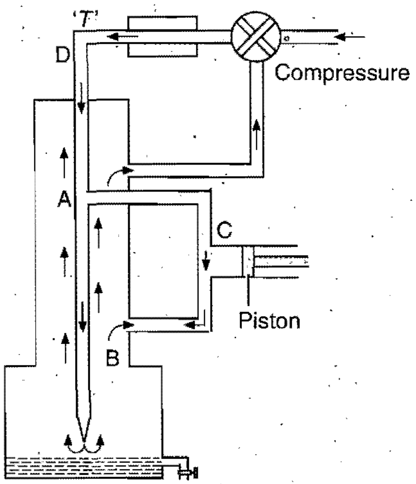


Fig. 4.11 (c) Claude's apparatus for liquefaction of air

The temperature of the gas thus falls. Cooled air then enters the chamber at B and cools the incoming air. The temperature of air is also reduced on expansion due to Joule-Thomson effect. The process continues until the air liquefies.

Tendency of Liquefaction of a Gas

Easily liquefiable gases have greater intermolecular force which is represented by high value of 'a'. *Thus, greater will be the value of 'a' more will be its liquefiability.*

Easily liquefiable gases are:

$$\underset{\substack{\text{Decreasing value of constant '}a\text{'}\\ \text{(Decreasing tendency of liquefiability)}}}{\xrightarrow{SO_2 > NH_3 > H_2O > CO_2,\ \text{etc.}}}$$

Above gases have higher value of 'a' as compared to the permanent gases O_2, N_2, H_2, He, Ne, etc.

Incompressibility of a Gas

van der Waals' constant 'b' represents the excluded volume, *i.e.*, four times the volume occupied by the gas per mole. Value of 'b' remains constant over a wide range of temperature and pressure which implies that gas molecules are incompressible.

Compressibility factor: Mathematically, it may be defined as,

$$Z = \frac{PV}{nRT}$$

The extent to which a real gas departs from ideal behaviour is expressed in terms of compressibility factor.

$$Z = \frac{\text{Molar volume of real gas } (V_m)}{\text{Molar volume of ideal gas } (V_m)} = \frac{PV_m}{RT}$$

When $Z > 1, V_m > 22.4$ L at STP and when $Z < 1, V_m < 22.4$ L at STP.

(i) $Z = 1$ for ideal gas. Deviation from the unity indicates extent of imperfection or non-ideality.

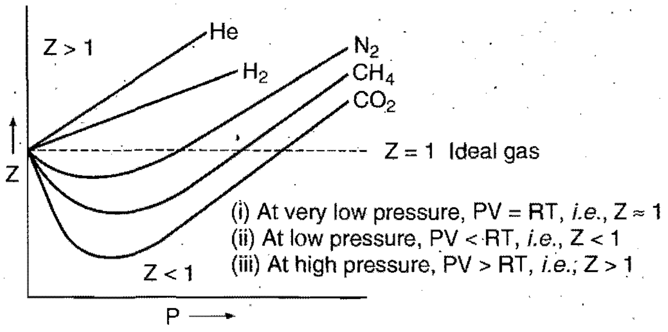
(ii) Real gases have $Z \approx 1$ at low pressure and high temperature. In this case, the real gas behaves like ideal gas.

(iii) $Z > 1$ shows that it is difficult to compress the gas as compared to ideal gas. It is possible at high pressure. In this case, repulsive forces dominate.

(iv) $Z < 1$ shows that the gas is easily compressible as compared to ideal gas. It is possible at intermediate pressure. In this case, attractive forces are dominant.

Plots of Compressibility Factor against Pressure

Figure 4.12(b) indicates that an increase in temperature shows decrease in deviation ideal behaviour, *i.e.*, Z approaches unity with increase in temperature.



(i) At very low pressure, PV = RT, *i.e.*, Z ≈ 1
(ii) At low pressure, PV < RT, *i.e.*, Z < 1
(iii) At high pressure, PV > RT, *i.e.*, Z > 1

Fig. 4.12(a) Variation of compressibility factor against

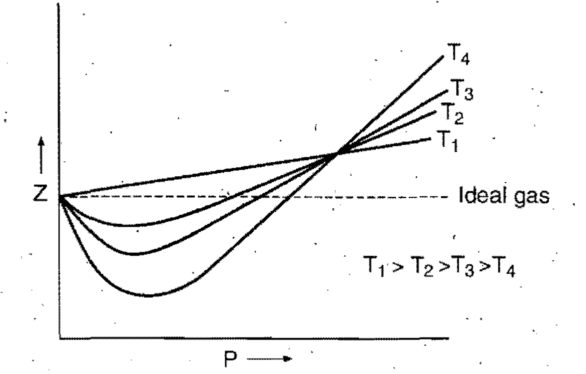


Fig. 4.12(b) Variation of compressibility factor against pressure at different temperature

Note: (i) In case of H_2, $Z > 1$ at 273 K and Z increases with the pressure. When temperature is less than 273 K, H_2 has $Z < 1$.

(ii) For gases other than hydrogen, at 273 K there is decrease in 'Z' at initial stage, with increase in pressure, value of 'Z' approaches a minimum, with increase in pressure.

(iii) In case of easily liquefiable gas like CO_2, Z dips largely below ideal line in low pressure region, see Fig. 4.12 (a).

Specific Heat of Gases

Amount of heat required to raise the temperature of 1 g of a substance through 1°C is called its specific heat. It can be measured at constant pressure and at constant volume.

Molar specific heat, *i.e.*, heat required to raise 1 gram mole of a substance through 1°C is called heat capacity.

Heat Capacity at Constant Volume

It is denoted by C_V. It may the heat supplied to one mole of a substance to increase the temperature through 1°C at constant volume.

We know from kinetic theory that,

$$PV = \frac{1}{3}mnc^2 \quad \text{or} \quad \frac{1}{2}mnc^2 = \frac{3}{2}RT$$

Thus, kinetic energy $E = \frac{3}{2}RT$

When temperature is raised through 1°C then the increase in kinetic energy may be given as:

$$\text{Increase in kinetic energy} = \frac{3}{2}R(T+1) - \frac{3}{2}RT = \frac{3}{2}R$$

Now, $C_V = \frac{3}{2}R$ since at constant volume, heat supplied to raise the temperature is used up to increase the kinetic energy only.

$C_V = \frac{3}{2}R$ [for monoatomic gases only, since monoatomic gases undergo translational motion only]

$C_V = \frac{3}{2}R + x$ [for di and polyatomic molecules; vibrational and rotational motions also contribute to the total kinetic energy]

where factor 'x' varies from gas to gas and its value is zero for monoatomic gases.

Heat Capacity at Constant Pressure

It is denoted by C_P; it may be defined as heat supplied to 1 mole of a substance in order to increase the temperature through 1°C at constant pressure.

Heat supplied at constant pressure will be used in:

(i) Increasing kinetic energy, which is equal to $\frac{3}{2}R + x$. For monoatomic gas increase in kinetic energy is equal to $\frac{3}{2}R$ when temperature is raised through 1°C.

(ii) Doing work due to volume expansion.

We know that, $PV = RT$ for 1 mole of gas ... (i)

When temperature changes to $(T+1)$, then

$$P(V + \Delta V) = R(T+1) \qquad \text{... (ii)}$$

Subtracting eq. (i) from eq. (ii), we have

$P\Delta V = R =$ Work done due to volume expansion

Thus, $C_P = \frac{3}{2}R + R = \frac{5}{2}R$ for monoatomic gases

$C_P = C_V + R$ or $C_P - C_V = R$ (general equation)

Ratio of Molar Heat Capacity

It is denoted as γ and it represents atomicity of the gas.

$$\text{For monoatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$$

$$\text{For diatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$$

$$\text{For triatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{4R}{3R} = 1.33$$

Name	C_P	C_V	$C_P - C_V$	$C_P/C_V = \gamma$	Atomicity
He	5	3.01	1.99	1.661	1
N_2	6.95	4.96	1.99	1.4	2
O_2	6.82	4.83	1.99	1.4	2
CO_2	8.75	6.71	2.04	1.30	3
H_2S	8.62	6.53	2.09	1.32	3

Example 46. *Specific heat of a monoatomic gas at constant volume is 315 $J\ kg^{-1}\ K^{-1}$ and at a constant pressure is 525 $J\ kg^{-1}\ K^{-1}$. Calculate the molar mass of the gas.*

Solution: $C_P = M \times 525$ and $C_V = M \times 315$

where, M is the molecular mass.

$$C_P - C_V = R \ (R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1})$$

$$M \times 525 - M \times 315 = 8.314$$

$$M\ (525 - 315) = 8.314$$

$$M = \frac{8.314}{210} = 0.0396\ \text{kg mol}^{-1} = 39.6\ \text{g mol}^{-1}$$

Example 47. *Calculate the pressure exerted by 16 g of methane in a 250 mL container at 300 K using van der Waals' equation. What pressure will be predicted by ideal gas equation?*

$a = 2.253\ atm\ L^2\ mol^{-2}$, $b = 0.0428\ L\ mol^{-1}$,

$R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$

Solution: Given, $16\text{ g } CH_4 = \frac{16}{16} = 1\text{ mole}$

Applying van der Waals' equation,

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

Substituting $n = 1$,

$R = 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1}$; $T = 300\ \text{K}$; $V = 0.250\ \text{L}$;

$a = 2.253\ \text{atm L}^2\ \text{mol}^{-2}$; $b = 0.0428\ \text{L mol}^{-1}$

$$P = \frac{1\times 0.0821\times 300}{(0.250-1\times 0.0428)} - \frac{1\times 2.253}{(0.250)^2} = 82.822 \text{ atm}$$

The ideal gas equation predicts that,

$$P = \frac{nRT}{V} = \frac{1\times 0.0821\times 300}{0.250} = 98.52 \text{ atm}$$

Example 48. *Calculate the temperature of the gas if it obeys van der Waals' equation from the following data. A flask of 2.5 litre contains 10 mole of a gas under 50 atm. Given* $a = 5.46$ *atm litre*^{2} *mol*$^{-2}$ *and* $b = 0.031$ *litre mol*$^{-1}$.

Solution: Given that,

$P = 50$ atm; $V = 2.5$ litre, $n = 10$; $a = 5.46$ atm litre^2 mol^{-2};

$b = 0.031$ litre mol^{-1}; $R = 0.0821$ litre-atm K^{-1} mol^{-1}.

Applying van der Waals' equation,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or

$$T = \frac{\left(P + \frac{an^2}{V^2}\right)(V - nb)}{nR}$$

$$= \frac{\left(50 + \frac{5.46\times 100}{(2.5)^2}\right)(2.5 - 10\times 0.031)}{10\times 0.0821} = 366.4 \text{ K}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

23. At high temperature and low pressure, the van der Waals' equation is reduced to:

(a) $\left(P + \frac{a}{V^2}\right)V = RT$ (b) $PV = RT$

(c) $P(V - b) = RT$ (d) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

[Ans. (b)]

[Hint: At high temperature and low pressure, V is large in comparison to 'b' and $\left(\frac{a}{V^2}\right)$ is negligible in comparison to P. Hence, the equation reduces to $PV = RT$.]

24. The constant 'a' in van der Waals' equation is maximum in:

(a) He (b) H_2

(c) O_2 (d) NH_3

[Ans. (d)]

[Hint: Intermolecular force of NH_3 is maximum, hence its van der Waals' constant (a) will also be maximum.]

25. The van der Waals' equation for 0.5 mol gas is:

(a) $\left(P + \frac{a}{4V^2}\right)\left(\frac{V-b}{2}\right) = \frac{2RT}{2}$

(b) $\left(P + \frac{a}{4V^2}\right)(2V - b) = RT$

(c) $\left(P + \frac{a}{4V^2}\right)(2V - 4b) = RT$

(d) $\left(P + \frac{a}{4V^2}\right) = \frac{2RT}{2(V - b)}$

[Ans. (b)]

[Hint: $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

For $n = \frac{1}{2}$, $\left(P + \frac{a}{4V^2}\right)\left(V - \frac{b}{2}\right) = \frac{1}{2}RT$

$\left(P + \frac{a}{4V^2}\right)(2V - b) = RT$]

26. van der Waals' constants of two gases X and Y are as given:

	a (litre-atm mol^{-2})	b (litre mol^{-1})
Gas X	5.6	0.065
Gas Y	5.1	0.012

What is correct about the two gases?

(a) $T_c(X) > T_c(Y)$ (b) $T_c(X) = T_c(Y)$

(c) $V_c(X) > V_c(Y)$ (d) $V_c(Y) > V_c(X)$

[Ans. (c)]

[Hint: Gas X Gas Y

$V_c = 3b$ $3\times 0.065 = 0.195$ $3\times 0.012 = 0.036$]

27. Select the correct statements about van der Waals' constant 'b':

1. It is excluded volume
2. Its unit is mol litre^{-1}
3. It depends on intermolecular force
4. Its value depends on molecular size

(a) 2, 3 (b) 1, 2, 4 (c) 2, 3, 4 (d) 3, 4

[Ans. (b)]

28. Gases X, Y, Z, P and Q have the van der Waals' constants 'a' and 'b' (in CGS units) as shown below:

	X	Y	Z	P	Q
a	6	6	20	0.05	30
b	0.025	0.15	0.1	0.02	0.2

The gas with the highest critical temperature is:

[PET (Kerala) 2006]

(a) P (b) Q (c) Y (d) Z

(e) X

[Ans. (e)]

[Hint: Critical temperature, $T_c = \frac{8a}{27Rb}$

$\therefore$ Greater is the value of (a/b), more is the critical temperature of gas.

For gas X, T_c will be maximum.

$$T_c = \frac{8a}{27Rb}$$

$\frac{a}{b}$ for $X = \frac{6}{0.025} = 240$; for all other gases, $\left(\frac{a}{b}\right)$ is lesser.]

29. At high pressure, van der Waals' equation becomes:

(DPMT 2006)

(a) $PV = RT$ (b) $PV = RT + \frac{a}{V}$

(c) $PV = RT - \frac{a}{V}$ (d) $PV = RT + Pb$

[Ans. (d)]

[**Hint:** $\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ for 1 mol gas}$$

At high pressure, $\left(P + \frac{a}{V^2}\right) \approx P$

$$\therefore \quad P(V - b) = RT$$

$$PV = RT + Pb]$$

SOME SOLVED EXAMPLES

Example 49. *Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases.*

Given that, $R = 0.082$ litre – atm K^{-1} mol^{-1}. **(IIT 1997)**

Solution:

$$n_{He} = \frac{0.4}{4} = 0.1,\ n_{O_2} = \frac{1.6}{32} = 0.05$$

$$n_{N_2} = 1.4 / 28 = 0.05$$

$$P_{He} \times V = n_{He} \times R \times T$$

$$P_{He} \times 10 = 0.1 \times 0.0821 \times 300$$

$$P_{He} = 0.2463 \text{ atm}$$

$$P \times V = (n_{He} + n_{O_2} + n_{N_2})RT$$

$$P \times 10 = (0.1 + 0.05 + 0.05) \times 0.0821 \times 300$$

$$P = 0.4926 \text{ atm}$$

Example 50. *An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g / mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.* **(IIT 1998)**

Solution: Mass of liquid = 148 – 50 = 98 g

$$\text{Volume of liquid} = \frac{\text{mass}}{\text{density}} = \frac{98}{0.98} = 100 \text{ mL}$$

Volume of vessel = Volume of liquid

Mass of gas = 50.5 – 50 = 0.5 g

On applying ideal gas equation, we have,

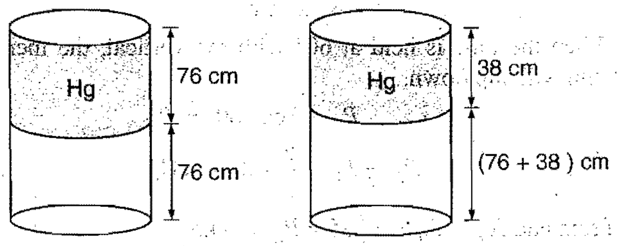
$$PV = \frac{w}{m}RT$$

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{m} \times 0.0821 \times 300$$

$$m = 123$$

Example 51. *A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.*

Solution:



(Initial state) (After heating)

At initial stage:

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 76 + 76 = 152 \text{ cm}$$

$$T = 300 \text{ K}$$

$V = V_1 / 2$ where, V_1 is volume of cylinder.

At final stage after heating:

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 38 + 76 = 114 \text{ cm}$$

$$V = \frac{3V_1}{4},\ T = ?$$

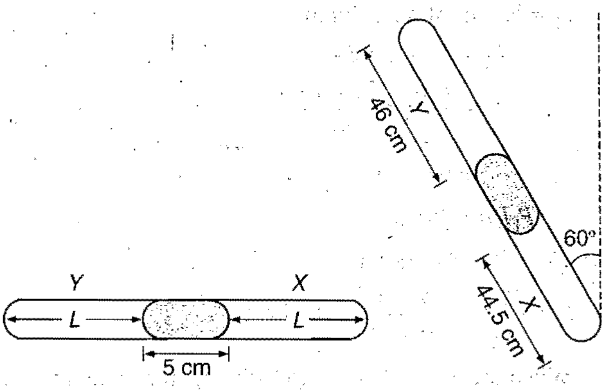
Applying gas equation, we have

$$\frac{152 \times V_1}{2 \times 300} = \frac{114 \times (3V_1 / 4)}{T}$$

$$T = \frac{114 \times 3 \times 2 \times 300}{4 \times 152}$$

$$= 337.5 \text{ K}$$

Example 52. *A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0. When the tube is held at an angle 60° with the vertical, the lengths of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate pressure P_0 in cm of Hg. (The temperature of the system is kept at 30°C).*



Solution: At horizontal position, let the length of air column in tube be L cm.

$$\therefore \quad 2L + 5 = 46 + 5 + 44.5 \text{ cm}$$

$$L = 45.25 \text{ cm}$$

When the tube is held at 60° with the vertical, the mercury column will slip down.

$$P_Y + 5\cos 60° = P_X$$

$$P_X - P_Y = \frac{5}{2} = 2.5 \text{ cm Hg} \qquad \text{... (i)}$$

From end X, $P_0 \times 45.25 = P_X \times 44.5$

$$P_X = \frac{45.25}{44.5} P_0 \qquad \text{.... (ii)}$$

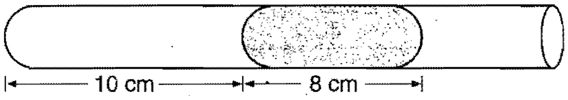
From end Y, $P_0 \times 45.25 = P_Y \times 46$

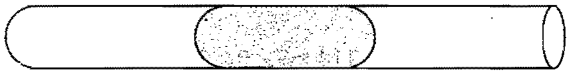
$$P_Y = \frac{45.25}{46} P_0 \qquad \text{... (iii)}$$

Substituting the values of P_X and P_Y in equation (i) we get

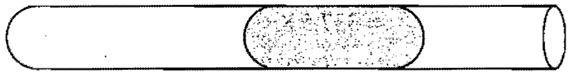
$$P_0 = 75.4$$

Example 53. *A 10 cm column of air is trapped by a column of Hg, 8 cm long, in a capillary tube horizontally fixed as shown below, at 1 atm pressure. Calculate the length of air column when the tube is fixed at the same temperature (a) vertically with open end up (b) vertically with open end down (c) at 45° with the horizontal with open end up.*





(a)



(b)

Solution: (a) $P_1V_1 = P_2V_2$

or $\quad P_1 l_1 a = P_2 l_2 a$

where, a = area of cross section of tube

l_1, l_2 = length of air column

$$\because \quad P_2 = 76 + 8 = 84 \text{ cm}$$

$$\therefore \quad l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{84}$$

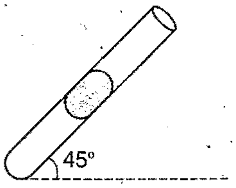
$$= 9.04 \text{ cm}$$

$$P_1 l_1 a = P_2 l_2 a$$

(b) $P_2 = 76 - 8 = 68$ cm

$$\therefore \quad l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{68} = 11.17 \text{ cm}$$

(c) When the tube is held at 45° with open end up, the weight of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg is a measure of additional pressure on gas, *i.e.,*



(c)

$$\therefore \quad l = \frac{8}{\sqrt{2}}$$

Also $\quad P_2 l_2 a = P_1 l_1 a$

$$\therefore \quad l_2 = \frac{P_1 l_1}{P_2}$$

$$= \frac{76 \times 10}{76 + \frac{8}{\sqrt{2}}} = 9.3 \text{ cm}$$

Example 54. *The stop cock connecting two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure in the two bulbs if the temperature remains the same?*

Solution: $\quad P_1V_1 + P_2V_2 = P_R(V_1 + V_2)$

$$9 \times 5 + 6 \times 10 = P_R(15)$$

$$P_R = 7 \text{ atm}$$

where, P_R = resultant pressure after mixing.

Example 55. *At what temperature is the average velocity of O_2 molecule equal to the root mean square velocity at 27°C?*

(CBSE-PMT 2005)

Solution: $\quad v_{\text{av}} = v_{\text{rms}}$

$$\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{3RT}{M}}$$

$$\frac{8RT}{\pi M} = \frac{3R \times 300}{M}$$

$$T = 353.57 \text{ K}$$

$$t = 80.57° \text{ C}$$

Example 56. *The composition of the equilibrium mixture for the equilibrium $Cl_2 \rightleftharpoons 2Cl$ at 1400 K may be determined by the rate of diffusion of mixture through a pin hole. It is found that at 1400 K, the mixture diffuses 1.16 times as fast as krypton diffuses under the same conditions. Find the degree of dissociation of Cl_2 equilibrium.* **(IIT 1995)**

Solution: Equilibrium of dissociation of Cl_2 may be represented as:

$$\begin{array}{lcc} & Cl_2(g) & \rightleftharpoons & 2Cl(g) \\ t = 0 & a & & 0 \\ t_{\text{eq}} & a(1-\alpha) & & 2a\alpha \end{array}$$

$$\text{Total moles} = a(1-\alpha) + 2a\alpha = a(1+\alpha)$$

$$M_{\text{mix}} = \frac{aM_{Cl_2}}{a(1+\alpha)} = \frac{M_{Cl_2}}{(1+\alpha)}$$

$$\frac{R_{\text{mix}}}{R_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{mix}}}}$$

$$1.16 = \frac{84(1+\alpha)}{M_{Cl_2}}$$

$$\frac{(1.16)^2 \times 71}{84} - 1 = \alpha; \quad \alpha = 0.1374$$

Example 57. *A gaseous mixture of helium and oxygen is found to have a density of* 0.518 *g* dm^{-3} *at* 25°C *and* 720 *torr. What is the per cent by mass of helium in this mixture?*

Solution: We know that, $Pm = dRT$

$$\frac{720}{760} \times m = 0.518 \times 0.0821 \times 298$$

$$m = 13.37 \text{ g / mol}$$

Let mole fraction of He in mixture be α.

$$\therefore \quad x_{He} = \alpha, \; x_{O_2} = (1-\alpha)$$

$$\text{Average } mw = \alpha \times M_{He} + (1-\alpha) M_{O_2}$$

$$13.37 = \alpha \times 4 + (1-\alpha)32$$

$$\alpha = 0.666$$

$$\% \text{ by mass of He} = 0.666 \times \frac{4}{0.666 \times 4 + 0.334 \times 32} \times 100$$

$$= 19.95\%$$

Example 58. *Find the temperature at which 3 moles of* SO_2 *will occupy a volume of* 10 *litre at a pressure of* 15 *atm.*

$a = 6.71$ *atm litre*^{2} *mol*$^{-2}$; $b = 0.0564$ *litre mol* $^{-1}$

Solution:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\left(15 + \frac{6.71 \times 9}{100}\right)(10 - 3 \times 0.0564) = 3 \times 0.082 \times T$$

$$T = 624 \text{ K}$$

Example 59. *van der Waals' constant 'b' of Ar is* 3.22×10^{-5} m^3 mol^{-1}. *Calculate the molecular diameter of Ar.*

Solution: We know that,

$b = 4 \times$ volume occupied by the molecules in one mole of a gas

$$= 4 \times N_0 \times \left(\frac{4}{3}\pi r^3\right)$$

$$3.22 \times 10^{-5} = 4 \times 6.02 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

or

$$r = \left(\frac{3.22 \times 10^{-5} \times 3 \times 7}{4 \times 6.02 \times 10^{23} \times 4 \times 22}\right)^{1/3}$$

$$= 0.1472 \times 10^{-9} \text{ m}$$

$$\therefore \quad \text{Diameter} = 2r = 2 \times 0.1472 \times 10^{-9}$$

$$= 0.2944 \times 10^{-9} \text{ m}$$

Example 60. *The compression factor (compressibility factor) for* 1 *mole of a van der Waals' gas at* 0°C *and* 100 *atmospheric pressure is found to be* 0.5. *Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant 'a'.* **(IIT 2001)**

Solution: We know that,

$$Z = \frac{PV}{RT}$$

$$0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$$V = 0.112 \text{ litre}$$

According to van der Waals' equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{for 1 mole}$$

$$\left[100 + \frac{a}{(0.112)^2}\right][0.112 - 0] = 0.0821 \times 273$$

On solving, we get $a = 1.253 \text{ L}^2 \text{ mol}^{-2}$ atm

Example 61. *The density of the vapours of a substance at* 1 *atm pressure and* 500 *K is* 0.36 *kg* m^{-3}. *The vapours effuse through a small hole at a rate of* 1.33 *times faster than oxygen under the same conditions:*

(*a*) *Determine:* (*i*) *molecular weight,* (*ii*) *molar volume,* (*iii*) *compressibility factor* (*Z*) *of the vapours,* (*iv*) *Which forces among gas molecules are dominating, the attractive or the repulsive?*

(*b*) *If the vapours behave ideally at* 1000 *K, determine the average translational kinetic energy of a molecule.* **(IIT 2002)**

Solution: (a) (i)

$$\frac{r_{vapour}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{vapour}}}$$

$$1.33 = \sqrt{\frac{32}{M_{vapour}}}$$

$$M_{vapour} = 18.1$$

(ii)

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}}$$

$$= \frac{18.1}{0.36} = 50.25 \times 10^{-3} \text{ m}^{-3}$$

(iii) Compressibility factor, $Z = \frac{PV}{RT} = \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500}$

$$= 1.225$$

(iv) $Z > 1$ shows that repulsive forces are dominant.

(b) Translational KE per molecule

$$= \frac{3}{2} \times \frac{R}{N} \times T$$

$$= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 1000$$

$$= 2.07 \times 10^{-20} \text{ J}$$

Example 62. *The ratio of rate of diffusion of helium and methane under identical conditions of pressure and temperature will be:* **[IIT (S) 2005]**

(*a*) 4 (*b*) 2 (*c*) 1 (*d*) 0.5

Solution:

$$\frac{r_{CH_4}}{r_{He}} = \sqrt{\frac{m_{He}}{m_{CH_4}}} = \sqrt{\frac{4}{16}} = \frac{1}{2}$$

$$r_{He} = 2r_{CH_4}$$

SECTION 2 : LIQUID STATE

4.11 THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids possess fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite volume but no definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

Properties of liquids can be explained on the basis of kinetic molecular theory which has the following postulates:

(i) A liquid is made up of molecules; atoms in rare cases, *e.g.*, Hg (mercury).
(ii) The molecules of the liquid are quite close together.
(iii) The intermolecular forces of attraction in a liquid are quite large.
(iv) The molecules of liquids are in a state of constant rapid motion.
(v) The average kinetic energy of the molecules of a liquid is directly proportional to their absolute temperature.

A liquid state is regarded as a condensed gas or a molten solid. Liquid state, however, has much more in common with solid state than with gaseous state. The following general characteristics are exhibited by liquids:

(i) Shape

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) Volume

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong. The molecules are not quite free to occupy any space.

(iii) Density

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100°C and 1 atmospheric pressure is 0.958 g mL^{-1} while that of water vapour under similar conditions as calculated from ideal gas law $\left(d=\dfrac{MP}{RT}\right)$ is 0.000588 g mL^{-1}.

(iv) Compressibility

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little with increased pressure. Thus, liquids are relatively incompressible compared to gases.

(v) Diffusion

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small, liquids diffuse slowly in comparison to gases.

(vi) Evaporation

The process of change of liquid into vapour state on standing is termed **evaporation.** Evaporation may be explained in terms of motion of molecules. At any given temperature, all the molecules do not possess the same kinetic energy (average kinetic energy is, however, same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation is accompanied by cooling as average kinetic energy of remaining molecules decreases.

Evaporation depends on the following factors:

(a) Nature of the liquid: The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order:

$$\begin{array}{c}\text{Ether} < \text{Alcohol} < \text{Water} \\ \text{Alcohol} < \text{Glycol} < \text{Glycerol} \\ \xrightarrow[\text{Increasing extent of hydrogen bonding}]{\hspace{8em}}\end{array}$$

(b) Surface area: Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

$$\text{Rate of evaporation} \propto \text{Surface area}$$

(c) Temperature: Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

$$\text{Rate of evaporation} \propto \text{Temperature}$$

(d) Flow of air current over the surface: Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation.

(vii) Heat of vaporisation

The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation or heat of evaporation. The heat of vaporisation depends on the strength of the intermolecular forces within the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation.** It is numerically equal to the heat of vaporisation at the same temperature.

(viii) Vapour pressure

When the space above the liquid is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they are

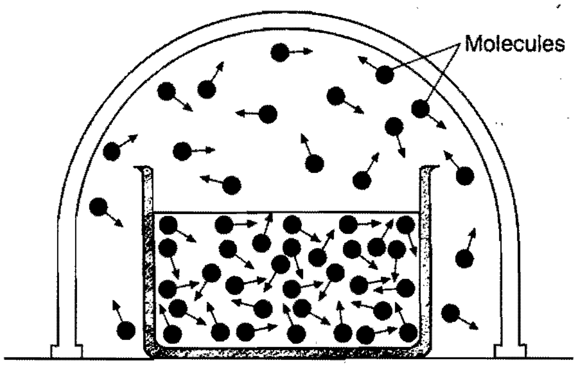


Fig. 4.13 (a) Evaporation in a closed vessel

trapped. The return of the molecules from the vapour state to the liquid state is known as **condensation.** As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, *i.e.*, the vapour in the closed container is in equilibrium with the liquid.

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapour}$$

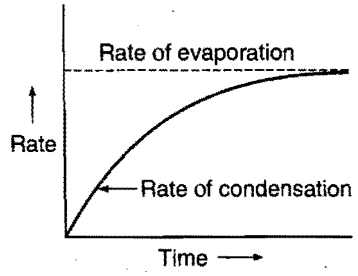


Fig. 4.13 (b)

At equilibrium, the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure.** Mathematically, it is given by the gas equation:

$$P = \frac{n}{V} RT = CRT$$

where, C is the concentration of vapour, in mol/litre.

In closed vessel,

Rate of evaporation $\propto e^{-E/RT}$ (Boltzmann factor)

Thus, rate of evaporation remains constant at constant temperature.

Since, the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporised liquids are called **volatile liquids** and they have relatively high vapour pressures. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table:

Substance	Temperatures				
	0°C	20°C	40°C	80°C	100°C
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	135.3	812.6	1693.3
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

It is observed that non-polar or less polar liquids such as diethyl ether and ethyl alcohol possess fairly high vapour pressures on account of weak intermolecular forces (cohesive forces) whereas polar molecules such as water which have stronger intermolecular forces possess relatively lower vapour pressures.

The simplest method for measuring vapour pressure is the **barometric method.** It consists of two barometer tubes as shown in Fig. 4.14. A small quantity of the liquid is introduced into one of the tubes. It changes into vapour and rises into vacuum above the mercury. Some more of the liquid is introduced and the process is continued till a small amount of the liquid is visible on the surface of mercury. The difference in the levels of mercury in the two tubes is noted and this measures the vapour pressure of the liquid at atmospheric temperature. The measurement can also be made at any desired temperature by surrounding the tubes with a jacket maintained at that temperature.

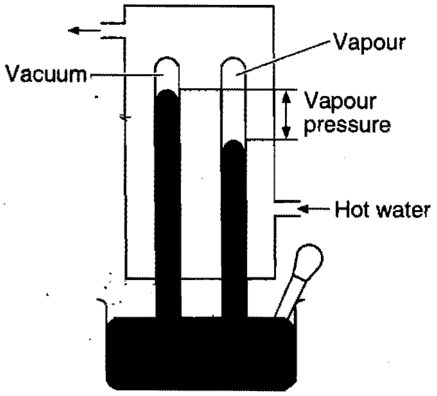


Fig. 4.14 The barometric method for measurement of vapour pressure

The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation.**

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where, ΔH is the latent heat of vaporisation and R is the molar gas constant.

The actual form of Clausius-Clapeyron equation is:

$$\log_{10} P = \frac{-\Delta H_{\text{vap}}}{2.303RT} + A$$

Note : Vapour and gas: A gas can be liquefied only below critical temperature, by applying pressure. There is no characteristic critical temperature for vapours.

When ΔH_{vap} = Latent heat of vaporisation and 'A' is constant. A graph between $\log_{10} P$ and $\frac{1}{T}$ will be a straight line with negative slope.

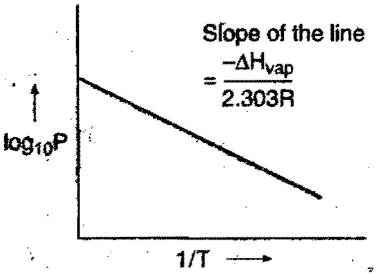


Fig. 4.15 Variation of vapour pressure with temperature

(ix) Boiling point

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling.** The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one standard atmospheric pressure (760 mm of Hg). Fig. 4.16 shows that normal boiling points of diethyl ether, ethyl alcohol and water are 34.6°C, 78.5°C and 100°C respectively.

The temperature of the boiling liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid. The higher rate at which heat is added to the boiling liquid, the faster it boils.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperature higher than normal under external pressure greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperature below its normal boiling point of 100°C. Food cooks more slowly at higher altitudes because the temperature of boiling water is lower than it would be nearer the sea level. The temperature of boiling water in a pressure cooker is higher than the normal, thus making it possible to cook foods faster than in open vessels.

If a liquid decomposes when heated, it can be made to boil at lower temperature by reducing the pressure. This is the principle of vacuum distillation. Unwanted water is removed from many food products by boiling it away under reduced pressure.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in the following respects:

(a) Evaporation takes place spontaneously at all temperatures but boiling occurs only at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.

(b) Evaporation is a surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

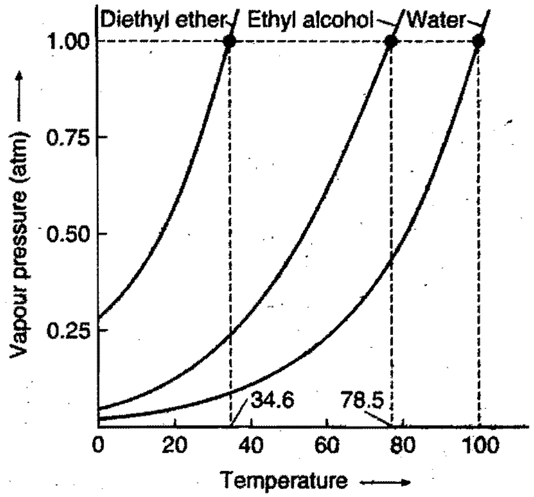


Fig. 4.16 Vapour pressure curves for diethyl ether, ethy alcohol and water

(c) In vaporisation, the vapour molecules diffuse from the liquid into the atmosphere but in boiling, molecules escape with sufficient pressure into the space over the surface of liquid.

(x) Freezing point

When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the translational motion is reduced to minimum. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point.**

Normal freezing point of a liquid is the temperature at which its liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid form. At the freezing point the temperature of the solid-liquid system remains constant until all the liquid is frozen. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point is called the **heat of fusion.**

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls.

(xi) Surface tension

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, *i.e.*, are pulled inward and the surface area is minimized. **Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface.** The unit of surface tension is dyne cm^{-1} or Newton metre^{-1} ($N\ m^{-1}$). It is a scalar quantity. Surface tension is, thus, defined as **the force acting on unit length of a line imagined to be drawn tangentially anywhere on the free surface of a liquid at rest. It acts at right angles on both sides of the line and along the tangent to the liquid surface.** Surface tension depends on the area, not on the length, like elastic properties.

As the intermolecular forces of attraction decrease with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid reduces its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

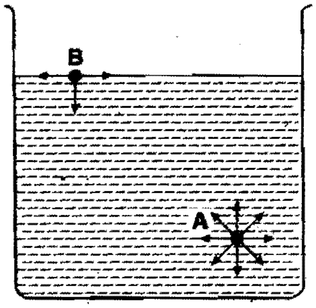


Fig. 4.17 (a) Molecules at the surface are under unequal tension

Many common phenomena can be explained with the help of surface tension. Some are described here:

(a) Small droplets are spherical in shape: The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b) Insects can walk on the surface of water: Many insects can walk on the surface of water without drowning. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c) Cleaning action of soap and detergents: Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) Capillary action: The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension. The force of adhesion between the molecules of water and the molecules of glass of the capillary tube is greater than the force of cohesion between water molecules. Due to this, surface of water in a glass capillary tube curves upwards in convex shape and then the force of surface tension of water pulls the water up into the tube. The water rises into a capillary tube to such a height that the weight of resulting water column is just balanced by the force of surface tension.

The rise of oil in a lamp wick and flow of water from the roots of a tree to upper parts are also the examples of capillary action. In general, the liquids which wet the material show capillary rise. Those liquids which do not wet the material of a capillary always show depression, *e.g.*, glycerine, honey, mercury, etc.

When a liquid rises in a column, its upper surface becomes concave and when the liquid goes down in a capillary, its upper surface becomes convex.

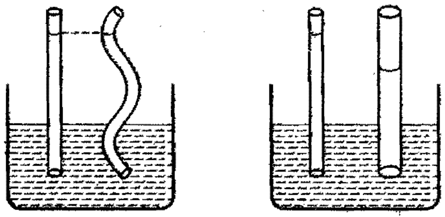

(i) (ii)

Fig. 4.17 (b) Effect of shape and radius on capillary rise

(i) Height of liquid in the column of capillary is independent of shape of capillary if its radius is same.

(ii) Thinner is the capillary, greater is the height of liquid in the column.

(e) Surface energy: The work in erg required to be done to increase or extend surface area by 1 sq. cm is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, *i.e.*, J m^{-2} in SI system). Surface tension of liquid is numerically equal to the surface energy.

Surface energy,

$$\gamma = \text{Work done to increase the surface area by one unit}$$

$$= \frac{\text{Work}}{\text{Change in area}}$$

$$= \frac{\text{force} \times \text{displacement in the direction of force}}{\text{area}}$$

$$= \frac{\text{Force}}{\text{Length}}$$

The unit of surface tension is therefore dyne cm^{-1} (force per unit length).

Measurement of surface tension: The surface tension of a liquid is measured by the drop count method using a stalagmometer.

Let γ_1 and d_1 be the surface tension and density of water and γ_2 and d_2 be surface tension and density of the liquid whose surface tension is to be determined. Using a stalagmometer the number of drops formed by the same volume of water and liquid is determined.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$$

Using the above relation, the surface tension of the liquid, γ_2, can be calculated.

Note: At the critical temperature, surface tension of liquid becomes zero (where the meniscus between the liquid and the vapour disappears). Surface tension is scalar quantity.

Surface tension of the liquid can also be measured by capillary rise method.

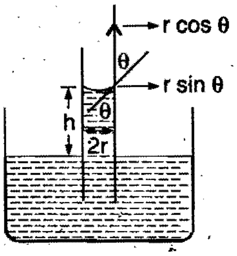


Fig. 4.18 Capillary rise

When liquid rises in a capillary, upward force due to surface tension is balanced by gravitational force.

$\therefore \quad 2\pi r\gamma \cos\theta = mg$

where, m = mass of liquid in column
r = radius of capillary
h = capillary rise
g = gravitational force

Mass of liquid in column $(m) = V \times \rho$

$$= \pi r^2 h \times \rho$$

$$\therefore \quad 2\pi r\gamma \cos\theta = \pi r^2 h\rho g$$

$$\gamma = \frac{rh\rho g}{2\cos\theta} \quad (\rho = \text{density of liquid})$$

If angle of contact between glass and liquid is zero, *i.e.*, $\cos\theta = 1$, then

$$\gamma = \frac{rh\rho g}{2}$$

Effect of temperature on surface tension : Surface tension decreases with rise in temperature because the intermolecular force also decreases with rise in temperature. The decrease in surface tension with rise in temperature continues till critical temperature at which the surface tension of liquid becomes zero, *i.e.*, meniscus between liquid and vapour disappears.

According to Eotvos equation,

$$\gamma = \left(\frac{M}{\rho}\right)^{2/3} = K(t_c - t)$$

$\therefore$ As t increases, γ decreases linearly, when $t = t_c$, $\gamma = 0$, here t_c is the critical temperature.

(xii) Viscosity

All liquids have a characteristic property of flow. Some liquids like water, alcohol, ether, etc., flow quickly while glycerine, castor oil, molasses, etc., flow very slowly. **The property of the liquids which determines their resistance to flow, is called viscosity.**

When a liquid flows through a pipe, all parts of it do not move at the same rate. The thin layer in immediate contact with the wall of the pipe is almost stationary. The velocity of flow of each successive layer of liquid increases progressively as we proceed inward towards the centre. At the centre, the flow becomes fastest. Each layer of liquid moving with greater velocity over the one having lower velocity will experience a retarding effect due to the internal friction between the two layers. **This internal friction or resistance is called viscosity.**

Imagine a liquid to be made up of a large number of thin cylindrical coaxial layers.

It has been found that force of friction 'f' between two cylindrical layers each having area 'A' sq. cm separated by a distance 'x' cm and having a velocity difference v cm/sec is given by:

$$f \propto A\frac{v}{x}$$

$$f = \eta A\frac{v}{x}$$

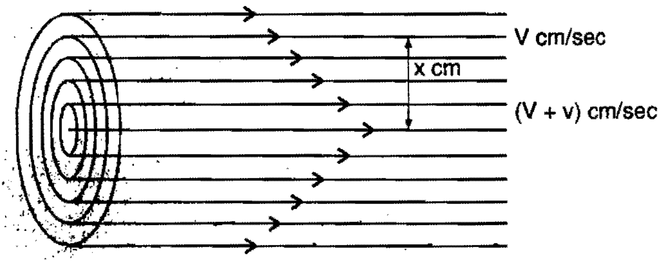


Fig. 4.19

Here, η is a constant known as coefficient of viscosity. If $x = 1$ cm, $A = 1\,\text{cm}^2$ and $v = 1$ cm/sec., then $f = \eta$.

Thus, coefficient of viscosity can be defined as **the force per unit area needed to maintain unit difference of velocity between two consecutive parallel layers of the liquid which are one centimetre apart.**

Coefficient of viscosity is expressed in dyne cm^{-2} sec. It is more commonly expressed as poise, centipoise (10^{-2} poise) and millipoise (10^{-3} poise), after the name of **Poiseuille** who derived the formula and gave the method for its determination. 1 poise is equal to a force of 1 dyne per unit area which maintains a velocity difference of 1 cm per second between two parallel consecutive layers of the liquid 1 cm apart.

The reciprocal of the coefficient of viscosity is called **Fluidity** (ϕ).

$$\phi = \text{Fluidity} = \frac{1}{\eta}$$

Liquids with low viscosity are termed mobile and others with high viscosity are called viscous.

Viscosity depends on the following factors:

(a) ***Intermolecular forces*:** The liquids with high intermolecular attractive forces offer greater resistance to the flow of molecules and thus possess high viscosity.

(b) ***Molecular mass*:** The flow of molecules is inversely proportional to its mass. Liquids having high molecular mass possess greater viscosity.

(c) ***The structure and shape of molecules*:** Viscosity generally increases as the branching in the chain increases. Symmetrical molecules have low viscosity.

(d) *Temperature*: Intermolecular forces decrease with rise in temperature. Thus, viscosity decreases with the increase of temperature. This property is used to select the lubricant for a machine and engine. The variation of viscosity with temperature can be expressed by the following relationship:

$$\eta = Ae^{-E_a/RT} \qquad \text{...(i)}$$

where, A = Pre-exponential factor (constant)

E_a = Activation energy

Taking logarithm of equation (i) we get :

$$\log_{10}\eta = \log_{10}A - \frac{E_a}{2.303R}\times\frac{1}{T} \qquad \text{...(ii)}$$

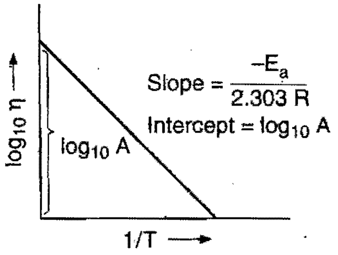


Fig. 4.20

This equation represents straight line with formula $y = mx + C$

Equation (ii) may also be given as

$$\log_{10}\frac{\eta_2}{\eta_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where η_2 is the coefficient of viscosity at temperature T_2 and η_1 is the coefficient of viscosity at temperature T_1.

(e) *Pressure*: The increase of pressure increases the intermolecular forces. Thus, the viscosity of a given liquid increases with increase of pressure.

(f) *Density* : Viscosity of a liquid increases with increase in density while that of gas decreases.

Measurement of viscosity: Viscosity is generally determined by Ostwald's method. It involves the comparison of time of flow of equal volumes of two liquids through the same capillary using an apparatus called **viscometer.**

$$\frac{\eta}{\eta_w} = \frac{d\times t}{d_w\times t_w}$$

where, η_w, η = coefficients of viscosity of water and liquid respectively; d = density of liquid; d_w = density of water; t = time of flow of liquid; t_w = time of flow of water.

Note: Viscosity of gases increases with increase in temperature.

Comparison between viscous force and solid friction

Points of differences :

Viscous force	Solid friction
1. It is directly proportional to the area of layers in contact.	It is independent of the area of the surfaces in contact.
2. It is directly proportional to the relative velocity between the two liquid layers.	It is independent of the relative velocity between two solid surfaces.

Point of similarities:

(i) Both viscous force and solid friction come into action where ever there is relative motion.

(ii) Both these forces oppose the motion.

(iii) Both are due to molecular attraction.

SECTION 3 : SOLID STATE

4.12 THE SOLID STATE

In solid state, the particles (molecules, ions or atoms) are closely packed. These are held together by strong intermolecular attractive forces (cohesive forces) and cannot move at random. These are held at fixed positions and surrounded by other particles. There is only one form of molecular motion in solids, namely vibrational motion by virtue of which the particles move about fixed positions and cannot easily leave the solid surface. The following general characteristics are exhibited by solids:

(i) Definite shape and volume: Unlike gases and liquids, solids have definite shape and rigidity. This is due to the fact that constituent particles do not possess enough energy to move about to take-up different positions. Solids are characterised by their definite volume which does not depend on the size and shape of the container. This is due to close packing of molecules and strong short range intermolecular forces between them.

(ii) High density and low compressibility: Solids have generally high density and low compressibility due to close packing of molecules which eliminates free space between molecules.

(iii) Very slow diffusion: The diffusion of solid is negligible or rather very slow as the particles have permanent positions from which they do not move easily.

(iv) Vapour pressure: The vapour pressure of solids is generally much less than the vapour pressure of liquids at a definite temperature. Some particles near the surface may have high energies (kinetic) as to move away and enter the vapour state.

(v) Melting point: The temperature at which the solid and the liquid forms of a substance exist at equilibrium or both the forms have same vapour pressure, is called the **melting point.** On supplying heat energy, the particles acquire sufficient energy and move away from their fixed positions in space. This results in the formation of liquid state. The solids have definite melting points depending on the strength of binding energy. However, in some solids (amorphous solids)* the melting point is not sharp.

4.13 FORMS OF SOLIDS

Solids are divided into two classes on the basis of haphazard and regular arrangement of the building constituents.

(i) Amorphous solids: The term 'amorphous' has been derived from a Greek word *'Omorphe'* meaning shapeless. In amorphous solids the arrangement of building constituents is not regular but haphazard. Although these solids possess some of the mechanical properties such as rigidity, incompressibility, refractive index, etc., but do not have characteristic shapes or geometrical forms. Amorphous solids in many respects resemble liquids which flow very slowly at room temperature and regarded as supercooled liquids in which the cohesive forces holding the molecules together are so great that the material is rigid but there is no regularity of the structure. Glass, rubber, plastics, etc., are some of the examples of amorphous solids.

Amorphous solids do not have sharp melting points. For example, when glass is heated, it softens and then starts flowing without undergoing any abrupt change from solid to liquid state.

Thus, amorphous substances are not true solids but can be regarded as intermediate between liquids and solids.

(ii) Crystalline solids: In crystalline solids, the building constituents arrange themselves in regular manner throughout the entire three-dimensional network. The ordered arrangement of building constituents (molecules, atoms or ions) extends over a large distance. Thus, crystalline solids have long range order. A crystalline solid consists of a large number of units, called crystals. **A crystal is defined as a solid figure which has a definite geometrical shape, with flat faces and sharp edges.**

A crystalline substance has a sharp melting point, *i.e.*, it changes abruptly into liquid state. Strictly speaking 'a solid state refers to crystalline state' or 'only a crystalline substance can be considered to be a true solid'.

4.14 ISOTROPY AND ANISOTROPY

The substances which show same properties in all directions are said to be isotropic and the substances exhibiting directional differences in properties are termed **anisotropic.**

Amorphous solids like liquids and gases are said to be isotropic as arrangement of building constituents is random and disordered. Hence, all directions are equal and therefore, properties are same in all the directions.

Crystalline solids are anisotropic. Magnitude of some of the physical properties of crystalline solids such as refractive index, coefficient of thermal expansion, electrical and thermal conductivities, etc., is different in different directions, within the crystal. For example, in the crystal of silver iodide (AgI), the coefficient of thermal expansion is positive in one direction and negative in the other direction.

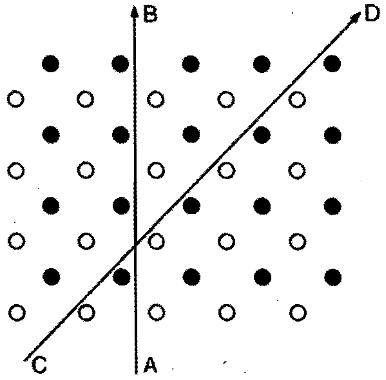


Fig. 4.21 Anisotropic behaviour of crystals

The phenomenon of anisotropy provides a strong evidence for the presence of ordered molecular arrangement in crystals. This can be explained with the help of Fig. 4.21 in which a simple two dimensional arrangement of two different kinds of atoms has been depicted. When a physical property is measured along the slanting line *CD*, it will be different from that measured in the direction of vertical line *AB*, as line *CD* contains alternate types of atoms while line *AB* contains one type of atoms only.

4.15 DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline solids	Amorphous solids
1. They have definite and regular geometry due to definite and orderly arrangement of atoms, ions or molecules in three dimensional space.	They do not have any pattern of arrangement of atoms, ions or molecules and, thus, do not have any definite geometrical shape.
2. They have sharp melting points and change abruptly into liquids.	Amorphous solids do not have sharp melting points and do not change abruptly into liquids.
3. Crystalline solids are anisotropic. Some of their physical properties are different in different directions.	Amorphous solids are isotropic. Their physical properties are same in all directions.
4. These are considered as true solids.	These are considered pseudo-solids or supercooled liquids.
5. Crystalline solids are rigid and their shape is not distorted by mild distorting forces.	Amorphous solids are not very rigid. These can be distorted by bending or compressing forces.

---

* Melting point of a solid depends on the structure of the solid. It is used for the identification of solids whether it is crystalline or amorphous.

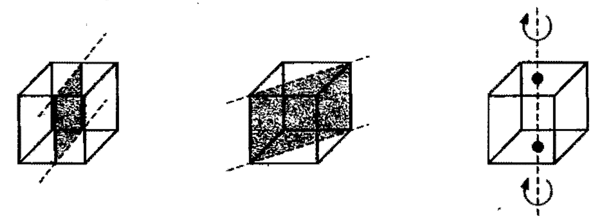
Crystalline solids	Amorphous solids
6. Crystals are bound by plane faces. The angle between any two faces is called interfacial angle. For a given crystalline solid, it is a definite angle and remains always constant no matter how the faces develop. When a crystalline solid is hammered, it breaks up into smaller crystals of the same geometrical shape.	Amorphous solids do not have well defined planes. When an amorphous solid is broken, the surfaces of the broken pieces are generally not flat and intersect at random angles.
7. An important property of crystals is their symmetry. There are: (i) plane of symmetry, (ii) axis of symmetry and (iii) centre of symmetry.	Amorphous solids do not have any symmetry.

4.16 TYPES OF SYMMETRY IN CRYSTALS

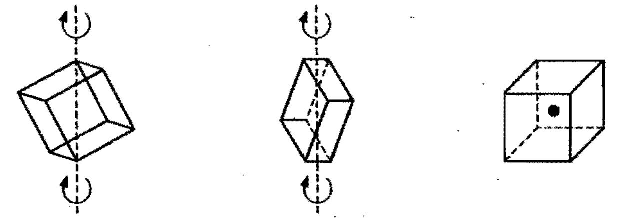
(i) Centre of symmetry: It is such an imaginary point within the crystal that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possesses only one centre of symmetry [Fig. 4.22 (f)].

(ii) Plane of symmetry: It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

A cubical crystal like NaCl possesses, in all, nine planes of symmetry; three rectangular planes of symmetry and six diagonal planes of symmetry. One plane of symmetry of each of the above is shown in Fig. 4.22 (a) and (b).



Rectangular plane of symmetry (a) | Diagonal plane of symmetry (b) | Axis of four-fold symmetry (three) (c)



Axis of three-fold symmetry (four) (d) | Axis of two-fold symmetry (six) (e) | Centre of symmetry (one) (f)

Fig. 4.22 Various elements of symmetry in a cubic crystal

(iii) Axis of symmetry: It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution. The axes of symmetry are called diad, triad, tetrad and hexad, respectively, if the original appearance is repeated twice (after an angle of 180°), thrice (after an angle of 120°), four times (after an angle of 90°) and six times (after an angle of 60°) in one rotation. These axes of symmetry are also called two-fold, three-fold, four-fold and six-fold, respectively.

In general, if the same appearance of a crystal is repeated on rotating through an angle of $\frac{360^\circ}{n}$, around an imaginary axis, the axis is called an n-fold axis.

In all, there are 13 axes of symmetry possessed by a cubical crystal like NaCl as shown in Fig. 4.22 (c), (d) and (e).

(iv) Elements of symmetry: The total number of planes, axes and centre of symmetry possessed by a crystal are termed as elements of symmetry. A cubic crystal possesses a total of 23 elements of symmetry.

Planes of symmetry = $(3 + 6) = 9$ [Fig. 4.22 (a) and (b)]

Axes of symmetry = $(3 + 4 + 6) = 13$ [Fig. 4.22 (c), (d) and (e)]

Centre of symmetry = 1 [Fig. 4.22 (f)]

Total number of symmetry elements = 23

4.17 SPACE LATTICE AND UNIT CELL

All crystals are polyhedra consisting of regularly repeating arrays of atoms, molecules or ions which are the structural units. A crystal is a homogeneous portion of a solid substance made of regular pattern of structural units bonded by plane surfaces making definite angles with each other. The geometrical form consisting only of a regular array of points in space is called a **lattice** or **space lattice** or it can be defined as an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space. Fig. 4.23 shows a space lattice. A space lattice can be subdivided into a number of small cells known as unit cells. It can be defined as the smallest repeating unit in space lattice which, when repeated over and over again, results in a crystal of the given substance or it is the smallest block or geometrical figure from which entire crystal can be built up by its translational repetition in three-dimensions. A unit cell of a crystal possesses all the structural properties of the given crystal. For example, if a crystal is a cube, the unit cell must also have its atoms, molecules or ions arranged so as to give a cube.

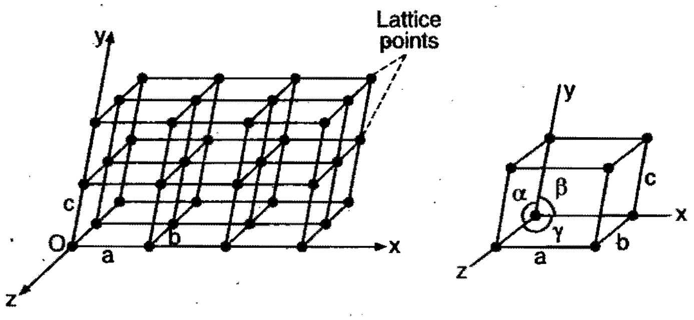


Fig. 4.23 Space lattice and unit cell

System	Edges	Angles	Maximum symmetry elements	Examples
1. Cubic $a = b = c,\ \alpha = \beta = \gamma = 90°$	All the three equal	All right angles	Nine planes, thirteen axes	NaCl, KCl, ZnS, diamond, alums
2. Orthorhombic $a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$	All unequal	All right angles	Three planes, three axes	KNO_3, $BaSO_4$, K_2SO_4, rhombic sulphur.
3. Tetragonal $a = b \neq c,\ \alpha = \beta = \gamma = 90°$	Two equal	All right angles	Five planes, five axes	TiO_2, $PbWO_4$, SnO_2, NH_4Br
4. Monoclinic $a \neq b \neq c,\ \alpha = \gamma = 90°, \beta \neq 90°$	All unequal	Two right angles	One plane, one axis	Monoclinic sulphur, $KClO_3$, $CaSO_4 \cdot 2H_2O$, $Na_2B_4O_7 \cdot 10H_2O$
5. Triclinic $a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$	All unequal	None right angles	No planes, no axis	$CuSO_4 \cdot 5H_2O$, H_3BO_3, $K_2Cr_2O_7$
6. Hexagonal $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	Two equal	Angle between equal edges = 120°	Seven planes, seven axes	ZnO, CdS, HgS, SiC, AgI
7. Rhombohedral $a = b = c,\ \alpha = \beta = \gamma \neq 90°$	All three equal	All equal but none 90°	Seven planes, seven axes	$NaNO_3$, ICl, quartz ($CaCO_3$)

Each unit cell has three vectors a, b and c as shown in Fig. 4.23. The distances a, b and c are the lengths of the edges of the unit cell and angles α, β and γ are the angles between three imaginary axes OX, OY and OZ, respectively.

For example: For a crystal system, $a = b = c$ and $\alpha = \beta = \gamma \neq 90°$:.

(a) tetragonal (b) hexagonal
(c) rhombohedral (d) monoclinic

[Ans. (c)]

[**Hint:** From the table $a = b = c$ for rhombohedral and cubic system both but $\alpha = \beta = \gamma \neq 90°$ for rhombohedral only.]

4.18 CRYSTAL SYSTEMS

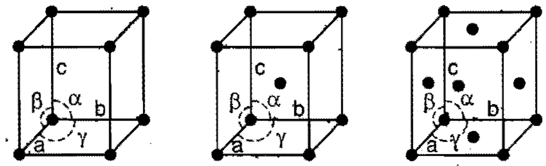
On the basis of geometrical considerations, theoretically there can be 32 different combinations of elements of symmetry of a crystal. These are called 32 systems. Some of the systems have been grouped together. In all, seven types of **basic** or **primitive unit cells** have been recognised among crystals. These are cubic, orthorhombic, tetragonal, monoclinic, triclinic, hexagonal and rhombohedral. These are shown in Fig. 4.24 and their characteristics are summarised in the following table.

All crystals do not have simple lattices. Some are more complex. Bravais pointed out that there can be 14 different ways in which similar points can be arranged in a three-dimensional space. Thus, the total number of space lattices belonging to all the seven crystal systems are 14.

The crystals belonging to cubic system have three kinds of Bravais lattices. These are:

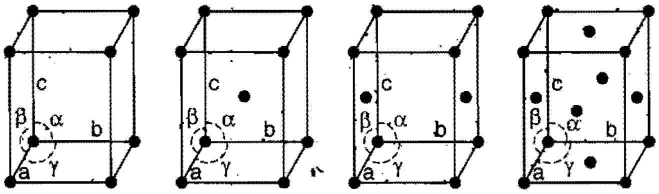
(i) ***Simple cubic lattice:*** There are points only at the corners of each unit.

(ii) ***Face-centred cubic lattice:*** There are points at the corners as well as at the centre of each of the six faces of the cube.



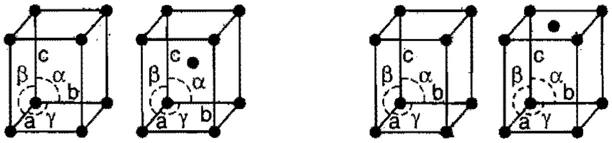
Simple or primitive Body-centred Face-centred

(a) Cubic space lattices



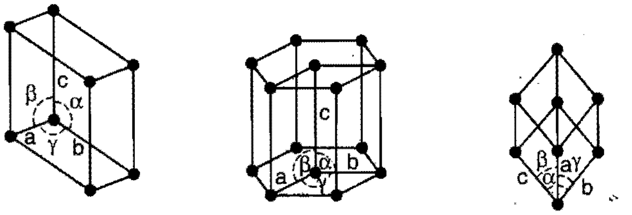
Simple or primitive Body-centred End-centred Face-centred

(b) Orthorhombic space lattices



Simple Body-centred Simple End-centred

(c) Tetragonal and monoclinic space lattices



Triclinic Hexagonal Rhombohedral

(d) Triclinic, hexagonal and rhombohedral space lattices

Fig. 4.24 Bravais lattices

(iii) ***Body-centred cubic lattice:*** There are points at the corners as well as in the body-centre of each cube.

The number of Bravais space lattices in a given system is listed in the following table and shown in Fig. 4.24.

Crystal system	No. of space lattices	Lattice type
1. Cubic	3	Simple, face-centred and body-centred.
2. Orthorhombic	4	Rectangular and body-centred rectangular prism; rhombic and body-centred rhombic prism.
3. Tetragonal	2	Simple and body-centred tetragonal prism.
4. Monoclinic	2	Monoclinic parallelopiped, monoclinic face-centred parallelopiped.
5. Triclinic	1	Triclinic parallelopiped.
6. Hexagonal	1	Hexagonal prism.
7. Rhombohedral	1	Rhombohedron.

In various unit cells, there are three kinds of lattice points: points located at the corners, points in the face-centres and points that lie entirely within the unit cell. In a crystal, atoms located at the corner and face-centre of a unit cell are shared by other cells and only a portion of such an atom actually lies within a given unit cell.

(i) A point that lies at the corner of a unit cell is shared among eight unit cells and, therefore, only one-eighth of each such point lies within the given unit cell.

(ii) A point along an edge is shared by four unit cells and only one-fourth of it lies within any one cell.

(iii) A face-centred point is shared by two unit cells and only one half of it is present in a given unit cell.

(iv) A body-centred point lies entirely within the unit cell and contributes one complete point to the cell.

Type of lattice point	Contribution to one unit cell
Corner	1/8
Edge	1/4
Face-centre	1/2
Body-centre	1

Total number of constituent units per unit cell

$$= \frac{1}{8} \times \text{occupied corners} + \frac{1}{4} \times \text{occupied edge-centres}$$

$$+ \frac{1}{2} \times \text{occupied face-centres} + \text{occupied body-centre.}$$

Determination of Number of Constituent units per unit cell:

Let edge length of cube $= a$ cm

Density of substance $= d \text{ g cm}^{-3}$

Volume of unit cell $= a^3 \text{ cm}^3$

Mass of unit cell = volume × density $= (a^3 \times d)$ g

$$\text{Number of mol per unit cell} = \frac{a^3 \times d}{M};$$

where, M = molar mass

Number of molecules per unit cell = Number of mole × Avogadro's number

$$Z = \frac{a^3 \times d}{M} \times N = \frac{a^3 \times d \times N}{M}$$

Calculation of number of constituent units in hexagonal unit cell

(i) Constituent units at each corner of unit cell is common among six unit cells hence contribute 1/6th to each unit cell.

(ii) Constituent unit at edge is common to three unit cells hence contribute 1/3rd to each unit cell.

(iii) Constituent units present at the body centre is considered in single unit cell.

(iv) Constituent unit at face centre is common between two unit cells hence contribute 1/2 to each unit cell.

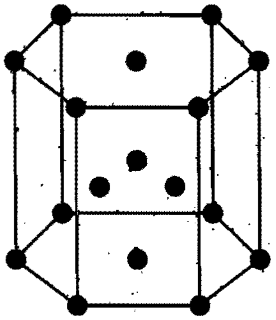


Fig. 4.25 Hexagonal unit cell

In the hexagonal unit cell (Fig 4.25), 12 corners, 2 face centres and 3 constituent units within the unit cells are occupied, hence effective number of constituent units present in the unit cell may be calculated as

$$z = \frac{1}{6} \times \begin{matrix}\text{occupied}\\\text{corners}\end{matrix} + \frac{1}{2} \times \begin{matrix}\text{occupied}\\\text{face clutres}\end{matrix} + \begin{matrix}\text{Central}\\\text{constituent units}\end{matrix}$$

$$= \frac{1}{6} \times 12 + \frac{1}{2} \times 2 + 3$$

$$= 6$$

4.19 DESIGNATION OF PLANES IN CRYSTALS—MILLER INDICES

Planes in crystals are described by a set of integers (h, k and l) known as Miller indices. Miller indices of a plane are the reciprocals of the fractional intercepts of that plane on the various crystallographic axes. For calculating Miller indices, a reference plane, known as parametral plane, is selected having intercepts a, b and c along x, y and z-axes, respectively (Fig. 4.26). Then, the intercepts of the unknown plane are given with respect to a, b and c of the parametral plane.

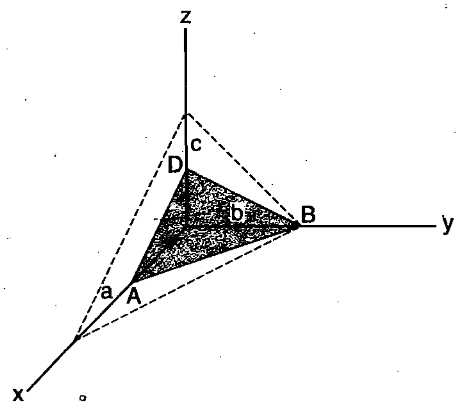


Fig. 4.26 Parametral (intercepts *a*, *b*, *c* along *x*, *y* and *z*-axes)

Thus, the Miller indices are:

$$h = \frac{a}{\text{intercept of the plane along } x\text{- axis}}$$

$$k = \frac{b}{\text{intercept of the plane along } y\text{- axis}}$$

$$l = \frac{c}{\text{intercept of the plane along } z\text{- axis}}$$

Consider the shaded plane *ABD* in Fig. 4.26. The intercepts of the shaded plane along *X*, *Y* and *Z*-axes are $a/2$, b and $c/2$, respectively. Thus,

$$h = \frac{a}{a/2} = 2;$$

$$k = \frac{b}{b} = 1;$$

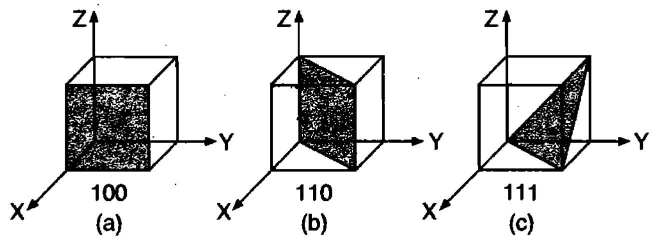
$$l = \frac{c}{c/2} = 2$$

The plane is, therefore, designed as (212) plane.

Note: (i) If a plane is parallel to an axis, its intercept with that axis is taken as infinite and the Miller indices will be zero.

(ii) While defining Miller indices for orthogonal crystal, *X*, *Y* and *Z*-axes are considered crystallographic axes.

Some of the important planes of cubic crystals are shown in Fig. 4.27.



100 (a) 110 (b) 111 (c)

Fig. 4.27 Miller indices of planes in cubic lattice

In (a) intercepts are	1	∞	∞
So, Miller indices are	1	0	0
The plane is designated (100)			
In (b) intercepts are	1	1	∞
So, Miller indices are	1	1	0
The plane is designated (110)			
In (c) intercepts are	1	1	1
So, Miller indices are	1	1	1
The plane is designated (111)			

The distances between the parallel planes in crystals are designated as d_{hkl}. For different cubic lattices these interplanar spacings are given by the general formula,

$$d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where, *a* is the length of the cube side while *h*, *k* and *l* are the Miller indices of the plane.

The spacings of the three planes (100), (110) and (111) of simple cubic lattice can be calculated.

$$d_{(100)} = \frac{a}{\sqrt{1^2 + 0 + 0}} = a$$

$$d_{(110)} = \frac{a}{\sqrt{1^2 + 1^2 + 0}} = \frac{a}{\sqrt{2}}$$

$$d_{(111)} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

The ratio is,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

Similarly, $d_{(hkl)}$ ratios for face-centred cubic and body-centred cubic can be calculated. For face-centred cubic,

$$d_{(100)} : d_{(110)} : d_{(111)} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} = 1 : 0.707 : 1.154$$

For body-centred cubic,

$$d_{(100)} : d_{(110)} : d_{(111)} = \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}}$$

$$= 1 : \sqrt{2} : \frac{1}{\sqrt{3}}$$

$$= 1 : 1.414 : 0.577$$

4.20 CRYSTALLOGRAPHY AND X-RAY DIFFRACTION

Crystallography is the branch of science which deals with the geometry, properties and structure of crystals and crystalline substances. Geometric crystallography is concerned with the external spatial arrangement of crystal planes and geometric shapes of crystals.

Atoms, molecules or ions are too small to be seen with naked eye. The arrangement of particles in crystalline solids is determined indirectly by X-ray diffraction. In 1912, **Von Laue** showed that any crystal could serve as a three-dimensional grating to the incident electromagnetic radiation with wavelength approximately equal to the internuclear separations ($\approx 10^{-8}$ cm) of atoms in the crystal. Such radiation is in the X-ray region of the electromagnetic spectrum.

The apparatus used is shown in Fig. 4.28. A monochromatic X-ray beam is directed towards the surface of a slowly rotated crystal so as to vary the angle of incidence θ. At various angles, strong beams of deflected X-rays strike the photographic plate. The photographic plate after developing shows a central spot due to primary beam and a set of symmetrically disposed spots due to deflected X-rays. Different kinds of crystals produce different arrangements of spots.

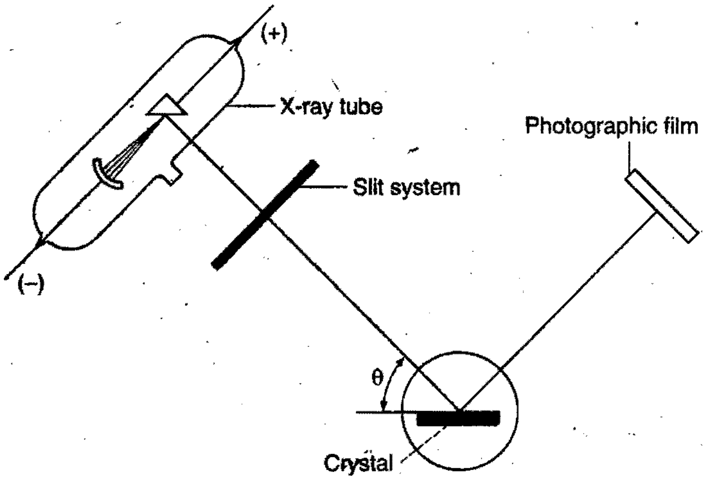


Fig. 4.28 X-ray diffraction of crystals

In 1913, **Bragg** found that Laue photographs are more easily interpreted by treating the crystals as a reflection grating rather than a diffraction grating. Fig. 4.29 illustrates the way by which the crystal spacings can be determined by use of X-rays of a single wavelength, λ. The rays strike the parallel planes of the crystal at angle θ. Some of the rays are reflected from the upper plane, some from the second and some from the lower planes. A strong reflected beam will result only if all the reflected rays are in phase. The waves reflected by different layer planes will be in phase with one another only if the difference in the path length of the waves reflected from the successive planes is equal to an integral number of wavelengths. OL and OM are the perpendiculars drawn to the incident and reflected beams. The difference in path lengths of waves deflected from the first two planes is given by:

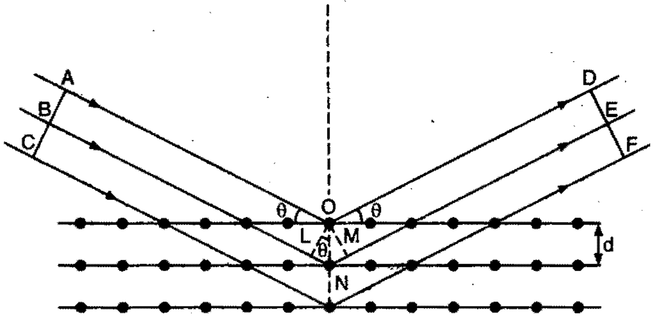


Fig. 4.29 X-ray reflection from crystals

$$LN + NM = n\lambda \quad (n = 1, 2, 3, \dots)$$

Since, the triangles OLN and OMN are congruent, hence $LN = NM$.

So, Path difference $= 2LN$

as $LN = d \sin\theta$ where, d is the distance between two planes.

So, Path difference $= 2d \sin\theta$

When two reflected waves reinforce each other (maximum reflection), the path difference should be $= n\lambda$ (where, $n = 1, 2, 3, \dots$).

So, for maximum reflection,

$$n\lambda = 2d \sin\theta$$

This relation is called Bragg's equation. Distance between two successive planes d can be calculated from this equation. With X-rays of definite wavelength, reflections at various angles will be observed for a given set of planes separated by a distance d. These reflections correspond to $n = 1, 2, 3$ and so on and are spoken of as first order, second order, third order and so on. With each successive order, the angle θ increases and the intensity of the reflected beam weakens.

The values of θ for the first order reflection from the three faces of sodium chloride crystal were found to be $5.9°$, $8.4°$ and $5.2°$ respectively. As n and a are same in each case, the distance d between successive planes in three faces will be in the ratio of

$$\frac{1}{\sin 5.9°} : \frac{1}{\sin 8.4°} : \frac{1}{\sin 5.2°} = 9.61 : 6.84 : 11.04$$

$$= 1 : 0.70 : 1.14$$

$$= 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}$$

This ratio corresponds to spacings along the three planes of a face-centred cubic structure. Thus, the NaCl crystal has face-centred cubic structure.

Example 63. *X-rays of wavelength 1.54 Å strike a crystal and are observed to be deflected at an angle of 22.5°. Assuming that n = 1, calculate the spacing between the planes of atoms that are responsible for this reflection.*

Solution: Applying Bragg's equation,

$$n\lambda = 2d \sin\theta$$

Given, $n = 1,\ \lambda = 1.54\,\text{Å},\ \theta = 22.5°$.

Using relation $n\lambda = 2d \sin\theta$,

$$d = \frac{1.54}{2 \sin 22.5°} = \frac{1.54}{2 \times 0.383} = 2.01\text{Å}$$

Example 64. *The first order reflection of a beam of X-rays of wavelength 1.54 Å from the (100) face of a crystal of the simple* *cubic type occurs at an angle of* 11.29°. *Calculate the length of the unit cell.*

Solution: Applying Bragg's equation,

$$2d \sin \theta = n\lambda$$

Given, $\theta = 11.29°$, $n = 1$, $\lambda = 1.54\ \text{Å} = 1.54 \times 10^{-8}$ cm

$$d = \frac{1.54 \times 10^{-8}}{2 \times \sin 11.29°} = \frac{1.54 \times 10^{-8}}{2 \times 0.1957} = 3.93 \times 10^{-8}\ \text{cm}$$

$$d_{\text{hkl}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = a$$

$$a = 3.93 \times 10^{-8}\ \text{cm} = \text{length of the unit cell}$$

Example 65. *When an electron in an excited state of Mo atom falls from L to K-shell, an X-ray is emitted. These X-rays are diffracted at angle of* 7.75° *by planes with a separation of* 2.64 Å. *What is the difference in energy between K-shell and L-shell in Mo, assuming a first order diffraction* (sin 7.75° = 0.1349)?

Solution: According to Bragg's equation:

$$n\lambda = 2d \sin \theta$$

$$1 \times \lambda = 2 \times 2.64 \sin 7.75° = 2 \times 2.64 \times 0.1349$$

$$\lambda = 0.712\ \text{Å}$$

Energy difference between K and L-shell of Mo

$$= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{0.712 \times 10^{-10}} = 2.791 \times 10^{-15}\ \text{J}$$

4.21 ANALYSIS OF CUBIC SYSTEMS

The following characteristics are reflected by cubic systems when analysed mathematically:

(i) Atomic Radius

It is defined as half the distance between nearest neighbouring atoms in a crystal. It is expressed in terms of length of the edge 'a' of the unit cell of the crystal.

(a) Simple cubic unit cell : In a simple cubic unit cell, atoms at the corners touch each other along the edge.

Distance between the nearest neighbours,

$$d = AB = a = 2r$$

(where r = radius of the atom)

or Atomic radius,

$$r = \frac{a}{2} = 0.5a$$

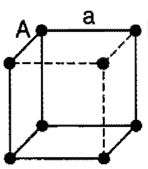


Fig. 4.30
Simple cubic unit cell

(b) Body-centred cubic unit cell : The distance between the two nearest neighbours is represented by length AE or ED, *i.e.*, half of the body diagonal, AD.

$$d = AE = ED = \frac{AD}{2}$$

In Δ ABC,

$$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$$

or $AC = \sqrt{2}a$

Now, in Δ ADC,

$$AD^2 = AC^2 + CD^2$$
$$= (\sqrt{2}a)^2 + a^2 = 3a^2$$

or $AD = \sqrt{3}a$

$$\therefore \quad d = \frac{\sqrt{3}}{2}a$$

$$d = 2r = \frac{\sqrt{3}}{2}a$$

or Atomic radius, $r = \dfrac{\sqrt{3}}{4}a$

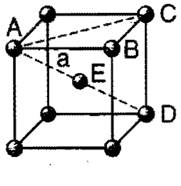


Fig. 4.31
Body-centred cubic unit cell

(c) Face-centred cubic unit cell : The distance between the two nearest neighbours is represented by length AB or BC, *i.e.*, half of the face diagonal, AC.

$$d = AB = BC = \frac{AC}{2}$$

In ΔACD, $AC^2 = CD^2 + AD^2$

$$= a^2 + a^2 = 2a^2$$

$$AC = \sqrt{2}a$$

or $d = \dfrac{AC}{2} = \dfrac{\sqrt{2}}{2}a = \dfrac{1}{\sqrt{2}}a$

$$d = 2r = \frac{1}{\sqrt{2}}a$$

or Atomic radius, $r = \dfrac{1}{2\sqrt{2}}a$

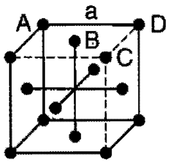
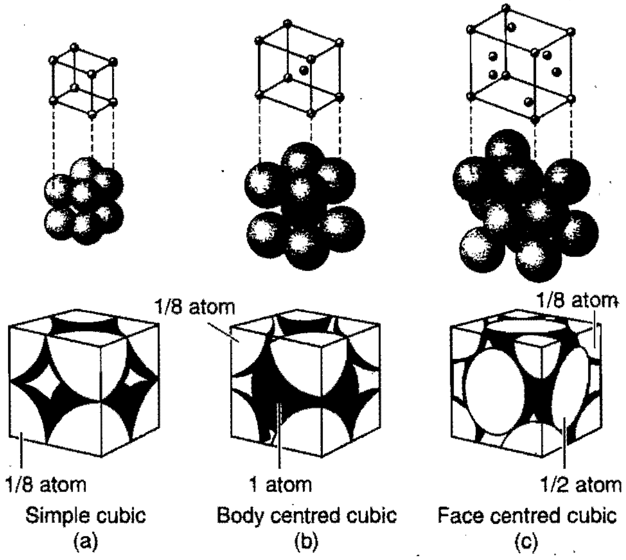


Fig. 4.32
Face-centred cubic unit cell

(ii) No. of Atoms Per Unit Cell

Different types of cubic unit cells are given in following figure:



Simple cubic (a)
Body centred cubic (b)
Face centred cubic (c)

Fig. 4.33 (a) Simple or primitive cubic lattice; (b) Body-centred cubic lattice; (c) Face-centred cubic lattice

(a) Simple cubic structure: Since, each corner atom is shared by eight surrounding cubes, therefore, it contributes for $\frac{1}{8}$ of an atom.

Thus, for simple cube $= 8 \times \frac{1}{8} = 1$ atom per unit cell

(b) Face-centred cubic structure: Since, the structure possesses 8 corner atoms and six at the centre of each face, the contribution will be

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} \quad \text{(Face atom is shared by two cubes)}$$

$$= 1 + 3 = 4 \text{ atoms per unit cell}$$

(c) Body-centred cubic structure: Since, the structure possesses 8 corner atoms and one body-centre, the contribution will be $= 8 \times \frac{1}{8} + 1 = 2$ atoms per unit cell.

(iii) Coordination Number

It is defined as the number of nearest neighbours that an atom has in a unit cell. It depends upon structure.

(a) Simple cubic structure: Coordination number = 6

(b) Face-centred cubic structure: Coordination number = 12

(c) Body-centred cubic structure: Coordination number = 8

(iv) Density of Lattice Matter

Knowing the unit cell dimensions, the theoretical density of a crystal can be calculated as:

$$\text{Density of the unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of the unit cell}}$$

$$\text{Mass of the unit cell} = \text{number of atoms in the unit cell} \times \text{mass of each atom}$$

$$\text{Mass of each atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

$$\text{So, density of a unit cell} = \frac{Z \times M}{N_0 \times V} = \frac{n \times M}{N_0 \times a^3} \quad \text{(For a cube)}$$

where, Z is the number of atoms in a unit cell and V is the volume of unit cell.

For a cube $V = a^3$ where, a is the edge length of the cubic unit cell.

(v) Packing Fraction or Density of Packing

It is defined as the ratio of volumes occupied by atoms in unit cell to the total volume of the unit cell.

$$\text{Packing fraction} = \frac{\text{Volume occupied by atoms in unit cell}}{\text{Total volume of the unit cell}} = \frac{v}{V}$$

(a) Simple cubic structure: Let a be the cube edge and r the atomic radius.

$$V = \text{volume of the unit cell} = a^3$$

Since, one atom is present in a unit cell, its

$$\text{Volume, } v = \frac{4}{3}\pi r^3 \qquad (r = a/2)$$

$$= \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

$$\text{Packing fraction} = \frac{v}{V} = \frac{\pi a^3/6}{a^3} = \frac{\pi}{6} = 0.52$$

i.e., 52% of the unit cell is occupied by atoms and 48% is empty.

(b) Face-centred cubic structure: Since, four atoms are present in a unit cell, their volume is

$$v = 4 \times \left(\frac{4}{3}\pi r^3\right)$$

Putting the value of $r = \frac{a}{2\sqrt{2}}$,

$$v = \frac{16}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3 = \frac{\pi}{3\sqrt{2}}a^3$$

Volume of unit cell, $V = a^3$

$$\text{Packing fraction} = \frac{\pi a^3}{3\sqrt{2}a^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

i.e., 74% of unit cell is occupied by atoms and 26% is empty.

(c) Body-centred cubic structure: Since, two atoms are present in a unit cell, their volume is

$$v = 2 \times \left(\frac{4}{3}\pi r^3\right)$$

Putting the value of $r = \frac{\sqrt{3}}{4}a$, $v = 2 \times \frac{4}{3}\pi \times \left(\frac{\sqrt{3}}{4}a\right)^3$

$$= \frac{\sqrt{3}\pi a^3}{8}$$

Volume of unit cell, $V = a^3$

$$\text{Packing fraction} = \frac{\sqrt{3}\pi a^3}{8a^3} = \frac{\sqrt{3}}{8}\pi = 0.68$$

i.e., 68% of the unit cell is occupied by atoms and 32% is empty.

Characteristics of cubic unit cells are summerised in following tables :

	Simple	**Body-centered**	**Face-centered**
Volume, conventional cell	a^3	a^3	a^3
Lattice points per cell	1	2	4
Volume, primitive cell	a^3	$\frac{1}{2}a^3$	$\frac{1}{4}a^3$
Lattice points per unit volume	$1/a^3$	$2/a^3$	$4/a^3$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	a	$3^{1/2}a/2 = 0.866a$	$a/2^{1/2} = 0.707a$
Number of second neighbors	12	6	6
Second neighbor distance	$2^{1/2}a$	a	a
Packing fraction	$\frac{1}{6}\pi = 0.524$	$\frac{1}{6}\pi\sqrt{3} = 0.680$	$\frac{1}{6}\pi\sqrt{2} = 0.740$

Hexagonal Unit Cell

Let us consider hexagonal unit cell of height 'h'; its constituent units are spherical having radius 'r'.

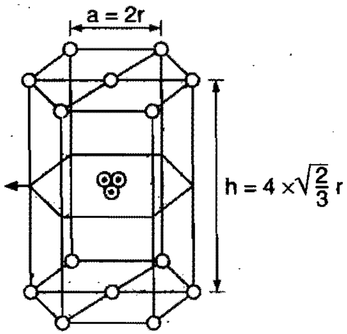


Fig. 4.34 Hexagonal unit cell

Number of constituent units in the hexagonal unit cell = 6

Thus, occupied volume in the unit cell $= 6\times\frac{4}{3}\pi r^3$

Volume of unit cell = Area of base × height

$$= 6\times \text{Area of equilateral triangle} \times \text{height}$$

$$= 6\times\frac{\sqrt{3}}{4}a^2\times 4r\sqrt{\frac{2}{3}}$$

$$= 6\times\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}$$

(Height of the unit cell can be calculated geometrically)

$$\text{Percentage occupied space} = \frac{\text{occupied volume}}{\text{volume of unit cell}}\times 100$$

$$= \frac{6\times\frac{4}{3}\pi r^3}{6\frac{\sqrt{3}}{4}(2r)^2\times 4r\sqrt{\frac{2}{3}}}\times 100 = 74.06\%$$

SOME SOLVED EXAMPLES

Example 66. *A compound formed by elements A and B crystallises in cubic structure where A atoms are at the corners of a cube and B atoms are at the face-centre. What is the formula of the compound?*

Solution: An atom at the corner of the cube contributes $\frac{1}{8}$ to the unit cell. Hence, number of atoms of A in the unit cell $= 8\times\frac{1}{8} = 1$.

An atom at the face of the cube contributes $\frac{1}{2}$ to the unit cell. Hence, number of atoms of B in the unit cell $= 6\times\frac{1}{2} = 3$.

Thus, the formula is AB_3.

Example 67. *At room temperature, sodium crystallises in body-centred cubic lattice with $a = 4.24$ Å. Calculate the theoretical density of sodium (At. mass of Na = 23.0).*

Solution: A body-centred cubic unit cell contains 8 atoms at the 8 corners and 1 in the centre.

Hence,

$$\text{Total number of atoms in a unit cell} = 8\times\frac{1}{8}+1 = 2$$

$$\text{Volume of unit cell} = a^3 = (4.24\times 10^{-8})^3\ \text{cm}^3$$

$$\text{So, Density} = \frac{Z\times M}{N_0\times V} = \frac{2\times 23}{(6.023\times 10^{23})(4.24\times 10^{-8})^3}$$

$$= 1.002\ \text{g cm}^{-3}$$

Example 68. *The density of KCl is 1.9893 g cm^{-3} and the length of a side of unit cell is 6.29082 Å as determined by X-ray diffraction. Calculate the value of Avogadro's number.*

Solution: KCl has face-centred cubic structure,

i.e., $Z = 4$

$$\text{Avogadro's number} = \frac{Z\times M}{d\times V}$$

Given that, $d = 1.9893$; $M = 74.5$; $V = (6.29082\times 10^{-8})^3\ \text{cm}^3$

$$\text{Avogadro's number} = \frac{4\times 74.5}{1.9893\times(6.29082\times 10^{-8})^3}$$

$$= 6.017\times 10^{23}$$

Example 69. *Silver crystallises in a face-centred cubic unit cell. The density of Ag is 10.5 g cm^{-3}. Calculate the edge length of the unit cell.*

Solution: For face-centred cubic unit, $Z = 4$.

$$\text{We know that,}\quad V = \frac{Z\times M}{N_0\times d}$$

$$= \frac{4\times 108}{(6.023\times 10^{23})\times 10.5} = 6.83\times 10^{-23}$$

$$= 68.3\times 10^{-24}$$

Let a be the edge length of the unit cell.

So, $V = a^3$

or $a^3 = 68.3\times 10^{-24}$

$$a = (68.3\times 10^{-24})^{1/3}\ \text{cm}$$

$$= 4.09\times 10^{-8}\ \text{cm}$$

$$= 409\ \text{pm}$$

Example 70. *An element occurs in bcc structure with a cell edge of 288 pm. The density of metal is 7.2 g cm^{-3}. How many atoms does 208 g of the element contain?*

Solution: Volume of the unit cell $= (288\times 10^{-10})^3$

$$= 23.9\times 10^{-24}\ \text{cm}^3$$

$$\text{Volume of 208 g of the element} = \frac{208}{7.2} = 28.88\ \text{cm}^3$$

$$\text{Number of unit cells in 28.88 cm}^3 = \frac{28.88}{23.9\times 10^{-24}}$$

$$= 12.08\times 10^{23}\ \text{unit cells}$$

Each bcc structure contains 2 atoms.

So, Total atoms in 12.08×10^{23} unit cells

$$= 2\times 12.08\times 10^{23}$$
$$= 24.16\times 10^{23}$$

Example 71. *Lithium forms body-centred cubic crystals. Calculate the atomic radius of lithium if the length of the side of a unit cell of lithium is 351 pm.*

Solution: In body-centred cubic crystals,

$$r = \frac{\sqrt{3}}{4}a$$
$$= \frac{\sqrt{3}}{4}\times 351\,\text{pm} = 151.98\,\text{pm}$$

Example 72. *Ammonium chloride crystallises in a body-centred cubic lattice with a unit distance of 387 pm. Calculate (a) the distance between oppositely charged ions in the lattice and (b) the radius of the NH_4^+ ion if the radius of Cl^- ion is 181 pm.*

Solution: (a) In a body-centred cubic lattice, oppositely charged ions touch each other along the cross-diagonal of the cube.

So, $$2r_c + 2r_a = \sqrt{3}a$$

or $$r_c + r_a = \frac{\sqrt{3}}{2}a$$
$$= \frac{\sqrt{3}}{2}\times 387 = 335.15\,\text{pm}$$

(b) Given that, $$r_a = 181\,\text{pm}$$
$$r_c = 335.15 - 181.0 = 154.15\,\text{pm}$$

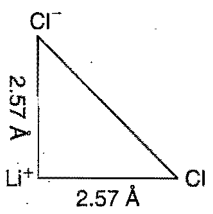
Example 73. *The unit cell cube length for LiCl (NaCl structure) is 5.14 Å. Assuming anion-anion contact, calculate the ionic radius for chloride ion.*

Solution: In a face-centred cubic lattice, anions touch each other along the face diagonal of the cube.

$$4r_{\text{Cl}^-} = \sqrt{2}a$$
$$r_{\text{Cl}^-} = \frac{\sqrt{2}}{4}a$$
$$= \frac{\sqrt{2}}{4}\times 5.14 = 1.82\,\text{Å}$$

Alternative: Distance between Li^+ and Cl^- ion

$$= \frac{5.14}{2} = 2.57\,\text{Å}$$



Thus, distance between two chloride ions

$$= \sqrt{(2.57)^2 + (2.57)^2}$$
$$= 3.63\,\text{Å}$$

Hence,

$$\text{radius of Cl}^- = \frac{3.63}{2} = 1.82\,\text{Å}$$

Example 74. *The density of crystalline sodium chloride is $2.165\,g\,cm^{-3}$. What is the edge length of the unit cell. What would be the dimensions of cube containing one mole of NaCl?*

Solution: We know that,

$$\rho = \frac{N}{a^3}\left(\frac{M}{N_A}\right)$$

where, ρ = density = $2.165\,\text{gcm}^{-3}$

M = molar mass = 58.5

N_A = Avogadro's number = 6.023×10^{23}

N = number of formula unit per unit cell

= 4 (for fcc)

$$a^3 = \frac{N}{\rho}\left(\frac{M}{N_A}\right) = \frac{4}{2.165}\left[\frac{58.5}{6.023\times 10^{23}}\right]$$
$$= 1.794\times 10^{-22}$$
$$a = 5.64\times 10^{-8}\,\text{cm}$$

$$\text{Molar volume} = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.8}{2.165}$$

$$\text{Edge length }(a) = \left[\frac{58.8}{2.165}\right]^{1/3} = 3\,\text{cm}$$

Example 75. *The density of potassium bromide crystal is $2.75\,g\,cm^{-3}$ and the length of an edge of a unit cell is 654 pm. The unit cell of KBr is one of three types of cubic unit cells. How many formula units of KBr are there in a unit cell? Does the unit cell have a NaCl or CsCl structure?*

Solution: We know that,

$$\rho = \frac{N}{a^3}\left[\frac{M}{N_A}\right]$$
$$N = \frac{\rho\times a^3\times N_A}{M}$$
$$= \frac{2.75\times(654\times 10^{-10})^3\times 6.023\times 10^{23}}{119} = 3.89\approx 4$$

Number of mass points per unit cell = 4

It is NaCl type crystal, *i.e.*, fcc structure.

Example 76. *A unit cell of sodium chloride has four formula units. The edge length of unit cell is 0.564 nm. What is the density of sodium chloride?* **(IIT May 1997)**

Solution: $$\rho = \frac{ZM}{a^3N} = \frac{4\times 58.5}{(5.64\times 10^{-8})^3\times 6.023\times 10^{23}}$$
$$= 2.16\,\text{g cm}^{-3}$$

Example 77. *Chromium metal crystallises with a body-centred cubic lattice. The length of the unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3?* **(IIT July 1997)**

Solution: In body-centred cubic unit cell,

$$a\sqrt{3} = 4r$$

where, a = edge length, r = radius of atom

$$r = \frac{a\sqrt{3}}{4} = \frac{\sqrt{3} \times 4.29}{4} = 1.8574 \text{ Å}$$

Example 78. *When heated above 916°C, iron changes its crystal structure from body-centred cubic to cubic closed packed structure. Assuming that the metallic radius of the atom does not change, calculate the ratio of density of the bcc crystal to that of the ccp crystal.*

Solution: In body-centred packing, the efficiency of packing is 67.92%. In the cubic closed packing, the packing efficiency is 74.02%.

Let d_1 be the density when packing efficiency is 74.02% and d_2 is the density when packing efficiency is 74.02%.

$$\frac{d_2}{d_1} = \frac{67.92}{74.02} = 0.918$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

30. An element 'A' has face-centred cubic structure with edge length equal to 361 pm. The apparent radius of atom 'A' is:

(a) 127.6 pm (b) 180.5 pm
(c) 160.5 pm (d) 64 pm

[Ans. (a)]

[Hint: For face-centred unit cell,

$$a\sqrt{2} = 4r$$

$$\therefore \quad \frac{361 \times 1.414}{4} = r$$

$$\therefore \quad r = 127.6 \text{ pm}]$$

31. The packing fraction of the element that crystallises in simple cubic arrangement is:

(a) $\frac{\pi}{4}$ (b) $\frac{\pi}{6}$ (c) $\frac{\pi}{3}$ (d) $\frac{\pi}{2}$

[Ans. (b)]

[Hint: In simple unit cell $a = 2r$

$$Z = 1$$

$$\therefore \quad \text{Packing fraction} = \frac{\text{Occupied volume}}{\text{Total volume}}$$

$$= \frac{\frac{4}{3}\pi r^3}{a^3} = \frac{\frac{4}{3}\pi r^3}{(2r)^3} = \frac{\pi}{6}]$$

32. How many unit cells are present in 39 g of potassium that crystallises in body-centred cubic structure?

(a) N_A (b) $\frac{N_A}{4}$ (c) $0.5\, N_A$ (d) $0.75\, N_A$

[Ans. (c)]

[Hint: $\text{Number of atoms} = \frac{\text{Mass}}{\text{Atomic mass}} \times N_A$

$$= \frac{39}{39} \times N_A = N_A$$

In bcc unit cell, $Z = 2$

$$\therefore \quad \text{Number of unit cells} = \frac{N_A}{2} = 0.5\, N_A]$$

33. Sodium metal exists in bcc unit cell. The distance between nearest sodium atoms is 0.368 nm. The edge length of the unit cell is:

(a) 0.368 nm (b) 0.184 nm
(c) 0.575 nm (d) 0.424 nm

[Ans. (d)]

[Hint: In bcc unit cell, $a\sqrt{3} = 4r$

$$a = \frac{4r}{\sqrt{3}} = \frac{2}{\sqrt{3}} \times 2r$$

$$= \frac{2}{\sqrt{3}} \times 0.368 = 0.425 \text{ nm}]$$

34. If the distance between Na^+ and Cl^- ions in NaCl crystal is 265 pm, then edge length of the unit cell will be?

(a) 265 pm (b) 530 pm (c) 795 pm (d) 132.5 pm

[Ans. (b)]

[Hint: In NaCl:

Edge length = 2 × distance between Na^+ and Cl^- ions

$$= 2 \times 265 = 530 \text{ pm}]$$

35. The interionic distance for caesium chloride crystal will be:

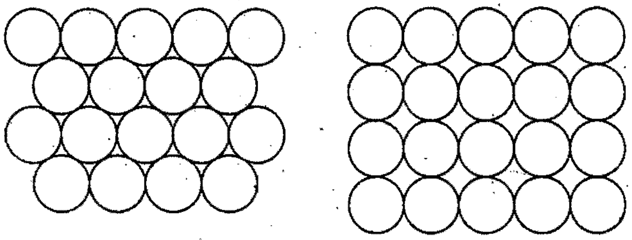
[PMT (MP) 2007]

(a) a (b) $\frac{a}{2}$ (c) $\frac{a\sqrt{3}}{2}$ (d) $\frac{2a}{\sqrt{3}}$

[Ans. (c)]

4.22 PACKING OF IDENTICAL SOLID SPHERES

The constituent particles in the formation of crystals are either atoms, ions or molecules. These particles may be of various shapes and thus, the mode of packing of these particles will change according to their shapes. The simplest way will be to consider these particles as spheres of equal size. The packing of spheres is done in such a way as to use the available space in the most economical manner.



Arrangement (i) Arrangement (ii)

Fig. 4.35 Two common ways of packing spheres of equal size

There are two common ways in which spheres of equal size can be packed. This has been shown in Fig. 4.35. The arrangement (i) is more economical in comparison to arrangement (ii) as 60.4% volume is occupied in arrangement (i) and 52.4% volume in arrangement (ii). Arrangement (i) represents a close packing of spheres.

In arrangement (i), the spheres are packed in such a manner that their centres are at the corners of an equilateral triangle. Each sphere is surrounded by six other similar spheres as shown in Fig. 4.36. This arrangement can be extended in three dimensions by adjusting spheres on the top of hollows or voids of the two-dimensional layer which is called the first layer or '*A*' layer. There are two types of hollows in the first layer which have been marked by dots (·) and cross (×). All the hollows are equivalent. The spheres of the second layer may be put either on hollows marked by dots or by crosses. Half of the hollows remain unoccupied in the second layer (Fig. 4.37). The second layer is marked as '*B*' layer. The spheres have been placed on the hollows marked by dots.

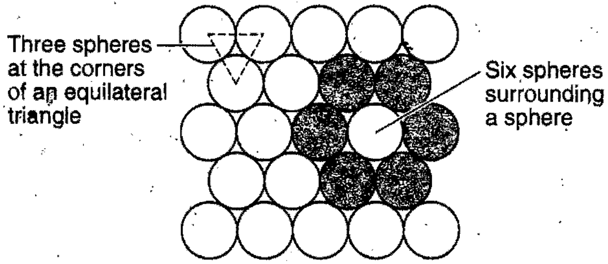


Fig. 4.36 Close packing of spheres

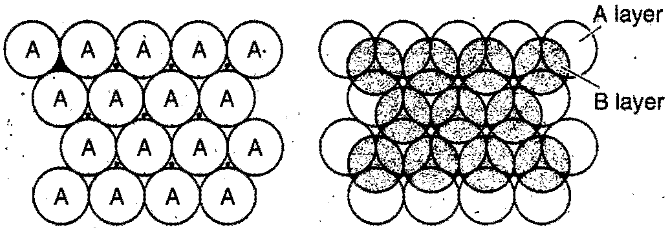


Fig. 4.37 Building of second layer (B, shown shaded) covering hollows marked by dots (•). The hollows marked by a cross (×) unoccupied

To build up the third layer of spheres, there are two alternative ways. In the first way the spheres are placed on the hollows of second layer. It is observed that each sphere of third layer lies exactly above the spheres of first layer. When this arrangement is continued indefinitely, the system obtained is found to possess hexagonal symmetry and is called hexagonal close packing of spheres and is abbreviated as hcp or *ABABAB*... This is shown in Fig. 4.38. In the second way, spheres are placed on the unoccupied hollows of the first layer, marked by 'crosses'. It is observed that spheres of the third layer do not come over those of first layer. This arrangement of close packing is referred to as *ABC*. However, it is noted that spheres in the fourth layer will correspond with those in the first layer. When such an arrangement is continued indefinitely, the system is found to possess cubic symmetry and called cubic close packing of spheres and is abbreviated as **ccp** or *ABCABC*... This is shown in Fig. 4.39. The system *ABCABC*... shows that there is a sphere at the centre of each face of the unit cube and thus, this system is also referred to as face-centred cubic or **fcc.**

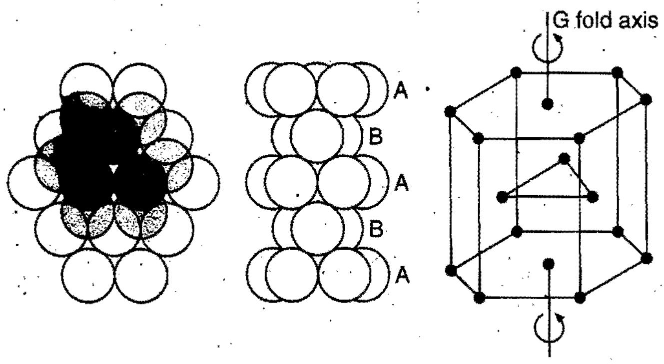
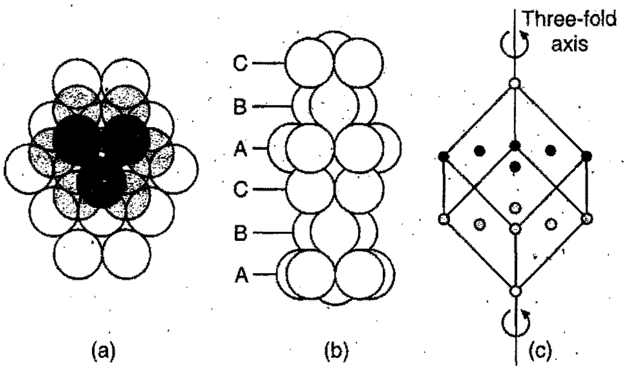


Fig. 4.38 *ABABAB*... or hexagonal close packing (hcp) of spheres



(a) (b) (c)

Fig. 4.39 *ABC ABC A*... or cubic close packing (ccp) of spheres

It is noted that in both the above systems **hcp** or **ccp**, each sphere is surrounded by twelve other spheres shown in Fig. 4.40. There is a third arrangement of packing of spheres which is known as **body-centred cubic** arrangement (bcc). This arrangement is obtained when the spheres in the first layer are slightly opened up, *i. e.*, none of the spheres touches each other. In the second layer, the spheres are placed at the top of hollows in the first layer. In the third layer, spheres are placed exactly above the first layer. Each sphere in this system of packing is in contact with eight spheres, four in the lower layer and four in the upper layer. This arrangement has been shown in Fig. 4.41.

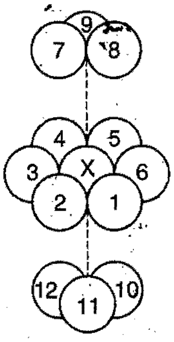


Fig. 4.40 Coordination number in hcp and ccp structure

Most of the metals belonging to *s*-block and *d*-block elements possess any one of the following close packing arrangements:

(i) Cubic closed packed, (ii) Hexagonal closed packed and (iii) Body-centred cubic packed.

Examples:

Metals	Structure
Mg, Zn, Mo, V, Cd	hcp
Cu, Ag, Au, Ni, Pt	ccp or fcc
Li, Na, K, Rb, Cs, Ba	bcc

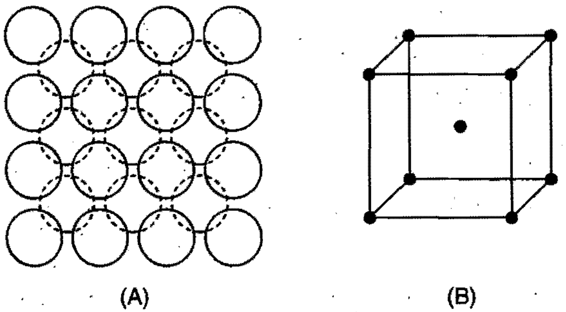


Fig. 4.41 (A) Body-centred cubic packing of spheres
(B) Body-centred cubic arrangement

Interstitial sites in close packed lattices: In a close packing of spheres, there is always some empty space left. The empty space is called hole or void or interstitial site. Common interstitial sites in closely packed spheres are tetrahedral and octahedral.

Tetrahedral site: When one sphere is placed upon the three other spheres which are touching each other, tetrahedral structure results. The four spheres leave a small space in between which is called a tetrahedral site. The site is much smaller than that of the spheres. However, when the spheres are bigger in size, the tetrahedral site becomes larger. In hcp and ccp, each sphere is in contact with three spheres above and three spheres below. Thus, there are two tetrahedral sites associated with each sphere.

Octahedral site: This site is formed at the centre of six spheres, the centres of which lie at the apices of a regular octahedron. Each octahedral site is created by superimposing two equilateral triangles with apices in opposite direction, drawn by joining centres of three spheres in one plane and three spheres in other plane. There is an octahedral site for each sphere. Thus, octahedral sites are half of tetrahedral sites. Tetrahedral and octahedral voids are represented in Fig. 4.42 and 4.43.

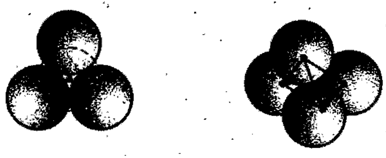


Fig. 4.42 Tetrahedral voids

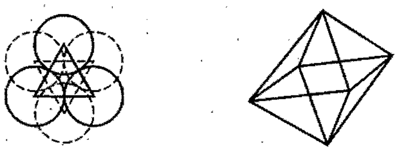


Fig. 4.43 Octahedral voids

Location of Octahedral and Tetrahedral Voids in Cubic Close Packing

Octahedral voids : In the Fig. 4.44 a unit cell of ccp or fcc lattice is drawn. Corners and face-centres are the packing sites. In the face-centred cubic unit cell; octahedral voids are located at the body-centre and all the edge centres of cube.

Number of constituent units at packing sites $= 8\times\frac{1}{8}+6\times\frac{1}{2}=4$

Number of octahedral voids (one at body-centre and twelve at edge-centres) $= 1+\frac{1}{4}\times 12 = 4$

∴ Number of octahedral voids is equal to the number of constituent units at packing sites. Each octahedral void is surrounded by six constituent units.

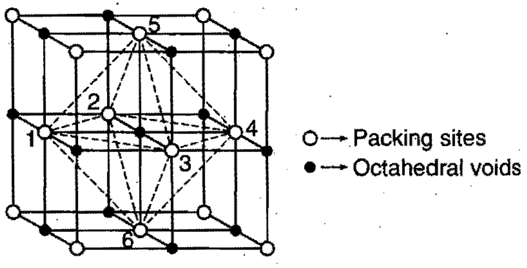


Fig. 4.44

Tetrahedral voids : In cubic close packing, there are eight tetrahedral voids in each unit cell. Tetrahedral voids are located on body diagonals. Two tetrahedral voids are located on each body diagonal; these are represented in the Fig. 4.45.

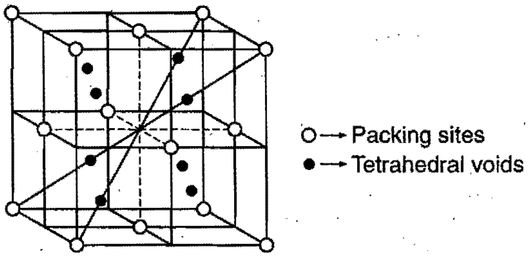


Fig. 4.45

Number of constituent units at packing sites (corners and face-centres) $= 8\times\frac{1}{8}+6\times\frac{1}{2}=4$

Number of tetrahedral voids = 8

Thus, number of tetrahedral voids is twice the number of constituent units present at packing sites.

In a multilayered closest-packed structure, there is a tetrahedral void above and below each atom, hence there are twice as many tetrahedral voids as those of closest-packed constituent units.

Tetrahedral and octahedral voids can be located as

———————— Second closest packed layer
———————— Tetrahedral voids
———————— Octahedral voids
———————— Tetrahedral voids
———————— First closest packed layer

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

36. In a compound, atoms of element Y form ccp lattice and those of element X occupy 2/3rd tetrahedral voids. The formula of the compound will be : (AIEEE 2008)
(a) X_3Y_4 (b) X_4Y_3 (c) X_2Y_3 (d) X_2Y
[**Ans.** (b)]
[**Hint** : Let number of atoms of Y used in packing $= n$

Number of tetrahedral voids = $2n$

Number of atoms of $X = \frac{2}{3} \times 2n = \frac{4}{3}n$

$$Y : X = n : \frac{4}{3}n = 3 : 4$$

Formula of compound = X_4Y_3]

37. A solid compound contains X, Y and Z atoms in a cubic lattice with X atoms occupying the corners, Y atoms in the body centred positions and Z atoms at the centre of the faces of the unit cell. What is the empirical formula of the compound ?

(a) XY_2Z_3 (b) XYZ_3 (c) $X_2Y_2Z_3$ (d) X_8YZ_6
(e) XYZ

[**Ans.** (b)]

[**Hint :** Number of atoms of X in a unit cell = $\frac{1}{8} \times 8 = 1$

Number of atoms of Y in a unit cell = 1

Number of atoms of Z in a unit cell = $\frac{1}{2} \times 6 = 3$

Empirical formula of the compound = XYZ_3]

38. In a crystalline solid, atoms of X form fcc packing and the atoms of Y occupy all octahedral voids. If all the atoms along one body diagonal are removed then the simplest formula of the crystalline solid will be :

(a) XY (b) X_4Y_3 (c) X_5Y_4 (d) X_4Y_5

[**Ans.** (c)]

[**Hint :** Number of atoms of X in fcc packing (at corners and face centres of cubic unit cell) = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Number of atoms of Y at octahedral voids = 4

Along one body diagonal there are two X atoms and one Y atom.

Number of effective atoms of X after removal

$$= 4 - 2 \times \frac{1}{8} = \frac{15}{4}$$

Number of effective atoms of Y after removal = 4 − 1 = 3

$$X : Y = \frac{15}{4} : 3$$

$$= 5 : 4$$

∴ Simplest formula = X_5Y_4]

4.23 TYPES OF CRYSTALS

Crystals are classified into four main types depending upon the nature of forces that hold the constituent particles together in the crystal lattice.

1. Ionic crystals: The forces operating in ionic crystals are electrostatic. The lattice points in such crystals are occupied by positively and negatively charged ions. Each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its **coordination number.** The coordination numbers of positive or negative ions may be same or different. For example, in sodium chloride, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Thus, both the ions have coordination number six. In CsCl, each Cs^+ ion is surrounded by eight Cl^- ions and *vice-versa*. Thus, both the ions have coordination number eight. In the case of CaF_2, the coordination number of Ca^{2+} is eight while that of F^- ion, is four.

The coordination numbers commonly encountered in ionic crystals are 8 (body-centred cubic arrangement), 6 (octahedral arrangement) and 4 (tetrahedral arrangement).

It is impossible for both anions and cations to have closed packed structures but if one of the ions is much bigger than the other, it is common for the bigger ions alone to approach a closed packed structure and smaller ions to fit into holes in this structure.

In ionic crystals, the coordination numbers as well as the geometrical shapes of the crystals depend mainly on the relative sizes of the ions. The ratio of the radii of the positive and negative ions is called radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of positive ion (cation)}}{\text{Radius of negative ion (anion)}} = \frac{r_{c^+}}{r_{a^-}}$$

Common coordination numbers are 3, 4, 6 and 8.

The following table shows the radius ratio values, permitted coordination numbers and the shapes of ionic crystals:

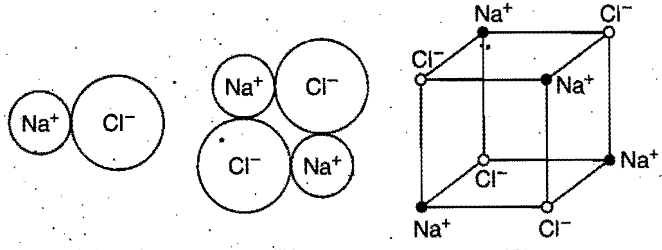
Radius ratio (r_c^+ / r_a^-)	**Permitted coordination number**	**Arrangement of anions round the cations**	**Example**
0.155– 0.225	3	Plane Triangular	B_2O_3
0.225– 0.414	4	Tetrahedral	ZnS
0.414– 0.732	6	Octahedral	NaCl
0.732–1.000	8	Cubic (body-centred)	CsCl

Types of Structure of Ionic Solids

Crystal structure of ionic solids are described into following types:

Crystal structure (Type)	**Example**
1. Rock salt	NaCl, LiCl, KBr, RbI, AgCl, AgBr, FeO, CaO
2. Cesium chloride	CsCl, CaS, CsCN
3. Fluorite	CaF_2, UO_2, $BaCl_2$, HgF_2
4. Antifluorite	K_2O, K_2S, Li_2O, Na_2O, Na_2S
5. Nickel Arsenite	NiAS, NiS, FeS, CoS
6. Rutile	TiO_2, MnO_2, SnO_2
7. Perovskite	$CaTiO_3$, $BaTiO_3$, $SrTiO_3$
8. Zinc blende (sphalerite)	ZnS, CuCl, CdS, HgS
9. Wurtzite	ZnS, ZnO, BeO, MnS, AgI

Packing of ions in ionic crystal (Formation of NaCl crystal): The formation of NaCl crystal can be explained in the following manner. The two ions form one ion-pair of opposite charges by the electrostatic force of attraction. Each of the ions has a strong residual field around it and will naturally attract another ion-pair much in the same way as two magnets attract each other, *i.e.*, a cluster is formed. Two clusters combine together to give a unit cell. Finally, large number of unit cells unite together to form three-dimensional cubic crystal.



(A) (B) (C)

Fig. 4.46 Filing up of ion pairs in stages: (A) shows an ion-pair, (B) two ion-pairs and (C) four ion-pairs of sodium chloride

An examination of NaCl crystal (Fig. 4.47) makes the following points clear:

(i) Each Na^+ ion is surrounded by six Cl^- ions at the corners of a regular octahedron and similarly each Cl^- ion is surrounded by six Na^+ ions. It is, therefore, termed as 6 : 6 arrangement. The radius ratio $[r^+_{Na} / r^-_{Cl} = 0.95/1.81 = 0.524]$ suggests that coordination number of each ion is six.

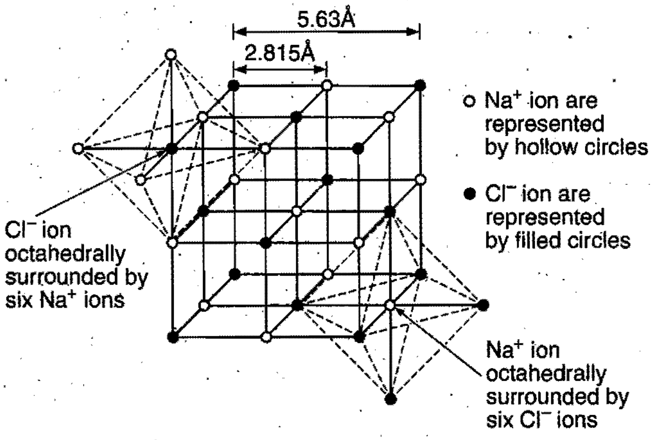


Fig. 4.47 Unit cell representation on NaCl structure

(ii) In the octahedral structure, Cl^- ions may be regarded as having a cubic closed packed (ccp) arrangement in which all octahedral holes are filled by Na^+ ions.

(iii) This type of structure is possessed by most of the alkali metal halides (KCl, NaI, RbF, RbI), alkaline earth metal oxides and AgF, AgCl, AgBr, NH_4Cl, NH_4Br, etc.

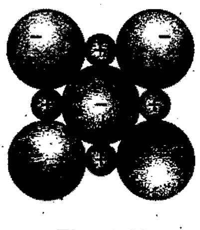


Fig. 4.48

Here, $4r_- = \sqrt{2}a$ and $(2r_- + 2r_+) = a$

Packing fraction (ϕ) :

$$\phi = 4 \times \frac{4}{3}\pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{\pi}{3\sqrt{2}}\left[\left(\frac{r_+}{r_-}\right)^3 + 1\right].$$

The unit cell of sodium chloride has four sodium ions and four chloride ions.

(a) Number of sodium ions = 12 (at the edge-centres) $\times \frac{1}{4}$ + 1 (at body-centre) = 4

(b) Number of chloride ions = 8 (at the corners) $\times \frac{1}{8}$ + 6 (at face-centres) $\times \frac{1}{2} = 4$

Structure of Some Other Ionic Compounds

In CsCl crystal, the coordination number of each ion is 8 as the radius ratio $\left(\frac{r_{Cs^+}}{r_{Cl^-}}\right)$ is 0.933. It is termed as 8 : 8 arrangement. The arrangement of the ions in this crystal is body-centred cubic type, *i.e.*, the unit cell has one ion at the centre and oppositely charged ions at the corners of the cube. This has been shown in Fig. 4.49. This type of structure is possessed by CsBr, CsI, TlCl, TlBr, etc.

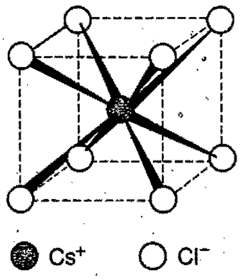


Fig. 4.49 Structure of CsCl

Here, Cs^+ ion is present at the body centre and chloride ions at eight corners. In their limiting case :

$$2r_- = a \text{ and } (2r_- + 2r_+) = \sqrt{3}a$$

a = edge length of unit cell

Packing fraction (ϕ):

$$\phi = \frac{4}{3}\pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{4\pi}{3 \times 8}\left[\left(\frac{r_+}{r_-}\right)^3 + 1\right]$$

ZnS crystal has two types of structures:

(i) Zinc blende structure and

(ii) Wurtzite structure.

(i) Zinc blende structure: It has cubic close-packed (ccp) structure. The S^{2-} ions are present at the corners of the cube and at the centre of each face. Zinc ions occupy half of the tetrahedral sites. Each zinc ion is surrounded by four sulphide ions which are disposed towards the corners of a regular tetrahedron. Similarly, each S^{2-} ion is surrounded by four Zn^{2+} ions. This structure is similar to diamond.

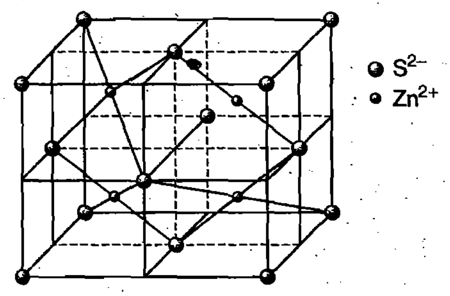


Fig. 4.50 Zinc blende

$$4r_- = \sqrt{2}a$$

Packing fraction (ϕ) :

$$= 4 \times \frac{4}{3}\pi \frac{(r_+^3 + r_-^3)}{a^3} = \frac{\pi}{3\sqrt{2}}\left[\left(\frac{r_+}{r_-}\right)^3 + 1\right]$$

(ii) **Wurtzite structure:** It has hexagonal close-packed (hcp) structure. S^{2-} ions adopt hcp arrangement and Zn^{2+} ions occupy half of the tetrahedral sites.

The above structures are termed 4 : 4 arrangement possessed by ZnO, AgI, SiC, etc.

CaF_2 crystal: The Ca^{2+} ions are arranged in ccp arrangement, *i.e.*, Ca^{2+} ions are present at all corners and at the centre of each face of the cube. The fluoride ions occupy all the tetrahedral sites. This is 8 : 4 arrangement, *i.e.*, each Ca^{2+} ion is surrounded by 8 F^- ions and each F^- ion by four Ca^{2+} ions.

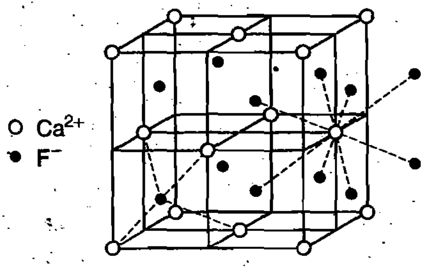


Fig. 4.51 Fluorite structure-Structure of calcium fluoride

Structure of Sodium Oxide (Na_2O)—Antifluorite Structure

Sodium oxide has antifluorite structure. The structure is similar to the structure of calcium fluoride with the difference that the anions occupy the positions of cations and *vice-versa*.

(i) It has cubic close packing arrangement of O^{2-} ions, *i.e.*, these ions are present at the corners and at the centres of all the six faces of the unit. Sodium ions on the other hand, are present at the sites of all the tetrahedral voids.

(ii) Each Na^+ ion is surrounded by four O^{2-} ions and each O^{2-} ion is surrounded by eight Na^+ ions. Thus, Na_2O has 4 : 8 coordination structure.

Other examples with antifluorite structures are :

Cl_2O, Na_2S, K_2O, Li_2S, K_2S, etc.

Structures of Oxides of Iron

Iron is known to form three major oxides, which are FeO, Fe_2O_3, Fe_3O_4. These oxides are interconvertible due to oxidation and reduction. Non-metal excess non-stoichiometry is also known in these oxides. Crystal structures of these oxides are very interesting.

1. **Structure of FeO :** This oxide has a structure like rock salt (NaCl). Oxide ions (O^{2-}) form a face-centred cubic close packing and Fe^{2+} ions occupy all octahedral voids. It is a perfect rock salt type structure with formula FeO. This oxide is known to form non-metal excess non-stoichiometric compound with the composition $Fe_{0.95}O$ (Wustite). In the non-stoichiometric compound some of the Fe^{2+} ions present in octahedral voids are replaced by Fe^{3+} ions. Three Fe^{2+} ions will be replaced by two Fe^{3+} ions to maintain electrical neutrality.

[**Normal Spinel Structure.:** Spinel is the common name of the mineral, $MgAl_2O_4$. The crystal structure of this mineral is also called spinel structure. In this type of structure, both tetrahedral and octahedral voids are simultaneously occupied. General formula of the compound having spinel structure is AB_2O_4 where 'A' stands for a divalent cation and 'B' stands for a trivalent cation. It has a cubic close packed arrangement of oxide ions. Half of the octahedral voids are occupied by trivalent cations and one-eighth of the tetrahedral voids are occupied by divalent cations.

Ferrites are the spinel type compounds having the general formula AFe_2O_4 where A stands for divalent cation such as Zn^{2+}. Ferrites are used for making powerful, permanent and non-rusting magnets. Ferrites are used in telephones and memory units of computers.]

2. **Structure of Fe_3O_4 :** Magnetite, Fe_3O_4, is considered as a mixed oxide. It contains mixture of FeO and Fe_2O_3. It has an **inverse spinel structure.** Oxide ions (O^{2-}) from face-centred cubic arrangement. Dipositive ions (Fe^{2+}) are present in octahedral voids and tripositive ions (Fe^{3+}) are equally distributed among tetrahedral and octahedral voids.

Number of O^{2-} ions in the unit cell = 4
Thus, Number of tetrahedral voids = 8
and Number of octahedral voids = 4
Number of Fe^{2+} ions present in octahedral void = 1
Number of Fe^{3+} ions present in tetrahedral void = 1
Number of Fe^{3+} ions present in octahedral void = 1

Thus, half of the octahedral voids are occupied by Fe^{2+} and Fe^{3+} ions and one-eighth of the tetrahedral voids are occupied by Fe^{3+} ions.

3. **Structure of Fe_2O_3 :** If all the Fe^{2+} ions are replaced by Fe^{3+} ions, then as every three Fe^{2+} ions can be replaced by two Fe^{3+} ions to maintain electrical neutrality, the ratio between Fe and O will now be 2 : 3, *i.e.*, we get Fe_2O_3.

Properties of Ionic Crystals

(i) **Physical state:** Ionic crystals are crystalline solids at room temperature. They are never liquids or gases under ordinary temperature and pressure as the ions do not have freedom of movement.

Since, high energy is required to separate cations and anions from one another from their alloted positions on account of very strong electrostatic forces of attraction, the **ionic crystals are quite hard, have low volatility and have high melting and boiling points.**

(ii) **Electrical conductivity: Ionic crystals are insulators,** *i.e.*, do not conduct electricity in solid state. The reason is that ions are held firmly in fixed positions in the crystal lattice and cannot move when electric field is applied. **However, when melted they become good conductors of electricity,** *i.e.*, ions are free to move in liquid medium.

(iii) **Solubility:** Ionic crystals are soluble in polar solvents or solvents having high values of dielectric constant. They are insoluble in non-polar solvents. When they dissolve in non-polar medium colloidal solutions are formed, *e.g.*, NaCl in kerosine oil. The dissolution of an ionic crystal in a polar solvent depends on the relative magnitudes of lattice and hydration energies.

$$\underset{\text{(Ionic crystal)}}{MX(s)} + \underset{\text{(Lattice energy)}}{\text{Energy}} \longrightarrow M^+(g) + X^-(g)$$

$$M^+(g) + x(\text{Solvent}) \longrightarrow \underset{\text{(Solvated ion)}}{[M(\text{Solvent})_x]^+} + \underset{\text{(Heat of hydration)}}{\text{Energy}}$$

$$X^-(g) + y(\text{Solvent}) \longrightarrow \underset{\text{(Solvated ion)}}{[X(\text{Solvent})_y]^-} + \underset{\text{(Heat of hydration)}}{\text{Energy}}$$

The ionic compound will be soluble if total hydration energy is higher than lattice energy.

Ionic crystals are good conductors in molten state or when dissolved in water.

(iv) **Brittleness:** Ionic solids are highly brittle in nature. When external force is applied, these are easily broken into pieces. Ionic solids are composed of parallel layers which contain cations and anions. When external force is applied, one layer slides a bit over the other and like ions come in front of each other. Due to repulsion between two layers the ionic solid breaks down.

Ionic crystals have high density due to close packing.

(v) **Isomorphism:** Ionic crystals possess same crystalline structure, *i.e.*, show isomorphism if the ions (cations and anions) have same electronic configuration. NaF and MgO are isomorphous compounds.

Na^+	F^-	and	Mg^{2+}	O^{2-}
2, 8	2, 8		2, 8	2, 8

2. **Covalent crystals:** In covalent crystals, the lattice points are occupied by neutral atoms either of same element or of different elements. These atoms are held together by covalent bonds. Covalent crystals are of two types:

(i) The covalent bonds extend in three-dimensions forming a giant interlocking structure. Examples are diamond, silicon carbide (SiC), aluminium nitride, etc.

In **diamond,** each carbon atom is sp^3-hybridized and thus, covalently bonded to four other carbon atoms present at the four corners of a regular tetrahedron. This leads to a rigid three-dimensional network. The entire crystal is regarded as one large carbon molecule and is called a **macromolecule.** The structure of diamond explains the properties such as high density, non-conducting nature, extreme hardness and high melting and boiling point of the diamond.

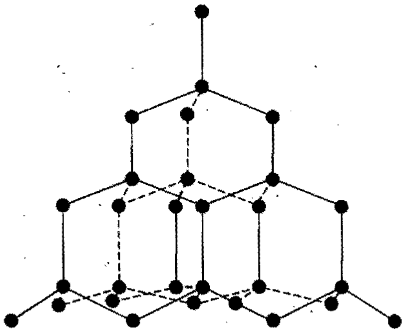


Fig. 4.52 Structure of diamond

(ii) The covalent bonds extend in two-dimensions forming a giant layer. These layers are then held together by van der Waals' forces. Examples are graphite, boron nitride (BN), cadmium iodide, etc.

In **graphite,** each carbon is sp^2-hybridized and is thus bonded to three carbon atoms in the same plane. The C—C distance is 1.42 Å which is intermediate between single bond distance (1.54 Å) and double bond distance (1.33 Å). The unit cell consists of a hexagon of six carbon atoms. The unit cells are interlocked giving a layer or sheet structure. The distance between two adjacent layers is 3.35 Å. The structure explains the properties of graphite such as being soft, good conductor of electricity, flaky and slippery.

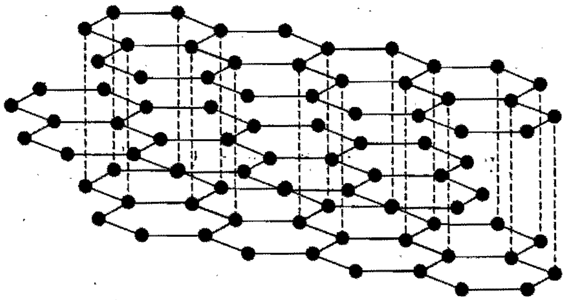


Fig. 4.53 Structure of graphite

In general, the packing of atoms in covalent crystals is loose in comparison to ionic and metallic crystals. Thus, covalent crystals have open structure.

3. Metallic crystals: The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons within its sphere of influence is known as **metallic bond.** Metallic crystals mostly belong to cubic face-centred (fcc), cubic body-centred (bcc) and hexagonal close-packed (hcp) systems. Metallic crystals exhibit the following properties:

(i) Good conductors: On account of the presence of mobile electrons, metals are good conductors of electricity. The electrical conductivity decreases with increase of temperature. This is due to the fact that positive ions also begin to oscillate with the increase of temperature. The oscillation of positive ions hinders the movement of mobile electrons. Metals are also good conductors of heat.

(ii) Lustre: When freshly cut or scratched, most of the metals have a shining surface. When light falls on freshly cut surface, the electrons get excited. The excited electrons give off energy in the form of light when they return to their original position and hence the metal looks bright. The metallic properties are explained on the basis that the metallic bond is non-directional and non-rigid. The result is that M^{n+} ions can be easily moved from one lattice site to another. The nearest neighbours can be thus changed easily and new metal bonds can be formed readily. This explains why metals are malleable and ductile.

(iii) Physical characteristics: Most of the metals are quite hard and tough. They are malleable and ductile. They have high tensile strength. Except alkali metals, they have high melting and boiling points. They also possess elasticity.

4. Molecular crystals: In molecular crystals, the lattice points are occupied by molecules which do not carry any charge. The forces responsible for binding these molecules are dipole-dipole attractions and van der Waals' forces. Dipole-dipole forces are present in solids when polar molecules occupy the lattice points as in the case of water. van der Waals' forces are more general and occur in all kinds of molecular crystals. The binding energy in molecular crystals is, therefore, weak. Molecular crystals show the following general properties:

(i) They are generally soft and easily compressible.

(ii) They have low melting or boiling points.

(iii) They are bad conductors of electricity as the electrons are localised in the bonds.

(iv) They have low density.

The following table provides a comparative summary of the properties of various types of crystals:

Property	Ionic crystals	Covalent crystals	Metallic crystals	Molecular crystals
1. Constituent particles occupying lattice points	Positive and negative ions	Neutral atoms	Positive ion in sea of electrons	Molecules polar or non-polar
2. Binding force	Electrostatic attraction	Shared pairs of electrons	Electrostatic attractions between positive ions and electrons	Weak polar forces or van der Waals' forces
3. Hardness	Hard and brittle	Very hard	Hard or soft	Very soft
4. Melting and boiling points	High	Very high	High or low	Low
5. Electrical conductivity	Bad conductors; Good conductors in fused state or in solution	Bad conductors with few exceptions	Good conductors	Bad conductors
6. Examples	NaCl, KNO_3, CaF_2	Diamond, graphite, carborundum	Cu, Na, Fe metals	Ice, solid CO_2

4.24 IMPERFECTION IN SOLIDS

An ideal crystal is one which has the same unit cell containing the same lattice points across the whole crystal. Any departure from perfectly ordered arrangement of constituent particles in the crystals is called imperfection or *defect.*

Perfect of ideal crystals can exist only at absolute zero or zero Kelvin. At absolute zero the crystalline substances have zero entropy, *i.e.*, have no randomness. Above absolute zero, entropy or randomness increases, *i.e.*, some deviations from perfectly ordered arrangement takes places.

The imperfection may be **intrinsic** or **extrinsic.** Crystalline defects can profoundly after the properties of a solid material. Imperfections or defects not only alter the properties but also give rise to new characteristics. Extrinsic defects due to presence of certain impurities give rise to interesting changes in the properties. For example, gem stones are crystals containing impurities that give them beautiful colours. The presence of Fe^{3+} ions makes sapphire blue and Cr^{3+} ions presence makes ruby red. (Gems are actually crystals of Al_2O_3 which is colourless).

There are mainly two types of imperfections.

1. Electronic imperfections
2. Atomic imperfections.

1. Electronic Imperfections

This type of imperfection arises due to irregular arrangement of electrons in the crystal structure. At 0 K (absolute zero), the electrons in both ionic and covalent solids are present in fully occupied lowest energy orbitals or states and these electrons do not move under the influence of applied electric field. However, when temperature is raised above 0 K, some electrons may occupy higher energy states. For example, in crystals of pure silicon or germanium, some electrons are released from the covalent bonds above 0 K. These free or mobile electrons become responsible for electrical conductance. The bonds from which the electrons have been removed on heating become electron deficient and these are referred to as **holes.** Like free electrons, holes also conduct electric current. Holes in an electric field move in a direction opposite to that in which electrons move. Both electrons and holes present in the solids give rise to electronic imperfection. Electrons and holes are denoted by the symbols '*e*' and '*h*' and their concentrations are represented by '*n*' and '*p*'. In pure covalent solids like silicon and germanium, the number of free electrons and holes will be equal. Electrons and holes can be obtained preferentially according to the requirement by adding appropriate impurities.

Silicon and germanium are the elements of group 14th; thus, they have maximum covalency of four. A number of solids can be obtained by the combination of the elements of groups 13 and 15 or groups 12 and 16 to get average valency of four as in silicon and germanium. Examples are : InSb; AlP; GaAs. In these materials, In, Al and Ga belong to group 13 and Sb, P and As belong to group 15 of the extended form of the periodic table. Other examples are : ZnS, CdS, CdSe, HgTe. In these materials, Zn, Cd and Hg belong to group 12 and S, Se and Te belong to group 16 of the periodic table. These combinations are not purely covalent but possess an ionic character due to difference in the electronegativities of the two elements. These combinations show interesting electrical, magnetic and optical properties which have been utilised in the electronic industries for photovoltaic cells, light emitting diodes, thermocouples and semiconductors, etc.

2. Atomic Imperfections or Point Defects

When the deviations exist in the regular or periodic arrangement of the constituent particles (atoms or ions) in the crystal, these defects are termed atomic imperfections or point defects.

These defects are caused by the following points.

(i) When some of the constituent particles are missing from their normal positions, these unoccupied position are termed **holes** or **vacancies.**

(ii) When some of the constituent particles are missing from their positions and these particles have shifted either to interstitial vacant sites or to positions which are meant for other particles.

Types of point defects : Point defects are classified into the following three types:

(A) Defects in stoichiometric crystals,
(B) Defects in non-stoichiometric crystals,
(C) Impurity defects

(A) Defects in stoichiometric crystals

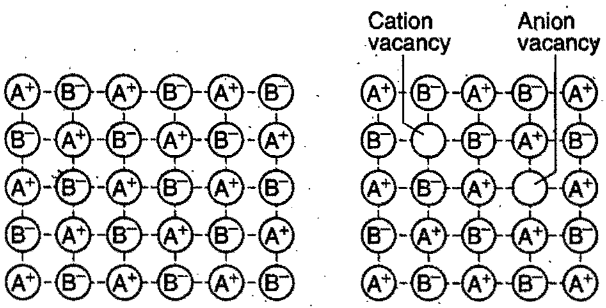
The crystals in which cations and anions are exactly in the same ratio as indicated by their molecular formulae are termed stoichiometric crystals. Points defects do not alter the stoichiometry of the solid; these defects are called as intrinsic or thermodynamic defect. Two types of point defects are observed in these crystals :

(i) Schottky defect, (ii) Frenkel defect.

(i) Schottky defect : This defect was first observed by the German scientist Schottky in 1930. In this defect equal number of cations and anions (from *AB* type crystal) are missing from their normal lattice sites, *i.e.*, equal number of cationic and anionic **vacancies** or **holes** will be developed. The crystal maintains electrical neutrality.

This defect is usually observed in strongly ionic compounds which have high coordination number and the sizes of two ions (cations and anions) are almost same.

Examples : NaCl, KCl, KBr, CsCl, AgBr etc.



(a) Ideal crystal (b) Schottky defect

Fig. 4.54

In 1 cm^3 of NaCl there are 10^{22} ions and 10^6 Schottky pairs, thus there is one Schottky defect per 10^{16} ions.

Consequences of Schottky defect

(a) Due to Schottky defect, the density of crystalline solid decreases.

(b) Lattice energy and thereby stability of the crystalline solid decreases.

(c) Entropy increases.

(ii) Frenkel defect : This defect was discovered and studied by a Russian scientist, Frenkel, in 1926. *This defect is caused if some of the ions (usually the cations) of the lattice occupy interstitial sites leaving a corresponding number of normal lattice sites vacant.* This defect creates **vacancy defect** at original site and **interstitial defect** at new site. Frenkel defect is also called **dislocation defect.**

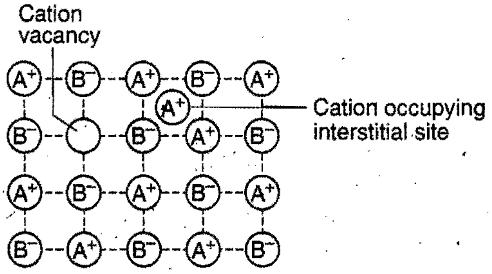


Fig. 4.55 Frenkel defect in the crystal

Main conditions for Frenkel defect are:

⟶ *Coordination number should be low.*

⟶ *Size of anion should be bigger than cation.*

Examples : This defect is not found in alkali metal halides because cations and anions have almost equal sizes and cations cannot be accommodate in interstitial sites. This defect is mainly found in transition metal halides like AgCl, AgBr, AgI, ZnS, etc. Silver ion (Ag^+) being smaller in size can be accommodated in interstitial site. AgBr shows both Frenkel and Schottky defect.

Consequences of Frenkel defect

(a) There is no change in the density of the solid.

(b) There is increase in the dielectric constant as the like charge ions come closer.

(c) The solids having Frenkel defect show conductivity and diffusion in solid state due to presence of vacant lattice sites.

(d) Lattice energy and thereby stability of crystalline solids decreases.

(e) This defect influences the chemical properties of ionic compound.

(f) Entropy of the solid increases.

Thermodynamic facts about point defects in stoichiometric solids : Frenkel and Schottky defects are also called as intrinsic or thermodynamic defects.

Number of point defects increases with temperature. The number of defects formed per unit volume (cm^3) 'n' is given by,

$$n = Ne^{-W/2RT}$$

where, N = number of sites per unit volume (cm^3) which could be left vacant

W = Work necessary to create a defect

T = Absolute temperature

Electrical conductance of crystals increases due to point defects. When potential difference is applied to the solid then ions may move from the lattice sites to occupy the holes or vacancies. Such movement is responsible for electrical conductance.

Difference between Schottky and Frenkel defect

Schottky defect	Frenkel defect
1. Equal number of cationic and anionic vacancies are present in this defect.	Some ions are displaced from normal lattice sites to the interstitial sites.
2. Density is lowered in this defect.	Density is unaffected in it.
3. Dielectric constant remains same.	Dielectric constant increases.
4. It is shown by those ionic compounds which have high coordination number, sizes of cations and anions are almost equal.	It is shown by those ionic compounds which have low coordination number and size of cations is smaller than size of anions.

(B) Defects in non-stoichiometric solids

The compounds in which the number of positive and negative ions are not exactly in the ratio as indicated by their chemical formulae are called non-stoichiometric compounds. Non-stoichiometric solids are also known as **Berthollide compounds.**

Examples :

(i) Ferrous oxide FeO exists in non-stoichiometric form as $Fe_{0.95}O$ called *wüstite.*

(ii) Vanadium oxide has non-stoichiometric formula VO_x, where x lies between 0.6 and 1.3.

(iii) ZnO exists as a non-stoichiometric compound having excess zinc.

(iv) Stoichiometric compounds like NaCl, KCl, etc., can be non-stoichiometric under suitable conditions.

The defects which bring change in overall chemical composition are termed as **non-stoichiometric defects.** In such crystals, there is excess of either positive particles (cations) or negative particles (anions). However, the crystal as a whole is neutral in nature. If positive particles are in excess, the charge is balanced by the presence of extra electrons. In case the negative particles are in excess, the charge is balanced by acquiring higher oxidation state by metal atoms.

Non-stoichiometric defects are of two types:

1. Metal excess defect, 2. Non-metal excess defect

1. Metal excess defect : In this defect, metal ions or cations are in excess. This defect may develop on account of the following two ways :

(a) Anion vacancies : A negative ion may be missing from its lattice site leaving behind a vacancy or hole. This vacancy or hole is occupied by an extra electron to maintain electrical neutrality. This defect is somewhat similar to Schottky defect but differs in having only one hole and not a pair as in the latter case.

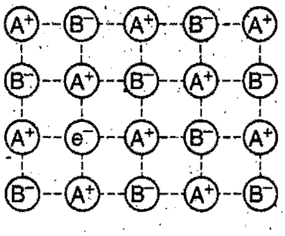


Fig. 4.56 Metal excess defect due to anion vacancy

Anion vacancies in alkali metal halides are produced by heating the metal halides in the atmosphere of alkali metal vapours. Metal atoms get adsorbed on the surface of the metal halides. Halide ions move towards the surface and combine with metal ions formed by the adsorbed atoms on account of their ionisation. The electrons released in the process diffuse into the crystal and occupy anion vacancies. The electrons trapped in anion vacancies are referred to as **F-centres.** 'F' stands for **Farben,** a German word, meaning colour. Greater is the number F-centres, more is the intensity of colour. For example, non-stoichiometric sodium chloride with excess sodium is yellow, non-stoichiometric; potassium chloride with excess of potassium is violet and non-stoichiometric; lithium chloride with excess of lithium is pink.

(b) Excess cations occupying interstitial positions : Metal excess defect may also be developed by the presence of extra cation in the interstitial site. Electrical neutrality is achieved by an electron presence in another interstitial site. This defect is similar to Frenkel defect. For example, when ZnO is heated, it loses oxygen and turns yellow.

$$ZnO \longrightarrow Zn^{2+} + (1/2)O_2 + 2e$$

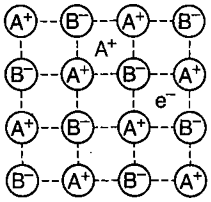


Fig. 4.57 Metal excess defect due to the presence of extra cation in the interstitial position

The Zn^{2+} ions thus formed occupy interstitial sites and the electrons occupy the neighbouring interstitial sites. The crystals having metal excess defects contain few free electrons and, thus, such solids act as semi-conductors.

2. Non-metal excess or metal deficiency defect : These contain lesser number of positive particles than negative particles. These defects arise due to cation vacancies or anions occupying interstitial sites. the extra negative charge is balanced by oxidation of some of the nearby metal ions. Thus, this defect occurs when metal shows variable valency, *i.e.*, especially in the case of transition metals. Examples are : FeO, FeS, NiO, etc. Crystals with metal deficient defects are semiconductors of *p*-type.

(C) Impurity defects in ionic crystalline solids

A defect in an ionic solid can be introduced by adding foreign ions. If the impurity ions have a different oxidation state than that of the host ions, vacancies are created. For example, if molten NaCl containing a little $SrCl_2$ or $CaCl_2$ as impurity is allowed to cool, some lattice sites will be occupied either by Ca^{2+} ions or Sr^{2+} ions in place of Na^+ ions. For every Ca^{2+} ion or Sr^{2+} ion, two Na^+ ions are removed in the crystal lattice in order to maintain electrical neutrality. Thus, one of these lattice sites is occupied by Ca^{2+} or Sr^{2+} ion and the other site remains vacant.

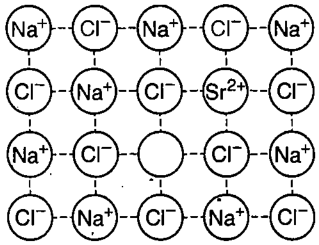


Fig. 4.58 Impurity defect

Cationic vacancies developed due to introduction of impurity cause higher electrical conductivity of ionic solids. Addition of about 0.1% $SrCl_2$ to NaCl increases the electrical conductivity by 10000 times. Solid solution of $CdCl_2$ and AgCl is another example of this type of impurity defect.

Electric Properties of Solids

On the basis of electrical conductivity, solids are divided into three categories:

(i) Metals (ii) Insulators (iii) Semiconductors

Metals have conductivity $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$ and insulators have $10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Metals: Metals have free electrons and fixed **kernels** at their lattice sites:

$$M \rightarrow \underset{\text{kernel}}{M^{n+}} + \underset{\text{free electrons}}{ne}$$

Free electrons make the metal good conductor of electricity and heat. Conductivity of metals is nearly independent of impurity of metals. Resistance ratio may be taken to check the impurity level of metals, *i.e.*, $\rho_{300K} / \rho_{4.2K}$. Conductivity of metals depends on number of valence electrons, *i.e.*, number of free electrons produced by the metal.

Nature of Metallic Bond

A metal is regarded as group of positively charged metal ions packed as closely as possible in a regular geometrical fashion and immersed in a sea or pool of mobile electrons. The attraction force that binds the metal ions and mobile electrons is called metallic bonding.

1. Conductivity: When potential difference is applied electrons (mobile) conduct electric current. It has been observed that the conductivity of most of the metals decreases with increase in temperature. At high temperature, positive metal ions start vibration and create resistance to the flow of electrons; thus resistance of metal increases.

Good thermal conductivity of metals can also be explained on the basis of mobile electrons.

2. Opaqueness and lustre: Mobile electrons absorb quantum energy of visible light and become excited; when excited electrons return to normal state, visible light is evolved. Since, the light is fully absorbed by metal hence it is opaque.

3. Elasticity: On applying mechanical stress, temporary deformation of the metal crystal takes place and the kernels with their electron cloud return to their original position as soon as mechanical stress is removed.

4. Microproperties of metals: Some other properties of metals are summarised ahead:

(a) Metals possess high tensile stress.

(b) Metals are usually hard and solid.

(c) Some metals like alkali and alkaline earth metals show photoelectric effect, *i.e.*, ejection of electron from metal surface when exposed to light of appropriate energy.

(d) Metals have low ionization energy.

(e) Strength of metallic bond depends on the following factors:

Strength increases with:

(i) increase in number of valence electrons,

(ii) increase in charge on the nucleus,

(iii) decrease in size of positive metal ion.

Valence band: Group of electrons containing valence electrons.

Conduction band: The free electrons for conduction constitute conduction band.

Band structure of metals may be given as shown in Fig. 4.59.

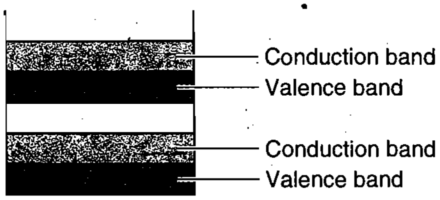


Fig. 4.59

There is no energy gap between valence and conduction band, *i.e.*, width of forbidden zone is zero. Thus, as soon as potential difference is applied electrons jump to conduction band from valence band and conduct electric current. All valence electrons are free to conduct electric current. **When temperature is raised conductance of metals decreases because at high temperature kernels vibrate and create obstruction in the flow of electron.**

Semiconductors: Conductivity of semiconductors is intermediate between metals and insulators. These are of two types:

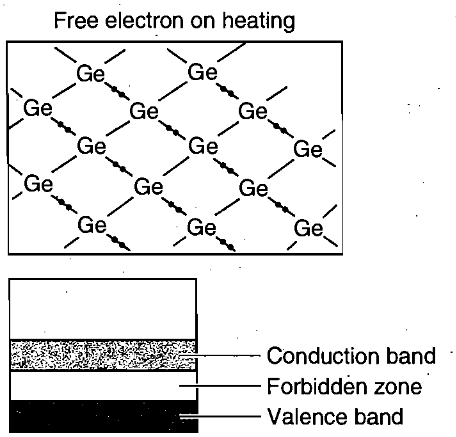


Fig. 4.60

(i) Intrinsic semiconductors: These are insulators at room temperature and become semiconductors when temperature is raised.

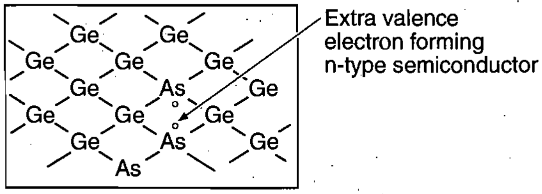
On heating, some covalent bonds are broken to give free electrons. These free electrons make it semiconductor.

Width of forbidden zone in semiconductors is very low; thus on heating, electrons are easily tossed to conduction band from valence band and conduct electric current.

(ii) Extrinsic semiconductors or Impurity semiconductors: These are formed by dopping impurity of lower or higher group.

n-type Semiconductor

Dopping of higher group impurity forms *n*-type semiconductor, *e.g.*, when 'As' is dopped to 'Ge', an extra valence electron of arsenic makes the mixture *n*-type semiconductor. Current carriers are negatively charged, hence called *n*-type.



n-type Semiconductors

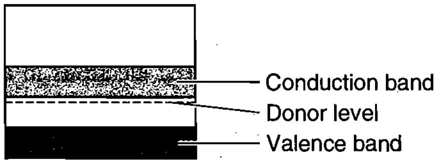


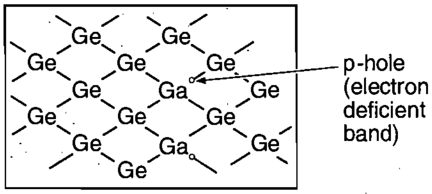
Fig. 4.61 *n*-type Semiconductor

Impurity dopping creates donor level just below the conduction band.

On applying potential difference, electrons jump from donor level to the conduction band and conduct electric current.

p-type Semiconductor

Impurity of lower group creates acceptor level just above the valence band. When electrons jump from valence band to acceptor level, a *p*-hole (positively charged hole) is created in valence band. On applying potential difference, these *p*-holes conduct electric current.



p-type Semiconductors

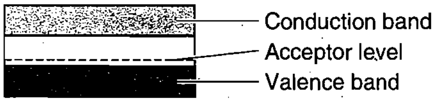


Fig. 4.62 *p*-type Semiconductor

Insulators: Such substances do not conduct electric current; their conductivity is very low. Width of forbidden zone between valence and conduction band is very big; hence electrons are not tossed from valence band to conduction band. On heating they decompose but do not give free conducting electrons.

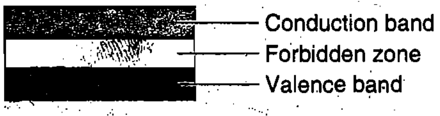


Fig. 4.63

Examples: Classification of transition metal oxides

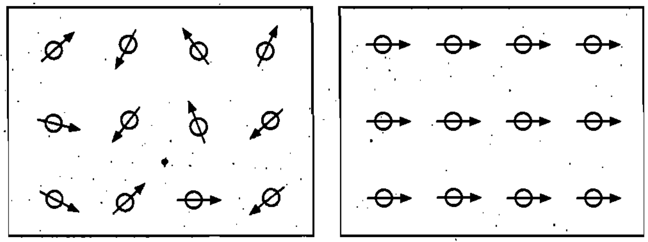
Metallic	Semiconductors	Insulators
VO	FeO, V_2O_5	MnO
TiO	Fe_2O_3, Mn_2O_3 Co_3O_4, Mn_3O_4	
CrO_2	CuO Cu_2O	

TiO and NbO become superconductors at low temperature, about 2 K.

4.25 MAGNETIC PROPERTIES

(i) Paramagnetic Solids

The presence of one or more unpaired electrons in an atom, molecule or ion gives rise to paramagnetism. Such materials are weakly attracted in the field. When they are placed in a magnetic field they become parallel to the field. Domain significance of unpaired electrons are given below:



(In absence of magnetic field) (In presence of magnetic field)

Fig. 4.64

Resultant magnetic field for n-unpaired electrons may be calculated as:

$$\mu_M = \sqrt{n(n+2)}$$

The magnetic field produced by unpaired electrons is due to—
(a) their spin and (b) their orbital motion.

Magnetic moment is measured in Bohr Magneton (BM)

$$\text{BM} = \frac{eh}{4\pi mc};$$

μ_S = 1.73 BM (one unpaired electron)
μ_S = 2.83 BM (two unpaired electrons)
μ_S = 3.87 BM (three unpaired electrons)
μ_S = 4.90 BM (four unpaired electrons)

5.92, 6.93, 7.94 values for five, six and seven unpaired electrons respectively.

(ii) Diamagnetic Solids

The solids, which are weakly repelled by external magnetic field, are called diamagnetic solids and the property thus exhibited is called diamagnetism.

In diamagnetic solids, all electrons have paired spins, *i.e.*, only fully filled orbitals are present. Examples are : NaCl, TiO_2, ZrO_2, KCl etc. Some diamagnetic solids like TiO_2 show para magnetism due to presence of slight non-stoichiometry.

(iii) Ferromagnetic Solids

The solids which are strongly attracted by external magnetic field and do not lose their magnetism when the external field is removed, are called ferromagnetic solids. The property thus, exhibited is termed ferromagnetism.

Ferromagnetic substances can be permanently magnetised. Only three elements, iron (Fe), cobalt (Co) and nickel (Ni) show ferromagnetism at room temperature. Some other examples are : EuO, CrO_2, etc. CrO_2 is the oxide used to make magnetic tapes for use in cassette recorders.

Ferromagnetism arises due to spontaneous alignment of magnetic moments due to unpaired electrons in the same direction as shown below (Fig. 4.65).

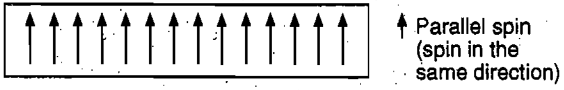


Fig. 4.65 Ferromagnetism

Mechanism of magnetisation of ferromagnetic substances: Unpaired electron in one atom interacts strongly with unpaired electron of neighbourhood atom, thus they align themselves spontaneously in a common direction in a small volume of solid called domains. Magnetic moments of all atoms in a domain are parallel to each other hence the domain possesses a net magnetic dipole moment. In absence of external magnetic field, the direction of magnetic moments in different domains are randomly oriented in different direction. When external magnetic field is applied then the domains in which the magnetic moments are parallel to external field, expand at the expense of remaining domains and ultimately all the magnetic moments align themselves in the direction of external magnetic field.

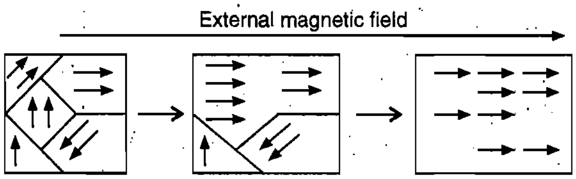


Fig. 4.66 Magnetisation of ferromagnetic substance

(iv) Antiferromagnetic Solids

The solids which are expected to show paramagnetism or ferromagnetism on the basis of unpaired electrons but actually *have zero net magnetic moment are called antiferromagnetic solids.*

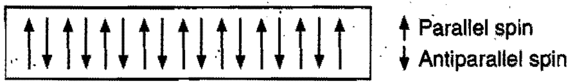


Fig. 4.67 Antiferromagnetism

Magnetic moments are aligned in a compensatory way so as to give zero net magnetic moment. Antiferromagnetism is due to the presence of equal number of magnetic moments in opposite directions as shown above (Fig. 4.67). The important examples are : MnO, MnO_2, Mn_2O_3, NiO, CoO, etc.

(v) Ferrimagnetic Solids

The solids which are expected to show large magnetism due to the presence of unpaired electrons but in fact have small net magnetic moment are called ferrimagnetic solids.

Ferrimagnetism arises due to alignment of magnetic moments in parallel and antiparallel directions in unequal numbers resulting in some net magnetic moment. This alignment has been shown ahead (Fig. 4.68).

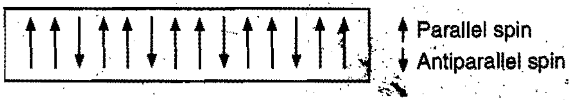


Fig. 4.68 Ferrimagnetism

Examples are : Fe_3O_4 and ferrites of the formula $M^{2+}Fe_2O_4$ where M = Zn, Cu, Mg, etc.

Influence of temperature on magnetic character of solids : All magnetically ordered solids (ferromagnetic, antiferromagnetic and ferrimagnetic) change into paramagnetic state on increasing temperature. This is due to randomisation of their spins. The following examples explain this point :

(i) Ferrimagnetic solid, Fe_3O_4, becomes paramagnetic when heated to 850 K.

(ii) Antiferromagnetic solid, V_2O_3, becomes paramagnetic when heated to 750 K.

It should be noted that each ferromagnetic solid has a characteristic temperature above which it becomes paramagnetic. The characteristic temperature is called **Curie point** for **Curie temperature.**

Table 4.1 Magnetic Properties of Solid at a Glance

Properties	Information	Magnetic alignment	Example	Application
1. Diamagnetic	Repelled weakly in magnetic field. Such solids have only paired electrons.	⇅ ⇅ ⇅ ⇅ ⇅	Benzene, NaCl, TiO_2, V_2O_5, etc.	Insulators
2. Paramagnetic	Have unpaired electrons; weakly attracted in magnetic field. They cannot be permanently magnetised.	↖↙→↑↘↗	O_2, VO, CuO, TiO	Electronic devices
3. Ferromagnetic	Also, have unpaired electrons. Strongly attracted in magnetic field. Such solids can be permanently magnetised. On heating to a temperature called **Curie Point,** these solids change to paramagnetic solid.	↑↑↑↑↑↑↑	Fe, Ni, Co, CrO_2	CrO_2 is used in audio, video tapes.
4. Antiferromagnetic	In these solids, unpaired electrons align themselves in such a way that resultant magnetic moment is zero.	↑↓↑↓↑↓↑↓	Cr_2O_3, CoO, Co_3O_4, Fe_2O_3, MnO, MnO_2	Used in the instruments of magnetic susceptibility measurement
5. Ferrimagnetic	Unpaired electrons align themselves in such a way that there is a net magnetic moment.	↑↓↓↑↓↓↑↓↓ OR ↑↑↓↓↓↑↑↓↓↓↑↑ and so on	Fe_3O_4, ferrites	—

Table 4.2 Dielectric Properties of Solid at a Glance

Properties	Information	Dipolar property	Example	Application
1. Piezoelectricity	When a crystal of dielectrics is subjected to mechanical stress, then small magnitude current is produced. It is called direct Piezoelectric effect.	Development of charge in some part of crystal.	Quartz and Rochelle salt	Used in mechanical electric transducer, *e.g.*, in record player, transmission of direct signals, sounding of sea depths.
2. Anti piezoelectricity	In some solids, electric field develops mechanical effect.	Crystal suffers elastic deformation in an electric field	—	
3. Ferroelectricity	Piezoelectric crystals having permanent dipoles are said to possess ferroelectricity.	↑↑↑↑↑↑	Ba TiO_3, KH_2PO_4 Rochelle salt	Electromagnetic appliances.
4. Anti ferroelectricity	Piezoelectric crystals with zero dipole are said to possess anti ferroelectricity.	↑↓ ↑↓ ↑↓	$PbZrO_3$ Lead zirconate	
5. Pyroelectricity	Some polar crystals produce electric impulse on heating.	—	Crystals of tartaric acid	Used in fire alarms, and thermostat

Superconductors

Copper and most other metals are good conductors of electricity. But even the best conductors present some resistance to the flow of electricity and a part of electrical energy is converted into heat energy. Thus, generators, turbines, motors of all kinds, transmission lines and other electrical equipment always operate at less than 100% efficiency.

A superconductor is a material that loses all electrical resistance below a characteristic temperature called the superconducting transition temperature, i.e., a superconductor presents no resistance to the flow of electricity.

Electrons move freely through a superconductor without any resistance or friction.

This phenomenon was discovered, in 1911, by the Dutch scientist **Heike Kamerlingh Onnes,** who found that mercury abruptly loses its electrical resistance when it is cooled with liquid helium to 4.2 K. Below its critical temperature (T_c), a superconductor becomes a perfect conductor and an electric current, once started, flows indefinitely without loss of energy. Most metals become superconductors at very low temperatures (generally around 2–5 K), but this temperature is far too cold for any commercial applications.

Since, 1911, scientists have been searching for materials that superconduct or at higher temperatures and more than 6000 superconductors are now known. Niobium alloys are particularly good superconductors and in 1973, a niobium alloy, Nb_3Ge, was found to show superconductivity at 23.2K. The situation changed dramatically in 1986 when **Müller** and **Bednorz** reported a T_c of 35K for the non-stoichiometric barium lanthanum copper oxide, $Ba_xLa_{2-x}CuO_4$, where x has a value of about 0.1. Soon thereafter even higher values of T_c for other copper containing oxides : 90 K for $YBa_2Cu_3O_7$, 125K for $Tl_2Ca_2Ba_2Cu_3O_{10}$ and 133 K for $HgCa_2Ba_2Cu_3O_{8+x}$. [$YBa_2Cu_3O_7$ is also called 1-2-3 compound, *i.e.*, 1 yttrium, 2 bariums and 3 coppers].

Room temperature 'T_c' superconductors are yet to be discovered. The great advantage of these materials that offer no electrical resistance is the elimination of heating effects as electricity passes through. The energy saving and efficiencies that would be realised are substantial. Superconducting coils of wire could store electricity (in principle) forever, since no energy is lost. Thus, the energy can be tapped as needed. One of the most dramatic properties of a superconductor is its ability to levitate a magnet. When a superconductor is cooled below its T_c and a magnet is lowered towards it, the superconductor and magnet repel each other and the magnet hovers above the superconductor as though suspended in midair. The potential application of this effect will be in the high speed magnetically levitated trains. Some applications of superconductors already exist. For example, powerful superconducting magnets are essential components in the magnetic resonance imaging (MRI) instruments used in medical diagnosis. Superconductors are also used to make the magnets that bend the path of the charged particles in high energy particle accelerators. All the present applications, however, use conventional superconductors ($T_c \leq 20$ K). Of course, the search goes on for materials with higher values of T_c. For applications such as long distance electric power transmission, the goal is a material that superconducts at room temperature.

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *There is a collection of crystalline substances in a hexagonal closed packing. If the density of matter is $2.6\,g/cm^3$, what would be the average density of matter in collection? What fraction of space is actually unoccupied ?*

Solution: In hexagonal closed packing, the packing efficiency is 74.05%.

$\therefore$ Density of matter = Packing fraction × Total density

$$= \frac{74.05}{100} \times 2.6 = 1.93\,g\,cm^{-3}$$

$$\%\text{ empty space} = 100 - 74.05 = 25.95\%$$

Example 2. *The unit cell length of NaCl is observed to be 0.5627 nm by X-ray diffraction studies; the measured density of NaCl is 2.164 gcm^{-3}. Correlate the difference of observed and calculated density and calculate % of missing Na^+ and Cl^- ions.*

Solution: We know that,

$$Z = \frac{a^3 \times d \times N}{M}$$

where, Z = number of constituent units per unit cell
= 4 in fcc
a = edge length = 0.5627×10^{-7} cm
d = density
N = Avogadro's number
M = molar mass

$$\frac{(0.5627 \times 10^{-7})^3 \times d \times 6.023 \times 10^{23}}{58.5} = 4$$

$$d = 2.1805\,g/cm^3$$

Observed density = $2.164\,g/cm^3$ which is less than calculated density because some places are missing.

Actual constituent units per unit cell can be calculated as:

$$Z = \frac{(0.5627 \times 10^{-7})^3 \times 2.164 \times 6.023 \times 10^{23}}{58.5} = 3.969$$

$$\text{Missing units} = 4 - 3.969 = 0.031$$

$$\%\text{ missing} = \frac{0.031}{4} \times 100 = 0.775\%$$

Example 3. *In a cubic lattice, the closed packed structure of mixed oxides of the lattice is made up of oxide ions ; one eighth of the tetrahedral voids are occupied by divalent ions (A^{2+}) while one half of the octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxides ?*

Solution: Let there be 80 O^{2-} in the crystal.

$\therefore$ Octahedral voids = 80

Tetrahedral voids = 160

$$A^{2+}\text{ ions} = \frac{1}{8} \times 160 = 20$$

$$B^{3+}\text{ ions} = \frac{1}{2} \times 80 = 40$$

$$A^{2+} : B^{3+} : O^{2-} = 20 : 40 : 80$$

$$= 1 : 2 : 4$$

$\therefore$ Formula is AB_2O_4.

Example 4. *At 1425°C, Fe crystallises in a body-centred cubic lattice whose edge length is 2.93 Å. Assuming the atoms to be packed spheres, calculate :*

(*a*) *the radius of the spheres,*
(*b*) *the distance between centres of neighbouring spheres,*
(*c*) *the number of atoms of Fe per unit lattice and*
(*d*) *the total volume occupied by an atom of Fe.*

Solution: (a) $a\sqrt{3} = 4r$ where, a = edge length

$$r = \frac{a\sqrt{3}}{4} = \frac{2.93 \times \sqrt{3}}{4} = 1.268\text{ Å}$$

(b) Distance between the centres of neighbouring spheres

$$= 2r = 2 \times 1.268 = 2.537\text{ Å}$$

(c) No. of atoms per unit cell = $8 \times \frac{1}{8} + 1 = 2$.

(d) Volume occupied by an atom of iron = $\frac{4}{3}\pi r^3$.

Example 5. *In face-centred cubic (fcc) crystal lattice, edge length of the unit cell is 400 pm. Find the diameter of the greatest sphere which can be fitted into the interstitial void without distortion of lattice.* (IIT 2005)

Solution: In fcc unit cell, we can use

$$a\sqrt{2} = 4r$$

$$r = \frac{a\sqrt{2}}{4} = \frac{400 \times \sqrt{2}}{4} = 141.4\text{ pm}$$

For octahedral void,

$$2(r + R) = a$$

$$2R = a - 2r$$

$$2R = a - 2r = 400 - 2 \times 141.4 = 117.16\text{ pm}$$

Diameter of greatest sphere = 117.16 pm.

Example 6. *The distance between planes of ions parallel to the face of the unit cell of sodium chloride is 282 pm. The smallest angle of reflection observed in the X-ray diffraction pattern is 5.97°. Calculate the wavelength of the incident radiation.*

Solution: Using Bragg's equation,

$$n\lambda = 2d\sin\theta$$

$$1 \times \lambda = 2 \times 282 \times 10^{-12}\sin 5.97$$

$$\lambda = 5.86 \times 10^{-11}\text{ m} = 58.6\text{ pm}$$

Example 7. *CsCl has cubic structure of ions in which Cs^+ ion is present in the body-centre of the cube. If density is 3.99 g cm^{-3}:*

(*a*) *Calculate the length of the edge of a unit cell.*

(*b*) *What is the distance between* Cs^+ *and* Cl^- *ions?*

(*c*) *What is the radius of* Cs^+ *ion if the radius of* Cl^- *ion is* 180 *pm?*

Solution: We know that,

(a) $$Z=\frac{a^3\times\rho\times N}{M}$$

$$Z=1,\ 1Cs^+ + 1Cl^- = 1CsCl$$

$$M=168.5$$

$$1=\frac{a^3\times 3.99\times 6.023\times10^{23}}{168.5}$$

$$a=4.123\times10^{-8}\ \text{cm}=412\ \text{pm}$$

(b) Distance between Cs^+ and Cl^- ions

$$=\frac{a\sqrt{3}}{2}=\frac{412\times\sqrt{3}}{2}=356.8\ \text{pm}$$

(c) $$r_{Cs^+}+r_{Cl^-}=356.8$$

$$r_{Cs^+}+180=356.8$$

$$r_{Cs^+}=176.8\ \text{pm}$$

Example 8. *If NaCl is doped with* 10^{-3} *mol per cent of* $SrCl_2$, *what is the concentration of cation vacancy?*

Solution:

Na^+	Cl^-	Na^+	Cl^-
Cl^-		Cl^-	Na^+
Sr^{2+}	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+

Number of cationic vacancies per mol

$$=\frac{10^{-3}\times6.023\times10^{23}}{100}=6.023\times10^{18}\ \text{vacancies per mol}$$

Example 9. *A metal crystallises into two cubic phases, face-centred cubic (fcc) and body-centred cubic (bcc) whose unit lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of fcc and bcc.* **(IIT 1999)**

Solution: Density of fcc $=\dfrac{Z_1\times\text{At. mass}}{\text{Av. no.}\times V_1}$

and density in bcc $=\dfrac{Z_2\times\text{At. mass}}{\text{Av. no.}\times V_2}$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}}=\frac{Z_1}{Z_2}\times\frac{V_2}{V_1}$$

For fcc $Z_1=4;\ V_1=a^3=(3.5\times10^{-8})^3$

For bcc $Z_2=2;\ V_2=a^3=(3.0\times10^{-8})^3$

$$\frac{d_{\text{fcc}}}{d_{\text{bcc}}}=\frac{4\times(3.0\times10^{-8})^3}{2\times(3.5\times10^{-8})^3}=1.259$$

Example 10. *A solid AB has the NaCl structure. If radius of the cation* A^+ *is 120 pm, calculate the maximum value of the radius of the anion* B^-.

Solution: Since, NaCl has octahedral structure,

$$\text{The limiting ratio }\frac{r_A^+}{r_B^-}=0.414$$

or $$r_B^-=\frac{r_A^+}{0.414}=\frac{120}{0.414}=290\ \text{pm}$$

Example 11. *You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bond by four lines each of length 40 mm. What will be the arrangement of marbles in a plane, so that, maximum number of marbles can be placed inside the area. Sketch the diagram and derive expression for the number of marbles per unit area.* **(IIT 2003)**

Solution: In order to accomodate maximum number of spheres, there should be hcp (hexagonal closed packing).

Area of square having spherical marbles $=16\,\text{cm}^2$

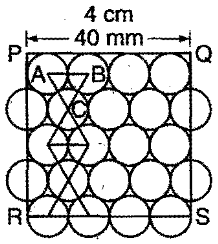
Maximum number of spheres = 14 (full) + 8 (half)

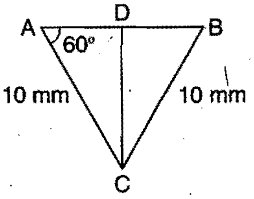
Number of spheres = 18

Per unit area (per cm^2) $=\dfrac{18}{16}=1.125$

Length PQ of square = 4 cm

Length $PR=5+4\times5\sqrt{3}=40\ \text{mm}=4\ \text{cm}$





$$CD=10\sin60^\circ=\frac{10\sqrt{3}}{2}=5\sqrt{3}$$

Example 12. *Calculate the density of diamond from the fact that it has face-centred cubic structure with two atoms per lattice point and a unit cell of edge length 3.569 Å.*

Solution: $Z=8, M=12$

$$Z=\frac{l^3\times\rho\times N}{M}$$

$$\text{Density }\rho=\frac{ZM}{l^3N}=\frac{8\times12}{(3.569\times10^{-8})^3\times6.023\times10^{23}}$$

$$=3.506\ \text{g cm}^{-3}$$

Example 13. *An element crystallises into a structure which may be described by a cubic unit cell having one atom at each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is 24×10^{-24} cm^3 and density of element is $7.2\,g/cm^3$. Calculate the number of atoms present in 200 g of the element.*

Solution: Number of atoms in a unit cell $(Z) = 1 + 2 = 3$

$$Z = \frac{l^3 \times \rho \times N}{M}$$

$$M = \frac{l^3 \times \rho \times N}{Z}$$

$$= \frac{24 \times 10^{-24} \times 7.2 \times 6.023 \times 10^{23}}{3} = 34.69$$

$$\text{Number of atoms} = \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23}$$

$$= \frac{200}{34.69} \times 6.023 \times 10^{23} = 3.47 \times 10^{24}$$

Example 14. *Analysis shows that nickel oxide has formula $Ni_{0.98}O_1$. What fraction of nickel exist as Ni^{2+} and Ni^{3+} ions?*

Solution: Let number of Ni^{3+} ions $= x$

$\therefore$ Number of Ni^{2+} ions $= (0.98 - x)$

Since, molecule is neutral, its total charge is zero.

$$(+3 \times x) + (0.98 - x) \times 2 - 2 = 0$$

$x = 0.04$, *i.e.*, $Ni^{3+} = 0.04$; $Ni^{2+} = 0.94$

Example 15. *Calcium crystallises in face-centred cubic unit cell with $a = 0.556\,nm$. Calculate density if*

(i) it contained 0.1% Frenkel defect.

(ii) it contained 0.1% Schottky defect.

Solution: (i) Frenkel defect does not alters the density of solid.

$$d = \frac{MZ}{l^3 N} = \frac{40 \times 4}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5455\,g/cm^3$$

(ii) Schottky defect lowers the density of solid

$$Z = 4 - \frac{4 \times 0.1}{100} = 3.996$$

$$d = \frac{40 \times 3.996}{(0.556 \times 10^{-7})^3 \times 6.023 \times 10^{23}}$$

$$= 1.5440\,g/cm^3$$

Example 16. *Density of lithium atom is $0.53\,g/cm^3$. The edge length of Li is $3.5\,\mathring{A}$. Find out the number of lithium atoms in a unit cell. Atomic mass of lithium is 6.94.*

[CBSE-PMT (Mains) 2005]

Solution: $$Z = \frac{a^3 \times \rho \times N_A}{M}$$

$$= \frac{(3.5 \times 10^{-8})^3 \times 0.53 \times 6.023 \times 10^{23}}{6.94}$$

$$= 2$$

Example 17. *Cu metal crystallises in face centred cubic lattice with cell edge, $a = 361.6$ pm. What is the density of Cu crystal? (Atomic mass of copper = 63.5 amu, $N_A = 6.023 \times 10^{23}$)*

[CBSE-PMT (Mains) 2008]

Solution: We know

$$Z = \frac{a^3 \times d \times N_A}{M}$$

$$\therefore \quad d = \frac{ZM}{a^3 N_A} \qquad \text{...(i)}$$

$Z = 4$ for fcc unit cell; $M = 63.5\text{ g mol}^{-1}$

$a = 361.6 \times 10^{-10}$ cm; $N_A = 6.023 \times 10^{23}$

Putting these values in (i), we get

$$d = \frac{4 \times 63.5}{(361.6 \times 10^{-10})^3 \times 6.023 \times 10^{23}} = 8.94\text{ g cm}^{-3}$$

Example 18. *An LPG cylinder weighs 14.8 kg when empty. When full, it weighs 29 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the weight of the full cylinder reduced to 23.2 kg. Find out the volume of n-butane in cubic metres used up at 27°C and 1 atm.*

[*Molecular mass of n butane* = 58] [CBSE-PMT (Mains) 2008]

Solution : Mass of n-butane used $= 29 - 23.2 = 5.8$ kg

$$\text{Number of moles of butane used} = \frac{5800}{58} = 100$$

$$V = \frac{nRT}{P} = \frac{100 \times 0.0821 \times 300}{1}$$

$$= 2463 \text{ litre}$$

$$= 2.463\text{ m}^3$$

Example 19. *r_{Na^+} and r_{Cl^-} represents radius of Na^+ and Cl^- ions respectively. If 'n' is the number of NaCl units per unit cell then give the equation you will use to obtain molar volume.*

[CBSE-PMT (Mains) 2009]

Solution: Edge length of unit cell 'a' $= 2(r_{Na^+} + r_{Cl^-})$

Volume of unit cell $= a^3 = 8(r_{Na^+} + r_{Cl^-})^3$

Volume occupied by one mole of NaCl

$$= \frac{8(r_{Na^+} + r_{Cl^-})^3}{n} \times N_A$$

where $N_A = 6.023 \times 10^{23}$

Example 20. *Two gases A and B of mass 70.6 g and 167.5 g (M_w of A = 32 and M_w of B = 20) are mixed. Then total pressure of mixture is 25 bar. Calculate partial pressure of A and B.*

[CBSE-PMT (Mains) 2009]

Solution: Number of moles A, $n_A = \frac{70.6}{32} = 2.2$

Number of moles of B, $n_B = \frac{167.5}{20} = 8.375$

Partial pressure of gas A, $p_A = \frac{n_A}{n_A + n_B} \times p$

$$= \frac{2.2}{2.2 + 8.375} \times 25 = 5.20 \text{ bar}$$

$$p_B = 25 - 5.20 = 19.8 \text{ bar}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Matter: Matter is anything which has mass and occupies space. Matter exists in three states, *viz.*, solid, liquid and gas. Any substance can exist in either of the three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

2. Gaseous state: It is the simplest state and shows greatest uniformity in behaviour. The gases show almost the same behaviour irrespective of chemical nature, colour or odour. The molecules in a gas possess random motion in all directions. A gas has neither a definite shape nor a definite volume. Gases are characterised by low density, high degree of compressibility and expandability. Gases exert uniform pressure on the walls of the container. They diffuse rapidly and intermix to form homogeneous mixtures. All gases obey certain laws called gas laws.

3. Gas laws: Gas laws are based on experiments.

(i) Boyle's law: It states that the volume of the given amount of a gas is inversely proportional to its pressure at a constant temperature.

$$V \propto \frac{1}{P} \text{ or } PV = \text{constant} \text{ or } P_1V_1 = P_2V_2 = P_3V_3 = \ldots$$

or $$\frac{P_1}{d_1} = \frac{P_2}{d_2} \quad \text{(at constant temperature)}$$

where, d_1 and d_2 are the densities of a gas at pressures P_1 and P_2. The curves between P and V at constant temperature are hyperbolas and called isotherms.

(ii) Charles' law: At constant pressure, the volume of a given amount of a gas is directly proportional to its absolute temperature.

$$V \propto T \text{ or } \frac{V}{T} = \text{constant} \text{ or } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \ldots$$

Absolute temperature scale or Kelvin scale starts with −273°C as zero.

Absolute temperature (in K) = $273 + t\,°\text{C}$

The absolute zero is that temperature where no gas can exist. The plots of volume against temperature (at constant pressure) are termed as isobars.

(iii) Pressure law or Gay-Lussac law: At constant volume, the pressure of a given amount of a gas varies directly as its absolute temperature.

$$P \propto T \text{ or } \frac{P}{T} = \text{constant} \text{ or } \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \ldots$$

(iv) Gas equation: $\frac{PV}{T} = \text{constant}$

For one mole of an ideal gas, $PV = RT$

For n moles of an ideal gas, $PV = nRT$

For w g of the gas (mol. mass M),

$$PV = \frac{w}{M} RT$$

or $$P = \frac{w}{V} \frac{RT}{M} = d \times \frac{RT}{M} \quad (d = \text{density})$$

R is a universal gas constant. It is expressed in the units of work per degree kelvin per mol. Value of R in different units is

$$R = 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$
$$= 82.1 \text{ mL-atm K}^{-1} \text{ mol}^{-1}$$
$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$
$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$= 1.987 \approx 2 \text{ cal K}^{-1} \text{ mol}^{-1}$$

(v) Avogadro's law: Equal volumes of all gases contain equal number of molecules under similar conditions of temperature and pressure. Volume occupied by one mole of any gas at NTP (0°C and 1 atm) is termed **molar volume.** It is 22.4 litre or 22400 mL.

[**Note :** At 25° C and 1 bar, one mole of a gas has a volume of 25 litre.]

(vi) Dalton's law of partial pressures: The total pressure exerted by a mixture of gases which do not react chemically is equal to the sum of their individual pressures (partial pressures) under similar conditions of temperature.

$$P = P_1 + P_2 + P_3 + \ldots$$

Partial pressure of a gas = Molar fraction × Total pressure of the gas

(vii) Graham's law of diffusion: The property of gases to mix with each other to form homogeneous mixture irrespective of gravity is called diffusion. Effusion is a special case of diffusion in which gas passes through a small aperture.

Under similar conditions of temperature and pressure, the relative rates of diffusion of gases are inversely proportional to the square root of their densities or vapour densities or molecular masses. This is Graham's law of diffusion.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{\text{VD}_2}{\text{VD}_1}} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

4. Kinetic theory of gases: The theory with the help of which behaviour of gases can be interpreted mathematically is termed kinetic theory of gases. The main postulates of the theory are:

(a) All gases consist of very large number of small spherical elastic particles called molecules. These are in constant rapid motion in all directions.

(b) There is a lot of empty space between the molecules. The actual volume of gas molecules is negligible in comparison to total volume of the gas.

(c) The pressure exerted by the gas molecules is due to its recorded by molecules against the walls of containing vessel. The collisions between gas molecules are perfectly elastic, *i.e.*, there is no loss of energy during collisions.

(d) There is no effective force of attraction or repulsion between gas molecules. There is no effect of gravity on the motion of gas molecules.

(e) The average kinetic energy of gas molecules is directly proportional to the absolute temperature of the gas.

On the basis of above postulates, the following equation, known as kinetic gas equation, has been derived.

$$PV = \frac{1}{3} mnc^2$$

where, P = pressure; V = volume; m = mass of gas molecules; n = number of gas molecules and c = root mean square speed of the gas molecules.

Also $\quad PV = RT = \frac{1}{3} mnc^2 = \frac{2}{3}\cdot\frac{1}{2} mnc^2 = \frac{2}{3}\text{KE}$

or $\quad \text{KE} = \frac{3}{2}RT = \frac{3}{2}PV$

$$\text{KE of single molecule} = \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$$

where, k = Boltzmann constant.

5. Molecular speeds: There are three kinds of speed.

(a) Root mean square speed: It is the square root of the mean of the squares of the speeds of all the molecules present in a gas.

$$\text{rms} = c = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots + c_n^2}{n}}$$

$$= \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

(b) Average speed: It is the arithmetic mean of speeds of the molecules present in the gas.

$$\text{Average speed} = \frac{c_1 + c_2 + c_3 + \ldots + c_n}{n} = \sqrt{\frac{8RT}{\pi M}}$$

$$= 0.9213 \times \text{rms}$$

(c) Most probable speed: It is the speed possessed by majority of the gas molecules. It is equal to

$$\sqrt{\frac{2RT}{M}} \quad \text{or } (0.8164 \times \text{rms})$$

Most probable speed : Average speed : rms speed

:: 1 : 1.128 : 1.224

6. van der Waals' equation: It is an improved form of ideal gas equation. It has been derived after applying two corrections due to two wrong assumptions in kinetic theory of gases. Two corrections are:

(i) volume correction, $V_i = (V - b)$ and

(ii) pressure correction, $P_i = P_{\text{obs}} + \frac{a}{V^2}$.

The equation is $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ for one mole

and $\quad \left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$ for 'n' moles,

a and b are constants. Units of a are atm lit^2 mol^{-2} or Pa m^6 mol^{-2} and units of b are litre or dm^3 or m^3. This equation is applicable to real gases.

Real gases: These do not obey various gas laws strictly under all conditions of temperature and pressure. Deviations are large under high pressure and low temperature.

Ideal gases: These obey laws strictly under all conditions. Actually no gas is ideal.

(a) At very low pressure or at very high temperature, V is large, so $\frac{a}{V^2}$ and b can be neglected. The equation becomes $PV = RT$, *i.e.*, the gas behaves like ideal gas.

(b) At moderate pressure, V is not so large and $\frac{a}{V^2}$ cannot be neglected. However, b can be neglected, so that we have

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV = RT - \frac{a}{V}$$

(c) At high pressure, V is so small that b cannot be neglected but a/V^2 can be neglected. Hence, the equation becomes

$$P(V - b) = RT$$

$$PV = RT + Pb$$

(d) In case of H_2 and He, the intermolecular forces of attraction are negligible, *i.e.*, a is very small, so that $\frac{a}{V^2}$ can be neglected. The equation becomes

$$P(V - b) = RT$$

$$PV = RT + Pb$$

7. **Compressibility factor:** The extent of deviation of a real gas from ideal behaviour is expressed in terms of compressibility factor, Z.

$$Z = \frac{PV}{nRT}; \; Z \text{ is unitless quantity.}$$

(i) For ideal gas $Z = 1$.

(ii) For real gas $Z \neq 1$.

When $Z < 1$, there is negative deviation from ideal behaviour and the gas is more compressible than ideal gas.

When $Z > 1$, there is positive deviation from ideal behaviour and the gas is less compressible than ideal gas.

8. **Critical phenomenon:** (i) **Critical temperature** is that temperature above which the gas cannot be liquefied with the help of pressure (ii) **Critical pressure** is the minimum pressure required to liquefy the gas at critical temperature (iii) **Critical volume** is the volume occupied by one mole of the gas at its critical temperature and critical pressure.

$$V_c = 3b; \; P_c = \frac{a}{27b^2}; \; T_c = \frac{8a}{27bR}$$

Boyle's temperature: It is the temperature above which the gas behaves like an ideal gas. In terms of van der Waals' constants,

$$\text{Boyle's temperature } (T_B) = \frac{a}{Rb}$$

$$T_B > T_c$$

Inversion temperature: It is the temperature to which the gas should be cooled so that expansion is accompanied by further cooling.

9. **Molar heat capacity:** It is the quantity of heat required to raise the temperature of one mole of a substance through 1°C.

Molar heat capacity = Specific heat capacity × Molar mass

(i) **Molar heat capacity at constant pressure (C_P):** It is the quantity of heat required to raise the temperature of 1 mole of gas through 1°C under constant pressure. It is equal to $\frac{5}{2}R$.

(ii) **Molar heat capacity at constant volume (C_V):** It is the quantity of heat required to raise the temperature of 1 mole of gas through 1°C under constant volume. It is equal to $\frac{3}{2}R$.

$$C_P - C_V = R$$

For monoatomic gases, $\frac{C_P}{C_V} = \gamma = 1.66$

For diatomic gases, $\frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

and for triatomic gases, $\frac{C_P}{C_V} = \frac{8R}{6R} = \frac{4}{3} = 1.33$

$$(C_P)_{\text{mixture}} = \frac{n_1 \times (C_P)_1 + n_2 (C_P)_2}{n_1 + n_2}$$

10. (i) Volume coefficient, $\alpha_V = \frac{V_t - V_0}{V_0 \times t}$

$$\alpha_V = \frac{1}{273} \quad \text{(for all gases)}$$

At constant pressure, increase in volume of a gas per degree rise of temperature per cc of gas at 0°C is called coefficient of volume expansion. Similarly, the pressure coefficient α_P is defined as,

$$\alpha_P = \frac{P_t - P_0}{P_0 \times t} = \frac{1}{273} \quad \text{(for all gases)}$$

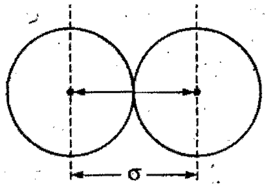
(ii) CO, N_2, C_2H_4 and B_2H_6 have same molar mass (28) and show same rate of diffusion under identical conditions.

(iii) **Atmolysis** is the process to separate two gases on the basis of difference in their densities and rate of diffusion.

(iv) Average molecular mass of air is 29. If a gas has molecular mass less than air, it is lighter than air and if it has molecular mass greater than air, it is heavier than air, *e.g.*, Cl_2 (71), CO_2 (44) and SO_2 (64) are heavier than air, while H_2 (2), He (4), NH_3 (17) and H_2O (18) are lighter than air.

11. **Transport phenomena of gases:**

(i) Collision diameter (σ) = Distance of closest approach when two molecules are under collision.



(ii) **Collision number:** It is the number of collisions of a molecule with other molecules in one second.

$$N_c = \frac{\sqrt{2}\pi v_{\text{av}} \sigma^2 N}{V}$$

where, v_{av} = Average velocity of molecules

N = Number of molecules

V = Volume of molecules

(iii) **Collision frequency (Z):** It is the number of molecula collisions taking place per second per unit volume of the gas.

$$Z = \frac{1}{\sqrt{2}} \pi v_{\text{av}} \sigma^2 \left(\frac{N}{V}\right)^2$$

(iv) **Mean free path λ:** It is the average distance travelled between two successive collisions.

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \left(\frac{N}{V}\right)}$$

$\lambda \propto T$ (at constant pressure)

$\lambda \propto \frac{1}{P}$ (at constant temperature)

$\lambda \propto \frac{1}{\sigma}$ (at constant temperature and pressure)

12. **Liquid state:** Liquid state is condensed gas or molten solid. Liquids have definite volume but no definite shape.

Liquids diffuse slowly and are almost incompressible. Some important properties of liquids are:

(i) Evaporation: It is the spontaneous change in which a liquid changes into vapours at the surface of liquid. It increases with increase of surface area, increase in temperature and decrease in intermolecular forces. It causes cooling.

(ii) Vapour pressure: It is the pressure exerted by the vapours of a liquid in equilibrium with the liquid at a given temperature. It increases with increase of temperature. Liquids with low intermolecular forces have high vapour pressure.

(iii) Boiling point: It is the temperature at which the vapour pressure of a liquid becomes equal to atmospheric pressure. Temperature of the liquid remains constant after it starts boiling as the energy supplied increases the potential energy but its kinetic energy remains constant. Boiling point changes with the pressure of surroundings.

$$\log\left(\frac{P_2}{P_1}\right)=\frac{\Delta H_V}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

where, ΔH_V = latent heat of vaporisation; P_2 and P_1 are vapour pressures at T_2 and T_1.

(iv) Surface tension: It is the force in dyne acting on the surface at right angles to any line of unit length. It decreases generally with increase in temperature. It is expressed in J m^{-2} or N m^{-1} or dyne cm^{-1}.

(a) Surface tension is molecular phenomenon of liquid involving the force of cohesion among the liquid molecules.

(b) Maximum potential energy of liquid molecules is on the surface.

(c) Surface tension is numerically equal to the surface energy. The work required to increase or extend the surface area by 1 sq. cm is called surface energy.

(d) Surface tension is a scalar quantity.

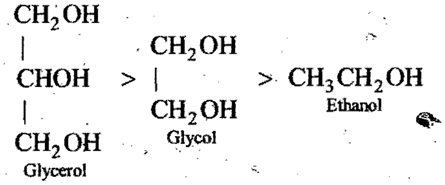
(e) Sparingly soluble solutes like soap and detergent decrease the surface tension of the liquid. However, fairly soluble solutes like sugar and salt increase the surface tension of the liquid.

(f) Liquid drops are spherical because liquid surface has a tendency to acquire minimum surface area.

(g) Greater is the intermolecular force, more is the surface tension.

e.g., Soap in water < Water < Mercury

$H_2O > C_2H_5OH > CH_3OCH_3$



$$\underset{\text{Glycerol}}{\begin{matrix}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{matrix}} > \underset{\text{Glycol}}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}} > \underset{\text{Ethanol}}{CH_3CH_2OH}$$

(v) Viscosity: It is the resistance in a liquid to flow. The force in newton per square metre required to maintain a difference of velocity of one metre per second between two parallel layers of a liquid at a distance of one metre from each other is called coefficient of viscosity. It is expressed in $\text{g m}^{-1}\text{s}^{-1}$.

Or

The force per unit area required to maintain unit difference of velocity between two consecutive parallel layers of the liquid which are one centimetre apart. It is expressed in $\text{dyne cm}^{-2}\text{ s}^{-1}$ or poise.

The reciprocal of coefficient of viscosity is called **fluidity**. Liquids with low viscosity are termed mobile while others with high viscosity are called viscous. Viscosity is high in liquids with high intermolecular forces, high molecular masses and having branching in the chain of the molecule. Viscosity decreases with increase in temperature.

(vi) Reynold's number: The nature of flow of a liquid through a tube depends on the value of Reynold's number N_R.

$$N_R=\frac{2r\bar{v}\rho}{\eta}$$

where, r = Radius of the tube
$\bar{v}$ = Average velocity of the fluid
ρ = Density of liquid
η = Coefficient of viscosity

Case I: When $N_R > 4000$, the flow is called turbulent flow.

Case II: When $N_R < 2100$, the flow is called laminar flow.

13. The solid state: The particles are closely packed and are held together by strong intermolecular forces. The particles cannot move at random. They have only vibrational motion. Solids have definite shape and definite volume. They possess high density and low compressibility. Solids are divided into two classes: (i) amorphous solids and (ii) crystalline solids. In amorphous solids, the arrangement of building constituents is not regular but haphazard. Their melting points are not sharp. These are isotropic in nature.

In crystalline solids, building constituents arrange themselves in regular manner throughout the entire three-dimensional network. Crystalline solids consist of large number of units called crystals. A crystal is defined as a solid figure which has definite geometrical shape with flat faces and sharp edges. It has a sharp melting point and anisotropic in nature.

14. Types of symmetry in crystals: The total number of planes, axes and centres of symmetry possessed by a crystal are termed as elements of symmetry.

(i) Centre of symmetry: It is an imaginary point within the crystal such that any line drawn through it intersects the surface of the crystal at equal distances in both directions. A crystal always possess only one centre of symmetry.

(ii) Plane of symmetry: It is an imaginary plane which passes through the centre of a crystal and divides it into two equal portions such that one part is exactly the mirror image of the other.

(iii) Axis of symmetry: It is an imaginary straight line about which, if the crystal is rotated, it will present the same appearance more than once during the complete revolution.

A cubic crystal possesses a total of 23 elements of symmetry.

15. Space lattice and unit cell: The geometrical form consisting of a regular array of points in space is called a space lattice or an array of points showing how molecules, atoms or ions are arranged in different sites, in three-dimensional space is called space lattice.

The smallest repeating unit in a space lattice which when repeated over and over again results in a crystal of the given substance is termed unit cell. A unit cell possesses all the structural properties of the given crystal. The edges of the unit cell are designated as a, b and c, and the angles between three imaginary axes as α, β and γ respectively.

16. Crystal systems: Seven types of basic or primitive unit cells have been recognised among crystals. These are:

1. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, KCl, ZnS
2. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	KNO_3, $BaSO_4$
3. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	NH_4Br, SnO_2
4. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$, $\beta \neq 90°$	Monoclinic sulphur, $CaSO_4 \cdot 2H_2O$
5. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4 \cdot 5H_2O$, H_3BO_3
6. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$; $\gamma = 120°$	ZnO, AgI, SiC
7. Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$NaNO_3$, $CaCO_3$

All crystals do not have simple lattices. There can be 14 different ways in which similar points can be arranged in a three dimensional space. The crystals belonging to a cubic system have three kinds of lattices:

(i) Simple cubic lattice: There are points only at the corners of each unit:

(ii) Face-centred cubic lattice: There are points at the corners as well as at the centre of each of the six faces of the cube.

(iii) Body-centred cubic lattice: There are points at the corners as well as in the centre of each cube.

Type of lattice point	Contribution to one unit cell
Corner	$1/8$
Edge	$1/4$
Face-centre	$1/2$
Body-centre	1

- Halides of alkali metals except those of Cs, ammonium halides, oxides and sulphides of alkaline earth metals except BeS and halides of silver except AgI have rock salt (NaCl type) structure.
- CsCl, CsBr, CsI, TiCl, TiBr, TiI have CsCl type structure.
- CuCl, CuBr, CuI, AgI, BeS have zinc blende structure (ZnS type).
- $SrCl_2$, SrF_2, $BaCl_2$, BaF_2, CdF_2, HgF_2 have fluorite (CaF_2) structure.
- Na_2O, K_2O, Na_2S, K_2S have antifluorite (Li_2O type) structure.

17. Bragg's law: When X-rays are incident on a crystal face, they penetrate into the crystal and strike the atoms in different planes. From each of these planes, X-rays are deflected. Bragg presented a relationship between the wavelength of the X-rays and the distance between the planes.

$$n\lambda = 2d \sin\theta$$

Where, n is an integer such as, 1, 2, 3, ..., λ is the wavelength, d is the distance between repeating planes of particles and θ the angle of deflection or glancing angle.

18. Characteristics of cubic systems:

(i) Number of atoms per unit cell: (a) Simple cubic structure—one atom per unit cell, (b) Face-centred cubic structure—4 atoms per unit cell and (c) Body-centred cubic structure—2 atoms per unit cell.

(ii) Density of lattice matter $= \dfrac{n \times M}{N_0 \times a^3}$

where, n is the number of atoms in unit cell, M is the atomic mass or molecular mass, N_0 is Avogadro's number and a = edge length of the cubic unit cell.

(iii) Atomic radius:

(a) Simple cubic cell—Radius of atom $= \dfrac{a}{2}$

(b) Face-centred cubic cell—Radius of atom $= \dfrac{a}{2\sqrt{2}}$

(c) Body-centred cubic cell—Radius of atom $= \dfrac{\sqrt{3}}{4} a$

19. Close packing of constituents: It refers to the arrangement in which constituents occupy maximum available space. The two common types of close packing are:

(a) *AB AB* ... arrangement. This gives hexagonal close packing.

(b) *ABC ABC* ... arrangement. This gives cubical close packing.

In the packing of constituents, some interstitial sites are left. These sites are termed voids. The interstitial site between four spheres is tetrahedral and between six spheres is octahedral.

The space occupied by hard spheres in hcp; ccp (fcc) is 74%; in bcc it is 68%; in simple cubic it is 52% and in diamond it is 34%; thus, only fcc and hcp are close packed structures.

(i) hcp is present in Be, Mg, Ca, Cr, Mo, V and Zn.

(ii) ccp is present in Fe, Cu, Ag, Au, Pt, Al and Ni.

(iii) bcc is present in alkali metals.

(iv) All noble gases have ccp structure except helium which has hcp structure.

If 'n' spheres are present in packing, then the numbers of tetrahedral and octahedral voids are $2n$ and n respectively.

20. The coordination number: The nearest neighbours with which a given sphere is in contact is called coordination number. It depends upon structure.

(a) Simple cubic structure: coordination number = 6

(b) Face-centred cubic structure: coordination number = 12

(c) Body-centred cubic structure: coordination number = 8

For ionic solids, the ratio of the radius of cation to that of anion is called radius ratio. The radius ratio for a given coordination number is fixed.

For radius ratio (0.155– 0.225) coordination number = 3

For radius ratio (0.225– 0.414) coordination number = 4

For radius ratio (0.414– 0.732) coordination number = 6

For radius ratio (0.732–1.0) coordination number = 8

21. Types of crystals: Depending upon the nature of forces that hold the constituent particles together in the crystal lattice, crystals are classified into four types:

(i) Ionic crystals: The forces are electrostatic. The lattice points are occupied by positively and negatively charged ions. These crystals are quite hard, have low volatility and have high melting and boiling points. These are insulators but become good conductors in molten state. These are soluble in polar solvents and highly brittle in nature. NaCl, KCl, $BaCl_2$, etc., belong to this class.

(ii) Covalent crystals: The constituent particles are the atoms of same or different elements which are held by strong covalent bonds. These solids are very hard and have very high melting points. Diamond and carborundum belong to this class.

(iii) Metallic crystals: The metallic crystals have positive metal ions as lattice points surrounded by a sea of mobile electrons. Each electron belongs to a number of positive ions and each positive ion belongs to a number of electrons. The force that binds a metal ion to a number of electrons is known as metallic bond. Metallic crystals mostly belong to fcc, bcc and hcp systems. These are good conductors, possess lustre and are hard, tough, malleable and ductile in nature.

(iv) Molecular crystals: The constituent units of molecular crystals are molecules. The forces holding the molecules are weak van der Waals' forces. Molecular solids are soft and vaporise easily. These are bad conductors of electricity and possess low density. Examples are ice, solid, CO_2, etc.

22. Defects in crystals: An ideal crystal is the one which has the same unit cell containing the same lattice points throughout the whole of the crystal. At absolute zero, the crystals are ideal but with rise in temperature, there is a chance of distortion. The defect may be at a point along a line or over a surface.

(i) Schottky defect: This defect is caused if some of the lattice points are unoccupied. The points which are unoccupied are called vacancies or holes. The number of missing positive and negative ions is the same and, thus, the crystal is neutral. Such defect is common in ionic compounds with high coordination number where the cations and anions are of similar size, *e.g.*, NaCl, KCl, KBr, etc.

(ii) Frenkel defect: This defect is caused when some of the ions of the lattice occupy interstitial sites leaving lattice sites vacant. This defect appears generally in ionic crystals in which anion is much larger in size than the cation, *e.g.*, AgBr, ZnS.

In Schottky defect, density decreases while in Frenkel defect it remains the same. In both the defects, electrical conductivity is observed to some extent. The overall chemical composition of the substance does not change. However, there are other defects in which there is change in overall chemical combination. Such defects are termed **non-stoichiometric defects.** In such crystals, there is excess of either positive particles or negative particles. However, the crystal is neutral in nature.

Positive particle excess defects: (i) A negative ion may be missing from the lattice site which is occupied by an extra electron. (ii) An extra positive particle is present in the interstitial position. To maintain neutrality, an extra electron also occupies a place in the interstitial space. Such crystals are usually coloured and semiconductors.

Positive particle deficiency defect: One of the positive particles may be missing from its lattice site. The extra negative charge may be balanced if a nearby positive particle acquires extra positive charge. Such crystals are also semiconductors. Examples are FeO, FeS, NiO, etc.

Certain defects in crystals arise due to presence of chemical impurities. These are known as impurity defects.

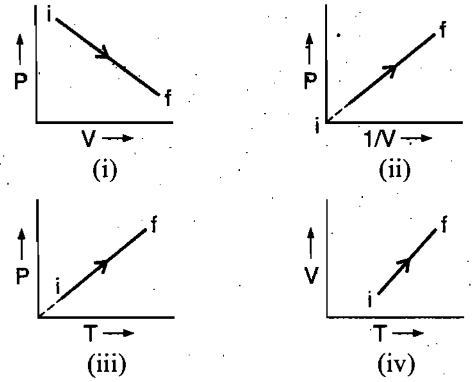
Questions

1. Matrix Match Type Questions:

[A] Match the crystalline solids in Column-I with the coordination number of their ions in Column-II:

Column-I	Column-II
(a) CsCl	(p) Coordination number of cation = 8
(b) CaF_2	(q) Coordination number of anion = 4
(c) ZnS	(r) Coordination number of cation = 4
(d) Na_2O	(s) Coordination number of anion = 8

[B] The diagrams below depict the different processes for a given amount of an ideal gas. Match the Column-I and Column-II:



(i) (ii) (iii) (iv)

i → initial state,
f → final state

Column-I	Column-II
(a) Fig. (i) : System proceeding from initial state to final state	(p) Temperature will remain constant
(b) Fig. (ii) : System from initial state to final state	(q) Pressure will decrease
(c) Fig. (iii) : System proceeding from initial state to final state	(r) Volume will be constant
(d) Fig. (iv) : System proceeding from initial state to final state	(s) Temperature may increase or decrease or may first increase and then decrease

[C] Match Column-I with Column-II for ideal gases:

Column-I	Column-II
(a) If temperature of given gas is increased	(p) Average speed of gas will increase
(b) If the pressure of a given gas is increased at constant temperature	(q) Root mean square speed of gas molecules will increase
(c) If the density of a given gas is lowered at constant temperature	(r) Most probable speed of gas molecules will increase
(d) If the volume of a given gas is increased at constant temperature	(s) Speed of gas molecules will not change

[D] Match the Column-I with Column-II:

Column-I	Column-II
(a) Boyle's temperature	(p) a/Rb
(b) $\frac{1}{2}$ (Inversion temperature)	(q) $8a/27Rb$
(c) Critical temperature	(r) The gas cannot be liquefied above this temperature, on applying pressure
(d) Critical pressure	(s) $a/27b^2$

[E] Match the Column-I with Column-II:

Column-I	Column-II
(a) Real gas at high pressure	(p) $PV = RT + Pb$
(b) Force of attraction among gas molecules is negligible	(q) $PV = nRT$
(c) At high temperature and low pressure	(r) $Z = 1$
(d) Real gas at N.T.P.	(s) $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$

[F] Match the Column-I with Column-II:

Column-I	Column-II
(a) Internal energy of gas	(p) $\frac{3}{2}RT$
(b) Translational kinetic energy of gas molecules	(q) $\frac{5}{2}RT$
(c) The temperature at which there is no molecular motion	(r) −273° C
(d) The lowest possible temperature at which gas molecules have no heat	(s) 3.716 kJ at 298 K

[G] Match the Column-I with Column-II:

Column-I	Column-II
(a) NaCl	(p) Schottky defect
(b) ZnS	(q) Frenkel defect
(c) AgBr	(r) Develops yellow colour on heating due to F-centre
(d) KCl	(s) Develops blue/violet colour on heating due to F-centre

[H] Match the crystalline solids in Column-I with packing arrangement in Column-II:

Column-I	Column-II
(a) CaF_2	(p) Cations are in ccp arrangement
(b) NaCl	(q) Anions are in tetrahedral voids
(c) ZnS	(r) Anions are in ccp arrangement
(d) Na_2O	(s) Cations are in octahedral voids

[I] Match the crystal system in Column-I with unit cell dimensions in Column-II:

Column-I	Column-II
(a) Cubic	(p) $a = b = c$
(b) Rhombohedral	(q) $\alpha = \beta = \gamma = 90°$
(c) Orthorhombic	(r) $a \neq b \neq c$
(d) Triclinic	(s) $\alpha \neq \beta \neq \gamma \neq 90°$

[J] Match the crystal system in Column-I with Bravais lattice in Column-II:

Column-I (Crystal System)	Column-II (Bravais lattice)
(a) Cubic	(p) Primitive only
(b) Hexagonal	(q) Primitive, body centred
(c) Tetragonal	(r) Primitive, face centred, body centred
(d) Orthorhombic	(s) Primitive, face centred, body centred and end centred

[K] Match the Column-I with Column-II:

Column-I	Column-II
(a) Root mean square velocity	(p) $\sqrt{\frac{3P}{d}}$
(b) Average velocity	(q) $\sqrt{\frac{3RT}{m}}$
(c) Most probable velocity	(r) $\sqrt{\frac{8P}{\pi d}}$
(d) Velocity possessed by maximum fraction of molecules	(s) $\sqrt{\frac{2RT}{m}}$

Answers

1. [A] (a — p, s); (b — p, q); (c — q, r); (d — r, s)
   [B] (a — s); (b — p); (c — r); (d — q)
   [C] (a — p, q, r); (b — s); (c — p, q, r); (d — s)
   [D] (a — p); (b — p); (c — q, r); (d — s)
   [E] (a — p); (b — p); (c — q, r); (d — s)
   [F] (a — p, q, s); (b — p, s); (c — r); (d — r)
   [G] (a — p, r); (b — q); (c — p, q); (d — p, s)
   [H] (a — p, q); (b — r, s); (c — q); (d — q)
   [I] (a — p, q); (b — p); (c — q, r); (d — r, s)
   [J] (a — r); (b — p); (c — q); (d — s)
   [K] (a — p, q); (b — r); (c — s); (d — s)

• PRACTICE PROBLEMS •

1. A gas occupies a volume of 250 cm^3 at 745 torr and 25°C. What additional pressure is required to reduce the gas volume to 200 cm^3 at the same temperature?
   [**Ans.** 186.25 torr]
2. A vessel of 120 cm^3 contains a certain mass of a gas at 20°C and 750 torr pressure. The gas was transferred to a vessel of volume 180 cm^3. Calculate the pressure of the gas at the same temperature.
   [**Ans.** 500 torr]
3. A gaseous system has a volume of 580 cm^3 at a certain pressure. If its pressure is increased by 0.96 atm, its volume becomes 100 cm^3. Determine the pressure of the system.
   [**Ans.** 0.2 atm]
   [**Hint:** $P \times 580 = (P + 0.96)100$]
4. A gas filled freely collapsible balloon is pushed from the surface level of a lake to a depth of 50 m. Approximately what per cent of its original volume will the balloon finally have, assuming that the gas behaves ideally and temperature is same at the surface and at 50 m depth?
   [**Ans.** 17.13]
   [**Hint:** P_1 = Pressure at the surface = 1 atm
   $= 76.0 \times 13.6 \times 981$ dyne/cm^2
   P_2 = Pressure at a depth of 50 m
   $= 76.0 \times 13.6 \times 981 + (50 \times 100) \times 1 \times 981$ dyne/cm^2
   $= 981[76.0 \times 13.6 + 5000]$
   $= 981 \times (6033.6)$ dyne/cm^2
   Now apply Boyle's law, $P_1V_1 = P_2V_2$
   or $\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{76.0 \times 13.6 \times 981}{981 \times 6033.6} = 0.1713$
   $\% = 0.1713 \times 100 = 17.13$]
5. A sample of gas at room temperature is placed in an evacuated bulb of volume 0.51 dm^3 and is found to exert a pressure of 0.24 atm. The bulb is connected to another evacuated bulb whose volume is 0.63 dm^3. What is the new pressure of the gas at room temperature?
   [**Ans.** 0.1074 atm]

6. It is desired to increase the volume of 800 cm^3 of a gas by 20% keeping the pressure constant. To what temperature should the gas be heated, if the initial temperature is 22°C?
[**Ans.** 81°C]

7. A chamber of constant volume contains hydrogen gas. When the chamber is immersed in a bath of melting ice (0°C) the pressure of the gas is 800 torr. What pressure will be indicated when the chamber is brought to 100°C?
[**Ans.** 1093 torr]

8. Calculate the volume occupied by 4.045×10^{23} molecules of oxygen at 27°C and having a pressure of 700 torr.
[**Ans.** 17.97 dm^3]
[**Hint:** No. of moles 'n' $= \frac{4.045 \times 10^{23}}{6.023 \times 10^{23}} = 0.672$; $P = \frac{700}{760}$ atm
Now use the gas equation, $PV = nRT$]

9. Calculate the moles of hydrogen present in a 500 cm^3 sample of hydrogen gas at a pressure of 760 mm of Hg and 27°C.
[**Ans.** 2.03×10^{-2} mol]
[**Hint:** 500 cm^3 = 0.5 L, 760 mm of Hg = 1 atm. Now apply the gas equation, $n = \frac{PV}{RT}$]

10. Calculate the volume occupied by 4 mole of an ideal gas at 2.5×10^5 Nm^{-2} pressure and 300 K temperature.
[**Ans.** 39.9 dm^3]
[**Hint:** $V = \frac{nRT}{P}$, Given, $n = 4$; $R = 8.314$ Nm K^{-1} mol^{-1}; $T = 300$; $P = 2.5 \times 10^5$ Nm^{-2}]

11. What is the volume occupied by 11 g of carbon dioxide at 27°C and 780 mm of Hg pressure?
[**Ans.** 6 litre]
[**Hint:** 780 mm of Hg $= \frac{780}{760}$ atm; $w = 11$ g; $M = 44$ g mol^{-1}.
Now apply $V = \frac{w}{M} \cdot \frac{RT}{P}$]

12. A certain quantity of a gas occupies 200 mL when collected over water at 15°C and 745 mm pressure. It occupies 182.6 mL in dry state at NTP. Find the vapour pressure of water at 15°C.
[**Ans.** 13 mm]

13. The density of a gas is found to be 2.07 g L^{-1} at 30°C and 2 atmospheric pressure. What is its density at NTP?
[**Ans.** 1.149 gL^{-1}]
[**Hint:** Apply $P_1 = \frac{D_1}{M} RT_1$, $P_2 = \frac{D_2}{M} RT_2$
So, $\frac{P_1}{D_1 T_1} = \frac{P_2}{D_2 T_2}$]

14. At the top of a mountain, the thermometer reads 0°C and the barometer reads 700 mm Hg. At the bottom of the mountain the thermometer reads 30°C and the pressure 760 mm Hg. Compare the density of the air at the top with that at the bottom.
[**Ans.** 1.02 : 1]
[**Hint:** Density is inversely proportional to volume.

$$\frac{d_{top}}{d_{bottom}} = \frac{V_b}{V_t} = \frac{T_b P_t}{T_t P_b} = \frac{303 \times 700}{273 \times 760} = \frac{1.02}{1}$$]

15. Calculate the volume occupied by 5 g of acetylene gas at 50°C and 740 mm of pressure. **(IIT 1991)**
[**Ans.** 5.23 litre]

16. Calculate the volume occupied by 7 g of nitrogen gas at 27°C and 750 mm Hg pressure. **(MLNR 1992)**
[**Ans.** 6.24 litre]

17. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atm and 27°C. The cylinder can hold 2.82 litre of water at NTP. Calculate the number of balloons that can be filled up. **(MLNR 1991)**
[**Ans.** 10]
[**Hint:** Volume of one balloon

$$= \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3 = 4851 \text{ cm}^3$$
$$= 4.851 \text{ litre}$$

Let n balloons be filled; thus, total volume of hydrogen used in filling balloons

$$= 4.851 \times n \text{ litre}$$

Total volume of hydrogen in the cylinder at NTP,

$$V = \frac{20 \times 2.82 \times 273}{300 \times 1} = 51.324 \text{ litre}$$

Actual volume of H_2 to be transferred to balloons

$$= 51.324 - 2.82 \text{ (2.82 litre retained in the cylinder)}$$
$$= 48.504 \text{ litre}$$

No. of balloons filled 'n' $= \frac{48.504}{4.851} \approx 10$]

18. An open vessel at 27°C is heated until three-fifth of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated? **(MLNR 1990)**
[**Ans.** 477°C]
[**Hint:** Both volume and pressure are constant as the vessel is open,
i.e., $n_1 RT_1 = n_2 RT_2$
or $\frac{n_1}{n_2} = \frac{T_2}{T_1}$
If $n_1 = 1$, $n_2 = 1 - \frac{3}{5} = \frac{2}{5}$
So, $\frac{5}{2} = \frac{T_2}{300}$ or $T_2 = 750 \text{ K} = 477° \text{C}$]

19. A gaseous mixture of He and O_2 is found to have a density of 0.518 g L^{-1} at 25°C and 720 torr. What is the per cent by mass of helium in this mixture?
[**Ans.** 19.88]
[**Hint:** First determine the average molecular mass and then number of moles of helium and oxygen.
Moles of helium = 0.665; Moles of oxygen = 0.335

$$\text{Mass per cent of helium} = \frac{4 \times 0.665}{4 \times 0.665 + 32 \times 0.335} \times 100$$
$$= 19.88$$]

20. A sample of natural gas is 85.2% methane and 14.8% ethane by mass. What is the density of this mixture at 18°C and 748 mm Hg?
[**Ans.** 0.74 g L^{-1}]

[**Hint:** Molecular mass of mixture,

$$M = \frac{85.2}{100} \times 16 + \frac{14.8}{100} \times 30 = 13.632 + 4.44 = 18.07$$

$$PM = dRT$$

$$d = \frac{PM}{RT} = \frac{748}{760} \times \frac{18.07}{0.0821 \times 291} = 0.74 \text{ g L}^{-1}$$]

21. 125 mL of a gas A of pressure 500 mm is mixed with 200 mL of another gas B at a pressure of 300 mm in a vessel of 150 mL capacity. What will be the total pressure of the resulting mixture if the temperature is kept constant?

[**Ans.** 816.67 mm]

22. Two vessels whose volumes are in the ratio 2 : 1 contain nitrogen and oxygen at 800 mm and 680 mm pressures respectively, when they are connected together what will be the pressure of the resulting mixture?

[**Ans.** 760 mm]

23. A 10 litre flask at 298 K contains a gaseous mixture of CO and CO_2 at a total pressure of 2 atm. If 0.20 mole of CO is present, find its partial pressure and also that of CO_2.

[**Ans.** Partial pressure of CO = 0.49 atm; partial pressure of CO_2 = 1.51 atm]

24. Calculate the total pressure in a mixture of 4 g of oxygen and 3 g of hydrogen confined in a total volume of one litre at 0°C. **(MLNR 1991)**

[**Ans.** 25.18 atm]

[**Hint:** Determine total number of moles and then apply $PV = n_{\text{total}}RT$]

25. A gas cylinder contains 55% nitrogen, 20% oxygen and 25% carbon dioxide by mass, at 760 mm pressure. Calculate the partial pressure of each gas.

[**Ans.** 472.8 mm, 150.44 mm, 136.74 mm]

26. The density of a mixture of N_2 and O_2 at NTP is 1.3 gL^{-1}. Calculate partial pressure of O_2.

[**Ans.** 0.28 atm]

[**Hint:** Let n_1 and n_2 moles of N_2 and O_2 be present in the mixture respectively.

Average molecular mass of the mixture $= \frac{28n_1 + 32n_2}{n_1 + n_2}$ ... (i)

Average molecular mass from general gas equation,

$$M = \frac{D}{P} \times RT = \frac{1.3}{1} \times 0.0821 \times 273 = 29.137 \quad \text{... (ii)}$$

So, $\frac{28n_1 + 32n_2}{n_1 + n_2} = 29.137$ or $\frac{4n_2}{n_1 + n_2} = 1.137$

or $\frac{n_2}{n_1 + n_2} = 0.28 =$ mole fraction of oxygen

Partial pressure of $O_2 = 0.28 \times 1 = 0.28$ atm]

27. At a definite pressure and temperature, 100 mL of hydrogen diffused in 20 minute. How long will 40 mL of oxygen take to diffuse under similar conditions?

[**Ans.** 32 minute]

28. At a given temperature and pressure, 20 mL of air diffused through a porous membrane in 15 second. Calculate the volume of carbon dioxide which will diffuse in 10 second if the vapour density of air is 14.48.

[**Ans.** 10.8 mL]

29. At room temperature, ammonia gas at one atmospheric pressure and hydrogen chloride at P atmospheric pressure are allowed to effuse through identical pinholes from opposite ends of a glass tube of one metre length and uniform cross reaction. NH_4Cl is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P?

[**Ans.** 2.198 atm]

[**Hint:** $\frac{r_{HCl}}{r_{NH_3}} = \sqrt{\frac{M_{NH_3}}{M_{HCl}}} \times \frac{P_{HCl}}{P_{NH_3}}$]

30. The rate of effusion of an unknown gas (X) through a pinhole is found to be 0.279 times the rate of effusion of hydrogen gas through the same pinhole, if both are at STP. What is the molecular mass of the unknown gas? **[CEE (Bihar) 1991]**

[**Ans.** 25.69]

31. In a 2 m long narrow tube, HCl is allowed to diffuse in the tube from one end and NH_3 from the other end. If diffusion is started at the same time, predict at what point the white fumes of NH_4Cl will form?

[**Ans.** NH_4Cl will form at 1.1886 m from the NH_3 end of the tube]

32. The composition of air is approximately 80% N_2 and 20% O_2 by mass. Calculate density of air at 293 K and 76 cm Hg pressure.

[**Ans.** 1.19 g L^{-1}]

[**Hint:** Determine first average molecular mass of air and then apply $D = \frac{P \times M_{av}}{RT}$]

33. Calculate the internal energy of one gram mole of nitrogen at 150°C assuming it to be an ideal gas.

[**Ans.** 5.275×10^{10} erg]

34. Calculate the kinetic energy of 5 mole of a gas at 27°C in erg and calorie.

[**Ans.** 1.8706×10^{11} erg, 4477 cal]

35. A glass tumbler containing 243 mL of air at 100 kPa and 20°C is turned upside down and immersed in a water bath to a depth of 20.5 metre. The air in the glass is compressed by the weight of water above it. Calculate the volume of air in the glass assuming the temperature and the barometric pressure have not changed.

[**Ans.** 80.7 mL]

[**Hint:** Hydrostatic pressure $= h \times d \times g$

$$= 20.5 \times 1 \times 9.81$$

$$= 201.105 \text{ kPa}$$

Inside the water bath atmospheric pressure and hydrostatic pressure acts:

$$P_{\text{total}} = 100 + 201.105 = 301.105 \text{ kPa}$$

$$P_1V_1 = P_2V_2$$

$$100 \times 243 = 301.105 \times V_2$$

$$V_2 = 80.70 \text{ mL}$$]

36. Calculate the rms speed of the molecules of ethane gas of volume 1.5 litre at 750 mm of Hg pressure.

[**Ans.** 1.225×10^4 cm/sec]

37. The density of a gas at 1.5 atm is 1.52 g L^{-1}. Calculate the rms speed of the molecules of the gas.

[**Ans.** 5.476×10^4 cm/sec]

38. At what temperature will the rms speed of hydrogen be the same as that of oxygen at 25°C?
[**Ans.** 18.62 K or $-254.38°$ C]

39. Calculate the average rms and most probable speed of SO_2 molecules at 27°C.
[**Ans.** 3.15×10^4 cm/sec, 3.419×10^4 cm/sec,
2.792×10^4 cm/sec]

40. The average speed at temperature T_1 and most probable speed at T_2 of CO_2 gas is 9×10^4 cm/sec. Calculate the values of T_1 and T_2.
[**Ans.** 1682.5 K, 2143.4 K]

41. How many times would the average molecular speed of nitrogen increase as its temperature is raised from -73°C and 127°C?
[**Ans.** 1.414 times]

42. A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially? **(IIT 1994)**
[**Ans.** 8 : 1]
[**Hint:** Partial pressure ratio of He and CH_4 is 16 : 4.

For diffusion
$$\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}} \times \frac{p_{He}}{p_{CH_4}}$$
$$\frac{n_{He}}{n_{CH_4}} = \sqrt{\frac{16}{4}} \times \frac{16}{4} = 8$$

i.e., mole ratio of diffusion for He and CH_4 is 8 : 1.]

43. Pure O_2 diffuses through an aperture in 224 second, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 second. What is the molecular mass of gas?
[**Ans.** 46.6]

44. 56 g of nitrogen are confined to a 6 litre flask at 37°C. Calculate its pressure using van der Waals' equation for nitrogen. $a = 4.17$ atm litre^2 mol^{-2} and $b = 0.037$ litre mol^{-1}.
[**Ans.** 8.1175 atm]

45. One mole of carbon dioxide was found to occupy a volume of 1.32 litre at 48°C under a pressure of 16.4 atm. Calculate the pressure that would have been expected from:
(i) the ideal gas equation,
(ii) van der Waals' equation.
($a = 3.59$ atm litre^2 mol^{-1}; $b = 4.27 \times 10^{-3}$ litre mol^{-1} and $R = 0.0821$ litre-atm K^{-1} mol^{-1})
[**Ans.** (i) 19.96 atm (ii) 18.64 atm]

46. Calculate the compressibility factor for SO_2, if 1 mole of it occupies 0.35 litre at 300 K and 50 atm pressure. Comment on the result.
[**Hint:** $Z = \frac{PV}{nRT} = \frac{50 \times 0.35}{1 \times 0.0821 \times 300} = 0.711$

Since, $Z < 1$; the gas SO_2 will be more compressible than ideal gas.]

47. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. **(IIT 2003)**
[**Ans.** 434 m/sec]

48. A chamber contains monoatomic 'He' at STP, determine its number density.
[**Ans.** 2.68×10^{25} m^{-3}]
[**Hint:** Number density $= \frac{P}{kT}$
(where, k = Boltzmann constant)
$$PV = nRT$$
$$= (n \times N)\frac{R}{N}T$$
$$= (n \times N)kT$$
$$\frac{P}{kT} = \frac{n \times N}{V} = \text{number density}$$
$$\therefore \quad \text{Number density} = \frac{1.01 \times 10^5}{1.38 \times 10^{-23} \times 273} = 2.68 \times 10^{25} \text{ m}^{-3}$$]

49. Two perfect gases at absolute temperature T_1 and T_2 are mixed. There is no loss of energy. Find the temperature of the mixture if masses of molecules are m_1 and m_2 and the number of moles of the gases are n_1 and n_2 respectively.
[**Ans.** $T = \frac{n_1T_1 + n_2T_2}{n_1 + n_2}$]
[**Hint:** Let final temperature is T
$$\frac{3}{2}n_1RT_1 + \frac{3}{2}n_2RT_2 = \frac{3}{2}(n_1 + n_2)RT$$
$$T = \frac{n_1T_1 + n_2T_2}{n_1 + n_2}$$]

50. van der Waals' constant 'b' for oxygen is 32 cm^3/mol. Assume b is four times the actual volume of a mole of "billiard-ball" O_2 molecules and compute the diameter of an O_2 molecule.

51. The speed of ten particles in metre/sec are 0, 1, 2, 3, 3, 3, 4, 4, 5 and 6. Find (a) average speed (b) the root mean square speed (c) most probable speed.
[**Ans.** $c_{av} = 3.1$ m sec^{-1}, $c_{rms} = 12.5$ m sec^{-1}, $c_{mp} = 3$ m sec^{-1}]

52. Using van der Waals' equation, calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11 atm at a temperature of 300 K. The value of 'b' is 0.05 litre mol^{-1}. **(IIT 1998)**
[**Ans.** 6.46 atm litre^2 mol^{-2}]

53. (a) Calculate the pressure exerted by 5 moles of CO_2 in one litre vessel at 47°C using van der Waals' equation. Also, report the pressure of the gas if it behaves ideally in nature. Given that $a = 3.592$ atm litre^2 mol^{-2}, $b = 0.0427$ litre mol^{-1}. **(IIT 2002)**
(b) If volume occupied by CO_2 molecule is negligible, then calculate the pressure exerted by one mol of CO_2 gas at 273 K. **(IIT 2000)**
[**Ans.** (a) 77.218 atm, 131.36 atm and (b) 0.9922 atm]

54. A compound alloy of gold and copper crystallises in a cubic lattice in which gold atoms occupy corners of cubic unit cell and copper atoms occupy the centre of faces of cube. What is formula of alloy compound?
[**Ans.** $AuCu_3$]

55. A compound formed by elements A and B crystallises in the cubic structure where A atoms are at the corners of the cube

and *B* atoms at the centre of the cube. What is the formula of the compound?

[Ans. *AB*]

56. A fcc element (atomic mass = 60) has a cell edge of 400 pm. What is its density?

[Ans. 6.23 g cm^{-3}]

[Hint: Apply density = $\frac{Z \times M}{N_0 \times V}$, $Z = 4$ and $V = (4 \times 10^{-8})^3$ cm^3 (1 pm = 10^{-12} m = 10^{-10} cm)]

57. The face-centred unit cell of nickel has an edge length of 352.39 pm. The density of nickel is 8.9 g cm^{-3}. Calculate the value of Avogadro's number. The atomic mass of nickel is 58.7 and 1 pm is equal to 10^{-10} cm.

[Ans. 6.029×10^{23}]

58. The unit cell of aluminium is a cube with an edge length of 405 pm. The density of aluminium is 2.70 g cm^{-3}. What type of unit cell of aluminium is?

[Ans. The unit cell is face-centred]

[Hint: Apply the formula, density = $\frac{Z \times M}{N_0 \times V}$ and find the value of *Z*.]

59. A substance forms face-centred cubic crystals. Its density is 1.984 g cm^{-3} and the edge length of the unit cell is 630 pm. Calculate the molar mass of the substance.

[Ans. 74.70 g mol^{-1}]

60. Molybdenum forms body-centred cubic crystals whose density is 10.3 g cm^{-3}. Calculate the edge length of the unit cell. The molar mass of Mo is 95.94 g mol^{-1}.

[Ans. 313.9 pm]

61. An element crystallises in a structure having a fcc unit cell of an edge 200 pm. Calculate its density if 200 g of this element contains 24×10^{23} atoms.

[Ans. 4.166 g cm^{-3}]

[Hint: Molar mass= $\frac{200}{24 \times 10^{23}} \times 6.023 \times 10^{23} = 50.19$ g mol^{-1}

For fcc, $Z = 4$, $V = a^3 = (200 \times 10^{-10})^3$

Apply density = $\frac{ZM}{N_0 \times V}$]

62. The element chromium exists in bcc lattice with unit cell edge 2.88×10^{-10} m. The density of chromium is 7.2×10^3 kg m^{-3}. How many atoms does 52×10^{-3} kg of chromium contain?

[Ans. 6.04×10^{23}]

63. A cubic solid is made up of two elements *P* and *Q*. Atoms *Q* are present at the corners of the cube and atoms *P* at the body-centre. What is the formula of the compound? What are the coordination numbers of *P* and *Q*?

[Ans. *PQ*, 8, 8]

64. A metallic element crystallises into a lattice containing a sequence of layers of *AB AB AB* ... Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space? **(IIT 1996)**

[Ans. 26%]

65. A lead(II) sulphide crystal has an NaCl structure. What is its density? The edge length of the unit cell is 500 pm. $N_0 = 6.023 \times 10^{23}$; atomic mass: Pb = 207.2, S = 32.

[Ans. 12.708 g cm^{-3}]

66. The unit cell of metallic gold is face-centred cubic.

(a) How many atoms occupy the gold unit cell?

(b) What is the mass of a gold unit cell?

[Ans. (a) 4 atoms (b) 1.308×10^{21} g]

67. Polonium crystallises in a simple cubic unit cell. It has atomic mass 209 and density 91.5 kg m^{-3}. What is the edge length of its unit cell?

[Ans. 15.59×10^{-8} cm]

68. The unit cell of nickel is a face-centred cube. The length of its side is 0.352 nm. Calculate the atomic radius of nickel.

[Ans. 0.124 nm]

69. Determine the simplest formula of an ionic compound in which cations are present at the corners and the anions occur at the centre of each face.

[Ans. AB_3; *A* and *B* are cation and anion respectively.]

70. Sodium metal crystallises in a body-centred cubic lattice with cell edge, $a = 4.29$ Å. What is the radius of sodium atom? **(IIT 1994)**

[Ans. 1.8576 Å]

[Hint: $4r = \sqrt{3}a$]

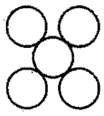
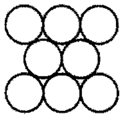
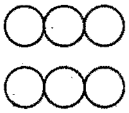
71. If three elements *P*, *Q* and *R* crystallise in a cubic type lattice with *P* atoms at the corners, *Q* atoms at the cube centre and *R* atoms at the edges, then write the formula of the compound.

[Ans. PQR_3]

72. The first order reflection of the beam of X-ray from a given crystal occurs at 5°15′. At what angle will be the third order reflection?

[Ans. 15° 56′]

73. The figures given below show the location of atoms in three crystallographic planes in a fcc lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **(IIT 2000)**

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. At constant temperature, the product of pressure and volume of a given amount of a gas is constant. This is:
(a) Gay-Lussac law (b) Charles' law
(c) Boyle's law (d) Pressure law

2. A curve drawn at constant temperature is called an isotherm. This shows the relationship between:
(a) P and $\frac{1}{V}$ (b) PV and V
(c) V and $\frac{1}{P}$ (d) P and V

3. Charles' law is represented mathematically as:
(a) $V_t = KV_0 t$ (b) $V_t = \frac{KV_0}{t}$
(c) $V_t = V_0\left(1+\frac{273}{t}\right)$ (d) $V_t = V_0\left(1+\frac{t}{273}\right)$

4. Correct gas equation is: [UGET (Manipal Medical) 2006]
(a) $\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$ (b) $\frac{V_1T_2}{P_1} = \frac{V_2T_1}{P_2}$
(c) $\frac{P_1T_1}{V_1} = \frac{P_2T_2}{V_2}$ (d) $\frac{V_1V_2}{T_1T_2} = P_1P_2$

5. In general gas equation, $PV = nRT$, V is the volume of:
(a) n moles of a gas (b) any amount of a gas
(c) one mole of a gas (d) one gram of a gas

6. In the equation of state of an ideal gas $PV = nRT$, the value of universal gas constant would depend only on: (CPMT 1991)
(a) the nature of the gas (b) the units of measurement
(c) the pressure of the gas (d) the temperature of the gas

7. The value of gas constant per degree per mol is approximately:
(a) 1 cal (b) 2 cal (c) 3 cal (d) 4 cal

8. Which one of the following is not the value of R?
(a) 1.99 cal K^{-1} mol^{-1} (b) 0.0821 litre-atm K^{-1} mol^{-1}
(c) 9.8 kcal K^{-1} mol^{-1} (d) 8.3 J K^{-1} mol^{-1}

9. One litre of a gas collected at NTP will occupy at 2 atmospheric pressure and 27°C:
(a) $\frac{300}{2\times 273}$ litre (b) $\frac{2\times 300}{273}$ litre
(c) $\frac{273}{2\times 300}$ litre (d) $\frac{2\times 273}{300}$ litre

10. 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping the volume constant; its pressure would become:
(a) $\frac{1}{2}$ atm (b) $\frac{1}{273}$ atm (c) 2 atm (d) 273 atm

11. 56 g of nitrogen and 96 g of oxygen are mixed isothermally and a total pressure of 10 atm. The partial pressures of oxygen and nitrogen (in atm) are respectively: [PET (Kerala) 2010]
(a) 4, 6 (b) 5, 5 (c) 2, 8 (d) 8, 2
(e) 6, 4

[**Hint:** $n_{N_2} = \frac{56}{28} = 2;\quad n_{O_2} = \frac{96}{32} = 3$

$$P_{N_2} = x_{N_2} \times P_{\text{Total}}$$
$$= \frac{2}{2+3}\times 10 = 4 \text{ atm},$$
$$P_{O_2} = 10 - 4 = 6 \text{ atm}$$]

12. 273 mL of a gas at STP was taken to 27°C and 600 mm pressure. The final volume of the gas would be: (CPMT 1992)
(a) 273 mL (b) 300 mL
(c) 380 mL (d) 586 mL

13. The density of the gas is equal to: (CBSE 1991)
(a) nP (b) MP/RT (c) P/RT (d) M/V
[P = Pressure; V = Volume; T = Temperature; R = Gas constant; n = number of mole; M = molecular mass]

14. The density of a gas is 1.964 g dm^{-3} at 273 K and 76 cm Hg. The gas is: (KCET 2006)
(a) CH_4 (b) C_2H_6 (c) CO_2 (d) Xe

15. Compressed oxygen is sold at a pressure of 100 atmosphere in a cylinder of 49 litre. The number of moles of oxygen in the cylinder is:
(a) 400 (b) 100 (c) 300 (d) 200
[**Hint:** One mole occupies a volume approximately 24.5 litre under ordinary atmospheric conditions.]

16. If the pressure and absolute temperature of 2 litre of carbon dioxide are doubled, the volume of carbon dioxide would become: (CBSE 1991)
(a) 7 litre (b) 5 litre (c) 4 litre (d) 2 litre

17. One gram mole of a gas at NTP occupies 22.4 litre as volume. This fact was derived from:
(a) Dalton's theory (b) Avogadro's hypothesis
(c) Berzelius hypothesis (d) law of gaseous volumes

18. 4.4 g of CO_2 contains how many litre of CO_2 at STP? (AFMC 2004)
(a) 2.4 litre (b) 2.24 litre (c) 44 litre (d) 22.4 litre

19. Five gram each of the following gases at 87°C and 750 mm pressure are taken. Which of them will have the least volume? (MLNR 1991)
(a) HF (b) HCl (c) HBr (d) HI

20. If molecular mass of O_2 and SO_2 are 32 and 64 respectively. If one litre of O_2 at 15°C and 750 mm pressure contains N molecules, the number of molecules in two litre of SO_2 under the same conditions of temperature and pressure will be: (MLNR 1991)
(a) $2N$ (b) N (c) $N/2$ (d) $4N$

21. Rate of diffusion of a gas is:
(a) directly proportional to its density
(b) directly proportional to its molecular mass
(c) directly proportional to the square of its molecular mass
(d) inversely proportional to the square root of its molecular mass

22. The rate of diffusion of hydrogen is about: (CPMT 1991)
(a) one-half that of helium (b) 1.4 times that of helium
(c) twice that of helium (d) four times that of helium

23. The rate of diffusion of methane at a given temperature is twice that of gas X. The molecular mass of gas X is: **(IIT 1990; MLNR 1995)**

(a) 64.0 (b) 32.0 (c) 4.0 (d) 8.0

24. Some moles of O_2 diffuse through a small opening in 18 second. Same number of moles of an unknown gas diffuse through the same opening in 45 second. Molecular mass of the unknown gas is:

(a) $32\times\frac{(45)^2}{(18)^2}$ (b) $32\times\frac{(18)^2}{(45)^2}$

(c) $(32)^2\times\frac{45}{18}$ (d) $(32)^2\times\frac{18}{45}$

25. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both the ends. The white ring first formed will be:

(a) at the centre of the tube
(b) near the ammonia bottle
(c) near the HCl bottle
(d) throughout the length of the tube

26. 0.5 mole of each H_2, SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be : **[CET (Karnataka) 2009]**

(a) $p_{SO_2} > p_{CH_4} > p_{H_2}$ (b) $p_{H_2} > p_{SO_2} > p_{CH_4}$

(c) $p_{H_2} > p_{CH_4} > p_{SO_2}$ (d) $p_{SO_2} > p_{H_2} > p_{CH_4}$

27. The mass of 6.02×10^{23} molecules of CO is:

(a) 28 g (b) 14 g (c) 7.0 g (d) 56 g

28. 10 g of hydrofluoric acid occupy 5.6 litre of volume at NTP. The empirical formula of the gas is HF. The molecular formula of the gas will be (At. mass of fluorine = 19):

(a) H_4F_4 (b) HF

(c) H_3F_3 (d) H_2F_2

29. A fire extinguisher contains 4.4 kg of CO_2. The volume of CO_2 delivered by this fire extinguisher at room temperature is:

(a) 24.5 litre (b) 100×24.5 litre

(c) 10×24.5 litre (d) 1000×24.5 litre

30. The number of moles of H_2 in 0.224 litre of hydrogen gas at STP is: **(MLNR 1994)**

(a) 1 (b) 0.1 (c) 0.01 (d) 0.001

31. A gas has a vapour density 11.2. The volume occupied by 1 g of the gas at NTP is:

(a) 1 L (b) 11.2 L (c) 22.4 L (d) 4 L

32. "The total pressure exerted by a number of non-reacting gases is equal to the sum of partial pressures of the gases under the same conditions" is known as:

(a) Boyle's law (b) Dalton's law

(c) Avogadro's law (d) Charles' law

33. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is:

(a) $\frac{1}{3}$ (b) $\frac{1}{2}$ (c) $\frac{2}{3}$ (d) $\frac{1}{3}\times\frac{273}{298}$

34. Equal masses of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is:

(a) $\frac{1}{2}$ (b) $\frac{8}{9}$

(c) $\frac{1}{9}$ (d) $\frac{16}{17}$

35. A gaseous mixture of 2 moles of A, 3 moles of B, 5 moles of C and 10 moles of D is contained in a vessel. Assuming that gases are ideal and the partial pressure of C is 1.5 atm, the total pressure is:

(a) 3 atm (b) 6 atm (c) 9 atm (d) 15 atm

[**Hint:** 5 moles of C produce pressure 1.5 atm; therefore partial pressures of $D = 3$ atm, $B=\frac{1.5}{5}\times3=0.9$ atm and $A=\frac{1.5}{5}\times2=0.6$ atm]

36. 50 mL of a gas A diffuse through a membrane in the same time as for the diffusion of 40 mL of gas B under identical conditions of pressure and temperature. If the molecular mass of A is 64, that of B would be: **(CBSE 1992)**

(a) 100 (b) 250 (c) 200 (d) 80

37. 3.2 g of oxygen (At. mass = 16) and 0.2 g of hydrogen (At. mass = 1) are placed in a 1.12 litre flask at 0°C. The total pressure of the gas mixture will be: **(CBSE 1992)**

(a) 1 atm (b) 2 atm (c) 3 atm (d) 4 atm

38. Select the correct statement:
In the gas equation, $PV = nRT$ **(CBSE 1992)**

(a) n is the number of molecules of a gas
(b) n moles of the gas have volume V
(c) V denotes volume of one mole
(d) P is the pressure of the gas when only one mole of gas is present

39. The density of a gas at 27°C and 1 atm is d. Pressure remaining constant, at which of the following temperatures will its density become $0.75d$? **(CBSE 1992)**

(a) 20°C (b) 30°C (c) 400 K (d) 300 K

40. If 4 g of oxygen diffuse through a very narrow hole, how much hydrogen would have diffused under identical conditions?

(a) 16 g (b) 1 g (c) $\frac{1}{4}$ g (d) 64 g

[**Hint:** $\frac{w/2}{4/32}=\sqrt{\frac{M_{O_2}}{M_{H_2}}}$]

41. A closed vessel contains equal number of hydrogen and nitrogen molecules. The total pressure is 740 mm of Hg. If N_2 molecules are removed, the pressure would become/remain:

(a) double of 740 mm of Hg
(b) one-ninth of 740 mm of Hg
(c) unchanged
(d) one-half of 740 mm of Hg

42. The pressure P exerted by a mixture of three gases having partial pressures P_1, P_2 and P_3 is given by:

(a) $P = P_1 + P_2 - P_3$ (b) $P=\sqrt{P_1+P_2+P_3}$

(c) $P = P_1 - P_2 + P_3$ (d) $P = P_1 + P_2 + P_3$

43. Two sealed containers of same capacity at the same temperature are filled with 44 g of hydrogen gas in one and 44 g of CO_2 in the other. If the pressure of CO_2 is 1 atm, what is the pressure in the hydrogen container?

(a) 1 atm (b) Zero atm (c) 22 atm (d) 44 atm

44. Absolute zero is the temperature where all gases are expected to have:
(a) different volumes (b) same volume
(c) zero volume (d) none of these

45. If a gas is heated at constant pressure, its density:
(a) will decrease (b) will increase
(c) may increase or decrease (d) will remain unchanged

46. Density of neon will be highest at:
(a) STP (b) 0°C, 2 atm
(c) 273°C, 1 atm (d) 273°C, 2 atm

47. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is: **(IIT 1993)**
(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

48. According to kinetic theory of gases:
(a) there are intermolecular attractions
(b) molecules have considerable volume
(c) there is no intermolecular attraction
(d) speed of molecules decreases for each collision

49. Postulate of kinetic theory is:
(a) atom is indivisible
(b) gases combine in simple ratio
(c) there is no influence of gravity on the molecules of the gas
(d) none of the above

50. Which of the following statements is not consistent with the postulates of kinetic theory of gases?
(a) Gases consist of large number of tiny particles
(b) Particles are in constant motion
(c) All the particles have same speed
(d) Pressure is due to hits recorded by particles against the walls of containing vessel

51. A helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is:
(a) two times that of a hydrogen molecule
(b) four times that of a hydrogen molecule
(c) half that of a hydrogen molecule
(d) same as that of a hydrogen molecule

52. The kinetic theory of gases predicts that total kinetic energy of a gas depends on:
(a) pressure of the gas
(b) temperature of the gas
(c) volume of the gas
(d) pressure, temperature and volume of the gas

53. If a gas is allowed to expand at constant temperature then:
(a) number of molecules of the gas decreases
(b) the kinetic energy of the gas molecules decreases
(c) the kinetic energy of the gas molecules increases
(d) the kinetic energy of the gas molecules remains the same

54. Gases deviate from ideal behaviour because molecules:
(a) are colourless (b) are spherical
(c) attract each other (d) have high speeds

55. Deviations from ideal behaviour will be more if the gas is subjected to:
(a) low temperature and high pressure
(b) high temperature and low pressure
(c) low temperature
(d) high temperature

56. In a closed vessel, a gas is heated from 300 K to 600 K; the kinetic energy becomes/remains:
(a) double (b) half (c) same (d) four times

57. A mixture contains 56 g of nitrogen, 44 g of CO_2 and 16 g of methane. The total pressure of the mixture is 720 mm Hg. The partial pressure of methane is: **(EAMCET 1991)**
(a) 180 mm (b) 360 mm (c) 540 mm (d) 720 mm

58. The root mean square speed of an ideal gas at 27°C is 0.3 m/sec. Its rms velocity at 927°C is: **(EAMCET 1991)**
(a) 3.0 m/sec (b) 2.4 m/sec (c) 0.9 m/sec (d) 0.6 m/sec

59. The rms speed at NTP of the species can be calculated from the expression: **(EAMCET 1990)**
(a) $\sqrt{\frac{3P}{d}}$ (b) $\sqrt{\frac{3PV}{M}}$ (c) $\sqrt{\frac{3RT}{M}}$ (d) all of these

60. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to:
(a) increase in average molecular speed
(b) increased rate of collisions amongst molecules
(c) increase in molecular attraction
(d) decrease in mean free path

61. Non-ideal gases approach ideal behaviour: **(IIT 1999; KCET 2004)**
(a) high temperature and high pressure
(b) high temperature and low pressure
(c) low temperature and high pressure
(d) low temperature and low pressure

62. The ratio of root mean square speed and average speed of a gas molecule, at a particular temperature, is:
(a) 1 : 1.086 (b) 1.086 : 1
(c) 2 : 1.086 (d) 1.086 : 2

63. Most probable speed, average speed and rms speed are related as:
(a) 1 : 1.224 : 1.128 (b) 1.128 : 1 : 1.224
(c) 1 : 1.128 : 1.224 (d) 1.224 : 1.128 : 1

64. In a closed flask of 5 litre, 1.0 g of H_2 is heated from 300–600 K. Which statement is not correct? **(CBSE 1991)**
(a) The rate of collision increases
(b) The energy of gaseous molecules increases
(c) The number of mole of the gas increases
(d) Pressure of the gas increases

65. The root mean square speed is expressed as:
(a) $\left[\frac{3}{2}RT\right]^{1/2}$ (b) $\left[\frac{2RT}{M}\right]^{1/2}$
(c) $\left[\frac{3RT}{M}\right]$ (d) $\left[\frac{3RT}{M}\right]^{1/2}$

66. The rms speed of hydrogen molecules at room temperature is 2400 m s^{-1}. At room temperature the rms speed of oxygen molecules would be:
(a) 400 ms^{-1} (b) 300 ms^{-1}
(c) 600 ms^{-1} (d) 1600 ms^{-1}

[**Hint:** $\frac{C_{O_2}}{C_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}$]

67. The molecules of which of the following gas have highest speed?
(a) Hydrogen at – 50°C (b) Methane at 298 K
(c) Nitrogen at 1000°C (d) Oxygen at 0°C

68. Which one of the following is an ideal gas?
(a) Hydrogen (b) Nitrogen
(c) Carbon dioxide (d) None of these

69. van der Waals' equation explains the behaviour of:
(a) ideal gases (b) real gases
(c) mixture of gases (d) diatomic gases

70. The critical temperature of a gas is that temperature:
(a) above which it can no longer remain in the gaseous state
(b) above which it cannot be liquefied by pressure
(c) at which it solidifies
(d) at which the volume of the gas becomes zero

71. The van der Waals' equation for a real gas is:
(a) $\left(P+\frac{a}{V^2}\right)(V-b)=nRT$
(b) $\left(P+\frac{an^2}{V^2}\right)(V-b)=nRT$
(c) $\left(P+\frac{a}{V^2}\right)(V+b)=nRT$
(d) $P=\frac{nRT}{(V-nb)}-\frac{n^2a}{V^2}$

72. In van der Waals' equation of state for a non-ideal gas the term that accounts for intermolecular force is:
(a) $\left(P+\frac{a}{V^2}\right)$ (b) $(V-b)$ (c) RT (d) $\frac{1}{RT}$

73. The units of 'a' in van der Waals' equation

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

are:
(a) atom litre^2 mol^{-2} (b) atom litre mol^{-2}
(c) atom litre mol^{-1} (d) atom litre^2 mol^{-1}

74. If 1000 mL of gas A at 600 torr and 500 mL of gas B at 800 torr are placed in a 2 litre flask, the final pressure will be:
(a) 2000 torr (b) 1000 torr
(c) 500 torr (d) 400 torr

75. Two samples of gases A and B are at the same temperature. The molecules of A are travelling four times faster than the molecules of B. The ratio of m_A/m_B of their masses will be:
(a) 16 (b) 4 (c) 1/4 (d) 1/16

[**Hint.** $\frac{m_A}{m_B}=\frac{C_2^2}{C_1^2}$]

76. The root mean square speed of a certain gas at 27°C is 3×10^4 cm s^{-1}. The temperature at which the velocity will be 6×10^4 cm s^{-1} is:
(a) 54°C (b) 108°C (c) 1200 K (d) 600 K

77. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called: **(DPMT 2009)**
(a) critical temperature (b) Boyle temperature
(c) inversion temperature (d) reduced temperature

78. The value of van der Waals' constant 'a' for gases O_2, N_2, NH_3 and CH_4 are 1.360, 1.390, 4.170 and 2.253 litre^2-atm mol^{-2} respectively. The gas which can be most easily liquefied is:
(a) O_2 (b) N_2 (c) NH_3 (d) CH_4

79. According to kinetic theory of gases for a diatomic molecule: **(IIT 1991)**
(a) the pressure exerted by the gas is proportional to the mean square speed of the molecules
(b) the pressure exerted by the gas is proportional to the root mean square speed of the molecules
(c) the root mean square speed is inversely proportional to the temperature
(d) the mean translational KE of the molecule is directly proportional to the absolute temperature

80. A real gas obeying van der Waals' equation will resemble an ideal gas if the:
(a) constants a and b are small
(b) a is large and b is small
(c) a is small and b is large
(d) constants a and b are large

81. When the universal gas constant (R) is divided by Avogadro's number (N), their ratio is called:
(a) Planck's constant (b) Rydberg's constant
(c) Boltzmann's constant (d) van der Waals' constant

82. The compressibility factor of a gas is defined as $Z=\frac{PV}{RT}$. The compressibility factor of an ideal gas is: **[PMT (MP) 2004]**
(a) 0 (b) 1 (c) –1 (d) infinity

83. An ideal gas is one which obeys:
(a) gas laws (b) Boyle's law
(c) Charles' law (d) Avogadro's law

84. A mixture of three gases X (density 1.0), Y (density 0.2) and Z (density 0.4) is enclosed in a vessel at constant temperature. When the equilibrium is established, the gas/gases:
(a) X will be at the top of the vessel
(b) Y will be at the top of the vessel
(c) Z will be at the top of the vessel
(d) will mix homogeneously throughout the vessel

85. 16 g of oxygen and 3 g of hydrogen are mixed and kept at 760 mm pressure at 0°C. The total volume occupied by the mixture will be nearly: **[CMC (Vellore) 1991]**
(a) 22.4 litre (b) 33.6 litre (c) 44800 mL (d) 4480 mL

86. Which of the following expressions does not represent Boyle's law?
(a) $PV=$ constant (b) $V\propto\frac{1}{P}$
(c) $V_1T_2=V_2T_1$ (d) $P_1V_1=P_2V_2$

87. When an ideal gas undergoes unrestricted expansion, no cooling occurs because the molecules:
(a) exert no attractive forces on each other
(b) do work equal to loss of kinetic energy
(c) collide without loss of energy
(d) are above the inversion temperature

88. Which of the following mixture of gases at room temperature does not follow Dalton's law of partial pressures?

(a) NO_2 and O_2 (b) NH_3 and HCl
(c) CO and CO_2 (d) SO_2 and O_2

89. The speed possessed by most of the gaseous molecules is:
(a) most probable speed (b) average speed
(c) root mean square speed (d) none of these

90. In which of the following pairs the gaseous species diffuse through a porous plug along with the same rate of diffusion? **(EAMCET 1990)**
(a) NO, CO (b) NO, CO_2
(c) NH_3, PH_3 (d) NO, C_2H_6

91. Which of the following statements is correct?
(a) $3PV = mnc^2$ is the expression for real gases
(b) At normal temperature and pressure most gases behave nearly as ideal gases
(c) The molecules of real gases have both volume and mutual attraction
(d) Pressure depends on number of molecules and volume

92. For one gram molecule of an ideal gas:
(a) $\frac{PV}{T} = \frac{3}{2}$ cal (b) $\frac{PV}{T} = 2$ cal
(c) $\frac{PV}{T} = 8.31$ cal (d) $\frac{PV}{T} = 0.0821$ cal

93. When helium is allowed to expand into vacuum, heating effect is observed. This is due to the fact that:
(a) helium is an inert gas
(b) helium is a noble gas
(c) helium is an ideal gas
(d) the inversion temperature of helium is very low

94. At STP, the order of mean square velocity of molecules of H_2, N_2, O_2 and HBr is: **(CBSE 1991)**
(a) $H_2 > N_2 > O_2 > HBr$ (b) $HBr > O_2 > N_2 > H_2$
(c) $HBr > H_2 > O_2 > N_2$ (d) $N_2 > O_2 > H_2 > HBr$

95. At constant temperature in a given mass of an ideal gas: **(CBSE 1991)**
(a) the ratio of pressure and volume always remains constant
(b) volume always remains constant
(c) pressure always remains constant
(d) the product of pressure and volume always remains constant

96. The non-compressible volume of a gas is . . . times the actual volume of gas molecules:
(a) 2 (b) 4 (c) 3 (d) 2.5

97. One mole of an ideal monoatomic gas is mixed with 1 mole of an ideal diatomic gas. The molar specific heat of the mixture at constant volume is:
(a) 3 cal (b) 4 cal (c) 5 cal (d) 8 cal

98. In an experiment during the analysis of a carbon compound, 145 mL of H_2 was collected at 760 mm Hg pressure and 27°C. The mass of H_2 is nearly:
(a) 10 mg (b) 6 g (c) 12 mg (d) 12 g

[**Hint:** Apply $PV = \frac{w}{M}RT$; $1 \times 0.145 = \frac{w}{2} \times 0.0821 \times 300$]

99. The kinetic energy of N molecules of O_2 is x joule at – 123°C. Another sample of O_2 at 27°C has a kinetic energy of $2x$ joule. The latter sample contains:
(a) N molecules of O_2 (b) $2N$ molecules of O_2
(c) $\frac{N}{2}$ molecules of O_2 (d) $\frac{N}{4}$ molecules of O_2

100. A balloon filled with N_2O is pricked with a sharper point and plunged into a tank of CO_2 under the same pressure and temperature. The balloon will:
(a) be enlarged (b) shrink
(c) collapse completely (d) remain unchanged in size

101. The three states of matter are solid, liquid and gas. Which of the following statements is true about them?
(a) Gases and liquids have viscosity as a common property
(b) The molecules in all the three states possess random translational motion
(c) Gases cannot be converted into solids without passing through the liquid phase
(d) Solids and liquids have pressure as a common property

102. Strong intermolecular forces exist in:
(a) gases (b) liquids
(c) amorphous solids (d) crystalline solids

103. Association of molecules in water is due to:
(a) covalent bonding (b) hydrogen bonding
(c) ionic bonding (d) van der Waals' forces

104. Which of the following statements is wrong?
(a) Evaporation is a spontaneous process
(b) Evaporation is a surface phenomenon
(c) Vapour pressure decreases with increase of temperature
(d) The vapour pressure of a solution is always less than the vapour pressure of a pure solvent

105. Normal boiling point of a liquid is that temperature at which vapour pressure of the liquid is equal to:
(a) zero (b) 380 mm of Hg
(c) 760 mm of Hg (d) 100 mm of Hg

106. Water boils at lower temperature on high altitudes because:
(a) atmospheric pressure is low there
(b) atmospheric pressure is high there
(c) water is weakly hydrogen bonded there
(d) water in pure form is found there

107. When a student was given a viscometer, the liquid was sucked with difficulty; the liquid may be:
(a) benzene (b) toluene (c) water (d) glycerine

108. Mark the statement which is correct:
(a) surface tension of a liquid increases with temperature
(b) addition of chemicals reduces the surface tension of a liquid
(c) stalagmometer is used for measuring viscosity of the liquid
(d) viscosity of the liquid does not depend on intermolecular forces

109. With the increasing molecular mass of a liquid, the viscosity: **(Jiwaji 1990)**
(a) decreases (b) increases
(c) no effect (d) all are wrong

110. The viscosity of which liquid is the maximum?
(a) water (b) glycol
(c) acetone (d) ethanol

111. The rise of a liquid in a capillary tube is due to:
(a) viscosity (b) osmosis
(c) diffusion (d) surface tension

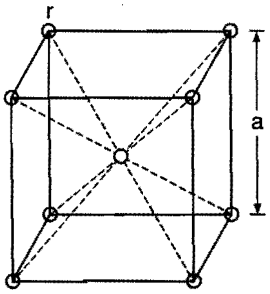
112. With increase in temperature, the fluidity of liquids:
(a) increases (b) decreases
(c) remains constant (d) may increase or decrease

113. If η_1 and η_2 are the coefficients of viscosity of two liquids, d_1 and d_2 their densities and t_1 and t_2 the flow times in Ostwald viscometer, then:
(a) $\frac{\eta_1}{\eta_2} = \frac{d_1 t_2}{d_2 t_1}$ (b) $\frac{\eta_1}{\eta_2} = \frac{d_2 t_2}{d_1 t_1}$
(c) $\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$ (d) $\frac{\eta_1}{\eta_2} = \frac{d_2 t_1}{d_1 t_2}$

114. Which of the following expressions regarding the unit of coefficient of viscosity is not true?
(a) dyne cm^{-2} sec (b) dyne cm^2 sec^{-1}
(c) Nm^{-2} sec (d) 1 poise $= 10^{-1}$ Nm^{-2} sec

115. The boiling points of water, ethyl alcohol and diethyl ether are 100°C, 78.5°C and 34.6°C respectively. The intermolecular forces will be in the order of:
(a) water > ethyl alcohol > diethyl ether
(b) ethyl alcohol > water > diethyl ether
(c) diethyl ether > ethyl alcohol > water
(d) diethyl ether > water > ethyl alcohol

116. The unit cell in a body centered cubic lattice is given in the figure. Each sphere has a radius, r and the cube has a side, a. What fraction of the total cube volume is empty. (TIFR 2010)



(a) $1-\frac{8}{3}\pi\frac{r^3}{a^3}$ (b) $\frac{4}{3}\cdot\pi\frac{r^3}{a^3}$
(c) $\frac{r}{a}$ (d) $2-\frac{4}{3}\pi\frac{r^3}{a^3}$

117. Which one is not the property of crystalline solid?
(a) Isotropic
(b) Sharp melting point
(c) A definite and regular geometry
(d) High intermolecular forces

118. The number of crystal systems known is:
(a) 7 (b) 8 (c) 6 (d) 4

119. Tetragonal crystal system has the following unit cell dimensions: [PMT (MP) 1993]
(a) $a = b = c$ and $\alpha = \beta = \gamma = 90°$
(b) $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$
(c) $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$
(d) $a = b \neq c$ and $\alpha = \beta = 90°, \gamma = 120°$

120. A match box exhibits: [PET (MP) 1993]
(a) cubic geometry (b) monoclinic geometry
(c) orthorhombic geometry (d) tetragonal geometry

121. In the crystal of CsCl, the nearest neighbours of each Cs ion are: [PET (MP) 1993]
(a) six chloride ions (b) eight Cs ions
(c) six Cs ions (d) eight chloride ions

122. How many chloride ions are there around sodium ion in sodium chloride crystal?
(a) 3 (b) 8 (c) 4 (d) 6

123. The number of atoms contained in one face-centred cubic unit cell of monoatomic substance is: [PMT (Vellore) 2006; PET (MP) 2007]
(a) 1 (b) 2 (c) 4 (d) 3

124. The number of close neighbours in a body-centred cubic lattice of identical spheres is:
(a) 4 (b) 12 (c) 6 (d) 8

125. The coordination number of each sphere in (hcc) arrangement is:
(a) 8 (b) 12 (c) 6 (d) 4

126. Bragg's law is given by the equation: (BHU 1990)
(a) $n\lambda = 2\theta \sin\theta$ (b) $n\lambda = 2d \sin\theta$
(c) $2n\lambda = d \sin\theta$ (d) $n\frac{\theta}{2} = \frac{d}{2}\sin\theta$

127. In Bragg's equation for diffraction of X-rays, 'n' represents:
(a) the number of mole (b) quantum number
(c) the order of reflection (d) Avogadro's number

128. The coordination number for an atom in a primitive cubic unit cell is:
(a) 6 (b) 8 (c) 10 (d) 12

129. The number of atoms per unit cell in a simple cubic, face-centred cubic and body-centred cubic are ...... respectively:
(a) 1, 4, 2 (b) 4, 1, 2
(c) 2, 4, 1 (d) 4, 8, 2

130. In a solid lattice, the cation has left a lattice site and is located at interstitial position, the lattice defect is: (VITEEE 2007)
(a) interstitial defect (b) vacancy defect
(c) Frenkel defect (d) Schottky defect

131. Schottky defects occur mainly in ionic compounds where : (VITEEE 2008)
(a) positive and negative ions are of different size
(b) positive and negative ions are of same size
(c) positive ions are small and negative ions are big
(d) positive ions are big and negative ions are small

132. What type of crystal defect is indicated in the diagram below?

Na^+	Cl^-	Na^+	Cl^-	Na^+	Cl^-
Cl^-		Cl^-	Na^+		Na^+
Na^+	Cl^-		Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+		Na^+

(AIEEE 2004)
(a) Frenkel defect (b) Schottky defect
(c) Interstitial defect (d) Frenkel and Schottky defects

133. In a closed packed array of N spheres, the number of tetrahedral holes is:
(a) $N/2$ (b) N
(c) $4N$ (d) $2N$

134. In a closed packed array of N spheres, the octahedral holes are:
(a) $N/2$ (b) $2N$ (c) $4N$ (d) N

135. AB crystallizes in a body centred cubic lattice with edge length 'a' equal to 387 pm. The distance between two oppositely charged ions in the lattice is: **[CBSE (PMT) 2010]**
(a) 335 pm (b) 250 pm
(c) 200 pm (d) 300 pm

[**Hint :** Distance between two oppositely charged ions

$$(r^+ + r^-) = \frac{a\sqrt{3}}{2} = \frac{387 \times \sqrt{3}}{2}$$
$$= 335.14 \text{ pm}]$$

136. Germanium or silicon becomes semiconductor due to:
(a) Schottky defect (b) chemical impurity
(c) Frenkel defect (d) none of these

137. A particular solid is very hard and has a high melting point. In solid state it is a non conductor and its melt is a conductor of electricity. Classify the solid: **[CMC Vellore (Med.) 2008]**
(a) metallic (b) molecular
(c) network (d) ionic
(e) amorphous

138. Which one has the highest melting point?
(a) Ionic crystal (b) Molecular crystal
(c) Covalent crystal (d) Metallic crystal

139. For an ionic crystal of general formula AX and coordination number 6, the value of radius ratio will be: **[PMT (MP) 1993]**
(a) greater than 0.73 (b) in between 0.73 and 0.41
(c) in between 0.41 and 0.22 (d) less than 0.22

140. The Ca^{2+} and F^- are located in CaF_2 crystal respectively at face-centred cubic lattice points and in: **(AIIMS 2006)**
(a) tetrahedral voids (b) half of tetrahedral voids
(c) octahedral voids (d) half of octahedral voids

141. In calcium fluoride structure, the coordination numbers of calcium and fluoride ions are:
(a) 8 and 4 (b) 6 and 8
(c) 4 and 4 (d) 4 and 8

142. The unit cell of a binary compound of A and B metals has a ccp structure with A atoms occupying the corners and B atoms occupying the centres of each faces of the cubic unit cell. If during the crystallisation of this alloy, in the unit cell two A atoms are missed, the overall composition per unit cell is: **[CET (J&K) 2009]**
(a) AB_6 (b) AB_4 (c) AB_8 (d) A_6B_{24}

[**Hint :** Number of atoms of $A = 6 \times \frac{1}{8} = \frac{3}{4}$

Number of atoms of $B = 6 \times \frac{1}{2} = 3$

$$A : B = \frac{3}{4} : 3 = 1 : 4$$

$\therefore$ Composition of alloy = AB_4]

143. In a solid lattice, the cation has left a lattice site and is located at an interstitial position. The lattice defect is : **[BHU (screening) 2008]**
(a) interstitial defect (b) vacancy defect
(c) Frenkel defect (d) Schottky defect

144. Which of the following statements is incorrect about amorphous solids? **(KCET 2004)**
(a) They are anisotropic
(b) They are rigid and incompressible
(c) They melt over a wide range of temperature
(d) There is no orderly arrangement of particles

145. Which defect causes decrease in the density of a crystal?
(a) Frenkel (b) Schottky
(c) Interstitial (d) F-centre

146. For tetrahedral coordination number, the radius ratio r_c^+ / r_a^- is: **(KCET 2008)**
(a) 0.732 – 1.0 (b) 0.225 – 0.414
(c) 0.414 – 0.732 (d) 0.155 – 0.225

147. What is the total number of ions present in one unit cell of sodium chloride lattice? **(EAMCET 2006)**
(a) 2 (b) 6 (c) 12 (d) 8

148. The formula for determination of density of cubic unit cell is:
(a) $\frac{a^3 N_0}{Z \times M}$ g cm^{-3} (b) $\frac{Z \times N_0}{M \times a^3}$ g cm^{-3}
(c) $\frac{a^3 \times M}{Z \times N_0}$ g cm^{-3} (d) $\frac{Z \times M}{N_0 \times a^3}$ g cm^{-3}

149. The closest-packing sequence $ABAB$ ..... represents:
(a) primitive cubic packing
(b) body-centred cubic packing
(c) face-centred cubic packing
(d) hexagonal packing

150. The closest-packing sequence $ABC\,ABC$ ..... represents:
(a) primitive cubic packing
(b) body-centred cubic packing
(c) face-centred cubic packing
(d) hexagonal packing

151. The edge length of face centred cubic cell of an ionic substance is 508 pm. If the radius of cation is 110 pm, the radius of anion is: **(AIEEE 2010)**
(a) 618 pm (b) 144 pm
(c) 288 pm (d) 398 pm

[**Hint :** Edge length = $2(r^+ + r^-)$

$$508 = 2(110 + r^-)$$
$$r^- = 144 \text{ pm}]$$

152. Close packing is maximum in the crystal lattice of:
(a) face-centred cubic (b) body-centred cubic
(c) simple-centred cubic (d) none of these

153. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is: **(IIT 1996)**
(a) 4 (b) 2 (c) 1 (d) 1/4

154. X mL of H_2 gas effused through a hole in a container in 5 second. The time taken for the effusion of the same volume of the gas specified below under identical conditions is: **(IIT 1996)**
(a) 10 second : He (b) 20 second : O_2
(c) 25 second : CO (d) 55 second : CO_2

155. The energy of a gas per litre is 300 joule. Its pressure will be:
(a) 3×10^5 N/m^2 (b) 6×10^5 N/m^2
(c) 10^5 N/m^2 (d) 2×10^5 N/m^2

156. If the universal gas constant is 8.3 joule mol^{-1} K^{-1} and the Avogadro's number is 6×10^{23}. The mean kinetic energy of the oxygen molecules at 327°C will be:

(a) 415×10^{-23} joule (b) 2490×10^{-22} joule
(c) 1245×10^{-23} joule (d) 830×10^{-22} joule

157. If increase in temperature and volume of an ideal gas is two times, then initial pressure of P changes to: **[JEE (Orissa) 2006]**

(a) $4P$ (b) $2P$ (c) P (d) $3P$

158. The average kinetic energy of one molecule of an ideal gas at 27°C and 1 atm pressure is: **(EAMCET 2009)**

(a) 900 cal K^{-1} mol^{-1}
(b) 6.21×10^{-21} J K^{-1} $molecule^{-1}$
(c) 336.7 J K^{-1} $molecule^{-1}$
(d) 3741.3 J K^{-1} mol^{-1}

[**Hint :** $\text{KE} = \frac{3}{2}\frac{R}{N}T$

$$= \frac{3}{2} \times \frac{8.314}{6.023 \times 10^{23}} \times 300$$

$$= 6.21 \times 10^{-21} \text{ J K}^{-1} \text{ molecule}^{-1}]$$

159. The respective speeds of five molecules are 2, 1.5, 1.6, 1.6 and 1.2 km/sec. The most probable speed in km/sec will be:

(a) 2 (b) 1.58 (c) 1.6 (d) 1.31

160. If one mole of a monoatomic gas $\left(\gamma = \frac{5}{3}\right)$ is mixed with one mole of diatomic gas $\left(\gamma = \frac{7}{5}\right)$, the value of γ for the mixture is:

(a) 1.40 (b) 1.50 (c) 1.53 (d) 3.07

161. The root mean square speed of hydrogen molecule of an ideal hydrogen gas kept in a gas chamber at 0°C is 3180 metre/second. The pressure on the hydrogen gas is: (density of hydrogen gas is 8.99×10^{-2} kg / m^3, 1 atmosphere = 1.01×10^5 N / m^2)

(a) 1.0 atmosphere (b) 1.5 atmosphere
(c) 2.0 atmosphere (d) 3.0 atmosphere

162. CH_4 diffuses two times faster than a gas X. The number of molecules present in 32 g of gas X is: (N is Avogadro number) **[EAMCET (Engg.) 2010]**

(a) N (b) $\frac{N}{2}$ (c) $\frac{N}{4}$ (d) $\frac{N}{16}$

[**Hint:** $\frac{r_{CH_4}}{r_{gas}} = \sqrt{\frac{m_{gas}}{m_{CH_4}}}$

$$2 = \sqrt{\frac{m_{gas}}{16}}$$

$$m_{gas} = 64$$

$$\text{Number of molecules} = \frac{w}{\text{molar mass}} \times N$$

$$= \frac{32}{64} \times N = \frac{N}{2}]$$

163. At what temperature would the rms speed of a gas molecule have twice its value at 100°C?

(a) 4192 K (b) 1492 K
(c) 9142 K (d) 2491 K

164. Find the rms speed of an argon molecule at 27°C (Molecular weight of argon = 40 gm / mol):

(a) 234.2 m / s (b) 342.2 m / s
(c) 432.2 m / s (d) 243.2 m / s

165. At a temperature T K, the pressure of 4 g argon in a bulb is P. The bulb is put in a bath having a temperature higher by 50 K than the first one. 0.8 g of argon gas had to be removed to maintain original pressure. The temperature T is equal to: **(IIT 1999)**

(a) 510 K (b) 200 K
(c) 100 K (d) 73 K

166. At 25°C and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure? **(CBSE 1999)**

(a) 265 mL (b) 365 mL (c) 569 mL (d) 621 mL

167. Which of the following solids shows electrical conduction? **(CBSE 1999)**

(a) Graphite (b) Potassium chloride
(c) Diamond (d) Sodium chloride

168. Schottky defect in solids is due to: **[PMT (Vellore) 2006; VITEEE 2006]**

(a) a pair of cation and anion vacancies
(b) occupation of interstitial site by a pair of cation and anion
(c) occupation of interstitial site by a cation
(d) occupation of interstitial site by an anion

169. Copper crystallises in face-centred cubic lattice with a unit cell length of 361 pm. What is the radius of copper atom in pm? **[CBSE (PMT) 2009; AIEEE 2009]**

(a) 108 (b) 128 (c) 157 (d) 181

[**Hint :** $a\sqrt{2} = 4r$

$$361 \times \sqrt{2} = 4r$$

$$r = 128 \text{ pm}]$$

170. The second order Bragg diffraction of X-rays with $X = 1$ Å from a set of parallel planes in a metal occurs at an angle of 60°. The distance between the scattering planes in the crystal is: **(CBSE 1998)**

(a) 0.575 Å (b) 1.00 Å
(c) 2.00 Å (d) 1.15 Å

171. According to Graham's law at a given temperature, the ratio of the rates of diffusion r_A / r_B of gases A and B is given by: **(IIT 1998)**

(a) $\frac{P_A}{P_B} \cdot \left(\frac{M_A}{M_B}\right)^{1/2}$ (b) $\frac{M_A}{M_B} \cdot \left(\frac{P_A}{P_B}\right)^{1/2}$

(c) $\frac{P_A}{P_B} \cdot \left(\frac{M_B}{M_A}\right)^{1/2}$ (d) $\frac{M_A}{M_B} \cdot \left(\frac{P_B}{P_A}\right)^{1/2}$

172. The root mean square velocity of an ideal gas at constant pressure varies with density as: **[IIT (Screening) 2000]**

(a) d^2 (b) d (c) $\sqrt{d}$ (d) $1/\sqrt{d}$

173. Match the following:

List-I	**List-II**
(A) Inversion temperature	(i) a / Rb
(B) Boyle's temperature	(ii) $8a / 27Rb$
(C) Critical temperature	(iii) $2a / Rb$

(a) A—(i), B—(ii), C—(iii) (b) A—(iii), B—(ii), C—(i)
(c) A—(iii), B—(i), C—(ii) (d) A—(i), B—(iii), C—(ii)

174. For three different gases values of van der Waals' constant 'a' and 'b' are given. What is the correct order of liquefaction of gases?

Gases	a	b
X_2	1.3	0.090
Y_2	4.1	0.023
Z_2	2.2	0.075

(a) $X_2 > Y_2 > Z_2$ (b) $Y_2 > Z_2 > X_2$
(c) $Z_2 > Y_2 > X_2$ (d) $X_2 > Z_2 > Y_2$

175. Match the following:

List-I	**List-II**
(A) P_c	(i) $3b$
(B) V_c	(ii) $8a/27bR$
(C) T_c	(iii) $a/27b^2$

(a) A—(i), B—(ii), C—(iii) (b) A—(iii), B—(ii), C—(i)
(c) A—(ii), B—(iii), C—(i) (d) A—(iii), B—(i), C—(ii)

176. By what factor does the average velocity of a gaseous molecule increases when the absolute temperature is doubled? **(DUMET 2010)**
(a) 1.4 (b) 2 (c) 2.8 (d) 4.0

177. The van der Waals' constant 'a' for different gases have been given as :

Gas	a (atm L^2 mol^{-2})
O_2	1.36
N_2	1.39
CH_4	2.25
NH_3	4.17

The gas that can be most easily liquefied is : **[JEE (Orissa) 2010]**
(a) O_2 (b) N_2 (c) CH_4 (d) NH_3

178. Match the following:

List-I	**List-II**
(A) U_{rms}/U_{av}	(i) 1.22
(B) U_{av}/U_{mp}	(ii) 1.13
(C) U_{rms}/U_{mp}	(iii) 1.08

(a) A—(iii), B—(ii), C—(i) (b) A—(i), B—(ii), C—(iii)
(c) A—(iii), B—(i), C—(ii) (d) A—(ii), B—(iii), C—(i)

179. Joule-Thomson coefficient is zero at:
(a) critical temperature (b) inversion temperature
(c) absolute temperature (d) Boyle's temperature

180. At a constant pressure, what should be the percentage increase in temperature for a 10% increase in volume?
(a) 10% (b) 11% (c) 8.9% (d) 12.5%

181. 5 g of unknown gas has pressure P at a temperature T K in a vessel. On increasing the temperature by 50°C, 1 g of the gas was given out to maintain the pressure P. The original temperature was:
(a) 73 K (b) 100 K
(c) 200 K (d) none of these

182. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, $\overline{KE}$ of CO and N_2 molecules at the same temperature? **[CBSE (PMT) 2000]**
(a) $\overline{KE}_{CO} = \overline{KE}_{N_2}$
(b) $\overline{KE}_{CO} > \overline{KE}_{N_2}$
(c) $\overline{KE}_{CO} < \overline{KE}_{N_2}$
(d) Cannot be predicted unless the volumes of the gases are given

183. Which of the following exhibits the weakest intermolecular forces? **(AIIMS 2000)**
(a) NH_3 (b) HCl (c) He (d) H_2O

184. The compressibility of a gas is less than unity at STP. Therefore: **[IIT 2000; PMT (MP) 2004]**
(a) $V_m > 22.4$ litre (b) $V_m < 22.4$ litre
(c) $V_m = 22.4$ litre (d) $V_m = 44.8$ litre

185. The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas: **(IIT 2000)**
(a) $T(H_2) = T(N_2)$ (b) $T(H_2) > T(N_2)$
(c) $T(H_2) < T(N_2)$ (d) $T(H_2) = \sqrt{7}T(N_2)$

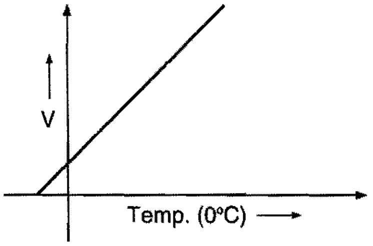
186. The kinetic energy of any gas molecule at 0°C is:
(a) zero (b) 3408 J
(c) 2 cal (d) 5.66×10^{-21} J

187. Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1; then the ratio of their respective pressures is: **(BHU 2000)**
(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 4 : 1

188. Gas equation $PV = nRT$ is obeyed by: **(BHU 2000)**
(a) only isothermal process (b) only adiabatic process
(c) both (a) and (b) (d) none of these

189. An ideal gas will have maximum density when: **(CPMT 2000)**
(a) $P = 0.5$ atm, $T = 600$ K (b) $P = 2$ atm, $T = 150$ K
(c) $P = 1$ atm, $T = 300$ K (d) $P = 1.0$ atm, $T = 500$ K

190. The following graph illustrates: **(JIPMER 2000)**



(a) Dalton's law (b) Charles' law
(c) Boyle's law (d) Gay-Lussac's law

191. 4.4 g of a gas at STP occupies a volume of 2.24 L. The gas can be: **[CET (Haryana) 2000]**
(a) O_2 (b) CO (c) NO_2 (d) CO_2

192. At 0°C and one atm pressure a gas occupies 100 cc. If the pressure is increased to one and a half time and temperature is increased by one-third of absolute temperature, then final volume of the gas will be: **(DCE 2000)**
(a) 80 cc (b) 88.9 cc (c) 66.7 cc (d) 100 cc

193. Pressure of a mixture of 4 g of O_2 and 2 g of H_2 confined in a bulb of 1 litre at 0°C is: **(AIIMS 2000)**
(a) 25.215 atm (b) 31.205 atm
(c) 45.215 atm (d) 15.210 atm

194. Density ratio of O_2 and H_2 is 16 : 1. The ratio of their rms velocities will be: **(AIIMS 2000)**
(a) 4 : 1 (b) 1 : 16 (c) 1 : 4 (d) 16 : 1

195. The rate of diffusion of a gas having molecular weight just double of nitrogen gas is 56 mL s^{-1}. The rate of diffusion of nitrogen will be: **(CPMT 2000)**

(a) 79.19 mL s^{-1} (b) 112.0 mL s^{-1}
(c) 56 mL s^{-1} (d) 90.0 mL s^{-1}

196. The density of air is 0.00130 g/mL. The vapour density of air will be: **(DCE 2000)**

(a) 0.00065 (b) 0.65 (c) 14.4816 (d) 14.56

197. If 300 mL of a gas at 27°C is cooled to 7°C at constant pressure, its final volume will be: **(AIIMS 2000)**

(a) 135 mL (b) 540 mL (c) 350 mL (d) 280 mL

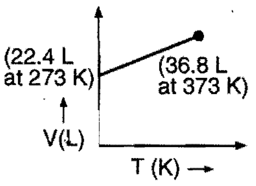
198. For an ideal gas, number of moles per litre in terms of its pressure P, gas constant R and temperature T is: **(AIEEE 2002)**

(a) PT/R (b) PRT (c) P/RT (d) RT/P

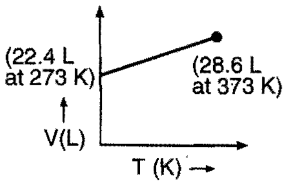
199. The van der Waals' equation reduces itself to the ideal gas equation at: **[MEE (Kerala) 2001; CBSE (PMT) 2002]**

(a) high pressure and low temperature
(b) low pressure and low temperature
(c) low pressure and high temperature
(d) high pressure alone

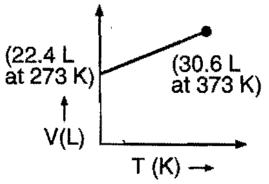
200. Which of the following volume (V), temperature (T) plots represents the behaviour of an ideal gas at one atmospheric pressure? **[IIT (Screening) 2002; PET (Kerala) 2007]**



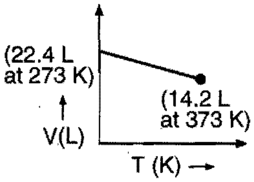
(a)



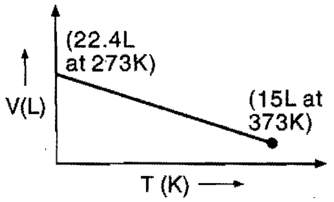
(b)



(c)



(d)



(e)

201. The following is a method to determine the surface tension of liquids: **[CET (J&K) 2007]**

(a) single capillary method (b) refractometric method
(c) polarimetric method (d) boiling point method

202. The crystalline structure of NaCl is: **[CET (J&K) 2007]**

(a) hexagonal close packing (b) face-centred cubic
(c) square planar (d) body-centred cubic

203. A crystal lattice with alternate +ve and −ve ions has radius ratio 0.524, its coordination number is: **[PMT (Manipal) 2002]**

(a) 4 (b) 3 (c) 6 (d) 12

204. The major binding force of diamond, silicon and quartz is: **[MEE (Kerala) 2002]**

(a) electrostatic force (b) electrical attraction
(c) covalent bond force (d) non-covalent bond force
(e) van der Waals' force

205. A compound is formed by elements A and B. This crystallizes in the cubic structure when atoms A are at the corners of the cube and atoms B are at the centre of the body. The simplest formula of the compound is: **(DPMT 2009)**

(a) AB (b) AB_2 (c) A_2B (d) AB_4

206. The coordination number of a metal crystallizing in a hexagonal close packed (hcp) structure is: **[PET (MP) 2004]**

(a) 6 (b) 12 (c) 8 (d) 4

207. The crystal system of a compound with unit cell dimensions $a = 0.387$, $b = 0.387$, $c = 0.504$ nm and $\alpha = \beta = 90°$ and $\gamma = 120°$ is: **(AIIMS 2004)**

(a) cubic (b) hexagonal
(c) orthorhombic (d) rhombohedral

208. The maximum number of molecules is present in: **[CBSE (PMT) 2004]**

(a) 15 L of H_2 gas at STP (b) 5 L of N_2 gas at STP
(c) 0.5 g of H_2 gas (d) 10 g of O_2 gas

209. The root mean square velocity of one mole of a monoatomic gas having molar mass M is U_{rms}. The relation between average kinetic energy (E) of the gas and U_{rms} is: **[IIT (S) 2004]**

(a) $U_{rms} = \sqrt{\frac{3E}{2M}}$ (b) $U_{rms} = \sqrt{\frac{2E}{3M}}$
(c) $U_{rms} = \sqrt{\frac{2E}{M}}$ (d) $U_{rms} = \sqrt{\frac{E}{3M}}$

210. Which of the following is not a property of liquid state? **[BHU (Pre) 2005]**

(a) Intermolecular force of attraction in a liquid is quite large
(b) All liquids accompanied by cooling on evaporation
(c) Lower the boiling point of a liquid, greater is its vapour pressure at room temperature
(d) A liquid boils at higher temperature at the top of a mountain than at the sea level

211. A certain sample of a gas has a volume of 0.2 litre measured at 1 atm pressure and 0°C. At the same pressure but 273°C, its volume will be: **[BHU (Pre) 2005]**

(a) 0.4 L (b) 0.8 L (c) 27.8 L (d) 55.6 L

212. When electrons are trapped into the crystal in anion vacancy, the defect is known as: **[BHU (Pre) 2005]**

(a) Schottky defect (b) Frenkel defect
(c) stoichiometric defect (d) F-centres

213. In the equation of state of an ideal gas $PV = nRT$, the value of the universal gas constant R would depend only on the: **(KCET 2005)**

(a) nature of the gas (b) pressure of the gas
(c) units of the measurement (d) none of these

214. If Z is the number of atoms in the unit cell that represents the closest packing sequence $ABC\ ABC\ \dots$, the number of tetrahedral voids in the unit cell is equal to: **(AIIMS 2005)**

(a) Z (b) $2Z$ (c) $\frac{Z}{2}$ (d) $\frac{Z}{4}$

215. Equation of Boyle's law is: **(DPMT 2005)**

(a) $\frac{dP}{P} = -\frac{dV}{V}$ (b) $\frac{dP}{P} = +\frac{dV}{V}$

(c) $\frac{d^2P}{P} = -\frac{dV}{dT}$ (d) $\frac{d^2P}{P} = +\frac{d^2V}{dt}$

[**Hint:** $PV = \text{constant}$

$$P\,dV + V\,dP = 0$$

$$\frac{dP}{P} = -\frac{dV}{V}\ ]$$

216. In a face-centred cubic unit cell, edge length is: **(DPMT 2005)**

(a) $\frac{4}{\sqrt{3}}r$ (b) $\frac{4}{\sqrt{2}}r$ (c) $2r$ (d) $\frac{\sqrt{3}}{2}r$

217. If v_{rms} is $30R^{1/2}$ at 27°C, then calculate the molar mass of the gas in kilogram: **(DPMT 2005)**

(a) 1 (b) 2 (c) 4 (d) 0.001

[**Hint:** $v_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

$$30R^{1/2} = \sqrt{\frac{3 \times R \times 300}{m}}$$

$$m = 0.001 \text{ kg}\ ]$$

218. The pressure exerted by 1 mole of methane in a 0.25 litre container at 300 K using van der Waals' equation (given $a = 2.253$ atm L^2 mol^{-2}, $b = 0.0428$ L mol^{-1}) is: **[JEE (Orissa) 2005]**

(a) 82.82 atm (b) 152.51 atm

(c) 190.52 atm (d) 70.52 atm

219. An ionic compound has a unit cell consisting of 'A' ions at the corners of a cube and 'B' ions on the centres of the faces of the cube. The empirical formula for this compound would be: **[AIEEE 2005; CET (Karnataka) 2009]**

(a) AB (b) A_2B

(c) AB_3 (d) A_3B

220. Which one of the following statements is not true about the effect of an increase in temperature on the distribution of molecular speeds in a gas?

(a) The most probable speed increases

(b) The fraction of the molecules with most probable speed increases

(c) The distribution becomes broader

(d) The area under the distribution curve remains the same as under the lower temperature

221. A gas can be liquefied: **(AFMC 2005)**

(a) above its critical temperature

(b) at its critical temperature

(c) below its critical temperature

(d) at any temperature

222. If the absolute temperature of a gas is doubled and the pressure is reduced to one-half, the volume of the gas will: **[PET (Kerala) 2005]**

(a) remain unchanged (b) be doubled

(c) increase fourfold (d) be halved

(e) be reduced to one-fourth

[**Hint:** Use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$]

223. To what temperature must a neon gas sample be heated to double the pressure, if the initial volume of a gas at 75°C is decreased by 15%? **[PET (Kerala) 2005]**

(a) 319°C (b) 592°C (c) 128°C (d) 60°C

(e) 90°C

[**Hint:** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{PV}{348} = \frac{2P \times 85V}{T_2 \times 100}$$

$$T_2 = 591.6 \text{ K}$$

$$t_2 = 318.6^\circ\text{C}\ ]$$

224. The surface tension of which of the following liquids is maximum? **[CBSE (Pre) 2005]**

(a) C_2H_5OH (b) CH_3OH (c) H_2O (d) C_6H_6

[**Hint:** (c) Due to hydrogen bonding, H_2O has the highest intermolecular force, hence its surface tension is also maximum.]

225. An element (with atomic mass = 250 g) crystallises in a simple cube. If the density of unit cell is 7.2 g cm^{-3}, what is the radius of the element? **[JEE (Orissa) 2006]**

(a) 1.93×10^{-6} cm (b) 1.93×10^{-8} cm

(c) 1.93×10^{-8} Å (d) 1.93×10^{-8} m

[**Hint:** $Z = \frac{l^3 \times \rho \times N_A}{M}$

$$1 = \frac{l^3 \times 7.2 \times 6.023 \times 10^{23}}{250}$$

$$l = 3.86 \times 10^{-8} \text{ cm}$$

$l = 2r$ (for simple cubic unit cell)

$$r = \frac{l}{2} = \frac{3.86 \times 10^{-8}}{2} = 1.93 \times 10^{-8} \text{ cm}\ ]$$

226. Dominance of strong repulsive forces among the molecules of the gas (Z = compressibility factor): **(AIIMS 2006)**

(a) depends on Z and indicated by $Z = 1$

(b) depends on Z and indicated by $Z > 1$

(c) depends on Z and indicated by $Z < 1$

(d) is independent of Z

[**Hint:** When $Z > 1$, the gas is less compressible than ideal gas and the repulsive forces dominate.]

227. Total volume of atoms present in a face-centred cubic unit cell of a metal is (r is atomic radius): **(AIEEE 2006)**

(a) $\frac{20}{3}\pi r^3$ (b) $\frac{24}{3}\pi r^3$ (c) $\frac{12}{3}\pi r^3$ (d) $\frac{16}{3}\pi r^3$

228. If we know the ionic radius ratio in a crystal of ionic solid, what can be known of the following? **[CET (Gujarat) 2006]**

(a) Magnetic property

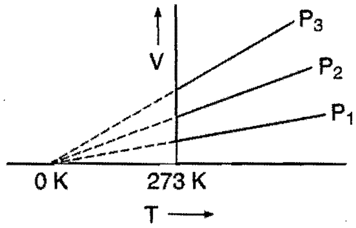
(b) Nature of chemical bond

(c) Type of defect

(d) Geometrical shape of crystal

229. If a volume containing gas is compressed to half, how many moles of gas remained in the vessel? (DCE 2006)
(a) Just double (b) Just half
(c) Same (d) More than double

230. The volume-temperature graphs of a given mass of an ideal gas at constant pressures are shown below. What is the correct order of pressures? (EAMCET 2006; AIIMS 2008)



(a) $P_1 > P_3 > P_2$ (b) $P_1 > P_2 > P_3$
(c) $P_2 > P_3 > P_1$ (d) $P_2 > P_1 > P_3$

231. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.023 \times 10^{23}$): [CBSE (Medical) 2007]
(a) 6.02×10^{16} mol^{-1} (b) 6.02×10^{17} mol^{-1}
(c) 6.02×10^{14} mol^{-1} (d) 6.02×10^{15} mol^{-1}

232. Coordination number of NaCl crystal will be: [PET (MP) 2007]
(a) 8:8 (b) 6:6 (c) 4:4 (d) 2:2

233. The unit cell of Al (molar mass 27 g mol^{-1}) has an edge length of 405 pm. Its density is 2.7 g / cm^3. The cubic unit cell is: [PET (Kerala) 2007]
(a) face-centred (b) body-centred (c) primitive
(d) edge-centred (e) simple

[Hint: $Z = \frac{a^3 \times d \times N_A}{M} = \frac{(405 \times 10^{-10})^3 \times 2.7 \times 6.023 \times 10^{23}}{27} = 4$

∴ It is a face-centred cubic unit cell.]

234. The 8 : 8 type packing is present in: (VITEEE 2007)
(a) MgF_2 (b) CsCl (c) KCl (d) NaCl

235. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is: [AIEEE 2007; EAMCET (Med.) 2010]
(a) $\frac{1}{2}$ (b) $\frac{2}{3}$ (c) $\frac{1}{3} \times \frac{273}{298}$ (d) $\frac{1}{3}$

236. Percentage of free space in a body centred cubic unit cell is: [CBSE (PMT) 2008]
(a) 34% (b) 28% (c) 30% (d) 32%

237. Which of the following statement is not correct? [CBSE (PMT) 2008]
(a) The number of carbon atoms in a unit cell of diamond is 4.
(b) The number of Bravis lattices in which a crystal can be categorized is 14.
(c) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48.
(d) Molecular solids are generally volatile.

238. If a stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively: [CBSE (PMT) 2008]
(a) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$ (b) $1a : \sqrt{3}a : \sqrt{2}a$
(c) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (d) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

[Hint: Simple unit cell, $r = a/2$

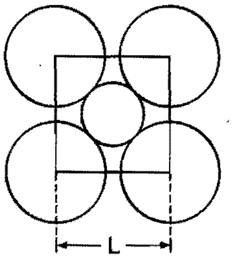
Body centred unit cell, $r = \frac{a\sqrt{3}}{4}$

Face centred unit cell, $r = \frac{a}{2\sqrt{2}}$]

239. The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is: (IIT 2009)
(a) nb (b) $\frac{an^2}{V^2}$ (c) $\frac{-an^2}{V^2}$ (d) $-nb$

240. Which is not the correct statement for ionic solids in which positive and negative ions are held by strong electrostatic attractive forces? (DCE 2009)
(a) The ratio $\frac{r^+}{r^-}$ increases as coordination number increases
(b) As the difference in size of ions increases coordination number increases
(c) When coordination number is eight, the $\frac{r^+}{r^-}$ ratio lies between 0.225 – 0.414
(d) In ionic solid of the type AX (ZnS, Wurtzite) the coordination number of Zn^{2+} and S^{2-} respectively are 4 and 4

241. The packing efficiency of the two-dimensional square unit cell shown below is: (IIT 2010)



(a) 39.27% (b) 68.02%
(c) 74.05% (d) 78.54%

[Hint: $a\sqrt{2} = 4r$

$a = 2\sqrt{2}\,r$

Packing fraction $= \frac{\text{Occupied area}}{\text{Total area}} \times 100$

$= \frac{2\pi r^2}{(2\sqrt{2}r)^2} \times 100 = 78.5\%$]

Set-2: The questions given below may have more than one correct answers

1. If force of attraction between the molecules is negligible, van der Waals' equation (for one mole) will become:
(a) $PV = RT + Pb$ (b) $P = \frac{RT}{V-b} - \frac{a}{V^2}$
(c) $PV = RT + a/V$ (d) $PV = RT - a/V$

2. van der Waals' equation for:

A. High pressure	(i) $PV = RT + Pb$
B. Low pressure	(ii) $PV = RT - a/V$
C. Force of attraction is negligible	(iii) $PV = RT + a/V$
D. Volume of molecules is negligible	(iv) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

(a) A (iv), B (ii), C (i), D (iii)
(b) A (i), B (ii), C (iii), D (iv)
(c) A (iv), B (iii), C (ii), D (i)
(d) A (iv), B (ii), C (iii), D (i)

3. van der Waals' constants for three different gases are given:

Gases	a	b
X	3.0	0.025
Y	10.0	0.030
Z	6.0	0.035

Which is correct?
(a) Maximum critical temperature—Y
(b) Most ideal behaviour—X
(c) Maximum molecular volume—Z
(d) All are correct

4. What is the ratio of mean speed of an O_3 molecule to the rms speed of an O_2 molecule at the same T ?
(a) $(3\pi/7)^{1/2}$ (b) $(16/9\pi)^{1/2}$
(c) $(3\pi)^{1/2}$ (d) $(4\pi/9)^{1/2}$

5. Boyle's law may be represented as:
(a) $\left(\frac{dP}{dV}\right)_T = K/V$ (b) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V}$
(c) $\left(\frac{dP}{dV}\right) = -\frac{K}{V^2}$ (d) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V^2}$
where, K = constant.

6. If pressure of a gas is increased by 1% when heated by 1°C, its initial temperature must be (if volume remains constant):
(a) 100 K (b) 100°C (c) 250 K (d) 250°C

7. Which of the following are not the units of gas constant, R?
(a) dyne K^{-1} mol^{-1} (b) erg deg^{-1} mol^{-1}
(c) cm^3 K^{-1} mol^{-1} (d) kPa dm^3 K^{-1} mol^{-1}

8. According to Charles' law:
(a) $V \propto \frac{1}{T}$ (b) $\left(\frac{dV}{dT}\right)_P = K$
(c) $\left(\frac{dT}{dV}\right)_P = K$ (d) $\left(\frac{1}{T} - \frac{V}{T^2}\right)_P = 0$

9. In the following statements :
(A) ideal gases are liquefied only at very low temperatures
(B) ideal gases can not be liquefied
(C) ideal gas behaviour is observed by real gases at low pressures
(D) ideal gases do not exist
The correct statements are : **(ISAT 2010)**
(a) A, B, C and D (b) A, B and C
(c) B, C and D (d) C and D

10. Which of the following relationships is/are not true?
(a) Most probable velocity = $\sqrt{\frac{2RT}{M}}$
(b) $PV = \frac{3}{2}kT$
(c) Compressibility factor $Z = \frac{PV}{nRT}$
(d) Average kinetic energy of gas = $\frac{1}{2}kT$

11. According to kinetic theory of gases: **(IIT 1991)**
(a) the pressure exerted by a gas is proportional to mean square velocity of the molecules
(b) the pressure exerted by the gas is proportional to the root mean square velocity of the molecules
(c) the root mean square velocity is inversely proportional to the temperature
(d) the mean translational KE of the molecule is directly proportional to the absolute temperature

12. A gas described by van der Waals' equation : **(IIT 2008)**
(a) behaves similar to an ideal gas in the limit of large molar volume
(b) behaves similar to an ideal gas in the limit of large pressures
(c) is characterised by van der Waals' constant that are dependent on identity of the gas but are independent of the temperature.
(d) has the pressure that is lower than the pressure exerted by the same behaving ideally.

Assertion-Reason TYPE QUESTIONS

Set-1

The questions given below consist of an **'Assertion' (A)** and the **'Reason' (R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. (A) The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.
(R) The volume occupied by the molecules of an ideal gas is zero. **(IIT 2000)**

2. (A) The pressure of a fixed amount of an ideal gas is proportional to its temperature.
(R) Frequency of collisions and their impact both increase in proportion of the square root of temperature. **(IIT 2000)**

3. (A) $C_P - C_V = R$ for an ideal gas.
   (R) $\left(\frac{\partial E}{\partial V}\right)_T = 0$ for an ideal gas.
4. (A) A lighter gas diffuses more rapidly than a heavier gas.
   (R) At a given temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density.
5. (A) On cooling, the brown colour of nitrogen dioxide disappears.
   (R) On cooling, NO_2 undergoes dimerisation resulting in the pairing of the odd electrons in NO_2.
6. (A) The value of the van der Waals' constant 'a' is larger for ammonia than for nitrogen.
   (R) Hydrogen bonding is present in ammonia.
7. (A) The Joule-Thomson coefficient for the ideal gas is zero.
   (R) There are no intermolecular attractive forces in an ideal gas.
8. (A) At 27°C, the kinetic energy of 8 gram of methane is equal to the kinetic energy of 16 gram of oxygen.
   (R) The total heat change in a reaction is the same whether the chemical reaction takes place in one single step or in several steps. **(EAMCET 2006)**
9. (A) A closed cylinder containing high pressure gas tends to rise against gravity when the gas is allowed to escape through an orifice at the bottom.
   (R) The velocity of escaping gas develops an upward thrust proportional to the area of cross-section of the orifice. **(SCRA 2007)**

   [**Hint:** Assertion is correct but reason is wrong as the velocity of escaping gas is inversely proportional to the area of cross- section of orifice.]
10. (A) Meniscus of a liquid disappears at the critical temperature.
    (R) Density of liquid and its gaseous phase become equal at the critical temperature. **[BHU (Screening) 2008]**
11. (A) Graphite is soft while diamond is hard.
    (R) Graphite has three dimensional structure while diamond has planar. **[BHU (Screening) 2008]**
12. (A) White tin is an example of tetragonal system.
    (R) For tetragonal system $a = b = c$ and $\alpha = \beta = \gamma \neq 90$.

Set-2

The questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions you are required to choose any one of the following four responses:

(a) If both (A) and (R) are true and (R) is the correct explanation for (A).
(b) If both (A) and (R) are true but (R) is not the correct explanation for (A).
(c) If (A) is true but (R) is false.
(d) If both (A) and (R) are false.

13. (A) Sulphur dioxide and chlorine are both bleaching agents.
    (R) Both are reducing agents. **(AIIMS 1994)**
14. (A) Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures (on heating or in the presence of catalysts).
    (R) In nitrogen molecule, there is extensive delocalisation of electrons. **(AIIMS 1996)**
15. (A) Noble gases can be liquefied.
    (R) Attractive forces can exist between non-polar molecules. **(AIIMS 1998)**
16. (A) Under similar conditions of temperature and pressure, O_2 diffuses 1.4 times faster than SO_2.
    (R) Density of SO_2 is 1.4 times greater than that of O_2.
17. (A) On compressing a gas to half the volume, the number of moles is halved.
    (R) The number of moles present decreases with decrease in volume.
18. (A) The plot of volume (V) *versus* pressure (P) at constant temperature is a hyperbola in the first quadrant.
    (R) $V \propto 1/P$ at constant temperature.
19. (A) At constant temperature, if pressure on the gas is doubled, density is also doubled.
    (R) At constant temperature, molecular mass of a gas is directly proportional to the density and inversely proportional to the pressure.
20. (A) If H_2 and Cl_2 enclosed separately in the same vessel exert pressures of 100 and 200 mm respectively, their mixture in the same vessel at the same temperature will exert a pressure of 300 mm.
    (R) Dalton's law of partial pressures states that total pressure is the sum of partial pressures.
21. (A) Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.
    (R) On collision, more and more molecules acquire higher speed at the same temperature.
22. (A) Compressibility factor (Z) for non-ideal gases is always greater than 1.
    (R) Non-ideal gases always exert higher pressure than expected.
23. (A) van der Waals' equation is applicable only to non-ideal gases.
    (R) Ideal gases obey the equation $PV = nRT$.
24. (A) Helium shows only positive deviations from ideal behaviour.
    (R) Helium is an inert gas.
25. (A) Gases are easily absorbed on the surface of metals, especially transition metals.
    (R) Transition metals have free valencies.
26. (A) SO_2 gas is easily liquefied while H_2 is not.
    (R) SO_2 has low critical temperature while H_2 has high critical temperature.
27. (A) Diffusion is used in the enrichment of U^{235}.
    (R) A lighter gas diffuses more rapidly than a heavier gas.
28. (A) Crystalline solids can cause X-rays to diffract.
    (R) Interatomic distance in crystalline solids is of the order of 0.1 nm. **(AIIMS 2004)**
29. (A) The effusion rate of oxygen is smaller than that of nitrogen.
    (R) Molecular size of nitrogen is smaller than that of oxygen. **(AIIMS 2004)**
30. (A) The compressibility factor for hydrogen varies with pressure with positive slope at all pressures.
    (R) Even at low pressures, the repulsive forces dominate in hydrogen gas. **(AIIMS 2005)**
31. (A) Graphite is an example of tetragonal crystal system.
    (R) For a tetragonal system $a = b \neq c, \alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. **(AIIMS 2006)**
32. (A) No compound has both Schottky and Frenkel defects.
    (R) Both defects change the density of the solid. **(AIIMS 2008)**

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (c) 2. (d) 3. (d) 4. (a) 5. (a) 6. (b) 7. (b) 8. (c)
9. (a) 10. (a) 11. (a) 12. (c) 13. (b) 14. (c) 15. (d) 16. (d)
17. (b) 18. (b) 19. (d) 20. (a) 21. (d) 22. (b) 23. (a) 24. (a)
25. (c) 26. (a) 27. (a) 28. (d) 29. (b) 30. (c) 31. (a) 32. (b)
33. (a) 34. (b) 35. (b) 36. (a) 37. (d) 38. (b) 39. (c) 40. (b)
41. (d) 42. (d) 43. (c) 44. (c) 45. (a) 46. (b) 47. (d) 48. (c)
49. (c) 50. (c) 51. (d) 52. (b) 53. (d) 54. (c) 55. (a) 56. (a)
57. (a) 58. (d) 59. (d) 60. (a) 61. (b) 62. (b) 63. (c) 64. (c)
65. (d) 66. (c) 67. (a) 68. (d) 69. (b) 70. (b) 71. (d) 72. (a)
73. (a) 74. (c) 75. (d) 76. (c) 77. (b) 78. (c) 79. (d) 80. (a)
81. (c) 82. (b) 83. (a) 84. (d) 85. (c) 86. (c) 87. (a) 88. (b)
89. (a) 90. (d) 91. (c) 92. (b) 93. (d) 94. (a) 95. (d) 96. (b)
97. (b) 98. (c) 99. (a) 100. (d) 101. (a) 102. (d) 103. (b) 104. (c)
105. (c) 106. (a) 107. (d) 108. (b) 109. (b) 110. (b) 111. (d) 112. (a)
113. (c) 114. (b) 115. (a) 116. (d) 117. (a) 118. (a) 119. (b) 120. (c)
121. (d) 122. (d) 123. (c) 124. (d) 125. (b) 126. (b) 127. (c) 128. (a)
129. (a) 130. (c) 131. (b) 132. (a) 133. (d) 134. (d) 135. (a) 136. (b)
137. (d) 138. (c) 139. (b) 140. (a) 141. (a) 142. (b) 143. (c) 144. (a)
145. (b) 146. (c) 147. (c) 148. (d) 149. (d) 150. (c) 151. (b) 152. (a)
153. (c) 154. (b) 155. (d) 156. (c) 157. (c) 158. (b) 159. (d) 160. (b)
161. (d) 162. (b) 163. (b) 164. (c) 165. (b) 166. (b) 167. (a) 168. (a)
169. (b) 170. (d) 171. (c) 172. (d) 173. (c) 174. (b) 175. (d) 176. (a)
177. (d) 178. (b) 179. (a) 180. (a) 181. (b) 182. (a) 183. (c) 184. (b)
185. (c) 186. (d) 187. (a) 188. (c) 189. (b) 190. (b) 191. (d) 192. (b)
193. (a) 194. (c) 195. (a) 196. (d) 197. (d) 198. (c) 199. (c) 200. (c)
201. (a) 202. (b) 203. (c) 204. (c) 205. (a) 206. (b) 207. (b) 208. (a)
209. (b) 210. (d) 211. (a) 212. (d) 213. (c) 214. (b) 215. (a) 216. (a)
217. (d) 218. (a) 219. (c) 220. (b) 221. (c) 222. (c) 223. (a) 224. (c)
225. (b) 226. (b) 227. (d) 228. (d) 229. (c) 230. (b) 231. (b) 232. (b)
233. (a) 234. (a) 235. (d) 236. (d) 237. (c) 238. (c) 239. (b) 240. (c)
241. (d)

- **Set–2**

1. (a) 2. (a) 3. (d) 4. (b) 5. (a) 6. (a) 7. (a , c) 8. (b, c, d)
9. (c) 10. (d) 11. (b, d) 12. (a, c)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (b) 2. (c) 3. (b) 4. (a) 5. (a) 6. (a) 7. (a) 8. (b)
9. (c) 10. (a) 11. (c) 12. (c) 13. (c) 14. (c) 15. (a) 16. (c)
17. (d) 18. (a) 19. (c) 20. (d) 21. (c) 22. (d) 23. (b) 24. (b)
25. (a) 26. (c) 27. (b) 28. (c) 29. (c) 30. (a) 31. (d) 32. (d)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions have single correct option:

1. Which of the following graphs is not a straight line for an ideal gas?

   (a) $V \to T$ (b) $T \to P$ (c) $n \to \frac{1}{T}$ (d) $n \to \frac{1}{P}$

2. The quantity (PV / k_BT) represents the:

   (a) number of molecules in the gas

   (b) mass of the gas

   (c) number of moles of the gas

   (d) translational energy of the gas

   [**Hint:** $PV = nRT$

   $$n = \frac{PV}{RT}$$

   $$\text{Number of molecules} = N_A \frac{PV}{RT} = \frac{PV}{(R/N_A)T} = \frac{PV}{k_BT}$$

   where, k_B = Boltzmann constant.]

3. 1 litre of N_2 and 7/8 litre of O_2 at the same temperature and pressure were mixed together. What is the relation between the masses of the two gases in the mixture?

   (a) $M_{N_2} = 3M_{O_2}$ (b) $M_{N_2} = 8M_{O_2}$

   (c) $M_{N_2} = M_{O_2}$ (d) $M_{N_2} = 16M_{O_2}$

   [**Hint:** $PV = \frac{M}{m} RT$

   $$P \times 1 = \frac{M_{N_2}}{28} RT \qquad \ldots (i)$$

   $$P \times \frac{7}{8} = \frac{M_{O_2}}{32} RT \qquad \ldots (ii)$$

   Dividing eq. (i) by eq. (ii), we get

   $M_{N_2} = M_{O_2}$]

4. A box is divided into two equal compartments by a thin partition and they are filled with gases X and Y respectively. The two compartments have a pressure of 250 torr each. The pressure after removing the partition will be equal to:

   (a) 125 torr (b) 500 torr (c) 250 torr (d) 750 torr

5. The density of a gas A is twice that of a gas B at the same temperature. The molecular mass of gas B is thrice that of A. The ratio of the pressures acting on A and B will be:

   (a) 6 : 1 (b) 7 : 8 (c) 2 : 5 (d) 1 : 4

   [**Hint:** $Pm = dRT$

   $$\frac{P_A m_A}{P_B m_B} = \frac{d_A RT}{d_B RT}$$

   $$\frac{P_A}{P_B} \times \frac{1}{3} = 2$$

   $P_A : P_B = 6 : 1$]

6. In the corrections made to the ideal gas equation for real gases, the reduction in pressure due to attractive forces is directly proportional to:

   (a) n / V (b) nb (c) $\frac{n^2}{V^2 b}$ (d) $\frac{n^2}{V^2}$

   [**Hint:** Pressure correction $= a \frac{n^2}{V^2}$

   $\therefore$ Pressure correction $\propto \frac{n^2}{V^2}$]

7. Which of the following conditions is favourable for liquefaction of gas?

   (a) $T > T_c; P > P_c$ (b) $T < T_c; P > P_c$

   (c) $T = T_c, P = P_c$ (d) $T = T_c, P < P_c$

8. An ideal gas of certain mass is heated in a small vessel and then in a large vessel, such that their volume remains unchanged. The P - T curves are:

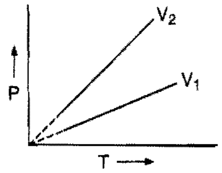
   (a) parabolic with same curvature

   (b) parabolic with different curvatures

   (c) linear with same slope

   (d) linear with different slopes

   [**Hint:**



   Straight lines with different slopes will be obtained.]

9. A spherical air bubble is rising from the depth of a lake when pressure is P atm and temperature is T K. The percentage increase in its radius when it comes to the surface of a lake will be: (Assume temperature and pressure at the surface to be respectively $2T$ K and P / 4.)

   (a) 100% (b) 50% (c) 40% (d) 200%

   [**Hint:** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; V_1 = initial volume, V_2 = final volume

   $$\frac{PV_1}{T} = \frac{P}{4} \times \frac{V_2}{2T}$$

   $$V_1 = \frac{V_2}{8}$$

   $$V_2 = 8V_1$$

   $$V_2 = 8 \times \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(8r)^3$$

   New radius $= 2r$ ($\therefore$ 100% radius will increase)]

10. It is easier to liquefy oxygen than hydrogen because:

    (a) oxygen has a higher critical temperature and lower inversion temperature than hydrogen

    (b) oxygen has a lower critical temperature and higher inversion temperature than hydrogen

(c) oxygen has a higher critical temperature and a higher inversion temperature than hydrogen

(d) the critical temperature and inversion temperature of oxygen is very low

11. 2 mole 'He' is mixed with 2 gm of H_2. The molar heat capacity at constant pressure for the mixture is:

(a) $\frac{17R}{6}$ (b) $\frac{11R}{6}$ (c) $4R$ (d) $\frac{3R}{2}$

[**Hint:** C_{P_1} for 'He' $= \frac{5}{2}R$; C_{P_2} for $H_2 = \frac{7}{2}R$

$$n_{He} = 2;\ n_{H_2} = 1$$

$$C_P = \frac{n_1 C_{P_1} + n_2 C_{P_2}}{n_1 + n_2} = \frac{2 \times \frac{5}{2}R + 1 \times \frac{7}{2}R}{3}$$

$$= \frac{17R}{6}\ ]$$

12. The van der Waals' constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.36, 1.39, 4.17 and 2.253 respectively, the gas which can be most easily liquefied is:

(a) O_2 (b) N_2 (c) NH_3 (d) CH_4

[**Hint:** The van der Waals' constant 'a' is directly proportional to the intermolecular force; hence, the gas with greater value of 'a' can be most easily liquefied.]

13. At what temperature will the molar kinetic energy of 0.3 mole of 'He' be the same as that of 0.4 mole of argon at 400 K?

(a) 700 K (b) 500 K (c) 800 K (d) 400 K

[**Hint:** $$\text{KE} = \frac{3}{2}nRT$$

$n = 1$, for molar kinetic energy

$$\left(\frac{3}{2} \times 1 \times R \times T\right)_{\text{Helium}} = \left(\frac{3}{2} \times 1 \times R \times 400\right)_{\text{Argon}}$$

$$T = 400\text{ K}\ ]$$

14. Let P_s and P be the saturated partial pressure and partial pressure of water respectively. Then the relative humidity is given by:

(a) $\frac{P_s + P}{P_s} \times 100$ (b) $\frac{P}{P_s} \times 100$

(c) $\frac{P_s}{P} \times 100$ (d) $(P + P_s) \times 100$

15. Molar volume of a monoatomic gas at P_0 and T_0 is 0.5 times its molar volume at $10P_0$ and at the same temperature. Ignoring the value of the van der Waals' constant 'a', the radius of the gas molecules is given by:

(a) $\frac{0.8RT_0}{P_0}$ (b) $\left(\frac{0.6RT_0}{P_0 N\pi}\right)^{1/3}$

(c) $\left(\frac{3RT_0}{20P_0\ N\pi}\right)^{1/3}$ (d) $\left(\frac{3RT_0}{20P_0\pi}\right)^{1/3}$

where, N = Avogadro's number

16. A vessel is filled with a mixture of oxygen and nitrogen. At what ratio of partial pressures will the mass of gases be identical?

(a) $P(O_2) = 0.785P(N_2)$ (b) $P(O_2) = 8.75P(N_2)$

(c) $P(O_2) = 11.4P(N_2)$ (d) $P(O_2) = 0.875P(N_2)$

[**Hint:** $$PV = nRT$$

$$PV = \frac{w}{m}RT$$

$$P_{O_2}V = \frac{w}{32}RT \quad \text{...(i)}$$

$$P_{N_2}V = \frac{w}{28}RT \quad \text{...(ii)}$$

$$\frac{P_{O_2}}{P_{N_2}} = \frac{28}{32}$$

$$P_{O_2} = 0.875P_{N_2}\ ]$$

17. KCl crystallises in the same type of lattice as does NaCl. Given that $r_{Na^+}/r_{Cl^-} = 0.55$ and $r_{K^+}/r_{Cl^-} = 0.74$. Calculate the ratio of the side of the unit cell for KCl to that of NaCl

[PET (Kerala) 2008]

(a) 1.123 (b) 0.891 (c) 1.414 (d) 0.414

(e) 1.732

[**Hint:** $$\frac{r_{Na^+}}{r_{Cl^-}} = 0.55, \quad \frac{r_{K^+}}{r_{Cl^-}} = 0.74$$

$$\frac{r_{Na^+}}{r_{Cl^-}} + 1 = 1.55 \quad \text{...(1)}$$

$$\frac{r_{K^+}}{r_{Cl^-}} + 1 = 1.74 \quad \text{...(2)}$$

Dividing (2) by (1)

$$\frac{1.74}{1.55} = \frac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} \times \frac{r_{Cl^-}}{r_{Na^+} + r_{Cl^-}}$$

$$\frac{r_{K^+} + r_{Cl^-}}{r_{Na^+} + r_{Cl^-}} = 1.122]$$

18. 8 : 8 coordination of CsCl is found to change into 6 : 6 coordination:

(a) on increasing the pressure

(b) on increasing the temperature

(c) on decreasing the pressure

(d) on decreasing the temperature

19. An alloy of Cu, Ag and Au is found to have copper constituting ccp lattice. If silver atoms occupy the edge-centres and gold is present at body-centre, the alloy has the formula:

(a) Cu_4Ag_2Au (b) Cu_4Ag_4Au

(c) Cu_4Ag_3Au (d) $CuAgAu$

[**Hint:** In ccp arrangement, Cu atoms occupy the corners and face-centres.

$$\therefore \text{Number of Cu atoms} = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$\text{Number of silver atoms} = \text{Number of edge-centres} \times \frac{1}{4}$$

$$= 12 \times \frac{1}{4} = 3$$

Number of gold atoms = 1 (at body-centre)

$\therefore$ Formula of alloy = Cu_4Ag_3Au]

20. The anions (A) form hexagonal closest packing and atoms (M) occupy only two-third of octahedral voids in it; then the general formula of the compound is:

(a) MA (b) A_2 (c) M_2A_3 (d) M_3A_2

21. In a face-centred cubic of A and B-atoms in which A atoms are at the corners of the unit cell and B-atoms at the face-centres, one of the A-atoms is missing from one corner in unit cell. The simplest formula of the compound is:
(a) A_7B_3 (b) AB_3 (c) A_7B_{24} (d) A_8B_{21}

[**Hint:** Number of A atoms $= \frac{1}{8} \times 7 = \frac{7}{8}$

Number of B atoms $= 6 \times \frac{1}{2} = 3$

$$A : B = \frac{7}{8} : 3 = 7 : 24$$

Molecular formula $= A_7B_{24}$]

22. Select the incorrect statement(s):
(a) Schottky defect is not shown by CsCl
(b) Frenkel defect is shown by ZnS
(c) hcp and ccp structures have different coordination numbers
(d) at high pressure, the coordination number increases

23. Select the incorrect statement:
(a) In CsCl unit cell, $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2} l$
(b) In NaCl unit cell, $r_{Na^+} + r_{Cl^-} = \frac{l}{2}$
(c) In CsCl unit cell, 68% space is void
(d) In NaCl unit cell, 26% space is void

24. The ionic radii of Rb^+ and I^- are 1.46 and 2.16 Å respectively. The most probable type of structure exhibited by it is:
(a) CsCl (b) NaCl (c) ZnS (d) CaF_2

25. Perovskite is a mineral with the formula $CaTiO_3$. Which of the positive ions in the crystal is more likely to be packed in the octahedral holes?
(a) Ti^{4+} (b) Ti^{2+} (c) Ca^{2+} (d) O_2^+

26. Which of the following is incorrect ?[**BHU (Screening) 2008**]
(a) A real gas behaves like ideal gas over a wide range of pressure (~ 100 atm) at Boyle point
(b) A real gas behaves like an ideal gas over a wide range of pressure (~ 100 atm) at critical temperature of the gas.
(c) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for an ideal gas
(d) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$ for a real gas obeying van der Waal's equation

[Hint: A real gas cannot behave like ideal gas at critical temperature.]

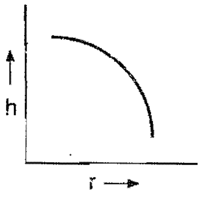
27. The number of atoms in 100 g of an fcc crystal with density $d = 10 \text{ g/cm}^3$ and cell edge as 200 pm is equal to:
(a) 3×10^{25} (b) 5×10^{24} (c) 1×10^{25} (d) 2×10^{25}

28. In a ccp structure, the:
(a) first and third layers are repeated
(b) first and fourth layers are repeated
(c) second and fourth layers are repeated
(d) first, third and sixth layers are repeated

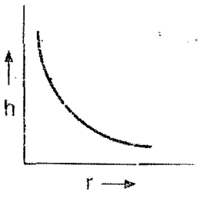
29. Which of the following compounds represents an inverse 2 : 3 spinel structure?
(a) $Fe^{III}[Fe^{II}Fe^{III}]O_4$ (b) PbO_2
(c) Al_2O_3 (d) Mn_3O_4

30. A solid solution of $CdBr_2$ in AgBr contains:
(a) Schottky defects
(b) Frenkel defects
(c) Colour centres
(d) Frenkel as well as Schottky defects

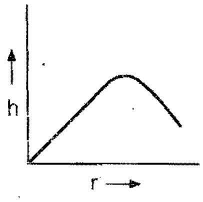
31. Which of the following correctly represents the relation between capillary rise 'h' and capillary radius 'r' ?



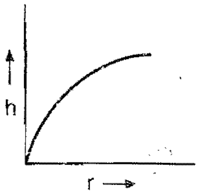
(a)



(b)



(c)



(d)

[**Hint:** Capillary rise decreases with increase in the radius of tube.]

32. There is a depression in the surface of the liquid in a capillary when:
(a) the cohesive force is smaller than the adhesive force
(b) the cohesive force is greater than the adhesive force
(c) the cohesive and adhesive forces are equal
(d) none of the above is true

[**Hint:** Depression in the surface takes place when intermolecular attraction force of liquid called cohesive force dominates the force of attraction between the liquid and the capillary called adhesive force.]

33. Surface tension does not vary with:
(a) temperature (b) vapour pressure
(c) the size of surface (d) concentration

34. Which among the following has the least surface tension?
(a) Benzene (b) Acetic acid
(c) Diethyl ether (d) Chlorobenzene

35. The SI unit of the coefficient of viscosity is:
(a) $N\,s^{-1}\,m^{-1}$ (b) $N\,s\,m^{-2}$ (c) $N\,s^{-2}\,m^{-2}$ (d) $N\,s^{-1}\,m^{-2}$

36. Compressibility factor for a gas under critical condition is:
(a) 3/8 (b) 8/3 (c) 1 (d) 1/4

[**Hint:** $P_cV_c = \frac{3}{8} RT_c$

$$Z = \frac{P_cV_c}{RT_c} = \frac{3}{8}$$]

37. Critical temperature of H_2O is greater than that of O_2 because H_2O molecules have:
(a) greater dipole moment
(b) V-shape
(c) lesser number of electrons
(d) it has only sigma bonds

38. For van der Waals' constants 'a' and 'b', the unit of the ratio $\frac{a}{b}$ will be:
(a) atm litre^{-1} (b) litre-atm mol^{-1}
(c) litre-atm mol^{-2} (d) litre mol^{-1}

[**Hint:** $P_{\text{correction}} = \frac{an^2}{V^2}$ Unit of a = atm litre^2 mol^{-2}

$V_{\text{correction}} = nb$ Unit of b = litre mol^{-1}

$$\text{Unit of}\left(\frac{a}{b}\right) = \frac{\text{atm litre}^2\ \text{mol}^{-2}}{\text{litre mol}^{-1}}$$
$$= \text{atm litre mol}^{-1}\ ]$$

39. Select the correct order of the following temperatures:
Boyle temp. (A) Critical temp. (B) Inversion temp. (C)
(a) $A > C > B$ (b) $B > A > C$
(c) $A > B > C$ (d) $C > A > B$

[**Hint:** T_B (Boyle temp.) $= \frac{a}{R_b}$; T_i (Inversion temp.) $= \frac{2a}{Rb}$

T_c (Critical temp.) $= \frac{8a}{27Rb}$

$\therefore$ $T_i > T_B > T_c$]

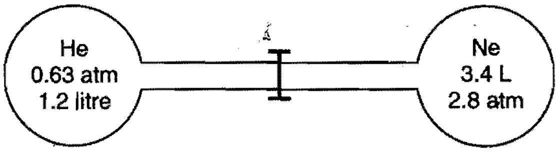
40. The gas equation for a real gas is:
$$P(V-b) = RT$$
Here, the parameter 'b' is van der Waals' constant. The graph of pressure against temperature (isochore) will give straight line of slope:
(a) zero (b) $\frac{R}{(V-b)}$ (c) R/P (d) negative

41. A crystalline solid is made of X, Y and Z elements. Atoms of X form fcc packing; atoms of Y occupy octahedral voids while atoms of Z occupy tetrahedral voids. What will be the simplest formula of solid if atoms along one body diagonal are removed:
(a) $X_5Y_4Z_8$ (b) XYZ (c) $X_8Y_4Z_5$ (d) X_2YZ

[**Hint:** Number of atoms of X (at packing site, *i.e.*, at corners and face-centres)
$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$
Number of atoms of $Y = 4$
Number of atoms of $Z = 8$
Along one body diagonal there will be two X atoms, one Y atom and two Z atoms are found and are removed.
Number of atoms of X will be $= 4 - \frac{1}{8} \times 2 = \frac{15}{4}$
Number of atoms of Y will be $= 4 - 1 = 3$
Number of atoms of Z will be $= 8 - 2 = 6$
$$X : Y : Z$$
$$\frac{15}{4} : 3 : 6$$
$$5 : 4 : 8$$
$\therefore$ Simplest formula will be $X_5Y_4Z_8$.]

42. Which of the following pattern has void fraction of 0.26 ?
(a) *AAAA*... (b) *ABABAB*...
(c) *ABCABCABC*... (d) *ABCCBAABC*...

43. Two gas bulbs are connected by a thin tube. Calculate the partial pressure of helium after the connective valve is opened at a constant temperature of 27°C :



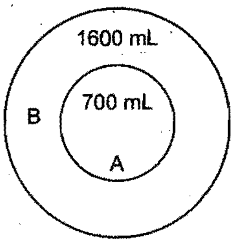
(a) 1 atm (b) 0.328 atm (c) 1.64 atm (d) 0.166 atm

[**Hint :** $n_{\text{He}} = \frac{PV}{RT} = \frac{0.63 \times 1.2}{0.0821 \times 300} = 0.03$
$$n_{\text{Ne}} = \frac{2.8 \times 3.4}{0.0821 \times 300} = 0.39$$
$$x_{\text{He}} = \frac{n_{\text{He}}}{n_{\text{He}} + n_{\text{Ne}}} = \frac{0.03}{0.03 + 0.39} = 0.0714$$
Total pressure after connecting the bulbs will be :
$$P_1V_1 + P_2V_2 = P_R\ (V_1 + V_2)$$
$$0.63 \times 1.2 + 2.8 \times 3.4 = P_R\ (1.2 + 3.4)$$
$$P_R = 2.33 \text{ atm}$$
$$P_{\text{He}} = x_{\text{He}} \times P_R = 0.0714 \times 2.33 = \mathbf{0.166\ atm}]$$

44. Ammonia gas at 76 cm Hg pressure was connected to a manometer. After sparking in the flask, ammonia is partially dissociated as follows:
$$2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$$
the level in the mercury column of the manometer was found to show the difference of 18 cm. What is the partial pressure of $H_2(g)$ at equilibrium?
(a) 18 cm Hg (b) 9 cm Hg
(c) 27 cm Hg (d) 24 cm Hg.

[**Hint :**
$$\begin{array}{llll} & 2NH_3\,(g) & \rightleftharpoons N_2(g) & +\ 3H_2(g) \\ t_0 & 76 & 0 & 0 \\ t_{\text{eq.}} & 76-2x & x & 3x \end{array}$$
Total pressure after dissociation $= 76 - 2x + x + 3x = 76 + 2x$
Increase in pressure $= 2x = 18$
$x = 9$ cm.
Partial pressure of $H_2 = 3x = 27$ cm]

45. Two balloons A and B are taken at 300K. Maximum capacity of balloon A and balloon B are 800 mL and 1800 mL respectively. When the balloon system is heated; which one will burst first?



(a) Inner balloon (A)
(b) Outer balloon (B)
(c) Both balloons simultaneously
(d) Cannot be predicted

[Hint : For balloon A :

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}$$

$$\frac{700}{300}=\frac{800}{T_2}$$

$$T_2 = 342.85\ \text{K}$$

For balloon B :

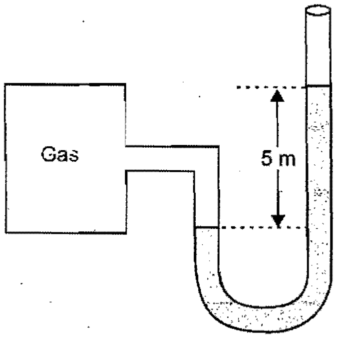
$$\frac{V_1}{T_1}=\frac{V_2}{T_2}$$

$$\frac{1600}{300}=\frac{1800}{T_2}$$

$$T_2 = 337.5\ \text{K}$$

Thus, outer balloon B will burst first.]

46.



A gas jar of 10 litre volume filled with O_2 at 300 K is connected to glycerine manometer. The manometer shows 5 m difference in the level as shown in figure. What will be the number of moles of O_2 in the gas jar ?
(Give $d_{\text{glycerine}} = 2.72$ g/mL; $d_{\text{mercury}} = 13.6$ g/mL).

(a) 0.64 mol (b) 0.4 mol (c) 0.94 mol (d) 0.36 mol

[Hint : $(h \times d \times g)_{\text{Hg}} = (h \times d \times g)_{\text{glycerine}}$

$$(h \times 13.6)_{\text{Hg}} = (5 \times 2.72)_{\text{glycerine}}$$

$$h_{\text{Hg}} = 1\text{m}$$

$$P_{\text{gas}} = (1 + 0.76)\ \text{m}$$

$$= 1760\ \text{mm Hg}$$

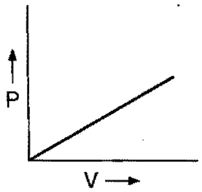
$$PV = nRT$$

$$\frac{1760}{760} \times 10 = n \times 0.0821 \times 300$$

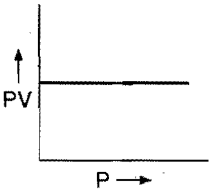
$$n = 0.94\ \text{mol}]$$

Following questions may have more than one correct options:

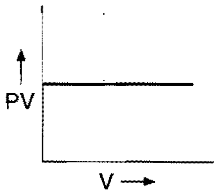
1. Which of the following graphs represent Boyle's law?



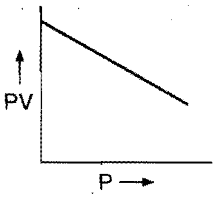
(a)



(b)



(c)



(d)

2. Which of the following equation(s) is/are correct on the basis of ideal gas equation?
   (a) $PV = \frac{N}{N_A} RT$ (b) $PV = Nk_BT$
   (c) $PV = \frac{d}{m} RT$ (d) $PV = dRT$
   where, N = number of molecules, N_A = Avogadro's number, k_B = Boltzmann constant
3. A gas can be easily liquefied:
   (a) when its inversion temperature equals the Boyle's temperature
   (b) under reversible adiabatic expansion
   (c) under pressure when it is cooled below the critical temperature
   (d) at low pressure and above critical temperature
   [Hint: (i) Reversible adiabatic expansion lowers the temperature hence facilitates the liquefaction of gas. (ii) A gas can be liquefied below the critical temperature by increasing the pressure.]
4. Which of the following quantities are same for all ideal gases at the same temperature?
   (a) The kinetic energy of 1 mole
   (b) The kinetic energy of 1 g
   (c) The number of molecules in 1 mole
   (d) The number of molecules in 1 g
   [Hint: (i) 1 mole of a gas always contains 6.023×10^{23} molecules.
   (ii) Kinetic energy of ideal gases depends only on temperature.]
5. Which of the following statements are correct?
   (a) Helium diffuses at a rate 8.65 times as much as CO does
   (b) Helium diffuses at a rate 2.65 times as fast as CO does
   (c) Helium diffuses at a rate of 4 times faster than CO_2
   (d) Helium diffuses at a rate 4 times as fast as SO_2 does
6. The viscosity of a liquid molecule depends on:
   (a) the volume of the liquid
   (b) the temperature of the liquid
   (c) the surface area of the liquid
   (d) the structure of the molecule
7. Viscosity is the property of:
   (a) liquids (b) gases (c) solids (d) all of these
8. Which of the following crystals have 6 : 6 coordination?
   (a) NH_4I (b) MgO (c) MnO (d) ZnS
9. Which of the following compounds represent a normal 2 : 3 spinel structure?
   (a) $Mg^{II}\,Al_2^{III}O_4$ (b) $Co^{II}\,(Co^{III})_2O_4$
   (c) $Zn(TiZn)\ O_4$ (d) $Ni(CO)_4$
10. Which type of crystals contain only one Bravis lattice?
    (a) Hexagonal (b) Triclinic
    (c) Rhombohedral (d) Monoclinic
11. At which temperature, is a ferrimagnetic solid converted to a ferromagnetic solid?

(a) 850 K (b) 300 K (c) 400 K (d) 600 K

12. In NaCl structure, all the:

(a) octahedral sites are occupied
(b) tetrahedral sites are unoccupied
(c) octahedral as well as tetrahedral sites are unoccupied
(d) octahedral as well as tetrahedral sites are occupied

13. The density of a certain solid *AB* (formula mass = 119) is 2.75 g/cm^3. The edge of the unit cell is 654 pm long. What is/are true about the solid *AB*?

(a) It has bcc unit cell
(b) There are four constituents per unit cell
(c) Unit cell constituted by anion is fcc
(d) Structure is similar to ZnS

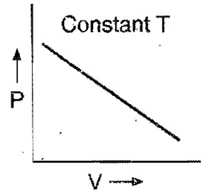
[**Hint:** $Z = \dfrac{a^3 \times d \times N}{M}$

$$= \frac{(654 \times 10^{-10})^3 \times 2.75 \times 6.023 \times 10^{23}}{119} \approx 4]$$

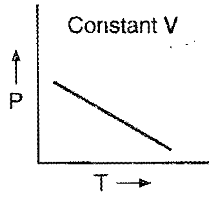
14. The unit cell of a crystalline solid is bounded by f (faces), e (edges) and c (interfacial angle). Which of the following relations is correct?

(a) $f + e = c + 2$ (b) $f + c = e + 2$
(c) $c + e = f + 2$ (d) None of these

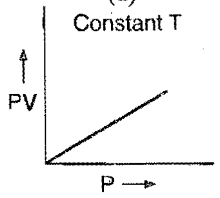
15. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K)
[PMT (Kerala) 2007; CMS Vellore (Med.) 2008; CET (Punjab) 2008]



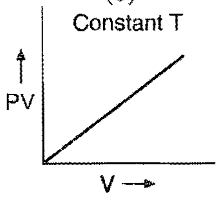
(a)



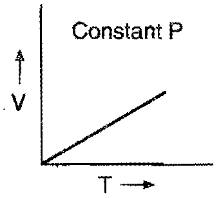
(b)



(c)



(d)

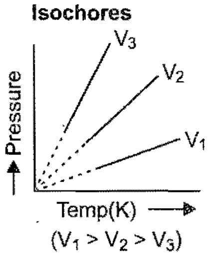


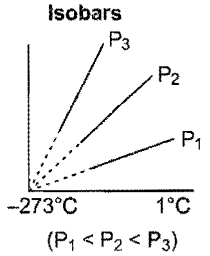
(e)

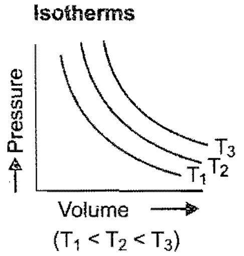
16. Molar mass of Ne atom is ten times of H_2 molecule. Which of the following statement is/are true?

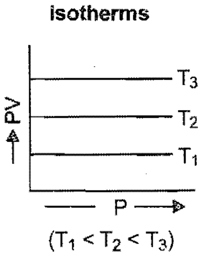
(a) Both these gases have same Kinetic Energy at 27°C
(b) H_2 molecule will travel 10 times faster than Ne atom at same temperature
(c) Pressure of 1 mol Ne atom and 1 mole H_2 molecules will be same
(d) Ten mole of H_2 and 1 mole of Ne will have same volume at a temperature of 27°C

17. Select the correct conditions indicated below the following plots:

(a)


(b)


(c)


(d)


Answers

Single correct option

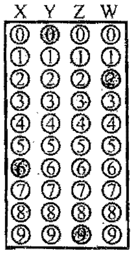
1. (d) 2. (a) 3. (c) 4. (c) 5. (a) 6. (d) 7. (b) 8. (d)
9. (a) 10. (c) 11. (a) 12. (c) 13. (d) 14. (b) 15. (c) 16. (d)
17. (a) 18. (b) 19. (c) 20. (c) 21. (c) 22. (a, c) 23. (c) 24. (b)
25. (a) 26. (c) 27. (b) 28. (b) 29. (a) 30. (d) 31. (b) 32. (b)
33. (c) 34. (c) 35. (b) 36. (a) 37. (a) 38. (b) 39. (d) 40. (b)
41. (a) 42. (c) 43. (d) 44. (c) 45. (b) 46. (c)

One or more than one correct options

1. (b, c) 2. (a, b) 3. (b, c) 4. (a, c) 5. (a, d) 6. (b, d) 7. (a, b) 8. (a, b)
9. (a, b) 10. (a, b, c) 11. (a) 12. (a, b) 13. (b, c) 14. (b) 15. (e) 16. (a, b, c)
17. (a, c, d)

Integer Answer TYPE QUESTIONS

This section contains 14 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. A substance $AxBy$ crystallises in a face centred cubic lattice. Atoms 'A' occupy each corner of unit cell and atoms of 'B' occupy centre of each face of the cube. Total number of atoms of A and B in one unit cell will be ....
2. In KBr crystal structure, the number of second nearest neighbour of K^+ ions are ....
3. Density of lithium atom is 0.53 g/cm^3. The edge length of Li is 3.5 Å. The number of lithium atoms in a unit cell will be .... (Atomic mass of lithium is 6.94)
4. A cubic solid is made up of two elements P and Q. Atoms of Q are present at the corners of the cube and atoms of P at the body centre. The coordination number of P and Q will be ....
5. If there are 3 moles of atoms present in the packing of pattern $ABC\,ABC\,ABC$ ..... . The number of moles of tetrahedral voids is equal to ....
6. The number of atoms in HCP unit cell is ....
7. How many effective Na^+ ions are present in rock salt NaCl? If ions along one axis joining opposite faces are removed?
8. How many moles of SO_2 will occupy a volume of 10 litre at a pressure of 15 atm and temperature 624 K? ($a = 6.71$ atm L^2 mol^{-2}; $b = 0.0564$ litre mol^{-1})
9. 3.2 g of oxygen and 0.2 g of hydrogen are placed in 1.12 litre flask at 0°C. The total pressure in atm of the gas mixture will be......... .
10. A mixture of non reacting gases exert a pressure of 5 atm. If one of the gases occupy 40% volume of the mixture, what would be its partial pressure in atm?
11. A gas is found to have the formula $(C_3O_2)_n$. Its vapour density is 34. The value of n will be ....
12. The weight of hydrogen gas obtained from 42 g of CaH_2 by treatment with water is .... gm.
13. The stop cock containing two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 60 atm respectively is opened. What is the final pressure in atm if the temperature remains the same?
14. At 400 K, the root mean square (rms) speed of gas X (molecular mass = 40) is equal to the most probable speed of gas Y at 60 K. The molecular mass of the gas Y is .... **(IIT 2009)**

[Hint : $\left(\sqrt{\frac{3RT}{m}}\right)_X = \left(\sqrt{\frac{2RT}{m}}\right)_Y$

$$\sqrt{\frac{3R400}{40}} = \sqrt{\frac{2R60}{m}}$$

$$\sqrt{30} = \sqrt{\frac{4\times 30}{m}}$$

$m = 4$]

Answers

1. (4) **2.** (12) **3.** (2) **4.** (8) **5.** (6) **6.** (6) **7.** (3) **8.** (3)
9. (4) **10.** (2) **11.** (1) **12.** (4) **13.** (7) **14.** (4)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

The gases which strictly follow the general equation ($PV = nRT$) are called ideal or perfect gases. Actually, there is no gas which is perfect or ideal. A real gas is one which actually exists, whether it obeys gas laws strictly or not. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc. The most easily liquefiable and highly soluble gases such as ammonia, carbon dioxide, sulphur dioxide show large deviations.

A very convenient method of studying deviation of real gases from ideal behaviour is through a compressibility factor (Z).

$$Z = \frac{PV}{nRT}$$

(i) $Z = 1$, *for ideal gases.*

(ii) $Z \neq 1$, *for real gases.*

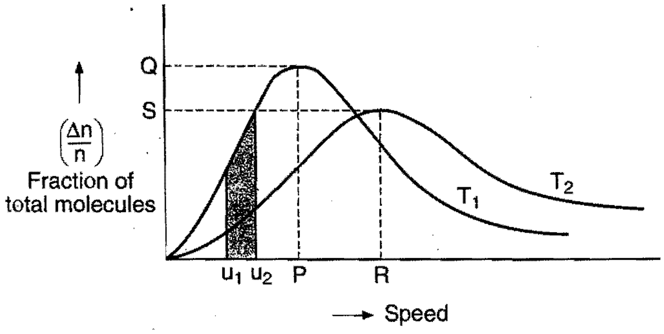
Answer the following questions:

1. Consider the equation $Z = \frac{PV}{nRT}$; which of the following statements is correct?
   (a) When $Z > 1$, real gases are easier to compress than the ideal gas
   (b) When $Z = 1$, real gases get compressed easily
   (c) When $Z > 1$, real gases are difficult to compress
   (d) When $Z = 1$, real gases are difficult to compress
2. The compressibility of a gas is less than unity at STP, therefore:
   (a) $V_m > 22.4$ L (b) $V_m < 22.4$ L
   (c) $V_m = 22.4$ L (d) $V_m = 44.8$ L
3. At low pressure, the van der Waals' equation is reduced to:
   (a) $Z = \frac{PV_m}{RT} = 1 - \frac{aP}{RT}$ (b) $Z = \frac{PV_m}{RT} = 1 + \frac{bP}{RT}$
   (c) $PV_m = RT$ (d) $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RT}$
4. At Boyle's temperature, compressibility factor Z for a real gas is:
   (a) $Z = 1$ (b) $Z = 0$
   (c) $Z > 1$ (d) $Z < 1$
   [**Hint:** At Boyle's temperature, the real gas behaves like an ideal gas.]
5. The behaviour of a real gas is usually depicted by plotting compressibility factor Z *versus* pressure P at a constant temperature. At high temperature and pressure, Z is usually more than one. This fact can be explained by van der Waals' equation when:
   (a) the constant 'a' is negligible but not 'b'
   (b) the constant 'b' is negligible but not 'a'
   (c) both the constants 'a' and 'b' are negligible
   (d) both the constants 'a' and 'b' are not negligible
6. The units of compressibility factor are:
   (a) atm L^{-1} (b) atm^{-1}
   (c) L^{-1} (d) unitless

• Passage 2

The gas molecules randomly move in all directions and collide with each other and with the wall of the container. It is difficult to determine the speed of an individual molecule but it has become possible to work out the distribution of molecules among different molecular speeds. This is known as Maxwell Boltzmann distribution.

Consider the following graph about Maxwell's distribution of speeds at two different temperatures T_1 and T_2:



Answer the following questions:

1. In the above graph the point 'P' refers to:
   (a) root mean square speed at T_1
   (b) average speed at T_1
   (c) most probable speed at T_1
   (d) highest possible speed at T_1
2. The shaded area represents:
   (a) number of molecules having speed between u_1 and u_2
   (b) number of molecules having speed less than the most probable speed
   (c) number of molecules having v_{rms} at T_1
   (d) fraction of total molecules having average speed
3. The point Q refers to:
   (a) number of molecules with speed at P
   (b) fraction of total molecules with speed at P
   (c) root mean square speed
   (d) total kinetic energy of molecules at P
4. Relation between T_1 and T_2 is:
   (a) $T_1 = T_2$ (b) $T_1 > T_2$
   (c) $T_1 < T_2$ (d) cannot be predicted
5. Total area under the curve at T_1 is:
   (a) equal to that under curve at T_2
   (b) less than that under curve at T_2
   (c) greater than that under curve at T_2
   (d) can be greater or less than that under curve at T_2, depending on the nature of the gas
6. Select the correct statement(s):
   (a) Most probable speed increases with increase in temperature
   (b) Fraction of total molecules with most probable velocity decreases with increase in temperature
   (c) Area under the curve increases with increase in the temperature
   (d) none of the above

7. The curve has which of the following characteristics?
   (i) It has symmetrical distribution of molecules against molecular velocity.
   (ii) The area under the curve gives the total number of molecules.
   (iii) The maxima of the curve shifts towards right as the temperature is raised.
   (iv) The area under the curve is independent of temperature.
   Select the correct statements from the codes given below:
   (a) (i), (ii) (b) (i), (ii) and (iii)
   (c) (ii), (iii) and (iv) (d) all are correct

• Passage 3

The essential conditions for liquefaction of gases were discovered by Andrews in 1869 as a result of his study of pressure-volume-temperature relationship for CO_2. It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature (T_c). The pressure required to liquefy a gas at this temperature is called the critical pressure (P_c). The volume occupied by one mole of the substance at the critical temperature and pressure is called critical volume. Critical constants are related with van der Waals' constant as follows:

$$V_c = 3b,\ P_c = \frac{a}{27b^2},\ T_c = \frac{8a}{27Rb}$$

Answer the following questions:

1. The relationship between P_c, V_c and T_c is:
   (a) $P_cV_c = RT$ (b) $P_cV_c = 3RT_c$
   (c) $P_cV_c = \frac{3}{5}RT_c$ (d) $P_cV_c = \frac{3}{8}RT_c$
2. Which of the following parameters is three times the van der Waals' constant 'b'?
   (a) Critical volume (b) Critical temperature
   (c) Vapour density (d) Critical pressure
3. The critical temperature of:
   (a) a substance means the temperature above which the substance is in vapour form
   (b) a gas is the temperature below which it can be liquefied by application of pressure
   (c) water is 100°C
   (d) none of the above
4. The pressure required to liquefy a gas at the critical temperature is called:
   (a) reduced pressure (b) critical pressure
   (c) vapour pressure (d) atmospheric pressure
5.

Gases	A	B	C	D
P_c (atm)	2.2	14	35	45
T_c (K)	5.1	33	127	140

   Which of the above gases cannot be liquefied at 100 K and 50 atm?
   (a) D only (b) A only
   (c) A and B (d) C and D
6. At critical point, the meniscus between liquid and vapour disappears due to:
   (a) zero refractive index (b) zero surface tension
   (c) zero viscosity (d) zero critical temperature
7. Gas A can be liquefied at room temperature by applying pressure but gas B cannot. This reflects:
   (a) critical temperature of B is less than that of A
   (b) critical temperature of B is greater than that of A
   (c) A and B have critical temperature greater than room temperature
   (d) critical temperatures of both are equal
8. The values of critical volumes of four gases A, B, C and D are 0.025 L, 0.312 L, 0.245 L and 0.432 L respectively. The gas with larger diameter will be:
   (a) A (b) D
   (c) B (d) C
   [**Hint:** $V_c = 3b = 3 \times 4N \times \frac{4}{3}\pi r^3$]

• Passage 4

Kinetic theory of gases is a generalization offered by Maxwell, Boltzmann, Clausius, etc., to explain the behaviour of ideal gases. This theory assumes that ideal gas molecules neither attract nor repel each other. Average kinetic energy of gas molecules is directly proportional to the absolute temperature. A gas equation called kinetic gas equation was derived on the basis of kinetic theory.

$$PV = \frac{1}{3}mnv^2$$

Answer the following questions:

1.

Gas	Density
A	0.82 g L^{-1}
B	0.26 g L^{-1}
C	0.51 g L^{-1}

   Pick up the correct statement/statements:
   1. gas A will tend to lie at the bottom.
   2. the number of atoms of various gases A, B and C are same.
   3. the gases will diffuse to form homogeneous mixture.
   4. average kinetic energy of each gas is same.
   (a) 2, 3 (b) 1, 4 (c) 1 (d) 3, 4
2. Select the incorrect statement(s) about the real gases:
   1. The molecules attract each other.
   2. They show deviation from Boyle's and Charles' law.
   3. Volume of gas molecules are negligible.
   4. The molecules have negligible mass.
   (a) 2, 3 (b) 1, 4 (c) 1 (d) 3, 4
3. The average kinetic energy per molecule of an ideal gas is equal to:
   (a) 0.5 kJ (b) $0.5RT$
   (c) $1.5kT$ (d) $1.5RT^2$
4. Which of the following do not pertain to the postulates of kinetic theory of gases?
   (a) The gas molecules are perfectly elastic
   (b) Speed of gas molecules are ever changing
   (c) Pressure exerted by the gas is due to the collision of molecules with the walls of the container
   (d) Kinetic energy of a gas is given by the sum of 273 and temperature in Celsius scale

SELF ASSESSMENT

ASSIGNMENT NO. 4

SECTION-I

Straight Objective Type Questions

This section contains 14 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Boyle's temperature of four gases are given below:

Gases	*A*	*B*	*C*	*D*
T_B	120 K	25 K	500 K	410 K

which gas can be liquified most easily?
(a) *A* (b) *B* (c) *C* (d) *D*

2. A gas is enclosed in a vessel of volume V at temperature T_1 and pressure P; the vessel is connected to another vessel of volume $V/2$ by a tube and a stop cock. The second vessel is initially evacuated. If the stop cock is opened, the temperature of second vessel becomes T_2. The first vessel is maintained at a temperature T_1. What is the final pressure P_1 in the apparatus?
(a) $\frac{2PT_2}{2T_2+T_1}$ (b) $\frac{2PT_2}{T_2+2T_1}$ (c) $\frac{PT_2}{2T_2+T_1}$ (d) $\frac{2PT_2}{T_1+T_2}$

3. The ratio of rate of diffusion of gases A and B is 1 : 4. If the ratio of their masses present in the mixture is 2 : 3, what is the ratio of their mole fraction?
(a) $\frac{1}{8}$ (b) $\frac{1}{12}$ (c) $\frac{1}{16}$ (d) $\frac{1}{24}$

4. Density of a gas at STP is 2g / L while the expected density is 1.8 g / L assuming its ideal behaviour. Then:
(a) gas behaves ideally
(b) forces of attraction are dominant among gas molecules
(c) forces of repulsion are dominant among gas molecules
(d) none of the above

5. In a crystalline solid, anions B are arranged in ccp lattice and cations A occupy 50% of the octahedral voids and 50% of the tetrahedral voids. What is the formula of the solid?
(a) AB (b) A_3B_2 (c) A_2B_2 (d) A_2B_3

6. In a compound XY_2O_4, oxide ions are arranged in ccp and cations X are present in octahedral voids. Cations Y are equally distributed among octahedral and tetrahedral voids. The fraction of the octahedral voids occupied is:
(a) $\frac{1}{4}$ (b) $\frac{1}{2}$ (c) $\frac{1}{6}$ (d) $\frac{1}{8}$

7. An ideal gas:
(a) can be liquefied if its temperature is more than critical temperature
(b) can be liquefied if its pressure is more than critical pressure
(c) cannot be liquefied at any pressure and temperature
(d) can be liquefied if its temperature is more than Boyle's temperature

8. A mineral is made of calcium, titanium and oxygen Ca^{2+} ions located at corners, Ti^{4+} ions at the body-centre and O^{2-} ions at face-centres of the unit cell. The molecular formula of the mineral is.......
(a) $CaTi_3O_4$ (b) $CaTiO_3$ (c) $CaTiO_2$ (d) $CaTi_2O_3$

9. If the graph is plotted for 1 mol gas in such a way that PV is plotted against P then intercept of the graph for real gas will be:
(a) $RT + Pb + a$ (b) RT
(c) $RT - Pb + a$ (d) $RT + Pb + ab + a$

10. The ratio of Boyle's temperature and critical temperature for a gas is:
(a) $\frac{8}{27}$ (b) $\frac{27}{8}$ (c) $\frac{1}{2}$ (d) $\frac{2}{1}$

11. With which of the following elements silicon should be doped so as to give *p*-type semiconductor ? [CBSE (PMT) 2008]
(a) Selenium (b) Boron (c) Germanium (d) Arsenic

12. Total volume of atoms present in a face centred cubic unit cell of a metal is (r is atomic radius): [JIPMER 2008]
(a) $\frac{16}{3}\pi r^3$ (b) $\frac{20}{3}\pi r^3$ (c) $\frac{24}{3}\pi r^3$ (d) $\frac{12}{3}\pi r^3$.

13. How many effective Na^+ and Cl^- ions are present respectively in the rocksalt (NaCl). If ions along the axis joining opposite faces are removed ?
(a) $4, \frac{7}{2}$ (b) $\frac{7}{2}, \frac{7}{2}$ (c) $\frac{7}{2}, 4$ (d) 3, 3

14. Kinetic energy and pressure of a gas of unit mole are related as :
(a) $P = 2E$ (b) $P = \frac{2}{3}E$ (c) $P = \frac{3}{2}E$ (d) $P = \frac{E}{2}$

SECTION-II

Multiple Answers Type Objective Questions

15. Which of the following measure the deviation from ideal behaviour of gas?
(a) Collision diameter (b) Collision frequency
(c) Compressibility factor (d) van der Waals' constant '*a*'

16. In face-centred cubic unit cell:
(a) face diagonal of the cube is $a\sqrt{2}$ or $4r$
(a = edge length, r = radius of constituent units)
(b) effective number of atoms in the unit cell is 4
(c) 8 tetrahedral voids per unit cell
(d) rank of the unit cell is 3

17. Which of the following mixtures of gases at room temperature follow Dalton's law of partial pressures?
(a) NO and O_2 (b) CO and CO_2
(c) NH_3 and HCl (d) SO_2 and O_2

18. A real gas can be liquefied:
(a) under adiabatic expansion
(b) above critical temperature
(c) when cooled below critical temperature under applied pressure
(d) at temperature lower than critical temperature and pressure higher than critical pressure

19. Which of the following statements is (are) correct?
(a) In body-centred cubic unit cell, the coordination number is 12
(b) The coordination number of each type of ion in CsCl is 8

(c) A unit cell of an ionic crystal shares some of its ions with neighbouring unit cell

(d) If $r_{Na^+} = 95$ pm; $r_{Cl^-} = 181$ pm; then edge length of unit cell of NaCl is 552 pm

SECTION-III

Assertion-Reason Type Questions

This section contains 6 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.

(c) Statement-1 is true; statement-2 is false.

(d) Statement-1 is false; statement-2 is true.

20. **Statement-1:** The pressure inside the LPG cylinder remains constant even when it is in use at room temperature.

Because

Statement-2: Vapour pressure of any liquid is independent of its amount; it depends only on temperature.

21. **Statement-1:** If a gas has compressibility factor (Z) greater than unity, then repulsive forces are dominant.

Because

Statement-2: Value of Z decreases with increase in pressure.

22. **Statement-1:** The value of Boyle's temperature for a real gas is $\left(T_B = \frac{a}{Rb}\right)$.

Because

Statement-2: At Boyle's temperature, T_B, real gases behave ideally over a long range of pressure.

23. **Statement-1:** $CaCO_3$ shows polymorphism.

Because

Statement-2: $CaCO_3$ exists in two forms called aragonite and calcite.

24. **Statement-1:** Lead zirconate is piezoelectric solid.

Because

Statement-2: Lead zirconate crystals have no dipole moment.

25. **Statement-1:** Band gap in germanium is small.

Because

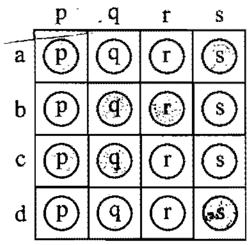
Statement-2: The energy spread of each germanium atomic energy level is infinitesimally small. (IIT 2007)

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as follows:



26. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) High temperature	(p) $Z \neq 1$
(b) Extremely low pressure	(q) $Pb < \frac{a}{V}$
(c) Very high pressure	(r) $Z = 1$
(d) Low pressure	(s) $Pb > \frac{a}{V}$

27. Match the Column-I with Column-II:

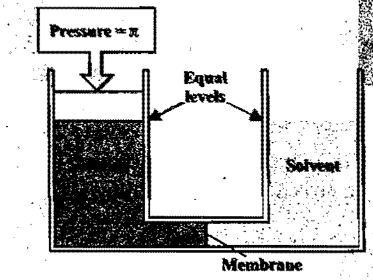
Column-I	**Column-II**
(a) Constituent units occupy only corners	(p) 67.98%
(b) Constituent units occupy corners as well as face-centres	(q) 26.17%
(c) Constituent units occupy corners and body-centre	(r) 74.01%
(d) Constituent units occupy corners and edge-centres	(s) 52.33%

28. Match the Column-I with Column-II: (IIT 2007)

Column-I	**Column-II**
(a) Simple cubic and face-centred cubic	(p) Have these cell parameters $a = b = c$ and $\alpha = \beta = \gamma$
(b) Cubic and rhombohedral	(q) Are two crystal systems
(c) Cubic and tetragonal	(r) Have only two crystallography angles of 90°
(d) Hexagonal and monoclinic	(s) Belong to same crystal system

Answers

1. (c) **2.** (a) **3.** (b) **4.** (b) **5.** (b) **6.** (b) **7.** (c) **8.** (b)
9. (b) **10.** (b) **11.** (b) **12.** (a) **13.** (d) **14.** (b) **15.** (c, d) **16.** (a, b, c)
17. (a, b, d) **18.** (a, c, d) **19.** (b, c, d) **20.** (c) **21.** (c) **22.** (b) **23.** (a) **24.** (c)
25. (c) **26.** (a-p) (b-p) (c-p, s) (d-p, q) **27.** (a-s) (b-r) (c-p) (d-q) **28.** (a-p, s) (b-p, q) (c-q) (d-q, r)



CHAPTER 5

SOLUTIONS

(General and Colligative Properties)

5.1 INTRODUCTION

When two or more chemically non-reacting substances are mixed, they form mixtures. A mixture may be **heterogeneous** or **homogeneous.** A heterogeneous mixture consists of distinct phases and the observed properties are just the sum of the properties of individual phases. However, a homogeneous mixture consists of a single phase which has properties that may differ drastically from those of the individual components.

A homogeneous mixture whose composition can be varied within certain limits is termed a true solution.

The constituents of a solution cannot be separated by filtration, settling or centrifugal action. All solutions are characterised by (i) homogeneity, (ii) absence of settling and (iii) the molecular or ionic state of sub-division of the components.

When the solution is composed of only two chemical substances, it is termed a **binary solution.** Similarly, it is called **ternary** and **quaternary** if it is composed of three and four components, respectively. **Thus, a solution may be regarded as a single phase containing more than one component.**

5.2 SOLVENT AND SOLUTE

Every solution consists of a solvent and one or more solutes. **Solvent in a solution is its constituent substance which has the same state of aggregation as that of the solution.** Generally, the component present in greater amount than any or all the other components is called the solvent. For the solubility of solids in liquids, where the liquid is present in large excess over the solid, there is no ambiguity in these terms, the solid being the solute and the liquid being the solvent. However, if the solution is such that the state of aggregation of the solution is the same as that of a component present in smaller amount, the latter is called the solvent. For example, in a syrup (liquid solution) containing 60% sugar (a solid) and 40% water (a liquid—same aggregation as solution), water is termed as the solvent. In a solution of alcohol and water, the substance present in a larger proportion by mass is called the solvent. But if both the liquids have same masses in solution, it becomes difficult to differentiate between solvent and solute.

5.3 TYPES OF SOLUTIONS

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be the following seven types of binary solutions:

S. No.	Solute	Solvent	Example
1.	Gas	Gas	Air
2.	Gas	Liquid	Aerated water (CO_2 + H_2O)
3.	Gas	Solid	Hydrogen in palladium
4.	Liquid	Liquid	Alcohol in water, benzene in toluene
5.	Liquid	Solid	Mercury in zinc amalgam
6.	Solid	Liquid	Sugar in water, common salt in water
7.	Solid	Solid	Various alloys

The solution of liquid in gas or solid in gas is not possible because the constituents cannot form a homogeneous mixture.

For a given solution, the amount of the solute dissolved in a unit volume of solution (or a unit amount of solvent) is termed as the concentration of the solute. Solutions containing relatively high concentration of solute are called **concentrated solutions** while those of relatively low concentration of solute are termed as **dilute solutions.**

In this chapter, we shall discuss only three types of solutions:

(i) Gas in liquid.
(ii) Liquid in liquid.
(iii) Solid in liquid.

5.4 METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

The concentration of a solution can be expressed in a number of ways. The important methods are:

(i) Mass percentage or Per cent by mass: It is defined as the amount of solute in gram present in 100 gram of the solution.

$$\text{Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

$$= \frac{\text{Mass of solute}}{\text{Mass of solute + Mass of solvent}} \times 100$$

$$= \frac{\text{Mass of solute}}{\text{Volume of solution} \times \text{Density of solution}} \times 100$$

The ratio $\frac{\text{Mass of solute}}{\text{Mass of solution}}$ is termed as **mass fraction.**

Thus,

$$\text{Mass percentage of solute} = \text{Mass fraction} \times 100$$

10% solution of sugar means that 10 gram of sugar is present in 100 gram of the solution, *i.e.*, 10 gram of sugar has been dissolved in 90 gram of water.

(ii) Per cent by volume: It is defined as the volume of solute in mL present in 100 mL solution.

$$\text{Per cent of solute by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

(iii) Per cent mass by volume: It is defined as the mass of solute present in 100 mL of solution.

Per cent of solute mass by volume

$$= \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(iv) Strength or concentration (Gram per litre): It is defined as the amount of the solute in gram present in one litre of the solution.

Concentration of solution

$$= \frac{\text{Mass of solute in gram}}{\text{Volume of the solution in litres}}$$

$$= \frac{\text{Mass of solute in gram}}{\text{Volume of the solution in mL}} \times 1000$$

Concentration in gram per litre is also termed as strength of the solution. Let w g of the solute be present in V litre of solution, then

$$\text{Strength or concentration of the solution} = \frac{w}{V}\ \text{gL}^{-1}$$

[**Note:** V is not the volume of the solvent. V is actually the final volume after dissolving a definite quantity of solute in the solvent.]

(v) Parts per million (ppm): When the solute is present in trace quantities, it is convenient to express the concentration in parts per million (ppm). It is defined as the quantity of the solute in gram present in 10^6 gram of the solution.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Atmospheric pollution in cities is also expressed in ppm by volume. It refers to the volume of the pollutant in 10^6 units of volume. 10 ppm of SO_2 in air means 10 mL of SO_2 is present in 10^6 mL of air.

(vi) Mole fraction: This method is used when the solution is constituted by mixing two or more components. It is defined as the ratio of number of moles of one component to the total number of moles of the solution (*i.e.*, all the components). Taking three components *A*, *B* and *C*.

Components	A	B	C
Mass (in gram)	w_1	w_2	w_3
Molecular mass	m_1	m_2	m_3
No. of g moles	$\frac{w_1}{m_1}$	$\frac{w_2}{m_2}$	$\frac{w_3}{m_3}$

$$\text{Total number of g moles} = \frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}$$

Thus,

$$\text{Mole fraction of } A = \frac{w_1 / m_1}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_A$$

$$\text{Mole fraction of } B = \frac{w_2 / m_2}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_B$$

$$\text{Mole fraction of } C = \frac{w_3 / m_3}{\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}} = f_C$$

The sum of mole fractions of a solution is equal to 1, *i.e.*,

$$f_A + f_B + f_C = 1$$

In a binary solution,

Mole fraction of solute + Mole fraction of solvent = 1

Let n moles of solute (B) and N moles of solvent (A) be present in a solution.

$$\text{Mole fraction of solute} = \frac{n}{N+n} = X_B$$

$$\text{Mole fraction of solvent} = \frac{N}{N+n} = X_A$$

Thus,

$$X_A + X_B = 1$$

Mole fraction is independent of temperature of the solution.

(vii) Molality: It is defined as the number of moles of the solute present in 1 kg of the solvent. It is denoted by *m*.

$$\text{Molality } (m) = \frac{\text{Number of moles of solute}}{\text{Number of kilo-grams of the solvent}}$$

Let w_B gram of the solute of molecular mass m_B be present in w_A gram of the solvent, then

$$\text{Molality } (m) = \frac{w_B}{m_B \times w_A} \times 1000$$

Relation between mole fraction and molality:

$$X_B = \frac{n}{N+n} \text{ and } X_A = \frac{N}{N+n}$$

$$\frac{X_B}{X_A} = \frac{n}{N} = \frac{\text{Moles of solute}}{\text{Moles of solvent}} = \frac{w_B \times m_A}{m_B \times w_A}$$

$$\frac{X_B \times 1000}{X_A \times m_A} = \frac{w_B \times 1000}{m_B \times w_A} = m$$

or
$$\frac{X_B \times 1000}{(1 - X_B)\, m_A} = m$$

Note: (i) Molality is the most convenient method to express the concentration because it involves the mass of liquids rather than their volumes. It is also independent of the variation in temperature.

(ii) Molality and solubility are related by the following relation :

$$\text{Molality} = \frac{\text{Solubility} \times 10}{\text{Molecular mass of the solute}}$$

$$\left[\text{Solubility} = \frac{\text{Mass of solute in gram}}{\text{Mass of solvent in gram}} \times 100\right]$$

(viii) Molarity (Molar concentration): It is defined as the number of moles of the solute per litre or per dm^3 of the solution, *i.e.*,

$$\text{Molarity } (M) = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$$

or
$$\text{Molarity} \times \text{Number of litres of solution} = \text{Number of moles of solute}$$

Let w_B g of the solute of molecular mass m_B be dissolved in V litre of solution.

$$\text{Molarity of the solution} = \frac{w_B}{m_B \times V}$$

or
$$\text{Molarity} \times m_B = \frac{w_B}{V} = \text{Strength of the solution}$$

If V is taken in mL (cm^3), then

$$\text{Molarity of the solution} = \frac{w_B}{m_B \times V} \times 1000$$

The unit of molarity is mol litre^{-1} or mol dm^{-3}.

Molarity (second method): Let d = density of solution in g/mL and let it contains x% solute by mass.

Then, mass of 1 litre solution = $(1000 \times d)$ g

$$\text{Mass of solute in 1 litre} = \frac{x}{100} \times (1000 \times d)\text{ g}$$
$$= (x \times d \times 10)\text{ g}$$

Number of moles of solute in 1 litre

$$= \frac{\text{Mass of solute in gram}}{\text{Gram molecular mass of solute}} = \frac{x \times d \times 10}{m_B}$$

where m_B = molecular mass of solute

$$\therefore \qquad \boldsymbol{M = \frac{x \times d \times 10}{m_B}}$$

Molarity of dilution:

Before dilution		*After dilution*
M_1V_1	=	M_2V_2

Molarity of mixing: Let there be three samples of solution (containing same solvent and solute) with their molarity M_1, M_2, M_3 and volumes V_1, V_2, V_3 respectively. These solutions are mixed; molarity of mixed solution may be given as:

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$

where, M_R = Resultant molarity

$V_1 + V_2 + V_3$ = Resultant volume after mixing

Note: Molarity is dependent on volume; therefore, it depends on temperature.

1 M	Molar solution, *i.e.*, molarity is 1
0.5 M or $M/2$	Semimolar
0.1 M or $M/10$	Decimolar
0.01 M or $M/100$	Centimolar
0.001 M or $M/1000$	Millimolar

Relationship between molality and molarity:

$$\frac{1}{m} = \frac{\rho}{M} - \frac{m_B}{1000}$$

where, ρ = density of solution

m = molality

M = molarity

m_B = molar mass of solute

Relation between molarity 'M' and mole fraction:

Let M be the molarity of solution, and x_A, x_B be mole fractions of solvent and solute, respectively.

Suppose n_A and n_B moles of solvent and solute are mixed to form solution.

$$\text{Mass of solution} = n_A m_A + n_B m_B \qquad \ldots \text{(i)}$$

where, m_A and m_B are molar masses of solvent and solute, respectively.

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_A m_A + n_B m_B)}{d}$$

$$\text{Molarity} = \text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution}}$$

$$M = n_B \times \frac{1000 \times d}{(n_A m_A + n_B m_B)}$$

Dividing both numerator and denominator by $(n_A + n_B)$,

$$M = \left\{\frac{n_B}{n_A + n_B}\right\} \times \frac{1000 \times d}{\frac{n_A}{n_A + n_B} \times m_A + \frac{n_B}{n_A + n_B} \times m_B}$$

$$M = \frac{x_B \times 1000 \times d}{x_A m_A + x_B m_B}$$

(ix) Normality: It is defined as the number of gram equivalents of solute present per litre of solution. It is denoted by 'N'.

$$\text{Normality } (N) = \frac{\text{Number of gram equivalents of solute}}{\text{Number of litres of the solution}}$$

or **Normality × Number of litres of the solution**
= Number of gram equivalents of the solute

Let w_B gram of the solute of equivalent mass E_B be present in V litre of the solution, then,

$$\text{Normality} = \frac{w_B/E_B}{V} = \frac{w_B}{E_B \times V}$$

$$\textbf{Normality} \times \textbf{Equivalent mass} = \frac{w_B}{V}$$

$$= \textbf{Strength of the solution in g/L}$$

Solutions are expressed as:

$$1\,N, 2\,N, \frac{N}{2}, \frac{N}{10}, \frac{N}{100}, \frac{N}{1000}, \text{etc.}$$

Like molarity, normality is also dependent on volume, therefore, it depends on temperature.

Normality of solution may be represented as,

$1\,N$	Normal solution, *i.e.*, normality is 1
$0.5\,N$ or $\frac{N}{2}$	Seminormal
$0.1\,N$ or $\frac{N}{10}$	Decinormal
$0.01\,N$ or $\frac{N}{100}$	Centinormal
$0.001\,N$ or $\frac{N}{1000}$	Millinormal

Relationship between normality and molarity: We know that,

Molarity × Molecular mass = Strength of the solution (g/L)

Similarly,

Normality × Equivalent mass = Strength of the solution (g/L)

Hence,

Molarity × Molecular mass = Normality × Equivalent mass

or
$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

So, $\quad$ **Normality = n × Molarity**

[Normality (second method): Let 'd' is the density of solution in g/mL and x is the percentage of the solute by mass. Then,

$$N = \frac{x \times d \times 10}{\text{Equivalent mass of solute}}\ ]$$

(x) Formality: It is the number of formula mass in gram present per litre of solution. In case, formula mass is equal to molecular mass, formality is equal to molarity. Like molarity and normality, the formality is also dependent on temperature. It is used for ionic compounds in which there is no existence of a molecule. Mole of ionic compounds is called **formole** and molarity as **formality.**

SOME SOLVED EXAMPLES

Example 1. *Calculate the masses of cane sugar and water required to prepare 250 g of 25% cane sugar solution.*

Solution: Mass percentage of cane sugar = 25

We know that,

$$\text{Mass percentage} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

So,
$$25 = \frac{\text{Mass of cane sugar}}{250} \times 100$$

or
$$\text{Mass of cane sugar} = \frac{25 \times 250}{100} = 62.5\text{ g}$$

$$\text{Mass of water} = (250 - 62.5) = 187.5\text{ g}$$

Example 2. *Calculate the molarity of the following solutions:*

(*a*) *4 g of caustic soda is dissolved in 200 mL of the solution.*

(*b*) *5.3 g of anhydrous sodium carbonate is dissolved in* 100 *mL of solution.*

(*c*) *0.365 g of pure HCl gas is dissolved in 50 mL of solution.*

Solution: (a) Molecular mass of NaOH = 40

$$\text{No. of gram moles in 4 g of NaOH} = \frac{4}{40} = 0.1$$

$$\text{Volume of solution in litre} = \frac{200}{1000} = 0.2$$

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litre}} = \frac{0.1}{0.2} = 0.5\,M$$

(b) Molecular mass of anhydrous $Na_2CO_3 = 106$

No. of gram moles in 5.3 g of anhydrous Na_2CO_3

$$= \frac{5.3}{106} = 0.05$$

$$\text{Volume of solution in litre} = \frac{100}{1000} = 0.1$$

$$\text{Molarity} = \frac{\text{No. of gram moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{0.05}{0.1} = 0.5\,M$$

(c) Molecular mass of HCl = 36.5

$$\text{No. of gram moles in 0.365 g of pure HCl} = \frac{0.365}{36.5}$$

$$\text{Volume of solution in litre} = \frac{50}{1000}$$

$$\text{Molarity} = \frac{\text{No. of gram moles of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{0.365}{36.5} \times \frac{1000}{50} = 0.2\,M$$

Example 3. *The density of a solution containing* 13% *by mass of sulphuric acid is* 1.09 *g/mL. Calculate the molarity and normality of the solution.*

Solution: Volume of 100 g of the solution

$$= \frac{100}{d} = \frac{100}{1.09} \text{ mL}$$

$$= \frac{100}{1.09 \times 1000} \text{ litre}$$

$$= \frac{1}{1.09 \times 10} \text{ litre}$$

Number of moles of H_2SO_4 in 100 g of the solution $= \frac{13}{98}$

$$\text{Molarity} = \frac{\text{No. of moles of } H_2SO_4}{\text{Volume of soln. in litre}} = \frac{13}{98} \times \frac{1.09 \times 10}{1}$$

$$= 1.445\, M$$

[**Note:** In solving such numericals, the following formula can be applied:

$$\text{Molarity} = \frac{\text{\% strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$$

Similarly,

$$\text{Normality} = \frac{\text{\% strength of soln.} \times \text{density of soln.} \times 10}{\text{Eq. mass}}\ ]$$

We know that,

$$\text{Normality} = \text{Molarity} \times n$$

$$= 1.445 \times 2 \qquad \left[n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2 \right]$$

$$= 2.89\, N$$

Example 4. *Calculate the molarity of pure water* $(d = 1\, g / mL)$.

Solution: Consider 1000 mL of water.

Mass of 1000 mL of water $= 1000 \times 1 = 1000$ g

No. of moles of water $= \frac{1000}{18} = 55.5$

$$\text{Molarity} = \frac{\text{No. of moles of water}}{\text{Volume in litre}}$$

$$= \frac{55.5}{1} = 55.5\, M$$

Example 5. *Calculate the quantity of sodium carbonate (anhydrous) required to prepare* 250 *mL* $\frac{M}{10}$ *solution.*

Solution: We know that,

$$\text{Molarity} = \frac{w}{M \times V}$$

where, w = mass of Na_2CO_3 in g,

M = molecular mass of Na_2CO_3 in gram = 106

V = volume of solution in litre $= \frac{250}{1000} = 0.25$

$$\text{Molarity} = \frac{1}{10}$$

Hence, $\frac{1}{10} = \frac{w}{106 \times 0.25}$

or $w = \frac{106 \times 0.25}{10} = 2.65$ g

Example 6. 214.2 *g of sugar syrup contains* 34.2 *g of sugar. Calculate (i) molality of the solution and (ii) mole fraction of sugar in the syrup.*

Solution: (i) Mass of sugar = 34.2 g

$$\text{No. of moles of sugar} = \frac{34.2}{\text{Mol. mass}} = \frac{34.2}{342} = 0.1$$

$$\text{Mass of water} = (214.2 - 34.2)$$

$$= 180 \text{ g} = \frac{180}{1000} \text{ kg}$$

No. of moles of water $= \frac{180}{18} = 10$

$$\therefore \text{Molality} = \frac{\text{No. of moles of sugar}}{\text{Mass of water in kg}} = \frac{0.1}{180} \times 1000$$

$$= 0.555\, m$$

(ii) Total number of moles $= 10.0 + 0.1 = 10.1$

$$\therefore \text{Mole fraction of sugar} = \frac{\text{No. of moles of sugar}}{\text{Total number of moles}}$$

$$= \frac{0.1}{10.1} = 0.0099$$

Example 7. *A solution contains* 410.3 *g of* H_2SO_4 *per litre of solution at* 20°C. *If the density is* 1.243 *g/mL, what will be its molarity and molality?*

Solution: Mol. mass of $H_2SO_4 = 98$

No. of moles of $H_2SO_4 = \frac{410.3}{98} = 4.186$

$$\text{Molarity of } H_2SO_4 \text{ solution} = \frac{\text{No. of moles of } H_2SO_4}{\text{Volume of soln. in litre}}$$

$$= \frac{4.186}{1} = 4.186\, M$$

Mass of 1 litre H_2SO_4 solution $= 1000 \times 1.243 = 1243$ g

Mass of water $= (1243 - 410.3) = 832.7 \text{ g} = \frac{832.7}{1000}$ kg

$$\text{Molality of solution} = \frac{\text{No. of moles of } H_2SO_4}{\text{Mass of water in kg}}$$

$$= \frac{4.186}{832.7} \times 1000$$

$$= 5.027\, m$$

Example 8. *The density of a 2.03 M solution of acetic acid (molecular mass 60) in water is 1.017 g/mL. Calculate the molality of the solution.*

Solution: Strength of the solution

$$= \text{Molarity} \times \text{mol. mass}$$

$$= 2.03 \times 60 = 121.8 \text{ g/L}$$

Density of solution $= 1.017$ g/mL

Mass of 1 litre of solution $= 1000 \text{ mL} \times 1.017 \text{ g/mL}$

$$= 1017 \text{ g}$$

$$\text{Mass of water} = 1017 - 121.8 = 895.2 \text{ g} = \frac{895.2}{1000} \text{ kg}$$

$$\text{Molality} = \frac{2.03}{895.2} \times 1000 = 2.267\ m$$

Example 9. *The density of a 3 M sodium thiosulphate solution ($Na_2S_2O_3$) is 1.25 g/mL. Calculate (i) the percentage by mass of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate and (iii) molalities of Na^+ and $S_2O_3^{2-}$ ions.*

Solution: (i) Mass of 1000 mL of $Na_2S_2O_3$ solution

$$= 1.25 \times 1000 = 1250 \text{ g}$$

Mass of $Na_2S_2O_3$ in 1000 mL of 3 M solution

$$= 3 \times \text{Mol. mass of } Na_2S_2O_3$$

$$= 3 \times 158 = 474 \text{ g}$$

Mass percentage of $Na_2S_2O_3$ in solution

$$= \frac{474}{1250} \times 100 = 37.92$$

Alternatively, $$M = \frac{x \times d \times 10}{m_A}$$

$$3 = \frac{x \times 1.25 \times 10}{158}$$

$$x = 37.92$$

(ii) $$\text{No. of moles of } Na_2S_2O_3 = \frac{474}{158} = 3$$

Mass of water $= (1250 - 474) = 776$ g

$$\text{No. of moles of water} = \frac{776}{18} = 43.1$$

$$\text{Mole fraction of } Na_2S_2O_3 = \frac{3}{43.1 + 3} = \frac{3}{46.1} = 0.065$$

(iii) No. of moles of Na^+ ions

$$= 2 \times \text{No. of moles of } Na_2S_2O_3$$

$$= 2 \times 3 = 6$$

$$\text{Molality of } Na^+ \text{ ions} = \frac{\text{No. of moles of } Na^+ \text{ ions}}{\text{Mass of water in kg}}$$

$$= \frac{6}{776} \times 1000$$

$$= 7.73\ m$$

No. of moles of $S_2O_3^{2-}$ ions = No. of moles of $Na_2S_2O_3$

$$= 3$$

$$\text{Molality of } S_2O_3^{2-} \text{ ions} = \frac{3}{776} \times 1000 = 3.86\ m$$

Example 10. *A solution is prepared by dissolving 5.64 g of glucose in 60 g of water. Calculate the following:*

(i) mass per cent of each of glucose and water,

(ii) molality of the solution,

(iii) mole fraction of each of glucose and water.

Solution: (i) Total mass of solution

$$= 5.64 + 60 = 65.64 \text{ g}$$

$$\text{Mass per cent of glucose} = \frac{5.64}{65.64} \times 100 = 8.59\%$$

Mass per cent of water = (100 − Mass per cent of glucose)

$$= (100 - 8.59) = 91.41\%$$

(ii) $$\text{No. of moles of glucose} = \frac{5.64}{180}$$

$$\text{Mass of water in kg} = \frac{60}{1000}$$

$$\text{Molality} = \frac{5.64}{180} \times \frac{1000}{60} = 0.522\ m$$

(iii) $$\text{No. of moles of glucose} = \frac{5.64}{180} = 0.0313$$

$$\text{No. of moles of water} = \frac{60}{18} = 3.333$$

$$\text{Mole fraction of glucose} = \frac{0.0313}{3.333 + 0.0313} = 0.0093$$

$$\text{Mole fraction of water} = \frac{3.333}{3.333 + 0.0313} = 0.9907$$

Example 11. *What would be the molality of a solution made by mixing equal volumes of 30.0% by mass of H_2SO_4 (density 1.218 g cm^{-3}) and 70% by mass of H_2SO_4 (density 1.610 g cm^{-3})?*

Solution: Let 100 mL of one solution be mixed with 100 mL of the other solution.

Mass of 100 mL of 30% H_2SO_4 $= 100 \times 1.218 = 121.8$ g

Mass of H_2SO_4 in 121.8 g of 30% H_2SO_4

$$= \frac{30}{100} \times 121.8 \text{ g} = 36.54 \text{ g}$$

Mass of water $= (121.8 - 36.54) = 85.26$ g

Mass of 100 mL of 70% H_2SO_4 $= 100 \times 1.61 = 161.0$ g

Mass of H_2SO_4 in 161.0 g of 70% H_2SO_4

$$= \frac{70}{100} \times 161.0 \text{ g} = 112.7 \text{ g}$$

Mass of water $= (161.0 - 112.7) = 48.30$ g

Total H_2SO_4 in solution $= 36.54 + 112.7 = 149.24$ g

$$\text{No. of moles of } H_2SO_4 = \frac{149.24}{98}$$

$$\text{Total mass of water in solution} = (85.26 + 48.30)$$

$$= 133.56 \text{ g} = \frac{133.56}{1000} \text{ kg}$$

$$\text{Molality} = \frac{\text{No. of moles of } H_2SO_4}{\text{Mass of water in kg}} = \frac{149.24}{98} \times \frac{1000}{133.56}$$

$$= 11.4\ m$$

Example 12. *The mole fraction of CH_3OH in an aqueous solution is 0.02 and its density is 0.994 g cm^{-3}. Determine its molarity and molality.*

Solution: Let x mole of CH_3OH and y mole of water be present in solution.

$$\text{Mole fraction of } CH_3OH = \frac{x}{x+y} = 0.02$$

$$\therefore \text{So,} \quad \frac{y}{x} = 49 \quad \text{or} \quad \frac{x}{y} = \frac{1}{49}$$

$$\text{Molality} = \frac{x}{18 \times y} \times 1000 = \frac{1000}{18 \times 49} = 1.13\ m$$

$$\text{Volume of solution} = \frac{\text{Total mass}}{\text{density}} = \frac{32x + 18y}{0.994} \text{ mL}$$

$$= \frac{32x + 18y}{0.994 \times 1000} \text{ litre} = \frac{32x + 18y}{994} \text{ litre}$$

$$\text{Molarity} = \frac{x}{32x + 18y} \times 994$$

$$= \frac{994}{32 + 18 \times y/x} = \frac{994}{32 + 18 \times 49} = 1.0875\ M$$

Example 13. *Calculate the concentration of NaOH solution in g/mL, which has the same normality as that of a solution of HCl of concentration 0.04 g/mL.*

Solution:

$$N_{\text{HCl}} = \frac{w_B \times 1000}{E_B \times V} = \frac{0.04 \times 1000}{36.5 \times 1} = 1.095$$

$$N_{\text{NaOH}} \equiv N_{\text{HCl}}$$

$$\therefore \quad 1.095 = \frac{w_B \times 1000}{40 \times 1}$$

$$w_B = 0.0438 \text{ g / mL}$$

Example 14. *How many Na^+ ions are present in 50 mL of a 0.5 M solution of NaCl?*

Solution:

$$\text{Number of moles of NaCl} = \frac{MV}{1000}$$

$$= \frac{0.5 \times 50}{1000} = 0.025$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$\text{Number of moles of } Na^+ = \text{Number of moles of NaCl}$$

$$= 0.025$$

$$\text{Number of ions of } Na^+ = 0.025 \times 6.023 \times 10^{23}$$

$$= 1.505 \times 10^{22}$$

Example 15. *Reaction,*

$$2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$$

is used for commercial preparation of bromine from its salts. Suppose we have 50 mL of a 0.06 M solution of NaBr. What volume of a 0.05 M solution of Cl_2 is needed to react completely with the Br^-?

Solution: $2Br^-(aq) + Cl_2(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$

$$\frac{M_1V_1(Br^-)}{n_1} = \frac{M_2V_2(Cl_2)}{n_2}$$

where, n_1 and n_2 are corresponding coefficients.

$$\frac{0.06 \times 50}{2} = \frac{0.05 \times V_2}{1}$$

$$\therefore \quad V_2 = 30 \text{ mL}$$

Example 16. *Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 95 mL prepared by adding 50 mL of ethyl alcohol (density = 0.789 mL^{-1}) to 50 mL water (density = 1.00 g mL^{-1}).*

Solution:

$$\text{No. of moles of ethyl alcohol} = \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}}$$

$$= \frac{50 \times 0.789}{46} = 0.8576$$

$$\text{No. of moles of water} = \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}} = \frac{50 \times 1}{18}$$

$$= 2.7777$$

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Vol. of sol. in mL}} \times 1000$$

$$= \frac{0.8576}{95} \times 1000 = 9.027\ M$$

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

$$= \frac{0.8576}{50} \times 1000 = [illegible]52\ m$$

$$\text{Mole fraction} = \frac{0.8576}{0.8576 + 2.7777} = \frac{0.8576}{3.6353} = 0.236$$

5.5 SOLUTIONS OF GASES IN LIQUIDS (Solubility of Gases)

All gases are soluble in water as well as in other liquids to a greater or lesser extent. Solutions of gases in water play an important role in our daily life. The common examples are carborated beverages, *i.e.*, soft drinks, household cleaners containing aqueous solutions of ammonia, formalin-an aqueous solution of formaldehyde, etc. The natural waters contain dissolved O_2 which is vital for the existence of aquatic life in sea, rivers and lakes.

The solubility of a gas in a liquid is expressed in terms of **absorption coefficient.** It is defined as the volume of the gas in mL that can be dissolved by 1 mL of a liquid solvent at the temperature of the experiment at one atmospheric pressure. The volume of the gas is measured at STP. Thus, if v is the volume of the gas dissolved, reduced to STP, V is the volume of the solvent and P is pressure of the gas in atmospheres, then the absorption coefficient, α, is given by

$$\alpha = \frac{v}{VP}$$

The following factors affect the solubilities of gases in liquids:

(i) Nature of the gas and solvent : Generally, the gases which can be easily liquefied are more soluble in common solvents. For example, CO_2 is more soluble in water than oxygen or hydrogen. The gases which react with the solvent posses higher solubility. For example, HCl and NH_3 are highly soluble in water.

Oxygen, nitrogen and carbon dioxide are much more soluble in ethyl alcohol than in water at the same temperature and pressure.

(ii) Temperature : The solubility of most of the gases in liquids decreases with increase of temperature as the dissolution is an exothermic process. When water is heated in a beaker, bubbles of air are formed on the sides of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to "boil out" of the solution long before the water itself boils.

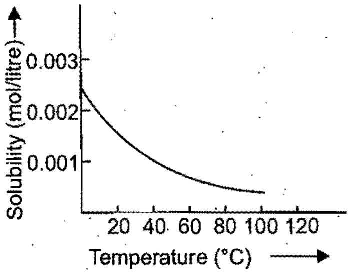


Fig. 5.1 Temperature dependence of O_2 gas solubility in water

The reduced solubility of molecular oxygen in hot water has a direct bearing on **thermal pollution,** *i.e., the heating of the environment*—usually waterways—*to temperatures that are harmful to its living inhibitants.*

(iii) Pressure : The most important factor which influences the solubility of a gas in a liquid is the **pressure.** The effect of pressure on the solubility of the gas in the liquid is given by Henry's law, which states that *the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution at a definite temperature.* The solubility is taken as the mass of the gas dissolved per unit volume of the liquid. Thus, if m is the mass of the gas dissolved per unit volume of the solvent and P is the pressure of the gas in equilibrium with the solution, then

$$m \propto P$$

or $$m = KP \qquad \text{...(i)}$$

where, K is the proportionality constant.

When $P = 1$, $m = K$, *i.e.*, the solubility of the gas at unit pressure is equal to constant K. The value of K is different for each gas at a particular temperature. The magnitude of K depends upon the nature of the gas, nature of solvent, temperature and the units of pressure. Equation (i) represents equation of straight line $(y = mx)$ passing through origin. Fig. 5.2 shows the variation of solubility of some gases against equilibrium pressure. The straight line graphs show the validity of Henry's law.

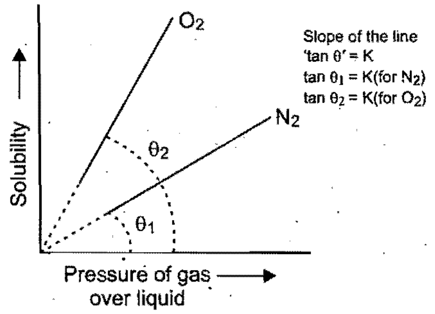


Fig. 5.2 Variation of solubility of a gas with pressure

If solubility of the gas is known at one particular pressure, then it can be calculated at other pressures using the following relation,

$$\frac{m_1}{m_2} = \frac{P_1}{P_2} \qquad \text{...(ii)}$$

where 'm_1' is the solubility of the gas at pressure 'P_1' and 'm_2' is the solubility of the gas at pressure 'P_2'.

When a mixture of two or more non-reacting gases is brought in contact with a solvent, each constituent gas dissolves in proportion to its own partial pressure. Henry's law can be applied to each individual gas independent of the presence of other gas. If we use the mole fraction of the gas in the solution as a measure of its solubility, then the law can be stated as, "*mole fraction of the gas in a solution is proportional to the partial pressure of the gas.*"

$$x \propto P$$

where, x = mole fraction of the gas in solution

and p = partial pressure of the gas.

or $x = K' p$

or $$p = \frac{1}{K'} x = K_H\, x \qquad \left(K_H = \frac{1}{K'}\right) \text{...(iii)}$$

K_H is called Henry's law constant. Different gases have different values of K_H at a definite temperature for a given solvent.

Table 5.1 Values of Henry's Law Constant (K_H) for Some Common Gases in Water

Gas	Temperature (K)	K_H (k bar)
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	393	46.82

From equation (iii), it can be inferred that higher is the value of Henry's law constant, the lower is the solubility of the gas in the liquid.

Limitations of Henry's Law

Henry's law holds good if the following conditions are fulfilled :

(i) The pressure is not too high,

(ii) The temperature is not very low,

(iii) The gas does not chemically combine with the solvent.

The gas molecules do not either dissociate or associate in the solvent. In case the dissolved gas reacts with the solvent, higher solubilities can result. The solubility of ammonia in water is much higher than expected because of the following reaction :

$$NH_3 + H_2O = NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Carbon dioxide also reacts with water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Another interesting example concerns the dissolution of oxygen in blood. Normally, oxygen gas is only sparingly soluble in water. However, its solubility in blood is abnormally high because of the high content of haemoglobin (Hb) molecules, which are eventually delivered to the tissues for use in metabolism.

$$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$$

Due to these processes, Henry's law is not strictly followed.

Applications of Henry's Law

1. Soft drink bottles are sealed at high pressure, to increase the solubility of CO_2 in the soft drink.

2. At high altitude, partial pressure of oxygen is low, it leads to low concentration of oxygen in blood of people living there. Low concentration of oxygen develops **anoxia,** *i.e.*, unable to think and act properly.

3. When scuba divers go deep in the sea, solubility of atmospheric gases increases in blood. When the divers come up, there is release of dissolved gases and it leads to the formation of bubbles of nitrogen in our blood capillaries and hence there is painful sensation called **bends.** To avoid bends; the tanks of scuba divers are filled with 11.7% He, 56.2% N_2 and 32.1% oxygen.

[**Note :** (i) Gases are less soluble in aqueous solutions of electrolytes than in pure water. It is called *salting out effect.*
(ii) Non-electrolytes such as sugar if present in a solution also reduce the solubility of gases in water.]

Example 17. *Calculate the concentration of CO_2 in a soft drink that is bottled at partial pressure of CO_2 of 4 atm over the liquid at 25° C. The Henry's Law constant for CO_2 in water at 25° C is 3.1×10^{-2} mol/litre-atm.*

Solution: According to Henry's Law:

$$S = KP = 3.1 \times 10^{-2} \times 4 = 0.12 \text{ mol litre}^{-1}$$

Example 18. *The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5×10^{-2} g of ethane, then what shall be the partial pressure of the gas?*

Solution:
$$\frac{S_1}{S_2} = \frac{P_1}{P_2}$$

$$\frac{6.56 \times 10^{-2}}{5 \times 10^{-2}} = \frac{1}{P_2}$$

$$P_2 = 0.762 \text{ bar}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 0.5 M H_2SO_4 is diluted from 1 litre to 10 litre, normality of the resulting solution is: (AFMC 2005)

(a) 1 N (b) 0.1 N (c) 10 N (d) 11 N

[**Ans.** (b)]

[**Hint:** $M_1V_1 = M_2V_2$

$$0.5 \times 1 = M_2 \times 10$$
$$M_2 = 0.05$$
$$N = M \times \text{basicity of acid} = 0.05 \times 2 = 0.1\, N$$]

2. Molar solution means 1 mole of solute present in: [BCECE (Medical) 2005]

(a) 1000 g of solvent (b) 1 litre of solvent
(c) 1 litre of solution (d) 1000 g of solution

[**Ans.** (c)]

3. The molarity of a solution containing 50 g of NaCl in 500 g of a solution and having a density of 0.936 g/cm³ is:

(a) 1.5 M (b) 1.6 M (c) 1.8 M (d) 1.2 M

[**Ans.** (b)]

[**Hint:** $M = \frac{x \times d \times 10}{m_B}$ ... (i)

$$x = \frac{50}{500} \times 100 = 10$$

$$\therefore \quad M = \frac{10 \times 0.936 \times 10}{58.5} = 1.6\, M$$]

4. 20 mL of 0.5 M HCl is mixed with 30 mL of 0.3 M HCl, the molarity of the resulting solution is:

(a) 0.8 M (b) 0.53 M (c) 0.38 M (d) 0.83 M

[**Ans.** (c)]

[**Hint:** $M_1V_1 + M_2V_2 = M_R(V_1 +$

$$0.5 \times 20 + 0.3 \times 30 = M_R \times 5$$
$$M_R = 0.38\, M$$

where, M_R = resultant molarity o mixture.]

5. How many moles and how many ams of NaCl are present in 250 mL of a 0.5 M NaCl solution?

(a) 0.125 mol; 7.32 g (b) 7.32 mol; 0.125 g
(c) 0.125 mol; 0.125 g (d) 7.32 mol; 7.32 g

[**Ans.** (a)]

[**Hint:** Number of moles $= \frac{MV}{1000} = \frac{0.5 \times 250}{1000} = 0.125$

Mass of NaCl = 58.5 × 0.125 = 7.32 g]

6. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is: (AIEEE 2006)

(a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}
(c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}

[**Ans.** (c)]

[**Hint:** $m = \frac{M \times 1000}{1000d - Mm_B} = \frac{2.05 \times 1000}{1000 \times 1.02 - 2.05 \times 60}$

$= 2.28$ mol kg^{-1}]

7. The hardness of water sample containing 0.002 mol of magnesium sulphate dissolved in a litre of water is expressed as: [PET (Kerala) 2007]
(a) 20 ppm (b) 200 ppm (c) 2000 ppm (d) 120 ppm
(e) 240 ppm
[**Ans.** (b)]

[**Hint:** 10^6 g water contains (0.002×1000) mol $MgSO_4$

$1 \text{ mol } MgSO_4 \cong 1 \text{ mol } CaCO_3$

$\therefore \quad 2 \text{ mol } MgSO_4 \cong 2 \text{ mol } CaCO_3$, *i.e.*, 2×100 g $CaCO_3$

$\therefore$ Hardness of water = 200 ppm]

8. The density (in g mL^{-1}) of a 3.6 M sulphuric acid solution, *i.e.*, 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be: (AIEEE 2007)
(a) 1.45 (b) 1.64 (c) 1.88 (d) 1.22
[**Ans.** (d)]

[**Hint:** $M = \dfrac{x \times d \times 10}{m_B}$

$$d = \frac{M \times m_B}{x \times 10} = \frac{3.6 \times 98}{29 \times 10} \approx 1.22 \text{ g mL}^{-1}]$$

9. 1 litre solution containing 490 g of sulphuric acid is diluted to 10 litre with water. What is the normality of the resulting solution? (SCRA 2007)
(a) 0.5 N (b) 1.0 N (c) 5.0 N (d) 10.0 N
[**Ans.** (b)]

[**Hint:** $N = \dfrac{w_B \times 1000}{E_B \times V} = \dfrac{490 \times 1000}{49 \times 1000} = 10$

$N_1V_1 = N_2V_2$

$10 \times 1 = N_2 \times 10$

$N_2 = 1$]

10. 250 mL of a Na_2CO_3 solution contains 2.65 g of Na_2CO_3. 10 mL of this solution is added to x mL of water to obtain 0.001 M Na_2CO_3 solution. The value of x is....
(Molecular mass of Na_2CO_3 = 106 amu) [BHU (Mains) 2008]
(a) 1000 (b) 990 (c) 9990 (d) 90
[**Ans.** (b)]
[**Hint :** Molarity of solution.

$$M = \frac{w_B \times 1000}{m_B \times V} = \frac{2.65 \times 1000}{106 \times 250} = 0.1$$

$M_1V_1 = M_2V_2$

$0.1 \times 10 = 0.001\,(10 + x)$

$x = 990$ mL]

11. The volumes of two HCl solutions A (0.5 N) and B (0.1 N) to be mixed for preparing 2 L of 0.2 N HCl are : [EAMCET (Med) 2008]
(a) 0.5 L of A + 1.5 L of B
(b) 1.5 L of A + 0.5 L of B
(c) 1 L of A + 1 L of B
(d) 0.75 L of A + 1.25 L of B
[**Ans.** (a)]
[**Hint :** Let x L of A and $(2 - x)$ L of B are mixed.

$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$

$0.5 \times x + 0.1\,(2 - x) = 0.2 \times 2$

$(0.5 - 0.1)\,x = 0.4 - 0.2$

$0.4\,x = 0.2$

$x = 0.5$ L

$\therefore$ 0.5 L of A and 1.5 L of B should be mixed.]

5.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

When one liquid dissolves in another, the molecules of the solvent are caused to move apart so as to accommodate the solute molecules. Similarly, the solute molecules must also be separated so that they can take their places in the mixture. In both these processes, energy is required. Finally, as the solute and solvent molecules are brought together, energy is released because of the attractive forces between them. When solute and solvent molecules are strongly attracted to each other, more energy is released in the final step. Three cases may arise under these circumstances. The overall dissolution process results either in evolution of heat or absorption of heat, or energy released in the final step is the same as the energy absorbed in the first two, *i.e.*, net change is zero.

Examples:

1. Benzene and carbon tetrachloride:	No evolution or absorption of heat.
2. Acetone and water:	Evolution of heat.
3. Ethyl alcohol and water:	Absorption of heat.

A liquid may or may not be soluble in another liquid. Depending upon the relative solubility of a liquid in another, the following three cases are possible:

Liquid-Liquid Systems

1. Liquids that are completely miscible.	2. Liquids that are partially miscible.	3. Liquids that are practically immiscible.
Examples: Benzene and toluene; Ethyl alcohol and water; Carbon tetrachloride and benzene.	*Examples*: Ether and water; Phenol and water; Nicotine and water.	*Examples*: Benzene and water; Carbon tetrachloride and water; Benzene and alcohol.

Miscible liquids form three types of solutions, which can be ideal or non-ideal solutions.

Ideal solution: An ideal solution is one in which the molecules attract one another with equal force irrespective of their nature. Thus, a solution composed of two components A and B will be an ideal one if the forces between A and A, B and B should be the same. An ideal solution possesses the following characteristics:

(i) Volume change of mixing should be zero.

$$\Delta V_{\text{mix}} = 0; \quad V_{\text{solvent}} + V_{\text{solute}} = V_{\text{solution}}$$

(ii) Heat change on mixing should be zero.

$$\Delta H_{\text{mix}} = 0 \text{ (Heat is neither absorbed nor evolved.)}$$

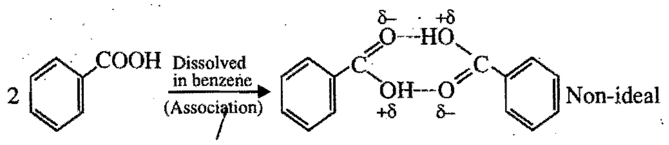
(iii) There should be no chemical reaction between solvent and solute.

$$\left.\begin{array}{lll} \text{Solvent} + & \text{Solute} & \longrightarrow \text{Solution} \\ H_2O & + NH_3 & \longrightarrow NH_4OH \\ H_2O & + CO_2 & \longrightarrow H_2CO_3 \\ H_2O & + CaO & \longrightarrow Ca(OH)_2 \end{array}\right\} \text{Non-ideal}$$

(iv) Solute molecules should not dissociate in the ideal solution.

$$\left.\begin{array}{l} NaCl \xrightarrow{\text{Aqueous medium}} Na^+ + Cl^- \\ H_2SO_4 \xrightarrow{\text{Aqueous medium}} 2H^+ + SO_4^{2-} \end{array}\right\} \text{Non-ideal}$$

(v) Solute molecules should not associate in ideal solution.



(vi) Ideal solutions must obey Raoult's law at all concentrations.

The following are some of the binary mixtures which show the properties of ideal solutions:

(a) Benzene and toluene,
(b) Carbon tetrachloride and silicon tetrachloride,
(c) *n*-Hexane and *n*-heptane,
(d) Ethylene dibromide and ethylene dichloride.

Raoult's Law

According to this law, **the partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.**

Let a mixture (solution) be prepared by mixing n_A mole of liquid A and n_B mole of liquid B. Let p_A and p_B be the partial pressures of two constituents A and B in solution and p_A^0 and p_B^0 the vapour pressures in pure state respectively.

Table 5.2 Comparison between Ideal and Non-ideal Solutions

Ideal solutions	**Non-ideal solutions**	
	Positive deviation from Raoult's law	**Negative deviation from Raoult's law**
1. Obey Raoult's law at every range of concentration.	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{mix} = 0$; neither heat is evolved nor absorbed during dissolution.	$\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{mix} < 0$. Exothermic dissolution; heat is evolved.
3. $\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{mix} > 0$. Volume is increased after dissolution.	$\Delta V_{mix} < 0$. Volume is decreased during dissolution.
4. $P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$ *i.e.*, $p_A = p_A^0 X_A$; $p_B = p_B^0 X_B$	$p_A > p_A^0 X_A$; $p_B > p_B^0 X_B$ $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$	$p_A < p_A^0 X_A$; $p_B < p_B^0 X_B$ $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$
5. $A - A$, $A - B$, $B - B$ interactions should be same, *i.e.*, 'A' and 'B' are identical in shape, size and character.	$A - B$ attractive force should be weaker than $A - A$ and $B - B$ attractive forces. 'A' and 'B' have different shape, size and character.	$A - B$ attractive force should be greater than $A - A$ and $B - B$ attractive forces. 'A' and 'B' have different shape, size and character.
6. Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing higher vapour pressure than the expected value.	Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
Examples: dilute solutions; benzene + toluene; *n*-hexane + *n*-heptane; chlorobenzene + bromobenzene; ethyl bromide + ethyl iodide; *n*-butyl chloride + *n*-butyl bromide.	**Examples:** acetone + ethanol; acetone + CS_2; water + methanol; water + ethanol; CCl_4 + toluene; CCl_4 + $CHCl_3$; acetone + benzene; CCl_4 + CH_3OH; cyclohexane + ethanol.	**Examples:** acetone + aniline; acetone + chloroform; CH_3OH + CH_3COOH; H_2O + HNO_3; chloroform + diethyl ether; water + HCl; acetic acid + pyridine; chloroform + benzene.

Thus, according to Raoult's law,

$$p_A = \frac{n_A}{n_A + n_B} p_A^0 = \text{mole fraction of } A \times p_A^0 = X_A \, p_A^0$$

and $$p_B = \frac{n_B}{n_A + n_B} p_B^0 = \text{mole fraction of } B \times p_B^0 = X_B \, p_B^0$$

If the total pressure be P, then

$$P = p_A + p_B$$

$$= \frac{n_A}{n_A + n_B} p_A^0 + \frac{n_B}{n_A + n_B} p_B^0$$

$$= X_A \, p_A^0 + X_B \, p_B^0$$

This law, in fact, is the major deciding factor, whether a solution will be ideal or non-ideal. Ideal solutions obey Raoult's law at every range of concentration. Non-ideal solutions do not obey Raoult's law. They show either **positive** or **negative** deviation from Raoult's law. For comparison between ideal and non-ideal solutions a table has been given below. (Only binary combinations of miscible liquids have been considered.)

Graphical Representation of Ideal and Non-ideal Solutions

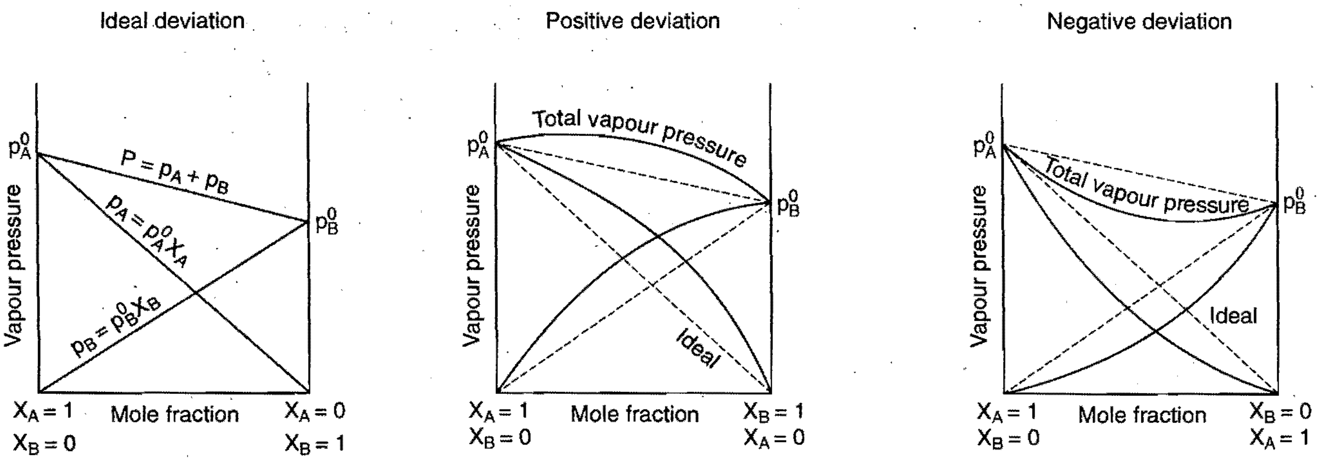


Fig. 5.3

Relation between Dalton's Law and Raoult's Law:

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fractions of vapours A and B be Y_A and Y_B respectively. Let p_A and p_B be the partial pressures of vapours A and B respectively and total pressure P.

$$p_A = Y_A \, P \quad \text{... (i)}$$

$$p_B = Y_B \, P \quad \text{... (ii)}$$

$$p_A = X_A \, p_A^0 \quad \text{... (iii)}$$

$$p_B = X_B \, p_B^0 \quad \text{... (iv)}$$

Equating eqs. (i) and (iii),

$$Y_A \, P = X_A \, p_A^0$$

or $$Y_A = \frac{X_A \, p_A^0}{P} = \frac{p_A}{P}$$

Similarly, equating eqs. (ii) and (iv),

$$Y_B = \frac{X_B \, p_B^0}{P} = \frac{p_B}{P}$$

Thus, in case of ideal solution the vapour phase is richer with more volatile component, *i.e.*, the one having relatively greater vapour pressure.

Example 19. *The vapour pressures of ethanol and methanol are* 44.5 *mm and* 88.7 *mm Hg respectively. An ideal solution is formed at the same temperature by mixing* 60 *g of ethanol with* 40 *g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.*

Solution: Mol. mass of ethyl alcohol = $C_2H_5OH = 46$

No. of moles of ethyl alcohol $= \frac{60}{46} = 1.304$

Mol. mass of methyl alcohol = $CH_3OH = 32$

No. of moles of methyl alcohol $= \frac{40}{32} = 1.25$

'X_A', mole fraction of ethyl alcohol $= \frac{1.304}{1.304 + 1.25} = 0.5107$

'X_B', mole fraction of methyl alcohol $= \frac{1.25}{1.304 + 1.25}$

$= 0.4893$

Partial pressure of ethyl alcohol $= X_A \cdot p_A^0 = 0.5107 \times 44.5$

$= 22.73$ mm Hg

Partial pressure of methyl alcohol $= X_B \cdot p_B^0 = 0.4893 \times 88.7$

$= 43.40$ mm Hg

Total vapour pressure of solution = 22.73 + 43.40

= 66.13 mm Hg

Mole fraction of methyl alcohol in the vapour

$$= \frac{\text{Partial pressure of } CH_3OH}{\text{Total vapour pressure}} = \frac{43.40}{66.13} = 0.6563$$

Example 20. *Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.*

Solution: Let the vapour pressure of pure A be $= p_A^0$; and the vapour pressure of pure B be $= p_B^0$.

Total vapour pressure of solution (1 mole A + 3 mole B)

$$= X_A \cdot p_A^0 + X_B \cdot p_B^0 \quad [X_A \text{ is mole fraction of } A \text{ and } X_B \text{ is mole fraction of } B]$$

$$550 = \frac{1}{4} p_A^0 + \frac{3}{4} p_B^0$$

or

$$2200 = p_A^0 + 3p_B^0 \qquad \dots \text{(i)}$$

Total vapour pressure of solution (1 mole A + 4 mole B)

$$= \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

$$560 = \frac{1}{5} p_A^0 + \frac{4}{5} p_B^0$$

or

$$2800 = p_A^0 + 4p_B^0 \qquad \dots \text{(ii)}$$

Solving eqs. (i) and (ii),

$p_B^0 = 600$ mm of Hg = vapour pressure of pure B

$p_A^0 = 400$ mm of Hg = vapour pressure of pure A

Example 21. *An aqueous solution containing 28% by mass of a liquid A (mol. mass = 140) has a vapour pressure of 160 mm at 37°C. Find the vapour pressure of the pure liquid A (The vapour pressure of water at 37°C is 150 mm).*

Solution: For two miscible liquids,

P_{total} = Mole fraction of $A \times p_A^0$ + Mole fraction of $B \times p_B^0$

No. of moles of $A = \frac{28}{140} = 0.2$

Liquid B is water. Its mass is $(100 - 28)$, *i.e.*, 72.

No. of moles of $B = \frac{72}{18} = 4.0$

Total no. of moles $= 0.2 + 4.0 = 4.2$

Given, $P_{\text{total}} = 160$ mm

$p_B^0 = 150$ mm

So,

$$160 = \frac{0.2}{4.2} \times p_A^0 + \frac{4.0}{4.2} \times 150$$

$$p_A^0 = \frac{17.15 \times 4.2}{0.2} = 360.15 \text{ mm}$$

Example 22. *Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25 g of heptane and 35 g of octane?*

Solution: (A) Heptane C_7H_{16} $m_A = 100$

(B) Octane C_8H_{18} $m_B = 114$

$$n_A = \frac{w_A}{m_A} = \frac{25}{100} = 0.25; \quad n_B = \frac{35}{114} = 0.3$$

$$x_A = \frac{0.25}{0.25 + 0.30}; \qquad x_B = \frac{0.3}{0.25 + 0.30}$$

$$= 0.45 \qquad\qquad = 0.55$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 105.2 \times 0.45 + 46.8 \times 0.55$$

$$= 47.34 + 25.74 = 73.08 \text{ kPa}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

12. Mole fraction of the component A in vapour phase is x_1 and the mole fraction of component A in liquid mixture is x_2, then (p_A^0 = vapour pressure of pure A; p_B^0 = vapour pressure of pure B), the total vapour pressure of liquid mixture is:

(a) $p_A^0 \frac{x_2}{x_1}$ (b) $p_A^0 \frac{x_1}{x_2}$ (c) $p_B^0 \frac{x_1}{x_2}$ (d) $p_B^0 \frac{x_2}{x_1}$

[Ans. (a)]

[Hint: $p_A = p_A^0 x_2$, vapour pressure of 'A'

Mole fraction of A in vapour $= \frac{p_A}{p_{\text{total}}}$

$$x_1 = \frac{p_A^0 x_2}{p}$$

$$p = \frac{p_A^0 x_2}{x_1}]$$

13. Vapour pressure of pure A (p_A^0) = 100 mm Hg

Vapour pressure of pure B (p_B^0) = 150 mm Hg

2 mole of liquid A and 3 mole of liquid B are mixed to form an ideal solution. The vapour pressure of solution will be:

(a) 135 mm (b) 130 mm (c) 140 mm (d) 145 mm

[Ans. (b)]

[Hint: $x_A = \frac{2}{5}, x_B = \frac{3}{5}$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 100 \times \frac{2}{5} + 150 \times \frac{3}{5} = 40 + 90 = 130]$$

14. The vapour pressure of a certain pure liquid A at 298 K is 40 m bar. When a solution of B is prepared in A at the same temperature, the vapour pressure is found to be 32 m bar. The mole fraction of A in the solution is:

(a) 0.5 (b) 0.2 (c) 0.1 (d) 0.8

[Ans. (d)]

[Hint: $p = p^0 x_A$

$32 = 40 \times x_A$ or $x_A = 0.8$]

15. 100 mL of liquid A and 25 mL of liquid B are mixed to form a solution of volume 125 mL. Then the solution is:

(a) ideal

(b) non-ideal with positive deviation

(c) non-ideal with negative deviation

(d) cannot be predicted

[Ans. (a)]

[Hint: $\Delta V_{\text{mix}} = 0$, hence the solution is ideal.]

16. The vapour pressure of pure benzene at 88°C is 957 mm and that of toluene at the same temperature is 379.5 mm. Calculate the composition of benzene-toluene mixture boiling at 88°C:

(a) $x_{\text{benzene}} = 0.66$; $x_{\text{toluene}} = 0.34$
(b) $x_{\text{benzene}} = 0.34$; $x_{\text{toluene}} = 0.66$
(c) $x_{\text{benzene}} = x_{\text{toluene}} = 0.5$
(d) $x_{\text{benzene}} = 0.75$; $x_{\text{toluene}} = 0.25$

[Ans. (a)]

[Hint: $p = p^0_{\text{benzene}}\, x_{\text{benzene}} + p^0_{\text{toluene}}\, x_{\text{toluene}}$

$$760 = 957 \cdot x_{\text{benzene}} + 379.5(1 - x_{\text{benzene}})$$

$$x_{\text{benzene}} = 0.66$$

and $x_{\text{toluene}} = 1 - 0.66 = 0.34$]

17. At 25°C, the total pressure of an ideal solution obtained by mixing 3 mole of A and 2 mole of B, is 184 torr. What is the vapour pressure (in torr) of pure B at the same temperature (Vapour pressure of pure A at 25°C is 200 torr.)? **[CET (J&K) 2006]**

(a) 180 (b) 160 (c) 16 (d) 100

[Ans. (b)]

[Hint: $x_A = \dfrac{n_A}{n_A + n_B} = \dfrac{3}{3+2} = \dfrac{3}{5} = 0.6$

$$x_B = 0.4$$

$$p = p^0_A x_A + p^0_B x_B$$

$$184 = 200 \times 0.6 + p^0_B \times 0.4$$

$$184 = 120 + p^0_B \times 0.4$$

$$p^0_B = \frac{64}{0.4} = 160 \text{ torr}]$$

18. The mass of glucose that would be dissolved in 50 g of water in order to produce the same lowering of vapour pressure as is produced by dissolving 1 g of urea in the same quantity of water is: **(KCET 2006)**

(a) 1 g (b) 3 g (c) 6 g (d) 18 g

[Ans. (b)]

[Hint: $(\Delta p)_{\text{glucose}} = (\Delta p)_{\text{urea}}$

$$(x_B)_{\text{glucose}} = (x_B)_{\text{urea}}$$

i.e., $\left(\dfrac{n_B}{n_A}\right)_{\text{glucose}} = \left(\dfrac{n_B}{n_A}\right)_{\text{urea}}$

$$\frac{w_B}{50} \times \frac{18}{180} = \frac{1 \times 18}{50 \times 60}$$

$$w_B = 3 \text{ g}]$$

5.7 THEORY OF FRACTIONAL DISTILLATION

The process of separation of one liquid from another liquid (binary mixture) having different boiling points by distillation is termed fractional distillation. The information, whether a particular solution of two liquids can be separated by distillation or not, is provided by the study of liquid-vapour equilibrium diagrams at constant pressure, say atmospheric pressure. **The separation is possible only when the vapour phase has a composition different from that of the boiling liquid mixture.**

Liquid pairs of type-I (Ideal solutions): The boiling temperature composition curves for liquid and vapour phases in the case of binary solutions of first type are represented in Fig. 5.4.

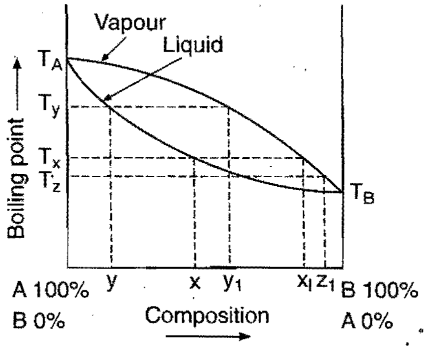


Fig. 5.4 Liquid-vapour equilibrium diagram of a solution of type-I

Suppose a solution of composition x is heated. When the temperature T_x is reached, the boiling will start. At this temperature, the vapour coming off from x will have the composition x_1. Since, x_1 is richer in B than x, the composition of the residual liquid will become richer in A. Let the new composition be y. This liquid cannot boil at temperature T_x but will require higher temperature T_y. The vapour coming off at temperature T_y will also be richer in B as represented by y_1. Hence, the composition of the residue will again be enriched in A. Thus, if the process is allowed to continue, the boiling point of solution will go on increasing towards T_A, the boiling point of pure liquid A. At the same time the solution becomes more and more rich in A. If the process is continued for a sufficiently long time, pure liquid A can be obtained.

Now, if the initial vapours are condensed, the solution obtained will have the composition x_1 and boils at temperature T_z. Evidently, the distillate is richer in B than before. If the process of condensation and redistilling is continued, the final distillate will be pure B component.

Thus, the two liquids forming a solution of type-I can be separated by fractional distillation.

Solution of type-II (Positive deviations from Raoult's law): The boiling temperature-composition curves for the liquid and vapour phases have been shown in Fig. 5.5. The two curves meet at a minimum point C where the liquid and vapour phases have the same composition. The liquid mixture at point C will boil at constant temperature T without undergoing any

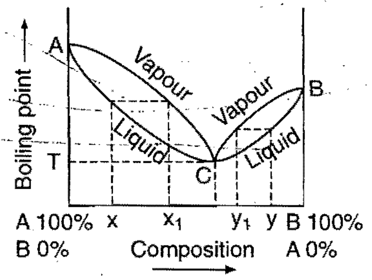


Fig. 5.5 Boiling point-composition curves in binary solution of type-II

change in composition. **Such a mixture which boils at constant temperature and distils over completely at the same temperature without any change in composition, is called constant boiling mixture or azeotropic mixture.**

Consider the distillation of a mixture of composition x. The vapour given off has the composition x_1. The composition of residual liquid will shift towards A. In the mean time the composition of the distillate shifts towards C. Ultimately by repeated fractional distillation, the mixture of composition C will be obtained as distillate and pure liquid A will be left as residue. It will never be possible to have pure B.

When a mixture of composition y is distilled, the vapour given off has the composition y_1, *i.e.*, the composition of residual liquid will shift towards B. Ultimately the mixture of composition C will be obtained as distillate and pure liquid B will be left as residue. It will never be possible to have pure A.

There are several liquid pairs which form minimum boiling point azeotropes. Some examples are given in the table:

Table 5.3 Some Azeotropic Mixtures

	Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1.	Water-Ethanol	95.97 Ethanol	78.15°C
2.	Pyridine-Water	57.00 Pyridine	92.60°C
3.	Ethanol-Benzene	32.40 Ethanol	67.80°C
4.	Acetic acid-Toluene	28.00 Acetic acid	105.40°C

Solutions of type-III (Negative deviations from Raoult's law): The boiling temperature-composition curves for the liquid and vapour phases have been shown in Fig. 5.6. The curves meet at point C. At this point, both liquid and vapour phases have same composition. The constant-boiling mixture has maximum boiling point.

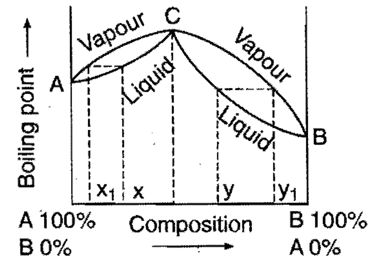


Fig. 5.6 Boiling temperature–composition curves in binary solution of type-III

Consider the distillation of a mixture of composition x. The vapour coming off is richer in A as indicated by composition x_1. The composition of the residual liquid shifts towards C. As the distillation proceeds, the composition of the distillate moves towards A and that of residue towards C.

Similarly, a mixture of composition lying between B and C, say y, on distillation will give vapour richer in B as indicated by composition y_1. The composition of residual liquid shifts towards C and distillate towards A on repeated distillation.

It is never possible to separate a mixture completely into the pure components A and B. It mainly gives a constant boiling mixture (azeotropes) which can never be separated by distillation.

There are several liquid pairs which form maximum boiling point azeotrope. Some examples are tabulated below:

	Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1.	Nitric acid-Water	68% Nitric acid	125.5°C
2.	Acetic acid-Pyridine	65% Pyridine	139.0°C
3.	Chloroform-Acetone	80% Chloroform	65.0°C
4.	Hydrogen chloride-Water	79.8% Water	108.6°C

5.8 SOLUTIONS OF SOLIDS IN LIQUIDS

Solutions of this type are most common. In solutions of solids in liquids, the liquid is invariably referred to as a solvent and the solid dissolved in it as the solute. If a solute is added in small amounts at a time to a given amount of a solvent at a constant temperature, with vigorous stirring of the solvent after each addition, a stage is reached when the added solute no more disappears, *i.e.*, goes into solution but remains undissolved. The solution is then said to be saturated. **A solution which remains in contact with undissolved solute is termed as saturated.** It can also be defined as **one which is in equilibrium with the excess of solid at a particular temperature.**

The amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature is termed the **solubility** of the solute in the given solvent at that temperature. Each substance has a characteristic solubility in a given solvent at a definite temperature.

When a solid is added to the solvent, the particles from the solid diffuse into it. The solute and solvent molecules move constantly in the solution phase. Some of the particles of the solute return to the solid state due to collisions. Thus, two opposite processes operate simultaneously.

(a) *Dissolution*: Particles of solute leaving the solid and dissolving in the solvent.

(b) *Recrystallisation*: Solute particles returning to the solid form.

When these two processes move with same speed, an equilibrium stage is reached,

$$\text{Solute (solid)} \rightleftharpoons \text{Solute (dissolved)}$$

Thus, a dynamic equilibrium exists in a saturated solution.

When a saturated solution prepared at a higher temperature is cooled, it gives a solution which contains usually more of solute than required for the saturated solution at that temperature. Such a solution is referred to as a **supersaturated solution.** It is usually unstable and changes to saturated solution when excess of solute comes out in solid state.

The following factors influence the solubility of a solute in a liquid:

(1) Nature of solute,
(2) Nature of solvent,
(3) Temperature.

1. Nature of solute: The solutes (solids) can be classified as ionic and non-ionic solids. The ionic solids consist of positively and negatively charged ions. It is the force of attraction between the ions, *i.e.*, lattice energy which opposes the tendency of a solute to dissolve. This force of attraction is different in different ionic solids depending on the charges present on the ions and distance between ions (ionic radii). The ionic solutes having high lattice energy like $BaSO_4$ are less soluble while those having less lattice energy have more solubility. The ions are solvated by the solvent molecules and in this process energy (known as hydration energy) is released. When the hydration energy is high, the ionic solid is more soluble.

Many non-ionic substances dissolve in polar solvents due to hydrogen bonding. Generally, if the solute and solvent have similar characteristics, *i.e.*, both are polar or both non-polar, the solubility is high and if both are dissimilar, the solubility is found low.

2. Nature of solvent: Ionic solids dissolve to a larger extent in a solvent having a high dielectric constant as compared to solvents of low dielectric constants. Dielectric constant of water is 80 while that of methyl alcohol is 33.5. An ionic solid, therefore, dissolves more readily in water than in methyl alcohol. Benzene has a very low dielectric constant of 2.3 and, hence, ionic solids do not dissolve in benzene.

For non-ionic solids, the guiding principle is *'like dissolves like'*, *i.e.*, if the solvent is polar, it will dissolve the polar solutes and if it is non-polar, it will dissolve the non-polar solutes in it.

3. Temperature: The solubility of a solute in a given solvent varies appreciably with temperature. A few curves drawn between solubility in water and temperature are given in Fig. 5.7.

It is observed that the solubility of NaCl increases very slightly with an increase in temperature whereas those of KNO_3, $NaNO_3$, $AgNO_3$ and KI, etc., increase greatly. A sharp break in a solubility curve indicates the formation of a compound whose solubility is different from that of the substance from which it has been formed as in the case of $Na_2SO_4 \cdot 10H_2O$. It losses its water of crystallisation at 32.3°C and is converted into anhydrous form. There are few substances like calcium acetate, cerium sulphate, calcium chromate, etc., which show a decrease in solubility with rise in temperature.

Generally, solubility depends on heat of solution. **If a substance dissolves with absorption of heat, the solubility increases with rise of temperature.** On the other hand, **if a substance dissolves with evolution of heat, the solubility decreases with rise of temperature.**

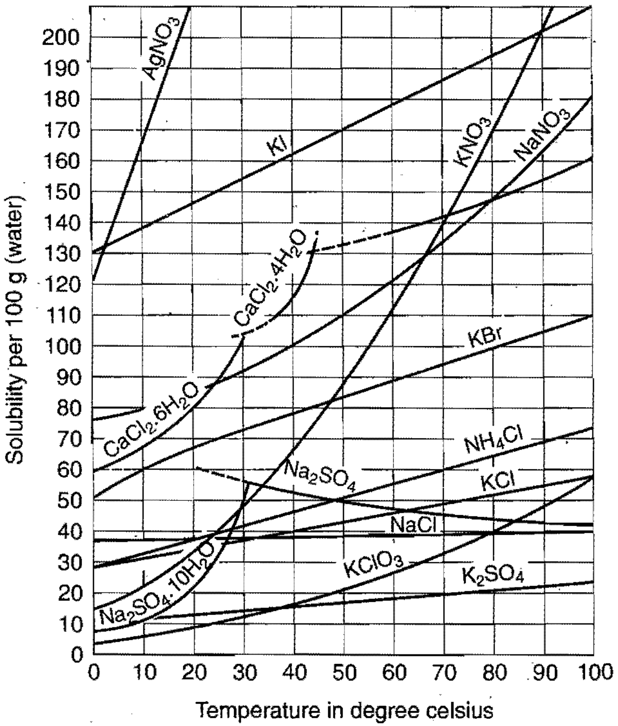


Fig. 5.7 Solubility curves of some compounds

Determination of solubility: The solubility of salts is generally determined by gravimetric method. First of all a saturated solution is prepared. Some part of this saturated solution is weighed out in a porcelain dish. The solution is evaporated slowly to dryness on a sand bath. The dish is cooled and weighed again. The observations are recorded as follows:

1. Mass of empty dish = w g
2. Mass of dish + solution = w_1 g
3. So, Mass of solution = $(w_1 - w)$ g
4. Mass of dish + residue = w_2 g

So, Mass of residue = $(w_2 - w)$ g = x g

and Mass of solvent = (Mass of solution − Mass of residue)

$$= (w_1 - w) - (w_2 - w)$$
$$= (w_1 - w_2) = y \text{ g}$$

Thus, the solubility of salt $= \frac{x}{y} \times 100$ g per 100 g of solvent.

Example 23. *50 g of a saturated aqueous solution of potassium chloride at* 30°C *is evaporated to dryness, when* 13.2 g *of dry KCl was obtained. Calculate the solubility of KCl in water at* 30°C.

Solution: Mass of water in solution = (50 − 13.2) = 36.8 g

$$\text{Solubility of KCl} = \frac{\text{Mass of KCl}}{\text{Mass of water}} \times 100 = \frac{13.2}{36.8} \times 100 = 35.87 \text{ g}$$

Example 24. *How much copper sulphate will be required to saturate* 100 g *of a dilute aqueous solution of* $CuSO_4$ *at* 25° C *if* 10 g *of the dilute solution leave on evaporation and drying* 1.2 g *of anhydrous* $CuSO_4$? *The solubility of* $CuSO_4$ *in water at* 25° C *is* 25.

Solution: 100 g of dilute solution of $CuSO_4$ contain

$$= 1.2 \times 10 = 12.0 \text{ g } CuSO_4$$

Mass of water present in dilute solution

$$= (100 - 12) = 88 \text{ g}$$

To saturate 100 g of water, $CuSO_4$ required = 25 g

So, to saturate 88 g of water, $CuSO_4$ required $= \frac{25}{100} \times 88$
$= 22\,g$

Thus, the mass of $CuSO_4$ to be added to 100 g of dilute solution to saturate it $= (22 - 12) = 10\,g$

5.9 COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent. The dilute solutions show more or less ideal behaviour as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

Dilute solutions containing non-volatile solute exhibit some special properties which depend only upon the number of solute particles present in the solution irrespective of their nature. These properties are termed as **colligative properties.** The colligative properties are:

(i) Lowering in the vapour pressure,
(ii) Elevation in the boiling point,
(iii) Depression in the freezing point and
(iv) Osmotic pressure.

Colligative properties are the properties of dilute solutions, that is why these are termed as *colligative properties of dilute solutions.* These properties are related to one another. Thus, if one is measured, the other can be calculated. The importance of these properties lies in the fact that they provide methods for the determination of molecular masses of dissolved solutes. The results are excellent if the following three conditions are satisfied:

(i) The solution should be very dilute.
(ii) The solute should be non-volatile.
(iii) The solute does not dissociate or associate in solution.

5.10 LOWERING IN THE VAPOUR PRESSURE

When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons:

(i) Percentage surface area occupied by the solvent decreases. Thus, the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the per cent surface area occupied by the solvent decreases.

(ii) According to Graham's law of evaporation,

$$\text{Rate of evaporation} \propto \frac{1}{\sqrt{\text{density}}}$$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus, both rate of evaporation and vapour pressure are lowered.

If p_0 is the vapour pressure of pure solvent and p_s is the vapour pressure of the solution, the difference $(p_0 - p_s)$ is termed **lowering in vapour pressure** and the ratio $\left[\frac{p_0 - p_s}{p_0}\right]$ is termed **relative lowering in vapour pressure.**

Raoult, in 1886, established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. The relationship is known as **Raoult's law.** It states that **the relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.**

If n moles of solute be dissolved in N moles of the solvent, the mole fraction of the solute will be $\frac{n}{n+N}$.

According to Raoult's law, $\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$

This is the mathematical expression for Raoult's law.

[**Modified form of Raoult's law:** The above relationship can be written as,

$$\frac{p_0}{p_0 - p_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

or
$$\frac{p_0}{p_0 - p_s} - 1 = \frac{N}{n} \text{ or } \frac{p_s}{p_0 - p_s} = \frac{N}{n}$$

or
$$\frac{p_0 - p_s}{p_s} = \frac{n}{N} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

This equation gives accurate results and is easy to apply.]

Derivation of Raoult's Law for a Dilute Solution

When a non-volatile solute is dissolved in a volatile solvent, a fraction of the surface of solvent is blocked by solute molecules where no evaporation occurs. Thus, under similar conditions, the vapour pressure is decreased. The vapour pressure of the solution, thus, depends upon the number of molecules of the solvent present on the surface of the solution. The number of such molecules is proportional to mole fraction of the solvent.

So, the vapour pressure of solution,

$$`p_s' \propto \frac{N}{n+N}$$

or
$$p_s = k \cdot \frac{N}{n+N} \quad \text{... (i)}$$

(k is proportionality factor)

For pure solvent, $n = 0$

and hence, $$p_0 = k\frac{N}{0+N} = k \quad \text{... (ii)}$$

Putting the value of k in eq. (i)

$$p_s = p_0 \frac{N}{n+N}$$

Note : Isopiestic solutions : Two solutions having same vapour pressure at same temperature are known as **isopiestic** solutions.

or $$\frac{p_s}{p_0}=\frac{N}{n+N}$$

or $$1-\frac{p_s}{p_0}=1-\frac{N}{n+N}$$

or $$\frac{p_0-p_s}{p_0}=\frac{n}{n+N} \qquad \text{... (iii)}$$

This is Raoult's equation.

If a solution is made by dissolving w_B g of solute (molecular mass m_B) in w_A g of the solvent (molecular mass m_A), the mole fraction of the solute will be

$$\frac{\dfrac{w_B}{m_B}}{\dfrac{w_A}{m_A}+\dfrac{w_B}{m_B}}$$

If the solution is very dilute, $\frac{w_B}{m_B}$ can be neglected in the denominator as compared to $\frac{w_A}{m_A}$. The eq. (iii), thus, becomes

$$\frac{p_0-p_s}{p_0}=\frac{w_B\times m_A}{m_B\times w_A} \qquad \text{... (iv)}$$

This relationship is useful in the determination of the molecular mass of dissolved solute by measuring relative lowering of vapour pressure.

Measurement of Relative Lowering in Vapour Pressure (Ostwald and Walker Method)

The apparatus used is shown in Fig. 5.8. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent. Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like P_2O_5, conc. H_2SO_4 etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature.

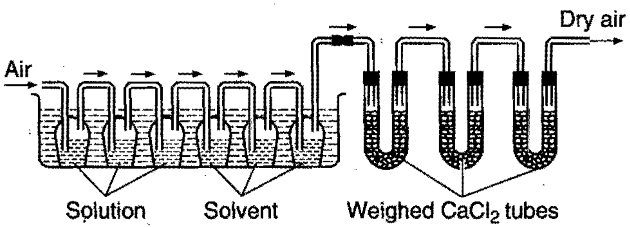


Fig. 5.8 Ostwald and Walker method

A current of pure dry air is bubbled through the series of bulbs as shown in Fig. 5.8. The air gets saturated with the vapours in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, *i.e.*, $p_0 - p_s$. The two sets of bulbs are weighed again. The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto p_s$

Loss in mass in the solvent bulbs $\propto (p_0 - p_s)$

Total loss in both sets of bulbs $\propto [p_s + (p_0 - p_s)]$

$\propto p_0$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

$$\text{Thus, } \frac{p_0-p_s}{p_0}=\frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$
$$=\frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

$$\frac{p_0-p_s}{p_0}=\frac{w_B/m_B}{w_A/m_A+w_B/m_B}$$

$$\therefore \quad \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}}=\frac{w_B/m_B}{w_A/m_A+w_B/m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied:

$$\frac{p_0-p_s}{p_0}=\frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of guard tubes}}=\frac{w_B\times m_A}{m_B\times w_A}$$

Vapour Pressure of Liquid and Temperature

$$\text{Liquid} \rightleftharpoons \text{Vapour} \qquad \Delta H_{\text{vap.}} > 0$$

Vapour pressure of liquid increases with temperature. Here, ΔH is enthalpy of vaporisation. A graphical representation of vapour pressure *versus* temperature is given below :

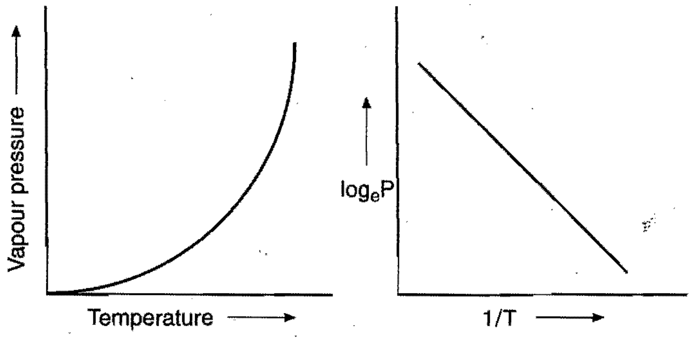


Fig. 5.9 Variation of vapour pressure with temperature

If vapour pressure of a liquid is known at a temperature; it can be calculated at another temperature using Clausius-Clapeyron equation :

$$\log_{10}\left(\frac{P_2}{P_1}\right)=\frac{\Delta H_{\text{vap.}}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Here, P_1 = Vapour pressure at temperature T_1

P_2 = Vapour pressure at temperature T_2

SOME SOLVED EXAMPLES

Example 25. *Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.*

Solution: According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

or $$\Delta p = \frac{n}{n+N} \cdot p_0$$

Given: $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

Example 26. *The vapour pressure of pure benzene at a certain temperature is* 640 *mm Hg. A non-volatile solid weighing* 2.175 *g is added to* 39.0 *g of benzene. The vapour pressure of the solution is* 600 *mm Hg. What is the molecular mass of the solid substance?* **(IIT 1990; MLNR 1992)**

Solution: According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

Let m be the molecular mass of the solid substance.

$$n = \frac{2.175}{m}; N = \frac{39}{78} = 0.5$$

(molecular mass of benzene = 78)

$$p_0 = 640 \text{ mm}; \; p_s = 600 \text{ mm}$$

Substituting the values in above equation,

$$\frac{640 - 600}{640} = \frac{\frac{2.175}{m}}{\frac{2.175}{m} + 0.5} = \frac{2.175}{2.175 + 0.5\,m}$$

$$m = \frac{2.175 \times 16 - 2.175}{0.5} = 65.25$$

Example 27. *A solution containing* 30 *g of a non-volatile solute in exactly* 90 *g of water has a vapour pressure of* 21.85 *mm of Hg at* 25°*C. Further,* 18 *g of water is then added to the solution; the new vapour pressure becomes* 22.15 *mm of Hg at* 25°*C. Calculate* (*a*) *molecular mass of the solute and* (*b*) *vapour pressure of water at* 25°*C.* **(MLNR 1990)**

Solution: Let the vapour pressure of water at 25°C be p_0 and molecular mass of the solute be m.

Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

For solution (I), $$\frac{(p_0 - 21.85)}{21.85} = \frac{30 \times 18}{90 \times m} \quad \text{... (i)}$$

For solution (II), $$\frac{(p_0 - 22.15)}{22.15} = \frac{30 \times 18}{108 \times m} \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii),

$$\frac{(p_0 - 21.85)}{21.85} \times \frac{22.15}{(p_0 - 22.15)} = \frac{108}{90} = \frac{6}{5}$$

$$p_0 = 23.87 \text{ mm of Hg}$$

Substituting the value of p_0 in eq. (i)

$$m = 67.9$$

Example 28. *What mass of non-volatile solute* (*urea*) *needs to be dissolved in* 100 *g of water in order to decrease the vapour pressure of water by* 25%. *What will be the molality of solution?* **(IIT 1993)**

Solution: Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

If $p_0 = 100$ mm, then $p_s = 75$ mm

$$\frac{100 - 75}{75} = \frac{w \times 18}{100 \times 60}$$

$$w = 111.1$$

$$\text{Molality} = \frac{w \times 1000}{m \times W} = \frac{111.1 \times 1000}{60 \times 100} = 18.52\, m$$

Example 29. *A current of dry air was bubbled through a bulb containing* 26.66 *g of an organic compound in* 200 *g of water, then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in bulb containing water was* 0.087 *g and gain in mass of the calcium chloride tube was* 2.036 *g. Calculate the molecular mass of the organic substance.*

Solution: $$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulb}}{\text{Gain in mass of CaCl}_2\text{ tube}}$$

$$= \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be m. According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{m}}{\frac{26.66}{m} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}m}$$

$$m = 53.75$$

Example 30. *The vapour pressure of a dilute aqueous solution of glucose is* 750 *mm Hg at* 373 *K. Calculate* (i) *molality,* (ii) *mole fraction of the solute.*

Solution: p_0 = Vapour pressure of water at 373 K = 760 mm Hg

Using Raoult's law in the following form,

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm}$$

or $$\frac{760 - 750}{750} = \frac{w}{Wm} \times 18$$

or $$\frac{w}{W \times m} = \frac{10}{750 \times 18}$$

$$\text{Molality} = \frac{w}{W \times m} \times 1000 = \frac{10 \times 1000}{750 \times 18} = 0.74\ m$$

$$p_s = \text{Mole fraction of solvent} \times p_0;$$

$$\text{Mole fraction of solvent} = \frac{750}{760}$$

So, $\text{Mole fraction of solute} = \left(1 - \frac{750}{760}\right) = 0.0132$

Example 31. *Calculate the vapour pressure of an aqueous solution which contains 5 mass per cent of urea. The vapour pressure of pure water is 23.5 mm Hg. Molar mass of urea is 60.*

Solution: Mass of urea = 5 g

Mass of water = (100 − 5) = 95 g

$$\text{No. of moles of urea} = \frac{5}{60} = 0.083$$

$$\text{No. of moles of water} = \frac{95}{18} = 5.278$$

$$\text{Total number of moles} = 5.278 + 0.083 = 5.361$$

$$\text{Mole fraction of solvent} = \frac{5.278}{5.361}$$

$$p_s = \text{Mole fraction of solvent} \times p_0 = \frac{5.278}{5.361} \times 23.5 = 23.14 \text{ mm}$$

Example 32. *10 g of glucose (molar mass 180) and 20 g of sucrose (molar mass 342) are dissolved in 100 g of water. What will be the vapour pressure of the resultant solution if the vapour pressure of water is 35 mm Hg?*

Solution: Mass of glucose = 10 g

No. of moles of glucose = 0.0556

Mass of sucrose = 20 g

No. of moles of sucrose = 0.0585

Mass of water = 100 g

No. of moles of water = 5.556

Total number of moles = 5.556 + 0.0585 + 0.0556 = 5.67

$$\text{Mole fraction of water} = \frac{5.556}{5.67}$$

$$\text{Vapour pressure of solution} = \text{Mole fraction of water} \times p_0 = \frac{5.556}{5.67} \times 35 = 34.3 \text{ mm Hg}$$

Example 33. *Calculate the vapour pressure of an aqueous solution of 1.0 molal glucose solution at 100°C.*

Solution: $\text{Molality} = \frac{w}{m \times W} \times 1000$

where, w = mass of solute in grams;
W = mass of solvent in grams

$$1.0 = \frac{w}{m \times W} \times 1000$$

or $$\frac{w}{m \times W} = \frac{1.0}{1000} = 0.001$$

Applying Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w}{m \times W} \times M \qquad (M = 18)$$

$$\frac{760 - p_s}{760} = 0.001 \times 18 \quad (p_0 = 760 \text{ mm at } 100°\text{C})$$

or $$p_s = 760 - 760 \times 0.001 \times 18 = 760 - 13.68 = 746.32 \text{ mm}$$

Example 34. *The vapour pressure of pure benzene at 50°C is 268 mm of Hg. How many moles of non-volatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure 167 mm of Hg at 50°C?*

Solution: Applying Raoult's law in the following form:

$$\frac{p_0 - p_s}{p_s} = \frac{wM}{Wm} = \frac{w/m}{W/M}$$

= No. of moles of solute per mole of benzene

or $$\frac{n}{N} = \frac{(268 - 167)}{167} = 0.6047 \approx 0.605$$

Alternative method: We know that, p_s = Mole fraction of solvent × p_0

or 167 = Mole fraction of solvent × 268

So, $\text{Mole fraction of solvent} = \frac{167}{268} = 0.623$

Mole fraction of solute = 1 − 0.623 = 0.377

$$\frac{n}{N} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} = \frac{0.377}{0.623} = 0.605$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The vapour pressure of water at 23°C is 19.8 mm. 0.1 mole glucose is dissolved in 178.2 g of water. What is the vapour pressure (in mm) of the resultant solution?

(a) 19 (b) 19.602 (c) 19.402 (d) 19.202

[Ans. (b)]

[Hint: $n_B = 0.1,\ n_A = \frac{178.2}{18} = 9.9$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{9.9}{9.9 + 0.1} = 0.99$$

$$p = p_0 x_A = 19.8 \times 0.99 = 19.602 \text{ mm}]$$

20. What is the vapour pressure of the solution containing 34.2 g of sucrose per 100 g of water at 25°C? The vapour pressure of water at 25°C is 23.75 mm.

(a) 20.3 mm (b) 23.10 mm

(c) unpredictable (d) 23.33 mm

[**Ans.** (d)]

[**Hint:** $$n_A = \frac{w_A}{m_A} = \frac{100}{18} = 5.55$$

$$n_B = \frac{34.2}{342} = 0.1$$

$$x_A = \frac{5.55}{5.55 + 0.1} = \frac{5.55}{5.65} = 0.982$$

$$p = p_0 x_A$$

$$= 23.75 \times 0.982 = 23.33 \text{ mm}]$$

21. Lowering of vapour pressure due to a solute in 1 molal aqueous solution at 100°C is:

(a) 13.44 mm Hg (b) 14.12 mm Hg
(c) 31.2 mm Hg (d) 35.2 mm Hg

[**Ans.** (a)]

[**Hint:** $$m = \frac{x_B \times 1000}{(1 - x_B)m_A}$$ x_B = mole fraction of solute
m_A = molar mass of solvent

$$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.0176$$

$$x_A = 1 - 0.0176 = 0.9824$$

$$p = p_0 x_A$$

$$= 760 \times 0.9824 = 746.62$$

$$\Delta p = p_0 - p = 760 - 746.62$$

$$\approx 13.4]$$

22. The mass of a non-volatile solute (molecular mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80% will be:

(a) 20 g (b) 30 g (c) 10 g (d) 40 g

[**Ans.** (c)]

[**Hint:** If $p_0 = 100$, then $p = 80$

$$p = p_0 x_A$$

$$80 = 100 \times x_A$$

$$x_A = 0.80$$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{114/114}{114/114 + w_B/40}$$

$$0.8 = \frac{1}{1 + w_B/40}$$

$$1 + \frac{w_B}{40} = \frac{1}{0.8}$$

$$w_B = 10 \text{ g}]$$

23. 3g urea is dissolved in 45g of water. The relative lowering of vapour pressure is : **[Comed (Karnataka) 2008]**

(a) 0.05 (b) 0.04 (c) 0.02 (d) 0.01

[**Ans.** (c)]

[**Hint:** $$n_B = \frac{3}{60} = 0.05; \quad n_A = \frac{45}{18} = 2.5$$

$$\frac{\Delta p}{p_0} = x_B = \frac{0.05}{2.5 + 0.05} = 0.0196 \approx 0.02]$$

24. When 25g of a non-volatile solute is dissolved in 100g of water, the vapour pressure is lowered by 0.225 mm. If the vapour pressure of water at 25°C is 17.5 mm, what is the molecular mass of the solute ? **[EAMCET (Engg) 2008]**

(a) 206 (b) 302 (c) 318 (d) 276

[**Ans.** (c)]

[**Hint :** $p = p_0 x_A$

$$(17.5 - 0.225) = 17.5 \times \frac{100/18}{100/18 + \frac{25}{m_B}}$$

$$\frac{17.275}{17.5}\left(\frac{100}{18} + \frac{25}{m_B}\right) = \frac{100}{18}$$

$$0.987\left(5.55 + \frac{25}{m_B}\right) = 5.55$$

$$5.55 + \frac{25}{m_B} = 5.628$$

$$m_B \approx 318 \text{ mm}]$$

5.11 ELEVATION OF BOILING POINT (Ebullioscopy)

The boiling point of a liquid is **the temperature at which its vapour pressure is equal to the atmospheric pressure.** The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, the temperature of the solution when its vapour pressure will be equal to atmospheric pressure will be higher than the temperature of the pure solvent. In other words, the boiling point of the solvent is elevated by the addition of non-volatile solute. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed **elevation of boiling point.**

Elevation of boiling point,

(ΔT) = Boiling point of the solution – Boiling point of pure solvent

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions of different concentrations. The curves of the solutions always lie below the curve of the pure solvent. The line P_0C represents the atmospheric pressure. T_0, T_1 and T_2 represent the boiling points of pure solvent, solution I and solution II respectively. The vapour pressure of pure solvent, solution I and solution II at temperature T_0 are P_0, P_1 and P_2 respectively.

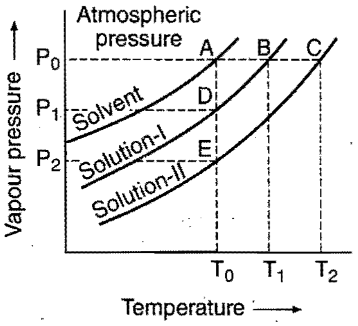


Fig. 5.10

Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus, ΔACE and ΔABD are similar.

Therefore, $$\frac{AC}{AB} = \frac{AE}{AD}$$

or $$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

or $$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or $$\Delta T \propto \Delta P$$

From Raoult's law for dilute solution,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B \times m_A}{m_B \times w_A}$$

(p_s = vapour pressure of solution)

or $$p_0 - p_s = \frac{w_B \times m_A}{m_B \times w_A} \cdot p_0$$

For the pure solvent, p_0 (its vapour pressure at the boiling point) and m_A (its molecular mass) are constant. Therefore,

$$p_0 - p_s \propto \frac{w_B}{m_B \times w_A}$$

or $$\Delta p \propto \Delta T \propto \frac{w_B}{m_B \times w_A}$$

or $$\Delta T = K \cdot \frac{w_B}{m_B \times w_A} \quad \text{... (i)}$$

where K is a constant, called as elevation constant.

When, $\frac{w_B}{m_B} = 1$, (one mole of solute) and $w_A = 1\,\text{g}$, then

$$\Delta T = K$$

Thus, boiling point constant is equal to the elevation in boiling point which would be theoretically produced when 1 mole of a non-volatile solute is dissolved in 1 g of the solvent.

If $\frac{w_B}{m_B} = 1$ and $w_A = 100\,\text{g}$,

Then, $$\Delta T = \frac{K}{100} = K'$$

K' is called **molecular elevation constant.** It is defined as the **elevation in boiling point produced when 1 mole of the solute is dissolved in 100 g of the solvent.**

Thus, $$K = 100K'$$

Putting this value in eq. (i),

$$\Delta T = 100K' \cdot \frac{w_B}{m_B\ w_A} \quad \text{... (ii)}$$

If $\frac{w_B}{m_B} = 1$ and $w_A = 1000\,\text{g}$,

Then, $$\Delta T = \frac{K}{1000} = K_b$$

K_b is called **molal elevation constant.** It is defined as the **elevation in boiling point produced when 1 mole of the solute is dissolved in 1000 g of the solvent.**

Thus, $$K = 1000\,K_b$$

Putting this value in eq. (i),

$$\Delta T = \frac{1000K_b\ w_A}{m_A\ w_B} \quad \text{... (iii)}$$

or $$\Delta T = \text{Molality} \times K_b$$

$$\left(\text{since } \frac{w_B}{m_B \times w_A} \times 1000 = \text{molality}\right)$$

The elevation in boiling point of a solution of non-electrolyte is proportional to its molality and equimolal solutions of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^{\,2}}{1000\,L_v}$$

where, R is molar gas constant, T_b is the boiling point of the solvent on kelvin scale and L_v the latent heat of vaporisation of solvent in calories per gram.

For water $$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

The molal elevation constants for some common solvents are given in the following table:

Table 5.4 Molal Elevation Constants of Some Solvents

Solvent	B.pt. (°C)	Molal elevation constant (K kg mol^{-1})
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.67
Carbon tetrachloride	76.8	5.02
Benzene	80.0	2.70
Ethyl alcohol	78.4	1.15

If $K_b, w_A, \Delta T$ and w_B are known, molecular mass of a non-volatile solute can be determined. The most convenient method for the determination of ΔT in the laboratory is the **Landsberger method.**

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* This relation may also be written as:

$$\Delta T = \frac{1000\,K_b \times w}{m \times W}$$

where, w and W are masses of solute and solvent respectively and m = molecular mass of solute.

5.12 DEPRESSION OF FREEZING POINT (Cryoscopy)

Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since, the addition of a non-volatile solute always lowers the vapour pressure of a solvent, therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of the pure solvent and its solution is called **depression of freezing point.**

Depression of freezing point

$$(\Delta T) = \text{Freezing point of the solvent} - \text{Freezing point of the solution}$$

This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions, solution I and solution II. CFB is a curve for a solid solvent. The solvent, solution I and solution II vapour pressure curves meet CFB curve at points B, F and C respectively. Thus, T_0, T_1 and T_2 are the freezing points of pure solvent, solution I and solution II respectively. The vapour pressures at temperatures T_0, T_1 and T_2 for solvent, solution I and solution II are, thus, P_0, P_1 and P_2 respectively.

For very dilute solutions, the curves FD and CE are almost straight lines and CB is also nearly a straight line. The ΔBEC and ΔBDF are similar.

So,
$$\frac{EC}{DF} = \frac{BE}{BD}$$

or
$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P_0 - P_2}{P_0 - P_1}$$

or
$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

or
$$\Delta T \propto \Delta P$$

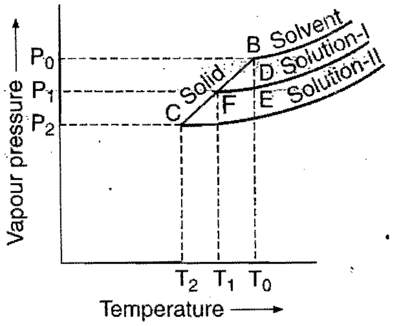

Fig. 5.11

From Raoult's law for dilute solutions,

$$\frac{p_0 - p_s}{p_0} = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A}$$

or
$$p_0 - p_s = \frac{w_B}{m_B} \cdot \frac{m_A}{w_A} \cdot p_0$$

For the pure solvent, p_0 and m_B are constants. Therefore,

$$p_0 - p_s \propto \frac{w_B}{m_B\ w_A}$$

or
$$\Delta p \propto \frac{w_B}{m_B\ w_A}$$

or
$$\Delta p \propto \Delta T \propto \frac{w_B}{m_B\ w_A}$$

or
$$\Delta T = K \cdot \frac{w_B}{m_B\ w_A} \quad \text{... (i)}$$

where, K is a constant, called depression constant.

When, $\frac{w_B}{m_B} = 1$ (one mole of solute) and $w_A = 1\text{g}$

$$\Delta T = K$$

Thus, depression constant is equal to the depression of the freezing point which would be theoretically produced when one mole of a non-volatile solute is dissolved in 1 g of the solvent.

If $\frac{w_B}{m_B} = 1$ and $w_B = 100\,\text{g}$,

$$\Delta T = \frac{K}{100} = K'$$

K' is called molecular depression constant.

It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus, $K = 100K'$

Putting this value in eq. (i),

$$\Delta T = \frac{100K' \times w_B}{m_B \times w_A} \quad \text{... (ii)}$$

If $\frac{w_B}{m_B} = 1$ and $w_A = 1000\,\text{g}$

$$\Delta T = \frac{K}{1000} = K_f$$

K_f is called molal depression constant.

It is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

Thus, $K = 1000K_f$

Putting this value in eq. (i),

$$\Delta T = 1000K_f \frac{w_B}{m_B\ w_A} \quad \text{... (iii)}$$

---

* This relation may also be written as:

$$\Delta T = \frac{1000\ K_f \times w}{m \times W}$$

where w and W are the masses of solute and solvent respectively and m = molecular mass of solute.

or $$\Delta T = \text{molality} \times K_f$$

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{0.002\,T_f^2}{L_f}$$

where, T_f is the freezing point of solvent in absolute scale and L_f the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80}$$

$$= 1.86\,\text{K kg mol}^{-1}$$

The molal depression constants for some common solvents are given in the following table:

Table 5.5 Molal Depression Constants of Some Solvents

Solvent	F.pt. (°C)	Molal elevation constant (K kg mol^{-1})
Water	0.0	1.86
Ethyl alcohol	–114.6	1.99
Chloroform	–63.5	4.70
Carbon tetrachloride	–22.8	29.80
Benzene	5.5	5.12
Camphor	179.0	39.70

If $K_f, w_A, \Delta T$ and w_B are known, molecular mass of a non-volatile solute can be determined. ΔT is measured by Beckmann's method in the laboratory.

The molecular mass of non-volatile and non-ionisable solute can be calculated using following formula:

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B}{w_A} \times 1000$$

where, w_B and w_A are the masses of solute and solvent respectively.

Anti-freeze solutions : Water is used in radiators of cars and other automobiles. In cold countries where the atmospheric temperature becomes less than zero degree, the water in the radiators would freeze. Anti-freeze solutions are useful under these conditions when the vehicles are used in the regions of sub-zero temperature so that the water does not freeze in radiators. Such solutions are made by dissolving ethylene glycol in water. Freezing point can be lowered to the desired extent by varying the concentration of ethylene glycol. Glycerol can also be used as anti-freeze.

Freezing mixture : It is a mixture of ice and common salt (NaCl). It is used in the making of ice-cream and in the laboratories to create low temperatures. With the help of this mixture, a temperature as low as –33°C (240 K) can be achieved.

Note: Ebullioscopic and cryoscopic methods are effective when :

(i) Solutions are dilute. Solutions obey Raoult's law.
(ii) The solute is non-volatile.
(iii) There is no association or dissociation of solute molecules in the solution.
(iv) Solute does not form a solid solution with solvent in frozen state, *i.e.*, only solvent separates in solid state on freezing the solution.
(v) Equimolal quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under identical conditions.

SOME SOLVED EXAMPLES

Example 35. *On dissolving* 10.8 g *glucose* (*m.wt.* = 180) *in* 240 g *of water, its boiling point increases by* 0.13° C. *Calculate the molecular elevation constant of water.*

Solution: $$\Delta T = \frac{100K' \times w}{W \times m}$$

or $$K' = \frac{\Delta T \times W \times m}{100 \times w}$$

Given, $\Delta T = 0.13°$ C, $W = 240$ g, $m = 180$ and $w = 10.8$ g

$$K' = \frac{0.13 \times 240 \times 180}{100 \times 10.8} = 5.2°.$$

Example 36. *A solution of* 2.5 g *of a non-volatile solid in* 100 g *benzene is boiled at* 0.42°C *higher than the boiling point of pure benzene. Calculate the molecular mass of the substance. Molal elevation constant of benzene is* 2.67 K kg mol^{-1}.

Solution: $$m = \frac{1000K_b \times w}{W \times \Delta T}$$

Given, $K_b = 2.67$, $w = 2.5\,\text{g}, W = 100\,\text{g}, \Delta T = 0.42$

$$m = \frac{1000 \times 2.67 \times 2.5}{100 \times 0.42} = 158.9$$

The molecular mass of substance is 158.9.

Example 37. *The molal elevation constant for water is* 0.56 K kg mol^{-1}. *Calculate the boiling point of a solution made by dissolving* 6.0 g *of urea* (NH_2CONH_2) *in* 200 g *of water.*

Solution: $$\Delta T = \frac{1000K_b \times w}{m \times W}$$

Given, $K_b = 0.56\,\text{K kg mol}^{-1}, w = 6.0\,\text{g}, W = 200\,\text{g}, m = 60$

$$\Delta T = \frac{1000 \times 0.56 \times 6.0}{200 \times 60} = 0.28°\,\text{C}$$

Thus, the boiling point of solution = b.pt. of water + ΔT

$$= (100°\,\text{C} + 0.28°\,\text{C}) = 100.28°\,\text{C}$$

Example 38. *By dissolving* 13.6 g *of a substance in* 20 g *of water, the freezing point decreased by* 3.7°C. *Calculate the molecular mass of the substance. (Molal depression constant for water* = 1.863 K kg mol^{-1})

Solution: $$m = \frac{1000K_f \times w}{W \times \Delta T}$$

Given, $K_f = 1.863\,\text{K kg mol}^{-1}$

$$w = 13.6\,\text{g}, W = 20\,\text{g}, \Delta T = 3.7°\,\text{C}$$

$$m = \frac{1000 \times 1.863 \times 13.6}{20 \times 3.7} = 342.39$$

Example 39. *On dissolving 0.25 g of a non-volatile substance in 30 mL benzene (density 0.8 g / mL), its freezing point decreases by 0.40°C. Calculate the molecular mass of non-volatile substance* ($K_f = 5.12\,K\ kg\ mol^{-1}$).

Solution: Mass of benzene, W = volume × density

$$= 30 \times 0.8 = 24\text{ g}$$

Given, $K_f = 5.12\text{ K kg mol}^{-1}$, $w = 0.25\text{ g}$, $\Delta T = 0.40°\text{C}$.

We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 0.25}{24 \times 0.40} = 133.33$$

Example 40. *A solution of 1.25 g of a certain non-volatile substance in 20 g of water freezes at 271.94 K. Calculate the molecular mass of the solute* ($K_f = 1.86\,K\ kg\ mol^{-1}$).

Solution: Freezing point of solution = 271.94 K

Freezing point of water = 273.0 K

$$\Delta T = (273 - 271.94) = 1.06\text{ K}$$

We know that, $$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

Given, $K_f = 1.86$ K kg mol^{-1}, $w = 1.25$ g, $W = 20$ g and $\Delta T = 1.06$ K.

$$m = \frac{1000 \times 1.86 \times 1.25}{20 \times 1.06} = 109.66$$

Example 41. *Two elements A and B form compounds having molecular formulae AB_2 and AB_4. When dissolved in 20.0 g of benzene, 1.0 g of AB_2 lowers the freezing point by 2.3°C, whereas 1.0 g of AB_4 lowers the freezing point by 1.3° C. The molal depression constant for benzene in 1000 g is 5.1. Calculate the atomic masses of A and B.*

Solution: We know that,

$$m = \frac{1000 K_f \times w}{W \times \Delta T}$$

Molecular mass of AB_2 (from given data) $= \dfrac{1000 \times 5.1 \times 1}{20 \times 2.3}$

$$= 110.86$$

and Molecular mass of AB_4 (from given data) $= \dfrac{1000 \times 5.1 \times 1}{1.3 \times 20}$

$$= 196.15$$

Further, $$AB_4 = A + 4B = 196.15 \quad \text{... (i)}$$

$$AB_2 = A + 2B = 110.86 \quad \text{... (ii)}$$

Subtracting eq. (ii) from (i),

$$2B = 85.29$$

$$B = 42.645$$

Putting the value of B in eq. (ii),

$$A + 85.29 = 110.86$$

or $$A = (110.86 - 85.29) = 25.57$$

Thus, the atomic masses of A and B are 25.57 and 42.645 respectively.

Example 42. *1.355 g of a substance dissolved in 55 g of CH_3COOH produced a depression in the freezing point of 0.618°C. Calculate the molecular weight of the substance* ($K_f = 3.85$). **[CECE (Mains) Bihar 2005]**

Solution: $$\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$

where, w_B = mass of solute, m_B = molar mass of solute, w_A = mass of solvent

$$0.618 = 3.85 \times \frac{1.355 \times 1000}{m_B \times 55}$$

$$m_B = 153.47$$

Example 43. *An aqueous solution of a non-volatile solute boils at 100.17°C. At what temperature will the solution freeze? (Given: $K_b = 0.512\,K\ kg\ mol^{-1}$ and $K_f = 1.86\,K\ kg\ mol^{-1}$)*

Solution: We know that,

$$\Delta T_b = \text{molality} \times K_b$$

$$0.17 = \text{molality} \times 0.512$$

Molality of the solution $= \dfrac{0.17}{0.512}\,m$

Let depression in freezing point be ΔT_f

$$\Delta T_f = \text{molality} \times K_f$$

$$= \frac{0.17}{0.512} \times 1.86 = 0.62°\text{ C}$$

Thus, the freezing point of the solution is

$$0.00 - 0.62 = -0.62°\text{C}$$

Example 44. *18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will the water boil (1.013 bar pressure)? K_b for water is 0.52 K kg mol^{-1}.*

Solution: $$\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$\Delta T = 0.52 \times \frac{18 \times 1000}{180 \times 1000}$$

$$T - T_0 = 0.052$$

$$T - 373 = 0.052$$

$$T = 373.052\text{ K}$$

Example 45. *A solution of urea in water has boiling point of 100.15°C. Calculate the freezing point of the same solution if K_f and K_b for water are 1.87 K kg mol^{-1} and 0.52 K kg mol^{-1} respectively.*

Solution: $$\Delta T_b = (100.15 - 100) = 0.15°\text{C}$$

We know that, $$\Delta T_b = \text{molality} \times K_b$$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$$\Delta T_f = \text{molality} \times K_f$$

$$= 0.2884 \times 1.87 = 0.54^\circ \text{C}$$

Thus, the freezing point of the solution $= -0.54\,^\circ\text{C}$

Example 46. *In a cold climate, water gets frozen causing damage to radiator of a car. Ethylene glycol is used as antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at $-6^\circ C$ (K_f for water = 1.85 K kg mol $^{-1}$).* **(IIT 1992)**

Solution: Given,

$$\Delta T = 6^\circ\text{C},\ W = 4\ \text{kg} = 4000\ \text{g},\ m = 62,\ K_f = 1.85$$

$$w = \frac{m \times W \times \Delta T}{1000 \times K_f}$$

$$= \frac{62 \times 4000 \times 6}{1000 \times 1.85} = 804.32\,\text{g}$$

Example 47. *A solution containing 0.2563 g of naphthalene (molecular mass $= 128$) in 50 g of carbon tetrachloride yields a boiling point elevation of 0.201°C while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.647°C. Find the molecular mass of the unknown solute.*

Solution: We know that,

$$K_b = \frac{\Delta T_b \times W \times m}{1000 \times w}$$

For CCl_4, $$K_b = \frac{0.201 \times 50 \times 128}{1000 \times 0.2563} = 5.019$$

K_b is now used in the second part of the problem.

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

$$= \frac{1000 \times 5.019 \times 0.6216}{0.647 \times 50} = 96.44$$

Example 48. *Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion $180.75\,J\,g^{-1}$.*

Solution: $$K_f = \frac{RT_f^{\,2}}{1000 \times L_f}$$

$$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1},$$

$$T_f = 16.6^\circ\text{C} = 273 + 16.6 = 289.6\,\text{K},$$

$$L_f = 180.75\ \ \text{J g}^{-1}.$$

Substituting the values in the above equation,

$$K_f = \frac{8.314 \times (289.6)^2}{1000 \times 180.75} = 3.86$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

25. Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1}: **[JEE (Orissa) 2005]**

(a) 2.68 (b) 3.86 (c) 4.68 (d) 2.86

[**Ans.** (b)]

[**Hint:** $K_f = \dfrac{RT_0^{\,2}}{1000L}$ $\qquad T_0 = 273 + 16.6 = 289.6$ K

$$= \frac{8.314 \times (289.6)^2}{1000 \times 180.75}$$

$$= 3.86]$$

26. The elevation in boiling point for 13.44 g of $CuCl_2$ dissolved in 1 kg of water as solvent will be (K_b = 0.52 K kg mol^{-1}; molar mass of $CuCl_2$ = 134.4 g/mol): **(IIT 2005)**

(a) 0.05 (b) 0.10 (c) 0.16 (d) 0.20

[**Ans.** (c)]

[**Hint:** $i = 3$, assuming complete ionization of $CuCl_2$

$$\Delta T = i \times K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$= 3 \times 0.52 \times \frac{13.44 \times 1000}{134.4 \times 1000} = 0.156 \approx 0.16]$$

27. A solution containing 7 g of a solute (molar mass 210 g mol^{-1}) in 350 g of acetone raised the boiling point of acetone from 56°C to 56.3°C. The value of ebullioscopic constant of acetone in K kg mol^{-1} is:

(a) 2.66 (b) 3.15 (c) 4.12 (d) 2.86

[**Ans.** (b)]

[**Hint:** $$\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = K_b \times \frac{7 \times 1000}{210 \times 350}$$

$$K_b = \frac{0.3 \times 210 \times 350}{7 \times 1000} = 3.15\ \text{K kg mol}^{-1}]$$

28. The normal boiling point of toluene is 110.7°C and its boiling point elevation constant is 3.32 K kg mol^{-1}. The enthalpy of vaporization of toluene is nearly:

(a) 17 kJ mol^{-1} (b) 21 kJ mol^{-1}

(c) 51 kJ mol^{-1} (d) 68 kJ mol^{-1}

[**Ans.** (b)]

[**Hint:** $K_b = \dfrac{RT_0^{\,2}}{1000L}$; $3.32 = \dfrac{(8.314 \times 10^{-3}) \times (383.7)^2}{1000 \times L}$

$$L = 0.368\ \text{kJ/g}$$

Latent heat per mol = 0.368 × molar mass of acetone

$$= 0.368 \times 58 = 21.344\ \text{kJ mol}^{-1}]$$

29. An aqueous solution freezes at -0.186°C (K_f = 1.86 K kg mol^{-1}, K_b = 0.512 K kg mol^{-1}). The elevation of b. pt. of the solution is:

(a) 0.186 (b) 0.512 (c) $\frac{0.512}{1.86}$ (d) 0.0512

[**Ans.** (d)]

[**Hint:**

$$\Delta T = K_f \times m$$

$$0.186 = 1.86 \times m$$

$$m = 0.1$$

$$\Delta T = K_b \times m = 0.512 \times 0.1 = 0.0512]$$

30. The amount of urea to be dissolved in 500 cc of water ($K_f = 1.86$) to produce a depression of 0.186°C in the freezing point is: **[UGET (Manipal) 2006]**

(a) 9 g (b) 6 g (c) 3 g (d) 0.3 g

[**Ans.** (c)]

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$0.186 = 1.86 \times \frac{w_B \times 1000}{60 \times 500}$$

$$w_B = 3 \text{ g}]$$

31. What should be the freezing point of aqueous solution containing 17 g of C_2H_5OH in 1000 g of water (K_f for water $= 1.86$ deg kg mol^{-1})?

(a) − 0.69°C (b) 0.34°C

(c) 0.0°C (d) − 0.34°C

[**Ans.** (a)]

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A} = 1.86 \times \frac{17 \times 1000}{46 \times 1000} = 0.69$

∴ Freezing point of solution $= 0 - 0.69 = -0.69$°C]

5.13 OSMOSIS AND OSMOTIC PRESSURE

Osmosis: When a semipermeable membrane is placed between a solution and a solvent, it is observed that solvent molecules enter the solution and the volume of solution increases. It is also observed that if two solutions of unequal concentrations are separated by a semipermeable membrane, the solvent molecules from a solution of lower concentration move towards a solution of higher concentration. This phenomenon was first observed by **Abbe Nollet** (1748) and termed as **Osmosis** (Greek, *osmos* = to push). Osmosis is defined **as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.**

The phenomenon of osmosis can be demonstrated by the following experiment:

Two eggs of same size are taken and their outer hard shell is removed by dissolving in dilute hydrochloric acid. One of the eggs is placed in distilled water and the other in saturated salt solution.

After sufficient time, it is noticed that the egg placed in water swells up and that placed in salt solution shrinks. In the first case, water enters the concentrated egg fluid while in the second case, water comes out of the egg as salt solution is more concentrated than the egg fluid.

Difference between Osmosis and Diffusion

The two processes, diffusion and osmosis, can be distinguished in terms of the following aspects:

(i) In diffusion, solute as well as solvent molecules flow in opposite directions while in osmosis the flow of solvent molecules occurs in one direction only.

(ii) For osmosis, a semipermeable membrane* is required while for diffusion it is not required.

Semipermeable membrane

"A membrane which allows the solvent molecules to pass through it but prevents the passage of solute molecules through it is called a semipermeable membrane."

Examples of semipermeable membranes are too many. Parchment paper, membranes covering the animal and plant cells and many gelatinous inorganic substances such as calcium phosphate and copper ferrocyanide, etc., act as semipermeable membranes. Animal and plant membranes are not all completely semipermeable. The best semipermeable membrane used is prepared by deposition of copper ferrocyanide, $Cu_2[Fe(CN)_6]$, in the pores of a porous pot.

Working of semipermeable membrane : Several theories have been put forward to explain the working of semipermeable membrane. These are :

(a) The sieve theory : The theory was suggested by Traube. According to this theory, a semipermeable membrane contains a large number of small pores which act like a sieve. The pores allow the smaller molecules of solvent to pass through it but does not allow the larger molecules of solute to do so. However, this theory fails in those cases of semipermeability where the solute molecules are smaller than the solvent molecules.

(b) The solution theory : According to this theory, a membrane is permeable to those substances which dissolve in it and is impermeable to those which are insoluble in it. Thus, a layer of phenol acts as a semipermeable membrane when placed between a solution of $Ca(NO_3)_2$. Phenol allows water to pass through it because water is soluble in phenol. It is impermeable to $Ca(NO_3)_2$ because $Ca(NO_3)_2$ is insoluble in phenol.

(c) Vapour pressure theory : According to this theory, a solvent can pass through a semipermeable membrane because the vapour pressure of the pure solvent is higher than the vapour pressure of the solution. This theory is widely accepted because it explains the phenomenon of osmosis.

Osmotic pressure: A porous pot is taken and a semipermeable membrane of copper ferrocyanide is deposited in its walls. It is fitted with a long glass tube with the help of a rubber stopper. It is filled with concentrated aqueous sugar solution and placed in distilled water. Osmosis occurs and the level of the solution in glass tube rises over a period of time. After a few days, the level becomes stationary. At this equilibrium state the hydrostatic pressure of the liquid column exactly balances the tendency which enables the water molecules to pass through semipermeable membrane.

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* Membranes which allow the passage of only solvent molecules through them are called semipermeable membranes. Egg membrane, goat's bladder and cell membranes can serve as semipermeable membranes but these are not perfect for laboratory measurements. Artificial membranes of gelatinous inorganic substances such as copper ferrocyanide are used these days as semipermeable membranes.

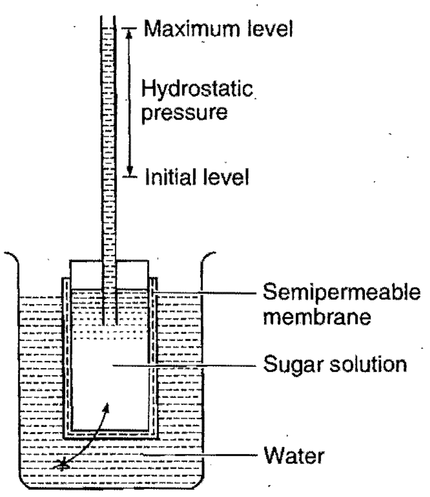


Fig. 5.12 Hydrostatic pressure determination

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution. Osmotic pressure is also defined **as the hydrostatic pressure built up on the solution which just stops the osmosis.**

Osmotic pressure = hydrostatic pressure

$$\pi = hdg$$

where, h = increase in level in the tube of unit cross section, d = density of solution and g = acceleration due to gravity.

Actually, this will not be an exact measure of osmotic pressure of the solution originally taken because sufficient dilution has taken place with time.

If osmosis takes place due to concentration gradient *i.e.*, when two solutions of different concentration are separated by semipermeable membrane then,

$$\pi = hdg = \Delta CRT$$

Alternative definition: An apparatus as shown in Fig. 5.13 consists of a water-tight chamber which is divided into two halves by a semipermeable membrane and fitted with a water-tight piston and a flow indicator in separate compartments. The compartment having a piston is filled with solution and the other compartment is filled with a pure solvent. Water (solvent) tries to flow into the solution side. To check this tendency, a certain pressure shall have to be applied by the piston. This external pressure is thus a measure of osmotic pressure of the solution. **The external pressure which must be applied on the solution in order to stop the flow of the solvent into the solution through semipermeable membrane is equal to osmotic pressure.**

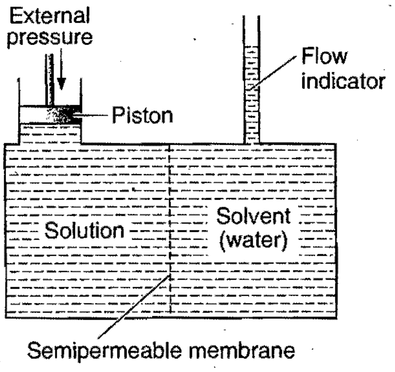


Fig. 5.13

Determination of Osmotic Pressure: Berkeley and Hartley's Method

Various methods are employed for the measurement of osmotic pressure but the best known method was suggested by Berkeley and Hartley. The apparatus used is shown in Fig. 5.14. A porcelain tube having copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. The porcelain tube is fitted with a reservoir of pure solvent at one end and a capillary tube at the other end. In a metallic jacket, there is an arrangement for applying external pressure which is measured with the help of pressure gauge.

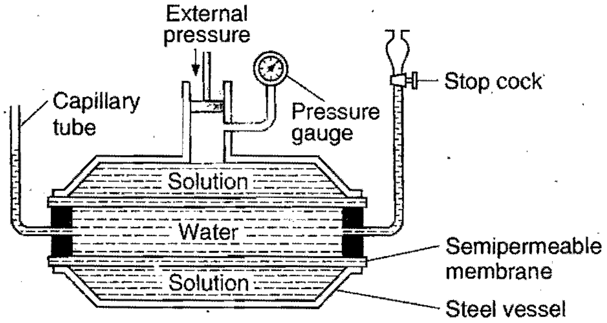


Fig. 5.14 Berkeley and Hartley's method

Procedure: The porcelain tube is filled with pure solvent and the metallic jacket with solution. The level in the capillary tube will tend to move down as the solvent flows towards solution due to osmosis. External pressure is now applied on the solution by the piston so that level in capillary remains stationary. The reading of pressure gauge is recorded. This is the osmotic pressure of the solution.

Advantages: (i) It is a quick and accurate method.

(ii) The concentration of the solution does not change because flow of solvent is not permitted into solution; so the results obtained by this method are reliable.

(iii) As the osmotic pressure is balanced by external pressure, there is no strain on membrane and the danger of its bursting is eliminated. So, this method can be used to measure high osmotic pressures also.

Comparison of osmotic pressures: de-Vries developed an approximate method for comparing the relative osmotic pressures of aqueous solutions. A solution of low osmotic pressure is termed **hypotonic** and solution of high osmotic pressure is termed **hypertonic.** The protoplasmic layer, lining the cell walls of plant cells is easily penetrated by water but is almost impermeable to the substances dissolved in the cellular fluid. When a plant cell is placed in hypotonic solution, the water is drawn in and the cell swells. If the cell is placed in a hypertonic solution, water will diffuse out of the cell fluid and partial collapse of the cell will take place when hypotonic solution is separated from hypertonic solution using semipermeable membrane, then osmosis takes place from hypotonic to hypertonic because solvent concentration is greater in hypotonic solution. This phenomenon is known as **plasmolysis.** The change in cell can be observed under a microscope. When the plant cell is placed in the solution of same osmotic pressure as that of the cell fluid, no change in the structure of the cell is observed. Such solutions having same osmotic pressures are termed **isotonic.** By putting, therefore, cells of the same kind into solutions of different concentrations, it can be ascertained whether the solution is hypertonic or hypotonic or isotonic.

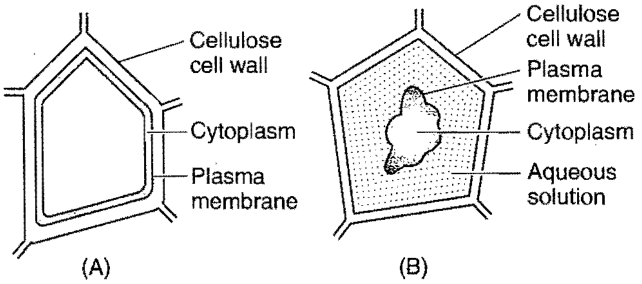


Fig. 5.15 Plasmolysis

Some biological explanation on the basis of osmosis are given below:

(i) In animals, circulation of water to all parts of body takes place due to osmosis.

(ii) Plant roots absorb water from soil due to osmosis. Concentration of cell sap inside the root hair cells is higher than that of water present in the soil. Water enters the root cells due to endosmosis.

(iii) Water absorbed by plant roots is circulated in the entire plant body and reaches to the top of a tall tree due to osmosis.

(iv) Osmosis helps in plant growth and germination of seeds.

(v) Red blood cells burst when placed in water; it is due to endosmosis.

(vi) Various functions of plants are controlled by osmosis, *e.g.*, stretching of leaves and flowers, opening and closing of flowers.

(vii) Use of salt and sugar in pickles and jams acts as preservatives. It prevents growth of bacteria and fungi by osmosis.

(viii) Dead bodies swell under water due to endosmosis.

(ix) When dried fruits and vegetables are placed in water, they slowly swell and return to the original form. It is again due to endosmosis of water into the fruits and vegetables.

Intravenous drip of saline water : Saline drip to the patients is also based on the principle of osmosis.

(i) A 0.91% solution of NaCl in water is isotonic to human blood. Hence, in this solution red blood cells neither swell nor shrink.

(ii) Aqueous solution of NaCl with concentration less than 0.91% is hypotonic to blood. On placing red blood cells in this solution, endosmosis results into bursting of RBCs.

(iii) Aqueous solution of NaCl with concentration more than 0.91% is **hypertonic** to blood. On placing red blood cells in it exosmosis or plasmolysis results into shrinking of cells.

5.14 VAN'T HOFF THEORY OF DILUTE SOLUTIONS

van't Hoff realised that an analogy exists between gases and solutions provided osmotic pressure of solutions is used in place of ordinary gas pressure. He showed that for dilute solutions of non-electrolytes the following laws hold good:

1. Boyle-van't Hoff law: The osmotic pressure (P or π) of a solution is directly proportional to its concentration (C) when the temperature is kept constant. The concentration of the solution containing one gram mole in V litre is equal to $\frac{1}{V}\left(C=\frac{1}{V}\right)$.

Thus, $$P \propto C \text{ (when temperature is constant)}$$

or $$P \propto \frac{1}{V}$$

or $$PV = \text{constant} \quad \text{or} \quad \pi V = \text{constant}$$

van't Hoff presumed that the osmotic pressure is due to the bombardment of solute molecules against the semipermeable membrane as the gas pressure is due to hits recorded by gas molecules against the walls of its container.

2. Pressure-Temperature law (Gay-Lussac-van't Hoff law): Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T), *i.e.*,

$$P \propto T$$

or $$\frac{P}{T} = \text{constant} \quad \text{or} \quad \frac{\pi}{T} = \text{constant}$$

Combining the two laws, *i.e.*, when concentration and temperature both are changing, the osmotic pressure will be given by:

$$P \propto C\,T$$

or $$P = kC\,T$$

or $$P = k \cdot \frac{1}{V} \cdot T \qquad \left(\text{since, } C = \frac{1}{V}\right)$$

or $$PV = ST \text{ or } \pi V = ST$$

S is called molar solution constant.

Here, V is the volume of solution containing one gram mole of the solute. The value of S comes out to 0.082 litre atm K^{-1} mol^{-1} which is in agreement with the value of R, the molar gas constant. In case, the solution contains n gram moles in V litre, the general equation would become:

$$PV = nST \quad \text{or} \quad \pi V = nST$$

3. Third law: Equimolecular solutions of different solutes exert equal osmotic pressure under identical conditions of temperature. Such solutions which have the same osmotic pressure are termed **isotonic or iso-osmotic.** When two isotonic solutions are separated by a semipermeable membrane, no flow of solvent molecules is observed on either side.

The law is similar to Avogadro's hypothesis. It can be stated as, **"Equal volumes of dilute solutions of different solutes, having the same temperature and osmotic pressure, contain equal number of molecules".**

For solution I, $PV = n_1ST$

For solution II, $PV = n_2ST$

Thus, n_1 must be equal to n_2 when P, V and T are same.

The analogy of dilute solutions with gases is thus perfect. This led van't Hoff to suggest **that a solute in dissolved state (*i.e.*, in solution) behaves as a gas and the osmotic pressure of the solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume as that of the solution.** This statement is known as van't Hoff theory of dilute solutions.

5.15 DETERMINATION OF MOLECULAR MASSES

In the case of dilute solutions, it has been stated that the equation $PV = nST$ holds good. Instead of one gram mole of the solute present in V litre of solution, let w_B gram of solute (mol. mass m_B) be present in V' litre of solution; then

$$n = \frac{w_B}{m_B} \text{ and } V = V'$$

Thus, the equation $PV = nST$ becomes:

$$PV' = \frac{w_B}{m_B} \cdot ST$$

or

$$m_B = \frac{w_B \times S \times T}{PV'}$$

Knowing the value of P experimentally, the value of m_A, *i.e.*, molecular mass of the solute can be determined.

Consider two solutions I and II having n_1 and n_2 moles of the solute in V_1 and V_2 litres of solution respectively. Let P_1 and P_2 be their osmotic pressures at the same temperature (T).

From the equation $PV = nST$,

For solution I, $P_1V_1 = n_1ST$

or

$$P_1 = \frac{n_1}{V_1} ST$$

For solution II, $P_2V_2 = n_2ST$

or

$$P_2 = \frac{n_2}{V_2} ST$$

If both solutions are isotonic, *i.e.*, $P_1 = P_2$, obviously,

$$\frac{n_1}{V_1} ST = \frac{n_2}{V_2} ST$$

or

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

or

$$\frac{w_1/m_1}{V_1} = \frac{w_2/m_2}{V_2}$$

or

$$\frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2}$$

This is the condition for isotonic solutions.

If molecular mass of one solute is known, the molecular mass of the other can be determined without using osmotic pressure values.

Osmotic pressure of mixture of two solutions:

Case I: Let two solutions of same substance having different osmotic pressures π_1 and π_2 are mixed. Osmotic pressure of the resultant solution can be calculated as,

$$\pi_1V_1 + \pi_2V_2 = \pi_R(V_1 + V_2)$$

where, V_1 and V_2 are the volumes of two solutions and π_R is the resultant osmotic pressure.

Case II: Let n_1 and n_2 are the number of moles of two different solutes present in V_1 and V_2 volumes respectively.

Osmotic pressure of the mixture can be calculated as,

$$\pi = \pi_1 + \pi_2 = \frac{n_1i_1RT}{(V_1 + V_2)} + \frac{n_2i_2RT}{(V_1 + V_2)}$$

$$\pi = \frac{(n_1i_1 + n_2i_2)}{(V_1 + V_2)} RT$$

Here, i_1 and i_2 are van't Hoff factor for the two solutes.

SOME SOLVED EXAMPLES

Example 49. *200 cm^3 of an aqueous solution contains 1.26 g of a polymer. The osmotic pressure of such solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the polymer.*

Solution:

$$\pi V = \frac{w_B}{m_B} RT$$

$$m_B = \frac{w_B}{V} \times \frac{RT}{\pi}$$

$$= \frac{1.26}{0.2} \times \frac{0.083 \times 300}{2.57 \times 10^{-3}} = 61038 \text{ g mol}^{-1}$$

Example 50. *A solution is prepared by dissolving 1.08 g of human serum albumin, a protein obtained from blood plasma, in 50 cm^3 of aqueous solution. The solution has an osmotic pressure of 5.85 mm Hg at 298 K:*

(a) What is molar mass of albumin?

(b) What is height of water column placed in solution?

$$d\,(H_2O) = 1\text{ g } cm^{-3}$$

Solution: (a) Molar mass of albumin can be calculated using following relation:

$$m_B = \frac{w_B \times RT}{\pi V} \qquad \text{...(i)}$$

Given, $w_B = 1.08$ g; $R = 0.0821$ litre atm K^{-1} mol^{-1}

$$T = 298\text{ K}, \pi = \frac{5.85}{760}\text{ atm}; V = \frac{50}{1000} = 0.05\text{ litre}$$

Substituting these values in eq. (i)

$$m_B = \frac{1.08 \times 0.0821 \times 298}{(5.85/760) \times 0.05} = 68655 \text{ g/mol}$$

(b) $$\pi = h \cdot d \cdot g$$

$$\frac{5.85}{760} \times 101325 = h \times 1 \times 10^{-3} \times 9.8$$

$$\therefore \quad h = 7.958 \times 10^4 \text{ m} = 7.958 \times 10^6 \text{ cm}$$

Example 51. *Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15°C.*

Solution: m = mol. mass of sucrose $(C_{12}H_{22}O_{11}) = 342$

$$w = 5 \text{ g}, \quad V = 100 \text{ mL} = 0.1 \text{ litre}$$

$$S = 0.082, \quad T = (15 + 273) = 288 \text{ K}$$

Applying the equation $PV = \frac{w}{m} ST$,

$$P = \frac{5}{342} \times \frac{1}{0.1} \times 0.082 \times 288$$

$$= 3.453 \text{ atm}$$

Example 52. *The solution containing 10 g of an organic compound per litre showed an osmotic pressure of 1.18 atmosphere at 0°C. Calculate the molecular mass of the compound ($S = 0.0821$ litre atm per degree per mol).*

Solution: Applying the equation,

$$m = \frac{w}{PV} \cdot ST$$

Given, $w = 10$ g, $P = 1.18$ atm, $V = 1$ litre, $S = 0.0821$ and $T = 273$ K.

$$m = \frac{10}{1.18 \times 1} \times 0.0821 \times 273 = 189.94$$

Example 53. *The osmotic pressure of a solution containing 30 g of a substance in 1 litre solution at 20°C is 3.2 atmosphere. Calculate the value of S. The molecular mass of solute is 228.*

Solution: Applying the equation,

$$PV = \frac{w}{m} \cdot ST$$

or $$S = \frac{m \times P \times V}{w \times T}$$

Given, $m = 228, P = 3.2$ atm, $V = 1$ litre, $w = 30$ g and

$$T = 20 + 273 = 293 \text{ K}$$

$$S = \frac{228 \times 3.2 \times 1}{30 \times 293}$$

$$= 0.083 \text{ litre atm per degree per mol}$$

Example 54. *What is the volume of solution containing 1 g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at 0°C?*

Solution: Applying the equation $PV = n \cdot ST$,

$$V = \frac{n}{P} \times S \times T$$

Given, $n = 1, P = 1$ atm, $S = 0.0821$ and $T = 273$ K

$$V = \frac{1}{1} \times 0.0821 \times 273 = 22.4 \text{ litre}$$

Example 55. *Find the osmotic pressure of M/20 solution of urea at 27°C ($S = 0.0821$ lit atm K^{-1} mol^{-1}).*

Solution: Applying the equation $PV = n \cdot ST$,

$$P = \frac{n}{V} \cdot ST$$

or $$P = \text{Molarity} \times S \times T$$

Given,

molarity $= \frac{1}{20} = 0.05, S = 0.0821$ and $T = 27 + 273 = 300$ K

Substituting values,

$$P = 0.05 \times 0.0821 \times 300 = 1.2315 \text{ atm}$$

Example 56. *The osmotic pressure of a solution of an organic substance containing 18 g in one litre of solution at 293 K is 2.414×10^5 Nm^{-2}. Find the molecular mass of the substance if $S = 8.3$ JK^{-1} per mol.*

Solution: Applying the equation,

$$PV = \frac{w}{m} \cdot ST$$

or $$m = \frac{w}{PV} \cdot ST$$

Given, $P = 2.414 \times 10^5 \text{ Nm}^{-2}, V = 1.0 \text{ lit} = 1 \times 10^{-3} \text{ m}^3$,

$S = 8.3 \text{ JK}^{-1}$ per mol, $w = 18$ g and $T = 293$ K

$$m = \frac{18}{2.414 \times 10^5 \times 1 \times 10^{-3}} \times 8.3 \times 293 = 181.33$$

Example 57. *A 5% solution of cane sugar is isotonic with 0.877% solution of urea. Calculate the molecular mass of urea if the molecular mass of cane sugar is 342.*

Solution: Let the molecular mass of urea be m_2.

$$\text{Molar concentration of sugar} = \frac{w_1}{m_1 \times V_1} = \frac{5}{342 \times 0.1}$$

and $$\text{Molar concentration of urea} = \frac{w_2}{m_2 \times V_2} = \frac{0.877}{m_2 \times 0.1}$$

For isotonic solutions,

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

$$\frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$

$$m_2 = \frac{0.877 \times 342}{5} = 59.987$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

32. Find out the osmotic pressure of 0.25 *M* aqueous solution of urea at 27°C ($R = 0.082$ litre atm K^{-1} mol^{-1}, $R = 1.987$ cal $K^{-1}mol^{-1}$). **[CET (Gujarat) 2008]**
(a) 6.15 atm (b) 0.615 atm (c) 0.0615 atm (d) 61.5 atm
[**Ans.** (a)]

[Hint : $\pi = CRT$

$= 0.25 \times 0.0821 \times 300$

$= 6.157$ atm]

33. Two solutions of glucose have osmotic pressures 1.5 and 2.5 atm. 1 litre of first solution is mixed with 2 litre of second solution. The osmotic pressure of the resultant solution will be:

(a) 1.62 atm (b) 6.12 atm (c) 1.26 atm (d) 2.16 atm

[Ans. (d)]

[Hint: $\pi_1 V_1 + \pi_2 V_2 = \pi_R (V_1 + V_2)$

$$1.5 \times 1 + 2.5 \times 2 = \pi_R \times 3$$

$$\pi_R = \frac{6.5}{3} = 2.16 \text{ atm}$$]

34. 18 g glucose and 6 g urea are dissolved in 1 litre aqueous solution at 27°C. The osmotic pressure of the solution will be:

(a) 3.826 atm (b) 4.926 atm

(c) 2.92 atm (d) 9.42 atm

[Ans. (b)]

[Hint: $\pi V = (n_1 + n_2)RT$

$$\pi V = \left(\frac{w_1}{m_1} + \frac{w_2}{m_2}\right) RT$$

$$\pi \times 1 = \left(\frac{18}{180} + \frac{6}{60}\right) \times 0.0821 \times 300$$

$$\pi = 4.926 \text{ atm}$$]

35. A solution containing 10 g per dm^3 of urea (m.w. = 60) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is: **[CBSE (Medical) 2006]**

(a) 250 g mol^{-1} (b) 300 g mol^{-1}

(c) 350 g mol^{-1} (d) 200 g mol^{-1}

[Ans. (b)]

[Hint: π_1 (urea) $= \pi_2$ (unknown solute)

C_1 (urea) $= C_2$ (unknown solute)

$$\left[\frac{w_B \times 1000}{m_B \times V}\right]_{\text{urea}} = \left[\frac{w_B \times 1000}{m_B \times V}\right]_{\text{unknown solute}}$$

$$\frac{10 \times 1000}{60 \times 1000} = \frac{5 \times 1000}{m_B \times 100}$$

$$m_B = 300 \text{ g mol}^{-1}$$]

36. The osmotic pressure of a solution at 0°C is 4 atm. What will be its osmotic pressure at 546 K under similar conditions?

(a) 4 atm (b) 2 atm (c) 8 atm (d) 1 atm

[Ans. (c)]

[Hint: $\frac{\pi_1}{\pi_2} = \frac{CRT_1}{CRT_2}$

$$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$

$$\frac{4}{\pi_2} = \frac{273}{546}$$

$$\pi_2 = 8 \text{ atm}$$]

37. The temperature at which 10% aqueous solution $\left(\frac{W}{V}\right)$ of glucose will exhibit the osmotic pressure of 16.4 atm, is : ($R = 0.082\, dm^3$ atm $K^{-1} mol^{-1}$) **[PMT (Kerala) 2008]**

(a) 360°C (b) 180 K (c) 90 K (d) 300 K

(e) 360 K

[Ans. (e)]

[Hint : $\pi V = nRT$

$$\pi V = \frac{W}{m} RT$$

$$16.4 \times \left(\frac{100}{1000}\right) = \frac{10}{180} \times 0.082 \times T$$

$$\therefore \quad T = 360 \text{ K}$$]

5.16 REVERSE OSMOSIS

When a solution is separated from pure water by a semipermeable membrane, water moves towards the solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, *i.e.*, in reverse direction of the ordinary osmosis. This type of osmosis is termed **reverse osmosis.** Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

5.17 ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of solutions depend on the number of solute particles present in solution. Various relations derived for colligative properties hold good in dilute solutions only when there is no change in molecular state of solute. In case, the total number of particles of the solute changes in solution, the colligative property shall also change accordingly. The number of particles in solution may change in two ways:

(i) By dissociation: When the substance is an electrolyte, *i.e.*, the substance undergoes ionisation and number of particles increases in solution, the ions act as particles. The number of particles, thus, increases on ionisation and the value of colligative property increases accordingly.

(ii) By association: When the substance undergoes association, *i.e.*, two or more molecules of the solute associate to form a single giant particle, the number of particles decreases and consequently the value of colligative property decreases. Thus,

Normal value of colligative property

∝ No. of particles of solute taken

Abnormal value of colligative property

∝ No. of particles of solute after ionisation or association

Thus, the ratio, $\frac{\text{Abnormal colligative property}}{\text{Normal colligative property}}$, may have the value either more than 1 or less than 1. The ratio is termed **van 't Hoff factor** which is represented by '*i*'. Thus,

Table 5.6 Illustrations of van't Hoff Factor '*i*' for Different Solutes

S. No.	Solute type	Example	Ionisation or association	No. of particles in the solution from 1 mole solute	van't Hoff factor '*i*'	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose	—	1	1	m_{normal}
2.	Binary electrolyte *AB* type	NaCl, KCl CH_3COOH, etc.	$\underset{1-\alpha}{AB} \rightleftharpoons \underset{\alpha}{A^+} + \underset{\alpha}{B^-}$	2	$1+\alpha$	$\frac{m_{\text{normal}}}{1+\alpha}$
3.	Ternary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$ H_2SO_4, $K_2[PtCl_6]$	$\underset{1-\alpha}{AB_2} \rightleftharpoons \underset{\alpha}{A^{2+}} + \underset{2\alpha}{2B^-}$ $\underset{1-\alpha}{A_2B} \rightleftharpoons \underset{2\alpha}{2A^+} + \underset{\alpha}{B^{2-}}$	3 3	$1+2\alpha$ $1+2\alpha$	$\frac{m_{\text{normal}}}{1+2\alpha}$ $\frac{m_{\text{normal}}}{1+2\alpha}$
4.	Quaternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_3]$ $FeCl_3$, K_3PO_4	$\underset{1-\alpha}{AB_3} \rightleftharpoons \underset{\alpha}{A^{3+}} + \underset{3\alpha}{3B^-}$ $\underset{1-\alpha}{A_3B} \rightleftharpoons \underset{3\alpha}{3A^+} + \underset{\alpha}{B^{3-}}$	4 4	$1+3\alpha$ $1+3\alpha$	$\frac{m_{\text{normal}}}{1+3\alpha}$ $\frac{m_{\text{normal}}}{1+3\alpha}$
5.	Association of solute	Benzoic acid forming dimer in benzene	$\underset{1-\alpha}{nA} \rightleftharpoons \underset{\frac{\alpha}{n}}{An}$	$\frac{1}{n}$	$\left[1-\left(1-\frac{1}{n}\right)\alpha\right]$	$\frac{m_{\text{normal}}}{\left[1-\left(1-\frac{1}{n}\right)\alpha\right]}$
6.	General electrolyte AB_{n-1}	One mole of solute giving *n* ions in the solution	$\underset{1-\alpha}{AB_{n-1}} \rightleftharpoons \underset{\alpha}{A^{+(n-1)}} + \underset{(n-1)\alpha}{(n-1)B^-}$	*n*	$[1+(n-1)\alpha]$	$\frac{m_{\text{normal}}}{[1+(n-1)\alpha]}$

$$i = \frac{P_{\text{obs.}}}{P_{\text{normal}}} = \frac{(\Delta p)_{\text{obs.}}}{(\Delta p)_{\text{normal}}}$$

$$= \frac{(\Delta T_b)_{\text{obs.}}}{(\Delta T_b)_{\text{normal}}} = \frac{(\Delta T_f)_{\text{obs.}}}{(\Delta T_f)_{\text{normal}}}$$

$$= \frac{\text{Actual no. of particles in solution}}{\text{No. of particles taken}}$$

(i) Suppose one molecule of an electrolyte gives '*n*' ions on dissociation and 'α' is its degree of ionisation. Obviously,

$$\text{Number of ions produced} = n\alpha$$

and $$\text{Number of unionised molecules} = 1-\alpha$$

$$\text{Total number of particles in solution} = 1-\alpha+n\alpha$$
$$= 1+(n-1)\alpha$$

Thus,

$$\text{van't Hoff factor '}i\text{'} = \frac{1+(n-1)\alpha}{1} > 1 \text{ if } n \text{ is 2 or more}$$

and $$\alpha = \frac{i-1}{n-1}$$

(ii) Suppose '*n*' molecules associate to form one giant molecule and 'α' is the degree of association; then

$$\underset{(1-\alpha)}{nA} \rightleftharpoons \underset{\alpha/n}{(A)_n}$$

$$\text{Total number of particles in solution} = 1-\alpha+\alpha/n$$
$$= 1+\left(\frac{1}{n}-1\right)\alpha$$

Thus, $$\text{van't Hoff factor '}i\text{'} = \frac{1+\left(\frac{1}{n}-1\right)\alpha}{1} < 1 \text{ if } n \text{ is 2 or more}$$

$$\alpha = \frac{1-i}{1-1/n}$$

As, $$\text{Colligative property} \propto \frac{1}{\text{mol. mass}}$$

So, $$\frac{\text{Observed colligative property}}{\text{Normal colligative property}} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

Thus, $$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

In case of dissociation,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1+(n-1)\alpha > 1$$

Observed mol. mass will always be less than normal mol. mass.

In case of association,

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = 1+\left(\frac{1}{n}-1\right)\alpha < 1$$

Observed mol. mass will always be higher than normal mol. mass.

Relation between osmotic pressure and vapour pressure

Let an aqueous dilute solution filled in a capillary tube is closed at one end by a semipermeable membrane. The tube is placed in pure solvent (water). Entire apparatus is closed by a belljar. At osmotic equilibrium, the belljar is saturated with water vapour. At equilibrium osmotic pressure (π) becomes equal to hydrostatic pressure.

$$\pi = h \times d \qquad \text{... (i)}$$

where '*h*' is height in the column, π is osmotic pressure.

Let, p_0 = Vapour pressure of pure solvent

p = Vapour pressure of solution

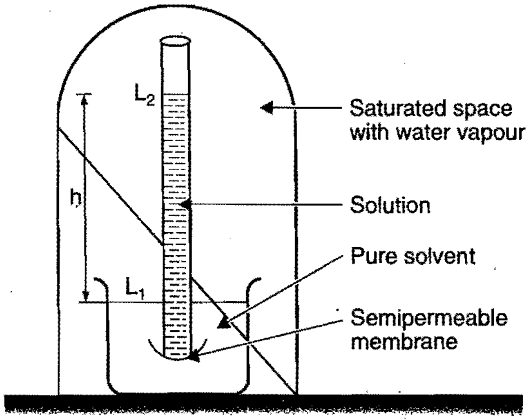


Fig. 5.16

Pressure at level $L_1 = p_0$; Pressure at level $L_2 = p$. Pressure at L_1 will be greater than pressure at L_2. Then

$$p_0 - p = hD \qquad \text{... (ii)}$$

where '*D*' is density of solvent vapour at pressure p_0.

Dividing eq. (i) by eq. (ii), we have,

$$\frac{\pi}{p_0 - p} = \frac{hd}{hD} = \frac{d}{D}$$

at a fixed temperature *d*/*D* is constant.

$$\therefore \qquad \pi = \text{constant}\,(p_0 - p) \qquad \text{... (iii)}$$

$$i.e., \qquad \pi \propto (p_0 - p) \text{ or } \Delta p \qquad \text{... (iv)}$$

Thus, *osmotic pressure is directly proportional to the lowering of vapour pressure.*

We know that,

$$p_0 V = nRT$$

$$p_0 V = \frac{W}{M} RT$$

$$i.e., \qquad p_0 M = \frac{W}{V} RT = DRT$$

$$\therefore \qquad p_0 = \frac{RTD}{M} \qquad \text{... (v)}$$

Dividing eq. (iii) by eq. (v), we get

$$\frac{p_0 - p}{p_0} = \pi \times \frac{D}{d} \times \frac{M}{RTD}$$

$$\frac{\Delta p}{p_0} = \pi \frac{M}{dRT}$$

At a fixed temperature, π and $\frac{M}{dRT}$ is constant.

Thus, $\frac{\Delta p}{p_0} \propto \pi$, *i.e., osmotic pressure is proportional to relative lowering of vapour pressure.*

Partial pressure of immiscible liquids

Let '*A*' and '*B*' be the two volatile and immiscible liquids; p_A and p_B be the partial pressures of '*A*' and '*B*' respectively.

Then,

$$\frac{p_A}{p_B} = \frac{n_A}{n_B}$$

where, M_A and M_B are molar concentrations of '*A*' and '*B*' respectively.

$$\frac{p_A}{p_B} = \frac{W_A / m_A}{W_B / m_B}$$

where, W_A and W_B are weights of '*A*' and '*B*', m_A and m_B are molecular weights of '*A*' and '*B*' respectively.

Example 58. *Phenol associates in benzene to a certain extent for a dimer. A solution containing* 20×10^{-3} *kg of phenol in* 1.0 *kg of benzene has its freezing point decreased by* 0.69 *K. Calculate the fraction of the phenol that has dimerised* (K_f *of benzene is* 5.12°*K kg mol* $^{-1}$).

Solution: Observed mol. mass

$$= \frac{1000 \times K_f \times w}{W \times \Delta T}$$

$$= \frac{1000 \times 5.12 \times 20 \times 10^{-3}}{1 \times 0.69} = 148.4$$

Normal mol. mass of phenol (C_6H_5OH) = 94

$$\text{So,} \qquad \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{94}{148.4}$$

$$= 1 + \left(\frac{1}{n} - 1\right)\alpha = 1 + \left(\frac{1}{2} - 1\right)\alpha$$

$$\frac{94}{148.4} = 1 - \frac{\alpha}{2}$$

$$\text{or} \qquad \alpha = 0.733 \quad \text{or} \quad 73.3\%$$

Example 59. *The freezing point depression of* 0.001 *m* $K_x[Fe(CN)_6]$ *is* 7.10×10^{-3} *K. Determine the value of x. Given,* $K_f = 1.86\,K\ kg\ mol^{-1}$ *for water.*

Solution:

$$\Delta x = i \times K_f \times m$$

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{3.817 - 1}{(x+1) - 1}$$

$$x = 2.817 \approx 3$$

$\therefore$ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

Example 60. *A* $\frac{M}{10}$ *solution of potassium ferrocyanide is* 46% *dissociated at* 18°*C. What will be its osmotic pressure?*

Solution: Normal osmotic pressure $= \dfrac{w}{m \times V} \times S \times T$

(when no dissociation has taken place)

$\dfrac{w}{m} = 0.1, V = 1\text{ litre}, S = 0.0821, T = 18 + 273 = 291\text{ K}$

Normal osmotic pressure $= \dfrac{0.1}{1} \times 0.0821 \times 291 = 2.389$ atm

Potassium ferrocyanide is an electrolyte. It dissociates as:

$$\underset{(1-\alpha)}{K_4Fe(CN)_6} \rightleftharpoons \underset{4\alpha}{4K^+} + \underset{\alpha}{[Fe(CN)_6]^{4-}}$$

Total number of particles $= 1 - \alpha + 4\alpha + \alpha = 1 + 4\alpha$

$\alpha = 0.46$; so, $1 + 4\alpha = 1 + 4 \times 0.46 = 2.84$

$$\frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{2.84}{1}$$

$$\text{Observed osmotic pressure} = 2.84 \times 2.389$$
$$= 6.785 \text{ atm}$$

Example 61. *A 0.5% aqueous solution of KCl was found to freeze at* $-0.24°$ *C. Calculate the van't Hoff factor and degree of dissociation of the solute at this concentration (* K_f *for water* $= 1.86 K\ kg\ mol^{-1}$ *).*

Solution: Observed mol. mass of KCl $= \dfrac{1000 \times K_f \times w}{\Delta T \times W}$

Given, $K_f = 1.86\text{K kg mol}^{-1}, w = 0.5\text{ g}, W = 100\text{ g}, \Delta T = 0.24$

So, Observed mol. mass of KCl $= \dfrac{1000 \times 1.86 \times 0.5}{0.24 \times 100} = 38.75$

Normal mol. mass of KCl $= 39 + 35.5 = 74.5$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$
$$= \frac{74.5}{38.75} = 1.92$$

$$\underset{(1-\alpha)}{KCl} \rightleftharpoons \underset{\alpha}{K^+} + \underset{\alpha}{Cl^-} \quad (\alpha \text{ is the degree of ionisation})$$

Total number of particles $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = 1 + \alpha$$
$$1.92 = 1 + \alpha$$

So, $\alpha = 1.92 - 1 = 0.92$

i.e., 92% dissociated.

Example 62. *The freezing point of a solution containing 0.2 g of acetic acid in 20 g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene (* K_f *for benzene is* $5.12 K\ kg\ mol^{-1}$*).* **(IIT 1994)**

Solution: Let the observed molecular mass of acetic acid be m_{obs}.

$$m_{\text{obs.}} = \frac{1000 \times K_f \times w}{W \times \Delta T}$$
$$= \frac{1000 \times 5.12 \times 0.2}{20 \times 0.45} = 113.78$$

Normal molecular mass of acetic acid = 60

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

	$2CH_3COOH$	$(CH_3COOH)_2$
Before association	1	0
After association	$(1-\alpha)$	$\alpha/2$

$$\text{van't Hoff factor} = \frac{\text{Normal mol. mass}}{\text{Obs. mol. mass}}$$
$$= \frac{1 - \alpha + \alpha/2}{1}$$

$$\frac{60}{113.78} = 1 - \frac{\alpha}{2}$$

or $\alpha = 0.945$

or 94.5% associated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

38. 0.002 molar solution of NaCl having degree of dissociation of 90% at 27°C has osmotic pressure equal to:

(a) 0.94 bar (b) 9.4 bar
(c) 0.094 bar (d) 9.4×10^{-4} bar

[**Ans.** (c)]

[**Hint:** $\alpha = \dfrac{i-1}{n-1}$

$$0.9 = \frac{i-1}{2-1}; i = 1.9$$
$$\pi = iCRT$$
$$= 1.9 \times 0.002 \times 0.082 \times 300$$
$$= 0.094 \text{ bar}]$$

39. A 0.2 molal solution of KCl freezes at -0.68°C. If K_f for H_2O is 1.86, the degree of dissociation of KCl is:

(a) 75% (b) 83% (c) 65% (d) 92%

[**Ans.** (b)]

[**Hint:** $\Delta T = i \times K_f \times m$

$$0.68 = i \times 1.86 \times 0.2$$
$$i = 1.83$$
$$\alpha = \frac{i-1}{n-1}$$
$$= \frac{1.83 - 1}{2 - 1} = 0.83$$

Ionization = 83%]

40. A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is:

(a) 122 (b) 31 (c) 244 (d) 62

[**Ans.** (d)]

[**Hint:** $\alpha = \dfrac{1-i}{1-\dfrac{1}{n}}$

$$0.8 = \frac{1-i}{1-\frac{1}{4}}; i = 0.4$$

$$\Delta T = iK_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$m_B = 62$]

41. van't Hoff factor of Hg_2Cl_2 in its aqueous solution will be (Hg_2Cl_2 is 80% ionized in the solution):

(a) 1.6 (b) 2.6 (c) 3.6 (d) 4.6

[**Ans.** (b)]

[**Hint:** $Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$

$n = 3$

$$\alpha = \frac{i-1}{n-1}$$

$$0.8 = \frac{i-1}{3-1}$$

$i = 2.6$]

42. 0.1 M aqueous solution of $MgCl_2$ at 300 K is 4.92 atm. What will be the percentage ionization of the salt?

(a) 49% (b) 29% (c) 39% (d) 69%

[**Ans.** (a)]

[**Hint:** $\pi = iCRT$

$$4.92 = i \times 0.1 \times 0.0821 \times 300$$

$i = 1.99$

$$\alpha = \frac{i-1}{n-1}$$

$$= \frac{1.99-1}{3-1} = \frac{0.99}{2} = 0.49$$

Percentage ionization = 49%]

43. Which of the following solutions will exhibit highest boiling point? **(KCET 2006)**

(a) 0.01 M Na_2SO_4 (b) 0.01 M KNO_3

(c) 0.015 M urea (d) 0.015 M glucose

[**Ans.** (a)]

[**Hint:** $\Delta T = i \times k_b \times m$

$i \times m$ of Na_2SO_4 is highest, hence its boiling point will also be highest.

Na_2SO_4	$i \times m = 3 \times 0.01 = 0.03$
KNO_3	$i \times m = 2 \times 0.01 = 0.02$
Urea	$i \times m = 1 \times 0.015 = 0.015$
Glucose	$i \times m = 1 \times 0.015 = 0.015$]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Calculate the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure of* 2.0 *atmosphere at* 300 *K.*

$(K_f = 1.86 K\ kg\ mol^{-1}, R = 0.821\ litre\text{-}atm\ K^{-1}\ mol^{-1})$

(IIT 1993)

Solution: We know that,

$$P = CRT$$

or, $$C = \frac{P}{RT} = \frac{2}{0.0821 \times 300}\ \text{mol lit}^{-1}$$

In dilute solution, the density of water can be taken as 1.0 g cm^{-3}.

Hence, $$\frac{2}{0.0821 \times 300}\ \text{mol lit}^{-1} = \frac{2}{0.0821 \times 300}\ \text{mol kg}^{-1}$$

Let ΔT be the depression in freezing point.

$$\Delta T = K_f \times \text{molality}$$

$$= 1.86 \times \frac{2}{0.0821 \times 300} = 0.151\ \text{K}$$

Freezing point $= (273 - 0.151) = 272.749$ K or $-0.151°$ C

Example 2. *Calculate the amount of NaCl which must be added to* 100 *g water so that freezing point is depressed by* 2 *K. For water,* $K_f = 1.86\ K\ kg\ mol^{-1}$.

Solution: NaCl is a strong electrolyte. It is completely dissociated in solution.

Degree of dissociation, $\alpha = 1$

$$NaCl \rightleftharpoons \underset{(n=2)}{Na^+ + Cl^-}$$

$$\text{No. of particles after dissociation} = 1 + (n-1)\alpha$$

$$= 1 + (2-1) \times 1 = 2$$

$$\frac{\Delta T_{\text{obs.}}}{\Delta T_{\text{theo.}}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$\frac{2}{\Delta T_{\text{theo.}}} = 2$$

or $$\Delta T_{\text{theo.}} = 1$$

Let w g of NaCl be dissolved in 100 g of water.

So, $$\Delta T_{\text{theo.}} = \frac{1000 \times K_f \times w}{W \times m}$$

or $$w = \frac{\Delta T_{\text{theo.}} \times W \times m}{1000 \times K_f} = \frac{1 \times 100 \times 58.5}{1000 \times 1.86}$$

$$= 3.145\ \text{g}$$

Example 3. *The degree of dissociation of* $Ca(NO_3)_2$ *in a dilute solution containing* 14 *g of the salt per* 200 *g of water at* 100°*C is* 70%. *If the vapour pressure of water is* 760 *mm, calculate the vapour pressure of solution.* **(IIT 1991)**

Solution:

$\Delta p_{\text{theo.}}$ = Lowering in vapour pressure when there is no dissociation

$$= p_0 \times \frac{wM}{Wm} \quad (\text{given, } p_0 = 760\ \text{mm},\ w = 14\ \text{g},\ W = 200\ \text{g}, M = 18, m = 164)$$

$$= \frac{760 \times 14 \times 18}{200 \times 164} = 5.84\ \text{mm}$$

$$\text{Degree of dissociation} = \frac{70}{100} = 0.7$$

$$Ca(NO_3)_2 \rightleftharpoons \underset{(n=3)}{Ca^{2+} + 2NO_3^-}$$

$$\frac{\Delta p_{\text{obs.}}}{\Delta p_{\text{theo.}}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles when there is no dissociation}}$$

$$= \frac{1 + (n-1)\alpha}{1} = \frac{1 + (3-1) \times 0.7}{1} = 2.4$$

So, $\Delta p_{\text{obs.}} = 2.4 \times \Delta p_{\text{theo.}} = 2.4 \times 5.84$

$= 14.02$ mm

$$p_0 - p_s = \Delta p_{\text{obs.}} = 14.02$$

$$p_s = p_0 - 14.02 = 760 - 14.02 = 745.98\ \text{mm}$$

Example 4. *Calculate the osmotic pressure of solution obtained by mixing* 100 *mL of* 3.4% *solution of urea (molecular mass* = 60) *and* 100 *mL of* 1.6% *solution of cane sugar (molecular mass* = 342) *at* 20°*C.*

Solution: $$\text{No. of moles of urea} = \frac{3.4}{60} = 0.0567$$

$$\text{No. of moles of cane sugar} = \frac{1.6}{342} = 0.0047$$

Total number of moles $= (0.0567 + 0.0047) = 0.0614$

Total volume of solution $= (100 + 100) = 200$ mL

$= 0.2$ litre

$$PV = (\text{Total number of moles}) \times S \times T$$

$$P = \frac{0.0614}{0.2} \times 0.0821 \times 293 = 7.385\ \text{atm}$$

Example 5. *Calculate the normal boiling point of a sample of sea water found to contain* 3.5% *of NaCl and* 0.13% *of* $MgCl_2$ *by mass. The normal boiling point of water is* 100°*C and* K_b *(water)* $= 0.51\ K\ kg\ mol^{-1}$. *Assume that both the salts are completely ionised.*

Solution: Mass of NaCl = 3.5 g

$$\text{No. of moles of NaCl} = \frac{3.5}{58.5}$$

Number of ions furnished by one molecule of NaCl is 2.

So, actual number of moles of particles furnished by sodium chloride $= 2 \times \frac{3.5}{58.5}$

Similarly, actual number of moles of particles furnished by magnesium chloride $= 3 \times \frac{0.13}{95}$

$$\text{Total number of moles of particles} = \left(2 \times \frac{3.5}{58.5} + 3 \times \frac{0.13}{95}\right)$$

$$= 0.1238$$

$$\text{Mass of water} = (100 - 3.5 - 0.13) = 96.37 \text{ g} = \frac{96.37}{1000} \text{ kg}$$

$$\text{Molality} = \frac{0.1238}{96.37} \times 1000 = 1.2846$$

$$\Delta T_b = \text{Molality} \times K_b$$

$$= 1.2846 \times 0.51 = 0.655 \text{ K}$$

Hence, boiling point of sea water = 373.655 K or 100.655°C.

Example 6. *A solution of a non-volatile solute in water has a boiling point of 375.3 K. Calculate the vapour pressure of water above this solution at 338 K. Given, p_0 (water) = 0.2467 atm at 338 K and K_b for water = 0.52.*

Solution: $\Delta T_b = (375.3 - 373.15) = 2.15 \text{ K}$

We know that,

$$\Delta T_b = \text{Molality} \times K_b$$

$$2.15 = \text{Molality} \times 0.52$$

$$\text{Molality} = \frac{2.15}{0.52} = 4.135$$

i.e., 4.135 moles of the solute present in 1000 g of water (55.5 moles).

$$\text{Mole fraction of water} = \frac{55.5}{4.135 + 55.5} = \frac{55.5}{59.635}$$

Vapour pressure of water above solution

$$= \text{Mole fraction} \times p_0$$

$$= \frac{55.5}{59.635} \times 0.2467 = 0.23 \text{ atm}$$

Example 7. *Sea water is 3.5% by mass of a salt and has a density 1.04 g cm^{-3} at 293 K. Assuming the salt to be sodium chloride, calculate the osmotic pressure of sea water. Assume complete ionisation of the salt.*

Solution: Mass of NaCl = 3.5 g

$$\text{No. of moles} = \frac{3.5}{58.5}$$

Actual number of moles of particles of solute in solution

$$= \frac{2 \times 3.5}{58.5}$$

$$\text{Volume of solution} = \frac{100}{1.04 \times 1000} \text{ litre}$$

$$\pi = \frac{2 \times 3.5}{58.5} \times \frac{1.04 \times 1000}{100} \times 0.0821 \times 293 = 29.93 \text{ atm}$$

Example 8. *Molality of a solution in aqueous medium is 0.8. Calculate its mole fraction and the percentage by mass of solute if molar mass of solute is 60.*

Solution: We know that,

$$m = \frac{x_B \times 1000}{(1 - x_B) \times m_A} \quad \ldots \text{(i)}$$

where, x_B = mole fraction of solute

m_A = molar mass of solvent

$$0.8 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$$

$$x_B = 0.014$$

Let $w_B = x \text{ g}$, $w_A = 100 \text{ g}$

$$m = \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.8 = \frac{x \times 1000}{60 \times 100}$$

$$x = 4.8\%$$

Example 9. *Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of $CS_2(l)$ assuming 84% dimerisation of the acid. The boiling point and K_b of CS_2 are 46.2° C and 2.3 K kg mol^{-1} respectively.* **(IIT 1997)**

Solution: $\Delta T = i \times K_b \times \text{Molality}$

$$= i \times K_b \times \frac{w \times 1000}{m \times W}$$

$$\alpha = \frac{1 - i}{1 - 1/n}$$

$$0.84 = \frac{1 - i}{1 - 1/2}$$

$$i = 0.58$$

$$\Delta T = 0.58 \times 2.3 \times \frac{0.61 \times 1000}{122 \times 50} = 0.1334$$

$$T - T_0 = 0.1334$$

$$T = T_0 + 0.1334 = 46.2 + 0.1334 = 46.3334$$

Example 10. *A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.8 mm Hg while that of benzene is 100 mm Hg. Find the molality of the solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?* **(IIT 1997)**

Solution:

$$\frac{\Delta p}{p_0} = X_A$$

$$\frac{100 - 98.8}{100} = X_A$$

$$X_A = 0.012$$

$$\text{Molality} = \frac{X_A \times 1000}{(1-X_A)m_B} = \frac{0.012\times 1000}{0.988\times 78} = 0.1557$$

$$\Delta T = K_f \times \text{Molality}$$

$$0.73 = K_f \times 0.1557$$

$$K_f = 4.688$$

Example 11. *The solution of a non-volatile solute in water freezes at $-0.30°$ C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and K_f for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K.* (IIT 1998)

Solution:

$$\Delta T = K_f \times \text{Molality}$$

$$0.3 = 1.86 \times \text{Molality}$$

$$\text{Molality} = 0.161$$

$$\text{Molality} = \frac{X_A \times 1000}{(1-X_A)\times m_B}$$

$$0.161 = \frac{X_A \times 1000}{(1-X_A)18}$$

$$X_A = 0.00289$$

$$\frac{\Delta p}{p_0} = X_A$$

$$\frac{23.51 - p_s}{23.51} = 0.00289$$

$$p_s = 23.442 \text{ mm}$$

Example 12. *x g of a non-electrolytic compound (molar mass = 200) is dissolved in 1.0 litre of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27° C. Calculate the value of 'x'. Assume complete dissociation of NaCl and ideal behaviour of this solution.* (IIT 1998)

Solution:

(i) For NaCl: $\pi = iCRT = 2\times 0.05\times 0.0821\times 300$

$= 2.463$ atm

(ii) For unknown compound:

$$\pi = CRT = \frac{x}{200}\times 0.0821\times 300 = 0.1231x \text{ atm}$$

Total osmotic pressure $\pi = \pi_1 + \pi_2$

$$4.92 = 2.463 + 0.1231x$$

$$x = 19.959 \text{ g}$$

Example 13. *The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g of water is found to be $-34°$ C. Assuming ideal behaviour, calculate the density of ethylene glycol (K_f for water = 1.86 K kg mol^{-1}).* (IIT 1999)

Solution:

$$\Delta T = K_f \times \frac{w\times 1000}{m\times W}$$

$$34 = 1.86\times \frac{w\times 1000}{62\times 50}$$

$$w = 56.66 \text{ g}$$

$$V = \frac{w}{d}$$

$$50 = \frac{56.66}{d}$$

$$d = 1.13 \text{ g/cm}^3$$

Example 14. *A 1.2% solution of NaCl is isotonic with 7.2% solution of glucose. Calculate the van't Hoff factor of NaCl.* (MLNR 1997)

Solution: NaCl glucose

$$\pi_{(\text{NaCl})} = \pi_{(\text{glucose})}$$

$$iC_1RT = C_2RT$$

$$iC_1 = C_2$$

$$i\left(\frac{1.2/58.5}{V}\right) = \frac{7.2/180}{V}$$

$$i = \frac{7.2\times 58.5}{1.2\times 180} = 1.95$$

Example 15. *1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.76 K. Calculate the molecular mass of (A).* (IIT 2000)

Solution: We know that,

$$\Delta T = K_f \times \frac{w\times 1000}{m\times W}$$

where, ΔT = Depression in freezing point

K_f = Molal depression constant of benzene

w = Mass of solute

m = Molecular mass of solute

W = Mass of solvent

Case I: $(278.4 - 277.12) = K_f \times \frac{1.4\times 1000}{58\times 100}$

$$1.28 = K_f \times \frac{14}{58} \quad \ldots(1)$$

Case II: $(278.4 - 277.76) = K_f \times \frac{2.8\times 1000}{m_{(A)}\times 100}$

$$0.64 = K_f \frac{28}{m_{(A)}} \quad \ldots(2)$$

Dividing eq. (1) by eq. (2), we get

$$m_{(A)} = 232$$

Example 16. *To 500 cm^3 of water, 3.0×10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3} respectively.* (IIT 2000)

Solution: Mass of solute = 3.0×10^{-3} kg = 3.0 g

Molecular mass of solute = 60

$$\text{Mass of solvent} = 500 \times 0.997 = 498.5 \text{ g}$$

We know that,

$$\text{Degree of dissociation } (\alpha) = \frac{i-1}{n-1}$$

$$0.23 = \frac{i-1}{2-1}$$

or

$$i = 1.23$$

$$\Delta T = i \times K_f \times \text{molality}$$

$$= 1.23 \times 1.86 \times \frac{3 \times 1000}{60 \times 498.5} = 0.229$$

i.e., depression in freezing point = 0.229

Example 17. *Osmotic pressure of a solution is* 1.3 *atm. The density of solution is* $1.1 g/cm^3$. *Calculate osmotic rise.*

($1\ atm = 76 cm\ Hg$, $d_{Hg} = 13.6 g/cm^3$)

Solution:

$$\pi = hdg$$

$$1.3 \times 76 \times 13.6 \times g = h \times 1.1 \times g$$

$$h = \frac{1.3 \times 76 \times 13.6}{1.1} \text{ cm}$$

$$= 1221 \text{ cm}$$

Example 18. (*a*) 10 *g of a certain non-volatile solute were dissolved in* 100 *g water at* 20°C. *The vapour pressure was lowered from* 17.3555 *mm to* 17.2350 *mm; calculate the m.wt. of the solute.*

(*b*) *The vapour pressure of pure water at* 25°C *is* 23.62 *mm. What will be the vapour pressure of a solution of* 1.5 *g urea in* 50 *g of water?* **(IIT 2001)**

Solution: (a) We know that, $\frac{p_0 - p}{p} = \frac{w_B \times m_A}{m_B \times w_A}$

$$\frac{17.3555 - 17.2350}{17.2350} = \frac{10 \times 18}{m_B \times 100}$$

$$m_B = 258.5$$

(b)

$$p = p_0 x_A$$

$$p = p_0 \frac{n_A}{n_A + n_B} = 23.62 \times \frac{\frac{50}{18}}{\frac{50}{18} + \frac{1.5}{60}}$$

$$p = 23.41 \text{ mm Hg}$$

Example 19. *Match the boiling point with* K_b *for x, y and z if molecular weight of x, y and z are same:*

	b. pt.	K_b
x	100	0.68
y	27	0.53
z	253	0.98

(IIT 2003)

Solution: Molal elevation constant may be calculated as,

$$K_{b_{1000}} = \frac{RT_0^2}{1000 L_V}$$

(where, T_0 = boiling point of pure solvent
L_V = latent heat of vaporization per gram
$L_V = \frac{\Delta H_V}{m_B}$)

$$= \frac{RT_0^2}{1000 \frac{\Delta H_V}{m_B}}$$

(here, ΔH_V = molar latent heat of vaporization
m_B = molar mass of solute)

$$= \frac{RT_0^2 m_B}{1000 \Delta H_V}$$

Since, $\Delta S_V = \frac{\Delta H_V}{T_0}$

$$K_{b_{1000}} = \frac{RT_0\, m_B}{1000 \Delta S_V}$$

here, ΔS_V = entropy of vaporization

By considering ΔS_V as almost constant, $K_b \propto T_0$.

$\therefore \quad K_b(x) = 0.68; \quad K_b(y) = 0.53 \quad$ and $\quad K_b(z) = 0.98$

Example 20. 1.22 *g* C_6H_5COOH *is added into two solvents and data of* ΔT_b *and* K_b *are given as:*

(*a*) *In* 100*g* CH_3COCH_3; $\Delta T_b = 0.17$; $K_b = 1.7$ *kg kelvin / mol*

(*b*) *In* 100*g benzene*; $\Delta T_b = 0.13$; $K_b = 2.6$ *kg kelvin / mol*

Find out the molecular weight of C_6H_5COOH *in both cases and interpret the result.* **(IIT 2004)**

Solution: (a)

$$\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.17 = 1.7 \times \frac{1.22 \times 1000}{m_B \times 100}$$

$$m_B = 122$$

(normal molecular mass of benzoic acid)

(b)

$$\Delta T = \frac{K_b \times w_B \times 1000}{m_B \times w_A}$$

$$0.13 = \frac{2.6 \times 1.22 \times 1000}{m_B \times 100}$$

$$m_B = 244$$

(Abnormally double molecular mass of benzoic acid, it shows association of benzoic acid in benzene.)

Example 21. *How much* C_2H_5OH *should be added to* 1 *litre* H_2O *so that it will not freeze at* −20°C?

$K_f = 1.86°C / m$ **(BCECE 2006)**

Solution: Mass of 1 litre water = 1000 g

$$\because \quad \Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$20 = 1.86 \times \frac{w_B \times 1000}{46 \times 1000}$$

$$w_B = 494.6 \text{ g}$$

Example 22. *Depression in freezing point of* 0.1 *molal solution of HF is* − 0.201°C. *Calculate percentage degree of dissociation of HF.* ($K_f = 1.86 K\,kg\,mol^{-1}$)

[AIPMT (Mains) 2008]

Solution : We know

$$\Delta T = i \times k_f \times m$$

$$0.201 = i \times 1.86 \times 0.1$$

$$i = 1.0806$$

The degree of dissociation HF may be calculated as.

$$\alpha = \frac{i-1}{n-1} = \frac{1.0806-1}{2-1} = 0.0806$$

Percentage dissociation $= \alpha \times 100 = 0.0806 \times 100$

$$= 8.06$$

Example 23. *There is KI and sucrose solution with* 0.1 *M concentration, if the osmotic pressure of KI and sucrose solution is* 0.465 *atm and* 0.245 *atm respectively. Then find the van't Hoff factor of KI and its degree of dissociation.* **[AIPMT (Mains) 2008]**

Solution : For KI

$$\pi = iCRT$$

$$0.465 = i \times 0.1 \times RT \qquad \text{...(i)}$$

For Sucrose

$$\pi = CRT$$

$$0.245 = 0.1 \times RT \qquad \text{...(ii)}$$

Dividing eq. (i) by (ii)

$$\frac{0.465}{0.245} = i$$

$$\therefore \quad i = 1.897$$

We know, $\alpha = \frac{i-1}{n-1} = \frac{1.897-1}{2-1}$

$$= 0.897$$

$\therefore$ Percentage ionization $= 0.897 \times 100$

$$= 89.7$$

Example 24. 102% *solution of glycerine and* 2% *solution of glucose are isotonic. Molecular mass of glucose is* 180 *then find out the molecular mass of glycerine.* **[AIPMT (Mains) 2009]**

Solution : $\pi_{\text{glycerine}} = \pi_{\text{glucose}}$

$$\therefore \quad C_{(\text{glycerine})} = C_{(\text{glucose})}$$

$$\frac{120 \times 1000}{m_{\text{glycerine}} \times 100} = \frac{2 \times 1000}{180 \times 100}$$

$$m_{\text{glycerine}} = 91.8$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Solution: It is a homogeneous mixture of two or more components whose concentration can be varied within certain limits. A solution containing only two components is termed a binary solution. One component is called the solute while other as solvent. The component having the same physical state as the solution is called the solvent. In solutions, in which the two components have the same physical state, the component present in larger proportion is termed the solvent and the other component is called solute.

2. Solubility: A solution is said to be saturated when it contains as much solute as it can dissolve at a particular temperature in presence of the undissolved solute. A super-saturated solution contains more quantity and an unsaturated solution contains less quantity of the solute than a saturated solution.

The amount of the solute in grams which can dissolve at a particular temperature in 100 grams of the solvent when the solution is saturated is termed solubility of the solute.

3. Solubility of a gas in a liquid: Gases which can be easily liquified are more soluble in common solvents. The gases which form ions in water are highly soluble in water. The solubility of a gas generally decreases with rise in temperature and increases with increase in pressure.

Mass of gas dissolved per unit volume of a solvent is directly proportional to the pressure of the gas at a given temperature. This is Henry's law.

$$m = KP \qquad \text{(at constant temperature)}$$

where, m is the mass of gas dissolved per unit volume of solvent, P is pressure of the gas in equilibrium with the solution and K is proportionality constant.

4. Solutions of liquids in liquids: Miscible liquids form three types of solutions which may be ideal or non-ideal solutions.

Ideal solution is that in which the attractive forces among the solute and solvent molecules are of the same order as that of solute intramolecular and solvent intramolecular forces. The ΔH mixing and ΔV mixing in such solutions is zero. Ideal solutions obey Raoult's law.

The solutions in which solute-solvent interactions are different from solute-solute and solvent-solvent interactions are called non-ideal solutions. The non-ideal solutions do not obey Raoult's law for all concentrations.

$\Delta H_{\text{mix}} \neq 0$ and $\Delta V \neq 0$ in these solutions. There are two types of deviations from the ideal behaviour.

(i) If $\Delta V_{\text{mix}} > 0$ and $\Delta H_{\text{mix}} > 0$, then non-ideal solutions show positive deviations. Such solutions form a constant boiling mixture of definite composition (azeotropic mixture) having boiling point less than either of both the liquids. In these solutions solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions. Examples are: $H_2O + CH_3OH$; $H_2O + C_2H_5OH$; $C_6H_6 + CH_3OH$; $C_6H_6 + CCl_4$; $(CH_3)_2CO + C_6H_6$; $(CH_3)_2CO + C_2H_5OH$.

(ii) If $\Delta V_{\text{mix}} < 0$ and $\Delta H_{\text{mix}} < 0$, then non-ideal solutions show negative deviations. In these solutions, solvent-solvent and solute-solute interactions are weaker than solvent-solute interactions. Such solutions also form azeotropic mixture having boiling point higher than either of the two solvents. Examples are:

$H_2O + HCl$; $H_2O + HNO_3$; $CHCl_3 + (CH_3)_2CO$; $CHCl_3 + C_6H_6$, etc.

5. Methods of expressing the concentration of a solution: Some of the methods are given in the table.

Name	Symbol	Formula	Definition	Effect of temperature
1. Mass percentage	% (*W/W*)	$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$	Number of parts by mass of solute per hundred parts of the solution.	No effect
2. Gram per litre	g/L	$\frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$	Amount of the solute in grams present in one litre of solution.	Changes with change of temperature.
3. Parts per million	ppm	$\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$	Number of parts by mass of solute per 10^6 parts of solution.	No effect
4. Molarity	*M*	$\frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$	Number of moles of solute per litre of solution.	Changes with change of temperature.
5. Molality	*m*	$\frac{\text{Number of moles of solute}}{\text{Number of kilograms of the solvent}}$	Number of moles of solute present in 1 kg of the solvent.	No effect
6. Normality	*N*	$\frac{\text{Number of gram equivalents of solute}}{\text{Number of litres of solution}}$	Number of gram equivalents of the solute present in one litre of the solution.	Changes with change of temperature.
7. Mole fraction	*X*	$\frac{n_A}{n_A + n_B}$	Ratio of number of moles of one component to the total number of moles of solution.	No effect
8. Formality	*F*	$\frac{\text{Number of formula mass}}{\text{Number of litres of solution}}$	Number of formula mass in grams present per litre of solution.	Changes with change of temperature.

6. Raoult's law: The partial pressure of any volatile constituent of a solution at a constant temperature is equal to the vapour pressure of pure constituent multiplied by mole fraction of that constituent in the solution.

$$p_A = \text{mole fraction of } A \times p_A^0 = X_A \times p_A^0$$

In the case of binary solution of two volatile liquids, the total vapour pressure of such solution can be given as:

$$\text{Total vapour pressure of solution} = p_A^0 \times X_A + p_B^0 \times X_B$$
$$= p_A + p_B$$

Mole fraction of component A in vapour phase,

i.e., $$Y_A = \frac{p_A}{p} = \frac{p_A^0 X_A}{p_A^0 X_A + p_B^0 X_B}$$

similarly, $$Y_B = \frac{p_B^0 X_B}{p_A^0 X_A + p_B^0 X_B}$$

7. Colligative properties: The properties of dilute solutions containing non-volatile solutes, which depend upon the number of solute particles in solution are called colligative properties. These properties do not depend upon the nature of solutes and solvents. The four colligative properties are:

(i) Relative lowering in vapour pressure
(ii) Elevation in the boiling point
(iii) Depression in the freezing point
(iv) Osmotic pressure.

All these properties are dependent on the concentration of solutes in solution.

8. Relative lowering in vapour pressure: When a non-volatile solute is dissolved in a solvent, its vapour pressure decreases. ($p_0 - p_s$) is known as lowering in vapour pressure. $\left(\frac{p_0 - p_s}{p_0}\right)$ is called relative lowering in vapour pressure.

The relative lowering in vapour pressure of a solution containing non-volatile solute is equal to the mole fraction of the solute present in the solution. This is Raoult's law. Mathematically,

$$\frac{p_0 - p_s}{p_0} = X_{\text{solute}} = \frac{n}{n + N}$$

Let w g of the solute (mol. mass $= m$) be dissolved in W g of solvent (molecular mass $= M$).

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{w/m + W/M}$$

If the solution is very dilute w/m in denominator can be neglected.

$$\frac{p_0 - p_s}{p_0} = \frac{w/m}{W/M} = \frac{wM}{mW} \quad \text{or} \quad \frac{\Delta p}{p_0} = \frac{w_A\, m_B}{m_A\, w_B}$$

9. Elevation of boiling point: The boiling point of a solution containing non-volatile solute is always higher than the boiling point of a pure solvent. The increase in boiling point is termed elevation and represented as ΔT_b.

$$\Delta T_b \propto \text{Molality of the solution}$$

or $$\Delta T_b = m \times K_b \qquad (K_b \text{ is a molal elevation constant})$$

or $$\Delta T_b = \frac{1000 \times K_b \times w}{W \times m} \quad \text{or} \quad \Delta T_b = \frac{1000 \times K_b \times w_A}{w_B \times m_A}$$

where, w = mass of solute; m = molecular mass of solute;
W = mass of solvent

K_b is equal to $\frac{RT_0^2}{1000L}$.

where, T_0 = boiling point of solvent in absolute scale;

L = latent heat of vaporization

The units of K_b are K kg mol^{-1}.

10. Depression in freezing point: The freezing point of a solution containing non-volatile solute is always less than the freezing point of a pure solvent. The decrease in freezing point is termed depression and represented as ΔT_f.

$$\Delta T_f \propto \text{molality of the solution}$$

or $$\Delta T_f = m \times K_f \qquad (K_f \text{ is a molal depression constant})$$

or $$\Delta T_f = \frac{1000 \times K_f \times w}{W \times m} \text{ or } \Delta T_f = \frac{1000 \times K_f \times w_A}{w_B \times m_A}$$

where, w = mass of solute; m = molecular mass of solute;

W = mass of solvent

K_f is equal to $\frac{RT_0^2}{1000L}$.

where, T_0 = freezing point of solvent in absolute scale;

L = latent heat of fusion

The units of K_f are K kg mol^{-1}.

11. Osmosis and osmotic pressure: When a solution is separated from the pure solvent with the help of a semipermeable membrane, the solvent molecules from the pure solvent move towards the solution. The movement of solvent molecules from low concentration to higher concentration through semipermeable membrane is termed as osmosis.

As a result of osmosis, a pressure is developed which is termed as osmotic pressure, *i.e.*, the hydrostatic pressure which develops on account of osmosis is called osmotic pressure. It is equal to $h \cdot d \cdot g$. It is also found that if an equal and opposite force is applied on the solution, the osmosis stops. Thus, the excess pressure that must be applied on the solution as to prevent osmosis is also the measure of osmotic pressure.

Osmotic pressure of a dilute solution is given by van't Hoff equation, $P = CRT$, where C = concentration, R = solution constant and T = absolute temperature.

$$C = \frac{n}{V} = \frac{w}{m \times V}$$

where, w = mass of solute in grams

V = volume of solution in litres

m = molecular mass of solute

i.e., $$P = \frac{w}{m \times V} \cdot RT$$

Best method for the determination of osmotic pressure is Berkeley and Hartley's method.

The term hypertonic and hypotonic are applied to compare the osmotic pressures of two solutions. The solution having lower osmotic pressure is termed hypotonic and the solution having higher osmotic pressure is termed hypertonic solution. The two solutions having equal osmotic pressures are termed as isotonic. Condition for isotonic solutions is

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

A 0.91% solution of pure NaCl is isotonic with human blood cells (RBC). An NaCl solution with concentration less than 0.91% is called hypotonic and RBC will swell and burst in the solution. An NaCl solution with concentration greater than 0.91% is called hypertonic and RBC will shrink in this solution, *i.e.*, will undergo **plasmolysis or crenation.**

12. van't Hoff factor: When the solute undergoes dissociation or association in solution, the number of particles in solution increases or decreases and thus, the colligative property changes accordingly. In 1886, van't Hoff introduced a factor 'i' known as van't Hoff factor to express the extent of dissociation or association of the solute in solution.

van't Hoff factor, i

$$= \frac{\text{Observed colligative property}}{\text{Theoretical or normal colligative property}}$$

$$= \frac{\text{No. of particles after dissociation or association}}{\text{No. of particles when there is no dissociation or association}}$$

$$= \frac{\text{Normal molecular mass of the solute}}{\text{Observed molecular mass of the solute}}$$

From the value of 'i' it is possible to determine the degree of dissociation or association.

In case of dissociation 'i' is greater than 1.

$$i = \frac{1 + (n-1)\alpha}{1}$$

where, n is the number of particles per molecule and α is the degree of dissociation.

or $$\alpha = \frac{i-1}{(n-1)}$$

Similarly, in case of association, 'i' is less than 1.

$$i = \frac{1 + \left(\frac{1}{n} - 1\right)\alpha}{1}$$

where, n is the number of molecules which are associated to form one giant molecule and α is the degree of association.

or $$\alpha = \frac{i-1}{\left(\frac{1}{n} - 1\right)}$$

Molecular masses of electrolytes observed by the methods based on colligative properties are always less than normal molecular masses.

13. Calculation of osmotic pressure from lowering of vapour pressure:

$$\frac{P_0 - P}{P_0} = \frac{\pi m_B}{RdT}$$

where, P_0 = vapour pressure of pure solvent

P = vapour pressure of solution

π = osmotic pressure

m_B = molecular mass of solvent

d = density of solution in gmL^{-1}

R = gas constant in atm mL / deg / mol, *i.e.*, 82.1 .

14. Variation of vapour pressure with temperature (Clausius-Clapeyron equation):

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where, P_1 = vapour pressure at T_1

P_2 = vapour pressure at T_2

ΔH = latent heat of vaporization per mole

15. Variation of vapour pressure of a liquid with external pressure:

$$\log_{10}\left(\frac{p_2}{p_1}\right) = \frac{V_l}{2.303RT}(P_2 - P_1)$$

where, p_1 = vapour pressure at external pressure P_1

p_2 = vapour pressure at external pressure P_2

V_l = molar volume of liquid.

16. Molecular masses of polymers are best determined by osmotic pressure method because other colligative properties give so low value that they cannot be measured accurately.

17. To avoid the freezing of water in a car radiator, in the sub-zero weather, ethylene glycol is added to lower the freezing point of water.

18. Freezing point is same as melting point. Hence, instead of depression in freezing point, depression in melting point can be determined. For this purpose camphor is used as solvent because it has high molal depression constant, *i.e.*, $40\,\text{K m}^{-1}$.

19. Relationship between different colligative properties:

(i) Osmotic pressure π and boiling point elevation ΔT_b:

$$\pi = \Delta T_b \times \frac{dRT}{1000K_b}$$

(ii) Osmotic pressure π and freezing point depression ΔT_f :

$$\pi = \Delta T_f \times \frac{dRT}{1000K_f}$$

(iii) Elevation in boiling point and relative lowering of vapour pressure:

$$\Delta T_b = \frac{1000K_b}{m_A} \times \frac{\Delta P}{P_0}; \quad m_A = \text{molar mass of solvent}$$

(iv) Depression in freezing point and relative lowering of vapour pressure:

$$\Delta T_f = \frac{1000K_f}{m_A} \times \frac{\Delta P}{P_0}$$

20. Hygroscopic and deliquescent substances both absorb moisture from the air. The former do not change their state, *e.g.*, glycerol, whereas the latter dissolve into it, *e.g.*, NaOH. They absorb moisture because the vapour pressure of their saturated solution is less than that of water vapours present in surroundings at that temperature.

The substances like $Na_2CO_3 \cdot 10H_2O$ which lose their water of crystallisation are called **efflorescent.**

Questions

1. Match the following:

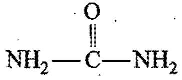
Set-I	Set-II
(A) 10 vol H_2O_2	1. Perhydrol
(B) 20 vol H_2O_2	2. 5.358 N
(C) 30 vol H_2O_2	3. 1.785 N
(D) 100 vol H_2O_2	4. 3.03 %

The correct match is :

(a) A – 4, B – 3, C – 2, D – 1
(b) A – 1, B – 2, C – 3, D – 4
(c) A – 1, B – 3, C – 2, D – 4
(d) A – 4, B – 2, C – 3, D – 1 **[CPMT (UP) 2008]**

2. Matrix Matching Problems (For IIT aspirants):

[A] Match the solutes in Column-I with the van't Hoff factors in Column-II:

Column-I	Column-II
(a) $K_4[Fe(CN)_6]$	(p) $1+\alpha$
(b) $Al_2(SO_4)_3$	(q) Greater than 1
(c)  $NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$	(r) $(1+4\alpha)$
(d) $CaCl_2$	(s) 1

α = Degree of ionization.

[B] Match the solutions in Column-I with their nature in Column-II:

Column-I	Column-II
(a) Benzene + toluene	(p) Non-ideal solution
(b) Ethanol + water	(q) Ideal solution
(c) Benzene + chloroform	(r) $\Delta H_{mix} > 0$
(d) Carbon tetrachloride + chloroform	(s) $\Delta H_{mixing} = 0$

[C] Match the solutions in Column-I with their nature in Column-II:

Column-I	Column-II
(a) n-hexane + n heptane	(p) Can be perfectly separated by distillation
(b) Acetone + chloroform	(q) Maximum boiling azeotrope
(c) Acetone + aniline	(r) Cannot be perfectly separated by distillation
(d) Ethanol + water	(s) Nearly ideal

[D] Match the solutions in Column-I with their osmotic properties in Column-II:

Column-I	Column-II
(a) S_1: 0.1 M glucose, S_2: 0.1 M urea ;	(p) S_1 and S_2 are isotonic
(b) S_1: 0.1 M NaCl, S_2: 0.1 M Na_2SO_4	(q) No migration of solvent across the membrane
(c) S_1: 0.1 M NaCl, S_2: 0.1 M KCl	(r) S_1 is hypertonic to S_2
(d) S_1: 0.1 M $CuSO_4$, S_2: 0.1 M sucrose	(s) S_1 is hypotonic to S_2

[**Note:** Assume that the electrolytes are completely ionised.]

[E] Match the solutions in Column-I with their colligative properties in Column-II:

Column-I	Column-II
(a) 0.1 M $Ca_3(PO_4)_2$	(p) Solution with highest boiling point
(b) 0.1 M NaCl	(q) Solution with van't Hoff factor greater than 1
(c) 0.1 M glucose	(r) Solution with lowest osmotic pressure
(d) 0.1 M $CaCl_2$	(s) Solution with lowest freezing point

[**Note:** Assume that the electrolytes are completely ionised.]

[F] Match the concentration terms of List-I with their informations in List-II:

List-I	List-II
(a) Molarity	(p) Number of gram formula mass of solute dissolved per litre of solution
(b) Molality	(q) Number of moles of solute dissolved per kg of solvent
(c) Formality	(r) Depends on temperature
(d) Strength of solution	(s) Number of moles of solute dissolved per litre of solution

Answers

1. (a) A-4, B-3, C-2, D-1.

2. [A] (a—q, r); (b—q, r); (c—s); (d—p, q)
[B] (a—q, s); (b—p, r); (c—p); (d—s)
[C] (a—p, s); (b—q, r); (c—q, r); (d—r)
[D] (a—p, q); (b—s); (c—p, q); (d—r)
[E] (a—p, q, s); (b—q); (c—r); (d—q)
[F] (a—r, s); (b—q); (c—p, r); (d—r)

• PRACTICE PROBLEMS •

1. 15 g of methyl alcohol is present in 100 mL of solution. If the density of solution is 0.96 g mL^{-1}, calculate the mass percentage of methyl alcohol in solution.
[**Ans.** 15.625%]

2. A solution is prepared by dissolving 15 g of cane sugar in 60 g water. Compute the mass per cent of each component of solution.
[**Ans.** Mass percentage of sugar 20%, Mass percentage of water 80%]

3. The density of the solution of a salt X is 1.15 g mL^{-1}. 20 mL of the solution when completely evaporated gave a residue of 4.6 g of the salt. Calculate the mass percentage of the solute in solution.
[**Ans.** 20%]

4. (a) 5.85 g of NaCl is dissolved in 200 mL of water. What will be the molarity of this solution?
[**Ans.** 0.5 M]
(b) Calculate the molarity of the solution obtained by dissolving 20.6 g NaBr in 500 mL of water.
[**Ans.** 0.4 M]

5. The density of a solution containing 40% by mass of HCl is 1.2 g/mL. Calculate the molarity of the solution.
[**Ans.** 13.15 M]

6. Concentrated sulphuric acid has density of 1.9 g/mL and 99% H_2SO_4 by mass. Calculate the molarity of the acid.
[**Ans.** 19.19 M]

7. A mixture of alcohol and water contains 54% water by mass. Calculate the mole fraction of alcohol in this solution.
[**Ans.** 0.25]

8. What amount of oxalic acid is required to prepare 250 mL 0.1 N solution (Given: molecular mass of oxalic acid = 126)?
[**Ans.** 1.575 g]

9. 7.45 g of potassium chloride is dissolved in 100 g of water. What will be the molality of the solution?
[**Ans.** 1 m]

10. A solution is prepared by mixing 50 g sugar in 100 g of water at 25° C. Calculate the following:
(i) Mass per cent of water.
(ii) Mole fraction of sugar.
(iii) Molality of the solution.
[**Ans.** (i) 66.6 (ii) 0.0256 (iii) 1.46 m]

11. A solution contains 25% water, 50% ethanoic acid and 25% ethanol by mass. Compute the mole fraction of each component.
[**Ans.** Mole fraction of water = 0.5022;
Mole fraction of ethanoic acid = 0.3013;
Mole fraction of ethanol = 0.1965]

12. Find the amount of 98% pure Na_2CO_3 required to prepare 5 litres of 2 N solution.
[**Ans.** 540.8 g impure Na_2CO_3]

13. Calculate the final molarity when 2.0 litre of 3.0 M sugar solution and 3.0 litre of 2.5 M sugar solution are mixed and then diluted to 10 litres with water.
[**Hint:** After mixing number of moles of sugar present $= 2 \times 3 + 3 \times 2.5 = 13.5$; Final molarity $= \frac{13.5}{10} = 1.35\ M$]

14. If 20.0 mL of 1.0 M calcium chloride and 60 mL of 0.2 M $CaCl_2$ are mixed, what will be the molarity of the final solution?
[**Ans.** 0.40 M]

15. Calculate the molarity of each of the ions in a solution when 3.0 litre of 4.0 M NaCl and 4.0 litre of 2.0 M $CoCl_2$ are mixed and diluted to 10 litre.
[**Ans.** Molarity $Na^+ = 1.2\ M$; Molarity $Co^{2+} = 0.8\ M$; Molarity $Cl^- = 2.8\ M$]

[**Hint:**

$$\underset{\substack{1\text{ mole}\\3\times 4\text{ mole}}}{NaCl} = \underset{\substack{1\text{ mole}\\12\text{ mole}}}{Na^+} + \underset{\substack{1\text{ mole}\\12\text{ mole}}}{Cl^-}$$

$$\underset{\substack{1\text{ mole}\\2\times 4\text{ mole}}}{CoCl_2} = \underset{\substack{1\text{ mole}\\8\text{ mole}}}{Co^{2+}} + \underset{\substack{2\text{ mole}\\16\text{ mole}}}{2Cl^-}$$

Total Cl^- ions = 28 mole]

16. What volume of 96% H_2SO_4 solution (density 1.83 g/mL) is required to prepare 4 litre of 3.0 M H_2SO_4 solution?
[**Ans.** 670 mL]
[**Hint:** First determine the molarity of 96% H_2SO_4 and then dilute to get the desired solution.]

17. Calculate the molarity of each ion in solution after 2.0 litre of 3.0 M $AgNO_3$ is mixed with 3.0 litre of 1.0 M $BaCl_2$.
[**Ans.** Molarity of $Ba^{2+} = 0.6\ M$; Molarity of $NO_3^- = 1.2\ M$]

[**Hint:**	$BaCl_2$ +	$2AgNO_3$ =	$2AgCl\downarrow + Ba(NO_3)_2$
Initial	3 mole Ba^{2+} 6 mole Cl^-	6 mole Ag^+ 6 mole NO_3^-,	6 mole Ag^+ will react with 6 mole Cl^- to form AgCl(s)
After reaction	3 mole Ba^{2+}	6 mole NO_3^-	

Total volume 3.0 + 2.0 = 5 litre.]

18. The density of a 10.0% by mass of KCl solution in water is 1.06 g/mL. Calculate molarity, molality and mole fraction of KCl in this solution.
[**Ans.** Molarity = 1.42 M; Molality = 1.489 m; mole fraction of KCl = 0.026]

19. Calculate the molality and mole fraction of the solute in an aqueous solution containing 6 g of urea per 500 g of water (Mol. mass of urea = 60).
[**Ans.** Molality = 0.2 M; Mole fraction = 0.00359]

20. Calculate the molality of 1 litre solution of 93% H_2SO_4 (mass/volume). The density of the solution is 1.84 g/mL. **(MLNR 1993)**
[**Ans.** 10.428 m]

21. Molarity of H_2SO_4 is 0.8 and its density is 1.06 g/cm^3. What will be its concentration in terms of molality and mole fraction. **[CBSE (Mains) 2005]**
[**Ans.** $m = 0.814$; $x_{H_2SO_4} = 0.014$]

22. A 6.90 M solution of KOH in water contains 30% by mass of KOH. Calculate the density of the solution.
[Ans. 1.288 g mL^{-1}]

23. How many kilograms of wet NaOH containing 10% water are required to prepare 60 litre of a 0.5 M solution?
[Ans. 1.33 kg]

24. In an experiment, 18.0 g of mannitol was dissolved in 100 g of water. The vapour pressure of solution at 20° C was 17.226 mm of mercury. Calculate the molecular mass of mannitol. The vapour pressure of water at 20° C is 17.535 mm of mercury.
[Ans. Molecular mass of mannitol = 181.02]

25. The vapour pressure of water at 20° C is 17.53 mm. Calculate the vapour pressure of a solution at 20° C containing 6 g of urea in 100 g of water (molecular mass of urea = 60).
[Ans. Vapour pressure of solution = 17.22 mm]

26. The vapour pressure of ether (molecular mass = 74) is 442 mm Hg at 293 K. If 3 g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426 mm Hg. Calculate the molecular mass of A assuming that the solution of A is very dilute.
[Ans. $m = 123$]

27. 18.2 g of urea is dissolved in 100 g of water at 50° C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50° C is 92 mm Hg.
[Ans. 57.05]
[Hint: Use $\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$, as the solution is not very dilute]

28. Calculate the vapour pressure of a solution at 100° C containing 3 g of cane sugar in 33 g of water.
[Ans. 756.36 mm of Hg]
[Hint: Apply $\frac{p_0 - p_s}{p_0} = \frac{wM}{Wm}$ as the solution is very dilute.
$p_0 = 760$ mm of Hg at 100° C and $m = 342$]

29. An aqueous solution containing 28% by mass of a liquid A (molecular mass = 140) has a vapour pressure of 160 mm at 37° C. Find the vapour pressure of pure liquid A (the vapour pressure of water at 37° C is 150 mm).
[Ans. $p_A = 358.3$ mm]
[Hint: Apply P_{total} = mole fraction of liquid $A \times p_A$ + mole fraction of water $\times\, p_w$. Mass of water = 100 − 28 = 72 g]

30. At 25° C, the vapour pressure of pure benzene is 100 torr, while that of pure ethyl alcohol is 44 torr. Assuming ideal behaviour, calculate the vapour pressure at 25° C of a solution which contains 10 g of each substance.
[Ans. 64.775 torr]

31. Estimate the lowering of the vapour pressure due to solute in a 1.0 molal aqueous solution at 100° C.
[Ans. 14 mm of Hg or 14 torr]

32. Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water. **(Dhanbad 1990)**
[Ans. 1.133 m]

33. Calculate the mass of a non-volatile solute of molecular mass 40, which should be dissolved in 114 g of octane to reduce the vapour pressure to 80%.
[Ans. 10 g]

34. 10 g of a certain non-volatile solute was dissolved in 100 g of water at 20° C. The vapour pressure was lowered from 17.3555 to 17.235 mm. Calculate the molecular mass of the solute.
[Ans. 257.45]

35. 0.534 g of solute is dissolved in 15 g of water then freezing point temperature changes from 0°C to −1.57°C. Molal depression constant of water, $K_f = 1.85$ K kg mol^{-1}. Find out:

(i) Molal concentration
(ii) Molecular mass of solute **[AIPMT (Mains) 2009]**
[Ans. (i) 0.848 (ii) 41.98 amu]

36. Addition of 0.643 g of a compound to 50 mL of benzene (density 0.879 g/mL) lowers the freezing point from 5.51° C to 5.03° C. If K_f for benzene is 5.12, calculate the molecular mass of the compound. **(IIT 1992)**
[Ans. 156]

37. A solution made by dissolving 0.32 g of a new compound in 25 g of water has freezing point − 0.201°C. Calculate the molecular mass of the new compound.
[Ans. 118.4]

38. The boiling point of a solution of 0.1050 g of a substance in 15.84 g of ether was found to be 0.1° C higher than that of pure ether. What is the molecular mass of the substance (Molecular elevation constant of ether per 100 g is 21.6)? **(MLNR 1991)**
[Ans. 143.18]

39. Calculate the freezing point and the boiling point at 1 atmosphere of a solution containing 30 g cane sugar (molecular mass 342) and 150 g water.
Given: $K_b = 0.513$ and $K_f = 1.86$.
[Ans. Boiling point = 100.3; Freezing point = − 1.09°C]

40. When 36.0 g of a solute having the empirical formula CH_2O is dissolved in 1.20 kg of water, the solution freezes at − 0.93° C. What is the molecular formula of the compound?
[Ans. $C_2H_4O_2$]

41. In winter, the normal temperature in Kullu valley was found to be − 11° C. Is a 28% (by mass) aqueous solution of ethylene glycol suitable for a car radiator?
K_f for water = 1.86 K kg mol^{-1}.
[Ans. Yes. The given solution freezes at − 11.66° C]

42. Latent heat of fusion of water is 80 cal/g and its normal freezing point is 0° C. Calculate molal depression constant for water. (R = 1.987 cal)
[Ans. 1.86 K kg mol^{-1}]

43. A solution containing 7.5 g of urea (molecular mass = 60) in 1 kg of water freezes at the same temperature as another solution containing 15 g of solute 'A' in the same amount of water. Calculate molar mass of 'A'.
[Ans. 120]

44. Calculate the osmotic pressure of a decinormal solution of NaCl which is ionised to 80% at 27° C.
[Ans. 4.43 atm]

45. What is the volume of a solution containing 2 g mole of sugar that will give rise to an osmotic pressure of 1 atmosphere at STP?
[Ans. 44.8 litre]

46. If the osmotic pressure of 5 g per litre solution of a compound at 27° C is 0.025 atm, calculate the molecular mass of the compound.
[**Ans.** 4926]

47. The osmotic pressure of blood is 7.65 atmosphere at 37° C. How much glucose should be used per litre for an intravenous injection that is to have same osmotic pressure as blood?
[**Ans.** 54.18 g of glucose per litre]

48. 10 g of cane sugar (molecular mass = 342) in 1×10^{-3} m^3 of solution produces an osmotic pressure of 6.68×10^4 Nm^{-2} at 273 K. Calculate the value of S in SI units.

[**Hint:** $$S = \frac{PV}{n \times T}$$

Given: $V = 1 \times 10^{-3}$ m^3; $P = 6.68 \times 10^4$ Nm^{-2};

$$n = \frac{10}{342}, T = 273$$

$$S = \frac{6.68 \times 10^4 \times 1 \times 10^{-3} \times 342}{10 \times 273} = 8.3684 \text{ J K}^{-1} \text{ mol}^{-1}$$]

49. A 250 mL water solution containing 48 g of sucrose (molecular mass = 342) at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied on solution as to prevent osmosis?
[**Ans.** 13.8 atm]

50. What would be the osmotic pressure of 0.05 M solution of sucrose at 5° C? Find out the concentration of a solution of glucose which would be isotonic with this solution of sucrose. (Molecular mass of sucrose = 342, Molecular mass of glucose = 180)
[**Ans.** 1.14 atm; Concentration of glucose soln. = 9.0 g/L]

51. Calculate the osmotic pressure of 0.5% solution of glucose (molecular mass 180) at 18° C. The value of solution constant is 0.0821 litre-atm K^{-1} mol^{-1}.
[**Ans.** 0.6628 atm]

52. At 10° C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25° C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

[**Hint:** Original solution $$\frac{500}{760} \times V_1 = \frac{w}{m} \times S \times 283 \quad \text{...(i)}$$

After dilution $$\frac{105.3}{760} \times V_2 = \frac{w}{m} \times S \times 298 \quad \text{...(ii)}$$

or $$\frac{V_2}{V_1} \times \frac{105.3}{500} = \frac{298}{283}$$

or $$\frac{V_2}{V_1} = \frac{298}{283} \times \frac{500}{105.3} = 5$$

i.e., the solution is diluted to the extent that V_2 is five times the original volume (V_1).]

53. Two solutions containing respectively 0.75 g of urea (molecular mass 60) and 1.5 g compound X in 100 g of water boil at the same temperature. Calculate the molecular mass of X.
[**Ans.** 120]

54. A 5% solution of glucose is isotonic with 1.1% solution of KCl at 30° C. Calculate the degree of ionisation of KCl.
[**Ans.** 0.88 or 88%]

55. What should be the osmotic pressure of a solution of urea in water at 30° C which has boiling point 0.052 K higher than pure water? Assume molarity and molality to be the same. K_b for water is 0.52 K kg mol^{-1}.
[**Ans.** 2.487 atm]

56. 4.0 g of a substance A dissolved in 100 g H_2O depressed the freezing point of water by 0.1° C while 4.0 g of another substance B depressed the freezing point by 0.2° C. Which one has higher molecular mass and what is the relation?
[**Ans.** $M_A = 2M_B$]

57. A solution containing 28 g of phosphorus in 315 g of CS_2 (boiling point 46.3° C) boils at 47.98° C. The molal elevation constant for CS_2 is 2.34 K kg mol^{-1}. Calculate the molecular mass of phosphorus and deduce its formula in CS_2.
[**Ans.** 123.8, P_4]

58. A solution of two volatile liquids A and B obeys Raoult's law. At a certain temperature it is found that when the pressure above the mixture in equilibrium is 402.5 mm of Hg, the mole fraction of A in the vapour is 0.35 and in the liquid it is 0.65. What are the vapour pressures of two liquids at this temperature?

[**Hint:** Let p_A and p_B be the partial pressures of vapours and p_A^0 and p_B^0 be the vapour pressures of two liquids respectively.

$$p_A = 0.65\, p_A^0 \quad \text{and} \quad p_B = 0.35 p_B^0$$
$$p_A + p_B = 402.5 \quad \text{(given)}$$

In vapour phase,

$$\frac{p_A}{p_A + p_B} = 0.35 \quad \text{or} \quad p_A = 0.35 \times 402.5 = 140.875 \text{ mm}$$

So, $$p_A^0 = 216.72 \text{ mm} \quad \text{and} \quad p_B^0 = 747.5 \text{ mm}$$]

59. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to − 9.3° C (K_f for water = 1.86 K kg mol^{-1}). (IIT 1995)

[**Hint:** $$\Delta T = K_f \times m$$
$$9.3 = 1.86 \times m$$

or $$m = 5$$

Thus, solution of 5.0 molality will have freezing point of − 9.3° C. Let W g water be needed to prepare 5.0 molal solution containing $\frac{50}{62}$ mole of ethylene glycol.

So, $$\frac{50 \times 1000}{62 \times W} = 5.0$$

or $$W = \frac{50 \times 1000}{62 \times 5} = 161.3 \text{ g}$$

Hence, ice separating out = (200 − 161.3) = 38.7 g]

60. At 293.2 K, the density of a 60% aqueous solution of methanol is 0.8946 g/mL. Calculate volume of 1 mole of the solution.
[**Ans.** 28.46 mL/mol]

[**Hint:** Let volume of solution be 100 mL

$$W = 100 \times 0.8946 = 89.46 \text{ g}$$
$$n_{CH_3OH} = \frac{60}{32} = 1.875$$
$$n_{H_2O} = \frac{29.46}{18} = 1.636$$

Total moles = 1.875 + 1.636 = 3.511

Volume per mole $= \dfrac{100}{3.511} = 28.48$ mL/mol]

61. 1.2 kg ethylene glycol $\left(\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}\right)$ was added in a car radiator containing 9 litre water. The freezing of water was just prevented when car was running in the Himalayan valley at temperature − 4°C. Sudden thunderstorm in the valley lowered the temperature to − 6°C. Calculate the amount of ice separated.

[**Ans.** 3 kg ice]

[**Hint:** $\Delta T = K_f \times \dfrac{w_A \times 1000}{m_A \times w_B}$ $A \rightarrow$ Solute ; $B \rightarrow$ Solvent

$$6 = 1.86 \times \frac{1200 \times 1000}{62 \times w_B}$$

$$w_B = 6000 \text{ g}$$

$$I_{\text{Weight of ice}} = \text{Total weight of } H_2O - \text{wt. of } H_2O \text{ at } -6°\text{C}$$
$$= 9000 - 6000 = 3000 \text{ g} = 3 \text{ kg}]$$

62. 2 g mixture of glucose and sucrose is dissolved in 1 litre water at 298 K to develop osmotic pressure of 0.207 atm. Calculate percentage composition of glucose and sucrose by mole as well as by mass.

[**Ans.**

Percentage by mole: glucose = 65.194, sucrose = 34.806;

Percentage by mass: glucose = 50, sucrose = 50.]

63. If benzoic acid (mol. mass = 122) is associated into double molecules when dissolved in benzene and the osmotic pressure of a solution of 5 g of benzoic acid in 100 mL benzene is 5.73 atm at 10°C, what is the percentage association of benzoic acid?

[**Ans.** 80%]

[**Hint:** $\pi = iCRT = i\dfrac{n}{V}RT$

$$5.73 = i \times \frac{5/122}{0.1} \times 0.0821 \times 283$$

$$i = 0.6017$$

$$\alpha = \frac{1-i}{1-1/n} = \frac{1-0.6017}{1-1/2} \approx 0.8$$

% association = 80%]

64. 0.1 formal solution of NaCl is found to be isotonic with 1.10% solution of urea. Calculate the apparent degree of ionization of NaCl.

[**Ans.** 0.83]

[**Hint:** $\pi_{\text{NaCl}} = \pi_{\text{urea}}$

$$= n \times \frac{1}{V} RT$$

$$i \times 0.1 \times RT = \frac{1.1}{60 \times 0.1} \times RT \qquad \left(\pi = \frac{n}{V} RT\right)$$

$$i = 1.83$$

$$\alpha = \frac{i-1}{n-1} = \frac{1.83-1}{2-1} = 0.83]$$

65. The vapour pressure of water at 100° C is 760 mm. What will be the vapour pressure at 95° C ? The latent heat of water at this temperature range is 548 cal/g.

[**Ans.** 634.3 mm]

[**Hint:** Use Clausius-Clapeyron equation.

$$\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)]$$

66. Calculate the increase in vapour pressure of water per atmosphere rise in external pressure at 10 °C. The vapour pressure of water at 10° C and 1 atm is equal to 9.2 mm.

[**Ans.** 0.1%]

[**Hint:** Use $\log_{10}\left(\dfrac{P_2}{P_1}\right) = \dfrac{V_l}{2.303RT}(P_2 - P_1)$

V_l = molar volume of liquid]

67. An aqueous solution of H_2SO_4 has density 1.84 g/mL. Solution contains 98% H_2SO_4 by mass. Calculate:

(i) molarity of solution

(ii) overall molarity of solution

(iii) molar volume

(iv) specific volume

(v) relative decrease in vapour pressure with respect to water, assuming H_2SO_4 as non-electrolyte at this high concentration.

[**Hint:** (i) $M = \dfrac{x \times d \times 10}{m_B}$

$$= \frac{98 \times 1.84 \times 10}{98} = 18.4$$

(ii) Weight of solution (1 litre) = 1000 × 1.84 = 1840 g

$$w_B \text{ (weight of } H_2SO_4) = \frac{98}{100} \times 1840 = 1803.2 \text{ g}$$

$$w_A \text{ (weight of water)} = 1840 - 1803.2 = 36.8 \text{ g}$$

$$\text{Total number of moles} = \frac{w_A}{m_A} + \frac{w_B}{m_B} = \frac{36.8}{18} + \frac{1803.2}{98}$$
$$= 2.044 + 18.4 = 20.444$$

Overall molarity = 20.444

(iii) Molar volume $= \dfrac{\text{Volume}}{\text{Total moles}} = \dfrac{1000}{20.444}$

$$= 48.914 \text{ mL/mol}$$

(iv) Specific volume $= \dfrac{1}{\text{density}} = \dfrac{1}{1.84}$ mL/g = 0.543 mL/g

(v) Molality $(m) = \dfrac{w_B \times 1000}{m_B \times w_A} = \dfrac{98 \times 1000}{98 \times 2} = 500$

$$m = \frac{x_B \times 1000}{(1-x_B)\,m_A}$$

$$500 = \frac{x_B \times 1000}{(1-x_B) \times 18}$$

$$x_B = 0.9$$

According to Raoult's law: $\dfrac{\Delta p}{p_0} = x_B = 0.9$]

68. You are given two samples of HCl with molarity 0.341 and 0.143; volume of each sample being 1 litre. What will be the maximum volume of 0.243 *M* HCl that can be obtained by mixing the given samples in the following two conditions?

(i) When water is added for dilution.

(ii) When no water is added.

[**Ans.** (i) 2.0204 litre; (ii) 1.98 litre]

[**Hint:** (i) Let x litre of 0.341 M HCl and 1 litre of 0.143 M HCl be mixed to obtain 0.243 M HCl.

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$
$$0.341 \times x + 0.143 \times 1 = 0.243\ (1 + x)$$
$$(0.341 - 0.243)x = 0.243 - 0.143$$
$$0.098x = 0.1$$
$$x = 1.0204 \text{ litre}$$
$$\text{Total volume} = 1 + x = 2.0204 \text{ litre}$$

Since, volume is greater than 2 litre, hence water is to be added.

(ii) Let x litre of 0.143 M HCl and 1 litre of 0.341 M HCl are mixed to obtain 0.243 M HCl.

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$
$$0.143 \times x + 0.341 \times 1 = 0.243(1 + x)$$
$$0.1x = 0.098$$
$$x = 0.98 \text{ litre}$$
$$\text{Total volume} = 1 + x = 1.98 \text{ litre}$$

Since, volume is less than two litres, no water is to be added.]

69. What is the vapour pressure of a solution of glucose which has an osmotic pressure of 3 atmosphere at 20° C? The vapour pressure of water at 20° C is 17.39 mm. Consider the density of solution equal to that of solvent.

[**Ans.** 17.35 mm]

[**Hint:** Use: $\frac{\Delta p}{p_0} = \frac{\pi m}{dRT}$]

70. The osmotic pressure of an aqueous solution of a non-electrolyte is 18.8 atm at 15° C. What will be the vapour pressure of this solution at 100° C (Density of water at 100° C ≈ 1 g/cc)?

[**Ans.** 0.958 atm]

[**Hint:** Use, $\frac{\pi_1}{T_1} = \frac{\pi_2}{T_2}$ to calculate osmotic pressure at 100°C.

$$\frac{18.8}{278} = \frac{\pi_2}{373}$$
$$\pi_2 = 25.224 \text{ atm}$$

Use, $\frac{p_0 - p}{p_0} = \frac{\pi m}{dRT}$

$$\frac{1 - p}{1} = \frac{25.224 \times 18}{(1 \times 10^3) \times 0.0821 \times 373}$$
$$p = 0.958 \text{ atm}]$$

71. Calculate the osmotic pressure at 25° C of a solution containing 1 g of glucose and 1 g of sucrose in 1 litre of solution.

If it were not known that the solute was a mixture of glucose and sucrose, what would be the molecular weight of solute corresponding to the calculated osmotic pressure?

[**Ans.** 0.207 atm, 236.384]

[**Hint:** Use; $\pi V = (n_1 + n_2)RT$ to calculate osmotic pressure

$$\pi \times 1 = \left(\frac{1}{180} + \frac{1}{342}\right) \times 0.0821 \times 298$$
$$= 0.207 \text{ atm}$$

Use; $\pi V = \frac{w}{m} RT$ to calculate molar mass of solute.

$$0.207 \times 1 = \frac{2}{m} \times 0.0821 \times 298$$
$$m = 236.384]$$

72. 100 mL aqueous solution of glucose with osmotic pressure 1.2 atm at 25° C is mixed with 300 mL aqueous solution of urea at 2.4 atm at 25° C. Calculate the osmotic pressure of mixture.

[**Ans.** 1.68 atm]

[**Hint:** Use: $\pi_1V_1 + \pi_2V_2 = \pi_R(V_1 + V_2)$

$$\pi_R = \frac{\pi_1V_1 + \pi_2V_2}{V_1 + V_2}$$
$$= \frac{1.2 \times 100 + 2.4 \times 300}{500} = 1.68 \text{ atm}]$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. A solution is defined as a:
(a) homogeneous mixture of two or more substances
(b) heterogeneous mixture of two or more substances
(c) homogeneous mixture of liquid and solid components only
(d) homogeneous mixture consisting of water as one of the components

2. Ideal solution is formed when its components:
(a) have zero heat of mixing only
(b) have zero volume change on mixing only
(c) have zero heat of mixing and zero volume change
(d) can be converted into gases

3. Solutions which distil without change in composition or temperature are called:
(a) amorphous (b) azeotropic mixture
(c) supersaturated (d) ideal

4. Azeotropic mixtures are:
(a) mixture of two solids
(b) those which boil at different temperatures
(c) those which can be fractionally distilled
(d) constant boiling mixtures

5. The solubility of a gas in a liquid is directly proportional to the pressure of the gas. This statement is:
(a) Raoult's law (b) Henry's law
(c) van't Hoff's law (d) None of these

6. Which of the following is not correct for an ideal solution?
(a) Raoult's law is obeyed for entire concentration range and temperatures
(b) $\Delta H_{\text{mix}} = 0$
(c) $\Delta V_{\text{mix}} = 0$
(d) $\Delta S_{\text{mix}} = 0$

7. The solubility of a gas in liquid increases with:
(a) increase in temperature
(b) reduction of gas pressure
(c) decrease in temperature and increase of gas pressure
(d) amount of liquid taken

8. Saturated solution of NaCl on heating becomes:
(a) supersaturated (b) unsaturated
(c) remains saturated (d) none of these

9. A supersaturated solution is a metastable solution whose concentration:
(a) is equal to the solubility of the substance in solvent
(b) is less than the solubility
(c) exceeds the solubility
(d) continuously changes

10. When a crystal of a solute is introduced into a supersaturated solution of the solute:
(a) the solute dissolves
(b) the solution becomes unsaturated
(c) the solution remains supersaturated
(d) the excess of solute crystallises out

11. An electrolyte dissolves in water if:
(a) lattice energy is less than hydration energy
(b) lattice energy is greater than hydration energy
(c) lattice energy is equal to hydration energy
(d) dissolution is endothermic

12. The solubility of a substance is defined as the amount of solute in grams:
(a) present in 100 g of the solvent
(b) present in 100 g of the solution
(c) present in 100 mL of the solution
(d) present in 1 litre of the solution

13. Which of the following will form an ideal solution?
(a) C_2H_5OH and water (b) HNO_3 and water
(c) $CHCl_3$ and CH_3COCH_3 (d) C_6H_6 and $C_6H_5CH_3$

14. Which of the following shows positive deviation from Raoult's law?
(a) C_6H_6 and $C_6H_5CH_3$ (b) C_6H_6 and CCl_4
(c) $CHCl_3$ and C_2H_5OH (d) $CHCl_3$ and CH_3COCH_3

15. Which of the following shows negative deviation from Raoult's law?
(a) $CHCl_3$ and acetone (b) C_6H_6 and C_2H_5OH
(c) $C_6H_5CH_3$ and C_6H_6 (d) C_6H_6 and CCl_4

16. An azeotropic mixture of two liquids boils at a lower temperature than either of them when:
(a) it is saturated
(b) it does not deviate from Raoult's law
(c) it shows negative deviation from Raoult's law
(d) it shows positive deviation from Raoult's law

17. A maxima or minima obtained in the temperature composition curve of a mixture of two liquids indicates:
(a) an azeotropic mixture
(b) an eutectic formation
(c) that the liquids are immiscible with one another
(d) that the liquids are partially miscible at the maximum or minimum

18. Among the following, that does not form an ideal solution is:
(a) C_6H_6 and $C_6H_5CH_3$ (b) C_2H_5Cl and C_2H_5OH
(c) C_6H_5Cl and C_6H_5Br (d) C_2H_5Br and C_2H_5I

19. Which of the following solution pairs can be separated by fractional distillation?
(a) Water-HNO_3 (b) Water-HCl
(c) Benzene-toluene (d) C_2H_5OH-water

20. When two liquids *A* and *B* are mixed, their boiling points become greater than both of them. The mixture is:
(a) ideal solution
(b) non-ideal solution with negative deviation from Raoult's law
(c) non-ideal solution with positive deviation from Raoult's law
(d) normal solution

21. The azeotropic mixture of water (b.pt. 100° C) and HCl (b.pt. 85° C) boils at 108.5 ° C. When this mixture is distilled, it is possible to obtain:
(a) pure HCl
(b) pure water
(c) pure water as well as HCl
(d) neither HCl nor H_2O in their pure states

22. Pressure cooker reduces cooking time because:(CPMT 1990)
(a) the heat is more evenly distributed inside the cooker
(b) a large flame is used
(c) boiling point of water is elevated
(d) whole matter is converted into steam

23. A molal solution is one that contains one mole of a solute in:
(a) 1000 g of the solvent (b) one litre of the solution
(c) one litre of the solvent (d) 22.4 litre of the solution

24. In which mode of expression, the concentration of the solution remains independent of temperature?
(a) Normality (b) Molality (c) Molarity (d) Formality

25. 8 g NaOH is dissolved in one litre of solution. Its molarity is:
(a) 0.8 *M* (b) 0.4 *M* (c) 0.2 *M* (d) 0.1 *M*

26. If 18 g of glucose is present in 1000 g of solvent, the solution is said to be:
(a) 1 molar (b) 0.1 molar (c) 0.5 molal (d) 0.1 molal

27. The molarity of pure water is: [CMC (Vellore) 1991]
(a) 100 *M* (b) 55.6 *M* (c) 50 *M* (d) 18 *M*

28. For preparing 0.1 *M* solution of H_2SO_4 in one litre, we need H_2SO_4:
(a) 9.8 g (b) 4.9 g (c) 49.0 g (d) 0.98 g

29. Mole fraction of $C_3H_5(OH)_3$ in a solution of 36 g of water and 46 g of glycerine is: (CPMT 1991)
(a) 0.46 (b) 0.36 (c) 0.20 (d) 0.40

30. H_2O_2 solution used for hair bleaching is sold as a solution of approximately 5.0 g H_2O_2 per 100 mL of the solution. The molecular mass of H_2O_2 is 34. The molarity of this solution is approximately:
(a) 0.15 *M* (b) 1.5 *M* (c) 3.0 *M* (d) 3.4 *M*

31. The number of moles of solute per kg of a solvent is called its:
(a) molarity (b) normality
(c) mole fraction (d) molality

32. 1000 g aqueous solution of $CaCO_3$ contains 10 g of calcium carbonate. Concentration of the solution is:

(a) 10 ppm (b) 100 ppm
(c) 1000 ppm (d) 10000 ppm

33. A solution of $CaCl_2$ is 0.5 mol/litre; then the moles of chloride ion in 500 mL will be:
(a) 0.5 (b) 0.25 (c) 1.0 (d) 0.75

34. If 5.85 g of NaCl are dissolved in 90 g of water, the mole fraction of solute is: [CMC (Vellore) 1991]
(a) 0.0196 (b) 0.01 (c) 0.1 (d) 0.2

35. What is the normality of 1 M H_3PO_4 solution? (AIIMS 1991)
(a) 0.5 N (b) 1.0 N
(c) 2.0 N (d) 3.0 N

36. The molarity of a 0.2 N Na_2CO_3 solution will be:
(a) 0.05 M (b) 0.2 M
(c) 0.1 M (d) 0.4 M

37. How many grams of H_2SO_4 are present in 0.25 g mole of H_2SO_4? (CPMT 1990)
(a) 2.45 (b) 24.5 (c) 0.25 (d) 0.245

38. Colligative properties of the solution depend upon:
(a) nature of the solution (b) nature of the solvent
(c) number of solute particles (d) number of moles of solvent

39. Which of the following is a colligative property? (AFMC 2009)
(a) Surface tension (b) Osmotic pressure
(c) Optical rotation (d) Viscosity

40. Which is not a colligative property?
(a) Osmotic pressure
(b) Lowering in vapour pressure
(c) Depression in freezing point
(d) Refractive index

41. Colligative properties are applicable to:
(a) ideal dilute solutions (b) concentrated solutions
(c) non-ideal solutions (d) all of these

42. The vapour pressure of a solution having solid as solute and liquid as solvent is: [PET (MP) 2004]
(a) directly proportional to mole fraction of the solvent
(b) inversely proportional to mole fraction of the solvent
(c) directly proportional to mole fraction of the solute
(d) inversely proportional to mole fraction of the solute

43. If p_0 and p are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and solute respectively, then correct relation is:
(a) $p = p_0 N_2$ (b) $p = p_0 N_1$
(c) $p_0 = pN_1$ (d) $p = p_0(N_1/N_2)$

44. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressure of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be : (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}) (AIEEE 2010)
(a) 96.2 kPa (b) 144.5 kPa
(c) 72 kPa (d) 36.1 kPa

[**Hint:** Heptane A, $n_A = \frac{25}{100} = 0.25$

Octane $B, n_B = \frac{35}{114} = 0.31$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{0.25}{0.25+0.31} = 0.45$$
$$x_B = 0.55$$
$$p = p_A^0 x_A + p_B^0 x_B$$
$$= 105 \times 0.45 + 45 \times 0.55$$
$$= 72 \text{ kPa}]$$

45. The vapour pressure of water at room temperature is 30 mm of Hg. If the mole fraction of the water is 0.9, the vapour pressure of the solution will be:
(a) 30 mm of Hg (b) 24 mm of Hg
(c) 21 mm of Hg (d) 27 mm of Hg

46. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be: (AIEEE 2007)
(a) 360 (b) 350
(c) 300 (d) 700

47. When a non-volatile solute is dissolved in a solvent, the relative lowering in vapour pressure is equal to: [AFMC 2004; PMT (Himachal) 2006]
(a) mole fraction of solvent
(b) mole fraction of solute
(c) concentration of solute in g L^{-1}
(d) concentration of solute in g per 100 mL

48. The vapour pressure of a dilute aqueous solution of glucose is 750 mm of mercury at 373 K. The mole fraction of solute is:
(a) $\frac{1}{10}$ (b) $\frac{1}{7.6}$ (c) $\frac{1}{35}$ (d) $\frac{1}{76}$

[**Hint:** $\frac{p - p_s}{p}$ = Mole fraction of solute

p = Vapour pressure of water at 373 K is 760 mm]

49. The vapour pressure of a pure liquid 'A' is 70 torr at 27 °C. It forms an ideal solution with another liquid B. The mole fraction of B is 0.2 and total pressure of the solution is 84 torr at 27 °C. The vapour pressure of pure liquid B at 27 °C is: [CET (Karnataka) 2009]
(a) 14 torr (b) 56 torr (c) 140 torr (d) 70 torr

[**Hint:** $p_A = (1 - 0.2) \times 70 = 0.8 \times 70 = 56$ torr
$p_B = 84 - 56 = 28$ torr
$28 = 0.2 \times p_B^0$ or $p_B^0 = 140$ torr]

50. The vapour pressure of water at room temperature is 23.8 mm Hg. The vapour pressure of an aqueous solution of sucrose with mole fraction 0.1 is equal to:
(a) 23.9 mm Hg (b) 24.2 mm Hg
(c) 21.42 mm Hg (d) 31.44 mm Hg

51. The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved in 20 g of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu, then the molecular mass of B is:
(a) 100 amu (b) 90 amu (c) 75 amu (d) 120 amu

52. If the various terms in the following expressions have usual meanings, the van't Hoff factor 'i' cannot be calculated by which of the following expression?
(a) $\pi V = \sqrt{i}\, nRT$
(b) $\Delta T_f = i \times K_f \times m$
(c) $\Delta T_b = i \times K_b \times m$
(d) $\frac{P^{\circ}_{\text{solvent}} - P_{\text{solution}}}{P^{\circ}_{\text{solvent}}} = i\left[\frac{n}{N+n}\right]$

53. Semipermeable membrane is that which permits the passage of: **(CPMT 1990)**
(a) solute molecules only
(b) solvent molecules only
(c) solvent and solute molecules both
(d) neither solute nor solvent molecules

54. Which inorganic precipitate acts as semipermeable membrane?
(a) Calcium sulphate (b) Barium oxalate
(c) Nickel phosphate (d) Copper ferrocyanide

55. During osmosis, flow of water through a semipermeable membrane is: **[CBSE (Medical) 2006]**
(a) from solution having higher concentration only
(b) from both sides of semipermeable membrane with equal flow rates
(c) from both sides of semipermeable membrane with unequal flow rates
(d) from solution having lower concentration only

56. At constant temperature, the osmotic pressure of a solution is:
(a) directly proportional to the concentration
(b) inversely proportional to the concentration
(c) directly proportional to the square of concentration
(d) directly proportional to the square root of concentration

57. Osmotic pressure observed when benzoic acid is dissolved in benzene, is less than that expected from theoretical considerations. This is because : **[MGIMS (Wardha) 2008]**
(a) benzoic acid is organic solute
(b) benzoic acid has higher molar mass than benzene
(c) benzoic acid gets associated in benzene
(d) benzoic acid gets dissociated in benzene

58. Blood cells do not shrink in blood because blood is: **[PMT (Med) 2007]**
(a) hypertonic (b) isotonic
(c) equimolar (d) hypotonic

59. Isotonic solutions have the same:
(a) density (b) molar concentration
(c) normality (d) strength

60. The osmotic pressure of solution increases if: **(CPMT 1991)**
(a) temperature is decreased
(b) concentration is decreased
(c) number of solute particles is increased
(d) volume is increased

61. The osmotic pressure of a 5% solution of cane sugar (molecular mass 342) at 15°C is:
(a) 3.46 atm (b) 3.64 atm (c) 4.0 atm (d) 2.45 atm

62. A solution has an osmotic pressure of 0.821 atm at 300 K. Its concentration would be: **(IIT 1990)**
(a) 0.66 M (b) 0.32 M (c) 0.066 M (d) 0.033 M

63. If 3 g of glucose (molecular mass 180) is dissolved in 60 g of water at 15°C, then the osmotic pressure of this solution will be:
(a) 0.34 atm (b) 0.65 atm (c) 6.57 atm (d) 5.57 atm

64. The relationship between the values of osmotic pressure of 0.1 M solutions of KNO_3 (P_1) and CH_3COOH (P_2) is:
(a) $P_1 = P_2$ (b) $P_2 > P_1$
(c) $\frac{P_1}{P_1 + P_2} = \frac{P_2}{P_1 + P_2}$ (d) $P_1 > P_2$

65. An electrolyte A gives 3 ions and B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure P, then 0.05 M solution of A will produce an osmotic pressure, assuming that the electrolyte is completely ionised:
(a) 1.5P (b) P (c) 0.5P (d) 0.75P

66. 1 molar solution of a non-volatile and non-electrolyte compound will produce an osmotic pressure .... at 0°C.
(a) 1 atm (b) 44.8 atm (c) 10.0 atm (d) 22.4 atm

67. If 0.1 M solution of glucose and 0.1 M urea solution are placed on two sides of a semipermeable membrane to equal heights, then it will be correct to say that: **(CBSE 1992)**
(a) there will be no net movement across the membrane
(b) glucose will flow towards urea solution
(c) urea will flow towards glucose solution
(d) water will flow from urea solution towards glucose solution

68. Which solution will exert highest osmotic pressure?
(a) 1 M glucose solution (b) 1 M urea solution
(c) 1 M alum solution (d) 1 M NaCl solution

69. Which is the correct relation between osmotic pressure of 0.1 M NaCl solution and 0.1 M Na_2SO_4 solution?
(a) The osmotic pressure of Na_2SO_4 is less than NaCl solution
(b) The osmotic pressure of Na_2SO_4 is more than NaCl solution
(c) Both have same osmotic pressure
(d) None of the above

70. A 0.6% urea solution would be isotonic with: **[CET (Karnataka) 2009]**
(a) 0.1 M glucose solution (b) 0.1 M KCl solution
(c) 0.6% glucose solution (d) 0.6% NaCl solution

71. Which one of the following solutions will have highest osmotic pressure? (Assume that all the salts are equally dissociated.)
(a) 0.1 M $Al_2(SO_4)_3$
(b) 0.1 M $BaCl_2$
(c) 0.1 M Na_2SO_4
(d) The solution obtained by mixing equal volumes of (b) and (c)

72. The following solutions have equal concentrations. Which one will show minimum osmotic pressure?
(a) $BaCl_2$ (b) $AgNO_3$
(c) Na_2SO_4 (d) $(NH_4)_3PO_4$

73. A solution of a substance containing 1.05 g per 100 mL was found to be isotonic with 3% glucose solution. The molecular mass of the substance is:
(a) 31.5 (b) 6.3 (c) 630 (d) 63

74. The osmotic pressure of equimolar solutions of $BaCl_2$, NaCl and glucose will be in the order:
(a) glucose > NaCl > $BaCl_2$ (b) $BaCl_2$ > NaCl > glucose
(c) NaCl > $BaCl_2$ > glucose (d) NaCl > glucose > $BaCl_2$

75. At 25°C, the highest osmotic pressure is exhibited by 0.1 M solution of: **(CBSE 1994)**
(a) $CaCl_2$ (b) KCl (c) glucose (d) urea

76. The plant cell will shrink when placed in:
(a) water (b) a hypotonic solution
(c) a hypertonic solution (d) an isotonic solution

77. The osmotic pressure of a solution at 273 K is 2.5 atm. Its osmotic pressure at 546 K under similar conditions will be:
(a) 0.5 atm (b) 1.0 atm (c) 2.5 atm (d) 5.0 atm

78. Which one of the following pairs of solutions will be expected to be isotonic under the same temperature?
[CET (Gujarat) 2006; AMU (Medical) 2009]
(a) 0.1 M urea and 0.1 M NaCl
(b) 0.1 M urea and 0.2 M $MgCl_2$
(c) 0.1 M NaCl and 0.1 M Na_2SO_4
(d) 0.1 M $Ca(NO_3)_2$ and 0.1 M Na_2SO_4

79. An aqueous solution of methanol in water has vapour pressure:
(a) less than that of water (b) equal to that of water
(c) more than that of water (d) equal to that of methanol

80. An aqueous solution is 1 molal in KI. Which change will cause the vapour pressure of the solution to increase?
[CBSE (PMT) 2010]
(a) Addition of NaCl (b) Addition of Na_2SO_4
(c) Addition of 1 molal KI (d) Addition of water

81. Osmotic pressure of a solution containing 0.1 mole of solute per litre at 273 K is (in atm):
(a) $\frac{0.1\times 273}{0.0821}$ (b) $\frac{0.1}{1}\times 0.0821\times 273$
(c) $\frac{1}{0.1}\times 0.0821\times 273$ (d) $\frac{0.1}{1}\times\frac{0.0821}{273}$

82. A solution of urea contains 8.6 g per litre. It is isotonic with a 5% solution of a non-volatile solute. The molecular mass of the solute will be:
(a) 349 (b) 34.9 (c) 3490 (d) 861

83. The hard shell of an egg was dissolved in HCl. The egg was then placed in a concentrated solution of NaCl. What will happen?
(a) The egg will shrink
(b) The egg will swell
(c) The egg will become harder
(d) There will be hardly any visible change

84. Blood has been found isotonic with:
(a) saturated solution of NaCl
(b) saturated solution of KCl
(c) saturated solution of 1 : 1 mixture of NaCl and KCl
(d) normal sodium chloride solution

85. When a solute is dissolved in a solvent:
(a) vapour pressure of the solvent is decreased
(b) freezing point of the solution becomes less than that of solvent
(c) boiling point of the solution becomes higher than that of solvent
(d) all are correct

86. The molal elevation constant is the ratio of the elevation in boiling point to:
(a) molarity (b) molality
(c) mole fraction of solute (d) mole fraction of solvent

87. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It results in:
(a) reducing viscosity (b) reducing specific heat
(c) reducing freezing point (d) reducing boiling point

88. The best colligative property used for the determination of molecular masses of polymers is:
(a) relative lowering in vapour pressure
(b) osmotic pressure
(c) elevation in boiling point
(d) depression in freezing point

89. Ebullioscopy is concerned with:
(a) osmotic pressure of a solution
(b) elevation of boiling point of a solution
(c) depression in freezing point of a solution
(d) relative lowering in vapour pressure of a solution

90. Cryoscopy is concerned with:
(a) osmotic pressure of a solution
(b) elevation of boiling point of a solution
(c) depression in freezing point of a solution
(d) relative lowering in vapour pressure of a solution

91. Molecular mass of a non-volatile solute can be determined by:
(a) Cryoscopic method (b) Victor-Meyer's method
(c) Graham's method (d) Duma's method

92. Beckmann's thermometer measures:
(a) boiling point of the solution
(b) freezing point of the solution
(c) any temperature
(d) elevation in boiling point or depression in freezing point

93. The freezing point of 1% of lead nitrate solution in water will be: **[UGET (Manipal) 2006]**
(a) 2°C (b) 1°C (c) 0°C (d) below 0°C

94. A solution of 1.25 g of non-electrolyte in 20 g of water freezes at 271.94 K. If K_f is 1.86 K kg mol^{-1} then molecular mass of the solute will be:
(a) 207.8 (b) 179.79 (c) 209.6 (d) 109.5

95. The ratio of the value of colligative property for KCl solution to that of sugar solution at the same concentration is nearly:
(a) 1 (b) 2 (c) 0.5 (d) 2.5

96. The freezing point order of the solution of glucose is:
(a) 10% > 3% > 2% > 1% (b) 1% > 2% > 3% > 10%
(c) 1% > 3% > 10% > 2% (d) 10% > 1% > 3% > 2%

97. Which one of the following solutions has the highest b.p.?
[UGET (Manipal) 2006]
(a) 0.1 M NaCl (b) 0.1 M urea
(c) 0.1 M $BaCl_2$ (d) 0.1 M glucose

98. The freezing point of 1 molal NaCl solution assuming NaCl to be 100% dissociated in water is:

(a) $-1.86°C$ (b) $-3.72°C$
(c) $+1.86°C$ (d) $+3.72°C$

99. Which of the following 0.1 M aqueous solutions will have the lowest freezing point? **(MLNR 1990)**
(a) K_2SO_4 (b) NaCl (c) Urea (d) Glucose

100. The freezing point of a 0.05 molal solution of a non-electrolyte in water is: **(MLNR 1990)**
(a) $-1.86°C$ (b) $-0.93°C$ (c) $-0.093°C$ (d) $0.93°C$

101. The freezing point of equimolal aqueous solution will be highest for: **(IIT 1990)**
(a) $C_6H_5NH_3Cl$ (b) $Ca(NO_3)_2$
(c) $La(NO_3)_3$ (d) $C_6H_{12}O_6$ (glucose)

102. Elevation in boiling point was 0.52°C when 6 g of a compound X was dissolved in 100 g of water. Molecular mass of the compound X is: (K_b for water is 0.52 per 1000 g of water.)
(a) 120 (b) 60 (c) 600 (d) 180

103. The molal freezing point constant for water is 1.86. If 342 g of cane sugar is dissolved in 1000 g of water, the solution will freeze at:
(a) 1.86°C (b) $-1.86°C$ (c) $-3.92°C$ (d) 3.92°C

104. The molal elevation constant of water is 0.51. The boiling point of 0.1 molal aqueous NaCl solution is nearly: **(IIT 1991)**
(a) 100.05°C (b) 100.1°C (c) 100.2°C (d) 101.0°C

105. The molal elevation of an unknown solution is equal to the molal elevation of 0.1 M solution of urea. The concentration of unknown solution is:
(a) 1 M (b) 0.01 M (c) 0.1 M (d) none of these

106. Benzoic acid dissolved in benzene will show a molecular mass of:
(a) 122 (b) 61 (c) 244 (d) 366

107. If the observed and normal osmotic pressures of a KCl solution are 5.85 and 3.20 atm, the degree of dissociation of KCl is:
(a) 1 (b) 0.082 (c) 0.82 (d) 0.28

108. The van't Hoff factor of a 0.005 M aqueous solution of KCl is 1.95. The degree of ionisation of KCl is:
(a) 0.95 (b) 0.97 (c) 0.94 (d) 0.96

109. If the observed and normal osmotic pressures of 1% NaCl solution are 5.7 and 3.0 atm, the degree of dissociation of NaCl is:
(a) 0.9 (b) 1.0 (c) 0.57 (d) 0.3

110. Which one of the following salts would have the same value of the van't Hoff factor as that of $K_3Fe(CN)_6$? **(CBSE 1994)**
(a) $Al_2(SO_4)_3$ (b) NaCl
(c) Na_2SO_4 (d) $Al(NO_3)_3$

111. Equimolal solutions of A and B show depression in freezing point in the ratio of 2 : 1. A remains in normal state in solution. B will be in . . . state in solution.
(a) normal (b) associated
(c) hydrolysed (d) dissociated

112. The values of observed and calculated molecular mass of $Ca(NO_3)_2$ are 65.4 and 164 respectively. The degree of ionisation of the salt will be:
(a) 0.25 (b) 0.50 (c) 0.60 (d) 0.75

113. Which of the following compounds corresponds to van't Hoff factor to be equal to 2 in dilute solution?
(a) KCl (b) $BaCl_2$ (c) K_2SO_4 (d) $C_6H_{12}O_6$

114. A solution containing 3.3 g of a substance in 125 g of benzene (b.pt. = 80°C) boils at 80.66°C. If K_b for benzene is 3.28 K kg mol^{-1} the molecular mass of the substance will be: **(CPMT 1992)**
(a) 130.20 (b) 129.20 (c) 132.20 (d) 131.20

115. The elevation in boiling point of a solution of 10 g of a binary electrolyte (molecular mass 100) in 100 g of water is ΔT_b. The value of K_b for water is:
(a) $\frac{\Delta T_b}{2}$ (b) 10 (c) $10\Delta T_b$ (d) $\frac{\Delta T_b}{10}$

116. The molal freezing point constant for water is 1.86 K kg mol^{-1}. Therefore, the freezing point of 0.1 M NaCl solution in water is expected to be: **(MLNR 1994)**
(a) $-1.86°C$ (b) $-0.186°C$ (c) $-0.372°C$ (d) $+0.372°C$

117. Equal volumes of $M/20$ urea solution and $M/20$ glucose solution are mixed. The mixture will have osmotic pressure:
(a) equal to either of the solution
(b) less than either of the solution
(c) higher than either of the solution
(d) zero

118. Assuming the salts to be unionised in solution, which of the following has highest osmotic pressure?
(a) 1% CsCl (b) 1% RbCl (c) 1% KCl (d) 1% NaCl

119. Pure benzene freezes at 5.3°C. A solution of 0.223 g of phenyl acetic acid ($C_6H_5CH_2COOH$) in 4.4 g of benzene ($K_f = 5.12$ K kg mol^{-1}) freezes at 4.47°C. From the observation one can conclude that: **(AFMC 2010)**
(a) phenyl acetic acid exists as such in benzene
(b) phenyl acetic acid undergoes partial ionization in benzene
(c) phenyl acetic acid undergoes complete ionization in benzene
(d) phenyl acetic acid dimerizes in benzene

120. The movement of solvent molecules from higher concentration to lower concentration through semipermeable membrane under pressure is termed:
(a) osmosis (b) reverse osmosis
(c) dialysis (d) diffusion

121. During depression of freezing point experiment, an equilibrium is established between the molecules of: **(EAMCET 2009)**
(a) liquid solvent and solid solvent
(b) liquid solute and solid solvent
(c) liquid solute and solid solute
(d) liquid solvent and solid solute

122. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to: **(IIT 1996)**
(a) ionisation of benzoic acid
(b) dimerization of benzoic acid
(c) trimerization of benzoic acid
(d) solvation of benzoic acid

123. If 0.15 g of a solute, dissolved in 15 g of solvent, increases the boiling point by 0.216° C over that of the pure solvent, the molecular mass of the substance is (Molal elevation constant for the solvent is 2.16): **(CBSE 1999)**

(a) 1.01 (b) 10
(c) 10.1 (d) 100

124. The vapour pressure of benzene at a certain temperature is 640 mm of Hg. A non-volatile and non-electrolytic solid, weighing 2.175 g, is added to 39.08 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is the molecular mass of the solid substance? **(CBSE 1999)**
(a) 49.50 (b) 59.6
(c) 69.5 (d) 79.8

125. A 5% solution of cane sugar (mol. mass = 342) is isotonic with 1% solution of a substance X. The molecular mass of X is: **(CBSE 1998)**
(a) 34.2 (b) 171.2
(c) 68.4 (d) 136.8

126. The vapour pressure of a solvent decreased by 10 mm of mercury when a non-volatile solute was added to the solvent. The mole fraction of the solute in the solution is 0.2. What should be the mole fraction of the solvent, if the decrease in the vapour pressure is to be 20 mm of mercury? **(CBSE 1998)**
(a) 0.8 (b) 0.6
(c) 0.4 (d) 0.2

[**Hint:** Mole fraction of solute = $\dfrac{\text{lowering in vapour pressure}}{\text{vapour pressure of solvent}}$

Comparing under the two conditions,

$$\frac{0.2}{\text{mole fraction of solute}} = \frac{10}{20}$$

or mole fraction of solute = 0.4

mole fraction of solvent = (1 − 0.4) = 0.6]

127. Which of the following 0.10 m aqueous solution will have the lowest freezing point? **(CBSE 1997)**
[✓ (a)] $Al_2(SO_4)_3$ (b) KI
(c) $C_6H_{12}O_6$ (d) $C_{12}H_{22}O_{11}$

128. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **(AIEEE 2009)**
(a) The solution formed is an ideal solution
(b) The solution is non-ideal, showing positive deviation from Raoult's law
(c) The solution is non-ideal, showing negative deviation from Raoult's law
(d) n-heptane shows positive deviation, while ethanol shows negative deviation from Raoult's law

129. X is a non-volatile solute and Y is volatile solvent. The following vapour pressures are obtained by dissolving X in Y.

X/mol L^{-1}	Y/mm Hg
0.1	P_1
0.25	P_2
0.01	P_3

The correct order of vapour pressure is : **[EAMCET (Engg.) 2010]**
(a) $P_1 < P_2 < P_3$ (b) $P_3 < P_2 < P_1$
(c) $P_3 < P_1 < P_2$ (d) $P_2 < P_1 < P_3$

130. 12.2 g of benzoic acid (M = 122) in 100 g water has elevation in boiling point of 0.27. K_b = 0.54 K kg mol^{-1}. If there is 100% polymerisation, the number of molecules of benzoic acid in associated state is:
(a) 1 (b) 2
(c) 3 (d) 4

131. For $[CrCl_3 \cdot xNH_3]$, elevation in boiling point of one molal solution is double of one molal solution of glucose; hence x is, if complex is 100% ionised:
(a) 4 (b) 5
(c) 6 (d) 3

132. If glycerol and methanol were sold at the same price in the market, which would be cheaper for preparing an antifreeze solution for the radiator of an automobile?
(a) Glycerol (b) Methanol
[✓ (c)] Both are equal (d) None of these

133. Two liquids A and B have $P_A^0 : P_B^0 = 1:3$ at a certain temperature. If the mole fraction ratio of $x_A : x_B = 1:3$, the mole fraction of A in vapour in equilibrium with the solution at a given temperature is:
(a) 0.1 (b) 0.2
(c) 0.5 (d) 1.0

134. Relationship between osmotic pressure at 273 K when 1% glucose (π_1), 1% urea (π_2), 81% sucrose (π_3) are dissolved in 1 litre of water:
(a) $\pi_1 > \pi_2 > \pi_3$ (b) $\pi_2 > \pi_1 > \pi_3$
(c) $\pi_3 > \pi_1 > \pi_2$ (d) $\pi_1 = \pi_2 = \pi_3$

135. Which of the following property indicates weak intermolecular forces of attraction in liquid?
(a) High heat of vaporization (b) High vapour pressure
(c) High critical temperature (d) High boiling point

136. One mole of sugar is dissolved in two moles of water. The vapour pressure of the solution relative to that of pure water is:
(a) 2/3 (b) 1/3
(c) 3/2 (d) 1/2

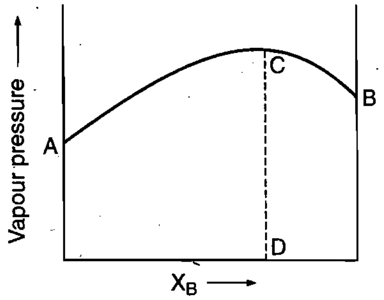
137. The highest temperature at which vapour pressure of a liquid can be measured is:
(a) critical temperature (b) inversion temperature
(c) critical solu. temperature (d) b.pt. of liquid

138. The expression relating molality (m) and mole fraction (x_2) of solute in a solution is:

(a) $x_2 = \dfrac{mM_1}{1 + mM_1}$ (b) $x_2 = \dfrac{mM_1}{1 - mM_1}$

(c) $x_2 = \dfrac{1 + mM_1}{mM_1}$ (d) $x_2 = \dfrac{1 - mM_1}{mM_1}$

139. The diagram given below is a vapour pressure composition diagram for a binary solution of A and B.



In the solution, $A - B$ interactions are:
(a) similar to $A - A$ and $B - B$ interactions
(b) greater than $A - A$ and $B - B$ interactions
(c) smaller than $A - A$ and $B - B$ interactions
(d) unpredictable

140. The best and accurate method for determining osmotic pressure is: **(AFMC 1995)**
(a) negative pressure method
(b) Berkeley and Hartely method
(c) Morse and Frazer method
(d) Preffer's method

141. If all the following four compounds were sold at the same price, which would be cheapest for preparing an antifreeze solution for a car radiator? **(AMU 1997)**
(a) CH_3OH (b) C_2H_5OH
(c) $C_2H_4(OH)_2$ (d) $C_3H_5(OH)_3$

142. What is the osmotic pressure of the solution obtained by mixing 300 cm^3 of 2% (mass-volume) solution of urea with 300 cm^3 of 3.42% solution of sucrose of 20°C?
($R = 0.082$ L atm K^{-1} mol^{-1}) **(SCRA 2009)**
(a) 5 atm (b) 5.2 atm (c) 2.6 atm (d) 4.5 atm

[Hint : $\pi V = \left[\left(\frac{w_B}{m_B}\right)_{\text{urea}} + \left(\frac{w_B}{m_B}\right)_{\text{sucrose}}\right] RT$

$$\pi \times \frac{600}{1000} = \left[\frac{6}{60} + \frac{3 \times 3.42}{342}\right] 0.082 \times 293$$
$$\pi \times 0.6 = (0.1 + 0.03) \times 0.082 \times 293$$
$$\pi = 5.2 \text{ atm}]$$

143. A solution of 1 molal concentration of a solute will have maximum boiling point elevation when the solvent is: **[PMT (MP) 2000]**
(a) ethyl alcohol (b) acetone
(c) benzene (d) chloroform

144. Isotonic solutions have: **(DPMT 2000)**
(a) same boiling point (b) same vapour pressure
(c) same melting point (d) same osmotic pressure

145. The depressions in freezing point for 1 M urea, 1 M glucose and 1 M NaCl are in the ratio: **[CET (Haryana) 2000]**
(a) 1 : 2 : 3 (b) 3 : 2 : 2
(c) 1 : 1 : 2 (d) none of these

146. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is: **(IIT 2001)**
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

147. The vapour pressure of a solvent A is 0.80 atm. When a non-volatile substance B is added to this solvent, its vapour pressure drops to 0.6 atm. The mole fraction of B in the solution is: **[PMT (MP) 2000]**
(a) 0.25 (b) 0.50 (c) 0.75 (d) 0.90

148. An aqueous solution of sucrose, $C_{12}H_{22}O_{11}$, containing 34.2 g/L has an osmotic pressure of 2.38 atmospheres at 17° C. For an aqueous solution of glucose, $C_6H_{12}O_6$, to be isotonic with this solution, it would have: **(AMU 1997)**
(a) 34.2 g/L (b) 17.1 g/L
(c) 18.0 g/L (d) 36.0 g/L of glucose

149. The molal b.pt. constant for water is 0.513° C kg mol^{-1}. When 0.1 mole of sugar is dissolved in 200 g of water, the solution boils under a pressure of 1 atm at: **(AIIMS 1991)**
(a) 100.513° C (b) 100.0513° C
(c) 100.256° C (d) 101.025° C

150. The correct expression relating molality (m), molarity (M), density (d) and molar mass (M_2) of a solute is:
(a) $m = \frac{M}{d + MM_2}$ (b) $m = \frac{M}{d - MM_2}$
(c) $m = \frac{d + MM_2}{M}$ (d) $m = \frac{d - MM_2}{M}$

151. The expression relating mole fraction of solute (x_2) and molarity (M) of the solution is:
(a) $x_2 = \frac{MM_1}{M(M_1 - M_2) + \rho}$ (b) $x_2 = \frac{MM_1}{M(M_1 - M_2) - \rho}$
(c) $x_2 = \frac{M(M_1 - M_2) + \rho}{MM_1}$ (d) $x_2 = \frac{M(M_1 - M_2) - \rho}{MM_1}$
(where ρ is the density of solution and M_1 and M_2 are the molar masses of solvent and solute, respectively.)

152. The boiling point of a solution of 0.11 g of a substance in 15 g of ether was found to be 0.1°C higher than that of pure ether. The molecular weight of the substance will be ($K_b = 2.16$) : **[PET (MP) 2002]**
(a) 148 (b) 158 (c) 168 (d) 178

153. 2.5 litre of 1 M NaOH solution are mixed with another 3 litre of 0.5 M NaOH solution. Then the molarity of the resulting solution is: **[CBSE (PMT) 2002]**
(a) 0.80 M (b) 1.0 M (c) 0.73 M (d) 0.50 M

154. In a mixture, 'A' and 'B' components show the negative deviations as: **(AIEEE 2002)**
(a) $\Delta V_{\text{mix}} > 0$
(b) $\Delta V_{\text{mix}} < 0$
(c) $A - B$ interaction is weaker than $A - A$ and $B - B$ interactions
(d) none of the above reasons is correct

155. A solution contains non-volatile solute of molecular mass M_2. Which of the following can be used to calculate the molecular mass of solute in terms of osmotic pressure? **[CBSE (PMT) 2002]**
(a) $M_2 = \frac{m_2}{\pi} VRT$ (b) $M_2 = \left(\frac{m_2}{V}\right)\frac{RT}{\pi}$
(c) $M_2 = \left(\frac{m_2}{V}\right)\pi RT$ (d) $M_2 = \left(\frac{m_2}{V}\right)\frac{\pi}{RT}$
(m_2 = mass of solute; V = volume of solution; π = osmotic pressure)

156. 0.6 g of an organic compound when dissolved in 21.7 g water freezes at 272.187 K. The molar mass of the organic compound is close to:
(K_f of water is 1.86 deg/molality; freezing point is 273 K) **(SCRA 2009)**
(a) 61 g mol^{-1} (b) 63 g mol^{-1}
(c) 65 g mol^{-1} (d) 67 g mol^{-1}

157. Osmotic pressure of urea solution at 10°C is 500 mm. Osmotic pressure of the solution becomes 105.3 mm, when it is diluted and temperature raised to 25°C. The extent dilution is: **[PMT (MP) 2004]**

(a) 8 times (b) 5 times (c) 4 times (d) 7 times

158. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in blood stream? **(AIIMS 2004)**

(a) 0.15 mol/L (b) 0.30 mol/L
(c) 0.45 mol/L (d) 0.60 mol/L

159. Camphor is often used in molecular mass determination because: **[CBSE-PMT (Pre.) 2004]**

(a) it is readily available
(b) it has very high cryoscopic constant
(c) it is volatile
(d) it is a solvent for organic substances

160. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is: **[IIT (S) 2004]**

(a) 25% (b) 50% (c) 75% (d) 85%

161. Which of the following liquid pairs shows a positive deviation from Raoult's law? **[AIEEE 2004; AMU (Med) 2007]**

(a) Water-hydrochloric acid (b) Benzene-methanol
(c) Water-nitric acid (d) Acetone-chloroform

162. Which one of the following statements is false? **(AIEEE 2004)**

(a) Raoult's law states that vapour pressure of a component over a solution is proportional to mole fraction
(b) The osmotic pressure (π) of a solution is given by the relation $\pi = MRT$ where M is molarity of the solution
(c) The correct order of osmotic pressure for 0.01 M aqueous solution of each component is:

$$BaCl_2 > KCl > CH_3COOH > \text{Sucrose}$$

(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

163. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be:
(K_f for water = 1.86 K kg mol^{-1}) **[CBSE (PMT) 2010]**

(a) –0.372°C (b) –0.520°C
(c) +0.372°C (d) –0.570°C

[Hint : $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$= 1.86 \times \dfrac{68.5 \times 1000}{342 \times 1000}$

$= 0.372$

Freezing point of solution = 0 – 0.372°C
= –0.372°C]

164. Which of the following is incorrect? **[CET (J&K) 2005]**

(a) Relative lowering of vapour pressure is independent of the nature of the solute and the solvent
(b) The vapour pressure is a colligative property
(c) Vapour pressure of a solution is lower than that of the solvent
(d) The relative lowering of vapour pressure is directly proportional to the original pressure

165. Calculate the molal depression constant of a solvent which has freezing point 16.6°C and latent heat of fusion 180.75 J g^{-1}. **[JEE (Orissa) 2005]**

(a) 2.68 (b) 3.86 (c) 4.68 (d) 2.86

166. If for a sucrose solution, elevation in boiling point is 0.1°C then what will be the boiling point of NaCl solution for same molal concentration? **[BHU (Pre.) 2005]**

(a) 0.1°C (b) 0.2°C (c) 0.08°C (d) 0.01°C

167. Which has minimum osmotic pressure? **(DCE 2005)**

(a) 200 mL of 2 M NaCl solution
(b) 200 mL of 1 M glucose solution
(c) 200 mL of 2 M urea solution
(d) All have same

168. Solution A contains 7 g/L of $MgCl_2$ and solution B contains 7 g/L of NaCl. At room temperature, the osmotic pressure of: **(DCE 2005)**

(a) solution A is greater than B
(b) both have same osmotic pressure
(c) solution B is greater than A
(d) can't determine

169. The van't Hoff factor for $BaCl_2$ at 0.01 M concentration is 1.98. The percentage dissociation of $BaCl_2$ at this concentration is: **[PET (Kerala) 2005]**

(a) 49 (b) 69 (c) 89 (d) 98
(e) 100

170. Equimolar solutions in the same solvent have: **(AIEEE 2005)**

(a) same boiling point but different freezing points
(b) same freezing point but different boiling points
(c) same freezing and boiling points
(d) different freezing and boiling points

171. A solution of urea (mol. mass 56 g mol^{-1}) boils at 100.18°C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol^{-1} respectively, the above solution will freeze at: **[CBSE-PMT (Pre.) 2005]**

(a) 0.654°C (b) – 0.654°C
(c) 6.54°C (d) – 6.54°C

172. If 0.5 g of a solute (molar mass 100 g mol^{-1}) in 25 g of solvent elevates the boiling point by 1 K, the molar boiling point constant of the solvent is: **[PMT (Kerala) 2006]**

(a) 2 (b) 8 (c) 5 (d) 0.5
(e) 10

173. Osmotic pressure observed when benzoic acid is dissolved in benzene, is less than that expected from theoretical considerations. This is because: **[KCET 2006]**

(a) benzoic acid is an organic solute
(b) benzoic acid has higher molar mass than benzene
(c) benzoic acid gets associated in benzene
(d) benzoic acid gets dissociated in benzene

174. A 5% solution by mass of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is: **(AIIMS 2006)**

(a) 271 K (b) 273.15 K (c) 269.07 K (d) 277.23 K

[Hint: $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$$2.15 = K_f \times \frac{5 \times 1000}{342 \times 95} \quad \ldots\text{(i)} \quad \text{(for sucrose)}$$

$$\Delta T = K_f \times \frac{5 \times 1000}{180 \times 95} \quad \ldots\text{(ii)} \quad \text{(for glucose)}$$

Dividing eq. (i) by eq. (ii), we get,

$$\Delta T = 4.18 \text{ K}$$

$$T = T_0 - 4.18$$

$$= 273.15 - 4.18 = 269.07 \text{ K}]$$

175. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is: **(AIEEE 2006)**

(a) 759 torr (b) 7.60 torr (c) 76 torr (d) 752.4 torr

176. Depression in freezing point is 6 K for NaCl solution. If K_f for water is 1.86 K/kg mol, amount of NaCl dissolved in 1 kg water is: **(DCE 2006)**

(a) 3.42 (b) 1.62 (c) 3.24 (d) 1.71

177. Observe the following observations:

π_{obs} = observed colligative property

π_{cal} = theoretical colligative property assuming normal behaviour of solute

van't Hoff factor (i) is given by: **[CET (J&K) 2006]**

(a) $i = \pi_{obs} \times \pi_{cal}$ (b) $i = \pi_{obs} + \pi_{cal}$

(c) $i = \pi_{obs} - \pi_{cal}$ (d) $i = \dfrac{\pi_{obs}}{\pi_{cal}}$

178. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1 g cm^{-3}, molar mass of the substance will be: **(AIEEE 2007)**

(a) 210.0 g mol^{-1} (b) 90.0 g mol^{-1}

(c) 115.0 g mol^{-1} (d) 105.0 g mol^{-1}

[Hint: For isotonic solutions:

$$\pi_1 = \pi_2 \quad \because \quad \pi = CRT$$

$$C_1 = C_2$$

$$\frac{1.5/60}{V} = \frac{5.25/m}{V}$$

$$\therefore \quad m = 210]$$

179. Concentrated aqueous sulphuric acid 98% H_2SO_4 by mass has a density of 1.80 g mL^{-1}. Volume of acid required to make one litre of $0.1M$ H_2SO_4 solution is: **[CBSE (Med) 2007]**

(a) 16.65 mL (b) 22.20 mL

(c) 5.55 mL (d) 11.10 mL

[Hint: $M = \dfrac{x \times d \times 10}{m_B} = \dfrac{98 \times 1.80 \times 10}{98} = 18$

$$M_1V_1 = M_2V_2$$

$$18 \times V_1 = 0.1 \times 1000$$

$$V_1 = \frac{100}{18} = 5.55 \text{ mL}]$$

180. If the vapour pressures of pure A and pure B at 298 K are 60 and 15 torr respectively, what would be the mole fraction of A in vapour phase (at this temperature) in a solution that contains 20 mole per cent of A in the $(A + B)$ binary mixture in the liquid phase? **(SCRA 2007)**

(a) 0.2 (b) 0.3

(c) 0.5 (d) 0.7

[Hint: $x_A = \dfrac{20}{100} = 0.2, \quad \therefore \quad x_B = 0.8$

$$p = p_A + p_B = p_A^0 x_A + p_B^0 x_B$$

$$= 60 \times 0.2 + 15 \times 0.8 = 12 + 12 = 24$$

Mole fraction of A in the vapour phase, *i.e.*, y_A may be calculated as:

$$p_A = y_A \times p$$

$$12 = y_A \times 24$$

$$y_A = \frac{12}{24} = 0.5]$$

181. When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene ($K_f = 1.72$ kg mol^{-1}), a freezing point depression of 2K is observed. The van't Hoff factor (i) is: **(IIT 2007)**

(a) 0.5 (b) 1

(c) 2 (d) 3

[Hint: $\Delta T = i \times K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$$2 = i \times 1.72 \times \frac{20 \times 1000}{172 \times 50}$$

$$i = 0.5]$$

182. At 80°C, the vapour pressure of pure liquid A is 520 mm of Hg and that of pure liquid B is 1000 mm of Hg. If a mixture of solution A and B boils at 80°C and 1 atm pressure, the amount of A in the mixture is: (1 atm = 760 mm of Hg) **(AIEEE 2008)**

(a) 50 mol per cent (b) 52 mol per cent

(c) 34 mol per cent (d) 48 mol per cent

[Hint : $p = p_A^0\, x_A + p_B^0\, x_B$

$$760 = 520 \times x_A + 1000\,(1 - x_A)$$

$x_A = 0.50$, *i.e.*, 50 mol per cent.]

183. The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of resulting solution will be : **(AIEEE 2008)**

(a) 17.325 mm Hg (b) 17.675 mm Hg

(c) 15.75 mm Hg (d) 16.5 mm Hg

[Hint : $p = p^0 x_A$

$$= 17.5 \times \frac{178.2/18}{178.2/18 + \dfrac{18}{180}}$$

$$= 17.325 \text{ mm Hg}]$$

184. Which of the following can be measured by the Ostwald-Walker dynamic method ? **(KCET 2008)**

(a) Vapour pressure of the solvent

(b) Relative lowering of vapour pressure

(c) Lowering of vapour pressure

(d) All of the above

185. Cryoscopic constant is the depression in freezing point produced by : **[Comed (Karnataka) 2008]**

(a) 1% solution (b) 1 molar solution

(c) 1 molal solution (d) 1 N solution

186. Which among the following gas will greatly deviate from Henry's law in water ? **[PMT (Kerala) 2008]**

(a) H_2 (b) N_2
(c) CH_4 (d) CO_2
(e) Ar

187. Vapour pressure increases with increase in : **[JEE (Orissa) 2008]**

(a) concentration of solution containing non-volatile solute
(b) temperature upto boiling point
(c) temperature upto triple point
(d) altitude of the concerned place of boiling

188. When mercuric iodide is added to the aqueous solution of potassium iodide: **[BHU (Mains) 2008]**

(a) freezing point is raised
(b) freezing point is lowered
(c) freezing point does not change
(d) boiling point is raised

[**Hint :** $2KI + HgI_2 \longrightarrow K_2[HgI_4]$

Number of particles decreases due to above reaction hence freezing point is raised.]

189. The Henry's law constant for the solubility of N_2 gas in water at 298 K is 1×10^5 atm. The mole fraction of N_2 in air is 0.8. The number of moles of N_2 from dissolved in 10 moles of water at 298 K and 5 atm pressure is: **(IIT 2009)**

(a) 4×10^{-4} (b) 4×10^{-5}
(c) 5×10^{-4} (d) 4×10^{-6}

[**Hint :** $p_{N_2} = x_{N_2} \times p_{\text{total}}$

$$= 0.8\times5 = 4 \text{ atm}$$

According to Henry's law :

$$p_{N_2} = K_H \times x_{N_2}$$

$$4 = 1\times10^5 \times \frac{n_{N_2}}{n_{N_2}\times n_{H_2O}}$$

$$\frac{n_{N_2}+n_{H_2O}}{n_{N_2}} = \frac{1\times10^5}{4}$$

$$\frac{n_{N_2}+10}{n_{N_2}} = 0.25\times10^5$$

$$n_{N_2} = 4\times10^{-4}\,]$$

190. A 0.002 *m* aqueous solution of an ionic compound $Co(NH_3)_5(NO_2)Cl$ freezes at –0.00732°C. Number of moles of ions which 1 mol of ionic compound produces on being dissolved in water will be : ($K_f = -1.86$°C/m) **[CBSE (Med) 2009]**

(a) 1 (b) 2 (c) 3 (d) 4

[**Hint :** $\Delta T = i\times K_f \times m$

$$0.00732 = i\times1.86\times0.002$$

$$i = 1.967 \approx 2\,]$$

191. A solution is separated from pure solvent by a semipermeable membrane at 298 K. The difference in the height of the solution and the solvent is 0.9 m. If K_f and freezing point of the solvent are 30 K kg mol^{-1} and 250.3 K, respectively, the temperature at which the solution freezes is: **(ISAT 2010)**

(a) 250.10 K (b) 250.25 K
(c) 250.20 K (d) 250.05 K

(Assume density of solution to be 1 g/cc)

[**Hint :** $\pi\times13.6\times g\times76 = 90\times g\times1$

$$\pi = 0.087 \text{ atm}$$

$$\pi = CRT$$

$$0.087 = C\times0.082\times298$$

$$C = 3.56\times10^{-3}\,M$$

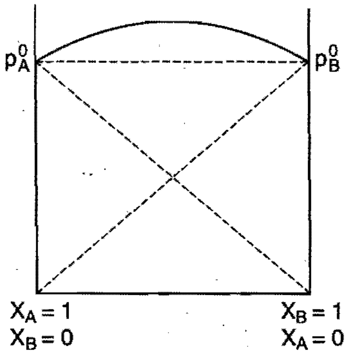
$$\Delta T = K_f\times m$$

$$= 30\times3.56\times10^{-3} \simeq 0.1$$

∴ Freezing point of solution will be : 250.3 – 0.1
= 250.2 K]

Set-2: The questions given below may have more than one correct answers

1. The given graph indicates:



(a) (+) deviation (b) (–) deviation
(c) no deviation (d) none of these

2. Which is the correct statement?

(a) Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components
(b) Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components
(c) Minimum boiling azeotropic mixture shows (+)ve deviation
(d) Maximum boiling azeotropic mixture shows (–)ve deviation

3. A certain non-volatile substance (non-electrolyte) contains 40% C, 6.7% H, 53.3% O. An aqueous solution containing 5% by mass of the solute boils at 100.15° C. Molecular formula of the compound is:

(a) CH_2O (b) $C_2H_4O_2$
(c) $C_6H_{12}O_6$ (d) $C_{12}H_{22}O_{11}$

4. Difference between diffusion and osmosis is:

(a) a semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane
(b) in osmosis the movement of molecules is only in one direction whereas in diffusion movement is on both sides
(c) in osmosis only the solvent moves while in diffusion solute and solvent both move
(d) none of the above

5. For a non-volatile solute:

(a) vapour pressure of solute is zero
(b) vapour pressure of solution = vapour pressure of pure solvent
(c) vapour pressure of solution = vapour pressure of solvent in solution
(d) all of the above

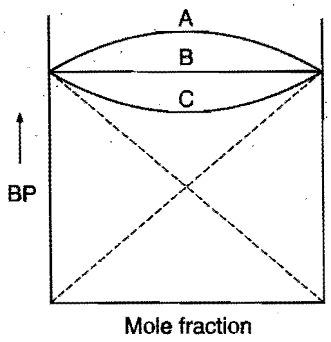
6. In which of the following cases does osmosis take place if the solutions are separated by a semipermeable membrane?
(a) 0.1 M NaCl and 0.2 M glucose
(b) 0.1 M sucrose and 0.1 M fructose
(c) 0.05 M $K_4[Fe(CN)_6]$ and 0.1 M $CaCl_2$
(d) 10^{-3} M $CaCl_2$ and 1.5×10^{-3} M NaCl

7. Match the following:

Solute (equimolar)	**π (OP) ratio**
(i) Urea, glucose, fructose	(A) 1 : 0.8 : 1
(ii) NaCl, $MgCl_2$, K_2SO_4	(B) 1 : 2 : 3
(iii) $Al_2(SO_4)_3$, Na_3PO_4, $K_4Fe(CN_6)$	(C) 1 : 1 : 1
(iv) Glucose, NaCl, $CaCl_2$	(D) 2 : 3 : 3

	(i)	(ii)	(iii)	(iv)
(a)	A	B	C	D
(b)	B	D	C	A
(c)	D	B	A	C
(d)	C	D	A	B

8. Match the following graph:



A (i) (+) deviation
B (ii) Ideal
C (iii) (–) deviation
(a) (A) (i), (B) (ii), (C) (iii)
(b) (A) (iii), (B) (ii), (C) (i)
(c) (A) (ii), (B) (iii), (C) (i)
(d) none of these

9. Vapour pressure of methyl alcohol and ethyl alcohol solutions is represented by $P = 115x_A + 140$ where x_A is the mole fraction of methyl alcohol. The value of $\lim\limits_{x_A \to 0} \frac{P_B^0}{x_B}$ is:
(a) 255 (b) 115
(c) 140 (d) 135

10. To 10 mL of 1 M $BaCl_2$ solution 5 mL of 0.5 M K_2SO_4 is added, $BaSO_4$ is precipitated out. What will happen?
(a) F.pt. is increased (b) B.pt. is increased
(c) F.pt. is lowered (d) B.pt. is lowered

11. Which is a dimensionless quantity?
(a) Mole fraction (b) Molality
(c) % by wt. of solvent (d) % by wt. of solution

12. Which of the following concentration terms is/are independent of temperature? **[PET (Kerala) 2006; CET (Gujarat) 2006; DCE 2007]**
(a) Molarity
(b) Molarity and mole fraction
(c) Mole fraction and molality
(d) Molality and normality
(e) Only molality

13. In the depression of freezing point experiment, it is found that: **(IIT 1999)**
(a) the vapour pressure of the solution is less than that of pure solvent
(b) the vapour pressure of solution is more than that of pure solvent
(c) only solute molecules solidify at the freezing point
(d) only solvent molecules solidify at the freezing point

14. Which of the following is/are correct for a solution of a particular concentration?
(a) Molarity is always less than molality
(b) Formality is equivalent to molarity
(c) Mole fraction is equivalent to mass fraction
(d) Normality of H_2SO_4 solution is double than its molarity

15. Effect of adding a non-volatile solute to a solvent is:
(a) to lower the vapour pressure
(b) to increase its freezing point
(c) to increase its boiling point
(d) to decrease its osmotic pressure

16. Which of the following form/s an ideal solution?
(a) Ethyl bromide + ethyl iodide
(b) Ethyl alcohol + water
(c) Chloroform + benzene
(d) Benzene + toluene

17. Osmotic pressure of a solution is:
(a) directly proportional to the molar concentration of the solution
(b) inversely proportional to the molecular weight of the solute
(c) inversely proportional to the temperature
(d) directly proportional to the volume of the solution

18. Which of the following is/are true?
(a) For the same solution, elevation in boiling point = depression in freezing point
(b) van't Hoff factor for a dilute solution of $BaCl_2$ is 3
(c) Elevation in boiling point is due to increase in vapour pressure
(d) Depression in freezing point is due to decrease in vapour pressure

19. In the following question, more than one of the answers given may be correct. Select correct answer and mark it according to the code : **[BHU (Mains) 2008]**
A solution containing components A and B exhibits positive deviation from Raoult's law only when

(1) $\Delta V_{\text{mixing}} = +\text{ve}$
(2) $\Delta H_{\text{mixing}} = -\text{ve}$
(3) $A - B$ attraction forces < $A - A$ and $B - B$ attraction forces
(4) $A - B$ attraction forces > $A - A$ and $B - B$ attraction forces

Codes:

(a) 1, 2 and 3 are correct
(b) 1 and 2 are correct
(c) 2 and 4 are correct
(d) 1 and 3 are correct

20. Consider the following statements in respect of an ideal solution:

1. Raoult's law is valid for an ideal solution over the whole concentration range
2. Enthalpy of mixing is zero, *i.e.*, $\Delta H_{\text{mix}} = 0$
3. Volume of mixing is not zero, *i.e.*, $\Delta V_{\text{mix}} \neq 0$
4. The components of ideal solution cannot be separated by fractional distillation.

Which of the statements given above is/are correct? **(SCRA 2009)**

(a) 3 and 4 (b) 1 and 4
(c) 1 and 2 (d) 2 and 3

21. Consider the following :

At constant pressure, boiling point of a solution is greater than the boiling point of its pure liquid solvent because

1. Solute is non-electrolyte
2. Solute is involatile
3. Chemical potential of solvent in solution is less than the chemical potential of solvent in its pure state at constant pressure

Which of the above are correct? **(SCRA 2009)**

(a) 1, 2 and 3 (b) 1 and 2 only
(c) 1 and 3 only (d) 2 and 3 only

22. Which values can be obtained from the information represented by the vapour pressure curve of a liquid?

1. Normal boiling point
2. Normal freezing point
3. Enthalpy of vaporisation **(DUMET 2010)**

(a) 1 only (b) 1 and 2 only
(c) 1 and 3 only (d) 1, 2 and 3

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as '**Assertion**' **(A)** and '**Reason**' **(R).** While answering these questions you are required to choose any one of the following four options:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) The dissolution of gases in water is always an endothermic process.
(R) Dissolution of gases in water proceed with negative value of ΔS.

2. (A) Water boiling at 100°C at 1 atmospheric pressure in a beaker is not at equilibrium.
(R) It refers to an open system.

3. (A) A solution which contains one gram equivalent of solute per litre of the solution is called a normal solution.
(R) A normal solution means a solution in which the solute does not associate or dissociate.

4. (A) The sum of mole fractions of all the components of a solution is unity.
(R) Mole fraction is a temperature dependent quantity.

5. (A) Iodine is more soluble in CCl_4 than in water.
(R) Non-polar solutes are more soluble in non-polar solvents.

6. (A) Vapour pressure of 0.5 M sugar solution is more than 0.5 M KCl solution.
(R) Lowering of vapour pressure is directly proportional to the number of species present in the solution.

7. (A) Non-ideal solutions form azeotropic mixture.
(R) Boiling point of azeotropic mixture is higher than boiling points of its both components.

8. (A) One molar solution is always more concentrated than one molal solution.
(R) The amount of solvent in 1 M and 1 m aqueous solution is not equal.

9. (A) Camphor is used as solvent in the determination of molecular mass of naphthalene and anthracene etc.
(R) Camphor has high molal elevation constant.

10. (A) 0.1 M solution of glucose has same increment in freezing point than 0.1 M solution of urea.
(R) K_f for both has different values. **(AIIMS 1997)**

11. (A) Molarity of 0.02 N solution of HNO_3 is 0.02 M.
(R) Molarity and normality of a solution are never equal.

12. (A) Larger the value of cryoscopic constant of the solvent, lesser will be the freezing point of the solution.
(R) Depression in the freezing point depends on the nature of the solvent.

13. (A) 0.1 M solution of NaCl has greater osmotic pressure than 0.1 M solution of glucose at same temperature.
(R) In solution, NaCl dissociates to produce more number of particles.

14. (A) Henry's law and Raoult's law are not independent, *i.e.*, one can be derived from the other.
(R) The partial pressure is directly proportional to the mole fraction of the concerned species for ideal solutions.

15. (A) The water pouch of instant cold pack for treating athletic injuries breaks when squeezed and NH_4NO_3 dissolves thus lowering the temperature.
(R) Addition of non-volatile solute into solvent results into depression of freezing point of solvent. **(AIIMS 2006)**

16. (A) In a pressure cooker, the water is brought to boil. The cooker is then removed from the stove. Now on removing the lid of pressure cooker, the water starts boiling again.
(R) The impurities in water bring down its boiling point.
[**Hint:** In pressure cooker, water boils above 100° C. When the lid of cooker is opened, pressure is lowered so that boiling point decreases and water boils again.]

17. (A) An increase in surface area increases the rate of evaporation.
(R) Stronger the inter-molecular attractive forces, faster is the rate of evaporation at a given temperature.

18. (A) An ideal solution obeys Raoult's law.
(R) In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interaction.

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (a)	2. (c)	3. (b)	4. (d)	5. (b)	6. (d)	7. (c)	8. (b)
9. (c)	10. (d)	11. (a)	12. (a)	13. (d)	14. (c)	15. (a)	16. (d)
17. (a)	18. (b)	19. (c)	20. (b)	21. (d)	22. (c)	23. (a)	24. (b)
25. (c)	26. (d)	27. (b)	28. (a)	29. (c)	30. (b)	31. (d)	32. (d)
33. (b)	34. (a)	35. (d)	36. (c)	37. (b)	38. (c)	39. (b)	40. (d)
41. (a)	42. (a)	43. (b)	44. (c)	45. (d)	46. (b)	47. (b)	48. (d)
49. (c)	50. (c)	51. (b)	52. (a)	53. (b)	54. (d)	55. (d)	56. (a)
57. (c)	58. (b)	59. (b)	60. (c)	61. (a)	62. (d)	63. (c)	64. (d)
65. (a)	66. (d)	67. (a)	68. (c)	69. (b)	70. (c)	71. (a)	72. (b)
73. (d)	74. (b)	75. (a)	76. (c)	77. (d)	78. (d)	79. (a)	80. (d)
81. (b)	82. (a)	83. (a)	84. (d)	85. (d)	86. (b)	87. (c)	88. (b)
89. (b)	90. (c)	91. (a)	92. (d)	93. (d)	94. (d)	95. (b)	96. (b)
97. (c)	98. (b)	99. (a)	100. (c)	101. (d)	102. (b)	103. (b)	104. (b)
105. (c)	106. (c)	107. (c)	108. (a)	109. (a)	110. (d)	111. (b)	112. (d)
113. (a)	114. (d)	115. (a)	116. (c)	117. (a)	118. (d)	119. (d)	120. (b)
121. (a)	122. (b)	123. (d)	124. (c)	125. (c)	126. (b)	127. (a)	128. (b)
129. (d)	130. (b)	131. (a)	132. (b)	133. (a)	134. (b)	135. (b)	136. (a)
137. (d)	138. (c)	139. (c)	140. (b)	141. (a)	142. (b)	143. (c)	144. (d)
145. (c)	146. (a)	147. (a)	148. (c)	149. (c)	150. (b)	151. (a)	152. (b)
153. (c)	154. (b)	155. (b)	156. (b)	157. (b)	158. (b)	159. (b)	160. (c)
161. (b)	162. (d)	163. (a)	164. (d)	165. (b)	166. (b)	167. (b)	168. (a)
169. (a)	170. (d)	171. (b)	172. (c)	173. (c)	174. (c)	175. (d)	176. (b)
177. (d)	178. (a)	179. (c)	180. (c)	181. (a)	182. (a)	183. (a)	184. (b)
185. (c)	186. (d)	187. (b)	188. (a)	189. (a)	190. (b)	191. (c)	

- **Set–2**

1. (a)	2. (a, b, c, d)	3. (c)	4. (a, b, c)	5. (a, c)	6. (c)	7. (d)	8. (b)
9. (c)	10. (b, c)	11. (a, c, d)	12. (c)	13. (a, d)	14. (b, d)	15. (a, c)	16. (a, d)
17. (a, d)	18. (b, d)	19. (d)	20. (c)	21. (d)	22. (b)		

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (d)	2. (a)	3. (c)	4. (c)	5. (a)	6. (a)	7. (c)	8. (d)
9. (a)	10. (c)	11. (c)	12. (a)	13. (a)	14. (b)	15. (a)	16. (c)
17. (c)	18. (a)						

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain single correct option:

1. Three solutions of HCl having normality 12 *N*, 6 *N* and 2 *N* are mixed to obtain a solution of 4 *N* normality. Which among the following volume ratio is correct for the above three components?

(a) 1 : 1 : 5 (b) 1 : 2 : 6 (c) 2 : 1 : 9 (d) 1 : 2 : 4

[Hint: $N_1V_1 + N_2V_2 + N_3V_3 = N_R(V_1 + V_2 + V_3)$

$$12 \times 1 + 6 \times 2 + 2 \times 6 = N_R(9)$$

$$N_R = 4]$$

2. 6.8 g H_2O_2 is dissolved in 224 mL solution. This solution will be labelled as:

(a) 0.224 V (b) 20 V (c) 5 V (d) 10 V

[Hint: $M = \frac{w_B \times 1000}{m_B \times V} = \frac{6.8}{34} \times \frac{1000}{224}$

$$= \frac{200}{224}$$

Volume strength $V = M \times 11.2$

$$= \frac{200}{224} \times 11.2 = 10]$$

3. A solution weighing *a* g has molality *b*. The molecular mass of solute if the mass of solute is *c* g, will be:

(a) $\frac{c}{b} \times \frac{1000}{(a-c)}$ (b) $\frac{b}{a} \times \frac{1000}{(a-b)}$

(c) $\frac{b}{c} \times \frac{1000}{(a-c)}$ (d) $\frac{c}{a} \times \frac{1000}{(b-a)}$

[Hint: Molality, $m = \frac{w_B}{m_B} \times \frac{1000}{w_A}$

$$b = \frac{c}{m_B} \times \frac{1000}{(a-c)}$$

$$m_B = \frac{c}{b} \times \frac{1000}{(a-c)}\ ]$$

4. Two solutions of H_2SO_4 of molarities *x* and *y* are mixed in the ratio of V_1 mL : V_2 mL to form a solution of molarity M_1. If they are mixed in the ratio of V_2 mL : V_1 mL, they form a solution of molarity M_2. Given $V_1/V_2 = \frac{x}{y} > 1$ and $\frac{M_1}{M_2} = \frac{5}{4}$, then *x* : *y* is:

(a) 2 : 1 (b) 4 : 1 (c) 1 : 2 (d) 3 : 1

[Hint: Molarity of the mixture can be calculated as:

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

where, M_R = resultant solution

$$V_1 \times x + V_2 \times y = M_1(V_1 + V_2) \quad \text{... (i)}$$

$$V_2 \times x + V_1 \times y = M_2(V_1 + V_2) \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{V_1x + V_2y}{V_2x + V_1y} = \frac{M_1}{M_2}$$

Substituting $\frac{M_1}{M_2} = \frac{5}{4}$ and $\frac{V_1}{V_2} = \frac{x}{y}$ we can calculate *x* : *y*.]

5. You are given 500 mL of 2 *N* HCl and 500 mL of 5 *N* HCl. What will be the maximum volume of 3 *M* HCl that you can make from these two solutions?

(a) 250 mL (b) 750 mL (c) 500 mL (d) 1000 mL

6. The mole fraction of a given sample of I_2 in C_6H_6 is 0.2. The molality of I_2 in C_6H_6 is:

(a) 0.32 (b) 3.2 (c) 0.032 (d) 0.48

[Hint: $m = \frac{x_B \times 1000}{(1 - x_B)m_A}$

$$m = \frac{0.2 \times 1000}{0.8 \times 78}$$

m = molality
x_B = mole fraction of solute
m_A = molar mass of solvent]

7. A 15-volume sample of an H_2O_2 solution is equivalent to:

(a) 5.30 *N* (b) 1.77 *N* (c) 2.68 *N* (d) 7.50 *N*

[Hint: $V = 5.6\,N$

$$15 = 5.6\,N$$

$$N = 2.68]$$

8. If P_A is the vapour pressure of a pure liquid *A* and the mole fraction of *A* in the mixture of two liquids *A* and *B* is *x*, the partial vapour pressure of *A* is:

(a) $(1 - x)P_A$ (b) xP_A (c) $\frac{x}{(1-x)} P_A$ (d) $\frac{1-x}{x} P_A$

9. Difference between diffusion and osmosis is:

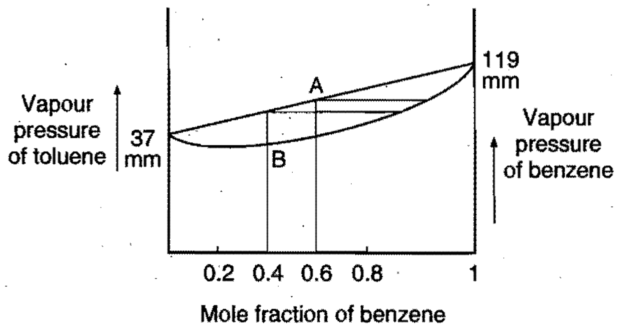
(a) a semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane

(b) in osmosis, movement of molecules is in one direction whereas in diffusion, the movement is on both sides

(c) in osmosis only the solvent moves while in diffusion solute and solvent both move

(d) all of the above

10.



Choose the correct option:

(a) '*A*' represents vapour composition and '*B*' the liquid composition

(b) '*A*' as well as '*B*' represent liquid composition

(c) Both '*A*' and '*B*' represent vapour composition

(d) '*A*' represents liquid composition and '*B*' the vapour composition

11. Insulin $(C_2H_{10}O_5)_n$ is dissolved in a suitable solvent and the osmotic pressure (π) of solutions of various concentrations (g/cc) C is measured at 20°C. The slope of the plot of π against 'C' is found to be 4.65×10^{-3}. The molecular weight of insulin is:

(a) 4.8×10^5 (b) 9×10^5 (c) 3×10^5 (d) 5.17×10^6

[**Hint:** $\pi V = \frac{w_B}{m_B} \times RT$

$$\pi = \left(\frac{w_B}{V}\right)\frac{RT}{m_B}$$

$$\pi = C \times \frac{RT}{m_B} \times 1000 \quad \text{... (i)}$$

where C = concentration in g/cc,

$$y = x \times m \quad \text{... (ii)}$$

Comparing eqs. (i) and (ii),

$$\text{Slope} = \frac{RT}{m_B} \times 1000$$

$$m_B = \frac{RT}{\text{Slope}} \times 1000$$

$$= \frac{0.0821 \times 293 \times 1000}{4.65 \times 10^{-3}}$$

$$= 5.17 \times 10^6]$$

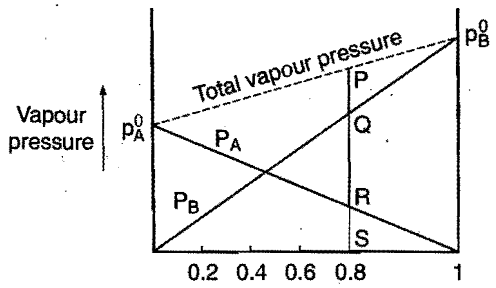
12. Solubility of deliquescent substances in water is generally:

(a) high (b) low

(c) moderate (d) cannot be predicted

[**Hint:** A deliquescent substance absorbs large amount of water, hence solubility is very high.]

13. Consider the following vapour pressure-composition graph, SP is equal to:



(a) $PQ + RS$ (b) $PQ + QR + RS$

(c) $SR + SQ$ (d) $PQ + QR$

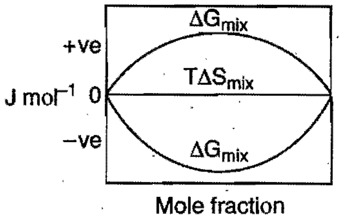
14. y g of a non-volatile organic substance of molecular mass M is dissolved in 250 g benzene. Molal elevation constant of benzene is K_b. Elevation in its boiling point is given by:

(a) $\frac{M}{K_b y}$ (b) $\frac{4K_b y}{M}$ (c) $\frac{K_b y}{4M}$ (d) $\frac{K_b y}{M}$

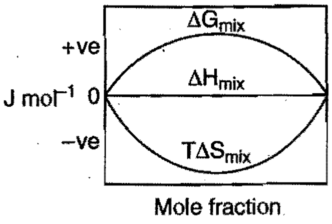
[**Hint:** $\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A}$

$$= K_b \times \frac{y \times 1000}{M \times 250} = \frac{4K_b y}{M}]$$

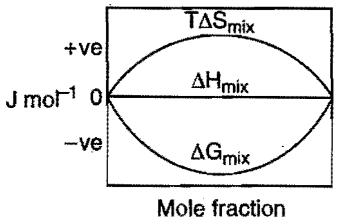
15. Which of the following represents correctly the changes in thermodynamic properties during the formation of 1 mole of an ideal binary solution?



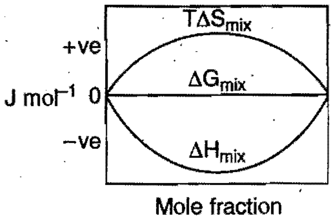
(a)



(b)



(c)



(d)

16. A solute forms a pentamer when dissolved in a solvent. The van't Hoff factor 'i' for the solute will be:

(a) 0.2 (b) 0.8 (c) 0.5 (d) 0.6

17. What is the molarity of HCl in a solution prepared by dissolving 5.5 g HCl in 200 g ethanol if the density of the solution is 0.79 g mL^{-1}?

(a) 21 M (b) 0.93 M (c) 6×10^{-4} M (d) 1.7 M

(e) 0.58 M

[**Hint:** $V = \frac{W\text{ (mass)}}{d} = \frac{205.5}{0.79} = 260.13$ mL

$$M = \frac{w_B \times 1000}{m_B \times V}$$

$$= \frac{5.5 \times 1000}{36.5 \times 260.13} = 0.58\ M]$$

18. Which statement about the composition of vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume the temperature is constant at 25°C.

Vapour pressure data (25°C):

Benzene	75 mm Hg
Toluene	22 mm Hg

(a) The vapour will contain higher percentage of benzene

(b) The vapour will contain higher percentage of toluene

(c) The vapour will contain equal amount of benzene and toluene

(d) Not enough information is given to make a prediction

[**Hint:** A : Benzene B : Toluene

$$p = p_A + p_B$$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 75 \times \frac{1}{2} + 22 \times \frac{1}{2}$$

$$= 37.5 + 11 = 48.5$$

Mole fraction of benzene in vapour, $y_A = \frac{p_A}{p} = \frac{37.5}{48} = 0.78$

Similarly, mole fraction of toluene in vapour, $y_B = 0.22$

∴ The vapour will contain higher percentage of benzene.]

19. When 1.2 g of sulphur is melted with 15 g of naphthalene, the solution freezes at 77.2°C. What is the molar mass of this form of sulphur?

Data for naphthalene:

Melting point (m.pt.)	80°C
Freezing point depression constant K_f	6.80 K m^{-1}

(a) 180 g mol^{-1} (b) 190 g mol^{-1}
(c) 260 g mol^{-1} (d) 450 g mol^{-1}

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$$m_B = \frac{K_f}{\Delta T} \times \frac{w_B \times 1000}{w_A}$$

$$= \frac{6.8}{2.8} \times \frac{1.2 \times 1000}{15} \approx 190]$$

20. Which concentrations can be calculated if the mole fraction and density of an aqueous solution of HCl are known?

1. Molality 2. Molarity 3. Percentage by mass

(a) 1 only (b) 3 only
(c) 1 and 2 only (d) 1, 2 and 3

21. The vapour pressure of a liquid in a closed container depends on:

(1) temperature of liquid (2) quantity of liquid
(3) surface area of the liquid

(a) 1 only (b) 2 only
(c) 1 and 3 only (d) 1, 2 and 3

22. A solution is prepared by dissolving a 2.5 g sample of an unknown compound in 34 g of benzene (C_6H_6) boils at 1.38°C higher than pure benzene. Which expression gives the molar mass of the unknown compound?

Compound	K_b
C_6H_6	2.53°C m^{-1}

(a) $2.53 \times \frac{2.50}{1.38}$ (b) $1.38 \times \frac{34}{2.53} \times 2.50$

(c) $2.5 \times 10^3 \times \frac{2.53}{34} \times \frac{1}{1.38}$ (d) $2.50 \times 10^3 \times \frac{1.38}{34} \times 2.53$

23. If liquids A and B form an ideal solution:

(a) the free energy of mixing is zero
(b) the free energy as well as entropy of mixing are zero
(c) enthalpy of mixing is zero
(d) the entropy of mixing is zero

24. Solute A is a ternary electrolyte and solute B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure of $2P$ at temperature $3T$ K then 0.05 M solution of A at T K will produce an osmotic pressure of:

(a) P (b) $1.5P$ (c) $2P$ (d) $10P$

25. Which of the following plots represents the behaviour of an ideal binary liquid solution?

(a) Plot of P_{total} *vs* y_A (mole fraction of A in vapour) is linear
(b) Plot of P_{total} *vs* y_B is linear
(c) Plot of $1/P_{\text{total}}$ *vs* y_A is linear
(d) Plot of $1/P_{\text{total}}$ *vs* y_B is non-linear

26. Total vapour pressure of mixture of 1 mol A ($p_A^0 = 150$ torr) and 2 mol B ($p_B^0 = 240$ torr) is 200 torr. In this case:

(a) there is positive deviation from Raoult's law
(b) there is negative deviation from Raoult's law
(c) there is no deviation from Raoult's law
(d) molecular masses of A and B are also required for calculating the deviation

[**Hint:** $x_A = \frac{1}{3}, x_B = \frac{2}{3}$

$$p = p_A^0 x_A + p_B^0 x_B$$

$$= 150 \times \frac{1}{3} + 240 \times \frac{2}{3} = 50 + 160 = 210 \text{ mm}$$

$$p_{\text{exp.}} < p_{\text{calculated}}$$

∴ There is negative deviation from Raoult's law.]

27. A compound MX_2 has observed and normal molar masses 65.6 and 164 respectively. Calculate the apparent degree of ionization of MX_2:

(a) 75% (b) 85% (c) 65% (d) 25%

[**Hint:** $i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$

$$= \frac{164}{65.6} = 2.5$$

$$\alpha = \frac{i-1}{n-1}, \qquad n = 3 \text{ (number of ions)}$$

$$= \frac{2.5-1}{3-1} = \frac{1.5}{2} = 0.75$$

∴ Percentage ionization of MX_2 will be 75%.]

28. Compound $PdCl_4 \cdot 6H_2O$ is a hydrated complex; 1 molal aqueous solution of it has freezing point 269.28 K. Assuming 100% ionization of complex, calculate the molecular formula of the complex (K_f for water = 1.86 K kg mol^{-1}):

(a) $[Pd(H_2O)_6]Cl_4$ (b) $[Pd(H_2O)_4Cl_2]Cl_2 \cdot 2H_2O$
(c) $[Pd(H_2O)_3Cl_3]Cl \cdot 3H_2O$ (d) $[Pd(H_2O)_2Cl_4] \cdot 4H_2O$

[**Hint:** $\Delta T = i \times K_f \times m$

$$(273 - 269.28) = i \times 1.86 \times 1$$

$$3.72 = i \times 1.86$$

$$i = 2$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{2-1}{n-1} \text{ or } n = 2$$

Thus, the complex should give two ions in the solution, *i.e.*, the complex will be $[Pd(H_2O)_3Cl_3]Cl \cdot 3H_2O]$

29. Inulin is dissolved in suitable solvent and the osmotic pressure (π) of solutions of various concentrations (g/cm^3) C is measured at 27°C. The slope of plot of π against C is found to be 4.1×10^{-3}. The molecular mass of inulin is:

(a) 6×10^6 (b) 3×10^6 (c) 6×10^3 (d) 3×10^3

[**Hint:** $\pi V = nRT$

$$\pi V = \frac{w}{m} RT$$

$$\pi = \left(\frac{w}{V}\right) \times \frac{1}{m} RT$$

$$\pi = C\left(\frac{RT}{m}\right) \qquad \text{... (i)}$$

$$y = MX \qquad \text{... (ii)}$$

Slope of the line will be $\frac{RT}{m}$,

i.e., $\frac{RT}{m} = 4.1 \times 10^{-3}$

$$m = \frac{RT}{4.1 \times 10^{-3}} = \frac{0.0821 \times 1000 \times 300}{4.1 \times 10^{-3}}$$

$$= 6 \times 10^{6}]$$

30. pH of a 0.1 M monobasic acid is measured to be 2. Its osmotic pressure at a given temperature T K is:

(a) $0.1RT$ (b) $0.11RT$ (c) $1.1RT$ (d) $0.01RT$

[**Hint:** $HA \rightleftharpoons H^+ + A^-$

$t = 0 \quad C \quad 0 \quad 0$

$t_{eq} \quad C - C\alpha \quad C\alpha \quad C\alpha$

$[H^+] = C\alpha; [H^+] = 10^{-pH}$

$\therefore \quad C\alpha = 10^{-2}$

$0.1\alpha = 10^{-2}$

$\alpha = 0.1$

$\alpha = \frac{i-1}{n-1}; 0.1 = \frac{i-1}{2-1}$

$i = 1.1$

$\therefore \quad \pi = iCRT$

$= 1.1 \times 0.1 \times RT = 0.11RT$]

31. The amount of ice that will separate on cooling a solution containing 50 g of ethylene glycol in 200 g water at –9.3°C, $K_f = 1.86 \text{ K kg mol}^{-1}$:

(a) 38.71 g (b) 38.71 mg (c) 42 g (d) 42 mg

[**Hint:** $\Delta T = K_f \times \frac{w_B \times 1000}{m_B \times w_A}$

$9.3 = 1.86 \times \frac{50 \times 1000}{62 \times w_A}$

$w_A = 161.29$ g (amount of water present at – 9.3°C)

$\therefore$ Amount of ice separated = 200 – 161.29

= 38.71 g]

32. 2 moles each of liquids A and B are dissolved to form an ideal solution. What will be the mole fraction of B in the vapour phase?

$p_A^0 = 120$ torr; $p_B^0 = 80$ torr.

(a) 1/4 (b) 1/2 (c) 3/5 (d) 2/5

[**Hint:** $p = p_A + p_B$

$p = p_A^0 x_A + p_B^0 x_B$

$= 120 \times \frac{2}{4} + 80 \times \frac{2}{4}$

$= 60 + 40 = 100$ torr

y_B = mole fraction of B in the vapour phase

$= \frac{p_B}{p_{\text{total}}} = \frac{40}{100} = \frac{2}{5}$]

33. Lowering of vapour pressure in 1 molal aqueous solution at 100°C is:

(a) 13.44 mm Hg (b) 14.12 mm Hg
(c) 31.2 mm Hg (d) 35.2 mm Hg

[**Hint:** Molality and mole fraction are related as follows:

$m = \frac{x_B \times 1000}{(1 - x_B)m_A}$ $\quad m = 1$

x_B = mole fraction of solute

m_A = molar mass of solvent

$1 = \frac{x_B \times 1000}{(1 - x_B) \times 18}$

$x_B = 0.0176, \quad x_A = 0.9824$

$p = p_0 x_A$

$p = 760 \times 0.9824$

$= 746.624$

$\Delta p = p_0 - p = 760 - 746.624$

≈ 13.4 mm Hg]

34. The temperature at which the molarity of pure water is equal to its molality is:

(a) 273 K (b) 298 K
(c) 277 K (d) none of these

35. Isopiestic solutions have:

(a) same vapour pressure (b) same osmotic pressure
(c) same freezing point (d) same boiling point

36. Molarity and molality of a solution of caustic soda are respectively 11.12 M and 94.12 m. The density of the solution is:

(a) 0.556 g mL^{-1} (b) 5.56 g mL^{-1}
(c) 55.6 g mL^{-1} (d) none of these

[**Hint:** $d = M\left(\frac{1}{m} + \frac{\text{molar mass of solute}}{1000}\right)$

$d = 11.12\left(\frac{1}{94.12} + \frac{40}{1000}\right)$

$= 0.556$ g mL^{-1}]

37. Which of the following solutions has osmotic pressure nearer to that of equimolar solution of $K_4[Fe(CN)_6]$?

(a) Na_2SO_4 (b) $BaCl_2$
(c) $Al_2(SO_4)_3$ (d) $C_{12}H_{22}O_{11}$

38. Equal amounts of a solute are dissolved in equal amounts of two solvents A and B. The lowering of vapour pressure for the solution A is twice the lowering of vapour pressure for the solution B. If M_A and M_B are the molecular weights of solvents A and B respectively, then:

(a) $M_A = M_B$ (b) $M_A = M_B / 2$
(c) $M_A = 4M_B$ (d) $M_A = 2M_B$

Following questions may have more than one correct options:

1. Consider the following solutions:

I. 1 M sucrose II. 1 M KCl
III. 1 M benzoic acid in benzene IV. 1 M $(NH_3)_3PO_4$

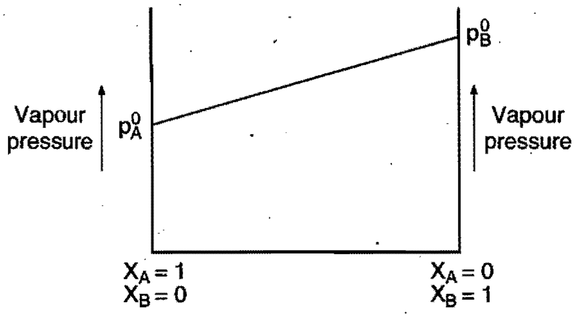
Which of the following is/are true?

(a) All solutions are isotonic
(b) III is hypotonic of I, II and IV
(c) I, II and III are hypertonic of IV
(d) IV is hypertonic of I, II and III

2. Osmotic pressure of the solution depends on:

(a) nature of solute
(b) nature of solvent
(c) temperature
(d) molar concentration of solute

3. The following is a graph plotted between the vapour pressures of two volatile liquids against their respective mole fractions.



Which of the following statements are correct?

(a) When $x_A = 1$ and $x_B = 0$, then $p = p_A^0$

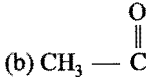
(b) When $x_B = 1$ and $x_A = 0$, then $p = p_B^0$

(c) When $x_A = 1$ and $x_B = 0$, then $p < p_B^0$

(d) When $x_B = 1$ and $x_A = 0$, then $p > p_A^0$

4. Which of the following combinations are correct for a binary solution, in which the solute as well as solvent are liquid?

(a) C_6H_6 and $C_6H_5CH_3$; $\Delta H_{Sol} > 0$; $\Delta V_{Sol} = 0$


(b) $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$ and $CHCl_3$; $\Delta H_{Sol} < 0$; $\Delta V_{Sol} < 0$

(c) H_2O and HCl; $\Delta H_{Sol} > 0$; $\Delta V_{Sol} < 0$

(d) H_2O and C_2H_5OH; $\Delta H_{Sol} > 0$; $\Delta V_{Sol} > 0$

5. A solution containing 0.1 g of a non-volatile organic substance P (molecular mass 100) in 100 g of benzene raises the boiling point of benzene by 0.2° C, while a solution containing 0.1 g of another non-volatile substance Q in the same amount of benzene raises the boiling point of benzene by 0.4° C. What is the ratio of molecular masses of P and Q? **(SCRA 2007)**

(a) 1:2 (b) 2:1 (c) 1:4 (d) 4:1

[Hint :

$$\frac{(\Delta T)_P}{(\Delta T)_Q} = \frac{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A}\right)_P}{K_b \times \left(\frac{w_B \times 1000}{m_B \times w_A}\right)_Q}$$

$$\frac{0.2}{0.4} = \frac{\left(\frac{0.1 \times 1000}{100 \times 100}\right)_P}{\left(\frac{0.1 \times 1000}{100 \times m_B}\right)_Q}$$

$$\frac{1}{2} = \frac{(m_B)_Q}{100}$$

$$m_B = 50$$

$$\therefore \ (m_B)_P : (m_B)_Q = 100 : 50$$
$$= 2:1]$$

6. Consider 0.1 M solution of two solutes X and Y. The solute X behaves as uni-univalent electrolyte while the solute Y dimerises in solution. Which of the following statements are correct regarding these solutions?

1. The boiling point of solution of X will be higher than that of Y
2. The osmotic pressure of solution of Y will be lower than that of X
3. The freezing point of the solution of X will be lower than that of Y
4. The relative lowering of vapour pressure of both the solutions will be the same

Select the correct answer from the codes given below:

(a) 1, 2, 3 (b) 2, 3, 4 (c) 1, 2, 4 (d) 1, 3, 4

7. For a given value of degree of dissociation, which of the following have correct van't Hoff factor?

(a) NaCl	$i = 2 + \alpha$
(b) $Ca(NO_3)_2$	$i = 1 + 2\alpha$
(c) $K_4[Fe(CN)_6]$	$i = 1 + 4\alpha$
(d) $(NH_3)_3PO_4$	$i = 3 + \alpha$

8. 1 mole benzene ($p^0_{\text{benzene}} = 42$ mm) and 2 mole toluene ($p^0_{\text{toluene}} = 36$ mm) will have:

(a) total vapour pressure 38 mm

(b) mole fraction of vapours of benzene above liquid mixture is 7/19

(c) positive deviation from Raoult's law

(d) negative deviation from Raoult's law

[Hint: $p = p_A^0 x_A + p_B^0 x_B$ $A \rightarrow$ Benzene, $B \rightarrow$ Toluene

$$= 42 \times \frac{1}{3} + 36 \times \frac{2}{3}$$
$$= \frac{114}{3} = 38 \text{ mm}$$

Mole fraction of benzene in vapour $= \frac{p_{\text{benzene}}}{p_{\text{total}}} = \frac{42/3}{38}$

$= 7/19]$

9. The decrease in freezing point of an aqueous solution of a substance is 1.395 K and that in the freezing point of a benzene solution of the same substance is 1.28 K. The substance:

(a) dissociates in aqueous solution as well as in the benzene solution

(b) forms complexes in the solution

(c) associates in the benzene solution

(d) dissociates in the aqueous solution and not in the benzene solution

10. The vapour pressure of water at T (K) is 20 mm Hg. The following solutions are prepared at T (K):

I. 6 g of urea (mol. wt. = 60) is dissolved in 178.2 g of water.

II. 0.01 mole of glucose is dissolved in 179.82 g of water.

III. 5.3 g of Na_2CO_3 (mol. wt. = 106) is dissolved in 179.1 g of water.

Identify the correct order in which the vapour pressures of solutions increase: **[EAMCET (Medical) 2006]**

(a) III, I, II (b) II, III, I (c) I, II, III (d) I, III, II

[Hint:

I. $x_B = \frac{n_B}{n_A + n_B} = \frac{6/60}{178.2/18} + \frac{6}{60}$

$$= 0.01$$

$$\frac{\Delta p}{p_0} = x_B = 0.01$$

II. $$x_B = \frac{n_B}{n_A + n_B} = \frac{0.01}{\frac{179.82}{18} + 0.01}$$

$$= 0.001$$

$$\frac{\Delta p}{p_0} = 0.001$$

III. $$x_B = \frac{n_B}{n_A + n_B} = \frac{5.3/106}{\frac{179.1}{18} + \frac{5.3}{106}} = 0.005$$

$$\frac{\Delta p}{p_0} = ix_B$$

$$= 3 \times 0.005$$

$$= 0.015$$

∴ Vapour pressures of solutions will increase in the following sequence:

(III) < (I) < (II).]

11. Consider lowering of vapour pressure (Δp), elevation in boiling point (ΔT_b) and depression in freezing point (ΔT_f) of a solvent for the same molar concentration of each of the following three solutes :

1. $BaCl_2$ 2. NaCl 3. $MgCl_2$

Which of the following is/are the correct sequence?

(SCRA 2009)

(a) $\Delta p : 3 < 2 < 1$
(b) $\Delta T_b : 1 > 2 > 3$
(c) $\Delta T_f : 3 < 2 < 1$
(d) None of these

[**Hint :** van't Hoff factor of both $BaCl_2$ and $MgCl_2$ are same, *i.e.*, 3, hence none of the given sequence are correct.]

Answers

• Single correct option

1. (b) **2.** (d) **3.** (a) **4.** (a) **5.** (b) **6.** (b) **7.** (c) **8.** (b)
9. (d) **10.** (c) **11.** (d) **12.** (a) **13.** (c) **14.** (b) **15.** (c) **16.** (a)
17. (e) **18.** (b) **19.** (b) **20.** (d) **21.** (a) **22.** (c) **23.** (c) **24.** (a)
25. (c) **26.** (b) **27.** (a) **28.** (c) **29.** (a) **30.** (b) **31.** (a) **32.** (d)
33. (a) **34.** (c) **35.** (a) **36.** (a) **37.** (c) **38.** (b)

• One or more than one correct options

1. (b, c, d) **2.** (c, d) **3.** (a, b) **4.** (b, d) **5.** (b) **6.** (a) **7.** (b, c) **8.** (a, b)
9. (c, d) **10.** (a) **11.** (d)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

A 1.24 M aqueous solution of KI has density of $1.15\ g/cm^3$.

Answer the following questions about this solution:

1. Percentage composition of solute in the solution is:
(a) 17.89 (b) 27.89 (c) 37.89 (d) 47.89
2. Molality of this solution will be:
(a) 2.61 (b) 1.31 (c) 4.12 (d) 3.12
3. What is the freezing point of the solution if the KI is completely dissociated in the solution?
(a) – 4.87°C (b) – 3.22°C
(c) – 1.22°C (d) None of these
4. Experimental freezing point of the solution is – 4.46°C. What % of KI is dissociated?
(a) 82% (b) 90% (c) 83% (d) None
5. Normality of this solution is:
(a) 0.62 (b) 1.24 (c) 2.48 (d) 3.72

• Passage 2

The colligative properties of electrolytes require a slightly different approach than the one used for the colligative properties of non-electrolytes. The electrolytes dissociate into ions in a solution. It is the number of solute particles that determines the colligative properties of a solution. The electrolyte solutions, therefore, show abnormal colligative properties. To account for this effect we define a quantity called the van't Hoff factor, given by:

$$i = \frac{\textit{Actual number of particles in solution after dissociation}}{\textit{Number of formula units initially dissolved in solution}}$$

$i = 1$ (*for non-electrolytes*);

$i > 1$ (*for electrolytes, undergoing dissociation*)

$i < 1$ (*for solutes, undergoing association*).

Answer the following questions:

1. Benzoic acid undergoes dimerisation in benzene solution. The van't Hoff factor 'i' is related to the degree of association 'α' of the acid as:
(a) $i = 1 - \alpha$ (b) $i = 1 + \alpha$
(c) $i = 1 - \frac{\alpha}{2}$ (d) $i = 1 + \frac{\alpha}{2}$
2. A substance trimerises when dissolved in a solvent A. The van't Hoff factor 'i' for the solution is:
(a) 1 (b) 1/3
(c) 3 (d) unpredictable
3. For a solution of a non-electrolyte in water, the van't Hoff factor is:
(a) always equal to 0 (b) ≤ 1
(c) always equal to 2 (d) > 1 but < 2
4. 0.1 M $K_4[Fe(CN)_6]$ is 60% ionized. What will be its van't Hoff factor?
(a) 1.4 (b) 2.4 (c) 3.4 (d) 4.4

[**Hint:** $\alpha = \frac{i-1}{n-1}$, $n = 5$ since, $K_4[Fe(CN)_6]$ gives 5 ions in the solution

$$0.6 = \frac{i-1}{5-1}$$

$$i = 3.4\ ]$$

5. A solution of benzoic acid dissolved in benzene such that it undergoes molecular association and its molar mass approaches 244. Benzoic acid molecules will exist as:
(a) dimer (b) monomer
(c) tetramer (d) trimer
6. The molar mass of the solute sodium hydroxide obtained from the measurement of the osmotic pressure of its aqueous solution at 27°C is 25 g mol^{-1}. Therefore, its dissociation percentage in this solution is: **[CET (J&K) 2009]**
(a) 75 (b) 60
(c) 80 (d) 70

[**Hint:**
$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}} \quad \ldots\text{(i)}$$

$$\alpha = \frac{i-1}{n-1}$$

$i = 1 + \alpha$ for binary electrolyte

$$\therefore \quad 1 + \alpha = \frac{40}{25};\ \alpha = 0.6$$

% ionisation = 60]

• Passage 3

Many chemical and biological processes depend on osmosis which is, the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one. The osmotic pressure π depends on molar concentration of the solution ($\pi = CRT$)*. If two solutions are of equal solute concentration and, hence, have the same osmotic pressure, they are said to be* ***isotonic.*** *If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be* ***hypertonic*** *and the more diluted solution is described as* ***hypotonic.***

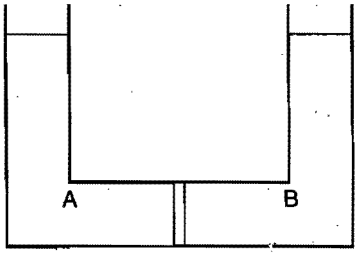
Osmosis is the major mechanism for transporting water upward in the plants. Transpiration in the leaves supports the transport mechanism of water. The osmotic pressure of seawater is about 30 atm; this is the pressure that must be applied to the seawater (separated from pure water using a semipermeable membrane) to get drinking water.

Answer the following questions:

1. A plant cell shrinks when it is kept in:
(a) hypotonic solution (b) hypertonic solution
(c) isotonic solution (d) pure water
2. 4.5% solution of glucose would be isotonic with respect to .... solution of urea.
(a) 4.5% (b) 13.5%
(c) 1.5% (d) 9%
3. Glucose solution to be injected into the bloodstream must have same ..... as that of the bloodstream.
(a) molarity (b) vapour pressure
(c) osmotic pressure (d) viscosity

4. Isotonic solutions have same:
(a) density (b) molarity
(c) molality (d) mole fraction
(e) normality
5. Osmotic rise of a solution depends on:
(a) density (b) temperature
(c) nature of solvent (d) none of these

• Passage 4



Compartments 'A' and 'B' have the following combinations of solutions:

	A	*B*
1.	0.1 *M KCl*	0.2 *M KCl*
2.	0.1% *(m/V) NaCl*	10% *(m/V) NaCl*
3.	18 *g/L glucose*	34.2 *g/L sucrose*
4.	20% *(m/V) glucose*	10% *(m/V) glucose*

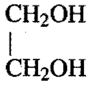
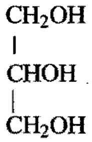
Answer the following questions:

1. Indicate the solutions which is/are isotonic:
(a) 1 only (b) 3 only (c) 4 only (d) 2 only
2. The solutions in which the compartment '*B*' is hypertonic:
(a) 1, 2 (b) 2, 3 (c) 3, 4 (d) 1, 4
3. Indicate the solution(s) in which the compartment '*A*' will show the increase in volume:
(a) 1 (b) 2 (c) 3 (d) 4
4. Indicate the solution(s) in which the compartment '*B*' will show the increase in volume:
(a) 1, 2, 4 (b) 1, 2 (c) 2, 3 (d) 3, 4
5. The solution in which there will be no change in the level of the solution in the compartments '*A*' and '*B*' is:
(a) 1 (b) 2 (c) 3 (d) 4

• Passage 5

The boiling point elevation and the freezing point depression of solutions have a number of practical applications. Ethylene glycol ($CH_2OH \cdot CH_2OH$) *is used in automobile radiators as an antifreeze because it lowers the freezing point of the coolant. The same substance also helps to prevent the radiator coolant from boiling away by elevating the boiling point. Ethylene glycol has low vapour pressure. We can also use glycerol as antifreeze. For boiling point elevation to occur, the solute must be non-volatile, but no such restriction applies to freezing point depression. For example, methanol* (CH_3OH)*, a fairly volatile liquid that boils only at 65°C is sometimes used as antifreeze in automobile radiators.*

Answer the following questions:

1. Which of the following is a better reagent for depression in freezing point but not for elevation in boiling point?
(a) CH_3OH (b)  $\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}$ (c)  $\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$ (d) $C_6H_{12}O_6$
2. 124 g each of the two reagents glycol and glycerol are added in 5 kg water of the radiators in the two cars. Which of the following statements is wrong?
(a) Both will act as antifreeze
(b) Glycol will be better
(c) Glycerol is better because its molar mass is greater than glycol
(d) Glycol is more volatile than glycerol
3. 620 g glycol is added to 4 kg water in the radiator of a car. What amount of ice will separate out at – 6°C? $K_f = 1.86$ K kg mol^{-1}:
(a) 800 g (b) 900 g (c) 600 g (d) 1000 g
4. If cost of glycerol, glycol and methanol are same, then the sequence of economy to use these compounds as antifreeze will be:
(a) glycerol > glycol > methanol
(b) methanol > glycol > glycerol
(c) methanol = glycol = glycerol
(d) methanol > glycol < glycerol
5. Which among the following is the most volatile and the best antifreeze?
(a) CH_3OH (b) C_2H_5OH (c) Glycol (d) Glycerol

• Passage 6

The solutions which boil at constant temperature like a pure liquid and possess same composition in liquid as well as vapour state are called azeotropes. The components of azeotropes cannot be separated by fractional distillation. Only non-ideal solutions form azeotropes. Solutions with negative deviation form maximum boiling azeotrope and the solutions with positive deviation form minimum boiling azeotrope. Boiling point of an azeotrope is never equal to the boiling points of any of the components of the azeotrope.

Answer the following questions:

1. The azeotropic solutions of two miscible liquids:
(a) can be separated by simple distillation
(b) may show positive or negative deviation from Raoult's law
(c) are supersaturated
(d) behave like single pure component and boil at a fixed temperature
2. Solutions which distill without any change in composition or temperature are called:
(a) saturated (b) supersaturated
(c) ideal (d) azeotrope
3. The azeotropic mixture of water and HCl boils at 108.5°C. This solution is:
(a) ideal
(b) non-ideal with positive deviation
(c) non-ideal with negative deviation
(d) cannot be predicted

4. 100 mL liquid A and 50 mL liquid B are mixed to form 138 mL solution. It is:
   (a) ideal solution (b) high boiling azeotrope
   (c) low boiling azeotrope (d) none of these
5. Which among the following combinations is maximum boiling azeotrope?
   (a) $H_2O + CH_3OH$ (b) $CCl_4 + CHCl_3$
   (c) $(CH_3)_2CO + C_2H_5OH$ (d) $H_2O + HNO_3$

• Passage 7

The properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water.

The mole fraction of ethanol in the mixture is 0.9.

Given : Freezing point depression constant of water (K_f *for water*) $= 1.86\,K\ kg\ mol^{-1}$

Freezing point depression constant of ethanol (K_f *for ethanol*) $= 2.0\,K\ kg\ mol^{-1}$

Boiling point elevation constant of water (K_b *for water*) $= 0.52\,K\ kg\ mol^{-1}$

Boiling point elevation constant of ethanol (K_b *for ethanol*) $= 1.2\,K\ kg\ mol^{-1}$

Standard freezing point of water = 273 *K*
Standard freezing point of ethanol = 155.7 *K*
Standard boiling point of water = 373 *K*
Standard boiling point of ethanol = 351.5 *K*
Vapour pressure of pure water = 32.8 *mm Hg*
Vapour pressure of pure ethanol = 40 *mm Hg*
Molecular weight of water $= 18\ g\ mol^{-1}$
Molecular weight of ethanol $= 46\ g\ mol^{-1}$

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

Answer the following questions:

1. The freezing point of the solution M is:
   (a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K
2. The vapour pressure of the solution M is:
   (a) 39.3 mm Hg (b) 36.0 mm Hg
   (c) 29.5 mm Hg (d) 28.8 mm Hg
3. Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is:
   (a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K

(IIT 2008)

[**Hint:**

1. Molality $m = \frac{x_B \times 1000}{(1 - x_B)\, m_A} = \frac{0.1 \times 1000}{0.9 \times 46}$

$$= 2.415$$

$$\Delta T = K_f \times m$$

$$= 2 \times 2.415 = 4.83$$

Freezing point of solution $= 155.7 - 4.83 = 150.9$ K

2. $p = p^0 x_A$

$$= 40 \times 0.9 = 36 \text{ mm Hg}$$

3. When water becomes solvent, the molality of solution will be :

$$m = \frac{x_B \times 100}{x_A \times m_A} = \frac{0.1 \times 1000}{0.9 \times 18} = 6.172$$

$$\Delta T = K_b \times m = 0.52 \times 6.172 = 3.209$$

Boiling point of solution $= 373 + 3.209$
$= 376.2$ K]

Answers

Passage 1.	1. (a)	2. (b)	3. (a)	4. (c)	5. (b)	
Passage 2.	1. (c)	2. (b)	3. (b)	4. (c)	5. (a)	6. (b)
Passage 3.	1. (b)	2. (c)	3. (c)	4. (b)	5. (a, b)	
Passage 4.	1. (b)	2. (a)	3. (d)	4. (b)	5. (c)	
Passage 5.	1. (a)	2. (c)	3. (b)	4. (b)	5. (a)	
Passage 6.	1. (b, d)	2. (d)	3. (c)	4. (b)	5. (d)	
Passage 7.	1. (d)	2. (b)	3. (b)			

SELF ASSESSMENT

ASSIGNMENT NO. 5

SECTION-I

Straight Objective Type Questions

This section contains 12 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. The relative lowering of vapour pressure of a dilute aqueous solution containing non-volatile solute is 0.0125. The molality of solution is about: **[PET (Kerala) 2007]**

(a) 0.70 (b) 0.50 (c) 0.90 (d) 0.80
(e) 0.60

2. If the elevation in boiling point of a solution of 10 gm of solute (mol. mass = 100) in 100 g of water is ΔT_b, the ebullioscopic constant of water is: **[PET (Kerala) 2007]**

(a) 10 (b) $100\,T_b$ (c) $\Delta\,T_b$ (d) $\frac{\Delta T_b}{10}$
(e) $10\,T_b$

3. Which one of the following aqueous solutions will exhibit highest boiling point? **(DPMT 2009)**

(a) 0.1 M KNO_3 (b) 0.1 M Na_3PO_4
(c) 0.1 M $BaCl_2$ (d) 0.1 M K_2SO_4

4. A solution containing 10 g per dm^3 of urea (molecular mass $= 60\ g\ mol^{-1}$) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is: **(AIIMS 2007)**

(a) $300\ g\ mol^{-1}$ (b) $350\ g\ mol^{-1}$
(c) $200\ g\ mol^{-1}$ (d) $250\ g\ mol^{-1}$

5. The molarity of 5 molal aqueous solution of NaOH having density 1.2 g / cc is:

(a) 5 M (b) 4.1 M (c) 6 M (d) 8 M

6. The value of osmotic pressure does not depend on:

(a) concentration of solution
(b) van't Hoff factor
(c) temperature
(d) structure of solute particles

7. Henry's law constants for O_2 and N_2 are:

$$k_{O_2} = 3.3 \times 10^7, k_{N_2} = 6.51 \times 10^7$$

Calculate the ratio of $\frac{x_{O_2}}{x_{N_2}}$, *i.e.*, the ratio of mole fractions of O_2 and N_2 dissolved in water at 25° C from air:

(a) 0.62 (b) 0.92 (c) 0.42 (d) 0.52

8. The molal lowering of vapour pressure of water at 100° C is:

(a) 13.68 mm (b) 46 mm
(c) 65 mm (d) 13.68 cm

9. USP ethanol in aqueous solution in containing 95% ethanol by volume. At 20° C, pure ethanol has a density of 0.789 g/mL and USP ethanol density 0.813 g/mL. What is the mass percentage of ethanol in USP ethanol?

(a) 46% (b) 90% (c) 86% (d) 92.3%

10. A solution of 7.45 g KCl in 1000 mL shows osmotic pressure of 4.68 atm at 300K. Calculate the percentage dissociation of KCl:

(a) 70% (b) 80% (c) 90% (d) 10%

11. The mass of glucose that should be dissolved in 50g of water in order to produce same lowering of vapour pressure as is produced by dissolving 1 g of urea in the same quantity of water is : **[MGIMS (Wardha) 2008]**

(a) 1 g (b) 3 g (c) 6 g (d) 18 g

12. Consider the following aqueous solutions and assume 100% ionisation in electrolytes :

I. 0.1 m urea II. 0.04 m $Al_2(SO_4)_3$
III 0.05 m $CaCl_2$ IV. 0.005 m NaCl

The correct statement regarding the above solutions is : **[BHU (Mains) 2008]**

(a) freezing point will be lowest for solution I
(b) freezing point will be highest for solution IV
(c) boiling point will be highest for solution IV
(d) Vapour pressure will be highest for solution II

SECTION-II

Multiple Answers Type Objective Questions

13. K_2HgI_4 is 50% ionised in aqueous solution. Which of the following are correct?

(a) $n = 7$ (b) $n = 3$ (c) $i = 2$ (d) $i = 4$

14. Henry's law is invalid for gases like.................

(a) CO_2 (b) SO_2 (c) HCl (d) N_2

15. The azeotropic mixture of two liquids:

(a) boils at constant temperature
(b) can be separated by simple distillation
(c) is super saturated
(d) deviates from Raoult's law

16. Cryoscopic constant of a liquid depends on:

(a) the latent heat of fusion of solvent
(b) the freezing point of solvent
(c) the concentration of solution
(d) the melting point of solute

17. Which of the following is/are influenced by the temperature?

(a) Freezing point (b) Boiling point
(c) Vapour pressure (d) Osmotic pressure

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

18. **Statement-1:** Solubility of ionic compounds in water depends on both the lattice energy and the hydration energy.

Because

Statement-2: Ionic compounds dissolve in water when their hydration energy exceeds the lattice energy.

19. **Statement-1:** Isotonic solutions have same molar concentration.

Because

Statement-2: Solutions which have same osmotic pressure at same temperature are known as isotonic solutions.

[**Hint:** It is not necessary that solutions at same molar concentration have same osmotic pressure, *eg.*, $\pi(0.1M \text{ NaCl}) > \pi(0.1\,M \text{ glucose})$ because NaCl is ionised]

20. **Statement-1:** The vapour pressure of 0.1 M Hg_2Cl_2 is equal to 0.1 M $AlCl_3$ solution.

Because

Statement-2: 0.1 M $AlCl_3$ and 0.1 M Hg_2Cl_2 give different numbers of ions in a solution.

21. **Statement-1:** Elevation in boiling point will be high if the molal elevation constant of solvent is high.

Because

Statement-2: Elevation in boiling point is a colligative property.

22. **Statement-1:** Ethylene glycol is used as antifreeze for the radiator of a car.

Because

Statement-2: Ethylene glycol dissolves in water with the help of hydrogen bond and it lowers the freezing point.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statements given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s), (b-q,r), (c-p,q) and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

23. Match the Column-I with Column II:

Column-I	Column-II
(a) $CCl_4 + CHCl_3$	(p) Raoult's law
(b) $C_6H_6 + H_2O$	(q) Nearly ideal solution
(c) $p_A \propto x_A$	(r) Negative deviation from Raoult's law
(d) $p_A < p_A^0 x_A$	(s) Positive deviation from Raoult's law

24. Match the Column-I with Column II:

Column-I (Species completely ionised)	Column-II (van't Hoff factor)
(a) Hg_2Cl_2	(p) 5
(b) $K_3[Fe(CN)_6]$	(q) 4
(c) $Ca_3(PO_4)_2$	(r) 1
(d) glucose	(s) 3

25. Match the Column-I with Column II:

Column-I	Column-II
(a) Mole fraction	(p) mol kg^{-1}
(b) Molality	(q) Depends on temperature
(c) Molarity	(r) Unitless
(d) Normality	(s) Independent of temperature

Answers

1. (a) **2.** (c) **3.** (b) **4.** (a) **5.** (a) **6.** (d) **7.** (d) **8.** (a)
9. (d) **10.** (c) **11.** (b) **12.** (b) **13.** (b, c) **14.** (a, b, c) **15.** (a, d) **16.** (a, b)
17. (c, d) **18.** (a) **19.** (d) **20.** (d) **21.** (b) **22.** (a) **23.** (a-q) (b-s) (c-p, q) (d-r)
24. (a-s) (b-q) (c-p) (d-r) **25.** (a-r,s) (b-p,s) (c-q) (d-q)

CHAPTER 6

THE COLLOIDAL STATE

6.1 INTRODUCTION

The foundation of colloid chemistry was laid down by an English scientist, **Thomas Graham,** in 1861. The credit for the various advances in this field goes to eminent scientists like **Tyndall, Hardy, Zsigmondy, N.R. Dhar, S.S. Bhatnagar** and **others.**

Thomas Graham classified the soluble substances into two categories depending upon the rate of their diffusion through animal and vegetable membranes or parchment paper. He observed that certain substances diffuse freely through the membrane, whereas others do not diffuse. The former type of substances on account of their crystalline nature like common salt, sugar, urea, etc., were named **crystalloids** while the second type of substances were termed as **colloids** (Greek word, *Kolla*, meaning glue-like). All inorganic acids, bases and salts and organic compounds such as sugar, urea, etc., were included in crystalloids while substances such as starch, gelatin, gums, silicic acid, etc., belonged to the colloidal group.

It was soon realised that the above classification was not perfect since many crystalline substances can be converted into colloidal form by suitable means. The colloidal form of sodium chloride, a crystalloid, can be obtained in benzene. Silver, copper, gold, etc., which are completely insoluble in water, can be transformed into colloidal state by suitable methods. X-ray examination of certain colloids like glue and gelatin revealed that these were crystalline in nature. Thus, the above classification was discarded, *i.e.*, **the term colloid does not apply to a particular class of substances but is a state of matter like solid, liquid and gas. Any substance can be brought into colloidal state by suitable means.**

6.2 PARTICLE SIZE AND COLLOIDAL STATE

The colloidal state depends on the particle size. **It is regarded as intermediate state between true solution and suspension.** In

Table 6.1 Comparison of Suspensions, Colloids and True Solutions

S.No.	Property	Suspension	Colloid	True solution
1.	Particle size	$> 10^{-5}$ cm or 10^3 Å or 100 mμ	10^{-7} cm to 10^{-5} cm or 10 Å to 10^3 Å or 1 mμ to 100 mμ	$< 10^{-7}$ cm or 10 Å or 1 mμ
2.	Visibility	Visible with naked eye	Visible with ultramicroscope	Not visible with any of the optical means
3.	Separation			
	(a) with filter paper	Possible	Not possible	Not possible
	(b) with membranes	Possible	Possible	Not possible
4.	Diffusion	Does not diffuse	Diffuses very slowly	Diffuses rapidly
5.	Settling	Settles under gravity	Does not settle but it may settle under centrifuge	Does not settle
6.	Nature	Heterogeneous	Heterogeneous	Homogeneous
7.	Appearance	Opaque	Generally clear	Clear

true solutions, the size of the particles of solute is very small and, thus, these cannot be detected by any optical means and freely diffuse through membranes while in suspensions the size of the particles is large enough and, thus, can be seen even by naked eye and do not pass through filter paper.

True solutions are homogeneous systems while suspensions are heterogeneous. These are two extreme systems and the colloidal state is an intermediate between the two. If we start with particles of large size (suspension) and go on subdividing them till we reach the size of particles found in solution, there is continuous change in the characteristics. During transition, the mixture passes through an intermediate state which shares the characteristics of both. This has been shown in Fig. 6.1.

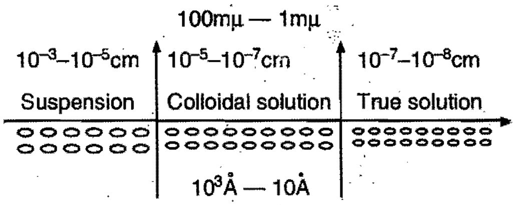


Fig. 6.1

A system is said to be in colloidal state if particles of one or more components have the size range* 10 Å to 10^3 Å. However, it is not possible to draw a sharp line of demarcation between colloidal state and suspension. The properties of one gradually appear into those of the other. **Roughly speaking, the colloidal state is a heterogeneous dispersion of solute particles of size ranging between 10 Å to 10^3 Å into a solvent.**

Some properties of the three systems (suspension colloids and true solutions) are summarized in table 6.1.

6.3 TYPES OF COLLOIDAL SOLUTIONS

The colloidal solutions consist of two-phases, one of which is dispersed in the other. This is called **dispersed phase**, the **internal phase** or the **discontinuous phase.** The phase in which the dispersion is done is termed **dispersion phase**, the **external phase** or the **continuous phase.** This phase forms the larger part of the colloidal solution. Depending upon the physical state of dispersed and dispersion phases, the types of colloidal solutions given in table 6.2 are possible.

A colloidal solution of gas in gas is not possible as gases are completely miscible and always form true solutions.

Lyophobic and Lyophilic Colloids

Colloidal solutions in which the dispersed phase has very little affinity for the dispersion phase are termed as **lyophobic** (solvent hating) colloids. These are also termed **suspensoids.** Colloidal solutions of metals which have negligible affinity for solvents are examples of this type. Generally, lyophobic sols are less stable. On evaporation of solvent, the residue cannot be easily transformed back into colloidal state by ordinary means. Lyophobic colloids are, therefore, also called **irreversible colloids.**

Table 6.2

S. No.	Dispersed phase (Colloidal particles)	Dispersion phase (Solvent)	Name	Examples
1.	Gas	Liquid	Foam	Froths of air
2.	Gas	Solid	Solid foam	Pumice stone, dried sea foam
3.	Liquid	Gas	Liquid aerosol	Cloud, mist
4.	Liquid	Liquid	Emulsion	Milk, cream
5.	Liquid	Solid	Gel	Jellies, curd, cheese
6.	Solid	Gas	Aerosol	Smoke, haze
7.	Solid	Liquid	Sol	Goldsol, sulphursol
8.	Solid	Solid	Solid-sol	Ruby glass, minerals, gems

Colloidal solutions in which the dispersed phase has considerable affinity for the dispersion phase, *i.e.*, colloidal solution, can be prepared by bringing them together, are called **lyophilic** (solvent loving) colloids. These are also known as

Table 6.3 Comparison of Lyophobic and Lyophilic Sols

S. No.	Property	Lyophobic sols (Suspensoid)	Lyophilic sols (Emulsoid)
1.	Preparation	Cannot be easily prepared. Special methods are required for preparation.	Can easily be prepared by shaking or warming the substance with solvent.
2.	Stability	Are less stable.	Are more stable.
3.	Reversibility	Are irreversible.	Are reversible.
4.	Viscosity	Viscosity is nearly the same as that of solvent.	Viscosity is much higher than that of solvent.
5.	Surface tension	Surface tension is almost the same as that of the solvent.	Surface tension is usually low.
6.	Hydration or solvation	These are less solvated as the particles have less affinity for solvent.	These are highly solvated as the particles have great affinity for solvent.
7.	Charge	The particles carry a characteristic charge either positive or negative.	The particles have little or no charge at all.
8.	Visibility	Particles can be seen under microscope.	Particles cannot be seen under microscope.
9.	Coagulation	Easily coagulated by addition of electrolytes.	Cannot be easily coagulated.

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* 1 Å (Angstrom unit) = 10^{-8} cm = 10^{-7} mm = 0.1 mμ (millimicron)

emulsoids. Gelatin, proteins, starch, etc., are the examples of this type. Colloidal solutions of this type are more stable and are also known as **reversible colloids** since the residue left on evaporation can be readily transformed back into colloidal state simply by adding solvent. When the dispersion medium is water, the above colloidal solutions are termed as **hydrophobic** and **hydrophilic.** (For comparison, see table 6.3)

The colloidal solutions are also named according to the dispersion phase or medium used. The colloidal solutions in alcohol and benzene are known as ***alcosols*** and ***benzosols*** respectively. The colloidal solutions where water is used as the dispersion medium are called ***hydrosols*** or ***aquasols.***

Note: Colloidal solutions of solids in liquids are abbreviated as sols.

6.4 PREPARATION OF COLLOIDAL SOLUTIONS

1. Preparation of lyophilic sols: The colloidal solutions of lyophilic colloids like starch, glue, gelatin, etc., can be readily prepared by dissolving these substances in water either in cold or on warming. Solutions of colloidal electrolytes such as soaps and dye stuffs can also be prepared similarly.

2. Preparation of lyophobic sols: To get a substance in colloidal form either the substance in bulk is broken down into fine particles of colloidal dimension (1 Å to 10^3 Å) or increasing the size of molecular particles as to form larger aggregates. In some cases, a third substance is usually added to increase the stability of the sol. These substances are called **stabilizers.** Thus, there are two ways by which the lyophobic sols can be prepared:

(i) Dispersion methods: By splitting coarse aggregates of a substance into colloidal size.

(ii) Condensation methods: By aggregating very small particles (atoms, ions or molecules) into colloidal size.

Table 6.4

S. No.	Dispersion methods	Condensation methods
1.	Mechanical dispersion	Exchange of solvents
2.	Electro-dispersion	Change of physical state
3.	Ultrasonic dispersion	Chemical methods:
4.	Peptization	(i) Double decomposition (ii) Oxidation (iii) Reduction (iv) Hydrolysis

Dispersion Methods

1. Mechanical dispersion: Solid material is first finely ground by usual methods. It is then mixed with dispersion medium which gives a coarse suspension. The suspension is now introduced into the **colloid mill.** The simplest form of colloid mill consists of two metal discs held at a small distance apart from one another and capable of revolving at a very high speed (about 7000 revolutions per minute) in opposite directions. The particles are ground down to colloidal size and are then dispersed in the liquid. A stabilizer is often added to stabilize the colloidal solution. Colloidal graphite (a lubricant) and printing ink are made by this method. Tannin is used as a stabilizer in the preparation of colloidal graphite and gum arabic in lampblack colloidal solution (Indian ink).

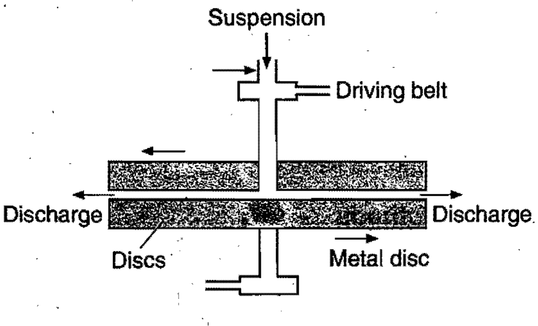


Fig. 6.2

2. Electro-dispersion (Bredig's arc method): This method is suitable for the preparation of colloidal solutions of metals like gold, silver, platinum, etc. An arc is struck between the metal electrodes under the surface of water containing some stabilizing agents such as a trace of KOH. The water is cooled by immersing the container in an ice bath. The intense heat of the arc vaporises some of the metal which condenses under cold water.

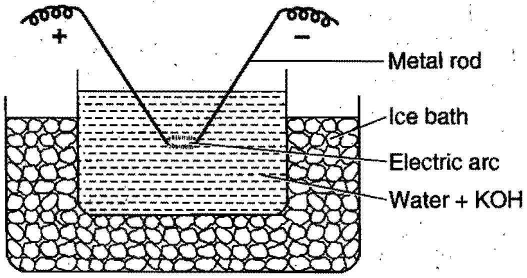


Fig. 6.3

Note: 1. This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.
2. This method comprises both dispersion and condensation.

3. Ultrasonic dispersion: The sound waves of high frequency are usually called ultrasonic waves. These waves can be produced when quartz crystal discs are connected with a high frequency generator. The application of ultrasonic waves for the preparation of colloidal solutions was first introduced by Wood and Loomis, in 1927. Various substances like oils, mercury, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves.

4. Peptization: The dispersion of a freshly precipitated material into colloidal solution by the action of an electrolyte in solution is termed peptization. The electrolyte used is called a **peptizing agent.**

A few examples of sols obtained by peptization are:

(i) Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution at once forms a dark reddish brown solution. Ferric chloride acts as a peptizing agent.

(ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal solution of stannic oxide.

(iii) Freshly precipitated silver chloride can be converted into a colloidal solution by adding a small amount of hydrochloric acid.

(iv) Cadmium sulphide can be peptized with the help of hydrogen sulphide.

The process of peptization thus involves the adsorption of suitable ions (supplied by the electrolyte added—particularly a common ion) and electrically charged particles then split from the precipitate as colloidal particles.

Condensation Methods

1. By exchange of solvents: If a solution of sulphur or phosphorus prepared in alcohol is poured into water, a colloidal solution of sulphur or phosphorus is obtained due to low solubility in water. Thus, there are a number of substances whose colloidal solutions can be prepared by taking a solution of the substance in one solvent and pouring it into another solvent in which the substance is relatively less soluble.

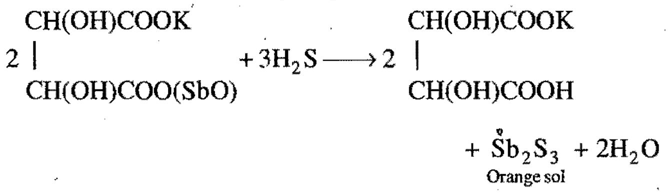
2. By change of physical state: Colloidal solutions of certain elements such as mercury and sulphur are obtained by passing their vapour through cold water containing a stabilizer (an ammonium salt or a citrate).

3. Chemical methods: The chemical methods involve chemical reactions in a medium in which the dispersed phase is sparingly soluble. A condition of supersaturation is produced but the actual precipitation is avoided. Some familiar reactions used are:

(a) *Double decomposition*: (i) Arsenious sulphide sol: A 1% solution of arsenious oxide is prepared in hot water. The solution is cooled, filtered and is then gradually added to water saturated with hydrogen sulphide, whilst a stream of H_2S is being passed through the solution. This is continued till an intense yellow-coloured solution is obtained. Excess of H_2S is removed by bubbling hydrogen through the solution.

$$As_2O_3 + 3H_2S \longrightarrow \underset{\text{Yellow sol}}{As_2S_3} + 3H_2O$$

(ii) Antimony sulphide sol: A 0.5% solution of potassium antimonyl tartarate is added drop by drop to water saturated with H_2S, whilst H_2S is being passed through the solution. Orange coloured solution of antimony sulphide is obtained.



$$2\begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COO(SbO)}\end{array} + 3H_2S \longrightarrow 2\begin{array}{l}\text{CH(OH)COOK}\\ |\\ \text{CH(OH)COOH}\end{array} + \underset{\text{Orange sol}}{Sb_2S_3} + 2H_2O$$

(b) *Oxidation*: A colloidal solution of sulphur is obtained by passing H_2S into a solution of sulphur dioxide.

$$2H_2S + SO_2 \longrightarrow 2H_2O + \underset{\text{Sol}}{3S}$$

Sulphur sol can also be obtained when H_2S is bubbled through an oxidising agent (bromine water or nitric acid).

(c) *Reduction*: Colloidal solutions of metals like gold, silver, platinum, lead, etc., can be obtained when their salts solutions are acted upon by reducing agents.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + \underset{\text{Sol}}{2Au}$$

Organic reducing agents such as formaldehyde, phenyl hydrazine, tannic acid, etc., can also be used.

$$AgNO_3 + \text{tannic acid} \longrightarrow \text{Silver sol}$$

$$AuCl_3 + \text{tannic acid} \longrightarrow \text{Gold sol}$$

(d) *Hydrolysis*: Colloidal solutions of some salts can be prepared by hydrolysis. A colloidal solution of ferric hydroxide is obtained by boiling a dilute solution of ferric chloride.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{Red sol}}{Fe(OH)_3} + 3HCl$$

The colloidal solution of silicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with $4N$ hydrochloric acid which is added drop by drop with constant stirring.

6.5 PURIFICATION OF COLLOIDAL SOLUTIONS

Colloidal solutions prepared by above methods generally contain excessive amount of electrolytes and some other soluble impurities. The presence of traces of electrolyte is essential for the stability of the colloidal solution but larger quantities coagulate it. It is, therefore, necessary to reduce the concentration of these soluble impurities to a requisite minimum. **The process used for reducing these impurities to a requisite minimum is known as purification of colloidal solution.** The purification of colloidal solution is carried out by the following methods:

(i) Dialysis*: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Since, particles in true solution (ions or smaller molecules) can pass through animal membranes (bladder) or parchment paper or cellophane sheet but colloidal particles do not, the above can be used for dialysis. The apparatus used for this purpose is called **dialyser.** A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flown (Fig. 6.4). The molecules and ions diffuse through the membrane into the outer water and pure colloidal solution is left behind.

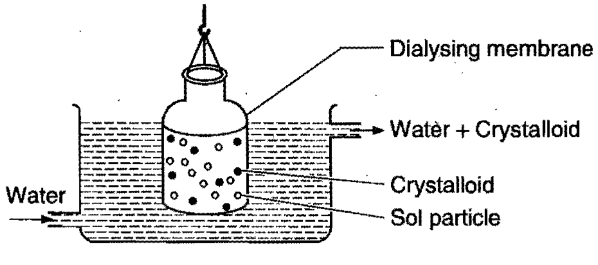


Fig. 6.4

(ii) Electro-dialysis: Ordinarily, the process of dialysis is quite slow. It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only electrolyte. The process is then named electro-dialysis. The colloidal solution is placed between two **electrodes** while pure water is taken in a compartment on each side. Electrodes are fitted in the compartment as shown in Fig. 6.5. The ions present

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*Blood is a colloidal solution. In case of kidney failure, blood cannot be purified. Under such condition, the blood is separated from dissolved toxic impurities by dialysis and re-introduced in the blood stream.

in the colloidal solution migrate out to the oppositely charged electrodes.

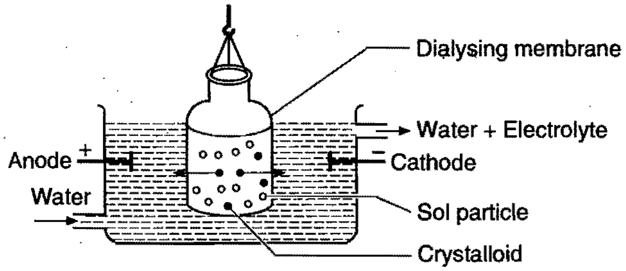


Fig. 6.5

(iii) Ultrafiltration: Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by especially prepared filters, which are permeable to all substances except the colloidal particles.

Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with colloidion solution and subsequently hardened by soaking in formaldehyde. The usual colloidion is a 4% solution of nitro-cellulose in a mixture of alcohol and ether. An ultra-filter paper may be prepared by soaking the filter paper in a colloidion solution and hardened by formaldehyde and finally drying it. Thus, by using ultra-filter paper, the colloidal particles are separated from rest of the materials. Ultrafiltration is a slow process. To speed up the process, pressure or suction is used.

The colloidal particles left on the ultra-filter paper are then stirred with fresh dispersion medium (solvent) to get a pure colloidal solution.

6.6 PROPERTIES OF COLLOIDAL SOLUTION

1. Heterogeneous character: Colloidal solutions are heterogeneous in character as they consist of two phases: (a) dispersed phase and (b) dispersion medium.

2. Visibility: It is not possible to see colloidal particles with naked eye or with the help of microscope. It is a well known fact that no particle is visible if its diameter is less than half the wavelength of the light used. The shortest wavelength of the visible light is about 4000 Å or 400 mμ. Hence, no particle of diameter less than 200 mμ can be seen. The size of colloidal particles is less than 200 mμ.

Recently, three new techniques have been developed to determine the size and shape of the colloidal particles. These are:

(i) Scanning electron microscope (SEM).
(ii) Transmission electron microscope (TEM).
(iii) Scanning transmission electron microscope (STEM).

3. Filtrability: Colloidal particles pass through an ordinary filter paper. However, the particles do not pass through parchment and other fine membranes.

4. Surface tension and viscosity: The surface tension and viscosity of lyophobic sols are not very different from those of the dispersion medium. On the other hand, lyophilic sols show higher viscosity and lower surface tension in comparison to the dispersion medium.

5. Colligative properties: Colloidal particles are bigger aggregates. Thus, the number of particles in the colloidal solution is comparatively small as compared to true solution and hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.

6. Tyndall effect: If a heterogeneous solution placed in dark is observed in the direction of light, it appears clear and if it is observed from a direction at right angles to the direction of light beam, it appears perfectly dark. Colloidal solutions show a mild to strong opalescence, when viewed at right angles to the path of light, *i.e.*, the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as **Tyndall effect.** The bright cone of the light is called **Tyndall cone** (Fig. 6.6). The Tyndall effect is due to the fact that colloidal particles absorb light energy and then scatter in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion.

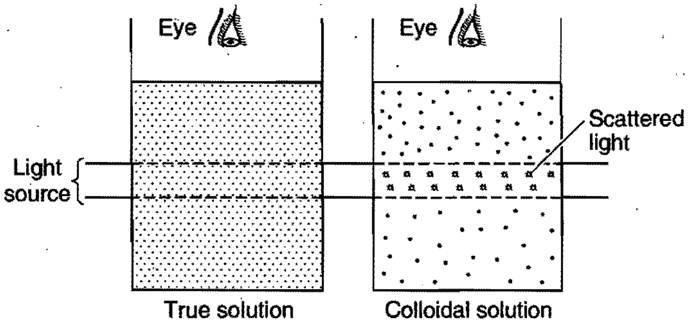


Fig. 6.6

Tyndall effect can be observed during the projection of picture in the cinema hall due to scattering of light by dust and smoke particles present there. Tyndall effect is observed only when the following two conditions are satisfied:

(i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and

(ii) The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude. This

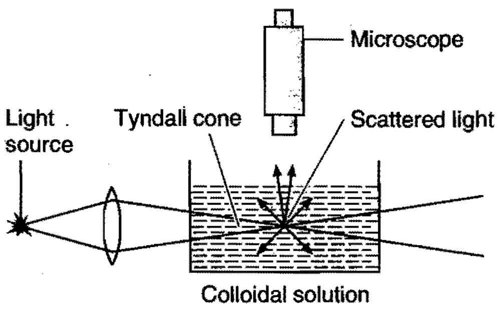


Fig. 6.7

condition is satisfied by lyophobic sols. The lyophilic sols show little or no Tyndall effect as there is very small difference in the refractive indices of the dispersed phase and the dispersion medium.

Some examples of Tyndall effects are:

(i) Blue colour of sky and seawater
(ii) Visibility of tails of comets
(iii) Twinkling of stars.

Tyndall effect is used to distinguish between a colloidal and true solution. **Zsigmondy,** in 1903, used Tyndall effect to set up an apparatus known as **ultramicroscope.** An intense beam of light is focussed on the colloidal solution contained in a glass vessel. The focus of the light is then observed with a microscope at right angles to the beam. Individual colloidal particles appear as bright stars against a dark background. Ultramicroscope does not render visible the actual colloidal particles but only the light scattered by them. Thus, ultramicroscope does not provide any information about the size and shape of colloidal particles.

7. Colour: The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of colloidal solution also changes with the way the observer receives the light. For example, milk and water mixture appears blue when viewed by the reflected light and looks red by the transmitted light. Finest gold sol is red in colour. As size of the particles increases, it becomes purple, then blue and finally golden yellow.

8. Brownian movement: When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous motion in zig-zag directions all over the field of view. This motion was first observed by the British botanist **Robert Brown** and hence is known as **Brownian movement** (Fig. 6.8). This motion is independent of the nature of the colloid but depends on the size of the particles and the viscosity of solution. **Smaller the size and lesser the viscosity, faster is the motion.** The motion becomes intense at high temperature. The distance between two points decreases at elevated temperature.

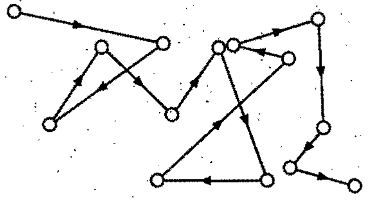


Fig. 6.8

The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium. The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.

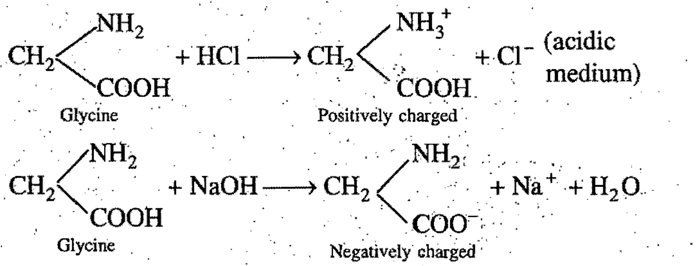
9. Charge on colloidal particles: Colloidal particles always carry an electric charge. This charge is of the same type on all the particles in a given colloidal solution and may be either positive or negative. A list of some common sols with the type of charge on their particles is given in table 6.5.

Table 6.5

S. No.	Positively charged	Negatively charged
1.	Metallic hydroxides, *e.g.*, $Cr(OH)_3$, $Al(OH)_3$ and $Fe(OH)_3$ sols.	Metals, *e.g.*, copper, silver, gold-sols.
2.	Basic dyestuffs, *e.g.*, methylene blue sol.	Metallic sulphides, *e.g.*, As_2S_3, Sb_2S_3, CdS sols.
3.	Proteins in acidic medium.	Acid dyestuffs, *e.g.*, eosin, congo red-sols.
4.	Oxides, *e.g.*, TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

The charge on the sol particles is due to one or more of the following reasons:

(i) Due to the presence of acidic or basic groups: A protein molecule has a carboxylic group and a basic NH_2 group. The particles of proteins in sols can either have positive charge or negative charge depending upon the pH of the medium.



$$CH_2(NH_2)COOH + HCl \longrightarrow CH_2(NH_3^+)COOH + Cl^- \quad \text{(acidic medium)}$$

$$CH_2(NH_2)COOH + NaOH \longrightarrow CH_2(NH_2)COO^- + Na^+ + H_2O$$

(alkaline medium)

Isoelectric point of a colloid: In case of colloidal solution proteins, the nature of charge depends on the pH of the solution called isoelectric point. Above this pH, the particles are negatively charged and below this pH, they have positive charge. At isoelectric point, colloidal particles exist in the form of Zwitter ion hence they do not migrate under the influence of external electric field.

Examples:	Colloidal sol	Isoelectric pH
	Haemoglobin	4.3—5.3
	Casein from human milk	4.1—4.7
	Gelatin	4.7

(ii) Due to self-dissociation: When colloidal particles such as soaps or detergents are dissolved in water, ionised molecules associate to form a micelle. The outer surface will be thus charged depending on the charge of the ions from which it is formed. Thus, sodium palmitate solution will have negative charge on its sol particles.

$$\underset{\text{Sodium palmitate}}{C_{15}H_{31}COONa} \longrightarrow C_{15}H_{31}COO^- + Na^+$$

(iii) Due to electron capture by sol particles: *e.g.*, during electro-dispersion of metals.

(iv) Due to preferential adsorption of ions: This is the most accepted view. The sol particles acquire positive or negative charge by preferential adsorption of +ve or –ve ions. **When two**

or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle usually takes place. This can be explained by taking the following examples:

(a) If silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide will adsorb iodide ions from the dispersion medium and negatively charged colloidal solution will result. However, when KI solution is added to $AgNO_3$ solution, positively charged sol will result due to adsorption of Ag^+ ions from dispersion medium.

$$\underset{\text{Negatively charged}}{AgI/I^-} \qquad \underset{\text{Positively charged}}{AgI/Ag^+}$$

(b) If $FeCl_3$ is added to excess of hot water, a positively charged sol of ferric hydroxide is formed due to adsorption of Fe^{3+} ions.

$$\underset{\text{Positively charged}}{Fe(OH)_3/Fe^{3+}}$$

However, when ferric chloride is added to NaOH a negatively charged sol is obtained with adsorption of OH^- ions.

$$Fe(OH)_3/OH^-$$

SnO_2 is positively charged colloidal sol due to adsorption of Sn^{4+} ions.

$$SnO_2 + 4H^+ \longrightarrow Sn^{4+} + 2H_2O$$

$$SnO_2 + Sn^{4+} \longrightarrow \underset{\text{Positive colloid}}{[SnO_2]Sn^{4+}}$$

On the other hand in alkaline medium, SnO_2 forms negatively charged colloidal sol due to adsorption of SnO_3^{2-} ions formed.

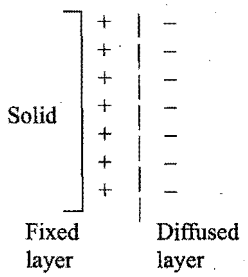
$$SnO_2 + 2OH^- \longrightarrow SnO_3^{2-} + H_2O$$

$$SnO_2 + SnO_3^{2-} \longrightarrow \underset{\text{Negative colloid}}{[SnO_2]SnO_3^{2-}}$$

Electrical double layer: The surface of a colloidal particle acquires a positive or a negative charge by selective adsorption of ions carrying positive or negative charge respectively as stated above. This layer attracts counter ions from the medium which form a second layer.

$$AgI/I^- \mid K^+ \qquad AgI/Ag^+ \mid I^-$$

The combination of the two layers of opposite charges around the colloidal particle is called **Helmholtz electrical double layer.** According to modern views, the first layer of ions is firmly held and is termed **fixed** layer while the second layer is mobile which is termed **diffused** layer. Since, separation of charge is a seat of potential, the charges of opposite signs on the fixed and diffused parts of the double layer results in a difference in potential between these layers. This potential difference between the fixed charged layer and the diffused layer of opposite charge is called the **electrokinetic potential** or **zeta potential.**



$$\xi = \frac{4\pi\eta u}{D}$$

where, η = Coefficient of viscosity
u = Velocity of colloidal particles
D = Dielectric constant of the medium

The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution because the forces of repulsion exist between same charged particles which prevent them from coalescing or aggregating when they come closer to one another.

10. Electrophoresis: When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. This movement of colloidal particles under an applied electric field is called **electrophoresis.** Positively charged particles move towards the cathode while negatively charged particles move towards anode. This can be demonstrated by the following experiment:

The apparatus consists of a U-tube provided with a stopcock through which it is connected to a funnel-shaped reservoir (Fig. 6.9). A small amount of water is first taken in the U-tube and then a requisite quantity of colloidal solution is placed in the reservoir. The stopcock is slightly opened and the reservoir is gradually raised as to introduce the colloidal solution into the U-tube. The water is displaced upwards producing a sharp boundary line in each arm. The platinum electrodes are fitted in the water layer and a voltage of 50 to 200 volts is applied. The movement of the particles can be observed towards one of the electrodes by seeing the position of boundary. When the colloidal particles are negatively charged, the boundary moves down in the cathodic arm and moves upwards in the anodic arm showing that particles move towards anode. It is, thus, possible to ascertain the charge on particles by noting the movement of boundary.

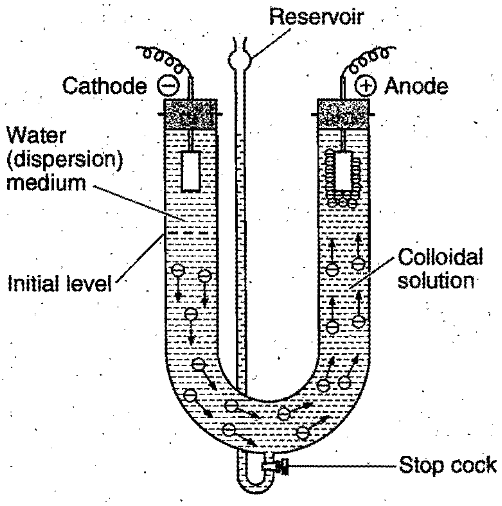


Fig. 6.9

When electrophoresis, *i.e.*, movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in an electric field. This phenomenon is termed **electro-osmosis.**

Summary of Electrokinetic Phenomena

Motion Causing Potential :

Sedimentation Potential	Streaming Potential
Medium rests but dispersed particles move.	Medium moves but dispersed particles rest.

Potential Causing Motion :

Electrophoresis	Electro-osmosis
Medium rests but dispersed particles move.	Medium moves but dispersed particles rest.

11. Coagulation or precipitation: The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If, some how, the charge is removed, the particles will come nearer to each other and thus, aggregate or flocculate and settle down under the force of gravity.

The flocculation and settling down of the colloidal particles is called coagulation or precipitation of the sol.

The coagulation of the lyophobic sols can be carried out by following methods:

(i) By electrophoresis: In electrophoresis, the colloidal particles move towards oppositely charged electrode. When these come in contact with the electrode for long, these are discharged and precipitated.

(ii) By mixing two oppositely charged sols: When oppositely charged sols are mixed in almost equal proportions, their charges are neutralised. Both sols may be partially or completely precipitated as the mixing of ferric hydroxide (+ve sol) and arsenious sulphide (–ve sol) bring them in precipitated form. This type of coagulation is called **mutual coagulation** or **meteral coagulation.**

(iii) By boiling: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately they settle down to form a precipitate.

(iv) By persistent dialysis: On prolonged dialysis, the traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable.

(v) By addition of electrolytes: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloidal particles take up ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation. The ion responsible for neutralisation of charge on the particles is called the **flocculating ion.** A negative ion causes the precipitation of positively charged sol and *vice-versa*.

It has been observed that, **generally, the greater the valency of the flocculating ion added, the greater is its power to cause precipitation.** This is known as **Hardy-Schulze rule.** In the coagulation of a negative sol, the flocculating power of Na^+, Ba^{2+} and Al^{3+} ions is in the order of:

$$Al^{3+} > Ba^{2+} > Na^+$$

Similarly, in the coagulation of a positive sol, the flocculation power of Cl^-, SO_4^{2-}, PO_4^{3-} and $[Fe(CN)_6]^{4-}$ is in the order of:

$$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$$

The minimum concentration of an electrolyte in millimole per litre required to cause precipitation of a sol in 2 hours is called flocculation value. The smaller the flocculating value, the higher will be the coagulating power of an ion.

Flocculation value of an ion depends on its charge :

$$\text{Flocculation value} \propto \frac{1}{(Z)^6} \text{ where } Z = \text{charge of ion}$$

Flocculation value of $M^{\pm}$, $M^{2\pm}$, $M^{3\pm}$, $M^{4\pm}$ ions lies in following ratio.

$$\frac{1}{(1)^6} : \frac{1}{(2)^6} : \frac{1}{(3)^6} : \frac{1}{(4)^6}$$

$$1 : 0.0156 : 0.00137 : 0.00024$$

$$100 : 1.56 : 0.137 : 0.024$$

Coagulation of lyophilic sols: There are two factors which are responsible for the stability of lyophilic sols. These factors are the charge and solvation of the colloidal particles. When these two factors are removed, a lyophilic sol can be coagulated. This is done (i) by adding electrolyte and (ii) by adding suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, the dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

12. Protection of colloids: Lyophilic sols are more stable than lyophobic sols. This is due to the fact that lyophilic colloids are extensively solvated, *i.e.*, colloidal particles are covered by a sheath of the liquid in which they are dispersed.

Lyophilic colloids have a unique property of protecting lyophobic colloids. When a lyophilic sol is added to the lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus, protect the latter from electrolytes. Lyophilic colloids used for this purpose are called **protective colloids.**

The lyophilic colloids differ in their protective power. The protective power is measured in terms of **Gold Number.** This number was introduced by Zsigmondy and is defined **as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 mL of a gold sol on the addition of 1 mL of 10% sodium chloride solution.**

The gold numbers of some of the common protective colloids are listed below:

Table 6.6

S.No.	Protective Colloid	Gold Number
1.	Gelatin	0.005–0.01
2.	Haemoglobin	0.03
3.	Gum arabic	0.15
4.	Egg albumin	0.08–0.10
5.	Potato starch	25
6.	Sodium oleate	0.4
7.	Gum tragacanth	2
8.	Starch	25–50

Higher is the gold number, lower will be the protective power. Thus, gelatin and starch have the maximum and minimum protective powers. The use of protective colloids is widespread. Gelatin is added in the preparation of ice cream as protective agent to the colloidal particles of ice. Argyrol, used as eye drops, is a silver sol protected by organic material.

Some facts :

(i) Blood is a colloidal solution, it is not coagulated by the electrolytes (NaCl, $Ca_3(PO_4)_2$ etc.) present in blood itself because proteins present in blood act as protective colloid.

(ii) Milk of human mother is better protected than cow's and buffaloes milk.

(iii) The proteins which are not coagulated at their iso-electric pH are better protective colloid.

(iv) Ageing : It is spontaneous destabilisation of colloidal solution. In this process, dispersed is separated from dispersion medium by itself, *i.e.*, no artificial method is used.

Congo Rubin Number

Ostwald proposed that it is the amount of protective colloid in mg which prevents the colour change in 100 mL of 0.01% Congo rubin dye solution to which 0.16 g equivalent of KCl are added when observed after 10–15 min.

13. Colligative properties: The value of colligative properties are of very small order because they have very small van't Hoff factor.

$$nAs_2S_3 \longrightarrow (As_2S_3)_n$$

$$n \approx 1000$$

$$\text{van't Hoff factor } i = \frac{1}{1000}$$

Colligative properties are directly proportional to the van't Hoff factor.

6.7 EMULSIONS

These are liquid-liquid colloidal systems, *i.e.*, the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called **emulsion.** Generally, one of the two liquids is water. There are two types of emulsions:

(i) Oil dispersed in water (O/W type),

(ii) Water dispersed in oil (W/O type).

In the first system, water acts as dispersion medium. Examples of this type of emulsions are milk and vanishing cream. In milk, liquid fat is dispersed in water.

In the second system, oil acts as dispersion medium. Common examples of this type are butter and cream.

Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For the stabilization of an emulsion, a third component called **emulsifying agent** is usually added. The emulsifying agents form an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid, when mixed, forms at once a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

Detection of emulsion: Following tests can be used to detect the type of emulsion:

(i) Dye test: An oil soluble dye is shaken up with the emulsion and a drop is seen under microscope. If coloured drops are seen, the emulsion is water in oil type otherwise of oil in water type.

(ii) Viscosity test: Water in oil type emulsion has greater viscosity than oil in water type emulsion.

(iii) Electrical conductivity test: Electrical conductivity of oil in water type emulsion is much greater than water in oil type emulsion. If electrolyte like NaCl is added to oil in water type emulsion, its conductivity greatly increases.

(iv) Spreading test: Water in oil type emulsion easily spread on the surface of an oil but not on the surface of water.

(v) Dilution test: Oil in water type emulsion can easily be diluted with water. On the other hand water in oil type emulsion cannot be diluted with water. For example, milk-which is oil in water type emulsion can be diluted with water, but butter or milk cream which are water in oil type emulsion cannot be diluted with water.

(vi) Coalescence: It is the phenomena of disappearance of the boundary between two particles (generally droplets or bubbles) in contact. Coalescence leads to the reduction of the total surface area. The flocculation of an emulsion, *viz.*, the formation of aggregates, may be followed by coalescence. In extensive condition, the coalescence leads to the formation of a macrophase and emulsion is said to break. Coalescence of solid particles is called sintering.

6.8 CLASSIFICATION OF COLLOIDS BASED ON THE TYPE OF PARTICLES OF DISPERSED PHASE

Depending upon the type of particles of dispersed phase, colloids are classified as:

(i) Multimolecular, (ii) Macromolecular, (iii) Associated colloids.

(i) Multimolecular colloids: On dissolution, a large number of atoms or smaller molecules of a substance aggregate together to form species having size in colloidal dimension (diameter less than 1 nm). The species thus formed are called multimolecular colloids. For example: Gold sol, sulphur sol. In these colloids, the particles are held together by van der Waals' forces.

(ii) Macromolecular colloids: Macromolecular substances dissolve in suitable solvent to form solutions in which the size of macromolecules lie in colloidal dimension. These are called macromolecular colloids and they are quite stable. For example: Starch, cellulose, proteins and enzymes, etc.

(iii) Associated colloids: Substances whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called **associated colloids.** These substances which when dissolved in a medium at low concentrations behave as normal, strong electrolytes, but at higher concentrations they exhibit colloidal properties due to the formation of aggregated particles (also called associated colloids). The molecules of soaps and detergents are usually smaller than the colloidal particles. However, in concentrated solutions, these molecules associate and form aggregates of colloidal size. These aggregates of soaps or detergent molecules are called **micelles.** The formation of micelles takes place only above a particular concentration called **critical micelle concentration** (CMC). For soaps, the CMC is 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain the aggregate of (30 – 100) molecules or more. Soaps and detergents are strong electrolytes and when dissolved in water they furnish ions.

$$\underset{\text{Soap}}{C_{17}H_{35}COONa} \longrightarrow C_{17}H_{35}COO^- + Na^+$$

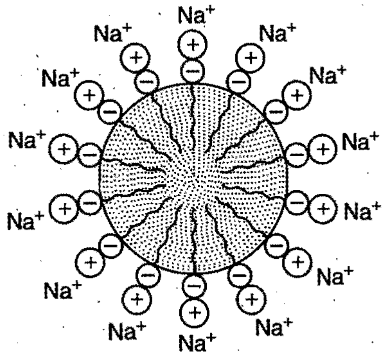


Fig. 6.10

The negative ions aggregate to form a micelle of colloidal size. The negative ion has a long hydrocarbon chain and a polar group ($—COO^-$) at one end. In micelle formation, the long hydrocarbon chain (tail) which is insoluble in water is directed towards the centre while the soluble polar head is on the surface in contact with water (Fig. 6.10). The charge on the micelle is responsible for the stability of this system. The cleansing action of soap is due to these micelles. The grease stain is absorbed into the interior of the micelle and gets detached from the fabric. The dust particles sticking to the stain are also removed. This action is similar to emulsification of grease.

Some other examples of micelle systems are as follows:

(i) Sodium lauryl sulphate $CH_3—(CH_2)_{11}SO_4^- \; Na^+$

(ii) Sodium oleate $C_{17}H_{35}COO^- \; Na^+$

(iii) Cetyltrimethyl ammonium bromide;

$$CH_3(CH_2)_{15}N^+(CH_3)_3Br$$

Micellisation with cationic terminals are also known, *e.g.*, in cetyltrimethyl ammonium chloride. It may be diagramatically represented as :

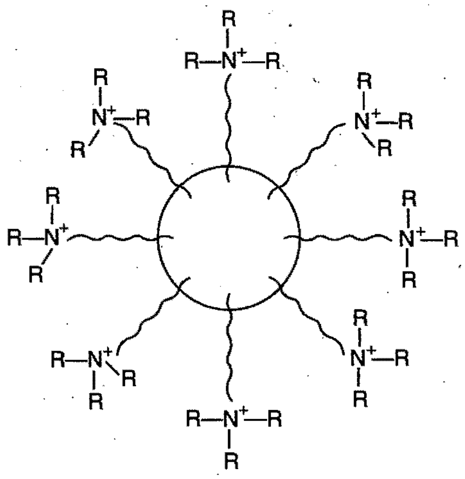
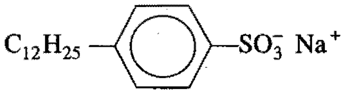


Fig. 6.11

(iv) *p*-Dodecyl benzene sulphonate;



$$C_{12}H_{25}—C_6H_4—SO_3^- \; Na^+$$

Surfactants are those substances which are preferentially adsorbed at the interfaces like air-water, oil-water and solid-water interfaces. Thus, it is the surfactant which is responsible for **micellisation** and emulsification. Surfactants are divided into three categories:

(i) Cationic surfactants: Such substances on ionisation give a cation having hydrophobic and hydrophilic group, *e.g.*, cetyl pyridinium chloride,

$$C_{16}H_{33}—C_5H_4N + Cl^-$$

Cetyltrimethyl ammonium chloride, $C_{16}H_{33}(CH_3)_3N^+Cl^-$

Octadecyl ammonium chloride, $C_{18}H_{37}NH_3^+Cl^-$

Ionisation of these compounds may be represented as,

$$C_{18}H_{37}NH_3^+Cl^- \xrightarrow{\text{Water}} \underset{\text{(Hydrophobic end)}}{C_{18}H_{37}} — \underset{\text{(Hydrophilic end)}}{NH_3^+} + Cl^-$$

(ii) Anionic surfactants: Such substances give anion which act as surfactant, *e.g.*,

Sodium Palmitate	$C_{15}H_{31}COONa$
Sodium Oleate	$C_{17}H_{35}COONa$

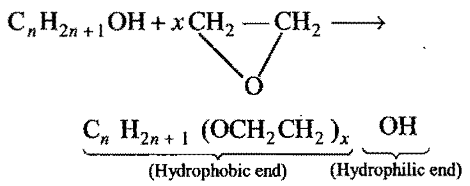
and salts of sulphonic acid having molecular formula

$$C_nH_{2n+1}SO_3M \quad \text{where,} \quad M^+ = Na^+, K^+, NH_4^+, \text{etc.}$$

$$C_{15}H_{31}COONa \xrightarrow{\text{Water}} \underset{\text{(Hydrophobic end)}}{C_{15}H_{31}} — \underset{\text{(Hydrophilic end)}}{COO^-} + Na^+$$

(iii) Non-ionogenic surfactants: These surfactants do not ionise or dissociate in aqueous medium, but these molecules also have hydrophobic and hydrophilic end.

High molecular mass alcohol adds to several molecules of ethylene oxide to form hydroxy surfactant.



$$C_nH_{2n+1}OH + xCH_2-CH_2 \longrightarrow \underbrace{C_n\,H_{2n+1}\,(OCH_2CH_2)_x}_{\text{(Hydrophobic end)}}\ \underbrace{OH}_{\text{(Hydrophilic end)}}$$

Kraft point: The temperature above which a surfactant forms micelle is called kraft point.

Some Important Features of Micelle

1. At critical micelle concentration (CMC), surfactants begins to form spherical aggregates made of 30 to 100 ions with their hydrocarbon tails in the interior of the aggregate and their charged terminals exposed to water on the out side (see Fig. 6.12).

2. Increase in temperature usually increases CMC.

3. CMC also depends on chain length, greater is the chain length of hydrocarbon tail, smaller is the CMC. Increase in the hydrophobic part of the surfactant molecules, favours the formation of micelles.

4. CMC of ionic micelles decreases on addition of simple electrolyte like NaCl. Screening action of added ions reduces the repulsion between charged groups at the surface of micelles.

5. Below the Kraft temperature, solubility of surfactant is not enough to form micelles. Kraft temperature increases with increase in the number of carbon atoms.

Number of carbon atoms in sodium alkyl sulphates	10	12	14
Kraft temperature °C	8	16	30

6. Micellisation is found to be spontaneous; it is confirmed by negative value of ΔG in following equation :

$$\Delta G = \Delta H - T\Delta S \qquad \ldots(1)$$

$\Delta H = -$ ve and $T\Delta S = +$ ve for micellisation

Standard enthalpy change of micellisation may be calculated as,

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

$$= -2.303RT^2\,\frac{d(\log CMC)}{dT}$$

Physical Properties of Critical Micelle Concentration

Physico-chemical properties of surfactant solution changes sharply in the region of the C.M.C. Variation of physico-chemical properties of surfactant solution with concentration is represented in following figure :

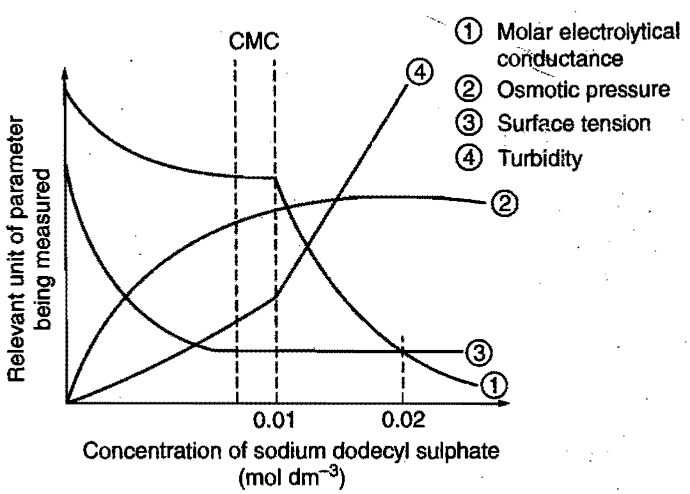


Fig. 6.12

6.9 GELS

When a colloidal solution is coagulated, a precipitate is usually formed which may or may not be gelatinous. Under certain set of conditions, it is possible to obtain the dispersed phase as more or less rigid mass enclosing within it all of the liquid. The product in this form is known as a **gel** and the process is called **gelation.** The gel is, thus, a colloidal semi-solid system rich in liquid phase. Gel usually consists of two components; one is solid, such as gelatin, silicic acid, sodium oleate, etc., and the other is a liquid such as water.

Gels may be elastic or non-elastic according to their mechanical properties. Elastic gels can be prepared by dissolving the substance in warm water and cooling it till sets. Examples are agar-agar and gelatin gels. Non-elastic gels are prepared by appropriate chemical action. The silica gel is formed by action of HCl with sodium silicate solution.

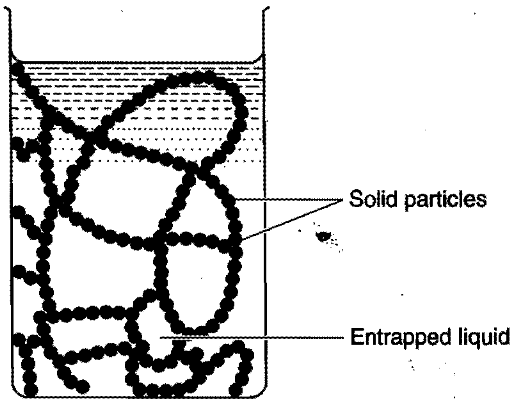


Fig. 6.13

Gel may shrink on keeping by loosing some of the liquid held by them. This is known as **syneresis** or weeping of gel. Some gels liquify on shaking and reset on being allowed to stand. This, reversible Sol-Gel transformation is known as **thixotropy.** The softening behaviour of a marshy land under trading is due to thixotropic behaviour of bentonite clay present in such soils.

Elastic gel can **imbibe** water when placed in it and undergo swelling, non-elastic gels are incapable of doing so. This phenomenon is known as imbibition or swelling.

6.10 APPLICATIONS OF COLLOIDS

Most of the substances, we come across in our daily life, are colloids. The meal we eat, the clothes we wear, the wooden furniture we use, the houses we live in, the newspapers we read, are largely composed of colloids.

The applications of colloid chemistry are limitless. These can be divided mainly into two classes:

1. Natural applications
2. Technical applications

1. Natural Applications

(i) Blue colour of the sky: Colloidal particles scatter blue light. Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.

(ii) Fog, mist and rain: When a large mass of air, containing dust particles, is cooled below its dewpoint, the moisture from the air condenses on the surfaces of these particles forming fine droplets. These droplets being colloidal in nature continue to float in the air in the form of mist or fog.

Clouds are aerosols having small droplets of water suspended in air. On account of condensation in the upper atmosphere, the colloidal droplets of water grow bigger and bigger in size, till they come down in the form of rain. Sometimes, the rainfall occurs when two oppositively charged clouds meet.

It is possible to cause artificial rain by throwing electrified sand or spraying a sol carrying charge opposite to the one on clouds from an aeroplane.

(iii) Food articles: Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in one form or the other.

(iv) Blood: Blood is a colloidal solution of an albuminoid substance. The styptic action of alum and ferric chloride solution is due to coagulation of blood forming a clot which stops further bleeding.

(v) Soils: Fertile soils are colloidal in nature in which humus acts as a protective colloid. On account of colloidal nature, soils absorb moisture and nourishing materials.

(vi) Formation of delta: River water is colloidal solution of clay. Seawater contains a number of electrolytes. When river water meets the seawater, the electrolytes present in seawater coagulate the colloidal solution of clay which gets deposited with the formation of delta.

2. Technical Applications

(i) Electrical precipitation of smoke: Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust, etc., in air. The smoke, before it comes out from the chimney, is led through a chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles thus, settle down on the floor of the chamber. The precipitator is called **cottrell precipitator.**

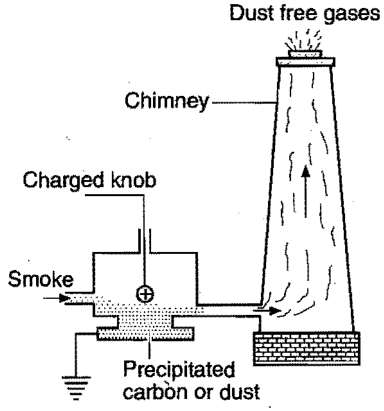


Fig. 6.14

(ii) Purification of drinking water: The water obtained from natural sources often contains bacteria and suspended impurities. Alum is added to such water so as to destroy the bacteria as well as to coagulate the suspended impurities and make water fit for drinking purposes.

(iii) Medicines: Most of the medicines in use are colloidal in nature. For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kala-azar. Colloidal gold is used for intramuscular injection. Milk of magnesia (an emulsion) is used for stomach disorders. Colloidal medicines are more effective because these are easily assimilated.

(iv) Tanning: Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin, which contains negatively charged colloidal particles, mutual coagulation takes place, which results in the hardening of leather. The process is termed as **tanning.** Chromium salts have also been used in place of tannin.

(v) Cleansing action of soaps and detergents: Already described in section 6.8.

(vi) Photographic plates and films: The photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

(vii) Rubber industry: Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

(viii) Industrial products: Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal solutions. Asphalt emulsion is used in road construction.

(ix) Disinfectants: The disinfectants such as dettol and lysol give emulsion of oil in water type when mixed with water.

(x) In metallurgy: Sulphide ores are concentrated by froth-flotation process. In this process; pulverised ore is treated with emulsion of pine oil.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. **Crystalloids and colloids:** Thomas Graham classified the soluble substances into two categories; crystalloids and colloids. Crystalloids are the substances which in solution diffuse readily through animal or vegetable membranes, *e.g.*, urea, sugar, salt and other crystalline compounds. Colloids (Greek word, *Kolla*, meaning glue-like) are the substances which in solution diffuse very slowly or do not diffuse through animal or vegetable membranes, *e.g.*, gelatin, glue, silicic acid, etc. It was soon realised that many of the crystalloids can be converted into colloidal form by suitable means. Thus, colloid is a state of matter like solid, liquid or gas in which any substance can be brought by suitable means.

2. **Colloidal state:** It depends upon the particle size. It is regarded as an intermediate state between true solution and suspension. Colloidal state is a heterogeneous system in which solute particles of size ranging between 10 Å to 10^3 Å (10^{-7} to 10^{-5} cm) are dispersed into a solvent (dispersion medium).

3. **Types of colloidal solutions:** A colloidal solution consists two types, *viz.*, dispersed or internal or discontinuous phase and the dispersion or external or continuous phase. Depending on these phases eight types of colloidal solutions are possible. The important ones are:

(i) Solid dispersed in liquid—It is called sol.
(ii) Liquid dispersed in liquid—It is called emulsion.
(iii) Solid dispersed in gas—It is called aerosol.
(iv) Liquid dispersed in solid—It is called gel.

Lyophobic: Colloidal solutions in which dispersed phase has very little affinity for the dispersion medium. These are less stable and irreversible in nature. These are also called suspensoids.

Lyophilic: Colloidal solutions in which dispersed phase has great affinity for dispersion medium. These are stable and reversible in nature. These are also called emulsoids.

The colloidal solutions are also named according to the dispersion phase or medium used.

Dispersion medium	Name of colloidal solution
Water	Hydrosols
Alcohol	Alcosols
Benzene	Benzosols
Air	Aerosols

4. **Preparation of colloidal solutions:** To get a substance in colloidal form either the substance is broken down into fine particles of colloidal dimension or increasing the size of molecular particles as to form large aggregates. Thus, there are two ways by which lyophobic sols can be prepared.

(i) **Dispersion methods:** By splitting coarse aggregates of a substance into colloidal size. The dispersion methods include (a) mechanical dispersion (b) electro-dispersion (c) ultrasonic dispersion and (d) peptization. Peptization is a process of converting precipitates into colloidal state by adding small amount of suitable electrolyte.

(ii) **Condensation methods:** By aggregating very small particles into colloidal particles. These include (a) exchange of solvents (b) change of physical state and (c) chemical methods such as double decomposition, oxidation, reduction, hydrolysis, etc.

5. **Purification of colloidal solutions:** The process of reducing the impurities (electrolytes or soluble substances) to a requisite minimum in a colloidal solution is known as purification of colloidal solution.

Dialysis: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane. Animal membranes, parchment paper or cellophane sheet can be used for this purpose. The electrolytes can be readily removed by electrodialysis.

6. **Properties of colloidal solutions:** Colloidal solutions possess the following properties:

(i) **Heterogeneous character:** Consist of two phases.

(ii) **Visibility:** Particles are not visible to naked eye or with the help of microscope.

(iii) **Filtrability:** Particles pass through ordinary filter paper but not through parchment and other fine membranes.

(iv) **Surface tension and viscosity:** These are not very different from those of dispersion medium in the case of lyophobic sols. Lyophilic sols show higher viscosity and lower surface tension.

(v) **Colligative properties:** These properties are of small order as compared to true solutions at same concentrations.

(vi) **Tyndall effect:** It is the scattering of light from the surface of colloidal particles. A beam of light passed through a colloidal solution becomes visible as a bright streak. The illuminated path is called Tyndall cone.

(vii) **Brownian movement:** It is a ceaseless zig-zag motion of colloidal particles. Smaller the size and lesser the viscosity, faster is the motion. This is due to unbalanced bombardment of particles by the molecules of dispersion medium. It is somewhat responsible for stability of sols as the particles are not allowed to settle.

(viii) **Charge on colloidal particles:** Colloidal particles are electrically charged either carrying positive or negative charge. The origin of charge in most cases is due to preferential adsorption of ions on the surface. When an electric current is passed through the colloidal solution, the particles move towards a particular electrode. This is termed electrophoresis or cataphoresis. When only the medium is allowed to migrate and not the particles, the phenomenon is known as electroosmosis.

(ix) **Coagulation:** The phenomenon of change of colloidal state to suspension state is known as coagulation or precipitation or flocculation of colloidal solution. The coagulation is affected either by boiling of colloidal solution or by mutual action of colloidal sols (by mixing oppositely charged colloidal solutions) or by electrophoresis or by the addition of electrolytes.

The positive ion is effective in coagulating negative sol and *vice-versa*. The effectiveness of anion is governed by Hardy-Schulze rule. The rule states that the precipitating power of an ion depends upon its valency, *i.e.*, higher the valency of the ion greater is the precipitating power of the ion.

For negative sol, the power varies as $M^{3+} > M^{2+} > M^{+}$ and for positive sol the power varies as $[\mathrm{Fe(CN)_6}]^{4-} > \mathrm{SO_4^{2-}} > \mathrm{Cl^-}$.

Flocculating value: It is the minimum concentration in millimoles per litre of an electrolyte required to cause precipitation of a sol in 2 hours. The smaller is the flocculating power greater shall be the precipitating power of an ion.

(x) Protective action: Lyophilic sols are more stable than lyophobic sols. Thus, lyophilic colloids have the property of protecting lyophobic sols. When a lyophilic sol is added to lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect them from electrolytes. The protective power of lyophilic colloid is measured in terms of gold number. It is defined as the number of milligrams of a lyophilic colloid that will just prevent the precipitation of 10 mL of a gold sol on the addition of 1 mL of 10% NaCl solution. Lower the gold number, higher will be the protective power. Gelatin (Gold Number 0.005–0.01) and starch (Gold Number 25–50) have the maximum and minimum protective powers.

(xi) Coacervation: The loss of the stability of a lyophilic sol, quite often results in a separation of the system into two liquid phases. The separation of colloidal sol into two liquid phases is called **coacervation.**

7. Emulsion: It is a colloidal solution of a liquid in another immiscible liquid. Emulsions are usually of two types:

(a) Oil in water—Examples: Milk, cream, face cream, etc.
(b) Water in oil—Examples: Butter, cold cream, etc.

Emulsifying agent: It is added to an oil and water emulsion to increase its stability. It has polar and non-polar groups; the former attaches to water and the latter to oil and so binds them together in an emulsion. Soaps and detergents act as emulsifying agents.

8. Gel: It is a colloidal system in which liquid is dispersed in solid. Fruit-jellies, cheese, etc., are the examples of gels. Gels may be elastic or non-elastic according to their mechanical properties.

9. Applications of colloids: The applications can be divided mainly into two classes:

(i) Natural applications:

(a) Blue colour of the sky
(b) Fog, mist and rain
(c) Food articles
(d) Blood
(e) Soils
(f) Formation of delta

(ii) Technical applications:

(a) Electrical precipitation of smoke
(b) Purification of drinking water
(c) Medicines
(d) Tanning
(e) Cleansing action of soaps and detergents
(f) Photographic plates and films
(g) Rubber industry
(h) Paints, inks, plastics, lubricants, cement, etc.

Questions

1. Match the following:

[A]

(i) Gold number	(a) Coagulation
(ii) Lyophobic	(b) An emulsion
(iii) Butter	(c) Gold sol
(iv) Hardy-Schulze rule	(d) Gel
(v) Micelles	(e) Purification of colloidal solution
(vi) Purple of cassius	(f) Protective colloids
(vii) Cheese	(g) Solvent hating
(viii) Dialysis	(h) Associated colloids

[B]

(i) Brownian movement	(a) Aerosol
(ii) Water loving colloids	(b) Ultramicroscope
(iii) Liquid dispersed in gas	(c) Irreversible
(iv) Tyndall effect	(d) Sewage disposal
(v) Hydrophobic	(e) Smoke precipitator
(vi) Coagulation	(f) Hydrophilic
(vii) Electrophoresis	(g) Emulsifying agent
(viii) Soap	(h) Robert Brown

[C]

Property	**Statement**	**Application / discoverer**
(i) Tyndall effect	(a) Due to unequal bombardment by solvent molecules	1. Sewage disposal
(ii) Coagulation	(b) Surface area is large	2. Smoke precipitator
(iii) Brownian movement	(c) Movement of colloidal particles under the influence of electric field	3. Ultramicroscope
(iv) Adsorption	(d) Due to neutralisation of charge	4. Ice cream
(v) Electrophoresis	(e) Due to scattering of light	5. Colloidal medicines
(vi) Stability	(f) Addition of protective colloid	6. Robert Brown

2. **Matrix Matching Problems (For IIT Aspirants):**

[A] Match the colloids in Column-I with the classifications in Column-II:

Column-I	**Column-II**
(a) Rain cloud	(p) Gel
(b) Smoke	(q) Foam
(c) Butter	(r) Aerosol
(d) Soap sud	(s) Gas as dispersion medium

[B] Match the terms of List-I with those of List-II:

List-I	**List-II**
(a) Coagulation	(p) Scattering of light
(b) Peptization	(q) Purification of colloidal solution
(c) Tyndall effect	(r) Addition of electrolyte
(d) Dialysis	(s) Precipitation of colloidal solution

[C] Match the Column-I with Column-II and Column-III:

Column-I (Colloidal solution)	**Column-II (Dispersed phase)**	**Column-III (Dispersion medium)**
(a) Colloidion	(p) Water	(u) Ethanol
(b) Fog	(q) Cellulose	(v) Oil
(c) Butter	(r) Fat	(w) Air
(d) Milk	(s) Water	(x) Water

[D] Match the terms in Column-I with their explanations in Column-II:

Column-I	**Column-II**
(a) Cottrell precipitation	(p) Purification of blood
(b) Electrophoresis	(q) Precipitation of colloidal particles by addition of electrolytes
(c) Hemidialysis	(r) Removal of pollutants from industrial waste gases
(d) Coagulation	(s) Movement of charged colloidal particles towards oppositely charged electrode

[E] Match the terms in Column-I with those of Column-II:

Column-I	**Column-II**
(a) Emulsifier	(p) Colloidal sol. of graphite
(b) Colloidal electrolyte	(q) Detergent
(c) Oil dag	(r) Cellophane
(d) Xerogel	(s) Dextrin

[F] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Milk	(p) Aerosol
(b) Dust	(q) Emulsion
(c) Cheese	(r) Gel
(d) Froth	(s) Foam

3. The coagulation of 100 mL of a colloidal solution of gold is completely prevented by adding 0.25 g of starch to it before adding 10 mL of 10% NaCl solution. Find out the gold number of starch.

[**Hint:** 10 mL of 10% NaCl solution is added to 100 mL of solution of gold.

Thus, 1 mL of 10% NaCl solution has been added to 10 mL solution of gold.

Since, 100 mL gold solution required = 0.25 g starch

$$= 0.25 \times 10^3 \text{ mg starch}$$

$$\text{So, 10 mL gold solution required} = \frac{0.25 \times 10^3}{100} \times 10$$

$$= 25 \text{ mg starch}$$

Thus, by definition, the gold number of starch is 25.]

4. For the coagulation of 100 mL of arsenious sulphide solution, 5 mL of 1 M NaCl is required. What is the coagulating power of NaCl?

[**Hint:** Total volume after addition of 5 mL of 1 M NaCl solution = 105 mL

Thus, 105 × molarity of NaCl in colloidal solution $= 5 \times 1$

$$\text{Molarity of NaCl in colloidal solution} = \frac{5}{105}$$

$$\text{Concentration in millimole} = \frac{5}{105} \times 1000$$

$$= 47.6]$$

Answers

1. [A] (i—f); (ii—g); (iii—b); (iv—a); (v—h); (vi—c); (vii—d); (viii—e)

[B] (i—h); (ii—f); (iii—a); (iv—b); (v—c); (vi—d); (vii—e); (viii—g)

[C] (i—e—3); (ii—d—1); (iii—a—6); (iv—b—5); (v—c—2); (vi—f— 4).

2. [A] (a—r, s) (b—r, s) (c—p) (d—q)

[B] (a—r, s) (b—r) (c—p) (d—q)

[C] (a—q—u) (b—p—w) (c—p—v) (d—r—x)

[D] (a—r, s) (b—s) (c—p) (d—q)

[E] (a—q, s) (b—q) (c—p) (d—r)

[F] (a—q) (b—p) (c—r) (d—s)

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Difference between crystalloid and colloid is of:
(a) particle size (b) chemical composition
(c) ionic character (d) solubility

2. Substances whose solutions can readily diffuse through animal membranes are called:
(a) colloids (b) crystalloids
(c) electrolytes (d) non-electrolytes

3. Suspensions are:
(a) visible to naked eye
(b) invisible through microscope
(c) not visible by any means
(d) invisible under electron microscope

4. The size of the colloidal particles is in between: (CPMT 1990)
(a) $10^{-7} - 10^{-9}$ cm (b) $10^{-9} - 10^{-11}$ cm
(c) $10^{-5} - 10^{-7}$ cm (d) $10^{-2} - 10^{-3}$ cm

5. The size of a colloidal particle is: [PMT (MP) 1990]
(a) $> 0.1\,\mu$ (b) 1 $m\mu$ to $0.1\,\mu$
(c) $< 0.1\, m\mu$ (d) more than 3000 $m\mu$

6. If liquid is dispersed in solid medium, then this is called: (DCE 2009)
(a) sol (b) emulsion
(c) liquid aerosol (d) gel

7. Which of the following forms a colloidal solution in water? (CPMT 1990)
(a) NaCl (b) Glucose (c) $Ba(NO_3)_2$ (d) Starch

8. The number of phases present in colloidal solution is:
(a) 2 (b) 4 (c) 3 (d) 1

9. The colloidal system of a solid dispersed in liquid medium is called: [CET (J&K) 2007]
(a) aerosol (b) sol (c) gel (d) foam

10. When dispersed phase is liquid and dispersion medium is gas, the colloidal system is called:
(a) smoke (b) emulsion (c) cloud (d) gel

11. Water loving colloids are called as:
(a) hydrophilic (b) hydrophobic
(c) lyophobic (d) irreversible

12. An emulsion is a colloidal solution consisting of:
(a) two solids (b) two liquids
(c) two gases (d) one solid and one liquid

13. The colloidal solution of gelatin is known as:
(a) solvent loving (b) reversible
(c) hydrophilic (d) all of these

14. Sol is a type of colloid in which: [PET (Raj.) 2008]
(a) solid is dispersed in liquid
(b) liquid is dispersed in solid
(c) gas is dispersed in liquid
(d) solid is dispersed in solid

15. Butter is a colloid formed when:
(a) fat is dispersed in fat
(b) fat is dispersed in water
(c) water is dispersed in fat
(d) suspension of casein in water

16. Milk is: **[PMT (MP) 2007; C.G. PET 2008]**
(a) fat dispersed in water (b) water dispersed in fat
(c) water dispersed in oil (d) fat dispersed in fat

17. Smoke is an example of: **(CPMT 1991)**
(a) solid dispersed in solid (b) solid dispersed in gas
(c) solid dispersed in liquid (d) gas dispersed in solid

18. Fog is a colloidal solution of: **[PMT (MP) 1991; CET (J&K) 2005; DUMET 2009]**
(a) gaseous particles dispersed in gas
(b) gaseous particles dispersed in liquids
(c) liquid dispersed in gas
(d) solid dispersed in liquid

19. Lyophobic colloids are:
(a) reversible (b) irreversible
(c) water loving (d) solvent loving

20. Sulphur sol contains:
(a) discrete sulphur atoms
(b) discrete sulphur molecules
(c) water dispersed in solid sulphur
(d) large aggregates of sulphur molecules

21. Which of the following is not a colloidal system?
(a) Bread (b) Muddy water
(c) Concrete (d) Sugar in water

22. Peptization denotes: **(MHT-CET 2007)**
(a) digestion of food
(b) hydrolysis of proteins
(c) breaking and dispersion into colloidal state
(d) precipitation of solid from colloidal dimension

23. Colloids are purified by: **(CPMT 1990)**
(a) Brownian motion (b) precipitation
(c) dialysis (d) filtration

24. The separation of colloidal particles from those of molecular dimension is known as:
(a) dialysis (b) electrophoresis
(c) peptization (d) pyrolysis

25. Bredig's arc method is used for the preparation of colloidal solution of:
(a) metals like silver, gold, etc.
(b) organic compounds
(c) two liquids
(d) inorganic compounds

26. Which of the following reactions is not used for the preparation of a colloidal solution?
(a) $2AuCl_3 + 3SnCl_2 \longrightarrow 3SnCl_4 + 2Au$
(b) $FeCl_3 + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$
(c) $2Mg + CO_2 \longrightarrow 2MgO + C$
(d) $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$

27. When freshly precipitated $Fe(OH)_3$ is boiled with water in the presence of few drops of dil. HCl, a hydrated ferric oxide sol is obtained. This method is termed:
(a) dialysis (b) peptization
(c) ultrafiltration (d) electro-dispersion

28. Which of the following substances gives a positively charged sol? **[PMT (MP) 1990]**
(a) Gold (b) Arsenious sulphide
(c) Starch (d) Ferric hydroxide

29. The kinetic activity of colloidal particles in dispersion medium is known as:
(a) electro-osmosis (b) cataphoresis
(c) Brownian movement (d) electrophoresis

30. Brownian movement was discovered by:
(a) Robert Brown (b) Zsigmondy
(c) Hardy-Schulze (d) Graham

31. The Brownian movement is due to:
(a) temperature fluctuations within the liquid phase
(b) attraction and repulsion between charges on colloidal particles
(c) impact of molecules of the dispersion medium on colloidal particles
(d) convection currents

32. Tyndall phenomenon is shown by:
(a) dilute solution (b) colloidal solution
(c) suspension (d) true solution

33. The sky looks blue due to:
(a) dispersion effect (b) reflection
(c) transmission (d) scattering

34. Tyndall effect in colloidal solution is due to: **(MHT-CET 2007)**
(a) absorption of light
(b) scattering of light
(c) reflection of light
(d) presence of electrically charged particles

35. The migration of colloidal particles under the influence of an electric field is known as:
(a) electro-osmosis (b) Brownian movement
(c) cataphoresis (d) dialysis

36. The stability of lyophilic colloids is due to: **[PMT (MP) 1990]**
(a) charge on their particles
(b) large size of their particles
(c) smaller size of their particles
(d) a layer of medium of dispersion on their particles

37. 'Greater the valency, the higher is the coagulating power of ion.' This rule was introduced by:
(a) Hardy-Schulze (b) Graham
(c) Kossel and Lewis (d) Faraday

38. Bleeding is stopped by the application of ferric chloride. This is because:
(a) the blood starts flowing in opposite direction
(b) the ferric chloride seals the blood vessel
(c) the blood reacts and forms a solid which seals the blood vessel
(d) the blood is coagulated and thus, the blood vessel is sealed

39. Which property of colloidal solution is used to determine the nature of charge on the particles?
(a) Sedimentation (b) Electrophoresis
(c) Dialysis (d) Ultrafiltration

40. When excess of electrolyte is added to a colloid it: **(CBSE 1990)**
(a) coagulates (b) gets diluted
(c) precipitates (d) does not change

41. The colloidal solutions of gold prepared by different methods have different colours. This is due to: **(MLNR 1993)**
(a) difference in size of colloidal particles
(b) different concentration of gold
(c) presence of different types of foreign particles
(d) the variable valency of gold

42. The capacity of an ion to coagulate a colloidal solution depends on:
(a) its shape
(b) the amount of its charge
(c) the sign of the charge
(d) both, the amount and the sign of the charge

43. Lyophilic sols are more stable than lyophobic sols because: **(AFMC 1998)**
(a) the colloidal particles have positive charge
(b) the colloidal particles have negative charge
(c) the colloidal particles are solvated
(d) there are strong electrostatic repulsions

44. Which of the following will have the highest coagulating power for As_2S_3 colloid?
(a) PO_4^{3-} (b) Al^{3+} (c) SO_4^{2-} (d) Na^+

45. A negatively charged suspension of clay in water will need for precipitation the minimum amount of:
(a) aluminium chloride (b) potassium sulphate
(c) sodium hydroxide (d) hydrochloric acid

46. Which of the following electrolytes is least effective in causing flocculation of ferric hydroxide sol? **(MLNR 1991)**
(a) $K_3Fe(CN)_6$ (b) K_2CrO_4
(c) KBr (d) K_2SO_4

47. Fe^{3+} ions coagulate blood. This show blood contains colloidal particles bearing:
(a) negative charge
(b) positive charge
(c) no charge
(d) either positive or negative charge

48. Gold number is a measure of: **(CPMT 1991)**
(a) stability of colloidal system
(b) coagulating power of a colloid
(c) size of colloidal particles
(d) efficiency of the protective colloid

49. Gold number is a measure of: **[PET (MP) 2004]**
(a) the amount of gold present in the colloidal solution
(b) the amount of gold required to break the colloid
(c) the amount of gold required to protect the colloid
(d) none of the above

50. Which of the following methods is used for destruction of a colloidal solution?
(a) Condensation
(b) Dialysis
(c) Diffusion through animal membrane
(d) Addition of an electrolyte

51. Which of the following is not a property of hydrophilic sols?
(a) High concentration of dispersed phase can be easily attained
(b) Coagulation is reversible
(c) Viscosity and surface tension are nearly as that of water
(d) The charge on the particles depends on the pH value of the medium; it may be positive, negative or even zero

52. Gelatin is added in manufacture of ice cream in order to:
(a) prevent formation of a colloid
(b) stabilise the colloid and prevent crystallisation
(c) cause the mixture to solidify easily
(d) improve flavour

53. Which one of the following will act as best protective colloid?
(a) Gelatin (Gold No. 0.005)
(b) Starch (Gold No. 25)
(c) Gum arabic (Gold No. 0.15)
(d) Egg albumin (Gold No. 0.08)

54. Gold number is a measure of the:
(a) protective action by a lyophilic colloid on lyophobic colloid
(b) protective action by a lyophobic colloid on lyophilic colloid
(c) number of mg of gold in a standard red gold sol
(d) none of the above

55. On addition of one mL solution of 10% NaCl to 10 mL gold sol in presence of 0.025 g of starch, the coagulation is just prevented. The gold number of starch is:
(a) 25.0 (b) 2.5 (c) 0.25 (d) 0.025

56. The stability of lyophobic sols is due to:
(a) Brownian motion only
(b) electric charge only
(c) both Brownian motion and electric charge
(d) particle size

57. Which one of the following colloidal solutions is positive sol.? **(CPMT 1992)**
(a) Blood
(b) Clay soil
(c) Smoke
(d) Gelatin in strongly acidic solution

58. All colloidal solutions show:
(a) very high osmotic pressure
(b) high osmotic pressure
(c) low osmotic pressure
(d) no osmotic pressure

59. Which of the following is associated colloid?
(a) Soap (b) Detergent
(c) Both (d) None of these

60. Which of the following is an emulsifier?
(a) Oil (b) Soap (c) Solvent (d) KCl

61. An emulsifier is a substance which:
(a) helps in the dispersion of liquid in liquid
(b) stabilises the emulsion
(c) coagulates the emulsion
(d) purifies the emulsion

62. The gold numbers of some colloidal solutions are given below:

Colloidal solution	Gold number
A	0.01
B	2.5
C	20

The projective powers of these colloidal solutions follow the order: **[CET (J&K) 2006; AIEEE 2008]**

(a) $C > B > A$ (b) $A > B > C$
(c) $A = B = C$ (d) $B > A > C$

63. Dialyser is a name given to:

(a) lyophilic colloids
(b) lyophobic colloids
(c) to a membrane which can separate colloids from the solution
(d) none of the above

64. Flocculation value is expressed in terms of:

(a) millimole per litre (b) mol per litre
(c) gram per litre (d) mol per millilitre

65. Which of the following has minimum flocculation value? **[PET (MP) 1990]**

(a) Pb^{2+} (b) Pb^{4+} (c) Sr^{2+} (d) Na^+

66. The charge of As_2S_3 sol is due to the absorbed:

(a) H^+ (b) OH^- (c) O^{2-} (d) S^{2-}

67. Which of the following has maximum flocculation value?

(a) $[Fe(CN)_6]^{4-}$ (b) Cl^-
(c) SO_4^{2-} (d) PO_4^{3-}

68. Above critical micelle concentration, particles get: **[AMU (Medical) 2006]**

(a) associated (b) dissociated
(c) both (a) and (b) (d) none of these

69. Continuous phase contains dispersed phase throughout. Example is: **(VITEEE 2008)**

(a) water in milk (b) fat in milk
(c) water droplets in mist (d) oil in water

70. The movement of dispersion medium in an electric field when the dispersed particles are prevented from moving is called:

(a) cataphoresis (b) electrophoresis
(c) electro-osmosis (d) Brownian movement

71. To coagulate gelatin sol, which of the following is most effective?

(a) NaCl (b) Na_3PO_4 (c) $AlCl_3$ (d) Alcohol

72. The emulsifying agent in milk is: **[EAMCET (Med.) 2010]**

(a) lactic acid (b) fat
(c) lactose (d) casein

73. Colloidal solutions of metals like Cu, Ag, Au and Pt are generally prepared by using:

(a) peptization (b) Bredig's arc method
(c) exchange of solvent (d) oxidation method

74. Silver iodide is used for producing artificial rain because AgI:

(a) has crystal structure similar to ice
(b) is easy to spray at high altitudes
(c) is easy to synthesise
(d) is soluble in water

75. The minimum concentration of an electrolyte required to cause coagulation of a sol. is called:

(a) flocculation value (b) gold number
(c) protective value (d) coagulation number

76. Purple of cassius is:

(a) colloidal solution of silver
(b) colloidal solution of gold
(c) colloidal solution of platinum
(d) oxy acids of gold

77. Which type of molecules form micelles?

(a) Polar molecules (b) Non-polar molecules
(c) Surfactant molecules (d) Any of these

78. The name aquadag is given to the colloidal solution of:

(a) copper in water (b) platinum in water
(c) gold in water (d) graphite in water

79. A liquid is found to scatter a beam of light but leaves no residue when passed through the filter paper. The liquid can be described as: **(AIIMS 1993)**

(a) a suspension (b) oil
(c) a colloidal sol. (d) true solution

80. Point out the false statement: **[CET (Punjab) 1991]**

(a) colloidal sols. are homogeneous
(b) colloidal sols. carry +ve or –ve charge
(c) colloidal sols. show Tyndall effect
(d) the size of colloidal particles ranges between 10–2000 Å

81. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called:

(a) colloidal potential (b) zeta potential
(c) electrostatic potential (d) none of these

82. An example of micelle is:

(a) As_2O_3 sol.
(b) ruby glass
(c) Na_2CO_3 solution
(d) sodium stearate concentrated solution

83. Surface tension of lyophilic sols. is: **[PMT (MP) 1992]**

(a) lower than H_2O (b) more than H_2O
(c) equal to H_2O (d) none of these

84. Which is not shown by sols.? **[PMT (MP) 1992]**

(a) Adsorption (b) Tyndall effect
(c) Flocculation (d) Paramagnetism

85. An example of solid-solid system is:

(a) smoke (b) coke
(c) synthetic gems (d) pumice stone

86. Detergent action of synthetic detergents is due to their:

(a) interfacial area (b) high molecular weight
(c) ionisation (d) emulsifying properties

87. Blood contains:

(a) positively charged particles
(b) negatively charged particles
(c) neutral particles
(d) negatively as well as positively charged colloids

88. A colloidal solution always has at least: **(CPMT 1993)**

(a) one-phase (b) more than two-phases
(c) a true solution (d) two phases

89. Silica gel is commonly used as:

(a) wetting agent (b) drying agent
(c) solvent (d) catalyst

90. Which is not a colloidal solution of gas in liquid?
(a) Froth (b) Foams with tiny bubbles
(c) Mist (d) Whipped cream

91. Fog is a colloidal solution of: **[MLNR 1995; PMT (MP) 1991]**
(a) liquid particles dispersed in gas
(b) gaseous particles dispersed in liquid
(c) solid particles dispersed in liquid
(d) solid particles dispersed in gas

92. Emulsions of polyvinyl acetate are used in:
(a) polishes (b) latex paints
(c) fireworks (d) rayons

93. When white light is passed through a colloidal solution containing fine suspended particles of gold, then the scattering light seen in a direction different from that of incident light is:
(a) yellow coloured (b) blue coloured
(c) green coloured (d) red coloured

94. When a sulphur sol is evaporated, solid sulphur is left. On mixing with water no colloidal sol is formed. The sulphur sol is:
(a) hydrophilic (b) hydrophobic
(c) reversible (d) lyophilic

95. Tails of comets are visible due to:
(a) Tyndall effect (b) reflection
(c) Brownian movement (d) none of these

96. Milk is an example of: **[CPMT 1995; PET (MP) 2004; CET (J&K) 2004]**
(a) fat dispersed in water
(b) water dispersed in fat
(c) water dispersed in oil
(d) fat dispersed in fat

97. Smog is an example of:
(a) ice dispersed in air
(b) water dispersed in air
(c) smoke dispersed in air
(d) smoke and water dispersed in air

98. Peptization denotes: **[ISM (Dhanbad) 1994]**
(a) digestion of food
(b) hydrolysis of proteins
(c) breaking of dispersion into colloidal state
(d) precipitation of a solid from colloidal state

99. Whipped cream is an example of:

	Dispersion Medium	**Dispersed Phase**
(a)	Liquid	Gas
(b)	Liquid	Liquid
(c)	Liquid	Solid
(d)	Gas	Liquid

100. Cottrell precipitator acts on which of the following principle?
(a) Hardy-Schulze rule
(b) Distribution law
(c) Le Chatelier's principle
(d) Neutralization of charge on the colloidal particles

101. CMC (critical micelle concentration) is:
(a) concentration at which micelles are destroyed
(b) concentration at which micelle formation starts
(c) concentration of electrolyte added to destroy the micelles
(d) concentration of micelles at room temperature

102. Cod liver oil is: **(CPMT 1997)**
(a) fat dispersed in water (b) water dispersed in fat
(c) water dispersed in oil (d) fat dispersed in fat

103. Which is not lyophilic colloid? **[PMT (MP) 1998]**
(a) Milk (b) Gum (c) Fog (d) Blood

104. At the critical micelle concentration, the surfactant molecules: **(CBSE 1998)**
(a) decompose (b) dissociate
(c) associate (d) become completely soluble

105. Which of the following ions can cause coagulation of proteins? **(KCET 2000)**
(a) Ag^+ (b) Na^+ (c) Mg^{2+} (d) Ca^{2+}

106. In Brownian movement or motion the paths of the particles are: **(KMEE 2000)**
(a) linear (b) zig-zag
(c) uncertain (d) curved

107. Which is used for ending charge on colloidal solutions? **(CBSE 2000)**
(a) Electrons (b) Electrolysis
(c) Positively charged ions (d) Compounds

108. Cloud or fog is a colloidal system in which the dispersed phase and the dispersion medium are: **(KCET 2000)**
(a) gas, liquid (b) liquid, gas
(c) liquid, liquid (d) solid, solid

109. The electrolyte which has the least effect in the coagulation of $Fe(OH)_3$ sol is: **[KCET 2008]**
(a) potassium carbonate (b) sodium sulphate
(c) potassium ferrocyanide (d) potassium iodide

110. Blood may be purified by: **[PMT (MP) 2000]**
(a) dialysis (b) electro-osmosis
(c) coagulation (d) filtration

111. Gold number was given by:
(a) Ostwald (b) Zsigmondy
(c) William and Chang (d) Langmuir

112. The diameter of colloidal particle ranges from: **(KCET 2004)**
(a) 10^{-9} m to 10^{-6} m (b) 10^{-9} m to 10^{-12} m
(c) 10^3 m to 10^{-3} m (d) 10^{-3} m to 10^{-6} m

113. The Tyndall effect is not observed in:
(a) suspensions (b) emulsions
(c) colloidal solutions (d) true solutions

114. Which one is example of Micelle's system?
(a) Soap + water (b) Rubber + benzene
(c) Protein + water (d) None of these

115. Sedimentation potential is the reverse of:
(a) electro-osmosis (b) electrophoresis
(c) electrokinetic potential (d) Dorn potential

116. Smoke has generally blue tinge. It is due to:
(a) scattering (b) coagulation
(c) Brownian motion (d) electrophoresis

117. On adding $AgNO_3$ solution to KI solution, a negatively charged colloidal sol will be formed in which of the following conditions?

(a) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.1 M KI
(b) 100 mL of 0.1 M $AgNO_3$ + 50 mL of 0.2 M KI
(c) 100 mL of 0.2 M $AgNO_3$ + 100 mL of 0.1 M KI
(d) 100 mL of 0.1 M $AgNO_3$ + 100 mL of 0.15 M KI

118. Peptization of SnO_2 by NaOH gives:
(a) $[SnO_2]SnO_3^{2-} : 2Na^+$ (b) $[SnO_2]Sn^{4+} : O^{2-}$
(c) $[SnO_2]Na^+ : OH^-$ (d) $[SnO_2]Sn^{4+} : OH^-$

119. Alum helps in purifying water by: (AIEEE 2002)
(a) forming Si complex with clay particles
(b) sulphate part which combines with the dirt and remove it
(c) aluminium which coagulates the mud particles
(d) making the mud water soluble

120. Surface tension of lyophilic sols is: [PMT (MP) 2002]
(a) lower than that of H_2O (b) equal to that of H_2O
(c) more than that of H_2O (d) none of these

121. Arsenic sulphide is negative sol. The reagent with least precipitating power is: [PMT (Manipal) 2002]
(a) $AlCl_3$ (b) NaCl (c) CaF_2 (d) glucose

122. Which one of the following is correctly matched? [CEE (Tamil Nadu) 2002]
(a) Emulsion-curd (b) Foam-mist
(c) Aerosol-smoke (d) Solid sol-cake

123. When H_2S gas is passed through nitric acid, the product is: [CEE (Kerala) 2002]
(a) rhombic sulphur (b) prismatic sulphur
(c) amorphous sulphur (d) monoclinic sulphur
(e) plastic sulphur

124. Tyndall effect is shown by: [CECE (Bihar) Pre 2004]
(a) precipitate (b) sol
(c) plasma (d) solution

125. On addition of one mL of 10% NaCl solution to 10 mL gold sol in presence of 0.25 gm of starch, the coagulation is just prevented, starch has gold number: [PMT (MP) 2004]
(a) 0.25 (b) 0.025 (c) 2.5 (d) none of these

126. Which of the following forms cationic micelles above certain concentration? [CBSE (PMT) 2004]
(a) Sodium dodecyl sulphate
(b) Sodium acetate
(c) Urea
(d) Cetyltrimethyl ammonium bromide

127. The smog is essentially caused by the presence of: (AIEEE 2004)
(a) O_2 and O_3
(b) O_2 and N_2
(c) oxides of sulphur and nitrogen
(d) O_3 and N_2

128. Which one of the following is most effective in causing the coagulation of an As_2S_3 sol? (EAMCET 2009)
(a) KCl (b) $AlCl_3$
(c) $MgSO_4$ (d) $K_3[Fe(CN)_6]$

129. The fresh precipitate can be transformed in colloidal solution by: [CET (J&K) 2004]
(a) peptization (b) coagulation
(c) diffusion (d) none of these

130. Potassium stearate is obtained by the saponification of an oil or a fat. It has formula $CH_3-(CH_2)_{16}-COO^- K^+$. The molecule has a lyophobic end (CH_3—) and a lypophilic end $COO^- K^+$. Potassium stearate is an example for: [PET (Kerala) 2005]
(a) lyophobic colloid
(b) lyophilic colloid
(c) multimolecular colloid
(d) macromolecular colloid
(e) associated colloid or micelle

131. Which one of the following forms micelles in aqueous solution above certain concentration? [CBSE (PMT) 2005]
(a) Dodecyl trimethyl ammonium chloride
(b) Glucose
(c) Urea
(d) Pyridinium chloride

132. Muddy water can be purified through coagulation using: [CET (J&K) 2005]
(a) common salt (b) alums
(c) sand (d) lime

133. The disperse phase in colloidal iron(III) hydroxide and colloidal gold is positively and negatively charged respectively. Which of the following is not correct? (AIEEE 2005)
(a) Magnesium chloride solution coagulates the gold sol more readily than iron(III) hydroxide sol
(b) Sodium sulphate solution causes coagulation in both sols
(c) Mixing of the sols has no effect
(d) Coagulation in both sols can be brought about by electrophoresis

134. An emulsifier is a substance which: (AIEEE 2005)
(a) stabilises the emulsion
(b) homogenises the emulsion
(c) coagulates the emulsion
(d) accelerates the dispersion of liquid in liquid

135. Gold number is associated with: [BHU (Mains) 2007; AMU (Engg.) 2010]
(a) electrophoresis
(b) purple of cassius
(c) protective colloid
(d) amount of pure gold

136. Which one of the following is a false statement? [PMT (Kerala) 2007]
(a) Cell fluid is an example of sol
(b) Butter is an example of gel
(c) Hair cream is an example of emulsion
(d) Whipped cream is an example of foam
(e) Cheese is an example of emulsion

137. The presence of electric charge on colloidal particles is indicated by the property, called: [CET (J&K) 2007]
(a) dialysis (b) solubility
(c) electrophoresis (d) osmosis

138. Which of the following properties are characteristic of lyophobic sols? (SCRA 2007)
1. Low viscosity, 2. High viscosity, 3. Reversibility and
4. Coagulation by electrolytes at low concentration

Select the correct answer using the codes given below:
(a) 2, 3 and 4 (b) 2 and 3 only
(c) 1 and 4 only (d) 1 and 3 only

139. In an electrical field, the particles of a colloidal system move towards cathode. The coagulation of the same sol is studied using K_2SO_4(I), Na_3PO_4(II), $K_4[Fe(CN)_6]$ (III) and NaCl (IV). Their coagulating power should be : **[PMT(Kerala) 2008]**
(a) (I) > (II) > (III) > (IV) (b) (III) > (II) > (I) > (IV)
(c) (III) > (I) > (II) > (IV) (d) (IV) > (III) > (I) > (II)
(e) (IV) > (I) > (II) > (III)

140. Cetyl trimethyl ammonium chloride is which type of detergent ? **[CET (Gujarat) 2008]**
(a) Cationic (b) Anionic (c) Biosoft (d) Non-ionic

141. The effective ion used in clarification of water is: **(KCET 2008)**
(a) Al^{3+} (b) Ca^{2+} (c) SO_4^{2-} (d) PO_4^{3-}

142. The number of moles of lead nitrate needed to coagulate 2 mole of colloidal $[Ag\,I]I^-$ is : **[PET (Kerala) 2008]**
(a) 2 (b) 1 (c) $\frac{1}{2}$ (d) $\frac{2}{3}$ (e) $\frac{5}{2}$
[**Hint :** $2[Ag\,I]I^- + Pb^{2+} \longrightarrow PbI_2 + 2AgI$
Thus, one mole of $Pb(NO_3)_2$ is required to coagulate 2 mole of $[AgI]\,I^-$]

143. Among the electrolytes $Na_2SO_4, CaCl_2, Al_2(SO_4)_3$ and NH_4Cl, the most effective coagulating agent for Sb_2S_3 sol is: **(IIT 2009)**
(a) Na_2SO_4 (b) $CaCl_2$
(c) $Al_2(SO_4)_3$ (d) NH_4Cl
[**Hint :** Sb_2S_3 sol is negative colloid, therefore, $Al_2(SO_4)_3$ will be most effective coagulating agent.

$$\xrightarrow[\text{Decreasing coagulating power for negatively charged colloidal particles of } Sb_2S_3]{Al^{3+} > Ca^{2+} > Na^+ > NH_4^+}\ ]$$

144. A micelle formed during the cleansing action of soap is : **[EAMCET (Engg.) 2010]**
(a) a discrete particle of soap
(b) aggregated particles of soap and dirt
(c) a discrete particle of dust
(d) an aggregated particle of dust and water

145. The dispersed phase and dispersion medium in soap lather are respectively : **[PET (Kerala) 2010]**
(a) gas and liquid (b) liquid and gas
(c) solid and gas (d) solid and liquid

Set-2: The questions given below may have more than one correct answers

1. Lysione is not used as:
(a) disinfectant (b) germ killer
(c) treating eye disease (d) anti-cancer drug

2. Which of the following are macromolecular colloids?
(a) Starch (b) Soap (c) Detergent (d) Cellulose

3. Multimolecular colloids are present in:
(a) sol of sulphur (b) sol of proteins
(c) sol of gold (d) soap solution

4. Methods used for the preparation of colloidal solutions are:
(a) peptization (b) hydrolysis
(c) ultrasonic dispersion (d) coagulation

5. Isoelectric point is the pH at which colloidal particles:
(a) coagulate
(b) become electrically neutral
(c) can move toward either electrode
(d) none of the above

6. Consider the following statements for micelles, which is/are correct?
(a) At critical micelle concentration, several properties of solution of surfactants such as molar conductivity, surface tension and osmotic pressure change
(b) Micelles from ionic surfactants can be formed only above a certain temperature called the Kraft temperature
(c) Micelle formation is exothermic
(d) Micelles are associated colloids

7. Which of the following are negative colloids?
(a) $Fe(OH)_3$ sol (b) As_2S_3 sol
(c) Blood (d) Gold sol

8. Which of the following are examples of aerosols?
(a) Whipped cream (b) Cloud
(c) Fog (d) Soap lather

9. Tyndall effect is applicable when:
(a) the diameter of the dispersed particles is not much smaller than the wavelength of the light used
(b) the diameter of the dispersed particles is much smaller than the wavelength of the light used
(c) the refractive indices of the dispersed phase and the dispersion medium must be same
(d) the refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions you are required to choose any one of the following four options:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) Colloidal silver iodide is prepared by adding silver nitrate in slight excess to potassium iodide solution. When subjected to an electric field, the colloidal particles migrate to the anode.
(R) Colloidal particles absorb ions and thus become electrically charged.

2. (A) Lyophilic colloids such as starch, gelatin, etc., act as protective colloids.
(R) Protective power of lyophilic colloids is expressed in terms of gold number.

3. (A) True solutions do not exhibit Tyndall effect.
(R) In true solutions, size of solute particles is much smaller than the wavelength of light used.

4. (A) The micelle formed by sodium stearate in water has —COO^- groups at the surface.
(R) Surface tension of water is reduced by the addition of stearate. **(AIIMS 2003)**

5. (A) Lyophilic sols. are more stable than lyophobic sols.
(R) Lyophilic sols. are highly hydrated in the solution.

6. (A) Colloidal sol. of $Fe(OH)_3$ formed by peptization carries positive charge.
(R) During the formation of positively charged colloidal particles of $Fe(OH)_3$, the electrons are lost by the colloidal particles of $Fe(OH)_3$.

7. (A) Colloidal solutions are purified by dialysis.
(R) In the process of dialysis, colloidal particles pass through parchment paper.

8. (A) Fe^{3+} can be used for coagulation of As_2S_3 sol.
(R) Fe^{3+} reacts with As_2S_3 to give Fe_2S_3. **(AIIMS 2006)**

9. (A) Fat is digested in the intestine by emulsification.
(R) Bile salts stabilize the emulsion so formed.

10. (A) NH_3Cl and *R*COONa are colloidal electrolyte.
(R) The substances which behave as electrolyte below a certain concentration limit, beyond this limit colloidal sol. is formed, are called colloidal electrolyte.

11. (A) Sulphide ores are concentrated by froth flotation process.
(R) Pine oil forms emulsion in water.

12. (A) The conversion of fresh precipitate to colloidal state is called peptization.
(R) It is caused by addition of common ions. **(AIIMS 2007)**

13. (A) Surfactant molecules form micelles above the critical micelle concentration (CMC).
(R) The conductance of solution of surfactant molecules decreases sharply at the (CMC).

14. (A) Soap and detergent are macro-molecular colloids.
(R) Soap and detergent are molecular of large size.

15. (A) Gold sol is hydrophobic and multimolecular.
(R) Gold sol is prepared by Bredig's arc method.

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (a) **2.** (b) **3.** (a) **4.** (c) **5.** (b) **6.** (d) **7.** (d) **8.** (a)
9. (b) **10.** (c) **11.** (a) **12.** (b) **13.** (d) **14.** (a) **15.** (c) **16.** (a)
17. (b) **18.** (c) **19.** (b) **20.** (d) **21.** (d) **22.** (c) **23.** (c) **24.** (a)
25. (a) **26.** (c) **27.** (b) **28.** (d) **29.** (c) **30.** (a) **31.** (c) **32.** (b)
33. (d) **34.** (b) **35.** (c) **36.** (d) **37.** (a) **38.** (d) **39.** (b) **40.** (a)
41. (a) **42.** (d) **43.** (c) **44.** (b) **45.** (a) **46.** (c) **47.** (a) **48.** (d)
49. (d) **50.** (d) **51.** (c) **52.** (b) **53.** (a) **54.** (a) **55.** (a) **56.** (c)
57. (d) **58.** (c) **59.** (c) **60.** (b) **61.** (b) **62.** (b) **63.** (c) **64.** (a)
65. (b) **66.** (d) **67.** (b) **68.** (a) **69.** (a) **70.** (c) **71.** (d) **72.** (d)
73. (b) **74.** (a) **75.** (a) **76.** (b) **77.** (c) **78.** (d) **79.** (c) **80.** (a)
81. (b) **82.** (d) **83.** (a) **84.** (d) **85.** (c) **86.** (d) **87.** (b) **88.** (d)
89. (b) **90.** (c) **91.** (a) **92.** (b) **93.** (b) **94.** (b) **95.** (a) **96.** (a)
97. (d) **98.** (c) **99.** (a) **100.** (c) **101.** (b) **102.** (c) **103.** (c) **104.** (c)
105. (a) **106.** (b) **107.** (b) **108.** (b) **109.** (c) **110.** (a) **111.** (b) **112.** (a)
113. (d) **114.** (a) **115.** (b) **116.** (a) **117.** (d) **118.** (a) **119.** (c) **120.** (a)
121. (d) **122.** (c) **123.** (c) **124.** (b) **125.** (d) **126.** (d) **127.** (c) **128.** (b)
129. (a) **130.** (e) **131.** (a) **132.** (b) **133.** (c) **134.** (a) **135.** (c) **136.** (e)
137. (c) **138.** (c) **139.** (b) **140.** (a) **141.** (a) **142.** (b) **143.** (c) **144.** (b)
145. (a)

- **Set–2**

1. (b, c, d) **2.** (a, d) **3.** (a, c) **4.** (a, b, c) **5.** (a, b, c) **6.** (a, b, d) **7.** (b, c, d) **8.** (b, c)
9. (a, d)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (d) **2.** (b) **3.** (a) **4.** (a) **5.** (a) **6.** (c) **7.** (c) **8.** (c)
9. (a) **10.** (a) **11.** (a) **12.** (b) **13.** (b) **14.** (d) **15.** (b)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain single correct option:

1. Which of the following statements are correct?
   1. On the application of an electric field, the particles of lyophobic sol may move in either direction or not move at all.
   2. Surface tension of lyophobic sols is similar to that of the dispersion medium.
   3. Electro-osmosis is the movement of the particles of dispersion medium under the influence of an electric field.

   Select the correct answer using codes given below:

   Codes:

   (a) 1, 2 and 3 (b) 1 and 3 (c) 2 and 3 (d) 1 and 2

2. Which of the following statements are correct?
   1. The smaller the gold number of lyophobic colloid, the larger will be its protective power.
   2. Lyophilic sols, in contrast to lyophobic sols are easily coagulated on addition of small amounts of electrolytes.
   3. Ferric chloride solution is used to stop bleeding from a fresh cut because it coagulates the blood.
   4. The flocculation value of arsenious sulphide sol is independent of the anion of the coagulating electrolyte.

   Codes:

   (a) 1, 2 and 3 (b) 1, 3 and 4 (c) 2, 3 and 4 (d) 1, 2 and 4

3. Match the List-I with List-II and select the correct answer using the codes given below the lists:

List-I	**List-II**
A. Coagulation	1. Scattering
B. Lyophilization	2. Washing of precipitates
C. Peptization	3. Purification of colloids
D. Tyndall effect	4. Electrolyte

Codes:

	A	B	C	D
(a)	4	—	2	1
(b)	2	—	3	4
(c)	—	1	2	4
(d)	4	3	1	—

4. The flocculating power of the given ions for the specified colloidal sols will be such that:

	Arsenic sulphide sol	**Ferric hydroxide sol**
(a)	$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$	$Al^{3+} > Ba^{2+} > Na^+$
(b)	$Al^{3+} > Ba^{2+} > Na^+$	$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$
(c)	$Na^+ > Ba^{2+} > Al^{3+}$	$Cl^- > SO_4^{2-} > PO_4^{3-} > Fe(CN)_6]^{4-}$
(d)	$Cl^- > SO_4^{2-} > PO_4^{3-} > [Fe(CN)_6]^{4-}$	$Na^+ > Ba^{2+} > Al^{3+}$

5. The coagulation value in millimoles per litre of electrolytes used for the coagulation of As_2S_3 are as below:

   I. NaCl = 52 II. KCl = 51

   III. $BaCl_2 = 0.69$ IV. $MgSO_4 = 0.22$

   The correct order of their flocculating power is:

   (a) I > II > III > IV (b) I > II > III = IV

   (c) IV > III > II > I (d) IV = III > II > I

6. Cotrell precipitator works on the principle of:

   (a) distribution law

   (b) addition of electrolyte

   (c) neutralisation of charge on colloids

   (d) Le Chatelier's principle

7. The substances involved in micellization are:

   (a) polyphilic in nature (b) non-polar in nature

   (c) diphilic in nature (d) uniphilic in nature

8. The swelling of 'gel' when placed in water is called:

   (a) gelation (b) imbibition (c) thixotropy (d) syneresis

9. A lyophilic sol is at its isoelectric point then it is:

   (a) negatively charged (b) positively charged

   (c) not charged (d) none of these

10. Sedimentation potential is reverse of:

    (a) electro-osmosis (b) electrophoresis

    (c) electrokinetic potential (d) streaming potential

11. The potential difference between the fixed charged layer and the diffused layer having opposite charge is called:

    (a) zeta potential (b) colloidal potential

    (c) Dorn potential (d) streaming potential

12. Silver iodide is used for producing artificial rains because AgI:

    (a) is easy to spray at high altitude

    (b) is insoluble in water

    (c) is easy to synthesize

    (d) has crystals similar to ice

13. All colloidal solutions show:

    (a) very high osmotic pressure

    (b) high osmotic pressure

    (c) low osmotic pressure

    (d) no osmotic pressure

14. Colloidion is a colloidal solution of:

    (a) sucrose in water

    (b) cellulose in water

    (c) cellulose nitrate in water

    (d) cellulose nitrate in ethyl alcohol

15. During micelle formation:

    (a) $\Delta H = +$ ve, $\Delta S = +$ ve (b) $\Delta H = -$ ve, $\Delta S = -$ ve

    (c) $\Delta H = -$ ve, $\Delta S = +$ ve (d) $\Delta H = +$ ve, $\Delta S = -$ ve

16. Which of the following is not the property of hydrophilic solutions?

    (a) High concentration of dispersed phase can be easily obtained

(b) Coagulation is reversible
(c) Viscosity and surface tension are nearly same as that of water
(d) The charge of the particles depends on the pH of the medium and it may be positive, negative or zero

17. The coagulation of 100 mL of colloidal solution of gold is completely prevented by addition of 0.25 g of a substance "X" to it before addition of 1 mL of 10% NaCl solution. The gold number of "X" is:
(a) 0.25 (b) 25 (c) 250 (d) 2.5
[**Hint:** Number of milligrams of protective colloid added in 10 mL of colloidal gold to prevent its coagulation on addition of 1 mL of 10% NaCl solution is called its gold number.
$\therefore$ Gold number of present colloid = 25]

18. Select the non-elastic gel out of the following:
(a) starch (b) agar-agar (c) silicic acid (d) gelatin

19. The colligative properties of a colloidal solution compared to the solution of non-electrolyte of same concentration will be:
(a) same (b) higher
(c) lower (d) higher or lower

20. 1 mole of AgI/Ag^+ sol. is coagulated by:
(a) 1 mole of KI (b) 500 mL of 1 M K_2SO_4
(c) 300 mL of 1 M Na_3PO_4 (d) 1 mole of AgI

21. Match the List-I (Colloidal dispersion) with List-II (Nature of the dispersion) and select the correct answer using the codes given below the lists: **(SCRA 2007)**

List-I **(Colloidal dispersion)**	**List-II** **(Nature of dispersion)**
A. Milk	1. Solid in liquid
B. Clouds	2. Liquid in gas
C. Paints	3. Solids in solid
D. Jellies	4. Liquids in liquid
	5. Liquid in solid

(a) A-4, B-2, C-1, D-5 (b) A-1, B-5, C-3, D-2
(c) A-4, B-5, C-1, D-2 (d) A-1, B-2, C-3, D-5

22. At CMC, the surfactant molecules undergo:
(a) association (b) aggregation
(c) micelle formation (d) all of these

23. The blue colour of the water of the sea is due to:
(a) reflection of blue light by salts present in water
(b) scattering of blue light by sol. particles
(c) refraction of blue coloured light by the impurities present in seawater
(d) absorption of radiation of different colours except blue light

24. **Statement :** To stop bleeding from an injury ferric chloride can be applied.
Which comment about the statement is justified?
[PMT (Kerala) 2008]
(a) It is not true, ferric chloride is a poison
(b) It is true, Fe^{3+} ions coagulate blood which is negatively charged sol
(c) It is not true, Cl^- ions form positively charged sol, profuse bleeding takes place
(d) It is true, coagulation takes place because of formation of negatively charged sol with Cl^- ions
(e) It is not true, ferric chloride is ionic and gets into blood stream

Answers

1. (c) **2.** (a) **3.** (a) **4.** (b) **5.** (c) **6.** (c) **7.** (c) **8.** (b)
9. (c) **10.** (b) **11.** (a) **12.** (a) **13.** (c) **14.** (c) **15.** (a) **16.** (c)
17. (b) **18.** (c) **19.** (c) **20.** (a) **21.** (a) **22.** (d) **23.** (b) **24.** (b)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

There are certain substances which behave as normal, strong electrolytes at low concentration but at higher concentration they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called ***micelles.*** *Soaps and detergents are the examples of associated colloids. The formation of micelles takes place above certain concentration called critical micellization concentration (CMC) and a characteristic temperature.*

Answer the following questions:

1. Micelles are:
(a) emulsions cum gels
(b) associated colloids
(c) adsorbed catalysts
(d) ideal solutions

2. What type of molecules form micelles?
(a) Non-polar molecules
(b) Polar molecules
(c) Surfactant molecules
(d) Salt of weak acid and weak base

3. Micelles are formed only:
(a) below the CMC and the Kraft temperature
(b) above the CMC and below the Kraft temperature
(c) above the CMC and above the Kraft temperature
(d) below the CMC and above the Kraft temperature

4. Above CMC, the surfactant molecules undergo:
(a) dissociation (b) aggregation
(c) micelle formation (d) all of these

5. Micelles are used in:
   (a) detergents
   (b) magnetic separation
   (c) petroleum recovery
   (d) all of these

• Passage 2

Emulsions are also the colloidal solutions in which disperse phase as well as dispersion medium are liquids. It may be oil in water or water in oil type. Bancroft proposed that the phase in which the emulsifier is more soluble becomes the outer phase of the emulsion. Emulsifiers can be used to stabilize the emulsion. Soaps, detergents, proteins and gum, etc., are used as emulsifiers.

Answer the following questions:

1. Addition of lyophilic solution to the emulsion forms:
   (a) a protective film around the dispersed phase
   (b) a protective film around the dispersion medium
   (c) an aerosol
   (d) true solution
2. Which of the following examples is/are oil in water type emulsion?
   (a) Ink
   (b) Detergent
   (c) Soap
   (d) Milk
3. Emulsions can be destroyed by:
   (a) the addition of emulsifier which tends to form another emulsion
   (b) electrophoresis with high potential
   (c) freezing
   (d) all of the above
4. Which of the following is homogeneous?
   (a) Milk
   (b) Paint
   (c) Shampoo
   (d) None of these
5. Milk is an emulsion in which:
   (a) milk fat is dispersed in water
   (b) a solid is dispersed in water
   (c) a gas is dispersed in water
   (d) lactose is dispersed in water

• Passage 3

The process of dialysis finds application in the purification of blood by artificial kidney. In this method, impure blood is introduced in the artificial kidney apparatus, where the waste material (electrolyte) diffuses through the membrane. The membrane used in the dialyser is different from the membrane used in osmosis. These membranes allow the movement of ions through them.

Blood is a negatively charged sol. The haemoglobin particles carry a positive charge. Blood is slightly alkaline (pH 7.36–7.42). Acidic salts like alum and $FeCl_3$ decrease the pH of the blood and the denaturation of globular proteins present in blood takes place. Due to denaturation, these globular proteins become fibrous which are insoluble and stop bleeding. Blood is lyophobic in nature.

Answer the following questions:

1. To stop bleeding, $FeCl_3$ is applied locally because:
   (a) $FeCl_3$ seals the blood vessels
   (b) $FeCl_3$ changes the direction of blood flow
   (c) $FeCl_3$ reacts with blood to form a solid substance which seals the blood vessel
   (d) $FeCl_3$ causes denaturation of proteins present in blood
2. Which of the following colloidal solutions does not contain negatively charged particles?
   (a) $Fe(OH)_3$ (b) As_2S_3 (c) Blood (d) Gold sol
3. The coagulating power of an electrolyte for blood decreases in the order:
   (a) Na^+, Al^{3+}, Ba^{2+}
   (b) $PO_4^{3-}, SO_4^{2-}, Cl^-$
   (c) Al^{3+}, Ba^{2+}, Na^+
   (d) $Cl^-, SO_4^{2-}, PO_4^{3-}$
4. Which of the following statements is/are not true?
   (a) Blood is positively charged sol
   (b) Soap solution contains ionic micelles as the colloidal particles
   (c) Blood is purified by the process of dialysis
   (d) Ca^{2+} and K^+ cause coagulation of blood if added in excess
5. Which of the following is/are lyophobic colloids?
   (a) Blood (b) Starch (c) Gelatin (d) Gold

Answers

Passage 1.	1. (b)	2. (c)	3. (c)	4. (b, c)	5. (a, c)
Passage 2.	1. (a)	2. (d)	3. (b, c)	4. (d)	5. (a)
Passage 3.	1. (d)	2. (a)	3. (c)	4. (a)	5. (a, d)

SELF ASSESSMENT

ASSIGNMENT NO. 6

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Dispersed phase and dispersion medium in butter are respectively: **[EAMCET (Medical) 2007]**
(a) solid and liquid (b) liquid and liquid
(c) liquid and solid (d) solid and solid

2. Which one of the following acts as the best coagulating agent for ferric hydroxide sol? **[PMT (Kerala) 2007]**
(a) Magnesium chloride (b) Hydrochloric acid
(c) Aluminium chloride (d) Potassium oxalate
(e) Potassium ferricyanide

3. The colloidal sol found effective in the treatment of eye disease is:
(a) colloidal sulphur (b) colloidal antimony
(c) colloidal silver (d) colloidal gold

4. When alcohol is added to the saturated solution of calcium acetate in water then we first of all get sol which changes to gelatinous mass called solid alcohol. Solid alcohol is........ .
(a) aerosol (b) gel
(c) solid foam (d) solid sol

5. Colloidal solutions of gold prepared by different methods are of different colours because of:
(a) variable valency of gold
(b) impurities produced by different methods
(c) different diameters of colloidal gold particles
(d) different concentration of gold particles

6. Emulsions of polyvinyl acetate are used in:
(a) polishes (b) latex paints
(c) fire works (d) rayons

7. The outcome of internal liquid of gel on shaking is called:
(a) syneresis (b) imbibition
(c) thixotropy (d) precipitation

8. Which of the following shows the maximum hydrophobic behaviour?
(a) Adenine (b) Glucose
(c) Stearic acid (d) Glycine

9. The solution of natural rubber in benzene is an example of:
(a) lyophobic colloids (b) macromolecular colloid
(c) multimolecular colloid (d) associated colloid

10. When NaCl solution is added to $Fe(OH)_3$ sol then:
(a) $[Fe(OH)_3]Fe^{3+}$ is formed
(b) $[Fe(OH)_3]Cl^-$ is formed
(c) $Fe(OH)_3$ is coagulated
(d) $[Fe(OH)_3]Na^+$ is formed

SECTION-II

Multiple Answers Type Objective Questions

11. Which of the following are lyophilic in nature?
(a) Gum (b) Sulphur (c) Starch (d) Protein

12. Surfactant molecules form micelles in aqueous solution, which:
(a) tend to congregate due to their hydrophobic tails
(b) are colloidal-sized cluster of molecules
(c) provide protection due to their hydrophobic head
(d) none of the above

13. Crystalloid and colloid differ with respect to:
(a) Tyndall effect
(b) particle size
(c) diffusion through animal or vegetable membrane
(d) number of particles per unit volume of solution

14. Select the correct statements among the following:
(a) Milk is emulsion of fat in water
(b) An emulsifier stabilizes the emulsion
(c) Emulsifier forms a thin film around the droplets of dispersed phase
(d) Milk is an emulsion of protein in water

15. Which of the following statements are true?
(a) Flocculation value is inversely proportional to the coagulating power
(b) Colloidal silica is a protective colloid
(c) Alum is used for cleaning muddy water
(d) Gelatin is added in ice cream, it acts as emulsifier

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.
(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. Statement-1: Micelles are formed by surfactant molecules above the critical micellar concentration (CMC).

Because

Statement-2: The conductivity of solution having surfactant molecules decreases sharply at the CMC. **(IIT 2007)**

[**Hint:** Micellisation takes place above certain minimum concentration called critical micellar concentration (CMC). Each micelle contains at least 100 molecules, therefore conductivity of solution decreases sharply at the CMC.]

17. **Statement-1:** Aqueous gold colloidal solution is red in colour.

Because

Statement-2: The colour arises due to scattering of light by colloidal gold particles.

18. **Statement-1:** An emulsion becomes stable if soap is added to it.

Because

Statement-2: Soap contains hydrophobic and hydrophilic parts.

19. **Statement-1:** Colloidal solutions are electrically neutral.

Because

Statement-2: Dispersed phase and dispersion medium are of same charge.

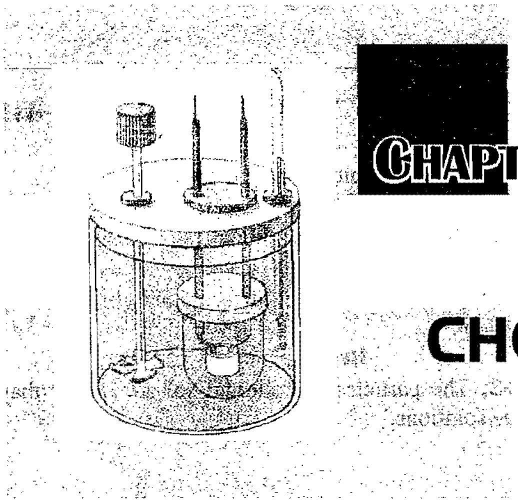
20. **Statement-1:** Colloidal sol scatter the beam of light while true solutions do not.

Because

Statement-2: The particles in colloidal sol are bigger than those of true solutions.

Answers

1. (b) **2.** (e) **3.** (c) **4.** (b) **5.** (c) **6.** (b) **7.** (c) **8.** (a)
9. (b) **10.** (c) **11.** (a, c, d) **12.** (a, b, c) **13.** (a, b, c) **14.** (a, b, c) **15.** (a, c, d) **16.** (b)
17. (b) **18.** (a) **19.** (c) **20.** (a)



CHAPTER 7

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

7.1 INTRODUCTION

Thermodynamics is a Greek word. Its literal meaning is motion or flow (dynamics) of heat (thermos). However, the term is used in a more general way. **Thermodynamics is the branch of science which deals with all changes in energy or transfers of energy that accompany physical and chemical processes.** It is concerned with interconversion of various forms of energy.

Chemical thermodynamics is the branch of thermodynamics which deals with the study of processes in which chemical energy is involved.

Or

Chemical thermodynamics is one of the branches of physical chemistry which deals with transport of heat either as a result of physical change or as a result of chemical change.

Chemical thermodynamics is concerned with the following questions:

(i) When two or more substances are put together, will they react?

(ii) If they do react, what energy changes will be associated with the reaction?

(iii) If a reaction occurs, at what concentrations of the reactants and their products will equilibrium be established?

Thermodynamics is not concerned with the total energy of the body but only with energy changes taking place during the transformation. The study of thermodynamics is based on three generalisations derived from experimental results. These generalisations are known as first, second and third law of thermodynamics based on human experience and there is no formal proof for them. Scientists are of the view that nothing contrary to these laws will ever occur.

Limitations of thermodynamics: (i) The laws of thermodynamics apply only to the matter in bulk, *i.e.*, macroscopic system and not to individual atoms or molecules of the macroscopic system. Thermodynamics does not deal with internal structure of atoms and molecules. (ii) Thermodynamics can only predict the feasibility or spontaneity of a process under a given set of conditions but does not tell anything about the rate at which the given process may proceed. It is only concerned with initial and final states of the system. For example, thermodynamics predicts that the reaction between oxygen and hydrogen is possible under ordinary conditions but does not tell whether the reaction is fast or slow.

7.2 TERMS USED IN THERMODYNAMICS

Before we study the laws of thermodynamics, it is necessary to define some of the basic terms which are frequently used in its discussion:

(i) System, Surroundings and Boundary: A system is defined as a specified part of the universe or specified portion of the matter which is under experimental investigation and the rest of the universe, *i.e.*, all other matter which can interact with the system, is surroundings.

Anything which separates system and surroundings is called **boundary.** The boundary may be real or imaginary; it may be rigid or non-rigid; it may be a conductor or a non-conductor of heat. The terms **diathermic wall** and **adiabatic wall** are used for conductor and non-conductor of heat boundaries respectively.

For example, a reaction is carried out in a beaker. The contents of the beaker constitute the system, beaker serves as boundary and the beaker, the air and anything else in the vicinity constitute the surroundings.

(ii) Types of System: There are three types of system:

(a) Isolated system: This type of system has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surroundings. A substance contained in an ideal thermos flask is an example of an isolated system.

(b) Closed system: This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed tube forms a closed system. Heat can be transferred through the walls of the tube to the surroundings but total amount of matter remains the same as vapours cannot escape.

(c) Open system: This type of system can exchange matter as well as energy with surroundings. The boundary is not sealed and not insulated. Sodium reacting with water in an open beaker is an example of open system as hydrogen escapes and heat of the reaction is transferred to the surroundings.

On the basis of composition, there are two types of systems:

(1) Homogeneous system: A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one-phase only. Examples are: a pure single solid, liquid or gas, mixture of gases and a true solution.

(2) Heterogeneous system: A system is said to be heterogeneous when it is not uniform throughout, *i.e.*, it consists two or more phases. Examples are: ice in contact with water, two or more immiscible liquids, insoluble solid in contact with a liquid, a liquid in contact with vapour, etc.

(iii) Thermodynamic Properties: These are of two types:

(a) Intensive properties: The properties which do not depend upon the quantity of matter present in the system or size of the system are called **intensive properties.** Pressure, temperature, density, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole, concentration, etc., are the examples of intensive properties of the system.

(b) Extensive properties: The properties whose magnitude depends upon the quantity of matter present in the system are called **extensive properties.**

Extensive property is an additive property of the system. For a heterogeneous system consisting of several phases, the total value of extensive property will be equal to the sum of contributions from several phases.

The following are some salient features of these properties :

(i) In a system having two or more substances, the extensive property will depend not only on the independent variables but also on the number of moles of different components present in it.

(ii) If an extensive property is expressed per mole or per gram, it becomes intensive property. For example, mass and volume are extensive properties but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

(iii) The product, sum and ratio of intensive properties are also intensive properties. Let X and Y be two intensive properties, then $(X+Y); XY; \frac{X}{Y}; \frac{\partial X}{\partial Y}$ are intensive properties.

(iv) Let X and Y be the two extensive properties, then

(a) $(X+Y)$ will also be an extensive variable.

(b) $\frac{X}{Y}$ and $\frac{\partial X}{\partial Y}$ will be intensive variables.

Extensive and intensive properties

Intensive properties	Extensive properties
Molarity	Heat capacity
Molality	Mass
Concentration	Volume
Density	Number of moles
Temperature	Gibbs free energy
Pressure	Enthalpy
Mole fraction	Entropy
Molar enthalpy	Internal energy
Molar entropy	
Refractive index	
Specific heat	
Viscosity	
Surface tension	
Dielectric constant	

When the total mass, temperature, volume, number of moles and composition have definite values, the system is said to be in a **definite state.** When there is any change in any one of these properties, it is said that the system has undergone a **change of state.**

(iv) State Functions or State Variables: Fundamental properties which determine the state of a system are referred to as **state variables** or **state functions** or **thermodynamic parameters.** The change in the state properties depends only upon the initial and final states of the system, but is independent of the manner in which the change has been brought about. In other words, the state properties do not depend upon a path followed.

Following are the state variables that are commonly used to describe the state of the thermodynamic system:

1. Pressure (P)
2. Temperature (T)
3. Volume (V)
4. Internal energy (E)
5. Enthalpy (H)
6. Entropy (S)
7. Free energy (G)
8. Number of moles (n)

(v) Thermodynamic Processes: When the thermodynamic system changes from one state to another, the operation is called a **process.** The various types of the processes are:

(a) Isothermal process: The process is termed **isothermal** if temperature remains fixed, *i.e.*, operation is done at constant temperature. This can be achieved by placing the system in a constant temperature bath, *i.e.*, thermostat. For an isothermal process $dT = 0$, *i.e.*, heat is exchanged with the surroundings and the system is not thermally isolated.

(b) Adiabatic process: If a process is carried out under such condition that no exchange of heat takes place between the system and surroundings, the process is termed **adiabatic.** The system is thermally isolated, *i.e.*, $dQ = 0$. This can be done by keeping the system in an insulated container, *i.e.*, thermos flask. In adiabatic process, the temperature of the system varies.

(c) Isobaric process: The process is known as **isobaric** in which the pressure remains constant throughout the change, *i.e.*, $dP = 0$.

(d) Isochoric process: The process is termed as **isochoric** in which volume remains constant throughout the change, *i.e.*, $dV = 0$.

(e) Cyclic process: When a system undergoes a number of different processes and finally returns to its initial state, it is termed **cyclic process.** For a cyclic process $dE = 0$ and $dH = 0$.

(f) Reversible process: A process which occurs infinitesimally slowly, *i.e.*, opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be **reversible process.** In fact, a reversible process is considered to proceed from initial state to final state through an infinite series of infinitesimally small stages and at every stage it is virtually in state of equilibrium. A reversible process is an ideal process and cannot be realised in practice.

(g) Irreversible process: When the process goes from initial to final state in single step in finite time and cannot be reversed, it is termed as **irreversible process.** In such a case equilibrium state exists only at the initial and final stages of the process. An irreversible process is spontaneous in nature. It is real and can be performed in practice. All natural processes are irreversible in nature.

Reversible process	Irreversible process
1. It is an ideal process and takes infinite time.	It is a spontaneous process and takes finite time.
2. The driving force is infinitesimally greater than the opposing force.	The driving force is much greater than the opposing force.
3. It is in equilibrium at all stages.	Equilibrium exists in the initial and final stages only.
4. Work obtained is maximum.	Work obtained is not maximum.
5. It is difficult to realise in practice.	It can be performed in practice.

Nature of Work and Heat

Work is a mode of energy transfer to or from a system with reference to the surroundings. If an object is displaced through a distance dx against a force of F, then the amount of work done is defined as

$$W = F \times dx$$

There are many types of work and all of them could be expressed as the product of two factors:

(i) an intensity factor,

(ii) a capacity factor.

Some of them are:

(a) Gravitational work $= (mg) \times h$

where, $m =$ mass of body, $g =$ acceleration due to gravity, $h =$ height moved.

(b) Electrical work = charge × potential

$$= Q \times V$$

where, $Q =$ charge, $V =$ potential gradient.

(c) Mechanical work $= P_{\text{ext}}\ (V_2 - V_1) = P_{\text{ext}}\ \Delta V$

where, $P_{\text{ext}} =$ external pressure, $\Delta V =$ increase or decrease in volume.

Work associated with change in volume of a system against external pressure is called mechanical work.

$P_{\text{ext}} =$ intensity factor

$\Delta V =$ capacity factor

Work (w) is a path-dependent function, it is a manifestation of energy. Work done on a system increases the energy of the system and work done by the system decreases the energy of the system.

Work done on the system, $w = +$ ve

Work done by the system, $w = -$ ve

Heat may be defined as the quantity of energy which flows between a system and its surroundings on account of temperature difference. Heat always flows from high temperature to low temperature.

Heat absorbed or evolved, $\Delta Q = ms\,\Delta t$

where, $m =$ mass of substance, $s =$ specific heat

and $\Delta t =$ temperature difference.

(i) Heat flowing into the system, ΔQ or $\Delta H = +$ ve.

The process in this case is endothermic in which the temperature of the system is raised and that of the surroundings is lowered.

(ii) Heat flowing out of the system, ΔQ or $\Delta H = -$ ve.

The process in this case is exothermic in which the temperature of the system is lowered and that of the surroundings is raised.

Units of Heat and Work: The unit of heat is calorie (cal). It is defined as the quantity of heat required to raise the temperature of one gram of water by 1°C.

Since, heat and work are interrelated, SI unit of heat is the joule (J).

$$1 \text{ joule} = 0.2390 \text{ cal}$$
$$1 \text{ calorie} = 4.184 \text{ J}$$
$$1 \text{ kcal} = 4.184 \text{ kJ}$$
$$1 \text{ litre-atm} = 101.3 \text{ J}$$
$$= 1.013 \times 10^9 \text{ erg}$$
$$= 24.206 \text{ cal}$$

SOME SOLVED EXAMPLES

Example 1. *A gas expands by 0.5 litre against a constant pressure of one atmosphere. Calculate the work done in joule and calorie.*

Solution: Work $= -P_{\text{ext}} \times$ volume change

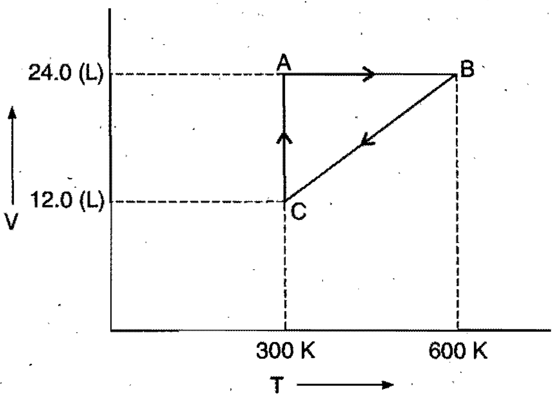
$$= -1 \times 0.5 = -0.5 \text{ litre-atm}$$
$$= -0.5 \times 101.328 \text{ J} = -50.664 \text{ J}$$
$$0.5 \text{ litre-atm} = -0.5 \times 24.20 \text{ cal} = -12.10 \text{ cal}$$

Example 2. *One mole of an ideal gas is put through a series of changes as shown in the graph in which A, B and C mark the three stages of the system. At each stage the variables are shown in the graph.*

(*a*) *Calculate the pressure at three stages of the system.*

(*b*) *Name the processes during the following changes:*

(*i*) *A to B* (*ii*) *B to C* (*iii*) *C to A and* (*iv*) *overall change.*



Solution: **(a) At stage A:**

$V = 24.0\,L; T = 300\,K; n = 1; R = 0.0821$ litre-atm K^{-1} mol^{-1}

Substituting these values in the ideal gas equation,

$$PV = nRT,$$

$$P = \frac{1 \times 0.0821 \times 300}{24.0} = 1.026\,\text{atm}$$

At stage B: Volume remains the same but temperature changes from 300 K to 600 K. Thus, according to pressure law, the pressure will be doubled at B with respect to A.

$$\text{Pressure at } B = 2 \times 1.026 = 2.052\,\text{atm}$$

At stage C: Temperature is 300 K and volume is half that of stage A. Thus, according to Boyle's law, the pressure at C will be doubled with respect to A.

$$\text{Pressure at } C = 2 \times 1.026 = 2.052\,\text{atm}$$

(b) (i) During the change from A to B, volume remains constant, the process is **isochoric.**

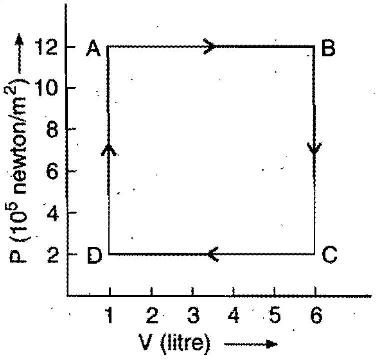
(ii) During the change from B to C the pressure remains constant, the process is **isobaric.**

(iii) During the change from C to A, the temperature remains constant, the process is **isothermal.**

(iv) Overall, the process is **cyclic** as it returns to initial state.

Example 3. *The diagram shows a P-V graph of a thermodynamic behaviour of an ideal gas. Find out from this graph (i) work done in the process $A \to B, B \to C, C \to D$ and $D \to A$, (ii) work done in the complete cycle $A \to B \to C \to D \to A$.*

Solution: (i) Work done in the process $A \to B$ (the process is expansion, hence work is done by the gas)



$$= -P \times dV = -12 \times 10^5 \times 5 \times 10^{-3}$$
$$= -6000\,\text{J}$$

Work done in the process $B \to C$ is zero as volume remains constant.

Work done in the process $C \to D$ (The process is contraction, hence work is done on the gas)

$$= P \times dV = 2 \times 10^5 \times 5 \times 10^{-3}$$
$$= 1000\,\text{J}$$

(ii) Work done in the process $D \to A$ is zero as volume remains constant.

Net work done in the whole cycle $= -6000 + 1000 = -5000\,\text{J}$

i.e., net work is done by the gas.

Example 4. *Calculate the work done when 1.0 mole of water at 373 K vaporizes against an atmospheric pressure of 1.0 atmosphere. Assume ideal gas behaviour.*

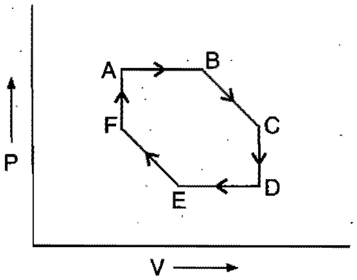
Solution: The volume occupied by water is very small and thus the volume change is equal to the volume occupied by one gram mole of water vapour.

$$V = \frac{nRT}{P} = \frac{1.0 \times 0.0821 \times 373}{1.0} = 31.0\,\text{litre}$$

$$W = -P_{ext} \times \Delta V = -(1.0) \times (31.0)\,\text{litre-atm}$$

$$= -(31.0) \times 101.3\,\text{J} = -3140.3\,\text{J}$$

Example 5. *Identify different steps in the following cyclic process:*



Temperature At A, B and F is T_1 and at C, D and E is T_2

$$T_1 > T_2$$

Solution: (i) $A \to B$ (Temperature and pressure are constant).

∴ It is **isothermal** and **isobaric** process.

(ii) $B \to C$: It is adiabatic expansion in which temperature falls from T_1 to T_2.

(iii) $C \to D$ (Temperature and volume are constant)

∴ This process is isothermal and isochoric.

(iv) $D \to E$ (Temperature and pressure are constant)

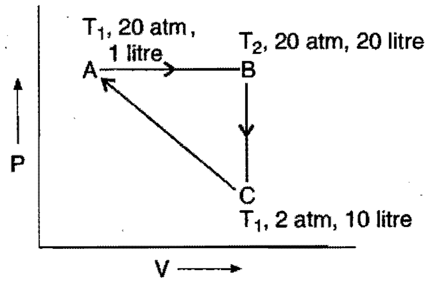
∴ It is isothermal and isobaric contraction.

(v) $E \to F$ (It is adiabatic compression in which temperature increases from T_2 to T_1).

(vi) $F \to A$ (Temperature and volume are constant).

∴ It is isothermal and isochoric process.

Example 6. *One mole of a monoatomic gas is subjected to following cyclic process:*



(*a*) *Calculate* T_1 *and* T_2.

(*b*) *Calculate* $\Delta E, q$ *and* W *in calories in each step of cyclic process.*

Solution: **(a) At** A **:**

$$PV = nRT$$
$$20 \times 1 = 1 \times 0.0821 \times T_1$$
$$T_1 = 243.6\text{ K}$$

At B **:**

$$PV = nRT$$
$$20 \times 10 = 1 \times 0.0821 \times T_2$$
$$T_2 = 2436.05\text{ K}$$

(b) Path AB **: Isobaric process** ($\Delta E = 0, q = W$)

$$W = P\Delta V = 20 \times 9 = 180\text{ litre-atm}$$
$$= \frac{180 \times 101.3}{4.185}\text{ cal}$$
$$= 4356.9\text{ cal} \quad \text{(Work in compression is positive)}$$

Path BC **: Isochoric process**

$$W = 0$$
$$q_V = \Delta U = nC_V\ \Delta T = 1 \times \frac{3}{2}R \times (2436 - 243.6)$$
$$= \frac{3}{2} \times 2 \times 2192.4 = 6577.2\text{ cal}$$

It is cooling process : $q_V = -6577.2\text{ cal}$

Path CA**: It is isothermal compression** ΔE_0

$$q = W = 2.303\, nRT \log \frac{V_2}{V_1}$$
$$q = W = 2.303 \times 1 \times 2 \times \log \frac{10}{1} = 1122.02\text{ cal}$$

7.3 INTERNAL ENERGY

Every system having some quantity of matter is associated with a definite amount of energy. This energy is known as internal energy. The exact value of this energy is not known as it includes all types of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational, the kinetic and potential energy of the nuclei and electrons within the individual molecules and the manner in which the molecules are linked together, etc. The internal energy is denoted by E.

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \ldots$$

Accurate measurements of some forms of energy which contribute to the absolute value of internal energy for a given substance in a given state is impossible. But one thing is certain that the internal energy of a particular system is a definite quantity at the given moment, irrespective of the manner by which it has been obtained. Internal energy like temperature, pressure, volume, etc., is a state function, *i.e.*, **total of all possible kinds of energy of a system is called its internal energy*.**

It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another. Let ΔE be the difference of energy of the initial state (E_i) and the final state (E_f), then

$$\Delta E = E_f - E_i$$

ΔE is positive if $E_f > E_i$ and negative if $E_f < E_i$.

A system may transfer energy to or from the surroundings as heat or work or both.

Characteristics of Internal Energy

(i) Internal energy of a system is an extensive property.

(ii) Internal energy is a state property.

(iii) The change in the internal energy does not depend on the path by which the final state is reached.

(iv) There is no change in internal energy in a cyclic process.

Thermal Equilibrium and Zeroth Law of Thermodynamics

When a hot body is kept in contact with a cold body, the cold body warms up and the hot body cools down. The internal energy of the hot body decreases and that of cold body increases. The transfer of energy from the hot body to a cold body is a non-mechanical process. The energy that is transferred from one body to the other, without any mechanical work involved, is called **heat.**

Two bodies are said to be in *thermal equilibrium* if no transfer of heat takes place when they are placed in contact.

The temperature concept can be stated precisely by the fact that systems in thermal equilibrium with each other have the same temperature.

Courses of thermodynamics usually deal with the three laws : the first, second and third laws, which constitute the subject matter of thermodynamics. However, at present an ever increasing use is made in thermodynamics of the law of thermal equilibrium formulated by R. Fowler in 1931, *i.e.*, the *Zeroth law of thermodynamics.* This law was formulated after the first and the second laws had been enunciated.

This law states : *If two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.*

Conversely, the law can be stated as follows :

If three or more systems are in thermal contact with each other by means of diathermal walls and are all in thermal equilibrium together, then any two systems taken separately are in thermal equilibrium with each other.

Now let us consider three systems A, B and C as shown in Fig. 7.1. It is an experimental fact that if system A is in thermal

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*The word internal is often omitted and the word energy implies internal energy of a system.

equilibrium with system C and system B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other.

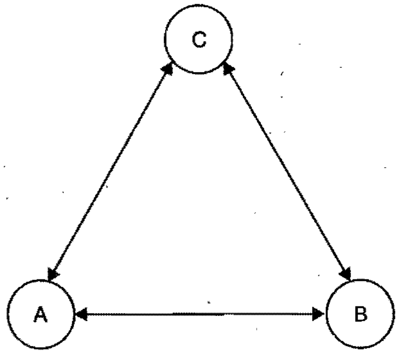


Fig. 7.1 Systems in thermal equilibrium

7.4 FIRST LAW OF THERMODYNAMICS

This law has been stated in various forms but is merely the law of conservation of energy. It was given by **Robert Mayer** and **Helmholtz.**

(i) Energy cannot be created or destroyed but it can be converted from one form to another.

(ii) The total energy of the universe is constant.

(iii) Whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of energy in some other form must appear.

(iv) It is impossible to construct a perpetual motion machine which could produce work without consuming energy.

(v) The total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from initial state to the final state, it undergoes a change in the internal energy from E_i to E_f. Thus, ΔE can be written as:

$$\Delta E = E_f - E_i$$

The change in internal energy can be brought about in two ways:

(a) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).

(b) By doing work on the system or the work done by the system.

Consider a system whose internal energy is E_1. If the system is supplied q amount of heat, the internal energy of the system will become $E_1 + q$. Now if work w is also done on the system, the final internal energy becomes E_2. Thus,

$$E_2 = E_1 + q + w$$

or $$E_2 - E_1 = q + w$$

or $$\Delta E = q + w$$

This is the mathematical statement of the first law of thermodynamics. In this statement, q is the heat absorbed and w is the work done on the system.

In case q is the heat absorbed and w the work done by the system, then the relationship becomes

$$\Delta E = q + (-w) = q - w$$

The first law of thermodynamics may also be stated as:

The net energy change of a closed system is equal to heat absorbed plus the work done on the system.

Or

The net energy change of a closed system is equal to heat absorbed minus the work done by the system.

Or

It is impossible to construct a mobile or perpetual machine that can work without consumption of any fuel energy.

Example 7. *If 500 calorie of heat energy are added to a system and the system does 350 calorie of work on the surroundings, what is the energy change of the system?*

Solution: Heat absorbed, $q = 500\,\text{cal}$

Work done by the system, $w = -350\,\text{cal}$

Applying the first law of thermodynamics,

$$\Delta E = q + w = 500 + (-350) = 150\,\text{calorie}$$

Example 8. *If 100 calorie of heat are added to the same system as in example 1 and a work of 50 calorie is done on the system, calculate the energy change of the system.*

Solution: Heat absorbed, $q = 100\,\text{cal}$

Work done on the system, $w = +50\,\text{cal}$

Applying the first law of thermodynamics,

$$\Delta E = q + w = (100 + 50) = 150\,\text{calorie}$$

In the above two examples, the final state is same but the paths adopted are different. Thus, the change in energy of the system depends on the initial and final states but does not depend on the path by which the final state has reached, q and w are, therefore, not state functions but ΔE is a state function.

Some useful conclusions drawn from the first law: $\Delta E = q + w$

(i) When a system undergoes a change $\Delta E = 0$, *i.e.*, there is no increase or decrease in the internal energy of the system, the first law of thermodynamics reduces to

$$0 = q + w$$

or $$q = -w$$

(heat absorbed from surroundings = work done by the system)

or $$w = -q$$

(heat given to surroundings = work done on the system)

(ii) If no work is done, $w = 0$ and the first law reduces to

$$\Delta E = q$$

i.e., increase in internal energy of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to heat lost by the system.

(iii) If there is no exchange of heat between the system and surroundings, $q = 0$, the first law reduces to

$$\Delta E = w$$

It shows that if work is done on the system, its internal energy will increase or if work is done by the system, its internal energy will decrease. This occurs in an adiabatic process.

(iv) In case of gaseous system, if a gas expands against the constant external pressure, P, let the volume change be ΔV. The mechanical work done by the gas is equal to $-P \times \Delta V$.

Substituting this value in $\Delta E = q + w$,

$$\Delta E = q - P\,\Delta V$$

When $\Delta V = 0$,

$$\Delta E = q \text{ or } q_V$$

The symbol q_V indicates the heat change at constant volume.

Example 9. *A gas contained in a cylinder fitted with a frictionless piston expands against a constant pressure* 1 *atmosphere from a volume of* 4 *litre to a volume of* 14 *litre. In doing so, it absorbs* 800 *J thermal energy from surroundings. Determine* ΔE *for the process.*

Solution: Given, $q = 800\,\text{J}$

$$\Delta V = (14 - 4) = 10\,\text{litre}$$

$$w = -P \times \Delta V = -1 \times 10 = -10\,\text{litre-atm}$$

But $0.082\,\text{litre-atm} = 1.987\,\text{cal}$

So, $$w = -\frac{10 \times 1.987}{0.082} = -242.3\,\text{cal}$$

But $1\,\text{calorie} = 4.184\,\text{J}$

So, $$w = -242.3 \times 4.184 = -1013.7\,\text{J}$$

Substituting the values in equation,

$$\Delta E = q + w = (800 - 1013.7) = -213.7\,\text{J}$$

7.5 ENTHALPY

Heat content of a system at constant pressure is called **enthalpy** denoted by 'H'.

From first law of thermodynamics;

$$Q = E + PV \qquad \text{... (i)}$$

Heat change at constant pressure can be given as

$$\Delta Q = \Delta E + P\,\Delta V \qquad \text{... (ii)}$$

At constant pressure heat can be replaced by enthalpy.

$$\Delta H = \Delta E + P\,\Delta V \qquad \text{... (iii)}$$

Constant pressures are common in chemistry as most of the reactions are carried out in open vessels.

At constant volume, $\Delta V = 0$; thus equation (ii) can be written as

$$\Delta Q = \Delta E$$

$\therefore \Delta H$ = Heat change or heat of reaction (in chemical process) at constant pressure

ΔE = Heat change or heat of reaction at constant volume.

(i) In case of solids and liquids participating in a reaction,

$$\Delta H \approx \Delta E \; (P\,\Delta V \approx 0)$$

(ii) Difference between ΔH and ΔE is significant when gases are involved in a chemical reaction.

$$\Delta H = \Delta E + P\,\Delta V$$

$$\boldsymbol{\Delta H = \Delta E + \Delta nRT}$$

Here, $$P\Delta V = \Delta nRT$$

Δn = Number of gaseous moles of products − Number of gaseous moles of reactants.

Using the above relation we can interrelate heats of reaction at constant pressure and at constant volume.

7.6 HEAT CAPACITY

Heat capacity of a system is defined as the quantity of heat required to raise the temperature of the system by one degree. Let a very small quantity of heat dq be given to a system and the temperature of the system rises by dT.

Thus, $$\text{Heat capacity} = \frac{dq}{dT}$$

The heat capacity of a system, particularly in a gaseous system, determined at constant volume, is different from that determined at constant pressure.

At constant volume, $q = \Delta E$

So, Heat capacity at constant volume, $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

At constant pressure, $q = \Delta E + P\Delta V = \Delta H$

So, Heat capacity at constant pressure, $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

For 1 mole of a gas, heat capacities at constant volume and constant pressure are denoted by C_V and C_P, respectively. These are termed as molar heat capacities. Thus, for 1 mole of a gas,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

and $$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

The difference between C_P and C_V is equal to the work done by 1 mole of gas in expansion when heated through 1°C.

Work done by the gas at constant pressure = $P\,\Delta V$.

For 1 mole of gas $PV = RT$.

When temperature is raised by 1°C, the volume becomes $V + \Delta V$;

So, $$P(V + \Delta V) = R(T + 1)$$

or $$P\,\Delta V = R$$

Hence, $$C_P - C_V = P\,\Delta V = R$$

Ratio of heat capacity $\left(\gamma = \frac{C_P}{C_V}\right)$ depends on atomicity of gas.

Atomicity	$\boldsymbol{C_V}$	$\boldsymbol{C_P = C_V + R}$	$\boldsymbol{\gamma = \frac{C_P}{C_V}}$
Monoatomic He, Ne, Ar etc.	$\frac{3}{2}R$	$\frac{5}{2}R$	$\gamma = \frac{5/2R}{3/2R} = 1.66$
Diatomic O_2, N_2, H_2, Cl_2	$\frac{5}{2}R$	$\frac{7}{2}R$	$\gamma = \frac{7/2R}{5/2R} = 1.40$
Tri and polyatomic CO_2, NH_3, SO_3 NO_2, CH_4 etc.	$3R$	$4R$	$\gamma = \frac{4R}{3R} = 1.33$

Let n_1 and n_2 moles of two non-reacting gases A and B are mixed then heat capacity of the mixture may be calculated as.

$$(C_V)_{\text{mixture}} = \frac{n_1\,(C_V)_1 + n_2\,(C_V)_2}{n_1 + n_2}$$

7.7 EXPANSION OF AN IDEAL GAS

(i) Isothermal Expansion

In an isothermal expansion, heat is allowed to flow into or out of the system so that temperature remains constant throughout the process of expansion. Since, for an ideal gas, the internal energy, ΔE, depends only on temperature, it follows that at constant temperature, the internal energy of the gas remains constant, *i.e.*, ΔE is zero.

$$\Delta E = 0$$

According to first law of thermodynamics,

$$\Delta E = q + w$$

Since, for isothermal process, $\Delta E = 0$, hence

$$q = -w$$

This shows that in isothermal expansion, the work is done by the system at the expense of heat absorbed. The magnitude of q or w depends on the manner in which the process of expansion is carried out, *i.e.*, whether it is carried reversibly or irreversibly.

Calculation of ΔH can be done according to the following equation:

$$H = E + PV$$

or $$\Delta H = \Delta E + \Delta(PV)$$

or $$\Delta H = \Delta E + \Delta(nRT)$$

Since, for isothermal process, ΔE and ΔT are zero respectively, hence,

$$\Delta H = 0$$

Work done in reversible isothermal expansion

Consider an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not insulated. The external pressure, P_{ext}, is equal to pressure of the gas, P_{gas}. Let it be P.

$$P_{\text{ext}} = P_{\text{gas}} = P$$

If the external pressure is decreased by an infinitesimal amount dP, the gas will expand by an infinitesimal volume, dV. As a result of expansion, the pressure of the gas within the cylinder falls to $P_{\text{gas}} - dP$, *i.e.*, it becomes again equal to the external pressure and, thus, the piston comes to rest. Such a process is repeated for a number of times, *i.e.*, in each step the gas expands by a volume dV.

Since, the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the surroundings and the temperature remains constant throughout the expansion.

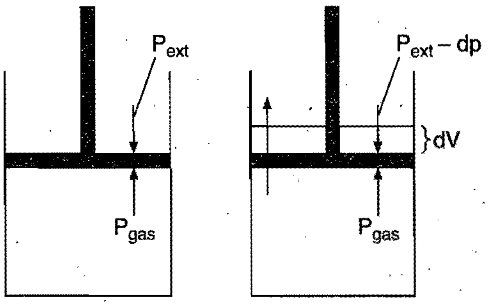


Fig. 7.2

The work done by the gas in each step of expansion can be given as,

$$d_w = -(P_{\text{ext}} - dP)\,dV = -P_{\text{ext}} \cdot dV = -P\,dV$$

$dP \cdot dV$, the product of two infinitesimal quantities, is neglected.

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, therefore,

$$w = -\int_{V_1}^{V_2} P\,dV$$

For an ideal gas, $$P = \frac{nRT}{V}$$

So, $$w = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

Integrating, $$w = -nRT\log_e \frac{V_2}{V_1} = -2.303nRT\log\frac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$$P_1V_1 = P_2V_2$$

or $$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

So, $$w = -2.303nRT\log\frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$w_{\text{compression}} = 2.303nRT\log\frac{V_1}{V_2} = 2.303nRT\log\frac{P_2}{P_1}$$

Work done in irreversible isothermal expansion

Two types of irreversible isothermal expansions are observed, *i.e.*, (i) Free expansion and (ii) Intermediate expansion. In free expansion, the external pressure is zero, *i.e.*, work done is zero when gas expands in vacuum. In intermediate expansion, the external pressure is less than gas pressure. So, the work done when volume changes from V_1 to V_2 is given by

$$w = -\int_{V_1}^{V_2} P_{\text{ext}} \times dV = -P_{\text{ext}}(V_2 - V_1)$$

Since, P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than the work done during reversible isothermal expansion in which P_{ext} is almost equal to P_{gas}.

Maximum work: The work done by the system always depends upon the external pressure. The higher the value of P_{ext}, the more work is done by the gas. As P_{ext} cannot be more than P_{gas}, otherwise compression will occur, thus the largest value of P_{ext} can be equal to P_{gas}. Under this condition when expansion occurs, the maximum work is done by the gas on the surroundings.

(ii) Adiabatic Expansion

In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$. When this value is substituted in first law of thermodynamics, $\Delta E = q + w$, we get $\Delta E = w$.

In expansion, work is done by the system on the surroundings, hence, w is negative. Accordingly ΔE is also negative, *i.e.*, internal energy decreases and therefore, the temperature of the system falls. In case of compression, ΔE is positive, *i.e.*, internal energy increases and therefore, the temperature of the system rises.

The molar specific heat capacity at constant volume of an ideal gas is given by

$$C_V = \left(\frac{dE}{dT}\right)_V$$

or $$dE = C_V \cdot dT \qquad \text{... (i)}$$

and for finite change $$\Delta E = C_V \, \Delta T \qquad \text{... (ii)}$$

So, $$w = \Delta E = C_V \, \Delta T \qquad \text{... (iii)}$$

The value of ΔT depends upon the process whether it is reversible or irreversible.

Reversible adiabatic expansion

Let P be the external pressure and ΔV the increase in volume. Thus, the work done by the system is

$$w = -P \, \Delta V \qquad \text{... (iv)}$$

If ΔT is the fall in temperature, then

$$C_V \, \Delta T = -P \, \Delta V \qquad \text{... (v)}$$

For very small change in reversible process,

$$C_V dT = -PdV = -\frac{RT}{V} \cdot dV \quad \text{(for 1 mole of the gas)}$$

$$C_V \cdot \frac{dT}{T} = -R \cdot \frac{dV}{V} \qquad \text{... (vi)}$$

Integrating the above equation between temperatures T_1 and T_2 when corresponding values are V_1 and V_2,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \log_e \frac{T_2}{T_1} = -R \log_e \frac{V_2}{V_1} = R \log_e \frac{V_1}{V_2}$$

or $$\log \frac{T_2}{T_1} = -\frac{R}{C_V} \log \frac{V_2}{V_1} = \frac{R}{C_V} \log \frac{V_1}{V_2} \qquad \text{... (vii)}$$

We know that, $$C_P - C_V = R$$

or $$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

or $$(\gamma - 1) = \frac{R}{C_V}$$

Putting the value of $\frac{R}{C_V}$ in eq. (vii),

$$\log \frac{T_2}{T_1} = (\gamma - 1) \log \frac{V_1}{V_2}$$

$$= \log \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \text{... (viii)}$$

or $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \text{... (ix)}$$

or $$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1} \qquad \text{... (x)}$$

or $$\frac{P_1V_1}{P_2V_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$$

or $$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad \text{... (xi)}$$

or $$PV^{\gamma} = \text{constant} \qquad \text{... (xii)}$$

Thus, knowing γ, V_1, V_2 and initial temperature, T_1, the final temperature, T_2, can be readily evaluated.

Modifying the eq. (x),

$$\frac{T_1}{T_2} = \left(\frac{\frac{RT_2}{P_2}}{\frac{RT_1}{P_1}}\right)^{\gamma - 1} = \left(\frac{P_1}{P_2} \cdot \frac{T_2}{T_1}\right)^{\gamma - 1}$$

or $$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma - 1} = \left(\frac{P_2}{P_1}\right)^{1 - \gamma} \qquad \text{... (xiii)}$$

Thus, knowing γ, P_1, P_2 and initial temperature, the final temperature, T_2, can be evaluated.

From eq. (v),

$$\text{Work done} = C_V \cdot \Delta T = C_V (T_2 - T_1) = \frac{R}{(\gamma - 1)} (T_2 - T_1)$$

$$\text{For } n \text{ moles} = \frac{nR}{(\gamma - 1)} (T_2 - T_1)$$

Irreversible adiabatic expansion

In free expansion, the external pressure is zero, *i.e.*, work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0$, $\Delta E = 0$, $w = 0$ and $\Delta H = 0$.

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure, P_{ext}.

$$w = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$

$$= -P_{\text{ext}} \left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right) \times R$$

or $$w = C_V (T_2 - T_1) = -RP_{\text{ext}} \left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)$$

Process	**Condition**	**Heat change q**	**Internal energy change ΔU**	**Work done**
Free expansion	(U) constant	—	0	0 as $P = 0$
Isochoric	(V) constant	ΔU	$nC_V \Delta T$	0 as $\Delta V = 0$
Isothermal	(T) constant	$-W$	0	$2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$ $= 2.303\, nRT \log\left(\frac{P_1}{P_2}\right)$

Isobaric	(P) constant	$nC_P\,\Delta T$	$nC_V\,\Delta T$	$P(V_2 - V_1)$ $= nR(T_2 - T_1)$
Adiabatic	(q) constant	0	$-W$	$C_V(T_1 - T_2)$ $= \frac{nR}{\gamma - 1}(T_1 - T_2)$ $= \frac{1}{\gamma - 1}(P_1V_1 - P_2V_2)$
Cyclic process	——	W	0	Area of cycle

7.8 GRAPHICAL REPRESENTATION OF VARIOUS THERMODYNAMIC PROCESSES AND THE CALCULATION OF WORK DONE BY GRAPHICAL METHODS

1. Graphically, different processes can be represented as follows.

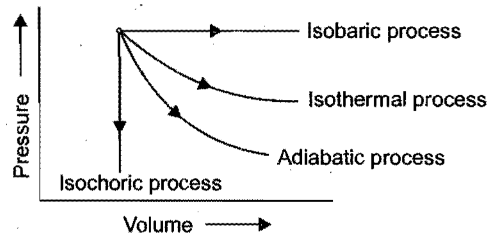


Fig. 7.3 (a)

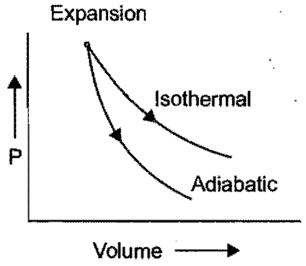


Fig. 7.3 (b)

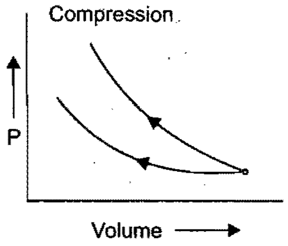


Fig. 7.3 (c)

2. Let a gas is compressed from V_i or V_f by an external pressure of P_{ext}. The work done on the gas can be calculated by the shaded area of the graph represented in following Fig. 7.4.

Work done on the gas, $w = -P_{ext}(V_f - V_i)$

$= +$ ve work, Since $V_f < V_i$

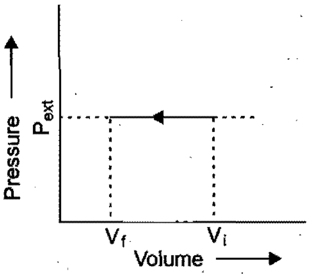


Fig. 7.4 Single step compression of ideal gas against external pressure P_{ext}

3. Let compression of gas takes place from volume V_i to V_f in the finite number of stages then the work done on the gas can be calculated by summing up the work of all stages.

Work done on the gas = Shaded area of the diagram.

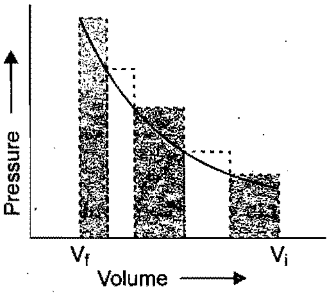


Fig. 7.5 Indicator diagram (P-V) plot in which the compression took place in the finite number of steps with varying pressure

4. Graphically, the work of expansion can also be determined. In case, if a graph is plotted between P and V, then the area under the curve gives the external work done by the gas.

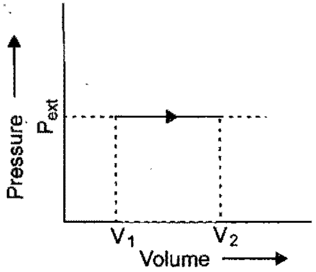


Fig. 7.6 Shaded area gives the work done by the gas when pressure remains constant

$$w_{exp} = -P_{ext}(V_2 - V_1)$$
$$= - \text{ ve work}$$

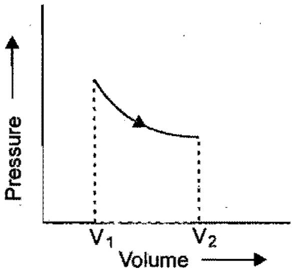
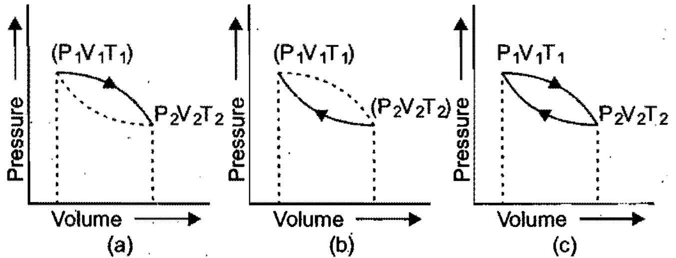


Fig. 7.7 Shaded area represents the work done by the gas when both pressure and volume vary

5. **Work done by a gas undergoing cyclic process :** It is determined with the help of following three graphs.



(a) Shaded area gives the work done by the gas

(b) Shaded area gives the work done on the gas

(c) Shaded area gives the net work done by the gas

Fig. 7.8 Complete cyclic process of a gas

6. Work done by the gas in a closed path *ABCA*.

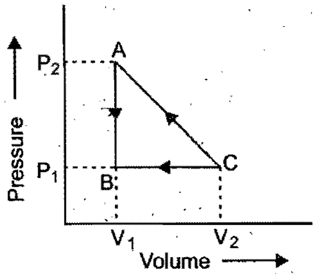


Fig. 7.9 The gas in closed cyclic process ABCA

$$\text{Work done} = \text{Area of shaded triangle}$$
$$= \frac{1}{2} \times \text{Length of base} \times \text{Length of perpendicular}$$
$$= \frac{1}{2} \times (V_2 - V_1)(P_2 - P_1)$$

7. Let a system of gas passes from initial state *A* to *B* in following three ways. The work done by the gas will be calculated by the shaded area.

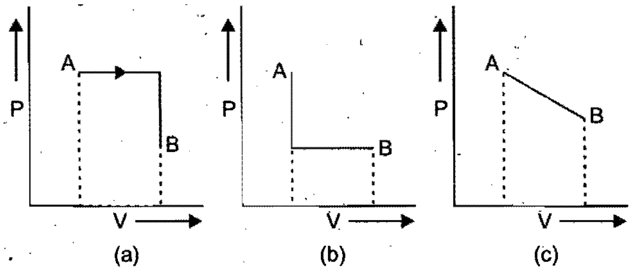


Fig. 7.10 Graphical proof that the work is not a state function

8. Work done in clockwise and anti-clockwise cyclic process :

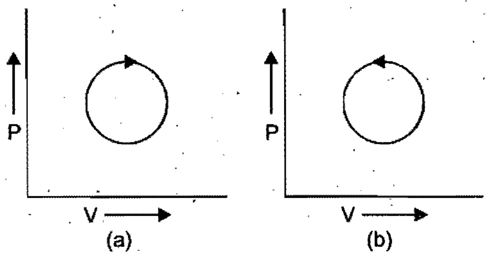


Fig. 7.11 Representation of closed cyclic process in clockwise and anti-clockwise direction

Shaded area represents the net work done in the cyclic process.

Case I : If the cyclic process is in clockwise direction then work done will be negative because the net work will be done by the system.

Case II : If the cyclic process is in anti-clockwise direction then work done will be positive because the net work is done on the system.

9. If the state of a system changes in such a way that its volume remains constant, the process is called isochoric. Following three plots represent isochoric process.

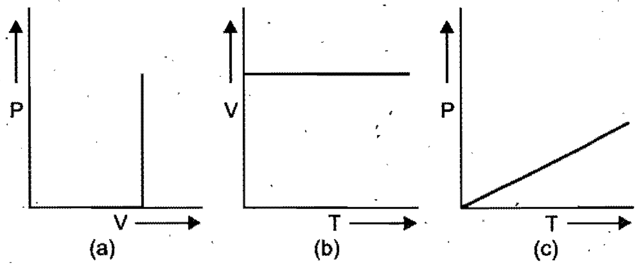


Fig. 7.12 Isochores of Ideal Gas

10. If the state of system changes in such a way that pressure is constant, the process is called isobaric.

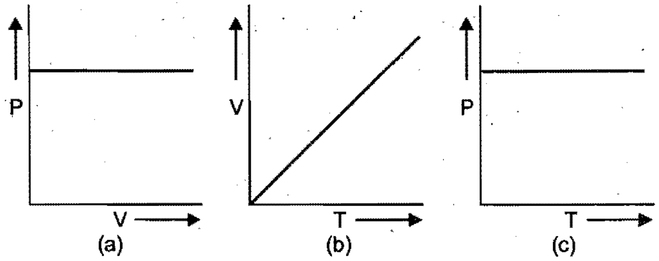


Fig. 7.13 Isobars of Ideal Gas

11. If the state of a system changes in such a way that temperature remains constant, the process is called isothermal.

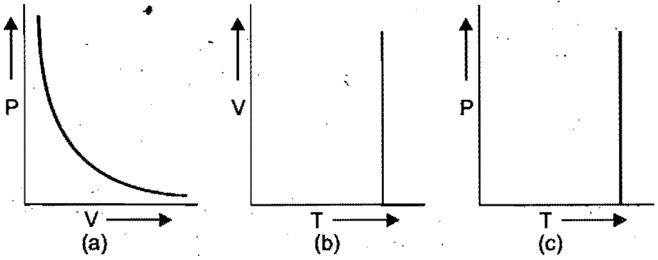


Fig. 7.14 Isotherm of Ideal Gas

7.9 JOULE-THOMSON EFFECT

An ideal gas is defined as the gas in which intermolecular forces of attraction are absent. If such a gas expands into vacuum adiabatically, no cooling is produced in the process, *i.e.*, there is no change in the internal energy which only depends upon the temperature.

However, when a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled. The greater the difference in pressure on the two sides, the higher shall be difference in temperature.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect.

The experimental set-up is shown in Fig. 7.15. It consists of a thermally insulated tube fitted with a porous plug and two weightless and frictionless pistons X and Y. Two sensitive thermometers are fitted on both the sides of the porous plug to record temperature.

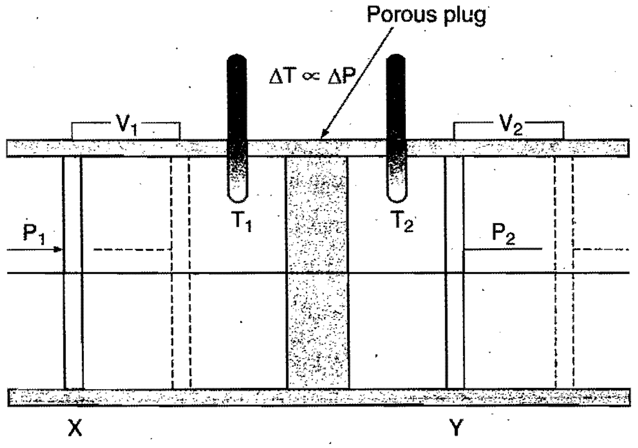


Fig. 7.15

Consider that a certain amount of the gas is passed through the porous plug by slow movement of piston X, *i.e.*, a volume V_1 of the gas at pressure P_1 be forced through the plug on the left side of the plug. The gas in the right hand chamber is allowed to expand to volume V_2 and pressure P_2 by moving the piston Y. The change in temperature is recorded from the thermometers.

Most of the gases are found to undergo cooling on expansion through the porous plug. However, helium and hydrogen are exceptions as these get warmed.

The gas is compressed on left hand side. Thus, work is done on the gas. It is equal to P_1V_1. The work done on right hand side by the gas is equal to P_2V_2.

$$\text{Total work done by the gas} = P_1V_1 - P_2V_2$$

As $q = 0$, the work done by the gas lowers its internal energy and consequently temperature falls.

$$\Delta E = P_1V_1 - P_2V_2$$
$$E_2 - E_1 = P_1V_1 - P_2V_2$$
$$(E_2 + P_2V_2) - (E_1 + P_1V_1) = 0$$

or $$H_2 - H_1 = 0$$

or $$\Delta H = 0$$

Thus, Joule-Thomson effect occurs at constant enthalpy.

Joule-Thomson Coefficient

The number of degrees of temperature change produced per atmospheric drop in pressure under constant enthalpy conditions when the gas is allowed to expand through porous plug is called **Joule-Thomson coefficient.** It is denoted by μ.

$$\mu = \frac{dT}{dP}$$

When μ has positive value, the gas cools on expansion. If it has negative value, the gas warms on expansion. Every gas has a definite value of temperature when the sign changes from negative to positive. This temperature is termed **inversion temperature.** Most of the gases have inversion temperature near about room temperature and thus cool at room temperature when expansion is done. However, the inversion temperature for H_2 is $-80°$ C. Thus, at room temperature hydrogen warms on expansion. In order to produce further cooling by Joule-Thomson effect in hydrogen, it is necessary that it should be first cooled to $-80°$ C by other cooling devices.

The value of inversion temperature has been calculated by using van der Waals' equation,

$$T_i = \frac{2a}{Rb}$$

Thus, inversion temperature depends upon van der Waals' constants a and b of the gas.

SOME SOLVED EXAMPLES

Example 10. *1 mole of Fe_2O_3 and 2 mole of Al are mixed at temperature 25° C and the reaction is completed to give :*

$$Fe_2O_3(s) + 2Al(s) \longrightarrow Al_2O_3(s) + 2Fe(l);\ \Delta H = -850\ kJ$$

The liberated heat is retained within the products, whose combined specific heat over a wide temperature range is about $0.8\,Jg^{-1}\,K^{-1}$. The melting point of iron is 1530° C. Show that the quantity of heat liberated is sufficient to raise the temperature of the product to the melting point of iron in order to get it welded.

Solution: Mass of products

$= $ Mass of one mole Al_2O_3 + Mass of two mole Fe

$= 214$ g

$$q = ms\,\Delta T = 214 \times 0.8 \times (1803 - 298)$$
$$= 257656\ \text{J} = 257.656\ \text{kJ}$$

Heat required is less than heat released, hence the temperature can be easily raised to the required value.

Example 11. *Calculate w and ΔE for the conversion of 0.5 mole of water at 100° C to steam at 1 atm pressure. Heat of vaporisation of water at 100° C is $40670\ J\,mol^{-1}$.*

Solution: Volume of 0.5 mole of steam at 1 atm pressure

$$= \frac{nRT}{P} = \frac{0.5 \times 0.0821 \times 373}{1.0} = 15.3\ \text{L}$$

Change in volume = Vol. of steam − Vol. of water

= 15.3 − negligible = 15.3 L

Work done by the system,

$$w = P_{ext} \times \text{volume change}$$
$$= 1 \times 15.3 = 15.3\ \text{litre-atm}$$
$$= 15.3 \times 101.3\ \text{J} = 1549.89\ \text{J}$$

'w' should be negative as the work has been done by the system on the surroundings.

$$w = -1549.89\ \text{J}$$

Heat required to convert 0.5 mole of water at 100° C to steam

$$= 0.5 \times 40670\ \text{J} = 20335\ \text{J}$$

According to first law of thermodynamics,

$$\Delta E = q + w = 20335 - 1549.89 = 18785.11\ \text{J}$$

Example 12. *Calculate the work done when 50 g of iron is dissolved in HCl at 25° C in (i) a closed vessel and (ii) an open beaker when the atmospheric pressure is 1 atm.*

Solution: (i) When the reaction is carried in a closed vessel, the change in volume is zero. Hence, the work done by the system will be zero. (ii) When iron dissolves in HCl, hydrogen is produced.

$$\underset{\substack{56\text{ g}\\50\text{ g}}}{\mathrm{Fe}} + 2\mathrm{HCl} \longrightarrow \mathrm{FeCl_2} + \underset{\substack{1\text{ mole}\\\frac{1}{56}\times 50\text{ mole}}}{\mathrm{H_2}}$$

Volume of hydrogen produced at 25° C

$$= \frac{nRT}{P} = \frac{50}{56} \times \frac{0.0821 \times 298}{1} = 21.84\text{ L}$$

This is equal to volume change when the reaction is carried in open beaker.

Work done by the system $= -P\,\Delta V = -1.0 \times 21.84$

$$= -21.84\text{ litre-atm} = -2212.39\text{ J}$$

Example 13. *5 mole of oxygen are heated at constant volume from 10° C to 20° C. What will be the change in the internal energy of gas? The molar heat of oxygen at constant pressure, $C_P = 7.03$ cal mol^{-1} deg^{-1} and $R = 8.31$ J mol^{-1} deg^{-1}.*

Solution: $R = 8.31\text{ J mol}^{-1}\text{ deg}^{-1} = \dfrac{8.31}{4.18}\text{ cal mol}^{-1}\text{ deg}^{-1}$

$$= 1.99\text{ cal mol}^{-1}\text{ deg}^{-1}$$

We know that, $C_P - C_V = R$

or $C_V = C_P - R = 7.03 - 1.99 = 5.04\text{ cal mol}^{-1}\text{ deg}^{-1}$

Heat absorbed by 5 mole of oxygen in heating from 10° C to 20° C

$$= 5 \times C_V \times \Delta T = 5 \times 5.04 \times 10 = 252\text{ cal}$$

Since, the gas is heated at constant volume, no external work is done,

i.e., $w = 0$

So, change in internal energy will be equal to heat absorbed,

$$\Delta E = q + w = 252 + 0 = 252\text{ cal}$$

Example 14. *Calculate the amount of work done by 2 mole of an ideal gas at 298 K in reversible isothermal expansion from 10 litre to 20 litre.*

Solution: Amount of work done in reversible isothermal expansion,

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

Given, $n = 2, R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}, T = 298\text{ K}, V_2 = 20\text{ L}$ and $V_1 = 10\text{ L}$.

Substituting the values in above equation,

$$w = -2.303 \times 2 \times 8.314 \times 298 \log \frac{20}{10}$$

$$= -2.303 \times 2 \times 8.314 \times 298 \times 0.3010 = -3434.9\text{ J}$$

i.e., work is done by the system.

Example 15. *5 moles of an ideal gas expand isothermally and reversibly from a pressure of 10 atm to 2 atm at 300 K. What is the largest mass which can be lifted through a height of 1 metre in this expansion?*

Solution: Work done by the system

$$= -nRT \log_e \frac{P_1}{P_2} = -2.303nRT \log \frac{P_1}{P_2}$$

$$= -2.303 \times 5 \times 8.314 \times 300 \log \frac{10}{2} = -20.075 \times 10^3\text{ J}$$

Let M be the mass which can be lifted through a height of 1 m.

Work done in lifting the mass

$$= Mgh = M \times 9.8 \times 1\text{ J}$$

So, $M \times 9.8 = 20.075 \times 10^3$

$$M = 2048.469\text{ kg}$$

Example 16. *Two moles of an ideal monoatomic gas at NTP are compressed adiabatically and reversibly to occupy a volume of 4.48 dm^3. Calculate the amount of work done, ΔE, final temperature and pressure of the gas. C_V for ideal gas $= 12.45\text{ J K}^{-1}\text{ mol}^{-1}$.*

Solution: For an ideal gas, $\gamma = \dfrac{C_P}{C_V} = 1.667$

Initial volume, $V_1 = 2 \times 22.4 = 44.8\text{ dm}^3$

Initial pressure, $P_1 = 1\text{ atm}$

Initial temperature, $T_1 = 273\text{ K}$

Final volume, $V_2 = 4.48\text{ dm}^3$

Let the final pressure be P_2 and temperature be T_2.

Applying $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

or $$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{4.48}{44.8}\right)^{1.667}$$

or $$\frac{P_2}{P_1} = (10)^{1.667}$$

$$P_2 = (10)^{1.667}\ (P_1 = 1\text{ given})$$

$$\log P_2 = 1.667 \log 10 = 1.667$$

$$P_2 = \text{antilog } 1.667 = 46.45\text{ atm}$$

$$\text{Final temperature} = \frac{P_2V_2}{P_1V_1} \cdot T_1 = \frac{46.45 \times 4.48}{1 \times 44.8} \times 273$$

$$= 1268\text{ K}$$

Work done on the system $= n \cdot C_V \cdot \Delta T$

$$= 2 \times 12.45 \times (1268 - 273)$$

$$= 2 \times 12.45 \times 995 = 24775.5\text{ J}$$

From the first law of thermodynamics,

$$\Delta E = q + w = 0 + 24775.5 = 24775.5\text{ J}$$

Example 17. *A certain volume of dry air at NTP is expanded reversibly to four times its volume (a) isothermally (b) adiabatically. Calculate the final pressure and temperature in each case, assuming ideal behaviour.*

$$\left(\frac{C_P}{C_V} \text{ for air} = 1.4\right)$$

Solution: Let V_1 be the initial volume of dry air at NTP.

(a) Isothermal expansion: During isothermal expansion, the temperature remains the same throughout. Hence, final temperature will be 273 K.

Since, $P_1V_1 = P_2V_2$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{1 \times V_1}{4V_1} = 0.25 \text{ atm}$$

(b) Adiabatic expansion:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$$

$$\frac{273}{T_2} = \left(\frac{4V_1}{V_1}\right)^{1.4-1} = 4^{0.4}$$

$$T_2 = \frac{273}{4^{0.4}} = 156.79 \text{ K}$$

Final pressure: $\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$

$$\frac{1}{P_2} = \left(\frac{4V_1}{V_1}\right)^{1.4} = 4^{1.4}$$

$$P_2 = \frac{1}{4^{1.4}} = 0.143 \text{ atm}$$

Example 18. *Calculate q, w, ΔE and ΔH for the reversible isothermal expansion of one mole of an ideal gas at 127° C from a volume of $10\,dm^3$ to $20\,dm^3$.*

Solution: Since, the process is isothermal,

$$\Delta E = \Delta H = 0$$

From first law of thermodynamics,

$$\Delta E = q + w = 0$$

$$q = -w$$

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 1 \times 8.314 \times 400 \log \frac{20}{10}$$

$$= -2.303 \times 1 \times 8.314 \times 400 \times 0.3010$$

$= -2305.3$ J (Work is done by the system)

$q = -w = 2305.3$ J (Heat is absorbed by the system)

Example 19. *A gas expands from a volume of $3.0\,dm^3$ to $5.0\,dm^3$ against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10.0 mole of water of temperature 290.0 K. Calculate the final temperature of water (specific heat of water = 4.184 $JK^{-1}\,g^{-1}$).* (IIT 1993)

Solution: Work done $= P \times dV = 3.0 \times (5.0 - 3.0)$

$$= 6.0 \text{ litre-atm} = 6.0 \times 101.3 \text{ J}$$

$$= 607.8 \text{ J}$$

Let ΔT be the change in temperature.

Heat absorbed $= m \times s \times \Delta T$

$$= 10.0 \times 18 \times 4.184 \times \Delta T$$

Given, $P \times dV = m \times s \times \Delta T$

or $$\Delta T = \frac{P \times dV}{m \times s} = \frac{607.8}{10.0 \times 18.0 \times 4.184} = 0.807$$

Final temperature = 290 + 0.807 = 290.807 K

Example 20. *10 g of argon gas is compressed isothermally and reversibly at a temperature of 27° C from 10 litre to 5 litre. Calculate q, w, ΔE and ΔH for this process. $R = 2\,cal\,K^{-1}\,mol^{-1}$, log 2 = 0.30. Atomic weight of Ar = 40.* (IIT 1997)

Solution: $w = -2.303nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log \frac{5}{10} = 103.635 \text{ cal}$$

$$\Delta E = 0$$

$$q = \Delta E - w$$

$\therefore$ $q = -w = -103.635$ cal

Example 21. *Calculate the maximum work done in expanding 16 g of oxygen at 300 K and occupying a volume of $5\,dm^3$ isothermally until the volume becomes $25\,dm^3$.*

Solution: Reversible work is maximum work.

$\therefore$ $$w = -2.303nRT \log \left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times \frac{16}{32} \times 8.314 \times 300 \log \frac{25}{5} = 2.01 \times 10^3 \text{ joule}$$

Example 22. *How much heat is required to change 10 g ice at 0° C to steam at 100° C? Latent heat of fusion and vaporization for H_2O are 80 cal / g and 540 cal / g, respectively. Specific heat of water is 1 cal / g.*

Solution: Total heat absorbed

$$= \Delta H_{\text{fusion}} + \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}}$$

$$= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200 \text{ cal}$$

Example 23. *A swimmer coming out of a pool is covered with a film of water weighing about 80 g. How much heat must be supplied to evaporate this water?*

Solution: $q = mL$

$$= \frac{80}{18} \times 40.79$$

$$= 181.28 \text{ kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. 5 moles of an ideal gas at 27°C expands isothermally and reversibly from a volume of 6 L to 60 L. The work done in kJ is:
(a) –14.7 (b) –28.72 (c) +28.72 (d) –56.72
[Ans. (b)]
[Hint: $w = -2.303nRT \log \frac{V_2}{V_1}$
$= -2.303 \times 5 \times 8.314 \times 300 \log \frac{60}{6}$
$= -28.72$ kJ]

2. 10 moles of an ideal gas confined to a volume of 10 L is released into atmosphere at 300 K where the pressure is 1 bar. The work done by the gas is:
($R = 0.083$ L bar K^{-1} mol^{-1})
(a) 249 L bar (b) 259 L bar (c) 239 L bar (d) 220 L bar
[Ans. (c)]
[Hint: Initial volume, $V_1 = 10$ L
$$V_2\,(\text{final}) = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$
$$W = P\,\Delta V = 1 \times (249 - 10)$$
$$= 239 \text{ L bar}]$$

3. 1 litre-atm work is approximately equal to:
(a) 101.3 J (b) 8.314 J (c) 931 J (d) 19.2 J
[Ans. (a)]
[Hint: 0.0821 litre-atm = 8.314 J (values of gas constant)
∴ 1 litre-atm = 101.3 J]

4. A system absorbs 20 kJ heat and also does 10 kJ of work. The net internal energy of the system:
(a) increases by 10 kJ (b) decreases by 10 kJ
(c) increases by 30 kJ (d) decreases by 30 kJ
[Ans. (a)]
[Hint: $\Delta U = q + w = 20 - 10 = 10$ kJ]

5. One mole of a gas is heated at constant pressure to raise its temperature by 1°C. The work done in joules is:
(a) – 4.3 (b) –8.314
(c) –16.62 (d) unpredictable
[Ans. (b)]
[Hint: $w = -nR\,\Delta T$ or $w = -P\,\Delta V$
$$= -1 \times 8.314 \times 1 = -P\left(\frac{nRT_2}{P} - \frac{nRT_1}{P}\right)$$
$$= -8.314 \text{ J}]$$

6. In open system:
(a) there will be exchange of both matter and energy
(b) there will be no exchange of matter and energy
(c) there will be exchange of energy only
(d) there will be exchange of matter only
[Ans. (a)]
[Hint : Open system has imaginary boundary, therefore, both energy and mass can be exchanged.]

7.10 THERMOCHEMISTRY

Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformations. It is also termed as chemical energetics. It is based on the first law of thermodynamics.

Chemical reactions are accompanied by evolution or absorption of heat energy. When reactants combine together to form new products, there is readjustment of energies. During a chemical reaction, the chemical bonds between atoms in the reactant molecules are rearranged in the product molecules, *i.e.*, chemical bonds in the reactants are broken down and new chemical bonds are formed in the products. Energy is needed to break the bonds of reactants and energy is released in the formation of new bonds of products.

Exothermic Reactions

Heat is evolved in these chemical reactions. It is possible when the bond energy of reactants is less than the bond energy of products.

At constant pressure,
$$\Delta H = (H_P - H_R) = -\text{ve}, \quad i.e., \quad H_P < H_R$$
At constant volume,
$$\Delta E = (E_P - E_R) = -\text{ve}, \quad i.e., \quad E_P < E_R$$

Endothermic Reactions

Heat is absorbed in these chemical reactions. It is possible when the bond energy of reactants is greater than the bond energy of products.

At constant pressure,
$$\Delta H = H_P - H_R = +\text{ve}, \quad i.e., \quad H_P > H_R$$
At constant volume,
$$\Delta E = E_P - E_R = +\text{ve}, \quad i.e., \quad E_P > E_R$$

Sign conventions:

	ΔQ	ΔE	ΔH
Exothermic	(–)	(–)	(–)
Endothermic	(+)	(+)	(+)

Exothermic and endothermic chemical equations can be represented as:

$$\text{Exothermic}\begin{cases} NaOH(aq.) + HCl(aq.) \longrightarrow NaCl(aq.) + H_2O(l) \\ \qquad\qquad\qquad\qquad\qquad\qquad + 13.7 \text{ kcal} \\ NaOH(aq.) + HCl(aq.) \longrightarrow NaCl(aq.) + H_2O(l); \end{cases}$$
$$\Delta H = -13.7 \text{ kcal}$$

$$\text{Endothermic}\begin{cases} C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g) - 31.4 \text{ kcal} \\ C(s) + H_2O(g) \longrightarrow CO(g) + H_2O(g); \end{cases}$$
$$\Delta H = +31.4 \text{ kcal}$$

7.11 HEAT OF REACTION OR ENTHALPY OF REACTION

Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (or heat of reaction)

$$= \Delta H = \Sigma H_P - \Sigma H_R$$

For example, the equation

$$H_2(g) + Cl_2(g) = 2HCl(g) + 44.0\,\text{kcal} \text{ or } \Delta H = -44\,\text{kcal}$$

indicates that when 2 g of hydrogen (1 mole) completely reacts with 71 g of chlorine (1 mole) to form 73 g of HCl (2 mole), the amount of heat evolved is 44.0 kcal or the enthalpy decreases by 44.0 kcal or the reacting system loses 44.0 kcal of heat or the enthalpy change of the reaction, $\Delta H = -44.0\,\text{kcal}$.

Consider the following reaction:

$$C_2H_4(g) + 3O_2(g) = 2CO_2 + 2H_2O(l);\ \Delta E = -335.8\,\text{kcal}$$

The equation indicates that reaction has been carried between 1 mole of C_2H_4 and 3 mole of oxygen at constant volume and 25° C. The heat evolved is 335.8 kcal or the internal energy of the system decreases by 335.8 kcal.

Consider another reaction:

$$C(s) + H_2O(g) = CO(g) + H_2(g) - 31.4\,\text{kcal}$$

or $$\Delta H = 31.4\,\text{kcal}$$

This reaction indicates that 1 mole of carbon (12 g) reacts with 1 mole of steam (18 g) to form 1 mole of CO and 1 mole of hydrogen and 31.4 kcal of heat is absorbed. The enthalpy of the system increases by 31.4 kcal or the total enthalpy of the products is 31.4 kcal more than the enthalpy of reactants.

Factors which Influence the Heat of Reaction

There are a number of factors which affect the magnitude of heat of reaction.

(i) Physical state of reactants and products: Heat energy is involved for changing the physical state of a chemical substance. For example, in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed.

Considering the following two reactions:

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g);\ \Delta H = -57.8\,\text{kcal}$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l);\ \Delta H = -68.32\,\text{kcal}$$

It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical state always affects the heat of reaction.

(ii) Allotropic forms of the element: Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.

$$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94.3\,\text{kcal}$$

$$C(\text{amorphous}) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -97.6\,\text{kcal}$$

The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is termed as **heat of transition.**

$$C(\text{diamond}) \longrightarrow C(\text{amorphous});\ \Delta H = 3.3\,\text{kcal}$$

(iii) Enthalpies of solution: Enthalpies of reaction differ when in one case dry substances react and in another case when the same substances react in solution. For example, in the reaction between hydrogen sulphide and iodine,

$$H_2S(g) + I_2(g) \longrightarrow 2HI + S;\quad \Delta H = -17.2\,\text{kcal}$$

$$H_2S(g) + I_2\ (\text{solution}) \longrightarrow 2HI\,(\text{solution}) + S;$$

$$\Delta H = -21.93\,\text{kcal}$$

(iv) Temperature: Heat of reaction or enthalpy of reaction also depends on the temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature. Due to this reason, enthalpies of reaction are calculated and expressed at a standard temperature of 25° C or 298 K. However, if the reaction is not carried out at 25° C, the temperature at which the reaction is performed, is indicated.

(v) Reaction carried out at constant pressure or constant volume: When a chemical reaction occurs at constant volume, the heat change is called the enthalpy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable. For this purpose see section 7.5.

$$\Delta E + \Delta nRT = \Delta H$$

or $$q_V + \Delta nRT = q_P$$

q_V = heat change at constant volume,

q_P = heat change at constant pressure.

Δn = total number of moles of products − total number of moles of reactants

Example 24. *The heat of combustion of ethylene at 18° C and at constant volume is –335.8 kcal when water is obtained in liquid state. Calculate the heat of combustion at constant pressure and at 18° C.*

Solution: The chemical equation for the combustion of C_2H_4 is

$$\underset{\text{1 mole}}{C_2H_4(g)} + \underset{\text{3 moles}}{3O_3(g)} = \underset{\text{2 moles}}{2CO_2(g)} + 2H_2O(l);\ \Delta E = -335.8\,\text{kcal}$$

No. of moles of reactants = (1 + 3) = 4

No. of moles of products = 2

So, $$\Delta n = (2 - 4) = -2$$

Given, $\Delta E = -335.8\,\text{kcal}$, $\Delta n = -2$, $R = 2 \times 10^{-3}$ kcal

and $$T = (18 + 273) = 291\,\text{K}$$

Applying
$$\Delta H = \Delta E + \Delta nRT$$
$$= -335.8 + (-2)(2 \times 10^{-3})(291)$$
$$= -336.964\,\text{kcal}$$

Example 25. *The enthalpy of formation of methane at constant pressure and 300 K is –75.83 kJ. What will be the heat of formation at constant volume?* ($R = 8.3\,J\,K^{-1}\,mol^{-1}$)

Solution: The equation for the formation of methane is

$$\underset{2\text{ moles}}{C(s) + 2H_2(g)} = \underset{1\text{ mole}}{CH_4(g)};\ \Delta H = -75.83\text{ kJ}$$

$$\Delta n = (1-2) = -1$$

Given, $\Delta H = -75.83\text{kJ}, R = 8.3\times10^{-3}\text{ kJ K}^{-1}\text{ mol}^{-1}, T = 300\text{K}$

Applying $\Delta H = \Delta E + \Delta nRT$

$$-75.83 = \Delta E + (-1)(8.3\times10^{-3})(300)$$

So, $\Delta E = -75.83 + 2.49$

$$= -73.34\text{ kJ}$$

7.12 ENTHALPY OF FORMATION OR HEAT OF FORMATION

The process in which a compound is formed from its constituent elements in their standard state is called **formation.**

The amount of heat absorbed or evolved when 1 mole of the substance is directly obtained from its constituent elements is called **heat of formation.**

$$\text{C (amorphous)} + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -97.6\text{ kcal/mol}$$

Enthalpy of formation of CO_2 is –97.6 kcal

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g);\ \Delta H = -44\text{ kcal}$$

Thus, enthalpy of formation of HCl is –22 kcal per mol.

Standard enthalpy of formation: The enthalpy of formation depends upon the conditions of formation, *i.e.*, temperature, pressure and physical states (gas, solid or liquid) or allotropic state of the reactants. If all substances of the chemical reaction are in their standard states (*i.e.*, at 25° C or 298 K and 1 atmospheric pressure), the heat of formation or enthalpy of formation is called **standard heat of formation** or **standard enthalpy of formation.** It is denoted by ΔE_f° (volume constant) or ΔH_f° (pressure constant).

It is very difficult to determine absolute values of enthalpies of substances. However, relative enthalpies of substances can be determined if the enthalpies of free elements at 25° C and 1 atmospheric pressure are taken arbitrarily as zero.

Consider the reaction between carbon and oxygen at 25° C to form carbon dioxide under atmospheric pressure.

$$C(s) + O_2(g) = CO_2(g);\ \Delta H = \Delta H_f = -393.5\text{ kJ}$$

$$\therefore\ \Delta H_f = \Delta H = H_P - H_R = -393.5\text{ kJ}$$

$H_R = 0$, *i.e.*, enthalpies of free elements are taken as zero.

So, $\Delta H_f = \Delta H = H_P =$ enthalpy of $CO_2 = -393.5$ kJ

Thus, $\Delta H_f^\circ = -393.5\text{ kJ}$.

The compounds which have positive enthalpies of formation are called **endothermic compounds** and are less stable than the reactants. The compounds which have negative enthalpies of formation are known as **exothermic compounds** and are more stable than reactants.

The knowledge of standard heats of formation of various substances can be used to calculate the heats of reactions under standard conditions, *i.e.*, ΔH°.

$$\begin{matrix}\Delta H^\circ\text{ for}\\ \text{the reaction}\end{matrix} = \begin{bmatrix}\text{Sum of the standard}\\ \text{heats of formation}\\ \text{of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard}\\ \text{heats of formation}\\ \text{of reactants}\end{bmatrix}$$

i.e., $\Delta H^\circ = \Sigma\,\Delta H_f^\circ{}_{(\text{products})} - \Sigma\,\Delta H_f^\circ{}_{(\text{reactants})}$

The heats of formation of all the elements in their standard states are arbitrarily assumed to be zero.

Intrinsic energy: It may be defined as:

Intrinsic energy = – Heat of formation

"Additional amount of energy which one gram mole of the compound possesses above that of its constituent elements."

Let us consider the combustion of carbon.

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94.38\text{ kcal}$$

When 1 mole CO_2 is formed, 94.38 kcal heat is evolved. It means, energy content of CO_2 is less than energy content of $C(s)$ and $O_2(g)$ by 94.38 kcal. Thus, intrinsic energy of CO_2 is 94.38 kcal.

If we assume that intrinsic energy of elements is zero, then intrinsic energy of compound may be calculated in the form of heat of formation. Hence, intrinsic energy may not be considered as internal energy of the compound.

Example 26. *Calculate the enthalpy change for the following reaction:*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

given, enthalpies of formation of CH_4, CO_2 and H_2O are –74.8 kJ mol^{-1}, –393.5 kJ mol^{-1} and –286.2 kJ mol^{-1} respectively.

Solution:

$$\Delta H^\circ = \Delta H_f^\circ{}_{(\text{products})} - \Delta H_f^\circ{}_{(\text{reactants})}$$

$$= [\Delta H_f^\circ{}_{(CO_2)} + 2\Delta H_f^\circ{}_{(H_2O)}] - [\Delta H_f^\circ{}_{(CH_4)} + 2\Delta H_f^\circ{}_{(O_2)}]$$

$$= [-393.5 + 2\times(-286.2)] - [-74.8 + 2\times 0]$$

$$= -393.5 - 572.4 + 74.8$$

$$= -891.1\text{ kJ}$$

Example 27. *The standard heats of formation at 298 K for $CCl_4(g), H_2O(g), CO_2(g)$ and $HCl(g)$ are –25.5, –57.8, –94.1 and –22.1 kcal mol^{-1} respectively. Calculate ΔH_{298}° for the reaction.*

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

Solution:

$$\Delta H^\circ = \Delta H_f^\circ{}_{(\text{products})} - \Delta H_f^\circ{}_{(\text{reactants})}$$

$$= [\Delta H_f^\circ{}_{(CO_2)} + 4\Delta H_f^\circ{}_{(HCl)}] - [\Delta H_f^\circ{}_{(CCl_4)} + 2\Delta H_f^\circ{}_{(H_2O)}]$$

$$= [-94.1 + 4\times(-22.1)] - [-25.5 + 2\times(-57.8)]$$

$$= -94.1 - 88.4 + 25.5 + 115.6$$

$$= -182.5 + 141.1 = -41.4\text{ kcal}$$

Example 28. *The molar heat of formation of* $NH_4NO_3(s)$ *is* -367.5 *kJ and those of* $N_2O(g)$ *and* $H_2O(l)$ *are* $+81.46$ *kJ and* -285.78 *kJ respectively at 25°C and 1 atmospheric pressure. Calculate the* ΔH *and* ΔE *for the reaction,*

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(l)$$

Solution: $\Delta H^\circ = \Delta H^\circ_{f\,(\text{products})} - \Delta H^\circ_{f\,(\text{reactants})}$

$$= [\Delta H^\circ_{f\,(N_2O)} + 2 \times \Delta H^\circ_{f\,(H_2O)}] - [\Delta H^\circ_{f\,(NH_4NO_3)}]$$

$$= 81.46 + 2 \times (-285.78) - (-367.5)$$

$$= 81.46 - 571.56 + 367.5$$

$$= -122.56 \text{ kJ}$$

We know that, $\Delta H = \Delta E + \Delta nRT$

or $\Delta E = \Delta H - \Delta nRT$

$\Delta n = 1;\; R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}; $T = 298$ K

$$\Delta E = -122.56 - (1)(8.314 \times 10^{-3})(298)$$

$$= -122.56 - 2.477$$

$$= -125.037 \text{ kJ}$$

7.13 ENTHALPY OF COMBUSTION OR HEAT OF COMBUSTION

Enthalpy of combustion is the amount of heat evolved or decrease in enthalpy when 1 mole of the substance (compound or element) is completely oxidised. The enthalpy of combustion, *i.e.*, ΔH is always negative. For example,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O; \quad \Delta H = -890.3 \text{ kJ}$$

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H = -1367.4 \text{ kJ}$$

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l); \quad \Delta H = -745.6 \text{ kcal}$$

Since, 2 mole of C_2H_6 are involved, hence enthalpy of combustion of ethane

$$= -\frac{745.6}{2} = -372.8 \text{ kcal}$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\; \Delta H = -26.0 \text{ kcal}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g);\; \Delta H = -94.3 \text{ kcal}$$

The enthalpy of combustion of carbon is not –26.0 kcal as combustion is not complete because carbon monoxide can further be oxidised to carbon dioxide. The enthalpy of combustion of carbon is thus –94.3 kcal.

The enthalpies of combustion have a number of applications. Some of these are described below:

(i) Calorific values of foods and fuels: Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas, etc., serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body. These substances undergo oxidation or combustion and release energy. These substances are, therefore, termed as fuels. An adult requires 2500 to 3000 kcal of energy per day. Since, the values of enthalpies of combustion of different food articles are known, it becomes easy to calculate our daily requirements and thus select the articles of food so as to secure a balanced diet.

The grading of food articles and various fuels can be done on the basis of the values of enthalpies of combustion.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as calorific value. **The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised.**

When methane burns, 890.3 kJ mol^{-1} of energy is released.

$$\underset{1\text{ mole }(16\text{ g})}{CH_4(g)} + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l),$$

$$\Delta H_{CH_4} = -890.3 \text{ kJ}$$

So, the calorific value of methane $= -\dfrac{890.3}{16} = -55.6$ kJ/g

Calorific values of some important foodstuffs and fuels are given below:

Fuel	Calorific value (kJ/g)	Food	Calorific value (kJ/g)
Wood	17	Milk	3.1
Charcoal	33	Egg	6.7
Kerosine	48	Rice	16.7
Methane	55	Sugar	17.3
LPG	55	Butter	30.4
Hydrogen	150	Ghee	37.6

Out of the fuels listed, hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel due to some technical problems. Of the various constituents of our food, fats and carbohydrates serve as the main sources of energy. The calorific value of proteins is quite low.

(ii) Enthalpies of formation: Enthalpies of formation of various compounds, which are not directly obtained, can be calculated from the data of enthalpies of combustions easily by the application of Hess's law.

Heat of reaction = Σ Heat of combustion of reactants

− Σ Heat of combustion of products

SOME SOLVED EXAMPLES

Example 29. *The heats of combustion of* CH_4 *and* C_4H_{10} *are* -890.3 *kJ mol*$^{-1}$ *and* -2878.7 *kJ mol*$^{-1}$ *respectively. Which of the two has greater efficiency as fuel per gram?*

Solution: Molar mass of methane = 16

$$\text{Heat produced per gram of methane} = -\frac{890.3}{16} = -55.64 \text{ kJ}$$

Molar mass of butane = 58

$$\text{Heat produced per gram of butane} = -\frac{2878.7}{58} = -49.63 \text{ kJ}$$

Thus, methane has greater fuel efficiency than butane.

Example 30. *In a Gobar gas plant, gobar gas is formed by bacterial fermentation of animal refuse. It mainly contains methane and its heat of combustion is* $-809\ kJ\ mol^{-1}$ *according to following equation:*

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H = -809\ kJ\ mol^{-1}$$

How much gobar gas would have to be produced per day for a small village of 50 families, if it is assumed that each family requires 20,000 kJ of energy per day? The methane content in gobar gas is 80% by mass.

Solution: Energy consumption of 50 families per day

$$= 50 \times 20{,}000\ \text{kJ} = 1 \times 10^6\ \text{kJ}$$

809 kJ of energy is obtained by burning methane = 16 g

1×10^6 kJ of energy will be obtained by burning methane

$$= \frac{16}{809} \times 10^6 = 1.98 \times 10^4\ \text{g}$$

$$= 19.8\ \text{kg}$$

Since, methane content in gobar gas is 80% by mass, hence, the mass of gobar gas needed

$$= \frac{100}{80} \times 19.8 = 24.75\ \text{kg}$$

Example 31. *The standard molar heats of formation of ethane, carbon dioxide and liquid water are −21.1, −94.1 and − 68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.*

Solution: The required chemical equation for combustion of ethane is

$$2C_2H_6(g) + 7O_2(g) = 4CO_2(g) + 6H_2O(l);\ \Delta H^\circ = ?$$

The equation involves 2 moles of C_2H_6; heat of combustion of ethane will be $= \dfrac{\Delta H^\circ}{2}$

$$\Delta H^\circ = \Delta H^\circ_{f\,(\text{products})} - \Delta H^\circ_{f\,(\text{reactants})}$$

$$= [4 \times \Delta H^\circ_{f\,(CO_2)} + 6\Delta H^\circ_{f\,(H_2O)}] - [2\Delta H^\circ_{f\,(C_2H_6)} + 7\Delta H^\circ_{f\,(O_2)}]$$

$$= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0]$$

$$= -376.4 - 409.8 + 42.2$$

$$= -744.0\ \text{kcal}$$

$$\frac{\Delta H^\circ}{2} = \text{Heat of combustion of ethane} = -\frac{744.0}{2} = -372.0\ \text{kcal}$$

Example 32. *An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per* cm^3 *of the mixture. Heats of formation and densities are as follows:*

$$H_{f\,(Al_2O_3)} = -399\ kcal\ mol^{-1};\ H_{f\,(Fe_2O_3)} = -199\ kcal\ mol^{-1}$$

Density of $Fe_2O_3 = 5.2\ g/cm^3$; *Density of* $Al = 2.7\ g/cm^3$

Solution: The required equation is:

$$2\text{Al} + \text{Fe}_2\text{O}_3 \longrightarrow \text{Al}_2\text{C}_3 + 2\text{Fe};\ \Delta H = ?$$

$$\Delta H = \Delta H_{f\,(\text{products})} - \Delta H_{f\,(\text{reactants})}$$

$$= [\Delta H_{f\,(Al_2O_3)} + 2\Delta H_{f\,(Fe)}] - [2\Delta H_{f\,(Al)} + \Delta H_{f\,(Fe_2O_3)}]$$

$$= (-399 + 2 \times 0) - [2 \times 0 + (-199)]$$

$$= -399 + 199 = -200\ \text{kcal}$$

At. mass of aluminium = 27, Mol. mass of $Fe_2O_3 = 160$

$$\text{Volume of reactants} = \frac{160}{5.2} + \frac{2 \times 27}{2.7} = 50.77\ \text{cm}^3$$

$$\text{Fuel value per cm}^3 = \frac{200}{50.77} = 3.92\ \text{kcal}$$

Example 33. *When 2 mole of* C_2H_6 *are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of* C_2H_6. ΔH_f *for* CO_2 *and* H_2O *are −395 kJ and −286 kJ respectively.*

Solution: The equation for the combustion of C_2H_6 is:

$$2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O;\ \Delta H = -3129\ \text{kJ}$$

$$\Delta H = \Delta H_{f\,(\text{products})} - \Delta H_{f\,(\text{reactants})}$$

$$= [4 \times \Delta H_{f\,(CO_2)} + 6 \times \Delta H_{f\,(H_2O)}] - [2 \times \Delta H_{f\,(C_2H_6)} + 7\Delta H_{f\,(O_2)}]$$

$$-3129 = [4 \times (-395) + 6 \times (-286)] - [2 \times \Delta H_{f\,(C_2H_6)} + 7 \times 0]$$

or $\qquad 2 \times \Delta H_{f\,(C_2H_6)} = -167$

So, $\qquad \Delta H_{f\,(C_2H_6)} = -\dfrac{167}{2} = -83.5\ \text{kJ}$

Example 34. *The standard heats of formation of* $CH_4(g)$, $CO_2(g)$ *and* $H_2O(g)$ *are −76.2, −398.8 and −241.6* $kJ\ mol^{-1}$ *respectively. Calculate the amount of heat evolved by burning* $1\ m^3$ *of methane measured under normal conditions.* **(IIT 1990)**

Solution: The required equation for the combustion of methane is:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O;\ \Delta H = ?$$

$$\Delta H = \Delta H_{f\,(\text{products})} - \Delta H_{f\,(\text{reactants})}$$

$$= \Delta H_{f\,(CO_2)} + 2 \times \Delta H_{f\,(H_2O)} - \Delta H_{f\,(CH_4)} - 2\Delta H_{f\,(O_2)}$$

$$= -398.8 - 2 \times 241.6 - (-76.2) - 2 \times 0$$

$$= -805.8\ \text{kJ mol}^{-1}$$

Heat evolved by burning 22.4 litre (1 mole) methane = − 805.8 kJ. So, heat evolved by burning 1000 litre ($1\ m^3$) methane

$$= -\frac{805.8}{22.4} \times 1000 = -35973.2\ \text{kJ}$$

Example 35. *A gas mixture of 3.67 litre of ethylene and methane on complete combustion at 25° C produces 6.11 litre of* CO_2. *Find out the heat evolved on burning 1 litre of the gas mixture. The heats of combustion of ethylene and methane are −1423 and −891* $kJ\ mol^{-1}$ *at 25° C.* **(IIT 1991)**

Solution: $$\underset{a\text{ litre}}{C_2H_4} + 3O_2 \longrightarrow \underset{2a\text{ litre}}{2CO_2} + 2H_2O$$

$$\underset{(3.67-a)\text{ litre}}{CH_4} + 2O_2 \longrightarrow \underset{(3.67-a)\text{ litre}}{CO_2} + 2H_2O$$

Given, $$2a + 3.67 - a = 6.11$$

$$a = 2.44 \text{ litre}$$

Volume of ethylene in mixture = 2.44 litre

Volume of methane in mixture = 1.23 litre

$$\text{Volume of ethylene in 1 litre mixture} = \frac{2.44}{3.67} = 0.6649 \text{ litre}$$

$$\text{Volume of methane in 1 litre mixture} = \frac{1.23}{3.67} = 0.3351 \text{ litre}$$

24.45 litre of a gas at 25° C correspond to 1 mole.

Thus, heat evolved by burning 0.6649 litre of ethylene

$$= -\frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

and heat evolved by burning 0.3351 litre of methane

$$= -\frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So, total heat evolved by burning 1 litre of mixture

$$= -38.69 - 12.21$$

$$= -50.90 \text{ kJ}$$

7.14 ENTHALPY OF SOLUTION OR HEAT OF SOLUTION

The amount of heat evolved or absorbed when 1 mole solute is dissolved in excess of solvent (about 200 mole) is called **heat of solution.**

Some examples, of heat of solution are:

$$H_2SO_4(l) + aq. = H_2SO_4(aq.); \quad \Delta H = -20.2 \text{ kcal}$$

$$KCl(s) + aq. = KCl(aq.); \quad \Delta H = 4.4 \text{ kcal}$$

$$KOH(s) + aq. = KOH(aq.); \quad \Delta H = -13.3 \text{ kcal}$$

Heat of ideal solution is taken zero.

Generally, dissolution of substances in a solvent is a disintegration process. This process needs energy. In such cases, energy is absorbed, *i.e.*, ΔH is positive. But in some cases, besides the process of breaking or ionisation, there is hydrate formation. During hydration heat is evolved. The net result is that heat is either evolved or absorbed. There are also cases in which heat of separation of ions is just equal to the heat of hydration and there is very little heat effect as in the case of sodium chloride. The heat of solution of NaCl is very small as the heat of ionisation is nearly equal to the heat of hydration.

7.15 ENTHALPY OF NEUTRALISATION OR HEAT OF NEUTRALISATION

The heat of neutralisation (or enthalpy of neutralisation) is defined as the heat evolved or decrease in enthalpy when 1 gram equivalent of an acid is neutralised by 1 gram equivalent of a base in dilute solution. Some examples are:

Strong acid + Strong base = Salt + Water; $\Delta H = -13.7$ kcal

$$HNO_3(aq.) + NaOH(aq.) = NaNO_3(aq.) + H_2O(l); \quad \Delta H = -13.7 \text{ kcal}$$

$$HCl(aq.) + NaOH(aq.) = NaCl(aq.) + H_2O(l); \quad \Delta H = -13.75 \text{ kcal}$$

$$\frac{1}{2}H_2SO_4(aq.) + NaOH(aq.) = \frac{1}{2}Na_2SO_4(aq.) + H_2O(l); \quad \Delta H = -13.7 \text{ kcal}$$

It is observed that heat of neutralisation of a strong acid against a strong base is always nearly the same, *i.e.*, 13.7 kcal or 57 kJ, no matter what acid or base is employed. This constant value is explained with the help of theory of ionisation. Both acid and base are present in aqueous solution in the form of ions and when mixed, the following reaction occurs:

$$\underset{\text{Strong acid}}{H^+ + A^-} + \underset{\text{Strong base}}{B^+ + OH^-} = \underset{\text{Salt}}{B^+ + A^-} + H_2O; \quad \Delta H = -13.7 \text{ kcal}$$

Cancelling the ions which are common on both the sides,

$$H^+ + OH^- = H_2O; \quad \Delta H = -13.7 \text{ kcal}$$

Thus, heat of neutralisation of a strong acid and a strong base is merely the heat of formation of water from H$^+$ and OH$^-$ ions. This is the common reaction whenever a strong acid and a strong base are mixed and that is why the heat of neutralisation is same.

However, when a strong acid and a weak base or a weak acid and a strong base or a weak acid and a weak base are mixed in equivalent amount, the heat evolved or change in enthalpy is less than 13.7 kcal. This is shown in the following examples:

$$\underset{\text{Strong}}{HCl(aq.)} + \underset{\text{Weak}}{NH_4OH(aq.)} = NH_4Cl(aq.) + H_2O(l); \quad \Delta H = -12.3 \text{ kcal}$$

$$\underset{\text{Weak}}{HCN(aq.)} + \underset{\text{Strong}}{NaOH(aq.)} = NaCN(aq.) + H_2O(l); \quad \Delta H = -12.3 \text{ kcal}$$

$$\underset{\text{Weak}}{CH_3COOH(aq.)} + \underset{\text{Weak}}{NH_4OH(aq.)} = CH_3COONH_4(aq.) + H_2O(l); \quad \Delta H = -11.9 \text{ kcal}$$

The reason for the lower value is that part of the heat energy evolved is utilised in the complete ionisation of a weak acid or a weak base or both. Hence, the net heat of neutralisation is less than 13.7 kcal. The neutralisation of NH_4OH with HCl can be explained in the following way:

$$NH_4OH(aq.) = NH_4^+(aq.) + OH^-(aq.); \quad \Delta H = Q$$

and $$NH_4^+(aq.) + Cl^-(aq.) + H^+(aq.) + OH^-(aq.) = NH_4^+(aq.) + Cl^-(aq.) + H_2O(l); \quad \Delta H = -13.7 \text{ kcal}$$

or $$NH_4OH(aq.) + H^+(aq.) + Cl^-(aq.) = NH_4^+(aq.) + Cl^-(aq.) + H_2O(l); \quad \Delta H = -12.3 \text{ kcal}$$

So, $Q - 13.7 = -12.3$

or $Q = 13.7 - 12.3 = 1.4$ kcal

Hence, 1.4 kcal of heat energy is absorbed for ionisation of NH_4OH which get subtracted from 13.7 kcal. Thus, the observed value of heat of neutralisation is not −13.7 kcal but −12.3 kcal.

Determination of Heat of Neutralisation

The heat of neutralisation of an acid or base can be easily determined in the laboratory with the help of polythene or polystyrene bottle. Bottle is fitted with rubber cork through which a thermometer and a stirrer are fitted as shown in the Fig. 7.16. 100 mL each of acid and alkali of equal normality are taken in separate bottles. The temperature of each solution is regularly recorded. When constant temperature is attained, the alkali solution is added to the acid solution. The mixture is quickly stirred and the maximum temperature attained is noted.

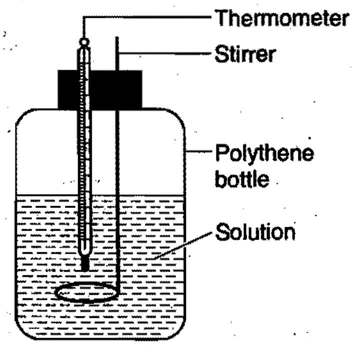


Fig. 7.16

Calculations:

Suppose, the initial temperature of acid and base $= T_1$

Final temperature of solution after mixing $= T_2$

Rise in temperature $= T_2 - T_1$

For the purpose of simplicity, the heat capacity of the bottle may be neglected as it is very small in comparison to that of solution. The specific heat capacity of the solution is assumed to be the same as that of water.

$$Q = \text{Heat change in reaction} = \text{Mass of solution} \times \text{sp. heat} \times (T_2 - T_1)$$

Q is the heat evolved by the neutralisation.

$$\text{Therefore, the enthalpy of neutralisation} = \frac{Q}{100} \times 1000 \times \frac{1}{x}$$

where, x = normality of the acid or base.

Example 36. *150 mL of 0.5 N nitric acid solution at 25.35°C was mixed with 150 mL of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.*

Solution: Total mass of solution $= 150 + 150 = 300$ g

$$Q = \text{Total heat produced} = 300 \times (28.77 - 25.35)\,\text{cal}$$
$$= 300 \times 3.42 = 1026\,\text{cal}$$

$$\text{Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5}$$
$$= \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68\,\text{kcal}$$

Since, heat is liberated, heat of neutralisation should be negative.

So, heat of neutralisation = −13.68 kcal.

Example 37. *Whenever an acid is neutralised by a base, the net reaction is*

$$H^+(aq.) + OH^-(aq.) \longrightarrow H_2O(l); \quad \Delta H = -57.1\,kJ$$

Calculate the heat evolved for the following experiments:

(*i*) *0.50 mole of HCl solution is neutralised by 0.50 mole of NaOH solution.*

(*ii*) *0.50 mole of HNO_3 solution is mixed with 0.30 mole of KOH solution.*

(*iii*) *100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M NaOH solution.*

(*iv*) *400 mL of 0.2 M H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution.*

Solution: According to the reaction,

$$H^+(aq.) + OH^-(aq.) \longrightarrow H_2O(l); \quad \Delta H = -57.1\,\text{kJ}$$

when 1 mole of H^+ ions and 1 mole of OH^- ions are neutralised, 1 mole of water is formed and 57.1 kJ of energy is released.

(i) 0.50 mole HCl ≡ 0.50 mole H^+ ions

0.50 mole NaOH ≡ 0.50 mole OH^- ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water

$= 57.1 \times 0.5 = 28.55$ kJ

(ii) 0.50 mole HNO_3 ≡ 0.50 mole H^+ ions

0.30 mole KOH ≡ 0.30 mole OH^- ions

i.e., 0.30 mole of H^+ ions react with 0.30 mole of OH^- ions to form 0.30 mole of water molecules.

Heat evolved in the formation of 0.3 mole of water

$= 57.1 \times 0.3 = 17.13$ kJ

(iii) 100 mL of 0.2 M HCl will give

$$\left(\frac{0.2}{1000} \times 100\right) = 0.02 \text{ mole of } H^+ \text{ ions}$$

and 100 mL of 0.3 M NaOH will give

$$\left(\frac{0.3}{1000} \times 100\right) = 0.03 \text{ mole of } OH^- \text{ ions}$$

i.e., 0.02 mole of H^+ ions react with 0.02 mole of OH^- ions to form 0.02 mole of water molecules.

Heat evolved in the formation of 0.02 mole of water

$= 0.02 \times 57.1 = 1.142$ kJ

(iv) 400 mL of 0.2 M H_2SO_4 will give

$$\left(\frac{2 \times 0.2}{1000} \times 400\right) = 0.16 \text{ mole of } H^+ \text{ ions}$$

and 600 mL of 0.1 M KOH will give

$$\left(\frac{0.1}{1000}\times 600\right) = 0.06 \text{ mole of } OH^- \text{ ions}$$

i.e., 0.06 mole of H^+ ions react with 0.06 mole of OH^- ions to form 0.06 mole of water molecules.

Heat evolved in the formation of 0.06 mole of water

$$= 0.06 \times 57.1 = 3.426 \text{ kJ}$$

Example 38. *100 cm^3 of 0.5 N HCl solution at 299.95 K were mixed with 100 cm^3 0.5 N NaOH solution at 299.75 K in a thermos flask. The final temperature was found to be 302.65 K. Calculate the enthalpy of neutralisation of HCl. Water equivalent of thermos flask is 44 g.*

Solution: The initial average temperature of the acid and the base

$$= \frac{299.95 + 299.75}{2} = 299.85 \text{ K}$$

Rise in temperature = (302.65 − 299.85) = 2.80 K

Heat evolved during neutralisation

$$= (100 + 100 + 44) \times 4.184 \times 2.8 = 2858.5 \text{ J}$$

$$\therefore \quad \text{Enthalpy of neutralisation} = -\frac{2858.5}{100} \times 1000 \times \frac{1}{0.50}$$

$$= -57.17 \text{ kJ}$$

Example 39. *When a student mixed 50 mL of 1 M HCl and 50 mL of 1 M NaOH in a coffee cup calorimeter, the temperature of the resultant solution increases from 21°C to 27.5°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the total volume of solution is 100 mL, its density 1 g mL^{-1} and that its specific heat is 4.18 J/g. Calculate :*

(a) the heat change during mixing,

(b) the enthalpy change for the reaction,

$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O(aq.)$$

Solution: (a) Number of moles of HCl and NaOH added

$$= \frac{MV}{1000} = \frac{1\times 50}{1000} = 0.05$$

Mass of mixture = $V \times d = 100 \times 1 = 100$ g

Heat evolved, $q = ms\Delta T = 100 \times 4.18 \times (27.5 - 21.0)$

$$= 100 \times 4.18 \times 6.5 \text{ J} = 2717 \text{ J} = 2.717 \text{ kJ}$$

(b) The involved reaction is:

$$HCl(aq.) + NaOH(aq.) \longrightarrow NaCl(aq.) + H_2O$$

ΔH = Heat evolved per mol

$$= \frac{-2.717}{0.05} = -54.34 \text{ kJ}$$

Example 40. *The enthalpies of neutralisation of a strong acid HA and weaker acid HB by NaOH are −13.7 and −12.7 kcal/eq. When one equivalent of NaOH is added to a mixture containing 1 equivalent of HA and HB ; the enthalpy change was −13.5 kcal. In what ratio is the base distributed between HA and HB?*

Solution: Let x equivalent of H*A* and y equivalent of H*B* are taken in the mixture

$$x + y = 1 \qquad \ldots(i)$$

$$x \times 13.7 + y \times 12.7 = 13.5 \qquad \ldots(ii)$$

Solving eqs. (i) and (ii), we get

$$x = 0.8, \ y = 0.2$$

$$x : y = 4 : 1$$

7.16 ENTHALPIES OF PHYSICAL CHANGES (Phase Changes)

Heat energy is involved whenever a physical state of a substance is changed. Some important enthalpies of physical changes are defined below:

(i) Enthalpy of fusion: It is the enthalpy change in converting 1 mole of the substance from solid state to liquid state at its melting point. The enthalpy of fusion equals latent heat of fusion per gram multiplied by the molecular mass. The value of enthalpy of fusion gives an idea about the strength of the intermolecular forces operating in a solid. The values of enthalpies of fusion for ionic solids are much more than molecular solids in which molecules are held together by weak van der Waals' forces.

$$H_2O(s) \xrightarrow{\text{Melting}} H_2O(l); \qquad \Delta H = 1.44 \text{ kcal}$$

$$H_2O(l) \xrightarrow{\text{Freezing}} H_2O(s); \qquad \Delta H_{(\text{freezing})} = -1.44 \text{ kcal}$$

(ii) Enthalpy of vaporization: It is the enthalpy change in converting 1 mole of the substance from liquid state to gaseous state (or vapour state) at its boiling point.

$$H_2O(l) \xrightarrow{\text{Boiling}} H_2O(g); \qquad \Delta H = 10.5 \text{ kcal}$$

$$H_2O(g) \xrightarrow{\text{Condensation}} H_2O(l); \quad \Delta H_{(\text{condensation})} = -10.5 \text{ kcal}$$

Enthalpy of vaporization of a liquid gives an idea about the strength of intermolecular forces operating between the molecules of the liquid.

(iii) Enthalpy of sublimation: Sublimation is the process in which a solid on heating is directly converted into vapour state. It is the heat change in converting 1 mole of a solid directly into its vapour at a given temperature below its melting point.

$$I_2(s) \longrightarrow I_2(g); \qquad \Delta H = 14.9 \text{ kcal}$$

The enthalpy of sublimation of a solid is equal to the sum of enthalpy of fusion and enthalpy of vaporization.

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

7.17 HESS'S LAW (The Law of Constant Heat Summation)

This law was presented by **Hess** in 1840. According to this law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, *i.e.*, the total enthalpy change is independent of intermediate steps involved in the change. The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance *A* be changed in three steps to *D* with enthalpy change from *A* to

B ΔH_1 calorie, from B to C ΔH_2 calorie and from C to D ΔH_3 calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps.

Total enthalpy change

$$\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Now if D is directly converted into A, let the enthalpy change be ΔH_{direct}. According to Hess's law $\Delta H_{\text{steps}} + \Delta H_{\text{direct}} = 0$, *i.e.*, ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more than ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.

Hess's law can also be verified experimentally with the help of following examples:

(i) Formation of carbon dioxide from carbon:

First method: Carbon is directly converted into $CO_2(g)$.

$$C(s) + O_2(g) = CO_2(g); \quad \Delta H = -94.0 \text{ kcal}$$

Second method: Carbon is first converted into $CO(g)$ and then $CO(g)$ into $CO_2(g)$, *i.e.*, conversion has been carried in two steps:

$$C(s) + \frac{1}{2}O_2 = CO(g); \qquad \Delta H = -26.0 \text{ kcal}$$

$$CO(g) + \frac{1}{2}O_2 = CO_2(g); \qquad \Delta H = -68.0 \text{ kcal}$$

$$\text{Total enthalpy change } C(s) \text{ to } CO_2(g); \qquad \Delta H = -94.0 \text{ kcal}$$

(ii) Formation of ammonium chloride from ammonia and hydrochloric acid:

First method:

$$\begin{array}{rl} NH_3(g) + HCl(g) = NH_4Cl(g); & \Delta H = -42.2 \text{ kcal} \\ NH_4Cl(g) + aq. = NH_4Cl(aq.); & \Delta H = +4.0 \text{ kcal} \\ \hline NH_3(g) + HCl(g) + aq. = NH_4Cl(aq.); & \Delta H = -38.2 \text{ kcal} \end{array}$$

Second method:

$$\begin{array}{rl} NH_3(g) + aq. = NH_3(aq.); & \Delta H = -8.4 \text{ kcal} \\ HCl(g) + aq. = HCl(aq.); & \Delta H = -17.3 \text{ kcal} \\ NH_3(aq.) + HCl(aq.) = NH_4Cl(aq.); & \Delta H = -12.3 \text{ kcal} \\ \hline NH_3(g) + HCl(g) + aq. = NH_4Cl(aq.); & \Delta H = -38.0 \text{ kcal} \end{array}$$

Conclusions

(i) The heat of formation of compounds is independent of the manner of its formation.

(ii) The heat of reaction is independent of the time consumed in the process.

(iii) The heat of reaction depends on the sum of enthalpies of products minus sum of the enthalpies of reactants.

(iv) Thermochemical equations can be added, subtracted or multiplied like algebraic equations.

Applications of Hess's Law

(i) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(ii) For the determination of enthalpies of extremely slow reactions.

(iii) For the determination of enthalpies of transformation of one allotropic form into another.

(iv) For the determination of bond energies.

$$\Delta H_{\text{reaction}} = \Sigma \text{ Bond energies of reactants} - \Sigma \text{ Bond energies of products}$$

(v) For the determination of resonance energy.

(vi) For the determination of lattice energy.

Thermochemical calculations: For making thermochemical calculations, the following points are kept in mind:

(i) Write down the required thermochemical equation. For example, if heat of formation of methane is to be determined, write down the following equation:

$$C(s) + 2H_2(g) = CH_4(g); \Delta H = ?$$

(ii) Try to obtain the required equation from the given data. This can be done in two ways:

(a) By adding, subtracting and multiplying the various given thermochemical equations. Or

(b) Heat of reaction = Total enthalpies of products − Total enthalpies of reactants

Note: In case of calculation of heat of formation, the enthalpies of free elements can be arbitrarily fixed as zero at 25° C and 1 atmospheric pressure.

Example 41. *Calculate the standard heat of formation of carbon disulphide (l). Given that the standard heats of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are* –393.3, 293.7 *and* –1108.76 *kJ mol*$^{-1}$ *respectively.*

Solution: Required equation is

$$C(s) + 2S(s) \longrightarrow CS_2(l); \ \Delta H_f = ?$$

Given,

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad (\Delta H = -393.3 \text{ kJ}) \quad ...(i)$$

$$S(s) + O_2(g) \longrightarrow SO_2(g) \qquad (\Delta H = -293.72 \text{ kJ}) \quad ...(ii)$$

$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) \quad ...(iii) \qquad (\Delta H = -1108.76 \text{ kJ})$$

First method: Multiply the eq. (ii) by 2.

$$2S(s) + 2O_2(g) \longrightarrow 2SO_2(g) \quad ...(iv) \quad (\Delta H = -587.44 \text{ kJ})$$

Adding eqs. (i) and (iv) and subtracting eq. (iii),

$$[C(s) + 2S(s) + 3O_2(g) - CS_2(l) - 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g) - CO_2 - 2SO_2]$$

$$C(s) + 2S(s) \longrightarrow CS_2(l)$$

This is the required equation.

Thus, $\Delta H_f = -393.3 - 587.44 + 1108.76 = 128.02$ kJ

Standard heat of formation of $CS_2(l) = 128.02$ kJ

Second method:

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad (\Delta H = -393.3 \text{ kJ}) \quad \ldots(i)$$

$$S(s) + O_2(g) \longrightarrow SO_2(g); \quad (\Delta H = -293.72 \text{ kJ}) \quad \ldots(ii)$$

$$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g); \quad (\Delta H = -1108.76 \text{ kJ}) \quad \ldots(iii)$$

From eqs. (i) and (ii),

Enthalpy of $CO_2 = -393.3$ kJ

Enthalpy of $SO_2 = -293.72$ kJ

Enthalpy of $O_2 = 0$ (By convention)

ΔH of eq. (iii) = Enthalpies of products − Enthalpies of reactants

$$-1108.76 = -393.3 + 2 \times (-293.72) - \Delta H_{CS_2(l)}$$

$$\Delta H_{CS_2(l)} = (1108.76 - 980.74) = 128.02 \text{ kJ}$$

Enthalpy of $CS_2(l) = 128.02$ kJ

Example 42. *Calculate the heat of formation of acetic acid from the following data:*

$$CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \quad ...(i) \quad (\Delta H = -207.9\ kcal)$$

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad (\Delta H = -94.48\ kcal) \quad ...(ii)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad (\Delta H = -68.4\ kcal) \quad ...(iii)$$

Solution: First method: The required equation is

$$2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l); \quad \Delta H = ?$$

This equation can be obtained by multiplying eq. (ii) by 2 and also eq. (iii) by 2 and adding both and finally subtracting eq. (i).

$$[2C + 2O_2 + 2H_2 + O_2 - CH_3COOH(l) - 2O_2 \longrightarrow 2CO_2 + 2H_2O - 2CO_2 - 2H_2O]$$

$$\Delta H_{CH_3COOH(l)} = 2 \times (-94.48) + 2 \times (-68.4) - (-207.9)$$

$$= -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

Second method: From eqs. (ii) and (iii)

Enthalpy of $CO_2 = -94.48$ kcal

Enthalpy of $H_2O = -68.4$ kcal

Enthalpy of $O_2 = 0$ (by convention)

ΔH of eq. (i) = Enthalpies of products − Enthalpies of reactants

$$-207.9 = 2 \times (-94.48) + 2(-68.4) - \Delta H_{CH_3COOH(l)}$$

$$\Delta H_{CH_3COOH(l)} = -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

Example 43. *Given the following standard heats of reactions :*

(a) heat of formation of water = − 68.3 kcal, (b) heat of combustion of $C_2H_2 = -310.6$ kcal and (c) heat of combustion of ethylene = − 337.2 kcal. Calculate the heat of the reaction for the hydrogenation of acetylene at constant volume and at 25° C.

Solution: The required equation is

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g); \quad \Delta H = ?$$

Given,

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ ...(i) ($\Delta H = -68.3$ kcal)

(b) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$ ...(ii) ($\Delta H = -310.6$ kcal)

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$ ...(iii) ($\Delta H = -337.2$ kcal)

The required equation can be achieved by adding eqs. (i) and (ii) and subtracting (iii).

$$C_2H_2(g) + H_2(g) + 3O_2(g) - C_2H_4(g) - 3O_2(g) \longrightarrow 2CO_2 + 2H_2O(l) - 2CO_2(g) - 2H_2O(l)$$

or $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$

$$\Delta H = -68.3 - 310.6 - (-337.2) = -378.9 + 337.2 = -41.7 \text{ kcal}$$

We know that,

$$\Delta H = \Delta E + \Delta nRT$$

or $$\Delta E = \Delta H - \Delta nRT$$

$$\Delta n = (1-2) = -1, R = 2 \times 10^{-3} \text{ kcal mol}^{-1} \text{ K}^{-1}$$

and $$T = (25 + 273) = 298 \text{ K}$$

Substituting the values in above equation,

$$\Delta E = -41.7 - (-1)(2 \times 10^{-3})(298)$$

$$= -41.7 + 0.596 = -41.104 \text{ kcal}$$

Example 44. *Determine the heat of transformation of $C_{(diamond)} \rightarrow C_{(graphite)}$ from the following data:*

$$C_{(diamond)} + O_2(g) \longrightarrow CO_2(g) \quad ...(i) \quad (\Delta H = -94.5\ kcal)$$

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \quad ...(ii) \quad (\Delta H = -94.0\ kcal)$$

Solution: Subtracting eq. (ii) from (i), the required equation is obtained.

$$\Delta H_{\text{transformation}} = -94.5 - (-94.0)$$

$$= -94.5 + 94.0 = -0.5 \text{ kcal}$$

Example 45. *Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst. The reaction is*

$$CO(g) + 2H_2(g) \longrightarrow CH_3OH(l).$$

Determine the enthalpy of this reaction by an appropriate combination of the following data:

$$C_{(graphite)} + \frac{1}{2}O_2(g) \longrightarrow CO(g) \quad ...(i) \quad (\Delta H = -110.5\ kJ\ mol^{-1})$$

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g) \quad ...(ii) \quad (\Delta H = -393.5\ kJ\ mol^{-1})$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad ...(iii) \quad (\Delta H = -285.9\ kJ\ mol^{-1})$$

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad ...(iv) \quad (\Delta H = -726.6\ kJ\ mol^{-1})$$

Solution: The required equation can be obtained in the following manner:

$$-\text{eq. (i)} + 2\text{eq. (iii)} + \text{eq. (ii)} - \text{eq. (iv)} = CO_2(g) + 2H_2(g) \longrightarrow CH_3OH(g)$$

So, $\Delta H = 110.5 - 571.8 - 393.5 + 726.6 = -128.2 \text{ kJ mol}^{-1}$

Example 46. *How much heat will be required to make 2 kg of calcium carbide (CaC_2) according to the following reaction?*

$$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$$

The heats of formation of $CaO(s)$, $CaC_2(s)$ and $CO(g)$ are −151.6, −14.2 and −26.4 kcal respectively.

Solution: $\Delta H = \Sigma \Delta H^\circ_{f\,(\text{products})} - \Sigma \Delta H^\circ_{f\,(\text{reactants})}$

$$= [\Delta H^\circ_{f\,(CaC_2)} + \Delta H^\circ_{f\,(CO)}] - [\Delta H^\circ_{f\,(CaO)} + 3\Delta H^\circ_{f\,(C)}]$$
$$= [-14.2 - 26.4] - [-151.6 + 3 \times 0]$$
$$= -40.6 + 151.6 = 111.0 \text{ kcal}$$

For formation of 64 g of CaC_2 111.0 kcal of heat is required.

So, heat required for making 2000 g of

$$CaC_2 = \frac{111.0}{64} \times 2000 = 3468.75 \text{ kcal}$$

7.18 INFLUENCE OF TEMPERATURE ON THE HEAT OF REACTION OR KIRCHHOFF'S EQUATION

Let us consider a reaction occurring at constant pressure. Heat of reaction at constant pressure may be given as:

$$\Delta H = H_P - H_R$$

Differentiating the above equation with respect to 'T' at constant pressure, we get:

$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_P}{dT}\right)_P - \left(\frac{dH_R}{dT}\right)_P$$
$$= (C_P)_P - (C_P)_R = \Delta C_P$$

or $$d(\Delta H) = \Delta C_P \, dT$$

Integrating above differential equation within proper limit, we get:

$$\int_{T_1}^{T_2} d\Delta H = \Delta C_P \int_{T_1}^{T_2} dT$$
$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_P (T_2 - T_1)$$
$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

Above equation is **Kirchhoff's equation.** It is used to calculate heat of reaction at a temperature provided it is known at another temperature.

Change in heat of reaction due to per degree change in temperature is equivalent to heat capacity difference between reactant and product.

Kirchhoff's equation at constant volume may be given as:

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$$

7.19 BOND ENERGY OR BOND ENTHALPIES

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the bond. The energy required to break the bond is termed bond dissociation energy. The more precise definition is:

The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, *i.e.*, to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy. For example,

$$H—H(g) \longrightarrow 2H(g); \qquad \Delta H = +433 \text{ kJ mol}^{-1}$$
$$Cl—Cl(g) \longrightarrow 2Cl(g); \qquad \Delta H = +242.5 \text{ kJ mol}^{-1}$$
$$H—Cl(g) \longrightarrow H(g) + Cl(g); \qquad \Delta H = +431 \text{ kJ mol}^{-1}$$
$$I—I(g) \longrightarrow 2I(g); \qquad \Delta H = +15.1 \text{ kJ mol}^{-1}$$
$$H—I(g) \longrightarrow H(g) + I(g); \qquad \Delta H = +299 \text{ kJ mol}^{-1}$$

The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. **This average bond dissociation energy required to break each bond in a compound is called bond energy.***

Consider the dissociation of water molecule which consists of two O—H bonds. The dissociation occurs in two stages.

$$H_2O(g) \longrightarrow H(g) + OH(g); \qquad \Delta H = 497.8 \text{ kJ mol}^{-1}$$
$$OH(g) \longrightarrow H(g) + O(g); \qquad \Delta H = 428.5 \text{ kJ mol}^{-1}$$

The average of these two bonds dissociation energies gives the value of bond energy of O—H.

$$\text{Bond energy of O—H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}$$

Similarly, the bond energy of N—H bond in NH_3 is equal to one-third of the energy of dissociation of NH_3 and those of C—H bond in CH_4 is equal to one-fourth of the energy of dissociation of CH_4.

$$\text{Bond energy C—H} = \frac{1664}{4} = 416 \text{ kJ mol}^{-1}$$
$$[CH_4(g) \longrightarrow C(g) + 4H(g); \Delta H = 1664 \text{ kJ mol}^{-1}]$$

Application of Bond Energy

1. Heat of a reaction = Σ Bond energy of reactants − Σ Bond energy of products

Note: In case of atomic species, bond energy is replaced by heat of atomization.

2. **Determination of resonance energy:** When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energie and that determined experimentally.

Resonance energy = Experimental or actual heat of formation ~ Calculated heat of formation.

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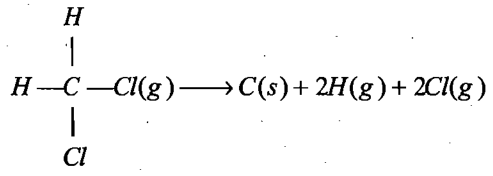
*Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.

$$H(g) + Cl(g) \rightarrow H—Cl(g); \qquad \Delta H = -431 \text{ kJ mol}^{-1}$$

Bond energy of H—Cl = − (enthalpy of formation) = −(−431) = +431 kJ mol^{-1}

SOME SOLVED EXAMPLES

Example 47. *Calculate the ΔH of the reaction,*



$$H-\underset{Cl}{\overset{H}{C}}-Cl(g)\longrightarrow C(s)+2H(g)+2Cl(g)$$

Bond energy for C—H bond and C—Cl bond are 415 *kJ and* 326 *kJ respectively.*

Solution: ΔH = Sum of bond energies of reactants − Sum of bond energies of products

$$=[2\times(C-H)+2\times(C-Cl)]-0$$

(All the products are free atoms)

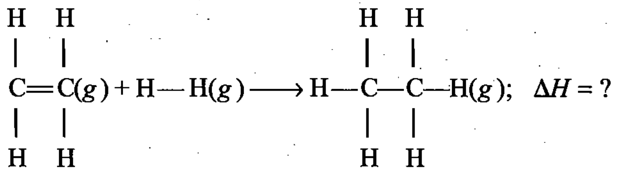
$$=2\times415+2\times326$$
$$=830+652=1482\text{ kJ}$$

Example 48. *Calculate the enthalpy of the following reaction:*

$$H_2C=CH_2(g)+H_2(g)\longrightarrow CH_3-CH_3(g)$$

The bond energies of C—H, C—C, C=C and H—H are 99, 83, 147 *and* 104 *kcal respectively.*

Solution: The reaction is:



$$\underset{H\;\;H}{\overset{H\;\;H}{C=C}}(g)+H-H(g)\longrightarrow H-\underset{H\;\;H}{\overset{H\;\;H}{C-C}}-H(g);\quad \Delta H=?$$

ΔH = Sum of bond energies of reactants − Sum of the bond energies of products

$$=[\Delta H_{C=C}+4\times\Delta H_{C-H}+\Delta H_{H-H}]-[\Delta H_{C-C}+6\times\Delta H_{C-H}]$$
$$=(147+4\times99+104)-(83+6\times99)=-30\text{ kcal}$$

Example 49. *The bond dissociation energies of gaseous H_2, Cl_2 and HCl are* 104, 58 *and* 103 *kcal mol^{-1} respectively. Calculate the enthalpy of formation of HCl(g).*

Solution: The required equation is

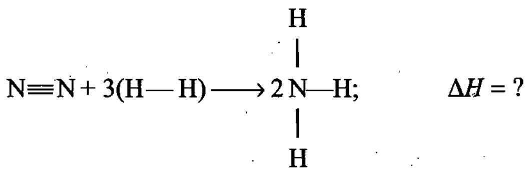
$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\longrightarrow HCl(g);\qquad \Delta H=?$$

$$\Delta H=[\frac{1}{2}\Delta H_{H-H}+\frac{1}{2}\Delta H_{Cl-Cl}]-[\Delta H_{H-Cl}]$$
$$=\frac{1}{2}\times104+\frac{1}{2}\times58-103=-22\text{ kcal mol}^{-1}$$

Example 50. *Calculate the enthalpy of formation of ammonia from the following bond energy data:*

(N—H) bond = 389 kJ mol^{-1}; (H—H) bond = 435 kJ mol^{-1} and (N≡N) bond = 945.36 kJ mol^{-1}.

Solution:



$$N\equiv N+3(H-H)\longrightarrow 2\,\underset{H}{\overset{H}{N}}-H;\qquad \Delta H=?$$

$$\Delta H=[\Delta H_{(N\equiv N)}+3\times\Delta H_{(H-H)}]-[6\Delta H_{(N-H)}]$$
$$=945.36+3\times435.0-6\times389.0=-83.64\text{ kJ}$$

$$\text{Heat of formation of NH}_3=\frac{\Delta H}{2}=-\frac{83.64}{2}=-41.82\text{ kJ mol}^{-1}$$

Example 51. *Calculate the resonance energy of N_2O from the following data:*

$$\Delta H_f^\circ \text{ of } N_2O=82\text{ kJ mol}^{-1}$$

Bond energy of N≡N, N=N, O=O and N=O bonds is 946, 418, 498 *and* 607 *kJ mol^{-1} respectively.* (IIT 1991)

Solution: $N\equiv N(g)+\frac{1}{2}(O=O)\longrightarrow N=N=O(g)$

$$\Delta H_{f(N_2O)}=[\Delta H_{(N\equiv N)}+\frac{1}{2}\Delta H_{(O=O)}]-[\Delta H_{(N=O)}+\Delta H_{(N=N)}]$$
$$=(946+\frac{1}{2}\times498)-(607+418)$$
$$=946+249-607-418$$
$$=1195-1025=170\text{ kJ mol}^{-1}$$

Resonance energy = Observed heat of formation ~ Calculated heat of formation

$$=82\sim170=88\text{ kJ mol}^{-1}$$

Example 52. *The enthalpies for the following reactions at 25° C are given:*

$$\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g)\longrightarrow OH(g);\quad \Delta H=10.06\text{ kcal}$$
$$H_2(g)\longrightarrow 2H(g);\quad \Delta H=104.18\text{ kcal}$$
$$O_2(g)\longrightarrow 2O(g);\quad \Delta H=118.32\text{ kcal}$$

Calculate the O—H bond energy in the OH group.

Solution: Required equation is

$$H(g)+O(g)\longrightarrow O-H(g);\qquad \Delta H=?$$

Given: $\frac{1}{2}H_2(g)+\frac{1}{2}O_2(g)\longrightarrow OH(g);\quad \Delta H=+10.06\text{ kcal}$

$$H(g)\longrightarrow\frac{1}{2}H_2(g);\quad \Delta H=-52.09\text{ kcal}$$
$$O(g)\longrightarrow\frac{1}{2}O_2(g);\quad \Delta H=-59.16\text{ kcal}$$

Adding, $H(g)+O(g)\longrightarrow OH(g);\quad \Delta H=-101.19\text{ kcal}$

Example 53. *The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25° C are −156 and + 49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25° C is −119 kJ mol^{-1}. Use these data to estimate the magnitude of resonance energy of benzene.*

(IIT 1996)

Solution:

Cyclohexene(l) + $H_2(g) \longrightarrow$ Cyclohexane(l); $\Delta H = -119$ kJ

Enthalpy of formation of cyclohexane(l) $= -156$ kJ mol^{-1}

So,enthalpy of formation of cyclohexane $= -156 - (-119)$ kJ

$= -37$ kJ mol^{-1}

Since, $\Delta H_{cyclohexane}$ is -156 kJ mol^{-1}, we can say that for every double bond the energy decreases by an amount $+119$ kJ mol^{-1} and therefore for the introduction of three double bonds (present in benzene ring) the energy required

$$= 3 \times 119 \text{ kJ mol}^{-1} = 357 \text{ kJ mol}^{-1}$$

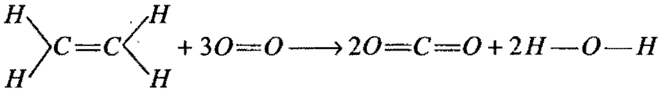
Hence, theoretical ΔH_f for benzene $= (357 - 156)$ kJ mol^{-1}

$= 201$ kJ mol^{-1}

Resonance energy = Theoretical ΔH_f − Observed ΔH_f

$= (201 \sim 49)$ kJ mol^{-1} $= 152$ kJ mol^{-1}

Example 54. *Calculate heat of combustion of ethene:*



$$H_2C{=}CH_2 + 3O{=}O \longrightarrow 2O{=}C{=}O + 2H{-}O{-}H$$

from bond energy data: $C{=}C$, $C{-}H$, $O{=}O$, $C{=}O$, $O{-}H$

BE kJ mol^{-1}: 619 414 499 724 460

Solution:

ΔH = Sum of bond energies of reactants

− Sum of bond energies of products

$$= [\Delta H_{(C=C)} + 4\Delta H_{(C-H)} + 3 \times \Delta H_{(O=O)}]$$
$$- [4 \times \Delta H_{(C=O)} + 4 \times \Delta H_{(O-H)}]$$
$$= [619 + 4 \times 414 + 3 \times 499] - [4 \times 724 + 4 \times 460]$$
$$= -964 \text{ kJ mol}^{-1}$$

Example 55. *Using the data (all values are in kilocalorie per mole at 25° C) given below, calculate the bond energy of C—C and C—H bonds.*

$$\Delta H^\circ_{combustion\ of\ ethane} = -372.0$$

$$\Delta H^\circ_{combustion\ of\ propane} = -530.0$$

$$\Delta H^\circ \ for\ C_{(graphite)} \longrightarrow C(g) = +172.0$$

Bond energy of H—H bond $= +104.0$

$$\Delta H^\circ_f \ of\ H_2O(l) = -68.0$$

$$\Delta H^\circ_f \ of\ CO_2(g) = -94.0$$

Solution:

$$C_2H_6(g) + \frac{7}{2}O_2 \longrightarrow 2CO_2(g) + 3H_2O(l); \ \Delta H = -372.0$$

$$\Delta H^\circ_{f\,(C_2H_6)} = 2 \times (-94.0) + 3 \times (-68.0) + 372.0 = -20 \text{ kcal}$$

$$C_3H_8(g) + 5O_2 \longrightarrow 3CO_2(g) + 4H_2O(l); \ \Delta H = -530.0$$

$$\Delta H^\circ_{f\,(C_3H_8)} = 2 \times (-94.0) + 4 \times (-68.0) + 530.0 = -24 \text{ kcal}$$

$$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g); \quad \Delta H = -20.0$$
$$2C(g) \longrightarrow 2C(s); \quad \Delta H = -344.0$$
$$6H(g) \longrightarrow 3H_2(g); \quad \Delta H = -312.0$$

Adding $2C(g) + 6H(g) \longrightarrow C_2H_6(g)$; $\Delta H = -676$ kcal

So, enthalpy of formation of 6C—H bonds and one C—C bond is -676.0 kcal.

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g); \quad \Delta H = -24.0$$
$$3C(g) \longrightarrow 3C(s); \quad \Delta H = -516.0$$
$$8H(g) \longrightarrow 4H_2(g); \quad \Delta H = -416.0$$

Adding $3C(g) + 8H(g) \longrightarrow C_3H_8(g)$; $\Delta H = -956.0$ kcal

So, enthalpy of formation of 8C—H and 2C—C bonds is

-956 kcal.

Let the bond energy of C—C be x and of C—H be y kcal.

In ethane $x + 6y = 676$

In propane $2x + 8y = 956$

On solving, $x = 82$ and $y = 99$

Thus, bond energy of C—C = 82 kcal and
bond energy of C—H = 99 kcal

Example 56. *Using the bond enthalpy data given below, calculate the enthalpy of formation of acetone* (g).

Bond energy C—H $= 413.4$ *kJ mol*$^{-1}$;

Bond energy C—C $= 347.0$ *kJ mol*$^{-1}$;

Bond energy C=O $= 728.0$ *kJ mol*$^{-1}$;

Bond energy O=O $= 495.0$ *kJ mol*$^{-1}$;

Bond energy H—H $= 435.8$ *kJ mol*$^{-1}$;

$\Delta H_{sub} C(s) = 718.4$ *kJ mol*$^{-1}$

Solution:

$$3C(g) + 6H(g) + O(g) \longrightarrow CH_3COCH_3(g)$$

In acetone, six C—H bonds, one C=O bond and two C—C bonds are present. Energy released in the formation of these bonds is

$$= -6 \times 413.4 - 728.0 - 2 \times 347.0 = -3902.4 \text{ kJ mol}^{-1}$$

The equation of the enthalpy of formation of acetone is

$$3C_{(graphite)} + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3COCH_3(g); \quad \Delta H = ?$$

This equation can be obtained from the following equations by adding:

$$3C(g) + 6H(g) + O(g) \longrightarrow CH_3COCH_3(g);$$
$$\Delta H = -3902.4 \text{ kJ mol}^{-1}$$
$$3C(s) \longrightarrow 3C(g); \quad \Delta H = 2155.2 \text{ kJ mol}^{-1}$$
$$3H_2(g) \longrightarrow 6H(g); \quad \Delta H = 1307.4 \text{ kJ mol}^{-1}$$

and $$\frac{1}{2}O_2(g) \longrightarrow O(g); \quad \Delta H = 247.5 \text{ kJ mol}^{-1}$$

$$3C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3COCH_3(g);$$
$$\Delta H = -192.3 \text{ kJ mol}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. ΔH_f° 298 K of methanol is given by the chemical equation: (AIIMS 2005)

(a) $CH_4(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(g)$

(b) C (graphite) $+ \frac{1}{2}O_2(g) + 2H_2(g) \longrightarrow CH_3OH(l)$

(c) C (diamond) $+ \frac{1}{2}O_2(g) + 2H_2(g) \longrightarrow CH_3OH(l)$

(d) $CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$

[Ans. (b)]

[Hint: In the process of formation, the compound must be formed from constituent elements in their standard state.]

8. The standard molar heat of formation of ethane, CO_2 and H_2O (l) are respectively –21.1, –94.1 and –68.3 kcal. The standard molar heat of combustion of ethane will be:

(a) –372 kcal	(b) –240 kcal
(c) 162 kcal	(d) 183.5 kcal

[Ans. (a)]

[Hint: $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$

$$\Delta H = 2\Delta H_{f(CO_2)} + 3\Delta H_{f(H_2O)} - \Delta H_{f(C_2H_6)}$$
$$= 2(-94.1) + 3(-68.3) - (-21.1) = -372 \text{ kcal}]$$

9. When ethyne is passed through a red hot tube, then formation of benzene takes place:

$$\Delta H^\circ_{f(C_2H_2)(g)} = 230 \text{ kJ mol}^{-1}$$
$$\Delta H^\circ_{f(C_6H_6)(g)} = 85 \text{ kJ mol}^{-1}$$

Calculate the standard heat of trimerisation of ethyne to benzene.

$$3C_2H_2(g) \longrightarrow C_6H_6(g)$$

(a) 205 kJ mol^{-1}	(b) 605 kJ mol^{-1}
(c) – 605 kJ mol^{-1}	(d) –205 kJ mol^{-1}

[Ans. (c)]

[Hint: $$\Delta H_{\text{reaction}} = \Delta H^\circ_{f(C_6H_6)} - 3\Delta H^\circ_{f(C_2H_2)}$$
$$= 85 - 3(230)$$
$$= -605 \text{ kJ mol}^{-1}]$$

10. $F_2(g) + 2HCl(g) \longrightarrow 2HF(g) + Cl_2(g)$;

$$\Delta H^\circ = -352.18 \text{ kJ}$$
$$\Delta H^\circ_{f(HF)} = -268.3 \text{ kJ}$$

The heat of formation of HCl will be:

(a) –22 kJ mol^{-1}	(b) 88 kJ mol^{-1}
(c) –92.21 kJ mol^{-1}	(d) –183.8 kJ mol^{-1}

[Ans. (c)]

[Hint: $$\Delta H^\circ_{\text{reaction}} = 2\Delta H^\circ_{f(HF)} - 2\Delta H^\circ_{f(HCl)}$$
$$-352.18 = 2 \times (-268.3) - 2x$$
$$2x = 2(-268.3) + 352.18$$
$$x = -92.21 \text{ kJ mol}^{-1}]$$

11. Given two processes:

$$\frac{1}{2}P_4(s) + 3Cl_2(g) \longrightarrow 2PCl_3(l); \ \Delta H = -635 \text{ kJ}$$
$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s); \quad \Delta H = -137 \text{ kJ}$$

The value of ΔH_f of PCl_5 is:

(a) 454.5 kJ mol^{-1}	(b) – 454.5 kJ
(c) –772 kJ mol^{-1}	(d) – 498 kJ mol^{-1}

[Ans. (b)]

[Hint: $\frac{1}{4}P_4(s) + \frac{3}{2}Cl_2(g) \longrightarrow PCl_5(l); \ \Delta H = -\frac{635}{2}$ kJ

$$PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s); \ \Delta H = -137 \text{ kJ}$$

On adding, $\frac{1}{4}P_4(s) + \frac{5}{2}Cl_2(g) \longrightarrow PCl_5(s); \ \Delta H = -454.5$ kJ]

12. The enthalpy of combustion at 25°C of H_2, cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) are –241, –3920 and –3800 kJ/mol respectively. The heat of hydrogenation of cyclohexene is: **[CBSE (Med.) 2006]**

(a) –121 kJ/mol	(b) +121 kJ/mol
(c) –242 kJ/mol	(d) +242 kJ/mol

[Ans. (a)]

[Hint: $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \ (\Delta H = -241 \text{ kJ})$ ...(i)

$$C_6H_{10} + \frac{17}{2}O_2(g) \longrightarrow 6CO_2(g) + 5H_2O(l) \quad \text{...(ii)}$$
$$(\Delta H = -3800 \text{ kJ})$$
$$C_6H_{12} + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \quad \text{...(iii)}$$
$$(\Delta H = -3920 \text{ kJ})$$

Eq. (i) + eq. (ii) – eq. (iii) gives

$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ}$$

for $C_6H_{10} + H_2 \longrightarrow C_6H_{12}$]

13. Given that:

$$2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s) \ (\Delta H = -193.4 \text{ kJ}) \ \text{...(i)}$$
$$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s) \ (\Delta H = -140.2 \text{ kJ}) \ \text{...(ii)}$$

What is ΔH of the reaction?

$3Mg + Fe_2O_3 \longrightarrow 3MgO + 2Fe$ **[JEE (Orissa) 2005]**

(a) –227.2 kJ	(b) –272.3 kJ
(c) 227.2 kJ	(d) 272.3 kJ

[Ans. (a)]

[Hint: Subtracting equation 1st from 2nd multiplied by 3,

$$2Fe(s) + \frac{3}{2}O_2(g) \longrightarrow Fe_2O_3(s) \quad (\Delta H = -193.4 \text{ kJ}) \ \text{...(i)}$$
$$3Mg(s) + \frac{3}{2}O_2(g) \longrightarrow 3MgO(s) \quad (\Delta H = -420.6 \text{ kJ}) \ \text{...(ii)}$$

Subtracting eq. (i) from (ii),

$$3Mg(s) + Fe_2O_3 \longrightarrow 3MgO + 2Fe; \ \Delta H = -420.6 - (-193.4)$$
$$= -227.2 \text{ kJ}]$$

14. Given that:

$$2C(s)+2O_2(g)\longrightarrow 2CO_2(g)\quad(\Delta H=-787\text{ kJ})\quad ...(i)$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l)\quad(\Delta H=-286\text{ kJ})\quad ...(ii)$$

$$C_2H_2(g)+\frac{5}{2}O_2(g)\longrightarrow 2CO_2(g)+H_2O(l)\quad ...(iii)$$

$$(\Delta H=-1301\text{ kJ})$$

Heat of formation of acetylene is: [JEE (Orissa) 2005]

(a) –1802 kJ (b) +1802 kJ

(c) –800 kJ (d) +228 kJ

[**Ans.** (d)]

[**Hint:** Required equation is:

$$2C(s)+H_2(g)\longrightarrow C_2H_2(g)$$

Eq. (i) + eq. (ii) – eq. (iii) gives

$$\Delta H=(-787)+(-286)-(-1301)$$
$$=+228\text{ kJ}]$$

15. The enthalpy changes for two reactions are given by the equations:

$$2Cr(s)+\frac{3}{2}O_2(g)\longrightarrow Cr_2O_3(s);\quad \Delta H=-1130\text{ kJ}$$

$$C(s)+\frac{1}{2}O_2(g)\longrightarrow CO(g);\quad \Delta H=-110\text{ kJ}$$

What is the enthalpy change in kJ for the following reaction?

$$3C(s)+Cr_2O_3(s)\longrightarrow 2Cr(s)+3CO(g)$$

(a) –1460 kJ (b) –800 kJ (c) +800 kJ (d) +1020 kJ

(e) +1460 kJ

[**Ans.** (c)]

[**Hint:** $3C(s)+\frac{3}{2}O_2(g)\longrightarrow 3CO(g);\quad \Delta H=-330\text{ kJ}$

$$Cr_2O_3(s)\longrightarrow 2Cr(s)+\frac{3}{2}O_2(g);\quad \Delta H=+1130\text{ kJ}$$

On adding, $3C(s)+Cr_2O_3(s)\longrightarrow 2Cr(s)+3CO(g);$

$$\Delta H=800\text{ kJ}]$$

16. The enthalpy change ΔH for the neutralisation of 1 M HCl by caustic potash in dilute solution at 298 K is: (DPMT 2005)

(a) 68 kJ (b) 65 kJ

(c) 57.3 kJ (d) 50 kJ

[**Ans.** (c)]

[**Hint:** Since, both HCl and KOH are strong, 57.3 kJ heat will be released.]

17. Enthalpy of neutralisation of the reaction between CH_3COOH ($aq.$) and NaOH($aq.$) is –13.2 kcal eq^{-1} and that of the reaction between $H_2SO_4(aq.)$ and KOH($aq.$) is –13.7 kcal eq^{-1}. The enthalpy of dissociation of $CH_3COOH(aq.)$ is:

(a) –0.5 kcal eq^{-1} (b) +0.5 kcal eq^{-1}

(c) –26.9 kcal eq^{-1} (d) +13.45 kcal eq^{-1}

[**Ans.** (b)]

[**Hint:** Dissociation enthalpy of $CH_3COOH=13.7-13.2$ $=0.5$ kcal eq^{-1}. Thus, 0.5 kcal eq^{-1} heat will be used to dissociate CH_3COOH completely.]

18. Calculate the enthalpy change when 50 mL of 0.01 M $Ca(OH)_2$ reacts with 25 mL of 0.01 M HCl. Given that $\Delta H°$ neutralisation of a strong acid and a strong base is 140 kcal mol^{-1}.

(a) 14 kcal (b) 35 cal (c) 10 cal (d) 7.5 cal

[**Ans.** (b)]

[**Hint:** Number of moles of HCl $=\frac{MV}{1000}=\frac{0.01\times 25}{1000}$

$$=25\times 10^{-5}$$

$$HCl\longrightarrow H^+ + Cl^-$$

$$n_{H^+}=25\times 10^{-5}$$

Number of moles of $Ca(OH)_2=\frac{MV}{1000}=\frac{0.01\times 50}{1000}=50\times 10^{-5}$

$$n_{OH^-}=2\times 50\times 10^{-5}=10^{-3}$$

In the process of neutralisation 25×10^{-5} mole H^+ will be completely neutralised

$\therefore\quad \Delta H=140\times 25\times 10^{-5}$ kcal $=0.035$ kcal $=35$ cal]

19. Equal volumes of 1 M HCl and 1 M H_2SO_4 are neutralised by 1 M NaOH solution and x and y kJ/equivalent of heat are liberated respectively. Which of the following relations is correct?

(a) $x=2y$ (b) $x=3y$ (c) $x=4y$ (d) $x=\frac{1}{2}y$

[**Ans.** (d)]

[**Hint:** Since, H_2SO_4 gives 2 moles H^+ while HCl gives 1 mole H^+ from 1 mole after ionisation. Hence, H_2SO_4 will release double amount of heat as compared to HCl,

i.e., $y=2x$ or $x=\frac{y}{2}$]

20. Which of the following acid will release maximum amount of heat when completely neutralised by strong base NaOH?

(a) 1 M HCl (b) 1 M HNO_3

(c) 1 M $HClO_4$ (d) 1 M H_2SO_4

[**Ans.** (d)]

[**Hint:** Ionisation of H_2SO_4 gives double amount of H^+ ions as compared to other acids.

$$H_2SO_4\longrightarrow 2H^+ + SO_4^{2-}\ ]$$

21. Determine the heat of the following reaction:

$$FeO(s)+Fe_2O_3(s)\longrightarrow Fe_3O_4(s)$$

Given informations:

$$2Fe(s)+O_2(g)\longrightarrow 2FeO(s);\quad \Delta H°=-544\text{ kJ}$$
$$4Fe(s)+3O_2(g)\longrightarrow 2Fe_2O_3(s);\quad \Delta H°=-1648.4\text{ kJ}$$
$$Fe_3O_4(s)\longrightarrow 3Fe(s)+2O_2(g);\Delta H°=+1118.4\text{ kJ}$$

(a) –1074 kJ (b) –22.2 kJ (c) +249.8 kJ (d) +2214.6 kJ

[**Ans.** (b)]

[**Hint:** $2FeO(s)\longrightarrow 2Fe(s)+O_2(g);\ \Delta H°=+544\text{ kJ}$

$$2Fe_2O_3(s)\longrightarrow 4Fe(s)+3O_2(g);\ \Delta H°=+1648.4\text{ kJ}$$

$$6Fe(s)+4O_2(g)\longrightarrow 2Fe_3O_4(s);\quad \Delta H°=-2\times 1118.4\text{ kJ}$$

On adding,

$$2FeO(s)+2Fe_2O_3(s)\longrightarrow 2Fe_3O_4(s);\quad \Delta H°=-44.4\text{ kJ}$$

$$\therefore\ FeO(s)+Fe_2O_3(s)\longrightarrow Fe_3O_4(s);\quad \Delta H°=-22.2\text{ kJ}]$$

22. Calculate the enthalpy of formation of ΔH_f for C_2H_5OH from tabulated data and its heat of combustion as represented by the following equations:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \text{...(i)}$$
$$(\Delta H^\circ = -241.8 \text{ kJ mol}^{-1})$$
$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \text{...(ii)}$$
$$(\Delta H^\circ = -393.5 \text{ kJ mol}^{-1})$$
$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 3H_2O(g) + 2CO_2(g) \qquad \text{...(iii)}$$
$$(\Delta H^\circ = -1234.7 \text{ kJ})$$

(a) –2747.1 kJ mol^{-1} (b) –277.7 kJ mol^{-1}
(c) 277.7 kJ mol^{-1} (d) 2747.1 kJ mol^{-1}
[**Ans.** (b)]
[**Hint:** Required equation:

$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$$
$$2C(s) + 2O_2(g) \longrightarrow 2CO_2(g);\ \Delta H^\circ = -2 \times 393.5 \text{ kJ}$$
$$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(g);\ \Delta H^\circ = -3 \times 241.8 \text{ kJ}$$
$$3H_2O(l) + 2CO_2(g) \longrightarrow C_2H_5OH(l) + 3O_2(g);$$
$$\Delta H^\circ = +1234.7 \text{ kJ}$$

On adding,

$$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l);$$
$$\Delta H^\circ = -277.7 \text{ kJ mol}^{-1}]$$

23. Which of the following methods for calculation of heat of a reaction is not correct?
(a) $\Delta H_{\text{reaction}} = \Sigma \Delta H_{f\ \text{products}} - \Sigma \Delta H_{f\ \text{reactants}}$
(b) $\Delta H_{\text{reaction}} = \Sigma(\text{BE})_{\text{reactants}} - \Sigma(\text{BE})_{\text{products}}$
(c) $\Delta H_{\text{reaction}} = \Sigma \Delta H_{\text{comb. (reactants)}} - \Sigma \Delta H_{\text{comb. (products)}}$
(d) $\Delta H_{\text{reaction}} = \Sigma \Delta H_{\text{solution (reactants)}} - \Sigma \Delta H_{\text{solution (products)}}$
[**Ans.** (d)]

24. Heat of combustion of diamond and graphite are –94.5 kcal and –94 kcal/mol respectively. What will be the heat of transition from diamond to graphite?
(a) – 0.5 kcal (b) +0.5 kcal (c) 1 kcal (d) –1 kcal
[**Ans.** (b)]
[**Hint:** $\Delta H = \Delta H_{\text{comb. (diamond)}} - \Delta H_{\text{comb. (graphite)}}$]

25. For the reaction,

$$3N_2O(g) + 2NH_3(g) \longrightarrow 4N_2(g) + 3H_2O(g);$$
$$\Delta H^\circ = -879.6 \text{ kJ}$$

If $\Delta H_f^\circ[NH_3(g)] = -45.9 \text{ kJ mol}^{-1}$;

$\Delta H_f^\circ[H_2O(g)] = -241.8 \text{ kJ mol}^{-1}$

then $\Delta H_f^\circ[N_2O(g)]$ will be:
(a) +246 kJ (b) +82 kJ
(c) –82 kJ (d) –246 kJ
[**Ans.** (b)]
[**Hint:** $\Delta H_{\text{reaction}} = \Sigma \Delta H_{f\ (\text{products})} - \Sigma \Delta H_{f\ (\text{reactants})}$

$$= 4\Delta H_f^\circ[N_2] + 3\Delta H_f^\circ[H_2O] - \{3\Delta H_f^\circ[N_2O]$$
$$+ 2\Delta H_f^\circ[NH_3]\}]$$

26. The bond energies of C═C and C—C at 298 K are 590 and 331 kJ mol^{-1} respectively. The enthalpy of polymerisation per mole of ethylene is:
(a) –70 kJ (b) –72 kJ (c) 72 kJ (d) –68 kJ
[**Ans.** (b)]

[**Hint:** The polymerisation of ethene may be represented as

$$nCH_2 = CH_2 \longrightarrow -\!\!\!\left[CH_2 - CH_2\right]\!\!\!-_n$$

one mole of C ═ C bond is decomposed and two moles of C—C bonds are formed per mole of ethene.

$\therefore\ \Delta H = 590 - 2 \times 331 = -72$ kJ per mol of ethylene.]

27. For the reaction,

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g); \qquad \Delta H = -571 \text{ kJ}$$

bond energy of (H—H) = 435 kJ; of (O═O) = 498 kJ; then calculate the average bond energy of (O—H) bond using the above data. **(DCE 2005)**
(a) 484 kJ (b) – 484 kJ (c) 271 kJ (d) –271 kJ
[**Ans.** (a)]

[**Hint:** $2(H—H) + O{=}O \longrightarrow 2(H—O—H)$

$$\Delta H = \Sigma(\text{BE})_{\text{reactants}} - \Sigma(\text{BE})_{\text{products}}$$
$$-571 = [2 \times 435 + 498] - 4 \times (\text{BE})_{O—H}$$
$$(\text{BE})_{O—H} = \frac{2 \times 435 + 498 + 571}{4} \approx 484 \text{ kJ}]$$

28. Use the bond energies in the table to estimate ΔH for this reaction:

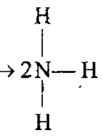
$$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2 - CH_2Cl$$

Bond	C—C	C═C	C—Cl	C—H	Cl—Cl
Bond energy (kJ/mol)	347	612	331	414	243

(a) $\Delta H = -684$ kJ (b) $\Delta H = -154$ kJ
(c) $\Delta H = +89$ kJ (d) $\Delta H = +177$ kJ
[**Ans.** (b)]
[**Hint:**

$$\Delta H_{\text{reaction}} = \Sigma(\text{BE})_{\text{reactants}} - \Sigma(\text{BE})_{\text{products}}$$
$$= [(\text{BE})_{C=C} + 4(\text{BE})_{C—H} + (\text{BE})_{Cl—Cl}]$$
$$- [4(\text{BE})_{C—H} + 2(\text{BE})_{C—Cl} + (\text{BE})_{C—C}]$$
$$= [(\text{BE})_{C=C} + (\text{BE})_{Cl—Cl}] - [2(\text{BE})_{C—Cl} + (\text{BE})_{C—C}]$$
$$= [612 + 243] - [2 \times 331 + 347] = -154 \text{ kJ}]$$

29. Heat of formation of 2 moles of $NH_3(g)$ is –90 kJ; bond energies of H—H and N—H bonds are 435 kJ and 390 kJ mol^{-1} respectively. The value of the bond energy of N≡N will be:
(a) – 472.5 kJ (b) – 945 kJ (c) 472.5 kJ (d) 945 kJ mol^{-1}
[**Ans.** (d)]



[**Hint:** $N{\equiv}N + 3(H—H) \longrightarrow 2\underset{\displaystyle H}{\overset{\displaystyle H}{\overset{|}{\underset{|}{N}}}}—H\ ; \qquad \Delta H = -90 \text{ kJ}$

$$\Delta H_{\text{reaction}} = \Sigma(\text{BE})_{\text{reactants}} - \Sigma(\text{BE})_{\text{products}}$$
$$-90 = [(\text{BE})_{N\equiv N} + 3(\text{BE})_{H—H}] - [6(\text{BE})_{N—H}]$$
$$-90 = x + 3 \times 435 - 6 \times 390$$
$$x = 945 \text{ kJ mol}^{-1}]$$

30. If values of ΔH_f° of $ICl(g)$, $Cl(g)$ and $I(g)$ are respectively 17.57, 121.34, 106.96 J mol^{-1}. The value of I—Cl (bond energy) in J mol^{-1} is:
(a) 17.57 (b) 210.73 (c) 35.15 (d) 106.96
[**Ans.** (b)]
[**Hint:** The process will be:

$$I(g) + Cl(g) \longrightarrow I—Cl(g); \quad \Delta H^\circ = 17.57 \text{ J mol}^{-1}$$

$$\Delta H = \text{Heat of atomisation of } I(g) \text{ and } Cl(g) - \text{Bond energy of I—Cl bond}$$

$$17.57 = 121.34 + 106.96 - x$$

$$x = 210.73 \text{ J mol}^{-1}]$$

31. Calculate the ΔH in joules for:

$$C\,(\text{graphite}) \longrightarrow C\,(\text{diamond})$$

from the following data:

$$C\,(\text{graphite}) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -393.5 \text{ kJ}$$

$$C\,(\text{diamond}) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -395.4 \text{ kJ}$$

[CET (J&K) 2006]

(a) 1900 (b) -788.9×10^3
(c) 190000 (d) $+788.9 \times 10^3$
[**Ans.** (a)]
[**Hint:** $C\,(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H^\circ = -393.5$ kJ

$CO_2(g) \longrightarrow C\,(\text{diamond}) + O_2(g)$; $\Delta H^\circ = +395.4$ kJ

On adding, $C\,(\text{graphite}) \longrightarrow C\,(\text{diamond})$; $\Delta H^\circ = +1900$ J $= +1.9$ kJ]

32. The enthalpy changes for the following processes are listed below:

$$Cl_2(g) \longrightarrow 2Cl(g); \quad \Delta H = 242.3 \text{ kJ mol}^{-1}$$

$$I_2(g) \longrightarrow 2I(g); \quad \Delta H = 151.0 \text{ kJ mol}^{-1}$$

$$ICl(g) \longrightarrow I(g) + Cl(g); \quad \Delta H = 211.3 \text{ kJ mol}^{-1}$$

$$I_2(s) \longrightarrow I_2(g); \quad \Delta H = 62.76 \text{ kJ mol}^{-1}$$

Given that, the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for ICl (g) is: (AIEEE 2006)
(a) -14.6 kJ mol^{-1} (b) -16.8 kJ mol^{-1}
(c) $+16.8$ kJ mol^{-1} (d) $+244.8$ kJ mol^{-1}
[**Ans.** (c)]
[**Hint:** The reaction is:

$$\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \longrightarrow ICl(g)$$

$$\Delta_f H_{I—Cl} = \left[\frac{1}{2} \Delta H_{I_2(s) \to I_2(g)} + \frac{1}{2} \Delta H_{I—I} + \frac{1}{2} \Delta H_{Cl—Cl}\right] - [\Delta H_{I—Cl}]$$

$$= [\frac{1}{2} \times 62.76 + \frac{1}{2} \times 151 + \frac{1}{2} \times 242.3] - [211.3]$$

$$= 16.73 \text{ kJ mol}^{-1}]$$

33. Given that:

$$2C(s) + O_2(g) \longrightarrow 2CO_2(g) \quad (\Delta H = -787 \text{ kJ}) \quad ...(i)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad (\Delta H = -286 \text{ kJ}) \quad ...(ii)$$

$$C_2H_2(g) + 2\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l) \quad ...(iii)$$

$$(\Delta H = -1310 \text{ kJ})$$

The heat of formation of acetylene is: (VITEEE 2007)
(a) -1802 kJ mol^{-1} (b) $+1802$ kJ mol^{-1}
(c) $+237$ kJ mol^{-1} (d) -800 kJ mol^{-1}
[**Ans.** (c)]
[**Hint:** Required equation is:

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$$

It can be obtained by adding eqs. (i) and (ii) and then subtracting eq. (iii) from it.
Heat of formation of acetylene

$$= (-787) + (-286) - (-1310)$$

$$= +237 \text{ kJ mol}^{-1}]$$

7.20 DETERMINATION OF LATTICE ENERGY (Born-Haber Cycle)

Lattice energy of an ionic compound is defined as the amount of energy released when one mole of the compound is formed by the interaction of constituent gaseous cations and gaseous anions.

$$A^+(g) + B^-(g) \longrightarrow \underset{1 \text{ mole}}{A^+B^-} + \underset{\text{(Lattice energy)}}{\text{Energy}}$$

It is represented by the symbol, U. It is given negative sign as the energy is always released. Since, it is difficult to find the lattice energy by direct experiment, it is generally calculated by indirect method known as **Born-Haber cycle** which is based on Hess's law. The cycle can be easily explained by taking the example of the formation of sodium chloride (NaCl). The formation of sodium chloride can be schematically represented as:

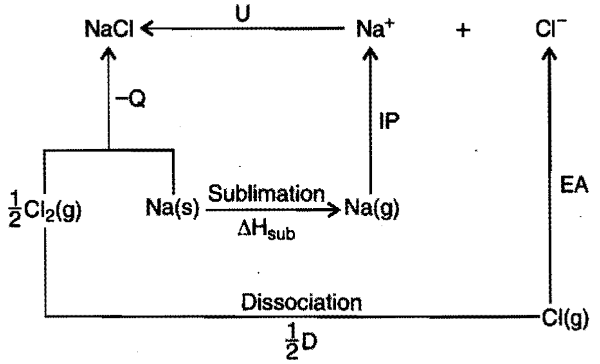


Fig. 7.17

The formation of sodium chloride can occur either by direct combination of sodium(s) and chlorine(g) or in various steps.

Let the heat of formation of sodium chloride by direct combination be $-Q$.

The various steps in the formation of NaCl are the following: In each step, either energy is absorbed or released.

	Steps involved	Energy change
(a)	Solid sodium changes into gaseous sodium. Energy is absorbed. It is sublimation energy. $Na(s) + \text{sublimation energy} \longrightarrow Na(g)$	$+\Delta H_{sub}$
(b)	Gaseous sodium atoms change into gaseous sodium ions. In this step, energy equivalent to ionisation potential is absorbed. $Na(g) + IP \longrightarrow Na^+(g) + e$	$+IP$
(c)	Half mole of molecular chlorine dissociate into one mole of gaseous atomic chlorine. In this step, energy equivalent to one half of the dissociation energy is absorbed. $\frac{1}{2}Cl_2(g) + \frac{1}{2}D = Cl(g)$	$+\frac{1}{2}D$
(d)	Gaseous chlorine atoms change into chloride ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $Cl(g) + e \longrightarrow Cl^-(g) + EA$	$-EA$
(e)	Sodium and chlorine ions are held together by electrostatic forces to form Na^+Cl^-. The energy equivalent to lattice energy is released.	U

Total energies involved in the above five steps

$$= \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$$

Thus, according to Hess's law

$$-Q = \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$$

Example 57. *Calculate the lattice energy for the reaction,*

$$Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$$

from the following data:

$$\Delta H_{sub(Li)} = 160.67\,kJ\,mol^{-1};\ \frac{1}{2}D(Cl_2) = 122.17\,kJ\,mol^{-1}$$

$$IP(Li) = 520.07\,kJ\,mol^{-1};\ EA(Cl) = -365.26\,kJ\,mol^{-1}$$

and $$\Delta H_f^\circ(LiCl) = -401.66\,kJ\,mol^{-1}.$$

Solution: Applying the equation

$$-Q = \Delta H + \tfrac{1}{2}D + IP - EA + U$$

and substituting the respective values,

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 + U$$

$$U = -839.31\,\text{kJ mol}^{-1}$$

Example 58. *When a mole of crystalline sodium chloride is prepared,* 410 *kJ of heat is produced. The heat of sublimation of sodium metal is* 180.8 *kJ. The heat of dissociation of chlorine gas into atoms is* 242.7 *kJ. The ionisation energy of Na and electron affinity of Cl are* 493.7 *kJ and* −368.2 *kJ respectively. Calculate the lattice energy of NaCl.*

Solution: Applying the equation

$$-Q = \Delta H_{sub} + \frac{1}{2}D + IP - EA + U$$

and substituting the respective values,

$$-410 = 108.8 + \frac{1}{2} \times 242.7 + 493.7 - 368.2 + U$$

$$U = -765.65\,\text{kJ mol}^{-1}$$

7.21 EXPERIMENTAL DETERMINATION OF THE HEAT OF REACTION

The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called **calorimeter.** The principle of measurement is that heat given out is equal to heat taken, *i.e.*,

$$Q = (W + m) \times s \times (T_2 - T_1),$$

where, Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of liquid in the calorimeter and s its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are:

(i) Water calorimeter and

(ii) Bomb calorimeter

(i) Water calorimeter

It is a simple form of a calorimeter which can be conveniently used in the laboratory. It is shown in Fig. 7.18.

It consists of a large vessel A in which a calorimeter B is held on corks. In between the calorimeter and the vessel, there is a packing of an insulating material such as cotton wool. Inside the calorimeter there are holes through which a thermometer, a stirrer and the boiling tube containing reacting substances are fitted. A known amount of water is taken in the calorimeter. Known amounts of reacting substances are taken in the boiling tube. The heat evolved during the reaction will be absorbed by the water. The rise in temperature is recorded with the help of thermometer. The heat evolved is then calculated from the formula

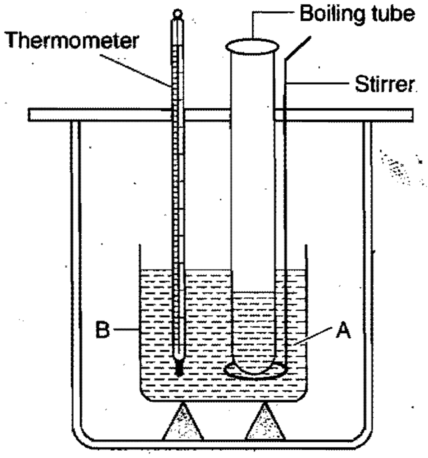


Fig. 7.18

$$(W + m) \times s \times (T_2 - T_1)$$

(ii) Bomb calorimeter

This is commonly used to find the heat of combustion of organic substances. It consists of a sealed combustion chamber, called a bomb. A weighed quantity of the substance in a dish along with oxygen under about 20 atmospheric pressure is placed in the bomb which is lowered in water contained in an insulated copper vessel. The vessel is fitted with a stirrer and a sensitive thermometer. The arrangement is shown in Fig. 7.19.

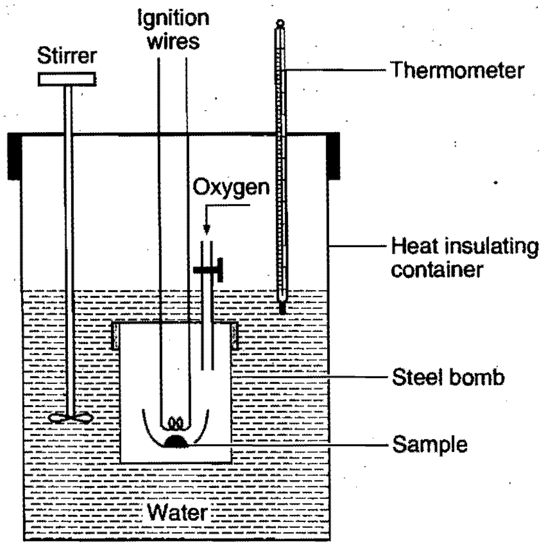


Fig. 7.19

The temperature of the water is noted and the substance is ignited by an electric current. After combustion, the rise in temperature of the system is noted. The heat of combustion can be calculated from the heat gained by water and calorimeter.

Since, the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE.

$$\Delta E = \frac{(W+m)(T_2 - T_1)\times s}{w_1} \times M \text{ kcal}$$

Where, M is the molecular mass of the substance and w_1 is the mass of substance taken.

ΔH can be calculated from the relation,

$$\Delta H = \Delta E + \Delta nRT$$

Example 59. *0.5 g of benzoic acid was subjected to combustion in a bomb calorimeter at 15°C when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the heat of combustion of benzoic acid (i) at constant volume and (ii) at constant pressure. The thermal capacity of the calorimeter including water was found to be 23.85 kJ.*

Solution: (i) Heat of combustion at constant volume, ΔE

= Heat capacity of calorimeter and its contents

$$\times \text{ rise in temperature} \times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 23.85 \times 0.55 \times \frac{122}{0.5} = 3200.67 \text{ kJ}$$

i.e., $\Delta E = -3200.67$ kJ mol

(ii) We know that, $\Delta H = \Delta E + \Delta nRT$

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$$

$\Delta n = 7 - 7.5 = -0.5$; $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}; $T = 288$ K

Substituting the values in the above equation,

$$\Delta H = -3200.67 + 8.314 \times 10^{-3} \times (-0.5) \times 288$$

$$= -3200.67 - 1.197 = -3201.867 \text{ kJ mol}^{-1}$$

Example 60. *A sample of 0.16 g CH_4 was subjected to combustion at 27° C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5° C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K $^{-1}$ and $R = 8.314\ J\ K^{-1}\ mol^{-1}$.* **(IIT 1998)**

Solution: (i) Heat of combustion at constant volume, ΔE

= Heat capacity of calorimeter system × rise in temperature

$$\times \frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

i.e., $\Delta E = -885$ kJ mol^{-1}

(ii) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta n = 1 - 3 = -2$, $T = 300$ K, $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

$$\Delta H = \Delta E + \Delta nRT$$

$$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$$

$$= -885 - 4.988 = -889.988 \text{ kJ mol}^{-1}$$

Example 61. *The heat of combustion of ethane gas is −368 kcal/mol. Assuming that 60% of heat is useful, how many m^3 of ethane measured at NTP must be burned to supply heat to convert 50 kg of water at 10° C to steam at 100° C?*

Solution: Heat required per gram of water

$$= (90 + 540) \text{ cal} = 630 \text{ cal}$$

Total heat needed for 50 kg of water

$$= 50 \times 10^3 \times 630 \text{ cal}$$

As the efficiency is 60%, the actual amount of heat required

$$= \frac{50 \times 10^3 \times 630}{60} \times 100 = 52500 \text{ kcal}$$

No. of mole of ethane required to produce 52500 kcal

$$= \frac{52500}{368} = 142.663 \text{ mole}$$

Volume of 142.663 mole at NTP = 142.663 × 22.4

= 3195.65 litre = 3.195 m^3

7.22 LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

The essence of first law of thermodynamics is that all physical and chemical processes occur in such a way that the total energy of the system and surroundings is constant. The law correlates the various forms of energy, *i.e.*, their interconversion into one another in exactly equivalent amounts. The law has stood the test of time as no transformation has violated the principle of conservation of energy. However, the first law of thermodynamics has a number of limitations.

1. The law does not give any information about the direction in which flow of energy takes place. For example, if two systems A and B which are capable of exchanging heat are brought in contact with each other, the first law of thermodynamics will only tell us that one system loses energy and other system gains the same amount of energy. But the law fails to tell whether the heat will flow from system A to B or from system B to A. In order to predict the direction of the flow of heat, one more parameter, *i.e.*, temperature is required. The heat actually flows from a system which has higher temperature. The process continues till both the systems attain the same temperature. The law fails to answer why heat energy does not flow from cold system to hot system though the energy is conserved in this way also.
2. The law does not explain why the chemical reactions do not proceed to completion.
3. The law does not explain why natural spontaneous processes are irreversible.
4. The law does not contradict the existence of self-acting refrigerator.
5. The law does not contradict the existence of 100% efficient engine.
6. The difference between spontaneous and non-spontaneous processes is insignificant in view of the first law.

The answers to above limitations are provided by second law of thermodynamics. However, before we study this law, let us understand the terms **spontaneous, entropy** and **free energy.**

7.23 SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a special set of conditions (for example, at a certain temperature, pressure and concentration). A reaction that occurs under the given set of conditions is called a **spontaneous reaction.** If a reaction does not occur under specified conditions, it is said to be **non-spontaneous.**

The term spontaneity means the feasibility of a process. In nature, we observe many processes which occur of their own. For example, water flows down the hill without the help of any external agency, heat flows from a conductor at high temperature to another at low temperature, electricity flows from high potential to low potential. There are processes which require some initiation before they can proceed. But once initiated, they proceed by themselves. The burning of carbon, burning of fuels and petrol, etc., require some initiation. These processes are termed as spontaneous on account of their feasibility, *i.e.*, these can occur without the help of external work.

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under the given set of conditions is known as spontaneous process.

Spontaneous process does not mean that it takes place **instantaneously.** It simply implies that the process has an urge to take place and is practically feasible. The actual speed of the process may vary from very low to extremely fast. The rusting of iron is a slow spontaneous process while the neutralisation reaction between an acid and an alkali is a fast spontaneous process. It is a matter of experience also that all natural processes are spontaneous and are **irreversible,** *i.e.*, move in one direction only. The reverse process which can be termed as non-spontaneous can be made to occur only by supplying external energy. For example, water can be made to flow upward by the use of some external agency or energy is always required to lift the ball from the ground. The natural (spontaneous) processes follow a non-equilibrium path and as such are irreversible but these processes proceed up to establishment of equilibrium. At equilibrium state, the process stops to occur any further. Heat flows from a hotter body to a colder body till the temperature of both bodies becomes equal; there is no further flow of heat and we say that the system has attained equilibrium. Some of the familiar examples of spontaneous processes are listed below:

(a) Spontaneous processes where no initiation is required

(i) Dissolution of sugar or salt in water

$$\text{Sugar} + \text{water} \longrightarrow \text{Aqueous solution of sugar}$$
$$\text{Salt} + \text{water} \longrightarrow \text{Aqueous solution of salt}$$

(ii) Evaporation of water from water reservoirs such as ponds, lakes, rivers, sea, open vessels, etc.

$$H_2O(l) \longrightarrow H_2O(g)$$

(iii) Flow of heat from a hot body to a cold body.

(iv) Mixing of different gases.

(v) Flow of water down a hill.

(vi) Reaction between $H_2(g)$ and $I_2(g)$ to form HI(g).

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

(vii) Reaction between nitric oxide gas and oxygen to form nitrogen dioxide.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

(viii) Melting of ice into water.

$$H_2O(s) \longrightarrow H_2O(l)$$

(ix) A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq.) + H_2(g)$$

(x) When a zinc rod is dipped in an aqueous solution of copper sulphate, copper is precipitated.

$$CuSO_4(aq.) + Zn(s) \longrightarrow ZnSO_4(aq.) + Cu(s)$$

(b) Spontaneous processes where initiation is required

(i) Reaction between H_2 and O_2: This reaction is initiated by passing electric spark through the mixture.

$$2H_2(g) + O_2(g) \xrightarrow[\text{spark}]{\text{Electric}} 2H_2O(l)$$

(ii) Coal burns in oxygen or air when ignited. Coal keeps on burning once initiated.

$$C(s)+O_2(g)\xrightarrow{\text{Ignition}}CO_2(g)$$

(iii) Methane burns with oxygen when ignited.

$$CH_4(g)+2O_2(g)\longrightarrow CO_2(g)+2H_2O(l)$$

(iv) A candle made up of wax burns only when ignited.

(v) Calcium carbonate evolves carbon dioxide upon heating.

$$CaCO_3(s)\xrightarrow{\text{Heat}}CaO(s)+CO_2(g)$$

A process which can neither occur by itself nor by initiation is called a non-spontaneous process.

Or

A process which has no natural tendency or urge to occur is said to be a non-spontaneous process.

Few examples of non-spontaneous processes are:

(i) Flow of heat from a cold body to a hot body.
(ii) Dissolution of gold or silver in water.
(iii) Flow of water from ground to overhead tank.
(iv) Hydrolysis of sodium chloride.
(v) Decomposition of water into hydrogen and oxygen.
(vi) Diffusion of gas from a low pressure to a high pressure.

It is not always true that non-spontaneous processes do not occur at all. Many of the non-spontaneous processes or changes can be made to take place when energy from some external source is supplied continuously throughout the change. (However, the processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction). For example, the decomposition of water into hydrogen and oxygen (non-spontaneous process) can occur when electrical energy is supplied to water. The process stops when the passage of electrical energy is stopped.

Driving force for a spontaneous process: After having learnt about spontaneous processes, a very obvious question arises in our minds that why some processes are spontaneous? Obviously there must be some kind of driving force which is responsible for driving the process or a reaction in a particular direction.

The force which is responsible for the spontaneity of a process is called the driving force.

Let us now discuss the nature of the driving force.

1. Tendency to acquire minimum energy: We know that, *lesser is the energy, greater is the stability.* Thus, every system tends to acquire minimum energy. For example:

(i) Heat flows from high temperature to low temperature so that heat content of hot body becomes minimum.
(ii) Water flows down a hill or a slope to have minimum energy (potential).
(iii) A wound watch spring tends to unwind so that mechanical energy of watch becomes minimum.

All the above processes are spontaneous because of a tendency to acquire minimum energy.

It has been observed that most of the spontaneous chemical reactions are exothermic. For example:

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l);\quad \Delta H=-286.2\text{ kJ mol}^{-1}$$

$$C(s)+O_2(g)\longrightarrow CO_2(g);\quad \Delta H=-395\text{ kJ mol}^{-1}$$

$$N_2(g)+3H_2(g)\longrightarrow 2NH_3(g);\quad \Delta H=-92.4\text{ kJ mol}^{-1}$$

In exothermic reactions, heat is evolved from the system, *i.e.*, energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthalpy of system $(\Delta H=-\text{ve})$.

Hence, it can be concluded that the negative value of ΔH may be the criterion of spontaneity.

Limitations of the criterion for minimum energy

(a) Spontaneous endothermic reactions or processes: A number of endothermic reactions and processes are known which are spontaneous, *i.e.*, when ΔH is +ve. Some examples are given below:

(i) Evaporation of water or melting of ice takes place by absorption of heat from surroundings, *i.e.*, these processes are endothermic $(\Delta H=+\text{ve})$.

$$H_2O(s)\longrightarrow H_2O(l);\quad \Delta H=+6.0\text{ kJ mol}^{-1}$$

$$H_2O(l)\longrightarrow H_2O(g);\quad \Delta H=+44\text{ kJ mol}^{-1}$$

(ii) The decomposition of $CaCO_3$ is non-spontaneous at room temperature but becomes spontaneous when the temperature is raised.

$$CaCO_3(s)\longrightarrow CaO(s)+CO_2(g);\ \Delta H=+178.3\text{ kJ mol}^{-1}$$

(iii) Compounds like NH_4Cl, KCl, etc., dissolve in water by absorption of heat from water. Temperature of the water decreases.

$$NH_4Cl(s)+aq.\longrightarrow NH_4^+(aq.)+Cl^-(aq.);\quad \Delta H=+15.1\text{ kJ mol}^{-1}$$

(iv) Dinitrogen pentoxide (N_2O_5) decomposes spontaneously at room temperature into NO_2 and O_2, although the reaction is highly endothermic.

$$2N_2O_5(g)\longrightarrow 4NO_2(g)+O_2(g);\quad \Delta H=219\text{ kJ mol}^{-1}$$

(v) The decomposition of HgO becomes spontaneous on heating.

$$2HgO(s)\longrightarrow Hg(l)+O_2(g);\quad \Delta H=90.3\text{ kJ mol}^{-1}$$

(b) Occurrence of reversible reactions: A large number of reactions are reversible in nature. In these reactions, both forward and backward reactions occur simultaneously in spite of the fact that one reaction is exothermic $(\Delta H=-\text{ve})$ and other endothermic $(\Delta H=+\text{ve})$.

(i)
$$\begin{array}{ll} H_2(g)+I_2(g)\longrightarrow 2HI(g); & \Delta H=-\text{ve} \\ 2HI(g)\longrightarrow H_2(g)+I_2(g); & \Delta H=+\text{ve} \\ \hline H_2(g)+I_2(g)\rightleftharpoons 2HI(g) & \end{array}$$

$$\begin{array}{ll}\text{(ii)}\; N_2(g)+3H_2(g)\longrightarrow 2NH_3(g); & \Delta H=-\text{ve}\\ \quad 2NH_3(g)\longrightarrow N_2(g)+3H_2(g); & \Delta H=+\text{ve}\\ \hline N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g) & \end{array}$$

(c) Reactions having zero ΔH: A number of reactions are known in which neither energy is evolved nor absorbed, but these are spontaneous. For example, esterification of acetic acid is a spontaneous process. ΔH of this reaction is zero.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

(d) Exothermic reactions fail to achieve completion: Every exothermic reaction rarely proceeds to completion even though ΔH remains negative throughout. In fact, all spontaneous reactions proceed in a direction until an equilibrium is attained.

Since, some spontaneous reactions are exothermic and others are endothermic, it is clear that enthalpy alone cannot account for spontaneity. There must be some other factor responsible for spontaneity or feasibility of a process.

2. Tendency to acquire maximum randomness: There is another natural tendency that must be taken into account to predict the direction of spontaneity.

Nature tends to move spontaneously from a state of lower probability to one of higher probability, *i.e.*, things tend to change from organized to disorganized. To illustrate what this statement means, we consider a spontaneous process of intermixing of two inert gases for which ΔH is zero. Two different inert gases, let us say helium (He) and neon (Ne), are originally contained in different glass bulbs, separated by a stopcock as shown in Fig. 7.20(a). To make the system as **closed** one, the entire system is perfectly insulated.

When the valve is opened, the intermixing of the two inert gases occurs due to diffusion into one another. As the gases are inert, there is no chemical interaction between them, the heat change during intermixing is negligible. The process of intermixing is a spontaneous process. If the process is examined critically, it is observed that when the valve is opened, both the gases are provided larger volume to occupy, *i.e.*, each gas achieves its own most probable distribution, independent of the presence of other gas. The final distribution is clearly much more probable than the initial distribution. There is, however, another useful way of looking at this process. The system has gone from a highly ordered state (all the helium molecules on the left, all the neon molecules on the right) to a more disordered or random state. Mixed gases cannot be separated on their own. Thus, diffusion is a spontaneous process acquiring more randomness.

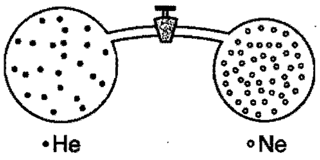


Fig. 7.20 (a)
Inert gases before mixing

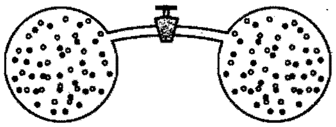


Fig. 7.20 (b)
Inert gases after mixing

In general, nature tends to move spontaneously from more ordered to more random states, or *a process proceeds spontaneously in a direction in which randomness of the system increases.*

Another example of achieving more randomness is the sugar dissolving in water. Before the solid sugar dissolves, the sugar molecules are organized in a crystal. As the molecules dissolve, they become distributed randomly and uniformly throughout the liquid. The opposite process never occurs, *i.e.*, sugar cubes do not form from the solution.

Thus, the second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness.

On the basis of second factor we may also explain the spontaneity of endothermic processes.

(i) *Decomposition of calcium carbonate*:

$$CaCO_3(s)\longrightarrow CaO(s)+CO_2(g);\quad \Delta H=+178.3\text{ kJ mol}^{-1}$$

This process is spontaneous because the gaseous CO_2 produced is more random than solid calcium carbonate.

(ii) *Evaporation of water*:

$$H_2O(l)\longrightarrow H_2O(g);\qquad \Delta H=+44\text{ kJ mol}^{-1}$$

The gaseous state of a substance is more random than the liquid state. Thus, evaporation of water is spontaneous which proceeds in the direction of more randomness.

Similarly, fusion of ice is also spontaneous because the process again proceeds in the direction of more random state, *i.e.*, liquid state is more random in comparison to solid state.

$$H_2O(s)\longrightarrow H_2O(l);\qquad \Delta H=+6.06\text{ kJ mol}^{-1}$$

(iii) *Dissolution of NH_4Cl in water*:

$$NH_4Cl(s)+aq.\longrightarrow NH_4^+(aq.)+Cl^-(aq.);\qquad \Delta H=+15.1\text{ kJ mol}^{-1}$$

When solid $NH_4Cl(s)$ is dissolved in water, its ions become free. Free ions move randomly in all directions. Thus, the solution is a more random state as compared to solid NH_4Cl. Thus, the process of dissolution will be spontaneous because randomness increases on dissolution.

(iv) *Decomposition of mercuric oxide*:

$$2HgO(s)\longrightarrow 2Hg(l)+O_2(g);\qquad \Delta H=+90.3\text{ kJ mol}^{-1}$$

Here again the process will be spontaneous because the product is more random than reactant due to presence of gaseous O_2.

Limitations of the criterion for maximum randomness: Like energy factor, the randomness factor has also certain limitations. For example, in the liquefaction of a gas or in the solidification of a liquid, the randomness of the particles decreases but still these processes are spontaneous. Thus, like energy factor, randomness alone cannot be the sole criterion for the spontaneity of a process.

Overall tendency as driving force for a spontaneous process

From the above discussion, it is apparent that the spontaneous processes occur because of the two tendencies:

(i) Tendency of a system to achieve a state of minimum energy.

(ii) Tendency of a system to achieve a state of maximum randomness.

The overall tendency of a process to be spontaneous depends on the resultant of the above two factors. The resultant of the two tendencies or overall tendency for a process to occur is termed the **driving force.**

Here, it should be noted that these tendencies are independent of each other. Both may act in the same or in opposite directions in a process.

Case I: *When enthalpy factor is absent then randomness factor decides spontaneity of a process.*

Case II: *When randomness factor is absent then enthalpy or energy factor decides spontaneity of a process.*

Case III: *When both factors take place simultaneously then magnitude of the tendencies becomes important to decide spontaneity.*

7.24 ENTROPY

Why do systems tend to move spontaneously to a state of maximum randomness or disorder? The answer is that a disordered state is more probable than an ordered state because the disordered state can be achieved in more ways. The following example illustrates the point. Suppose that you shake a box containing 10 identical coins and then count the number of heads (H) and tails (T). It is very unlikely that all the 10 coins will come up heads; *i.e.*, perfectly ordered arrangement is much less probable than the totally disordered state in which heads and tails come up randomly. The perfectly ordered state of 10 heads can be achieved in only one way and the totally disordered state can be achieved in 2^{10} (1024) ways, *i.e.*, the totally disordered state is 2^{10} times more probable than the perfectly ordered state. If the box contained 1 mol of coins, the perfectly ordered state would be only one, but the disordered states would be much higher ($2^{N_A} = 2^{6.02 \times 10^{23}}$). It is thus, concluded that a change which brings about randomness is more likely to occur than one that brings about order. The extent of disorder or randomness is expressed by a property known as **entropy.**

Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol 'S'. It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state. The change in entropy from initial to final state of a system is represented by ΔS. The entropy is a state function and depends only on the initial and final states of the system.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When $S_{\text{final}} > S_{\text{initial}}$, ΔS is positive.

For a chemical reaction,

$$\Delta S = S_{\text{(products)}} - S_{\text{(reactants)}}$$

Mathematical Definition of Entropy

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature (isothermally).

$$\int dS = \frac{1}{T}\int \delta q_{\text{rev}}$$

or

$$\Delta S = \frac{q_{\text{rev}}}{T} \qquad \text{... (i)}$$

If heat is absorbed, then ΔS is positive (increase in entropy). If heat is evolved, ΔS is negative (decrease in entropy). The value of ΔS, like ΔE and ΔH, is a definite quantity and depends on the initial and final states of the system. It is independent of the manner in which the change has been brought about, *i.e.*, whether the change has been brought about reversibly or irreversibly.

Several factors influence the amount of entropy that a system has in a particular state. In general,

(i) The value of entropy depends on the mass of the system. Hence, it is an extensive property.

(ii) A liquid has a higher entropy than the solid from which it is formed. In a solid, the atoms, molecules or ions are fixed in position; in the liquid, these particles are free to move past one another, *i.e.*, liquid structure is more random and the solid more ordered.

(iii) A gas has a higher entropy than the liquid from which it is formed. When vaporization occurs, the particles acquire greater freedom to move about.

(iv) Increasing temperature of a substance increases its entropy. Raising the temperature increases the kinetic energy of the molecules (atoms or ions) and hence their freedom of motion. In the solid, the molecules vibrate with a greater amplitude at higher temperatures. In a liquid or a gas, they move about more rapidly.
In other words, the more heat the system absorbs, the more disordered it becomes. Furthermore, if heat is absorbed at low temperature, it becomes more disordered than when the same amount of heat is added at higher temperature.

Units of Entropy and Entropy Change

Since, entropy change is expressed by a heat term divided by temperature, it is expressed in terms of calories per degree, *i.e.*, cal K^{-1}. In SI units, the entropy change is expressed in terms of joules per degree, *i.e.*, J K^{-1}. Entropy is an extensive property, *i.e.*, it depends on the mass of the substance; hence units of entropy are expressed as cal deg^{-1} mol^{-1} (cal K^{-1} mol^{-1}) or joule deg^{-1} mol^{-1} (J K^{-1} mol^{-1}).

Spontaneity in Terms of Entropy Change

In an isolated system, such as mixing of gases, there is no exchange of energy or matter between the system and surroundings. However, the mixing of gases is accompanied by randomness, *i.e.*, there is increase in entropy. Therefore, it can be stated that **for a spontaneous process in an isolated system, the change in entropy is positive, *i.e.*, $\Delta S > 0$.**

However, if a system is not isolated, the entropy changes of both the system and surroundings are to be taken into account because system and surroundings together constitute the **isolated system.** Thus, the total entropy change (ΔS_{total}) is sum of the change in entropy of the system (ΔS_{system}) and the change in entropy of the surroundings ($\Delta S_{\text{surroundings}}$), *i.e.*,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \qquad \text{... (ii)}$$

For a spontaneous process, ΔS_{total} must be positive, *i.e.*,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \qquad \text{... (iii)}$$

ΔS_{total} is also termed as $\Delta S_{\text{universe}}$

During a spontaneous process, the entropy of the system goes on increasing till the system attains the equilibrium state, *i.e.*, entropy of the system becomes maximum and, therefore, no more increase in the entropy of the system is possible. The mathematical condition for equilibrium is,

$$\Delta S = 0 \, (\text{at equilibrium for an isolated system}) \qquad \text{... (iv)}$$

If ΔS_{total} is negative, the direct process is non-spontaneous whereas the reverse process is spontaneous.

This can be illustrated by considering the entropy changes in the conversion of water to ice at three different temperatures. The relevent entropy changes for the system and surroundings and total change are given in the following table:

Temperature		ΔS_{system}	$\Delta S_{\text{surrounding}}$	ΔS_{total}
°C	K	$\text{J K}^{-1}\text{ mol}^{-1}$	$\text{J K}^{-1}\text{ mol}^{-1}$	$\text{J K}^{-1}\text{ mol}^{-1}$
−1	272	−21.85	+21.93	+0.08
0	273	−21.99	+21.99	0.00
+1	274	−22.13	+22.05	−0.08

At 272 K: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$= -21.85 + 21.93 = +0.08 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\therefore \quad \Delta S_{\text{process}} > 0 \quad \text{at } 272 \text{ K}$$

Thus, *freezing of ice at 272 K, $H_2O(l) \rightarrow H_2O(s)$ will be spontaneous.*

At 273 K: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$= -21.99 + 21.99 = 0$$

$$\Delta S_{\text{total}} = 0$$

Thus, *at this temperature, water and ice will be at equilibrium.*

$$H_2O(l) \rightleftharpoons H_2O(s); \quad \Delta S = 0 \text{ at } 273 \text{ K} \quad (\text{at equilibrium})$$

At 274 K: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$$= -22.13 + 22.05 = -0.08 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta S < 0$$

Thus, *freezing of water will be non-spontaneous at* 274 *K.*

$$H_2O(l) \longrightarrow H_2O(s) \qquad \Delta S < 0 \, (\text{non-spontaneous})$$

Entropy Change in Reversible Process

Consider an isothermal reversible process. In this process, let the system absorb q amount of heat from surroundings at temperature T. The increase in the entropy of the system will be

$$\Delta S_{\text{system}} = +\frac{q}{T}$$

On the other hand, surroundings lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will

$$\Delta S_{\text{surroundings}} = -\frac{q}{T}$$

Total change in entropy of the process = entropy change in system + entropy change in surroundings

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= \frac{q}{T} - \frac{q}{T} = 0$$

When the reversible process is **adiabatic,** there will be no heat exchange between system and surroundings, *i.e.*, $q = 0$

$$\therefore \quad \Delta S_{\text{system}} = 0, \; \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

Entropy Change in Irreversible Processes

Consider a system at higher temperature T_1 and its surroundings at lower temperature T_2. 'q' amount of heat goes irreversibly from system to surroundings.

$$\therefore \quad \Delta S_{\text{system}} = -\frac{q}{T_1}$$

$$\Delta S_{\text{surroundings}} = +\frac{q}{T_2}$$

$$\Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= -\frac{q}{T_1} + \frac{q}{T_2} = q\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

But $T_1 > T_2$, $\therefore$ $T_1 - T_2 = +\text{ve}$

or $\quad \Delta S_{\text{process}} > 0$

Hence, *entropy increases in an irreversible process.*

Entropy Change for Ideal Gases

Change in entropy for an ideal gas under different conditions may be calculated as:

(i) *When changes from initial state* (1) *to final state* (2):

$$\Delta S = 2.303 n C_V \log\left(\frac{T_2}{T_1}\right) + 2.303 nR \log\left(\frac{V_2}{V_1}\right)$$

(when T and V are variables)

$$\Delta S = 2.303 n C_P \log\left(\frac{T_2}{T_1}\right) + 2.303 nR \log\left(\frac{P_1}{P_2}\right)$$

(when T and P are variables)

(ii) *Entropy change for isothermal process*:

$$\Delta S = 2.303 nR \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$$

(iii) *Entropy change for isobaric process (at constant pressure)*:

$$\Delta S = 2.303nC_P \log\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2.303nC_P \log\left(\frac{V_2}{V_1}\right)$$

(iv) *Entropy change for isochoric process (at constant volume)*:

$$\Delta S = 2.303nC_V \log\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2.303nC_V \log\left(\frac{P_2}{P_1}\right)$$

(v) *Entropy change in mixing of ideal gases*: Let n_1 mole of gas A and n_2 mole of gas B are mixed; then total entropy change can be calculated as:

$$\Delta S = -2.303R[n_1 \log x_1 + n_2 \log x_2]$$

x_1, x_2 are mole fractions of gases A and B,

i.e., $$x_1 = \frac{n_1}{n_1 + n_2}; x_2 = \frac{n_2}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303R\left[\frac{n_1}{n_1 + n_2}\log x_1 + \frac{n_2}{n_1 + n_2}\log x_2\right]$$

$$\Delta S/\text{mol} = -2.303R[x_1 \log x_1 + x_2 \log x_2]$$

Entropy change in adiabatic expansion will be zero, $\Delta S = 0$.

Physical Significance of Entropy at a Glance

1. **Entropy as unavailable energy:** Entropy is unavailable energy of the system.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature in K}}$$

2. **Entropy and randomness:** Entropy is a measure of disorderness or randomness in the system. Increase in entropy means change from an ordered to less ordered (or disordered) state.

3. **Entropy and probability:** Entropy may be defined as a function of probability of the thermodynamic state. Since, we know that both the entropy and thermodynamic probability increase simultaneously in a process, hence the state of equilibrium is the state of maximum probability.

Characteristics of Entropy

The important characteristics of entropy are summarised below:

(i) Entropy is an extensive property. It is difficult to determine the absolute value of entropy of a substance but its value depends on mass of the substance present in the system.

(ii) Entropy of a system is a state function. It depends on the state variables such as T, P, V and n which govern the state of the system.

(iii) The change in entropy taking place in going from one state to another state does not depend on the path adopted. It actually depends on the final and initial states of the system.

$$\text{Change in entropy, } \Delta S = S_{\text{final}} - S_{\text{initial}}$$

(iv) The entropy change for a cyclic process is zero.

(v) The entropy change in the equilibrium state is zero ($\Delta S = 0$).

(vi) For natural processes, entropy of universe is increasing.

$$\Delta S_{\text{universe}} > 0$$

(vii) In a reversible process, ΔS_{total} or $\Delta S_{\text{universe}} = 0$ and therefore

$$\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$$

(viii) For adiabatic reversible process,

$$\Delta S_{\text{system}} = \Delta S_{\text{surroundings}} = \Delta S_{\text{total}} = 0$$

In a spontaneous (irreversible process),

$$\Delta S_{\text{total}} \text{ or } \Delta S_{\text{universe}} > 0,$$

i.e., in spontaneous processes, there is always increase in entropy of the universe.

7.25 ENTROPY CHANGE DURING PHASE TRANSITIONS

Solid, liquid and gas are the three forms of a matter. The change of a substance from one form to another is known as **phase transformation.** Such changes occur at definite temperatures and are accompanied by entropy change. During these transformations either heat is absorbed or evolved, *i.e.*, the entropy either increases or decreases accordingly.

The entropy change for these transformations is given by

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where, q_{rev} is the heat absorbed or evolved and T is the temperature of transition. q_{rev} is actually the molar enthalpy change of the substance.

(i) Entropy of fusion: The entropy of fusion is defined as the change in entropy when one mole of a solid substance changes into liquid form at the melting temperature.

The heat absorbed is equal to the latent heat of fusion

$$\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

For example, when ice melts, the change in entropy is given by

$$\Delta S_{\text{fusion (ice)}} = S_{\text{water}} - S_{\text{ice}} = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{6000 \text{ J mol}^{-1}}{273}$$

$$= 21.98 \text{ J K}^{-1} \text{ mol}^{-1}$$

(ii) Entropy of vaporisation: It is defined as the change in entropy when one mole of the liquid substance changes into vapours (gas) at its boiling point.

$$\Delta S_{\text{vapour}} = S_{\text{vapour}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}}$$

Where, ΔH_{vapour} is the latent heat of vaporisation and T_{bp} is the boiling point.

For example, when water is converted into steam, the change in entropy is given by

$$\Delta S_{\text{vapour (water)}} = S_{\text{steam}} - S_{\text{water}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}} = \frac{40626\ \text{J mol}^{-1}}{373}$$

$$= 108.9\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(iii) Entropy of sublimation: Sublimation involves the direct conversion of a solid into its vapour. The entropy of sublimation is defined as the change in entropy when one mole of a solid changes into vapour at a particular temperature.

$$\Delta S_{\text{sub}} = S_{\text{vapour}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

Where, ΔH_{sub} = heat of sublimation at temperature T.

SOME SOLVED EXAMPLES

Example 62. *The enthalpy change, for the transition of liquid water to steam, ΔH_{vapour} is 40.8 kJ mol^{-1} at 373 K. Calculate entropy change for the process.*

Solution: The transition under consideration is:

$$H_2O(l) \longrightarrow H_2O(g)$$

We know that, $\quad \Delta S_{\text{vapour}} = \dfrac{\Delta H_{\text{vapour}}}{T}$

Given, $\quad \Delta H_{\text{vapour}} = 40.8\ \text{kJ mol}^{-1}$

$$= 40.8 \times 1000\ \text{J mol}^{-1}$$

$$T = 373\ \text{K}$$

Thus, $\quad \Delta S_{\text{vapour}} = \dfrac{40.8 \times 1000}{373} = 109.38\ \text{J K}^{-1}\ \text{mol}^{-1}$

Example 63. *What is entropy change for the conversion of one gram of ice to water at 273 K and one atmospheric pressure? ($\Delta H_{fusion} = 6.025\ kJ\ mol^{-1}$)*

Solution: $\quad \Delta H_{\text{fusion}} = 6.025 \times 1000\ \text{J mol}^{-1}$

$$= \frac{6025}{18}\ \text{J g}^{-1} = 334.72\ \text{J g}^{-1}$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$= \frac{334.72}{273} = 1.226\ \text{J K}^{-1}\ \text{g}^{-1}$$

Example 64. *Calculate the enthalpy of vaporisation per mole for ethanol. Given, $\Delta S = 109.8\ J\ K^{-1}\ mol^{-1}$ and boiling point of ethanol is 78.5°C.*

Solution: We know that,

$$\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T_{\text{bp}}}$$

Given, $\quad \Delta S_{\text{vapour}} = 109.8\ \text{J K}^{-1}\ \text{mol}^{-1}$

$$T_{\text{bp}} = 78.5 + 273 = 351.5\ \text{K}$$

Substituting these values in above equation, we get

$$109.8 = \frac{\Delta H_{\text{vapour}}}{351.5}$$

$$\Delta H_{\text{vapour}} = 38594.7\ \text{J mol}^{-1}$$

$$= 38.594\ \text{kJ mol}^{-1}$$

Example 65. *Calculate the entropy change for the following reversible process:*

$$\underset{1\ mol\ at\ 1\ atm}{\alpha\text{-}Tin} \rightleftharpoons \underset{1\ mol\ at\ 1\ atm}{\beta\text{-}Tin} \qquad at\ 13°C$$

$(\Delta H_{trans} = 2090\ J\ mol^{-1})$

Solution: $\quad \Delta S_{\text{trans}} = \dfrac{\Delta H_{\text{trans}}}{T} = \dfrac{2090}{286}$

$$= 7.3076\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 66. *At 0°C, ice and water are in equilibrium and enthalpy change for the process $H_2O(s) \rightleftharpoons H_2O(l)$ is 6 kJ mol^{-1}. Calculate the entropy change for the conversion of ice into liquid water.*

Solution: We know that for the process of fusion,

$$H_2O(s) \rightleftharpoons H_2O(l)$$

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

$$= \frac{6 \times 1000}{273} = 21.98\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 67. *The enthalpy of vaporisation of liquid diethyl ether $(C_2H_5)_2O$ is 26 kJ mol^{-1} at its boiling point 35°C. Calculate $\Delta S°$ for conversion of:*

(a) liquid to vapour,
(b) vapour to liquid at 35°C.

Solution: (a) $\quad \Delta S_{\text{vaporisation}} = \dfrac{\Delta H_{\text{vaporisation}}}{T_{\text{bp}}} = \dfrac{26000}{308}$

$$= 84.42\ \text{J K}^{-1}\ \text{mol}^{-1}$$

(b) $\quad \Delta S_{\text{condensation}} = -\Delta H_{\text{vaporisation}}$

$$= -84.42\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Example 68. *Calculate entropy change when 10 moles of an ideal gas expands reversibly and isothermally from an initial volume of 10 litre to 100 litre at 300 K.*

Solution: $\quad \Delta S = 2.303 nR \log\left(\dfrac{V_2}{V_1}\right)$

$$= 2.303 \times 10 \times 8.314 \log\left(\frac{100}{10}\right)$$

$$= 191.24\ \text{J K}^{-1}$$

Example 69. *Oxygen gas weighing 64 g is expanded from 1 atm to 0.25 atm at 30°C. Calculate entropy change, assuming the gas to be ideal.*

Solution:
$$n = \frac{w}{\text{m. wt.}} = \frac{64}{32} = 2$$
$$\Delta S = 2.303 nR \log\left(\frac{P_1}{P_2}\right)$$
$$= 2.303 \times 2 \times 8.314 \log\left(\frac{1}{0.25}\right)$$
$$= 23.053 \text{ J K}^{-1}$$

Example 70. *Calculate the change in entropy when 1 mole nitrogen gas expands isothermally and reversibly from an initial volume of 1 litre to a final volume of 10 litre at 27° C.*

Solution:
$$\Delta S = 2.303\, nR \log\left(\frac{V_2}{V_1}\right)$$
$$= 2.303 \times 1 \times 8.134 \log\left(\frac{10}{1}\right)$$
$$= 19.12 \text{ J K}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. For a liquid, enthalpy of fusion is 1.435 kcal mol^{-1} and molar entropy change is 5.26 cal mol^{-1} K^{-1}. The melting point of the liquid is:

(a) 0°C (b) – 273°C
(c) 173 K (d) 100°C

[Ans. (a)]

[Hint: $\Delta S_{\text{fusion}} = \dfrac{\Delta H_{\text{fusion}}}{T_{\text{mp}}}$
$$5.26 = \frac{1.435 \times 1000}{T_{\text{mp}}}$$
$$T_{\text{mp}} = \frac{1435}{5.26} = 273 \text{ K, i.e., } 0° \text{C}]$$

35. Latent heat of vaporisation of water is 540 cal g^{-1} at 100°C. Calculate the entropy change when 1000 g water is converted to steam at 100°C.

(a) 1447 cal (b) 2447 cal (c) 3447 cal (d) 4447 cal

[Ans. (a)]

[Hint: $\Delta S_{\text{vap}} = \dfrac{\Delta H_{\text{vap}}}{T} = \dfrac{540 \times 1000}{373} = 1447 \text{ cal}$]

36. Enthalpy of fusion of water is 6.01 kJ mol^{-1}. The entropy change of 1 mole of ice at its melting point will be:

(a) 22 kJ mol^{-1} (b) 109 kJ mol^{-1}
(c) 44 kJ mol^{-1} (d) 11 kJ mol^{-1}

[Ans. (a)]

[Hint: $\Delta S_{\text{fusion}} = \dfrac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \dfrac{6.01 \times 1000}{273} = 22 \text{ kJ mol}^{-1}$]

37. For spontaneous process:

(a) $\Delta S_{\text{total}} = 0$ (b) $\Delta S_{\text{total}} > 0$
(c) $\Delta S_{\text{total}} < 0$ (d) none of these

[Ans. (b)]

[Hint: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$
$= +$ ve for spontaneous process]

38. Melting point of a solid is x K and its latent heat of fusion is 600 cal mol^{-1}. The entropy change for fusion of 1 mol solid is 2 cal mol^{-1} K^{-1}. The value of x will be:

(a) 100 K (b) 200 K (c) 300 K (d) 400 K

[Ans. (c)]

[Hint: $\dfrac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$
$$\frac{600}{T} = 2$$
$$T = 300 \text{ K}]$$

39. The entropy change involved in the conversion of 1 mole of liquid water at 373 K to vapour at the same temperature will be:
$$\Delta H_{\text{vap}} = 2.257 \text{ kJ/g}$$

(a) 0.119 kJ (b) 0.109 kJ
(c) 0.129 kJ (d) 0.120 kJ

[PMT (MP) 2007]

[Ans. (b)]

[Hint: $\Delta S = \dfrac{\Delta H_{\text{vap}}}{T} = \dfrac{2.257 \times 18}{373} = 0.109 \text{ kJ/g}$]

7.26 SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics tells us whether a given process can occur spontaneously and to what extent. It also helps us to calculate the maximum fraction of heat that can be converted into work in a given process.

The second law of thermodynamics like first law is a postulate and has not been derived from any prior concepts. It is stated in various forms. However, all the statements of second law have the same meaning.

1. Clausius statement: *"It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency."*

It means that work can always be completely converted into heat but heat cannot be converted completely into work without leaving some permanent change in the system or surroundings. For example, heat produced in heat engine is never fully utilized, as part of it is always lost to surroundings or in overcoming friction, etc. Thus, it can be said that *the complete conversion of heat into work is impossible without leaving some effect elsewhere.*

Or

It is not possible to convert heat into work without compensation.

Or

All forms of energy can be converted into heat energy but heat cannot be converted into other forms of energy fully by any process.

The other similar statements are:

2. Thomson statement: *The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work.*

3. Kelvin-Planck statement: *It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

4. *It is impossible to construct a heat engine of 100 % thermal efficiency.*

5. Ludwig Boltzmann statement: In 1886, Ludwig Boltzmann gave a most useful statement of the second law of thermodynamics. *Nature tends to pass from a less probable to more probable state.*

The connection between entropy and the spontaneity of a reaction or a process is expressed by the second law of thermodynamics in a number of ways.

6. *All spontaneous processes or naturally occurring processes are thermodynamically irreversible. Without the help of an external agency, a spontaneous process cannot be reversed.*

For example, the mixing of non-reacting gases is a spontaneous process. But these cannot be separated from the mixture without the application of special methods.

Heat energy can flow from a hot body to a cold body of its own (spontaneously) but not from a cold body to a hot body unless the former is heated.

7. *The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.*

Since, the universe is made up of the system and the surroundings, the entropy change in the universe ($\Delta S_{\text{universe}}$) for any process is the sum of the entropy changes in the system (ΔS_{system}) and in the surroundings ($\Delta S_{\text{surroundings}}$). Mathematically, the second law of thermodynamics can be expressed as:

A spontaneous process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

An equilibrium process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For a spontaneous process, the law says that $\Delta S_{\text{universe}}$ must be greater than zero, but it does not place a restriction on either ΔS_{system} or $\Delta S_{\text{surroundings}}$. Thus, it is possible for either ΔS_{system} or $\Delta S_{\text{surroundings}}$ to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, $\Delta S_{\text{universe}}$ is zero, *i.e.*, ΔS_{system} and $\Delta S_{\text{surroundings}}$ must be equal in magnitude but opposite in sign.

Thus, *the entropy of the universe is continuously increasing.* The main ideas of the first and second law of thermodynamics may be summarised as:

First law states that the energy of the universe is constant whereas the second law states that the entropy of the universe is continuously increasing and tends to a maximum.

First law deals with the conservation of energy whereas the second law tells the direction of flow of energy.

For a reversible process,

$$dS = \frac{dq}{T} \quad \text{or} \quad dq = T\,dS$$

For an irreversible process,

$$dS > \frac{dq}{T}$$

$$\therefore \qquad dS \geq \frac{dq}{T}$$

This is the mathematical statement of second law of thermodynamics.

$dq = dE + P\,dV$ This is the mathematical statement of first law of thermodynamics

Combining both the laws of a reversible process,

$$T\,dS = dE + P\,dV$$

7.27 GIBBS FREE ENERGY, (*G*), CHANGE IN FREE ENERGY AND SPONTANEITY

As discussed earlier, there are two thermodynamic quantities that affect reaction spontaneity. One of these is enthalpy, *H*; the other is the entropy, *S*. The problem is to put these two quantities together in such a way as to arrive at a single function whose sign will determine whether a reaction is spontaneous. This problem was first solved more than a century ago by **J. Willard Gibbs,** who introduced a new quantity, now called the **Gibbs free energy** and given the symbol, *G*. Gibbs showed that for a reaction taking place at constant pressure and constant temperature, ΔG represents that portion of the total energy change that is available (*i.e.*, free) to do useful work. If, for example, ΔG for a reaction is – 300 kJ, it is possible to obtain 300 kJ of useful work from the reaction. Conversely, if ΔG is + 300 kJ, at least that much energy in the form of work must be supplied to make the reaction to take place. Gibbs free energy of a system is defined as:

"The thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system."

Mathematically, it may be defined as:

$$G = H - TS \qquad \text{... (i)}$$

where, H = enthalpy; S = entropy and T = absolute temperature.

We know that, $H = E + PV$ ... (ii)

From eqs. (i) and (ii),

$$G = E + PV - TS$$

Free energy change at constant temperature and pressure can be given as:

$$\Delta G = \Delta E + P\,\Delta V - T\,\Delta S$$

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{... (iii)}$$

(Gibbs-Helmholtz equation)

Here, $\Delta H = \Delta E + P\,\Delta V$

Gibbs-Helmholtz equation is used to discuss the **driving force, *i.e.*, the overall criterion of spontaneity.**

[**Note:** Since, '*H*' and '*S*' are extensive property hence '*G*' will also be an extensive property. Moreover, Gibbs function '*G*' is a state function.]

Free Energy Change and Spontaneity

Let us consider a system which is not isolated from its surroundings. In this case, total entropy change can be calculated as:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \qquad \text{... (i)}$$

Let us consider the process at constant temperature and pressure. Let q_P amount of heat be given by the system to the surroundings.

$$(q_P)_{\text{surroundings}} = -(q_P)_{\text{system}} = -\Delta H_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{(q_P)_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} \qquad \text{... (ii)}$$

From equations (i) and (ii),

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$$

or $$T\,\Delta S_{\text{total}} = T\,\Delta S_{\text{system}} - \Delta H_{\text{system}}$$

or $$-T\,\Delta S_{\text{total}} = \Delta H_{\text{system}} - T\,\Delta S_{\text{system}} \qquad \text{... (iii)}$$

According to Gibbs-Helmholtz equation,

$$\Delta G = \Delta H - T\,\Delta S$$

$$\therefore \quad \Delta G_{\text{system}} = \Delta H_{\text{system}} - T\,\Delta S_{\text{system}} \qquad \text{... (iv)}$$

From equations (iii) and (iv),

$$\Delta G_{\text{system}} = -T\,\Delta S_{\text{total}}$$

We know that for spontaneous process, $\Delta S_{\text{total}} > 0$

$\therefore$ $\Delta G = -$ ve for spontaneous process.

Thus, *for spontaneous process $T\,\Delta S_{total}$ should be positive or ΔG should be negative.*

Case I: Let entropy and energy, both factors are favourable to a process, *i.e.*, $\Delta H = -$ ve and $T\,\Delta S = +$ ve

$\therefore$ From $\Delta G = \Delta H - T\,\Delta S$

$= (-\text{ve}) - (+\text{ve}) = -\text{ve}$

Thus, $\Delta G = -$ *ve for spontaneous process.*

Case II: Let both energy and entropy factors oppose a process, *i.e.*, $\Delta H = +$ ve, $T\,\Delta S = -$ ve.

$\therefore$ From $\Delta G = \Delta H - T\,\Delta S$

$= +\text{ve} - (-\text{ve}) = +\text{ve}$

Thus, ΔG *is positive for a non-spontaneous process.*

Case III: Let both tendencies be equal in magnitude but opposite, *i.e.*,

$$\Delta H = +\text{ve} \quad \text{and} \quad T\,\Delta S = +\text{ve} \quad \text{and} \quad \Delta H = T\,\Delta S$$

$\therefore$ From $\Delta G = \Delta H - T\,\Delta S$

$= 0$

In this condition, the process is said to be at equilibrium.

Coupled Reactions

We know that the reactions which have $\Delta G = +$ ve are non-spontaneous. However, such reactions can be made spontaneous when coupled with a reaction having very large negative free energy of reaction,

e.g., $2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g)$; $\Delta G^\circ = +1487$ kJ/mol

$6CO(g) + 3O_2(g) \longrightarrow 6CO_2(g)$; $\Delta G^\circ = -1543.2$ kJ/mol

On adding, $2Fe_2O_3(s) + 6CO(g) \longrightarrow 4Fe(s) + 6CO_2(g)$;

$\Delta G^\circ = -52.2$ kJ/mol

Thus, both reactions proceed simultaneously.

The free energy of a reaction is the chemical analogue of potential energy of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free energy, *i.e.*, ΔG is negative.

In a chemical reaction, $\Delta G = G_{\text{products}} - G_{\text{reactants}}$. Thus, spontaneous changes occur with a decrease in free energy, *i.e.*, ΔG is negative.

To sum up, the criteria for spontaneity of a process in terms of ΔG is as follows:

(i) If ΔG is negative, the process is spontaneous.
(ii) If ΔG is zero, the system is in equilibrium. The process does not occur.
(iii) If ΔG is positive, the process does not occur in the forward direction. It may occur in the backward direction.

Conditions for ΔG to be negative or the process to be spontaneous

We know that, $\Delta G = \Delta H - T\,\Delta S$

ΔH	$T\,\Delta S$	Conditions	ΔG
–ve (favourable)	+ve (favourable)	(any)	–ve spontaneous
–ve (favourable)	–ve (unfavourable)	$\lvert \Delta H \rvert > (T\,\Delta S)$	–ve spontaneous
+ve (unfavourable)	+ve (favourable)	$\lvert T\,\Delta S \rvert > \lvert \Delta H \rvert$	–ve spontaneous

Role of Temperature on Spontaneity

In Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T\,\Delta S,$$

not only ΔH and ΔS but also temperature 'T' is a determining factor for spontaneity, *i.e.*, for ΔG to be –ve. Let us discuss exothermic and endothermic reactions to show the influence of temperature.

1. Exothermic processes: In exothermic reactions,

$$\Delta H = -\text{ ve (favourable condition)}$$

Case I: When $T\,\Delta S$ is positive, *i.e.*, favourable, then ΔG will be negative and the process will be spontaneous at all temperatures.

Case II: When $T\,\Delta S$ is negative, *i.e.*, unfavourable, then ΔG will be negative when $|\Delta H| > |T\,\Delta S|$. To reduce the magnitude of $T\,\Delta S$, the temperature should be low. Thus, *exothermic reactions can be made favourable (when $T\,\Delta S = -$ ve) by lowering the temperature.*

2. Endothermic reactions: In endothermic reactions, $\Delta H = +$ ve (unfavourable conditions).

In case of endothermic reactions, ΔG will be negative when $|\Delta H| < |T\,\Delta S|$. To increase the magnitude of $T\,\Delta S$, temperature

(T) should be increased. Thus, *endothermic reactions can be made favourable by increasing the temperature.*

Thus, temperature also plays an important role in deciding the spontaneity of a reaction. A reaction which is non-spontaneous at low temperature becomes spontaneous at high temperature and *vice-versa.*

Sign of ΔH, ΔG and ΔS and prediction of spontaneity

ΔH	ΔS	ΔG	Remarks
–ve	+ve	–ve	Spontaneous at all temperatures
–ve	–ve	–ve (at low temperature)	Spontaneous
		+ve (at high temperature)	Non-spontaneous
+ve	+ve	+ve (at low temperature)	Non-spontaneous
		–ve (at high temperature)	Spontaneous
+ve	–ve	+ve	Non-spontaneous at all temperatures

		ΔH	
		+	–
ΔS	+	Spontaneous at high temperature and non-spontaneous at low temperatures	Spontaneous at all temperatures
	–	Non-spontaneous at all temperatures	Non-spontaneous at high temperatures and spontaneous at low temperatures

SOME SOLVED EXAMPLES

Example 71. *ΔH and ΔS for the reaction,*

$$Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2\,(g)$$

are $30.56\,kJ\,mol^{-1}$ and $66.0\,J\,K^{-1}\,mol^{-1}$ respectively. Calculate the temperature at which free energy change for the reaction will be zero. Predict whether the forward reaction will be favoured above or below this temperature.

Solution: We know that,

$$\Delta G = \Delta H - T\,\Delta S$$

At equilibrium, $\Delta G = 0$

so that $0 = \Delta H - T\,\Delta S$

or $T = \dfrac{\Delta H}{\Delta S}$

Given that, $\Delta H = 30.56\text{ kJ mol}^{-1}$

$= 30560\text{ J mol}^{-1}$

$\Delta S = 66.0\text{ J K}^{-1}\text{ mol}^{-1}$

$$T = \frac{30560}{66} = 463\text{ K}$$

Above this temperature, ΔG will be negative and the process will be spontaneous in forward direction.

Example 72. *For the reaction,*

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Calculate ΔG at 700 K when enthalpy and entropy changes are $-113.0\,kJ\,mol^{-1}$ and $-145\,J\,K^{-1}\,mol^{-1}$ respectively.

Solution: We know that, $\Delta G = \Delta H - T\,\Delta S$

Given, $\Delta H = -113\text{ kJ mol}^{-1}$

$= -113000\text{ J mol}^{-1}$

$\Delta S = -145\text{ J K}^{-1}\text{ mol}^{-1}$

$T = 700\text{ K}$

Substituting these values in the above equation,

we get $\Delta G = -113000 - 700 \times (-145)$

$= -11500\text{ J mol}^{-1}$

$= -11.5\text{ kJ mol}^{-1}$

Example 73. *In the reaction $A^+ + B \longrightarrow A + B^+$, there is no entropy change. If enthalpy change is 22 kJ of A^+, calculate ΔG for the reaction.*

Solution: For the given reaction,

$\Delta H = 22\text{ kJ}, \Delta S = 0$

$\therefore$ From, $\Delta G = \Delta H - T\,\Delta S$

$\Delta G = 22 - T \times 0 = 22\text{ kJ mol}^{-1}$

Example 74. *ΔH and ΔS for the reaction $Br_2(l) + Cl_2(g) \rightarrow 2BrCl(g)$ are 29.37 kJ and $104.0\,J\,K^{-1}$ respectively. Above what temperature will this reaction become spontaneous?*

Solution: According to Gibbs-Helmholtz equation,

$$\Delta G = \Delta H - T\,\Delta S$$

For spontaneous process, $\Delta G < 0$

i.e., $\Delta H - T\,\Delta S < 0$

$T\,\Delta S > \Delta H$

$T > \dfrac{\Delta H}{\Delta S}$

$T > \dfrac{29.37 \times 1000}{104}$ $\quad T > 282.4\text{ K}$

Example 75. *Calculate the temperature at which liquid water will be in equilibrium with water vapour.*

$\Delta H_{vap} = 40.73\,kJ\,mol^{-1}$ *and* $\Delta S_{vap} = 0.109\,kJ\,mol^{-1}\,K^{-1}$

Solution: Given, $\Delta H = 40.73\text{ kJ mol}^{-1}$

$\Delta S = 0.109\text{ kJ mol}^{-1}\text{ K}^{-1}$

and $\Delta G = 0$

Applying $\Delta G = \Delta H - T\,\Delta S$

$0 = 40.73 - T \times 0.109$

$$T = \frac{40.73}{0.109} = 373.6\text{ K}$$

Example 76. *Zinc reacts with dilute hydrochloric acid to give hydrogen at 17° C. The enthalpy of the reaction is $-12.55\,kJ\,mol^{-1}$ of zinc and entropy change equals $5.0\,J\,K^{-1}\,mol^{-1}$ for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.*

Solution: Given, $\Delta H = -12.55 \text{ kJ mol}^{-1}$

$$\Delta S = 5.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 0.005 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 17 + 273 = 290 \text{ K}$$

Applying $\Delta G = \Delta H - T\,\Delta S$

$$= -12.55 - 0.005 \times 290$$

$$= -12.55 - 1.45 = -14.00 \text{ kJ mol}^{-1}$$

Since, ΔG is negative, the reaction will be spontaneous.

Example 77. *ΔH and ΔS for the system $H_2O(l) \rightleftharpoons H_2O(g)$ at 1 atmospheric pressure are 40.63 kJ mol^{-1} and 108.8 $J\,K^{-1}\,mol^{-1}$ respectively. Calculate the temperature at which the rates of forward and backward reactions will be the same. Predict the sign of free energy for this transformation above this temperature.*

Solution: Given, $\Delta H = 40.63 \text{ kJ mol}^{-1}$

$$\Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1} = 0.1088 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$\Delta G = 0$ (when the system is in equilibrium)

Applying $\Delta G = \Delta H - T\,\Delta S$

$$0 = 40.63 - T \times 0.1088$$

$$T = \frac{40.63}{0.1088} = 373.4 \text{ K}$$

The sign of ΔG above 373 K, *i.e.*, say 374 K, may be calculated as follows:

Again applying $\Delta G = \Delta H - T\,\Delta S$

$$= 40.63 - 374 \times 0.1088$$

$$= 40.63 - 40.69 = -0.06 \text{ kJ}$$

ΔG will be negative; hence, the reaction will be spontaneous.

Example 78. *For the reaction,*

$$SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl,$$

the enthalpy of reaction is 49.4 kJ and the entropy of reaction is $336\,J\,K^{-1}$. Calculate ΔG at 300 K and predict the nature of the reaction.

Solution: $\Delta G = \Delta H - T\,\Delta S$

$$= 49.4 - (300 \times 336 \times 10^{-3})$$

$$= -51.4 \text{ kJ}$$

Since, the free energy change is negative, the given reaction is spontaneous.

Example 79. *The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:*

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$\Delta H^\circ_{300\,K} = -41.16\,kJ\,mol^{-1}$$

$$\Delta S^\circ_{300\,K} = -4.24 \times 10^{-2}\,kJ\,mol^{-1}$$

$$\Delta H^\circ_{1200\,K} = -32.93\,kJ\,mol^{-1}$$

$$\Delta S^\circ_{1200\,K} = -2.96 \times 10^{-2}\,kJ\,mol^{-1}$$

Calculate K_P at each temperature and predict the direction of reaction at 300 K and 1200 K, when $P_{CO} = P_{CO_2} = P_{H_2} = P_{H_2O} = 1$ atm at initial state.

Solution: At 300 K: $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

$$= -41.16 - 300 \times (-4.24 \times 10^{-2})$$

$$= -28.44 \text{ kJ}$$

Since, ΔG° is negative hence reaction is spontaneous in forward direction,

$$\Delta G^\circ = -2.303\,RT \log K_P$$

$$-28.44 = -2.303 \times 8.314 \times 10^{-3} \times 300 \log K_P$$

$$K_P = 8.93 \times 10^4$$

At 1200 K: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -32.93 - 1200(-2.96 \times 10^{-2}) = +2.59 \text{ kJ}$$

Positive value of ΔG° shows that the reaction is spontaneous in backward direction

$$\Delta G^\circ = -2.303\,RT \log K_P$$

$$2.59 = -2.303 \times 8.314 \times 10^{-3} \times 1200 \log K_P$$

$$K_P = 0.77$$

Example 80. *The standard Gibbs free energies for the reactions at 1773 K are given below:*

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta G^\circ = -380\,kJ\,mol^{-1}$$

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g); \quad \Delta G^\circ = -500\,kJ\,mol^{-1}$$

Discuss the possibility of reducing Al_2O_3 and PbO with carbon at this temperature,

$$4Al + 3O_2(g) \longrightarrow 2Al_2O_3(s); \quad \Delta G^\circ = -22500\,kJ\,mol^{-1}$$

$$2Pb + O_2(g) \longrightarrow 2PbO(s); \quad \Delta G^\circ = -120\,kJ\,mol^{-1}$$

Solution: Let us consider the reduction of Al_2O_3 by carbon:

$$2Al_2O_3 + 3C(s) \longrightarrow 4Al(s) + 3CO_2(g);$$

$$\Delta G^\circ = -380 \times 3 + (22500) = +21360 \text{ kJ}$$

$$2Al_2O_3 + 6C(s) \longrightarrow 4Al(s) + 6CO(g);$$

$$\Delta G^\circ = -500 \times 3 + 22500 = +21000 \text{ kJ}$$

Positive values of ΔG° show that the reduction of Al_2O_3 is not possible by any of the above methods.

Now, let us consider the reduction of PbO.

$$2PbO(s) + C \longrightarrow 2Pb + CO_2;$$

$$\Delta G^\circ = +120 + (-380) = -260 \text{ kJ}$$

$$2PbO(s) + 2C \longrightarrow 2Pb + 2CO;$$

$$\Delta G^\circ = +120 + (-500) = -380 \text{ kJ}$$

Negative value of ΔG° shows that the process is spontaneous and PbO can be reduced by carbon.

Example 81. *In a fuel cell, methanol is used as fuel and oxygen gas is used as an oxidiser. The reaction is:*

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Calculate standard Gibbs free energy change for the reaction that can be converted into electrical work. If standard enthalpy of combustion for methanol is $-726\,kJ\ mol^{-1}$; *calculate the efficiency of conversion of Gibbs energy into useful work.*

ΔG_f° *for* CO_2, H_2O, CH_3OH, O_2 *are* -394.36; -237.13; -166.27 *and zero respectively.*

Solution: The reaction for combustion of methanol is:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\begin{aligned}\Delta G^\circ_{\text{reaction}} &= [\Delta G_f^\circ\ CO_2(g) + 2\,\Delta G_f^\circ\ H_2O(l)] \\ &\quad - [\Delta G_f^\circ\ CH_3OH(l) + \frac{3}{2}\,\Delta G_f^\circ\ O_2(g)] \\ &= [-394.36 + 2(-237.13)] - [-166.27 + 0] \\ &= -702.35\ \text{kJ mol}^{-1}\end{aligned}$$

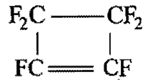
Efficiency of conversion of Gibbs free energy into useful work

$$= \frac{\Delta G^\circ_{\text{reaction}} \times 100}{\Delta H^\circ_{\text{reaction}}} = \frac{-702.35 \times 100}{-726} = 96.7\%$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

40. The free energy for a reaction having $\Delta H = 31400$ cal, $\Delta S = 32\ \text{cal K}^{-1}\ \text{mol}^{-1}$ at 1000°C is: **[JEE (Orissa) 2005]**
(a) −9336 cal (b) −7386 cal (c) −1936 cal (d) +9336 cal
[Ans. (a)]
[Hint: $\Delta G = \Delta H - T\,\Delta S = 31400 - 1273 \times 32 = -9336$ cal]

41. $F_2C{=}CF{-}CF{=}CF_2 \longrightarrow$



For this reaction (ring closure), $\Delta H = -49\ \text{kJ mol}^{-1}$, $\Delta S = -40.2\ \text{J K}^{-1}\ \text{mol}^{-1}$. Upto what temperature is the forward reaction spontaneous?
(a) 1492°C (b) 1219°C (c) 946°C (d) 1080°C
[Ans. (c)]
[Hint: For spontaneous process,

$$\Delta G = \Delta H - T\,\Delta S \quad \text{(should be negative)}$$

$$\therefore \quad T > \frac{\Delta H}{\Delta S}$$

$$T > \frac{-49 \times 1000}{-40.2}$$

$$T > 1219\ \text{K}, \textit{i.e.}, 946^\circ\text{C}]$$

42. For the equilibrium reaction, the value of Gibbs free energy change is: **(DCE 2005)**
(a) > 0 (b) < 0 (c) = 0 (d) ≠ 0
[Ans. (c)]
[Hint: $\Delta G = 0$ at equilibrium]

43. At 0°C, ice and water are in equilibrium and $\Delta H = 6\,\text{kJ mol}^{-1}$. For this process:

$$H_2O(s) \rightleftharpoons H_2O(l)$$

The values of ΔS and ΔG for conversion of ice into liquid water at 0°C are:
(a) $-21.9\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0 (b) $0.219\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0
(c) $21.9\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0 (d) $0.0219\ \text{J K}^{-1}\ \text{mol}^{-1}$ and 0
[Ans. (c)]
[Hint: $\Delta G = 0$,

$$\therefore \quad \Delta H - T\Delta S = 0$$

$$\Delta S = \frac{\Delta H}{T} = \frac{6000}{273} = 21.9\ \text{J K}^{-1}\ \text{mol}^{-1}]$$

44. For a reaction:

$$Ag_2O(s) \rightleftharpoons 2Ag(s) + \frac{1}{2}O_2(g)$$

$\Delta H, \Delta S$ and T are 40.63 kJ mol^{-1}; 108.8 J K^{-1} mol^{-1} and 373.4 K respectively. Predict the feasibility of the reaction.
(a) feasible (b) non-feasible
(c) remains at equilibrium (d) not predicted
[Ans. (c)]
[Hint: $\Delta G = \Delta H - T\,\Delta S$

$$= 40.63 \times 1000 - 373.4 \times 108.8 = 0]$$

45. For the homogeneous reactions:

$$xA + yB \longrightarrow lY + mZ$$

$\Delta H = -30\ \text{kJ mol}^{-1}$, $\Delta S = -100\ \text{J K}^{-1}\ \text{mol}^{-1}$.
At what temperature the reaction is at equilibrium? **[PMT (Kerala) 2006]**
(a) 50°C (b) 250°C (c) 100 K (d) 27°C
(e) 500 K
[Ans. (d)]
[Hint: $\Delta G = \Delta H - T\,\Delta S$
At equilibrium, $\Delta G = 0$

$$\therefore \quad T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-100} = 300\ \text{K}, \ \textit{i.e.}, 27^\circ\text{C}]$$

46. For the reaction $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, ΔH and ΔS are −283 kJ and −87 J K^{-1} mol^{-1} respectively. It was intended to carry out this reaction at 1000, 1500, 3000 and 3500 K. At which of these temperatures would this reaction be thermodynamically spontaneous? **[PMT (Kerala) 2006]**
(a) 1500 and 3500 K (b) 3000 and 3500 K
(c) 1000, 1500 and 3000 K (d) 1500, 3000 and 3500 K
(e) At all of the above temperatures
[Ans. (c)]
[Hint: $\Delta G = \Delta H - T\,\Delta S$
At 1000 K, $\Delta G = -283 - (-1000 \times 0.087)$ (Spontaneous) $= -196$
At 1500 K, $\Delta G = -283 - (-1500 \times 0.087)$ (Spontaneous) $= -152.5$ kJ
At 3000 K, $\Delta G = -283 - (-3000 \times 0.087)$ (Spontaneous) $= -22$ kJ
At 3500 K, $\Delta G = -283 - (-3500 \times 0.087)$ (Non-spontaneous) $= +21.5$ kJ]

47. For a reaction,

$$\Delta H = +29\ \text{kJ mol}^{-1}; \quad \Delta S = -35\ \text{JK}^{-1}\ \text{mol}^{-1}$$

at what temperature, the reaction will be spontaneous? **[PMT (Haryana) 2007]**

(a) 828.7°C
(b) 828.7 K
(c) Spontaneous at all temperature
(d) Not possible

[Ans. (d)]

[Hint: $\Delta G = \Delta H - T\,\Delta S$

When $\Delta H = +$ ve, $\Delta S = -$ ve then ΔG will be positive and the reaction is non-spontaneous.]

7.28 STANDARD FREE ENERGY CHANGE

Just like enthalpy and internal energies, we cannot determine absolute value of *Gibbs free energy.* The standard free energy change can be determined and it is defined as *the free energy change for a process at* 298 *K and* 1 *atm pressure in which the reactants in their standard state are converted to products in their standard state.* It is denoted as $\Delta G°$; it can be related to standard enthalpy and entropy change in the following manner:

$$\Delta G° = \Delta H° - T\,\Delta S°$$

Like that of $\Delta H°$, $\Delta G°$ can be calculated from the standard free energies of formation of the products and the reactants.

$$\Delta G° = \Sigma G_f^\circ \text{ (products)} - \Sigma G_f^\circ \text{ (reactants)}$$

$$= \begin{bmatrix}\text{Sum of standard free}\\ \text{energies of formation}\\ \text{of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of standard free}\\ \text{energies of formation}\\ \text{of reactants}\end{bmatrix}$$

Let us consider a general reaction:

$$n_1A + n_2B \longrightarrow n_3L + n_4M$$

$$\Delta G° = \Sigma G_f^\circ \text{ (products)} - \Sigma G_f^\circ \text{ (reactants)}$$

$$= [n_3 G_f^\circ(L) + n_4 G_f^\circ(M)] - [n_1 G_f^\circ(A) + n_2 G_f^\circ(B)]$$

The standard free energy of formation (ΔG_f°) may be defined as *the free energy change when* 1 *mole of a compound is formed from its constituent elements in their standard state. The standard free energy of formation of an element in its standard state is assumed to be zero.*

Standard Gibbs Free Energy of Formation (kJ mol^{-1} at 298 K)

HCl	–95.27	C_4H_8 (*iso*-butene)	294
H_2O	–228.6	BaO	–528.4
H_2O_2	–103.3	$BaCO_3$	–1139
CO	–137.3	$BaSO_4$	–1465
CO_2	–394.4	CaO	– 604.2
SO_2	–300.4	$Ca(OH)_2$	–896.6
SO_3	–370.4	$CaCO_3$	–1129
NO_2	51.84	CuO	–127
N_2O	104	NaCl	–384.0
NH_3	–16.6	KCl	– 408.3
O_3	163.4	NH_4Cl	–203.0
NO	86.69	Al_2O_3	–1582.4
CH_4	–50.79	Fe_2O_3	–741.0
C_2H_6 (ethane)	229	ZnO	–318.2
C_3H_8 (propane)	270	SiO_2	–805
C_4H_{10} (*n*-butane)	310	PbO_2	–219
C_4H_{10} (*iso*-butane)	310	CH_3OH	–166.2
C_2H_2 (acetylene)	209.2	C_2H_5OH	–174.8
C_2H_4 (ethylene)	219.4	C_6H_6	–124.5
C_3H_6 (propylene)	266.9	CH_3COOH	–392
C_4H_8 (1-butene)	307.4		

Example 82. *Will the reaction,*

$$I_2(s) + H_2S(g) \longrightarrow 2HI(g) + S(s)$$

proceed spontaneously in the forward direction at 298 K, $\Delta G_f^\circ HI(g) = 1.8\,kJ\ mol^{-1}$, $\Delta G_f^\circ H_2S(g) = 33.8\,kJ\ mol^{-1}$ *?*

Solution:

$$\Delta G° = \Sigma G_f^\circ \text{(products)} - \Sigma G_f^\circ \text{(reactants)}$$

$$= [2G_f^\circ \text{HI}(g) + G_f^\circ \text{S}(s)] - [1 \times G_f^\circ \text{I}_2(s) + G_f^\circ \text{H}_2\text{S}(g)]$$

$$= [2 \times 1.8 + 0] - [0 + 33.8] = -30.2 \text{ kJ}$$

–ve value shows that the process is spontaneous in forward direction.

Example 83. *Compute the standard free energy of the reaction at 27° C for the combustion of methane using the given data:*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Species	CH_4	O_2	CO_2	H_2O
$\Delta H_f^\circ / (kJ\ mol^{-1})$	– 74.8	—	– 393.5	– 285.8
$S°/(J\,K^{-1}\ mol^{-1})$	186	205	214	70

Solution: $\Delta H° = \Delta H^\circ_{f\,(CO_2)} + 2\Delta H^\circ_{f\,(H_2O)} - \Delta H^\circ_{f\,(CH_4)}$

$$= -393.5 + 2 \times (-285.8) - (-74.8)$$

$$= -890 \text{ kJ mol}^{-1}$$

$$\Delta S° = S^\circ_{(CO_2)} + 2S^\circ_{(H_2O)} - S^\circ_{(CH_4)} - 2S^\circ_{(O_2)}$$

$$= 214 + 2 \times 70 - 186 - 2 \times 205$$

$$= -242 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta G° = \Delta H° - T\Delta S°$$

$$= -890 - 300 \times (-242 \times 10^{-3})$$

$$= -890 + 72.6 = -817.4 \text{ kJ mol}^{-1}$$

7.29 RELATIONSHIP BETWEEN STANDARD FREE ENERGY CHANGE ($\Delta G°$) AND EQUILIBRIUM CONSTANT

For any reversible reaction, $A + B \rightleftharpoons C + D$, the free energy change and standard free energy change are related with each other by the following relation:

$$\Delta G = \Delta G° + RT \log_e Q$$

where, R is universal constant; T is temperature and Q is reaction quotient $Q = \dfrac{[C][D]}{[A][B]}$.

At equilibrium state, $\Delta G = 0$ and $Q = K_{eq}$

$$0 = \Delta G° + RT \log_e K_{eq}$$

or

$$\Delta G° = -RT \log_e K_{eq}$$

or $$\Delta G^\circ = -2.303RT \log K_{eq}$$

This equation helps in the calculation of K_{eq} if ΔG° of the reaction is known and *vice-versa.* The value of K_{eq} can give an idea about the extent of chemical reaction before the equilibrium is attained.

Alternatively,

$$K = e^{-\Delta G^\circ/RT}$$

Equilibrium constant of unity implies that standard free energy change ΔG° is zero and that the positive values of ΔG° implies the equilibrium constant to be less than unit.

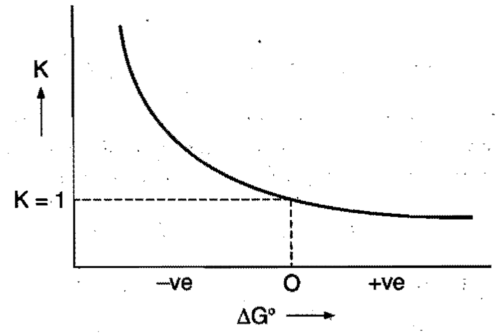


Fig. 7.21 Variation of equilibrium constant against standard free energy change

If we draw a graph of free energy against extent of reaction, we get U-shaped graph Fig. 7.22.

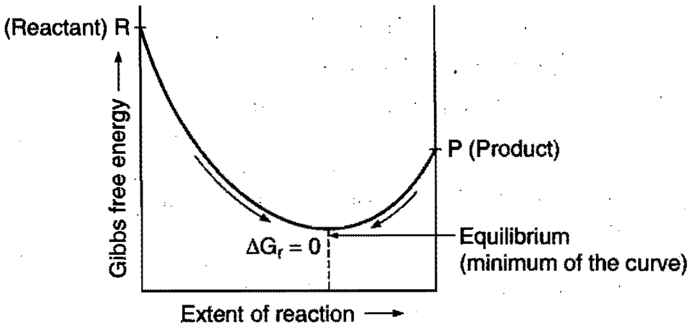


Fig. 7.22 Plot of free energy against extent of reaction

If the minimum in the curve lies closer to products, it means that reaction is in favour of products ($K >>> 1$). The reaction in this case will be closer to completion. On the other hand, if the minimum in the curve lies closer to the reactants, the reaction favours reactants ($K <<< 1$). The reaction in this case will be farthest from completion. (See. Fig. 7.23)

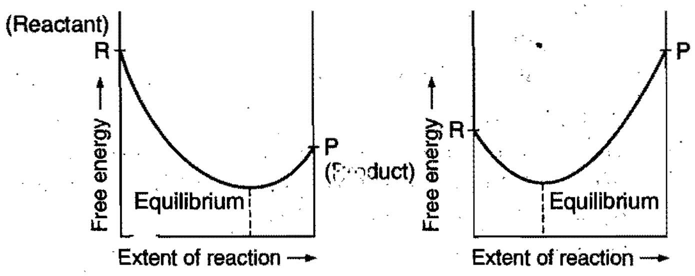


Fig. 7.23 Prediction of extent of reaction by the plot of free energy against extent of reaction

Example 84. *What is the equilibrium constant K_c for the following reaction at 400K?*

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$
$$\Delta H^\circ = 77.2\,kJ \text{ and } \Delta S^\circ = 122\,J\,K^{-1} \text{ at } 400\,K.$$

Solution: According to Gibbs-Helmholtz equation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= 77.2 - 400 \times 122 \times 10^{-3}$$
$$= 28.4 \text{ kJ} = 28.4 \times 10^3 \text{ J}$$

We know that, $\Delta G^\circ = -2.303RT \log K_c$

$$\therefore \quad \log K_c = \frac{-\Delta G^\circ}{2.303RT} = -\frac{28.4 \times 10^3}{2.303 \times 8.314 \times 400}$$
$$= -3.7081$$
$$K_c = \text{antilog } (-3.7081) = 1.958 \times 10^{-4}$$

Example 85. *For the equilibrium,*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \text{ at } 25^\circ C$$
$$K_c = 1.8 \times 10^{-7}$$

Calculate ΔG° for the reaction ($R = 8.314\,J\,K^{-1}\,mol^{-1}$).

Solution: We know that,

$$\Delta G^\circ = -2.303RT \log K_c$$
$$= -2.303 \times 8.314 \times 298 \log (1.8 \times 10^{-7})$$
$$= 38484 \text{ J mol}^{-1} = 38.484 \text{ kJ mol}^{-1}$$

Example 86. *The equilibrium constant at 25°C for the process:*

$$Co^{3+}(aq.) + 6NH_3(aq.) \rightleftharpoons [Co(NH_3)_6]^{3+}(aq.)$$

is 2×10^7.

Calculate the value of ΔG° at 25°C. ($R = 8.314\,J\,K^{-1}mol^{-1}$)

In which direction, the reaction is spontaneous when the reactants and products are in standard state?

Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 2 \times 10^7, T = 298\text{K}, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Thus, from above equation,

$$\Delta G^\circ = -2.303 \times 8.314 \times 298 \log 2 \times 10^7$$
$$= -12023.4 \text{ J} = -12.023 \text{ kJ}$$

Example 87. *The equilibrium constant for the reaction,*

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \text{ at } 298\,K$$

is 73. Calculate the value of the standard free energy change ($R = 8.314\,J\,K^{-1}\,mol^{-1}$).

Solution: We know that, $\Delta G^\circ = -2.303RT \log K_c$

Given, $K_c = 73, R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, T = 298\text{ K}$

$\therefore$ From above equation,

$$\Delta G^\circ = -2.303 \times 8.314 \times 298 \log 73$$
$$= -10.632 \text{ kJ}$$

Example 88. *For the water gas reaction,*

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

the standard Gibbs free energy of reaction (at $1000\,K$ *) is* -8.1 *kJ/mol. Calculate its equilibrium constant.*

Solution: We know that,

$$K = \text{antilog}\left(\frac{-\Delta G^\circ}{2.303RT}\right) \qquad \ldots(i)$$

Given that, $\Delta G^\circ = -8.1\,\text{kJ/mol}$

$R = 8.314 \times 10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}$

$T = 1000\,\text{K}$

Substituting these values in eq. (i), we get

$$K = \text{antilog}\left[\frac{-(-8.1)}{2.303 \times 8.314 \times 10^{-3} \times 1000}\right]$$

$$K = 2.65$$

Example 89. *Calculate* ΔG° *for the conversion of oxygen to ozone,* $(3/2)O_2(g) \rightleftharpoons O_3(g)$ *at 298 K, if* K_p *for this conversion is* 2.47×10^{-29}.

Solution: We know that,

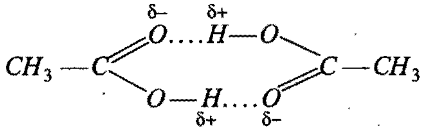
$$\Delta G^\circ = -2.303RT \log K_p$$

$$= -2.303 \times 8.314 \times 298 \log 2.47 \times 10^{-29}$$

$$= 163228\,\text{J/mol}$$

$$= 163.228\,\text{kJ/mol}$$

Example 90. *Acetic acid* CH_3COOH *can form a dimer* $(CH_3COOH)_2$ *in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mol of dimer*



If at 25° C, the equilibrium constant for the dimerization is 1.3×10^3. *Calculate* ΔS° *for the reaction:*

$$2CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

Solution: $\Delta G^\circ = -2.303\,RT \log K$

$$= -2.303 \times 8.314 \times 298 \log (1.3 \times 10^3)$$

$$= -17767.688\,\text{J} = -17.767\,\text{kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-17.767 = -66.5 - 298 \times \Delta S^\circ$$

$$\Delta S^\circ = \frac{-66.5 + 17.767}{298} = -0.163\,\text{kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

48. What is ΔG° for this reaction?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g);\ K_P = 4.42 \times 10^4 \text{ at } 25^\circ\text{C}$$

(a) -26.5 kJ mol^{-1} (b) -11.5 kJ mol^{-1}

(c) -2.2 kJ mol^{-1} (d) -0.97 kJ mol^{-1}

[Ans. (a)]

[Hint: $\Delta G^\circ = -2.303RT \log K_P$

$= -2.303 \times 8.314 \times 298 \log (4.42 \times 10^4)$

$= -26.5$ kJ mol^{-1}]

49. What is the sign of ΔG° and the value of K for an electrochemical cell for which $E^\circ_{\text{cell}} = 0.80$ volt?

	ΔG°	K
(a)	$-$	>1
(b)	$+$	>1
(c)	$+$	<1
(d)	$-$	<1

[Ans. (a)]

[Hint: $\Delta G^\circ = -nFE^\circ$; $\Delta G^\circ = -2.303RT \log K$]

50. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K?

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$$

(a) 8.4×10^{-5} (b) 7.1×10^{-9}

(c) 4.2×10^{-10} (d) 1.7×10^{-19}

[Ans. (a)]

[Hint: $K = \text{antilog}\left[\frac{-\Delta G^\circ}{2.303RT}\right]$

$= \text{antilog}\left[\frac{-78 \times 1000}{2.303 \times 8.314 \times 1000}\right]$

$= 8.4 \times 10^{-5}$]

51. Equilibrium constant for the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is $K_c = 50$ at 25°C.

The standard Gibbs free energy change for the reaction will be:

(a) -6.964 kJ (b) -9.694 kJ

(c) -4.964 kJ (d) -6.496 kJ

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K_c$

$= -2.303 \times 8.314 \times 298 \log 50$

$= -9694\text{ J} = -9.694\text{ kJ}$]

52. Standard Gibbs free energy change ΔG° for a reaction is zero. The value of the equilibrium constant will be:

(a) 10 (b) 1 (c) 100 (d) ∞

[Ans. (b)]

[Hint: $\Delta G^\circ = -2.303RT \log K$

When $K = 1$, $\Delta G^\circ = 0$]

53. The standard free energy change of a reaction is $\Delta G^\circ = -115$ kJ at 298 K. Calculate the equilibrium constant K_P in $\log K_P$. ($R = 8.314$ JK^{-1} mol^{-1})

(a) 20.16 (b) 2.303 (c) 2.016 (d) 13.83

(VITEEE 2008)

[Ans. (a)]

[**Hint:** $\log K_P = \dfrac{-\Delta G^\circ}{2.303\,RT}$

$= \dfrac{-(-115 \times 1000)}{2.303 \times 8.314 \times 298}$

$= 20.16$]

7.30 PHYSICAL SIGNIFICANCE OF GIBBS FREE ENERGY CHANGE (Free Energy and Useful Work)

According to first law of thermodynamics,

$$\Delta E = q - w \qquad \text{... (i)}$$

(–ve sign as the work is done by system)

Here, q is heat absorbed by the system and w is the work done by the system while ΔE is the change in internal energy. The work (w) actually includes two types of work, *i.e.*, $w_{\text{expansion}}$ (or $P\Delta V$) and $w_{\text{non-expansion}}$ (useful work). The two types of works can be understood by taking an example of the electrolysis of water to form $H_2(g)$ and $O_2(g)$ leading to an increase in the volume of the system. The work non-expansion (non-mechanical) is done to cause the decomposition of water while the work expansion (mechanical) is due to expansion in volume of the system. Thus, the electrical work is called non-pressure-volume work or non-expansion work or non-mechanical work. The non-expansion work is also known as useful work. Thus,

$$\Delta E = q - w_{\text{expansion}} - w_{\text{non-expansion}} \qquad \text{... (ii)}$$

$$= q - P\,\Delta V - w_{\text{non-expansion}} \qquad (\because w_{\text{expansion}} = P\,\Delta V)$$

or $$q = \Delta E + P\Delta V + w_{\text{non-expansion}} \qquad \text{... (iii)}$$

We know that,

$$\Delta E + P\,\Delta V = \Delta H$$

or $$q = \Delta H + w_{\text{non-expansion}} \qquad \text{... (iv)}$$

According to second law of thermodynamics, for a reversible change taking place at constant temperature, T

$$\Delta S = \frac{q_{\text{rev.}}}{T}$$

or $$q_{\text{rev.}} = T\,\Delta S \qquad \text{... (v)}$$

Substituting in equation (iv)

$$T\,\Delta S = \Delta H + w_{\text{non-expansion}} \qquad \text{... (vi)}$$

or $$\Delta H - T\,\Delta S = -\,w_{\text{non-expansion}}$$

or $$\Delta G = -\,w_{\text{non-expansion}} \qquad (\because \Delta H - T\,\Delta S = \Delta G)$$

or $$-\Delta G = w_{\text{non-expansion}} = w_{\text{useful work}} \qquad \text{... (vii)}$$

Thus, *the decrease in Gibbs free energy is a measure of useful work or non-expansion work done by the system.* The greater the free energy change, the greater is the amount of work that can be obtained from the process. This relation is useful in assessing the electrical work that may be produced by electrochemical cells and fuel cells.

Free Energy Change and Electrical Work Done in a Cell

Free energy change in electrochemical cells is related to the electrical work done in the cell.

ΔG and emf of the cell (E) are related by the following relation:

$$\Delta G = -\,nFE$$

where, F = faraday = 96500 coulomb

E = emf of the cell

n = Number of moles of electrons involved in balanced electrochemical reaction

If the reactants and products are in their standard states, then

$$\Delta G^\circ = -\,nFE^\circ$$

when E° = standard emf of the cell.

Example 91. *The emf of the cell reaction,*

$$Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$$

is 1.1 V. Calculate free energy change for the reaction. If enthalpy of the reaction is -216.7 *kJ mol*$^{-1}$*, calculate the entropy change for the reaction.*

Solution: $-\Delta G^\circ = n \times F \times E^\circ = 2 \times 96500 \times 1.1 = 212.3$ kJ

$$\Delta G^\circ = -212.3 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-216.7 - (-212.3)}{298}$$

$$= -0.01476 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= -14.76 \text{ J K}^{-1} \text{ mol}^{-1}$$

Example 92. *Calculate equilibrium constant for the following reaction:*

$$Cu(s) + 2Ag^{+}(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$$

At 25°C, $E^\circ_{cell} = 0.47$ *volt,* $R = 8.314\ J\ K^{-1}\ mol^{-1}$, $F = 96500$ *coulomb.*

Solution: Let us apply Nernst equation at equilibrium

$$E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K_c$$

$$0.47 = \frac{0.0591}{2} \log K_c$$

$$K_c = \text{antilog}\left[\frac{0.47 \times 2}{0.0591}\right]$$

$$= 8.5 \times 10^{15}$$

7.31 ABSOLUTE ENTROPIES AND THIRD LAW OF THERMODYNAMICS

Third law of Thermodynamics was given by T.W. Richards, Walter Nernst and Max Planck. Some statements for third law of thermodynamics are given below:

Statement-1. *"Every substance has a finite positive entropy but at the absolute zero temperature the entropy may become zero and does so become in the case of perfectly crystalline solids."*

Because

Statement-2. *"Entropy of a solid or liquid approaches zero at the absolute zero of temperature."*

It can be mathematically expressed as

$$\lim_{T \to 0\,\mathrm{K}} S \to 0$$

Because

Statement-3. *"It is impossible by any method, no matter how idealised it is, to reduce the temperature of any system to the absolute zero in a finite number of operations."*

Application of Third Law of Thermodynamics

The third law of thermodynamics has been useful in calculating the absolute entropies of solids, liquids and gases at different temperatures. Moreover, this law is also useful to calculate entropy changes of a chemical or physical process. Let us calculate absolute entropy.

$$dS = \frac{dQ}{T}$$

$$dS = C_P \frac{dT}{T}$$

On integrating the above equation between temperature limits of 0 and T K, we get

$$S_T - S_0 = \int_0^T C_P \frac{dT}{T}$$

or

$$S_T - S_0 = \int_0^T C_P \, d \ln T$$

From third law of thermodynamics, $S_0 = 0$

$$\therefore \quad S_T = \int_0^T C_P \, d \ln T$$

When entropy of one mole of a substance is expressed at 298 *K and* 1 *atm pressure, it is called* **standard entropy** *of that substance.* It is denoted by $S°$. The standard entropy change $\Delta S°$ for a chemical reaction can be calculated as

$$\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$$

$$= \begin{bmatrix}\text{Sum of the standard}\\ \text{entropies of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard}\\ \text{entropies of reactants}\end{bmatrix}$$

e.g., in the reaction:

$$\mathrm{C_2H_6}(g) \longrightarrow \mathrm{H_2}(g) + \mathrm{C_2H_4}(g)$$

$$\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$$

$$= [S°_{\mathrm{H_2}} + S°_{\mathrm{C_2H_4}}] - [S°_{\mathrm{C_2H_6}}]$$

Standard molar entropies in J/K mol at 298 K

Solids	Entropy	Solids	Entropy
C (graphite)	5.7	N_2	191.6
C (diamond)	2.4	O_2	205.1
Fe	27.3	CO_2	213.7
Pb	64.8	NO_2	240.1
Cu	33.1	N_2O_4	304.3
Al	96.2	NH_3	192.3
Fe_2O_3	87.4	CH_4	186.2
$CuSO_4 \cdot 5H_2O$	300.4	Hg	76.0
$C_{12}H_{22}O_{11}$ (sucrose)	360.8	H_2O	69.9
CaO	39.8	C_2H_5OH	160.7
$CaCO_3$ (calcite)	92.9	C_6H_6	173.3
H_2	130.7	CH_3COOH	159.8

Tephigraph

Graph of entropy of a substance against temperature is called tephigraph. In the following graph variation of entropy with temperature is represented:

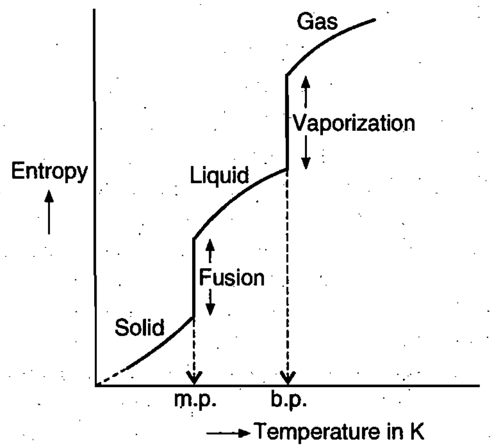


Fig. 7.24

From the graph it is clear that entropy of a substance increases with increase in temperature; there is sudden change in entropy at the stage of phase transformation.

Example 93. *Calculate $\Delta G°$ for the following reaction:*

$$CO(g) + (\tfrac{1}{2})O_2(g) \longrightarrow CO_2(g); \ \Delta H° = -282.84 \, kJ$$

Given,

$S°_{CO_2} = 213.8 \, J \, K^{-1} \, mol^{-1}$, $S°_{CO(g)} = 197.9 \, J \, K^{-1} \, mol^{-1}$,

$S°_{O_2} = 205.0 \, J \, K^{-1} \, mol^{-1}$.

Solution: $\Delta S° = \Sigma S°_{(\text{products})} - \Sigma S°_{(\text{reactants})}$

$$= [S°_{\mathrm{CO_2}}] - [S°_{\mathrm{CO}} + \frac{1}{2} S°_{\mathrm{O_2}}]$$

$$= 213.8 - [197.9 + \frac{1}{2} 205]$$

$$= -86.6 \, \mathrm{J \, K^{-1}}$$

According to Gibbs-Helmholtz equation,

$$\Delta G° = \Delta H° - T \, \Delta S°$$

$$= -282.84 - 298 \times (-86.6 \times 10^{-3})$$

$$= -282.84 + 25.807$$

$$= -257.033 \, \mathrm{kJ}$$

Example 94. *For the reaction;*

$$A(s) \longrightarrow B(s) + C(s)$$

calculate the entropy change at 298 *K and* 1 *atm if absolute entropies (in $J \, K^{-1} \, mol^{-1}$) are:*

$$A = 130, B = 203, C = 152$$

Solution: $\Delta S^\circ = \Sigma S^\circ_{\text{(products)}} - \Sigma S^\circ_{\text{(reactants)}}$

$$= [S^\circ_B + S^\circ_C] - [S^\circ_A]$$
$$= [203 + 152] - [130]$$
$$= 225\ \text{J K}^{-1}$$

7.32 CONVERSION OF HEAT INTO WORK—THE CARNOT CYCLE

Carnot, a French engineer, in 1824, employed merely theoretical and an imaginary reversible cycle known as Carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston which is subjected to a series of four successive operations. The four operations are:

(i) Isothermal reversible expansion
(ii) Adiabatic reversible expansion
(iii) Isothermal reversible compression
(iv) Adiabatic reversible compression

The four operations have been shown in Fig. 7.25.

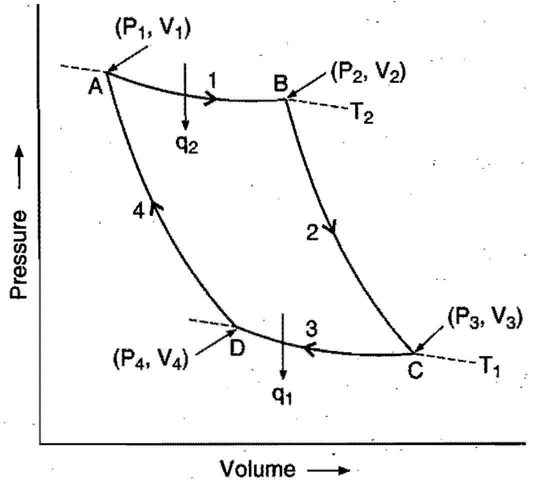


Fig. 7.25

First operation—Isothermal reversible expansion

The gas is allowed to expand reversibly and isothermally at the temperature T_2 through AB path. The volume V_1 (point A) increases to volume V_2 (point B). In this operation, let the heat absorbed by the system be q_2 (+ve) and the work done by the system on the surroundings be w_1 (−ve).

Since, the expansion is isothermal, $\Delta E = 0$. The heat absorbed, q_2, should be equal to the work done by the system on the surroundings, *i.e.*,

$$q_2 = -w_1 = RT_2 \log_e \frac{V_2}{V_1} \qquad \text{... (i)}$$

Second operation—Adiabatic reversible expansion

The gas is now allowed to expand reversibly and adiabatically through BC path. The volume increases from V_2 (point B) to volume V_3 (point C). In this operation, no heat is absorbed and thus, the work, w_2, is done by the system at the expense of internal energy, *i.e.*, the temperature of the system falls from temperature T_2 to temperature T_1.

$$\Delta E = -w_2 = -C_V(T_2 - T_1) \qquad \text{... (ii)}$$

Third operation—Isothermal reversible compression

The gas at point C is subjected to reversible isothermal compression at temperature T_1. The path followed is CD when the volume decreases from V_3 to V_4 (point D). In this operation work is done on the system and heat q_1 is given out by the system to surroundings.

$$-q_1 = w_3 = RT_1 \log_e \frac{V_4}{V_3} \qquad \text{... (iii)}$$

Fourth operation—Adiabatic reversible compression

Finally, the gas at point D is subjected to reversible adiabatic compression through the path DA at temperature T_1. The volume changes from V_4 to V_1, *i.e.*, the original volume is restored. The temperature increases from T_1 to T_2 (original temperature). The work done increases the internal energy of the system as $q = 0$.

$$w_4 = C_V(T_2 - T_1) \qquad \text{... (iv)}$$

The net heat absorbed, q, by the ideal gas in the cycle is given by

$$q = q_2 + (-q_1) = RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3}$$
$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \qquad \text{... (v)}$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma - 1} \qquad \text{(For adiabatic expansion)}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma - 1} \qquad \text{(For adiabatic compression)}$$

or $$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting the value of $\frac{V_3}{V_4}$ in eq. (v),

$$q = q_2 - q_1 = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$
$$= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \qquad \text{... (vi)}$$

Similarly, net work done by the gas is given by

$$w = -w_1 - w_2 + w_3 + w_4$$

$$= RT_2 \log_e \frac{V_2}{V_1} - C_V(T_2 - T_1) + RT_1 \log_e \frac{V_4}{V_3} - C_V(T_2 - T_1)$$

$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4}$$

$$= RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

$$= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \quad \text{... (vii)}$$

Thus, $q = w$. For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a Carnot cycle.

Calculation of thermodynamic efficiency of Carnot engine

Total work done from eq. (vii),

$$w = R(T_2 - T_1) \log_e \frac{V_2}{V_1}$$

and the heat absorbed at temperature T_2 from eq. (i),

$$q_2 = RT_2 \log_e \frac{V_2}{V_1}$$

Dividing both equations,

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since, $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means that only a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less than 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Example 95. *Calculate the maximum efficiency of an engine operating between* $100° C$ *and* $25° C$.

Solution: Efficiency $= \frac{T_2 - T_1}{T_2}$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$\text{Efficiency} = \frac{373 - 298}{373} = \frac{75}{373} = 0.20 = 20\%$$

Example 96. *Heat supplied to a Carnot engine is* 453.6 *kcal. How much useful work can be done by the engine which works between* $10° C$ *and* $100° C$?

Solution: $T_2 = 100 + 273 = 373$ K; $T_1 = 10 + 273 = 283$ K;

$$q_2 = 453.6 \times 4.184 = 1897.86 \text{ kJ}$$

We know that,

$$w = q_2 \cdot \frac{T_2 - T_1}{T_2}$$

$$= 1897.86 \times \frac{(373 - 283)}{373}$$

$$= \frac{1897.86 \times 90}{373} = 457.92 \text{ kJ}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

54. For which of the following reactions, the entropy change will be positive? **[JEE (WB) 2008]**
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $HCl(g) + NH_3(g) \rightleftharpoons NH_4Cl(s)$
(c) $NH_4NO_3(s) \rightleftharpoons N_2O(g) + 2H_2O(g)$
(d) $MgO(s) + H_2(g) \rightleftharpoons Mg(s) + H_2O(l)$
[Ans. (c)]
[Hint: $\Delta n_g = 3 - 0 = 3$,
Since $\Delta n_g > 0$, there will be increase in entropy change.]

55. If an endothermic reaction occurs spontaneously at constant temperature T and pressure P, then which of the following is true ? **(VITEEE 2008)**
(a) $\Delta G > 0$ (b) $\Delta H < 0$ (c) $\Delta S > 0$ (d) $\Delta S < 0$
[Ans. (c)]
[Hint: $\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
$\Delta S > 0$ for spontaneous process.]

56. Which is the correct expression that relates changes of entropy with the change of pressure for an ideal gas at constant temperature, among the following ? **[PET (MP) 2008]**
(a) $\Delta S = nRT \ln \frac{P_2}{P_1}$ (b) $\Delta S = T(P_2 - P_1)$
(c) $\Delta S = nR \ln \left(\frac{P_1}{P_2}\right)$ (d) $\Delta S = 2.303\, nRT \ln \left(\frac{P_1}{P_2}\right)$
[Ans. (c)]
[Hint: From first law, $\Delta U = q - W$

$$0 = q - W \quad \text{(for isothermal process)}$$

$$q = W = PdV$$

$$dS = \frac{q}{T} = \frac{PdV}{T}$$

$$dS = nR\frac{dV}{V}$$

On integration, $\Delta S = nR \ln \left(\frac{V_2}{V_1}\right)$

$\Delta S = nR \ln \left(\frac{P_1}{P_2}\right)$. Since $P_1V_1 = P_2V_2$ according to Boyle's law.]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are 436.0 kJ mol^{-1} and 941.8 kJ mol^{-1} and enthalpy of formation of $NH_3(g)$ is -46 kJ mol^{-1}. What is enthalpy of atomization of $NH_3(g)$? What is the average bond enthalpy of N—H bond?*

Solution: $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$;

$$\Delta H = -2 \times 46 \text{ kJ/mol}$$

$$\Delta H = \Sigma(\text{BE})_R - \Sigma(\text{BE})_P$$

$$= (941.8 + 3 \times 436) - (6x) = -2 \times 46$$

(Here, x = BE of N—H bonds)

$$x = 390.3 \text{ kJ mol}^{-1}$$

$$NH_3 \longrightarrow N + 3(H)$$

Heat of atomization $= 3 \times 390.3 = 1170.9$ kJ mol^{-1}

Example 2. *Ethanol was oxidised to acetic acid in a catalyst chamber at 18° C. Calculate the rate of removal of heat to maintain the reaction chamber at 18° C with the feed rate of 30 kg per hour ethanol along with excess oxygen to the system at 18° C, given that a 42 mole per cent yield based on ethanol is obtained. Given that,*

$$\Delta H_{f\,H_2O(l)} = -68.4 \textit{ kcal mol}^{-1}$$

$$\Delta H_{f\,C_2H_5OH\,(l)} = -66 \textit{ kcal mol}^{-1}$$

$$\Delta H_{f\,CH_3COOH\,(l)} = -118 \textit{ kcal mol}^{-1}$$

Solution: $C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$

$$\Delta H = \Sigma(H_f)_P - \Sigma(H_f)_R = (-118 - 68.4) - (-66) = -120.4 \text{ kcal}$$

Yield is 42%. Thus, energy produced per hour will be

$$= \frac{120.4 \times 42 \times 30000}{100 \times 46} = 32979.13 \text{ kcal hour}^{-1}$$

Example 3. *The standard heat of formation listed for gaseous NH_3 is -11.02 kcal/mol at 298 K. Given that at 298 K, the constant pressure heat capacities of gaseous N_2, H_2 and NH_3 are respectively 6.96, 6.89, 8.38 cal/mol. Determine $\Delta H^\circ_{298\,K}$ and $\Delta H_{773\,K}$ for the reaction,*

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$$

Solution: $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

$$\Delta H_{298\,K} = \Sigma(H_f)_P - \Sigma(H_f)_R = (-11.02 - 0)$$

$$= -11.02 \text{ kcal mol}^{-1}$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_2 - (-11.02)}{773 - 298} = (8.38 - \frac{1}{2} \times 6.96 - \frac{3}{2} \times 6.89) \times 10^{-3}$$

$$\Delta H_2 = -13.6 \text{ kcal mol}^{-1}$$

Example 4. *The heat of combustion of glycogen is about 476 kJ/mol of carbon. Assume that average rate of heat loss by an adult male is 150 watt. If we were to assume that all the heat comes from oxidation of glycogen, how many units of glycogen (1 mole carbon per unit) must be oxidised per day to provide for this heat loss?*

Solution: Total energy required in the day

$$= \frac{150 \times 24 \times 60 \times 60}{1000} \text{ kJ} \quad (1 \text{ watt} = \text{J sec}^{-1})$$

$$= 12960 \text{ kJ}$$

Units of glycogen required $= \frac{12960}{476} = 27.22$ units

Example 5. *At 25° C, the following heat of formations are given :*

Compound	$SO_2(g)$	$H_2O(l)$
ΔH_f° *kJ/mol*	−296.81	−285.83

For the reactions at 25° C,

$$2H_2S(g) + Fe(s) \longrightarrow FeS_2(s) + 2H_2(g); \Delta H^\circ = -137 \textit{ kJ/mol}$$

$$H_2S(g) + \frac{3}{2}O_2(g) \longrightarrow H_2O(l) + SO_2(g); \Delta H^\circ = -562 \textit{ kJ/mol}$$

Calculate heat of formation of $H_2S(g)$ and $FeS_2(s)$ at 25° C.

Solution: Heat of formation of $H_2S = x$ kJ/mol

Heat of formation of $FeS_2 = y$ kJ/mol

$$2H_2S(g) + Fe(s) \longrightarrow FeS_2(s) + 2H_2(g); \; \Delta H^\circ = -137 \text{ kJ/mol}$$

$$-137 = y - 2x \qquad \text{... (i)}$$

$$H_2S(g) + \frac{3}{2}O_2(g) \longrightarrow H_2O(l) + SO_2(g); \Delta H^\circ = -562 \text{ kJ/mol}$$

$$-562 = -285.83 - 296.81 - x \qquad \text{... (ii)}$$

From eq. (ii), $x = -20.64$ kJ mol^{-1}

From eq. (i), we get

$$y = 2x - 137 = 2(-20.64) - 137 = -178.28 \text{ kJ mol}^{-1}$$

$$\Delta H_{f\,H_2S} = 20.64 \text{ kJ/mol}$$

$$\Delta H_{f\,FeS_2} = -178 \text{ kJ/mol}$$

Example 6. *The "heat of total cracking" of hydrocarbons ΔH_{TC} is defined as ΔH at 298.15 K and 101.325 kPa for the process below:*

$$C_nH_m + \left(2n - \frac{m}{2}\right) H_2(g) \longrightarrow nCH_4(g)$$

Given that, ΔH_{TC} is -65.2 kJ for C_2H_6 and -87.4 kJ for C_3H_8, calculate ΔH for

$$CH_4(g) + C_3H_8(g) \longrightarrow 2C_2H_6(g)$$

Solution: ΔH_{TC} of $CH_4 = 0$

$$CH_4(g) + C_3H_8(g) \longrightarrow 2C_2H_6(g)$$

$$\Delta H = 2\Delta H_{TC}(C_2H_6) - \Delta H_{TC}(C_3H_8)$$

$$= 2(-65.2) - (-87.4) = -43 \text{ kJ}$$

Example 7. *A constant pressure calorimeter consists of an insulated beaker of mass 92 g made up of glass with heat capacity 0.75 $J\,K^{-1}\,g^{-1}$. The beaker contains 100 mL of 1 M HCl at 22.6°C to which 100 mL of 1M NaOH at 23.4°C is added. The final temperature after the reaction is complete at 29.3°C. What is ΔH per mole for this neutralization reaction? Assume that the heat capacities of all solutions are equal to that of same volumes of water.*

Solution: Initial average temperature of the acid and base

$$= \frac{22.6 + 23.4}{2} = 23.0°\text{C}$$

Rise in temperature $= (29.3 - 23.0) = 6.3°$ C

Total heat produced $= (92 \times 0.75 + 200 \times 4.184) \times 6.3$

$$= (905.8) \times 6.3 = 5706.54 \text{ J}$$

Enthalpy of neutralization $= -\dfrac{5706.54}{100} \times 1000 \times 1$

$$= -57065.4 \text{ J} = -57 \text{ kJ}$$

Example 8. $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$

$$\Delta H = -270.6 \text{ kJ mol}^{-1} K^{-1};\ \Delta S = -139\ JK^{-1}$$

(i) Is the reaction favoured by entropy, enthalpy both or none?

(ii) Find ΔG if $T = 300K$. **[CBSE (Mains) 2005]**

Solution: (i) Since, $\Delta H = -$ve, exothermic process and is favoured, *i.e.*, it will be spontaneous.

(ii) $\Delta G = \Delta H - T\Delta S$

$$= -270.6 \times 1000 - 300 \times (-139)$$

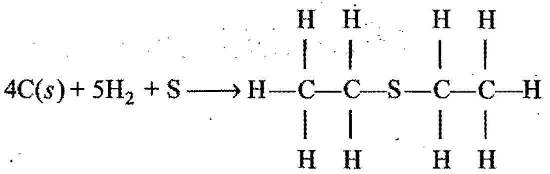
$$= -228900 \text{ J}$$

$$= -228.9 \text{ kJ}$$

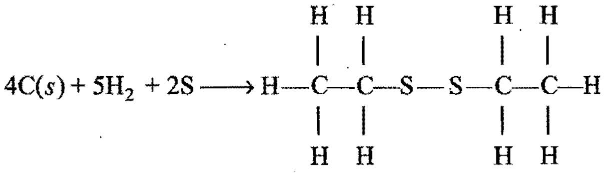
Example 9. *Find bond enthalpy of S—S bond from the following data:*

$C_2H_5—S—C_2H_5$;	$\Delta H_f^\circ = -147.2$ kJ mol^{-1}
$C_2H_5—S—S—C_2H_5$;	$\Delta H_f^\circ = -201.9$ kJ mol^{-1}
$S(g)$;	$\Delta H_f^\circ = 222.8$ kJ mol^{-1}

Solution:



$$4C(s) + 5H_2 + S \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}S{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H$$



$$4C(s) + 5H_2 + 2S \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}S{-}S{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H$$

$$\Delta H = \Sigma(BE)_R - \Sigma(BE)_P$$

(i) $-147.2 =$ Heat of atomization of 4C, 10H, 1S

$-$BE of 10(C—H), 2(C—S), 2(C—C)

(ii) $-201.9 =$ Heat of atomization of 4C, 10H, 2S

$-$BE of 10(C—H), 2(C—S), 2(C—C), (S—S)

Subtracting (i) from (ii),

$-201.9 + 147.2 =$ Heat of atomization of 1S $-$ BE of (S—S)

$= 222.8$ kJ $-$ BE of (S—S)

BE of (S—S) $= 277.5$ kJ

Example 10. *A natural gas may be assumed to be a mixture of methane and ethane only. On complete combustion of 10 litre of gas at STP, the heat evolved was 474.6 kJ. Assuming $\Delta H_{comb} CH_4(g) = -894$ kJ mol^{-1} and $\Delta H_{comb}\, C_2H_6 = -1500$ kJ. Calculate the percentage composition of the mixture by volume.*

Solution:

x litre $\longrightarrow CH_4$; mole of $CH_4 = x/22.4$

$(10-x)$ litre $\longrightarrow C_2H_6$; mole of $C_2H_6 = (10-x)/22.4$

$$\text{Heat evolved} = \frac{x}{22.4} \times 894 + \frac{(10-x)}{22.4} \times 1500$$

$$474.6 = \frac{x}{22.4} \times 894 + \frac{(10-x)}{22.4} \times 1500$$

$$x = 0.745, \quad \%\,CH_4 = 74.5\%$$

Example 11. *From the data at 25°C:*

$$Fe_2O_3(s) + 3C_{(graphite)} \longrightarrow 2Fe(s) + 3CO(g); \quad \Delta H^\circ = 492.6 \text{ kJ/mol}$$

$$FeO(s) + C_{(graphite)} \longrightarrow Fe(s) + CO(g); \Delta H^\circ = 155.8 \text{ kJ/mol}$$

$$C_{(graphite)} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -393.51 \text{ kJ/mol}$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -282.98 \text{ kJ/mol}$$

Calculate standard heat of formation of FeO(s) and $Fe_2O_3(s)$.

Solution:

$$Fe(s) + CO(g) \longrightarrow FeO(s) + C(\text{graphite}); \quad \Delta H^\circ = -158.88 \text{ kJ/mol}$$

$$\text{C(graphite)} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -393.5 \text{ kJ/mol}$$

$$CO_2(g) \longrightarrow CO(g) + \frac{1}{2}O_2(g); \quad \Delta H^\circ = 282.98 \text{ kJ/mol}$$

On adding $Fe(s) + \frac{1}{2}O_2(g) \longrightarrow FeO(s); \ \Delta H = -266.3$ kJ/mol

Similarly we may calculate heat of formation of Fe_2O_3.

Example 12. *Calculate, the ΔH at 85° C for the reaction:*

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$$

The data are: $\Delta H^\circ_{298} = -33.29$ *kJ/mol and*

Substance	$Fe_2O_3(s)$	$Fe(s)$	$H_2O(l)$	$H_2(g)$
C°_P *J/K mol*	103.8	25.1	75.3	28.8

Solution: $Fe_2O_3(s) + 3H_2 \longrightarrow 2Fe + 3H_2O$

$$\Delta C_P = (C_P)_P - (C_P)_R$$
$$= (2 \times 25.1 + 3 \times 75.3) - (103.8 + 3 \times 28.8)$$
$$= 276.1 - 190.2 = 85.9 \text{ J}$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

$$\frac{\Delta H_{558} - (-33.29)}{358 - 298} = 85.9 \times 10^{-3}$$

$$\Delta H_{358} = -28.14 \text{ kJ/mol}$$

Example 13. *The standard heats of formation at 298 K for $CCl_4(g)$, $H_2O(g)$, $CO_2(g)$ and $HCl(g)$ are $-25.5, -57.8, -94.1$ and -22.1 kcal mol^{-1} respectively, calculate $\Delta H^\circ_{298\,K}$ for the reaction:*

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

[BCECE (Mains) 2005]

Solution:

$\Delta H_{\text{reaction}} = \Sigma$ Heat of formation of products

$-\Sigma$ Heat of formation of reactants

$$= [\Delta H_{f(CO_2)} + 4\Delta H_{f(HCl)}] - [\Delta H_{f(CCl_4)} + 2\Delta H_{f(H_2O)}]$$
$$= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)]$$
$$= -41.4 \text{ kcal}$$

Example 14. *Calculate $Q, W, \Delta E$ and ΔH for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.* **(IIT 2000)**

Solution: In isothermal process as temperature remains constant both ΔE and ΔH are zero.

$$\Delta E = 0; \quad \Delta H = 0$$

Applying first law of thermodynamics,

$$\Delta E = W + Q$$
$$0 = W + Q$$

or $$Q = -W = -2.303\, nRT \log\left(\frac{P_1}{P_2}\right)$$

$$= -2.303 \times 1 \times 8.314 \times 273 \log\left(\frac{1}{0.1}\right)$$

$$= 5227.169 \text{ J} = 5.227 \text{ kJ}$$

Example 15. *A sample of argon at 1 atm pressure and 27° C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{v.m.}$ for argon is 12.48 J K^{-1} mol^{-1}.* **(IIT 2000)**

Solution: Number of moles of argon present in the sample

$$= \frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05075$$

For adiabatic expansion,

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{r-1}$$

or $$\frac{300}{T_2} = \left(\frac{2.50}{1.25}\right)^{1.66-1}$$

or $$T_2 = 188.55 \text{ K}$$

$$C_P = C_V + R$$
$$= 12.48 + 8.314$$
$$= 20.794 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = n \times C_P \times \Delta T$$
$$= 0.05075 \times 20.794 \times (300 - 188.55)$$
$$= 117.6 \text{ J}$$

Example 16. *Show that the reaction,*

$$CO(g) + \left(\frac{1}{2}\right)O_2(g) \longrightarrow CO_2(g)$$

at 300 K is spontaneous and exothermic, when the standard entropy change is -0.094 kJ mol^{-1} K^{-1}. The standard Gibb's free energies of formation for CO_2 and CO are -394.4 and -137.2 kJ mol^{-1} respectively. **(IIT 2000)**

Solution: The given reaction is,

$$CO(g) + \left(\frac{1}{2}\right)O_2(g) \longrightarrow CO_2(g)$$

$$\Delta G^\circ \text{ (for reaction)} = G^\circ_{CO_2} - G^\circ_{CO} - \left(\frac{1}{2}\right)G^\circ_{O_2}$$
$$= -394.4 - (-137.2) - 0$$
$$= -257.2 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$-257.2 = \Delta H^\circ - 298 \times (0.094)$$

or $$\Delta H^\circ = -288.2 \text{ kJ}$$

ΔG° is – ve, hence the process is spontaneous, and ΔH° is also –ve, hence the process is also exothermic.

Example 17. *Diborane is a potential rocket fuel which undergoes combustion according to the reaction,*

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

From the following data, calculate the enthalpy change for the combustion of diborane:

$$2B(s) + \left(\frac{3}{2}\right)O_2(g) \longrightarrow B_2O_3(s);\ (\Delta H = -1273\ kJ\ mol^{-1})\ldots(i)$$

$$H_2(g) + \left(\frac{1}{2}\right)O_2(g) \longrightarrow H_2O(l);\ (\Delta H = -286\ kJ\ mol^{-1})\ldots(ii)$$

$$H_2O(l) \longrightarrow H_2O(g);(\Delta H = \ 44\ kJ\ mol^{-1})\ \ldots(iii)$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g);\ (\Delta H = \ 36\ kJ\ mol^{-1})\ldots(iv)$$

(IIT 2000)

Solution: The required equation,

$$\mathrm{B_2H_6}(g) + 3\mathrm{O_2}(g) \longrightarrow \mathrm{B_2O_3}(s) + 3\mathrm{H_2O}(g)$$

can be obtained from

$$\begin{aligned}&\text{eq. (i)} + 3\text{eq. (ii)} + 3\text{eq. (iii)} - \text{eq. (iv)}\\ &= -1273 - 858 + 132 - 36\\ &= -2035\ \text{kJ mol}^{-1}\end{aligned}$$

i.e., Enthalpy of combustion of diborane is -2035 kJ mol^{-1}.

Example 18. *An insulated container contains* 1 *mole of a liquid, molar volume* 100 *mL at* 1 *bar. When liquid is steeply passed to* 100 *bar, volume decreases to* 99 *mL. Find* ΔH *and* ΔU *for the process.* **[IIT 2004 (Memory based)]**

Solution: From first law of thermodynamics:

$$\begin{aligned}\Delta U &= q + W\\ \Delta U &= q + P\,\Delta U = 0 + \{-100\,(99 - 100)\}\\ &= 100\ \text{bar mL}\\ \Delta H &= \Delta U + (P_2V_2 - P_1V_1)\\ &= 100 + (100 \times 99 - 1 \times 100)\\ &= 9900\ \text{bar mL}\end{aligned}$$

Example 19. *In the following equilibrium:*

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

when 5 *mole of each are taken and temperature is kept at* 298 *K, the total pressure was found to be* 20 *bar.*

Given: $\Delta G_f^\circ\ N_2O_4 = 100\ kJ$

$\Delta G_f^\circ\ NO_2 = 50\ kJ$

(*i*) *Find* ΔG *of the reaction at* 298 *K.*

(*ii*) *Find the direction of the reaction.*

[IIT 2004 (Memory based)]

Solution: The reaction is:

$$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g)$$

Since, number of moles of both $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ are same hence their partial pressure will also be same.

$$p_{\mathrm{N_2O_4}} = p_{\mathrm{NO_2}} = \frac{20}{2} = 10\ \text{bar}$$

$$Q_P = \frac{[p_{\mathrm{NO_2}}]^2}{[p_{\mathrm{N_2O_4}}]} = \frac{10^2}{10} = 10\ \text{bar}$$

$$\Delta G^\circ_{\text{reaction}} = 2\Delta G_f^\circ\ \mathrm{NO_2} - \Delta G_f^\circ\ \mathrm{N_2O_4}$$

$$= 2 \times 50 - 100 = 0$$

We know that, $\Delta G = \Delta G^\circ - 2.303\,RT \log Q$

$$\begin{aligned}&= 0 - 2.303 \times 8.314 \times 298 \log 10\\ &= -5705\ \text{J}\end{aligned}$$

Since, ΔG is negative hence reaction will be spontaneous in forward direction.

Example 20. *When* 1*-pentyne* (*A*) *is treated with* 4*N alcoholic KOH at* 175°C*, it is slowly converted into an equilibrium mixture of* 1.3 % *of* 1*-pentyne* (*A*), 95.2% 2*-pentyne* (*B*) *and* 3.5% *of* 1,2*-pentadiene* (*C*). *The equilibrium was maintained at* 175°C. *Calculate* ΔG° *for the following equilibria:*

$$B \rightleftharpoons A;\quad \Delta G_1^\circ = ?$$

$$B \rightleftharpoons C;\quad \Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° *and* ΔG_2° *indicate the order of stability of* (*A*), (*B*) *and* (*C*). *Write a reasonable reaction mechanism showing all intermediates leading to* (*A*), (*B*) *and* (*C*). **(IIT 2001)**

Solution: Pentyne-1 $\rightleftharpoons$ Pentyne-2 + 1, 2-pentadiene

$$\begin{array}{llll} & (A) & (B) & (C)\\ t_{\text{eq}} & 1.3 & 95.2 & 3.5\end{array}$$

$$K_{\text{eq}} = \frac{[B][C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$

$$B \rightleftharpoons A$$

$$K_1 = \frac{[A]}{[B]} = \frac{[C]}{K_{\text{eq}}} = \frac{3.5}{256.31} = 0.013$$

$$\begin{aligned}\Delta G_1^\circ &= -2.303RT \log K_1\\ &= -2.303 \times 8.314 \times 448 \log 0.013\\ &= 16178\ \text{J} = 16.178\ \text{kJ}\end{aligned}$$

for $\quad B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_{\text{eq}}[A]}{[B]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$$\begin{aligned}\Delta G_2^\circ &= -2.303RT \log K_2\\ &= -2.303 \times 8.314 \times 448 \log 0.037\\ &= 12282\ \text{J} = 12.282\ \text{kJ}\end{aligned}$$

Stability will lie in the order

$$B > C > A$$

Example 21. *Two moles of a perfect gas undergo the following process:*

(*a*) *A reversible isobaric expansion from* (1 *atm* 20 *L*) *to* (1 *atm* 40 *L*).

(*b*) *A reversible isochoric change of state from* (1 *atm* 40 *L*) *to* (0.5 *atm* 40 *L*).

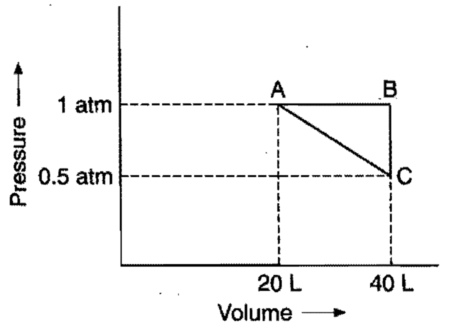
(*c*) *A reversible isothermal compression from* (0.5 *atm* 40 *L*) *to* (1 *atm* 20 *L*).

(*i*) *Sketch with labels each of the process on the same P-V diagram.*

(ii) Calculate the total work (W) and the total heat change (q) involved in the above process.

(iii) What will be the value of $\Delta U, \Delta H$ and ΔS for the overall process? **(IIT 2002)**

Solution:



$AB \rightarrow$ Isobaric process

$BC \rightarrow$ Isochoric process

$CA \rightarrow$ Isothermal compression

$$\text{Total work} = W_{AB} + W_{BC} + W_{CA}$$

$$= -P \times \Delta V + 0 + 2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= -1 \times 20 \times 101.3 + 0 + 2.303 \times 2 \times 8.314 \times T \log\left(\frac{40}{20}\right) \quad \ldots(1)$$

$$PV = nRT \text{ (At } A)$$

$$1 \times 20 = 2 \times 0.0821 \times T$$

$$T = \frac{20}{2 \times 0.0821} = 121.8\text{ K}$$

From eq. (1),

$$\text{Total work} = -2026 + 2.303 \times 2 \times 8.314 \times 121.8 \log 2$$

$$= -622.06\text{ J}$$

$$W = q = -622.06\text{ J}$$

In cyclic process:

$$\Delta U = 0, \Delta H = 0 \text{ and } \Delta S = 0$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. **Thermodynamics:** It is the branch of science which deals with all changes in energy or transfer of energy that accompany physical and chemical processes. It is not concerned with the total energy of body but only with energy changes taking place. The laws of thermodynamics apply only to matter in bulk, *i.e.*, to macroscopic system and not to individual atoms or molecules.

2. **Terms used in thermodynamics:**

(a) System, surroundings and boundary: A **system** is defined as a specified part of the universe which is under experimental investigation and the rest of the universe which can interact with the system is **surroundings.** Anything which separates system and surroundings is called **boundary.** It may be real or imaginary, conductor or non-conductor.

(b) Types of system: There are three types of system: **(i) Isolated system** is one which has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surroundings. **(ii) Closed system** is one which can exchange energy but not matter with surroundings. **(iii) Open system** is one which can exchange matter as well as energy with surroundings. A system is said to be **homogeneous** if it is made of one-phase only. A system is said to be **heterogeneous** when it consists of two or more phases.

(c) Thermodynamic properties: These are of two types: **(i) Intensive properties** are those which do not depend upon the quantity of matter present in the system such as pressure, temperature, specific heat, surface tension, viscosity, melting and boiling points, etc. **(ii) Extensive properties** are those whose magnitude depends upon the quantity of matter present in the system such as volume, total energy, enthalpy, entropy, etc.

(d) State variables: The fundamental properties which determine the state of the system are termed **state variables.** The change in state property depends only upon the initial and final states of the system, *i.e.*, do not depend on the path followed. Pressure, volume, temperature, internal energy, enthalpy, entropy, force, energy and number of moles are the state variables.

(e) Thermodynamic equilibrium: A system in which the fundamental properties do not undergo any change with time is said to be in thermodynamic equilibrium. Actually the system should be in thermal equilibrium, mechanical equilibrium and chemical equilibrium.

(f) Thermodynamic processes: When the system changes from one state to another, the operation is called a **process.** The various types of processes are:

(i) Isothermal: Temperature remains fixed, *i.e.*, $dT = 0$. This is achieved by placing the system in a thermostat.

(ii) Adiabatic: When no exchange of heat occurs between the system and surroundings, *i.e.*, the system is thermally isolated $(dq = 0)$.

(iii) Isobaric: Pressure remains constant throughout the change, *i.e.*, $dP = 0$.

(iv) Isochoric: Volume remains constant throughout the change, *i.e.*, $dV = 0$.

(v) Cyclic: When a system undergoes a number of different processes and finally returns to initial state, $dE = 0$ and $dH = 0$

(vi) Reversible: A process which occurs infinitesimally slowly and at every small change it is virtually in a state of equilibrium. It takes infinite time.

(vii) Irreversible: When the process goes from initial to final state in single step in finite time. All natural processes are irreversible.

3. Nature of work and heat: Work is a mode of transfer of energy to or from a system with reference to surroundings. If an object is displaced through a distance dx against a constant force F, then the amount of work which has to be done is equal to $F \times dx$. The mechanical work or pressure volume work is equal to $P_{\text{ext}}(V_2 - V_1)$ or $P \times dV$. The work done on the system increases its energy while work done by the system decreases its energy. On this basis, the work done has the sign convention.

$$\text{Work done by the system} = -w$$
$$\text{Work done on the system} = +w$$

The unit of work is erg. It is very small. The bigger unit is joule or kilojoule.

$$1 \text{ joule} = 10^7 \text{ ergs; } 1 \text{ kJ (kilojoule)} = 1000 \text{ J}$$

Heat is the quantity of energy which flows between system and surroundings on account of temperature difference. It is equal to $m \times s \times \Delta t$ where m is the mass, s is the specific heat and Δt is the temperature difference. The sign convention for heat is:

$$\text{Heat gained by system} = +q$$
$$\text{Heat lost by system} = -q$$

The unit of heat is calorie (cal). Since, heat and work are correlated the SI unit of heat is joule.

$$1 \text{ joule} = 0.2390 \text{ cal}$$
$$1 \text{ calorie} = 4.184 \text{ J}$$
$$1 \text{ kcal} = 4.184 \text{ kJ}$$
$$1 \text{ litre-atm} = 101.3 \text{ J} = 1.013 \times 10^9 \text{ erg} = 24.206 \text{ cal}$$

4. Internal energy: Sum of all forms of energy that a system possesses is termed internal energy. It is denoted by E. It is an extensive property. It is also a state property.

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \ldots$$

The internal energy of a particular system is a definite quantity but it is impossible to determine its exact value. It is a state function. In thermodynamics, one is concerned only with energy change which occurs when the system moves from one state to another, *i.e.*, $\Delta E = E_f - E_i$. ΔE is +ve if $E_f > E_i$ and negative if $E_f < E_i$. ΔE does not depend on the path by which final state is achieved. For a cyclic process, $\Delta E = 0$.

5. First law of thermodynamics: Energy can neither be created nor destroyed but it can be converted from one form to another.

Or

The energy of the universe is constant.

Or

Total energy of an isolated system remains constant, though it may change from one form to another.

When heat energy (q) is given to a system and work (w) is also done on it, its energy increases from E_1 to E_2.

$$E_2 = E_1 + q + w \quad \text{or} \quad E_2 - E_1 = q + w \quad \text{or} \quad \Delta E = q + w$$

In case heat energy (q) is given to a system and work (w) is done by the system then

$$\Delta E = q + (-w) = q - w$$

6. Enthalpy or heat content: The quantity $E + PV$ is known as enthalpy or heat content. It is denoted by H. It represents the total energy stored in a system.

$$\Delta E = q - P(V_2 - V_1) \quad \text{or} \quad E_2 - E_1 = q - PV_2 + PV_1$$
$$\text{or} \quad (E_2 + P_2V_2) - (E_1 + P_1V_1) = q \quad \text{or} \quad H_2 - H_1 = q$$
$$\text{or} \quad \Delta H = q \quad \text{or} \quad \Delta E + P\,\Delta V = \Delta H = q_P$$
$$\text{when} \quad V_2 = V_1, \ \textit{i.e.}, \ \Delta V = 0, \Delta E = q_V$$
$$q_V + \Delta nRT = q_P \qquad \text{in the case of gases}$$

where, Δn = total number of moles of products − total number of moles of reactants

7. Heat capacity: It is the quantity of heat required to raise the temperature of the system by one degree.

$$\text{Heat capacity} = \frac{dq}{dT}$$

In the case of gases,

$$C_V \text{ (at constant volume)} = \left(\frac{\partial E}{\partial T}\right)_V$$

= Molar heat capacity at constant volume

$$\text{and } C_P \text{ (at constant pressure)} = \left(\frac{\partial H}{\partial T}\right)_P$$

= Molar heat capacity at constant pressure

$$C_P - C_V = R$$

8. Isothermal expansion of an ideal gas: The expansion in an ideal gas at constant temperature can be done reversibly or irreversibly.

w = Work done by gas in reversible expansion

$$= -2.303nRT \log \frac{V_2}{V_1} = -2.303nRT \log \frac{P_1}{P_2}$$

q = Heat absorbed from surroundings

$$= -w = 2.303nRT \log \frac{V_2}{V_1}$$

w = Work done by gas in irreversible expansion

$$= -P_{\text{ext}}(V_2 - V_1)$$

Maximum work is done in reversible isothermal expansion. In isothermal process, $\Delta E = 0$ and $\Delta H = 0$.

Adiabatic expansion of an ideal gas: q in the process is zero, hence $\Delta E = w$. Work is done by the gas during expansion at the expense of internal energy. In expansion, ΔE decreases while in compression ΔE increases.

$$\Delta E = w = C_V \times \Delta T$$

The value of ΔT depends upon the process whether carried reversibly or irreversibly. The following relationships are followed by an ideal gas under adiabatic conditions:

$$PV^{\gamma} = \text{constant} \qquad \left(\gamma = \frac{C_P}{C_V}\right)$$

$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma - 1} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$$

9. Joule-Thomson effect: The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson effect. This effect is observed below the inversion temperature of a gas. The inversion temperature of a gas depends upon the van der Waals' constants of a gas. It is expressed in terms of van der Waals' constants 'a' and 'b' as:

$$T_i = \frac{2a}{Rb}$$

10. Thermochemistry: It is concerned with heat changes accompanying physical and chemical transformations. It is also termed as chemical energetics. It is based on the first law of thermodynamics. If E_1 and E_2 represent total energies associated with reactants and products respectively, three cases may arise:

Case I: $E_1 = E_2$. Neither heat is evolved nor absorbed. Such reactions are very rare.

Case II: $E_1 > E_2$. The difference $(E_1 - E_2)$ of energy will be evolved, *i.e.*, heat is evolved.

Case III: $E_1 < E_2$. The difference $(E_2 - E_1)$ of energy will be absorbed, *i.e.*, heat is absorbed.

11. Exothermic reactions: Reactions which occur with evolution of heat

$$H_{\text{products}} < H_{\text{reactants}}, \qquad i.e., \qquad \Delta H = -\text{ve}$$

Endothermic reactions: Reactions which occur with absorption of heat

$$H_{\text{products}} > H_{\text{reactants}}, \qquad i.e., \qquad \Delta H = +\text{ve}$$

Sign conventions	q	ΔE	ΔH
Exothermic	(–)	(–)	(–)
Endothermic	(+)	(+)	(+)

12. Heat of reaction or enthalpy of reaction: The amount of heat evolved or absorbed when quantities of the substances indicated by chemical equation have completely reacted, it is represented as ΔH.

$$\text{Enthalpy of reaction} = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

The factors which affect the magnitude of heat of reaction are :

(i) Physical state of reactants and products, (ii) Allotropic forms of the elements (iii) Reaction carried at constant pressure or constant volume $(\Delta H = \Delta E + \Delta nRT)$ (iv) Enthalpy of solution (v) Temperature at which the reaction is carried out.

13. Heat of formation or enthalpy of formation: It is the amount of heat evolved or absorbed when one gram mole of substance is directly obtained from its constituent elements. It is represented as ΔH_f.

If all the substances of the chemical reaction are in their standard states (*i.e.*, at 25° C or 298 K and one atmospheric pressure), the heat of reaction or formation is called standard heat of reaction or formation respectively. These are denoted as ΔH° or ΔH_f° respectively. The enthalpies of free elements at standard conditions are taken arbitrary as zero.

The compounds which have positive enthalpies of formation are called endothermic compounds (less stable) and which have negative enthalpies of formation are called exothermic compounds (stable).

14. Heat of combustion or enthalpy of combustion: It is the amount of heat evolved when one mole of the substance is completely oxidised. It has a number of applications:

(i) Determination of calorific values of foods and fuels.
(ii) Enthalpy of formation can be determined by application of Hess's law.
(iii) Structural problems can be evaluated.

15. Enthalpy of hydrogenation: The enthalpy change associated when one mole of an unsaturated organic compound is fully hydrogenated.

16. Enthalpy of solution: The amount of heat evolved or absorbed when one mole of the substance is dissolved in excess of water so that further dilution does not bring any heat change.

17. Enthalpy or heat of neutralisation: The amount of heat evolved when one gram equivalent of an acid is neutralised by one gram equivalent of a base in dilute solution. Heat of neutralisation of a strong acid against a strong base is always constant, *i.e.*, 13.7 kcal or 57.1 kJ. It is due to common reaction between H^+ and OH^- ions. The heat of formation of water from these ions is 13.7 kcal.

$$H^+ + OH^- \longrightarrow H_2O; \qquad \Delta H = -13.7\,\text{kcal}$$

In the case of weak acids and weak bases, the heat of neutralisation is always less than 13.7 kcal because some of the evolved heat energy is utilised in bringing about complete ionisation of acid or base in solution.

18. Enthalpy of fusion: Heat absorbed in converting one mole of solid into liquid at its melting point.

19. Enthalpy of vaporisation: Heat absorbed in converting one mole of a liquid into its vapours at its boiling point.

Enthalpy of sublimation: Heat absorbed in converting one mole of solid directly into its vapour.

20. Laws of thermochemistry:

(i) Lavoisier and Laplace law: The heat which is required to break a compound into its elements is equal to the heat evolved during its formation from its elements.

$$\Delta H_{\text{decomposition}} = -\Delta H_f$$

(ii) Hess's law (the law of constant heat summation): If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total change is always the same, *i.e.*, heat change depends upon the initial and final stages only and independent of intermediate steps. The thermochemical equations can be added, subtracted or multiplied by a number to obtain a desired equation.

21. Bond energy: The energy required to break one mole of bond of a particular type is termed bond dissociation energy. It depends upon the nature of bond and also the molecule in which the bond is present. The bond energies can be used for determining heats of reactions.

[Heat of reaction = Sum of bond energies of reactants
– Sum of bond energies of products]

The bond energies can also be used for determining resonance energy.

Resonance energy = Observed heat of formation
– Calculated heat of formation

22. Experimental determination of heat of reaction: The apparatus used is called calorimeter. Two of the common types of calorimeters are: (i) Water calorimeter (ii) Bomb-calorimeter. The principle of measurement is that heat given out is equal to heat taken, *i.e.*,

$$Q = (W + m) \times s \times (T_2 - T_1)$$

where, W = Water equivalent of the calorimeter, m = mass of the liquid, s = its sp. heat, T_2 = final temperature and T_1 = initial temperature.

23. Spontaneous process: A process which proceeds of its own accord without any outside help is termed spontaneous process. All natural processes proceed spontaneously and are thermodynamically irreversible.

Driving force: It is the force which makes the process to occur by itself. It is the resultant of two basic tendencies:

(i) Tendency to attain a state of minimum energy.
(ii) Tendency to attain a state of maximum randomness.

The disorder or randomness in a system is measured in terms of a thermodynamic property known as **entropy.** The absolute value of entropy cannot be determined. The change in entropy is denoted by ΔS.

$$\Delta S = \frac{q_{\text{reversible}}}{T}$$

where, q is the heat supplied at temperature T.

$\Delta S = +$ indicates increase in randomness whereas, $\Delta S = -$ indicates the decrease in randomness.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

24. Free energy: Free energy change, ΔG, was introduced by Gibbs. The Gibbs-Helmholtz equation is:

$$\Delta G = \Delta H - T\,\Delta S \quad \text{or} \quad G = H - TS$$

and $$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

where, G is known as free energy. This is the maximum energy available to a system during a process which can be converted into useful work.

Negative value of ΔG indicates that the process is spontaneous. Zero value means that there is a state of equilibrium.

25. Second law of thermodynamics: It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency.

Or

Work can always be converted into heat but the conversion of heat into work does not take place under all conditions.

26. Carnot cycle: It demonstrates the maximum convertibility of heat into work in a theoretical and an imaginary cycle.

$$\text{Thermodynamic efficiency} = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

The efficiency of a heat engine is always less than 1.

27. Third law of thermodynamics: The entropy of all pure crystals is zero at the absolute zero of temperature.

Questions

1. **Matrix-Matching Problems (For IIT Aspirants):**

[A] Match the List-I with List-II:

List-I	List-II
(a) $\Delta S_{\text{system}} > 0$ (Isolated system)	(p) Spontaneous
(b) $\Delta G < 0$	(q) Non-spontaneous photochemical reaction
(c) $\Delta S_{\text{Total}} = 0$	(r) Equilibrium
(d) $(\Delta G)_{TP} > 0$	(s) Non-spontaneous

[B] Match the Column-I with Column-II:

Column-I	Column-II
(a) Isothermal process (reversible)	(p) $W = 2.303nRT \log\left(\frac{P_1}{P_2}\right)$
(b) Adiabatic process	(q) $PV^{\gamma} = \text{constant}$
(c) $W = \frac{nR}{r-1}(T_2 - T_1)$	(r) $W = 2.303nRT \log\left(\frac{V_2}{V_1}\right)$
(d) Irreversible isothermal process	(s) $W = -P_{\text{ext}}(V_2 - V_1)$

[C] Match the physical properties in List-I with their relations in List-II:

List-I (Quantity)	List-II (Relation)
(a) ΔG	(p) $-nFE$ or $-nFE^{\circ}$
(b) ΔG°	(q) $\Delta H - T\,\Delta S$
(c) W or $W_{\max}$	(r) $-RT \log_e K$
(d) ΔS°	(s) $2.303nR \log_{10}\left(\frac{V_2}{V_1}\right)$

[D] Match the Column-I with Column-II:

Column-I (Gas)	Column-II (Thermodynamic property)
(a) O_2	(p) $\gamma = 1.4$
(b) N_2	(q) $C_P = \frac{7}{2}R$
(c) CO_2, CH_4	(r) $\frac{23}{6}R$
(d) 1 mol O_2 + 2 mol O_3	(s) $\gamma = 1.33$

Here: C_P = Heat capacity at constant pressure
$\gamma = C_P/C_V$

[E] Match the reactions in Column-I with relations of Column - II:

Column-I (Reaction)	Column-II (Relation)
(a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	(p) $\Delta H = \Delta U + RT$
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	(q) $\Delta H = \Delta U$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(r) $\Delta H = \Delta U - 2RT$
(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(s) Forward shift by increasing pressure

[F] Match the processes of Column-I with entropy or enthalpy changes in Column-II:

Column-I	Column-II
(a) $N_2(g) + O_2(g) \rightarrow 2NO(g)$	(p) $\Delta S = 0$
(b) $2KI(aq.) + HgI_2(aq.) \rightarrow K_2[HgI_4](aq.)$	(q) $\Delta S < 0$
(c) $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$	(r) $\Delta H > 0$
(d) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$	(s) $\Delta H < 0$

[G] Match the List-I with List-II:

List-I (Reaction)	List-II (Process)
(a) $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$	(p) Combustion
(b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	(q) Neutralization
(c) $NaOH(aq.) + HCl(aq.) \rightarrow NaCl(aq.) + H_2O$	(r) Process of formation
(d) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	(s) Reaction of apollo fuel cell

[H] Match the relations of Column-I with their names in Column-II:

Column-I	Column-II
(a) $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$	(p) Trouton equation
(b) $\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V$	(q) Effect of temperature on the heat of reaction
(c) $\frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \Delta S_{\text{fusion}}$	(r) Kirchhoff's equation
(d) $\lim\limits_{T \to 0\,\text{K}} S \rightarrow 0$	(s) Third law of thermodynamics

[I] Match the Column-I with Column-II:

	Column-I		Column-II
(a)	Amount of heat required to raise the temperature of 1 mol substance by 1°C	(p)	Specific heat × molar mass
(b)	$\frac{\Delta H}{\Delta T}$ or $\frac{\Delta U}{\Delta T}$	(q)	Heat capacity = C, C_P or C_V
(c)	Heat evolved in the combustion of 1 g of a substance	(r)	Electron gain enthalpy
(d)	Heat evolved when an extra electron is added to valence shell of an isolated gaseous atom	(s)	Calorific value

[J] Match the Column-I with Column-II :

	Column-I		Column-II
(a)	$\Delta H = +$ ve, $\Delta S = +$ ve	(p)	Spontaneous at all temperature
(b)	$\Delta H = -$ ve, $\Delta S = +$ ve	(q)	Non-spontaneous at all temperature
(c)	$\Delta H = +$ ve, $\Delta S = -$ ve	(r)	Non-spontaneous at high temperature
(d)	$\Delta H = -$ ve, $\Delta S = -$ ve	(s)	Spontaneous at high temperature

Answers

1. [A] (a—p); (b—p, q); (c—r); (d—s)
   [B] (a—p, r); (b—q); (c—q); (d—s)
   [C] (a—p, q); (b—p, r); (c—p); (d—s)
   [D] (a—p, q); (b—p, q); (c—s); (d—r)
   [E] (a—q); (b—q); (c—p); (d—r, s)
   [F] (a—p, r); (b—q, s); (c—q, r); (d—q, s)
   [G] (a—p, r); (b—p); (c—q); (d—p, r, s)
   [H] (a—q, r); (b—q, r); (c—p); (d—s)
   [I] (a—p, q); (b—p, q); (c—s); (d—r)
   [J] (a—s); (b—p); (c—q); (d—r)

• PRACTICE PROBLEMS •

1. Write 'yes' if heat, work or matter are able to cross the boundary of the corresponding system and 'no' if passage is forbidden:

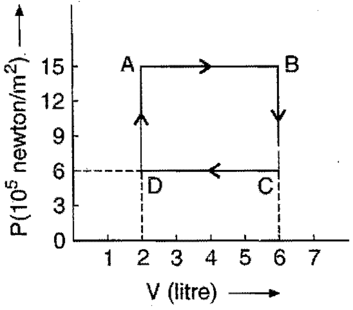
Property	Open system	Close system	Isolated system	Adiabatic system
Heat	Yes/No	Yes/No	Yes/No	Yes/No
Work	Yes/No	Yes/No	Yes/No	Yes/No
Matter	Yes/No	Yes/No	Yes/No	Yes/No

2. Which of the following are state functions?
(i) Q (ii) W (iii) $Q + W$ (iv) $Q - W$ (v) Q_V (vi) Q_P
(vii) $\frac{Q}{W}$ (viii) $\frac{Q}{T}$ (ix) $\frac{\Delta H}{T}$ (x) $E + PV$ (xi) $E - PV$

[**Ans.** (iv), (v), (vi), (viii), (ix), (x).]

3. In the adjoining diagram, the P-V graph of an ideal gas is shown. Find out from the graph (i) Work done in taking the gas from the state $A \rightarrow B$ (ii) Work done in taking the gas from $B \rightarrow C$ (iii) Work done in a complete cycle. (1 litre = 10^{-3} m^3)

[**Ans.** (i) -60×10^2 J (ii) zero (iii) 36×10^2 J, *i.e.,* net work is done by the gas]



4. A sample of a gas contracts 200 cm^3 by an average of 0.5 atmosphere while 8.5 J heat flows out into the surroundings. What is the change in energy of the system?
(1 litre-atm = 101.3 J)

[**Ans.** Energy of the system increases by 1.63 J]

5. Calculate the pressure-volume work done by the system when the gas expands from 1.0 litre to 2.0 litre against a constant external pressure of 10 atmospheres. Express the answer in calorie and joule.

[**Ans.** –10 litre-atm, –242.2 cal, –1013.28 J]

6. A sample of a gas in a cylinder contracts by 7.5 litre at a constant pressure of 5.0 atmosphere. How much work is done on the gas by the surroundings?

[**Ans.** 37.5 litre-atm or 3801.75 J]

7. A sample of a gas expands from 200 cm^3 to 500 cm^3 against an average pressure of 750 torr while 1.5 J heat flows into the system. What is the change in energy of the system? (1 litre-atm = 101.3 J)

[**Ans.** Energy of the system is decreased by 28.5 J; $\Delta E = -28.5$ J]

8. Calculate the work done when 65.38 g of zinc dissolves in hydrochloric acid in an open beaker at 300 K. (At. mass of Zn = 65.38)

[**Ans.** – 2494.2 J, *i.e.*, work is done by the system]

9. 6 moles of an ideal gas expand isothermally and reversibly from a volume of 1 dm^3 to a volume of 10 dm^3 at 27° C. What is the maximum work done? Express your answer in joule.
[**Ans.** – 34464.8 J, work is done by the system]

10. 1 mole of an ideal gas at 25° C is allowed to expand reversibly at constant temperature from a volume of 10 litre to 20 litre. Calculate the work done by the gas in joule and calorie.
[**Ans.** – 1717.46 J or –411 cal, *i.e.*, work is done by the gas]

11. Find the work done when 1 mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25° C.
[**Ans.** – 3984 J]
[**Hint:** Use $w = -2.303\, nRT \log \frac{P_1}{P_2}$]

12. How much energy is absorbed by 10 moles of an ideal gas if it expands from an initial pressure of 8 atmosphere to 4 atmosphere at a constant temperature of 27° C?
($R = 8.31\,J\,mol^{-1}\,K^{-1}$)
[**Ans.** 1.728×10^4 J]
[**Hint:** In isothermal process, $\Delta E = 0$,
so q (heat absorbed) = – w. Thus, apply the equation

$$q = 2.303 nRT \log \frac{P_1}{P_2}]$$

13. A given mass of a gas at 0° C is compressed reversibly and adiabatically to a pressure 20 times the initial value. Calculate the final temperature of the gas. $\left[\frac{C_P}{C_V} = 1.42\right]$
[**Ans.** $T_2 = 662.2$ K]
[**Hint:** Apply the formula $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$]

14. 3 moles of hydrogen are compressed isothermally and reversibly from 60 dm^3 to 20 dm^3 and 8.22 kJ of work is done on it. Assuming ideal behaviour, calculate the temperature of the gas.
[**Ans.** 300 K]

15. To what pressure must a certain ideal gas ($\gamma = 1.4$) at 373 K and 1 atmospheric pressure be compressed adiabatically in order to raise its temperature to 773 K?
[**Ans.** 7.89 atm]

16. 1 mole of an ideal gas ($C_V = 12.55\,J\,K^{-1}\,mol^{-1}$) at 300 K is compressed adiabatically and reversibly to one-fourth of its original volume. What is the final temperature of the gas?
[**Ans.** 752 K]

17. Calculate $q, w, \Delta E$ and ΔH for the reversible isothermal expansion of 1 mole of ideal gas at 27° C from a volume of 10 dm^3 to a volume of 20 dm^3.
[**Ans.** $q = -w = 1729$ J]

18. Calculate the internal energy change for the process in which 1.0 kcal of heat is added to 1.2 litre of O_2 gas in a cylinder at constant pressure of 1.0 atm and the volume changes to 1.5 litre.
[**Ans.** 0.993 kcal]

19. Calculate ΔE and ΔH when 10 dm^3 of helium at NTP is heated in a cylinder to 100° C, assuming that the gas behaves ideally. ($C_V = 3/2R$)
[**Ans.** $\Delta E = 556.74$ J
$\Delta H = 927.9$ J]
[**Hint:** $\Delta E = n \cdot C_V \cdot \Delta T$ and $\Delta H = n \cdot C_P \cdot \Delta T$

$$= \frac{10}{22.4} \times \frac{3}{2} \times 8.314 \times 100 \qquad = \frac{10}{22.4} \times \frac{5}{2} \times 8.314 \times 100$$
$$= 556.74 \text{ J} \qquad = 927.9 \text{ J}]$$

20. For the conversion of 1 mole of $SO_2(g)$ into $SO_3(g)$ the enthalpy of reaction at constant volume, ΔE, at 298 K is –97.027 kJ. Calculate the enthalpy of reaction, ΔH, at constant pressure.
[**Ans.** $\Delta H = -98.267$ kJ]
[**Hint:** Use the reaction,

$$SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g), \ \Delta n = 1 - \frac{3}{2} = -\frac{1}{2}]$$

21. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured at constant volume and at 27° C. Calculate the heat of combustion of benzene at constant pressure. ($R = 8.3\,JK^{-1}\,mol^{-1}$) **(IIT 1996)**
[**Ans.** –3273.7 kJ mol^{-1}]

22. 1 mole of naphthalene ($C_{10}H_8$) was burnt in oxygen gas at 25° C at constant volume. The heat evolved was found to be 5138.8 kJ. Calculate the heat of reaction at constant pressure. ($R = 8.3\,JK^{-1}\,mol^{-1}$)
[**Ans.** 5143.8 kJ]
[**Hint:** Water is present in liquid state at 25° C and naphthalene in solid state.]

23. The enthalpy of formation of methane at constant pressure and 300 K is –75.83 kJ. What will be the heat of formation at constant volume? ($R = 8.3\,J\,K^{-1}\,mol^{-1}$)
[**Ans.** –73.34 kJ]

24. The heat change for the reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

is – 92.2 kJ. Calculate the heat of formation of ammonia.
[**Ans.** – 46.1 kJ mol^{-1}]

25. $\Delta H°$ for the reaction,

$$4S(s) + 6O_2(g) \longrightarrow 4SO_3(g)$$

is –1583.2 kJ. Calculate ΔH_f° of sulphur trioxide.
[**Ans.** – 395.8 kJ]

26. Calculate the heat change in the reaction,

$$4NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(l)$$

at 298 K given that heats of formation at 298 K for $NH_3(g)$ and $H_2O(l)$ are – 46.0 and – 286.0 kJ mol^{-1} respectively.
[**Ans.** $\Delta H° = -1532$ kJ]

27. Calculate the heat of combustion of 1 mole of $C_2H_4(g)$ to form $CO_2(g)$ and $H_2O(g)$ at 398 K and 1 atmosphere, given that the heats of formation of $CO_2(g)$, $H_2O(g)$ and $C_2H_4(g)$ are – 94.1, – 57.8 and + 12.5 kcal mol^{-1} respectively.
[**Ans.** – 316.3 kcal]

28. The heats of combustion of $CH_4(g)$ and $C_2H_6(g)$ are –890.3 and – 1560 kJ mol^{-1} respectively. Which has higher calorific value?
[**Ans.** Methane has higher calorific value.]

29. The heat of combustion of butane is 2880 kJ mol^{-1}. What is the heat liberated by burning 1 kg of butane in excess of oxygen supply?
[**Ans.** 49655 kJ]

30. The heat of formation of $CH_4(g)$, $C_2H_6(g)$ and $C_4H_{10}(g)$ are – 74.8, – 84.7 and – 126.1 kJ mol^{-1} respectively. Arrange them in order of their efficiency as fuel per gram. Heats of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 and – 285.8 kJ mol^{-1} respectively.
[**Ans.** $CH_4 > C_2H_6 > C_4H_{10}$]
[**Hint:** First determine heat of combustion in each case and then find the calorific value.]

31. The heat of combustion of carbon to $CO_2(g)$ is – 393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of $CO_2(g)$ from carbon and oxygen gas.
[**Ans.** – 315 kJ]

32. Calculate ΔH_f° of $C_6H_{12}O_6(s)$ from the following data:
ΔH_{comb} of $C_6H_{12}O_6(s) = -2816$ kJ mol^{-1}, ΔH_f° of $CO_2(g)$ $= -393.5$ kJ mol^{-1} and $\Delta H^\circ_{f\,(H_2O)} = -285.9$ kJ mol^{-1}.
[**Ans.** – 1260 kJ mol^{-1}]

33. Calculate the amount of heat released when:
(i) 100 mL of 0.2 *M* HCl solution is mixed with 50 mL of 0.2 *M* KOH.
(ii) 200 mL of 0.1 *M* H_2SO_4 is mixed with 200 mL of 0.2 *M* KOH solution.
[**Ans.** (i) 0.57 kJ (ii) 2.18 kJ]

34. When 100 mL each of HCl and NaOH solutions are mixed, 5.71 kJ of heat was evolved. What is the molarity of two solutions? The heat of neutralisation of HCl is 57.1 kJ.
[**Ans.** 1 *M*]

35. Determine the enthalpy of the reaction,

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$$

at 25° C, using the given heat of combustion values under standard conditions.

Compound	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	C (graphite)
ΔH° (kJ mol^{-1})	–285.8	–890.0	–1560.0	–393.5

The standard heat of formation of $C_3H_8(g)$ is – 103.8 kJ mol^{-1}. (IIT 1992)
[**Ans.** – 55.7 kJ]
[**Hint:**

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O; \quad (\Delta H = -285.8 \text{ kJ}) \quad ...(i)$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O; \quad ...(ii) \quad (\Delta H = -890.0 \text{ kJ})$$

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O; \quad ...(iii) \quad (\Delta H = -1560.0 \text{ kJ})$$

$$C + O_2(g) \longrightarrow CO_2(g); \quad (\Delta H = -393.5 \text{ kJ}) \quad ...(iv)$$

$$3C + 4H_2(g) \longrightarrow C_3H_8(g); \quad (\Delta H = -103.8 \text{ kJ}) \quad ...(v)$$

Multiplying eq. (i) by 5 and eq. (iv) by 3 and adding both the equations and subtracting eqs. (ii), (iii) and (v).]

36. The standard enthalpy of combustion at 25° C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are – 241, – 3800 and – 3920 kJ mol^{-1} respectively. Calculate the heat of hydrogenation of cyclohexene. [ISM (Dhanbad) 1992]
[**Ans.** –121 kJ mol^{-1}]
[**Hint:**

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \quad ...(i) \quad (\Delta H = -241 \text{ kJ mol}^{-1})$$

$$C_6H_{10}(g) + \frac{17}{2}O_2(g) \longrightarrow 6CO_2(g) + 5H_2O(g); \quad ...(ii) \quad (\Delta H = -3800 \text{ kJ mol}^{-1})$$

$$C_6H_{12}(g) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g); \quad ...(iii) \quad (\Delta H = -3920 \text{ kJ mol}^{-1})$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$C_6H_{10}(s) + H_2(g) \longrightarrow C_6H_{12}(s);$$

$$\Delta H = -241 - 3800 - (-3920) = -121 \text{ kJ mol}^{-1}]$$

37. From the following data of heats of combustion, find the heat of formation of $CH_3OH(l)$:

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -726 \text{ kJ}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -394 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -286 \text{ kJ}$$

[BIT (Ranchi) 1991]
[**Ans.** –240 kJ mol^{-1}]

38. Calculate the heat of formation of methane, given that
heat of formation of water = – 286 kJ mol^{-1}
heat of combustion of methane = – 890 kJ mol^{-1}
heat of combustion of carbon = – 393.5 kJ mol^{-1}
[ISM (Dhanbad) 1993]
[**Ans.** – 75.5 kJ mol^{-1}]

39. Calculate the standard heat of formation of $C_{10}H_8$ (naphthalene) if standard heat of combustion of naphthalene is – 1231.0 kcal at 298 K and standard heat of formation of $CO_2(g)$ and $H_2O(l)$ are – 94.0 kcal and – 68.4 kcal respectively.
[**Ans.** 17.4 kcal]

40. The heat of combustion of liquid ethanol is – 327.0 kcal. Calculate the heat of formation of ethanol, given that the heats of formation of $CO_2(g)$ and $H_2O(l)$ are – 94.0 kcal and – 68.4 kcal respectively.
[**Ans.** – 66.2 kcal]

41. Calculate heat of formation of cane sugar from following data:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \quad \Delta H = -68.4 \text{ kcal}$$

$$C(g) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -94.4 \text{ kcal}$$

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l); \quad \Delta H = -1350.0 \text{ kcal}$$

[**Ans.** – 535.2 kcal]

42. The heats of formation of $C_6H_6(l)$, $H_2O(l)$ and CO_2(g) are 11.70, – 68.4 and – 94.0 kcal respectively. Calculate the heat of combustion of benzene (l).
[**Ans.** –780.9 kcal]

[**Hint:** $C_6H_6(l) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l); \Delta H = ?$

$\Delta H = 6 \times \Delta H_{f\,(CO_2)} + 3 \times \Delta H_{f\,(H_2O)} - \Delta H_{f\,(C_6H_6)}$]

43. Calculate the heat of hydrogenation of C_2H_2 to C_2H_4.

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -68.32 \text{ kcal}$$

$$C_2H_2(g) + \frac{5}{2} O_2(g) \longrightarrow 2CO_2(g) + H_2O(l);$$

$$\Delta H = -310.61 \text{ kcal}$$

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l);$$

$$\Delta H = -337.32 \text{ kcal}$$

[**Ans.** -41.61 kcal]

44. Calculate the heat of hydrogenation,

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

given that, the heat of combustion of ethylene, hydrogen and ethane are -337.0, -68.4 and -373.0 kcal respectively.

[**Ans.** -32.4 kcal]

45. If the heat of formation of $Al_2O_3(s)$ and $Cr_2O_3(s)$ are 1596 kJ and 1134 kJ (both exothermic) respectively. Calculate ΔH of the thermite reaction.

$$Cr_2O_3(s) + 2Al(s) \longrightarrow 2Cr(s) + Al_2O_3(s)$$

[**Ans.** -462 kJ]

46. Calculate the enthalpy of transition of rhombic sulphur to monoclinic sulphur from the following data:

$$S_{(rhombic)} + O_2(g) \longrightarrow SO_2(g); \quad \Delta H = -297.5 \text{ kJ}$$

$$S_{(monoclinic)} + O_2(g) \longrightarrow SO_2(g); \quad \Delta H = -299.9 \text{ kJ}$$

[**Ans.** $+2.4$ kJ]

47. Calculate ΔH for the reaction,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

given that bond energies of H—H and O$=$O bond and O—H bond are 433 kJ mol^{-1}, 492 kJ mol^{-1} and 464 kJ mol^{-1}.

[**Ans.** -249 kJ]

48. Using the bond enthalpy data, calculate ΔH of the following reaction:

$$2Cl_2(g) + 2H_2O(g) \longrightarrow 4HCl(g) + O_2(g)$$

given that, bond energies of Cl—Cl, H—Cl, O—H and O$=$O are 242.8, 431.8, 464 and 442 kJ mol^{-1} respectively.

[**Ans.** 172.4 kJ mol^{-1}]

49. Calculate the enthalpy of the reaction,

$$SnO_2(s) + 2H_2(g) \longrightarrow Sn(s) + 2H_2O(l)$$

given that, enthalpy of formation of $SnO_2(s)$ and $H_2O(l)$ are -580.7 kJ and -285.8 kJ respectively.

[**Ans.** $+9.1$ kJ]

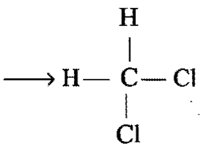
50. Calculate the enthalpy change for the reaction,

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

given that, bond energies of H—H, Cl—Cl and H—Cl are 436, 243 and 432 kJ mol^{-1}.

[**Ans.** -185 kJ mol^{-1}]

51. Use the bond energy data and calculate the enthalpy change for:



$$2C(g) + 2H(g) + 2Cl(g) \longrightarrow H-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-Cl$$

The bond energies of C—H and C—Cl are 413 and 328 kJ mol^{-1} respectively.

[**Ans.** -1482 kJ mol^{-1}]

52. Calculate the heat of formation of ammonia from the following data:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The bond energies of N$\equiv$N, H—H and N—H bonds are 226, 104 and 93 kcal respectively.

[**Ans.** -10 kcal]

53. Use the following bond dissociation energies to compute the C—H bond energy in methane:

(i) $CH_4(g) \longrightarrow CH_3(g) + H(g); \quad \Delta H = 475 \text{ kJ mol}^{-1}$

(ii) $CH_3(g) \longrightarrow CH_2(g) + H(g); \quad \Delta H = 470 \text{ kJ mol}^{-1}$

(iii) $CH_2(g) \longrightarrow CH(g) + H(g); \quad \Delta H = 416 \text{ kJ mol}^{-1}$

(iv) $CH(g) \longrightarrow C(g) + H(g); \quad \Delta H = 335 \text{ kJ mol}^{-1}$

[**Ans.** 424 kJ mol^{-1}]

54. Calculate ΔH_f° for chloride ion from the following data:

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g); \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

$$HCl(g) + nH_2O \longrightarrow H^+(aq.) + Cl^-(aq.);$$

$$\Delta H = -74.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{f\,(H^+\,aq.)} = 0.0 \text{ kJ mol}^{-1}$$

(IIT 1992)

[**Hint:** Required equation is

$$\frac{1}{2} Cl_2(g) + nH_2O \longrightarrow Cl^+(aq.); \; \Delta H = ?$$

Adding both equations.

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) + nH_2O \longrightarrow H^+(aq.) + Cl^-(aq.);$$

$$\Delta H = -167.2$$

$$\frac{1}{2} H_2(g) \longrightarrow H^+(aq.); \quad \Delta H = 0$$

So, $\frac{1}{2} Cl_2(g) + nH_2O \longrightarrow Cl^-(aq.); \quad \Delta H = -167.2 \text{ kJ mol}^{-1}$]

55. The heat of ionisation of formic acid is 1.5 kJ/mol. 9.2 g formic acid on reaction with 7 g ammonium hydroxide gives 10.8 kJ of heat. Calculate the heat of ionisation of ammonium hydroxide. (1 cal = 4.2 J)

[**Ans.** 2.04 kJ/mol]

56. Assuming that 50% of the heat of useful, how many kg of water at 15°C can be heated to 95.0°C by burning 200 litre of methane measured at NTP? The heat of combustion of methane is 211 kcal mol^{-1}.

[**Ans.** 11.76 kg]

57. The standard potential for the reaction,

$$Ag^+(aq.) + Fe^{2+}(aq.) \longrightarrow Fe^{3+}(aq.) + Ag(s)$$

is 0.028 V. What is the standard free energy change for this reaction?

[**Ans.** -2.702 kJ mol^{-1}]

58. Calculate the theoretical maximum efficiency of a heat engine operating between 373 K and 173 K.

[Ans. 0.536 or 53.6%]

59. The standard free energy of formation in the gaseous state of methanol, dimethyl ether and water are – 38.7, – 27.3 and –54.6 kcal respectively. Is the transformation of methanol to dimethyl ether and water in gaseous state possible?

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

[Hint: ΔG° for the transformation

$$= \Sigma\, \Delta G^\circ_{\text{(products)}} - \Sigma\, \Delta G^\circ_{\text{(reactants)}}$$

$=$ – ve (the transformation is possible)]

60. Ethanol boils at 78.4° C and standard enthalpy of vaporization of ethanol is 42.4 kJ mol^{-1}. Calculate the entropy of vaporization of ethanol.

[Ans. 120.9 J K^{-1} mol^{-1}]

61. The following data is known about the melting of KCl:

$$\Delta H = 7.25 \text{ kJ mol}^{-1} \text{ and } \Delta S = +\,0.007 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate its melting point.

[Ans. 1035.7 K]

[Hint: At melting point $\Delta G = 0$]

62. For the reaction,

$$Ag_2O \rightleftharpoons 2Ag(s) + \frac{1}{2} O_2(g)$$

Calculate the temperature at which free energy change is zero. At a temperature lower than this, predict whether the forward or the reverse reaction will be favoured. Give reason.

($\Delta H = +\,30.56$ kJ and $\Delta S = +\,0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at one atmosphere)

[Hint: Calculate T by applying the formula

$$\Delta G = \Delta H - T\,\Delta S \text{ and } \Delta G = 0.$$

Then find the value of ΔG at lower temperature than T. The value of ΔG comes positive; hence, the reverse reaction will be favoured. At temperature higher than T, the reaction is spontaneous.]

63. Calculate the boiling point of the liquid if its entropy of vaporization is 110 J K^{-1} mol^{-1} and the enthalpy of vaporization is 40.85 kJ mol^{-1}.

[Ans. 371.36 K]

64. Using S° values, calculate the entropy of the reaction,

$$SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g)$$

The S° values for SO_2, O_2 and SO_3 are 248.5, 205.0 and 256.2 J K^{-1} mol^{-1}.

[Ans. $= -\,94.2 \text{ J K}^{-1} \text{ mol}^{-1}$]

[Hint: $\Delta S^\circ_{\text{reaction}} = \Sigma\, S^\circ_{\text{products}} - \Sigma\, S^\circ_{\text{reactants}}$]

65. Calculate the entropy change for the following reaction:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$S^\circ \quad 92.9 \qquad\qquad 39.7 \qquad 213.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

[Ans. $+160.4 \text{ J K}^{-1} \text{ mol}^{-1}$]

66. Compute the value of ΔS at 298 K for the reaction,

$$H_2(g) + {}^1\!/_2 O_2(g) \longrightarrow H_2O(g)$$

given that, $\Delta G = -\,228.6$ kJ and $\Delta H = -\,241.8$ kJ.

[Ans $-\,44.3 \text{ J K}^{-1}$]

67. An engine operating between 150° C and 25° C takes 500 J heat from a high temperature reservoir. Assuming there is no frictional loss, calculate the work that can be done by the engine.

[Ans. 148 J]

68. At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ and $H_2O(l)$ are –408, –393 and –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$) **(IIT 1995)**

[Ans. (i) $\Delta H = -\,3201 \text{ kJ mol}^{-1}$;
(ii) $\Delta E = -\,3199.75 \text{ kJ mol}^{-1}$]

69. For the reaction,

$$Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$$

$\Delta H = 29.37 \text{ kJ mol}^{-1}$ and $\Delta S = 104 \text{ J K}^{-1} \text{ mol}^{-1}$. Find the temperature above which the reaction would become spontaneous.

[Ans. Above 282.4 K]

70. For the synthesis of ammonia,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Calculate ΔH°, ΔS° and ΔG° at 300 K using the following data:

Species	N_2	H_2	NH_3
ΔH°_f / (kJ mol^{-1})	0	0	– 46.2
S°/(J K^{-1} mol^{-1})	191.5	130.6	192.5

[Ans. $\Delta H^\circ = -\,92.4 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -\,198.3 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta G^\circ = -\,32.91 \text{ kJ mol}^{-1}$]

71. How much heat is required to change 15.6 g of benzene from liquid into vapour at its boiling point of 80° C? Entropy of vaporization of benzene is 87 J K^{-1} mol^{-1}.

[Ans. 6142.2 J]

72. Calculate the standard free energy change for the combustion of glucose at 298 K, using the given data.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

$$\Delta H^\circ = -\,2820 \text{ kJ mol}^{-1}, \Delta S^\circ = 210 \text{ J K}^{-1} \text{ mol}^{-1}.$$

[Ans. $\Delta G^\circ = -\,2882.58 \text{ kJ mol}^{-1}$]

73. The specific heat at constant volume for a gas is 0.075 cal/g and at constant pressure it is 0.125 cal/g. Calculate:
(i) the molecular weight of gas,
(ii) atomicity of gas.

[Hint: (i) $C_P - C_V = \dfrac{R}{M}$ where, M = molecular weight of gas

$$0.125 - 0.075 = \frac{1.987}{M}$$

$$M = 39.74 \approx 40$$

(ii) $$\frac{C_P}{C_V} = \gamma$$

$$\therefore \quad \gamma = \frac{0.125}{0.075} = 1.66$$

$\therefore$ 1.66 value of γ shows that the gas is monoatomic.]

74. The polymerisation of ethylene to linear polyethylene is represented by the reaction,

$$nCH_2{=}CH_2 \longrightarrow -\!\!\left(-CH_2-CH_2-\right)\!\!-_n$$

where, n has a large integral value. Given that the average enthalpies of bond dissociation for $C{=}C$ and $C{-}C$ at 298 K are +590 and + 331 kJ mol^{-1} respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K. **(IIT 1994)**

[**Hint:** $nCH_2{=}CH_2 \longrightarrow -\!\!\left(-CH_2-CH_2-\right)\!\!-_n$

There are equal number of C—H bonds on both sides but on reactant side there are $nC{=}C$ bonds and on product side $(2n+1)C{-}C$ bonds.

Enthalpy of polymerisation

$$= n\Delta H_{(C=C)} - (2n+1)\Delta H_{(C-C)}$$
$$= 590n - (2n+1)(331)$$
$$= 590n - 662n \qquad [2n+1 \rightarrow 2n \text{ as } n \text{ is very large}]$$
$$= -72n \text{ kJ}$$

Enthalpy of polymerisation per mole

$$= \frac{\Delta H}{n} = -\frac{72n}{n} = -72 \text{ kJ mol}^{-1}]$$

75. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilises 50% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ mol^{-1}.

[**Hint:** Unused energy $= \frac{1560}{2} = 780$ kJ

Mass of water needed for perspiration $= 18 \times \frac{780}{44} = 318.96$ g]

76. Calculate the entropy of ideal mixing when 2 moles of N_2, 3 moles of H_2 and 2 moles of NH_3 are mixed at constant temperature, assuming no chemical reaction is occurring.

[**Ans.** 62.80 J K^{-1}]

[**Hint:** Use the relation,

$$\Delta S = -R\,\Sigma\, n_i \log_e x_i$$

when n_i = no. of moles of component

x_i = mole fraction of the component]

77. Calculate free energy change for the reaction:

$$H_2(g) + Cl_2(g) \rightarrow 2H{-}Cl(g)$$

by using the bond energy and entropy data.

Bond energies of H—H, Cl—Cl and H—Cl bonds are 435 kJ mol^{-1}, 240 kJ mol^{-1} and 430 kJ mol^{-1} respectively. Standard entropies of H_2, Cl_2 and HCl are 130.59, 222.95 and 186.68 J K^{-1} mol^{-1} respectively.

[**Ans.** 190.9 kJ]

[**Hint:** ΔG° can be calculated by using:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$\Delta H^\circ = \Sigma\,(BE)_{reactants} - \Sigma\,(BE)_{products}$$
$$= 435 + 240 - 2 \times 430 = -185 \text{ kJ}$$
$$\Delta S^\circ = \Sigma\, S^\circ_{products} - \Sigma\, S^\circ_{reactants}$$
$$= 2 \times 186.68 - 130.59 - 222.95$$
$$= 19.82 \text{ J K}^{-1} = 19.82 \times 10^{-3} \text{ kJ K}^{-1}$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -185 - 298 \times 19.82 \times 10^{-3} = -190.9 \text{ kJ}]$$

78. For the reaction,

$$4C\,(\text{graphite}) + 5H_2(g) \longrightarrow nC_4H_{10}(g);$$
$$\Delta H^\circ = -124.73 \text{ kJ mol}^{-1}$$
$$\Delta S^\circ = -365.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$4C\,(\text{graphite}) + 5H_2(g) \longrightarrow iso\text{-}C_4H_{10}(g)$$
$$\Delta H^\circ = -131.6 \text{ kJ mol}^{-1}$$
$$\Delta S^\circ = -381.079 \text{ J K}^{-1} \text{ mol}^{-1}$$

Indicate whether *normal butane* can be spontaneously converted to *iso-butane* or not.

[**Ans.** Yes, $\Delta G^\circ = -2.32$ kJ]

[**Hint:** For nC_4H_{10},

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -124.73 - 298(-365.8 \times 10^{-3}) = -15.72 \text{ kJ}$$

For *iso*-butane (*iso*-C_4H_{10}),

$$\Delta G^\circ = -131.6 - 298(-381.079 \times 10^{-3})$$
$$= -18.04 \text{ kJ}$$

For conversion of $nC_4H_{10} \longrightarrow iso\text{-}C_4H_{10}$,

$$\Delta G^\circ = -18.04 - (-15.72) = -2.32 \text{ kJ}$$

Negative value shows that the process is spontaneous.]

79. The temperature of a bomb calorimeter was found to rise by 1.617 K, when a current of 3.20 amp was passed for 27 sec from a 12 V source. Calculate the calorimeter constant.

[**Hint:** Energy absorbed by the calorimeter

$$= I \times t \times V = 3.2 \times 27 \times 12 = 1036.8 \text{ J}$$

Calorimeter constant (ms) can be calculated as,

$$q = ms\,\Delta t$$
$$1036.8 = ms \times 1.617$$
$$ms = 641.187 \text{ kJ}]$$

80. 1 mole of an ideal gas is allowed to expand isothermally at 27°C until its volume is tripled. Calculate ΔS_{sys} and ΔS_{univ} under the following conditions:

(a) the expansion is carried out reversibly.

(b) the expansion is a free expansion.

[**Ans.** (a) $\Delta S_{sys} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$

$$\Delta S_{surr} = -9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{univ} = 0$$

(b) $\Delta S_{univ} = \Delta S_{sys} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$]

[**Hint:** (a) In isothermal reversible process:

$$\Delta S = \frac{q_{rev}}{T}$$
$$q = -W = 2.303RT \log\frac{V_2}{V_1}$$
$$= 2.303 \times 8.314 \times 300 \log 3 = 2740.6 \text{ J mol}^{-1}$$
$$\Delta S_{system} = \frac{q_{rev}}{T} = \frac{2740.6}{300} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{surr} = -\Delta S_{system} = -9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{univ} = 0$$

(b) In case of free expansion:

$$\Delta S = 2.303nR \log\left(\frac{V_2}{V_1}\right) = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} = 9.135 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{\text{surr}} = 0]$$

81. One kilogram water at 0° C is brought into contact with a heat reservoir at 100° C. Find:

(a) change in entropy when temperature reaches to 100° C.
(b) what is the change in entropy of reservoir?
(c) change in entropy of universe.
(d) the nature of process.

[**Ans.** (a) 312 cal K^{-1}, (b) −268.1 cal K^{-1}, (c) 43.9 cal K^{-1} (d) spontaneous]

[**Hint:** (a) $\Delta S = 2.303 nC_P \log\left(\frac{T_2}{T_1}\right)$

$$= 2.303 \times \frac{1000}{18} \times 18 \log\left(\frac{373}{273}\right) = 312 \text{ cal K}^{-1}$$

(b) $\Delta S_{\text{reservoir}} = -\frac{\Delta Q}{T}$

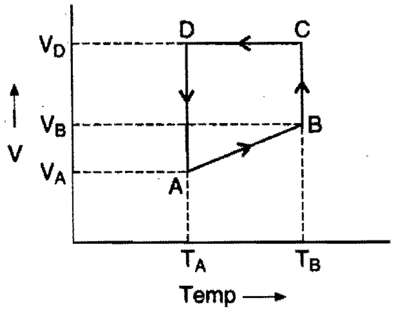
$$\Delta Q = ms\,\Delta t = 1000 \times 1 \times 100 = 10^5 \text{ cal}$$

$$\Delta S = \frac{-10^5}{373} = -268.1 \text{ cal K}^{-1}$$

(c) $\Delta S_{\text{universe}} = 312 - 268.1 = 43.9 \text{ cal K}^{-1}$

(d) $\Delta S > 0$, the process will be spontaneous.]

82. A monoatomic ideal gas of two moles is taken through a cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C. Calculate:



(a) the temperature of gas at B.
(b) heat absorbed or evolved in each process.
(c) total work done in cyclic process.

[**Hint:** $A \to B$: (It is isobaric process)

$$\frac{V_A}{T_A} = \frac{V_B}{T_B}$$

$$\therefore \quad T_B = \frac{V_B}{V_A} \times T_A = 2 \times 300 = 600 \text{ K}$$

$$q_{AB} = nC_P\,\Delta T = 2 \times \frac{5}{2} R\,\Delta T$$
$$= 2 \times \frac{5}{2} \times 2 \times 300 = 3000 \text{ cal}$$

$B \to C$: (Isothermal process)

$$\Delta U = 0$$

$$\therefore \quad q_{BC} = W = 2.303\, nRT \log\left(\frac{V_C}{V_B}\right)$$
$$= 2.303 \times 2 \times 2 \times 600 \log\frac{4}{2}$$
$$= 1.663 \times 10^3 \text{ cal}$$

$C \to D$: (Isochoric process)

$$q_{CD} = nC_V\,\Delta T = 2 \times \frac{3}{2} \times 2\,(-300) = -1800 \text{ cal}$$

$D \to A$: (Isothermal process)

$$q_{DA} = 2.303 nRT_A \log\frac{V_A}{V_D}$$
$$= 2.303 \times 2 \times 2 \times 300 \log\frac{1}{4}$$
$$= -1.663 \times 10^3 \text{ cal}$$

Total heat change $= 3000 + 1.663 \times 10^3 - 1800 - 1.663 \times 10^3$
$= 1200$ cal

Work done = − 1200 cal]

83. The reaction, $SOCl_2 + H_2O \longrightarrow SO_2 + 2HCl$ is endothermic by 49.4 kJ and exoergonic by 50.8 kJ. What is the factor that makes the reaction to be spontaneous? Calculate the entropy change at 298 K.

[**Ans.** $\Delta S^\circ = 0.3362 \text{ kJ K}^{-1}$]

[**Hint:** Exoergonic means $\Delta G^\circ = -$ ve.

$\Delta G^\circ = -50.8$ kJ,
$\Delta H^\circ = 49.4$ kJ

Substitute these values in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to calculate entropy.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{49.4 - (-50.8)}{298}$$
$$= 0.3362 \text{ kJ K}^{-1}]$$

84. What amount of ice will remain when 52 g ice is added to 100 g of water at 40° C?
Specific heat of water is 1 cal/g and latent heat of fusion of ice is 80 cal/g.

[**Ans.** 2 g ice]

[**Hint:** At the stage of thermal equilibrium at 0° C,
Heat lost by water = Heat absorbed by ice to melt.

$$ms\,\Delta T = mL$$
$$100 \times 1 \times 40 = m \times 80$$
$$m = 50 \text{ g}$$

Remaining ice = 52 − 50 = 2 g]

85. Calculate the ΔH_f° of $C_6H_{12}O_6(s)$ from the following data:

$\Delta H_{\text{comb}}\,[C_6H_{12}O_6(s)] = -2816$ kJ / mol
ΔH_f° of $CO_2(g) = -393.5$ kJ / mol
ΔH_f° of $H_2O(l) = -285.9$ kJ / mol [BCECE 2006]

[**Ans.** −1260 kJ/mol]

86. A liquid freezes into solid ($\Delta H = -500 \text{ J mol}^{-1}$) at 100 K and 1 atm. Find the values of:

(i) Gibbs free energy change
(ii) entropy change. [CBSE (Mains) 2006]

[**Hint:** Liquid $\rightleftharpoons$ Solid

(i) $\Delta G = 0$, at equilibrium

(ii) $\Delta S = \frac{\Delta H}{T} = \frac{-500}{100} = -5 \text{ J K}^{-1} \text{ mol}^{-1}$]

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Thermodynamics is concerned with:
   (a) total energy of a system
   (b) energy changes in a system
   (c) rate of a chemical change
   (d) mass changes in nuclear reactions
2. An isolated system is that system in which: [PET (MP) 1993]
   (a) there is no exchange of energy with the surroundings
   (b) there is exchange of mass and energy with the surroundings
   (c) there is no exchange of energy and mass with the surroundings
   (d) there is exchange of mass with the surroundings
3. Identify the intensive property from the following:
   (a) volume (b) mass
   (c) enthalpy (d) temperature
4. Which one of the following is an extensive property? [Comed (Karnataka) 2008]
   (a) Enthalpy (b) Concentration
   (c) Density (d) Viscosity
5. For an adiabatic process, which of the following relations is correct? (CPMT 1990)
   (a) $\Delta E = 0$ (b) $P\,\Delta V = 0$ (c) $q = 0$ (d) $q = +w$
6. Which one is true from the following for isobaric process ? [CET (Gujarat) 2008]
   (a) $\Delta P = 0$ (b) $\Delta q = 0$
   (c) $\Delta H = 0$ (d) $\Delta E = 0$
7. For an ideal gas, the value of $\left(\frac{dE}{dV}\right)_T$ is: [PET (MP) 1993]
   (a) positive (b) zero
   (c) negative (d) interchangeable
8. A process, in which pressure remains constant, is called:
   (a) isochoric process (b) isothermal process
   (c) adiabatic process (d) isobaric process
9. A process in which volume remains constant, is called:
   (a) isochoric process (b) isothermal process
   (c) adiabatic process (d) isobaric process
10. For a cyclic process, the condition is:
   (a) $\Delta E = 0$ (b) $\Delta H = 0$
   (c) $\Delta E > 0$ and $\Delta H > 0$ (d) both $\Delta E = 0$ and $\Delta H = 0$
11. Which one of the following is a state property?
   (a) Heat (b) Work
   (c) Internal energy (d) Potential energy
12. Internal energy of a system of molecules is determined by taking into consideration its:
   (a) kinetic energy
   (b) vibrational energy
   (c) rotational energy
   (d) all kinds of energies present in the molecules
13. A thermodynamic quantity is that:
   (a) which is used in thermochemistry
   (b) which obeys all laws of thermodynamics
   (c) quantity whose value depends only upon the state of the system
   (d) quantity which is used in measuring thermal change
14. Thermodynamic equilibrium involves: [CET (Pb.) 1991]
   (a) chemical equilibrium (b) thermal equilibrium
   (c) mechanical equilibrium (d) all the three
15. For the reaction of one mole zinc dust with one mole sulphuric acid in a bomb calorimeter, ΔU and w correspond to: (AIIMS 2005)
   (a) $\Delta U < 0, w = 0$ (b) $\Delta U < 0, w < 0$
   (c) $\Delta U > 0, w = 0$ (d) $\Delta U > 0, w > 0$
   [Hint: In bomb calorimeter, $w = 0, \Delta U = q(-\text{ve})$]
16. A system is provided with 50 joules of heat and the work done on the system is 10 joules. What is the change in internal energy of the system in joules? [EAMCET (Engg.) 2010]
   (a) 60 (b) 40 (c) 50 (d) 10
17. During an isothermal expansion of an ideal gas, its: (CBSE 1991)
   (a) internal energy increases
   (b) enthalpy decreases
   (c) enthalpy remains unaffected
   (d) enthalpy reduces to zero
18. The work done in ergs for a reversible expansion of one mole of an ideal gas from a volume of 10 litre to 20 litre at 25° C is: [CMC (Vellore) 1991]
   (a) $2.303 \times 8.31 \times 10^7 \times 298 \log 2$
   (b) $2.303 \times 0.0821 \times 298 \log 2$
   (c) $2.303 \times 0.0821 \times 298 \log 0.5$
   (d) $2.303 \times 2 \times 298 \log 2$
19. When an ideal gas is compressed adiabatically and reversibly, the final temperature is:
   (a) higher than the initial temperature
   (b) lower than the initial temperature
   (c) the same as initial temperature
   (d) dependent upon the rate of compression
20. Adiabatic reversible expansion of a gas is represented by:
   (a) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$ (b) $\left(\frac{T_1}{T_2}\right) = \left(\frac{P_1}{P_2}\right)^{1-\gamma}$
   (c) $\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$ (d) all are correct
21. Total energy change for a reversible isothermal cycle is:
   (a) always positive (b) zero
   (c) always negative (d) always 100 kJ per degree
22. "Heat energy cannot be completely transformed into work without producing some change somewhere", is the statement of:

(a) Hess's law
(b) first law of thermodynamics
(c) Kirchhoff's law
(d) second law of thermodynamics

23. The heat content of the system is called:
(a) internal energy (b) enthalpy
(c) free energy (d) entropy

24. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then : **(KCET 2008)**
(a) $\Delta H < \Delta U$
(b) $\Delta H > \Delta U$
(c) $\Delta H = \Delta U$
(d) there is no relationship between ΔH and ΔU

25. An exothermic reaction is one in which the reacting substances:
(a) have same energy as products
(b) have less energy than the products
(c) have more energy than the products
(d) are at higher temperature than the products

26. In endothermic reactions, the reactants:
(a) have more energy than products
(b) have as much energy as the products
(c) are at lower temperature than products
(d) have less energy than the products

27. Identify the reaction in which the heat liberated corresponds to the heat of formation (ΔH): **(EAMCET 2006)**
(a) C (diamond) + $O_2(g) \rightarrow CO_2(g)$ + heat
(b) $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ + heat
(c) C (diamond) + $2H_2(g) \rightarrow CH_4(g)$ + heat
(d) S (rhombic) + $O_2(g) \rightarrow SO_2(g)$ + heat

28. In an exothermic reaction, ΔH is:
(a) positive (b) negative
(c) zero (d) may be positive or negative

29. Evaporation of water is:
(a) a process in which neither heat is evolved nor absorbed
(b) a process accompanied by chemical reaction
(c) an exothermic change
(d) an endothermic change

30. An endothermic reaction is one in which:
(a) heat is converted into electricity
(b) heat is absorbed
(c) heat is evolved
(d) heat changes to mechanical work

31. If total enthalpy of reactants and products is H_R and H_P respectively, then for exothermic reaction:
(a) $H_R = H_P$ (b) $H_R < H_P$
(c) $H_R > H_P$ (d) $H_R - H_P = 0$

32. Calculate the work done when 1 mol of an ideal gas is compressed reversibly from 1 bar to 4 bar at a constant temperature of 300 K : **(DPMT 2009)**
(a) 4.01 kJ (b) –8.02 kJ
(c) 18.02 kJ (d) –14.01 kJ

[**Hint :** $w = 2.303\, nRT \log\left(\frac{P_2}{P_1}\right)$

$= 2.303 \times 1 \times 8.314 \times 300 \log \frac{4}{1}$

$= 3458.3\text{ J} = 3.458\text{ kJ}$]

33. Under which of the following conditions is the relation, $\Delta H = \Delta E + P\,\Delta V$ valid for a closed system?
(a) Constant pressure
(b) Constant temperature
(c) Constant temperature and pressure
(d) Constant temperature, pressure and composition

34. Which of the following is an endothermic reaction?
(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
(b) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(c) $NaOH(aq.) + HCl(aq.) \longrightarrow NaCl(aq.) + H_2O(l)$
(d) $C_2H_5OH(aq.) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

35. Which of the following reactions is endothermic?
(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(b) $Fe(s) + S(s) \longrightarrow FeS(s)$
(c) $NaOH(aq.) + HCl(aq.) \longrightarrow NaCl(aq.) + H_2O(l)$
(d) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

36. The formation of water from $H_2(g)$ and $O_2(g)$ is an exothermic process because:
(a) the chemical energy of $H_2(g)$ and $O_2(g)$ is more than that of water
(b) the chemical energy of $H_2(g)$ and $O_2(g)$ is less than that of water
(c) the temperature of $H_2(g)$ and $O_2(g)$ is higher than that of water
(d) the temperature of $H_2(g)$ and $O_2(g)$ is lower than that of water

37. Which one of the following reactions is an exothermic reaction?
(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(b) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(c) $2HgO(s) \longrightarrow 2Hg(s) + O_2(g)$
(d) $C(s) + O_2(g) \longrightarrow CO_2(g)$

38. Which one of the following is not applicable for a thermochemical equation?
(a) It tells about physical state of reactants and products
(b) It tells whether the reaction is spontaneous
(c) It tells whether the reaction is exothermic or endothermic
(d) It tells about the allotropic form (if any) of the reactants

39. The enthalpies of all elements in their standard state at 25° C and one atmospheric pressure are:
(a) same (b) always positive
(c) always negative (d) zero

40. The heat of reaction does not depend upon:
(a) physical state of the reactants and products
(b) whether the reaction has been carried at constant pressure or constant volume
(c) the manner by which the reaction has been carried
(d) the temperature at which the reaction has been carried

41. The value of $\Delta H - \Delta U$ for the following reaction at 27°C will be:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

[AMU (Medical) 2007]
(a) $8.314 \times 273 \times (-2)$ (b) $8.314 \times 300 \times (-2)$
(c) $8.314 \times 273 \times 2$ (d) $8.314 \times 300 \times 2$

42. Since, the enthalpy of the elements in their standard states is taken to be zero, the heat of formation (ΔH_f) of compounds:
(a) is always negative (b) is always positive
(c) is zero (d) may be positive or negative

43. The difference between heats of reaction at constant pressure and constant volume for the reaction,
$2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$ at 25° C in kJ is: **(IIT 1991)**
(a) +7.43 (b) +3.72 (c) −7.43 (d) −3.72

44. For a gaseous reaction, $A(g) + 3B(g) \rightarrow 3C(g) + 3D(g)$, ΔE is 17 kcal at 27°C. Assuming $R = 2\,\text{cal K}^{-1}\,\text{mol}^{-1}$, the value of ΔH for the above reaction is:
(a) 15.8 kcal (b) 18.2 kcal
(c) 20.0 kcal (d) 16.4 kcal

45. Which of the following statements is correct for the reaction, $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ at constant temperature and pressure?
(a) $\Delta H = \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H > \Delta E$ (d) None of these

46. For the reaction, $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$ which one of the following is true?
(a) $\Delta H = \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H > \Delta E$ (d) $\Delta H = \frac{1}{2}\Delta E$

47. Thermochemistry is the study of relationship between heat energy and:
(a) chemical energy (b) activation energy
(c) friction energy (d) none of these

48. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta U$? **[CBSE (Med.) 2006]**
(a) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
(b) $C(s) + 2H_2O(g) \longrightarrow 2H_2(g) + CO_2(g)$
(c) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$
(d) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$

49. The enthalpy change in the reaction, $2CO + O_2 \longrightarrow 2CO_2$ is termed as:
(a) enthalpy of reaction (b) enthalpy of fusion
(c) enthalpy of formation (d) enthalpy of combustion

50. Reaction, $H_2(g) + I_2(g) \longrightarrow 2HI$; $\Delta H = 12.40$ kcal
According to this, heat of formation of HI will be: **[PET (MP) 1990]**
(a) 12.40 kcal (b) −12.4 kcal
(c) − 6.20 kcal (d) 6.20 kcal

51. For the reactions,
(i) $H_2(g) + Cl_2(g) = 2HCl(g) + x$ kJ
(ii) $H_2(g) + Cl_2(g) = 2HCl(l) + y$ kJ
which one of the following statements is correct? **[PET (MP) 2007]**
(a) $x > y$ (b) $x < y$ (c) $x - y = 0$ (d) $x = y$

52. For the reactions,
(i) $H_2(g) + Cl_2(g) = 2HCl(g) + x$ kJ
(ii) $2HCl(g) = H_2(g) + Cl_2(g) - y$ kJ
which one of the following statements is correct?
(a) $x - y > 0$ (b) $x - y < 0$
(c) $x - y = 0$ (d) None of these

53. According to the equation,
$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l);$$
$$\Delta H = -3264.4\ \text{kJ mol}^{-1}$$
the energy evolved when 7.8 g benzene is burnt in air will be: **[PET (MP) 1990]**
(a) 163.22 kJ (b) 32.64 kJ (c) 3.264 kJ (d) 326.4 kJ

54. $\Delta H_{f\,(x)}, \Delta H_{f\,(y)}, \Delta H_{f\,(R)}$ and $\Delta H_{f\,(S)}$ denote the enthalpies of formation of x, y, R and S respectively. The enthalpy of the reaction, $x + y \longrightarrow R + S$ is given by:
(a) $\Delta H_{f\,(x)} + \Delta H_{f\,(y)}$
(b) $\Delta H_{f\,(R)} + \Delta H_{f\,(S)}$
(c) $\Delta H_{f\,(x)} + \Delta H_{f\,(y)} - \Delta H_{f\,(R)} - \Delta H_{f\,(S)}$
(d) $\Delta H_{f\,(R)} + \Delta H_{f\,(S)} - \Delta H_{f\,(x)} - \Delta H_{f\,(y)}$

55. The enthalpy change for the reaction,
$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$ is called:
(a) enthalpy of formation (b) enthalpy of combustion
(c) enthalpy of vaporisation (d) enthalpy of sublimation

56. The heat of combustion of methane is −880 kJ mol^{-1}. If 3.2 g of methane is burnt .... of heat is evolved.
(a) 88 kJ (b) 264 kJ (c) 176 kJ (d) 440 kJ

57. The enthalpy change for the reaction,
$$2C_{(graphite)} + 3H_2(g) \longrightarrow C_2H_6(g)$$
is called:
(a) enthalpy of formation (b) enthalpy of combustion
(c) enthalpy of hydrogenation (d) enthalpy of vaporisation

58. The enthalpy of formation of water from hydrogen and oxygen is − 286.0 kJ mol^{-1}. The enthalpy of decomposition of water into hydrogen and oxygen is ...... kJ mol^{-1}:
(a) − 286.0 (b) − 143.0 (c) 286.0 (d) 143.0

59. The heat of combustion of $C_{(graphite)}$ is −393.5 kJ mol^{-1}. The heat of formation of CO_2 from graphite is ..... kJ mol^{-1}:
(a) 393.5 (b) −393.5 (c) −787.0 (d) 787.0

60. The enthalpies of formation of organic compounds are conveniently determined from their:
(a) boiling points
(b) melting points
(c) enthalpies of neutralization
(d) enthalpies of combustion

61. ΔH combustion of a compound is always:
(a) positive (b) negative (c) zero (d) uncertain

62. The apparatus used for measuring the heat changes of a reaction is called:
(a) a thermometer (b) a colorimeter
(c) a calorimeter (d) none of these

63. The heat of neutralization of any strong acid and strong base is always constant and $\Delta H = -57.3$ kJ. This is because: **[Comed (Karnataka) 2008]**
(a) both the acid and base undergo complete ionization.
(b) during neutralization, salt and water are formed.
(c) 1 mole of water is formed from H^+ and OH^- ions.
(d) the reaction is exothermic.

64. The enthalpy of neutralization of oxalic acid by a strong base is -25.4 k cal mol^{-1}. The enthalpy of neutralization of strong acid and strong base is -13.7 kcal eq^{-1}. The enthalpy of dissociation of oxalic acid is: (DPMT 2009)
(a) 1 kcal mol^{-1} (b) 2 kcal mol^{-1}
(c) 18.55 kcal mol^{-1} (d) 11.7 kcal mol^{-1}
[Hint : Oxalic acid is dibasic acid hence expected heat of neutralization will be $(2 \times -13.7 \text{ kcal})$.
The dissociation energy of oxalic acid $= 2 \times 13.7 - 25.4$
$= 2 \text{ kcal mol}^{-1}$]

65. The amount of heat liberated when one mole of NH_4OH reacts with one mole of HCl is: (IIT 1990)
(a) 13.7 kcal (b) more than 13.7 kcal
(c) less than 13.67 kcal (d) cannot be predicted

66. Heat of neutralisation for the reaction,
$$NaOH + HCl \longrightarrow NaCl + H_2O$$
is 57.1 kJ mol^{-1}. The heat released when 0.25 mole of NaOH is titrated against 0.25 mole of HCl will be:
(a) 22.5 kJ (b) 57.1 kJ
(c) 28.6 kJ (d) 14.3 kJ

67. If $H^+ + OH^- = H_2O + 13.7 \text{ kcal}$, then heat of complete neutralisation of one gram mole of H_2SO_4 with strong base will be: [PMT (MP) 1990]
(a) 13.7 kcal (b) 27.4 kcal
(c) 6.85 kcal (d) 3.425 kcal

68. In which of the following neutralization reactions, the heat of neutralization will be highest?
(a) HCl and NaOH (b) CH_3COOH and NaOH
(c) CH_3COOH and NH_4OH (d) HCl and NH_4OH

69. "The enthalpy of formation of a compound is equal in magnitude but of opposite sign to the enthalpy of decomposition of that compound under the same conditions." This law was presented by:
(a) Hess (b) Le Chatelier
(c) Kirchhoff (d) Lavoisier and Laplace

70. "The change of enthalpy of a chemical reaction is the same whether the reaction takes place in one step or in several steps". This law was presented by:
(a) Hess (b) Le Chatelier
(c) van't Hoff (d) Kirchhoff

71. The enthalpy change in a reaction does not depend on the:
(a) conditions under which the reaction is carried out
(b) initial and final enthalpies of the reactants and products
(c) state of reactants and products
(d) number of intermediate steps to convert reactants to products

72. Hess's law deals with:
(a) changes in heat of reaction
(b) rate of reaction
(c) equilibrium constant
(d) influence of pressure on volume of a gas

73. From the thermochemical reactions,
$$C_{(\text{graphite})} + \frac{1}{2}O_2 \longrightarrow CO; \quad \Delta H = -110.5 \text{ kJ}$$
$$CO + \frac{1}{2}O_2 \longrightarrow CO_2; \ \Delta H = -283.2 \text{ kJ}$$
the heat of reaction of $C_{(\text{graphite})} + O_2 \longrightarrow CO_2$ is:
(a) +393.7 kJ (b) −393.7 kJ (c) −172.7 kJ (d) +172.7 kJ

74. If $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \quad \Delta H = -68.09 \text{ kcal}$
$$K + H_2O + \text{water} \longrightarrow KOH(aq.) + \frac{1}{2}H_2; \ \Delta H = -48.0 \text{ kcal}$$
$$KOH + \text{water} \longrightarrow KOH(aq.); \quad \Delta H = -14.0 \text{ kcal}$$
the heat of formation of KOH is:
(a) $-68.39 + 48 - 14.0$ (b) $-68.39 - 48.0 + 14.0$
(c) $+68.39 - 48.0 + 14.0$ (d) $+68.39 + 48.0 - 14.0$

75. The enthalpies of combustion of $C_{(\text{graphite})}$ and $C_{(\text{diamond})}$ are −393.5 and −395.4 kJ/mol respectively. The enthalpy of conversion of $C_{(\text{graphite})}$ to $C_{(\text{diamond})}$ in kJ/mol is:
(a) −1.9 (b) −788.9
(c) 1.9 (d) 788.9

76. The heat of combustion of yellow phosphorus and red phosphorus are −9.91 kJ and −8.78 kJ respectively. The heat of transition of yellow phosphorus to red phosphorus is: [CEE (Bihar) 1992]
(a) −18.69 kJ (b) +1.13 kJ
(c) +18.69 kJ (d) −1.13 kJ

77. What will be the heat of formation of methane, if the heat of combustion of carbon is '$-x$' kJ, heat of formation of water is '$-y$' kJ and heat of combustion of methane is '$-z$' kJ? (AIIMS 2008)
(a) $(-x - y + z)$ kJ (b) $(-z - x + 2y)$ kJ
(c) $(-x - 2y - z)$ kJ (d) $(-x - 2y + z)$ kJ

78. Given,
$$C(s) + O_2(g) \longrightarrow CO_2(g) + 94.2 \text{ kcal}$$
$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 68.3 \text{ kcal}$$
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) + 210.8 \text{ kcal}$$
The heat of formation of methane in kcal will be: [PET (MP) 1990]
(a) 45.9 (b) 47.8 (c) 20.0 (d) 47.3

79. On combustion carbon forms two oxides CO and CO_2, heat of formation of CO_2 is −94.3 kcal and that of CO is −26.0 kcal. Heat of combustion of carbon is: [EAMCET (Med.) 2010]
(a) −26.0 kcal (b) − 68.3 kcal
(c) −94.3 kcal (d) −120.3 kcal

80. The heat of combustion of ethanol determined in a bomb calorimeter is −670.48 kcal mol^{-1} at 298 K. What is ΔE at 298 K for the reaction?
(a) −760 kcal mol^{-1} (b) − 670.48 kcal mol^{-1}
(c) +760 kcal mol^{-1} (d) + 670.48 kcal mol^{-1}

81. 1 calorie is equivalent to:
(a) 4.184 J (b) 41.84 J (c) 418.4 J (d) 0.4184 J

82. For an endothermic reaction, where ΔH represents the enthalpy of reaction, the minimum value for the energy of activation will be: [IIT 1991; PMT (MP) 1993]
(a) less than ΔH (b) zero
(c) equal to ΔH (d) more than ΔH

83. If $S + O_2 \longrightarrow SO_2;$ $\qquad \Delta H = -298.2 \text{ kJ}$

$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3;$ $\qquad \Delta H = -98.7 \text{ kJ}$

$SO_3 + H_2O \longrightarrow H_2SO_4;$ $\qquad \Delta H = -130.2 \text{ kJ}$

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O;$ $\qquad \Delta H = -227.3 \text{ kJ}$

the heat of formation of H_2SO_4 will be:

(a) –754.4 kJ (b) + 320.5 kJ (c) – 650.3 kJ (d) – 433.7 kJ

84. Which of the following units represents the largest amount of energy?

(a) Electron-volt (b) Erg
(c) Joule (d) Calorie

85. If ΔH_f° for $H_2O_2(l)$ and $H_2O(l)$ are –188 kJ mol^{-1} and –286 kJ mol^{-1}, what will be the enthalpy change of the reaction $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$? |PMT (MP) 1992|

(a) 146 kJ mol^{-1} (b) –196 kJ mol^{-1}
(c) – 494 kJ mol^{-1} (d) –98 kJ mol^{-1}

86. The bond dissociation energies for Cl_2, I_2 and ICl are 242.3, 151 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ / mol. What is the standard enthalpy of formation of ICl(*g*)?

(a) – 211.3 kJ/mol (b) – 14.6 kJ/mol
(c) 16.8 kJ/mol (d) 33.5 kJ/mol

[**Hint:** $Cl_2(g) \longrightarrow 2Cl(g);$ $\qquad \Delta H_1 = 242.3 \text{ kJ/mol}$

$I_2(g) \longrightarrow 2I(g);$ $\qquad \Delta H_2 = 151 \text{ kJ/mol}$

$ICl(g) \longrightarrow I(g) + Cl(g);$ $\qquad \Delta H_3 = 211.3 \text{ kJ/mol}$

$I_2(s) \longrightarrow I_2(g);$ $\qquad \Delta H_4 = 62.8 \text{ kJ/mol}$

Required equation:

$$\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl(g); \quad \Delta H = ?$$

$$\Delta H = \frac{62.8 + 151 + 242.3}{2} - 211.3$$

$$= 16.75 \text{ kJ / mol}]$$

87. Standard heat of formation for CCl_4, H_2O, CO_2 and HCl at 298K are – 25.5, – 57.8, – 94.1 and – 22.1 kJ/ mol respectively. For the reaction,

$$CCl_4 + 2H_2O \longrightarrow CO_2 + 4HCl$$

what will be ΔH? (SCRA 2007)

(a) 36.4 kJ (b) 20.7 kJ (c) –20.7 kJ (d) – 41.4 kJ

88. Heat of combustion of CH_4, C_2H_6, C_2H_4 and C_2H_2 are –212.8, –373.0, –337.0 and –310.5 kcal respectively at the same temperature. The best fuel among these gases is:

(a) CH_4 (b) C_2H_6
(c) C_2H_4 (d) C_2H_2

89. Given, $C(s) + O_2(g) \longrightarrow CO_2(g);$ $\qquad \Delta H = -395 \text{ kJ}$

$S(s) + O_2(g) \longrightarrow SO_2(g);$ $\qquad \Delta H = -295 \text{ kJ}$

$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g);$ $\Delta H = -1110 \text{ kJ}$

The heat of formation of $CS_2(l)$ is: |CEE (Bihar) 1992|

(a) 250 kJ (b) 62.5 kJ (c) 31.25 kJ (d) 125 kJ

90. The heats of combustion of rhombic and monoclinic sulphur are –70960 and –71030 calorie respectively. What will be the heat of conversion of rhombic sulphur to monoclinic sulphur?

(a) –70960 cal (b) –71030 cal
(c) 70 cal (d) –70 cal

91. The bond dissociation energy of C—H in CH_4 from the equation

$$C(g) + 4H(g) \longrightarrow CH_4(g); \qquad \Delta H = -397.8 \text{ kcal}$$

is:

(a) + 99.45 kcal (b) –99.45 kcal
(c) + 397.8 kcal (d) +198.9 kcal

92. The dissociation energy of CH_4 is 400 kcal mol^{-1} and that of ethane is 670 kcal mol^{-1}. The C—C bond energy is:

(a) 270 kcal (b) 70 kcal (c) 200 kcal (d) 240 kcal

93. Heat of reaction at constant volume is measured in the apparatus:

(a) bomb calorimeter (b) calorimeter
(c) pyknometer (d) pyrometer

94. When 10 mL of a strong acid is added to 10 mL of an alkali, the temperature rises by 5° C. If 100 mL of the same acid is mixed with 100 mL of the same base, the temperature rise would be:

(a) 5° C (b) 50°C
(c) 20°C (d) cannot be predicted

95. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25° C. The bond energy of H—H bond will be:

(a) 1.04 cal (b) 10.4 kcal
(c) 104 kcal (d) 1040 kcal

96. The heat of neutralisation of strong base and strong acid is 57.0 kJ. The heat released when 0.5 mole of HNO_3 solution is added to 0.20 mole of NaOH solution is: (KCET 1993)

(a) 57.0 kJ (b) 28.5 kJ
(c) 11.40 kJ (d) 34.9 kJ

97. The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are respectively –3920, –3800 and –241 kJ mol^{-1}. The heat of hydrogenation of cyclohexene is: (AIIMS 2007)

(a) –121 kJ mol^{-1} (b) 121 kJ mol^{-1}
(c) –242 kJ mol^{-1} (d) 242 kJ mol^{-1}

98. If $C(s) + O_2(g) \longrightarrow CO_2(g);$ $\qquad \Delta H = r$

and $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);$ $\qquad \Delta H = s$

then the heat of formation of CO is:

(a) $r + s$ (b) $r - s$ (c) $s - r$ (d) $r \times s$

99. Given that, heat of neutralisation of strong acid and strong base is 57.1 kJ. Calculate the heat produced when 0.25 mole of HCl is neutralised with 0.25 mole of NaOH in aqueous solution: (CPMT 1990)

(a) 22.5 kJ (b) 57 kJ
(c) 14.275 kJ (d) 28.55 kJ

100. Which one of the following values of ΔH° represents that the product is least stable?

(a) – 94.0 kcal mol^{-1} (b) –231.6 kcal mol^{-1}
(c) +21.4 kcal mol^{-1} (d) + 64.8 kcal mol^{-1}

101. The value of ΔH_{O-H} is 109 kcal mol^{-1}. The formation of one mole of water in gaseous state from H(*g*) and O(*g*) is accompanied by: (CBSE 1990)

(a) 218 kcal (b) –109 kcal
(c) –218 kcal (d) unpredictable

102. Heat of neutralisation of a strong dibasic acid in dilute solution by NaOH is nearly:
(a) –27.4 kcal/eq
(b) –13.7 kcal/eq
(c) +13.7 kcal/eq
(d) –13.7 kcal/mol

103. The enthalpy changes at 298 K in successive breaking of O—H bonds of water are

$$H_2O(g) \longrightarrow H(g) + OH(g); \quad \Delta H = 498 \text{ kJ mol}^{-1}$$

and $$OH(g) \longrightarrow H(g) + O(g); \quad \Delta H = 428 \text{ kJ mol}^{-1}$$

The bond enthalpy of O—H bond is:
(a) 498 kJ mol^{-1}
(b) 428 kJ mol^{-1}
(c) 70 kJ mol^{-1}
(d) 463 kJ mol^{-1}

104. ΔH and ΔE for the reaction, $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g)$ are related as:
(a) $\Delta H = \Delta E - 0.5RT$
(b) $\Delta H = \Delta E - 1.5RT$
(c) $\Delta H = \Delta E + RT$
(d) $\Delta H = \Delta E + 1.5RT$

105. A spontaneous change is one in which the system suffers: **(VITEEE 2008)**
(a) an increase in internal energy
(b) lowering in entropy
(c) lowering in free energy
(d) no energy change

106. The free energy change for a reversible reaction at equilibrium is:
(a) zero
(b) positive
(c) negative
(d) none of these

107. In the evaporation of water, the entropy:
(a) decreases
(b) increases
(c) does not change
(d) sometimes increases, sometimes decreases

108. In which of the following change entropy decreases?
(a) Crystallisation of sucrose from solution
(b) Dissolving sucrose in water
(c) Melting of ice
(d) Vaporisation of camphor

109. For the precipitation reaction of Ag^+ ions with NaCl which of the following statements is true?
(a) ΔH is zero for the reaction
(b) ΔG is zero for the reaction
(c) ΔG is negative for the reaction
(d) ΔG should be equal to ΔH

110. If enthalpy of vaporisation of water is 186.5 kJ/mol, the entropy of its vaporisation will be:
(a) 0.5
(b) 1.0
(c) 1.5
(d) 2.0

111. A reaction is non-spontaneous when: **[AMU (Medical) 2006]**
(a) ΔH is +ve, ΔS is –ve
(b) both ΔH and ΔS are –ve
(c) ΔH is –ve and ΔS is +ve
(d) none of the above

112. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 $JK^{-1}mol^{-1}$ respectively. For the reaction:

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3; \quad \Delta H = -30 \text{ kJ}$$

to be at equilibrium, the temperature should be : **[CBSE (PMT) 2010]**
(a) 750 K
(b) 1000 K
(c) 1250 K
(d) 500 K

[**Hint :** $\Delta S = \Sigma S_{\text{Products}} - \Sigma S_{\text{Reactants}}$

$$= 50 - \left[\frac{1}{2} \times 60 + \frac{3}{2} \times 40\right]$$

$$= 50 - (30 + 60) = -40 \text{ JK}^{-1} \text{ mol}^{-1}$$

At equilibrium, $\Delta G = \Delta H - T\Delta S = 0$

i.e., $\Delta H = T\Delta S$

$$T = \frac{\Delta H}{\Delta S} = \frac{-30 \times 1000}{-40} = 750 \text{ K}$$]

113. 'At absolute zero the entropy of a perfect crystal is zero.' This statement corresponds to which law of thermodynamics?
(a) First law
(b) Second law
(c) Third law
(d) None of these

114. Unit of entropy is: **[PMT (Punjab) 2007]**
(a) $J K^{-1} mol^{-1}$
(b) $J mol^{-1}$
(c) $J^{-1} K^{-1} mol^{-1}$
(d) $J K mol^{-1}$

115. Given that $\Delta H_f(H) = 218$ kJ/mol, express the H—H bond energy in kcal/mol: **(EAMCET 2009)**
(a) 52.15
(b) 911
(c) 109
(d) 5.2153

116. For which reaction from the following, ΔS will be maximum?
(a) $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)$
(b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(c) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(d) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

117. A particular reaction at 27° C for which $\Delta H > 0$ and $\Delta S > 0$ is found to be non-spontaneous. The reaction may proceed spontaneously if:
(a) the temperature is decreased
(b) the temperature is kept constant
(c) the temperature is increased
(d) it is carried in open vessel at 27° C

118. The least random state of water system is:
(a) ice
(b) liquid water
(c) steam
(d) randomness is same in all

119. Although the dissolution of ammonium chloride in water is an endothermic reaction, even then it is spontaneous because:
(a) ΔH is positive, ΔS is –ve
(b) ΔH is +ve, ΔS is zero
(c) ΔH is positive, $T\,\Delta S < \Delta H$
(d) ΔH is +ve, ΔS is positive and $\Delta H < T\,\Delta S$

120. For an exothermic reaction to be spontaneous:
(a) temperature must be high
(b) temperature must be zero
(c) temperature may have any magnitude
(d) temperature must be low

121. For the reversible process, the value of ΔS is given by the expression:
(a) $\frac{q_{\text{rev}}}{T}$
(b) $T - q_{\text{rev}}$
(c) $q_{\text{rev}} \times T$
(d) $q_{\text{rev}} - T$

122. In an electrochemical cell, if E° is the emf of the cell involving n mole of electrons, then ΔG° is:
(a) $\Delta G^\circ = nFE^\circ$ (b) $\Delta G^\circ = -nFE^\circ$
(c) $E^\circ = nF\,\Delta G^\circ$ (d) $\Delta G^\circ = nF/E^\circ$

123. The correct relation between equilibrium constant (K), standard free energy (ΔG°) and temperature (T) is: **[CET (J&K) 2006]**
(a) $\Delta G^\circ = RT \ln K$ (b) $K = e^{-\Delta G^\circ/2.303\,RT}$
(c) $\Delta G^\circ = -RT \log K$ (d) $K = 10^{-\Delta G^\circ/2.303\,RT}$
(e) $\Delta G^\circ = R \ln K$

124. The value of entropy in the universe is:
(a) constant (b) decreasing
(c) increasing (d) zero

125. Which of the following thermodynamic relation is correct? **[JEE (WB) 2010]**
(a) $dG = VdP - SdT$ (b) $dU = PdV + TdS$
(c) $dH = -VdP + TdS$ (d) $dG = VdP + SdT$

[**Hint :** $dG = dH - TdS - SdT$
$(G = H - TS)$
$dH = dU + PdV + VdP$
$(H = U + PV)$
and $dU = TdS - PdV$
$\therefore$ $dG = (TdS - PdV) + PdV + VdP - TdS - SdT$
$dG = VdP - SdT$]

126. If enthalpies of formation for $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1 atm pressure be 52, –394 and –286 kJ mol^{-1} respectively, enthalpy of combustion of $C_2H_4(g)$ will be: **(CBSE 1995)**
(a) +141.2 kJ mol^{-1} (b) +1412 kJ mol^{-1}
(c) –141.2 kJ mol^{-1} (d) –1412 kJ mol^{-1}

127. Identify the correct statement regarding entropy: **(CBSE 1998)**
(a) at absolute zero, the entropy of a perfectly crystalline substance is + ve.
(b) at absolute zero, the entropy of a perfectly crystalline substance is zero.
(c) at 0°C the entropy of a perfectly crystalline substance is taken to be zero.
(d) at absolute zero of temperature the entropy of all crystalline substances is taken to be zero.

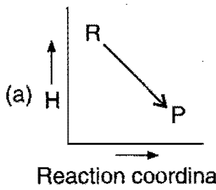
128. The enthalpy and entropy change for a chemical reaction are -2.5×10^{-3} cal and 7.4 cal deg^{-1} respectively. Predict whether the nature of reaction at 298 K is: **(AFMC 1998)**
(a) spontaneous (b) reversible
(c) irreversible (d) non-spontaneous

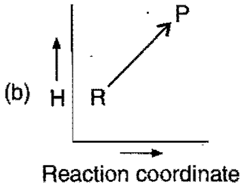
129. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The ΔE for this process is: ($R = 2$ cal K^{-1} mol^{-1}) **(CBSE 1998)**
(a) 163.7 cal (b) 1381.1 cal
(c) 9 litre-atm (d) zero

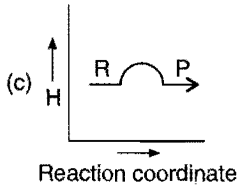
130. The latent heat of vaporisation of a liquid at 500 K and 1 atm pressure is 10 kcal/mol. What will be the change in internal energy (ΔE) of 3 moles of liquid at the same temperature? **(CBSE 1998)**
(a) 13.0 kcal (b) –13.0 kcal
(c) 27.0 kcal (d) –27.0 kcal

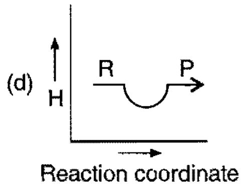
131. The enthalpy change of a reaction does not depend on: **(AIIMS 1997)**
(a) state of reactants and products
(b) nature of reactants and products
(c) different intermediate reactions
(d) initial and final enthalpy change of reaction

132. Which plot represents an exothermic reaction?









133. $S + \frac{3}{2}O_2 \longrightarrow SO_3 + 2x$ kcal;
$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 + y$ kcal
The heat of formation of SO_2 is: **[AIIMS 1997; PET (Kerala) 2008]**
(a) $y - 2x$ (b) $2x + y$ (c) $x + y$ (d) $2x/y$

134. Given,
$NH_3(g) + 3Cl_2(g) \rightleftharpoons NCl_3(g) + 3HCl(g)$; $-\Delta H_1$
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $-\Delta H_2$
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$; ΔH_3
The heat of formation of $NCl_3(g)$ in terms of ΔH_1, ΔH_2 and ΔH_3 is: **(EAMCET 1998)**
(a) $\Delta H_f = -\Delta H_1 + \frac{1}{2}\Delta H_2 - \frac{3}{2}\Delta H_3$
(b) $\Delta H_f = \Delta H_1 + \frac{1}{2}\Delta H_2 - \frac{3}{2}\Delta H_3$
(c) $\Delta H_f = \Delta H_1 - \frac{1}{2}\Delta H_2 - \frac{3}{2}\Delta H_3$
(d) none of the above

135. The word 'standard' in standard molar enthalpy change implies:
(a) temperature 298 K
(b) pressure 1 atm
(c) temperature 298 K and pressure 1 atm
(d) all temperatures and all pressures

136. The heat of formation (ΔH_f°) of $H_2O(l)$ is equal to:
(a) zero
(b) molar heat of combustion of $H_2(l)$
(c) molar heat of combustion of $H_2(g)$
(d) sum of heat of formation of $H_2O(g)$ and $O_2(g)$

137. An example of extensive property is:
(a) temperature (b) internal energy
(c) viscosity (d) molar heat capacity

138. For a diatomic molecule AB, the electronegativity difference between A and $B = 0.2028\sqrt{\Delta}$ [where, Δ = bond energy of

AB – geometric mean of the bond energies of A_2 and B_2]. The electronegativities of fluorine and chlorine are 4.0 and 3.0 respectively and the bond energies are of F—F: 38 kcal mol^{-1} and of Cl—Cl: 58 kcal mol^{-1}. The bond energy of Cl—F is:

(a) ~ 71 kcal/mol (b) ~ 61 kcal/mol
(c) ~ 48 kcal/mol (d) ~ 75 kcal/mol

139. The value of $\Delta H°$ for the reaction $Cu^+(g) + I^-(g) \rightarrow CuI(g)$ is – 446 kJ mol^{-1}. If the ionisation energy of Cu(g) is 745 kJ mol^{-1} and the electron affinity of I(g) is –295 kJ mol^{-1}, then the value of $\Delta H°$ for the formation of one mole of CuI(g) from Cu(g) and I(g) is:

(a) – 446 kJ (b) 450 kJ (c) 594 kJ (d) 4 kJ

140. If the enthalpy change for the reaction,
$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$; $\Delta H = -25$ kcal,
Bond energy of C—H is 20 kcal mol^{-1} greater than the bond energy of C—Cl and bond energies of H—H and H—Cl are same in magnitude, then for the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$, ΔH = ?

(a) –22.5 kcal/mol (b) –20.5 kcal/mol
(c) –32.5 kcal/mol (d) –12.5 kcal/mol

141. The standard heat of formation of sodium ions in aqueous solution from the following data:

Heat of formation of NaOH($aq.$) at 25° C = – 470.7 kJ
Heat of formation of OH^-($aq.$) at 25° C = – 228.8 kJ

is:

(a) –251.9 kJ (b) 241.9 kJ (c) – 241.9 kJ (d) 251.9 kJ

142. AB, A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2, AB and B_2 are in the ratio 1 : 1 : 0.5 and the enthalpy of formation of AB from A_2 and B_2 is –100 kJ mol^{-1}, what is the bond enthalpy of A_2?

(a) 400 kJ mol^{-1} (b) 200 kJ mol^{-1}
(c) 100 kJ mol^{-1} (d) 300 kJ mol^{-1}

143. The lattice energy of solid NaCl is 180 kcal per mol. The dissolution of the solid in water in the form of ions is endothermic to the extent of 1 kcal per mol. If the solvation energies of Na^+ and Cl^- ions are in the ratio 6 : 5, what is the enthalpy of hydration of sodium ion?

(a) – 85.6 kcal/mol (b) – 97.5 kcal/mol
(c) 82.6 kcal/mol (d) +100 kcal/mol

144. Which one of the following statements is false? **[IIT (Screening) 2000, 01]**

(a) Work is a state function
(b) Temperature is a state function
(c) Work appears at the boundary of the system
(d) Change in the state is completely defined when the initial and final states are specified

145. $\Delta G°$ for the reaction $x + y \rightleftharpoons z$ is – 4.606 kcal. The value of equilibrium constant of the reaction at 227° C is: **(IIT 1999)**

(a) 100 (b) 10 (c) 2 (d) 0.01
(R = 2.0 cal K^{-1} mol^{-1})

[Hint: $\Delta G° = -RT \times 2.303 \times \log K$]

146. The enthalpy of solution of $BaCl_2$ (s) and $BaCl_2 \cdot 2H_2O(s)$ are –20.6 and 8.8 kJ mol^{-1}, respectively. The enthalpy change for the reaction is: **(IIT 1998)**

(a) 29.8 kJ (b) –11.8 kJ
(c) –20.6 kJ (d) –29.4 kJ

147. For the reaction,

$$A(g) + 2B(g) \longrightarrow 2C(g) + 3D(g)$$

the value of ΔH at 27° C is 19.0 kcal. The value of ΔE for the reaction would be: (Given, R = 2.0 cal K^{-1} mol^{-1}): **(IIT 1998)**

(a) 20.8 kcal (b) 19.8 kcal (c) 18.8 kcal (d) 17.8 kcal

148. In thermodynamics, a process is called reversible when: **[IIT (Screening) 2000, 01]**

(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

149. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at 25°C increases the temperature of 18.94 kg of water by 0.632°C. If the specific heat of water at 25°C is 0.998 cal $g^{-1}deg^{-1}$, the value of heat of combustion of benzoic acid is: **(AFMC 2010)**

(a) 881.1 kcal (b) 771.4 kcal
(c) 981.1 kcal (d) 871.2 kcal

[Hint: Heat liberated by 1.89 g of benzoic acid,

$$q = ms\Delta T$$
$$= 18940 \times 0.998 \times 0.632$$
$$= 11946.14 \text{ cal}$$

Heat liberated by the combustion of
1 mol benzoic acid, *i.e.*,
122 g benzoic acid

$$= \frac{11946.14}{1.89} \times 122 = 771126.5 \text{ cal}$$
$$= 771.12 \text{ kcal mol}^{-1}]$$

150. One mole of a non-ideal gas undergoes a change state (2 atm, 3 L, 95 K) to (4 atm, 5 L, 245 K) with a change of internal energy, ΔU = 30 L atm. The change in enthalpy (ΔH) of the process in L atm.: **[IIT (S) 2002]**

(a) 40.0 (b) 42.3
(c) 44.0
(d) not defined, because pressure is not constant

151. Which of the following reactions defines $\Delta H_f°$? **[IIT (S) 2003]**

(a) $C_{(diamond)} + O_2(g) \longrightarrow CO_2(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(g)$
(c) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

152. If the enthalpies of formation of Al_2O_3 and Cr_2O_3 are –1596 kJ and –1134 kJ respectively, then the value of ΔH for the reaction;

$2Al + Cr_2O_3 \longrightarrow 2Cr + Al_2O_3$ is: **(AIIMS 2004)**

(a) –462 kJ (b) –1365 kJ
(c) –2530 kJ (d) +2530 kJ

153. Which of the following is true for spontaneous process? **[PMT (Himachal) 2006]**

(a) $\Delta G > 0$ (b) $\Delta G < 0$ (c) $\Delta G = 0$ (d) $\Delta G = T\,\Delta S$

154. Considering entropy(s) as a thermodynamic parameter, the criterion for the spontaneity of any process is: **[CBSE (PMT) 2004]**

(a) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
(b) $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$
(c) $\Delta S_{\text{system}} > 0$ only
(d) $\Delta S_{\text{surroundings}} > 0$ only

155. An ideal gas expands in volume from $1 \times 10^{-3}\ \text{m}^3$ to $1 \times 10^{-2}\ \text{m}^3$ at 300 K against a constant pressure of $1 \times 10^5\ \text{Nm}^{-2}$. The work done is: **(AIEEE 2004)**

(a) −900 J (b) −900 kJ
(c) 270 kJ (d) +900 kJ

156. What is the value of internal energy change (ΔU) at 27°C of a gaseous reaction $2A_2(g) + 5B_2(g) \longrightarrow 2A_2B_5(g)$ (whose heat change at constant pressure is −50700 J)? $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ **(SCRA 2009)**

(a) −50700 J (b) −63171 J
(c) −38229 J (d) +38229 J

[**Hint:** $\Delta H = \Delta U + \Delta n_g RT$

$-50700 = \Delta U + (-5) \times 8.314 \times 300$

$\Delta U = -38229$ J]

157. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is: **[IIT (S) 2004]**

(a) 11.4 kJ (b) −11.4 kJ (c) 0 kJ (d) 4.8 kJ

158. The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75 J $\text{mol}^{-1}\ \text{K}^{-1}$. The boiling point of the liquid at 1 atm is: **[IIT (S) 2004]**

(a) 250 K (b) 400 K (c) 450 K (d) 600 K

159. The sublimation energy of $I_2(s)$ is 57.3 kJ/mol and the enthalpy of fusion is 15.5 kJ/mol. The enthalpy of vaporisation of I_2 is: **(DCE 2005)**

(a) 41.8 kJ/mol (b) − 41.8 kJ/mol
(c) 72.8 kJ/mol (d) − 72.8 kJ/mol

[**Hint:** $\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporisation}}$]

160. ΔH and ΔS for a reaction are +30.558 kJ mol^{-1} and 0.066 kJ $\text{K}^{-1}\ \text{mol}^{-1}$ at 1 atm pressure. The temperature at which free energy change is zero and the nature of the reaction below this temperature is: **[PET (Kerala) 2005]**

(a) 483 K, spontaneous (b) 443 K, non-spontaneous
(c) 443 K, spontaneous (d) 463 K, non-spontaneous
(e) 463 K, spontaneous

161. What would be the amount of heat released when an aqueous solution containing 0.5 mole of HNO_3 is mixed with 0.3 mole of OH^- (enthalpy of neutralisation is −57.1 kJ)? **[PET (Kerala) 2005]**

(a) 28.5 kJ (b) 17.1 kJ (c) 45.7 kJ (d) 1.7 kJ
(e) 2.85 kJ

[**Hint:** 0.3 mole OH^- ion will be completely neutralised,

$\therefore \quad \Delta H = -57.1 \times 0.3 = -17.13$ kJ]

162. A process in which the system does not exchange heat with the surroundings is known as: **[CET (J&K) 2005]**

(a) isothermal (b) isobaric (c) isochoric (d) adiabatic

163. The entropy of a crystalline substance at absolute zero on the basis of third law of thermodynamics should be taken as: **[CET (J&K) 2005]**

(a) 100 (b) 50
(c) zero (d) different for different substances

164. Which of the following expressions is correct? **[JEE (Orissa) 2005]**

(a) $\Delta G^\circ = -nFE^\circ$ (b) $\Delta G^\circ = +nFE^\circ$
(c) $\Delta G^\circ = -2.303RTnFE^\circ_{\text{cell}}$ (d) $\Delta G^\circ = -nF \log K_c$

165. Consider the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; carried out at constant temperature and pressure. If ΔH and ΔU are enthalpy change and internal energy change respectively, which of the following expressions is true? **(AIEEE 2005)**

(a) $\Delta H = 0$ (b) $\Delta H = \Delta U$
(c) $\Delta H < \Delta U$ (d) $\Delta H > \Delta U$

[**Hint:** $\Delta H = \Delta U + \Delta nRT, \Delta n = 2 - 4 = -2$

$\therefore \quad \Delta H < \Delta U$]

166. The absolute enthalpy of neutralisation of the reaction,

$$\text{MgO}(s) + 2\text{HCl}(aq.) \longrightarrow \text{MgCl}_2(aq.) + \text{H}_2\text{O}(l)$$

will be: **[CBSE-PMT (Pre) 2005]**

(a) −57.33 kJ mol^{-1}
(b) greater than −57.33 kJ mol^{-1}
(c) less than −57.33 kJ mol^{-1}
(d) 57.33 kJ mol^{-1}

[**Hint:** Since, MgO is an oxide of a weak base, hence its neutralisation will evolve the heat less than 57.33 kJ mol^{-1}]

167. The entropy values (in J $\text{K}^{-1}\ \text{mol}^{-1}$) of $H_2(g) = 130.6$, $Cl_2(g) = 223$ and $\text{HCl}(g) = 186.7$ at 298 K and 1 atm pressure are given. Then entropy change for the reaction,

$$H_2(g) + Cl_2(g) \longrightarrow 2\text{HCl}(g)$$

is: **[BHU (Pre) 2005]**

(a) + 540.3 (b) + 727.3 (c) − 166.9 (d) + 19.8

168. A mixture of 2 mole of $\text{CO}(g)$ and one mole of O_2, in a closed vessel, is ignited to convert the carbon monoxide to carbon dioxide. If ΔH and ΔU are enthalpy and internal energy change, then: **(KCET 2005)**

(a) $\Delta H > \Delta U$
(b) $\Delta H < \Delta U$
(c) $\Delta H = \Delta U$
(d) the relationship depends on the capacity of the vessel

169. Consider the following reactions at 1000°C:

A. $\text{Zn}(s) + \frac{1}{2}O_2(g) \longrightarrow \text{ZnO}(s); \quad \Delta G^\circ = -360\ \text{kJ mol}^{-1}$

B. $\text{C (graphite)} + \frac{1}{2}O_2(g) \longrightarrow \text{CO}(g); \quad \Delta G^\circ = -460\ \text{kJ/mol}$

Choose the correct statement at 1000°C: **[PMT (Kerala) 2006]**

(a) zinc can be oxidised by carbon monoxide.
(b) ZnO can be reduced by graphite.
(c) both (a) and (b) are true.
(d) both (a) and (b) are false.
(e) carbon monoxide can be reduced by zinc.

170. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process? **[PET (Kerala) 2006]**

(a) Isothermal process : $q = -w$
(b) Cyclic process : $q = -w$
(c) Isochoric process : $\Delta U = q$
(d) Adiabatic process : $\Delta U = -w$
(e) Expansion of gas into vacuum : $\Delta U = q$

[**Hint:** In adiabatic process : $q = 0$

$\therefore$ From $\Delta U = q - w$

Work is done by the system,

$\Delta U = -w$ for adiabatic process]

171. The enthalpy and entropy changes for the reaction:

$$Br_2(l) + Cl_2(g) \rightleftharpoons 2BrCl(g)$$

are 30 kJ mol^{-1} and 105 J K^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is: **[CBSE (Med.) 2006]**

(a) 285.7 K (b) 273 K (c) 450 K (d) 300 K

172. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its element at 298 K is: $(R = 8.314\ J\ K^{-1}\ mol^{-1})$ **(AIEEE 2006)**

(a) −1238.78 J mol^{-1} (b) 1238.78 J mol^{-1}
(c) −2477.57 J mol^{-1} (d) 2477.57 J mol^{-1}

[**Hint:** $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$

$$\Delta H - \Delta U = \Delta nRT$$
$$= \frac{1}{2} \times 8.314 \times 298 = 1238.786\ J\ mol^{-1}]$$

173. For a phase change:

$$\underset{0°\,C,\,1\,bar}{H_2O(l) \rightleftharpoons H_2O(s)}$$

(AIIMS 2006)

(a) $\Delta G = 0$ (b) $\Delta S = 0$
(c) $\Delta H = 0$ (d) $\Delta U = 0$

174. We can drive any thermodynamically forbidden reaction in the desired direction by coupling with: **[PET (Kerala) 2006]**

(a) highly exothermic reaction
(b) highly endothermic reaction
(c) highly exergonic reaction
(d) highly endergonic reaction
(e) reaction with large positive ΔS values

175. Given that, bond energies of H — H and Cl — Cl are 430 kJ/mol and 240 kJ/mol respectively. ΔH_f for HCl is − 90 kJ/ mol. Bond enthalpy of HCl is: **[CBSE (Med.) 2007]**

(a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}
(c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}

176. The amount of heat released, when 20 mL of 0.5 M NaOH is mixed with 100 mL of 0.1 M HCl, is x kJ. The heat of neutralization (in kJ mol^{-1}) is: **[BHU (Mains) 2007]**

(a) $-100x$ (b) $-50x$ (c) $+100x$ (d) $+50x$

[**Hint:** Number of moles of NaOH $= \frac{MV}{1000} = \frac{0.5 \times 20}{1000} = 0.01$

$$\text{Number of moles of HCl} = \frac{MV}{1000} = \frac{0.1 \times 100}{1000} = 0.01$$

$$\text{Heat of neutralization} = \frac{-x}{0.01} = -100x\,]$$

177. In the conversion of limestone to lime,

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

the values of $\Delta H°$ and $\Delta S°$ are $+179.1\ kJ\ mol^{-1}$ and 160.2 JK^{-1} mol^{-1} respectively at 298 K and 1 bar. Assuming that, $\Delta H°$ and $\Delta S°$ do not change with temperature; temperature above which conversion of limestone to lime will be spontaneous is: **(AIEEE 2007)**

(a) 1118 K (b) 1008 K (c) 1200 K (d) 845 K

178. Assuming that, water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vaporised at 1 bar pressure and 100°C, (given: molar enthalpy of vaporisation of water at 1 bar and 373K = 41 kJ mol^{-1} and $R = 8.3\ J\ K^{-1}\ mol^{-1}$) will be: **(AIEEE 2007)**

(a) 41.00 kJ mol^{-1} (b) 4.100 kJ mol^{-1}
(c) 3.7904 kJ mol^{-1} (d) 37.904 kJ mol^{-1}

[**Hint:** $\Delta U = \Delta H - \Delta nRT$

$$= 41000 - 1 \times 8.314 \times 373$$
$$= 37898.878\ J\ mol^{-1}$$
$$= 37.9\ kJ\ mol^{-1}\,]$$

179. For the process,

$$H_2O(l)\ (1\ bar, 373K) \longrightarrow H_2O(g)\ (1\ bar, 373K).$$

The correct set of thermodynamic parameters is: **(IIT 2007)**

(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$
(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve$

180. For the reaction,

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g); \quad \Delta H° = -573.2\ kJ$$

The heat of decomposition of water per mol is: **(MHT-CET 2007)**

(a) 286.6 kJ (b) 573.2 kJ (c) − 28.66 kJ (d) zero

181. The free energy change $\Delta G = 0$, when: **[CET (J&K) 2007]**

(a) the reactants are completely consumed
(b) a catalyst is added
(c) the system is at equilibrium
(d) the reactants are initially mixed

182. In a closed container, a liquid is stirred with a paddle to increase the temperature, which of the following is true? **[PMT (Pb.) 2007]**

(a) $\Delta U = \Delta W \neq 0, q = 0$ (b) $\Delta U = W = 0, q \neq 0$
(c) $\Delta U = 0, W = q \neq 0$ (d) $W = 0, \Delta U = q \neq 0$

183. For the gas phase reaction,

$$PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Which of the following conditions are correct ? **[CBSE-PMT (Pre) 2008]**

(a) $\Delta H < 0, \Delta S < 0$ (b) $\Delta H > 0$ and $\Delta S < 0$
(c) $\Delta H = 0, \Delta S < 0$ (d) $\Delta H > 0$ and $\Delta S > 0$

184. Which of the following is correct ? **[BHU (Screening) 2008]**

(a) $C_V = \left(\frac{\partial U}{\partial T}\right)_P$ (b) $C_P = \left(\frac{\partial H}{\partial T}\right)_V$

(c) $C_P - C_V = R$ (d) $\left(\frac{\partial U}{\partial V}\right)_t = \frac{-a}{V^2}$

(Internal pressure in van dar Waals' equation)

185. Which of the following represents total kinetic energy of one mole of gas? **[JEE (Orissa) 2008]**

(a) $\frac{1}{2}RT$ (b) $\frac{3}{2}RT$ (c) $(C_P - C_V)RT$ (d) $\frac{2}{3}RT$

186. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 $\mathrm{JK^{-1}\ mol^{-1}}$ respectively. For the reaction :

$$\frac{1}{2}X_2+\frac{3}{2}Y_2 \longrightarrow XY_3, \qquad \Delta H=-30\ \mathrm{kJ},$$

to be at equilibrium, the temperature will be : **(AIEEE 2008)**

(a) 1000K (b) 1250K (c) 500K (d) 750K

[**Hint :** $\frac{1}{2}X_2+\frac{3}{2}Y_2 \rightarrow XY_3$

$$\Delta S^\circ_{\text{Reaction}}=\Delta S^\circ_{XY_3}-\frac{1}{2}\Delta S^\circ_{X_2}-\frac{3}{2}\Delta S^\circ_{Y_2}$$

$$=50-\frac{1}{2}\times 60-\frac{3}{2}\times 40=-40\ \mathrm{JK^{-1}\ mol^{-1}}$$

$\Delta G=\Delta H-T\,\Delta S=0$ at equilibrium.

$$\therefore \quad T=\frac{\Delta H}{\Delta S}=\frac{-30\times 1000}{40}=750\ \mathrm{K}\ ]$$

187. 4.48 L of an ideal gas at S.T.P requires 12 calories to raise its temperature by 15C° at constant volume. The C_P of the gas is : **[PMT (Kerala) 2009]**

(a) 3 cal (b) 4 cal (c) 7 cal (d) 6 cal
(e) 9 cal

[**Hint :** $C_V=\dfrac{\Delta U}{n\,\Delta T}$, $\quad n=\dfrac{4.48}{2.24}=0.2$

$$=\frac{12}{0.2\times 15}=4\ \text{cal}$$

$C_P=C_V+R=4+2=6$ cal]

188. On the basis of following thermochemical data : $[\Delta_f G^\circ\,\mathrm{H^+}(aq)=0]$

$$\mathrm{H_2O}(l)\longrightarrow \mathrm{H^+}(aq)+\mathrm{OH^-}(aq)\ ;\quad \Delta H=57.32\ \mathrm{kJ}$$

$$\mathrm{H_2}(g)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{H_2O}(l)\quad ;\quad \Delta H=-286.2\ \mathrm{kJ}$$

The value of enthalpy of formation of $\mathrm{OH^-}$ ion at 25°C is: **(AIEEE 2009)**

(a) −22.88 kJ (b) −228.88 kJ
(c) +228.88 kJ (d) −343.52 kJ

[**Hint :** The equation for the formation of $\mathrm{OH^-}(aq)$ is:

$$\mathrm{H_2}(g)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{H^+}(aq)+\mathrm{OH^-}(aq)$$

It is obtained by adding the two given equations :

$\Delta H=57.32+(-286.2)=-228.88$ kJ]

189. The values of ΔH and ΔS for the reaction, C(graphite) + $\mathrm{CO_2}(g)\longrightarrow 2\mathrm{CO}(g)$ are 170 kJ and 170 $\mathrm{JK^{-1}}$ respectively. This reaction will be spontaneous at : **[CBSE (PMT) Pre 2009]**

(a) 510 K (b) 710 K (c) 910 K (d) 1110 K

[**Hint :** $\Delta G=\Delta H-T\Delta S$, ΔG should be negative for spontaneous process.

$$\therefore \quad \Delta H-T\Delta S<0$$

$$\Delta H<T\Delta S$$

$$\text{or} \quad T>\frac{\Delta H}{\Delta S},\quad T>\frac{170\times 1000}{170}$$

$T>1000$ K]

190. In which reaction, there will be increase in entropy? **(DCE 2009)**

(a) $\mathrm{Na}(s)+\mathrm{H_2O}(l)\longrightarrow \mathrm{NaOH}(aq)+\frac{1}{2}\mathrm{H_2}(g)\uparrow$

(b) $\mathrm{Ag^+}(aq)+\mathrm{Cl^-}(aq)\longrightarrow \mathrm{AgCl}(s)$

(c) $\mathrm{H_2}(g)+\frac{1}{2}\mathrm{O_2}(g)\longrightarrow \mathrm{H_2O}(l)$

(d) $\mathrm{Cu^{2+}}(aq)+4\mathrm{NH_3}(g)\longrightarrow [\mathrm{Cu(NH_3)_4}]^{2+}_{(aq.)}$

191. The species which by definition has zero standard molar enthalpy of formation at 298 K is: **(IIT 2010)**

(a) $\mathrm{Br_2}(g)$ (b) $\mathrm{Cl_2}(g)$
(c) $\mathrm{H_2O}(g)$ (d) $\mathrm{CH_4}(g)$

192. The standard enthalpy of formation of $\mathrm{NH_3}$ is −46 kJ $\mathrm{mol^{-1}}$. If the enthalpy of formation of $\mathrm{H_2}$ from its atoms is −436 kJ $\mathrm{mol^{-1}}$ and that of $\mathrm{N_2}$ is −712 kJ $\mathrm{mol^{-1}}$, the average bond enthalpy of N—H bond in $\mathrm{NH_3}$ is: **(AIEEE 2010)**

(a) + 1056 kJ $\mathrm{mol^{-1}}$ (b) −1102 kJ $\mathrm{mol^{-1}}$
(c) −964 kJ $\mathrm{mol^{-1}}$ (d) +352 kJ $\mathrm{mol^{-1}}$

[**Hint :** $\frac{1}{2}(\mathrm{N\equiv N})+\frac{3}{2}(\mathrm{H-H})\longrightarrow \mathrm{H-N}\begin{matrix}\diagup\mathrm{H}\\ \diagdown\mathrm{H}\end{matrix}$

$\Delta H=-46$ kJ $\mathrm{mol^{-1}}$

BE $(\mathrm{N\equiv N})=-712$ kJ $\mathrm{mol^{-1}}$

BE $(\mathrm{H-H})=-436$ kJ $\mathrm{mol^{-1}}$

Let B.E. of $(\mathrm{N-H})=x$ kJ $\mathrm{mol^{-1}}$

$$\Delta H=\Sigma(\mathrm{B.E.})_{\text{Reactants}}-\Sigma(\mathrm{B.E.})_{\text{Products}}$$

$$-46=\left[\frac{1}{2}(712)+\frac{3}{2}(436)\right]-3x$$

$x=352$ kJ $\mathrm{mol^{-1}}$]

193. A 1 g sample of substance A at 100°C is added to 100 mL of $\mathrm{H_2O}$ at 25°C. Using separate 100 mL portion of $\mathrm{H_2O}$, the procedure is repeated with substance B and then with substance C. How will the final temperatures of the water compare?

Substance	Specific heat
A	0.6 $\mathrm{J\,g^{-1}\,{}^\circ C^{-1}}$
B	0.4 $\mathrm{J\,g^{-1}\,{}^\circ C^{-1}}$
C	0.2 $\mathrm{J\,g^{-1}\,{}^\circ C^{-1}}$

(DUMET 2010)

(a) $T_C>T_B>T_A$ (b) $T_B>T_A>T_C$
(c) $T_A>T_B>T_C$ (d) $T_A=T_B=T_C$

[**Hint :** $q=ms\Delta T$

$$s\propto\frac{1}{\Delta T}$$

Higher is the temperature of given solution, lesser is the temperature difference, so higher is the specific heat. Order of specific heat is $A>B>C$. Hence order of temperature will be :

$T_A>T_B>T_C$]

194. For vaporisation of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 kJ $\mathrm{mol^{-1}}$ and 108.8 J $\mathrm{K^{-1}mol^{-1}}$ respectively. The temperature when Gibbs free energy change (ΔG) for transformation will be zero, is: **[CBSE (PMT) 2010]**

(a) 273.4 K (b) 393.4 K
(c) 373.4 K (d) 293.4 K

[**Hint :** $\Delta G=\Delta H-T\Delta S$

$0=40.63\times 1000-T\times 108.8$

$T=373.4$ K]

Set-2: The questions given below may have more than one correct answers

1. Which is intensive property?
(a) Mass (b) Mass/volume
(c) Volume (d) Volume/mass

2. Which is an irreversible process?
(a) Mixing of two gases by diffusion
(b) Evaporation of water at 373 K and 1 atm pressure
(c) Dissolution of NaCl in water
(d) All of the above

3. One mole of anhydrous $MgCl_2$ dissolves in water and liberates 25 cal/mol of heat. $\Delta H_{\text{hydration}}$ of $MgCl_2 = -30$ cal/mol. Heat of dissolution of $MgCl_2 \cdot H_2O$ is:
(a) +5 cal/mol (b) –5 cal/mol
(c) 55 cal/mol (d) –55 cal/mol

4. Following enthalpy changes are given:
$\alpha\text{-}D$ glucose$(s) \longrightarrow \alpha\text{-}D$ glucose$(aq.)$; $\Delta H = 10.72$ kJ
$\beta\text{-}D$ glucose$(s) \longrightarrow \beta\text{-}D$ glucose$(aq.)$; $\Delta H = 4.68$ kJ
$\alpha\text{-}D$ glucose$(s) \longrightarrow \beta\text{-}D$ glucose$(aq.)$; $\Delta H = 1.16$ kJ
Calculate the enthalpy change in,
$\alpha\text{-}D$ glucose$(s) \longrightarrow \beta\text{-}D$ glucose(s)
(a) 14.24 kJ (b) 16.56 kJ (c) –7.2 kJ (d) 4.88 kJ

5. If x and y are arbitrary extensive variables, then:
(a) $(x+y)$ is an extensive variable
(b) x/y is an intensive variable
(c) dx/dy is an intensive variable
(d) both (b) and (c)

6. If x and y are arbitrary intensive variables, then:
(a) xy is an intensive variable
(b) x/y is an intensive variable
(c) $(x+y)$ is an extensive property
(d) dx/dy is an intensive property

7. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta H = x$
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = y$
Heat of vaporization of water is:
(a) $x+y$ (b) $x-y$ (c) $y-x$ (d) $-(x+y)$

8. Which is correct about ΔG?
(a) $\Delta G = \Delta H - T\,\Delta S$ (b) At equilibrium, $\Delta G^\circ = 0$
(c) At eq. $\Delta G = -RT \log K$ (d) $\Delta G = \Delta G^\circ + RT \log K$

9. Dissociation of sodium azide is given by,
$$NaN_3 \longrightarrow Na + 3/2N_2;$$
ΔH for this is:
(a) $\frac{3}{2}\Delta H^\circ_{f\,(N_2)} - \Delta H^\circ_{f\,(NaN_3)}$
(b) $-\Delta H^\circ_{f\,(NaN_3)}$
(c) $\Delta H^\circ_{f\,(NaN_3)} - [\Delta H^\circ_{f\,(Na)} + \frac{3}{2}\Delta H^\circ_{f\,(N_2)}]$
(d) $\Delta H^\circ_{f\,(Na)} + \frac{3}{2}\Delta H^\circ_{f\,(N_2)} - \Delta H^\circ_{f\,(NaN_3)}$

10. The lattice energy of KCl is 202 kcal/mol. When KCl is dissolved in water 2 kcal/mol is absorbed. If the sol energies of K^+ and Cl^- are in the ratio 2 : 3; then $\Delta H_{\text{hydration}}$ of K^+ is:
(a) –80 kJ/mol (b) –120 kJ/mol
(c) –150 kJ/mol (d) 133.3 kJ/mol

11. Which is a correct relationship?
(a) $\left[\frac{dH}{dT}\right]_P - \left[\frac{dE}{dT}\right]_T = (+\text{ve})$
(b) $\left[\frac{dE}{dV}\right]_T = 0$ (for ideal gas)
(c) $\left[\frac{dV}{dT}\right]_P = \frac{nR}{P}$ (for ideal gas)
(d) All of the above

12. The standard Gibbs free energy ΔG° is related to equilibrium constant K_P as:
(a) $K_P = -RT \log \Delta G^\circ$ (b) $K_P = [e/RT]^{\Delta G^\circ}$
(c) $K_P = -\Delta G^\circ/RT$ (d) $K_P = e^{-\Delta G^\circ/RT}$

13. For the two equations given below:
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) + x_1 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) + x_2 \text{ kJ}$$
Select the correct answer:
(a) $x_1 > x_2$ (b) $x_2 > x_1$
(c) $x_1 = x_2$ (d) $x_1 + x_2 = 0$

14. $\Delta E = 0$, for which process?
(a) Cyclic process (b) Isothermal expansion
(c) Isochoric process (d) Adiabatic process

15. For a reaction to be spontaneous in neither direction, which of the following is/are correct regarding the closed system? **[BHU (Mains) 2007]**
(1) $(\Delta G)_{T,P} = 0$ (2) $(\Delta G)_{T,P} < 0$
(3) $(\Delta S)_{U,V} = 0$ (4) $(\Delta S)_{U,V} > 0$
Codes:
(a) 1, 2 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 4 are correct (d) 1 and 3 are correct

Assertion-Reason TYPE QUESTIONS

Set-1

The questions given below consist of an '**Assertion**' **(A)** and the '**Reason**' **(R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.
(R) When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of the change.

2. (A) $C_P - C_V = R$ for an ideal gas.
(R) $\left[\frac{\partial E}{\partial V}\right]_T = 0$ for an ideal gas.

3. (A) When hydrogen gas at high pressure and room temperature expands adiabatically into a region of low pressure, there is a decrease in temperature.
(R) Hydrogen gas at room temperature is above its inversion temperature.

4. (A) The thermodynamic factor which determines the spontaneity of a process is the free energy. For a process to be spontaneous the free energy must be –ve.
(R) The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must always be positive if it is spontaneous.

5. (A) The Joules-Thomson coefficient for an ideal gas is zero.
(R) There are no intermolecular attractive forces in an ideal gas.

6. (A) As temperature increases, heat of reaction also increases for exothermic as well as endothermic reactions.
(R) $\Delta H_{\text{reaction}}$ varies according to the relation:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

7. (A) All exothermic reactions are spontaneous at room temperature.
(R) $\Delta G = -$ ve for above reactions and for spontaneous reactions $\Delta G = -$ ve.

8. (A) Efficiency of a reversible engine is 100% (maximum) when the temperature of sink is $-273°C$.
(R) Efficiency of engine, $\eta = \frac{T_2 - T_1}{T_2}$.

Set-2

The questions given below consist of statements '**Assertion**' **(A)** and '**Reason**' **(R).**

(a) If both (A) and (R) are correct and (R) is the correct reason for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is true but (R) is false.
(d) If both (A) and (R) are false.

1. (A) Enthalpy of graphite is lower than that of diamond.
(R) Entropy of graphite is lower than that of diamond. **(AIIMS 1994)**

2. (A) The enthalpy of formation of gaseous oxygen molecules at 298 K and under a pressure of one atm is zero.
(R) The entropy of formation of gaseous oxygen molecules under the same condition is zero. **(AIIMS 1996)**

3. (A) Heat of neutralization for both HNO_3 and HCl with NaOH is 53.7 kJ per mol.
(R) NaOH is a strong electrolyte/base. **(AIIMS 1997)**

4. (A) Decrease in free energy causes spontaneous reaction.
(R) Spontaneous reactions are invariably exothermic. **(AIIMS 1997)**

5. (A) Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
(R) Entropy of the system increases with increase in temperature. **(AIIMS 1998)**

6. (A) The enthalpy of formation of $H_2O(l)$ is greater than that of $H_2O(g)$.
(R) Enthalpy change is negative for the condensation reaction

$$H_2O(g) \longrightarrow H_2O(l)$$

7. (A) For a particular reaction, heat of combustion at constant pressure (q_P) is always greater than that at constant volume (q_V).
(R) Combustion reactions are invariably accomplished by increase in number of moles. **(AIIMS 1998)**

8. (A) The enthalpy of both graphite and diamond is taken to be zero, being elementary substances.
(R) The enthalpy of formation of an elementary substance in any state is taken as zero.

9. (A) Heat of neutralization of perchloric acid, $HClO_4$, with NaOH is same as that of HCl with NaOH.
(R) Both HCl and $HClO_4$ are strong acids.

10. (A) Heat of ionization of water is equal to the heat of neutralization of a strong acid with a strong base.
(R) Water ionizes to a very small extent while H^+ ions from acid combine very rapidly with OH^- from base to form H_2O.

11. (A) Enthalpy of formation of HCl is equal to the bond energy of HCl.

(R) Enthalpy of formation and bond energy both involve formation of one mole of HCl from the elements.

12. (A) Pressure, volume and temperature are all extensive properties.

(R) Extensive properties depend upon the amount and nature of the substance.

13. (A) When a gas at high pressure expands against vacuum, the work done is maximum.

(R) Work done in expansion depends upon the pressure inside the gas and increase in volume.

14. (A) When a real gas is allowed to expand adiabatically through a fine hole from a region of high pressure to a region of low pressure, the temperature of the gas falls.

(R) Work is done at the cost of internal energy of the gas.

15. (A) Internal energy change in a cyclic process is zero.

(R) Internal energy is a state function.

16. (A) An exothermic process, non-spontaneous at high temperature, may become spontaneous at low temperature.

(R) With decrease in temperature, randomness (entropy) decrease.

17. (A) There is no reaction known for which ΔG is positive, yet it is spontaneous.

(R) For photochemical reaction, ΔG is negative.

18. (A) A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.

(R) All exothermic reactions are accompanied by decrease of randomness.

19. (A) Molar entropy of vaporization of water is different from ethanol.

(R) Water is more polar than methanol.

20. (A) Heat of neutralization for both HNO_3 and HCl with NaOH is 53.7 kJ/mol.

(R) NaOH is a strong electrolyte/base.

21. (A) In the following reaction:

$$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = \Delta U - RT$$

(R) ΔH is related to ΔU by the equation,

$$\Delta H = \Delta U - \Delta n_g RT$$

22. (A) Enthalpy of graphite is lower than that of diamond.

(R) Entropy of graphite is greater than that of diamond.

23. (A) For a reaction

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g); \qquad \Delta H > \Delta E$$

(R) Enthalpy change is always greater than internal energy change. **(AIIMS 2008)**

Answers : OBJECTIVE QUESTIONS

Set–1

1. (b) **2.** (c) **3.** (d) **4.** (a) **5.** (c) **6.** (a) **7.** (b) **8.** (d)
9. (a) **10.** (d) **11.** (c) **12.** (d) **13.** (c) **14.** (d) **15.** (a) **16.** (a)
17. (c) **18.** (a) **19.** (a) **20.** (a) **21.** (b) **22.** (d) **23.** (b) **24.** (a)
25. (c) **26.** (d) **27.** (d) **28.** (b) **29.** (d) **30.** (b) **31.** (c) **32.** (a)
33. (c) **34.** (b) **35.** (a) **36.** (a) **37.** (d) **38.** (b) **39.** (d) **40.** (c)
41. (d) **42.** (d) **43.** (c) **44.** (b) **45.** (b) **46.** (c) **47.** (a) **48.** (a)
49. (a) **50.** (d) **51.** (b) **52.** (c) **53.** (d) **54.** (d) **55.** (b) **56.** (c)
57. (a) **58.** (c) **59.** (b) **60.** (d) **61.** (b) **62.** (c) **63.** (a) **64.** (b)
65. (c) **66.** (d) **67.** (b) **68.** (a) **69.** (d) **70.** (a) **71.** (d) **72.** (a)
73. (b) **74.** (b) **75.** (c) **76.** (d) **77.** (d) **78.** (c) **79.** (c) **80.** (b)
81. (a) **82.** (c) **83.** (a) **84.** (d) **85.** (b) **86.** (c) **87.** (d) **88.** (a)
89. (d) **90.** (c) **91.** (a) **92.** (b) **93.** (a) **94.** (a) **95.** (c) **96.** (c)
97. (a) **98.** (b) **99.** (c) **100.** (d) **101.** (c) **102.** (b) **103.** (d) **104.** (a)
105. (c) **106.** (a) **107.** (b) **108.** (a) **109.** (c) **110.** (a) **111.** (a) **112.** (a)
113. (c) **114.** (a) **115.** (c) **116.** (b) **117.** (c) **118.** (a) **119.** (d) **120.** (d)
121. (a) **122.** (b) **123.** (d) **124.** (c) **125.** (a) **126.** (d) **127.** (b) **128.** (a)
129. (d) **130.** (c) **131.** (c) **132.** (a) **133.** (a) **134.** (a) **135.** (b) **136.** (c)
137. (b) **138.** (a) **139.** (d) **140.** (a) **141.** (c) **142.** (a) **143.** (b) **144.** (a)
145. (a) **146.** (a) **147.** (d) **148.** (c) **149.** (b) **150.** (c) **151.** (b) **152.** (a)
153. (b) **154.** (a) **155.** (a) **156.** (c) **157.** (b) **158.** (b) **159.** (a) **160.** (d)
161. (b) **162.** (d) **163.** (c) **164.** (a) **165.** (c) **166.** (c) **167.** (d) **168.** (b)
169. (b) **170.** (d) **171.** (a) **172.** (b) **173.** (a) **174.** (c) **175.** (b) **176.** (a)
177. (a) **178.** (d) **179.** (a) **180.** (a) **181.** (c) **182.** (a) **183.** (d) **184.** (c)
185. (b) **186.** (d) **187.** (d) **188.** (b) **189.** (d) **190.** (a) **191.** (b) **192.** (d)
193. (c) **194.** (c)

Set–2

1. (b, d) **2.** (a, c) **3.** (a) **4.** (d) **5.** (a, b, c) **6.** (a, b, d) **7.** (b) **8.** (a, d)
9. (b) **10.** (a) **11.** (d) **12.** (d) **13.** (a) **14.** (a, b) **15.** (d)

Answers : ASSERTION-REASON TYPE QUESTIONS

Set–1

1. (d) **2.** (b) **3.** (d) **4.** (c) **5.** (a) **6.** (d) **7.** (a) **8.** (a)

Set–2

1. (b) **2.** (c) **3.** (b) **4.** (c) **5.** (b) **6.** (a) **7.** (d) **8.** (d)
9. (a) **10.** (b) **11.** (d) **12.** (d) **13.** (d) **14.** (a) **15.** (a) **16.** (b)
17. (d) **18.** (c) **19.** (b) **20.** (a) **21.** (d) **22.** (b) **23.** (c)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain single correct option :

1. In which of the following pairs, both properties are intensive?
(a) Pressure, temperature (b) Density, volume
(c) Temperature, density (d) Pressure, volume

2. Although the dissolution of ammonium chloride (NH_4Cl) in water is an endothermic reaction, even then it is spontaneous because:
(a) $\Delta S = -$ ve (b) $\Delta S =$ zero
(c) $T\,\Delta S < \Delta H$ (d) $\Delta S = +$ ve and $\Delta H < T\,\Delta S$

3. The S—S bond energy is if $\Delta H^\circ_f(E_t - S - E_t) = -147$ kJ/mol; $\Delta H^\circ_f(E_t - S - S - E_t) = -202$ kJ/mol and $\Delta H^\circ_f S(g) = +223$ kJ/mol:
(a) 168 kJ (b) 126 kJ (c) 278 kJ (d) 572 kJ

[**Hint:**

$$C_2H_5 — S — C_2H_5 + S(s) \longrightarrow C_2H_5 — S — S — C_2H_5$$

$$\Delta H_{\text{reaction}} = \Sigma\Delta H^\circ_{f\,(\text{products})} - \Sigma\Delta H^\circ_{f\,(\text{reactants})}$$
$$= (-202) - (-147) = -55 \text{ kJ}$$
$$\Delta H_{\text{reaction}} = \Sigma\,(\text{BE})_{\text{reactants}} - \Sigma(\text{BE})_{\text{products}}$$

$-55 =$ Heat of sublimation or enthalpy of atomisation of sulphur $-$ BE(S — S)

$-55 = 223 -$ BE(S — S)

BE(S — S) $= 223 + 55 = 278$ kJ

(Common bonds of reactants and products are rejected.)]

4. Standard enthalpies of formation of O_3, CO_2, NH_3 and HI are 142.2, –393.2, – 46.2 and +25.9 kJ mol^{-1} respectively. The order of their increasing stabilities will be:
(a) O_3, CO_2, NH_3, HI (b) CO_2, NH_3, HI, O_3
(c) O_3, HI, NH_3, CO_2 (d) NH_3, HI, CO_2, O_3

[**Hint:** (i) Exothermic compounds are more stable than endothermic compounds.
(ii) Greater is the amount of heat evolved in the formation of a compound, more will be its stability.]

5. Combustion of octane takes place in an automobile engine. The homogeneous equation of combustion is:

$$C_8H_{18}(g) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$$

The signs of ΔH, ΔS and ΔG for the reaction will be:
(a) +ve, –ve, +ve (b) –ve, +ve, –ve
(c) –ve, +ve, +ve (d) +ve, +ve, –ve

6. Which among the following represents the reaction of formation of the product?
(a) $C_{(\text{diamond})} + O_2(g) \longrightarrow CO_2(g)$
(b) $S_{(\text{monoclinic})} + O_2(g) \longrightarrow SO_2(g)$
(c) $2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$
(d) None of the above

7. How much energy must be supplied to change 36 g of ice at 0° C to water at room temperature 25°C?

Data for water	
$\Delta H^\circ_{\text{fusion}}$	6.01 kJ/mol
$C_{p\,\text{liquid}}$	4.18 J K^{-1} g^{-1}

(a) 12 kJ (b) 16 kJ (c) 19 kJ (d) 22 kJ

[**Hint:** $\Delta H = \Delta H_{\text{fusion}}$ of two moles $+ ms\,\Delta T$
$= 6.01 \times 2 + 36 \times 4.18 \times 25 \times 10^{-3}$
≈ 16 kJ]

8. A large positive value of ΔG° corresponds to which of these?
(a) Small positive K (b) Small negative K
(c) Large positive K (d) Large negative K

9. Consider the values for ΔH° (in kJ mol^{-1}) and for ΔS° (in J mol^{-1} K^{-1}) given for four different reactions. For which reaction will ΔG° increase the most (becoming more positive) when the temperature is increased from 0°C to 25°C?
(a) $\Delta H^\circ = 50, \Delta S^\circ = 50$ (b) $\Delta H^\circ = 90, \Delta S^\circ = 20$
(c) $\Delta H^\circ = -20, \Delta S^\circ = -50$ (d) $\Delta H^\circ = -90, \Delta S^\circ = -20$

[**Hint:** Use the relation, $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$]

10.
$$Fe_2O_3(s) + \frac{3}{2}C(s) \longrightarrow \frac{3}{2}CO_2(g) + 2Fe(s); \quad \Delta H^\circ = +234.1 \text{ kJ}$$
$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -393.5 \text{ kJ}$$

Use these equations and ΔH° values to calculate ΔH° for this reaction:

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$

(a) –1648.7 kJ (b) –1255.3 kJ
(c) –1021.2 kJ (d) –129.4 kJ

[**Hint:** $2Fe(s) + \frac{3}{2}CO_2(g) \longrightarrow Fe_2O_3(s) + \frac{3}{2}C(s)$ ...(i)
($\Delta H^\circ = -234.1$ kJ)
$C(s) + O_2(g) \longrightarrow CO_2(g)$ ($\Delta H^\circ = -393.5$ kJ) ...(ii)
Multiplying eq. (i) by 2 and eq. (ii) by 3 and on adding both equations, we get:
$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$;
$\Delta H^\circ = (-234.1 \times 2) + (-3 \times 393.5)$
$= -1648.7$ kJ]

11. Consider this equation and the associated value for ΔH°:

$$2H_2(g) + 2Cl_2(g) \longrightarrow 4HCl(g); \quad \Delta H^\circ = -92.3 \text{ kJ}$$

Which statement about this information is incorrect?
(a) If the equation is reversed, the ΔH° value equals + 92.3 kJ
(b) The four HCl bonds are stronger than four bonds in H_2 and Cl_2
(c) The ΔH° value will be –92.3 kJ if HCl is produced as a liquid
(d) 23.1 kJ of heat will be evolved when 1 mole of HCl(g) is produced

12. If the internal energy of an ideal gas decreases by the same amount as the work done by the system, the process is:
(a) cyclic (b) isothermal (c) adiabatic (d) isolated

13. The enthalpy of neutralization of a strong acid by a strong base is –57.32 kJ mol^{-1}. The enthalpy of formation of water is –285.84 kJ mol^{-1}. The enthalpy of formation of hydroxyl ion is:
(a) +228.52 kJ mol^{-1} (b) –114.26 kJ mol^{-1}
(c) –228.52 kJ mol^{-1} (d) +114.2 kJ mol^{-1}

[**Hint:** The process of neutralization is:

$H^+(aq.) + OH^-(aq.) \longrightarrow H_2O(l); \Delta H^\circ = -57.32\ \text{kJ mol}^{-1}$

$\Delta H_{\text{reaction}} = \Sigma$ Heat of formation of products − Σ Heat of formation of reactants

$$= \Delta H^\circ_{f\,H_2O(l)} - [\Delta H^\circ_{f\,H^+(aq.)} + \Delta H^\circ_{f\,OH^-(aq.)}]$$

$$-57.32 = -285.84 - (0 + x)$$

$$x = -285.84 + 57.32$$

$$= -228.52\ \text{kJ}]$$

14. For which process will ΔH° and ΔG° be expected to be most similar?

(a) $2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$

(b) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq.) + H_2(g)$

(c) $2NO_2(g) \longrightarrow N_2O_4(g)$

(d) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

[**Hint:** (a) In this reaction, $\Delta S^\circ \approx 0$

$\therefore \quad \Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

$\Delta G^\circ \approx \Delta H^\circ$]

15. For a particular reaction, $\Delta H^\circ = -38.3$ kJ and $\Delta S^\circ = -113$ $\text{J K}^{-1}\ \text{mol}^{-1}$. This reaction is:

(a) spontaneous at all temperatures

(b) non-spontaneous at all temperatures

(c) spontaneous at temperatures below 66°C

(d) spontaneous at temperatures above 66°C

[**Hint:** $\Delta G = \Delta H - T\,\Delta S$

For spontaneous process, $\Delta G < 0$.

$$\therefore \quad \Delta H - T\,\Delta S < 0$$

$$\frac{\Delta H}{\Delta S} < T$$

$$\frac{-38.3 \times 1000}{-113} < T$$

i.e., $T > 338.93$ K, *i.e.*, 66° C]

16. Which halogen in its standard state has the greatest absolute entropy per mole?

(a) $F_2(g)$ (b) $Cl_2(g)$ (c) $Br_2(l)$ (d) $I_2(s)$

17. For which of these processes is the value of ΔS negative?

I. Sugar is dissolved in water.

II. Steam condenses on a surface.

III. $CaCO_3$ is decomposed into CaO and CO_2.

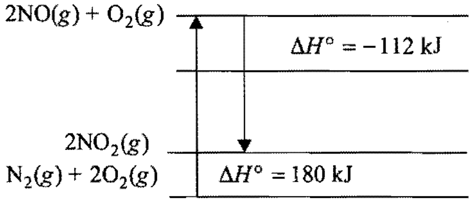
(a) I only (b) II only

(c) I and III only (d) II and III only

18. When solid NH_4NO_3 is dissolved in water at 25°C, the temperature of the solution decreases. What is true about the signs of ΔH and ΔS for this process?

	ΔH	ΔS
(a)	−	+
(b)	−	−
(c)	+	+
(d)	+	−

19. The diagram below shows the heat of reaction between N_2, O_2, NO and NO_2:



Which of the following statements pertaining to the formation of NO and NO_2 are correct?

1. The standard heat of formation of NO_2 is 68 kJ mol^{-1}.
2. NO_2 is formed faster than NO at higher temperature.
3. The oxidation reaction of nitrogen to NO_2 is endothermic.
4. These two reactions often take place in troposphere and causes green house effect.
5. These two reactions often take place and are responsible for city smog.

(a) 1 and 2 (b) 1 and 3 (c) 1 and 4 (d) 3 and 4

(e) 3 and 5

20. The enthalpy changes for two reactions are given by the equations:

$$2Cr(s) + 1\frac{1}{2}O_2(g) \longrightarrow Cr_2O_3(s); \quad \Delta H = -1130\ \text{kJ}$$

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta H = -110\ \text{kJ}$$

What is the enthalpy change, in kJ, for the reaction?

$$3C(s) + Cr_2O_3(s) \longrightarrow 2Cr(s) + 3CO(g)$$

(a) −1460 kJ (b) −800 kJ (c) +800 kJ (d) +1020 kJ

(e) +1460 kJ

[**Hint:** The given equations can be written as:

$$Cr_2O_3(s) \longrightarrow 2Cr(s) + \frac{3}{2}O_2(g); \quad \Delta H = +1130\ \text{kJ}$$

$$3C(s) + \frac{3}{2}O_2(g) \longrightarrow 3CO(g); \quad \Delta H = -330\ \text{kJ}$$

Adding the above equations, we get:

$$Cr_2O_3(s) + 3C(s) \longrightarrow 2Cr(s) + 3CO(g); \quad \Delta H = +800\ \text{kJ}]$$

21. The enthalpy change at 298 K for decomposition is given in the following two steps:

Step I: $H_2O(g) \longrightarrow H(g) + OH(g); \quad \Delta H = 498\ \text{kJ mol}^{-1}$

Step II: $OH(g) \longrightarrow H(g) + O(g); \quad \Delta H = 428\ \text{kJ mol}^{-1}$

The bond enthalpy of the O—H bond is:

(a) 498 kJ mol^{-1} (b) 463 kJ mol^{-1}

(c) 428 kJ mol^{-1} (d) 70 kJ mol^{-1}

22. Consider the following two reactions:

(i) Propene + $H_2 \longrightarrow$ Propane; ΔH_1

(ii) Cyclopropane + $H_2 \longrightarrow$ Propane; ΔH_2

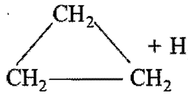
Then, $\Delta H_2 - \Delta H_1$ will be:

(a) 0 (b) $2BE_{C-C} - BE_{C=C}$

(c) $BE_{C=C}$ (d) $2BE_{C=C} - BE_{C-C}$

[**Hint:** $CH_3-CH=CH_2 + H_2 \longrightarrow CH_3-CH_2-CH_3$;

$$\Delta H_1 = (BE_{C=C} + BE_{H-H}) - (2BE_{C-H} + BE_{C-C})$$



$+ H_2 \longrightarrow CH_3-CH_2-CH_3$;

$$\Delta H_2 = (BE_{C-C} + BE_{H-H}) - (2 \times BE_{C-H})$$

$$\Delta H_2 - \Delta H_1 = 2BE_{C-C} - BE_{C=C}\ ]$$

23. Under which circumstances would the free energy change for a reaction be relatively temperature independent?
(a) ΔH° is negative
(b) ΔH° is positive
(c) ΔS° has a large positive value
(d) ΔS° has a small magnitude

24. Use the free energy change, $\Delta G^\circ = +63.3\,\text{kJ}$, for this reaction, to calculate the K_{sp} of $Ag_2CO_3(s)$ in water at 25°C :

$$Ag_2CO_3(s) \rightleftharpoons Ag^+(aq.) + CO_3^{2-}(aq.)$$

(a) 3.2×10^{-26} (b) 8×10^{-12} (c) 2.9×10^{-3} (d) 7.9×10^{-2}

25. Which statement(s) is/are true?
1. S° values for all elements in their states are positive.
2. S° values for all aqueous ions are positive.
3. ΔS° values for all spontaneous reactions are positive.

(a) 1 only (b) 1 and 2 only
(c) 2 and 3 only (d) All of these

26. The enthalpy of a reaction does not depend upon:
(a) the intermediate reaction steps
(b) the temperature of initial and final state of the reaction
(c) the physical states of reactants and products
(d) use of different reactants for the formation of the same product

27. When a solution of 500 mL of 2 M KOH is added to 500 mL of 2 M HCl, then the rise in temperature T_1 is noted. When the same experiment is repeated by mixing 250 mL of each solution, the rise in temperature T_2 is noted:
(a) $T_1 = T_2$ (b) $T_1 = 2T_2$ (c) $T_2 = 2T_1$ (d) $T_1 = 4T_2$

28. The heat of combustion of solid benzoic acid at constant volume is −321.30 kJ at 27°C. The heat of combustion at constant pressure is:
(a) $-321.30 - 300R$ (b) $-321.30 + 300R$
(c) $-321.30 - 150R$ (d) $-321.30 + 900R$

[Hint:

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l),$$

$$\Delta n = 7 - \frac{15}{2} = -\frac{1}{2}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$= -321.30 - \frac{1}{2} \times R \times 300 = -321.30 - 150R]$$

29. $A \longrightarrow B;$ $\Delta U = 40\ \text{kJ mol}^{-1}$

If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy?
(a) More than 40 kJ (b) Zero
(c) Less than 40 kJ (d) 40 kJ

30. For the process, $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$:
(a) $\Delta H = +\text{ve}, \Delta S = +\text{ve}$ (b) $\Delta H = -\text{ve}, \Delta S = +\text{ve}$
(c) $\Delta H = +\text{ve}, \Delta U = -\text{ve}$ (d) $\Delta H = -\text{ve}, \Delta S = -\text{ve}$

31. Match the thermodynamic properties **(List-I)** with their relation **(List-II):**

List-I	**List-II**
A. Free energy change (ΔG°)	(i) $RT \log_e K$
B. Entropy change ΔS°	(ii) $-nFE$
C. ΔH° enthalpy change of a reaction in standard state	(iii) $RT^2\left(\frac{d \ln K}{dT}\right)_P$
D. Standard free energy change (ΔG°)	(iv) $-\left\{\frac{d\,\Delta G}{dT}\right\}_P$

Select the correct answer:

Codes:	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(ii)	(iv)	(iii)	(i)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(i)	(ii)	(iv)	(iii)

32. An ideal gas is allowed to expand under adiabatic conditions. The zero value is of:
(a) ΔT (b) ΔS
(c) ΔG (d) none of these

33. Match the physical changes in **List-I** with their relations given in **List-II:**

List-I	**List-II**
A. ΔG	(i) $\Delta U + P\Delta V$
B. ΔH	(ii) $-nFE$
C. ΔS°	(iii) $-RT \log_e K$
D. ΔG°	(iv) $nR \log_e\left(\frac{V_2}{V_1}\right)$

Select the correct answer from the given codes:

Codes:	A	B	C	D
(a)	(ii)	(i)	(iv)	(iii)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(iii)	(ii)	(i)
(d)	(i)	(ii)	(iv)	(iii)

34. Given the following data:

Substance	**ΔH°(kJ/mol)**	**S°(J/mol K)**	**ΔG°(kJ/mol)**
FeO(s)	−266.3	57.49	−245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	−110.5	197.6	−137.15

Determine at what temperature the following reaction is spontaneous?

$$FeO(s) + C\,(\text{Graphite}) \longrightarrow Fe(s) + CO(g)$$

(a) 298 K
(b) 668 K
(c) 966 K
(d) ΔG° is +ve, hence the reaction will never be spontaneous.

[Hint: $\Delta H_{\text{reaction}} = \Sigma\{\Delta H^\circ_{f\,Fe(s)} + \Delta H^\circ_{f\,CO(g)}\}$

$$-\{\Delta H^\circ_{f\,FeO(s)} + \Delta H^\circ_{f\,C(\text{graphite})}\}$$

$$= (0 - 110.5) - (-266.3 + 0) = 155.8\ \text{kJ mol}^{-1}$$

$$\Delta S_{\text{reaction}} = \Sigma[S^\circ_{Fe(s)} + S^\circ_{CO(g)}] - [S^\circ_{FeO(s)} + S^\circ_{C(\text{graphite})}]$$

$$= (27.28 + 197.6) - (57.49 + 5.74)$$

$$= 161.65\ \text{JK}^{-1}\ \text{mol}^{-1}$$

For spontaneous reaction, $T > \frac{\Delta H}{\Delta S}$; $T > \frac{155.8 \times 1000}{161.65}$

$\therefore \quad T > 966$ K]

35. Which of the following equations has/have enthalpy changes equal to ΔH_{comb} C?

I. $C(s) + O_2(g) \longrightarrow CO_2(g)$

II. $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

III. $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

(a) I and II (b) I, II and III
(c) I and III (d) I only

36. The enthalpy change of which reaction corresponds to ΔH_f° for $Na_2CO_3(s)$ at 298 K?

(a) $2Na(s) + C(s) + \frac{3}{2}O_2(g) \longrightarrow Na_2CO_3(s)$
(b) $Na_2O(s) + CO_2(g) \longrightarrow Na_2CO_3(s)$
(c) $2Na^+(aq.) + CO_3^{2-}(aq.) \longrightarrow Na_2CO_3(s)$
(d) $2Na^+(aq.) + 2OH^-(aq.) + CO_2(aq.) \rightarrow Na_2CO_3(s) + H_2O$

37. Enthalpy is equal to: **(VITEEE 2007)**

(a) $T^2\left[\frac{\partial(G/T)}{\partial T}\right]_P$ (b) $-T^2\left[\frac{\partial(G/T)}{\partial T}\right]_P$

(c) $T^2\left[\frac{\partial(G/T)}{\partial T}\right]_V$ (d) $-T^2\left[\frac{\partial(G/T)}{\partial T}\right]_V$

[**Hint:**

$$G = H - TS \qquad \text{...(i)}$$

$$G = U + PV - TS$$

$$\Delta G = \Delta U + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

From the first and second laws,

$$T\Delta S = \Delta U + P\Delta V$$

$$\therefore \quad \Delta G = V\Delta P - S\Delta T$$

At constant pressure, $\Delta P = 0$

$$\frac{\Delta G}{\Delta T} = -S \qquad \text{...(ii)}$$

From eqs. (i) and (ii),

$$G = H + T\frac{\Delta G}{\Delta T}$$

OR

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$-\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P$$

$$= \left[\frac{\partial(G/T)}{\partial T}\right]_P$$

$$H = -T^2\left[\frac{\partial(G/T)}{\partial T}\right]_P$$]

38. When a bomb calorimeter is used to determine the heat of reaction, which property of the system under investigation is most likely to remain constant?

(a) Number of molecules (b) Pressure
(c) Temperature (d) Volume

39. For the reaction shown, which is closest to the value of ΔH?

$$2Cr^{3+}(aq.) + 3Ni(s) \longrightarrow 2Cr(s) + 3Ni^{2+}(aq.)$$

ΔH_f°	(kJ mol^{-1})
$Cr^{3+}(aq.)$	−143
$Ni^{2+}(aq.)$	−54

(a) 124 kJ (b) 89 kJ
(c) −89 kJ (d) −124 kJ

40. An ice cube at 0.00°C is placed in 200 g of distilled water at 25° C. The final temperature after the ice is completely melted is 5°C. What is the mass of the ice cube?
($\Delta H_{\text{fus}} = 340$ J g^{-1}, $C_p = 4.18$ J g^{-1}°C^{-1})

(a) 23.6 g (b) 46.3 g
(c) 50.0 g (d) 800 g

41. Which reaction occurs with the greatest increase in entropy?

(a) $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$
(b) $2NO(g) \longrightarrow N_2(g) + O_2(g)$
(c) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(d) $Br_2(g) + Cl_2(g) \longrightarrow 2BrCl(g)$

42. The bond dissociation energies for single covalent bonds formed between carbon and A, B, C, D and E atoms are:

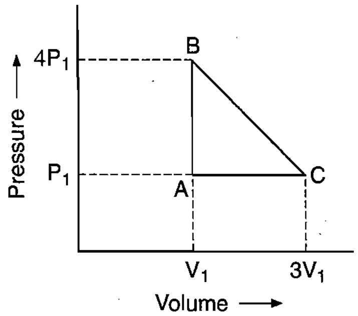
	Bond	Bond energy (kcal mol^{-1})
(i)	C—A	240
(ii)	C—B	382
(iii)	C—D	276
(iv)	C—E	486

This indicates that the smallest atom is:

(a) A (b) B (c) C (d) E

[**Hint:** C—E bond has highest bond energy; it means that the covalent bond C—E will be strongest. Smaller is the size of atom, stronger is the covalent bond.]

43. An ideal gas is taken around the cycle $ABCA$ as:



(a) $12P_1V_1$ (b) $6P_1V_1$ (c) $3P_1V_1$ (d) P_1V_1

[**Hint:** Work done in the cyclic process

$= \text{Area bounded } (ABCA)$

$= \frac{1}{2} \times AC \times AB$

$= \frac{1}{2} \times 2V_1 \times 3P_1 = 3P_1V_1$]

44. One gram mole of graphite and diamond were burnt to form CO_2 gas.

$$C_{(\text{graphite})} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -399.5 \text{ kJ}$$

$$C_{(\text{diamond})} + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -395.4 \text{ kJ}$$

(a) graphite is more stable than diamond
(b) diamond is more stable than graphite
(c) graphite has greater affinity with oxygen
(d) diamond has greater affinity with oxygen

[**Hint:** Thermal stability of one isotope is directly proportional to the heat of combustion.]

45. Which among the following is not an exact differential?
(a) Q (dQ = heat absorbed)
(b) U (dU = change in internal energy)
(c) S (dS = entropy change)
(d) G (dG = Gibbs free energy change)

[**Hint:** Heat 'Q' is a path dependent function, hence its exact differentiation is not possible; however, internal energy, entropy and Gibbs free energy are state functions, hence can be differentiated exactly.]

46. A gas expands adiabatically at constant pressure such that:

$$T \propto \frac{1}{\sqrt{V}}$$

The value of γ, *i.e.*, (C_P / C_V) of the gas will be:
(a) 1.30 (b) 1.50 (c) 1.70 (d) 2

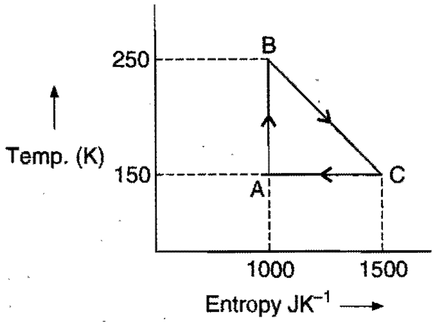
[**Hint:**
$$T \propto \frac{1}{\sqrt{V}}$$
$$TV^{1/2} = \text{constant}$$
For adiabatic process, $TV^{1/2} = TV^{\gamma - 1}$ = constant
$$\therefore \quad \gamma - 1 = \frac{1}{2}, \quad \gamma = \frac{3}{2}]$$

47.
$$2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}; \quad \Delta G^\circ = -616 \text{ J} \quad \ldots \text{(i)}$$
$$2\text{Zn} + \text{S} \longrightarrow 2\text{ZnS}; \quad \Delta G^\circ = -293 \text{ J} \quad \ldots \text{(ii)}$$
$$2\text{S} + 2\text{O}_2 \longrightarrow 2\text{SO}_2(g); \quad \Delta G^\circ = -408 \text{ J} \quad \ldots \text{(iii)}$$

ΔG° for the following reaction:
$$2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$$
would be:
(a) −731 J (b) −1317 J (c) +731 J (d) +1317 J

[**Hint:** $\Delta G^\circ = 2\Delta G^\circ_{\text{ZnO}} + 2\Delta G^\circ_{\text{SO}_2} - 2\Delta G^\circ_{\text{ZnS}}$
$$= [-616 - 408] - [-293]$$
$$= -1024 + 293$$
$$= -731 \text{ J}]$$

48. The efficiency of the reversible cycle shown in the figure will be:
(a) 33.33% (b) 56% (c) 66% (d) 25%



[**Hint:** Efficiency of cycle $= \dfrac{\text{Area of closed cycle}}{\text{Area under the curve}} \times 100$

$$= \frac{\frac{1}{2} \times (1500 - 1000) \times (250 - 150)}{\frac{1}{2} \times (1500 - 1000) \times (250 - 150) + (1500 - 1000) \times (150 - 0)} \times 100$$
$$= \frac{\frac{1}{2} \times 500 \times 100}{\frac{1}{2} \times 500 \times 100 + 500 \times 150} \times 100$$
$$= \frac{500 \times 50 \times 100}{500 \times 50 + 500 \times 150} = 25]$$

49. In Haber's process of ammonia manufacture:
$$\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g);$$
$\Delta H^\circ_{25^\circ\text{C}} = -92.2$ kJ

Molecules	$\text{N}_2(g)$	$\text{H}_2(g)$	$\text{NH}_3(g)$
C_P J K^{-1} mol^{-1}	29.1	28.8	35.1

If C_P is independent of temperature, then reaction at 100°C as compared to that of 25°C will be:
(a) more endothermic (b) less endothermic
(c) more exothermic (d) less exothermic

[**Hint:** Use: $\dfrac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$]

50. Consider the following statements:
I. Change in enthalpy is always smaller than change in internal energy.
II. The variation in enthalpy of a reaction with temperature is given by Kirchhoff's equation.
III. The entropy change in reversible adiabatic process is equal to zero.

Select the correct answer:
(a) I and II (b) II and III
(c) III and I (d) all are correct

51. In C_2H_4, energy of formation of (C=C) and (C—C) are −145 kJ/mol and −80 kJ/mol respectively. What is the enthalpy change when ethylene polymerises to form polythene? **[JEE (Orissa) 2006]**
(a) +650 kJ/mol (b) +65 kJ/mol
(c) −650 kJ mol^{-1} (d) −65 kJ mol^{-1}

[**Hint:** Polymerisation of ethene may be given as:
$$n\text{CH}_2{=}\text{CH}_2 \longrightarrow \text{-(}\text{CH}_2{-}\text{CH}_2\text{)-}_n$$
$$\Delta H = \Sigma(\text{BE})_{\text{reaetants}} - \Sigma(\text{BE})_{\text{products}}$$
$$= (+145) - (+80) = +65 \text{ kJ/mol}]$$

[**Note:** C—H bonds are common in both reactants and products.]

52. If 150 kJ of energy is needed for muscular work to walk a distance of 1 km, then how much of glucose one has to consume to walk a distance of 5 km, provided only 30% of energy is available for muscular work. The enthalpy of combustion of glucose is 3000 kJ mol^{-1}: **[PMT (Kerala) 2007]**
(a) 75 g (b) 30 g (c) 180 g (d) 150 g
(e) 45 g

53. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is:
(Given, $\Delta_r H^\circ_{298\text{K}} = -54.07$ kJ mol^{-1},
$\Delta_r S^\circ_{298\text{K}} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ J K^{-1} mol^{-1};
$2.303 \times 8.314 \times 298 = 5705$) **(IIT 2007)**
(a) 5 (b) 10 (c) 95 (d) 100

[**Hint:** $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -54.07 \times 1000 - 298 \times 10$

$= -57050$ J

$\Delta G^\circ = -2.303\, RT \log_{10} K$

$-57050 = -5705 \log_{10} K$

$\log_{10} K = 10$]

54. The lattice enthalpy and hydration enthalpy of four compounds are given below :

Compound	Lattice enthalpy (kJ/mol)	Hydration enthalpy (kJ/mol)
P	+ 780	− 920
Q	+ 1012	− 812
R	+ 828	− 878
S	+ 632	− 600

The pair of compounds which is soluble in water is : **[PET (Kerala) 2008]**

(a) P and Q (b) Q and R (c) R and S (d) Q and S
(e) P and R

[**Hint :** For solubility of ionic compounds, hydration energy must be greater than lattice energy.]

Following questions may have more than one correct options :

1. Which of the following are correct about irreversible isothermal expansion of ideal gas ?

(a) $W = -q$ (b) $\Delta U = 0$
(c) $\Delta T = 0$ (d) $W = -nRT \ln \dfrac{P_1}{P_2}$

2. The work done during adiabatic expansion or compression of an ideal gas is given by :

(a) $n\, C_V\, \Delta T$ (b) $\dfrac{nR}{(\gamma - 1)}(T_2 - T_1)$
(c) $-nR\, P_{\text{ext}} \left[\dfrac{T_2P_1 - T_1P_2}{P_1P_2}\right]$ (d) $-2.303\, RT \log \dfrac{V_2}{V_1}$

3. For an ideal gas $\left(\dfrac{C_{Pm}}{C_{Vm}} = \gamma\right)$; of molar mass M, its specific heat capacity at constant volume is :

(a) $\dfrac{\gamma R}{(\gamma - 1)M}$ (b) $\dfrac{\gamma}{M(\gamma - 1)}$ (c) $\dfrac{M}{R(\gamma - 1)}$ (d) $\dfrac{\gamma RM}{\gamma - 1}$

[**Hint :** $\dfrac{C_{Pm}}{C_{Vm}} = \gamma,\ C_{Pm} - C_{Vm} = R$

$C_{Vm} = \dfrac{R}{\gamma - 1}$ and $C_{Pm} = \dfrac{R\gamma}{\gamma - 1}$

$\dfrac{\gamma}{\gamma - 1} = C_{Vm} \times M$

$C_{Vm} = \dfrac{x}{M(\gamma - 1)}$]

Answers

- **Single correct option**

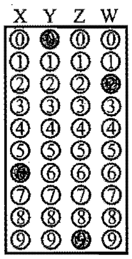
1. (c) **2.** (d) **3.** (c) **4.** (c) **5.** (b) **6.** (d) **7.** (b) **8.** (a)
9. (c) **10.** (a) **11.** (c) **12.** (c) **13.** (c) **14.** (a) **15.** (d) **16.** (b)
17. (b) **18.** (c) **19.** (e) **20.** (c) **21.** (b) **22.** (b) **23.** (d) **24.** (b)
25. (a) **26.** (a) **27.** (a) **28.** (c) **29.** (b) **30.** (d) **31.** (b) **32.** (d)
33. (a) **34.** (c) **35.** (d) **36.** (a) **37.** (b) **38.** (d) **39.** (a) **40.** (b)
41. (a) **42.** (d) **43.** (c) **44.** (a) **45.** (a) **46.** (b) **47.** (a) **48.** (d)
49. (d) **50.** (b) **51.** (b) **52.** (d) **53.** (b) **54.** (e)

- **One or more than one correct options**

1. (a,b,c,d) **2.** (a,b,c) **3.** (b)

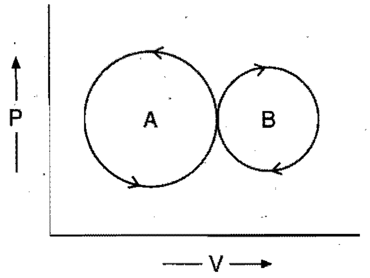
Integer Answer TYPE QUESTIONS

This section contains 11 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. A bubble of 8 moles of helium is submerged at certain depth in water. The temperature of water increases by 30°C. How much heat is added approximately to helium (in kJ) during expansion?
2. For a liquid, enthalpy of fusion is 1.435 kcal mol^{-1} and molar entropy change is 5.26 cal $\text{mol}^{-1}\ \text{K}^{-1}$. The freezing point of liquid in celcius will be :
3. For the reaction, $\text{Ag}_2\text{O}(s) \rightleftharpoons 2\text{Ag}(s) + \frac{1}{2}\text{O}_2(g)$

   $\Delta H, \Delta S$ and T are 40.63 kJ mol^{-1}, 108.8 J $\text{K}^{-1}\ \text{mol}^{-1}$ and 373.4 K respectively. Free energy change ΔG of the reaction will be:
4. Standard Gibbs Free energy change $\Delta G°$ for a reaction is zero. The value of equilibrium constant of the reaction will be:
5. $\Delta G°$ for the reaction $x + y \rightleftharpoons z$ is -4.606 kcal. The value of equilibrium constant of the reaction at 227°C is $(x \times 10^2)$. The value of 'x' is :
6. 4.48 L of an ideal gas at STP requires 12 cal to raise the temperature by 15°C at constant volume. The C_P of the gas is .... cal.
7.



In the present graph, the area of circle A and B are 25 unit and 20 unit respectively. Work done will be .... unit.

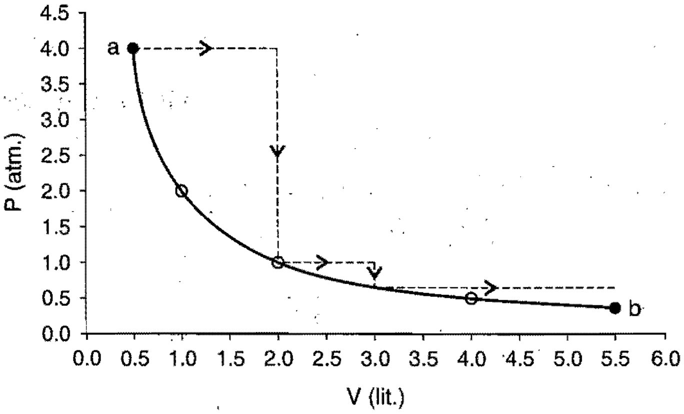
8. For the reaction,

   $$\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$$

   Heat of reaction at constant volume exceeds the heat of reaction at constant pressure by the value of xRT. The value of x is :
9. Gas (A_x) has the ratio of specific heat, equal to 1.66. The value of x will be :
10. For a liquid the vapour pressure is given by :

    $$\log_{10} P = \frac{-400}{T} + 10$$

    Vapour pressure of the liquid is 10^x mm Hg. The value of x will be :
11. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d, then the integer closest to the ratio w_d / w_s is:



(IIT 2010)

[**Hint :** w_d = work done along dotted line

$$= \Sigma P\Delta V$$

$$= 4 \times 1.5 + 1 \times 1 + 2.5 \times \frac{2}{3} = 8.65 \text{ L atm}$$

w_s = It is reversible isothermal process

$$= 2.303 nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times (PV) \log\left(\frac{V_2}{V_1}\right)$$

$$= 2.303 \times 2 \log\frac{5.5}{0.5} = 4.79 \text{ L atm}$$

$$\frac{w_d}{w_s} = \frac{8.65}{4.79} \approx 2 \text{]}$$

Answers

1. (3)	2. (0)	3. (0)	4. (1)	5. (1)	6. (6)	7. (5)	8. (2)
9. (1)	10. (9)	11. (2)					

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

Chemical reactions are invariably associated with the transfer of energy either in the form of heat or light. In the laboratory, heat changes in physical and chemical processes are measured with an instrument called calorimeter. Heat change in the process is calculated as:

$$q = ms\,\Delta T; \quad s = \text{Specific heat}$$
$$= c\Delta T; \quad c = \text{Heat capacity}$$

Heat of reaction at constant volume is measured using bomb calorimeter.

$$q_V = \Delta U = \text{Internal energy change}$$

Heat of reaction at constant pressure is measured using simple or water calorimeter.

$$q_P = \Delta H$$
$$q_P = q_V + P\,\Delta V$$
$$\Delta H = \Delta U + \Delta nRT$$

The amount of energy released during a chemical change depends on the physical state of reactants and products, the condition of pressure, temperature and volume at which the reaction is carried out. The variation of heat of reaction with temperature and pressure is given by Kirchhoff's equation:

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P \quad ; \quad \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V$$

(At constant pressure) *(At constant volume)*

Answer the following questions:

1. Match the **List-I** with **List-II** and select the answer from the given codes:

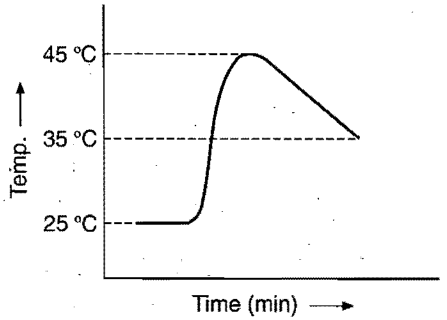
List-I	List-II
A. $C(s) + O_2(g) \longrightarrow CO_2(g)$	1. $\Delta H = \Delta U + RT$
B. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	2. $\Delta H = \Delta U$
C. $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$	3. $\Delta H = \Delta U - 2RT$
D. $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$	4. $\Delta H = \Delta U + 2RT$
E. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	5. $\Delta H = \Delta U - RT$

Codes:	A	B	C	D	E
(a)	1	2	3	4	5
(b)	5	2	3	4	1
(c)	1	3	4	2	5
(d)	2	3	4	1	5

2. The heat capacity of a bomb calorimeter is 500 J/K. When 0.1 g of methane was burnt in this calorimeter, the temperature rose by 2°C. The value of ΔU per mole will be:
(a) +1 kJ (b) −1 kJ (c) +160 kJ (d) −160 kJ

3. For which reaction will $\Delta H = \Delta U$? Assume each reaction is carried out in an open container:
(a) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$
(b) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
(c) $C(s) + 2H_2O(g) \longrightarrow 2H_2(g) + CO_2(g)$
(d) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

4. What value of ΔT should be used for the calorimetry experiment that gives the following graphical results?



(a) 10°C (b) 25°C (c) 20°C (d) 35°C

5. The enthalpy of fusion of ice is 6.02 kJ mol^{-1}. The heat capacity of water is 4.18 J g^{-1} C^{-1}. What is the smallest number of ice cubes at 0°C, each containing one mole of water, that are needed to cool 500 g of liquid water from 20°C to 0°C?
(a) 1 (b) 7 (c) 14 (d) 125
[**Hint:** Heat released to cool 500 g water from 20°C to 0°C,
$$q = ms\,\Delta T$$
$$= 500 \times 4.18 \times 20 = 41800\ \text{J} = 41.8\ \text{kJ}$$
Number of moles of water (ice) that will melt to absorb 41.8 kJ
$$= \frac{41.8}{6.02} \approx 7$$
∴ Number of cubes of ice that will melt = 7]

6. The enthalpy change (ΔH) for the reaction,
$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$
is −92.38 kJ at 298 K. The internal energy change ΔU at 298 K is: **(AIIMS 2006)**
(a) −92.38 kJ (b) −87.42 kJ (c) −97.34 kJ (d) −89.9 kJ
[**Hint:** $\Delta n_g = 2 - 4 = -2$
$$\Delta H = \Delta U + \Delta n_g RT$$
$$\Delta U = \Delta H - \Delta n_g RT$$
$$= -92.38 \times 1000 - (-2) \times 8.314 \times 298$$
$$= -87424\ \text{J} = -87.424\ \text{kJ}]$$

7. The specific heat of I_2 in vapour and solid state are 0.031 and 0.055 cal/g respectively. The heat of sublimation of iodine at 200°C is 6.096 kcal mol^{-1}. The heat of sublimation of iodine at 250°C will be:
(a) 3.8 kcal mol^{-1} (b) 4.8 kcal mol^{-1}
(c) 2.28 kcal mol^{-1} (d) 5.8 kcal mol^{-1}
[**Hint:** $I_2(s) \rightleftharpoons I_2(g)$
$$\Delta C_P = (0.031 - 0.055) \times 10^{-3} \times 254$$
$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$
$$\frac{\Delta H_2 - 6.096}{50} = (0.031 - 0.055) \times 10^{-3} \times 254$$
$$\Delta H_2 = 5.79\ \text{kcal mol}^{-1}]$$

• Passage 2

In a chemical reaction, the bonds of reactants are decomposed and new bonds of products are formed. The amount of energy required to break a particular bond in a gaseous molecule under standard conditions homolytically is called the standard bond dissociation enthalpy of that bond (ΔH°_{A-B}).

Bond energies can be used to obtain an approximate value for a reaction enthalpy of a gas phase reaction if the appropriate enthalpies of formation are not available.

$$\Delta H^{\circ}_{\text{reaction}} = \Sigma \textit{ Bond energy of bonds, broken in the reactants}$$
$$- \Sigma \textit{ Bond energy of bonds, formed in the products}$$

Bond energy depends on three factors:

(*a*) *Greater is the bond length, lesser is the bond energy.*
(*b*) *Bond energy increases with the bond multiplicity.*
(*c*) *Bond energy increases with the electronegativity difference between the bonding atoms.*

Answer the following questions:

1. Arrange N—H, O—H and F—H bonds in the decreasing order of bond energy:
(a) F—H > O—H > N—H (b) O—H > N—H > F—H
(c) N—H > O—H > F—H (d) F—H > N—H > O—H

2. X_2 represents halogen molecule. Bond energy of different halogen molecules will lie in following sequences:
(a) $F_2 > Cl_2 > Br_2 > I_2$ (b) $Cl_2 > Br_2 > F_2 > I_2$
(c) $I_2 > Cl_2 > Br_2 > I_2$ (d) $Br_2 > F_2 > I_2 > Cl_2$
[**Hint:** Bond energy of F_2 is surprisingly low due to strong repulsion between the lone pairs of two fluorine atoms.]

3. Which among the following sequences is correct about the bond energy of C—C, C=C and C≡C bonds?
(a) $C\equiv C > C=C > C-C$ (b) $C\equiv C < C=C < C-C$
(c) $C=C > C\equiv C > C-C$ (d) $C\equiv C > C-C > C=C$

4. In CH_4 molecule, which of the following statements is correct about the C—H bond energy?
(a) All C—H bonds of methane have same energy
(b) Average of all C—H bond energies is considered
(c) Fourth C—H bond requires highest energy to break
(d) None of the above

5. Use the bond energies to estimate ΔH for this reaction:

$$H_2(g) + O_2(g) \longrightarrow H_2O_2(g)$$

Bond	Bond energy
H—H	436 kJ mol^{-1}
O—O	142 kJ mol^{-1}
O=O	499 kJ mol^{-1}
H—O	460 kJ mol^{-1}

(a) −127 kJ (b) −209 kJ (c) −484 kJ (d) −841 kJ

6. The heat of formation of NO from its elements is +90 kJ mol^{-1}. What is the approximate bond dissociation energy of the bond in NO?

$$BE_{N\equiv N} = 941 \text{ kJ mol}^{-1} \quad BE_{O=O} = 499 \text{ kJ mol}^{-1}$$

(a) 630 kJ mol^{-1} (b) 720 kJ mol^{-1}
(c) 760 kJ mol^{-1} (d) 810 kJ mol^{-1}

• Passage 3

The change in Gibbs free energy (ΔG) *of the system alone provides a criterion for the spontaneity of a process at constant temperature and pressure. A change in the free energy of a system at constant temperature and pressure will be:*

$$\Delta G_{system} = \Delta H_{system} - T\,\Delta S_{system}$$

At constant temperature and pressure:

$$\Delta G_{system} < 0 \,(\textit{spontaneous})$$
$$\Delta G_{system} = 0 \,(\textit{equilibrium})$$
$$\Delta G_{system} > 0 \,(\textit{non-spontaneous})$$

Free energy is related to the equilibrium constant, as:

$$\Delta G^{\circ} = 2.303RT \log_{10} K_e$$

Answer the following questions:

1. The free energy for a reaction having $\Delta H = 31400$ cal, $\Delta S = 32 \text{ cal K}^{-1} \text{ mol}^{-1}$ at 1000°C is: **[JEE (Orissa) 2005]**
(a) −9336 cal (b) −7386 cal (c) −1936 cal (d) +9336 cal

2. For a spontaneous reaction ΔG, equilibrium 'K' and E°_{cell} will be respectively: **(AIEEE 2005)**
(a) −ve, > 1, +ve (b) +ve, > 1, −ve
(c) −ve, < 1, −ve (d) −ve, > 1, −ve

3. For a system in equilibrium, $\Delta G = 0$, under conditions of constant........: **(KCET 2005)**
(a) temperature and pressure (b) temperature and volume
(c) pressure and volume (d) energy and volume

4. If both ΔH and ΔS are negative, the reaction will be spontaneous:
(a) at high temperature (b) at low temperature
(c) at all temperatures (d) at absolute zero

5. A reaction has positive values of ΔH and ΔS. From this you can deduce that the reaction:
(a) must be spontaneous at any temperature
(b) cannot be spontaneous at any temperature
(c) will be spontaneous only at low temperature
(d) will be spontaneous only at high temperature

6. For a reaction to be spontaneous at all temperatures:
(a) ΔG − ve, ΔH + ve and ΔS + ve
(b) ΔG + ve, ΔH − ve and ΔS + ve
(c) ΔG − ve, ΔH − ve and ΔS − ve
(d) ΔG − ve, ΔH − ve and ΔS + ve

3 *moles of* CO_2 *gas expands isothermally against external pressure of* 1 *bar. Volume increases from* 10 *L to* 30 *L respectively. The system is in thermal contact of surroundings at temperature* 15°C. *Entropy change in isothermal process is:*

$$\Delta S = 2.303\, nR \log\left(\frac{V_2}{V_1}\right)$$

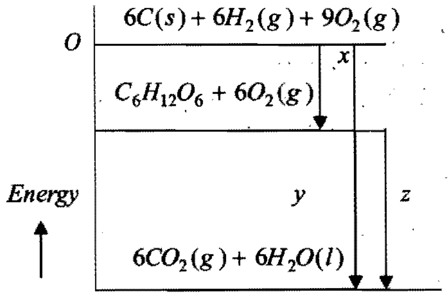
Answer the following questions:

7. If CO_2 behaves like an ideal gas, then entropy change of system (ΔS_{system}) will be:
(a) +27.4 J K^{-1} (b) 9.1 J K^{-1}
(c) −27.4 J K^{-1} (d) −9.1 J K^{-1}

8. Select the correct relation:
(a) $\Delta S_{\text{system}} > 0, \Delta S_{\text{surr.}} = 0$ (b) $\Delta S_{\text{surr.}} < 0, \Delta S_{\text{system}} > 0$
(c) $\Delta S_{\text{system}} = 0, \Delta S_{\text{surr.}} = 0$ (d) $\Delta S_{\text{surr.}} > 0, \Delta S_{\text{system}} < 0$

• Passage 4

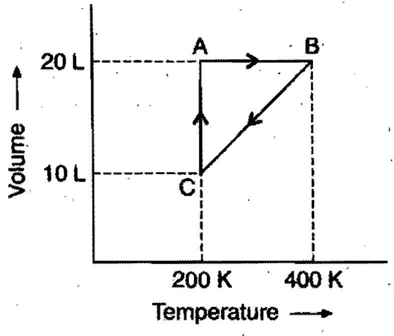
Consider the following energy level diagram:



Answer the following questions on the basis of the given diagram:

1. The heat of formation of glucose is:
   (a) $-x$ (b) $-y$ (c) $x - y$ (d) $-x + z$
2. In the given diagram z refers to:
   (a) $6 \times \Delta H^\circ_{f\,CO_2}$ (b) $\Delta H^\circ_{f\,C_6H_{12}O_6}$
   (c) $\Delta H^\circ_{\text{combustion } C_6H_{12}O_6}$ (d) $\Delta H^\circ_{\text{combustion } C(s)} + \Delta H^\circ_{f\,H_2O(l)}$
3. The quantity y is equal to:
   (a) $\Delta H_{\text{combustion } C(s)} + \Delta H_{\text{combustion } H_2(g)}$
   (b) $x + z$
   (c) $x - z$
   (d) $\Delta H_{f\,CO_2} + \Delta H_{H_2O}$
4. Select the incorrect statement(s):
   (a) combustion of glucose is exothermic process
   (b) standard state of glucose is $C_6H_{12}O_6(s)$
   (c) heat of formation of glucose = Heat of combustion of glucose
   (d) $x + y = z$

• Passage 5



Graph for one mole gas

Answer the following questions based on the above diagram:

1. Process, $A \longrightarrow B$ represents:
   (a) isobaric (b) isochoric (c) isothermal (d) adiabatic
2. The pressure at C is:
   (a) 3.284 atm (b) 1.642 atm (c) 0.0821 atm (d) 0.821 atm
3. Work done in the process $C \longrightarrow A$ is:
   (a) zero (b) 8.21 L atm
   (c) 16.2 L atm (d) unpredictable
4. The process which occurs in going from, $B \longrightarrow C$ is:
   (a) isothermal (b) adiabatic (c) isobaric (d) isochoric
5. The pressures at A and B in the atmosphere are respectively:
   (a) 0.821 and 1.642 (b) 1.642 and 0.821
   (c) 1 and 2 (d) 0.082 and 0.164

• Passage 6

The thermodynamic property that measures the extent of molecular disorder is called entropy. The direction of a spontaneous process for which the energy is constant is always the one that increases the molecular disorder. Entropy change of phase transformation can be calculated using Trouton's formula $\left(\Delta S = \dfrac{\Delta H}{T}\right)$. *In the reversible adiabatic process, however, ΔS will be zero. The rise in temperature in isobaric and isochoric conditions is found to increase the randomness or entropy of the system.*

$$\Delta S = 2.303C\ log\ (T_1 / T_2)$$
$$C = C_P\ or\ C_V$$

Answer the following questions:

1. The entropy change in an adiabatic process is:
   (a) zero
   (b) always positive
   (c) always negative
   (d) sometimes positive and sometimes negative
2. If, water in an insulated vessel at $-10°C$, suddenly freezes, the entropy change of the system will be:
   (a) $+10\ J\ K^{-1}\ mol^{-1}$
   (b) $-10\ J\ K^{-1}\ mol^{-1}$
   (c) zero
   (d) equal to that of surroundings
3. The melting point of a solid is 300 K and its latent heat of fusion is 600 cal mol^{-1}. The entropy change for the fusion of 1 mole of the solid (in cal K^{-1}) at the same temperature would be:
   (a) 200 (b) 2 (c) 0.2 (d) 20
4. For which of the following cases $\Delta S = \dfrac{\Delta H}{T}$?
   (a) A process for which $\Delta C_P = 0$ but $\Delta C_V = 0$
   (b) An adiabatic process
   (c) An isobaric or isothermal process
   (d) An isothermal reversible phase transition process
5. When 1 mol of an ideal gas is compressed to half of its volume, its temperature becomes double; then the change in entropy (ΔS) would be:
   (a) $C_V\ \ln 2$ (b) $C_P\ \ln 2$
   (c) $C_V\ R\ \ln 2$ (d) $(C_V - R)\ln 2 \times C_P$

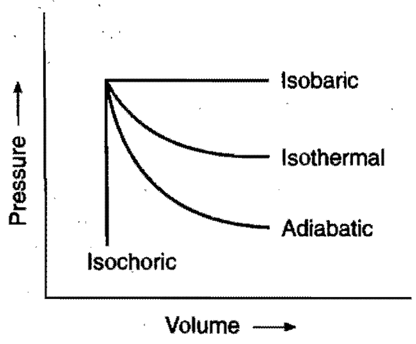
   [Hint: $\Delta S = 2.303 C_P \log_{10}\left(\dfrac{V_1}{V_2}\right)$

   $= C_P \ln\left(\dfrac{V_1}{V_2}\right) = C_P \ln_e\left(\dfrac{1}{1/2}\right)$

   $= C_P \ln_e 2$]

• Passage 7

The pressure-volume behaviour of various thermodynamic processes is shown in graphs:



Work is the mode of transference of energy. If the system involves gaseous substance and there is difference of pressure between system and surroundings, such a work is referred to as pressure-volume work ($w_{PV} = -P_{ext}\,\Delta V$)*. It has been observed that reversible work done by the system is the maximum obtainable work.*

$$w_{rev} > w_{irr}$$

The works of isothermal and adiabatic processes are different from each other.

$$w_{isothermal\ reversible} = 2.303nRT\log_{10}\left(\frac{V_2}{V_1}\right) = 2.303nRT\log_{10}\left(\frac{P_1}{P_2}\right)$$

$$w_{adiabatic\ reversible} = C_V(T_1 - T_2)$$

Answer the following questions:

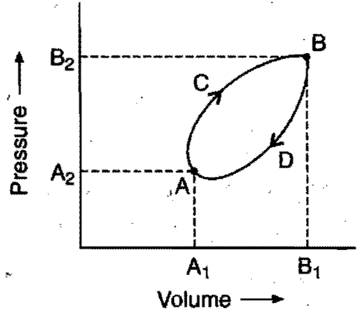
1. If w_1, w_2, w_3 and w_4 are work done in isothermal, adiabatic, isobaric and isochoric reversible processes, then the correct sequence (for expansion) would be:

   (a) $w_1 > w_2 > w_3 > w_4$ (b) $w_3 > w_2 > w_1 > w_4$

   (c) $w_3 > w_2 > w_4 > w_1$ (d) $w_3 > w_1 > w_2 > w_4$

   [**Hint:** w = Work done = Area under curve.]

2. A thermodynamic system goes in acyclic process as represented in the following P-V diagram:



The net work done during the com[illegible] cycle is given by the area:

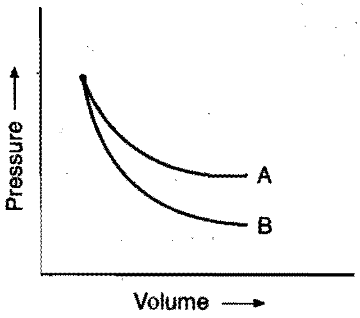
(a) cycle $ACBDA$

(b) AA_1B_1BDA

(c) AA_2B_2B

(d) half of area bounded by curve

3. $P-V$ plots for two gases during adiabatic processes are given in the given figure:



Plot A and plot B should correspond to:

(a) He and O_2 (b) He and Ar (c) O_2 and He (d) O_2 and F_2

[**Hint:** Slope of the adiabatic curve $\propto \gamma$

Slope of B > Slope of A

He ($\gamma = 1.66$); O_2 ($\gamma = 1.44$)

Thus, correct answer will be (c).]

4. The q value and work done in isothermal reversible expansion of one mole of an ideal gas from initial pressure of 1 bar to final pressure of 0.1 bar at constant temperature 273 K are:

   (a) 5.22 kJ, –5.22 kJ (b) –5.22 kJ, 5.22 kJ

   (c) 5.22 kJ, 5.22 kJ (d) –5.22 kJ, –5.22 kJ

   [**Hint:** $w = -2.303nRT\log\left(\frac{P_1}{P_2}\right)$

   $= -2.303 \times 1 \times 8.314 \times 273\log\left(\frac{1}{0.1}\right)$

   $= -5.227$ kJ

   $q = -w = +5.227$ kJ for isothermal process]

5. Calculate work done when 1 mole of an ideal gas is expanded reversibly from 20 L to 40 L at a constant temperature of 300 K.

   (a) 7.78 kJ (b) –1.73 kJ (c) 11.73 kJ (d) – 4.78 kJ

Answers

Passage 1.	**1.** (d)	**2.** (d)	**3.** (b)	**4.** (c)	**5.** (b)	**6.** (b)	**7.** (d)	
Passage 2.	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (b)	**5.** (a)	**6.** (a)		
Passage 3.	**1.** (a)	**2.** (a)	**3.** (a)	**4.** (c)	**5.** (d)	**6.** (d)	**7.** (a)	**8.** (b)
Passage 4.	**1.** (a)	**2.** (c)	**3.** (b)	**4.** (c, d)				
Passage 5.	**1.** (b)	**2.** (b)	**3.** (b)	**4.** (c)	**5.** (a)			
Passage 6.	**1.** (a)	**2.** (c)	**3.** (b)	**4.** (d)	**5.** (b)			
Passage 7.	**1.** (d)	**2.** (a)	**3.** (c)	**4.** (a)	**5.** (b)			

SELF ASSESSMENT

ASSIGNMENT NO. 7

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. Reaction of silica with mineral acids may be given as:

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O; \quad \Delta H = -10.17$ kcal

$SiO_2 + 4HCl \longrightarrow SiCl_4 + 2H_2O; \quad \Delta H = +36.7$ kcal

which among the following is correct?

(a) HF and HCl both will react with silica

(b) Only HF will react with silica

(c) Only HCl will react with silica

(d) Neither HF nor HCl will react with silica

[**Hint:** Exothermic reactions are spontaneous]

2. In Mayer's relation,

$$C_P - C_V = R$$

'R' stands for:

(a) translational kinetic energy of 1 mol gas

(b) rotational kinetic energy of 1 mol gas

(c) vibrational kinetic energy of 1 mol gas

(d) work done to increase the temperature of 1 mol gas by one degree

[**Hint:** $PV = RT$ (For 1 mol gas) ...(i)

$P(V + \Delta V) = R(T + 1)$ ...(ii)

From eqs. (i) and (ii)

$P\Delta V = R$

i.e., $W = R$ (work done)]

3. For an ideal gas, the Joule-Thomson coefficient is:

(a) zero (b) positive

(c) negative (d) depends on atomicity of gas

4. Entropy change in reversible adiabatic process is:

(a) infinite (b) zero

(c) equal to $C_V \Delta T$ (d) equal to $nR \ln \left(\frac{V_2}{V_1}\right)$

5. For a process to be in equilibrium, it is necessary that:

(a) $\Delta S_{\text{system}} = \Delta S_{\text{surr.}}$ (b) $\Delta S_{\text{system}} = -\Delta S_{\text{surr.}}$

(c) $\Delta S_{\text{system}} = 0$ (d) $\Delta S_{\text{surr.}} = 0$

6. Predict the sign of ΔS for each of the following processes, which occur at constant temperature:

I. The volume of 2 mol of $O_2(g)$ increases from 44L to 54L

II. The pressure of 2 mol of $O_2(g)$ increases from 1 atm to 1.2 atm.

	I	II
(a)	$\Delta S = -$ ve	$\Delta S = -$ ve
(b)	$\Delta S = -$ ve	$\Delta S = +$ ve
(c)	$\Delta S = +$ ve	$\Delta S = -$ ve
(d)	$\Delta S = +$ ve	$\Delta S = +$ ve

7. Which of the following statements must be true for the entropy of a pure solid to be zero?

I. The temperature must be zero kelvin

II. The solid must be perfectly crystalline

III. The solid must be an element

IV. The solid must be ionic

(a) I (b) I and II

(c) I, II and III (d) All are correct

8. Which of the following statements is correct?

(a) Slope of adiabatic $P-V$ curve is smaller than that in isothermal one

(b) Slope of adiabatic $P-V$ curve will be same as that in isothermal one

(c) Slope of adiabatic $P-V$ curve will be larger than in isothermal one

(d) Slope of adiabatic $P-V$ curve will be zero

9. $\left(\frac{\partial H}{\partial P}\right)_T$ for an ideal gas is equal to:

(a) zero (b) $\frac{\Delta VRT}{P}$ (c) $\frac{P\Delta V}{T}$ (d) $nR\Delta T$

10. A refrigerator is used to remove heat from enclosure at 0° C at the rate of 600 watt. If the surroundings temperature is 30° C, calculate the power needed:
(a) 303 watt (b) 11000 watt
(c) 65.9 watt (d) 110 watt

SECTION-II

Multiple Answers Type Objective Questions

11. ΔU will be zero for which processes?
(a) Cyclic process (b) Isothermal expansion
(c) Isochoric process (d) Adiabatic process

12. If x and y are two intensive variables then:
(a) xy is an intensive variable
(b) $\frac{x}{y}$ is an intensive variable
(c) $(x + y)$ is an intensive variable
(d) $\frac{dx}{dy}$ is an extensive property

13. Which of the following expressions is/are correct for an adiabatic process?
(a) $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$ (b) $\frac{P_2}{P_1} = \left(\frac{T_1}{T_2}\right)^{\gamma - 1/\gamma}$
(c) $P_2V_2^{\gamma} = P_1V_1^{\gamma}$ (d) $P_1V_1^{\gamma - 1} = P_2V_2^{\gamma - 1}$

14. Select the state functions among the following:
(a) temperature (b) entropy
(c) work (d) enthalpy

15. Select the correct expressions among the following:
(a) $\frac{\Delta G - \Delta H}{T} = \left(\frac{\partial \Delta G}{\partial T}\right)_P$ (b) $\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T}\right]_V$
(c) $\frac{\Delta S}{nF} = \left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_P$ (d) $\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_{T/C_P}$

16. Which of the following are correct for an ideal gas?
(a) $\left(\frac{\partial U}{\partial V}\right)_T = 0$ (b) $\left(\frac{\partial H}{\partial P}\right)_T = 0$
(c) $\left(\frac{\partial T}{\partial P}\right)_H = 0$ (d) $\left(\frac{\partial P}{\partial T}\right)_V = 0$

17. The Clausius-Clapeyron equation may be given as:
(a) $\log_{10}\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$
(b) $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$
(c) $\frac{dP}{dT} = \frac{q}{T\Delta V}$
(d) $\frac{dP}{dT} = \frac{\Delta V}{\Delta S}$

18. Which of the following is/are not state function?
(a) q (b) $q - w$
(c) $\frac{q}{w}$ (d) $q + w$

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

19. **Statement-1:** Most of the combustion reactions are exothermic.

Because

Statement-2: Products are more stable than reactants in exothermic process.

20. **Statement-1:** There is no exchange in internal energy in a cyclic process.

Because

Statement-2: In a cyclic process, the system returns to original state in a number of steps.

21. **Statement-1:** The value of enthalpy of neutralization of weak acid and strong base is always numerically less than 57.1 kJ.

Because

Statement-2: All the OH^- ions furnished by 1 gram equivalent of strong base are not completely neutralized.

22. **Statement-1:** Heat of solution is positive when $Na_2SO_4 \cdot 10H_2O$ is dissolved in water but it is negative when anhydrous $CuSO_4$ is dissolved in water.

Because

Statement-2: Molar masses of $Na_2SO_4.10H_2O$ and $CuSO_4$ are different.

23. **Statement-1:** The extensive property of a single pure substance depends upon the number of moles of the substance present.

Because

Statement-2: Any extensive property expressed per mole becomes intensive.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○ q	○ r	●
b	○ p	●	●	○ s
c	●	●	○ r	○ s
d	○ p	○ q	○ r	●

24. Match the List-I with List-II:

List-I	List-II
(a) $\left(\frac{\partial T}{\partial P}\right)_H$	(p) V
(b) $\left(\frac{\partial G}{\partial P}\right)_T$	(q) T
(c) $\left(\frac{\partial H}{\partial S}\right)_P$	(r) $-S$
(d) $\left(\frac{\partial G}{\partial T}\right)_P$	(s) μ_{jT}

25. Match the List-I with List-II and select the correct answer from the given codes:

List-I (Thermodynamic properties)	List-II (Expression)
(I) ΔG	(A) $-RT \log_e K$
(II) $\Delta H°$	(B) $RT^2\left(\frac{d \ln K}{dT}\right)_P$
(III) ΔS	(C) nFE
(IV) $\Delta G°$	(D) $-\left[\frac{\partial \Delta G}{\partial T}\right]_P$

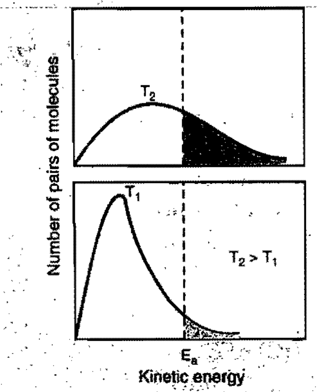
Codes:
(a) I-C, II-B, III-D, IV-A
(b) I-B, II-C, III-D, IV-A
(c) I-A, II-B, III-C, IV-D
(d) I-D, II-A, III-B, IV-C

26. Match the List-I with List-II:

List-I	List-II
(a) Perfectly crystalline solid	(p) $\Delta U = 0$
(b) Reversible reaction at equilibrium	(q) T = constant
(c) Isothermal process	(r) $\lim\limits_{T \to 0K} S \to 0$
(d) $\left(\frac{\partial G}{\partial P}\right) = -S$	(s) $\Delta S_{\text{universe}} = 0$

Answers

1. (b) 2. (d) 3. (a) 4. (b) 5. (b) 6. (c) 7. (b) 8. (c)
9. (a) 10. (c) 11. (a, b) 12. (a, b, d) 13. (a, c) 14. (a, b, d) 15. (a, c, d) 16. (a, b, c)
17. (a, b, c) 18. (a, b, c) 19. (a) 20. (a) 21. (c) 22. (c) 23. (b)
24. (a-s) (b-p) (c-q) (d-r) 25. (a) 26. (a-r) (b-s) (c-p, q) (d-q)



CHAPTER 8

CHEMICAL KINETICS

8.1 INTRODUCTION

Thermodynamics deals with the feasibility of a chemical change. The free energy change, ΔG, of a reaction helps us to understand whether the reaction will occur or not. Even though there may be decrease in free energy but reactants do not always form the products instantaneously and actual rate of the reaction may vary from extremely slow to very fast. Thermodynamics is concerned only with initial and final states of reacting systems but offers no explanation about the various stages through which the reactants pass to reach the final state. This leads to following questions concerning chemical changes.

(i) How fast do the chemical reactions go?

(ii) How can the speed of the reaction change?

(iii) What intermediate steps, the reactants follow to reach the final state of products, *i.e.*, the mechanism of the reaction.

The branch of physical chemistry which deals with the rate at which the chemical reactions occur, the mechanism by which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure, catalyst, etc., on the reaction rates, is called the **chemical kinetics.**

Different chemical reactions occur at different rates. On the basis of rates, the chemical reactions are broadly divided into three categories:

(a) Very fast or instantaneous reactions: These reactions are so fast that they occur as soon as the reactants are brought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

(i) Precipitation of AgCl when solutions of silver nitrate and sodium chloride are mixed.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

(ii) Precipitation of $BaSO_4$ when solutions of barium chloride and sulphuric acid are mixed.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

(iii) Neutralisation of an acid with a base when their aqueous solutions are mixed.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{NaCl} + H_2O$$

(b) Very slow reactions: There are certain reactions which are extremely slow. They may take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions.

Some examples are:

(i) Reaction between hydrogen and oxygen at room temperature.

$$2H_2 + O_2 \xrightarrow{\text{Room temperature}} 2H_2O \text{ (Very slow reaction)}$$

(ii) Reaction of atmospheric H_2S on basic lead acetate.

White basic lead acetate paint $\xrightarrow[H_2S]{\text{Atmospheric}}$ Blackening of paint occurs very slowly (due to formation of PbS.)

(iii) Reaction between carbon and oxygen.

$$C + O_2 \xrightarrow{\text{Room temperature}} CO_2$$

Carbon and oxygen are thermodynamically less stable than CO_2 at 298 K, yet coke does not spontaneously catch fire in air and remains unreacted even for years.

(iv) Reaction between carbon monoxide and hydrogen.

$$CO + 2H_2 \xrightarrow{\text{Room temperature}} CH_3OH$$

The reaction is thermodynamically feasible at 298 K but in actual practice the reaction proceeds infinitesimally slowly.

(v) Rusting of iron occurs very slowly.

(c) Moderate reactions: Between the above two extremes, there are a number of reactions which take place at moderate and measurable rates at room temperature and it is these reactions which are studied in chemical kinetics. Mostly these reactions are molecular in nature. Some common examples of such type are given below:

(i) Decomposition of hydrogen peroxide.

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

(ii) Decomposition of nitrogen pentoxide.

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

(iii) Hydrolysis of an ester.

$$\underset{\text{Ester}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + C_2H_5OH$$

(iv) Inversion of cane sugar in aqueous solution.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(v) Reaction between nitrogen dioxide and carbon monoxide.

$$NO_2 + CO \longrightarrow NO + CO_2$$

(vi) Reaction between ferric chloride and stannous chloride.

$$2FeCl_3(aq.) + SnCl_2(aq.) \longrightarrow 2FeCl_2(aq.) + SnCl_4(aq.)$$

(vii) Decolourisation of acidified potassium permanganate with sodium oxalate.

(viii) Reaction between nitric oxide and chlorine.

$$NO + Cl_2 \longrightarrow NOCl_2$$

The chemical reactions can be slowed down or speeded up by changing conditions under which they occur. For example, very slow reaction, $CO + 2H_2 \longrightarrow CH_3OH$, can be speeded up by maintaining temperature around 400°C, pressure about 300 atmospheres and using a catalyst containing ZnO and Cr_2O_3. The decay of food articles can be slowed down by preserving them in refrigerators. There are two principal reasons for studying chemical kinetics.

(i) To predict the rate of a particular reaction under specified conditions: The conditions can be adjusted to make the reaction to go at a desired rate, either rapidly or slowly or moderately. The field of chemical kinetics is useful in industry as the conditions for maximum yields of industrial products can be ascertained.

(ii) To predict the mechanism of the reaction: The intelligent guess regarding various elementary processes responsible for the formation of products can be made which should be consistent with experimental data.

8.2 RATE OF REACTION (Average and Instantaneous Rate)

We are all familiar with processes in which something changes with time. Rate is usually expressed as the ratio of the amount of change in some quantity to the time required to produce that change.

$$\text{Rate} = \frac{\text{Change in some quantity}}{\text{Time taken for the change}} = \frac{\Delta X}{\Delta t}$$

The term ΔX means $X_{\text{final}} - X_{\text{initial}}$ and Δt is the amount of time elapsed. For example, a car driver starts his journey at 9.0 a.m. with odometer reading x miles. At 11.0 a.m. he reaches his destination. The odometer reading at destination is y miles. The rate of his travel can be calculated as:

$$\text{Rate} = \frac{\Delta(\text{distance})}{\Delta(\text{time})} = \frac{\text{distance}_{(f)} - \text{distance}_{(in)}}{\text{time}_{(f)} - \text{time}_{(in)}}$$

$$= \frac{y-x}{11.0-9.0} = \frac{y-x}{2}\ \text{miles hr}^{-1}$$

The above example indicates that the car has been driven with uniform rate but actually it has been driven sometimes faster and sometimes slower depending upon the conditions of the road. Thus, the overall rate is an average rate and the rate at which the car was moving at any instant, *i.e.*, instantaneous rate was changeable.

The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.

In a chemical change, reactants and products are involved. As the chemical reaction proceeds, the concentration of the reactants decreases, *i.e.*, reactants are consumed and the concentration of products increases, *i.e.*, products are produced. **The rate of reaction (average rate) is defined as the change of concentration of any one of its reactants (or products) per unit time.**

Average rate of reaction,

$$r_{\text{av}} = \frac{\text{Change of concentration of one of the reactants or products}}{\text{Time taken for the change}}$$

Consider a common hypothetical reaction,

$$A \to B$$

The average rate of reaction may be expressed either in terms of decrease in concentration of A (reactants) or in terms of increase in concentration of B (product).

$$\text{Average rate of reaction} = \frac{\text{Decrease in concentration of } A}{\text{Time taken}}$$

$$\text{or Average rate of reaction} = \frac{\text{Increase in concentration of } B}{\text{Time taken}}$$

The concentrations of reactants or products are expressed as number of moles per litre. The symbol for the molar concentration consists of the formula of the substance enclosed in bracket. The symbol $[A]$ stands for the molar concentration of A. The symbol $\Delta[A]$, therefore, stands for the change in molar concentration of A.

The rate of decrease or increase in the concentration of reactants or products may also be expressed in terms of change in their concentration during the time interval, Δt, as:

$$\text{Average rate of reaction} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{or} \quad \text{Average rate of reaction} = +\frac{\Delta[B]}{\Delta t}$$

(A negative sign placed before a reaction rate symbol signifies a decrease in concentration of the reactant with increase of time and a positive sign before the rate symbol signifies that the concentration of the product increases with increase in time. The

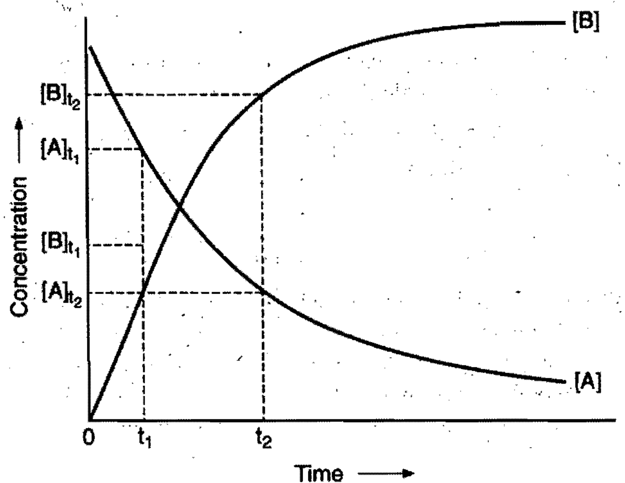


Fig. 8.1

concentration change may be positive or negative but the rate of reaction is always positive. The minus sign is always written when required but the plus sign is usually not mentioned.)

Figure 8.1 shows the change of concentrations of reactant (A) and product (B) as the chemical reaction $A \rightarrow B$ progresses with time. Let $[A]_{t_1}$ and $[A]_{t_2}$ be the concentrations of A at time t_1 and t_2, respectively.

$$\Delta[A] = [A]_{t_2} - [A]_{t_1}$$

and

$$\Delta t = t_2 - t_1$$

$$r_{\text{av}} = -\frac{\Delta[A]}{\Delta t} = -\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}$$

Over the same time interval t_1 to t_2, the concentration of B changes from $[B]_{t_1}$ to $[B]_{t_2}$.

$$r'_{\text{av}} = \frac{\Delta[B]}{\Delta t} = \frac{[B]_{t_2} - [B]_{t_1}}{t_2 - t_1}$$

Since, one mole of A produces one mole of B, the rate of decrease in concentration of A should be equal to the rate of increase in concentration of B. Thus,

$$r_{\text{av}} = r'_{\text{av}}$$

$$-\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Reaction rate has the units of concentration or molarity divided by time. Therefore, the units of rate of reaction may be expressed as:

mole/litre sec (mol L^{-1} s^{-1})

or mole/litre min (mol L^{-1} min^{-1})

or mole/litre hour (mol L^{-1} h^{-1})

or mole/litre day (mol L^{-1} d^{-1})

or mole/litre year (mol L^{-1} y^{-1})

SOME SOLVED EXAMPLES

Example 1. *In a reaction, the concentration of a reactant* (A) *changes from* 0.200 *mol litre*$^{-1}$ *to* 0.150 *mol litre*$^{-1}$ *in* 10 *minutes. What is the average rate of reaction during this interval?*

Solution: $\Delta[A] = [A]_{\text{final}} - [A]_{\text{initial}}$

$$= [0.150 - 0.200] = -0.050 \text{ mol litre}^{-1}$$

$$\Delta t = 10 \text{ minutes}$$

$$\text{Average rate of reaction} = \frac{-\Delta[A]}{\Delta t} = \frac{-[-0.050]}{10}$$

$$= \frac{0.050}{10} = 0.005 \text{ mol litre}^{-1} \text{ min}^{-1}$$

Expression of Rate

Consider the following reaction between CO and NO_2:

$$CO + NO_2 \longrightarrow CO_2 + NO$$

The equation shows that when one mole of CO reacts with one mole of NO_2, one mole each of CO_2 and NO are formed. The average rate of reaction can be expressed either by decrease of concentration of any one of the reactants (CO or NO_2) or by the increase in concentration of any one of the products (CO_2 or NO):

Thus, $-\frac{\Delta[CO]}{\Delta t} = -\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = \frac{\Delta[NO]}{\Delta t}$

However, for the reaction,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

it is observed that when 2 moles of H_2O_2 decompose, one mole of O_2 is formed in the same time interval. The rate of increase in the concentration of O_2, therefore, is half that of the disappearance of the concentration of H_2O_2 in the same time interval;

So, $\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t}$

In general, for a reaction,

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

the rate expression may be expressed as:

$$-\frac{1}{n_1}\frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2}\frac{\Delta[B]}{\Delta t} = \frac{1}{m_1}\frac{\Delta[C]}{\Delta t} = \frac{1}{m_2}\frac{\Delta[D]}{\Delta t}$$

Thus, for the reaction,

$$H_2 + I_2 \rightleftharpoons 2HI$$

the rate may be expressed as:

$$-\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

Note : In case of gaseous reaction, pressure may be taken in place of concentration. Thus, rate will have the unit of atm sec^{-1} or atm min^{-1}.

$$PV = nRT \quad \text{or} \quad P = \left[\frac{n}{V}\right]RT \quad \text{or} \quad P = CRT$$

$$\frac{\Delta[P]}{\Delta t} = \frac{\Delta[C]}{\Delta t} \cdot RT \quad \text{or} \quad \text{Rate in [atm/sec]} = \text{Rate in [molarity/sec]} \times RT$$

Similarly, for the decomposition of N_2O_5 in CCl_4 medium, the rate may be expressed as:

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

$$-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Example 2. *Decomposition of N_2O_5 is expressed by the equation,*

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$

If during a certain time interval, the rate of decomposition of N_2O_5 is 1.8×10^{-3} mol litre^{-1} min^{-1}, what will be the rates of formation of NO_2 and O_2 during the same interval?

Solution: The rate expression for the decomposition of N_2O_5 is:

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = 2\cdot\frac{\Delta[O_2]}{\Delta t}$$

So, $$\frac{\Delta[NO_2]}{\Delta t} = 2\frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3}$$

$$= 3.6 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

and $$\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3}$$

$$= 0.9 \times 10^{-3} \text{ mol litre}^{-1} \text{ min}^{-1}$$

(Rate is always positive and hence $-\frac{\Delta[N_2O_5]}{\Delta t}$ is taken positive.)

Instantaneous Rate

In chemical kinetics, the rate at any particular instant, *i.e.*, instantaneous rate rather than the average rate over a time interval has much more practical application and importance. It is defined as **the rate of change of concentration of any one of the reactants or products over a very small interval of time.**

If we take infinitesimal small interval of time dt, it may be assumed that the rate is uniform through this interval; then if dx is amount of substance A transformed to B during this interval, the rate of reaction at that instant is given as $-\frac{dx}{dt}$.

[In differential calculus, when Δt becomes very small and approaches zero, the ratio $\frac{\Delta[A]}{\Delta t}$ may be replaced by the derivative, $\frac{d[A]}{dt}$, *i.e.*,

$$r_{\text{inst}} = \lim_{\Delta t \to 0} -\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}\Bigg]$$

On the other hand, if the rate of reaction is expressed in terms of the concentration of any of the products which goes on increasing, then rate of reaction at particular instant $= \frac{dx}{dt}$:

In general, for a reaction,

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

The instantaneous rate may be expressed as:

$$r_{\text{inst}} = -\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = \frac{1}{m_1}\frac{d[C]}{dt} = \frac{1}{m_2}\frac{d[D]}{dt}$$

Experimental Determination of Instantaneous Rate of Reaction

In order to determine changes in concentration of reactants or products, it is customary to take small portions of the reaction mixture at suitable intervals of time and freeze them rapidly to about 0°C as to stop the reaction. The concentration is then measured with the help of a suitable method. In several cases, concentration changes are measured by observing changes in certain physical properties which are proportional to it such as optical densities, electrical conductivity, optical rotation, etc. A curve is plotted between concentration and time. A tangent is drawn to the curve at the point corresponding to time interval 't'. The slope of this tangent gives the instantaneous rate of reaction. This is shown in Fig. 8.2 (a).

Instantaneous rate of reaction = Slope of curve

$$= \frac{\text{Intercept along ordinate}}{\text{Intercept along abscissa}} = \frac{\Delta x}{\Delta t}$$

Since, the concentrations of the reactants keep on decreasing with time, the rate of reaction correspondingly decreases with time. Thus, the rate of reaction will depend on the stage considered during progress of the reaction. The rate of reaction is maximum at the initial stage and decreases with time. Theoretically, infinite time would be required for a reaction to complete. But the reaction rate becomes so slow after a certain time that for all practical purposes, the reaction can be considered to be completed. It is evident from Fig. 8.2 (b) that the rate of reaction is varying from moment to moment.

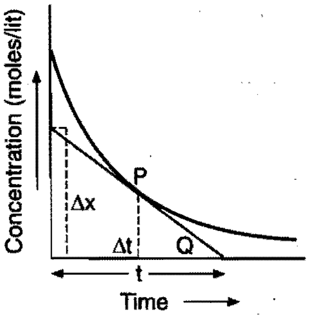


Fig. 8.2(a) Determination of rate of reaction

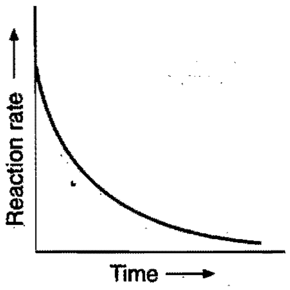


Fig. 8.2(b) Variation of rate

Reaction Life Time

It is defined as the time taken by a reaction to proceed to 98% of completion. The shorter the life time, the faster the reaction. Reaction life times are used to compare the various reactions. Reactions are also compared with half life periods. The half life period is defined as the time during which the concentration of a reactant is reduced to one-half of its initial value or the time in which half of the reaction is completed. It is generally denoted by $t_{1/2}$. The shorter the half life period, the faster is the reaction.

Example 3. *For each of the following reactions express the given rate of change of concentration of the reactant or product in terms of the rate of change of concentration of other reactants or products in that reaction :*

(a) $H_2O_2 + 2H^+ + 3I^- \longrightarrow I_3^- + 2H_2O$; $-\frac{d[I^-]}{dt} = ?$; $-\frac{d[H^+]}{dt} = ?$

(b) $16H^+ + 2MnO_4^- + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$; $-\frac{d[MnO_4^-]}{dt} = ?$

(c) $4NH_3 + 5O_2 \longrightarrow 4NO_2 + 6H_2O$; $-\frac{d[NH_3]}{dt} = ?$

Solution: We have,

(a) $H_2O_2 + 2H^+ + 3I^- \longrightarrow I_3^- + 2H_2O$

The equality in this case is:

$$-\frac{d[H_2O_2]}{dt} = -\frac{1}{2}\frac{d[H^+]}{dt} = -\frac{1}{3}\frac{d[I^-]}{dt} = \frac{d[I_3^-]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

$$\text{So,} -\frac{d[I^-]}{dt} = -3\frac{d[H_2O_2]}{dt} = -\frac{3}{2}\frac{d[H^+]}{dt} = 3\frac{d[I_3^-]}{dt} = \frac{3}{2}\frac{d[H_2O]}{dt}$$

$$\text{and} -\frac{d[H^+]}{dt} = -2\frac{d[H_2O_2]}{dt} = -\frac{2}{3}\frac{d[I^-]}{dt} = 2\frac{d[I_3^-]}{dt} = \frac{d[H_2O]}{dt}$$

(b) $16H^+ + 2MnO_4^- + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

The equality in this case is:

$$-\frac{1}{16}\frac{d[H^+]}{dt} = -\frac{1}{2}\frac{d[MnO_4^-]}{dt} = -\frac{1}{10}\frac{d[I^-]}{dt}$$
$$= \frac{1}{2}\frac{d[Mn^{2+}]}{dt} = \frac{1}{8}\frac{d[H_2O]}{dt} = \frac{1}{5}\frac{d[I_2]}{dt}$$

$$\text{So,} -\frac{d[MnO_4^-]}{dt} = -\frac{1}{8}\frac{d[H^+]}{dt} = -\frac{1}{5}\frac{d[I^-]}{dt}$$
$$= \frac{d[Mn^{2+}]}{dt} = \frac{1}{4}\frac{d[H_2O]}{dt} = \frac{2}{5}\frac{d[I_2]}{dt}$$

(c) $4NH_3 + 5O_2 \longrightarrow 4NO_2 + 6H_2O$

The equality in this case is:

$$-\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

$$\text{So,} \quad -\frac{d[NH_3]}{dt} = -\frac{4}{5}\frac{d[O_2]}{dt} = \frac{d[NO_2]}{dt} = \frac{2}{3}\frac{d[H_2O]}{dt}$$

Example 4. *The following reaction was carried out in water:*

$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$

The initial concentration of I^- *was* $0.25\ mol\ L^{-1}$ *and the concentration after* 10 *minutes* $0.23\ mol\ L^{-1}$. *Calculate the rate of disappearance of* I^- *and appearance of* I_2.

Solution: $\Delta[I^-] = [I^-]_{final} - [I^-]_{initial}$

$$= 0.23 - 0.25 = -0.02\ \text{mol L}^{-1}$$

$$\Delta t = 10 - 0 = 10\ \text{min}$$

$$-\frac{\Delta[I^-]}{\Delta t} = -\frac{(-0.02)}{10} = 0.002\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$\text{Rate of appearance of } I_2 = -\frac{1}{2}\frac{\Delta[I^-]}{\Delta t} = \frac{0.002}{2}$$
$$= 0.001\ \text{mol L}^{-1}\ \text{min}^{-1}$$
$$= 1\times10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

Example 5. *The reaction between* $Cr_2O_7^{2-}$ *and* HNO_2 *in an acidic medium is:*

$$Cr_2O_7^{2-} + 5H^+ + 3HNO_2 \rightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

The rate of disappearance of $Cr_2O_7^{2-}$ *is found to be* $2.4\times10^{-4}\ mol\ L^{-1}\ s^{-1}$ *during a measured time interval. Find the rate of disappearance of* HNO_2 *and the rate of appearance of* Cr^{3+} *during this time interval.*

Solution: The equality in this case is:

$$-\frac{\Delta[Cr_2O_7^{2-}]}{\Delta t} = -\frac{1}{3}\frac{\Delta[HNO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[Cr^{3+}]}{\Delta t}$$

It is given that,

$$-\frac{\Delta[Cr_2O_7^{2-}]}{\Delta t} = 2.4\times10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$\text{So,} \quad -\frac{\Delta[HNO_2]}{\Delta t} = 3\times2.4\times10^{-4} = 7.2\times10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$\text{and} \quad \frac{\Delta[Cr^{3+}]}{\Delta t} = 2\times2.4\times10^{-4} = 4.8\times10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. For the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$ rate of reaction is: **(AIIMS 2006)**

(a) $\frac{1}{2}\frac{d}{dt}[N_2O_5]$ (b) $2\frac{d}{dt}[N_2O_5]$

(c) $\frac{1}{4}\frac{d}{dt}[NO_2]$ (d) $4\frac{d}{dt}[NO_2]$

[Ans. (c)]

[Hint: For the reaction:

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = \text{Rate}]$$

2. Observe the following reaction:

$$A(g) + 3B(g) \longrightarrow 2C(g)$$

The rate of this reaction $\left\{\frac{-d[A]}{dt}\right\}$ is 3×10^{-3} mol litre^{-1} min^{-1}. What is the value of $\frac{-d[B]}{dt}$ in mol litre^{-1} min^{-1}? **(EAMCET 2006)**

(a) 3×10^{-3} (b) 9×10^{-3} (c) 10^{-3} (d) 1.5×10^{-3}

[Ans. (b)]

[Hint: $\frac{-d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt}$

$$\therefore \quad \frac{-d[B]}{dt} = 3\left\{\frac{-d[A]}{dt}\right\} = 3\times3\times10^{-3}$$
$$= 9\times10^{-3}\ \text{mol litre}^{-1}\ \text{min}^{-1}\ ]$$

3. For the reaction, $2A + B \longrightarrow 3C + D$, which of the following does not express the reaction rate? **[CBSE (Med.) 2006]**

(a) $\frac{-d[C]}{3\,dt}$ (b) $\frac{-d[B]}{dt}$ (c) $\frac{d[D]}{dt}$ (d) $\frac{-d[A]}{2\,dt}$

[Ans. (a)]

[Hint: $-\frac{1}{2}\frac{d[A]}{dt} = \frac{-d[B]}{dt} = +\frac{1}{3}\frac{d[C]}{dt} = +\frac{d[D]}{dt} = \text{Rate}$]

4. Consider the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is: **[CBSE (Med.) 2006]**

(a) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$ (b) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

(c) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$ (d) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

[Ans. (b)]

[Hint: $-\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$]

5. For a reaction $\frac{1}{2}A \longrightarrow 2B$ rate of disappearance of A is related to the rate of appearance of B by the expression: **(AIEEE 2008)**

(a) $\frac{-d[A]}{dt} = 4\frac{d[B]}{dt}$ (b) $\frac{-d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

(c) $\frac{-d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt}$ (d) $\frac{-d[A]}{dt} = +\frac{d[B]}{dt}$

[Ans. (c)]

[Hint: The reaction may be given as

$$A \longrightarrow 4B$$

$$\frac{-d[A]}{dt} = +\frac{1}{4}\frac{d[B]}{dt} = \text{Rate of reaction.}]$$

6. In a reaction of acidified hydrogen peroxide with potassium iodide, the concentration of iodine formed rises from 0 to 10^{-5} mol dm^{-3} in 10 seconds. What is the rate of reaction ? **[PET (Raj.) 2008]**

(a) 10^{-6} mol dm^{-3}s^{-1} (b) 10^{6} mol dm^{-3}s^{-1}

(c) 10^{-5} mol dm^{-3}s^{-1} (d) 10^{4} mol dm^{-3}s^{-1}

[Ans. (a)]

[Hint: The reaction is

$$2I^- + H_2O_2 + 2H^+ \longrightarrow I_2 + 2H_2O$$

$$\text{Rate} = +\frac{d[I_2]}{dt} = \frac{10^{-5}}{10} = 10^{-6}\ \text{mol dm}^{-3}\text{s}^{-1}]$$

8.3 LAW OF MASS ACTION (Guldberg and Waage, 1864)

This law relates rate of reaction with active mass or molar concentration of reactants.

"At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction."

Active mass = molar concentration of the substance

$$= \frac{\text{number of gram moles of the substance}}{\text{volume in litres}}$$

$$= \frac{w/M}{V} = \frac{n}{V}$$

where, w = mass of substance and 'M' is the molecular mass in gram, 'n' is the number of gram moles and V is volume in litre.

Example 6. *4 g of hydrogen and 128 g of hydrogen iodide are present in a 2 litre flask. What are their active masses?*

Solution: Mass of hydrogen = 4 g

Mol. mass of hydrogen = 2

Volume of the flask = 2 litre

$$\text{Active mass of hydrogen} = \frac{4}{2 \times 2} = 1\ \text{mol L}^{-1}$$

Mass of HI = 128 g

Mol. mass of HI = 128

Volume of the flask = 2 litre

$$\text{Active mass of hydrogen iodide} = \frac{128}{128 \times 2} = 0.5\ \text{mol L}^{-1}$$

8.4 RATE CONSTANT

Consider a simple reaction $A \rightarrow B$.

If C_A is the molar concentration or active mass of A at a particular instant, then

$$\frac{dx}{dt} \propto C_A \text{ or } \frac{dx}{dt} = kC_A$$

where, k is a **proportionality constant,** called **velocity constant** or **rate constant** or **specific reaction rate.**

At a fixed temperature, if $C_A = 1$, then

$$\text{Rate} = \frac{dx}{dt} = k \quad \text{... (i)}$$

Let us consider a general reaction.

$$aA + bB \longrightarrow \text{Product}$$

$$\text{Rate} = \left(\frac{dx}{dt}\right) \propto [A]^a[B]^b$$

$$\text{Rate} = k[A]^a[B]^b \quad \text{...(ii)}$$

When $[A] = [B] = 1$ mol/litre, then

$$\text{Rate} = k$$

Rate of a reaction at unit concentration of reactants is called rate constant.

The value of rate constant depends on:

(i) Nature of reactant

(ii) Temperature

(iii) Catalyst

Unit of Rate Constant

Rate constant has different units for reactions of different order. General rule for rate of reaction may be given as:

$$\text{Unit of rate constant} = \left[\frac{1}{\text{unit of concentration}}\right]^{n-1} \times \text{time}^{-1}$$

$$= \left[\frac{1}{\text{mol / litre}}\right]^{n-1} \times \text{sec}^{-1}$$

$$= \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$$

where, n = order of reaction.

S. No.	Rate of reaction	Reaction rate constant
1.	It is the speed with which reactants are converted into products.	It is proportionality constant.
2.	It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time.	It is equal to the rate of reaction when the concentration of each of the reactants is unity.
3.	It depends upon the initial concentration of reactants.	It is independent of the initial concentration of the reactants. It has a constant value at fixed temperature.

8.5 COLLISION THEORY OF REACTION RATE (Arrhenius Theory of Reaction Rate)

(1) A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as **collision frequency (Z).** The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.

(2) Every collision does not bring a chemical change. The collisions that actually produce the products are **effective collisions.** The effective collisions which bring chemical change are few in comparison to the total number of collisions. The collisions that do not form a product are **ineffective elastic collisions,** *i.e.*, molecules just collide and disperse in different directions with different velocities. For a collision to be effective, the following two barriers are to be cleared:

Energy Barrier

The minimum amount of energy which the colliding molecules must possess as to make the chemical reaction to occur, is known as threshold energy.

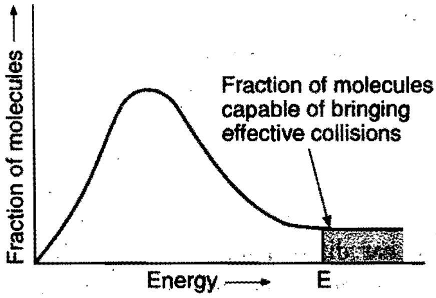


Fig. 8.3

In the graph (Fig. 8.3), 'E' corresponds to minimum or threshold energy for effective collision in a hypothetical reaction.

There is an energy barrier for each reaction. The reacting species must be provided with sufficient energy as to cross the energy barrier.

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy − average kinetic energy of reacting molecules

Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the **activated complex.** The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, *i.e.*, products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions *versus* the progress of the reaction are shown in Fig. 8.4.

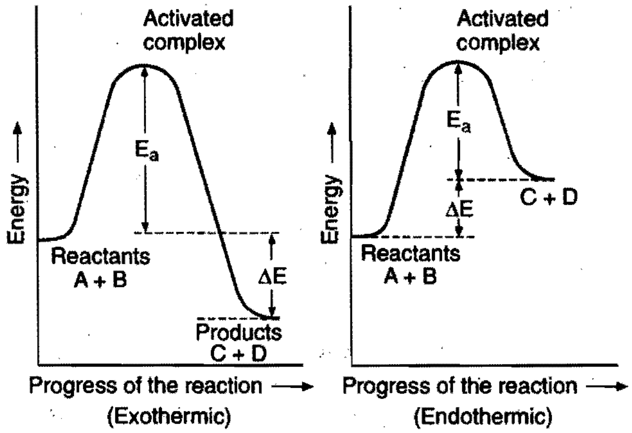


Fig. 8.4 Activation energy of exothermic and endothermic reaction

Thus, every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after collision and then they can go to the right side of the slope and consequently change into products. If the activation energy for a reaction is low, the fraction of effective collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of active molecules increases, *i.e.*, the number of effective collisions will increase and the rate of reaction will increase.

$$\text{Activation energy } E_a = E_{(\text{activated complex})} - E_{(\text{ground state})}$$

$$\Delta H = \text{activation energy of forward reaction} - \text{activation energy of backward reaction.}$$

Orientation Barrier

Energy alone does not determine the effectiveness of the collision. The reacting molecules must collide in proper manner if the reaction is to occur. This has been shown in Fig. 8.5.

Rate of reaction is directly proportional to the number of effective collisions.

$$\text{Rate} = -\frac{dx}{dt} = \text{collision frequency} \times \text{fraction of effective collisions}$$

$$= Z \times f$$

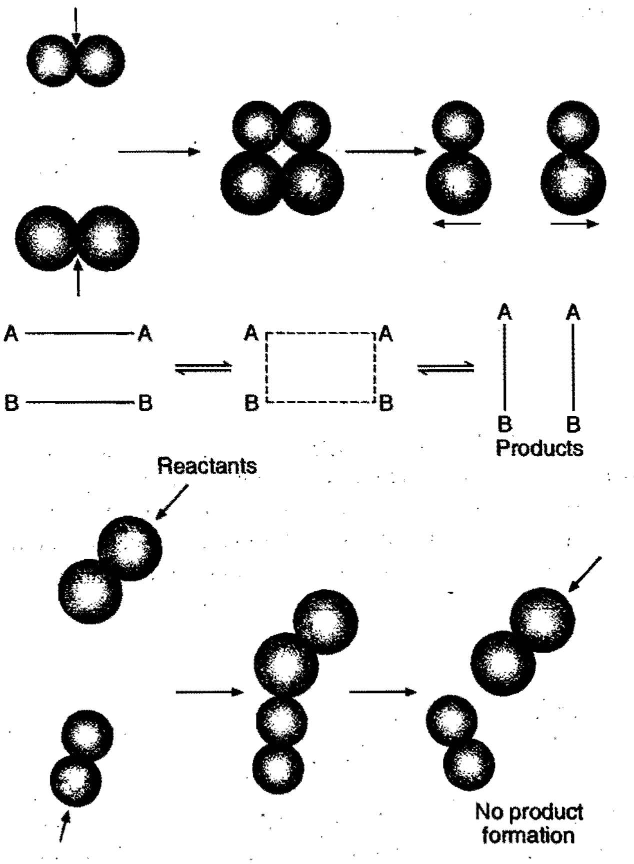


Fig. 8.5 Orientation of collisions

Factors Affecting Rate of Reaction

(i) Nature of the reactants

(a) Physical state of reactants: This has considerable effect over rate of reaction.

$$\underset{\text{Decreasing rate of reaction}}{\xrightarrow{\text{Gaseous state} > \text{Liquid state} > \text{Solid state}}}$$

Similarly, in a heterogeneous system, collision is not so effective as in homogeneous system. Thus, reactions in liquid phase or solution phase will be faster in comparison to heterogeneous conditions when same concentrations of the reactants are taken.

(b) Physical size of the reactants: Among the solids, rate increases with decrease in particle size. In powdered state rate of reaction is maximum because in powdered state, surface area is maximum.

(c) Chemical nature of reactants: Consider the following two reactions:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \text{... (i)}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O \qquad \text{... (ii)}$$

The first reaction is faster than the second because in the first reaction only $N{\equiv}O$ bond is to be broken whereas in the second reaction four (C—H) bonds are to be broken.

Similarly, consider another example of two similar reactions:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad \text{... (iii)}$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \text{... (iv)}$$

NO bond is weaker than CO bond, hence broken easily. Thus, reaction (iii) is faster than (iv).

(ii) Concentration of reactants

Let us consider the reaction:

$$A + B \longrightarrow C + D;$$

$$\text{Rate} = k\,[A][B]$$

Rate of the above reaction decreases with the passage of time because the concentration of reactants A and B will decrease as time passes on.

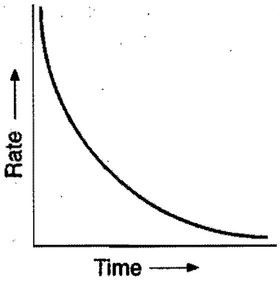


Fig. 8.6

Let us consider the following reversible reaction:

$$A + B \rightleftharpoons C + D$$

$$\text{Rate of forward reaction} = k_f\,[A][B]$$

$$\text{Rate of backward reaction} = k_b[C][D]$$

Rate of forward reaction decreases and that of backward reaction increases with passage of time. At equilibrium both the rates become equal.

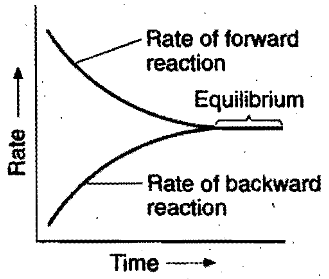


Fig. 8.7

(iii) Effect of temperature

The rate of reaction increases considerably with an increase in temperature. The rates of many reactions are approximately doubled or tripled for every 10°C rise in temperature. The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperatures differing by 10°C.

$$\mu = \text{Temperature coefficient} = \frac{k_{t+10}}{k_t}$$

Let temperature coefficient of a reaction be 'μ' when temperature is raised from T_1 to T_2; then the ratio of rate constants or rate may be calculated as:

$$\frac{k_{T_2}}{k_{T_1}} = (\mu)^{(T_2 - T_1)/10} = \mu^{\Delta T/10}$$

$$\log_{10}\left(\frac{k_{T_2}}{k_{T_1}}\right) = \frac{\Delta T}{10}\log_{10}\mu$$

$$\frac{k_{T_2}}{k_{T_1}} = \text{antilog}\left[\frac{\Delta T}{10}\log_{10}\mu\right]$$

Its value lies generally between 2 and 3.

When the temperature is increased, heat energy is supplied which increases the kinetic energy of the reacting molecules. This will increase the number of collisions and ultimately the rate of reaction will be enhanced. Arrhenius suggested an equation which describes k as a function of temperature, *i.e.*,

$$k = Ae^{-E_a/RT}$$

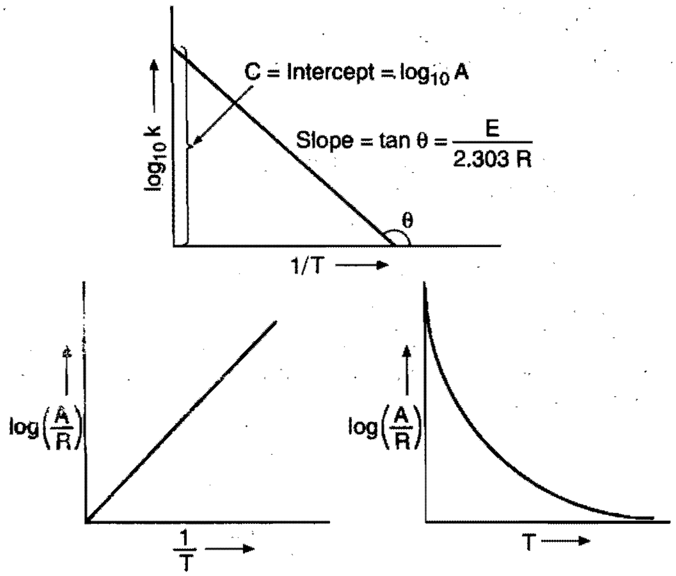


Fig. 8.8

where, $k \rightarrow$ rate constant

$A \rightarrow$ a constant (frequency factor)

$E_a \rightarrow$ energy of activation

At two temperatures T_1 and T_2, taking log of Arrhenius equation, we get

$$\log_e k_1 = \log A - \frac{E_a}{RT_1}\log_e e \quad \text{... (i)}$$

and

$$\log_e k_2 = \log A - \frac{E_a}{RT_2}\log_e e \quad \text{... (ii)}$$

Subtracting eq. (ii) from eq. (i) and converting the log to the base 10, we get

$$\log_{10}\frac{k_1}{k_2} = -\frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \text{ or } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

This equation can be used for calculation of energy of activation.

Logarithmic Arrhenius equation is:

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303R}\left[\frac{1}{T}\right]$$

$$Y = C + M\,X$$

It is the equation of straight line with negative slope. On plotting $\log_{10} k$ against $[1/T]$ we get a straight line as shown in Fig. 8.8. The graph gives two kinetic parameters.

The slope gives **activation energy** and intercept gives **frequency factor.**

The dependence of rate constant on temperature for two reactions is shown in the Fig. 8.9.

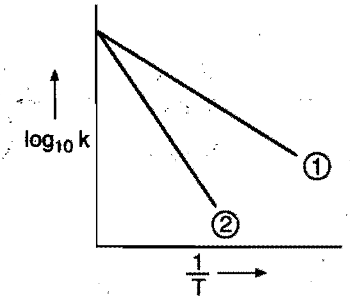
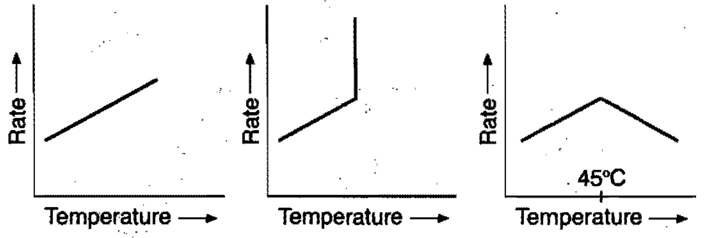


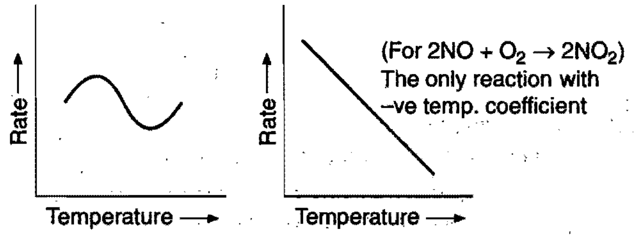
Fig. 8.9

In the reaction (2), the modulus of slope is greater than that of reaction (1), hence reaction (2) has higher activation energy. The reaction (2) will be more sensitive to temperature change.

Reactions on the basis of influence of temperature are classified into five types. These are shown in the graphs.



(Normal reactions) (a) (Explosive reactions) (b) (Biological reactions) (c)



(Oxidation of carbon) (d) (e)

Fig. 8.10

(iv) Presence of a positive catalyst

The function of a positive catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In the presence of a catalyst, the reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. Fig. 8.11 shows how the activation energy is lowered in presence of a catalyst.

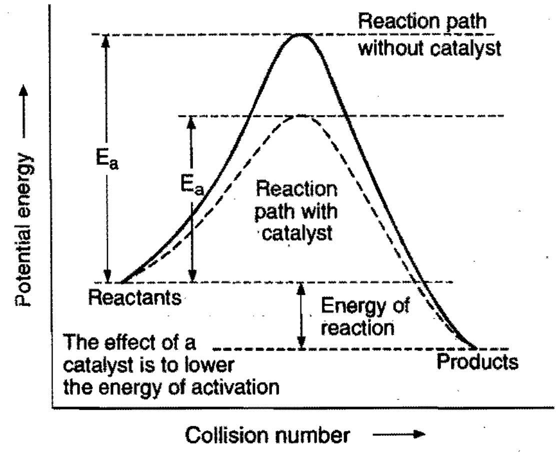


Fig. 8.11 A catalyst changes the reaction path (Positive catalyst)

(v) Presence of negative catalyst

A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy, *i.e.*, by changing the reaction mechanism.

Due to increased activation energy, some active molecules become inactive, therefore, rate of reaction decreases.

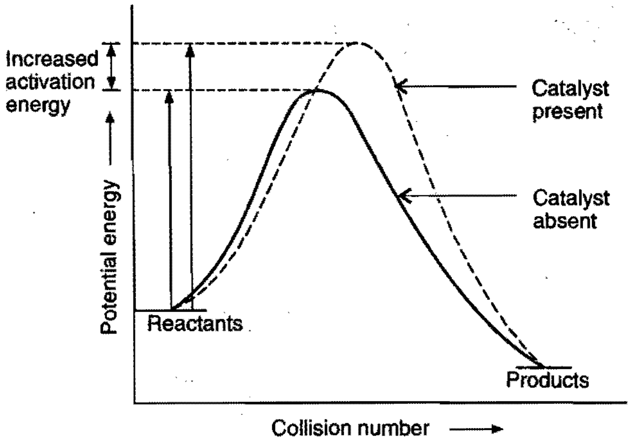


Fig. 8.12 Negative catalyst

Let 'p' denote presence of catalyst and 'a' denote absence of catalyst.

$$k_p = Ae^{-E_p/RT} \quad \text{... (i)}$$

$$k_a = Ae^{-E_a/RT} \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{k_p}{k_a} = e^{(E_a - E_p)/RT} = e^{\Delta E/RT}$$

$$\frac{k_p}{k_a} = \text{antilog}\left[\frac{\Delta E}{2.303RT}\right]$$

SOME SOLVED EXAMPLES

Example 7. *The rate of a reaction triples when temperature changes from 20°C to 50°C. Calculate energy of activation for the reaction.* ($R = 8.314\ JK^{-1}\ mol^{-1}$)

Solution: The Arrhenius equation is,

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{R \times 2.303}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Given: $\frac{k_2}{k_1} = 3$; $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$; $T_1 = 20 + 273 = 293\ \text{K}$

and $T_2 = 50 + 273 = 323\ \text{K}$

Substituting the given values in the Arrhenius equation,

$$\log_{10} 3 = \frac{E_a}{8.314 \times 2.303}\left[\frac{323 - 293}{323 \times 293}\right]$$

$$E_a = \frac{2.303 \times 8.314 \times 323 \times 293 \times 0.477}{30}$$

$$= 28811.8\ \text{J mol}^{-1}$$

$$= 28.8118\ \text{kJ mol}^{-1}$$

Example 8. *In Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. At what temperature, the reaction will have specific rate constant 1.1×10^{-3} sec^{-1}?*

Solution: According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

or $$\log_e k = \log_e A - \frac{E_a}{RT}\log_e e$$

or $$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

or $$2.303 \log (1.1 \times 10^{-3}) = 2.303 \log (4 \times 10^{13}) - \frac{98.6 \times 10^3}{8.314 \times T}$$

$$T = \frac{98.6 \times 10^3}{8.314 \times 2.303 \times 16.56}\ \text{K}$$

$$= 310.96\ \text{K}$$

Example 9. *The rate constant is given by Arrhenius equation,*

$$k = Ae^{-E_a/RT}$$

Calculate the ratio of the catalysed and uncatalysed rate constants at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

Solution: Let k_{ca} and k_{un} be the rate constants for catalysed and uncatalysed reactions.

$$2.303 \log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT} \quad \text{... (i)}$$

and $$2.303 \log_{10} k_{un} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT} \quad \text{... (ii)}$$

Subtracting eq. (ii) from eq. (i)

$$\log_{10} \frac{k_{ca}}{k_{un}} = \frac{10^3}{2.303RT}(350 - 162)$$

$$= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95$$

$$\frac{k_{ca}}{k_{un}} = 8.88 \times 10^{32}$$

Example 10. *Calculate the rate constant of a reaction at 293 K when the energy of activation is 103 kJ mol $^{-1}$ and the rate constant at 273 K is 7.87×10^{-7} s $^{-1}$.*
($R = 8.314 \times 10^{-3}$ kJ mol $^{-1}$ K $^{-1}$)

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Given: $k_1 = 7.87 \times 10^{-7}\ \text{s}^{-1}$; $E_a = 103\ \text{kJ mol}^{-1}$;
$R = 8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1}$;
$T_1 = 273$ K and $T_2 = 293$ K

Substituting the values in Arrhenius equation,

$$\log_{10} \frac{k_2}{7.87 \times 10^{-7}} = \frac{103 \times 20}{2.303 \times 8.314 \times 10^{-3} \times 293 \times 273}$$

$$= 1.345$$

$$\therefore k_2 = 1.74 \times 10^{-5}\ \text{s}^{-1}$$

Example 11. *At 407 K, the rate constant of a chemical reaction is 9.5×10^{-5} s $^{-1}$ and at 420 K, the rate constant is 1.9×10^{-4} s $^{-1}$. Calculate the frequency factor of the reaction.*

Solution: The Arrhenius equation is,

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Given: $k_1 = 9.5 \times 10^{-5}\ \text{s}^{-1}$; $k_2 = 1.9 \times 10^{-4}\ \text{s}^{-1}$;
$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$;
$T_1 = 407$ K and $T_2 = 420$ K

Substituting the values in Arrhenius equation

$$\log_{10} \frac{1.9 \times 10^{-4}}{9.5 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314}\left[\frac{420 - 407}{420 \times 407}\right]$$

$$E_a = 75782.3\ \text{J mol}^{-1}$$

Applying now $\log k_1 = \log A - \dfrac{E_a}{2.303RT_1}$

$$\log 9.5 \times 10^{-5} = \log A - \frac{75782.3}{2.303 \times 8.314 \times 407}$$

or $$\log \frac{A}{9.5 \times 10^{-5}} = \frac{75782.3}{2.303 \times 8.314 \times 407} = 9.7246$$

$$A = 5.04 \times 10^5\ \text{s}^{-1}$$

Example 12. *The energy of activation for a reaction is 100 kJ mol $^{-1}$. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20° C, other things being equal?*

Solution: The Arrhenius equation is,

$$k = Ae^{-E_a/RT}$$

In absence of catalyst, $k_1 = Ae^{-100/RT}$

In presence of catalyst, $k_2 = Ae^{-25/RT}$

So, $$\frac{k_2}{k_1} = e^{75/RT} \text{ or } 2.303 \log \frac{k_2}{k_1} = \frac{75}{RT}$$

or $$2.303 \log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293}$$

or $$\log \frac{k_2}{k_1} = \frac{75}{8.314 \times 10^{-3} \times 293 \times 2.303}$$

or $$\frac{k_2}{k_1} = 2.34 \times 10^{13}$$

As the things being equal in presence or absence of a catalyst,

$$\frac{k_2}{k_1} \text{ must be} = \frac{\text{rate in presence of catalyst}}{\text{rate in absence of catalyst}}$$

i.e., $$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.34 \times 10^{13}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. For a reaction $E_a = 0$ and $k = 3.2 \times 10^4\ \text{s}^{-1}$ at 300 K. The value of k at 310 K would be:

(a) $6.4 \times 10^4\ \text{s}^{-1}$ (b) $3.2 \times 10^4\ \text{s}^{-1}$
(c) $3.2 \times 10^8\ \text{s}^{-1}$ (d) $3.2 \times 10^5\ \text{s}^{-1}$

[Ans. (b)]

[Hint: $k = Ae^{-E_a/RT}$
When $E_a = 0$, $k = A$ = constant
$\therefore$ $k_{310} = k_{300} = 3.2 \times 10^4\ \text{s}^{-1}$]

8. For a gaseous reaction, following data is given:

$$A \longrightarrow B, k_1 = 10^{15} e^{-2000/T}$$
$$C \longrightarrow D, k_2 = 10^{14} e^{-1000/T}$$

The temperature at which $k_1 = k_2$ is:

(a) 1000 K (b) 2000 K (c) 868.82 K (d) 434.2 K

[Ans. (d)]

[Hint: When $k_1 = k_2$,

$$10^{15} e^{-2000/T} = 10^{14} e^{-1000/T}$$
$$10 = e^{1000/T}$$
$$2.303 \log 10 = \frac{1000}{T}$$
$$T = 434.2\ \text{K}]$$

9. For $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + 22$ kcal, E_a for the reaction is 70 kcal. Hence, the activation energy for $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$ is:
(a) 92 kcal (b) 70 kcal (c) 48 kcal (d) 22 kcal
[**Ans.** (a)]
[**Hint:**

$$\Delta H = E_f - E_b$$
$$-22 = 70 - E_b$$
$$E_b = 92 \text{ kcal}]$$

10. On introducing a catalyst at 500 K, the rate of a first order reaction increases by 1.718 times. The activation energy in the presence of a catalyst is 6.05 kJ mol^{-1}. The slope of the plot of $\ln k$ (sec^{-1}) against $1/T$ in the absence of catalyst is:
(a) +1 (b) −1 (c) +1000 (d) −1000
[**Ans.** (d)]
[**Hint:** $\dfrac{\text{Rate in presence of catalyst}}{\text{Rate in absence of catalyst}} = \text{Antilog}\left[\dfrac{+\Delta E}{2.303RT}\right]$.

$$1.718 = \text{Antilog}\, \frac{E_a - E_p}{2.303 \times 8.314 \times 500}$$
$$E_a - E_p = 2.25 \text{ kJ}$$
$$E_a = E_p + 2.25 = 6.05 + 2.25 = 8.30 \text{ kJ mol}^{-1}$$
$$= 8.3 \text{ kJ mol}^{-1}$$
$$\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T}$$
$$\text{Slope} = \frac{-E_a}{R} = \frac{-8.3 \times 1000}{8.3} = -1000]$$

11. For which of the following reactions k_{310}/k_{300} would be maximum?
(a) $A + B \longrightarrow C$; $E_a = 50$ kJ
(b) $X + Y \longrightarrow Z$; $E_a = 40$ kJ
(c) $P + Q \longrightarrow R$; $E_a = 60$ kJ
(d) $E + F \longrightarrow G$; $E_a = 100$ kJ
[**Ans.** (d)]
[**Hint:** Increase in rate constant is maximum for the reaction having maximum activation energy.]

12. The activation energy of exothermic reaction $A \longrightarrow B$ is 80 kJ mol^{-1}. The heat of reaction is 200 kJ mol^{-1}. The activation energy for the reaction $B \longrightarrow A$ (in kJ/mol) will be: **[PET (Kerala) 2007]**
(a) 80 (b) 120 (c) 40 (d) 200
(e) 280
[**Ans.** (e)]
[**Hint:**

$$\Delta H = E_f - E_b$$
$$-200 = 80 - E_b$$
$$E_b = 280 \text{ kJ/mol}]$$

13. Which equation is true to calculate the energy of activation, if the rate of reaction is doubled by increasing temperature from T_1 K to T_2 K? **[CET (Gujarat) 2008]**
(a) $\log_{10}\left(\dfrac{k_1}{k_2}\right) = \dfrac{E_a}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$
(b) $\log_{10}\left(\dfrac{k_2}{k_1}\right) = \dfrac{E_a}{2.303\,R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$
(c) $\log_{10}\dfrac{1}{2} = \dfrac{E_a}{2.303}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$
(d) $\log_{10} 2 = \dfrac{E_a}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$
[**Ans.** (d)]
[**Hint:** We know, $\log\left(\dfrac{k_2}{k_1}\right) = \dfrac{E_a}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

When reaction rate becomes double then $\dfrac{k_2}{k_1}$ will be equal to 2.

Then, $\log_{10} 2 = \dfrac{E_a}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$]

8.6 MOLECULARITY OF REACTION

In general, **molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.**

OR

The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

e.g.,
$PCl_5 \longrightarrow PCl_3 + Cl_2$ (Unimolecular)
$2HI \longrightarrow H_2 + I_2$ (Bimolecular)
$2SO_2 + O_2 \longrightarrow 2SO_3$ (Trimolecular)
$NO + O_3 \longrightarrow NO_2 + O_2$ (Bimolecular)
$2CO + O_2 \longrightarrow 2CO_2$ (Trimolecular)
$2FeCl_3 + SnCl_2 \longrightarrow SnCl_4 + 2FeCl_2$ (Trimolecular)

The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of a reaction.

For example, decomposition of H_2O_2 takes place in the following two steps:

$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ (overall reaction)
Step 1: $H_2O_2 \longrightarrow H_2O + [O]$ (slow)
Step 2: $[O] + [O] \longrightarrow O_2$ (fast)

The slowest step is rate-determining. Thus, from step 1, reaction appears to be unimolecular.

Note: (i) Molecularity is a theoretical concept.
(ii) Molecularity cannot be zero, –ve, fractional, infinite and imaginary.
(iii) Molecularity cannot be greater than three because more than three molecules may not mutually collide with each other.

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, *e.g.*, in

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$
$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the first reaction, molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions involve two or more steps; each step has its own molecularity not greater than three, *e.g.*, in first reaction,

$$HBr + O_2 \longrightarrow HOOBr$$
$$HOOBr + HBr \longrightarrow 2HOBr$$
$$[HOBr + HBr \longrightarrow H_2O + Br_2] \times 2$$
$$\overline{4HBr + O_2 \longrightarrow 2H_2O + Br_2}$$

Molecularity of each of the above steps is 2.

(a) Reaction between Br^- and H_2O_2 in acidic medium: The overall reaction is:

$$2Br^- + H_2O_2 + 2H^+ \longrightarrow Br_2 + 2H_2O$$

The proposed mechanism is:

$$Br^- + H_2O_2 + H^+ \longrightarrow HOBr + H_2O \quad \text{(slow)}$$
$$HOBr + H^+ + Br^- \longrightarrow Br_2 + H_2O \quad \text{(fast)}$$
$$\text{Rate} = k[Br^-][H_2O_2][H^+]$$

The reaction is trimolecular.

(b) Reaction between NO_2 and F_2: The overall reaction is:

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

The proposed mechanism is:

$$NO_2 + F_2 \longrightarrow NO_2F + F \quad \text{(slow)}$$
$$NO_2 + F \longrightarrow NO_2F \quad \text{(fast)}$$
$$\text{Rate} = k[NO_2][F_2]$$

The reaction is bimolecular.

(c) Decomposition of H_2O_2: The overall reaction is:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The proposed mechanism is:

$$H_2O_2 \longrightarrow H_2O + O \quad \text{(slow)}$$
$$H_2O_2 + O \longrightarrow H_2O + O_2 \quad \text{(fast)}$$
$$\text{Rate} = k[H_2O_2]$$

The reaction is unimolecular.

8.7 ORDER OF REACTION

Let us consider a general reaction:

$$m_1 A + m_2 B + m_3 C \longrightarrow \text{Product}$$

Let active moles of 'A', 'B' and 'C' be 'α', 'β' and 'γ' respectively. Then, rate of reaction may be given as:

$$\text{Rate} = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

$$\alpha + \beta + \gamma = \text{order}$$

When $\alpha + \beta + \gamma = m_1 + m_2 + m_3$, then

Order of reaction = molecularity of reaction.

Order is an experimentally determined quantity. It may be equal to zero, positive, negative, fractional and greater than three. Infinite and imaginary values are not possible.

Examples:

(i) $$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$-\frac{dx}{dt} = k[H_2O_2]^2$$

(observed from law of mass action)

Step 1: $$H_2O_2 \longrightarrow H_2O + [O] \quad \text{(slow)}$$

Step 2: $$[O] + [O] \longrightarrow O_2 \quad \text{(fast)}$$

Actual rate $$-\frac{dx}{dt} = k[H_2O_2]$$

Thus, order of reaction is unity.

(ii) $$2NO_2 + F_2 \longrightarrow 2NO_2F$$

Rate law from law of mass action:

$$-\frac{dx}{dt} = k[NO_2]^2[F_2]$$

Experimentally observed rate law:

$$-\frac{dx}{dt} = k[NO_2][F_2]$$

Slowest step is $NO_2 + F_2 \longrightarrow NO_2F + [F]$

Thus, order of reaction = 1 + 1 = 2

(iii) $$CH_3CHO \longrightarrow CH_4 + CO$$

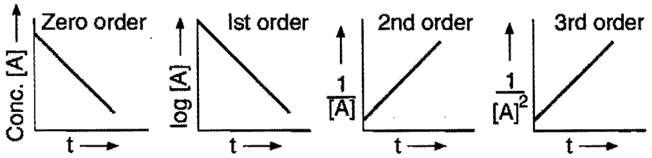
The rate equation derived from experimental data is found to be

$$-\frac{dx}{dt} = k[CH_3CHO]^{1.5}$$

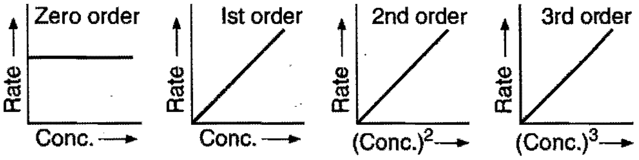
The order of reaction is 1.5.

Some typical linear plots for the reactions of different orders:

(a) Plots of rate *vs* concentrations [Rate = $k(\text{conc.})^n$]



(b) Plots from integrated rate equations:



From the study of the kinetics of many simple reactions, it is observed that for a large number of reactions, the molecularity and order are the same. Some examples are given below to justify this point.

1. Dissociation of N_2O_5,

$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$$

Order = 1, Molecularity = 1

2. Dissociation of H_2O_2,

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

Order = 1, Molecularity = 1

3. Dissociation of HI,

$$2HI \longrightarrow H_2 + I_2$$

Order = 2, Molecularity = 2

4. Formation of NO_2,

$$2NO + O_2 \longrightarrow 2NO_2$$

Order = 3, Molecularity = 3

8.8 PSEUDO-ORDER REACTION

Reactions whose actual order is different from that expected using rate law expression are called **pseudo-order reactions,** *e.g.*,

(i) $$RCl + H_2O \longrightarrow ROH + HCl$$

Expected rate law:

Rate = $k\,[RCl][H_2O]$ Expected order = 1 + 1 = 2

Actual rate law:

Rate = $k'\,[RCl]$; Actual order = 1

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, **pseudo first order.** Similarly, the acid catalysed hydrolysis of ester, *viz.*,

$$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$$

follow first order kinetics:

$$\text{Rate} = k\,[RCOOR']$$

It is also a pseudo first order reaction.

The main differences between molecularity and order of reaction are given below:

Molecularity	Order of reaction
1. It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentrations of the reacting species in the rate equation of the reaction.
2. It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.
3. It is a theoretical concept.	It is experimentally determined.
4. It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.	It is meant for the reaction and not for its individual steps.

Example 13. *The experimental data for the reaction,*

$$2A + B_2 \longrightarrow 2AB$$

is as follows:

Expt. No.	$[A]$ (*mol* L^{-1})	$[B_2]$ (*mol* L^{-1})	*Rate* (*mol* $L^{-1}\,s^{-1}$)
1.	0.50	0.50	1.6×10^{-4}
2.	0.50,	1.00	3.2×10^{-4}
3.	1.00	1.00	3.2×10^{-4}

Write the most probable equation for the rate of reaction giving reason for your answer. (IIT 1991)

Solution: From an examination of above data, it is clear that when the concentration of B_2 is doubled, the rate is doubled. Hence, the order of reaction with respect to B_2 is one.

Further, when concentration of A is doubled, the rate remains unaltered. So, order of reaction with respect to A is zero.

The probable rate law for the reaction will be

$$-\frac{dx}{dt} = k[B_2][A]^0 = k[B_2]$$

Alternatively, $\text{Rate} = k[B_2]^{\alpha}$

$$1.6 \times 10^{-4} = k[0.5]^{\alpha}$$

$$3.2 \times 10^{-4} = k[1]^{\alpha}$$

On dividing we get, $\alpha = 1$

$\therefore$ $\text{Rate} = k[A]^0[B_2]^1 = k[B_2]$

Example 14. *For the reaction,*

$$A + 2B \longrightarrow 2C$$

the following data were obtained:

Expt. No.	*Initial concentrations (mol L^{-1})*		*Initial reaction rates* (*mol* L^{-1} min^{-1})
	$[A]$	$[B]$	
1.	1.0	1.0	0.15
2.	2.0	1.0	0.30
3.	3.0	1.0	0.45
4.	1.0	2.0	0.15
5.	1.0	3.0	0.15

Write down the rate law for the reaction.

Solution: Let the rate law be

$$-\frac{dx}{dt} = k[A]^x[B]^y$$

By keeping the concentration of B constant in experiments (1), (2) and (3) and increasing the concentration uniformly, the rate also increases uniformly. Thus,

$$\text{Rate} \propto [A], \quad i.e., \quad x = 1$$

By keeping the concentration of A constant in experiments (1), (4) and (5) and increasing the concentration of B, the rate remains the same.

Hence, $y = 0$

The rate law is $-\dfrac{dx}{dt} = k[A]$

Alternative method:

From expt. (1), $k[1.0]^x[1.0]^y = 0.15$ ... (i)

From expt. (2), $k[2.0]^x[1.0]^y = 0.30$ ... (ii)

Dividing eq. (ii) by eq. (i),

$$\frac{[2.0]^x}{[1.0]^x} = \frac{0.30}{0.15} = 2$$

So, $x = 1$

From expt. (1), $k[1.0]^x[1.0]^y = 0.15$ ... (i)

From expt. (4), $k[1.0]^x[2.0]^y = 0.15$ ... (iii)

Dividing eq. (iii) by eq. (i),

$$\frac{[2.0]^y}{[1.0]^y} = 1$$

So, $y = 0$

Hence, the rate law is $-\frac{dx}{dt} = k[A]$

Example 15. *For the reaction,*

$$2NO + Cl_2 \longrightarrow 2NOCl$$

at 300K, following data are obtained:

Expt. No.	*Initial Concentration*		*Initial rate*
	[NO]	*[Cl₂]*	
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-4}

Write rate law for the reaction. What is the order of the reaction? Also calculate the specific rate constant.

Solution: Let the rate law for the reaction be

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

From expt. (1), $1.2 \times 10^{-4} = k[0.010]^x[0.010]^y$ ... (i)

From expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$ ... (ii)

Dividing eq. (ii) by eq. (i),

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^y}{[0.010]^y}$$

or $$2 = (2)^y$$

$$y = 1$$

From expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$ ... (ii)

From expt. (3), $9.6 \times 10^{-4} = k[0.020]^x[0.020]^y$ ... (iii)

Dividing eq. (iii) by eq. (ii),

$$\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^x}$$

or $$4 = 2^x$$

$$x = 2$$

Order of reaction $= x + y = 2 + 1 = 3$

Rate law for the reaction is

$$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$$

Considering eq. (i) again,

$$1.2 \times 10^{-4} = k[0.010]^2[0.010]$$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Example 16. *For the hypothetical reaction*

$$2A + B \rightarrow \text{Products}$$

the following data are obtained:

Expt. No.	*Initial conc. of (A) (mol L⁻¹)*	*Initial conc. of (B) (mol L⁻¹)*	*Initial rate mol L⁻¹ s⁻¹*
1.	0.10	0.20	3×10^2
2.	0.30	0.40	3.6×10^3
3.	0.30	0.80	1.44×10^4
4.	0.10	0.40	...
5.	0.20	0.60	...
6.	0.30	1.20	...

Find out how the rate of the reaction depends upon the concentration of A and B and fill in the blanks.

Solution: From expt. (2) and (3), it is clear that when concentration of A is kept constant and that of B is doubled, the rate increases four times. This shows that the reaction is of second order with respect to B.

Similarly, from expt. (1) and (2), it is observed that when concentration of A is increased three times and that of B two times, the rate becomes twelve times. Hence, the reaction is first order with respect to A.

Thus, the rate law for the reaction is:

$$\text{Rate} = k[A][B]^2$$

Fill in the blanks: Substituting the values of expt. (1) in the rate equation,

$$3 \times 10^2 = k[0.10][0.20]^2$$

or $$k = \frac{3 \times 10^2}{[0.10][0.20]^2} = 7.5 \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

Expt. (4): $\text{Rate} = k[0.10][0.40]^2$

$$= 7.5 \times 10^4 \times 0.10 \times 0.40 \times 0.40$$

$$= 1.2 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$$

Expt. (5): $\text{Rate} = k[0.20][0.60]^2$

$$= 7.5 \times 10^4 \times 0.20 \times 0.60 \times 0.60$$

$$= 5.4 \times 10^3 \text{ mol L}^{-1} \text{ s}^{-1}$$

Expt. (6): $\text{Rate} = k[0.30][1.20]^2$

$$= 7.5 \times 10^4 \times 0.30 \times 1.20 \times 1.20$$

$$= 3.24 \times 10^4 \text{ mol L}^{-1} \text{ s}^{-1}$$

Example 17. *The table given below gives kinetic data for the following reaction at 298 K:*

$$OCl^- + I^- \rightarrow OI^- + Cl^-$$

Expt. No.	$[OCl^-]$ *mol dm*$^{-3}$	$[I^-]$ *mol dm*$^{-3}$	$[OH^-]$ *mol dm*$^{-3}$	$10^{-4} \times d[IO^-]/dt$ *mol dm*$^{-3}$*s*$^{-1}$
1.	0.0017	0.0017	1.0	1.75
2.	0.0034	0.0017	1.0	3.50
3.	0.0017	0.0034	1.0	3.50
4.	0.0017	0.0017	0.5	3.50

What is the rate law and what is the value of rate constant?

Solution: Let the rate law be $= k[OCl^-]^x[I^-]^y[OH^-]^z$

From expt. (1), $1.75 \times 10^{-4} = k[0.0017]^x[0.0017]^y[1.0]^z$ ...(i)

From expt. (2), $3.50 \times 10^{-4} = k[0.0034]^x[0.0017]^y[1.0]^z$ ...(ii)

Dividing eq. (ii) by eq. (i),

$$\frac{3.50 \times 10^{-4}}{1.75 \times 10^{-4}} = \frac{[0.0034]^x}{[0.0017]^x}$$

or $$2 = 2^x$$

or $$x = 1, \text{ i.e., first order w.r.t. } OCl^-$$

From expt. (1), $1.75 \times 10^{-4} = k[0.0017]^x[0.0017]^y[1.0]^z$ ...(i)

From expt. (3),

$$3.50 \times 10^{-4} = k[0.0017]^x[0.0034]^y[1.0]^z \quad \text{...(iii)}$$

Dividing eq. (iii) by eq. (i),

$$\frac{3.50 \times 10^{-4}}{1.75 \times 10^{-4}} = \frac{[0.0034]^y}{[0.0017]^y}$$

or $$2 = 2^y$$

or $$y = 1, \text{ i.e., first order w.r.t. } I^-$$

From expt. (1), $1.75 \times 10^{-4} = k[0.0017]^x[0.0017]^y[1.0]^z$ ...(i)

From expt. (4),

$$3.50 \times 10^{-4} = k[0.0017]^x[0.0017]^y[0.5]^z \quad \text{...(iv)}$$

Dividing eq. (i) by eq. (iv),

$$\frac{1.75 \times 10^{-4}}{3.50 \times 10^{-4}} = \frac{[1.0]^z}{[0.5]^z}$$

or $$\frac{1}{2} = 2^z$$

or $$2^{-1} = 2^z$$

$$z = -1, \text{ i.e., order w.r.t. } OH^- \text{ is } -1.$$

$$\text{Rate law} = \frac{k[OCl^-][I^-]}{[OH^-]}$$

From expt. (1) $$k = \frac{1.75 \times 10^{-4}[OH^-]}{[OCl^-][I^-]} = \frac{1.75 \times 10^{-4} \times 1.0}{0.0017 \times 0.0017}$$

$$= 60.55 \text{ s}^{-1}$$

Example 18. *The rate law for the reaction,*

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

at 200°C is found to be: $\quad rate = k[Cl_2O]^2$.

(a) How would the rate change if $[Cl_2O]$ is reduced to one-third of its original value?

(b) How should the $[Cl_2O]$ be changed in order to double the rate?

(c) How would the rate change if $[Cl_2O]$ is raised to threefold of its original value?

Solution: (a) Rate equation for the reaction,

$$r = k[Cl_2O]^2$$

Let the new rate be r'; so, $r' = k\left[\frac{Cl_2O}{3}\right]^2 = \frac{1}{9}r$

(b) In order to have the rate $= 2r$, let the concentration of Cl_2O be x.

So, $$2r = kx^2 \quad \text{... (i)}$$

We know that, $$r = k[Cl_2O]^2 \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii),

$$\frac{2r}{r} = \frac{kx^2}{k[Cl_2O]^2}$$

or $$2 = \frac{x^2}{[Cl_2O]^2}$$

or $$x^2 = 2[Cl_2O]^2$$

or $$x = \sqrt{2}[Cl_2O]$$

(c) New rate $= k[3Cl_2O]^2 = 9k[Cl_2O]^2 = 9r$

i.e., nine times of the original rate.

Example 19. *For a reaction in which A and B form C, the following data were obtained from three experiments:*

Expt. No.	*Initial conc. (mol L*$^{-1}$*)*		*Initial rate (mol L*$^{-1}$ *s*$^{-1}$*)*
	[A]	*[B]*	
1.	0.03	0.03	0.3×10^{-4}
2.	0.06	0.06	1.2×10^{-4}
3.	0.06	0.09	2.7×10^{-4}

What is the rate equation of the reaction and what is the value of rate constant?

Solution: Let the rate equation be $k[A]^x[B]^y$.

From expt. (1), $0.3 \times 10^{-4} = k[0.03]^x[0.03]^y$ ... (i)

From expt. (2), $1.2 \times 10^{-4} = k[0.06]^x[0.06]^y$ ... (ii)

$$\frac{1.2 \times 10^{-4}}{0.3 \times 10^{-4}} = \frac{[0.06]^x[0.06]^y}{[0.03]^x[0.03]^y}$$

$$= 2^x \times 2^y = 4 \quad \text{... (iii)}$$

Similarly, from expt. (1) and expt. (3),

$$2^x \times 3^y = 9 \qquad \text{... (iv)}$$

Solving eqs. (iii) and (iv),

$$x = 0, y = 2$$

Rate equation, $\text{Rate} = k[B]^2$

Considering eq. (i) again,

$$k = \frac{0.3 \times 10^{-4}}{[0.03]^2} = 3.33 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

14. For the decomposition of HI at 1000 K ($2HI \longrightarrow H_2 + I_2$), the following data were obtained:

[HI], M	**Rate of decomposition of HI (mol L^{-1} s^{-1})**
0.1	2.75×10^{-8}
0.2	11×10^{-8}
0.3	24.75×10^{-8}

The order of reaction is:

(a) 1 (b) 2 (c) 0 (d) 1.5

[Ans. (b)]

[Hint: $\text{Rate} = k\,[\text{HI}]^n$

$$11 \times 10^{-8} = k\,[0.2]^n \qquad \text{... (i)}$$

$$2.75 \times 10^{-8} = k\,[0.1]^n \qquad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii),

$$4 = 2^n, n = 2]$$

15. Consider a reaction, $A \longrightarrow B + C$. If the initial concentration of A was reduced from 2 M to 1 M in 1 hour and from 1 M to 0.25 M in 2 hours, the order of the reaction is:

(a) 1 (b) 0 (c) 2 (d) 3

[Ans. (a)]

[Hint: Half life of the given reaction is independent of initial concentration, hence, it is a first order reaction.

$$t_{1/2} \propto \frac{1}{a^{n-1}} \,]$$

16. The rate of a gaseous reaction is given by the expression $k\,[A]^2[B]^3$. The volume of the reaction vessel is suddenly reduced to one half of the initial volume. The reaction rate relative to the original rate will be:

(a) 1/24 (b) 1/32 (c) 32 (d) 24

[Ans. (c)]

[Hint: $\text{Rate} = k\,[A]^2[B]^3 \qquad \text{... (i)}$

When volume is halved, the concentration will become double.

$$\therefore \quad \text{Rate} = k\,[2A]^2[2B]^3$$

$$= 32k\,[A]^2[B]^3$$

$$= 32 \times \text{Original rate from (i)}]$$

17. For a chemical reaction, $A \longrightarrow B$, the rate of reaction increases by a factor of 1.837 when the concentration of A is increased by 1.5 times. The order of reaction with respect to A is:

(a) 1 (b) 1.5 (c) 2 (d) –1

[Ans. (b)]

[Hint: $\text{Rate} = k\,[A]^n \qquad \text{... (i)}$

$$1.837 \times \text{Rate} = k\,[1.5A]^n \qquad \text{... (ii)}$$

Dividing eq. (ii) by eq. (i),

$$1.837 = 1.5^n$$

$\therefore \quad n = 3/2$ (solving by logarithmic method)]

18. The rate of the reaction,

$$3A + 2B \longrightarrow \text{Products}$$

is given by the rate expression:

$$\text{Rate} = k\,[A][B]^2$$

If A is taken in excess, the order of the reaction would be:

(a) 3 (b) 2 (c) 1 (d) 5

[Ans. (b)]

[Hint: When A is taken in excess, its concentration will become constant; the rate law may, therefore, be given as:

$$\text{Rate} = k'[B]^2 \quad \text{Order} = 2]$$

19. For a reaction $A + B \longrightarrow C + D$, if the concentration of A is doubled without altering the concentration of B, the rate gets doubled. If the concentration of B is increased by nine times without altering the concentration of A, the rate gets tripled. The order of the reaction is: **(KCET 2006)**

(a) 2 (b) 1 (c) 3/2 (d) 4/3

[Ans. (c)]

[Hint: $\text{Rate} = k[A]^\alpha[B]^\beta \qquad \text{... (i)}$

$$2 \times \text{rate} = k[2A]^\alpha[B]^\beta \qquad \text{... (ii)}$$

$$3 \times \text{rate} = k[A]^\alpha[9B]^\beta \qquad \text{... (iii)}$$

From eqs. (i) and (ii), $\alpha = 1$

From eqs. (i) and (iii), $\beta = 1/2$

$$\text{Order} = \alpha + \beta = 1 + \frac{1}{2} = \frac{3}{2}\,]$$

20. Inversion of cane sugar in dilute acid is: **[CET (J&K) 2007]**

(a) bimolecular reaction

(b) pseudo-unimolecular reaction

(c) unimolecular reaction

(d) trimolecular reaction

[Ans. (b)]

[Hint: $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}][H_2O]$$

When water is in excess, its concentration will be constant.

$$\therefore \quad \text{Rate} = k'[C_{12}H_{22}O_{11}]$$

The reaction is, therefore, pseudo first order or pseudo unimolecular reaction.]

21. The bromination of acetone that occurs in acid solution is represented by

$$CH_3COCH_3(aq.) + Br_2(aq.) \longrightarrow CH_3COCH_2Br\,(aq.) + H^+(aq.) + Br^-\,(aq.)$$

These kinetic data were obtained for given reaction concentrations:

Initial concentrations (M)			Initial rate of disappearance of Br_2, $M\,s^{-1}$
$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$	
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

[CBSE (PMT) 2008]

Based on these data, rate equation is :

(a) Rate $= k[CH_3COCH_3][Br_2][H^+]^2$

(b) Rate $= k[CH_3COCH_3][Br_2][H^+]$

(c) Rate $= k[CH_3COCH_3][H^+]$

(d) Rate $= k[CH_3COCH_3][Br_2]$

[Ans. (c)]

[Hint : Rate $= k[CH_3COCH_3]^{\alpha}[Br_2]^{\beta}[H^+]^{\gamma}$

$$5.7\times10^{-5} = k[0.30]^{\alpha}[0.05]^{\beta}[0.05]^{\gamma} \quad ...(i)$$

$$5.7\times10^{-5} = k[0.30]^{\alpha}[0.10]^{\beta}[0.05]^{\gamma} \quad ...(ii)$$

$$1.2\times10^{-4} = k[0.30]^{\alpha}[0.10]^{\beta}[0.10]^{\gamma} \quad ...(iii)$$

$$3.1\times10^{-4} = k[0.40]^{\alpha}[0.05]^{\beta}[0.20]^{\gamma} \quad ...(iv)$$

Dividing eq. (i) by eq. (ii),

$$1 = \left[\frac{1}{2}\right]^{\beta}, \quad i.e., \quad \beta = 0$$

Dividing eq. (ii) by eq. (iii),

$$\frac{1}{2} = \left[\frac{1}{2}\right]^{\gamma}, \quad i.e., \quad \gamma = 1$$

Dividing eq. (i) by eq. (iv),

$$\frac{5.7\times10^{-5}}{3.1\times10^{-4}} = \left[\frac{3}{4}\right]^{\alpha}\times\left[\frac{1}{4}\right]^{1}$$

$$\alpha \simeq 1$$

Thus, rate law will be

rate $= k[CH_3COCH_3]^1[H^+]^1$]

8.9 REACTION MECHANISM

Knowledge about involved steps in a reaction, and to determine which step is slowest or rate determining, is called mechanism.

The intelligent guess depending on the observed rates of reactions about the series of steps (known as elementary processes) leading to the formation of products is called the reaction mechanism.

For illustration a few examples of reaction mechanisms are given below:

1. The reaction between H_2 and I_2 to form hydrogen iodide was originally postulated as a simple one step reaction.

$$H_2 + I_2 = 2HI$$

$$\text{Rate} = k[H_2][I_2]$$

But, the formation of HI has been explained on the basis of the following mechanism:

$$\begin{array}{lll} I_2 \longrightarrow 2I & \text{(fast)} & ...(i) \\ H_2 + I \longrightarrow H_2I & \text{(fast)} & ...(ii) \\ H_2I + I \longrightarrow 2HI & \text{(slow)} & ...(iii) \\ \hline \end{array}$$

$$\text{Overall reaction:} \quad H_2 + I_2 \longrightarrow 2HI$$

2. The reaction of NO and Br_2 is known to be of second order in NO and first order in Br_2.

$$2NO + Br_2 \longrightarrow 2NOBr$$

$$\text{Rate} = k[NO]^2[Br_2]$$

The likelihood of three molecules (2 molecules of NO and 1 molecule of Br_2) colliding simultaneously is far less than the likelihood that two molecules will collide.

The mechanism is believed to be as under:

$$\begin{array}{lll} NO + Br_2 \xrightarrow{k'} NOBr_2 & \text{(fast)} & ...(i) \\ NOBr_2 + NO \xrightarrow{k''} 2NOBr & \text{(slow)} & ...(ii) \\ \hline \end{array}$$

$$\text{Overall reaction: } 2NO + Br_2 \xrightarrow{k} 2NOBr$$

The rate determining step involves 1 molecule of NO and 1 molecule of $NOBr_2$. Thus, the expected rate expression should be

$$\text{Rate} = k''[NOBr_2][NO]$$

However, $NOBr_2$ is a reaction intermediate and its concentration at the beginning of second step cannot be directly measured.

Concentration of $NOBr_2$ will be equal to

$$[NOBr_2] = k'[NO][Br_2]$$

If this is substituted in the above equation, we get

$$\text{Rate} = k'k''[NO]^2[Br_2]$$

$$= k[NO]^2[Br_2]$$

3. Depletion of ozone takes place in the following steps:

Overall reaction:

$$2O_3 \longrightarrow 3O_2$$

Step 1: $O_3 \rightleftharpoons O_2 + [O]$ (fast)

(Equilibrium constant K_c)

Step 2: $O_3 + [O] \xrightarrow{k} 2O_2$ (slow)

$$\text{Rate} = k[O_3][O] \quad ...(i)$$

Nascent oxygen [O] is not present in overall reaction; thus it should be eliminated.

$$K_c = \frac{[O_2][O]}{[O_3]}; \; [O] = K_c\frac{[O_3]}{[O_2]} \quad ...(ii)$$

From eqs. (i) and (ii),

$$\text{Rate} = k[O_3]\cdot K_c\frac{[O_3]}{[O_2]}$$

$$= k\,K_c[O_3]^2[O_2]^{-1}$$

$$= K[O_3]^2[O_2]^{-1}$$

$$K = k\times K_c$$

$$\text{Order} = 2 - 1 = 1$$

8.10 REACTIONS OF VARIOUS ORDERS

(i) Zero order reactions

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, *i.e.*, the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction

$$A \longrightarrow \text{Products}$$

to be of zero order,

$$-\frac{dx}{dt} = k[A]^0 = k$$

Some photochemical reactions and a few heterogeneous reactions are zero order reactions. Such reactions are not common.

Examples:

1. Photochemical reaction between hydrogen and chlorine:

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

This photochemical reaction is zero order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissolution of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2, *i.e.*, the concentration of the gases per unit volume in the gaseous phase will not change with time, although the quantities will change.

2. Decomposition of N_2O on hot platinum surface:

$$N_2O \longrightarrow N_2 + \frac{1}{2}O_2$$

$$\text{Rate} \propto [N_2O]^0 = k[N_2O]^0 = k$$

or

$$\frac{d[N_2O]}{dt} = k$$

3. Decomposition of NH_3 in presence of molybdenum or tungsten is a zero order reaction.

$$2NH_3 \xrightarrow{[Mo]} N_2 + 3H_2$$

The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot change by increasing the pressure or concentration of NH_3. Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction shows zero order kinetics.

Other examples of zero order are:

4. Decomposition of HI on the gold surface.
5. Iodation of acetone in presence of H^+ ions,

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$$

The rate equation of this reaction does not include $[I_2]$ factor, *i.e.*,

$$-\frac{dx}{dt} = k[CH_3COCH_3][H^+]$$

Characteristics of zero order reaction

(a) The concentration of reactant decreases linearly with time.

$$[A]_t = [A]_0 - kt$$

(b) The time required for the reaction to be complete, *i.e.*, time at which $[A]$ is zero.

$$t_{\text{Completion}} = \frac{[A]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

(c) The units of k are mol L^{-1} time^{-1}.

(ii) First order reactions

A reaction is said to be of first order if its rate is determined by the change of one concentration term only.

Consider the reaction,

$$A \longrightarrow \text{Products}$$

Let a be the concentration of A at the start and after time t, the concentration becomes $(a-x)$, *i.e.*, x has been changed into products. The rate of reaction after time 't' is given by the expression

$$\frac{dx}{dt} = k(a-x)$$

or

$$\frac{dx}{(a-x)} = k\,dt$$

upon integration of above equation,

$$\int \frac{dx}{(a-x)} = k\int dt$$

or

$$-\log_e (a-x) = kt + c$$

where c is integration constant.

When $t = 0$, $x = 0$,

$$\therefore \quad c = -\log_e a$$

Putting the value of 'c',

$$-\log_e (a-x) = kt - \log_e a$$

or

$$\log_e a - \log_e (a-x) = kt$$

or

$$\log_e \frac{a}{(a-x)} = kt$$

or

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

This is known as the kinetic equation for a reaction of the first order. The following two important conclusions are drawn from this equation:

(a) A change in concentration unit will not change the numerical value of *k*. Let the new unit be n times the first one.

So,

$$k = \frac{2.303}{t}\log_{10}\frac{na}{n(a-x)}$$

or

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

Thus, for first order reactions, any quantity which is proportional to concentration can be used in place of concentration for evaluation of 'k'.

(b) The time taken for the completion of same fraction of change is independent of initial concentration. For example, for half change,

$$x = 0.5a \quad \text{and} \quad t = t_{1/2}$$

So,

$$k = \frac{2.303}{t_{1/2}}\log_{10}\frac{a}{0.5a} = \frac{2.303}{t_{1/2}}\log_{10} 2$$

$$= \frac{0.693}{t_{1/2}}$$

or $$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration 'a'.

This time 't' in which the initial concentration becomes half is termed as **half life period.** Half life period of a first order reaction is independent of the initial concentration of the reactant.

Since, the velocity constant is independent of concentration and depends inversely on the time, the unit of k will be time^{-1}, *i.e.*, sec^{-1} or min^{-1} or hour^{-1}. The equation of the first order can also be written in the following form when initial concentration is not known:

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)}$$

$(a - x_1)$ is the concentration after time t_1 and $(a - x_2)$ the concentration after time t_2 when $t_2 > t_1$.

When the log of the concentration of the reactant at various intervals of time is plotted against the time intervals, a straight line is obtained (Fig. 8.13). The slope of this line gives the value 2.303/k, from which k can be evaluated.

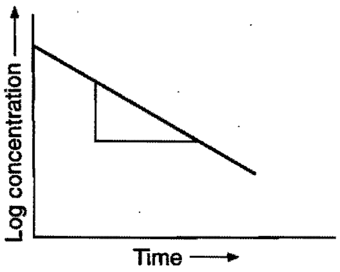


Fig. 8.13

Examples of first order reactions

1. Decomposition of H_2O_2 in aqueous solution.

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2} O_2$$

2. Hydrolysis of methyl acetate in presence of mineral acids.

$$CH_3COOCH_3 + H_2O \xrightarrow{\text{Acid}} CH_3COOH + CH_3OH$$

3. Inversion of cane sugar in presence of mineral acids.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Acid}} C_6H_{12}O_6 + C_6H_{12}O_6$$

4. Decomposition of ammonium nitrite in aqueous solution.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

5. Hydrolysis of diazo derivatives.

$$C_6H_5N{=}NCl + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$$

Note: In case of gases, pressure can be used in place of concentration.

First order growth kinetics

It is used for population growth and bacteria multiplication, *e.g.*,

Time	*Population*
0	a
dt	$(a + x)$

Growth rate is directly proportional to present population.

$$\frac{dx}{dt} \propto (a + x)$$

$$= k(a + x)$$

$$\frac{dx}{(a + x)} = k\,dt \qquad \text{... (i)}$$

It is a differential equation of first order and first degree in variable separable form. It may be solved on integration.

$$\int \frac{dx}{(a + x)} = k \int dt + c$$

$$\log_e (a + x) = kt + c \qquad \text{... (ii)}$$

Here, c = integration constant

At $t = 0$, $x = 0$

$\therefore$ $$\log_e a = k \times 0 + c$$

$$c = \log_e a \qquad \text{... (iii)}$$

Substituting the value of 'c' in eq. (ii), we get

$$\log_e (a + x) = kt + \log_e a$$

$$kt = -\log_e \frac{a}{(a + x)}$$

$$k = -\frac{2.303}{t} \log_{10} \left(\frac{a}{a + x}\right)$$

This is the kinetics for first order growth kinetics.

Note: (1) If volumes of reagents are given in volumetric analysis then we use the following equation to determine rate constant:

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

where, V_0 = volume used at zero time,
V_t = volume used at time 't',
V_∞ = volume used at infinite time

Case I: When V_0 is not given, we use

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Case II: When V_∞ is not given, then

$$k = \frac{2.303}{t} \log_{10} \left(\frac{V_0}{V_t}\right)$$

(2) If information is given in terms of angle of rotation of optically active compounds, measured by polarimeter with respect to time, then

$$k = \frac{2.303}{t} \log_{10} \left\{\frac{r_\infty - r_0}{r_\infty - r_t}\right\}$$

where, r_0 = angle of rotation at zero time,
r_t = angle of rotation at time 't',
r_∞ = angle of rotation at infinite time

Case I: If r_0 is not given, then

$$k = \frac{2.303}{t}\log_{10}\left\{\frac{r_\infty}{r_\infty - r_t}\right\}$$

Case II: If r_∞ is not given, then

$$k = \frac{2.303}{t}\log_{10}\left\{\frac{r_0}{r_t}\right\}$$

(3) If pressure is given in gaseous reactions, then we use the following kinetic equation:

$$k = \frac{2.303}{t}\log_{10}\left\{\frac{p_0}{p_0 - x}\right\}$$

where, p_0 = pressure of reactant at initial stage,

$(p_0 - x)$ = pressure of such a reactant at 't' time.

Values of 'p_0' and 'x' can be calculated using the following examples:

	$A(g) \longrightarrow$	$B(g) +$	$C(g) +$	$D(g)$
At $t = 0$	p_0	0	0	0
Pressure after time 't'	$(p_0 - x)$	x	x	x
Pressure after a long time or infinite time	0	p_0	p_0	p_0

Case I: If total pressure of reaction mixture is given in place of pressure of reactant, then

$$p_t = (p_0 - x + x + x + x)$$

where, p_t = pressure of vessel at time 't'.

Case II: If pressure of vessel after a long time or infinite time is given, then

$$p_\infty = p_0 + p_0 + p_0$$

(iii) Second order reactions

A reaction is said to be of second order if its reaction rate is determined by the variation of two concentration terms.

The kinetics of second order reactions are given as follows:

(a) When concentrations of both reactants are equal or two molecules of the same reactant are involved in the change, *i.e.*,

$$A + B \longrightarrow \text{Products}$$

or

$$2A \longrightarrow \text{Products}$$

$$\frac{dx}{dt} = k(a - x)^2,$$

On solving this equation,

$$k = \frac{1}{t}\cdot\frac{x}{a(a - x)}$$

where, a = initial concentration of the reactant or reactants and
x = concentration of the reactant changed in time t.

(b) When the initial concentrations of the two reactants are different, *i.e.*,

$$A + B \longrightarrow \text{Products}$$

Initial conc. $\quad a \quad b$

$$\frac{dx}{dt} = k(a - x)(b - x)$$

$$k = \frac{2.303}{t(a - b)}\log_{10}\frac{b(a - x)}{a(b - x)}$$

$(a - x)$ and $(b - x)$ are the concentrations of A and B after time interval, t.

Characteristics of the second order reactions

(i) The value of k (velocity constant) depends on the unit of concentration. The unit of k is expressed as $(\text{mol/litre})^{-1}\ \text{time}^{-1}$ or litre $\text{mol}^{-1}\ \text{time}^{-1}$.

(ii) Half life period $(t_{1/2}) = \dfrac{1}{k}\cdot\dfrac{0.5a}{a \times 0.5a} = \dfrac{1}{ka}$

Thus, half life is inversely proportional to initial concentration.

(iii) Second order reaction conforms to the first order when one of the reactants is present in large excess.

Taking, $k = \dfrac{2.303}{t(a - b)}\log_{10}\dfrac{b(a - x)}{a(b - x)}$, if $a >>> b$ then

$$(a - x) \approx a \text{ and } (a - b) \approx a$$

Hence, $$k = \frac{2.303}{ta}\log_{10}\frac{ba}{a(b - x)}$$

or $$ka = k' = \frac{2.303}{t}\log_{10}\frac{b}{(b - x)}$$

(since, 'a' being very large, may be treated as constant after the change). Thus, the reaction follows first order kinetics with respect to the reactant taken relatively in small amount.

Examples of second order reactions

1. Hydrolysis of ester by an alkali (saponification).

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

2. The decomposition of NO_2 into NO and O_2.

$$2NO_2 \longrightarrow 2NO + O_2$$

3. Conversion of ozone into oxygen at 100°C.

$$2O_3 \longrightarrow 3O_2$$

4. Thermal decomposition of chlorine monoxide.

$$2Cl_2O \longrightarrow 2Cl_2 + O_2$$

(iv) Third order reactions

A reaction is said to be of third order if its rate is determined by the variation of three concentration terms.

When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as:

$$3A \longrightarrow \text{Products}$$

$$A + B + C \longrightarrow \text{Products}$$

$$\frac{dx}{dt} = k(a - x)^3$$

On solving this equation,

$$k = \frac{1}{t}\cdot\frac{x(2a - x)}{2a^2(a - x)^2}$$

Characteristics of third order reactions

1. Half life period

$$= \frac{1}{k}\cdot\frac{0.5a(2a - 0.5a)}{2a^2(0.5a)^2} = \frac{1}{k}\,\frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a}$$

$$= \frac{3}{2a^2k}$$

Thus, half life is inversely proportional to the square of initial concentration.

2. The change in the unit of concentration changes the numerical value of k.

3. The unit of k is expressed as $(\text{mol/litre})^{-2}\ \text{time}^{-1}$ or $\text{litre}^2\ \text{mol}^{-2}\ \text{time}^{-1}$.

Examples of third order reactions

1. Reaction between nitric oxide and oxygen.

$$2NO + O_2 \longrightarrow 2NO_2$$

2. Reaction between nitric oxide and chlorine.

$$2NO + Cl_2 \longrightarrow 2NOCl$$

3. Reduction of $FeCl_3$ by $SnCl_2$.

$$2FeCl_3 + SnCl_2 \longrightarrow SnCl_4 + 2FeCl_2$$

Expressions for rate constant for reactions of different orders:

Reaction	Order	Rate law eqn.	Expression for rate const.
$A \to$ Products	0	Rate $= k$	$k = \frac{1}{t}\left[[A]_0 - [A]\right]$
$A \to$ Products	1	Rate $= k[A]$	$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$
$2A \to$ Products	2	Rate $= k[A]^2$	$k = \frac{1}{t}\left[\frac{1}{[A]} - \frac{1}{[A]_0}\right]$
$A + B \to$ Products	2	Rate $= k[A][B]$	$k = \frac{2.303}{t([A]_0 - [B]_0)}\log\frac{[B]_0[A]}{[A]_0[B]}$
$3A \to$ Products	3	Rate $= k[A]^3$	$k = \frac{1}{2t}\left[\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right]$

Parallel or Competing reaction

The reaction in which a substance reacts or decomposes in more than one way are called parallel or side reactions,

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$

$$\frac{-d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

$$k_1 = \text{fractional yield of } B \times k_{av}$$
$$k_2 = \text{fractional yield of } C \times k_{av}$$

If $k_1 >> k_2$ then,

$A \longrightarrow B$ main and
$A \longrightarrow C$ is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$\frac{x}{y} = \frac{k_1}{k_2}$$

i.e.,
$$\frac{d[B]}{dt} \Big/ \frac{d[C]}{dt} = \frac{k_1}{k_2}$$

Variation of concentration A, B and C with time may be graphically represented as,

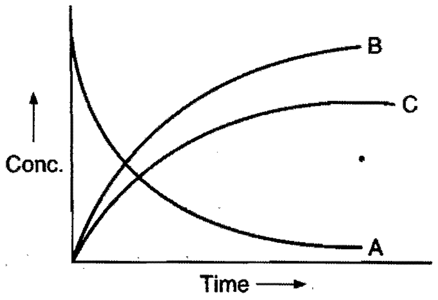
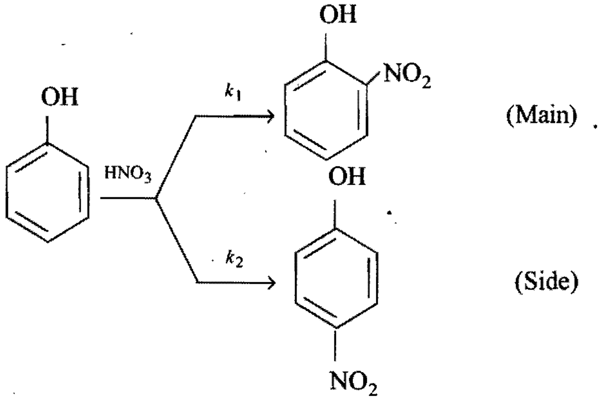


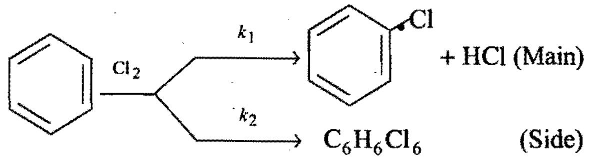
Fig. 8.14

Examples:

(i)



(ii)



Consecutive reaction

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

$$A \longrightarrow B \longrightarrow C \text{ and so on}$$

Examples: (i) Decomposition of ethylene oxide:

$$(CH_2)_2O \xrightarrow{k_1} CH_3CHO$$
$$CH_3CHO \xrightarrow{k_2} CO + CH_4$$

(ii) The pyrolysis of acetone:

$$(CH_3)_2CO \longrightarrow CH_4 + \underset{\text{Ketene}}{CH_2{=}C{=}O}$$

$$CH_2 = C = O \longrightarrow \frac{1}{2} C_2H_4 + CO$$

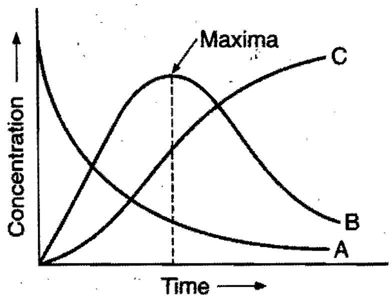


Fig. 8.15
Variation of concentration of various substances during the progress of reaction ($A \rightarrow B \rightarrow C$)

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Let initially ($t = 0$), $[B] = 0$ and $k_1 < k_2$ then maximum concentration of $[B]$ may be calculated as,

$$[B]_{\max} = [A]_0 \left[\frac{k_1}{k_2}\right]^{k_2/k_1 - k_2}$$

where, $[A]_0$ = initial concentration of A

Time in which B attains maximum concentration may be given as,

$$t_{\max} = \frac{2.303}{k_2 - k_1} \log\left(\frac{k_2}{k_1}\right)$$

Concentration of $[B]$ after time 't' may be calculated as,

$$[B]_t = \frac{k_1 [A]_0}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}]$$

Activation energy diagram of a composite reaction involves more than one peaks and number of peaks indicate the number of different types of activated complexes involved. The number of valleys in the activation energy diagram indicates the number of different types of reactive intermediates involved.

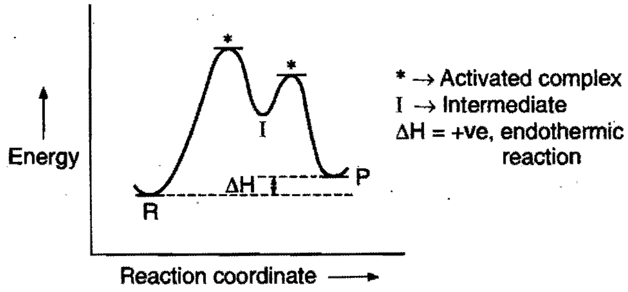


Fig. 8.16 Activation energy diagram of a two steps composite reaction

Energy Diagram of two Steps Reaction

Let us consider a reaction of the type :

$$A \xrightarrow{\text{Step 1}} B \xrightarrow{\text{Step 2}} C \quad \text{(Exothermic)}$$

These are two possibilities in this reaction

First possibility :

Step 1 $A \longrightarrow A^* \longrightarrow B$

Step 2 $B \longrightarrow B^* \longrightarrow C$

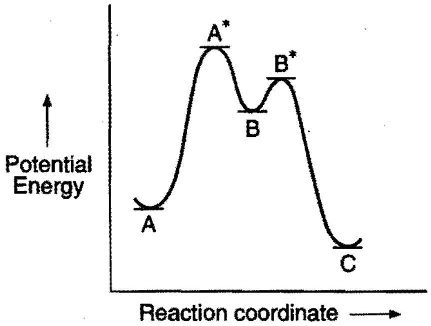


Fig. 8.17

Activation energy of **step 1** is greater than that of **step 2** thus **step 1** will be slow and rate determining.

Second possibility :

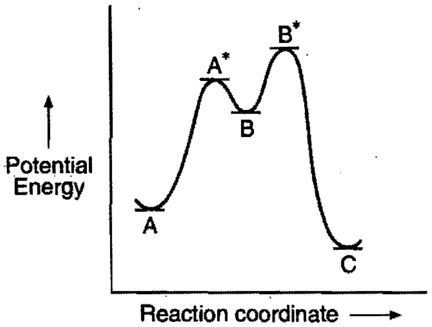


Fig. 8.18

Activation energy of **step 2** is greater than that of **step 1** hence **step 2** will be slow and rate determining

Reversible Reactions

The reactions in which the products of chemical change react together to form the original reactants, are called reversible reactions. These are also called opposing or counter reactions.

Let us consider a reversible reaction in which both forward and backward reactions are of first order.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Initial state ($t = 0$)	a	0
Conc. at time (t)	$a - x$	x
Equilibrium conc.	$(a - x_e)$	x_e

$$k_1 + k_2 = \frac{2.303}{t} \log_{10}\left\{\frac{x_e}{x_e - x}\right\}$$

8.11 METHODS FOR DETERMINATION OF ORDER OF A REACTION

The important methods used are the following:

1. Method of integration (Hit and trial method)

The most simple method is the one in which the quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}, \text{ for first order reactions;}$$

$$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right], \quad \text{for second order reactions;}$$

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right], \text{ for third order reactions.}$$

2. Graphical method

A graphical method based on the respective rate laws can also be used.

If the plot of $\log (a-x)$ *versus* 't' is a straight line, the reaction follows first order.

If the plot of $\frac{1}{(a-x)}$ *versus* 't' is a straight line, the reaction follows second order.

If the plot of $\frac{1}{(a-x)^2}$ *versus* 't' is a straight line, the reaction follows third order.

In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}}$ *versus* 't' must be a straight line.

3. Half life method

A general expression for the half life, $(t_{1/2})$, is given by

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where, 'n' is the order of the reaction.

Starting with two different initial concentrations a_1 and a_2 for the same reaction, the half lives are $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively are determined. As we know that,

$$(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}} \quad \text{... (i)}$$

and

$$(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}} \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii),

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \quad \text{... (iii)}$$

Taking logarithms on both sides,

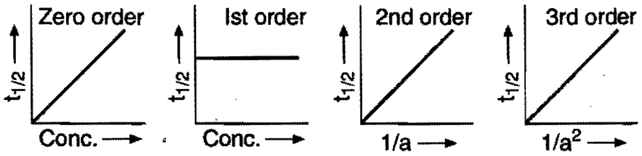
$$\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2 = (n-1)[\log_{10} a_2 - \log_{10} a_1]$$

$$(n-1) = \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1}$$

or

$$n = 1 + \frac{\log_{10} (t_{1/2})_1 - \log_{10} (t_{1/2})_2}{\log_{10} a_2 - \log_{10} a_1} \quad \text{... (iv)}$$

Plots of half lives *vs.* concentration $(t_{1/2} \propto a^{1-n})$:



This relation can be used to determine order of reaction 'n'.

4. van't Hoff differential method

As we know that, the rate of a reaction varies as the nth power of the concentration of the reactant where 'n' is the order of the reaction. Thus, for two different initial concentrations C_1 and C_2, equations can be written in the form

$$-\frac{dC_1}{dt} = kC_1^n \text{ and } -\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms,

$$\log_{10}\left(-\frac{dC_1}{dt}\right) = \log_{10} k + n \log_{10} C_1 \quad \text{... (i)}$$

and

$$\log_{10}\left(-\frac{dC_2}{dt}\right) = \log_{10} k + n \log_{10} C_2 \quad \text{... (ii)}$$

Subtracting eq. (ii) from eq. (i),

$$\log_{10}\left(-\frac{dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right) = n(\log_{10} C_1 - \log_{10} C_2)$$

or

$$n = \frac{\log_{10}\left(-\frac{dC_1}{dt}\right) - \log_{10}\left(-\frac{dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \quad \text{... (iii)}$$

$-\frac{dC_1}{dt}$ and $-\frac{dC_2}{dt}$ are determined from concentration *vs.* time graphs and the value of 'n' can be determined.

SOME SOLVED EXAMPLES

Example 20. *Rate of a reaction $A + B \longrightarrow$ product, is given as a function of different initial concentrations of A and B.*

$[A]$ (*mol* L^{-1})	$[B]$ (*mol* L^{-1})	*Initial rate* (*mol* L^{-1} *min*$^{-1}$)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and w.r.t. B. What is the half life of A in the reaction?

Solution: Let the rate of reaction be

$$\text{Rate} = k[A]^x[B]^y$$

From the data given, it is clear that by doubling the concentration of A, the rate also becomes double when B is kept constant. Thus, the rate is directly proportional to concentration of A.

$$\text{Rate} \propto [A], \quad i.e., \quad x = 1$$

Or the order of reaction w.r.t. A is 1.

When the concentration of A is kept constant and the concentration of B is doubled, the rate does not change, *i.e.*, $y = 0$; or the order of reaction w.r.t. B is zero.

Thus, reaction rate, $$-\frac{dx}{dt} = k[A]$$

Again $$k = \frac{0.005}{0.01} = 0.5\ \text{min}^{-1}$$

$$\text{Half life of } A = \frac{0.693}{k} = \frac{0.693}{0.5} = 1.386\ \text{min}$$

Example 21. *Thermal decomposition of a compound is of the first order. If 50% of a sample of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose?*

Solution: Half life of reaction = 120 min

We know that,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.77 \times 10^{-3}\ \text{min}^{-1}$$

Applying first order reaction equation,

$$t = \frac{2.303}{k}\log_{10}\frac{a}{a-x}$$

If $a = 100$, $x = 90$ or $(a - x) = 10$,

So, $$t = \frac{2.303}{5.77 \times 10^{-3}} \cdot \log_{10} 10 = \frac{2.303}{5.77 \times 10^{-3}} = 399\ \text{min}$$

Example 22. *The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.*

(i) After 55 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.

Solution: (i) As pressure ∝ concentration,

$$k = \frac{2.303}{t}\log_{10}\frac{P_i\ \text{(initial pressure)}}{P_t\ \text{(pressure after time } t)}$$

$$= \frac{2.303}{55}\log_{10}\frac{0.062}{0.044} = 6.2 \times 10^{-3}\ \text{s}^{-1}$$

(ii) Again applying the first order kinetic equation,

$$k = \frac{2.303}{t}\log_{10}\frac{P_i\ \text{(initial pressure)}}{P_t\ \text{(pressure after time } t)}$$

$$6.2 \times 10^{-3} = \frac{2.303}{100}\log_{10}\frac{0.062}{P_t}$$

or $$\frac{6.2 \times 10^{-3} \times 100}{2.303} = \log_{10} 0.062 - \log_{10}(P_t)$$

or $$0.2692 = \log_{10} 0.062 - \log_{10}(P_t)$$

or $$\log_{10}(P_t) = \log_{10} 0.062 - 0.2692$$

$$= (\bar{2}.7924 - 0.2692)$$

$$P_t = 0.033\ \text{atmosphere}$$

Pressure after 100 sec = 0.033 atm

Example 23. *The half life of a first order reaction is 60 min. How long will it take to consume 90% of the reactant?*

Solution: For the first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 11.55 \times 10^{-3}\ \text{min}^{-1}$$

Applying first order kinetic equation,

$$t = \frac{2.303}{k}\log_{10}\frac{a}{(a-x)}$$

Given: $a = 100, x = 90$, *i.e.*, $(a - x) = (100 - 90) = 10$

Hence, $$t = \frac{2.303}{11.55 \times 10^{-3}} \cdot \log_{10} 10$$

$$= 199\ \text{min}$$

Example 24. *A first order reaction has a rate constant of $15 \times 10^{-3}\ s^{-1}$. How long will 5.0 g of this reactant take to reduce to 3.0 g?*

Solution: Applying first order kinetic equation,

$$t = \frac{2.303}{k}\log_{10}\frac{a}{(a-x)}$$

Given: $k = 15 \times 10^{-3}\ \text{sec}^{-1}, a = 5\ \text{g}, (a - x) = 3\ \text{g}$

So, $$t = \frac{2.303}{15 \times 10^{-3}}\log_{10}\frac{5}{3} = 34.07\ \text{sec}$$

Example 25. *Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minutes and 73% in 100 minutes.*

(a) What is the order of reaction?

(b) How much it will decompose in 100 minutes at the same temperature but at an initial pressure of 600 mm? **(IIT 1990)**

Solution: (a) Using first order kinetic equation and substituting given values,

In first case: $$k = \frac{2.303}{53}\log_{10}\frac{200}{200-100} = 0.0131\ \text{min}^{-1}$$

In second case: $$k = \frac{2.303}{100}\log_{10}\frac{200}{200-146} = 0.0131\ \text{min}^{-1}$$

As the values of k come out to be the same in both cases, the reaction is of first order.

(b) As in the first order reaction, the time required for the completion of same fraction is independent of initial concentration; the percentage decomposition in 100 minutes when the initial pressure is 600 mm will also be 73%.

Example 26. *A substance reacts according to the first order rate law and the specific reaction rate for the reaction is* $1\times 10^{-2}\ s^{-1}$. *If the initial concentration is* 1.0 *M.*

(*a*) *What is the initial rate?*

(*b*) *What is the reaction rate after* 1 *minute?*

Solution: (a) Initial rate of a first order reaction = kC

$$=1\times 10^{-2}\times 1.0=1\times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

(b) Concentration after 60 seconds is calculated by applying first order kinetic equation,

$$k=\frac{2.303}{60}\log_{10}\frac{1}{(1-x)}$$

or
$$1\times 10^{-2}=\frac{2.303}{60}[-\log(1-x)]$$

or
$$\frac{60\times 10^{-2}}{2.303}=-\log(1-x)=0.2605$$

$$\log(1-x)=-0.2605$$
$$=\bar{1}.7395$$

$$(1-x)=\text{antilog of }(\bar{1}.7395)=0.5489\ \text{mol L}^{-1}$$

Rate of reaction after 1 minute $=k\times C$

$$=1\times 10^{-2}\times 0.5489$$
$$=5.489\times 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Example 27. *A first order reaction is 50% completed in* 30 *minutes at 27°C and in* 10 *minutes at 47°C. Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ mol*$^{-1}$.

Solution: For first order reaction $k=\dfrac{0.693}{t_{1/2}}$

At 27°C, $$k_{27°\text{C}}=\frac{0.693}{30}=0.0231\ \text{min}^{-1}$$

At 47°C, $$k_{47°\text{C}}=\frac{0.693}{10}=0.0693\ \text{min}^{-1}$$

Now applying the following equation:

$$\log_{10}\frac{k_1}{k_2}=\frac{-E_a}{2.303\times R}\cdot\left(\frac{T_2-T_1}{T_2\cdot T_1}\right)$$

or
$$\log_{10}\frac{0.0231}{0.0693}=\frac{-E_a}{2.303\times 8.314}\cdot\left(\frac{320-300}{320\times 300}\right)$$

or
$$-\log_{10}0.3333=\frac{E_a}{19.1471}\times\frac{20}{96000}$$

$$E_a=-\frac{19.1471\times 96000}{20}\times\log 0.3333$$
$$=-91906\times(-0.4772)$$
$$=43857\ \text{J mol}^{-1}=43.857\ \text{kJ mol}^{-1}$$

Example 28. *In Arrhenius equation for a certain reaction, the values of A and* E_a *(activation energy) are* 4×10^{13} *sec*$^{-1}$ *and* 98.6 *kJ mol*$^{-1}$ *respectively. If the reaction is of first order, at what temperature will its half life period be* 10 *minutes?*

(IIT 1990)

Solution: According to Arrhenius equation,

$$k=Ae^{-E_a/RT}$$

or
$$\log_e k=\log_e A-\frac{E_a}{RT}$$

or
$$2.303\log_{10}k=2.303\log_{10}A-\frac{E_a}{RT}$$

For a first order reaction $t_{1/2}=\dfrac{0.693}{k}$

So, $$k=\frac{0.693}{600}\ \text{sec}^{-1}\quad(t_{1/2}=10\ \text{min}=600\ \text{sec})$$
$$=1.1\times 10^{-3}\ \text{sec}^{-1}$$

Hence, $$\log(1.1\times 10^{-3})=\log(4\times 10^{13})-\frac{98.6\times 10^{3}}{2.303\times 8.314\times T}$$

$$T=310.95\ \text{K}$$

Example 29. *A second order reaction, in which both the reactants have same concentration, is* 20% *completed in* 500 *seconds. How much time it will take for* 60% *completion?*

Solution: The second order equation when both the reactants have same concentration is

$$k=\frac{1}{t}\cdot\frac{x}{a(a-x)}$$

If $a=100,\ x=20,\ t=500$ seconds.

So, $$k=\frac{1}{500}\times\frac{20}{100\times(100-20)}$$

When $a=100,\ x=60,\ t=?$

$$t=\frac{1}{k}\cdot\frac{60}{100\times 40}$$

Substituting the value of k,

$$t=\frac{500\times 100\times 80}{20}\times\frac{60}{100\times 40}$$

or $$t=3000\ \text{seconds}$$

Example 30. *A first order reaction is* 20% *complete in* 10 *minutes. Calculate the time taken for the reaction to go to* 80% *completion.*

Solution: Applying first order equation,

$$k=\frac{2.303}{t}\log_{10}\frac{100}{(100-20)}$$

$$=\frac{2.303}{10}\log_{10}\frac{100}{80}=0.0223\ \text{min}^{-1}$$

Again applying first order equation,

$$t = \frac{2.303}{k} \log_{10} \frac{100}{(100-80)}$$

$$= \frac{2.303}{0.0223} \log_{10} \frac{100}{20}$$

$$= 72.18 \text{ min}$$

Example 31. *The decomposition of dinitrogen pentoxide* (N_2O_5) *follows first order rate law. Calculate the rate constant from the given data:*

$t = 800\, sec \qquad [N_2O_5] = 1.45\, mol\, L^{-1} = [A_1]$

$t = 1600\, sec \qquad [N_2O_5] = 0.88\, mol\, L^{-1} = [A_2]$

Solution: Applying the formula,

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A_1]}{[A_2]}$$

$$= \frac{2.303}{(1600-800)} \log_{10} \frac{1.45}{0.88}$$

$$= \frac{2.303}{800} \times 0.2169 = 6.24 \times 10^{-4} \text{ sec}^{-1}$$

Example 32. *The decomposition of* N_2O_5 *according to the equation,*

$$N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.4 mm Hg and on completion, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

(IIT 1991)

Solution: $2N_2O_5 \longrightarrow 4NO_2 + O_2$

On decomposition of 2 moles of N_2O_5, 4 moles of NO_2 and 1 mole of O_2 are produced. Thus, the total pressure after completion corresponds to 5 moles and initial pressure to 2 moles.

Initial pressure of N_2O_5, $p_0 = \frac{2}{5} \times 584.5 = 233.8$ mm Hg

After 30 minutes, the total pressure = 284.5 mm Hg

$$\underset{p_0 - 2p}{2N_2O_5} \longrightarrow \underset{4p}{4NO_2} + \underset{p}{O_2}$$

or $\quad p_0 + 3p = 284.5$

or $\quad 3p = 284.5 - 233.8 = 50.7$ mm Hg

or $\quad p = \frac{50.7}{3} = 16.9$ mm Hg

Pressure of N_2O_5 after 30 minutes $= 233.8 - (2 \times 16.9)$

$= 200$ mm Hg

$$k = \frac{2.303}{30} \log_{10} \frac{233.8}{200.0} = 5.2 \times 10^{-3} \text{ min}^{-1}$$

Example 33. *The gas phase decomposition of dimethyl ether follows first order kinetics.*

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure after 12 minutes? Assume ideal gas behaviour.

(IIT 1993)

Solution: $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 0.047793 \text{ min}^{-1}$

Let the pressure of dimethyl ether after 12 minutes be p atm. Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{p_0}{p}$$

$$\log_{10} \frac{0.4}{p} = \frac{0.047793 \times 12}{2.303} = 0.2490$$

or $\quad \frac{0.4}{p} = 1.7743$

or $\quad p = \frac{0.4}{1.7743} = 0.2254$ atm

Decrease in pressure, $x = 0.4 - 0.2254 = 0.1746$ atm

$$\underset{p_0 - x}{CH_3OCH_3(g)} \longrightarrow \underset{x}{CH_4(g)} + \underset{x}{H_2(g)} + \underset{x}{CO(g)}$$

Total pressure $= p_0 + 2x$

$= 0.4 + 2 \times 0.1746$

$= 0.7492$ atm

Example 34. *The half life of first order decomposition of nitramide is 2.1 hours at 15°C.*

$$NH_2NO_2(aq.) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 *is allowed to decompose calculate (i) time taken for* NH_2NO_2 *to decompose 99% and (ii) the volume of dry* N_2O *produced at this point, measured at STP.* **(IIT 1994)**

Solution: (i) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33 \text{ hr}^{-1}$

Applying kinetic equation of first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

or $\quad t = \frac{2.303}{0.33} \log_{10} \frac{100}{(100-99)}$

$= 13.96$ hrs

(ii) No. of moles of NH_2NO_2 decomposed

$= 0.99 \times \frac{6.2}{62}$

$= 0.099$

No. of moles of N_2O formed = 0.099

Volume of N_2O at STP = 0.099 × 22400 mL

= 2217.6 mL

Example 35. *From the following data for the reaction between A and B:*

Expt. No.	$[A]$ ($mol\ L^{-1}$)	$[B]$ ($mol\ L^{-1}$)	Initial rate ($mol\ L^{-1}\ s^{-1}$)	
			300 K	**320 K**
(1)	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
(2)	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	...
(3)	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	...

Calculate the following:

(*i*) *The order of the reaction with respect to A and with respect to B,*

(*ii*) *The rate constant at 300K,*

(*iii*) *The energy of activation and*

(*iv*) *The pre-exponential factor.* (IIT 1994)

Solution: (i) Let the rate law be:

$$\text{Rate} = k[A]^x[B]^y$$

From expt. (1), $5.0\times10^{-4} = k[2.5\times10^{-4}]^x[3.0\times10^{-5}]^y$ ... (i)

From expt. (2), $4.0\times10^{-3} = k[5.0\times10^{-4}]^x[6.0\times10^{-5}]^y$ ... (ii)

Dividing eq. (ii) by eq. (i), $\dfrac{4.0\times10^{-3}}{5.0\times10^{-4}} = 2^x\cdot2^y = 8$

From expt. (3), $1.6\times10^{-2} = k[1.0\times10^{-3}]^x[6.0\times10^{-5}]^y$ ... (iii)

Dividing eq. (iii) by eq. (ii), $\dfrac{1.6\times10^{-2}}{4.0\times10^{-3}} = 2^x = 4$

or $x = 2$ and $y = 1$

Hence, order w.r.t. A is 2nd and order w.r.t. B is 1st.

(ii) $\text{Rate} = k\cdot[A]^2[B]$

From expt. (1), $5\times10^{-4} = k[2.5\times10^{-4}]^2[3.0\times10^{-5}]$

or $k = \dfrac{5\times10^{-4}}{[2.5\times10^{-4}]^2[3.0\times10^{-5}]} = 2.67\times10^8\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$

(iii) From Arrhenius equation,

$$\log_{10}\frac{2.0\times10^{-3}}{5.0\times10^{-4}} = \frac{E_a}{2.303\times8.314}\times\frac{20}{300\times320}$$

$$E_a = \frac{2.303\times8.314\times300\times320}{20}\times\log_{10}4$$

$$= 55.333\ \text{kJ mol}^{-1}$$

(iv) Applying $\log_{10}k = \log_{10}A - \dfrac{E_a}{2.303RT}$

$$\log_{10}\frac{A}{k} = \frac{55.333}{2.303\times8.314\times300} = 9.633$$

or $$\frac{A}{k} = 4.29\times10^9$$

or $$A = 4.29\times10^9\times2.67\times10^8$$

$$= 1.145\times10^{18}$$

Example 36. *At a certain temperature, the half change period for the catalytic decomposition of ammonia were found as follows:*

Pressure (Pascals):	6667	13333	26666
Half life period in hours:	3.52	1.92	1.0

Calculate the order of reaction.

Solution: $\dfrac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\dfrac{a_2}{a_1}\right)^{n-1}$ where, n is order of reaction

From the given data,

$$\frac{3.52}{1.92} = \left(\frac{13333}{6667}\right)^{n-1} \quad (a \propto \text{initial pressure})$$

$$= (2)^{n-1}$$

$$\log\frac{3.52}{1.92} = (n-1)\log 2$$

$$= 0.3010\times(n-1)$$

$$0.2632 = 0.3010\times(n-1)$$

$$n = 1.87 \approx 2$$

Similar calculations are made between first and third observations. n comes equal to $1.908\ (\approx 2)$.

Thus, the reaction is of second order.

Example 37. *On heating, arsine (AsH_3) decomposes as:*

$$2AsH_3(g) \longrightarrow 2As(s) + 3H_2(g)$$

The total pressure measured at constant temperature and constant volume varies with time as follows:

t (min)	0	5	7.5	10
p/mm Hg	760	836	866.4	896.8

Calculate the rate constant assuming the reaction to follow the first order rate law.

Solution: For first order, the rate equation is

Initially after time t

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{t}\log\frac{p_0}{p}$$

given, $p_0 = 760$ mm Hg.

The decomposition reaction is:

$$\begin{array}{ccccc} 2\text{AsH}_3(g) & \rightarrow & \text{As}(s) & + & 3\text{H}_2(g) \\ p_0 & & 0 & & 0 \\ p_0-2x & & & & 3x \end{array}$$

Total pressure, $p_t = p_0 - 2x + 3x = p_0 + x$

$$x = p_t - p_0$$

$$p_{\text{AsH}_3} = (p_0 - 2x) = p_0 - 2p_t + 2p_0 = 3p_0 - 2p_t$$

After 5 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 836)$

$$= 608 \text{ mm Hg}$$

$$k = \frac{2.303}{5} \log_{10} \frac{760}{608} = 0.0446 \text{ min}^{-1}$$

After 7.5 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 866.4)$

$$= 547.2 \text{ mm Hg}$$

$$k = \frac{2.303}{7.5} \log_{10} \frac{760}{547.2} = 0.0438 \text{ min}^{-1}$$

After 10 minutes, $p_{\text{AsH}_3} = (3 \times 760) - (2 \times 896.8)$

$$= 486.4 \text{ mm Hg}$$

$$k = \frac{2.303}{10} \log_{10} \frac{760}{486.4} = 0.0446 \text{ min}^{-1}$$

Example 38. *Cane sugar is gradually converted into dextrose and laevulose by dilute acid. The rate of inversion is observed by measuring the polarisation angle, at various times, when the following results are obtained:*

Time (min)	0	10	20	30	40	100	∞
Angle	32.4	28.8	25.5	22.4	19.6	−6.1	−14.1

Show that the reaction is of first order. Calculate the value of t, when the solution is optically inactive.

Solution: In case, the inversion of cane sugar is a first order change, then

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]} = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

When, $t = 10$, $r_0 = 32.4$, $r_t = 28.8$, $r_\infty = -14.1$

$$k = \frac{2.303}{10} \log_{10} \frac{32.4 - (-14.1)}{28.8 - (-14.1)}$$

$$= \frac{2.303}{10} \log_{10} \frac{46.5}{42.9} = 0.008 \text{ min}^{-1}$$

When, $t = 20$, $r_0 = 32.4$, $r_t = 25.5$, $r_\infty = -14.1$

$$k = \frac{2.303}{20} \log_{10} \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = \frac{2.303}{20} \log \frac{46.5}{39.6}$$

$$= 0.008 \text{ min}^{-1}$$

When, $t = 30$, $r_0 = 32.4$, $r_t = 22.4, r_\infty = -14.1$

$$k = \frac{2.303}{30} \log_{10} \frac{32.4 - (-14.1)}{22.4 - (-14.1)} = \frac{2.303}{30} \log_{10} \frac{46.5}{36.5}$$

$$= 0.008 \text{ min}^{-1}$$

Thus, the reaction is of first order as the value of k is constant.

The solution will be optically inactive when half of the cane sugar is inverted.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.008} = 86.6 \text{ min}$$

Example 39. *1 mL of methyl acetate was added to a flask containing 20 mL of N/20 HCl maintained at 25° C. 2 mL of the reaction mixture were withdrawn at different intervals and titrated with a standard alkali solution. The following results were obtained:*

Time (min)	0	75	119	183	∞
Alkali used (mL)	19.24	24.20	26.60	29.32	42.03

Show that the reaction follows first order kinetics.

Solution: In case the hydrolysis follows first order kinetics, then

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]} = \frac{2.303}{t} \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

When, $t = 75$ min, $V_\infty = 42.03$, $V_0 = 19.24$, $V_t = 24.20$

$$k = \frac{2.303}{75} \log_{10} \frac{(42.03 - 19.24)}{(42.03 - 24.20)} = \frac{2.303}{75} \log_{10} \frac{22.79}{17.83}$$

$$= 0.00327 \text{ min}^{-1}$$

$t = 119$ min, $V_\infty = 42.03$, $V_0 = 19.24$, $V_t = 26.60$

$$k = \frac{2.303}{119} \log_{10} \frac{(42.03 - 19.24)}{(42.03 - 26.60)} = \frac{2.303}{119} \log_{10} \frac{22.79}{15.43}$$

$$= 0.00327 \text{ min}^{-1}$$

Since, the values of k are constant, hence, it follows first order kinetics.

Example 40. *The gaseous decomposition of ozone*

$$2O_3 \rightarrow 3O_2$$

obeys the rate law $r = -\frac{d[O_3]}{dt} = \frac{k[O_3]^2}{[O_2]}$

Show that the following mechanism is consistent with the above rate law:

$$O_3 \overset{K_{eq}}{\rightleftharpoons} O_2 + O \qquad \textit{(fast)}$$

$$O + O_3 \xrightarrow{k_1} 2O_2 \qquad \textit{(slow)}$$

Solution: From the slow rate determining step

$$r = -\frac{d[\text{O}_3]}{dt} = k \qquad {}_3]$$

From the fast reaction,

$$K_{\text{eq}} = \frac{[\text{O}_2][}{[\text{O}_3}$$

or $$[\text{O}] = \frac{K_{\text{eq}}[\text{O}_3]}{[\text{O}_2]}$$

Substituting the value of [O] in the above expression

$$r = -\frac{d[\text{O}_3]}{dt} = \frac{k_1 K_{\text{eq}}[\text{O}_3]^2}{[\text{O}_2]} = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$$

Example 41. *For the formation of phosgene from $CO(g)$ and chlorine,*

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$

the experimentally determined rate equation is,

$$\frac{d[COCl_2]}{dt} = k[CO][Cl_2]^{3/2}$$

Is the following mechanism consistent with the rate equation?

(*i*) $Cl_2 \rightleftharpoons 2Cl$ *(fast)*

(*ii*) $Cl + CO \rightleftharpoons COCl$ *(fast)*

(*iii*) $COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$ *(slow)*

Solution: Multiplying equation (ii) by 2 and adding (i), we get:

$$Cl_2 + 2CO \rightleftharpoons 2COCl$$

$$K = \frac{[COCl]^2}{[Cl_2][CO]^2}$$

$$[COCl] = (K)^{1/2}\,[Cl_2]^{1/2}[CO] \qquad \ldots(i)$$

Slowest step is rate determining, hence,

$$\text{Rate} = k[COCl][Cl_2] \qquad \ldots(ii)$$

From eqs. (i) and (ii), we get

$$\text{Rate} = kK^{1/2}[Cl_2]^{1/2}[Cl_2][CO]$$

$$\text{Rate} = k'[Cl_2]^{3/2}[CO]$$

Thus, rate law is in accordance with the mechanism.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

22. A first order reaction has half life of 14.5 hrs. What percentage of the reactant will remain after 24 hrs?

(a) 18.3% (b) 31.8% (c) 45.5% (d) 68.2%

[Ans. (b)]

[Hint: $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

$$\frac{0.693}{14.5} = \frac{2.303}{24}\log\frac{100}{(a-x)}$$

On solving, $(a - x) = 31.8\%$]

23. Half life of a first order reaction is 10 min. What % of reaction will be completed in 100 min?

(a) 25% (b) 99.9% (c) 75% (d) 80%

[Ans. (b)]

[Hint: $\frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$

$$\frac{0.693}{10} = \frac{2.303}{100}\log\left(\frac{100}{100-x}\right)$$

$x = 99.9\%$]

24. A certain zero order reaction has $k = 0.025\,M\,s^{-1}$ for the disappearance of A. What will be the concentration of A after 15 seconds if the initial concentration is 0.5 M?

(a) 0.5 M (b) 0.32 M (c) 0.12 M (d) 0.06 M

[Ans. (c)]

[Hint: $x = kt = 0.025 \times 15 = 0.375\,M$

Remaining conc. $= 0.5 - 0.375 = 0.125\,M$]

25. A first order reaction:

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

has a rate constant of $1.3 \times 10^{-11}\,s^{-1}$ at 270°C and $4.5 \times 10^{-10}\,s^{-1}$ at 350°C. What is the activation energy for this reaction?

(a) 15 kJ (b) 30 kJ (c) 68 kJ (d) 120 kJ

[Ans. (d)]

[Hint: $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log\left(\frac{4.5 \times 10^{-10}}{1.3 \times 10^{-11}}\right) = \frac{E_a}{2.303 \times 8.314 \times 10^{-3}}\left[\frac{1}{543} - \frac{1}{623}\right]$$

$E_a = 120$ kJ]

26. The reaction of O_3 with chlorine atom is given as:

$$O_3(g) + Cl(g) \longrightarrow O_2(g) + ClO(g); \quad k_1 = 5.2 \times 10^9\ \text{L mol}^{-1}\ \text{sec}^{-1}$$

$$ClO(g) + O(g) \longrightarrow Cl(g) + O_2(g); \quad k_2 = 2.6 \times 10^{10}\ \text{L mol}^{-1}\ \text{sec}^{-1}$$

Which of these values is closest to the rate constant of the overall reaction?

$$O_3(g) + O(g) \longrightarrow 2O_2(g)$$

(a) 5.2×10^9 (b) 2.6×10^{10}

(c) 3.1×10^{10} (d) 1.4×10^{20}

[Ans. (a)]

[Hint: Lowest value of k shows that the step is rate determining.]

27. If a first order reaction takes 32 minutes for 75% completion, then time required for 50% completion is: [AMU (Medical)

(a) 32 min (b) 16 min (c) 8 min (d) 4 min

[Ans. (b)]

[Hint: $k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right)$

When, $a = 100$, $x = 75$, $t = 32$

$$k = \frac{2.303}{32}\log_{10}\left(\frac{100}{25}\right) = 0.0433\ \text{min}^{-1}$$

Time for 50% completion $(t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{0.0433} \approx 16$ min]

28. Rate constant of a reaction is 175 $\text{litre}^{-2}\ \text{mol}^{-2}\ \text{sec}^{-1}$. What is the order of reaction? [CET ([illegible])]

(a) First (b) Second (c) Third (d) Zero

[Ans. (c)]

[Hint: Unit of $k = \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$ ... (i)

Given unit of $k = \text{litre}^2\ \text{mol}^{-2}\ \text{sec}^{-1}$ ... (ii)

Comparing the unit of litre,

$$n - 1 = 2$$

$n = 3$]

29. The half life of a first order reaction having rate constant $k = 1.7 \times 10^{-5}\ \text{sec}^{-1}$ is: **(JIPMER 2006)**

(a) 12.1 hrs (b) 9.7 hrs (c) 11.3 hrs (d) 1.8 hrs

[Ans. (c)]

[Hint: $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.7 \times 10^{-5}} = 40764$ sec $= 11.3$ hrs]

30. At 500 K, the half life period of a gaseous reaction at an initial pressure of 80 kPa is 350 sec. When the pressure is 40 kPa, the half life period is 175 sec; the order of the reaction is: **[PET (Kerala) 2007]**

(a) zero (b) one (c) two (d) three

(e) half

[Ans. (a)]

[Hint: $\dfrac{(t_{1/2})_1}{(t_{1/2})_2}=\left(\dfrac{p_2}{p_1}\right)^{n-1}$

$$\frac{350}{175}=\left(\frac{40}{80}\right)^{n-1}$$

$$2=\left(\frac{1}{2}\right)^{n-1}$$

$$n-1=-1$$

$n=0$ (zero order reaction)]

31. 90% of the first order reaction is completed in 70 minutes. The velocity constant of the reaction is: [Comed (Karnataka) 2008]
(a) 0.0329 (b) 0.329 (c) 3.29 (d) 0.0293
[Ans. (a)]

[Hint : $k=\dfrac{2.303}{t}\log\dfrac{a}{a-x}$

$$=\frac{2.303}{70}\log\frac{100}{100-90}$$

$=0.0329\ \text{min}^{-1}$]

32. The half life period of a first order reaction is 1 min 40 seconds. Calculate its rate constant. (VITEEE 2008)
(a) $6.93\times10^{-3}\ \text{min}^{-1}$ (b) $6.93\times10^{-3}\ \text{sec}^{-1}$
(c) 6.93×10^{-3} sec (d) 6.93×10^{3} sec
[Ans. (b)]
[Hint : $k=\dfrac{0.693}{t_{1/2}}=\dfrac{0.693}{100}=6.93\times10^{-3}\ \text{sec}^{-1}$]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Ammonia and oxygen react at higher temperature as,*

$$4NH_3(g)+5O_2(g)\longrightarrow 4NO(g)+6H_2O(g)$$

in an experiment, the concentration of NO increases by 1.08×10^{-2} *mol litre*$^{-1}$ *in 3 seconds. Calculate:*

(*i*) *rate of reaction,* (*ii*) *rate of disappearance of ammonia,* (*iii*) *rate of formation of water.*

Solution:

(i) $\text{Rate}=-\dfrac{1}{4}\dfrac{d[NH_3]}{dt}=-\dfrac{1}{5}\dfrac{d[O_2]}{dt}=\dfrac{1}{4}\dfrac{d[NO]}{dt}=\dfrac{1}{6}\dfrac{d[H_2O]}{dt}$

$$\text{Rate}=\frac{1}{4}\times\frac{1.08\times10^{-2}}{3}=9\times10^{-4}\ \text{mol litre}^{-1}\ \text{sec}^{-1}$$

(ii) $\dfrac{-d[NH_3]}{dt}=4\times\text{rate}=4\times9\times10^{-4}$

$$=36\times10^{-4}\ \text{mol litre}^{-1}\ \text{sec}^{-1}$$

(iii) $\dfrac{d[H_2O]}{dt}=6\times\text{rate}=6\times9\times10^{-4}$

$$=54\times10^{-4}\ \text{mol litre}^{-1}\ \text{sec}^{-1}$$

Example 2. *Decomposition of* $N_2O_5(g)$ *into* $NO_2(g)$ *and* $O_2(g)$ *is a first order reaction. If initial concentration of* $N_2O_5(g)$, *i.e.,* $[N_2O_5]_0$ *is 0.03 mol litre*$^{-1}$, *what will be its concentration after 30 minutes? Rate constant of the reaction is* $1.35\times10^{-4}\ s^{-1}$.

Solution: $k=\dfrac{2.303}{t}\log_{10}\dfrac{[A_0]}{[A]}$

$$1.35\times10^{-4}=\frac{2.303}{30\times60}\log_{10}\frac{0.03}{[A]}$$

$$[A]=0.0235\ \text{mol litre}^{-1}$$

Example 3. *Rate constant for the decomposition of ethylene oxide into* CH_4 *and* CO *may be described by the equation,* $\log k\ (s^{-1})=14.34-\dfrac{1.25\times10^4}{T}$.

(*a*) *What is the energy of activation of this reaction?*
(*b*) *What is the value of k at 670 K?*

Solution: (a) We know that,

$$\log_{10}k=\log_{10}A-\frac{E}{2.303RT}\quad\text{... (i)}$$

$$\log_{10}k\ (\text{s}^{-1})=14.34-\frac{1.25\times10^4}{T}\quad\text{... (ii)}$$

Comparing eq. (i) and eq. (ii), we get

$$\frac{E}{2.303R}=1.25\times10^4$$

$$E=1.25\times10^4\times2.303\times8.314\times10^{-3}$$

$$E=239.339\ \text{kJ/mol}$$

(b) Substituting the value of T, *i.e.*, at 670 K, in equation (ii), we get,

$$\log k\ (\text{s}^{-1})=14.34-\frac{1.25\times10^4}{670}=-4.3167$$

$$k=4.82\times10^{-5}\ \text{s}^{-1}$$

Example 4. *A drug becomes ineffective after 30% decomposition. The original concentration of a sample was 5 mg/mL, which becomes 4.2 mg/mL during 20 months. Assuming the decomposition of first order, calculate the expiry time of the drug in months. What is the half life of the product?*

Solution: $k=\dfrac{2.303}{t}\log_{10}\left(\dfrac{a}{a-x}\right)=\dfrac{2.303}{20}\log_{10}\left(\dfrac{5}{4.2}\right)$

$$=0.00872\ \text{month}^{-1}$$

Expiry time 't' may be calculated as:

$$k=\frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

$$0.00872=\frac{2.303}{t}\log_{10}\frac{100}{70}$$

$$t=40.9\approx41\ \text{month}$$

$$t_{1/2}=\frac{0.693}{0.00872}=79.4\ \text{month}$$

Example 5. *Two reactions of the same order have equal exponential factors but their activation energies differ by* 24.9 *kJ/mol. Calculate the ratio between the rate constants of these reactions at* $27°C$. $(R = 8.31 J\,K^{-1}\,mol^{-1})$ (Dhanbad 1990)

Solution: We know that,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303RT}$$

So, $$\log_{10} k_2 = \log_{10} A - \frac{E_2}{2.303RT}$$

and $$\log_{10} k_1 = \log_{10} A - \frac{E_1}{2.303RT}$$

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{(E_1 - E_2)}{2.303RT}$$

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{24.9 \times 1000}{2.303 \times 8.314 \times 300}$$

$$\frac{k_2}{k_1} = 2.199 \times 10^4$$

Example 6. *Pseudo first order rate for the reaction,*

$$A + B \longrightarrow P$$

when studied in 0.1 *M of B is given by*

$$-\frac{d[A]}{dt} = k[A]$$

where, $k = 1.85 \times 10^4\ sec^{-1}$. *Calculate the value of second order rate constant.*

Solution: $$A + B \longrightarrow P$$

$$-\frac{d[A]}{dt} = k[A]$$

$$-\frac{d[A]}{dt} = 1.85 \times 10^4 \times [A] \qquad \text{... (i)}$$

Assuming the reaction to be of second order,

$$-\frac{d[A]}{dt} = k'[A][B]$$

$$-\frac{d[A]}{dt} = k'[A][0.1] \qquad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii), we get

$$1 = \frac{1.85 \times 10^4}{k'[0.1]}$$

$$k' = 1.85 \times 10^5 \text{ litre mol}^{-1} \text{ sec}^{-1}$$

Example 7. *The time required for* 10% *completion of a first order reaction at* 298 *K is equal to that required for its* 25% *completion at* 308 *K. If the pre-exponential factor for the reaction is* $3.56 \times 10^9\ sec^{-1}$, *calculate its rate constant at* 318 *K and also the energy of activation.* (IIT 1997)

Solution: We know that,

$$k = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$$

At 298 K, $x = 10, \quad a = 100,$

$$k_{298} = \frac{2.303}{t_1} \log_{10} \frac{100}{90} \qquad \text{... (i)}$$

At 308 K, $a = 100, x = 25, (a - x) = 75$

$$k_{308} = \frac{2.303}{t_2} \log_{10}\left(\frac{100}{75}\right) \qquad \text{... (ii)}$$

$t_1 = t_2$, dividing eq. (ii) by eq. (i)

$$\therefore \quad \frac{k_{308}}{k_{298}} = 2.73$$

$$\log \frac{k_{308}}{k_{298}} = \frac{E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log 2.73 = \frac{E}{2.303 \times 8.314}\left(\frac{1}{308} - \frac{1}{298}\right)$$

$$E = 76.622 \text{ kJ/mol}$$

Similarly, we can solve for k_{318} which is equal to $9.22 \times 10^{-4}\ s^{-1}$.

Example 8. *The rate constant of a reaction is* $1.5 \times 10^7\ s^{-1}$ *at* $50°C$ *and* $4.5 \times 10^7\ s^{-1}$ *at* $100°C$. *Calculate the Arrhenius parameter A and* E_a. (IIT 1998)

Solution: $$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log_{10} \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{323} - \frac{1}{373}\right)$$

$$E_a = 2.2 \times 10^4 \text{ J/mol}$$

We know that,

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\log_{10}(1.5 \times 10^7) = \log_{10} A - \frac{2.2 \times 10^4}{2.303 \times 8.314 \times 323}$$

$$A = 5.42 \times 10^{10}\ s^{-1}$$

Example 9. *In hydrogenation reaction at* $25°C$, *it is observed that hydrogen gas pressure falls from* 2 *atm to* 1.2 *atm in* 50 *min. Calculate the rate of reaction in molarity per sec.* $(R = 0.0821\ litre-atm\ degree^{-1}\ mol^{-1})$

Solution: $$\text{Rate} = \frac{dP}{dt} = \frac{2 - 1.2}{50 \times 60}$$

$$= 2.666 \times 10^{-4} \text{ atm s}^{-1}$$

$$PV = nRT$$

$$\frac{P}{\text{sec}} = \left(\frac{n}{V}\right)\frac{RT}{\text{sec}}$$

$$\left[\frac{n}{V}\right]\frac{1}{\text{sec}}=\left[\frac{P}{\text{sec}}\right]\frac{1}{RT}$$

$$\text{Rate (molarity/sec)}=\frac{2.666\times10^{-4}}{0.0821\times298}$$

$$=1.09\times10^{-5}\ \text{mol litre}^{-1}\ \text{s}^{-1}$$

Example 10. *A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole H^+ ions. If the rate of disappearance of the H^+ ions is 1×10^{7} mol litre^{-1} sec^{-1}, how long would it take for H^+ ions in the drop to disappear?*

Solution:

$$\text{Concentration of drop}=\frac{\text{mole}}{\text{volume in mL}}\times1000$$

$$=\frac{3\times10^{-6}}{0.05}\times1000=0.06\ \text{mol litre}^{-1}$$

$$\text{Rate of disappearance}=\frac{\text{conc. change}}{\text{time}}$$

$$1\times10^{7}=\frac{0.06}{\text{time}}$$

$$\text{Time}=6\times10^{-9}\ \text{sec}$$

Example 11. *A constant temperature and volume X decomposes as,*

$$2X(g)\longrightarrow3Y(g)+2Z(g)$$

P_X is the partial pressure of X.

Observation No.	*Time (min)*	*P_X (in mm Hg)*
1	0	800
2	100	400
3	200	200

(*i*) *What is the order of the reaction with respect to X?*
(*ii*) *Find the rate constant.*
(*iii*) *Find the time for 75% completion of the reaction.*
(*iv*) *Find the total pressure when pressure of X is 700 mm Hg.* **(IIT 2005)**

Solution: (i) Data shows that half life of the reaction is constant, *i.e.*, 100 min; hence, it is a first order reaction.

(ii) $k=\frac{0.693}{t_{1/2}}=\frac{0.693}{100}=6.93\times10^{-3}\ \text{min}^{-1}$

(iii) $t_{75\%}$, *i.e.*, $t_{3/4}=2\times t_{1/2}=2\times100=200$ min

(iv) $2X(g)\longrightarrow3Y(g)+2Z(g)$

$t=0$ 800 0 0

dt $800-2X$ $3X$ $2X$

$$\text{Total pressure}=800-2X+3X+2X=800+3X \quad ...(i)$$

$$800-2X=700$$

$$X=50$$

$\therefore$ Total pressure $=800+3\times50=950$ mm Hg

Example 12. *Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply.*

A study at 35° C gave the following results:

Time (minute)	0	15	30	45	60
Number of bacteria	50	100	200	400	800

Show that the rate of production of bacteria is of first order. How many bacteria will be there after 3 hours?

Solution: For bacterial growth,

$$k=-\frac{2.303}{t}\log_{10}\left(\frac{a}{a+x}\right)$$

At 15 minutes: $k=-\frac{2.303}{15}\log_{10}\left(\frac{50}{100}\right)$

$$=0.0462\ \text{min}^{-1}$$

At 30 minutes: $k=-\frac{2.303}{30}\log_{10}\left(\frac{50}{200}\right)$

$$=0.0462\ \text{min}^{-1}$$

At 45 minutes: $k=-\frac{2.303}{45}\log_{10}\left(\frac{50}{400}\right)=0.0462\ \text{min}^{-1}$

Same values of rate constants show that the process corresponds to first order.

Let there be '*n*' bacteria after 3 hrs.

$$k=-\frac{2.303}{t}\log_{10}\left(\frac{a}{a+x}\right)$$

$$0.0462=-\frac{2.303}{180}\log_{10}\frac{50}{n}$$

$$n=2.04\times10^{5}$$

Example 13. *A viral preparation was inactivated in a chemical bath. The inactivation process was found to be of first order in virus concentration, and at the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate 'k' for the inactivation process.*

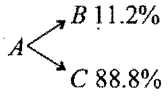
Solution: $a=100,\quad a-x=98,\quad t=60$ sec

$$k=\frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$$

$$=\frac{2.303}{60}\log_{10}\left(\frac{100}{98}\right)=3.3\times10^{-4}\ \text{sec}^{-1}$$

Example 14. *Trans-1,2-dideuterocyclopropane (A) undergoes a first order decomposition. The observed rate constant at a certain temperature, measured in terms of disappearance of 'A' was 1.52×10^{-4} sec^{-1}. Analysis of products showed that the reaction followed two parallel paths, one leading to dideuteropropane (B) and the other to cis-1,2-dideutero-cyclopropane (C). (B) was found to constitute 11.2% of the reaction product, independently of extent of reaction. What is the order of reaction for each path and what is the value of the rate constant for the formation of each of the products?*

Solution:



In case of parallel path reaction,

$$k_B = k_A \times \text{fractional yield of } B$$
$$= 1.52 \times 10^{-4} \times 0.112 = 1.7 \times 10^{-5}\ \text{sec}^{-1}$$
$$k_C = k_A \times \text{fractional yield of } C$$
$$= 1.52 \times 10^{-4} \times 0.888 = 1.35 \times 10^{-4}\ \text{sec}^{-1}$$

The reaction will be first order for each individual path.

Example 15. *In milk, at* 37°C, *lactobacillus acidophilus has a generation time of about* 75 *minutes. Calculate the population relative to the initial value at* 30, 60, 75, 90 *and* 150 *minutes.*

Solution: For growth kinetics,

$$k = -\frac{2.303}{t}\log_{10}\left(\frac{a}{a+x}\right)$$
$$k = -\frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$$

Generation time = 75 minutes; $a = 1,\ a + x = 2$

$$k = -\frac{2.303}{75}\log_{10}\left(\frac{1}{1+1}\right) = 0.00924\ \text{min}^{-1}$$

After 30 minutes,

$$k = \frac{-2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$$
$$0.00924 = -\frac{2.303}{30}\log_{10}\left(\frac{N_0}{N}\right)$$
$$\frac{N}{N_0} = 1.319 \approx 1.32$$

Similarly, we may calculate after 60, 75, 90 and 150 minutes.

Example 16. *Rate law for ozone layer depletion is,*

$$\frac{d[O_3]}{dt} = \frac{K[O_3]^2}{[O_2]}$$

Give the probable mechanism of reaction?

Solution: $O_3 \rightleftharpoons O_2 + O$ (fast reaction)

(equilibrium constant K_c)

$O_3 + O \longrightarrow 2O_2$ (slow reaction, rate constant k)

$$\text{Rate} = k[O_3][O] \qquad \dots \text{(i)}$$
$$K_c = \frac{[O_2][O]}{[O_3]} \text{ or } [O] = K_c\frac{[O_3]}{[O_2]},$$

putting the value in eq. (i)

From eq. (i),

$$\text{Rate} = k \cdot [O_3] \cdot K_c\frac{[O_3]}{[O_2]} = k \cdot K_c \cdot \frac{[O_3]^2}{[O_2]} = K \cdot \frac{[O_3]^2}{[O_2]}$$

Here, $K = k \times K_c$

Example 17. *In hypothetical reaction* $A_2 + B_2 \longrightarrow 2AB$, *follows the mechanism as given below:*

$$A_2 \rightleftharpoons A + A \qquad (\textit{fast reaction})$$
$$A + B_2 \longrightarrow AB + B \qquad (\textit{slow reaction})$$
$$A + B \longrightarrow AB \qquad (\textit{fast reaction})$$

Give the rate law and order of reaction.

Solution: Slowest step is rate determining.

$$\text{Rate} = k[A][B_2] \qquad \dots \text{(i)}$$

Here, $[A]$ should be eleminated.

$$K_c = \frac{[A][A]}{[A_2]} = \frac{[A]^2}{[A_2]}$$
$$[A] = K_c^{1/2}[A_2]^{1/2}$$

From eq. (i), $\text{Rate} = kK_c^{1/2}[A_2]^{1/2}[B_2]$

$$= K[A_2]^{1/2}[B_2]; \qquad [K = k \cdot K_c]$$
$$\text{Order} = 1 + 1/2 = 3/2$$

Example 18. *Calculate order of reaction from the following data:*

$$2NH_3 \longrightarrow N_2 + 3H_2\ (\textit{reaction})$$

Pressure (mm Hg)	50	100	200
Half lives (min)	3.52	1.82	0.93

Solution: We know that,

$$n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{\log_{10}p_2 - \log_{10}p_1}$$
$$= 1 + \frac{\log_{10}3.52 - \log_{10}1.82}{\log_{10}100 - \log_{10}50}$$
$$= 1.95 \approx 2$$

Similarly, we may calculate for other set of conditions.

Example 19. *The chemical reaction between mercuric chloride and potassium oxalate proceeds as under:*

$$2HgCl_2 + K_2C_2O_4 \longrightarrow KCl + 2CO_2 + Hg_2Cl_2$$

the mass of Hg_2Cl_2 *precipitated from different solutions in a given time, at* 100°C *was as follows:*

Expt. No.	**$HgCl_2$ (mol L^{-1})**	**$K_2C_2O_4$ (mol L^{-1})**	**Time (minutes)**	**Hg_2Cl_2 precipitated (mole)**
(1)	0.0836	0.404	65	0.0068
(2)	0.0836	0.202	120	0.0031
(3)	0.0418	0.404	60	0.0032

From these data calculate order of the reaction.

Solution: $\text{Rate} = k[\text{HgCl}_2]^{\alpha}[\text{K}_2\text{C}_2\text{O}_4]^{\beta};$

$$\frac{0.0068}{65} = k[0.0836]^{\alpha}[0.404]^{\beta}; \qquad \dots \text{(i)}$$

$$\frac{0.0031}{120} = k[0.0836]^{\alpha}[0.202]^{\beta}; \qquad \ldots \text{(ii)}$$

$$\frac{0.0032}{60} = k[0.0418]^{\alpha}[0.404]^{\beta} \qquad \ldots \text{(iii)}$$

Dividing eq. (i) by eq. (ii), we get $4 = 2^{\beta}; \beta = 2$

Dividing eq. (i) by eq. (iii), we get $2 = 2^{\alpha}; \alpha = 1$

Thus, overall order $= \alpha + \beta = 3$

Example 20. *The rate constant of the reaction $A \rightarrow B$ is $k = 0.5$; the initial concentration of A being 1 mol/litre. Calculate the degree of conversion of substance 'A' within 1 hour if the reaction is of zeroth, first and second order. How does the degree of conversion depend on the order of reaction?*

Solution: Zero order:

$$x = kt$$

$$x = 0.5 \times 1 = 0.5$$

First order: $$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

$k = 0.5$; $t = 1$ hr; $a = 1M$

$$0.5 = \frac{2.303}{1}\log_{10}\frac{1}{(1-x)}$$

$$x = 0.39$$

Second order: $$k = \frac{1}{t}\frac{x}{a(a-x)}$$

$$0.5 = \frac{1}{1}\cdot\frac{x}{1(1-x)}$$

$$x = 0.33$$

Example 21. *Two first order reactions proceed at 25° C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75° C.*

Solution: For first order reaction, $r_1 = k[A]^1$

$\therefore \quad r_1/r_2 = k_1/k_2 =$ temperature coefficient

Let the rate of reaction for Ist at 25°C be R_1 and the rate of reaction for IInd at 25°C be R_2.

Also, $R_1 = R_2$

	Rates of reaction	
∴ At 25°C	R_1	R_2
35°C	$2R_1$	$3R_2$
45°C	$(2)^2R_1$	$(3)^2R_2$
55°C	$(2)^3R_1$	$(3)^3R_2$
65°C	$(2)^4R_1$	$(3)^4R_2$
75°C	$(2)^5R_1$	$(3)^5R_2$

$\therefore$ Temperature coefficient for 1st reaction $= \dfrac{k_{35}}{k_{25}} = \dfrac{R_{35}}{R_{25}} = 2$

i.e., for each 10°C rise in temperature, rate becomes 2 times.

Similarly, for 2nd reaction it becomes 3 times,

$\therefore$ At 75°C

$$\frac{\text{rate of reaction for 2nd}}{\text{rate of reaction for 1st}} = \frac{(3)^5 R_2}{(2)^5 R_1} = 7.5937 \; (\because R_1 = R_2)$$

Example 22. *The reaction, $A + OH^- \rightarrow$ Products, obeys rate law expression as:*

$$\frac{-d[A]}{dt} = k[A][OH^-]$$

If initial concentrations of $[A]$ and $[OH^-]$ are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C, calculate the rate constant for the reaction.

Solution:

	A	+	OH^-	$\rightarrow$ Products
$t = 0$	0.002		0.3	
$t = 30$	$\left[0.002 - \frac{0.002 \times 1}{100}\right]$		$\left[0.3 - \frac{0.002 \times 1}{100}\right]$	

Using $k = \dfrac{2.303}{t(a-b)}\log_{10}\dfrac{b(a-x)}{a(b-x)}$,

$$k = \frac{2.303}{30 \times (0.002 - 0.3)}\log_{10}\frac{0.3\left[0.002 - \frac{0.002 \times 1}{100}\right]}{0.002\left[0.3 - \frac{0.002 \times 1}{100}\right]}$$

$$k = 1.12 \times 10^{-3} \text{ litre mol}^{-1}\text{ s}^{-1}$$

Example 23. *A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}.* **(IIT 2000)**

Solution: Arrhenius equation may be given as,

$$k = Ae^{-E_a/RT}$$

Let k_{500} and k_{400} be the rate constants at temperatures 500 K and 400 K (in presence of catalyst) respectively. E_{500} and E_{400} be the activation energies at temperatures 500 K and 400 K respectively.

$$k_{500} = Ae^{-E_{500}/R \times 500} \qquad \ldots \text{(i)}$$

$$k_{400} = Ae^{-E_{400}/R \times 400} \qquad \ldots \text{(ii)}$$

Given, $k_{500} = k_{400}$ (same rates in presence and absence of a catalyst).

On comparing eq. (i) with eq. (ii),

$$\frac{E_{500}}{R \times 500} = \frac{E_{400}}{R \times 400}$$

or $$\frac{E_{500}}{5} = \frac{E_{400}}{4}$$

or $$E_{500} = \frac{E_{400}}{4} \times 5 \qquad \ldots \text{(iii)}$$

Given, $$E_{500} = E_{400} + 20$$

Substituting in eq. (iii),

$$E_{400} + 20 = E_{400} \times 1.25$$

or $$E_{400} = \frac{20}{0.25} = 80 \text{ kJ mol}^{-1}$$

So, $$E_{500} = 80 + 20 = 100 \text{ kJ mol}^{-1}$$

Example 24. *Some $PH_3(g)$ is introduced into a fask at 600°C containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. Total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant,*

Time (sec)	0	60	120	∞
Pressure (mm Hg)	262.40	272.90	275.51	276.40

(IIT 2001)

Solution: $4PH_3(g) + \text{Inert gas} \longrightarrow P_4(g) + 6H_2(g) + \text{Inert gas}$

$t=0$	P	P_i	0	0	0
$t=t$	$(P-x)$	P_i	$x/4$	$6x/4$	P_i
$t=\infty$	0	P_i	$P/4$	$6P/4$	P_i

At $t=0$, $$262.40 = P + P_i \quad \ldots \text{(i)}$$

$t = 60$ sec $$272.90 = P_{PH_3(\text{left})} + P_{P_4(g)} + P_{H_2(g)} + P_i$$

$t = 120$ sec $$275.51 = P_{PH_3(\text{left})} + P_{P_4(g)} + P_{H_2(g)} + P_i$$

$t = \infty$ $$276.40 = P_{P_4(g)} + P_{H_2(g)} + P_i$$

$$276.40 = \frac{P}{4} + \frac{6P}{4} + P_i$$

$$276.40 \times 4 = 7P + 4P_i \quad \ldots \text{(ii)}$$

At $t = 0$, $$262.40 = P + P_i \quad \ldots \text{(iii)}$$

On solving eqs. (ii) and (iii), we get

$$P = 18.66 \text{ mm}, P_i = 243.74 \text{ mm}$$

At 60°C: $$272.90 = (P - x) + P_i + \frac{x}{4} + \frac{6x}{4}$$

$$272.90 = 18.66 - x + 243.74 + \frac{7x}{4}$$

$$x = 14 \text{ mm}$$

$$k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right) = \frac{2.303}{60} \log \frac{18.66}{18.66 - 14}$$

$$k = 2.32 \times 10^{-2} \text{ sec}$$

Similarly, at 120 sec $k = 2.30 \times 10^{-2}$ sec^{-1} (do yourself)

Since, ∵ values of '*k*' are same, hence the reaction belongs to first order.

Example 25. *For the given reaction, $A + B \longrightarrow$ Products following data were obtained:*

	$[A_0]$	$[B_0]$	R_0 *mol litre*$^{-1}$ *sec*$^{-1}$
1.	0.1 *M*	0.2 *M*	0.05
2.	0.2 *M*	0.2 *M*	0.10
3.	0.1 *M*	0.1 *M*	0.05

(*i*) *Write the rate law expression.*

(*ii*) *Find the rate constant.* **[IIT 2004 (Memory based)]**

Solution: Let order with respect to *A* and *B* are α and β respectively. Rate law expression may be given as,

$$\text{Rate} = k[A]^\alpha [B]^\beta$$

$$0.05 = k[0.1]^\alpha [0.2]^\beta \quad \ldots \text{(i)}$$

$$0.10 = k[0.2]^\alpha [0.2]^\beta \quad \ldots \text{(ii)}$$

$$0.05 = k[0.1]^\alpha [0.1]^\beta \quad \ldots \text{(iii)}$$

Dividing eq. (i) by eq. (ii), we get

$$\frac{1}{2} = \left[\frac{1}{2}\right]^\alpha, \quad i.e., \quad \alpha = 1$$

Dividing eq. (i) by eq. (iii), we get

$$1 = [2]^\beta, i.e., \beta = 0$$

∴ $$\text{Rate} = k[A]^1 [B]^0$$

Substituting the value of α and β in eq. (i), we get

$$0.05 = k[0.1]^1 [0.2]^0$$

$$k = 0.5 \text{ sec}^{-1}$$

Example 26. $A + 2B \longrightarrow 3C + 2D$

The rate of disappearance of B is 1×10^{-2} mol litre^{-1} sec^{-1}. What will be the (i) rate of the reaction and (ii) rate of change in concentration of A and C? **[CBSE (Mains) 2005]**

Solution: (i) $$\text{Rate} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$= -\frac{1}{2}[-1 \times 10^{-2}]$$

$$= 0.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

(ii) $$-\frac{d[A]}{dt} = -\frac{1}{2}\left[\frac{d[B]}{dt}\right] = 0.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$\frac{1}{3}\frac{d[C]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$\frac{d[C]}{dt} = -\frac{3}{2} \times (-1 \times 10^{-2})$$

$$= 1.5 \times 10^{-2} \text{ mol litre}^{-1} \text{ sec}^{-1}$$

Example 27. *For the reaction, $A + B \longrightarrow$ Products, rate is given as, rate $= k[A][B]^2$.*

How will the rate change if volume of the reaction mixture is reduced to 1/3rd of its original volume? **(BCECE 2006)**

Solution: When volume is reduced to 1/3rd, then concentration will increase three times.

∴ $$r_1 = k[A][B]^2 \quad \ldots \text{(i)}$$

$$r_2 = k[3A][3B]^2 \quad \ldots \text{(ii)}$$

From eqs. (i) and (ii),

$$\frac{r_1}{r_2} = \frac{1}{27}$$

$$r_2 = 27r_1$$

∴ Rate will increase 27 times.

Example 28. *For first order reaction, if rate constant at* $17°C$ *is* $2.8 \times 10^{-5}\ s^{-1}$ *and at* $27°C$ *is* $2.8 \times 10^{-4}\ s^{-1}$.

(*i*) *Write the equation for calculation of activation energy.*

(*ii*) *Calculate the activation energy.*

($R = 8.3\ J\ mol^{-1}\ k^{-1}$) [AIPMT (Mains) 2008]

Solution. We know,

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{2.8 \times 10^{-4}}{2.8 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.3}\left[\frac{1}{290} - \frac{1}{300}\right]$$

$$E_a = \frac{2.303 \times 8.3 \times 290 \times 300}{10}$$

$$= 166299.6 \text{ J mol}^{-1}$$

$$= 166.3 \text{ kJ mol}^{-1}$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Chemical kinetics: It is the branch of chemistry which deals with the rates of reactions, the factors which influence it and the mechanism by which the reactions occur.

2. Rate of reaction: It is the speed with which the reactants are converted into products. It may be expressed in terms of rate of disappearance of any of the reactants or rate of appearance of any of the products.

The rate measured over a long time interval is called the average rate.

$$\text{Average rate of reaction} = -\frac{\text{Decrease in conc. of reactant}}{\text{Time taken}}$$

$$= +\frac{\text{Increase in conc. of product}}{\text{Time taken}}$$

A –ve sign signifies a decrease in concentration of the reactant and +ve sign indicates an increase in concentration of the product.

In general, for a reaction,

$$n_1 A + n_2 B + n_3 C + \ldots \rightarrow m_1 X + m_2 Y + m_3 Z + \ldots$$

$$-\frac{1}{n_1}\frac{\Delta A}{\Delta t} = -\frac{1}{n_2}\frac{\Delta B}{\Delta t} = -\frac{1}{n_3}\frac{\Delta C}{\Delta t} = \ldots$$

$$\frac{1}{m_1}\frac{\Delta X}{\Delta t} = \frac{1}{m_2}\cdot\frac{\Delta Y}{\Delta t} = \frac{1}{m_3}\frac{\Delta Z}{\Delta t} = \ldots$$

Average rate is not very useful as it does not remain constant throughout its life span. It is more appropriate to express instantaneous rate.

Rate of reaction with reference to a particular instant of time is called instantaneous rate of reaction. It is defined as the rate of change of concentration of any one of the reactant or product species over a small interval of time.

$$\text{Rate of reaction} = -\frac{dx}{dt} \text{ or } +\frac{dx}{dt}$$

Units of rate of reaction are conc. time^{-1}, *e.g.*, mol L^{-1}s^{-1} or mol L^{-1} hr^{-1}, etc.

3. Law of mass action: It was presented by Guldberg and Waage in 1864. At a given temperature, the rate of a reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to powers which are numerically equal to the numbers of their respective molecules in the stoichiometric equation describing the reaction. Consider the following general reaction,

$$m_1 A_1 + m_2 A_2 + m_3 A_3 + \ldots \longrightarrow \text{Products}$$

$$\text{Rate of reaction} \propto [A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3} \ldots$$

4. Rate constant: It is equal to rate of reaction when concentration of each reactant is unity, *i.e.*, one mole litre^{-1}. It is a constant for a particular reaction at a given temperature and also known as specific rate constant or specific reaction rate.

Consider a general reaction,

$$aA + bB + \ldots \longrightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]^a[B]^b \ldots$$

If $\quad C_A = C_B = 1 \quad \text{or} \quad [A] = [B] = 1$

Then, $\quad \dfrac{dx}{dt} = k$

5. Collision theory of reaction rate: A chemical reaction occurs when the existing bonds of the reactants are broken down and new bonds come into existence in the molecules of products. The basic requirement for a reaction to occur is that there should be physical contact between reacting species, *i.e.*, they must collide with one another. Effective collisions which bring chemical change are few inspite of large number of actual collisions. For a collision to be effective, the following two conditions must be satisfied:

(i) Reacting species must possess adequate energy to overcome the energy barrier.

(ii) Reacting molecules must be properly oriented at the time of collision.

The minimum amount of energy which the colliding particles must possess as to make the chemical reaction to occur is called threshold energy. The excess energy (over and above the average energy of the reacting species) required by the reacting species to undergo chemical reaction is called activation energy (E_a).

Activation energy = Threshold energy – Average kinetic energy of the reacting molecules

Every chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before the reactants can be transformed into products. The reacting molecules must have sufficient energy as to cross this energy barrier. The effective collisions increase with increase of temperature, *i.e.*, rate of reaction increases with increase of temperature.

6. Factors influencing the reaction rate: The chief factors which influence the rates of reactions are:

(i) Nature of reactants: The reactants with weak bonds react quickly whereas the reactions involving reactants with strong bonds are slow. The molecular reactions are generally slow while ionic reactions are fast.

(ii) Concentration of reactants: The rate of reaction increases with increase in concentration of reactants as the number of collisions increases.

(iii) Catalyst: Positive catalysts increase the reaction rate by providing an alternative path involving lesser amount of activation energy.

(iv) Temperature: The rate of reaction increases with an increase in temperature. The number of effective collisions increases with increase of temperature. The rates of many reactions are approximately doubled or tripled for every 10° C rise in temperature. The temperature coefficient is defined as the ratio of specific reaction rates of a reaction at two temperatures differing by 10° C.

$$\text{Temp. coefficient} = \frac{k_{t+10}}{k_t} \text{ (value lies generally between 2 and 3)}$$

Arrhenius suggested an equation which describes k as a function of temperature, *i.e.*,

$$k = Ae^{-E_a/RT}$$

where, k = rate constant, A = a frequency factor (constant), E_a = energy of activation, R = gas constant and T = temperature.

At two temperatures T_1 and T_2,

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

7. Molecularity and order of reaction:

(i) Molecularity of reaction: The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products is called the molecularity of the reaction. The reactions are termed as unimolecular, bimolecular or trimolecular, etc., depending upon the number of reacting particles as 1, 2, 3, etc., in the rate determining step. Simultaneous collisions involving more than three molecules are very rare and hence reactions with molecularity more than three are also rare.

$NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Unimolecular)

$NO + O_3 \rightarrow NO_2 + O_2$ (Bimolecular)

$2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$ (Trimolecular)

In simple reactions involving one step only, the molecularity is equal to the sum of number of molecules of the reactants involved in the balanced equation. There are number of reactions which are complex in nature and occur in several steps; the molecularity of such reactions is determined by the slowest step. Thus, molecularity depends upon the mechanism of the reaction.

(ii) Order of reaction: Rate equation or rate law is an experimentally determined mathematical expression relating the molar concentrations of the reactants to the actual reaction rate.

Consider a general reaction,

$$n_1A + n_2B + n_3C + \ldots \rightarrow \text{Products}$$

The rate law or rate equation is

$$\text{Rate} = -\frac{dx}{dt} = k[A]^x[B]^y[C]^z \ldots$$

Order of reaction is the sum of the exponents (powers) to which molar concentration terms are raised in the rate law.

Order of reaction = $(x + y + z + \ldots)$

The value of $(x + y + z + \ldots)$ usually ranges between 0 and 2 and even 3. It may have positive, negative, zero and fractional values. It is termed overall order. The reactions are classified as zero, first, second, third order according as $(x + y + z + \ldots)$ is zero, one, two or three respectively. The order can be expressed either in terms of the order of the specific reactant or in terms of overall order of the reaction.

The reactions which obey a first order rate equation, although they are not unimolecular, are said to be pseudo first order.

8. Reactions of various orders: In such reactions, the concentrations of various reactants except one remain practically constant during the course of reaction.

(i) Zero order reactions:. A reaction in which the rate is independent of the concentration of the reactant molecules, *i.e.*, the rate is proportional to the zeroth power of the concentration of the reactants.

$$-\frac{dx}{dt} = k[A]_0 = k$$

i.e., the reaction velocity remains constant throughout the progress of the reaction. The concentration decreases linearly with time.

$$[A]_t = [A]_0 - kt$$

$$t_{\text{completion}} = \frac{[A]_0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

The units of k are mol L^{-1} time^{-1}.

(ii) First order reactions: The rate depends upon the concentration of one reactant only.

$$-\frac{dx}{dt} = k[A]$$

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

t = time, a = initial concentration and $(a - x)$ = concentration at time t.

A change in concentration unit does not affect the numerical value of k. Thus, for first order reactions, any quantity which is proportional to concentration can be used in place of concentration in the integrated equation.

The time taken for the completion of same fraction of change is independent of initial concentration. When $x = 0.5a$ and $t = t_{1/2}$,

$$k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2 = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k}$$

Thus, $t_{1/2}$ is independent of initial concentration.

The equation of the first order can also be written in the following form when initial concentration is not known.

$$k = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{(a - x_1)}{(a - x_2)} = \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A]_{t_1}}{[A]_{t_2}}$$

The unit of k is time^{-1}.

(iii) Second order reactions: Reaction rate depends upon the concentration of two reactants.

$$\frac{dx}{dt} = k[A][B] = k[A]^2$$

$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

[$(a-x)$ and $(b-x)$ are the concentrations of A and B after time interval t.]

When concentrations of both the reactants are same,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

(x is the concentration changed in time interval t)

Half life period, $t_{1/2} = \frac{1}{ka}$, *i.e.*, inversely proportional to initial concentration. The units of k are litre mol^{-1} time^{-1}.

(iv) Third order reactions: Expression for third order reactions of the type

$$3A \rightarrow \text{Products}$$

$$\frac{dx}{dt} = k[A]^3$$

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2 (a-x)^2}$$

The units of k are L^2 mol^{-2} time^{-1}.

9. Methods for the determination of order of a reaction:

(i) Initial rate method: A number of experiments are carried out by varying concentration of a reactant w.r.t. which the order is to be determined keeping the concentrations of all other reactants constant. The initial rate of the reaction at each concentration is determined by concentration-time curves. The order of the reactant is then calculated from the rates at various concentrations. The experiments are repeated with other reactants in a similar way. Likewise, the orders w.r.t. all reactants are determined. The overall order is the sum of the orders of all the reactants.

(ii) Integration method: The quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most consistent values for the specific rate constant (k) for a series of time intervals is the one corresponding to order of reaction.

$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ for first order reactions

$k = \frac{1}{t} \cdot \left[\frac{a}{a(a-x)}\right]$ for second order reactions

Rate $= k$ for zero order reactions

(iii) Graphical method: If the plot of $\log(a-x)$ *versus* 't' is a straight line, the reaction follows first order.

If a plot of $\frac{1}{(a-x)}$ *versus* 't' is a straight line, the reaction follows second order.

If a plot of $\frac{1}{(a-x)^2}$ *versus* 't' is a straight line, the reaction follows third order.

(iv) Half life method: Starting with two different concentrations a_1 and a_2 for the same reaction, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$ are determined.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \quad \text{or} \quad n = 1 + \frac{\log (t_{1/2})_1 - \log (t_{1/2})_2}{\log a_2 - \log a_1}$$

n is the order of reaction.

(v) van't Hoff differential method: For two different initial concentrations C_1 and C_2 equations can be written in the form

$$-\frac{dC_1}{dt} = kC_1^n \text{ and } -\frac{dC_2}{dt} = kC_2^n$$

Taking logarithms of two equations and then subtracting

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2}$$

10. Mechanism: An intelligent guess depending upon the observed rates of reactions about the series of steps (known as elementary processes) leading to the formation of products is called the reaction mechanism. The overall reaction is the summation of all elementary steps. The slowest step is taken as the rate determining step.

Questions

1. **Matrix Matching Problems:**
(According to the new pattern of IIT Screening)

[A] Match the reactions of List-I with their orders in List-II:

List-I	**List-II**
(a) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$	(p) Pseudo first order
(b) $CH_3COOC_2H_5 \xrightarrow[H^+ \text{ or } OH^-]{HOH} CH_3COOH + C_2H_5OH$	(q) Zero order
(c) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$	(r) Second order
(d) $CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$	(s) First order

[B] Match the reactions in Column-I with the units of their rate constant in Column-II:

Column-I **(Reactions)**	**Column-II** **(Unit of k)**
(a) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	(p) sec^{-1}
(b) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$	(q) min^{-1}
(c) $2H_2O_2 \longrightarrow 2H_2O + O_2$	(r) $L\ mol^{-1}\ min^{-1}$
(d) $H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$	(s) $L\ mol^{-1}\ s^{-1}$

[C] Match the kinetic equations of Column-I with the units of their rate constant in Column-II:

Column-I **(Kinetic equations)**	**Column-II** **(Units of rate constant)**
(a) $x = kt$	(p) sec^{-1}
(b) $k = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$	(q) $L\ mol^{-1}\ sec^{-1}$
(c) $k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$	(r) $mol\ L^{-1}\ sec^{-1}$
(d) $k = \frac{2.303}{t(a-b)}\log\left[\frac{b(a-x)}{a(b-x)}\right]$	(s) $atm^{-1}\ sec^{-1}$

[D] Match the half lives in Column-I with the orders in Column-II:

Column-I **(Half life)**	**Column-II** **(Order)**
(a) $t_{1/2}$ = constant	(p) First order
(b) $t_{1/2} \propto a$	(q) Pseudo first order
(c) $t_{1/2} \propto \frac{1}{a}$	(r) Second order
(d) $t_{1/2} \propto p^{-1}$	(s) Zero order

where, a = Initial concentration of the reactant
p = Initial pressure of the reactant

[E] Match the reactions of List-I with the increase in rate when concentration is raised two times in List-II:

List-I **(Reactions)**	**List-II** **(Increase in rate when conc. of reactant is doubled)**
(a) $CH_3CHO \longrightarrow CH_4 + CO$	(p) 2 times
(b) $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	(q) $2^{1.5}$ times
(c) $2H_2O_2 \longrightarrow 2H_2O + O_2$	(r) 2 times in acid medium
(d) $CH_3COOC_2H_5 \xrightarrow{HOH} CH_3COOH + C_2H_5OH$	(s) 2^2 times in basic medium

[F] Match the List-I with Liwst-II and List-III:

List-I	**List-II**	**List-III**
(a) x is plotted against 't' in zero order reaction	(p) Slope= $-k/2.303$	(u) Intercept = 0
(b) $\log(a-x)$ is plotted against 't' in first order reaction	(q) Slope = $2k$	(v) Intercept $= 1/a$
(c) $(a-x)^{-1}$ is plotted against 't' in second order reaction	(r) Slope = $-k$ (when log is natural)	(w) Intercept $= 1/a^2$
(d) $(a-x)^2$ is plotted against 't' in second order reaction	(s) Slope = k	(x) Intercept $= \log_{10} a$

where, a = Initial concentration of reactant
x = Extent of reaction in time 't' sec

[G] Match the List-I with List-II:

List-I	**List-II**
(a) Molecularity	(p) 0
(b) Order	(q) 1/2
(c) Temperature coefficient	(r) Between 2 to 3
(d) Activation energy for participation of all reactant molecules	(s) 2

[H] Match the Column-I with Column-II:

Column-I **(Rate law)**	**Column-II** **(Order)**
(a) Rate = $k \times$ Intensity of light	(p) Second order
(b) Rate = $k[A]^1[B]^1$	(q) Zero order
(c) Rate = $k[A]^{3/2}[B]^{1/2}$	(r) First order when A is excess
(d) Rate = $k[A]^2[B]^1$	(s) Second order when B is excess

[I] Match the Column-I with Column-II:

Column-I	Column-II
(a) $t_{1/2} = \frac{0.693}{k}$	(p) Zero order
(b) $t_{1/2} = \frac{a}{2k}$	(q) First order
(c) $\tau = \frac{1}{k}$	(r) Average life
(d) $t_{3/4} = 2t_{1/2}$	(s) 75% completion
	(t) 25% completion

[J] Match the Column-I with Column-II:

Column-I	Column-II
(a) $t_{3/4} = \frac{3}{2} \times t_{1/2}$	(p) 99% completion
(b) $t_{3/4} = 2 \times t_{1/2}$	(q) Zero order
(c) $6.909/k$	(r) First order
(d) $2.303/k$	(s) 90% completion

Here, $t_{1/2}$ = half life
$t_{3/4}$ = 3/4th life
k = rate constant

[K] Match the Column-I with Column-II:

Column-I	Column-II
(a) First order reaction	(p) $C_0 = 0.1\,M$; $t_{1/2} = 25$ min $C_0 = 0.05\,M$; $t_{1/2} = 12.5$ min
(b) Second order reaction	(q) $C_0 = 0.1\,M$; $t_{1/2} = 12$ min $C_0 = 0.05\,M$; $t_{1/2} = 24$ min
(c) Zero order reaction	(r) Radioactive decay
(d) $t_{1/2}$ varies inversely to the concentration of the reactants	(s) $C_0 = 0.1\,M$; $t_{1/2} = 8$ min $C_0 = 0.05\,M$; $t_{1/2} = 8$ min

Answers

1. [A] (a–p), (b–r, s), (c–q), (d–r)
[B] (a–p, q), (b–r, s), (c–p, q), (d–r, s)
[C] (a–r), (b–p), (c–q, s), (d–q, s)
[D] (a–p, q), (b–s), (c–r, s), (d–r, s)
[E] (a–q), (b–p), (c–p), (d–r, s)
[F] (a–s–u), (b–p, r–x), (c–s–v), (d–q–w)
[G] (a–s), (b–p, q, s), (c–r), (d–p)
[H] (a–q), (b–p), (c–p), (d–r, s)
[I] (a–q), (b–p), (c–q, r), (d–q, s)
[J] (a–q), (b–r), (c–p, r), (d–r, s)
[K] (a–r, s), (b–q), (c–p), (d–q)

• PRACTICE PROBLEMS •

1. For the reaction $A \rightarrow B$, it was found that the concentration of B increased by 0.3 mol L^{-1} in 2 hours. What is the average rate of reaction?
[Ans. 0.15 mol L^{-1} hr^{-1}]

2. In the reaction $X \rightarrow Y$, the initial concentration of X is 2.5 mol L^{-1} and its concentration after 3 hours is 0.7 mol L^{-1}. What is the average rate of the reaction?
[Ans. 6.0×10^{-1} mol $L^{-1}hr^{-1}$]

3. For the reaction $2A + B \rightarrow C$, the rate of formation of C is 0.25 mol L^{-1} hr^{-1}. What is the rate of disappearance of A and B?
[Ans. 0.5 mol L^{-1} hr^{-1}; 0.25 mol L^{-1} hr^{-1}]

4. For each of the following reactions express the given rate of change of the concentration of the reactant or product in terms of the rate of change of concentration of the other reactants or products in that reaction.

(i) $N_2 + 3H_2 \rightarrow 2NH_3$; $-\frac{d[H_2]}{dt} = ?$

(ii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $-\frac{d[O_2]}{dt} = ?$

(iii) $2NO + Cl_2 \rightarrow 2NOCl$; $\frac{d[NOCl]}{dt} = ?$

(iv) $CO + NO_2 \rightarrow CO_2 + NO$; $-\frac{d[NO_2]}{dt} = ?$

[Ans. (i) $-\frac{d[H_2]}{dt} = -3 \cdot \frac{d[N_2]}{dt} = +\frac{3}{2}\frac{d[NH_3]}{dt}$;

(ii) $-\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[H_2]}{2 \cdot dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$;

(iii) $\frac{d[NOCl]}{dt} = -\frac{d[NO]}{dt} = 2 \cdot \frac{d[Cl_2]}{dt}$

(iv) $-\frac{d[NO_2]}{dt} = -\frac{d[CO]}{dt} = \frac{d[CO_2]}{dt} = \frac{d[NO]}{dt}$]

5. When ammonia is treated with O_2 at elevated temperatures, the rate of disappearance of ammonia is found to be 3.5×10^{-2} mol dm^{-3} s^{-1} during a measured time interval. Calculate the rate of appearance of nitric oxide and water.
[Ans. $\frac{\Delta[NO]}{dt} = 3.5 \times 10^{-2}$ mol dm^{-3} s^{-1};
$\frac{\Delta[H_2O]}{dt} = 5.3 \times 10^{-2}$ mol dm^{-3} s^{-1}]

[**Hint:** Consider the following equation:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The equality in this case is

$$-\frac{1}{4}\frac{\Delta[NH_3]}{dt} = \frac{1}{4}\frac{\Delta[NO]}{dt} = \frac{1}{6}\frac{\Delta[H_2O]}{dt}\ ]$$

6. In a reaction, $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$, the rate of disappearance of N_2O_5 is 6.5×10^{-3} mol L^{-1} s^{-1}. Compute the rates of formation of NO_2 and O_2.

[**Ans.** $\frac{d[NO_2]}{dt} = 1.25 \times 10^{-2}$ mol L^{-1} s^{-1};

$\frac{d[O_2]}{dt} = 3.125 \times 10^{-3}$ mol L^{-1} s^{-1}]

7. For the reaction,

$$2O_3 \rightleftharpoons 3O_2$$

$-\frac{\Delta[O_3]}{dt}$ was found to be 4.0×10^{-4} atm s^{-1}.

Determine the value of $\frac{\Delta[O_2]}{\Delta t}$ in atm s^{-1} during this period of time.

[**Ans.** 6.0×10^{-4} atm s^{-1}]

8. The following reaction was carried out at 44° C:

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$

The concentration of NO_2 is 6.0×10^{-3} M after 10 minutes of the start of the reaction. Calculate the rate of production of NO_2 over the first ten minutes of the reaction.

[**Ans.** 6.0×10^{-4} mol L^{-1} min^{-1}]

9. The rate of a particular reaction doubles when temperature changes from 27°C to 37°C. Calculate the energy of activation for such reaction. ($R = 8.314$ J K^{-1} mol^{-1})

[**Ans.** 53.59 kJ mol^{-1}]

10. The rate constant of a reaction is 2×10^{-2} s^{-1} at 300 K and 8×10^{-2} s^{-1} at 340 K. Calculate the energy of activation of the reaction.

[**Ans.** 29.39 kJ mol^{-1}]

11. For a chemical reaction the energy of activation is 85 kJ mol^{-1}. If the frequency factor is 4.0×10^{9} L mol^{-1} s^{-1}, what is the rate constant at 400 K?

[**Ans.** $k = 3.19 \times 10^{-2}$ L mol^{-1}s^{-1}]

12. The energy of activation of a reaction is 140 kJ mol^{-1}. If its rate constant at 400 K is 2.0×10^{-6} s^{-1}, what is the value at 500 K?

[**Ans.** 9.06×10^{-3} s^{-1}]

13. Calculate the ratio of the catalysed and uncatalysed rate constant at 20°C if the energy of activation of a catalysed reaction is 20 kJ mol^{-1} and for the uncatalysed reaction is 75 kJ mol^{-1}.

[**Ans.** 6.4×10^{9}]

14. The decomposition of methyl iodide,

$$2CH_3I(g) \rightarrow C_2H_6(g) + I_2(g)$$

at 273° C has a rate constant of 2.418×10^{-5} s^{-1}. If activation energy for the reaction is +179.9 kJ mol^{-1}, what is the value of collision factor 'A' at 273° C?

[**Ans.** 3.9×10^{12} s^{-1}]

15. The reaction,

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2$$

occurs in carbon tetrachloride. The rate constant is 2.35×10^{-4} sec^{-1} at 20° C and 9.15×10^{-4} sec^{-1} at 30° C. Calculate the activation energy of the reaction.

[**Ans.** 100.343 kJ mol^{-1}]

16. For the inversion of cane sugar,

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6,$$

the rate constant is 2.12×10^{-4} L mol^{-1} sec^{-1} at 27° C. The activation energy of the reaction is 1.07×10^{5} J mol^{-1}. What is the rate constant of the reaction at 37° C?

[**Ans.** 8.46 L mol^{-1} sec^{-1}]

17. From the data given below for the reaction $2A + B \rightarrow 3C$ at 298 K, find out the rate law expression for the reaction.

Expt. No.	[A] (mol L^{-1})	[B] (mol L^{-1})	Rate of formation of C
1.	0.10	0.10	4.0×10^{-4}
2.	0.30	0.30	1.2×10^{-3}
3.	0.10	0.30	4.0×10^{-4}
4.	0.20	0.40	8.0×10^{-4}

[**Ans.** Rate $= k[A]$]

18. What is the rate law expression for the reaction,

$$A + B \rightarrow C\ ?$$

The following data were collected from the experiments:

Expt. No.	Initial [A] (mol L^{-1})	Initial [B] (mol L^{-1})	Rate of formation of C
1.	0.10	0.10	4.0×10^{-4}
2.	0.20	0.20	3.2×10^{-3}
3.	0.10	0.20	1.6×10^{-3}

[**Ans.** Rate $= k[A][B]^2$]

19. The reaction,

$$2N_2O_5 \rightarrow 2NO_2 + O_2,$$

was studied and the following data were collected:

Expt. No.	[N_2O_5] (mol L^{-1})	Rate of disappearance of N_2O_5 (mol L^{-1} min^{-1})
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine (i) order the reaction (ii) the rate law and (iii) rate constant for the reaction.

[**Hint:** Let the rate law for the reaction be

$$\text{Rate} = k[N_2O_5]^x$$

$$34 \times 10^{-5} = k[1.13 \times 10^{-2}]^x$$

$$25\times10^{-5}=k[0.84\times10^{-2}]^x$$

or $$\frac{34\times10^{-5}}{25\times10^{-5}}=\frac{[1.13\times10^{-2}]^x}{[0.84\times10^{-2}]^x}$$

$$1.36=[1.345]^x$$

$$x=1$$

Order of the reaction is 1. Rate law = $k[N_2O_5]$

$$k=\frac{\text{Rate}}{[N_2O_5]}=\frac{34\times10^{-5}}{1.13\times10^{-2}}=30.08\times10^{-3}\ \text{min}^{-1}]$$

20. For the reaction,

$$2NO+2H_2\rightarrow N_2+2H_2O,$$

the following kinetic data were obtained:

Expt. No.	$[H_2]$ (mol L^{-1})	[NO] (mol L^{-1})	Rate of reaction (mol L^{-1} s^{-1})
1.	0.12	0.12	0.25×10^{-4}
2.	0.12	0.24	1.0×10^{-4}
3.	0.24	0.24	2.0×10^{-4}

Determine the rate law and the rate constant.

[**Ans.** Rate = $k[H_2][NO]^2$; $k=1.45\times10^{-2}$ L^2 mol^{-2} s^{-1}]

21. Fill in the blanks in the following table which treats reaction of a compound A with a compound B, that is of the first order with respect to A and zero order with respect to B:

Expt. No.	$[A]$ (mol L^{-1})	$[B]$ (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1.	0.1	0.1	2.0×10^{-2}
2.	...	0.2	4.0×10^{-2}
3.	0.4	0.4	...
4.	...	0.2	2.0×10^{-2}

[**Ans.** (2) $[A]=0.2$ mol L^{-1}
(3) Rate = 8.0×10^{-2} mol L^{-1} s^{-1}
(4) $[A]=0.1$ mol L^{-1}]

22. The reaction $2NO+O_2\rightarrow2NO_2$, follows the rate law $=k[NO]^2[O_2]$. What is the order of the reaction? If $k=2.0\times10^{-6}$ mol^{-2} L^2 s^{-1}, what is the rate of the reaction when [NO] = 0.04 mol L^{-1} and $[O_2]=0.2$ mol L^{-1}?

[**Ans.** Order of the reaction = 3;
Rate = 6.4×10^{-10} mol L^{-1} s^{-1}]

23. From the following data of initial concentrations and rates, calculate the order of reaction $aA\rightarrow$ Products; and its rate constant.

$[A]$ mol L^{-1}	0.1	0.2	0.4
Rate mol L^{-1} s^{-1}	9×10^{-5}	36×10^{-5}	144×10^{-5}

[**Ans.** Order of reaction = 2;
Rate constant = 9.0×10^{-3} mol^{-1} L s^{-1}]

24. For a reaction $aA+bB\rightarrow mM+nN$, the rate of reaction is given as $k[A]^x[B]^y$.

Calculate the order of the reaction and the rate constant from the given initial concentrations and the corresponding rates.

$[A]$ mol L^{-1}	0.1	0.1	0.2
$[B]$ mol L^{-1}	0.2	0.4	0.2
Rate mol $L^{-1}s^{-1}$	4×10^4	16×10^4	8×10^4

[**Ans.** Order of the reaction = 3, $k=1.0\times10^7$ L^2 mol^{-2} s^{-1}]

25. The data given in the following table pertain to the reaction,

$$2A+B\rightarrow C.$$

Determine the form of the rate equation and the value of the rate constant.

Expt. No.	Initial concentration (mol L^{-1})		Initial rate (mol L^{-1} s^{-1})
	$[A]$	$[B]$	
1.	1×10^{-3}	1×10^{-3}	7×10^{-6}
2.	1×10^{-3}	2×10^{-3}	14×10^{-6}
3.	1×10^{-3}	3×10^{-3}	21×10^{-6}
4.	2×10^{-3}	3×10^{-3}	84×10^{-6}

[**Ans.** Rate = $k[A]^2[B]$; $k=7\times10^3$]

26. The following initial rate data were obtained for the reaction:

$$2NO(g)+Br_2(g)\rightarrow2NOBr(g)$$

Run	[NO]/M	$[Br_2]$/ M	Rate/M min^{-1}
1.	1.0	1.0	1.30×10^{-3}
2.	2.0	1.0	5.20×10^{-3}
3.	4.0	2.0	4.16×10^{-2}

Determine the reaction rate law and the value of the rate constant. **(Dhanbad 1992)**

[**Ans.** $-\frac{dx}{dt}=k[NO]^2[Br_2]$; $K=1.30\times10^{-3}$ mol^{-2} L^2 s^{-1}]

27. The data below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

Expt. No.	$[Cl_2]$ (mol L^{-1})	[NO] (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})
1.	0.05	0.05	1.0×10^{-3}
2.	0.15	0.05	3.0×10^{-3}
3.	0.05	0.15	9.0×10^{-3}

(a) What is the order w.r.t. NO and Cl_2 in the reaction?
(b) Write the rate expression.
(c) Calculate the rate constant.
(d) Determine the reaction rate when concentrations of Cl_2 and NO are 0.2 M and 0.4 M respectively. **(IIT 1993)**

[**Ans.** (a) Order w.r.t. NO = 2; order w.r.t. Cl_2 = 1
(b) Rate expression, $r=k[NO]^2[Cl_2]$
(c) $k=8.0$ L^2 mol^{-2} s^{-1}
(d) Rate = 0.256 mol L^{-1} s^{-1}]

28. In the hydrolysis of propyl acetate in presence of dilute HCl in aqueous solution, the following data were recorded:

Time from start (in minute)	60	350
% of ester decomposed	18.17	69.12

Calculate the rate constant of decomposition and time in which half of the ester was decomposed.

[**Ans.** 3.34×10^{-3} min^{-1}; 207.6 min]

29. In a first order reaction the concentration of the reactant is reduced to one-fourth of its initial value in 50 seconds. Calculate the rate constant of the reaction.

[**Ans.** 2.77×10^{-2} s^{-1}]

30. For a first order reaction, the rate constant is 0.1 s^{-1}. How much time will it take to reduce the concentration from initial value of 0.6 mol L^{-1} to 0.06 mol L^{-1}?

[**Ans.** 23.0 second]

31. A substance decomposes following first order reaction. If the half life period of the reaction is 35 minutes, what is the rate constant of this reaction?

[**Ans.** 1.98×10^{-2} min^{-1}]

32. For a certain first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.2 mol L^{-1}. What is the rate constant for this reaction? [log 3 = 0.4771].

[**Ans.** 0.2197 min^{-1}]

33. Find the two-thirds life ($t_{2/3}$) of a first order reaction in which $k = 5.48 \times 10^{-1}$ sec^{-1} (log 3 = 0.4771; log 2 = 0.3010).

[**Ans.** 2.005 s]

[**Hint:** $t_{2/3} = \dfrac{2.303}{k} \log_{10} \dfrac{a}{a - \frac{2}{3}a}$]

34. A first order reaction has a specific rate of 10^{-3} sec^{-1}. How much time will it take from 10 g of the reactant to reduce to 7.5 g (log 2 = 0.3010; log 4 = 0.6020 and log 6 = 0.7782)?

[**Ans.** 287.7 s]

35. In a reaction 5 g ethyl acetate is hydrolysed per litre in presence of dilute HCl in 300 min. If the reaction is of first order and initial concentration is 22 g per litre, calculate the rate constant for the reaction.

[**Ans.** $k = 8.59 \times 10^{-4}$ min^{-1}]

36. Calculate the half life of the reaction $A \to B$, when the initial concentration of A is 0.01 mol L^{-1} and initial rate is 0.00352 mol L^{-1} min^{-1}. The reaction is of the first order.

[**Ans.** 1.969 min]

[**Hint:** Evaluate k from $\dfrac{dx}{dt} = k[A]$]

37. In a reaction, $A \to B + C$, the following data were obtained:

t in seconds	0	900	1800
Concentration of A	50.8	19.7	7.62

Prove that it is a first order reaction.

[**Hint:** Calculate the value of k in both cases by using first order equation.]

38. The first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200° C. If the reaction is allowed to run for 10 hours at the same temperature, what percentage of the initial concentration would have changed into the product? What is the half life period of this reaction?

[**Ans.** $t_{1/2} = 128.3$ hours; 5.27%]

39. A first order reaction is 20% completed in 10 minutes. Calculate (i) the specific rate constant of the reaction and (ii) the time taken for the reaction to go to 75% completion.

[**Ans.** $k = 2.232 \times 10^{-2}$ min^{-1}; $t = 62.12$ min]

40. The rate constant of a reaction with respect to reactant A is 6 min^{-1}. If we start with $[A] = 0.8$ mol L^{-1}, when would $[A]$ reach the value of 0.08 mol L^{-1}?

[**Ans.** 0.3838 min]

41. What will be the initial rate of a reaction if the rate constant is 10^{-3} min^{-1} and the concentration is 0.2 mol dm^{-3}? How much of the reactant will be converted into the product in 200 minutes? [illegible]

[**Ans.** Initial rate = 2×10^{-4} mol L^{-1} s^{-1}; 0.036 mol]

42. A substance A decomposes by the first order reaction. Starting initially with $[A] = 2.00\,M$, after 200 minutes $[A] = 0.25\,M$. For this reaction what is $t_{1/2}$ and k? [illegible]

[**Ans.** $t_{1/2} = 66.66$ min, $k = 0.01039$ min^{-1}]

43. The specific rate constant for the concentration of H_2 and I_2 to form HI is 0.0234 mol^{-1} L s^{-1} at 400° C and 750 mol^{-1} L s^{-1} at 500° C. Calculate the activation energy of the reaction.

[CEE (Bihar) [illegible]]

[**Ans.** 107.9 kcal]

44. For a certain reaction it takes 10 minutes for the initial concentration of 2.0 mol L^{-1} to become 1.0 mol L^{-1} and another 10 minutes to become 0.5 mol L^{-1}. Calculate the rate constant of the reaction. [illegible]

[**Ans.** 0.0693 min^{-1}]

45. The catalytic decomposition of H_2O_2 was studied by titrating it at different intervals with $KMnO_4$ and the following data were obtained:

t (seconds)	0	600	1200
V of $KMnO_4$ (mL)	22.8	13.8	8.3

Calculate the velocity constant for the reaction assuming it to be a first order reaction.

[**Ans.** 8.4×10^{-3} s^{-1}]

[**Hint:** Volume of $KMnO_4$ used $\propto$ concentration of H_2O_2

Hence, $k = \dfrac{2.303}{t} \log_{10} \dfrac{V_0}{V_t}$]

46. The half life of a first order reaction is 10 seconds. Calculate the time for completion of 99.9% of the reaction.

[**Ans.** 99.7 sec ≈ 100 sec]

47. A first order reaction is 40% complete after 8 min. How long will it take before it is 90% complete? What is the value of the rate constant?

[**Ans.** $k = 0.06386$ min^{-1}; $t = 36.06$ min]

48. The reaction $SO_2Cl_2 \to SO_2 + Cl_2$, is a first order gas reaction with $k = 2.2 \times 10^{-5}$ s^{-1} at 573 K. What per cent of SO_2Cl_2 is decomposed on heating at 573 K for 90 min?

[**Ans.** 11.2]

49. The decomposition of $AB(g) \rightarrow A(g) + B(g)$, is first order reaction with a rate constant $k = 4 \times 10^{-4}\ \text{s}^{-1}$ at 318 K. If AB has 26664.5 Pa pressure at the initial stage, what will be the partial pressure of AB after half an hour?

[**Ans.** 12981.7 Pa]

50. In the first order reaction $A(g) \rightarrow B(g) + C(g)$, the initial pressure of A is 11200 Pa and the total pressure at the end of 16 minutes is 14667 Pa. Calculate the half life period of reaction.

[**Ans.** 30 min]

51. It was found that a solution of cane sugar was hydrolysed to the extent of 25% in 1 hr. Calculate the time taken for the sugar to be 50% hydrolysed assuming that the reaction is of first order.

[**Ans.** 2.408 hours]

52. A reaction is 20% complete in 20 minutes. How long will it take for 80% completion if the order of reaction is (a) zero and (b) one?

[**Ans.** (a) 80 minutes (b) 144.27 minutes]

53. A second order reaction where $a = b$ is 20% completed in 500 seconds. How long will the reaction take to be 60% complete?

[**Hint:** Apply

$$k = \frac{x}{ta(a - x)} = \frac{20}{500\,[100 \times (100 - 20)]} = \frac{1}{200000}\ \text{mol}^{-1}\ \text{L s}^{-1}$$

$$t = \frac{60}{k \times 100 \times 40} = \frac{60 \times 200000}{100 \times 40} = 3000 \text{ seconds]}$$

54. At a certain temperature, the half life periods of a reaction at different initial pressures were as follows:

p (kPa)	100	66.67	33.33
t (min)	105	235	950

Find out the order of the reaction.

[**Ans.** 3]

55. The time for half change for a gaseous reaction was measured for various initial pressures and the following data were obtained:

p (kPa)	26.6	40	53.3
t (min)	150	99.8	75.3

Find out the order of the reaction.

[**Ans.** 2]

56. Show that for a first order reaction the time required for 99% completion is twice the time required for the completion of 90% of the reaction.

57. Show that for a first order reaction the time required to complete 99.9% of the reaction is 10 times that required for half the reaction.

58. Show that for a first order reaction, the time required for a 50% reaction is half that for 75% reaction.

59. The decomposition of an aqueous solution of ammonium nitrite was studied. The volume of nitrogen gas collected at different intervals of time was as follows:

Time (minutes)	10	15	20	∞
Vol. of N_2 (mL)	6.25	9.00	11.40	35.05

From the above data prove that the reaction is of the first order.

[**Hint:** $[A]_0 =$ volume of nitrogen at $\infty = 35.05$

$$[A]_t = V_\infty - V_t$$

when $t = 10$, $k = \dfrac{2.303}{10} \log \dfrac{35.05}{(35.05 - 6.25)} = 0.0196$

when $t = 15$, $k = 0.0198$

when $t = 20$, $k = 0.0196$]

60. Optical rotation of sucrose in 1 N HCl at various times was found as shown below:

Time (sec)	0	7.18	18.0	27.05	∞
Rotation (deg)	+ 24.09	+ 21.7	+ 17.7	+15.0	−10.74

Show that the inversion of sucrose is a first order reaction.

[**Hint:** Initial concentration, $[A]_0 = r_0 - r_\infty$

At time t, $[A]_t = r_t - r_\infty$

$$k = 11.8 \times 10^{-3}\ \text{s}^{-1}\,]$$

61. The rate law for the decomposition of gaseous N_2O_5

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

is observed to be:

$$-\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

A reaction mechanism which has been suggested to be consistent with this is:

$$N_2O_5 \overset{K}{\rightleftharpoons} NO_2 + NO_3 \qquad \text{(fast)}$$

$$NO_2 + NO_3 \xrightarrow{k_1} NO_2 + NO + O_2 \qquad \text{(slow)}$$

$$NO + NO_3 \xrightarrow{k_2} 2NO_2 \qquad \text{(fast)}$$

Show that the mechanism is consistent with the observed law.

[**Hint:** $r = k_1[NO_2][NO_3]$,

$$K = \frac{[NO_2][NO_3]}{[N_2O_5]} \quad \text{or} \quad [NO_3] = \frac{K[N_2O_5]}{[NO_2]}$$

$$r = k_1K[N_2O_5] = k[N_2O_5]\,]$$

62. Write the overall reaction and the rate law equation from the following elementary steps:

$$NO + Br_2 \rightleftharpoons NOBr_2$$

$$NOBr_2 + NO \rightarrow 2NOBr$$

[**Hint:** Adding both the steps, we get overall reaction,

$$2NO + Br_2 \rightarrow 2NOBr.$$

The second step is slow and, therefore, a rate determining step.

$$r = k'[NOBr_2][NO]$$

$$K = \frac{[NOBr_2]}{[NO][Br_2]} \quad \text{or} \quad [NOBr_2] = K[NO][Br_2]$$

$$r = k'K[NO]^2[Br_2]\,]$$

63. The reaction, $2NO + O_2 \rightarrow 2NO_2$ proceeds in two steps. If one elementary reaction is $NO + O_2 \rightarrow NO_3$, write the second elementary reaction. Write the rate law of the reaction.

[**Ans.** $NO + NO_3 \rightarrow 2NO_2$, rate $= k[NO]^2[O_2]$]

64. At 380° C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450° C. **(IIT 1995)**

[**Ans.** 20.39 min]

65. Calculate the average rate of decomposition of N_2O_5 by the reaction,

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g).$$

During the time interval from $t = 600$ s to $t = 1200$ s using the following data:

Time	$[N_2O_5]$
600 s	$1.24 \times 10^{-2}\ M$
1200 s	$0.93 \times 10^{-2}\ M$

[CEE (Bihar) 1995]

[**Ans.** $5.166 \times 10^{-6}\ M\ s^{-1}$]

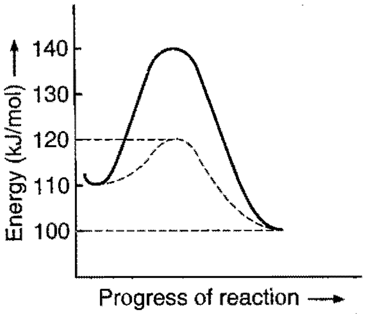
66. Consider the diagram for reaction:

$$A_2 + B_2 \rightleftharpoons 2AB$$

(a) Calculate the ΔH of the reaction.

(b) Calculate the energy of activation for forward and backward reaction.

(c) The dotted line curve is the path in the presence of a catalyst. What is the energy of activation for the forward and backward reactions in the presence of the catalyst?



What is the lowering in activation energy in the presence of the catalyst?

(d) Will the catalyst change the extent of the reaction?

[**Ans.** (a) $\Delta H = -10$ kJ / mol;

(b) $E_f = 30$ kJ / mol; $E_b = 40$ kJ / mol;

(c) $E_f = 10$ kJ / mol; $E_b = 20$ kJ / mol; 20 kJ / mol;

(d) no]

67. Temperature coefficient, $\mu = \dfrac{k_{35°C}}{k_{25°C}}$ of a reaction is 1.82. Calculate the energy of activation in calories. ($R = 1.987$ cal degree^{-1} mol^{-1}).

[**Ans.** 10.924 kcal/mol]

68. For first order gaseous reaction, log k when plotted against $\dfrac{1}{T}$ gives a straight line with a slope of -8000. Calculate the activation energy of the reaction.

[**Ans.** 36.6 kcal]

69. The rate at 27° C of a chemical reaction increases 1000 times when a suitable catalyst is introduced. Calculate the change in the energy of activation that the catalyst has brought in.

[**Ans.** 4118 cal]

70. Dehydration of tertiary butyl alcohol follows a first order reaction,

$$(CH_3)_3C{-}OH(g) \rightarrow (CH_3)_2C{=}CH_2(g) + H_2O(g)$$

the rate constant at 300° C is $2.27 \times 10^{-8}\ s^{-1}$. Calculate the rate constant at 400° C if the energy of activation for the reaction is 58 kcal.

[**Ans.** $4.392 \times 10^{-5}\ s^{-1}$]

71. Let us consider the following mechanism:

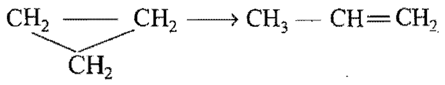
$$CH_3CN + H^+ \rightleftharpoons CH_3CNH^+ \qquad \text{(fast)}$$

$$CH_3CNH^+ + H_2O \rightarrow \text{Product} \qquad \text{(slow)}$$

What would be the rate law?

[**Ans.** Rate $= k[CH_3CN][H_2O][H^+]$]

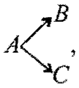
72. The thermal isomerization of cyclopropane occurs according to the equation:



The specific reaction rate constant for this reaction at 499° C was 5.95×10^{-4} sec^{-1}. What is the half life of the reaction? What fraction of the cyclopropane will remain after 1 hour at 499.5° C?

[**Ans.** 1165 s; 11.7%]

73. A substance 'A' was found to undergo two parallel first order reactions,



, i.e., $A \rightarrow B$ and $A \rightarrow C$,

with rate constants $1.26 \times 10^{-4}\ s^{-1}$ and $3.8 \times 10^{-5}\ s^{-1}$ respectively. What were the percentage distributions of B and C?

[**Ans.** 76.83% of B and 23.17% of C]

74. Two reactions proceed at 25° C at the same rate; the temperature coefficient of the rate of the first reaction is 2 and that of the second reaction is 2.5. Find the ratio of rates of these reactions at 95° C.

[**Ans.** 5 times]

75. The population of India in the year 1988 was 800 million. Growth rate is 25 per thousand per year. What will be the population in the year 2000 if the growth follows first order kinetics?

[**Ans.** 1075 million]

76. Half lives against initial pressure are given below. Calculate the order of the reaction.

p (mm)	750	500	250
t (min)	105	235	950

Find out the order of the reaction.

[**Ans.** 3]

77. For a given reaction at temperature T, the velocity constant k, is expressed as:

$$k = Ae^{-27000\,k'/T} \quad (k' = \text{Boltzmann constant})$$

Given, $R = 2$ cal K^{-1} mol^{-1}. Calculate the value of energy of activation. Comment on the results.

[**Ans.** $E = 18 \times 10^{-20}$ cal]

[**Hint:** Compare the equation with Arrhenius equation

$$k = Ae^{-E_a/RT} \qquad \text{... (i)}$$

$$k = Ae^{-27000k'/T} \qquad \text{... (ii)}$$

$$\frac{E_a}{RT} = \frac{27000k'}{T}$$

$$E_a = 27000Rk'$$

$$= 27000\,R \times \frac{R}{N} = \frac{27000 \times (2)^2}{6.023 \times 10^{23}}$$

$$= 18 \times 10^{-20} \text{ cal}$$

Activation energy is low, therefore reaction will be fast.]

78. If the activation energy of a reaction is 80.9 kJ mol^{-1}, calculate the fraction of molecules at 400°C which have enough energy to react to form the products.

[**Ans.** 5.257×10^{-7}]

[**Hint:** Fraction of total molecules which are active at a temperature is given as,

$$= \frac{k}{A} = e^{-E_a/RT}$$

$$\log \frac{k}{A} = \frac{-E_a}{2.303\,RT}$$

$$\frac{k}{A} = \text{antilog}\left(\frac{-E_a}{2.303RT}\right)$$

Substituting the values of E and T we can solve the problem.]

79. The following data were obtained for a given reaction at 300 K:

Reaction	**Energy of activation (kJ/mol)**
1. Uncatalysed	76
2. Catalysed	57

Calculate by what factor the rate of catalysed reaction is increased?

[**Ans.** 2000]

[**Hint:** Use: $\frac{k_p}{k_a} = \text{antilog}\left(\frac{\Delta E}{2.303RT}\right)$

k_p = rate constant in presence of catalyst

k_a = rate constant in absence of catalyst

$\Delta E = 76 - 57 = 19 \text{ kJ/mol}$]

80. The Arrhenius equations for *cis-trans* isomerization of but-2-ene ($CH_3-CH{=}CH-CH_3$) and but-2-ene, 1-nitrile ($CH_3-CH{=}CH-CN$) are,

$$k(\text{s}^{-1}) = 10^{13.8} \exp(-263.5 \text{ kJ mol}^{-1}/RT)$$

$$k^{-1}(\text{s}^{-1}) = 10^{11} \exp(-214.5 \text{ kJ mol}^{-1}/RT)$$

Calculate the temperature at which $k = k^{-1}$.

[**Ans.** 914 K]

81. The half life for a reaction between fixed concentration of reactants varies with temperature as follows:

t °C	520	533	555	574
$t_{1/2}$ sec	1288	813	562	477

Calculate the activation energy of this reaction.

[**Ans.** 86.47 kJ mol^{-1}]

[**Hint:** Use: $\log\left(\frac{k_2}{k_1}\right) = \frac{E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$k_2 = 0.693/t_2$$

$$k_1 = 0.693/t_1$$

$$\therefore \quad \log\left(\frac{t_1}{t_2}\right) = \frac{E}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)]$$

82. What percentage of reactant molecules will crossover the energy barrier at 325 K? Heat of reaction is 0.12 kcal and activation energy of backward reaction is 0.02 kcal.

[**Hint:** Activation energy of forward reaction = 0.12 − 0.02

= 0.10 kcal

Fraction of molecules which are active or which crossover the energy barrier $\left(\frac{k}{A}\right) = e^{-E/RT}$

$$\log_e\left(\frac{k}{A}\right) = -\frac{E}{RT}$$

$$\frac{k}{A} = \text{antilog}\left[\frac{-E}{2.303\,RT}\right]$$

$$= \text{antilog}\left[\frac{-0.10 \times 1000}{2.303 \times 2 \times 325}\right]$$

$$= \text{antilog}[-0.06680] = 0.8574$$

∴ Percentage of reactant molecules crossing over the barrier

$= 0.8574 \times 100 = 85.74$]

83. In a milk at 37°C Lactobacillus acidophillus has a generation time of about 75 minutes. Calculate the population relative to the initial value at 30, 60, 75, 90 and 150 minutes.

[**Ans.**

t_{min}	30	60	75	90
N/N_0	1.32	1.74	2	2.30]

[**Hint:** In the case of population growth we have to use growth kinetics.

$$-k = \frac{2.303}{t}\log\left(\frac{a}{a+x}\right)$$

a = initial population

x = growth in population in time 't'

Here, $N_0 = a$; $N = a + x$]

84. Two reactions of same order have equal pre-exponential factors but their activation energies differ by 41.9 J/mol. Calculate the ratios between rate constants of these reactions at 600 K.

[**Ans.** 0.002]

[**Hint:** Use the relation,

$$\log_{10} k = \log_{10} A - \frac{E}{2.303RT} \quad \text{... (i)}$$

$$\log_{10} k_1 = \log_{10} A - \frac{E_1}{2.303 \times 8.314 \times 600} \quad \text{... (ii)}$$

$$\log_{10} k_2 = \log_{10} A - \frac{E_2}{2.303 \times 8.314 \times 600} \quad \text{... (iii)}$$

$$E_1 - E_2 = 41.95/\text{mol} \quad \text{... (iv)}$$

Subtract eq. (iii) from eq. (ii) to determine the ratio.]

85. A decomposition reaction has following mechanism

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \quad \text{(overall)}$$

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \quad \text{(fast decomposition)}$$

$$NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2 \quad \text{(slow)}$$

$$NO + NO_3 \longrightarrow 2NO_2 \quad \text{(fast)}$$

Determine rate law, is the mechanism corresponds to first order reaction.

[**Ans.** $\frac{-d[N_2O_5]}{dt} = \frac{2k_1k_3}{k_1 + k_3}[N_2O_5]$]

86. Rate constant of a reaction changes by 2% by 0.1°C rise in temperature at 25°C. The standard heat of reaction is 121.6 kJ mol^{-1}. Calculate E_a of reverse reaction.

[**Ans.** 24.7 kJ/mol]

[Hint: $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$\log\frac{102}{100} = \frac{E}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{298.1}\right)$$

$$E = 1.463 \times 10^5 \text{ J/mol} = 146.3 \text{ kJ/mol}$$

$$\Delta H = E_f - E_b$$

$$121.6 = 146.3 - E_b$$

$E_b = 24.7$ kJ/mol]

87. Urea $(NH_2)_2CO$ can be prepared by heating ammonium cyanate NH_4OCN.

$$NH_4OCN \longrightarrow (NH_2)_2CO$$

The reaction may occur by the following mechanism:

$$NH_4^+ + OCN^- \underset{k-1}{\overset{k_1}{\rightleftharpoons}} NH_3 + HOCN \qquad \text{(fast, equilibrium)}$$

$$NH_3 + HOCN \xrightarrow{k_2} (NH_2)_2CO \qquad \text{(slow)}$$

What is rate law predicted by this mechanism?

[Ans. Rate $= \frac{k_2k_1}{k-1}[NH_4^+][OCN^-] = k[NH_4]^+[OCN^-]^-$]

88. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, under certain conditions of pressure and temperature of the reactants, the rate of formation of NH_3 is 0.001 kg hr^{-1}. Calculate the rate of reaction for N_2 and H_2.

[Ans. 1.76×10^{-4} kg hr^{-1}]

[Hint: $-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$

$$\frac{d[NH_3]}{dt} = 0.001 \text{ kg hr}^{-1} = \frac{0.001 \times 1000}{17} \text{ mol hr}^{-1}$$

$$= 0.058 \text{ mol hr}^{-1}$$

$$\frac{-d[N_2]}{dt} = \frac{1}{2} \times 0.058 \text{ mol hr}^{-1}$$

$$= 0.029 \text{ mol hr}^{-1}$$

$$= 0.029 \times 28 \times 10^{-3} \text{ kg hr}^{-1}$$

$$= 8.12 \times 10^{-4} \text{ kg hr}^{-1}$$

Similarly, $-\frac{d[H_2]}{dt} = 1.76 \times 10^{-4}$ kg hr^{-1}]

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. Chemical kinetics, a branch of physical chemistry, deals with:
(a) heat changes in a reaction
(b) physical changes in a reaction
(c) rates of reactions
(d) structure of molecules

2. The rate at which a substance reacts depends upon its:
(a) atomic mass (b) equivalent mass
(c) molecular mass (d) active mass

3. The rate of a chemical reaction:
(a) increases as the reaction proceeds
(b) decreases as the reaction proceeds
(c) may increase or decrease during the reaction
(d) remains constant as the reaction proceeds

4. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, rate is expressed as:
(a) $-3\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt}$
(b) $-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$
(c) $-\frac{d[N_2]}{dt} = -\frac{3d[H_2]}{dt} = \frac{2d[NH_3]}{dt}$
(d) $-\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

5. For the reaction, $2NO_2 \longrightarrow 2NO + O_2$, rate is expressed as:
(a) $-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$
(b) $-\frac{1}{2}\frac{d[NO_2]}{dt} = -\frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$
(c) $-\frac{2d[NO_2]}{dt} = \frac{2d[NO]}{dt} = \frac{d[O_2]}{dt}$
(d) $-\frac{d[NO_2]}{dt} = \frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$

6. The rate of reaction that does not involve gases, is not dependent on:
(a) pressure (b) temperature
(c) concentration (d) catalyst

7. For the reaction, $A + B \longrightarrow 2C + D$, which one is the incorrect statement?
(a) Rate of disappearance of A = Rate of disappearance of B
(b) Rate of disappearance of A = Rate of appearance of D
(c) Rate of disappearance of B = 2 × rate of appearance of C
(d) Rate of disappearance of $B = \frac{1}{2} \times$ rate of appearance of C

8. In a reaction, $2A_2 + B_2 \longrightarrow 2A_2B$, the reactant A will disappear at:
(a) half the rate that B will decrease
(b) the same rate that B will decrease
(c) double the rate that A_2B will form
(d) twice the rate that B will decrease

9. In the reaction $3A \rightarrow 2B$, rate of reaction $+\frac{d[B]}{dt}$ is equal to: **[JEE (WB) 2008]**
(a) $-\frac{1}{3}\frac{d[A]}{dt}$ (b) $-\frac{2}{3}\frac{d[A]}{dt}$ (c) $+2\frac{d[A]}{dt}$ (d) $-\frac{3}{2}\frac{d[A]}{dt}$

10. For the reaction, $2NO \longrightarrow N_2 + O_2$, the expression $-\frac{1}{2}\frac{d[NO]}{dt}$ represents:

(a) the rate of formation of NO
(b) the average rate of the reaction
(c) the instantaneous rate of the reaction
(d) all of the above

11. The term $-\frac{dx}{dt}$ in the rate expression refers to the:
(a) instantaneous rate of reaction
(b) average rate of reaction
(c) increase in the concentration of reactants
(d) concentration of reactants

12. According to collision theory of reaction rates:
(a) every collision between reactant molecules leads to a chemical reaction
(b) rate of reaction is proportional to the velocity of the molecules
(c) rate of reaction is proportional to the average energy of the molecules
(d) rate of reaction is proportional to the number of collisions per second

13. According to collision theory:
(a) all collisions are sufficiently violent
(b) all collisions are responsible for product formation
(c) all collisions are effective
(d) only a fraction of collisions are effective which have enough energy to form products

14. Which of the following has been used to explain the subject of chemical kinetics?
(a) Collision theory of bimolecular reactions
(b) The activated complex theory
(c) Arrhenius equation
(d) All of the above

15. The activation energy for a chemical reaction depends upon:
(a) temperature
(b) nature of reacting species
(c) concentration of the reacting species
(d) collision frequency

16. In a reaction, the threshold energy is equal to:
(a) activation energy + normal energy of reactants
(b) activation energy – normal energy of reactants
(c) normal energy of reactants – activation energy
(d) average kinetic energy of molecules of reactants

17. The influence of temperature on the rate of reaction is determined by:
(a) Nernst's equation (b) Gibbs-Helmholtz equation
(c) Arrhenius equation (d) van't Hoff equation

18. According to the collision theory of reaction rates, the rate of reaction increases with temperature due to:
(a) greater number of collisions
(b) higher velocity of reacting molecules
(c) greater number of molecules having the activation energy
(d) decrease in the activation energy

19. The temperature coefficient of a reaction is:
(a) ratio of rate constants at two temperatures differing by 1°C
(b) ratio of rate constants at temperature 35°C and 25°C
(c) ratio of rate constants at temperature 30°C and 25°C
(d) specific reaction rate at 25°

20. In general, with every 10°C rise in temperature, the rate of reaction becomes approximately ....
(a) ten times (b) double
(c) half (d) one tenth

21. Activation energy of the reaction is:
(a) the energy released during the reaction
(b) the energy evolved when activated complex is formed
(c) minimum amount of energy needed to overcome the potential barrier
(d) the energy needed to form one mole of the product

22. The temperature coefficient of most of the reactions lies between:
(a) 2 and 3 (b) 1 and 2
(c) 2 and 4 (d) 3 and 4

23. According to Arrhenius equation, rate constant of a chemical reaction is equal to:
(a) $Ae^{-E_a/RT}$ (b) $Ae^{E_a/RT}$
(c) Ae^{RT/E_a} (d) Ae^{-RT/E_a}

24. The correct expression for Arrheniu[illegible] the effect of temperature on the rate constant is ($T_2 > T_1$): (DCE 2009)

(a) $\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_1T_2}{T_2-T_1}\right]$

(b) $\log_{10}\frac{k_2}{k_1}=\frac{R}{2.303E_a}\left[\frac{T_2-T_1}{T_1T_2}\right]$

(c) $\log_{10}\frac{k_2}{k_1}=\frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$

(d) $\log_{10}\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_2T_1}\right]$

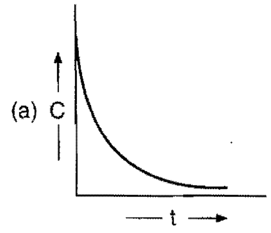
25. In order to react, a molecule, at the time of collision, must possess a certain amount of energy known as:
(a) free energy (b) kinetic energy
(c) threshold energy (d) internal energy

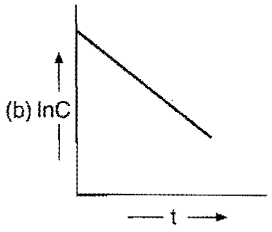
26. The activation energy of a reaction is zero. The rate constant of the reaction: [CET (Pb.) 1991]
(a) increases with increase of temperature
(b) decreases with decrease of temperature
(c) decreases with increase of temperature
(d) is nearly independent of temperature

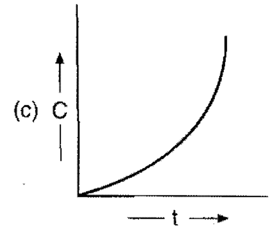
27. The activation energy of a reaction can be lowered by:
(a) using a positive catalyst
(b) increasing temperature
(c) decreasing temperature
(d) increasing concentration of the reactants

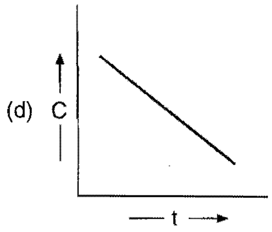
28. The activation energy for a hypothetical reaction $A \longrightarrow$ Product is 12.49 kcal/mol. If temperature is raised from 295 to 305, the rate of reaction increases by:
(a) 60% (b) 100%
(c) 50% (d) 20%

29. The plot between concentration versus time for a zero order reaction is represented by: [AMU (Engg.) 2009]









30. The rate of reaction increases with rise in temperature because of: **[Comed (Karnataka) 2008]**
(a) increase in the number of activated molecules
(b) increase in the activation energy
(c) decrease in the activation energy
(d) increase in the number of molecular collisions

31. Which of the following is a first order reaction?
(a) $2HI \longrightarrow H_2 + I_2$ (b) $2NO_2 \longrightarrow 2NO + O_2$
(c) $2NO + O_2 \longrightarrow 2NO_2$ (d) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

32. Which one of the following is not a first order reaction?
(a) $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$
(b) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
(c) $2H_2O_2 \longrightarrow 2H_2O + O_2$
(d) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

33. Rate expression of a chemical change is $-\dfrac{dx}{dt} = k[A]^2[B][C]^0$.
The order of reaction is:
(a) 3 (b) 2 (c) 1 (d) zero

34. For a reaction, $2A + B \longrightarrow C + D$, the concentration of B is kept constant and that of A is tripled the new rate of reaction will be:
(a) nine times (b) three times
(c) same (d) zero

35. The rate of the reaction, $A + B + C \longrightarrow$ Products, is given by

$$-\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$$

The order of the reaction is:
(a) 1/2 (b) 13/12
(c) 1 (d) 2

36. Which of the following rate laws has an overall order of 0.5 for the reaction involving substances x, y and z?
(a) Rate $= k[C_x][C_y][C_z]$
(b) Rate $= k[C_x]^{0.5}[C_y]^{0.5}[C_z]^{0.5}$
(c) Rate $= k[C_x]^{1.5}[C_y]^{-1}[C_z]^0$
(d) Rate $= k[C_x][C_y]^{-2}[C_z]^0$

37. If the rate of reaction between A and B is given by rate $= k[A][B]^2$, then the reaction is:
(a) first order in A (b) second order in B
(c) third order overall (d) all are correct

38. For the reaction $A \longrightarrow B$, the rate of reaction is quardrupled when the concentration of A is doubled; the rate of the reaction is $r = k[A]^n$; the value of n is:
(a) 1 (b) zero (c) 3 (d) 2

39. Select the rate law that corresponds to the data shown for the following reaction: $A + B \longrightarrow C$ **(CBSE 1994)**

Expt. No.	$[A]_0$	$[B]_0$	Initial rate
1.	0.012	0.035	0.10
2.	0.024	0.070	0.80
3.	0.024	0.035	0.10
4.	0.012	0.070	0.80

(a) rate $= k[B]^3$ (b) rate $= k[B]^4$
(c) rate $= k[A][B]^3$ (d) rate $= k[A]^2[B]^2$

40. For a chemical reaction, $A \longrightarrow E$, it is found that rate of reaction is doubled when the concentration of A is increased four times. The order of the reaction is:
(a) 1 (b) 2
(c) 1/2 (d) zero

41. The rate of reaction, $A + B \longrightarrow$ Products, is given by the equation, $r = k[A][B]$. If B is taken in large excess, the order of reaction would be: **(BIT 1992)**
(a) 2 (b) 1
(c) zero (d) unpredictable

42. The rate of reaction between A and B increases by a factor of 100, when the concentration of A is increased 10 folds. The order of reaction with respect to A is:
(a) 10 (b) 2 (c) 1 (d) 20

43. The rate law for the reaction,

$$RCl + NaOH(aq.) \longrightarrow ROH + NaCl$$

is given by, Rate $= k[RCl]$. The rate of reaction will be:
(a) unaffected by increasing temperature of the reaction
(b) doubled on doubling the concentration of NaOH
(c) halved on reducing the concentration of NaOH to one half
(d) halved on reducing the concentration of RCl to one half

44. A zero order reaction is one:
(a) in which reactants do not react
(b) in which one of the reactants is in large excess
(c) whose rate is uniform and not affected by time
(d) whose rate increases with time

45. The rates of a certain reaction at different time intervals are as follows:

Time (second)	0	10	20
Rate	1.8×10^{-2}	1.82×10^{-2}	1.79×10^{-2} mol L^{-1} s^{-1}

The reaction is of:
(a) zero order (b) first order
(c) second order (d) third order

46. For which of the following, the units of rate and rate constant of the reaction are identical?
(a) First order reaction (b) Zero order reaction
(c) Second order reaction (d) Fractional order reaction

47. The unit of rate constant for a zero order reaction is:
(a) mol time^{-1} (b) L time^{-1}
(c) mol L^{-1} time^{-1} (d) L mol^{-1} time^{-1}

48. For a zero order reaction: (EAMCET 1990)
(a) $t_{1/2} \propto a$ (b) $t_{1/2} \propto \frac{1}{a}$ (c) $t_{1/2} \propto a^2$ (d) $t_{1/2} \propto \frac{1}{a^2}$

49. The rate of the first order reaction, $A \longrightarrow$ Products, is 7.5×10^{-4} mol L^{-1} s^{-1}, when the concentration of A is 0.2 mol L^{-1}. The rate constant of the reaction is:
(a) 2.5×10^{-5} s^{-1} (b) 8.0×10^{-4} s^{-1}
(c) 6.0×10^{-4} s^{-1} (d) 3.75×10^{-3} s^{-1}

50. If the concentration is expressed in mole per litre and time in second, the units of rate constant for a first order reaction is:
(a) mol L^{-1} sec^{-1} (b) sec^{-1}
(c) mol L^{-1} (d) mol^{-1}

51. Which one of the following formula represents a first order reaction?
(a) $k = \frac{2.303}{t} \log \frac{[A]_t}{[A]_0}$ (b) $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$
(c) $k = \frac{2.303}{t} \log \frac{a}{a-x}$ (d) $k = \frac{2.303}{t} \log \frac{a}{x}$

52. 75% of a first order reaction was completed in 32 minute; when was 50% of the reaction completed?
(a) 4 min (b) 8 min (c) 24 min (d) 16 min

53. The first order rate constant for the decomposition of N_2O_5 is 6.2×10^{-4} s^{-1}. The half life period for this decomposition is: (MLNR 1991)
(a) 1117.7 s (b) 1117 s (c) 223.4 s (d) 160.9 s

54. The half life period of a first order reaction is:
(a) $\frac{0.693}{a}$ (b) $\frac{0.693}{k}$ (c) $\frac{0.693}{t}$ (d) $\frac{0.693}{ak}$

55. The specific rate constant of a first order reaction depends on:
(a) concentration of the reactants
(b) concentration of the products
(c) time
(d) temperature

56. For a given reaction of first order, it takes 20 minutes for the concentration to drop from 1.0 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be:
(a) more than 20 minutes (b) less than 20 minutes
(c) equal to 20 minutes (d) infinity

57. For the first order reaction $A \longrightarrow$ Product, the half life is 200 seconds. The rate constant of the reaction is:
(a) 3.46×10^{-2} s^{-1} (b) 3.46×10^{-3} s^{-1}
(c) 3.46×10^{-4} s^{-1} (d) 3.46×10^{-5} s^{-1}

58. The following data were obtained for the thermal decomposition of nitrous oxide on finely divided gold:

t (minutes)	0	20	40	60	80
Concentration of N_2O (mol L^{-1})	0.10	0.08	0.06	0.04	0.02

The order of reaction is:
(a) zero (b) 1 (c) 2 (d) 3

59. The following data are for the decomposition of ammonium nitrite in aqueous solution:

Vol. of N_2 in cm^3	6.25	9.0	11.42	13.65	35.02
Time (min)	10	15	20	25	∞

The order of reaction is:
(a) 3 (b) 2 (c) 1 (d) zero
[**Hint:** $a = 35.02, (a-x) = 35.02 - V_t$
Apply, $k = \frac{2.303}{t} \log \frac{35.02}{(35.02 - V_t)}$]

60. In the first order reaction, the concentration of reactant decreases from 1.0 M to 0.25 M in 20 minutes. The value of specific rate is:
(a) 69.32 (b) 6.932 (c) 0.6932 (d) 0.06932

61. The half life period of a first order reaction is 10 minutes. The time required for the concentration of the reactant to change from 0.08 M to 0.02 M is: (IIT 1990)
(a) 10 min (b) 20 min (c) 30 min (d) 40 min

62. The rate constant for the hydrolysis reaction of an ester by dilute acid is 0.6931×10^{-3} s^{-1}. The time required to change the concentration of ester from 0.04 M to 0.01 M is:
(a) 6931 sec (b) 4000 sec
(c) 2000 sec (d) 1000 sec

63. The rate of a gaseous reaction is given by the expression $k[A][B]$. If the volume of reaction vessel is suddenly reduced to one-fourth of the initial volume, the reaction rate relative to the original rate will be: (IIT 1992)
(a) 1/16 (b) 1/8 (c) 8 (d) 16

64. The velocity of a reaction is doubled for every 10°C rise in temperature. If the temperature is raised to 50°C, the reaction velocity increases by about:
(a) 12 times (b) 16 times (c) 32 times (d) 50 times

65. If the rate expression for a reaction is $\frac{dx}{dt} = k[A]^{1/2}[B]^{3/2}$, the overall order of the reaction is: [CEE (Bihar) 1992]
(a) 2 (b) 1/2 (c) 3/2 (d) 1

66. The rates of a certain reaction at different times are as follows:

Time (second)	0	10	20	30
Rate (mol L^{-1} s^{-1})	2.8×10^{-2}	2.78×10^{-2}	2.81×10^{-2}	2.79×10^{-2}

The reaction is of:
(a) third order (b) second order
(c) first order (d) zero order

67. The second order rate constant is usually expressed as:
(a) mol L^{-1} s^{-1} (b) mol^{-1} L^{-1} s^{-1}
(c) mol^{-1} L s^{-1} (d) mol L s^{-1}

68. The hydrolysis of ethyl acetate is a reaction of:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

(a) zero order (b) first order
(c) second order (d) third order

69. The inversion of cane sugar is represented by,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

It is a reaction of: **[PMT (MP) 1993]**
(a) second order (b) unimolecular
(c) pseudo-unimolecular (d) zero order

70. In a second order reaction, the time needed for the initial concentration of the reactant to reduce to half that value is:
(a) independent of the initial concentration
(b) proportional to the initial concentration
(c) inversely proportional to initial concentration
(d) proportional to the square of the initial concentration

71. Which of the following statements regarding molecularity of the reaction is wrong?
(a) It may be either whole number or fractional
(b) It is calculated from the reaction mechanism
(c) It depends on the rate determining step
(d) It is number of molecules of reactants taking part in a single step chemical reaction

72. For the reaction, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the reaction rate is:

$$\text{rate} = k[H_2][Br_2]^{1/2}$$

Which one of the following statements is true for this reaction?
(a) The reaction is of second order
(b) The molecularity of the reaction is 3/2
(c) The unit of k is $\sec^{-1}$
(d) The molecularity of the reaction is two

73. Molecularity of the reaction:
(a) is always a whole number
(b) is never a whole number
(c) can have a fractional value
(d) can be zero

74. For a single step reaction, $A + 2B \longrightarrow$ Products, the molecularity is:
(a) zero (b) three (c) two (d) one

75. The hypothetical reaction, $A_2 + B_2 \longrightarrow 2AB$, follows the following mechanism:

$A_2 \longrightarrow A + A$ (fast)
$A + B_2 \longrightarrow AB + B$ (slow)
$A + B \longrightarrow AB$ (fast)

The order of the overall reaction is: **[PMT (Pb.) 1991]**
(a) zero (b) 1 (c) 2 (d) 3/2

76. The molecularity of a reaction is:
(a) same as its order
(b) different from order
(c) may be same or different as compared to order
(d) always zero

77. The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows:

$O_3 \longrightarrow O_2 + O$ (fast)
$O + O_3 \longrightarrow 2O_2$ (slow)

The rate law expression should be:
(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2[O_2]^{-1}$
(c) $r = k[O_3][O_2]$ (d) $r = [O_3][O_2]^2$

[**Hint:** $r = k'[O_3][O] = \dfrac{k'k''[O_3][O_3]}{[O_2]} = k[O_3]^2[O_2]^{-1}$]

78. Time required to decompose half of the substance for nth order reaction is inversely proportional to:
(a) a^{n+1} (b) a^{n-1}
(c) a^{n-2} (d) a^n

79. What is the order of the reaction which obeys the expression $t_{1/2} = \dfrac{1}{ka}$?
(a) Zero (b) Third
(c) First (d) Second

80. The order of reaction can be deduced from:
(a) experiment (b) chemical equation
(c) rate constant (d) thermochemical equations

81. The order of a reaction may be determined by:
(a) differential method (b) initial rate method
(c) graphical method (d) all of these

82. A graph between time (t) and the substance consumed at any time is found to be a straight line passing through the origin. This indicates that the reaction is of:
(a) second order (b) first order
(c) zero order (d) fractional order

83. A plot of log $(a - x)$ against time 't' is a straight line. This indicates that the reaction is of:
(a) zero order (b) first order
(c) second order (d) third order

84. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as: **[CBSE (PMT) 2010]**
(a) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$
(b) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$
(c) 6.25×10^{-3} mol $L^{-1}s^{-1}$ and 3.125×10^{-3} mol $L^{-1}s^{-1}$
(d) 1.25×10^{-2} mol $L^{-1}s^{-1}$ and 6.25×10^{-3} mol $L^{-1}s^{-1}$

[**Hint:** $\dfrac{-d[N_2O_5]}{dt} = +\dfrac{1}{2}\dfrac{d[N_2O_5]}{dt} = +2\dfrac{d[O_2]}{dt}$

$$\therefore \quad \frac{d[N_2O_5]}{dt} = 2\left\{\frac{-d[N_2O_5]}{dt}\right\} = 2 \times 6.25 \times 10^{-3}$$
$$= 1.25 \times 10^{-2} \text{mol } L^{-1}s^{-1}$$
$$\frac{d[O_2]}{dt} = \frac{1}{2}\left\{\frac{-d[N_2O_5]}{dt}\right\} = \frac{1}{2} \times 6.25 \times 10^{-3}$$
$$= 3.125 \times 10^{-3} \text{mol } L^{-1}s^{-1}$$]

85. The ratio of the time required for $\frac{3}{4}$th of the reaction of first order to complete to that required for half of the reaction:
(a) 4 : 3 (b) 3 : 2
(c) 2 : 1 (d) 1 : 2

86. In pseudo-unimolecular reactions:
(a) one of the reactants is present in large excess
(b) both the reactants have same concentration
(c) both the reactants are present in low concentration
(d) one of the reactants is less reactive

87. The reaction,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g),$$

is first order with respect to N_2O_5. Which of the following graph, would yield a straight line?

(a) log ($p_{N_2O_5}$) *versus* time with −ve slope

(b) ($p_{N_2O_5}$)$^{-1}$ *versus* time

(c) ($p_{N_2O_5}$) *versus* time

(d) log ($p_{N_2O_5}$) *versus* time with +ve slope

88. Consider the following statements :

(i) increase in concentration of reactant increases the rate of a zero order reaction

(ii) rate constant k is equal to collision frequency 'A' if $E_a = 0$

(iii) rate constant k is equal to collision frequency A if $E_a = \infty$

(iv) $\log_e k$ *vs* T is a straight line

(v) $\log_e k$ *vs* $1/T$ is a straight line

Correct statement are : **[PMT (Kerala) 2010]**

(a) (i) and (iv) (b) (ii) and (v)

(c) (iii) and (iv) (d) (ii) and (iii)

(e) (i) and (v)

89. If we plot a graph between log k and $\frac{1}{T}$ by Arrhenius equation, the slope is: **[EAMCET (Engg.) 2010]**

(a) $-E_a/R$ (b) $+E_a/R$ (c) $-\frac{E_a}{2.303R}$ (d) $+\frac{E_a}{2.303R}$

90. The rate of the reaction,

$$CCl_3CHO + NO \longrightarrow CHCl_3 + NO + CO,$$

is given by the equation, rate $= k[CCl_3CHO][NO]$. If concentration is expressed in mol / litre, the units of k are: **[PMT (MP) 1993]**

(a) $mol^{-2}\ L^2\ s^{-1}$ (b) $mol\ L^{-1}\ s^{-1}$

(c) $L\ mol^{-1}\ s^{-1}$ (d) s^{-1}

91. In a reaction, $2A + B \longrightarrow A_2B$, the reactant A will disappear at: **[PMT (MP) 1993]**

(a) half the rate that B will decrease

(b) twice the rate that B will decrease

(c) the same rate that B will decrease

(d) the same rate that A_2B will form

92. The rate of the reaction, $2NO + O_2 \longrightarrow 2NO_2$, at 25°C is 0.028 mol $L^{-1}\ s^{-1}$. The experimental rate is given by

$$r = k[NO]^2[O_2]$$

If the initial concentrations of the reactants are $O_2 = 0.040$ mol L^{-1} and NO = 0.01 mol L^{-1}, the rate constant of the reaction is:

(a) $7.0 \times 10^{-2}\ L\ mol^{-1}\ s^{-1}$ (b) $7.0 \times 10^{-4}\ L^2\ mol^{-2}\ s^{-1}$

(c) $7.0 \times 10^{2}\ L^2\ mol^{-2}\ s^{-1}$ (d) $7.0 \times 10^{3}\ L^2\ mol^{-2}\ s^{-1}$

[Hint: $0.028 = k[0.01]^2[0.040]$]

93. For the reaction,

$$2NO + Cl_2 \longrightarrow 2NOCl,$$

the following mechanism has been proposed.

$$NO + Cl_2 \rightleftharpoons NOCl_2 \quad \text{(fast)}$$
$$NOCl_2 + NO \longrightarrow 2NOCl \quad \text{(slow)}$$

The rate law for the reaction is:

(a) rate $= k[NO]^2[Cl_2]$ (b) rate $= k[NO][Cl_2]^2$

(c) rate $= k[NOCl_2]$ (d) rate $= k[NOCl]^2$

[Hint:
rate $= k'[NO][NOCl_2] = k'K[NO][NO][Cl_2] = k[NO]^2[Cl_2]$]

94. The rate of a reaction can be increased in general by all the following factors except:

(a) by increasing the temperature

(b) using a suitable catalyst

(c) by increasing the concentration of reactants

(d) by an increase in activation energy

95. How will the rate $r = k[SO_2][O_2]$ of reaction,

$$2SO_2 + O_2 \longrightarrow 2SO_3,$$

change if the volume of the reaction vessel is tripled?

(a) It will be $\frac{1}{3}$rd of its initial value

(b) It will be 3 times of its initial value

(c) It will be 9 times of its initial value

(d) It will be $\frac{1}{9}$th of its initial value

96. Radioactive disintegration is an example of:

(a) zero order reaction (b) first order reaction

(c) second order reaction (d) third order reaction

97. In the formation of sulphur trioxide by the contact process, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of reaction was measured as $-\frac{d[O_2]}{dt} = 3.0 \times 10^{-4}$ mol $L^{-1}\ s^{-1}$.

The rate of reaction expressed in terms of SO_3 will be:

(a) 3.0×10^{-4} mol $L^{-1}\ s^{-1}$ (b) 6.0×10^{-4} mol $L^{-1}\ s^{-1}$

(c) 1.5×10^{-4} mol $L^{-1}\ s^{-1}$ (d) 4.5×10^{-4} mol $L^{-1}\ s^{-1}$

98. The rate constant for a first order reaction is 6.909 min^{-1}. Therefore, the time required in minutes for the participation of 75% of the initial reactant is: **[PET (J&K) 2009]**

(a) $\frac{2}{3}\log 2$ (b) $\frac{2}{3}\log 4$ (c) $\frac{3}{2}\log 2$ (d) $\frac{3}{2}\log 4$

99. For the reaction,

$$A + 2B \longrightarrow C + D, \frac{d[A]}{dt} = k[A][B]^2$$

the expression for $\frac{d[B]}{dt}$ will be:

(a) $2k[A][B]^2$ (b) $\frac{1}{2}k[A][B]^2$

(c) $k[A][B]^2$ (d) $k[A][B/2]^2$

100. Which of the following statements is not correct for the reaction,

$$4A + B \longrightarrow 2C + 2D?$$

(a) The rate of appearance of C is one-half the rate of disappearance of B

(b) The rate of disappearance of B is one-fourth of the rate of disappearance of A

(c) The rate of formation of D is one-half of the rate of consumption of A

(d) The rates of formation of C and D are equal

101. The overall rate of a reaction is governed by:
(a) the rate of the fastest intermediate step
(b) the sum total of the rates of all the intermediate steps
(c) the average of the rates of all the intermediate steps
(d) the rate of the slowest intermediate step

102. The rate constant of a reaction does not depend upon:
(a) temperature
(b) activation energy
(c) catalyst
(d) concentration of reactants and products

103. The half-life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be : (log 2 = 0.301) (AIEEE 2009)
(a) 230.3 minutes (b) 23.03 minutes
(c) 46.06 minutes (d) 460.6 minutes

104. For the chemical reaction $x \longrightarrow y$, it is found that the rate of reaction increases 2.25 times when the concentration of x is increased 1.5 times. What is the order of reaction?
(a) One (b) Two (c) Three (d) Zero
[**Hint:** $r = k[x]^a$ and $2.25r = k[1.5x]^a$
So, $2.25 = (1.5)^a$ or $a = 2$]

105. The half life period of a reaction is constant for:
(a) zero order (b) first order
(c) second order (d) none of these

106. From different sets of data of $t_{1/2}$ at different initial concentrations say 'a' for a given reaction, the $[t_{1/2} \times a]$ is found to be constant. The order of reaction is:
(a) zero (b) 1 (c) 2 (d) 3

107. Diazonium salt decomposes as

$$C_6H_5N_2^+Cl^- \longrightarrow C_6H_5Cl + N_2.$$

At 0°C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is: (MLNR 1994)
(a) a first order reaction
(b) a second order reaction
(c) independent of the initial concentration of the salt
(d) a zero order reaction

108. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, under certain conditions of temperature and pressure of the reactants, the rate of formation of ammonia is 0.001 kg hr^{-1}. The rate of consumption of hydrogen under the same conditions is ...... kg hr^{-1}.
(a) 0.001 (b) 0.003 (c) 0.002 (d) 0.0015

109. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4}\ s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$ respectively. The value of rate constant at $T \longrightarrow \infty$ is: (IIT 1996)
(a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$
(c) infinity (d) $3.6 \times 10^{30}\ s^{-1}$

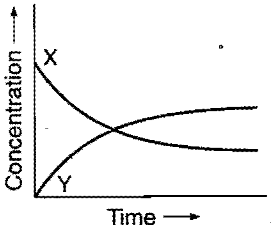
110. In the reaction

$$BrO_3^-(aq.) + 5Br^-(aq.) + 6H^+ \longrightarrow 3Br_2(l) + 3H_2O(l)$$

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following: [CBSE (PMT) 2009]
(a) $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$ (b) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$
(c) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (d) $\frac{d[Br_2]}{dt} = +\frac{5}{3}\frac{d[Br^-]}{dt}$

111. Given that k is the rate constant for some order of any reaction at temp. T, then the value of $\lim_{T \to \infty} \log k$, (where, A is the Arrhenius constant) is:
(a) $A/2.303$ (b) A (c) $2.303A$ (d) $\log A$

112. The curve depicts the change in concentration of species X and Y as a function of time. The point of intersection of the two curves represents:
(a) $t_{1/2}$
(b) $t_{3/4}$
(c) $t_{2/3}$
(d) data insufficient to predict



113. In gaseous reactions, important for the understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and E_a is 77 kJ mol^{-1}; then E_a for the bimolecular recombination of two OH radicals to form H_2O and O is:
(a) 3 kJ mol^{-1} (b) 4 kJ mol^{-1}
(c) 5 kJ mol^{-1} (d) 7 kJ mol^{-1}

114. From the following data, the activation energy for the reaction (cal/mol) is:

$$H_2 + I_2 \longrightarrow 2HI$$

T (K)	$1/T$ (K^{-1})	log K
769	1.3×10^{-3}	2.9
667	1.5×10^{-3}	1.1

(a) 4×10^4 (b) 2×10^4
(c) 8×10^4 (d) 3×10^4

115. The hydrolysis of an ester was carried out separately with 0.05 N HCl and 0.05 N H_2SO_4. Which of the following will be true?
(a) $k_{HCl} > k_{H_2SO_4}$ (b) $k_{H_2SO_4} > k_{HCl}$
(c) $k_{H_2SO_4} = 2k_{HCl}$ (d) $k_{H_2SO_4} = k_{HCl}$

116. For an endothermic reaction, where, ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be:
(a) less than ΔH (b) zero
(c) more than ΔH (d) equal to ΔH

117. In the following first order competing reactions;

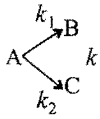
$$A + \text{Reagent} \longrightarrow \text{Product}$$
$$B + \text{Reagent} \longrightarrow \text{Product}$$

The ratio of k_1/k_2 if only 50% of B will have been reacted when 94% of A has been reacted is:
(a) 4.06 (b) 3.06
(c) 2.06 (d) 0.06

118. Two reactions $A \to$ Products and $B \to$ Products, have rate constants k_A and k_B at temperature T and activation energies E_A and E_B respectively. If $k_A > k_B$ and $E_A < E_B$ and assuming that A for both the reactions is same, then:

(a) at higher temperatures k_A will be greater than k_B
(b) at lower temperatures k_A and k_B will be close to each other in magnitude
(c) as temperature rises, k_A and k_B will be close to each other in magnitude
(d) at lower temperature $k_B > k_A$

119. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as:



$k_1 = 1.26 \times 10^{-4}\ \text{s}^{-1}$ and $k_2 = 3.8 \times 10^{-5}\ \text{s}^{-1}$

The percentage distributions of B and C are:
(a) 80% B and 20% C (b) 76.83% B and 23.17% C
(c) 90% B and 10% C (d) 60% B and 40% C

120. Inversion of a sugar follows first order rate equation which can be followed by noting the change in rotation of the plane of polarisation of light in a polarimeter. If r_∞, r_t and r_0 are the rotations at $t = \infty$, $t = t$ and $t = 0$, then first order reaction can be written as:
(a) $k = \frac{1}{t}\log_e \frac{r_t - r_\infty}{r_0 - r_\infty}$ (b) $k = \frac{1}{t}\log_e \frac{r_0 - r_\infty}{r_t - r_0}$
(c) $k = \frac{1}{t}\log_e \frac{r_\infty - r_0}{r_\infty - r_t}$ (d) $k = \frac{1}{t}\log_e \frac{r_\infty - r_t}{r_\infty - r_0}$

121. Rate of a chemical reaction can be kept constant by: **(BHU 1993)**
(a) stirring the compounds
(b) keeping the temperature constant
(c) both (a) and (b)
(d) none of the above

122. The number of molecules of the reactants taking part in a single step of the reaction tells about: **(AMU 1992)**
(a) molecularity of the reaction
(b) mechanism of the reaction
(c) order of reaction
(d) all of the above

123. Number of moles of a substance present in 1 litre volume is known as: **[PMT (MP) 1993]**
(a) activity (b) molar concentration
(c) active mass (d) none of these

124. The inversion of cane sugar into glucose and fructose is:
(a) I order (b) II order (c) III order (d) zero order

125. The unit of rate constant obeying the rate expression $r = k[A]'[B]^{2/3}$ is:
(a) $\text{mol}^{-2/3}\ \text{litre}^{2/3}\ \text{time}^{-1}$ (b) $\text{mol}^{2/3}\ \text{litre}^{-2/3}\ \text{time}^{-1}$
(c) $\text{mol}^{-5/3}\ \text{litre}^{5/3}\ \text{time}^{-1}$ (d) none of these

126. For the reaction,

$$N_2O_5 \longrightarrow 2NO_2 + 1/2O_2,$$
$$-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$$
$$\frac{d[NO_2]}{dt} = k_2[N_2O_5]$$
$$\frac{d[O_2]}{dt} = k_3[N_2O_5]$$

The relation in between k_1, k_2 and k_3 is:
(a) $2k_1 = k_2 = 4k_3$ (b) $k_1 = k_2 = k_3$
(c) $2k_1 = 4k_2 = k_3$ (d) none of these

127. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true for the rates of the three reactions if the concentration of the reactant is greater than 1 M?
(a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
(c) $r_1 < r_2 < r_3$ (d) All of these

128. In the Q.No. 127, if the concentration of the reactant is less than 1 M, then:
(a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
(c) $r_1 < r_2 < r_3$ (d) all of these

129. In the Q.No. 127, if the concentration of the reactant is 1 M, then:
(a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$
(c) $r_1 < r_2 < r_3$ (d) all of these

130. For a first order reaction, $A \longrightarrow$ Product, the rate of reaction at $[A] = 0.2\,\text{mol L}^{-1}$ is $1.0 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$. The half life period for the reaction is: **(IIT 1999)**
(a) 832 s (b) 440 s (c) 416 s (d) 14 s

131. The rate constant of a first order reaction, $A \longrightarrow$ Products, is $60 \times 10^{-4}\ \text{min}^{-1}$. Its rate at $[A] = 0.01\,\text{mol L}^{-1}$ would be: **(IIT 1997)**
(a) $60 \times 10^{-6}\ \text{mol L}^{-1}\ \text{min}^{-1}$ (b) $36 \times 10^{-4}\ \text{mol L}^{-1}\ \text{min}^{-1}$
(c) $60 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$ (d) $36 \times 10^{-1}\ \text{mol L}^{-1}\ \text{min}^{-1}$

132. For a first order reaction, the half life is independent of: **(CBSE 1999)**
(a) initial concentration
(b) cube root of initial concentration
(c) first power of final concentration
(d) square root of final concentration

133. Activation energy of a chemical reaction can be determined by: **(CBSE 1998)**
(a) changing concentration of reactants
(b) evaluating rate constant at standard temperature
(c) evaluating rate constants at two different temperatures
(d) evaluating velocities of reaction at two different temperatures

134. The experimental data for the reaction $2A + B_2 \rightarrow 2AB$, is:

Expt. No.	**$[A]$**	**$[B_2]$**	**Rate (mol s^{-1})**
1.	0.50	0.50	1.6×10^{-4}
2.	0.50	1.00	3.2×10^{-4}
3.	1.0	1.00	3.2×10^{-4}

The rate equation for the above data is: **(CBSE 1997)**
(a) rate $= k[B_2]^2$ (b) rate $= k[B_2]$
(c) rate $= k[A]^2[B]^2$ (d) rate $= k[A]^2[B]$

135. For the reaction $A \rightarrow B$, the rate law is: rate $= k[A]$. Which of the following statements is incorrect? **[PMT (Pb.) 1998]**
(a) The reaction follows first order kinetics
(b) The $t_{1/2}$ of the reaction depends on initial concentration
(c) k is constant for the reaction at a constant temperature
(d) The rate law provides a simple way of predicting the concentration of reactants at any time after the start of the reaction

136. Cyclopropane rearranges to form propene:

$$\Delta \longrightarrow CH_3-CH=CH_2$$

This follows first order kinetics. The rate constant is $2.714 \times 10^{-3}\ \text{sec}^{-1}$. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec? **[JEE (Orissa) 2009]**

(a) 0.035 M (b) 0.22 M
(c) 0.145 M (d) 0.0018 M

137. The rate constant for the reaction,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g),$$

is $2.3 \times 10^{-2}\ \text{sec}^{-1}$. Which equation given below describes the change of $[N_2O_5]$ with time $[N_2O_5]_0$ and $[N_2O_5]_t$ correspond to concentration of N_2O_5 initially and time 't'? **(AIIMS 2004)**

(a) $[N_2O_5]_0 = [N_2O_5]_t\, e^{kt}$

(b) $\log_e \dfrac{[N_2O_5]_0}{[N_2O_5]_t} = kt$

(c) $\log_{10}[N_2O_5]_t = \log_{10}[N_2O_5]_0 - kt$

(d) $[N_2O_5]_t = [N_2O_5]_0 + kt$

138. The reaction, $X \longrightarrow Y$ (Product) follows first order kinetics. In 40 minutes, the concentration of X changes from 0.1 M to 0.025 M, then the rate of reaction when concentration of X is 0.01 M is: **[IIT (S) 2004]**

(a) $1.73 \times 10^{-4}\ M/\text{min}$ (b) $3.47 \times 10^{-5}\ M/\text{min}$
(c) $3.47 \times 10^{-4}\ M/\text{min}$ (d) $1.73 \times 10^{-5}\ M/\text{min}$

139. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is:

(a) 30 min (b) 15 min (c) 7.5 min (d) 60 min

140. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as;

$$A \begin{cases} \xrightarrow{k_1} B & k_1 = 1.26 \times 10^{-4}\ \text{sec}^{-1} \\ \xrightarrow{k_2} C & k_2 = 3.8 \times 10^{-5}\ \text{sec}^{-1} \end{cases}$$

The percentage distribution of B and C are: **[PMT (Kerala) 2004]**

(a) 75% B and 25% C (b) 80% B and 20% C
(c) 60% B and 40% C (d) 90% B and 10% C
(e) 76.83% B and 23.17% C

141. For a reaction $2NH_3 \longrightarrow N_2 + 3H_2$, it is observed that

$$\frac{-d(NH_3)}{dt} = k_1(NH_3), \frac{d(N_2)}{dt} = k_2(NH_3), \frac{d(H_2)}{dt} = k_3(NH_3).$$

What is the relation between k_1, k_2 and k_3?

(a) $k_1 = k_2 = k_3$ (b) $3k_1 = 6k_2 = 2k_3$
(c) $2k_1 = 3k_2 = 6k_3$ (d) $6k_1 = 3k_2 = 2k_3$

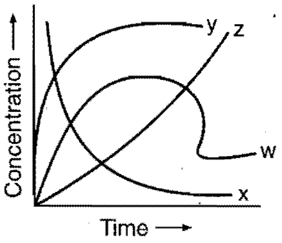
142. In Arrhenius equation $k = Ae^{-E_a/RT}$, factor $e^{-E_a/RT}$ is known as:

(a) frequency factor (b) activation factor
(c) pre-exponential factor (d) Boltzmann factor

143. Unit of frequency factor (A) is:

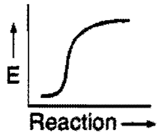
(a) moles/lit (b) moles/lit/sec
(c) depends upon order (d) no unit

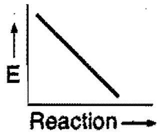
144. For the reaction $A + B \longrightarrow C + D$, the variation of the concentration of the products is given by the curve:

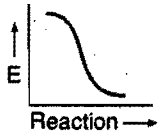


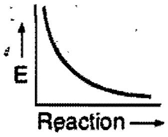
(a) x (b) y (c) z (d) w

145. Which graph shows zero activation energy?

(a)


(b)


(c)


(d)


146. $E_{\text{Threshold}}$ can never be:

(a) $> E_R$ (b) $> E_P$
(c) $< E_P$ (d) $> E_R$ as well as $> E_P$

147. A reaction takes place in three steps; the rate constants are k_1, k_2 and k_3. The overall rate constant $k = \dfrac{k_1 k_3}{k_2}$. If energies of activation are 40, 30 and 20 kJ, the overall energy of activation is:

(a) 10 (b) 15 (c) 30 (d) 60

148. For hypothetical reaction $A \rightarrow B$ takes place according to

$$A \overset{k_1}{\rightleftharpoons} C, \quad A + C \xrightarrow{k_2} D\ \text{(slow)}$$

Rate law will be:

(a) $k_2[A][C]$ (b) $k_1k_2[A]$ (c) $k_1k_2[A]^2$ (d) $k_1k_2[A][C]$

149. If concentration of reactant is increased by 'm'; then k becomes:

(a) $e^{k/m}$ (b) k (c) k/m (d) mk

150. $aA + bB \longrightarrow P$; $dx/dt = k[A]^a \cdot [B]^b$. If conc. of A is doubled, rate is doubled. If B is doubled, rate becomes four times. Which is correct?

(a) $\dfrac{-d[A]}{dt} = \dfrac{-d[B]}{dt}$ (b) $\dfrac{-d[A]}{dt} = \dfrac{-2d[B]}{dt}$

(c) $\dfrac{-2d[A]}{dt} = \dfrac{-d[B]}{dt}$ (d) None of these

151. A drop of solution (volume 0.05 mL) contains 3×10^{-6} mole of H^+. If the rate constant of disappearance of H^+ is 10^7 mol litre^{-1} sec^{-1}, how long would it take for H^+ in the drop to disappear?

(a) 6×10^{-8} sec (b) 6×10^{-9} sec

(c) 6×10^{-10} sec (d) 6×10^{-12} sec

152. For the reaction, $H_2 + I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2HI$. The rate law expression is:

(a) $\left[-\frac{1}{2}\frac{d[HI]}{dt}\right] = k_1[H_2][I_2]$

(b) $\left[-\frac{1}{2}\frac{d[HI]}{dt}\right] = \frac{k_1[HI]^2}{k_2[H_2][I_2]}$

(c) $\left[-\frac{1}{2}\frac{d[HI]}{dt}\right] = k_1[H_2][I_2] - k_2[HI]^2$

(d) $\left[-\frac{1}{2}\frac{d[HI]}{dt}\right] = k_1k_2[H_2][I_2]$

153. The chemical reaction, $2O_3 \rightarrow 3O_2$ proceeds as;

$O_3 \rightleftharpoons O_2 + O$ (fast), $O + O_3 \rightarrow 2O_2$ (slow)

The rate law expression will be:

(a) rate $= k[O][O_3]$ (b) rate $= k[O_3]^2$

(c) rate $= k[O_3]^2[O_2]^{-1}$ (d) can't be determined

154. For the reaction $NH_4^+ + OCN^- \longrightarrow NH_2CONH_2$, the probable mechanism is,

$NH_4^+ + OCN^- \rightleftharpoons NH_4OCN$ (fast)

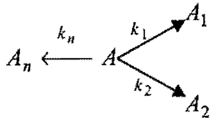
and $NH_4OCN \longrightarrow NH_2CONH_2$ (slow)

The rate law will be:

(a) rate $= k[NH_2CONH_2]$ (b) rate $= k[NH_4]^+[OCN]^-$

(c) rate $= k[NH_4OCN]$ (d) none of these

155. For a 1st order decomposition,



overall k will be given by:

(a) $k = k_1 + k_2 + \ldots + k_n$ (b) $k = (k_1 + k_2 + \ldots + k_n)/n$

(c) $k = k_1 \times k_2 \times \ldots \times k_n$ (d) none of these

156. For a reaction $A + 3B \rightarrow P$, Rate $= \frac{-d[A]}{dt}$, the expression for the rate of reaction in terms of change in the concentration of $B, \frac{-d[B]}{dt}$ will be :

(a) $k[A]^2[B]$ (b) $k[A]^2[3B]$

(c) $3k[A]^2[B]$ (d) $(\frac{1}{3})k[A]^2[B]$

157. Which of the following statements is correct?

(a) Rate of reaction $\propto \frac{1}{E_a}$

(b) At lower temp., increase in temp. causes more change in the value of k

(c) Both (a) and (b) are correct

(d) None is correct

158. For $X \rightarrow Y$; $k = 10^{10}e^{-500/T}$, and for $W \rightarrow Z$; $k = 10^{12}e^{-1000/T}$ at what temperature 'T' both reactions will have same value of k?

(a) 500 K (b) 1500 K

(c) $\frac{4.606}{500}$ K (d) $\frac{2.303}{5000}$ K

159. For a reversible reaction where the forward reaction is exothermic, which of the following statements is correct? **[JEE (WB) 2010]**

(a) The backward reaction has higher activation energy than the forward reaction

(b) The backward and the forward processes have same activation energy

(c) The backward reaction has lower activation energy

(d) No activation energy is required at all since energy is liberated in the process

160. For the reaction, $A + 3B \longrightarrow 2C + D$

which one of the following is not correct? **[EAMCET (Med.) 2010]**

(a) Rate of disappearance of A = Rate of formation of D

(b) Rate of formation of $C = \frac{2}{3} \times$ Rate of disappearance of B

(c) Rate of formation of $D = \frac{1}{3} \times$ Rate of disappearance of B

(d) Rate of disappearance of $A = 2 \times$ Rate of formation of C

161. $2A \longrightarrow B + C$, would be a zero order reaction when: **[CBSE (PMT) 2002]**

(a) the rate of reaction is proportional to square of concentration of 'A'

(b) the rate of reaction is same at any concentration of 'A'

(c) the rate remains unchanged at any concentration of 'B' and 'C'

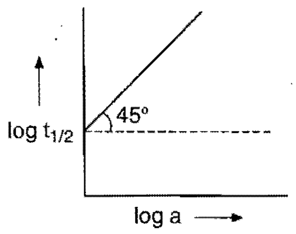
(d) the rate of reaction doubles if concentration of 'B' is increased to double

162. Units of rate constants for first and zero order reactions in terms of molarity M unit are respectively: **(AIEEE 2002)**

(a) sec^{-1}, M sec^{-1} (b) sec^{-1}, M

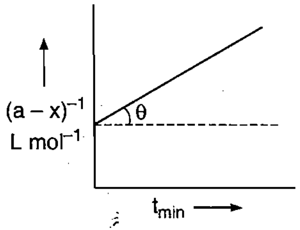
(c) M sec^{-1}, sec^{-1} (d) M, sec^{-1}

163. Following is the graph between log $t_{1/2}$ and log a (a = initial concentration) for a given reaction at 27°C. Hence, order is:



(a) 0 (b) 1 (c) 2 (d) 3

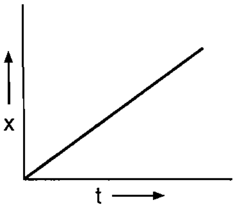
164. Following is the graph between $(a - x)^{-1}$ and time t for second order reaction. $\theta = \tan^{-1}(1/2)$; $OA = 2$ L mol^{-1}, hence rate at the start of reaction will be:



(a) 1.25 L mol^{-1} min^{-1} (b) 0.5 mol L^{-1} min^{-1}

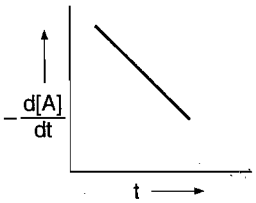
(c) 0.125 mol L^{-1} min^{-1} (d) 1.25 mol L^{-1} min^{-1}

165. Graph between concentration of the product 'x' and time 't' for $A \rightarrow B$ is given ahead:

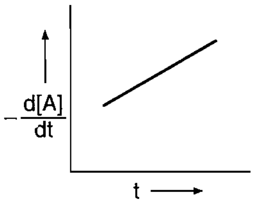


The graph between $-\frac{d[A]}{dt}$ and time will be of the type:

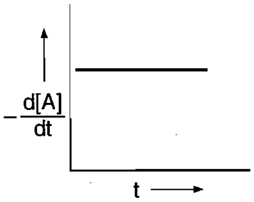
(a)



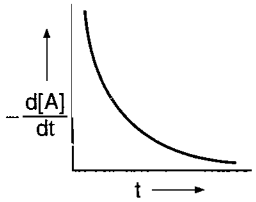
(b)



(c)



(d)



166. Consider the chemical reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The rate of reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions: **(IIT 2002)**

(a) $\text{rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$

(b) $\text{rate} = -\frac{d[N_2]}{dt} = -3\frac{d[H_2]}{dt} = +2\frac{d[NH_3]}{dt}$

(c) $\text{rate} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

(d) $\text{rate} = -\frac{d[N_2]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[NH_3]}{dt}$

167. For the reaction,

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, if

$\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol L^{-1}s^{-1}, the value of $\frac{-d[H_2]}{dt}$ would be: **[CBSE (PMT) 2009]**

(a) 1×10^{-4} mol L^{-1}s^{-1} (b) 3×10^{-4} mol L^{-1}s^{-1}

(c) 4×10^{-4} mol L^{-1}s^{-1} (d) 6×10^{-4} mol L^{-1}s^{-1}

168. Temperature dependent equation can be written as: **[JEE (Orissa) 2005]**

(a) $\ln k = \ln A - e^{E_a/RT}$ (b) $\ln k = \ln A + e^{E_a/RT}$

(c) $\ln k = \ln A - e^{RT/E_a}$ (d) all of these

169. If the rate of reaction $A \longrightarrow B$ doubles on increasing the concentration of A by 4 times, the order of reaction is: **[CET (J&K) 2005]**

(a) 2 (b) 1 (c) 1/2 (d) 4

170. For the reaction: $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ if the concentration of NO_2 increases by 5.2×10^{-3} M in 100 sec, then the rate of reaction is: **[PET (Kerala) 2005]**

(a) 1.3×10^{-5} M s^{-1} (b) 5×10^{-4} M s^{-1}

(c) 7.6×10^{-4} M s^{-1} (d) 2×10^{-3} M s^{-1}

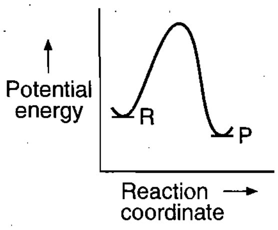
(e) 2.5×10^{-5} M s^{-1}

171. A first order reaction is 10% complete in 20 min. The time taken for 19% completion is: **[PET (Kerala) 2005]**

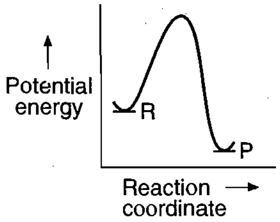
(a) 30 min (b) 40 min (c) 50 min (d) 38 min

(e) 45 min

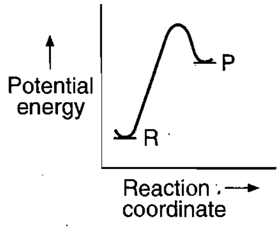
172. An endothermic reaction with high activation energy for the forward reaction is given by the diagram: **(AIIMS 2005)**



(a)



(b)



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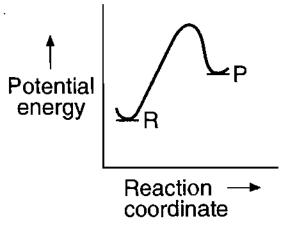


(d)

173. For reaction $aA \longrightarrow xP$, when $[A] = 2.2$ m-M, the rate was found to be 2.4 m M s^{-1}. On reducing concentration of A to half, the rate changes to 0.6 m M s^{-1}. The order of reaction with respect to A is: **(AIIMS 2005)**

(a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0

[Hint: Rate = $k[A]^a$

$2.4 = k[2.2]^a$ ... (i)

$0.6 = k[1.1]^a$ ... (ii)

Dividing eq. (i) by eq. (ii), $a = 2$ ∴ order = 2]

174. According to the law of mass action, rate of a chemical reaction is proportional to: **(AFMC 2005)**

(a) concentration of reactants
(b) molar concentration of reactants
(c) concentration of products
(d) molar concentration of products

175. Consider the endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for backward and forward reactions, respectively. In general: **(AIEEE 2005)**
(a) $E_b < E_f$
(b) $E_b > E_f$
(c) $E_b = E_f$
(d) there is no definite relation between E_f and E_b

176. Which one of the following statements for order of reaction is not correct? **[IIT (S) 2005]**
(a) Order can be determined experimentally
(b) Order of reaction is equal to sum of powers of concentration terms in differential rate law
(c) It is not affected by the stoichiometric coefficient of the reactants
(d) Order cannot be fractional

177. The rate constant of a reaction is found to be 3×10^{-3} mol L^{-1} min^{-1}. The order of the reaction is: **[CET (J&K) 2006]**
(a) zero (b) 1 (c) 2 (d) 1.5
[**Hint:** Unit of rate and rate constants are same for zero order reaction.]

178. In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half life period of the reaction is: **[UGET (Manipal) 2005]**
(a) 2 hrs (b) 4 hrs (c) 1/2 hr (d) 1/4 hr
[**Hint:** $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$

$$k = \frac{2.303}{1} \log\left(\frac{100}{25}\right) = 2 \times 0.693$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2 \times 0.693} = \frac{1}{2} \text{ hr}]$$

179. A substance reacts with initial concentration of a mol dm^{-3} according to zero order kinetics. The time it takes for the completion of the reaction is: (k = rate constant) **[[illegible] 2006; CET (Karnataka) 2009]**
(a) $\frac{k}{a}$ (b) $\frac{a}{2k}$ (c) $\frac{a}{k}$ (d) $\frac{2k}{a}$
(e) ka
[**Hint:** $x = k \times t$

$$t = \frac{x}{k}$$

Time for completion of reaction (when $x = a$), i.e., $t = \frac{a}{k}$]

180. Rate of a reaction can be expressed by Arrhenius equation as, $k = Ae^{-E/RT}$. In this equation, E represents: **(AIEEE 2006)**
(a) the energy above which all the colliding molecules will react
(b) the energy below which colliding molecules will not react
(c) the total energy of the reacting molecules at a temperature T
(d) the fraction of molecules with energy greater than the activation energy of the reaction

181. The rate constant of a first order reaction at 27°C is 10^{-3} min^{-1}. The temperature coefficient of this reaction is 2. What is the rate constant (in min^{-1}) at 17°C for this reaction? **(ET 2006)**
(a) 10^{-3} (b) 5×10^{-4} (c) 2×10^{-3} (d) 10^{-2}
[**Hint:** $\frac{k_{T_2}}{k_{T_1}} = (\mu)^{\Delta T/10}$

$$\frac{10^{-3}}{k_{T_1}} = (\mu)^{10/10} = 2$$

$$k_{T_1} = \frac{10^{-3}}{2} = 0.5 \times 10^{-3}$$

$$= 5 \times 10^{-4} \text{ min}^{-1}]$$

182. In a chemical reaction, two reactants take part. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The order of the reaction is: **[PMT (Raj.) 2006]**
(a) zero (b) 1 (c) 2 (d) 4

183. According to Arrhenius equation, the rate constant (k) is related to temperature (T) as: **(VITEEE 2007)**
(a) $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
(b) $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
(c) $\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$
(d) $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$

184. Consider a reaction $aG + bH \longrightarrow$ Products. When concentration of both the reactants G and H are doubled, the rate increases by eight times. However, when the concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of reaction is: **(IIT 2007)**
(a) 0 (b) 1 (c) 2 (d) 3
[**Hint:** Order with respect to 'G' will two and with respect to 'H' the order will be one.

$$\text{Rate} = k[G]^2[H]^1$$

When concentration of both G and H are doubled, the rate will increase eight times.]

185. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation $k = Ae^{-E_a/RT}$. Activation energy (E_a) of the reaction can be calculated by plotting: **(MS 2007)**
(a) $\log k$ *vs* T (b) $\log k$ *vs* $\frac{1}{T}$ (c) k *vs* T (d) k *vs* $\frac{1}{\log T}$

186. Consider the reaction, $2A + B \longrightarrow$ Products. When concentration of B alone was doubled, the half life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is: **(AIEEE 2007)**
(a) s^{-1} (b) L $mol^{-1}s^{-1}$ (c) unitless (d) mol $L^{-1}s^{-1}$

[**Hint:** Concentration change in 'B' does not change half life, it means the reaction is first order with respect to B. When concentration of only 'A' is doubled, the rate of reaction becomes double, thus order with respect to A will also be one.

Overall order of reaction = 2

unit of rate constant = L $\text{mol}^{-1}\text{s}^{-1}$]

187. In a first order reaction $A \longrightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M then half life is: **[CBSE (Med) 2007]**

(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

188. For the first order reaction, half life is 14 sec, the time required for the initial concentration to reduce to 1/8 of its value is: **[CET (J&K) 2007]**

(a) $(14)^3$ sec (b) 28 sec (c) 42 sec (d) $(14)^2$ sec

189. 75% of a first order reaction was completed in 32 min, when was 50% of the reaction completed? **[BHU (Mains) 2007]**

(a) 24 min (b) 16 min (c) 8 min (d) 48 min

190. For a zero order reaction,

$$A \longrightarrow P$$

$t_{1/2}$ is: (k is rate constant) **[BHU (Mains) 2007]**

(a) $\frac{[A]_0}{2k}$ (b) $\frac{\ln 2}{k}$ (c) $\frac{1}{k[A]_0}$ (d) $\frac{\ln 2}{[A]_0 k}$

191. The rate constants k_1 and k_2 for two different reactions are $10^{16}\, e^{-2000/T}$ and $10^{15} e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is : **[CBSE (PMT) 2008]**

(a) 2000 K (b) $\frac{1000}{2.303}$ K (c) 1000 K (d) $\frac{2000}{2.303}$ K

[**Hint :** $10^{15}\, e^{-1000/T} = 10^{16} e^{-2000/T}$

$$\frac{e^{-2000/T}}{e^{-1000/T}} = \frac{10^{15}}{10^{16}}$$

$$e^{-1000/T} = 10^{-1}$$

$$\log_e e^{-1000/T} = \log_e 10^{-1}$$

$$\frac{-1000}{T} = 2.303 \log_{10} 10^{-1}$$

$$= -2.303$$

$$T = \frac{1000}{2.303}\text{K}]$$

192. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constant for first order (k_1) and zero order (k_0) of the reaction is : **(IIT 2008)**

(a) 0.5 mol^{-1} dm^3 (b) 1 mol dm^{-3}

(c) 1.5 mol dm^{-3} (d) 2 mol^{-1} dm^3

[**Hint :** $t_{1/2} = \frac{0.693}{k_1}$, $t_{1/2} = \frac{a_0}{2k_0}$

$40 = \frac{0.693}{k_1}$, $20 = \frac{1.386}{2k_0} = \frac{0.693}{k_0}$

$$\frac{20}{40} = \frac{0.693/k_0}{0.693/k_1} = \frac{k_1}{k_0}$$

$$\frac{k_1}{k_0} = 0.5\, \frac{\text{sec}^{-1}}{\text{mol dm}^{-3}\ \text{sec}^{-1}} = 0.5\ \text{mol}^{-1}\ \text{dm}^3\ ]$$

193. The decomposition of HI on the surface of gold is : **[Comed (Karnataka) 2008]**

(a) Pseudofirst order (b) zero order

(c) first order (d) second order

194. Consider following two reactions

$$A \longrightarrow \text{Product},\qquad -\frac{d[A]}{dt} = k_1[A]_0$$

$$B \longrightarrow \text{Product},\qquad -\frac{d[B]}{dt} = k_2[B]_0$$

k_1 and k_2 are expressed in terms of molarity (mol L^{-1}) and time (s^{-1}) as: **[BHU (Mains) 2008]**

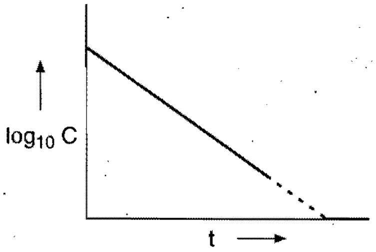
(a) $\text{s}^{-1}, M\ \text{s}^{-1}\ \text{L}^{-1}$ (b) $M\ \text{s}^{-1}, M\ \text{s}^{-1}$

(c) $\text{s}^{-1}, M^{-1}\text{s}^{-1}$ (d) $M\ \text{s}^{-1}, \text{s}^{-1}$

195. If a plot of $\log_{10} C$ versus t gives a straight line for a given reaction, then the reaction is : **(VITEEE 2008)**

(a) zero order (b) first order (c) second oder (d) third order

[**Hint:**



In first order reaction, $\log_{10} C$ when plotted against time 't' then we get straight line. Slope of the line $\left(\frac{2.303}{k}\right)$ gives the value of rate constant.]

196. For a zero order reaction the plot of concentration of reactant versus time is: (intercept refers to concentration axis) **[PET (Kerala) 2008]**

(a) linear with +ve slope and zero intercept

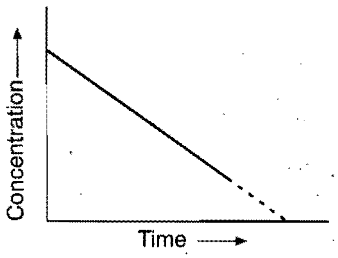
(b) linear with –ve slope and zero intercept

(c) linear with –ve slope and non zero intercept

(d) linear with +ve slope and non zero intercept

(e) a curve asymptotic to concentration axis

[**Hint :**



Linear with negative slope and non zero intercept.]

197. T_{50} of first order reaction is 10 min. Starting with 10 mol L^{-1}, rate after 20 min is : **(AIIMS 2008)**

(a) 0.0693 mol L^{-1} min^{-1}

(b) 0.0693 × 2.5 mol L^{-1} min^{-1}

(c) $0.0693 \times 5 \text{ mol L}^{-1} \text{ min}^{-1}$
(d) $0.0693 \times 10 \text{ mol L}^{-1} \text{ min}^{-1}$

[**Hint :** Remaining concentration of reactant after 20 min

$$= \frac{1}{4} \times 10 = 2.5 \text{ mol L}^{-1}$$

$$\begin{aligned} \text{Rate} &= k \times [\text{Reactant}] \\ &= \frac{0.693}{t_{1/2}} \times [\text{Reactant}] \\ &= \frac{0.693}{10} \times 2.5 = 0.0693 \times 2.5 \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$]

198. For the decomposition of AB at 600 K, the following data were obtained

[AB] mol dm^{-3}	**Rate of decomposition of AB in mol dm^{-3}s^{-1}**
0.20	2.75×10^{-8}
0.40	11×10^{-8}
0.60	24.75×10^{-8}

The order of the decomposition of AB is :
[CET (Karnataka) 2009]

(a) 0 (b) 1 (c) 2 (d) 1.5

199. For a reaction between A and B, the initial rate of reaction is measured for various initial concentrations of A and B. The data provided are: **(DCE 2009)**

Exp. No.	**[A]**	**[B]**	**Initial reaction rate (mol L^{-1}s^{-1})**
1.	0.2 M	0.3 M	5×10^{-5}
2.	0.2 M	0.1 M	5×10^{-5}
3.	0.4 M	0.05 M	7.5×10^{-5}

The overall order of the reaction is: **(DCE 2009)**

(a) one (1) (b) two (2)
(c) two and a half (2.5) (d) between 1 and 2

200. For a first order reaction $A \longrightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation:

$$\log k = -(2000)\frac{1}{T} + 6.0$$

The pre exponential factor A and the activation energy E_a respectively, are : **(IIT 2009)**

(a) $1 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}
(b) 6 s^{-1} and 16.6 kJ mol^{-1}
(c) $1 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}
(d) $1 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol^{-1}

[**Hint :** $\log k = \log_{10} A - \frac{E_a}{2.303} \times \frac{1}{T}$

Comparing this equation with the given equation we get,

$$A = 10^6 \text{ s}^{-1}, \; E_a = 38.3 \text{ kJ mol}^{-1}$$]

201. The time for half-life period of a certain reaction, $A \rightarrow$ Product is 1 hour. When the initial concentration of the reactant 'A' is 2 mol L^{-1}. How much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction? **(AIEEE 2010)**

(a) 0.25 h (b) 1 h (c) 4 h (d) 0.5 h

[**Hint :** $\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$

$$\frac{1}{t_2} = \left(\frac{0.5}{2}\right)^{0-1}$$

$$t_2 = 0.25 \text{ h}$$]

202. Consider the reaction :

$$Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is :

$$\text{Rate} = k\,[Cl_2][H_2S]$$

Which of these mechanisms is/are consistent with this rate equation?

A. $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)
$Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

B. $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)
$Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

(AIEEE 2010)

(a) neither A nor B (b) A only
(c) B only (d) both A and B

Assertion-Reason TYPE QUESTIONS

he questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions ou are required to choose any one of the following four options:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) is incorrect but (R) is correct.

1. (A) The rate of reaction sometimes does not depend on concentration.
   (R) The order of reaction can be negative.
2. (A) The rate of reaction increases generally by 2 to 3 times for every 10°C rise in temperature.
   (R) Increase in temperature increases the collision frequency.
3. (A) Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas in presence of alkali, it is a reaction of second order.
   (R) Acid acts as catalyst only whereas alkali acts as one of the reactant.
4. (A) The molecularity of the reaction,
   $H_2 + Br_2 \longrightarrow 2HBr$ is 2.
   (R) The order of this reaction is 3/2.
5. (A) Positive catalysts lower the activation energy of the reaction whereas heat of reaction remains same.
   (R) Heat of reaction is equal to the difference between activation energies for forward and the backward reactions.
6. (A) Positive catalysts increase the rate of reaction.
   (R) Catalysts decrease the value of ΔG°.
7. (A) $k = Ae^{-E_a/RT}$, the Arrhenius equation represents the dependance of rate constant with temperature.
   (R) Plot of log k against $1/T$ is linear and the activation energy can be calculated with this plot.
8. (A) If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
   (R) Lower the activation energy, faster is the reaction.
9. (A) Order with respect to any reactant or product can be zero, positive, negative and fractional.
   (R) Rate cannot decrease with increase in concentration of a reactant or product.
10. (A) Formation of HI is a bimolecular reaction.
    (R) Two molecules of reactants are involved in this reaction.
11. (A) The order of the reaction,
    $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$
    is 2.
    (R) The molecularity of this reaction is 2.
12. (A) For: $aA + bB \longrightarrow$ Product. The order of the reaction is equal to $(a + b)$.
    (R) Rate of reaction $= k\,[A]^a[B]^b$.
13. (A) The hydrolysis of methyl acetate by dil HCl is a pseudo first order reaction.
    (R) HCl acts as a catalyst for the hydrolysis. **(AIIMS 2007)**
14. (A) The order of a reaction can have fractional value.
    (R) The order of a reaction cannot be written from balanced equation of a reaction. **(AIIMS 2008)**

Answers : OBJECTIVE QUESTIONS

1. (c)	2. (d)	3. (b)	4. (b)	5. (a)	6. (a)	7. (c)	8. (d)
9. (b)	10. (c)	11. (a)	12. (d)	13. (d)	14. (d)	15. (b)	16. (a)
17. (c)	18. (c)	19. (b)	20. (b)	21. (c)	22. (a)	23. (a)	24. (d)
25. (c)	26. (d)	27. (a)	28. (b)	29. (d)	30. (d)	31. (d)	32. (b)
33. (a)	34. (a)	35. (b)	36. (c)	37. (d)	38. (d)	39. (a)	40. (c)
41. (b)	42. (b)	43. (d)	44. (c)	45. (a)	46. (b)	47. (c)	48. (a)
49. (d)	50. (b)	51. (c)	52. (d)	53. (a)	54. (b)	55. (d)	56. (c)
57. (b)	58. (a)	59. (c)	60. (d)	61. (b)	62. (c)	63. (d)	64. (c)
65. (a)	66. (d)	67. (c)	68. (b)	69. (c)	70. (c)	71. (a)	72. (d)
73. (a)	74. (b)	75. (d)	76. (c)	77. (b)	78. (b)	79. (d)	80. (a)
81. (d)	82. (c)	83. (b)	84. (b)	85. (c)	86. (a)	87. (a)	88. (b)
89. (c)	90. (c)	91. (b)	92. (d)	93. (a)	94. (d)	95. (d)	96. (b)
97. (b)	98. (a)	99. (a)	100. (a)	101. (d)	102. (d)	103. (c)	104. (b)
105. (b)	106. (c)	107. (a)	108. (d)	109. (b)	110. (b)	111. (d)	112. (a)
113. (c)	114. (a)	115. (a)	116. (c)	117. (a)	118. (a, c)	119. (b)	120. (b)
121. (b)	122. (a)	123. (c)	124. (a)	125. (a)	126. (a)	127. (c)	128. (b)
129. (a)	130. (a)	131. (a)	132. (a)	133. (c)	134. (b)	135. (b)	136. (b)
137. (b)	138. (c)	139. (a)	140. (e)	141. (c)	142. (d)	143. (b)	144. (b)
145. (c)	146. (c)	147. (c)	148. (c)	149. (b)	150. (c)	151. (b)	152. (c)
153. (c)	154. (b)	155. (a)	156. (c)	157. (c)	158. (c)	159. (a)	160. (d)
161. (b)	162. (a)	163. (a)	164. (c)	165. (c)	166. (a)	167. (b)	168. (a)
169. (c)	170. (a)	171. (b)	172. (c)	173. (b)	174. (b)	175. (a)	176. (d)
177. (a)	178. (c)	179. (c)	180. (b)	181. (b)	182. (a)	183. (a)	184. (d)
185. (b)	186. (b)	187. (c)	188. (c)	189. (b)	190. (a)	191. (b)	192. (a)
193. (b)	194. (d)	195. (b)	196. (c)	197. (b)	198. (c)	199. (d)	200. (d)
201. (a)	202. (b)						

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (b)	2. (b)	3. (a)	4. (b)	5. (b)	6. (c)	7. (a)	8. (b)
9. (c)	10. (a)	11. (d)	12. (b)	13. (b)	14. (b)		

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. Which of the following is correct?
   (a) Molecularity of a reaction can be fractional
   (b) Zero order reaction never stops
   (c) A first order reaction must be homogeneous
   (d) The frequency factor 'A' in Arrhenius equation ($k = Ae^{-E_a/RT}$) increases with increase in temperature

2. The rate constant of the reaction,
$$2H_2O_2(aq.) \rightarrow 2H_2O(l) + O_2(g),$$
is $3 \times 10^{-3}\ \text{min}^{-1}$.
At what concentration of H_2O_2, the rate of the reaction will be $2 \times 10^{-4}\ M\,s^{-1}$?
   (a) $6.67 \times 10^{-3}\ M$ (b) $2\ M$
   (c) $4\ M$ (d) $0.08\ M$

[**Hint:** Rate $= k[H_2O_2]^1$
$$2 \times 10^{-4} = \frac{3 \times 10^{-3}}{60} \times [H_2O_2]$$
$$[H_2O_2] = 4\ M]$$

3. The mechanism of the reaction,
$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g),$$
is:

Step 1: $2NO(g) + H_2(g) \xrightarrow{\text{slow}} N_2 + H_2O_2$

Step 2: $H_2O_2 + H_2 \xrightarrow{\text{fast}} 2H_2O$

   (a) rate $= k[NO]^2[H_2]^2$
   (b) rate $= k[H_2O_2][H_2]$
   (c) on doubling the concentration of H_2, keeping the concentration of NO constant, the rate will become double
   (d) if the initial concentration of H_2 and NO is C_0 and after time 't' the concentration of N_2 is x, then
   Rate $= k(C_0 - 2x)^x$

[**Hint:** Slowest step is rate determining
$\therefore$ Rate $= k[NO]^2[H_2]$
$\therefore$ On doubling the concentration of H_2 without changing the concentration of NO, the rate will become double.]

4. The rate law for a reaction between A and B is given by:
$$\text{Rate} = k[A]^n[B]^m$$
On doubling the concentration of A and halving the concentration of B, the ratio of new rate to the earlier rate of the reaction will be as:
   (a) $n - m$ (b) 2^{n-m} (c) $2^{1/(n+m)}$ (d) 2^{m-n}

5. The reaction $A \xrightarrow{k}$ Product, is zero order while the reaction $B \xrightarrow{k}$ Product, is first order reaction. For what initial concentration of A are the half lives of the two reactions equal?
   (a) $(\log_e 4)M$ (b) $2\ M$ (c) $2 \log 2\ M$ (d) $\ln 2\ M$

[**Hint:** For zero order reaction,
$$x = kt$$
$$\therefore \quad \frac{a}{2} = k \times t_{1/2},\ i.e.,\ t_{1/2} = \frac{a}{2k} \qquad \text{... (i)}$$
For first order reaction,
$$t_{1/2} = \frac{\log_e 2}{k} \qquad \text{... (ii)}$$
From eqs. (i) and (ii), $\dfrac{a}{2k} = \dfrac{\log_e 2}{k}$
$$a = \log_e 4\ M]$$

6. Which of the following is pseudo-unimolecular reaction?
   (a) $2H_2O_2 \longrightarrow 2H_2O + O_2$
   (b) $C_6H_5N_2Cl + HOH \longrightarrow C_6H_5OH + N_2 + HCl$
   (c) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
   (d) $2O_3 \longrightarrow 3O_2$

7. The order and molecularity of the chain reaction,
$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2HCl\ (g),$$
are:
   (a) 2, 0 (b) 0, 2 (c) 1, 1 (d) 3, 0

8. A reactant (A) forms two products:
$$A \xrightarrow{k_1} B \quad \text{Activation energy } E_{a_1}$$
$$A \xrightarrow{k_2} C \quad \text{Activation energy } E_{a_2}$$
If $E_{a_2} = 2E_{a_1}$, then k_1 and k_2 will be related as:
   (a) $k_2 = k_1 e^{E_{a_1}/RT}$ (b) $k_2 = k_1 e^{E_{a_2}/RT}$
   (c) $k_1 = Ak_2 e^{E_{a_1}/RT}$ (d) $k_1 = 2k_2 e^{E_{a_2}/RT}$

[**Hint:** $k_2 = Ae^{-E_{a_2}/RT}$
$$k_1 = Ae^{-E_{a_1}/RT}$$
$$\therefore \quad \frac{k_2}{k_1} = e^{(-E_{a_2} + E_{a_1})/RT}$$
$$\frac{k_2}{k_1} = e^{E_{a_1}/RT} \qquad \text{Since, } E_{a_2} = 2E_{a_1}$$
$$k_2 = k_1 e^{E_{a_1}/RT}]$$

9. Collision theory is satisfactory for:
   (a) first order reactions (b) second order reactions
   (c) bimolecular reactions (d) zeroth order reactions

10. Initial concentration of reactant for nth order reaction is 'a'. Which of the following relations is correct about $t_{1/2}$ of the reaction?
   (a) $\ln t_{1/2} = \ln(\text{constant}) - (n-1)\log_e a$
   (b) $\ln t_{1/2} = \ln n + \ln(\text{constant}) - \ln a$
   (c) $t_{1/2} \ln n = \ln(\text{constant}) + \ln a_0$
   (d) $\ln t_{1/2} = n \ln a_0$

[Hint: $t_{1/2} \propto \frac{1}{a^{n-1}}$

$$t_{1/2} = k\,\frac{1}{a^{n-1}}$$

$\ln t_{1/2} = \ln k - (n-1)\log_e a$]

11. Half life of a reaction becomes half when initial concentrations of reactants are made double. The order of the reaction will be:
(a) 1 (b) 2 (c) 0 (d) 3

[Hint: $t_{1/2} \propto \frac{1}{a^{n-1}}$

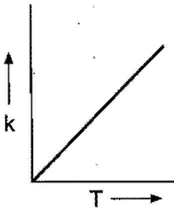
$$t_{1/2} \propto \frac{1}{a}$$

where, n = order of reaction for second order reaction.]

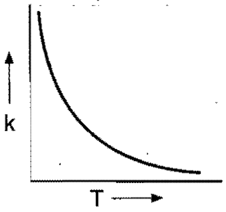
12. Arrhenius equation is:

$$k = Ae^{-E/RT}$$

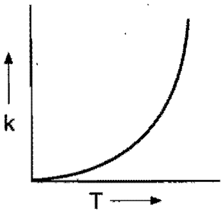
Which of the following graphs represents the variation of rate constant k against temperature T ? **(IIT 2010)**



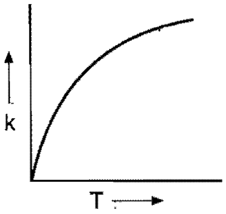
(a)



(b)

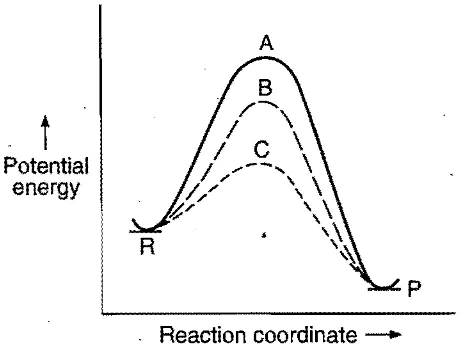


(c)



(d)

13. If a homogeneous catalytic reaction follows three alternative paths A, B and C, then which of the following indicates the relative ease with which the reaction moves?



(a) $A > B > C$ (b) $C > B > A$ (c) $A > C > B$ (d) $A = B = C$

14. The rate constant for the reaction,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is 3×10^{-5} sec^{-1}. If the rate is 2.4×10^{-5} mol litre^{-1} sec^{-1}, then the concentration of N_2O_5 in mol litre^{-1} will be:
(a) 1.4 (b) 2.1 (c) 1.27 (d) 0.8

[Hint: $\because$ Rate $= k\,[N_2O_5]$

$$2.4 \times 10^{-5} = 3 \times 10^{-5}\,[N_2O_5]$$

$[N_2O_5] = 0.8\,M$]

15. Consider the following statements:
1. The rate of reaction is always proportional to the concentrations of reactants.
2. The order of an elementary chemical reaction step can be determined by examining its stoichiometry.
3. The first order reactions follow an exponential time course.

Of these statements:
(a) 1, 2 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 3 are correct (d) 1 and 3 are correct

[Hint: Statement (1) cannot be correct because the rate of zero order reactions does not depend on concentration of reactant.]

16. Two different first order reactions have rate constants k_1 and k_2 at T_1 $(k_1 > k_2)$. If temperature is increased from T_1 to T_2, then new constants become k_3 and k_4 respectively. Which among the following relations is correct?
(a) $k_1 > k_2 = k_3 = k_4$ (b) $k_1 < k_3$ and $k_2 < k_4$
(c) $k_1 = k_3 = k_4$ (d) $k_1 > k_2 > k_3 > k_4$

17. In the reaction, $A + B \longrightarrow C + D$, the rate $\left(\frac{dx}{dt}\right)$ when plotted against time 't' gives a straight line parallel to time axis. The order and rate of reaction will be:
(a) $1, k+1$ (b) $0, k$ (c) $1, k+1$ (d) $k, k+1$

18. In the Haber's process of ammonia manufacture,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

the rate of appearance of NH_3 is:

$$\frac{d[NH_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

The rates of the reaction expressed in terms of N_2 and H_2 will be:

	Rates in terms of H_2 (mol L^{-1} sec^{-1})	**Rates in terms of N_2 (mol L^{-1} sec^{-1})**
(a)	3×10^{-4}	2×10^{-4}
(b)	3×10^{-4}	1×10^{-4}
(c)	1×10^{-4}	3×10^{-4}
(d)	2×10^{-4}	2×10^{-4}

[Hint: Rate $= +\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[N_2]}{dt}$

$$\frac{-d[H_2]}{dt} = \frac{3}{2} \times \frac{d[NH_3]}{dt}$$

$$= \frac{3}{2} \times 2 \times 10^{-4} = 3 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

$$\frac{-d[N_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt} = \frac{1}{2} \times 2 \times 10^{-4}$$

$= 1 \times 10^{-4}$ mol L^{-1} sec^{-1}]

19. A reaction $A \longrightarrow B$, involves following mechanism:

Step 1: $A \xrightarrow{k_1} B$ (fast)

Step 2: $B \xrightarrow{k_2} C$ (slow)

Step 3: $C \xrightarrow{k_3} D$ (fast)

The rate law of the reaction may be given as:

(a) rate $= k_1[A]$ (b) rate $= k_2[B]$
(c) rate $= k_3[C]$ (d) rate $= k_1k_2k_3[B][C]$

20. For a gaseous reaction, the following data were recorded:

Concentration in mol L^{-1}	0.1	0.05	0.025	0.0125
Half life in sec	30	29.9	30.1	30

The order of reaction is:

(a) second (b) first (c) zero (d) fractional

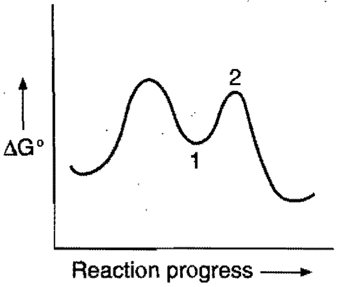
21. The half life of second order reaction is:

(a) inversely proportional to the square of the initial concentration of the reactants
(b) inversely proportional to the initial concentration of reactants
(c) proportional to the initial concentration of reactants
(d) independent of the initial concentration of reactants

[**Hint:** $t_{1/2} \propto \frac{1}{a^{n-1}}$; where, a = initial conc., n = order

$t_{1/2}$ (second order) $\propto \frac{1}{a}$]

22. What names apply to chemical species corresponding to locations 1 and 2 on this reaction coordinate diagram?



	Location 1	**Location 2**
(a)	Activated complex	Activated complex
(b)	Reaction intermediate	Activated complex
(c)	Activated complex	Intermediate
(d)	Reaction intermediate	Intermediate

23. Consider this reaction:

$$2NO_2(g) + O_3(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction of nitrogen dioxide and ozone represented is first order in $NO_2(g)$ and in $O_3(g)$. Which of these possible reaction mechanisms is consistent with the rate law?

Mechanism I: $NO_2(g) + O_3(g) \longrightarrow NO_3(g) + O_2(g)$ (slow)
$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$ (fast)

Mechanism II: $O_3(g) \rightleftharpoons O_2(g) + [O]$ (fast)
$NO_2(g) + [O] \longrightarrow NO_3$ (slow)
$NO_3(g) + NO_2(g) \longrightarrow N_2O_5$ (fast)

(a) I only (b) II only
(c) Both I and II (d) Neither I nor II

[**Hint:** Mechanism I, Rate $= k[NO_2][O_2]$. Slow step is rate determining

Mechanism II, Rate $= k\,[NO_2][O]$ ... (i)

$$K = \frac{[O_2][O]}{[O_3]}, [O] = K\frac{[O_3]}{[O_2]}$$

From eq. (i), Rate $= kK[NO_2][O_3][O_2]^{-1}$

$\therefore$ Both mechanisms show that reaction is first order with respect to NO_2 and O_3.]

24. Use the experimental data in the table to determine the rate law for this reaction:

$$A + B \longrightarrow AB$$

These data were obtained when the reaction was studied:

$[A]$	$[B]$	$\frac{\Delta[AB]}{\Delta t}$ mol L^{-1} sec^{-1}
0.1 M	0.1 M	2×10^{-4}
0.2 M	0.1 M	2×10^{-4}
0.3 M	0.3 M	1.8×10^{-3}

What is the rate equation for the reaction?

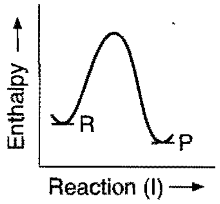
(a) Rate $= k[A][B]$ (b) Rate $= k[A]^2$
(c) Rate $= k[B]$ (d) Rate $= k[B]^2$

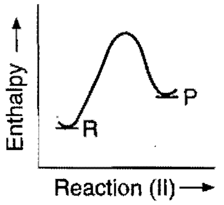
25. In which of the following reactions, the increase in the rate of reaction will be maximum?

	E_a	**Temperature rise**
(a)	40 kJ/mol	200 – 210 K
(b)	90 kJ/mol	300–320 K
(c)	80 kJ/mol	300–310 K

(d) All will have same rate

26. Which of the reactions represented in these diagrams will show the greatest increase in rate for a given increase in temperature?





(a) Reaction I forward (b) Reaction I reversed
(c) Reaction II forward (d) Reaction II reversed

27. Which function of $[X]$, plotted against time, will give a straight line for a second order reaction?

$$X \longrightarrow \text{Product}$$

(a) $[X]$ (b) $[X]^2$ (c) $\ln[X]$ (d) $\frac{1}{[X]}$

28. Decomposition of H_2O_2 is a first order reaction. A 16 volume solution of H_2O_2 of half life 30 min is present at start. When will the solution become one volume?

(a) After 120 min (b) After 90 min
(c) After 60 min (d) After 150 min

29. What is the activation energy for the reverse of this reaction?

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$

Data for the given reaction is: $\Delta H = +54$ kJ and $E_a = +57.2$ kJ:

(a) –54 kJ (b) +3.2 kJ (c) +60.2 kJ (d) +111.2 kJ

30. The reaction between chloroform, $CHCl_3(g)$ and chlorine $Cl_2(g)$ to form $CCl_4(g)$ and $HCl(g)$ is believed to occur by this series of steps:

Step 1: $Cl_2(g) \longrightarrow Cl(g) + Cl(g)$

Step 2: $CHCl_3(g) + Cl(g) \longrightarrow CCl_3(g) + HCl(g)$

Step 3: $CCl_3(g) + Cl(g) \longrightarrow CCl_4(g)$

If this reaction is first order in $CHCl_3$ and half order in Cl_2, which statement about the relative rates of steps 1, 2 and 3 is correct?

(a) Step 1 is the slowest
(b) Steps 1 and 2 must both be slow
(c) Step 2 must be slower than step 1
(d) Step 3 must be the slowest

31. In the reaction,

$3BrO^- \longrightarrow BrO_3^- + 2Br^-$ (aqueous alkaline medium at 80°C)

the value of the rate constant in the rate law in terms of $-\frac{d}{dt}[BrO^-]$ is 0.056 L mol^{-1} s^{-1}. What will be the rate constant when the rate law is stated in terms of $\frac{d}{dt}[BrO_3^-]$?

(a) 18.7×10^{-3} L mol^{-1} s^{-1} (b) 37.4×10^{-3} L mol^{-1} s^{-1}
(c) 0.0187 L mol^{-1} s^{-1} (d) 18.7×10^{-2} L mol^{-1} s^{-1}

[Hint $-\frac{1}{3}\frac{d[BrO^-]}{dt} = \frac{d[BrO_3^-]}{dt} = +\frac{1}{2}\frac{d[Br^-]}{dt}$

Required rate constant $= \frac{1}{3} \times 0.056$ L mol^{-1} s^{-1}

$= 0.0187$ L mol^{-1} s^{-1}]

32. The dependence of the rate constant for a reaction on temperature is given by the equation $k = Ae^{-E_a/RT}$.

Under what conditions is the rate constant k the smallest?

(a) High T and large E_a (b) High T and small E_a
(c) Low T and large E_a (d) Low T and small E_a

33. The activation energy of a certain reaction is 87 kJ mol^{-1}. What is the ratio of the rate constants for this reaction when the temperature is decreased from 37°C to 15°C?

(a) 5/1 (b) 8.3/1 (c) 13/1 (d) 24/1

34. Consider this reaction,

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The rate law for this reaction is:

$$\text{Rate} = k[H_2][NO]^2$$

Under what conditions could these steps represent the mechanism?

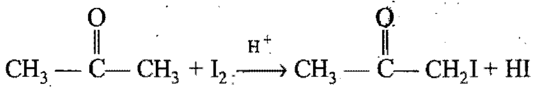
Step 1: $2NO \rightleftharpoons N_2O_2$

Step 2: $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$

Step 3: $N_2O + H_2 \longrightarrow N_2 + H_2O$

(a) These steps cannot be the mechanism under any circumstances
(b) These steps could be the mechanism if step 1 is the slow step
(c) These steps could be the mechanism if step 2 is the slow step
(d) These steps could be the mechanism if step 3 is the slow step

35. Propanone reacts with iodine in acid medium according to the following equation:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + I_2 \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-CH_2I + HI$$

These data were obtained when the reaction was studied:

$[CH_3-\overset{\overset{O}{\|}}{C}-CH_3]$, M	$[I_2]$, M	$[H^+]$, M	Relative rate
0.010	0.010	0.010	1
0.020	0.010	0.010	2
0.020	0.020	0.010	2
0.020	0.010	0.020	4

What is the rate equation for the reaction?

(a) Rate $= k[CH_3-\overset{\overset{O}{\|}}{C}-CH_3][I_2]$

(b) Rate $= k[CH_3-\overset{\overset{O}{\|}}{C}-CH_3]^2$

(c) Rate $= k[CH_3-\overset{\overset{O}{\|}}{C}-CH_3][I_2][H^+]$

(d) Rate $= k[CH_3-\overset{\overset{O}{\|}}{C}-CH_3][H^+]$

36. Arrhenius equation $k = Ae^{-E_a/RT}$

If the activation energy of the reaction is found to be equal to RT, then:

(a) the rate of reaction does not depend upon initial concentration
(b) the rate constant becomes about 37% of the Arrhenius constant A
(c) the rate constant becomes equal to 73% of the Arrhenius constant A
(d) the rate of the reaction becomes infinite or zero

37. At 25°C, the values of rate constant, activation energy and Arrhenius constant of a reaction are 3×10^{-4} sec^{-1}, 129 kJ/mol and 2×10^{15} sec^{-1} respectively.

The value of rate constant as $T \to \infty$ is:

(a) zero (b) 2×10^{15} (c) 3×10^{-4} (d) 6×10^{11}

38. The observed rate of a chemical reaction is substantially lower than the collision frequency. One or more of the following statements is/are true to account for this fact.

A. the reactants do not have the required energy.
B. the partners do not collide in the proper orientation
C. collision complex exists for a very short time.
D. collision frequency over estimates the number of effective collisions **(ISAT 2010)**

(a) A, B and C (b) A, B and D
(c) B, C and D (d) A, C and D

39. The reaction between NO and Cl_2 takes place in the following two steps:

I. $NO + Cl_2 \underset{k_2 \text{ fast}}{\overset{k_1}{\rightleftharpoons}} NOCl_2$

II. $NOCl_2 + NO \xrightarrow[\text{slow}]{k_2} 2NOCl$

The rate law of overall reaction,

$$2NO + Cl_2 \longrightarrow 2NOCl$$

can be given by:

(a) rate = $k[NO]^2[Cl_2]$ (b) rate = $k[NO][Cl_2]$

(c) rate = $k[NOCl][NO]$ (d) rate = $k[NO][Cl_2]^2$

40. Which of the following reactions will have fractional order for A_2 or B_2?

(a)
$A_2 \rightleftharpoons A + A$ (fast)
$A + B_2 \rightleftharpoons AB + B$ (slow)
$A + B \rightleftharpoons AB$ (fast)

(b)
$A_2 \rightleftharpoons C$ (slow)
$C + B_2 \rightleftharpoons D$ (fast)
$D + A_2 \rightleftharpoons$ Products

(c)
$B_2 \rightleftharpoons B + B$ (fast)
$A_2 + B \rightleftharpoons AB + A$ (slow)
$AB \longrightarrow$ Products (fast)

(d) All have fractional order

41. In which of the following, E_a for backward reaction is greater than E_a for forward reaction?

(a) $A \xrightarrow{E_a = 50 \text{ kcal}} B;$ $\Delta H = -10$ kcal

(b) $A \xrightarrow{E_a = 50 \text{ kcal}} B;$ $\Delta H = +10$ kcal

(c) $A \xrightarrow{E_a = 60 \text{ kcal}} B;$ $\Delta H = +20$ kcal

(d) All of the above

[Hint: $\Delta H = (E_a)_f - (E_a)_b$

$(E_a)_b = (E_a)_f - \Delta H = 50 + 10 = 60$ kcal]

42. For n th order reaction $\frac{t_{1/2}}{t_{3/4}}$ depends on $(n \neq 1)$:

(a) initial concentration only

(b) 'n' only

(c) initial concentration and 'n' both

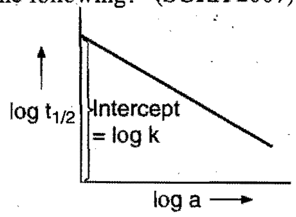
(d) sometimes 'n' and sometimes initial concentration

[Hint: Time for fractional change $\propto \frac{1}{a^{n-1}}$]

43. For a second order reaction, $2A \longrightarrow$ Products, a plot of log $t_{1/2}$ *vs* log a (where, a is initial concentration) will give an intercept equal to which one of the following? **(SCRA 2007)**

(a) $\frac{1}{k}$ (b) $\log\left(\frac{1}{2k}\right)$

(c) $\log\left(\frac{1}{k}\right)$ (d) $\log k$



[Hint: Kinetic equation for second order reaction is:

$$k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$$

when $x = \frac{a}{2}, t = t_{1/2}$

$$\therefore \quad t_{1/2} = \frac{1}{k} \times \frac{1}{a}$$

$\log t_{1/2} = -\log k - \log a$]

44. For a reaction taking place in three steps, the rate constants are k_1, k_2 and k_3. The overall rate constant $k = \frac{k_1 k_2}{k_3}$. If the energy of activation values for the first, second and third stages are respectively 40, 50 and 60 kJ mol^{-1}, then the overall energy of activation in kJ mol^{-1} is: **[PMT (Kerala) 2008]**

(a) 30 (b) 40 (c) 60 (d) 50

(e) 150

[Hint : $k = \frac{k_1 k_2}{k_3}$

$$Ae^{-E/RT} = \frac{Ae^{-E_1/RT} \times Ae^{-E_2/RT}}{Ae^{-E_3/RT}}$$

$$e^{-E/RT} = e^{(-E_1 - E_2 + E_3)/RT}$$

$$E = E_1 + E_2 - E_3$$

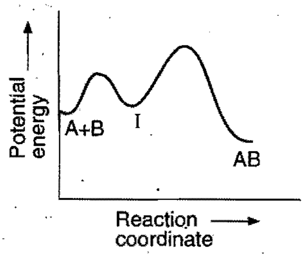
$$= 40 + 50 - 60 = 30 \text{ kJ mol}^{-1}]$$

45. For an exothermic reaction, following two steps are involved.

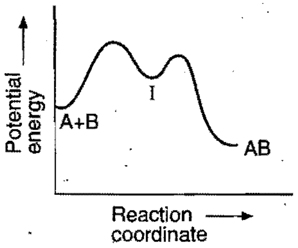
Step 1. $A + B \longrightarrow I$ (slow)

Step 2. $I \longrightarrow AB$ (fast)

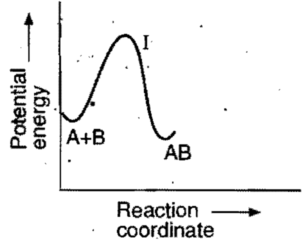
Which of the following graphs correctly represent this reaction ?



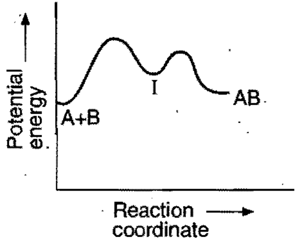
(a)



(b)



(c)



(d)

46. A reaction takes place in three steps with individual rate constant and activation energy,

	Rate constant	Activation energy
Step 1	k_1	$E_{a_1} = 180$ kJ/mol
Step 2	k_2	$E_{a_2} = 80$ kJ/mol
Step 3	k_3	$E_{a_3} = 50$ kJ/mol

overall rate constant, $k = \left(\frac{k_1 k_2}{k_3}\right)^{2/3}$

overall activation energy of the reaction will be :

(a) 140 kJ/mol (b) 150 kJ/mol

(c) 130 kJ/mol (d) 120 kJ/mol

[Hint : $Ae^{-E_a/RT} = \left[\frac{Ae^{-E_{a_1}/RT} Ae^{-E_{a_2}/RT}}{Ae^{-E_{a_3}/RT}}\right]^{2/3}$

$$= [Ae^{(-E_{a_1} - E_{a_2} + E_{a_3})/RT}]^{2/3}$$

$$E_a = \frac{2}{3}[E_{a_1} + E_{a_2} - E_{a_3}]$$

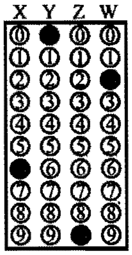
$$= \frac{2}{3}[180 + 80 - 50] = 140 \text{ kJ/mol}]$$

Answers

1. (d) 2. (c) 3. (c) 4. (b) 5. (a) 6. (b) 7. (b) 8. (a)
9. (c) 10. (a) 11. (b) 12. (c) 13. (b) 14. (d) 15. (c) 16. (b)
17. (b) 18. (b) 19. (b) 20. (b) 21. (b) 22. (b) 23. (c) 24. (d)
25. (b) 26. (b) 27. (d) 28. (a) 29. (b) 30. (c) 31. (c) 32. (c)
33. (c) 34. (c) 35. (d) 36. (b) 37. (b) 38. (a) 39. (a) 40. (a, c)
41. (a) 42. (c) 43. (d) 44. (a) 45. (a) 46. (a)

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. In the reaction, $A \longrightarrow B$ when the initial concentration of reactant is halved, the half-life increases by a factor of eight, what will be the order of the reaction?
2. Rate of a chemical reaction increases by 1024 times by 100°C rise in temperature; the temperature coefficient of the reaction will be:
3. The rate of a reaction at 10 sec intervals are as follows :

Time (sec)	Rate (mol L^{-1} sec^{-1})
0	4.8×10^{-2}
10	4.79×10^{-2}
20	4.78×10^{-2}
30	4.81×10^{-2}

What will be the order of the reaction?

4. How many times of the half-life will require to complete 75% of a reaction of first order?
5. Ozone depletion takes place as :

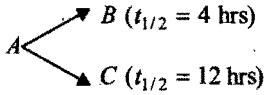
$$2O_3(g) \longrightarrow 3O_2(g)$$

Step 1 : $O_3(g) \overset{k}{\rightleftharpoons} O_2(g) + O(g)$ (fast)

Step 2 : $O_3(g) + [O] \xrightarrow{k} 2O_2(g)$ (slow)

order of the reaction will be :

6. If the $t_{1/2}$ for a first order reaction is 0.4 min, the time of or 99.9% completion of the reaction is .... min.
7. Consider following parallel first order reactions



The half-life for the decay of A is ....hrs.

8. The half-life period of a first order reaction is 1 hr. What is the time in hour taken for 87.5% completion of the reaction?
9. The half-life of a reaction is doubled when the initial concentration is doubled. The order of reaction is :
10. For the reaction $A_2 + 2B \longrightarrow 2AB$, the following data were observed :

Exp. No.	$[A_2]$	$[B]$	Rate (mol L^{-1} s^{-1})
1.	0.1	0.01	1.5×10^{-3}
2.	0.1	0.04	6.0×10^{-3}
3.	0.2	0.01	3.0×10^{-3}

The overall order of the reaction will be :

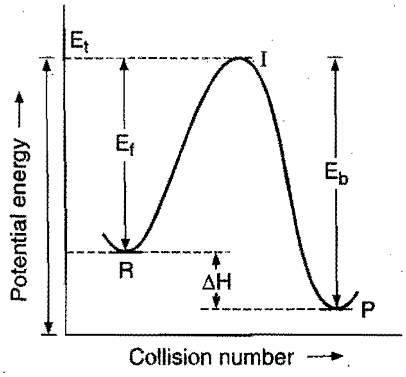
Answers

1. (4) 2. (2) 3. (0) 4. (2) 5. (1) 6. (4) 7. (3) 8. (3)
9. (0) 10. (2)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

A collision between reactant molecules must occur with a certain minimum energy before it is effective in yielding product molecules. This minimum energy is called activation energy E_a. Larger is the value of activation energy, smaller is the value of rate constant. Larger is the value of activation energy, greater is the effect of temperature rise on rate constant k.



E_f = *Activation energy of forward reaction*

E_b = *Activation energy of backward reaction*

$\Delta H = E_f - E_b$

E_t = *Threshold energy*

Answer the following questions:

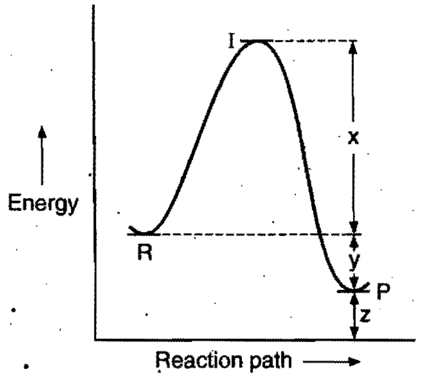
1. If a reaction, $A + B \longrightarrow C$, is exothermic to the extent of 30 kJ/mol and the forward reaction has an activation energy of 249 kJ/mol, the activation energy for reverse reaction in kJ/mol is:
   (a) 324 (b) 279 (c) 40 (d) 100
2. For the following reaction at a particular temperature, according to the equations,
   $$2N_2O_5 \longrightarrow 4NO_2 + O_2$$
   $$2NO_2 + \tfrac{1}{2}O_2 \longrightarrow N_2O_5$$
   the activation energies are E_1 and E_2 respectively. Then:
   (a) $E_1 > E_2$ (b) $E_1 < E_2$ (c) $E_1 = 2E_2$ (d) $\sqrt{E_1E_2^2} = 1$
3. In a hypothetical reaction, $A \rightarrow Y$, the activation energies for the forward and backward reactions are 15 and 9 kJ mol^{-1} respectively. The potential energy of A is 10 kJ mol^{-1}. Which of the following is wrong?
   (a) Threshold energy of the reaction is 25 kJ
   (b) The potential energy of B is 16 kJ
   (c) Heat of reaction is 6 kJ
   (d) The reaction is exothermic
4. For two reactions, activation energies are E_{a_1} and E_{a_2}; rate constants are k_1 and k_2 at the same temperature. If $k_1 > k_2$, then:
   (a) $E_{a_1} > E_{a_2}$ (b) $E_{a_1} = E_{a_2}$ (c) $E_{a_1} < E_{a_2}$ (d) $E_{a_1} \geq E_{a_2}$
5. The rate constant of a certain reaction is given by $k = Ae^{-E_a/RT}$ (where A = Arrhenius constant). Which factor should be lowered so that the rate of reaction may increase?
   (a) T (b) Z (c) A (d) E_a
6. The activation energies for forward and backward reactions in a chemical reaction are 30.5 and 45.4 kJ mol^{-1} respectively. The reaction is:
   (a) exothermic
   (b) endothermic
   (c) neither exothermic nor endothermic
   (d) independent of temperature

• Passage 2

The energy profile diagram for the reaction:

$$CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$$

is given below:



Answer the following questions:

1. The activation energy of the forward reaction is:
   (a) x (b) y (c) $x + y$ (d) $x - y$
2. The activation energy of the backward reaction is:
   (a) x (b) y (c) $x + y$ (d) $x - y$
3. The heat of the reaction is:
   (a) x (b) y (c) $x + y$ (d) $x - y$
4. The threshold energy of the reaction is:
   (a) $x + y - z$ (b) $x - y + z$ (c) $x + y + z$ (d) $x - y - z$

• Passage 3

Population growth of humans and bacteria follows first order growth kinetics. Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply. A study at 35°C gave the following results:

Time (minutes)	0	15	30	45	60
Number of bacteria	100	200	400	800	1600

Answer the following questions:

1. The rate constant for the first order growth of bacteria can be calculated using:
   (a) $k = \dfrac{2.303}{t}\log_{10}\left(\dfrac{a}{a-x}\right)$ (b) $k = -\dfrac{2.303}{t}\log\left(\dfrac{a}{a+x}\right)$

(c) $k = \frac{0.693}{t}$ (d) $k = \frac{x}{t}$

2. Unit of rate constant for first order growth is:
(a) min^{-1} (b) min^{2} (c) min^{-3} (d) unitless
3. The rate constant for the reaction is:
(a) $0.0462\ \text{min}^{-1}$ (b) $0.462\ \text{min}^{-1}$
(c) $4.62\ \text{min}^{-1}$ (d) $46.2\ \text{min}^{-1}$
4. The rate of growth initially is:
(a) 4.62 bacteria per min (b) 23.1 bacteria per min
(c) 23.1 bacteria per sec (d) 0.231 bacteria per sec
5. At what time, there will be 6400 bacteria in the flask?
(a) 150 min (b) 90 min (c) 160 min (d) 120 min

• Passage 4

Order of reaction is an experimentally determined quantity. It may be zero, positive, negative and fractional. The kinetic equation of nth order reaction is:

$$k \times t = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

Half life of nth order reaction depends on initial concentration according to the following relation:

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

Unit of the rate constant varies with the order but general relation for unit of nth order reaction is:

$$\textit{Unit of } k = \left[\frac{1}{\textit{conc.}}\right]^{n-1} \times \textit{time}^{-1}$$

The differential rate law for nth order reaction may be given as:

$$\frac{dx}{dt} = k[A]^n$$

where, A denotes the reactant.

Answer the following questions:

1. The unit of rate and rate constant are same for a:
(a) zero order reaction (b) first order reaction
(c) second order reaction (d) half order reaction
2. The rate constant for zero order reaction is:
(a) $k = \frac{C_0}{2t}$ (b) $k = \frac{C_0 - C_t}{t}$
(c) $k = \ln\frac{C_0 - C_t}{2t}$ (d) $k = \frac{C_0}{C_t}$
where C_0 and C_t are concentrations of reactants at respective times.
3. The half life for a zero order reaction equals to:
(a) $\frac{1}{2}\frac{k}{a^2}$ (b) $\frac{a^2}{2k}$ (c) $\frac{2k}{a}$ (d) $\frac{a}{2k}$
4. For a reaction:
$$I^- + OCl^- \longrightarrow IO^- + Cl^-$$
in an aqueous medium, the rate of the reaction is given by
$$\frac{d[IO^-]}{dt} = k\frac{[I^-][OCl^-]}{[OH^-]}$$
The overall order of the reaction is:
(a) -1 (b) 1 (c) zero (d) 2
5. In a chemical reaction $A \longrightarrow B$, it is found that the rate of the reaction doubles when the concentration of A is increased four times. The order of the reaction with respect to A is:
(a) 0 (b) 1/2 (c) 1 (d) 2

• Passage 5

Consider the reaction represented by the equation:

$$CH_3Cl(g) + H_2O(g) \longrightarrow CH_3OH(g) + HCl(g)$$

These kinetic data were obtained for the given reaction concentrations:

Initial conc. (*M*)		**Initial rate of disappearance of CH_3Cl $M\,s^{-1}$**
$[CH_3Cl]$	**$[H_2O]$**	
0.2	0.2	1
0.4	0.2	2
0.4	0.4	8

Answer the following questions based on these data:

1. The rate law for the reaction will be:
(a) $r = k[CH_3Cl][H_2O]$ (b) $r = k[CH_3Cl]^2[H_2O]$
(c) $r = k[CH_3Cl][H_2O]^2$ (d) $r = k[CH_3Cl]^2[H_2O]^4$
2. Order with respect to $[CH_3Cl]$ will be:
(a) 0 (b) 1 (c) 2 (d) 3
3. Overall order of the reaction will be:
(a) 0 (b) 1 (c) 2 (d) 3
4. Unit of rate constant will be:
(a) sec^{-1} (b) $\text{litre}^2\ \text{mol}^{-2}\ \text{sec}^{-1}$
(c) $\text{litre mol}^{-1}\ \text{sec}^{-1}$ (d) $\text{mol litre}^{-1}\ \text{sec}^{-1}$
5. If H_2O is taken in large excess, the order of the reaction will be:
(a) 1 (b) 0 (c) 3 (d) 2

Answers

Passage 1.	1. (d)	2. (a)	3. (d)	4. (c)	5. (d)	6. (a)
Passage 2.	1. (a)	2. (c)	3. (b)	4. (c)		
Passage 3.	1. (b)	2. (a)	3. (a)	4. (a)	5. (b)	
Passage 4.	1. (a)	2. (b)	3. (d)	4. (b)	5. (b)	
Passage 5.	1. (c)	2. (b)	3. (d)	4. (b)	5. (a)	

SELF ASSESSMENT

ASSIGNMENT NO. 8

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. What is the order of reaction,

$$A_2 + B_2 \longrightarrow 2AB\ ?$$

Mechanism:

$$A_2 \rightleftharpoons A + A \quad \text{(fast)}$$
$$A + B_2 \longrightarrow AB + B \quad \text{(slow)}$$
$$A + B \longrightarrow AB \quad \text{(fast)}$$

(a) 2 (b) 1 (c) $3/2$ (d) $1/2$

2. For a gaseous reaction, $A(g) \longrightarrow$ Product, which one of the following is correct relation among $\frac{dP}{dt}$, $\frac{dn}{dt}$ and $\frac{dc}{dt}$?

($\frac{dP}{dt}$ = Rate of reaction in atm sec^{-1}; $\frac{dc}{dt}$ = Rate of reaction in molarity sec^{-1}; $\frac{dn}{dt}$ = Rate of reaction in mol sec^{-1})

(a) $\frac{dc}{dt} = \frac{dn}{dt} = -\frac{dP}{dt}$ (b) $-\frac{dc}{dt} = -\frac{1}{V}\frac{dn}{dt} = -\frac{dP}{dt}$

(c) $\frac{dc}{dt} = \frac{V}{RT}\frac{dn}{dt} = \frac{dP}{dt}$ (d) None of these

3. The rate law for a reaction between the substances A and B is given by the, rate $= k[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as:

(a) $\frac{1}{2^{m+n}}$ (b) $m + n$ (c) $n - m$ (d) $2^{(n-m)}$

4. A substance having initial concentration 'a' reacts according to zero order kinetics. What will be the time for the reaction to go to completion?

(a) $\frac{a}{k}$ (b) $\frac{k}{a}$ (c) $\frac{a}{2k}$ (d) $\frac{2k}{a}$

5. The rate constant for the reaction,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

is $3 \times 10^{-5}\ \text{sec}^{-1}$. If the rate of reaction is 2.4×10^{-5} mol $\text{litre}^{-1}\ \text{sec}^{-1}$, then the concentration of N_2O_5 in mol litre^{-1} is:

(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8

6. Half life of a reaction is inversely proportional to cube of initial concentration. The order of reaction is:

(a) 4 (b) 3 (c) 5 (d) 2

7. The oxidation of ammonia takes place as,

$$NH_3(g) + 3O_2(g) \longrightarrow 2N_2(g) + 6H_2O(g)$$

if the rate of formation of N_2 is 0.7 M/s, determine the rate at which NH_3 is consumed:

(a) 1.4 mol $L^{-1}s^{-1}$ (b) 0.7 mol $L^{-1}s^{-1}$

(c) 1.5 mol $L^{-1}s^{-1}$ (d) none of these

8. Consider the reaction:

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The rate law for this reaction is:

$$\text{Rate} = k[H_2][NO]^2$$

Under what conditions could these steps represent the mechanism?

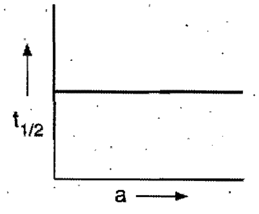
Step 1: $2NO(g) \rightleftharpoons N_2O_2(g)$

Step 2: $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$

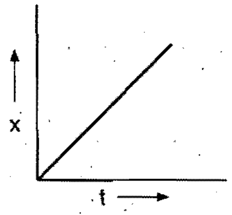
Step 3: $N_2O + H_2 \longrightarrow H_2O + N_2$

(a) These steps can never satisfy the rate law
(b) Step 1 should be the slowest step
(c) Step 2 should be the slowest step
(d) Step 3 should be the slowest step

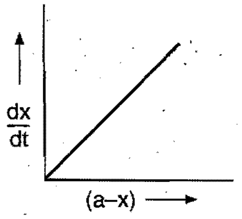
9. Which of the following is not for zero order reaction?



(a)



(b)



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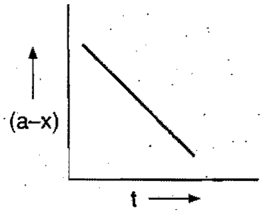


(d)

10. I. $E_a = 15\ \text{kJ mol}^{-1}$; $\Delta H = -70\ \text{kJ mol}^{-1}$

II. $E_a = 30\ \text{kJ mol}^{-1}$; $\Delta H = -15\ \text{kJ mol}^{-1}$

III. $E_a = 60\ \text{kJ mol}^{-1}$; $\Delta H = +20\ \text{kJ mol}^{-1}$

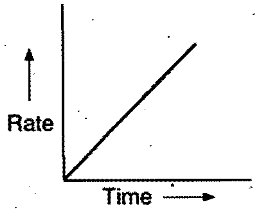
If above reactions are at same frequency factor then fastest and slowest reactions are:

(a) III is fastest, II is slowest
(b) I is fastest, III is slowest
(c) II is fastest, III is slowest
(d) III is fastest, I is slowest

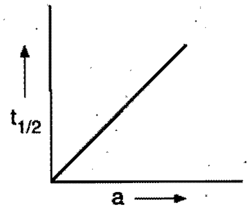
SECTION-II

Multiple Answers Type Objective Questions

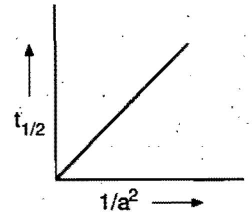
11. Which of the following graphs are correct?



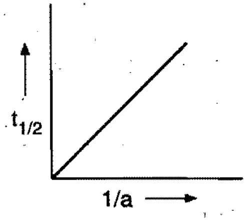
(a)



(b)



(c)



(d)

Here 'a' denotes initial concentration of reactants.

12. Arrhenius equation may be given as:

(a) $\ln \frac{A}{k} = \frac{E_a}{RT}$
(b) $\log A = \log k + \frac{E_a}{2.303\,RT}$
(c) $\log\left[\frac{-E_a}{RT}\right] = \frac{k}{a}$
(d) $\frac{d \ln k}{dt} = \frac{E_a}{RT}$

13. Which of the following is/are correct for second order reaction?

(a) $t_{1/2}$ is inversely proportional to initial concentration
(b) $k = \frac{1}{t}\left[\frac{1}{(a-x)} - \frac{1}{a}\right]$
(c) $k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$
(d) $k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$

14. For a 1st order reaction:

$A \longrightarrow B$, with initial concentration = a

(a) $t_{1/2} = \frac{k}{a}$
(b) $t_{3/4} = 2t_{1/2}$
(c) $t_{1/2} = \frac{0.693}{k}$
(d) $t_{1/2} = k \times 0.693$

15. Select the correct statement for Arrhenius equation

$$k = Ae^{-Ea/RT}$$

(a) 'A' may be termed as the rate constant at very high temperature
(b) 'A' may be termed as the rate constant at zero activation energy
(c) E_a is the activation energy of reaction
(d) k is rate of reaction at zero concentration

SECTION-III

Assertion-Reason Type Questions

This section contains 3 questions. Each question of this section contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; Statement-2 is true; Statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; Statement-2 is true; Statement-2 is not a correct explanation for Statement-1.
(c) Statement-1 is true; Statement-2 is false.
(d) Statement-1 is false; Statement-2 is true.

16. **Statement-1:** If temperature does not affect the rate of reaction, $E_a = 0$.

Because

Statement-2: Lesser is the activation energy, slower is the rate.

17. **Statement-1:** In the reaction:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$
$$\text{Rate} = k[NO_2]^2$$

The rate of reaction does not depend on the concentration of CO.

Because

Statement-2: Carbon monoxide is involved in fast step.

18. **Statement-1:** The reciprocal of time in which 66% of the reactant is converted to product is equal to the rate constant of first order reaction.

Because

Statement-2: The rate constant for first order reaction depends on initial concentration of reactants.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

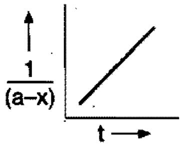
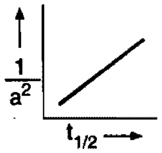
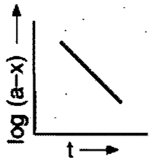
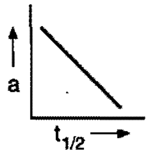
If the correct matches are (a-p,s); (b-q,r); (c-p,q); and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

19. Match the Column-I with Column-II:

Column-I	Column-II
(a) Rate of reaction	(p) May be fractional
(b) Rate constant	(q) Whole number
(c) Order of reaction	(r) Independent of temperature
(d) Molecularity of reaction	(s) Increase with temperature

20. Match the Column-I with Column-II:

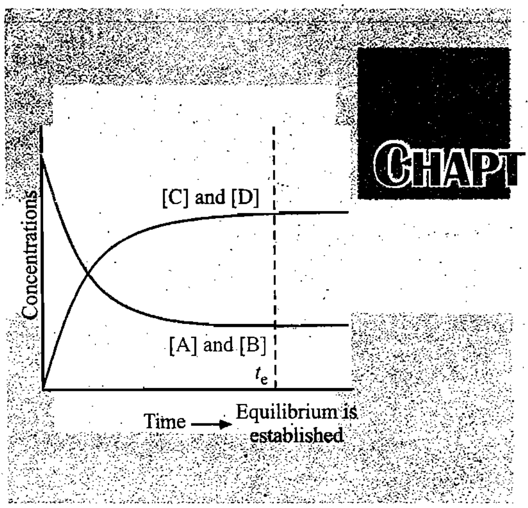
Column-I (Order of reaction)	**Column-II (Graph)**
(a) First order	(p) 
(b) Second order	(q) 
(c) Third order	(r) 
(d) Zero order	(s) 

21. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) First order	(p) Unit of $k = \text{sec}^{-1}$
(b) Pseudo first order	(q) Unit of $k = \text{dm}^6\text{mol}^{-2}\text{s}^{-1}$
(c) Third order	(r) $t_{1/2} \propto 1/a^2$
(d) Second order	(s) $t_{1/2} \propto \frac{1}{a}$

Answers

1. (c) 2. (b) 3. (d) 4. (a) 5. (d) 6. (a) 7. (a) 8. (c)
9. (c) 10. (b) 11. (b,c) 12. (a,b) 13. (a,b) 14. (b,c) 15. (a,b,c) 16. (c)
17. (a) 18. (c) 19. (a-s) (b-s) (c-p,r) (d-q,r) 20. (a-r) (b-p) (c-q) (d-s) 21. (a-p) (b-p) (c-q,r) (d-s)



CHAPTER 9

CHEMICAL EQUILIBRIUM

9.1 INTRODUCTION

It is a well established fact that many reactions do not go to completion. They proceed to some extent leaving considerable amounts of unreacted reactants, *i.e.*, the resulting mixture contains both reactants and products. When such a stage is reached in a course of reaction that no further reaction is apparent, it is said in chemical language that the reaction has attained the state of equilibrium where the composition of the system becomes fixed. At equilibrium state both the forward and backward reactions move with equal speeds, *i.e.*, the rate of disappearance of reactants is exactly equal to rate of the appearance of reactants from the products. The study of chemical equilibrium helps in the elucidation of the optimum conditions for the greater yields of the products in the case of those reactions which attain equilibrium in the course of reaction.

Chemical reactions can be classified as **irreversible** and **reversible** reactions.

Irreversible reactions: The chemical reactions which proceed in such a way that reactants are completely converted into products, *i. e.*, the reactions which move in one direction, *i.e.*, forward direction only are called **irreversible reactions.** In such reactions, products do not react together to produce reactants again, *i. e.*, the reaction does not move in backward direction. For example, when solutions containing equimolar concentrations of barium chloride and sodium sulphate are mixed, reaction occurs and practically whole of barium is precipitated as barium sulphate.

$$BaCl_2 + Na_2SO_4 \longrightarrow \underset{\text{ppt.}}{BaSO_4} + 2NaCl$$

The reaction between $BaSO_4$ and NaCl, *i. e.*, backward reaction, is not possible under the experimental conditions. In such reactions the arrow (→) is placed between reactants and products which indicates the direction of the chemical change. Some more examples of irreversible reactions are given below:

1. (a) Thermal decomposition of potassium chlorate,

$$2KClO_3 \xrightarrow[\text{Heat}]{MnO_2} 2KCl + 3O_2$$

   (b) Decomposition of ammonium nitrite,

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

2. Precipitation reactions,

   (a) $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

   (b) $Pb(NO_3)_2 + 2KI \longrightarrow PbI_2 + 2KNO_3$

3. Neutralisation reactions,

$$\underset{\text{Strong acid}}{H_2SO_4} + \underset{\text{Strong base}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$$

4. Redox and combustion reactions,

   (a) $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$

   (b) $2Mg + O_2 \longrightarrow 2MgO$

   (c) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

Reversible reactions: The chemical reactions which take place in both directions under similar conditions are called **reversible reactions.** In such reactions, the products also react with each other and produce reactants again. For example, when hydrogen is passed over heated magnetic oxide, metallic iron and water are produced.

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

On the other hand, if steam is passed over powdered iron at the same temperature, magnetic oxide of iron and hydrogen are formed.

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

If the reaction is carried out in a closed vessel, it is found that in no case the reaction proceeds to completion. It is, thus, clear that either of the two reactions can take place independently if steam or hydrogen is allowed to escape from system by carrying out the reaction in open vessel but if a closed vessel is used and nothing is allowed to escape both forward and backward reactions can take place in the vessel.

Reactions which thus proceed in both the directions and do not reach to completion are known as reversible reactions. The reaction proceeding from left to right is conventionally called the **forward reaction** and the opposite one proceeding from right to left is called the **reverse** or **backward reaction.** In such reactions the arrow (→) or sign of equality (=) is replaced by two half arrows ($\rightleftharpoons$) pointing the reaction in both the directions. This sign ($\rightleftharpoons$) represents the reversibility of the reaction.

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

Some examples of reversible reactions are given below:

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$2HI \rightleftharpoons H_2 + I_2$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$NH_4HS \rightleftharpoons NH_3 + H_2S$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

9.2 STATE OF CHEMICAL EQUILIBRIUM

The most important characteristic property of a reversible reaction is that it always attains a state of chemical equilibrium. Consider a general reversible reaction in a closed vessel.

$$A + B \rightleftharpoons C + D$$

In the initial state only A and B are present both react with each other, *i.e.*, rate of forward reaction is maximum as only the concentrations of A and B are involved (at the beginning, the concentrations of products C and D are nil). As soon as the products C and D are produced, the backward reaction starts functioning. By the expiry of time, the rate of forward reaction decreases as the concentrations of A and B decrease while the rate of backward reaction increases as the concentrations of products C and D increase. Ultimately, a stage comes when the rate of forward reaction becomes equal to rate of backward reaction. This state is called the **equilibrium state.**

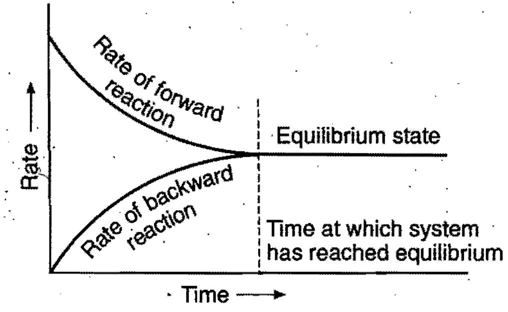


Fig. 9.1

At equilibrium state,

Rate of forward reaction = Rate of backward reaction.

It can be shown graphically as in Fig. 9.1.

Thus, chemical equilibrium in a reversible reaction is the state at which both forward and backward reactions or two opposing reactions occur at the same speed.

This state will continue indefinitely if the conditions such as temperature and concentration are not changed. At the state of equilibrium, the concentrations of reactants and products in the reaction mixture attain a constant value and the concentrations do not change with time.

When hydrogen gas and iodine vapours are heated in a closed vessel at a constant temperature 717 K, the two react to form hydrogen iodide. In the initial stage, the colour of the reaction mixture is deep violet due to the presence of large amounts of iodine. But as the reaction progresses, the intensity of the colour decreases as more and more iodine is converted into hydrogen iodide. After sometime, the intensity of the colour of the reaction mixture becomes constant. The constancy of intensity of colour indicates that concentration of both reactants and products have become constant and state of equilibrium has been attained.

The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the equilibrium state.

Or

The state in which the measurable properties of the system (such as pressure, density, colour or concentration) do not undergo any further noticeable change with time under given set of conditions is said to be a state of equilibrium.

The equilibrium state is **dynamic** and not static in nature. The reaction does not stop but both the opposing reactions are going on continuously with same speeds. At this stage, the number of moles of substances produced per second in the forward reaction is equal to the number of moles of substances which disappear per second in the backward reaction.

Characteristics of Equilibrium State

(i) Equilibrium state can only be achieved if a reversible reaction is carried out in closed space.

No product can leave nor any reactant from outside can enter the space. If the system is not closed, some of the products may escape and thus, the backward reaction will not occur.

(ii) Chemical equilibrium, at a given temperature, is characterised by constancy of certain properties such as pressure, concentration, density or colour.

(iii) Chemical equilibrium can be attained from either side, *i.e.*, from the side of reactants or products.

$$2HI \rightleftharpoons H_2 + I_2$$

or

$$H_2 + I_2 \rightleftharpoons 2HI$$

At equilibrium, each reactant and each product has a fixed concentration and this is independent of the fact whether we start the reaction with the reactants or with the products.

This reaction can be graphically represented as,

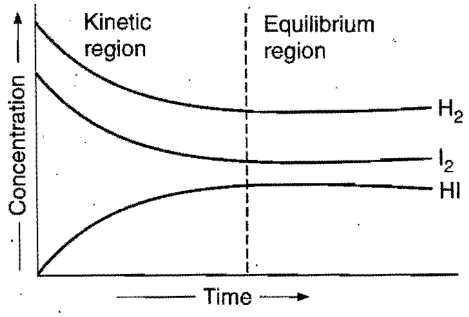


Fig. 9.2

(iv) Equilibrium state can be attained in a lesser time by the use of a positive catalyst, *i.e.*, the relative concentrations of reactants and products remain the same irrespective of the presence or absence of a catalyst. Thus, a catalyst does not change the equilibrium state but it helps in attaining it rapidly.

(v) It is dynamic in nature, *i.e.*, both the reactions move with same speed. However, the reaction seems to have come to stand still because the concentrations of reactants and products do not change.

Reversible chemical reactions are classified into two types heterogeneous and homogeneous reactions.

Heterogeneous reactions: The reversible reaction in which more than one-phase is present.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$
$$2Na_2O_2(s) + 2H_2O(l) \rightleftharpoons 4NaOH(l) + O_2(g)$$
$$3Fe(s) + 4H_2O(l) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Homogeneous reactions: The reversible reaction in which only one-phase is present, *i.e.*, all the reactants and products are in the same physical state.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Homogeneous reversible reactions are further classified into three types:

First type: When there is no change in number of molecules. Examples are:

(i) $H_2 + I_2 \rightleftharpoons 2HI$

(ii) $2NO \rightleftharpoons N_2 + O_2$

(iii) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

Second type: When there is an increase in number of molecules.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Third type: When there is a decrease in number of molecules.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

9.3 THE LAW OF CHEMICAL EQUILIBRIUM (Application of Law of Mass Action)

Consider a reversible homogeneous reaction which has attained equilibrium state at a particular temperature.

$$A + B \rightleftharpoons C + D$$

Let the active masses of A, B, C and D be $[A], [B], [C]$ and $[D]$ respectively at equilibrium.

According to law of mass action,

$$\text{Rate of forward reaction} \propto [A][B]$$

or $$\text{Rate of forward reaction} = k_f\,[A][B]$$

(where, k_f is the velocity constant for forward reaction).

Similarly,

$$\text{Rate of backward reaction} \propto [C][D]$$

or $$\text{Rate of backward reaction} = k_b[C][D]$$

(where, k_b is the velocity constant for backward reaction).

At equilibrium,

Rate of forward reaction = Rate of backward reaction,

i.e., $$k_f\,[A][B] = k_b[C][D]$$

or $$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Since, k_f and k_b are both constants, the ratio k_f/k_b is also a new constant say K_c, *i.e.*,

$$K_c = \frac{[C][D]}{[A][B]} \qquad \text{... (i)}$$

K_c is known as equilibrium constant. K_c has a definite value for every chemical reaction at a given temperature regardless of the concentration of the reactants.

Considering a more general homogeneous reversible reaction at a particular temperature which is under chemical equilibrium,

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

$$\text{Rate of forward reaction} = k_f\,[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots$$

$$\text{Rate of backward reaction} = k_b[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots$$

At equilibrium,

$$k_f\,[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots = k_b[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots$$

or $$\frac{k_f}{k_b} = \frac{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots}{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots} = K_c \qquad \text{... (ii)}$$

The equilibrium constant, at a given temperature, is the ratio of the rate constants of forward and backward reactions.

Or

The equilibrium constant may be defined as the ratio between the product of the molar concentrations of the products to that of the product of the molar concentrations of the reactants with each concentration term raised to a power equal to stoichiometric coefficient in the balanced chemical equation.

The value of equilibrium constant is independent of the following factors:

1. Initial concentrations of the reactants involved.
2. The presence of a catalyst.
3. The direction from which the equilibrium has been attained.
4. The presence of inert materials.

The value of equilibrium constant depends on the following factors:

1. The mode of representation of the reaction: Conventionally, the concentrations of the products are put in the numerator and the concentrations of the reactants in denominator in the equilibrium law equation. Consider the reversible reaction,

$$A + B \rightleftharpoons C + D$$

The equilibrium constant for the reaction,

$$K_c = \frac{[C][D]}{[A][B]} \qquad \text{... (i)}$$

Now, if the products are made reactants, *i.e.*, the reaction is reversed,

$$C + D \rightleftharpoons A + B$$

The equilibrium constant for the reaction is

$$K_c' = \frac{[A][B]}{[C][D]} \qquad \text{... (ii)}$$

The equilibrium constant, K_c', is actually the reciprocal of K_c, *i.e.*,

$$K_c' = \frac{1}{K_c}$$

2. Stoichiometric representation of the chemical equation: (a) When a reversible reaction can be written with the help of two or more stoichiometric equations, the value of equilibrium constant will be numerically different in these cases. For example, the dissociation of NO_2 can be represented as:

$$2NO_2 \rightleftharpoons N_2 + 2O_2 \qquad \text{... (i)}$$

or

$$NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2 \qquad \text{... (ii)}$$

For equation (i), the value of $K_c = \dfrac{[N_2][O_2]^2}{[NO_2]^2}$ ... (iii)

For equation (ii), the value of $K_c' = \dfrac{[N_2]^{1/2}[O_2]}{[NO_2]}$ ... (iv)

Thus, the two constants are related to each other as:

$$K_c' = \sqrt{K_c} \qquad \text{... (v)}$$

In general, when a balanced equation having equilibrium constant K_c, is multiplied by a certain value n, the equilibrium constant for the new equation will be equal to $(K_c)^n$.

$$A + B \rightleftharpoons C + D, \qquad K_c = \frac{[C][D]}{[A][B]}$$

$$nA + nB \rightleftharpoons nC + nD, \qquad K_c' = \frac{[C]^n[D]^n}{[A]^n[B]^n} = (K_c)^n$$

(b) Consider the following chemical equation,

$$N_2(g) + O_2(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

$$K_c = \frac{[NOCl]^2}{[N_2][O_2][Cl_2]} \qquad \text{... (i)}$$

Suppose the above equation is split into two as:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g); \qquad K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad \text{... (ii)}$$

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g); \qquad K_2 = \frac{[NOCl]^2}{[NO]^2[Cl_2]} \qquad \text{... (iii)}$$

Combining above two equations,

$$K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NOCl]^2}{[NO]^2[Cl_2]} = \frac{[NOCl]^2}{[N_2][O_2][Cl_2]} = K_c$$

Thus, when an equation (having equilibrium constant, K_c) is written in two steps (having equilibrium constant K_1 and K_2), then $K_c = K_1 \times K_2$.

3. Use of partial pressures instead of concentrations: When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature, as the partial pressure of a substance is proportional to its concentration in the gas phase.

Consider a general reversible homogeneous gaseous reaction

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

Let the partial pressures of various reactants and products be $pA_1, pA_2, pA_3, \ldots,$ and $pB_1, pB_2, pB_3, \ldots$ respectively at equilibrium. The equilibrium constant for the reaction,

$$K_p = \frac{(pB_1)^{n_1}(pB_2)^{n_2}(pB_3)^{n_3}\ldots}{(pA_1)^{m_1}(pA_2)^{m_2}(pA_3)^{m_3}\ldots} \qquad \text{... (i)}$$

The value of K_c for the above reaction can be given as:

$$K_c = \frac{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots}{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots} \qquad \text{... (ii)}$$

For an ideal gas, $pV = nRT$

or

$$p = \frac{n}{V}RT$$

$$= \text{Active mass} \times RT$$

(where, n = number of moles and V = volume in litres. Thus, $\frac{n}{V}$ = molar concentration or active mass).

Substituting the values of partial pressures in eq. (i),

$$K_p = \frac{[B_1]^{n_1}(RT)^{n_1} \cdot [B_2]^{n_2}(RT)^{n_2} \cdot [B_3]^{n_3}(RT)^{n_3}\ldots}{[A_1]^{m_1}(RT)^{m_1} \cdot [A_2]^{m_2}(RT)^{m_2} \cdot [A_3]^{m_3}(RT)^{m_3}\ldots}$$

or

$$K_p = \frac{\{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots\}(RT)^{n_1+n_2+n_3+\ldots}}{\{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots\}(RT)^{m_1+m_2+m_3+\ldots}}$$

or

$$K_p = K_c \cdot \frac{(RT)^{\Sigma n}}{(RT)^{\Sigma m}}$$

$$= K_c (RT)^{\Sigma n - \Sigma m}$$

$$= K_c (RT)^{\Delta n} \qquad \text{... (iii)}$$

Δn = total number of molecules of gaseous products
– total number of molecules of gaseous reactants.

Three cases may arise:

First case: When, $\Delta n = 0$,

$$K_p = K_c\,(RT)^0 = K_c$$

Second case: When, $\Delta n = +\text{ve}$ or $\Delta n > 0$,

$$K_p > K_c$$

Third case: When, $\Delta n = -\text{ve}$ or $\Delta n < 0$,

$$K_p < K_c$$

4. **Temperature:** According to Arrhenius equation,

$$k = Ae^{-E/RT} \qquad \text{... (i)}$$

where, k = rate constant, E = activation energy, R = gas constant, T = absolute temperature and e = exponential constant.

$$\log \frac{k_2}{k_1} = -\frac{E}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (ii)}$$

when, $T_2 > T_1$

for forward reaction,

$$\log\left(\frac{k_{f_2}}{k_{f_1}}\right) = -\frac{E_f}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (iii)}$$

for backward reaction,

$$\log\left(\frac{k_{b_2}}{k_{b_1}}\right) = -\frac{E_b}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (iv)}$$

Subtracting eq. (iv) from eq. (iii), we get

$$\log\left(\frac{k_{f_2}/k_{b_2}}{k_{f_1}/k_{b_1}}\right) = -\frac{(E_f - E_b)}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or

$$\log\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{... (v)}$$

where, ΔH is the heat of reaction at constant volume and K_1 and K_2 are the equilibrium constants of a reaction at temperatures T_1 and T_2 $(T_2 > T_1)$.

The effect of temperature can be studied in the following three cases:

First case: $\Delta H = 0$, *i.e.*, neither heat is evolved, nor absorbed.

So, $\log K_2 - \log K_1 = 0$

or $\log K_2 = \log K_1$

or $K_2 = K_1$

Thus, equilibrium constant remains the same at all temperatures.

Second case: When, $\Delta H = +\text{ve}$, *i.e.*, heat is absorbed, the reaction is endothermic. The temperature T_2 is higher than T_1.

Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is negative.

So, $\log K_2 - \log K_1 = +\text{ve}$

or $\log K_2 > \log K_1$

or $K_2 > K_1$

The value of equilibrium constant is higher at higher temperature in the case of endothermic reactions.

Third case: When $\Delta H = -\text{ve}$, *i.e.*, heat is evolved, the reaction is exothermic. The temperature T_2 is higher than T_1.

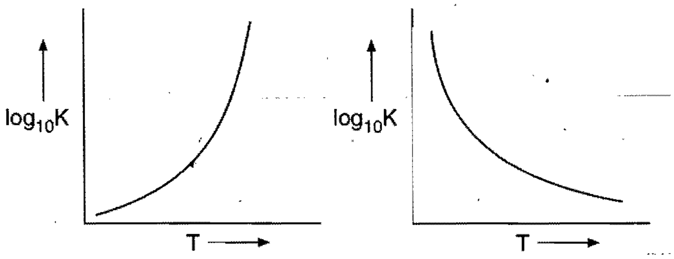
Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is negative.

So, $\log K_2 - \log K_1 = -\text{ve}$

or $\log K_1 > \log K_2$

or $K_1 > K_2$

The value of equilibrium constant is lower at higher temperature in the case of exothermic reactions.



(a) Endothermic reaction
(Plots of log K versus T)

(b) Exothermic reaction

Fig. 9.3

Units of Equilibrium Constant

The units of equilibrium constant vary in case of different reactions. 'K' has no units for a reaction in which total number of moles of reactants and products are the same. For example, for dissociation of nitric oxide, K_c has no units.

$$2NO \rightleftharpoons N_2 + O_2$$

$$K_c = \frac{[N_2][O_2]}{[NO]^2}$$

K_c will have units for a reaction in which the total number of moles of reactants and products are different. For example, for decomposition of PCl_5, the K_c has mol/litre units.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

In the formation of ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

K_c has litre^2 mol^{-2} units.

In general; unit of $K_c = [M]^{\Delta n}$

where, M = mol litre^{-1} and Δn = number of gaseous moles of product or products – number of gaseous moles of reactant or reactants.

Note: (i) The above relation can be used in homogeneous liquid system also

Δn = number of moles of product or products – number of moles of reactant or reactants

(ii) Similarly, the unit of $K_p = [\text{atm}]^{\Delta n}$

where, Δn = number of gaseous moles of product or products – number of gaseous moles of reactant or reactants.

9.4 REACTION QUOTIENT OR MASS ACTION RATIO

Let us consider a reaction:

$$A + B \rightleftharpoons C + D$$

$$Q = \frac{[C][D]}{[A][B]}$$

Q is denoted as Q_c or Q_p depending upon whether the concentration is taken in terms of moles per litre or partial pressures respectively. With the help of mass action ratio we can determine whether the reaction is at equilibrium or not.

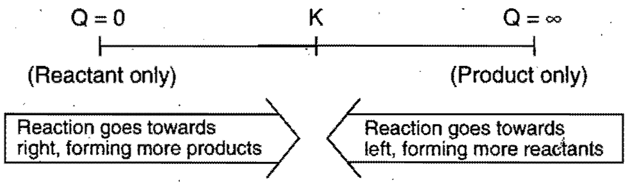
(I) When, $Q_c = K_c$ or $Q_p = K_p$ then the reversible reaction is at equilibrium, *i.e.*, the rate of forward and backward reaction becomes equal.

(II) When, $Q_c < K_c$ or $Q_p < K_p$ then the reaction is not at equilibrium. The reaction will be fast in forward direction, *i.e.*, reaction has a tendency to form product/products.

Rate of forward reaction > Rate of backward reaction.

(III) When, $Q_c > K_c$ or $Q_p > K_p$ then again the reaction is not at equilibrium. The reaction will be fast in backward direction, *i.e.*, have a tendency to form reactant/reactants.

Rate of forward reaction < Rate of backward reaction.



SOME SOLVED EXAMPLES

Example 1. *For the reactions,*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

and $$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$$

write down the expression for equilibrium constant K_c and K'_c. *How is* K_c *related to* K'_c *?*

Solution: For equation $N_2 + 3H_2 \rightleftharpoons 2NH_3$,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{... (i)}$$

and for equation, $\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$,

$$K'_c = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} \quad \text{... (ii)}$$

Squaring equation (ii),

$$(K'_c)^2 = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{... (iii)}$$

Equations (i) and (iii) are same

Thus, $$K_c = (K'_c)^2$$

or $$\sqrt{K_c} = K'_c$$

Example 2. *The equilibrium constant for the reaction,*

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

at a particular temperature is 100. *Write down the equilibrium law equations for the following reactions and determine the values of equilibrium constants:*

$$2NO_2 \rightleftharpoons N_2 + 2O_2 \quad \text{... (i)}$$

$$NO_2 \rightleftharpoons \tfrac{1}{2}N_2 + O_2 \quad \text{... (ii)}$$

Solution: The equilibrium constant for the reaction,

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

$$K_c = \frac{[NO_2]^2}{[N_2][O_2]^2} = 100 \quad \text{... (a)}$$

The equilibrium constant equation for reaction (i),

$$K_1 = \frac{[N_2][O_2]^2}{[NO_2]^2} \quad \text{... (b)}$$

This equation is reciprocal of eq. (a)

So, $$K_1 = \frac{1}{K_c} = \frac{1}{100} = 1 \times 10^{-2}$$

The equilibrium constant equation for reaction (ii),

$$K_2 = \frac{[N_2]^{1/2}[O_2]}{[NO_2]} \quad \text{... (c)}$$

Comparing eqs. (b) and (c),

$$K_2 = \sqrt{K_1} = \sqrt{10^{-2}} = 10^{-1} = 0.1$$

Example 3. *The value of* K_c *for the reaction,*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 0.50 *at* 400°C. *Find the value of* K_p *at* 400°C *when concentrations are expressed in mol litre*$^{-1}$ *and pressure in atmosphere.*

Solution: Applying the relationship,

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = 0.50, \quad R = 0.082 \text{ litre-atm deg}^{-1} \text{ mol}^{-1}$$

$$T(400 + 273) = 673\text{ K}, \quad \Delta n = (2 - 4) = -2$$

$$K_p = 0.5(0.082 \times 673)^{-2}$$

$$= 0.5(55.185)^{-2} = 1.64 \times 10^{-4}$$

Example 4. *Determine K_c for the reaction,*

$$\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g)+\frac{1}{2}Br_2(g)\rightleftharpoons NOBr(g)$$

from the following data at 298 K;

The equilibrium constants for the following reactions,

$$2NO(g)\rightleftharpoons N_2(g)+O_2(g)$$

and $$NO(g)+\frac{1}{2}Br_2(g)\rightleftharpoons NOBr(g)$$

are 2.4×10^{30} and 1.4 respectively.

Solution: The net reaction is,

$$\frac{1}{2}\mathrm{N_2}(g)+\frac{1}{2}\mathrm{O_2}(g)+\frac{1}{2}\mathrm{Br_2}(g)\rightleftharpoons \mathrm{NOBr}(g)$$

$$K_{c(\mathrm{net})}=\frac{[\mathrm{NOBr}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}[\mathrm{Br_2}]^{1/2}}$$

Considering the given equations:

$2\mathrm{NO}(g)\rightleftharpoons \mathrm{N_2}(g)+\mathrm{O_2}(g)$; equilibrium constant $=2.4\times 10^{30}$

$\mathrm{N_2}(g)+\mathrm{O_2}(g)\rightleftharpoons 2\mathrm{NO}(g)$; equilibrium constant $=\dfrac{1}{2.4\times 10^{30}}$

$$\frac{1}{2}\mathrm{N_2}(g)+\frac{1}{2}\mathrm{O_2}(g)\rightleftharpoons \mathrm{NO}(g);$$

$$\text{Equilibrium constant}=\left(\frac{1}{2.4\times 10^{30}}\right)^{1/2}$$

$$=0.6455\times 10^{-15}$$

$$\frac{[\mathrm{NO}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}}=K_c'=0.6455\times 10^{-15} \qquad \text{... (i)}$$

$$\mathrm{NO}(g)+\frac{1}{2}\mathrm{Br_2}(g)\rightleftharpoons \mathrm{NOBr}(g)$$

$$\frac{[\mathrm{NOBr}]}{[\mathrm{NO}][\mathrm{Br_2}]^{1/2}}=K_c''=1.4 \qquad \text{... (ii)}$$

Multiplying both equations

$$\frac{[\mathrm{NO}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}}\times\frac{[\mathrm{NOBr}]}{[\mathrm{NO}][\mathrm{Br_2}]^{1/2}}=K_c'\times K_c''=0.6455\times 10^{-15}\times 1.4$$

or $$\frac{[\mathrm{NOBr}]}{[\mathrm{N_2}]^{1/2}[\mathrm{O_2}]^{1/2}[\mathrm{Br_2}]^{1/2}}=K_{c(\mathrm{net})}=0.9037\times 10^{-15}$$

$$=9.037\times 10^{-16}$$

Example 5. *The equilibrium constant, K_p, for the reaction*

$N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$ is 1.6×10^{-4} atm^{-2} at 400°C.

What will be the equilibrium constant at 500°C if heat of reaction in this temperature range is -25.14 kcal?

Solution: Using the relation,

$$\log\frac{K_{p_2}}{K_{p_1}}=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_2T_1}\right]$$

Given,

$K_{p_1}=1.6\times 10^{-4}$; $\quad \Delta H=-25.14$ kcal;

$R=2\times 10^{-3}$ kcal deg^{-1} mol^{-1}

$T_1=400+273=673\ \mathrm{K}$, $\quad T_2=500+273=773\ \mathrm{K}$

$$\log\frac{K_{p_2}}{(1.6\times 10^{-4})}=\frac{-25.14}{2.303\times 2\times 10^{-3}}\left[\frac{773-673}{773\times 673}\right]$$

$$\log K_{p_2}=\log(1.6\times 10^{-4})-\frac{25.14\times 10^3\times 100}{2.303\times 2\times 773\times 673}$$

$$=-3.7960-1.049=-4.8450$$

$$K_{p_2}=1.429\times 10^{-5}\ \mathrm{atm}^{-2}$$

Example 6. *The equilibrium constant for the reaction,*

$$H_2(g)+S(s)\rightleftharpoons H_2S(g)$$

is 18.5 at 925 K and 9.25 at 1000 K respectively. Calculate the enthalpy of the reaction.

Solution: Using the relation,

$$\log\frac{K_2}{K_1}=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{9.25}{18.5}=\frac{\Delta H}{2.303\times 8.314}\times\frac{75}{925\times 1000}$$

$$-0.301=\frac{\Delta H\times 75}{2.303\times 8.314\times 925\times 1000}$$

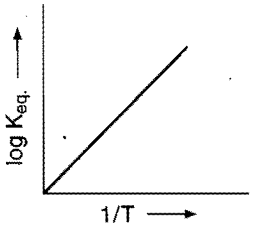
or $$\Delta H=-71080.57\ \mathrm{J\ mol^{-1}}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. For the hypothetical reactions, the equilibrium constant (K) values are given:
$A\rightleftharpoons B$; $K_1=2$; $B\rightleftharpoons C$; $K_2=4$; $C\rightleftharpoons D$; $K_3=3$
The equilibrium constant (K) for the reaction $A\rightleftharpoons D$ is: **[PMT (Kerala) 2005]**
(a) 48 (b) 6 (c) 2.7 (d) 12
(e) 24
[**Ans.** (e)]
[**Hint:** The reaction $A\rightleftharpoons D$ is obtained by adding the three given reactions.
$\therefore \quad K=K_1\times K_2\times K_3=2\times 4\times 3=24$]

2. If, in the reaction $\mathrm{N_2O_4}(g)\rightleftharpoons 2\mathrm{NO_2}(g)$, x is that part of $\mathrm{N_2O_4}$ which dissociates, then the number of molecules at equilibrium will be: **(KCET 2005)**
(a) 1 (b) 3
(c) $(1+x)$ (d) $(1+x)^2$
[**Ans.** (c)]
[**Hint:**
$$\begin{array}{lccc} & \mathrm{N_2O_4} & \rightleftharpoons & 2\mathrm{NO_2} \\ t=0 & 1 & & 0 \\ t_{\mathrm{eq.}} & 1-x & & 2x \end{array}$$
Total number of molecules at equilibrium $=1-x+2x=(1+x)$]

3. A schematic plot of ln $K_{eq.}$ *vs* inverse of temperature for a reaction is shown in the figure. The reaction must be: (AIEEE 2005)



(a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature

[**Ans.** (a)]

[**Hint:** $K_e = Ae^{-\Delta H°/RT}$

$$\log K_{eq.} = \log A - \frac{\Delta H°}{2.303\,RT}$$

$$Y = C + MX$$

Slope of the line will be positive, when, $\Delta H° = -$ve, *i.e.*, the reaction is exothermic.]

4. Given:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ K_1$$
$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g);\ K_2$$
$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g);\ K_3$$

The equilibrium constant for

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

will be: [CBSE (Med.) 2007]

(a) $K_1K_2K_3$ (b) $\frac{K_1K_2}{K_3}$ (c) $\frac{K_1K_3^{\,2}}{K_2}$ (d) $\frac{K_2K_3^{\,3}}{K_1}$

[**Ans.** (d)]

[**Hint:** $K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$; $K_2 = \frac{[NO]^2}{[N_2][O_2]}$; $K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$

The equilibrium constant for

$$2NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g)$$

will be:

$$\frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}} = \frac{K_2 \times K_3^{\,3}}{K_1}]$$

5. What is the equation for the equilibrium constant (K_c) for the following reaction? (EAMCET 2006)

$$\frac{1}{2}A(g) + \frac{1}{3}B(g) \overset{T\,K}{\rightleftharpoons} \frac{2}{3}C(g)$$

(a) $K_c = \frac{[A]^{1/2}[B]^{1/3}}{[C]^{3/2}}$ (b) $K_c = \frac{[C]^{3/2}}{[A]^2[B]^3}$

(c) $K_c = \frac{[C]^{2/3}}{[A]^{1/2}[B]^{1/3}}$ (d) $K_c = \frac{[C]^{2/3}}{[A]^{1/2} + [B]^{1/3}}$

[**Ans.** (c)]

[**Hint:** Coefficient goes to the power of respective active mass.

$$\therefore \quad K_c = \frac{[C]^{2/3}}{[A]^{1/2}[B]^{1/3}}]$$

6. For the following three reactions (i), (ii) and (iii), equilibrium constants are given:

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g);\ K_1$
(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g);\ K_2$
(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g);\ K_3$

Which of the following relations is correct? (AIEEE 2008)

(a) $K_3K_2^3 = K_1^2$ (b) $K_1\sqrt{K_2} = K_3$
(c) $K_2K_3 = K_1$ (d) $K_3 = K_1K_2$

[**Ans.** (d)]

[**Hint :** Reaction (iii) is obtained by adding (i) and (ii) hence $K_3 = K_1 \times K_2$]

9.5 ACTIVATION ENERGIES FOR FORWARD AND BACKWARD REACTIONS

In a reversible reaction, the molecules of the reactants in the forward reaction and the molecules of the products in the backward reaction follow the same path and form the same activated complex. However, the activation energies of both forward and backward reactions are different. Fig. 9.4 (a) and (b) show the activation energies, $E_a(f)$ and $E_a(b)$ respectively, for the forward and backward reactions for exothermic and endothermic reactions. Mathematically, $E_a(f)$ and $E_a(b)$ are related to overall energy change, ΔE, in the process as:

$$\Delta E = E_a(f) - E_a(b) = \Delta H \qquad \text{(At constant volume)}$$

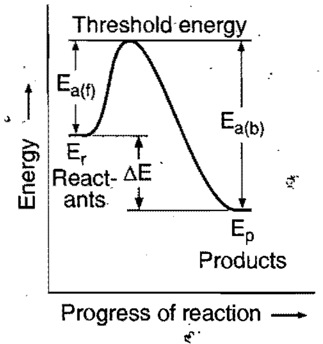


Fig. 9.4 (a) Activation energies for the forward and backward reactions where forward reaction is exothermic

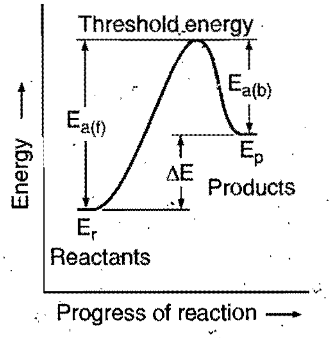


Fig. 9.4 (b) Activation energies for the forward and backward reactions where forward reaction is endothermic

For exothermic reaction,

$$E_a(f) < E_a(b)$$

Thus, ΔE is negative.

On the other hand, for the endothermic reaction,

$$E_a(f) > E_a(b).$$

Thus, ΔE is positive

Heat of reaction ΔH = Activation energy of forward reaction −Activation energy of backward reaction.

Example 7. *For the dissociation of gaseous HI, the energy of activation is 44.3 kcal. Calculate the energy of activation for the reverse reaction. Given, ΔH for the formation of 1 mole of HI from H_2 and I_2 is -1.35 kcal.*

Solution:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g); \quad E_a = 44.3\ \text{kcal}$$

$$\frac{1}{2}H_2(g)+\frac{1}{2}I_2(g) \rightleftharpoons HI(g); \qquad \Delta H=-1.35\,\text{kcal}$$

$$2HI(g) \rightleftharpoons H_2(g)+I_2(g);\ \Delta H=2\times1.35=2.70\,\text{kcal}$$

$$\Delta H=E_a(f)-E_a(b)$$

$$2.70=44.3-E_a(b)$$

$$E_a(b)=(44.3-2.70)$$

or $$=41.60\,\text{kcal}$$

Example 8. *For a reaction $X \rightarrow Y$, heat of reaction is $+83.68$ kJ, energy of reactant X is 167.36 kJ and energy of activation is 209.20 kJ. Calculate (i) threshold energy (ii) energy of product Y and (iii) energy of activation for the reverse reaction ($Y \rightarrow X$).*

Solution: (i) Given, $E_a(f)=209.20$ kJ

$$\Delta E=+83.68\,\text{kJ}$$

Energy of reactant, $X=167.36$ kJ

Threshold energy = Energy of reactant X + Activation energy for forward reaction

$$=167.36+209.20=376.56\,\text{kJ}$$

(ii) Energy of reaction, ΔE = Energy of product − Energy of reactant

Energy of product $=83.68+167.36=251.04$ kJ

(iii) Activation energy for backward reaction

= Threshold energy − Energy of product

$=376.56-251.04=125.52$ kJ

9.6 STANDARD FREE ENERGY CHANGE OF A REACTION AND ITS EQUILIBRIUM CONSTANT

Let $\Delta G°$ be the difference in free energy of the reaction when all the reactants and products are in the standard state (1 atmospheric pressure and 298 K) and K_c or K_p be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by the following relation:

$$\Delta G°=-2.303\,RT\log K_c$$

and $$\Delta G°=-2.303\,RT\log K_p \quad \text{(in case of ideal gases)}$$

This equation represents one of the most important results of thermodynamics and relates to the equilibrium constant of a reaction to a thermochemical property. It is sometimes easier to calculate the free energy in a reaction rather than to measure the equilibrium constant.

Standard free energy change can be thermodynamically calculated as:

$$\Delta G°=\Delta H°-T\Delta S°$$

Here, $\Delta H°$ = standard enthalpy change,

$\Delta S°$ = standard entropy change.

$$-RT\log_e K_p=\Delta H°-T\Delta S°$$

$$\log_e K_p=\frac{\Delta S°}{R}-\frac{\Delta H°}{RT}$$

$$\log_{10} K_p=\frac{\Delta S°}{2.303R}-\frac{\Delta H°}{2.303RT}$$

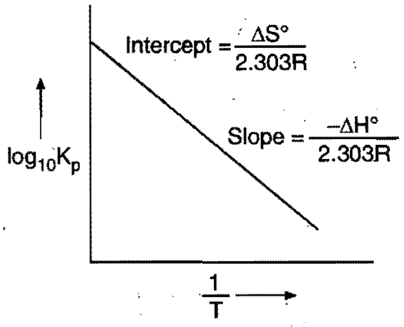


Fig. 9.5

(i) When, $\Delta G°=0$, then $K_c=1$.

(ii) When, $\Delta G°>0$, *i.e.*,+ve, then $K_c<1$. In this case reverse reaction is feasible, *i.e.*, less concentration of products at equilibrium state.

(iii) When, $\Delta G°<0$, *i.e.*, −ve, then $K_c>1$. In this case forward reaction is feasible showing thereby a large concentrations of products till the equilibrium is reached.

Example 9. *For the reaction,*

$$2NOCl(g) \rightleftharpoons 2NO(g)+Cl_2(g),$$

calculate the standard equilibrium constant at 298 K. Given that the values of $\Delta H°$ and $\Delta S°$ of the reaction at 298 K are 77.2 kJ mol^{-1} and 122 JK^{-1} mol^{-1}.

Solution: Using the relation,

$$\Delta G°=\Delta H°-T\Delta S°$$

$$=77200-298\times122$$

$$=40844\ \text{J mol}^{-1}$$

Let the equilibrium constant be $K_c°$. We know that,

$$\Delta G°=-2.303RT\log K_c°$$

or $$\log K_c°=-\frac{\Delta G°}{2.303\times8.314\times298}=-\frac{40844}{2.303\times8.314\times298}$$

$$=-7.158$$

$$K_c°=6.95\times10^{-8}$$

Example 10. *$\Delta G°$ for $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ is -16.5 kJ mol^{-1}. Find out K_p for the reaction at 25°C. Also report K_p and $\Delta G°$ for $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ at 25°C.*

Solution:

$$\log K_p=-\frac{\Delta G°}{2.303RT}=-\frac{(-16.5\times10^3)}{2.303\times8.314\times298}=2.8917$$

$$K_p=779.41$$

K_p for reaction $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ is equal to $(779.41)^2=6.07\times10^5$

$$\Delta G°=-2.303\times8.314\times298\log 6.07\times10^5\ \text{joule}$$

$$=-32.998\ \text{kJ mol}^{-1}$$

9.7 EQUILIBRIUM CONSTANT EXPRESSIONS FOR SOME REACTIONS

Case I: Homogeneous gaseous equilibria when, $\Delta n = 0$.

Synthesis of hydrogen iodide: The formation of hydrogen iodide from hydrogen and iodine is represented by the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Let a start be made with 'a' moles of hydrogen and 'b' moles of I_2. These are heated in a sealed bulb having a volume V litre by keeping the bulb in a thermostat till equilibrium is established. If at equilibrium, x moles of each of H_2 and I_2 have reacted, $2x$ moles of HI will be formed.

Thus, the active masses of various reactants and products present at equilibrium are:

$$[H_2] = \frac{(a-x)}{V} \text{ mol L}^{-1}$$

$$[I_2] = \frac{(b-x)}{V} \text{ mol L}^{-1}$$

$$[HI] = \frac{2x}{V} \text{ mol L}^{-1}$$

Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

When, $a = b = 1$, x becomes degree of formation of HI and

$$K_c = \frac{4x^2}{(1-x)^2}$$

The equilibrium constant, K_p, can also be calculated considering partial pressures of reactants and products at equilibrium.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial no. of moles	a	b	0
No. of moles at equilibrium	$(a-x)$	$(b-x)$	$2x$

Total number of moles at equilibrium

$$= (a-x) + (b-x) + 2x = (a+b)$$

Let the total pressure of the system at equilibrium be P atmosphere.

Partial pressure of H_2, $p_{H_2} = \frac{(a-x)}{(a+b)} \cdot P$

Partial pressure of I_2, $p_{I_2} = \frac{(b-x)}{(a+b)} \cdot P$

Partial pressure of HI, $p_{HI} = \frac{2x}{(a+b)} \cdot P$

$$K_p = \frac{(p_{HI})^2}{(p_{H_2})(p_{I_2})} = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)P \times \left(\frac{b-x}{a+b}\right)P} = \frac{4x^2}{(a-x)(b-x)}$$

Thus, $K_p = K_c$

This also follows from the relationship, $K_p = K_c(RT)^{\Delta n}$.

$$\Delta n = 0, \text{ So } K_p = K_c,$$

i.e., for all gaseous reactions of first type, K_p and K_c are identical. Both K_p and K_c have no units.

(a) Effect of pressure: The equation, $K_c = \frac{4x^2}{(a-x)(b-x)}$, does not include the volume term; hence K_c is independent of pressure. **Thus, change of pressure will not alter the final state of equilibrium.**

(b) Effect of adding substances (Reactants or products): On adding H_2 to the equilibrium mixture, the value of denominator of equation $K_c = 4x^2/[(a-x)(b-x)]$ will increase. To maintain the constant value of K_c, the value of numerator must also increase. This can happen if more of HI is formed, *i.e.*, hydrogen combines with iodine to form more of HI. Thus, the reaction moves in a direction in which the added hydrogen is used up. A similar effect is observed when iodine is added to the equilibrium mixture.

The reverse effect is observed when HI is added to the equilibrium mixture, *i.e.*, HI decomposes into H_2 and I_2.

(c) Effect of temperature: The formation of HI from H_2 and I_2 is an exothermic reaction, *i.e.*, by increasing temperature, the value of equilibrium constant, K_c, decreases. Thus, the yield of HI decreases, *i.e.*, high temperature is not favourable for greater yield of HI.

(d) Effect of adding an inert gas: Addition of an inert gas to equilibrium mixture will make no effect on equilibrium state as in the first type of reactions, volume and pressure changes have no effect on equilibrium state.

Case II: Homogeneous gaseous reaction when, $\Delta n > 0$.

Dissociation of PCl_5: The dissociation of PCl_5 takes place according to the equation:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Let a moles of PCl_5 be taken in a closed vessel of volume V litre. It is heated and by the time equilibrium is established, x moles are dissociated into PCl_3 and Cl_2. One molecule of PCl_5 on dissociation gives one molecule of PCl_3 and one molecule of Cl_2. Thus, x moles of PCl_5 will give x moles of PCl_3 and x moles of Cl_2.

At equilibrium,

$$[PCl_5] = \frac{(a-x)}{V}, [PCl_3] = \frac{x}{V}, [Cl_2] = \frac{x}{V}$$

Applying law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(a-x)}{V}} = \frac{x^2}{(a-x)V}$$

When, $a = 1$, x becomes degree of dissociation and

$$K_c = \frac{x^2}{(1-x)V} \qquad (\text{units} = \text{mol L}^{-1})$$

Calculation of K_p: Let the total pressure at equilibrium be P. Total number of moles at equilibrium

$$= (a-x)+x+x=(a+x)$$

$$p_{PCl_5} = \left(\frac{a-x}{a+x}\right)\cdot P;\quad p_{PCl_3} = \frac{x}{(a+x)}\cdot P;\quad p_{Cl_2} = \frac{x}{(a+x)}\cdot P$$

$$K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{\dfrac{x}{(a+x)}\cdot P\times\dfrac{x}{(a+x)}\cdot P}{\left(\dfrac{a-x}{a+x}\right)\cdot P} = \frac{x^2P}{(a-x)(a+x)};$$

(units = atm)

(a) Effect of pressure: In this case, $K_c = x^2/(a-x)V$. If pressure is increased, the value of 'V' decreases, *i.e.*, the value of denominator decreases. To maintain constant value of K_c, x must also decrease. In other words, the dissociation of PCl_5 decreases. Thus, the increase of pressure would suppress the dissociation of PCl_5.

(b) Effect of concentration: If PCl_5 is added to the equilibrium mixture, the rate of forward reaction increases, *i.e.*, dissociation of PCl_5 increases. In case PCl_3 or Cl_2 is added, the rate of backward reaction increases. This shall decrease the dissociation of PCl_5.

(c) Effect of temperature: The dissociation of PCl_5 is an endothermic reaction. Thus, the value of equilibrium constant increases with increase of temperature. It is thus concluded that dissociation increases with the increase of temperature.

(d) Effect of adding an inert gas: When an inert gas is added at constant volume the equilibrium state is not disturbed. In case an inert gas is added at constant pressure, the volume increases. To maintain the constant value of K_c, x must also increase. Thus, the addition of an inert gas at constant pressure increases the degree of dissociation of PCl_5.

Case III: Homogeneous gaseous reaction when, $\Delta n < 0$.

Synthesis of ammonia: The formation of ammonia from nitrogen and hydrogen is represented by the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Let a start be made by mixing 'a' moles of N_2 and 'b' moles of hydrogen in a closed vessel of V litre capacity. By the time equilibrium is established 'x' moles of nitrogen have combined with $3x$ moles of hydrogen and produced $2x$ moles of ammonia.

At equilibrium, $$[N_2] = \frac{(a-x)}{V}$$

$$[H_2] = \frac{(b-3x)}{V}$$

$$[NH_3] = \frac{2x}{V}$$

Applying law of mass action,

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

If $a = 1$ and $b = 3$, then,

$$K_c = \frac{4x^2V^2}{27(1-x)^4};\qquad (\text{units} = \text{mol}^{-2}\ \text{L}^2)$$

The effect of various factors at equilibrium is discussed here.

(a) Effect of pressure: By increasing pressure, the volume term decreases. The value of x must increase to maintain the constant value of K_c. In other words, the formation of ammonia increases with increase of pressure.

(b) Effect of concentration: By increasing the concentration of either nitrogen or hydrogen in the reaction mixture, the rate of forward reaction increases, *i.e.*, the formation of ammonia increases.

(c) Effect of temperature: The synthesis of ammonia is an exothermic reaction. The value of equilibrium constant decreases with increase of temperature. Thus, high temperature is not favourable for the synthesis of ammonia.

Calculation of K_p: Let the total pressure at equilibrium be P.

Total number of moles at equilibrium

$$= (a-x)+(b-3x)+2x = (a+b-2x)$$

$$p_{NH_3} = \frac{2x}{(a+b-2x)}\times P;\qquad p_{N_2} = \frac{(a-x)}{(a+b-2x)}\times P;$$

$$p_{H_2} = \frac{(b-3x)}{(a+b-2x)}\times P$$

$$K_p = \frac{[p_{NH_3}]^2}{[p_{N_2}][p_{H_2}]^3} = \frac{\left[\dfrac{2x}{(a+b-2x)}P\right]^2}{\left[\dfrac{(a-x)}{(a+b-2x)}P\right]\left[\dfrac{(b-3x)}{(a+b-2x)}P\right]^3}$$

$$= \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3P^2}\qquad (\text{units} = \text{atm}^{-2})$$

Case IV: Homogeneous liquid system: Formation of ethyl acetate:

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Let a start be made by mixing 'a' moles of an acid and 'b' moles of an alcohol. By the time equilibrium is established, x moles of ester and 'x' moles of water are formed, *i.e.*, x moles of acid and x moles of alcohol have been consumed. Let V be the total volume. At equilibrium, the active masses of reactants and products are:

$$[CH_3COOH] = \frac{(a-x)}{V},\ [C_2H_5OH] = \frac{(b-x)}{V},$$

$$[CH_3COOC_2H_5] = \frac{x}{V} \text{ and } [H_2O] = \frac{x}{V}$$

Applying law of mass action,

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{\dfrac{x}{V}\times\dfrac{x}{V}}{\left(\dfrac{a-x}{V}\right)\times\left(\dfrac{b-x}{V}\right)}$$

$$= \frac{x^2}{(a-x)(b-x)}$$

If $a = b = 1$, then $K_c = \dfrac{x^2}{(1-x)^2}$, ($K_c$ has no units)

This does not involve the volume term. Thus, K_c is not affected by the change of volume.

Case V: Heterogeneous equilibria:

Law of mass action can also be applied to the study of equilibria in which the substances are not in the same phase. Considering the decomposition of solid $NaHCO_3$ to produce solid Na_2CO_3, gaseous CO_2 and H_2O.

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Applying the law of mass action,

$$K'_c = \frac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]^2}$$

It involves two pure solids, Na_2CO_3 and $NaHCO_3$. It is customary not to include the concentrations of pure solids in equilibrium expressions.

$$\therefore \quad \frac{K'_c[NaHCO_3]^2}{[Na_2CO_3]} = [CO_2][H_2O]$$

or $$K_c = [CO_2][H_2O]$$

In terms of partial pressures we have $K_p = p_{CO_2} \times p_{H_2O}$. Similarly, in reactions in which a reactant or product occurs as a pure liquid phase, the concentration of that substance in the pure liquid is also constant. **As a result, the concentrations of pure solid and pure liquid phases do not appear in the equilibrium constant expression.**

Many other examples of heterogeneous equilibria are available. Such as:

1. Decomposition of $CaCO_3$,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c = [CO_2] \quad \text{or} \quad K_p = p_{CO_2}$$

When $CaCO_3$ is heated in a closed vessel at a definite temperature, the pressure or concentration of CO_2 produced becomes constant irrespective of the amount of $CaCO_3$ taken.

2. Reaction of steam on heated iron,

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

$$K_c = \frac{[H_2]^4}{[H_2O]^4} \text{ or } K'_p = \frac{p_{H_2}}{p_{H_2O}} = \sqrt[4]{K_p}$$

3. Reaction of steam on heated carbon,

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

$$K_c = \frac{[CO][H_2]}{[H_2O]} \quad \text{or} \quad K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}}$$

4. Dissociation of ammonium carbamate,

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

$$K_c = [NH_3]^2[CO_2]; \quad K_p = [p_{NH_3}]^2 \times [p_{CO_2}]$$

SOME SOLVED EXAMPLES

Example 11. *For the following reaction,*

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g),$$

If initially 25 mL of H_2 and 20 mL of I_2 are present in a container and at equilibrium 30 mL of HI is formed then calculate equilibrium constant. **[AIPMT (Mains) 2009]**

Solution: The given reaction is :

$$\begin{array}{lccc} & H_2(g) & +\ I_2(g) \rightleftharpoons & 2HI(g), \\ t_0 & 25\text{ mL} & 20\text{ mL} & 0 \\ t_{eq.} & 25-x & 20-x & 2x \end{array}$$

Give, $2x = 30\text{ mL} \quad \therefore \quad x = 15\text{ mL}$

Equilibrium constant may be calculated as,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{[30]^2}{[10][5]} = \frac{900}{15} = 60$$

Example 12. *In the reaction,*

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

the amounts of H_2, I_2 and HI are 0.2 g, 9.2525 g and 44.8 g respectively at equilibrium at a certain temperature. Calculate the equilibrium constant of the reaction.

Solution: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$,

Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Let the total volume be V litre, then

$$[H_2] = \frac{0.2}{2V} = \frac{0.1}{V}; [I_2] = \frac{9.2525}{254V} = \frac{0.0364}{V}$$

$$[HI] = \frac{44.8}{128V} = \frac{0.35}{V} \text{ mol L}^{-1} \text{ respectively}$$

So, $$K_c = \frac{\left(\frac{0.35}{V}\right)^2}{\frac{0.1}{V} \times \frac{0.0364}{V}} = \frac{0.35 \times 0.35}{0.1 \times 0.0364} = 33.65$$

Example 13. 0.5 *mole of hydrogen and* 0.5 *mole of iodine react in a* 10 *litre evacuated vessel at* 448°C; *hydrogen iodide is formed. The equilibrium constant, K_c for the reaction is* 50.

(*a*) *Calculate the number of moles of iodine which remain unreacted at equilibrium.*

(*b*) *What is the value of K_p?*

Solution: (a)

$$\begin{array}{lccc} & H_2(g) & +\ I_2(g) \rightleftharpoons & 2HI(g) \\ \text{Initial moles} & 0.5 & 0.5 & 0 \\ \text{No. of moles at equilibrium} & (0.5-x) & (0.5-x) & 2x \end{array}$$

$$K_c = \frac{4x^2}{(0.5-x)(0.5-x)} = 50$$

$$\frac{2x}{(0.5-x)} = \sqrt{50} = 7.07$$

$$2x = 0.5 \times 7.07 - 7.07x$$

or $$2x + 7.07x = 0.5 \times 7.07$$

$$x = \frac{0.5 \times 7.07}{9.07} = 0.39 \text{ mole}$$

(b) No. of moles of I_2 at equilibrium $= (0.5 - 0.39) = 0.11$ mole

$$K_p = K_c(RT)^{\Delta n}$$

As $\Delta n = 0$, $\quad K_p = K_c = 50$

Example 14. *25 mL of H_2 and 18 mL of I_2 vapours were heated in a sealed glass tube at 465°C and at equilibrium 30.8 mL of HI was formed. Calculate the percentage degree of dissociation of HI at 465°C.*

Solution: Since, the number of moles in a gas under the same conditions of temperature and pressure are proportional to volumes (Avogadro's Law), the volumes in mL of gases may be used instead of concentrations in the case of reversible reactions in which there is no change in the number of molecules of reactants and products.

Given, $\quad 2x = 30.8$ mL

So, $\quad x = 15.4$ mL

Vol. of H_2 at equilibrium $= (25 - 15.4) = 9.6$ mL

Vol. of I_2 at equilibrium $= (18 - 15.4) = 2.6$ mL

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(30.8)^2}{9.6 \times 2.6} = 38.0$$

Consider the equation,

$$2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$$

Let the degree of dissociation be x

$$K_c' = \frac{x^2}{4(1-x)^2} \qquad \left(K_c' = \frac{1}{K_c} = \frac{1}{38}\right)$$

$$\frac{1}{38} = \frac{x^2}{4(1-x)^2} \quad \text{or} \quad \frac{1}{6.1644} = \frac{x}{2(1-x)}$$

or $\quad x = 0.245$, *i.e.*, 24.5% dissociated

Example 15. *3.2 mole of HI were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation was found to be 20%. Calculate the number of moles of hydrogen iodide, hydrogen and iodine present at the equilibrium point and determine the equilibrium constant.*

Solution: The dissociation of HI is represented by the equation,

$$\begin{array}{ccc} 2\text{HI}(g) \rightleftharpoons & \text{H}_2(g) & +\text{I}_2(g) \\ (1-x) & x/2 & x/2 \end{array}$$

Degree of dissociation, $x = 0.20$ and initial concentration of HI, $a = 3.2$ mole.

At equilibrium,

No. of moles of HI $= a(1-x) = 3.2 \times 0.8 = 2.56$

No. of moles of $H_2 = \dfrac{a \cdot x}{2} = 3.2 \times 0.1 = 0.32$

No. of moles of $I_2 = \dfrac{a \cdot x}{2} = 3.2 \times 0.1 = 0.32$

$$K_c = \frac{x^2}{4(1-x)^2} = \frac{0.2 \times 0.2}{4 \times 0.8 \times 0.8} = 0.0156$$

Also, $$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{0.32 \times 0.32}{2.56 \times 2.56} = 0.0156$$

Example 16. *The equilibrium constant of the reaction,*

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K?

Solution: $\quad A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

	$A_2(g)$	$B_2(g)$	$2AB(g)$
Initial no. of moles	1	2	0
No. of moles at equilibrium	$(1-x)$	$(2-x)$	$2x$
(Total volume = 3 litre)			
Active masses	$\frac{(1-x)}{3}$	$\frac{(2-x)}{3}$	$\frac{2x}{3}$

Applying law of mass action,

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)} = \frac{4x^2}{(1-x)(2-x)}$$

But, $$\frac{4x^2}{(1-x)(2-x)} = 50$$

or $\quad 4x^2 = (2 - 3x + x^2)50$

or $\quad 2x^2 = (2 - 3x + x^2)25$

or $\quad 23x^2 - 75x + 50 = 0$

$$x = \frac{75 \pm \sqrt{(75)^2 - 4 \times 23 \times 50}}{2 \times 23}$$

$x = 2.317$ or 0.934

The value of x cannot be more than 1, *i.e.*, greater than the number of moles of A_2 and hence $x = 0.943$.

No. of moles of $AB = 2x = (2 \times 0.934)$

$= 1.868$

Example 17. *The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.*

Solution: $\quad \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

Mol. mass of $\text{N}_2\text{O}_4 = (28 + 64) = 92$

Vapour density, $D = \dfrac{92}{2} = 46$

Let the degree of dissociation be x

Given, $d = 30$

Applying the relationship,

$$x = \frac{D - d}{d} = \frac{(46 - 30)}{30} = \frac{16}{30} = 0.533$$

Degree of dissociation = 53.3%

Example 18. *3 g mole of phosphorus pentachloride is heated in a flask of 4 litre volume. At equilibrium it dissociates to give 40% of phosphorus trichloride and chlorine. Calculate the equilibrium constant.*

Solution: Degree of dissociation = 0.4

$$\begin{array}{llll} PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) & \\ a(1-x) & ax & ax & \text{(at equilibrium)} \end{array}$$

Given, $a = 3, x = 0.4$ and $V = 4$.

So, at equilibrium,

$$[PCl_5] = \frac{3(1-0.4)}{4} = \frac{3\times 0.6}{4}\ \text{mol L}^{-1}$$

$$[PCl_3] = \frac{3\times 0.4}{4}\ \text{mol L}^{-1}$$

$$[Cl_2] = \frac{3\times 0.4}{4}\ \text{mol L}^{-1}$$

Applying law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{3\times 0.4\times 3\times 0.4}{4\times 3\times 0.6} = 0.2\ \text{mol L}^{-1}$$

Example 19. *N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C.*

Solution: (i)

$$\begin{array}{lcc} & N_2O_4(g) \rightleftharpoons & 2NO_2(g) \\ \text{Initial} & 1 & 0 \\ \text{At equilibrium} & (1-x) & 2x \end{array}$$

$$\text{Total moles} = (1-x) + 2x = (1+x)$$

$$p_{N_2O_4} = \left(\frac{1-x}{1+x}\right)P, \quad p_{NO_2} = \frac{2x}{(1+x)}\cdot P$$

Given, $x = 0.25$ and $P = 1$ atm

$$p_{N_2O_4} = \left(\frac{1-0.25}{1+0.25}\right)\times 1 = 0.6\ \text{atm}$$

$$p_{NO_2} = \left(\frac{2\times 0.25}{1+0.25}\right)\times 1 = 0.4\ \text{atm}$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{0.4\times 0.4}{0.6} = 0.267\ \text{atm}$$

(ii) Let the degree of dissociation of N_2O_4 at 0.1 atm be 'α', then,

$$p_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right)\times 0.1 \text{ and } p_{NO_2} = \frac{2\alpha}{(1+\alpha)}\times 0.1$$

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2\times (0.1)^2}{\left(\frac{1-\alpha}{1+\alpha}\right)\times 0.1} = \frac{4\alpha^2\times 0.1}{(1-\alpha)(1+\alpha)} = \frac{0.4\alpha^2}{(1-\alpha^2)}$$

or $$0.267 = \frac{0.4\alpha^2}{(1-\alpha^2)} \text{ or } 0.267 = 0.667\alpha^2$$

$$\alpha = 0.632$$

Hence, dissociation of $N_2O_4 = 63.2\%$

Example 20. *1.0 mole of nitrogen and 3.0 moles of PCl_5 are placed in 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction,*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Solution:

$$\begin{array}{lccc} & PCl_5(g) \rightleftharpoons & PCl_3(g) + & Cl_2(g) \\ \text{Initial} & 3 & 0 & 0 \\ \text{At equilibrium} & 3(1-x) & 3x & 3x \end{array}$$

(x = degree of dissociation)

$$\text{Total moles} = 3(1-x) + 3x + 3x = 3(1+x)$$

1 mole of nitrogen is present, hence actual total number of moles at equilibrium $= 3(1+x) + 1$

According to gas equation,

$$PV = nRT$$

Given, $P = 2.05$ atm, $V = 100$ litres, $R = 0.082$

and $T = (273 + 227) = 500\ \text{K}$

So, $$n = \frac{2.05\times 100}{0.082\times 500} = 5$$

or $$3(1+x) + 1 = 5$$

$$3x = 1 \text{ or } x = 0.333$$

Thus, $3(1+x) + 1 = 3 + 3\times 0.333 + 1 = 4 + 0.999$

At equilibrium, $$p_{PCl_5} = \frac{3(1-x)}{(3x+4)}\times 2.05$$

$$p_{PCl_3} = p_{Cl_2} = \frac{3x}{(3x+4)}\times 2.05$$

$$K_p = \frac{\frac{3x}{(3x+4)}\times 2.05\times \frac{3x}{(3x+4)}\times 2.05}{\frac{3(1-x)}{(3x+4)}\times 2.05}$$

$$= \frac{9x^2\times 2.05}{3(3x+4)(1-x)} = \frac{3\times (0.333)^2\times 2.05}{(4+0.999)(0.667)}$$

$$= 0.204\ \text{atm}$$

Example 21. *For a gas reaction, $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere, respectively. The total pressure of the entire system is 2.8 atmosphere. What will be the value of K_p if all the concentrations are given in atmospheres?*

Solution:

$$\begin{array}{lccc} & N_2(g) + & 3H_2(g) \rightleftharpoons & 2NH_3(g) \\ \text{Partial pressures at equilibrium} & 0.8 & 0.4 & [2.8 - (0.8 + 0.4) = 1.6] \end{array}$$

Applying law of mass action,

$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3} = \frac{1.6\times 1.6}{0.8\times 0.4\times 0.4\times 0.4}$$

$$= 50\ \text{atm}^{-2}$$

Example 22. *One mole of nitrogen and three moles of hydrogen are mixed in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction:*

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

calculate the equilibrium constant (K_c) in concentration units. What will be the value of K for the following equilibrium?

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

Solution:

	$N_2(g)$	+ $3H_2(g)$	$\rightleftharpoons$ $2NH_3(g)$
At equilibrium	$(1-x)$	$(3-3x)$	$2x (x=0.0025)$
Active masses	$\frac{(1-0.0025)}{4}$	$\frac{(3-0.0075)}{4}$	$\frac{(0.0050)}{4}$

Applying law of mass action,

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}=\frac{\left(\frac{0.0050}{4}\right)^2}{\left(\frac{0.9975}{4}\right)\left(\frac{2.9925}{4}\right)^3}$$

$$=1.49\times10^{-5}\ \text{litre}^2\ \text{mol}^{-2}$$

K for the reaction,

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

is equal to $\sqrt{K_c}$.

$$K=\sqrt{K_c}=\sqrt{1.49\times10^{-5}}$$

$$=3.86\times10^{-3}\ \text{litre mol}^{-1}$$

Example 23. *In an experiment one mole of acetic acid and one mole of alcohol were allowed to react until equilibrium was established. The equilibrium mixture was found to contain 2/3 mole of ester. Calculate the equilibrium constant of the reaction.*

Solution:

$$CH_3COOH(l)+C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l)+H_2O(l)$$

	$CH_3COOH(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$H_2O(l)$
Initial no. of moles	1	1	0	0
No. of moles at equilibrium	$\left(1-\frac{2}{3}\right)$	$\left(1-\frac{2}{3}\right)$	$\frac{2}{3}$	$\frac{2}{3}$
Active masses	$\frac{1}{3V}$	$\frac{1}{3V}$	$\frac{2}{3V}$	$\frac{2}{3V}$

V is the total volume in litres.

Applying law of mass action,

$$K_c=\frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]}$$

$$=\frac{\frac{2}{3V}\times\frac{2}{3V}}{\frac{1}{3V}\times\frac{1}{3V}}=4$$

Example 24. *Ammonium hydrogen sulphide dissociates according to the equation:*

$$NH_4HS(s) \rightleftharpoons NH_3(g)+H_2S(g)$$

If the observed pressure at equilibrium is 1.12 atm at 380 K, what is the equilibrium constant K_p of the reaction?

Solution: $NH_4HS(s) \rightleftharpoons NH_3(g)+H_2S(g)$

$$p_{NH_3}=p_{H_2S}=\frac{1}{2}\times1.12=0.56\ \text{atm}$$

$$K_p=p_{NH_3}\times p_{H_2S}=0.56\times0.56=0.3136$$

Example 25. *A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K_p if total pressure at equilibrium is 0.8 atm.*

(IIT 1993)

Solution:

	$CO_2(g)$ + $C(s)$	$\rightleftharpoons$ $2CO(g)$
Initial	0.5 atm	0 atm
At equilibrium	$(0.5-x)$ atm	$2x$ atm

At equilibrium, the total pressure is 0.8 atm.

$$p_{\text{total}}=p_{CO_2}+p_{CO}$$

$$0.8=(0.5-x)+2x=0.5+x$$

or $x=0.3$ atm

Applying law of mass action,

$$K_p=\frac{(p_{CO})^2}{p_{CO_2}}=\frac{(2\times0.3)^2}{0.2}=\frac{0.36}{0.2}=1.8\ \text{atm}$$

Example 26. *A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.654 litre and heated to 1000 K until equilibrium is reached. The equilibrium constant for the reaction,*

$$CaCO_3(s) \rightleftharpoons CaO(s)+CO_2(g),$$

is 3.9×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

Solution: $CaCO_3(s) \rightleftharpoons CaO(s)+CO_2(g)$

$$K_p=p_{CO_2}$$

Let the number of moles of CO_2 be formed $= n$

$$n=\frac{p_{CO_2}\times V}{RT}=\frac{3.9\times10^{-2}\times0.654}{0.082\times1000}$$

$$=3.11\times10^{-4}\ \text{mol}$$

The amount of CaO(s) formed will also be $=3.11\times10^{-4}$ mol

Hence, mass of CaO formed $=3.11\times10^{-4}\times56=0.0174$ g

Example 27. *The decomposition of ammonium carbamate at 30°C is represented as:*

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g)+CO_2(g)$$

The equilibrium constant K_p is 2.9×10^{-5} atm^3.

What is the total pressure of gases in equilibrium with $NH_2COONH_4(s)$ at 30°C?

Solution: $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g)+CO_2(g)$

	$NH_2COONH_4(s)$	$2NH_3(g)$	$CO_2(g)$
At equilibrium	$(1-x)$	$2x$	x

$$K_p=(p_{NH_3})^2\times p_{CO_2}$$

$$2.9\times10^{-5}=(2x)^2\times x=4x^3$$

$$x = \left(\frac{2.9 \times 10^{-5}}{4}\right)^{1/3} = 0.0194 \text{ atm}$$

Total pressure $= 2x + x = 3x = 3 \times 0.0194 = 0.0582$ atm

Example 28. *In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at 100°C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Calculate the equilibrium constant of this reaction.*

Solution:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initial	1	1	0	1
At equilibrium	$1-x$	$1-x$	x	$1+x$
	$1-0.543$	$1-0.543$	0.543	$1+0.543$

Given, $x = 0.543$.

Applying law of mass action,

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$$

Example 29. *The equilibrium constant for the reaction, $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ is 4. What will be the composition of the equilibrium mixture when one mole of acetic acid is taken along with 4 moles of ethyl alcohol?*

Solution:

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initial	1	4	0	0
At equilibrium	$1-x$	$4-x$	x	x

$$K_c = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} = \frac{x^2}{(1-x)(4-x)} = 4$$

$$x^2 = 4(1-x)(4-x)$$

$$= 4[4 - 5x + x^2]$$

$$= 16 - 20x + 4x^2$$

or $$3x^2 - 20x + 16 = 0$$

$$x = \frac{20 \pm \sqrt{400 - 192}}{6} = \frac{20 \pm 14.42}{6}$$

$$x = 0.93 \quad \text{or} \quad 5.7366$$

The value 5.7366 is not possible, hence $x = 0.93$

Thus, the composition of mixture at equilibrium is

$$[CH_3COOH] = (1 - 0.93) = 0.07 \text{ mole}$$

$$[C_2H_5OH] = (4 - 0.93) = 3.07 \text{ mole}$$

$$[CH_3COOC_2H_5] = 0.93 \text{ mole}$$

$$[H_2O] = 0.93 \text{ mole}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

7. For the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the value of K_c at 300°C is 0.1. When the equilibrium concentrations of both the reactants is 0.5 mol, what is the value of K_p at the same temperature? (KCET 2005)

(a) 0.5 (b) 0.1 (c) 0.01 (d) 0.025

[**Ans.** (b)]

[**Hint:** $K_p = K_c(RT)^{\Delta n}$

Since, $\Delta n = 0$, hence, $K_p = K_c$]

8. $A(g) + 3B(g) \rightleftharpoons 4C(g)$, initial concentration of A is equal to that of B. The equilibrium concentrations of A and C are equal. K_c of the reaction will be:

(a) 0.08 (b) 0.8 (c) 8 (d) 80 (e) 1/8

[**Ans.** (c)]

[**Hint:** $A(g) + 3B(g) \rightleftharpoons 4C(g)$

$t = 0$	a	a	0
$t_{eq.}$	$a - x$	$a - 3x$	$4x$

$a - x = 4x$ given

$a = 5x$

$$K_c = \frac{[C]^4}{[A][B]^3} = \frac{[4x]^4}{[4x][2x]^3} = \frac{256}{32} = 8]$$

9. For a hypothetical reaction:

$$4A(g) + 5B(g) \rightleftharpoons 4P(g) + 6Q(g)$$

The equilibrium constant K_c has units:

(a) mol L^{-1} (b) mol^{-1} L
(c) $(mol\ L^{-1})^{-2}$ (d) unitless

[**Ans.** (a)]

[**Hint:** Unit of $K_c = (mol\ L^{-1})^{\Delta n}$

$= (mol\ L^{-1})^1 = mol\ L^{-1}$]

10. Starting with 1 mol of O_2; 2 mol of SO_2, the equilibrium for the formation of $SO_3(g)$ was established at a certain temperature. If V is the volume of the vessel and $2x$ is the number of moles of SO_3 present, the equilibrium constant will be:

(a) $\frac{x^2V}{(1-x)^3}$ (b) $\frac{4x^2}{(2-x)(1-x)}$

(c) $\frac{(1-x)^3}{2V}$ (d) $\frac{x^2}{(2-x)(1-x)}$

[**Ans.** (a)]

[**Hint:** $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$t = 0$	2	1	0
$t_{eq.}$	$\left[\frac{2-2x}{V}\right]$	$\left[\frac{1-x}{V}\right]$	$\left[\frac{2x}{V}\right]$

$$\therefore K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[2x/V]^2}{\left[\frac{2-2x}{V}\right]^2\left[\frac{1-x}{V}\right]} = \frac{x^2V}{(1-x)^3}]$$

11. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K = 47.6$, if the initial number of moles of each reactant and product is 1 mole, then at equilibrium: [JEE (Orissa) 2006]

(a) $[I_2] = [H_2]; [I_2] > [HI]$ (b) $[I_2] < [H_2]; [I_2] = [HI]$
(c) $[I_2] = [H_2]; [I_2] < [HI]$ (d) $[I_2] > [H_2]; [I_2] = [HI]$

[**Ans.** (c)]

[**Hint:** $K_c = \frac{[HI]^2}{[H_2][I_2]}$

$[H_2] = [I_2]$ will be same at equilibrium, since it is same at initial state.

$$K_c = \frac{[HI]^2}{[I_2]^2}$$

$$K_c [I_2]^2 = [HI]^2$$
$$47.6 [I_2]^2 = [HI]^2$$
$$\therefore \quad [I_2] < [HI]]$$

12. In a closed vessel of volume V, a mol of nitrogen and b mol of oxygen are made to react to give nitric oxide, according to the reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

If at equilibrium, $2x$ mol of NO are obtained, then: **[BV (Pune) 2006]**

(a) $K_c = \dfrac{4x^2}{(a-x)(b-x)} \times \dfrac{1}{V}$

(b) $K_c = \dfrac{4x^2}{(a-x)(b-x)} \times V$

(c) $K_c = \dfrac{x^2}{(a-x)(b-x)} \times V$

(d) $K_c = \dfrac{4x^2}{(a-x)(b-x)}$

[Ans. (d)]

[Hint:

$$\begin{array}{llll} & N_2(g) & + \; O_2(g) \rightleftharpoons & 2NO(g) \\ t = 0 & a & b & 0 \\ t_{eq.} & \dfrac{(a-x)}{V} & \left(\dfrac{b-x}{V}\right) & \dfrac{2x}{V} \end{array}$$

$$K_c = \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}]$$

13. Equivalent amounts of H_2 and I_2 are heated in a closed till equilibrium is obtained. If 80% of the hydrogen can be converted to HI, the K_c at this temperature is: **(VITEEE 2007)**

(a) 64 (b) 16 (c) 0.25 (d) 4

[Ans. (a)]

[Hint:

$$\begin{array}{llll} & H_2(g) & + \; I_2(g) \rightleftharpoons & 2HI(g) \\ t = 0 & 1 & 1 & 0 \\ t_{eq.} & \dfrac{1-0.8}{V} & \dfrac{1-0.8}{V} & \dfrac{2 \times 0.8}{V} \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\dfrac{1.6}{V}\right]^2}{\dfrac{0.2}{V} \times \dfrac{0.2}{V}} = 64]$$

14. Equimolar concentration of H_2 and I_2 are heated to equilibrium in a 2 litre flask. At equilibrium, the forward and backward rate constants are found to be equal. What percentage of initial concentration of H_2 has reacted at equilibrium? **[PMT (Kerala) 2008]**

(a) 33% (b) 66%
(c) 50% (d) 40%
(e) 20%

[Ans. (a)]

[Hint :

$$\begin{array}{llll} & H_2(g) & + \; I_2(g) \rightleftharpoons & 2HI(g) \\ t_0 & 1 & 1 & 0 \\ t_{eq.} & \dfrac{1-x}{2} & \dfrac{1-x}{2} & \dfrac{2x}{2} \end{array}$$

$$K = \frac{k_f}{k_b} = 1 = \frac{[HI]^2}{[H_2][I_2]} = \frac{(x)^2}{\left(\dfrac{1-x}{2}\right)\left(\dfrac{1-x}{2}\right)}$$

$$1 = \frac{4x^2}{(1-x)^2}$$

$$1 = \frac{2x}{1-x}$$

$$x = 0.33$$

% of H_2 reacted = 33]

9.8 LE CHATELIER'S PRINCIPLE

There are three main factors which can change the state of equilibrium in a reversible system. These are concentration, pressure and temperature. Le Chatelier, a French chemist, presented a qualitative principle known as Le Chatelier's principle which can describe the effect of change in concentration, pressure and temperature on any reversible system whether physical or chemical.

According to this principle, **if a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.**

Or

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to annul the effect of that change.

(a) Change in concentration: If an additional amount of any reactant or product is added to the system, the stress is relieved as the reaction that consumes the added substance occurs more rapidly than its reverse reaction, *i.e.*, if any of the reactants is added, the rate of forward reaction increases and if any of the products is added, the rate of backward reaction increases.

In general, in a chemical equilibrium, increasing the concentrations of the reactants results in shifting the equilibrium in favour of products while increasing concentrations of the products results in shifting the equilibrium in favour of reactants.

(b) Change in pressure: If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more than before. According to Le Chatelier's principle, the equilibrium will shift in the direction in which there is decrease in number of moles, *i.e.*, towards the direction in which there is decrease in volume.

In general, **an increase in pressure applied to a system at equilibrium, favours the reaction in the direction that produces smaller number of moles of gases and a decrease in pressure favours the opposite reaction.** If there is no change in number of moles of gases in a reaction, a pressure change does not affect the equilibrium.

(c) Change in temperature: A chemical reaction (reversible) involves two opposing reactions, forward and backward. If one reaction is endothermic, the other will be exothermic in nature. When heat energy is added by raising temperature, the system can relieve itself from the stress if the reaction which absorbs heat moves faster, *i.e.*, **endothermic reaction is always favoured with increase of temperature.**

Conclusions:

(i) Increase in concentration of any substance favours the reaction in which it is used up.
(ii) High pressure is favourable for the reaction in which there is decrease in volume.
(iii) A rise in temperature favours the endothermic reaction.

(d) Role of catalyst: Positive catalyst increases the rate of both forward and backward reactions equally; the equilibrium will be attained in less time, *i.e.*, same amount of product will be formed in less time.

On the other hand, negative catalyst lowers the rate of both forward and backward reactions equally. Same amount of product will be formed in more time.

Catalyst does not affect equilibrium constant and heat of reaction.

Summary of Le Chatelier's Principle

Effect of inert gas addition

Condition		Effect
$\Delta V = 0, V = \text{Constant}$	$\Delta n = 0, +\text{ve or } -\text{ve}$	No effect
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n = 0$	No effect
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n > 0$	Forward shift
$\Delta V \neq 0, V \neq \text{Constant}$	$\Delta n < 0$	Backward shift

where, Δn = number of gaseous moles of product − number of gaseous moles of reactant

Effect of temperature and pressure

	Nature of reaction	Effect of increased temperature	Δn; Side with fewer mole of gas	Effect of increase in P
1.	Exothermic	backward shift	0; neither	no shift
2.	Exothermic	backward shift	−ve; right	forward shift
3.	Endothermic	forward shift	−ve; right	forward shift
4.	Endothermic	forward shift	+ve; left	backward shift
5.	Exothermic	backward shift	+ve; left	backward shift
6.	Exothermic	backward shift	−ve; right	forward shift
7.	Endothermic	forward shift	+ve; left	backward shift
8.	Endothermic	forward shift	+ve; left	backward shift

Application of Le Chatelier's Principle

(a) Formation of HI:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + 3000 \text{ cal}$$

Effect of concentration: When concentration of H_2 or I_2 is increased at equilibrium, the system moves in a direction which decreases the concentration, *i.e.*, the rate of forward reaction increases thereby increasing the concentration of HI.

Effect of pressure: As there is no change in the number of moles in the reaction, the equilibrium state remains unaffected by change of pressure.

Effect of temperature: By increasing temperature, the equilibrium state shifts towards the reaction which moves with absorption of heat. The formation of HI is an exothermic reaction. Thus, the backward reaction moves faster when temperature is increased.

In short, we can say that the favourable conditions for greater yield of HI are:

(i) High concentrations of H_2 and I_2 and
(ii) Low temperature.

(b) Formation of nitric oxide:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43200 \text{ cal}$$

Effect of concentration: When concentration of N_2 or O_2 is increased, the system moves in a direction in which N_2 or O_2 is used up, *i.e.*, rate of forward reaction increases thereby increasing the concentration of NO.

Effect of pressure: In the formation of nitric oxide, the number of moles remains the same, *i.e.*, no change in volume occurs. Consequently, the equilibrium state is not affected by any change in pressure.

Effect of temperature: The formation of NO is endothermic in nature. If the temperature is raised, the equilibrium shifts in the direction in which heat is absorbed. The concentration of NO will, therefore, be higher at higher temperature.

Thus, favourable conditions for greater yield of nitric oxide are:

(i) High concentrations of N_2 and O_2 and
(ii) High temperature

(c) Dissociation of PCl_5:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - 15000 \text{ cal}$$

Effect of concentration: When concentration of PCl_5 is increased at equilibrium, the rate of forward reaction increases as to decrease the added concentration. Thus, more of PCl_3 and Cl_2 are formed.

Effect of pressure: The volume increases in the dissociation of PCl_5. When pressure is increased, the system moves in the direction in which there is decrease in volume. Thus, high pressure does not favour dissociation of PCl_5.

Effect of temperature: The dissociation of PCl_5 is an endothermic reaction. Thus, increase of temperature favours the dissociation.

Thus, favourable conditions for dissociation of PCl_5 are:

(i) High concentration of PCl_5,
(ii) Low pressure and
(iii) High temperature.

(d) Formation of ammonia:

$$N_2(g) + 3H_2(g) \overset{Fe}{\rightleftharpoons} 2NH_3(g); \Delta H = -22.4 \text{ kcal/mol}$$

(i) At high pressure reaction will shift in forward direction to form more product.
(ii) When concentration of N_2 and H_2 is raised or concentration of NH_3 is lowered, then again the equilibrium shifts in forward direction to form more ammonia.

If concentration of only one reactant is raised, then again the equilibrium shifts in forward direction till the other reactant is available for reaction.

(iii) The reaction shifts in forward direction at low temperature. But at very low temperature the rate of reaction becomes very low; thus moderate temperature is favourable for this reaction.

9.9 APPLICATION OF LE CHATELIER'S PRINCIPLE TO PHYSICAL EQUILIBRIA

(i) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Gas

When temperature is raised, the above equilibrium shifts in forward direction.

(ii) Effect of pressure on boiling point: When pressure is raised, condensation of vapour takes place. Thus, vapour pressure is lowered. Now more heat is required to equate vapour pressure with atmospheric pressure as a result of which boiling point increases.

(iii) Effect of pressure on melting point: There are two types of solids:

(a) Solids whose volume decreases on melting, *e.g.*, ice, diamond, carborundum, magnesium nitride and quartz.

$$\text{Solid (higher volume)} \rightleftharpoons \text{Liquid (lower volume)}$$

The process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solids whose volume increases on melting, *e.g.*, Fe, Cu, Ag, Au, etc.

$$\text{Solid (lower volume)} \rightleftharpoons \text{Liquid (higher volume)}$$

In this case the process of melting become difficult at high pressure; thus melting point becomes high.

(c) Solubility of substances: When solid substances are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

$$\text{KCl} + aq. \rightleftharpoons \text{KCl}(aq.) - \text{heat}$$

In such cases, solubility increases with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.

$$\text{KOH} + aq. \rightleftharpoons \text{KOH}(aq.) + \text{heat}$$

In such cases, solubility decreases with increase in temperature.

(d) Solubility of gases in liquids: When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

15. Consider the following reversible reaction at equilibrium:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g);\ \Delta H = +24.7\ \text{kJ}$$

which one of the following changes in conditions will lead to maximum decomposition of $H_2O(g)$?

(a) Increasing both temperature and pressure
(b) Decreasing temperature and increasing pressure
(c) Increasing temperature and decreasing pressure
(d) Increasing temperature at constant pressure
(e) Increasing pressure at constant temperature

[**Ans.** (c)]

[**Hint:** Reaction is endothermic and $\Delta n > 0$, hence, the formation of product will be favoured by increasing the temperature and decreasing the pressure.]

16. The exothermic formation of ClF_3 is represented by the equation:

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g);\ \Delta H = -329\ \text{kJ}$$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3? (AIEEE 2005)

(a) Increasing the temperature
(b) Removing Cl_2
(c) Increasing the volume of the container
(d) Adding F_2

[**Ans.** (d)]

[**Hint:** Equilibrium will shift in forward direction by increasing the concentration of reactant.]

17. Which among the following reactions will be favoured at low pressure?

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

[**Ans.** (c)]

[**Hint:** On lowering the pressure, equilibrium favours the direction of higher volume.]

18. At constant pressure, the addition of argon to:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

will:

(a) shift the equilibrium in forward direction
(b) shift the equilibrium in backward direction
(c) not affect the equilibrium
(d) stop the reaction

[**Ans.** (b)]

[**Hint:** If volume is not constant, the addition of inert gas favours the direction where volume is increasing.]

19. The equilibrium reaction that is not influenced by volume change at constant temperature is: [CET (J&K) 2006]

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(d) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

[**Ans.** (a)]

[**Hint:** When, $\Delta n = 0$, there is no effect of pressure and volume change on the equilibrium.]

20. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

What is the effect of the increase of temperature on the equilibrium of the reaction? (KCET 2008)

(a) Equilibrium is unaltered
(b) Reaction rate does not change
(c) Equilibrium is shifted to the left
(d) Equilibrium is shifted to the right

[**Ans.** (c)]

[**Hint:** The given reaction is exothermic, therefore, the equilibrium will shift in backward direction by the increase of temperature.]

9.10 CALCULATION OF DEGREE OF DISSOCIATION FROM DENSITY MEASUREMENTS

Degree of dissociation is defined as the fraction of one molecule dissociated. It is denoted by x or α. Its value is always less than 1. When the value becomes equal to 1, it is said that the substance is completely dissociated.

The degree of dissociation in the case of second type of reactions (reversible) is determined by measuring density of reaction mixture at equilibrium.

Consider the general reversible reaction,

	A	$\rightleftharpoons$	nB
Initial no. of moles	1		0
No. of moles at equilibrium	$(1-x)$		nx

Total number of moles at equilibrium $= (1-x) + nx$
$= 1 + (n-1)x$

Let the initial volume be V litre. Thus, the volume at equilibrium $= [1+(n-1)x]V$.

Let 'd' be the observed vapour density at a particular temperature when degree of dissociation is 'x' and D be the vapour density when there is no dissociation. Again,

$$D \propto \frac{1}{V} \quad \text{... (i)}$$

and
$$d \propto \frac{1}{[1+(n-1)x]V} \quad \text{... (ii)}$$

Dividing eq. (i) by eq. (ii),

$$\frac{D}{d} = 1 + (n-1)x$$

or
$$\frac{D}{d} - 1 = (n-1)x$$

or
$$\frac{D-d}{d} = (n-1)x$$

or
$$x = \frac{D-d}{(n-1)d} \quad \text{... (iii)}$$

$$x = \frac{M-m}{(n-1)m}$$

where, M = initial molecular mass

m = molecular mass at equilibrium.

In the dissociation of PCl_5, NH_4Cl and N_2O_4, the value of $n = 2$.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$NH_4Cl \rightleftharpoons NH_3 + HCl$$
$$N_2O_4 \rightleftharpoons 2NO_2$$

So,
$$x = \frac{D-d}{(2-1)d} = \frac{D-d}{d}$$

Calculation of Degree of Reaction using Pressure-Temperature Determination

Let us consider the following gaseous reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Initial pressure and temperature are P_1 and T_1. At equilibrium, pressure and temperature are P_2 and T_2 respectively. The volume of vessel is constant, equal to 'V'.

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$	n	V	T	P
$t = 0$	a	0	0	a	V	T_1	P_1
$t_{eq.}$	$a - ax$	ax	ax	$a + ax$	V	T_2	P_2

Initial state $\quad P_1V = aRT_1 \quad$ ... (i)

Equilibrium state $\quad P_2V = (a + ax)RT_2 \quad$ ... (ii)

Dividing equation (i) by eq. (ii), we get

$$\frac{P_1}{P_2} = \frac{T_1}{(1+x)T_2}$$

$$(1+x) = \frac{T_1P_2}{T_2P_1}$$

$$x = \frac{T_1P_2 - T_2P_1}{T_2P_1}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

21. At equilibrium:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

the observed molecular weight of N_2O_4 is 80 g mol^{-1} at 350 K. The percentage dissociation of $N_2O_4(g)$ at 350 K is:

[PMT (Kerala) [illegible]]

(a) 10% (b) 15% (c) 20% (d) 18%
(e) 13%

[Ans. (b)]

[Hint: Degree of dissociation may be calculated as,

$$x = \frac{M-m}{(n-1)m} \quad \because n = 2 \text{ (number of gas moles produced by 1 mol reactant)}$$

$$= \frac{92-80}{(2-1)80} \quad (M = 92, m = 80)$$

$$= \frac{12}{80} = 0.15$$

Percentage dissociation $= 0.15 \times 100 = 15$]

22. The vapour density of PCl_5 is 104.25 but when heated to 230°C, its vapour density is reduced to 62. The degree of dissociation of PCl_5 at this temperature will be:

(a) 6.8% (b) 68% (c) 46% (d) 64%

[Ans. (b)]

[Hint: The reaction is:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$n = 2$$

$$\alpha = \frac{D-d}{(n-1)d} = \frac{104.25-62}{(2-1)\times 62}$$

$$= 0.68$$

Percentage dissociation $= 0.68 \times 100 = 68\%$]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *At a certain temperature, equilibrium constant (K_c) is 16 for the reaction:*

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole of each of the four gases in one litre container, what would be the equilibrium concentration of NO and NO_2?

Solution:	$SO_2(g)$ +	$NO_2(g) \rightleftharpoons$	$SO_3(g)$ +	$NO(g)$
Initial concentration	1	1	1	1
Equilibrium concentration	$1-x$	$1-x$	$1+x$	$1+x$

Applying law of mass action,

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = 16$$

$$\frac{1+x}{1-x} = 4 \text{ or } 1+x = 4-4x$$

or $$5x = 3, \textit{i.e.}, x = \frac{3}{5} = 0.6$$

Conc. of NO_2 at equilibrium $= (1-0.6) = 0.4$ mole

Conc. of NO at equilibrium $= (1+0.6) = 1.6$ mole

Example 2. *At 817°C, K_p for the reaction between $CO_2(g)$ and excess of hot graphite (s) is 10 atm.*

(*a*) *What are the equilibrium concentrations of the gases at 817°C and a total pressure of 5 atm?*

(*b*) *At what total pressure does the gas contain 5% CO_2 by volume?* (IIT 2000)

Solution: (a) $CO_2(g) + C(s) \rightleftharpoons 2CO(g); K_p = 10$ atm

Given: $p_{CO(g)} + p_{CO_2(g)} = 5$ atm

Let $p_{CO(g)} = x$ atm

So, $p_{CO_2(g)} = (5-x)$ atm

$$K_p = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{x^2}{(5-x)}$$

or $$10 = \frac{x^2}{(5-x)}$$

or $$x^2 + 10x - 50 = 0$$

On solving, we get

$$x = 3.66$$

$$p_{CO(g)} = 3.66 \text{ atm}$$

or Mole fraction CO at equilibrium = 73.2% (by volume)

$$p_{CO_2(g)} = 1.34 \text{ atm}$$

or Mole fraction CO_2 at equilibrium = 26.8% (by volume)

(b) Let the total pressure be P atm

Given, % CO_2 (by volume) = 5 and % CO (by volume) = 95

$$p_{CO_2} = \frac{5}{100} \times P = 0.05P \text{ and } p_{CO} = \frac{95}{100} \times P = 0.95P$$

$$K_p = 10 = \frac{[p_{CO}]^2}{p_{CO_2}} = \frac{0.95P \times 0.95P}{0.05P} = 18.05P$$

or $$P = 0.554 \text{ atm}$$

Example 3. *At 700 K, CO_2 and H_2 react to form CO and H_2O. For this process K_c is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K.*

(*i*) *Find out the amount of each gas at equilibrium state.*

(*ii*) *After equilibrium is reached another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find the composition of the mixture at the new equilibrium state.*

Solution: (i)	$CO_2(g)$ +	$H_2(g) \rightleftharpoons$	$CO(g)$ +	$H_2O(g)$
Initial no. of moles	0.45	0.45	0	0
of moles at equilibrium	$0.45-x$	$0.45-x$	x	x

Applying law of mass action,

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{x \times x}{(0.45-x)(0.45-x)} = \frac{x^2}{(0.45-x)^2} = 0.11$$

So, $$\frac{x}{(0.45-x)} = 0.33$$

$$x = 0.11$$

At equilibrium, $[CO_2] = [H_2] = 0.34$ mole

$[CO] = [H_2O] = 0.11$ mole

(ii)	CO_2 +	$H_2 \rightleftharpoons$	CO +	H_2O
Initial moles	$0.34 + 0.34$ $= 0.68$	$0.34 + 0.34$ $= 0.68$	0.11	0.11
At equilibrium	$0.68-y$	$0.68-y$	$0.11+y$	$0.11+y$

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{(0.11+y)(0.11+y)}{(0.68-y)(0.68-y)} = 0.11$$

or $$\frac{0.11+y}{0.68-y} = 0.33$$

or $$0.11 + y = 0.33 \times 0.68 - 0.33y$$

or $$y = 0.086$$

At equilibrium, $[CO] = [H_2O] = 0.11 + 0.086 = 0.196$ mole

$[CO_2] = [H_2] = 0.68 - 0.086 = 0.594$ mole

Example 4. *A mixture of SO_3, SO_2 and O_2 gases is maintained in a 10 litre flask at a temperature at which the equilibrium constant for the reaction is 100:*

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(*i*) *If the number of moles of SO_2 and SO_3 in the flask are equal, how many moles of O_2 are present?*

(*ii*) *If the number of moles of SO_3 in the flask is twice the number of moles of SO_2, how many moles of oxygen are present?*

Solution: (i) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

At equilibrium, let the number of moles of each of SO_2 and SO_3 be n_1 and of oxygen n_2, *i.e.*,

$$[SO_2] = \frac{n_1}{10}$$

$$[O_2] = \frac{n_2}{10}$$

$$[SO_3] = \frac{n_1}{10}$$

Applying law of mass action,

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{\left(\frac{n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2\left(\frac{n_2}{10}\right)} = 100$$

or $$n_2 = 0.1 \text{ mole}$$

Oxygen = 0.1 mole

(ii) Let the number of moles of SO_2 be $= n_1$

So, number of moles of $SO_3 = 2n_1$

Let the number of moles of oxygen be $= n_2$

$$K_c = \frac{\left(\frac{2n_1}{10}\right)^2}{\left(\frac{n_1}{10}\right)^2\left(\frac{n_2}{10}\right)} \text{ or } 100 = \frac{40}{n_2}$$

$$n_2 = 0.4 \text{ mole}$$

Oxygen = 0.4 mole

Example 5. *At 250°C and 1 atmospheric pressure, the vapour density of PCl_5 is 57.9. Calculate (i) K_p for the reaction,*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g),$$

at 250°C, (ii) the percentage dissociation when pressure is doubled.

Solution: (i) Mol. mass of $PCl_5 = 208.5$

$$\text{Vapour density, } D = \frac{208.5}{2} = 104.25$$

Observed vapour density, $d = 57.9$

$$\text{Degree of dissociation, } \alpha = \frac{D-d}{d} = \frac{104.25 - 57.9}{57.9}$$

$$= 0.80$$

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$
At equilibrium	$1-\alpha$	α	α
	$(1-0.80)$	0.80	0.80

Total number of moles $= (1+\alpha) = (1+0.80) = 1.80$

$$\text{Partial pressure of } PCl_5 = \frac{0.2}{1.80} \times 1 = \frac{1}{9}$$

$$\text{Partial pressure of } PCl_3 = \frac{0.80}{1.80} \times 1 = \frac{4}{9}$$

$$\text{Partial pressure of } Cl_2 = \frac{0.80}{1.80} \times 1 = \frac{4}{9}$$

So, $$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{4/9 \times 4/9}{1/9} = \frac{16}{9} = 1.78$$

(ii) Let the degree of dissociation be α when pressure is 2 atmospheres.

At equilibrium

$$p_{PCl_5} = \frac{(1-\alpha)}{(1+\alpha)} \cdot P = \frac{(1-\alpha)}{(1+\alpha)} \times 2$$

$$p_{PCl_3} = \frac{\alpha}{(1+\alpha)} \cdot P = \frac{\alpha}{(1+\alpha)} \times 2$$

$$p_{Cl_2} = \frac{\alpha}{(1+\alpha)} \cdot P = \frac{\alpha}{(1+\alpha)} \times 2$$

$$K_p = \frac{\frac{\alpha}{(1+\alpha)} \times 2 \times \frac{\alpha}{(1+\alpha)} \times 2}{\frac{(1-\alpha)}{(1+\alpha)} \times 2} = \frac{\alpha^2}{(1-\alpha^2)} \times 2 = 1.78$$

or $$\frac{\alpha^2}{(1-\alpha^2)} = 0.89$$

or $$\alpha^2 = 0.89 - 0.89\alpha^2$$

or $$1.89\alpha^2 = 0.89$$

$$\alpha^2 = \frac{0.89}{1.89}$$

$$\alpha = 0.686$$

Thus, PCl_5 is 68.6% dissociated.

Example 6. *For the reaction,*

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of $CO(g)$ and a catalyst, until the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constants K_p and K_c. (IIT 1993)

Solution: Let the number of moles of hydrogen introduced be m moles.

Total moles of CO and hydrogen $= 0.2 + m$

Applying, $PV = nRT$

$$P = 4.92 \text{ atm}, \ V = 5 \text{ litre}, \ R = 0.082,$$

$$T = (273 + 327) = 600 \text{ K}$$

$$4.92 \times 5 = 0.082 \times 600 \times (0.2 + m)$$

or $$0.2 + m = \frac{4.92 \times 5}{0.082 \times 600}$$

or $$m = 0.3 \text{ mole}$$

	$CO(g) +$	$2H_2(g) \rightleftharpoons$	$CH_3OH(g)$	
	$0.2-x$	$0.3-2x$	x	(No. of moles
or	$0.2-0.1$	$0.3-0.2$	0.1	at equilibrium)
or	0.1	0.1	0.1	
	$\frac{0.1}{5}$	$\frac{0.1}{5}$	$\frac{0.1}{5}$	(Active masses)

Applying law of mass action,

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{\frac{0.1}{5}}{\frac{0.1}{5} \times \left(\frac{0.1}{5}\right)^2} = 2500 \text{ mol}^{-2} \text{ L}^2$$

We know that, $K_p = K_c(RT)^{\Delta n}, \Delta n = -2$

or $K_p = 2500(0.082 \times 600)^{-2}$

or $$K_p = \frac{2500}{49.2 \times 49.2} = 1.0327 \text{ atm}^{-2}$$

Example 7. *When sulphur in the form of S_8 is heated at 900 K the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2. Find the value of equilibrium constant for this reaction.*

Solution: $S_8(g) \rightleftharpoons 4S_2(g)$

	$S_8(g)$	$4S_2(g)$
Initial mole	1	0
At equilibrium	$1-x$	$4x$
	$(1-0.29)$ $= 0.71$	(4×0.29) $= 1.16$

Applying law of mass action,

$$K_p = \frac{[p_{S_2}]^4}{[p_{S_8}]} = \frac{(1.16)^4}{0.71} = 2.5582 \text{ atm}^3$$

Example 8. *For the equilibrium,*

$$AB(g) \rightleftharpoons A(g) + B(g),$$

K_p is equal to four times the total pressure. Calculate the number of moles of A formed.

Solution: Let the total equilibrium pressure be = P atm

Given, $K_p = 4P$

Let the start be made with 1 mole of $AB(g)$ and the degree of dissociation be x.

	$AB(g) \rightleftharpoons$	$A(g) +$	$B(g)$
At equilibrium	$1-x$	x	x

Total moles at equilibrium $= 1 - x + x + x = 1 + x$

Thus, p_A = Partial pressure of $A = \frac{x}{1+x} \cdot P$

p_B = Partial pressure of $B = \frac{x}{1+x} \cdot P$

p_{AB} = Partial pressure of $AB = \frac{1-x}{1+x} \cdot P$

Applying the law of mass action,

$$K_p = \frac{p_A \times p_B}{p_{AB}} = \frac{\left(\frac{x}{1+x} \cdot P\right)\left(\frac{x}{1+x} \cdot P\right)}{\left(\frac{1-x}{1+x} \cdot P\right)}$$

So, $$4P = \frac{x^2}{1-x^2} \cdot P$$

or $4 - 4x^2 = x^2$

or $5x^2 = 4$

or $$x = \frac{2}{\sqrt{5}}$$

Hence, number of moles of A formed $= \frac{2}{\sqrt{5}}$ times initial moles of AB taken

Example 9. *0.15 mole of CO taken in a 2.5 litre flask is maintained at 705 K along with a catalyst so that the following reaction can take place:*

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. (IIT 1993)

Solution: (i) Let the total number of moles of gases be n at equilibrium.

Applying equation, $PV = nRT$

Given, $P = 8.5$ atm; $V = 2.5$ L;

$R = 0.0821$ atm L mol^{-1} K^{-1} and $T = 705$ K

$$n = \frac{8.5 \times 2.5}{0.0821 \times 705} = 0.367 \text{ mol}$$

	$CO(g) +$	$2H_2(g) \rightleftharpoons$	$CH_3OH(g)$
Initial mole	0.15	$(nH_2)_0$	0
At equilibrium	$0.15 - x$	$[(nH_2)_0 - 2x]$	$x = 0.08$

Number of moles of CO at equilibrium

$= (0.15 - 0.08) = 0.07$ mole

Number of moles of H_2 at equilibrium

= total moles − moles of CO − moles of CH_3OH

$= (0.367 - 0.07 - 0.08)$

$= 0.217$ mole

Applying law of mass action,

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{\frac{0.08}{2.5}}{\frac{0.07}{2.5} \times \left(\frac{0.217}{2.5}\right)^2} = 151.6 \text{ mol}^{-2} \text{ L}^2$$

Now, $K_p = K_c(RT)^{\Delta n} = 151.6 \times (0.0821 \times 705)^{-2}$

$= 0.045 \text{ atm}^{-2}$

(ii) Since, $[(n_{H_2})_0 - 2x] = 0.217$

or $(n_{H_2})_0 = 0.217 + 2 \times 0.08$

$= 0.377$ mole

$(n_{CO})_0 = 0.15$

Total moles $(n_0) = 0.377 + 0.15 = 0.527$

Hence, $$p_0 = \frac{n_0RT}{V} = \frac{0.527 \times 0.0821 \times 705}{2.5}$$

$= 12.20$ atm

Example 10. *The equilibrium constant for the reaction,*

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$$

at 986°C is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0 atm.

(*i*) *How many moles of H_2 are present at equilibrium?*

(*ii*) *Calculate the partial pressures of gases in equilibrium mixture.* (IIT 1992)

Solution: (i) In the given reaction, $\Delta n = 0$, hence, $K_c = K_p$

$$\begin{array}{lcccc} & \text{CO}(g) + & \text{H}_2\text{O}(g) \rightleftharpoons & \text{CO}_2(g) + & \text{H}_2(g) \\ \text{At equilibrium} & (3-x) & (1-x) & x & x \end{array}$$

Applying law of mass action,

$$\frac{x \times x}{(3-x)(1-x)} = 0.63$$

$$x^2 = 0.63(3 - 4x + x^2)$$

$$0.37x^2 + 2.52x - 1.89 = 0$$

or $$x^2 + 6.81x - 5.1 = 0$$

$$x = \frac{-6.81 \pm [6.81 \times 6.81 - 4 \times (-5.1)]^{1/2}}{2} = 0.68 \text{ mole} = \text{H}_2$$

(ii) Partial pressure of CO_2 = partial pressure of H_2

$$= \text{mole fraction} \times \text{total pressure}$$

$$= \frac{0.68}{4} \times 2 = 0.34 \text{ atm}$$

$$\text{Partial pressure of CO}(g) = \frac{(3-0.68)}{4} \times 2 = 1.16 \text{ atm}$$

$$\text{Partial pressure of H}_2\text{O}(g) = \frac{(1-0.68)}{4} \times 2 = 0.16 \text{ atm}$$

Example 11. *The equilibrium constant K_p for the reaction,*

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

Solution: The system in the initial stage does not contain SO_2. SO_3 will, thus, decompose to form SO_2 and O_2 until equilibrium is reached. The partial pressure of SO_3 will decrease. Let the decrease in partial pressure be $2x$.

$$\begin{array}{lccc} & 2\text{SO}_2(g) + & \text{O}_2(g) \rightleftharpoons & 2\text{SO}_3(g) \\ \text{At equilibrium} & (2x) & (2+x) & (1-2x) \end{array}$$

Applying law of mass action,

$$K_p = \frac{(1-2x)^2}{(2x)^2(2+x)} \qquad (2+x) \to 2$$

$$900 = \frac{(1-2x)^2}{8x^2}$$

or $$\frac{1-2x}{x} = 84.85$$

or $$x = 0.0115 \text{ atm}$$

Thus, the partial pressures at equilibrium are:

$$p_{\text{SO}_2} = 2 \times 0.0115 = 0.023 \text{ atm}$$

$$p_{\text{O}_2} = 2 + 0.0115 = 2.0115 \text{ atm}$$

$$p_{\text{SO}_3} = 1 - 2 \times 0.0115 = 0.977 \text{ atm}$$

Example 12. *What is the concentration of CO in equilibrium at 25°C in a sample of a gas originally containing 1.00 mol L^{-1} of CO_2? For the dissociation of CO_2 at 25°C, $K_c = 2.96 \times 10^{-92}$.*

Solution:
$$\begin{array}{lccc} & 2\text{CO}_2(g) \rightleftharpoons & 2\text{CO}(g) + & \text{O}_2(g) \\ \text{At equilibrium} & (1-2x) & (2x) & (x) \end{array}$$

Applying law of mass action,

$$K_c = \frac{[\text{O}_2][\text{CO}]^2}{[\text{CO}_2]^2} = \frac{x \times (2x)^2}{(1-2x)^2} = 2.96 \times 10^{-92}$$

It can be assumed that $1 - 2x \approx 1.0$ as K_c is very small.

So, $$4x^3 = 2.96 \times 10^{-92}$$

or $$x = 1.95 \times 10^{-31} \text{ mol L}^{-1}$$

$$[\text{CO}] = 2x = 2 \times 1.95 \times 10^{-31}$$

$$= 3.90 \times 10^{-31} \text{ mol L}^{-1}$$

Example 13. *Ammonia is heated at 15 atm from 27°C to 347°C assuming volume constant. The new pressure becomes 50 atm at equilibrium. Calculate % of NH_3 actually decomposed.* (MLNR 1995)

Solution: Pressure of NH_3 at 27°C = 15 atm

Pressure of NH_3 at 347° C = P atm

$$\frac{P}{620} = \frac{15}{300}$$

$$P = 31 \text{ atm}$$

Let a moles of ammonia be present. Total pressure at equilibrium = 50 atm

$$\begin{array}{lccc} & 2\text{NH}_3(g) \rightleftharpoons & \text{N}_2(g) + & 3\text{H}_2(g) \\ \text{At equilibrium} & (a-2x) & x & 3x \\ \text{Total moles} & \multicolumn{3}{l}{a - 2x + x + 3x = a + 2x} \end{array}$$

$$\frac{\text{Initial number of moles}}{\text{Moles at equilibrium}} = \frac{\text{Initial pressure}}{\text{Equilibrium pressure}}$$

$$\frac{a}{(a+2x)} = \frac{31}{50}$$

$$x = \frac{19}{62}a$$

$$\text{Amount of ammonia decomposed} = 2x = 2 \times \frac{19}{62}a = \frac{19}{31}a$$

$$\%\text{ of ammonia decomposed} = \frac{19 \times a}{31 \times a} \times 100$$

$$= 61.3$$

Example 14. *Calculate the per cent dissociation of $H_2S(g)$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K for the reaction,*

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

The value of K_c is 1.0×10^{-6}.

Solution: $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

$$\begin{array}{llll} \text{At equilibrium} & (0.1-x) & x & x/2 \\ \text{Molar conc.} & \dfrac{(0.1-x)}{0.4} & \dfrac{x}{0.4} & \dfrac{x}{0.8} \end{array}$$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{x}{0.4}\right)^2\left(\frac{x}{0.8}\right)}{\left(\frac{0.1-x}{0.4}\right)^2} = 1.0 \times 10^{-6}$$

or $$\frac{x^3}{0.8(0.1-x)^2} = 1.0 \times 10^{-6}$$

as x is very small; $0.1 - x \rightarrow 0.1$

$$\frac{x^3}{0.8 \times (0.1)^2} = 1.0 \times 10^{-6}$$

$$x^3 = 8 \times 10^{-9}$$

or $$x = 2 \times 10^{-3}$$

So, per cent dissociation $= \dfrac{2 \times 10^{-3}}{0.1} \times 100 = 2.0$

Example 15. *The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 38.3 at 26.7° C. Calculate the number of moles of NO_2 in 100 grams of the mixture.* (MLNR 1993)

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\begin{array}{lll} \text{At equilibrium} & (1-x) & 2x \end{array}$$

$$x \text{ (degree of dissociation)} = \frac{D-d}{(n-1)d}$$

Given, $d = 38.3$, $D = \dfrac{\text{Mol. mass of } N_2O_4}{2} = \dfrac{92}{2} = 46$, $n = 2$

So, $$x = \frac{46 - 38.3}{38.3} = 0.2$$

At equilibrium, amount of $N_2O_4 = 1 - 0.2 = 0.8$ mol

and amount of $NO_2 = 2 \times 0.2 = 0.4$ mol

Mass of the mixture $= 0.8 \times 92 + 0.4 \times 46$

$= 73.6 + 18.4 = 92.0$ g

Since, 92 gram of the mixture contains = 0.4 mol NO_2

So,

100 gram of the mixture contains $= \dfrac{0.4 \times 100}{92} = 0.43$ mol NO_2

Example 16. *At temperature T, the compound $AB_2(g)$ dissociates according to the reaction,*

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation, x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p and the total pressure, P. (IIT 1994)

Solution: $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

$$\begin{array}{llll} \text{At equilibrium} & (1-x) & x & x/2 \end{array}$$

Total moles at equilibrium $= 1 - x + x + x/2$

$$= \frac{2+x}{2}$$

$$p_{AB_2} = \frac{2(1-x)}{(2+x)} \cdot P;\ p_{AB} = \frac{2x}{(2+x)} \cdot P;\ p_{B_2} = \frac{x}{(2+x)} \cdot P;$$

$$K_p = \frac{(p_{AB})^2(p_{B_2})}{(p_{AB_2})^2} = \frac{\left[\frac{2x}{(2+x)}P\right]^2\left(\frac{x}{2+x}\right)P}{\left(\frac{2(1-x)}{(2+x)}P\right)^2}$$

$$= \frac{x^3P}{(2+x)(1-x)^2}$$

As x is very small, $(2+x) \rightarrow 2$ and $(1-x) \rightarrow 1$.

So, $$K_p = \frac{x^3P}{2}$$

or $$x^3 = \frac{2K_p}{P}$$

or $$x = \left(\frac{2K_p}{P}\right)^{1/3}$$

Example 17. *At 25°C and one atmospheric pressure, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atmosphere, respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25°C and at a total pressure of 10 atmospheres.* (MLNR 1990)

Solution: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$\begin{array}{lll} \text{At equilibrium} & 0.7 & 0.3 \text{ atm} \end{array}$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{0.3 \times 0.3}{0.7} = 0.1285 \text{ atm}$$

Let the degree of dissociation of N_2O_4 be x when total pressure is 10 atmosphere.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$\begin{array}{lll} \text{At equilibrium} & (1-x) & 2x \end{array}$$

Total number of moles $= 1 - x + 2x = 1 + x$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10;\ p_{NO_2} = \frac{2x}{(1+x)} \times 10$$

$$K_p = 0.1285 = \frac{\left(\frac{2x}{1+x}\right)^2 \times 10^2}{\left(\frac{1-x}{1+x}\right) \times 10} = \frac{40x^2}{1-x^2}$$

Since, x is very small, $(1-x^2) \rightarrow 1$

So, $$x^2 = \frac{0.1285}{40}$$

or $$x = 0.0566$$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)} \times 10 = \frac{1-0.0566}{1+0.0566} \times 10 = \frac{0.9436\times 10}{1.0566} = 8.93 \text{ atm}$$

$$p_{NO_2} = \frac{2x}{(1+x)} \times 10 = \frac{2\times 0.0566}{1+0.0566} \times 10 = \frac{0.1132}{1.0566} \times 10 = 1.07 \text{ atm}$$

Example 18. *At 450°C, the equilibrium constant, K_p, for the reaction,*

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

was found to be 1.6×10^{-5} at a pressure of 200 atm. If N_2 and H_2 are taken in 1 : 3 ratio what is % of NH_3 formed at this temperature?

Solution: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium $(1-x)$ $(3-3x)$ $2x$

Total number of moles $= 1 - x + 3 - 3x + 2x = 4 - 2x$

$$p_{N_2} = \frac{(1-x)}{(4-2x)}P;\ p_{H_2} = \frac{(3-3x)}{(4-2x)}P;\ p_{NH_3} = \frac{2x}{(4-2x)}P$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2}\times(p_{H_2})^3} = \frac{\left(\frac{2x}{4-2x}P\right)^2}{\left(\frac{1-x}{4-2x}P\right)\left(\frac{3-3x}{4-2x}P\right)^3}$$

$$= \frac{4x^2(4-2x)^2}{(1-x)\times 27\times(1-x)^3P^2}$$

$$1.6\times 10^{-5} = \frac{16}{27}\times\frac{x^2(2-x)^2}{(1-x)^4\times(200)^2}$$

or $$\frac{x^2(2-x)^2}{(1-x)^4} = \frac{1.6\times 10^{-5}\times 27\times(200)^2}{16}$$

$$= \frac{16\times 10^{-6}\times 27\times(200)^2}{16}$$

or $$\frac{x(2-x)}{(1-x)^2} = 200\times 10^{-3}\times\sqrt{27} = 1.039$$

or $x = 0.30$

Moles of ammonia formed $= 2\times 0.30 = 0.60$

Total moles at equilibrium $= (4-2x) = (4 - 2\times 0.30) = 3.40$

$$\% \text{ of } NH_3 \text{ at equilibrium} = \frac{0.60}{3.40}\times 100 = 17.64$$

Example 19. *A mixture of SO_2 and O_2 at 1 atmosphere in the ratio of 2 : 1 is passed through a catalyst at 1170°C for attainment of equilibrium. The exit gas is found to contain 87% SO_3 by volume. Calculate K_p for the reaction,*

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

Solution: The volume of SO_2 and O_2 at equilibrium

$= (100 - 87) = 13$ mL

$$\text{Volume of } SO_2 = \frac{2}{3}\times 13 = 8.67 \text{ mL}$$

$$\text{Volume of oxygen} = \frac{1}{3}\times 13 = 4.33 \text{ mL}$$

$$p_{SO_3} = \frac{87}{100}\times 1 = 0.87 \text{ atm}$$

$$p_{SO_2} = \frac{8.67}{100}\times 1 = 0.0867 \text{ atm}$$

$$p_{O_2} = \frac{4.33}{100}\times 1 = 0.0433 \text{ atm}$$

$$K_p = \frac{p_{SO_3}}{p_{SO_2}\times(p_{O_2})^{1/2}} = \frac{0.87}{(0.0867)\times(0.0433)^{1/2}}$$

$$= \frac{0.87}{(0.0867)\times 0.208}$$

$$= 48.24 \text{ atm}^{-1/2}$$

Example 20. *N_2O_4 dissociates as.*

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

at 55°C and one atmosphere % decomposition of N_2O_4 is 50.3%. At what pressure and same temperature, the equilibrium mixture has the ratio of $N_2O_4 : NO_2$ as 1 : 8?

Solution:

Case I: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

At equilibrium $(1-x)$ $2x$

$$p_{N_2O_4} = \frac{(1-x)}{(1+x)}\times P;\ p_{NO_2} = \frac{2x}{(1+x)}\times P$$

$$K_p = \frac{\left(\frac{2x}{1+x}\cdot P\right)^2}{\left(\frac{1-x}{1+x}\cdot P\right)} = \frac{4x^2P}{(1-x^2)}$$

Given, $x = 0.503$ and $P = 1$

$K_p = 1.3548$ atm

Case II: $N_2O_4 \rightleftharpoons 2NO_2$

$(1-x)$ $2x$

Given, $$\frac{(1-x)}{2x} = \frac{1}{8}$$

$x = 0.8$

Let the new pressure be P atm.

$$K_p = \frac{4x^2P}{(1-x^2)} = \frac{4\times 0.8\times 0.8\times P}{(1+0.8)(1-0.8)} = 1.3548$$

$P = 0.19$ atm

Example 21. *At 627°C and one atmosphere SO_3 is partially dissociated into SO_2 and O_2 by the reaction,*

$$SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g).$$

The density of the equilibrium mixture is $0.925\ g\ L^{-1}$. What is the degree of dissociation?

Solution: Let the molecular mass of the mixture at equilibrium be M_{mix}.

Applying the relation,

$$M_{mix} = \frac{dRT}{P} = \frac{0.925\times 0.0821\times 900}{1}$$

$$= 68.348$$

$$\text{Molecular mass of } SO_3 = 80$$

$$\text{Vapour density of } SO_3, D = \frac{80}{2} = 40$$

$$\text{Vapour density of mixture, } d = \frac{68.348}{2} = 34.174$$

Let the degree of dissociation be x.

$$x = \frac{D-d}{(n-1)d} = \frac{40 - 34.174}{\left(\frac{3}{2} - 1\right) \times 34.174} = \frac{5.826 \times 2}{34.174} = 0.34$$

or $\quad x = 34\%$ dissociated

i.e., SO_3 is 34% dissociated.

Example 22. *Density of equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 384 K is 1.84 g dm^{-3}. Calculate the equilibrium constant of the reaction.*

$$N_2O_4 \rightleftharpoons 2NO_2$$

Solution: We know that,

$$Pm = dRT$$

$$1 \times m = 1.84 \times 0.0821 \times 384$$

$$m = 29 \times 2$$

Vapour density (d) at equilibrium = 29

Initial vapour density $= M/2 = 92/2 = 46$

$$x = \frac{D-d}{(n-1)\,d} = \frac{46-29}{29} = 0.586$$

	$N_2O_4 \rightleftharpoons$	$2NO_2$	
$t = 0$	1	0	
$t_{eq.}$	$1-x$	$2x$	(Total moles = $1 + x$)

$$p_{N_2O_4} = \frac{1-x}{1+x} \times P; \; p_{NO_2} = \frac{2x}{1+x} \times P$$

$$K_p = \frac{4x^2P}{1-x^2} = \frac{4 \times (0.586)^2 \times 1}{1-(0.586)^2} = 2.09 \text{ atm}$$

Example 23. *For the reaction,*

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

show that degree of dissociation of NH_3 is given as:

$$\alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right]^{-1/2}$$

where, 'p' is equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C, calculate K_c.

Solution:

	$NH_3(g) \rightleftharpoons$	$\frac{1}{2}N_2$ +	$\frac{3}{2}H_2(g)$	Total moles
$t = 0$	1	0	0	1
$t_{eq.}$	$1-\alpha$	$\alpha/2$	$3\alpha/2$	$1+\alpha$
p_i	$\left(\frac{1-\alpha}{1+\alpha}\right)p$	$\left(\frac{\alpha}{2(1+\alpha)}\right)p$	$\left(\frac{3\alpha}{2(1+\alpha)}\right)p$	($P_i \rightarrow$ partial pressure)

$$K_p = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]}$$

$$= \frac{\left[\frac{\alpha}{2(1+\alpha)}p\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}p\right]^{3/2}}{\left[\frac{1-\alpha}{1+\alpha}p\right]} = \frac{p\alpha^2\sqrt{27}}{4(1-\alpha^2)}$$

$$\text{Solving for } \alpha \text{, we get } \quad \alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right]^{-1/2}$$

K_c can be calculated by using $K_p = K_c(RT)^{\Delta n}$

$K_p = 78.1; T = 673\text{K}; \Delta n = 1$

Example 24. *The equilibrium constant K_p for the reaction,*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

is 1.64×10^{-4} at 400°C and 0.144×10^{-4} at 500°C. Calculate the mean heat of formation of 1 mole of NH_3 from its elements in this temperature range.

Solution: We know that, $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$$\log \frac{0.144}{1.64} = \frac{\Delta H}{2.303 \times 1.987 \times 10^{-3}}\left(\frac{1}{673} - \frac{1}{773}\right)$$

$$\Delta H = -25.14 \text{ kcal for 2 mole}$$

$$= -12.57 \text{ kcal mol}^{-1}$$

Example 25. *When limestone is heated, quicklime is formed according to the equation,*

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The experiment was carried out in the temperature range 800–900°C. Equilibrium constant K_p follows the relation,

$$\log K_p = 7.282 - 8500/T$$

where, T is temperature in Kelvin. At what temperature the decomposition will give $CO_2(g)$ at 1 atm?

Solution: $\quad K_p = p_{CO_2} = 1$

$$\log K_p = 7.282 - \frac{8500}{T}$$

$$\log 1 = 7.282 - \frac{8500}{T}$$

$$T = \frac{8500}{7.282} = 1167.26 \text{ K}$$

$$= 894.26°\text{C}$$

Example 26. *Equilibrium constant for the reaction of iodine with propane according to the following equation was determined.*

Some results obtained at 545 K were as given ahead:

Initial Pressures (mm Hg)			Equilibrium Pressures (mm)	
I_2	**C_3H_6**	**HI**	**HI**	**C_3H_5I**
23.9	505.8	0	1.80	1.80
16.1	355.3	1.62	2.27	0.645

Calculate equilibrium constant according to the following equation,

$$I_2(g)+C_3H_6(g)\rightleftharpoons C_3H_5I(g)+HI(g)$$

Solution: Ist experiment:

$$\begin{array}{lcccccc} & I_2(g) & + & C_3H_6(g) & \rightleftharpoons & C_3H_5I(g) & + \; HI(g) \\ t=0 & 23.9 & & 505.8 & & 0 & 0 \\ t_{eq.} & (23.9-1.8) & & (505.8-1.8) & & 1.80 & 1.80 \end{array}$$

$$K_p=\frac{p_{C_3H_5I}\times p_{HI}}{p_{I_2}\times p_{C_3H_6}}=\frac{1.8\times 1.8}{22.1\times 504}=2.9\times 10^{-4}$$

Similarly, solve for second experiment.

Example 27. *At 817°C K_p for the reaction between CO_2 and excess hot graphite to form $2CO(g)$ is 10.*

(*i*) *What is the analysis (mole fraction) of the gases at equilibrium at 817°C and a total pressure of 4 atm? What is the partial pressure of CO_2 at equilibrium?*

(*ii*) *At what total pressure will the gas mixture have 6% CO_2 by volume?*

Solution: (i) $CO_2(g)+C(s)\rightleftharpoons 2CO(g)$

$$\begin{array}{lcc} t=0 & 1 & 0 \\ t_{eq.} & 1-\alpha & 2\alpha \\ p_{eq.} & \left(\frac{1-\alpha}{1+\alpha}\right)p & \left(\frac{2\alpha}{1+\alpha}\right)p \end{array}$$

$$K_p=\frac{4\alpha^2 p}{1-\alpha^2};\ 10=\frac{4\alpha^2 4}{1-\alpha^2}$$

On solving, we get $\alpha = 0.62$

$$x_{CO_2}=\frac{1-\alpha}{1+\alpha}=\frac{1-0.62}{1+0.62}=0.2345=23.45\%\text{ (by volume)}$$

$$x_{CO}=0.7655=76.55\%\text{ (by volume)}$$

$$p_{CO_2}=(0.2345\times 4.0)\text{ atm}=0.938\text{ atm}$$

(ii) Let the total pressure be P atm.

$$K_p=10=\frac{[p_{CO}]^2}{p_{CO_2}}=\frac{0.94\times P\times 0.94\times P}{0.06\times P}$$

$$P=0.68\text{ atm}$$

Example 28. *Ammonia under a pressure of 20 atm at 127°C is heated to 327°C in a closed vessel. Under these conditions NH_3 is partially decomposed to N_2 and H_2 according to the equation:*

$$2NH_3(g)\rightleftharpoons N_2(g)+3H_2(g)$$

After decomposition at constant volume in a vessel the pressure increases to 45 atm. What is the percentage of ammonia dissociated?

Solution:

$$\begin{array}{lccccccc} 2NH_3(g)\rightleftharpoons & N_2(g) & +\,3H_2(g) & n & P & V & T \\ t=0\quad a & 0 & 0 & a & 20 & V & 400 \\ t_{eq.}\quad a-a\alpha & a\alpha/2 & 3a\alpha/2 & a+a\alpha & 40 & V & 600 \end{array}$$

$$V=\frac{nRT}{P}=\frac{a\times R\times 400}{20} \qquad \text{... (1)}$$

$$V=\frac{nRT}{P}=\frac{a(1+\alpha)\times R\times 600}{45} \qquad \text{... (2)}$$

On dividing, we get $1=\dfrac{400\times 45}{(1+\alpha)20\times 600}$

$$\alpha=0.5$$

Percentage dissociation of $NH_3 = 50$

Example 29. *When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?* (IIT 1999)

Solution: $NH_4HS(s)\rightleftharpoons NH_3(g)+H_2S(g)$

$$\text{Moles of }NH_4HS=\frac{3.06}{51}=0.06$$

Degree of dissociation = 0.3

At equilibrium,

$$[NH_3(g)]=\frac{0.3\times 0.06}{2};\quad [H_2S(g)]=\frac{0.3}{2}\times 0.06$$

$$K_c=[NH_3(g)][H_2S(g)]=\frac{0.3\times 0.06\times 0.3\times 0.06}{2\times 2}$$

$$=8.1\times 10^{-5}$$

Now applying,

$$K_p=K_c(RT)^{\Delta n}=8.1\times 10^{-5}\times(0.082\times 300)^2$$

$$=0.049$$

Since, NH_4HS is solid, so it causes no change in equilibrium.

Example 30. *At 540 K, 0.10 mole of PCl_5 are heated in a 8 litre flask. The pressure of equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.* (IIT 1998)

Solution: $PCl_5\rightleftharpoons PCl_3+Cl_2$

$$\begin{array}{lccc} \text{At equilibrium (mole)} & (0.1-x) & x & x \end{array}$$

Total number of moles, $n=(0.1-x)+x+x=(0.1+x)$

$$PV=nRT$$

$$1\times 8=(0.1+x)\times 0.082\times 540$$

or $$x=0.08$$

$$K_c=\frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{x^2}{(0.1-x)\times 8}$$

$$=\frac{0.08\times 0.08}{(0.1-0.08)8}=4\times 10^{-2}\text{ mol L}^{-1}$$

$$K_p=K_c(RT)^{\Delta n}=K_c\,RT\ (\Delta n=+1)$$

$$=4\times 10^{-2}\times 0.082\times 540=1.77\text{ atm}$$

Example 31. *At 817°C, K_p for the reaction between $CO_2(g)$ and excess hot graphite(s) is 10 atm.*

(a) What are the equilibrium concentrations of gases at 817°C and a total pressure of 5 atm?

(b) At what total pressure, the gas contains 5% CO_2 by volume? (IIT 2000)

Solution: (a) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

$$\begin{array}{lcc} \text{At equilibrium} & (5-x)\,\text{atm} & x\,\text{atm} \end{array}$$

$$K_p = \frac{[CO]^2}{[CO_2]} = \frac{x^2}{(5-x)}$$

$$10 = \frac{x^2}{5-x}$$

$$x^2 = 50 - 10x$$

$$x^2 + 10x - 50 = 0$$

$$x = \frac{-10 \pm \sqrt{100+200}}{2} = 3.66$$

i.e., $p_{CO} = 3.66$ atm; $p_{CO_2} = 1.34$ atm

$$\text{Concentration of CO} = \frac{p}{RT} = \frac{3.66}{0.0821 \times 1090} = 0.041\ \text{mol litre}^{-1}$$

$$\text{Concentration of CO}_2 = \frac{p}{RT} = \frac{1.34}{0.0821 \times 1090} = 0.015\ \text{mol litre}^{-1}$$

(b) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

$$\begin{array}{lccc} t=0 & 1 & 0 & 0 \\ t_{eq.} & 1-\alpha & & 2\alpha \\ p_i & \frac{1-\alpha}{1+\alpha}p & & \frac{2\alpha}{1+\alpha}p \end{array}$$

$$K_p = \frac{\left[\frac{2\alpha}{1+\alpha}p\right]^2}{\left[\frac{1-\alpha}{1+\alpha}p\right]} = \frac{4\alpha^2 p}{1-\alpha^2} \quad \text{... (i)}$$

$$\frac{5}{100} = \frac{1-\alpha}{1+\alpha}$$

$$\alpha = 0.95$$

$$\therefore \text{ From eq. (i), } 10 = \frac{4 \times (0.95)^2}{1-(0.95)^2} \times p$$

$$p = 0.27\ \text{atm}$$

Example 32. *The value of K_p is 1×10^{-3} atm^{-1} at 25°C for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$. A flask contains NO at 0.02 atm and at 25°C. Calculate the mole of Cl_2 that must be added if 1% of the NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 mole of gas produces 1 atm pressure at 25°C. (Ignore probable association of NO to N_2O_2).* (IIT 2001)

Solution: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$

$$\begin{array}{lccc} t=0 & 0.02 & 0 & 0 \\ t_{eq.} & \frac{0.02 \times 99}{100} & p & \frac{0.02 \times 1}{100} \end{array}$$

$$K_p = \frac{[p_{NOCl}]^2}{[p_{NO}]^2[p_{Cl_2}]} = \frac{(0.02 \times 0.01)^2}{(0.99 \times 0.02)^2 \times p} = 10^{-3}$$

$$\therefore \quad p = 0.102\ \text{atm}$$

$$PV = nRT$$

$$0.102 \times V = n \times R \times T \quad \text{... (i)}$$

$$1 \times V = 0.2 \times R \times T \quad \text{... (ii)}$$

From eqs. (i) and (ii), $n = 0.0204$ (no. of moles of Cl_2 at equilibrium)

Pressure of Cl_2 involved in reaction

$$= \frac{1}{2} \times \text{pressure of NOCl}$$

$$= \frac{1}{2} \times \frac{0.02}{100} = 0.0001\ \text{atm}$$

$$PV = nRT$$

$$0.0001 \times V = n \times RT \quad \text{... (iii)}$$

From eqs. (ii) and (iii), $n = 2 \times 10^{-5}$ (moles of Cl_2 involved in reaction)

Initial moles of Cl_2 taken $= 0.0204 + 2 \times 10^{-5}$

$= 0.02042$

Example 33. *In the following equilibrium,*

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

when 5 moles of each is taken and the temperature is kept at 298 K, the total pressure was found to be 20 bar.

Given : $\Delta G^\circ_{f\,N_2O_4} = 100\,kJ, \Delta G^\circ_{f\,NO_2} = 50\,kJ$

(a) Find ΔG of the reaction at 298 K.

(b) Find the direction of the reaction. (IIT 2004)

Solution: $\text{Reaction Quotient} = \frac{[p_{NO_2}]^2}{p_{N_2O_4}} = \frac{100}{10} = 10$

$$\Delta G^\circ_{\text{reaction}} = 2\Delta G^\circ_{f\,NO_2} - \Delta G^\circ_{f\,N_2O_4}$$

$$= 2 \times 50 - 100 = 0$$

We know that, $\Delta G = \Delta G^\circ - 2.303\,RT \log Q_p$

$$= 0 - 2.303 \times 8.314 \times 298 \log 10$$

$$= -5705.8\ \text{J} = -5.705\ \text{kJ}$$

Negative value shows that reaction will be in forward direction..

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Irreversible and reversible reactions: Chemical reactions can be classified as irreversible and reversible reactions. The reactions which move in one direction only are called **irreversible reactions.** In these reactions products do not react to produce original reactants. In such reactions an arrow (→) is placed between reactants and products. The chemical reactions which take place in both directions under similar conditions are called **reversible reactions.** In such reactions products also react with each other to produce reactants again. The sign ($\rightleftharpoons$) is placed between reactants and products.

2. Chemical equilibrium: Chemical equilibrium is the most important characteristic property of reversible reactions. It is the state at which both forward and backward reactions occur at the same speed.

At equilibrium state,

Rate of forward reaction = Rate of backward reaction

At equilibrium state, the concentrations of the reactants and products do not change with time. The following are the characteristics of the equilibrium state:

(i) It can be achieved only if the reversible reaction is carried out in a closed space.

(ii) It is characterised by constancy of certain properties such as concentration, pressure, density, colour, etc.

(iii) It can be attained from either side of the reaction.

(iv) It can be attained in lesser time by use of a catalyst.

(v) It is dynamic in nature, *i.e.,* reaction does not stop, but both the forward and backward reactions move with the same speed.

(vi) Change of pressure, concentration or temperature favours one of the reaction and thus shifts the equilibrium point in one direction.

Reversible chemical reactions are classified into two types:

(i) **Heterogeneous reactions:** The reversible reactions in which more than one-phase is present.

(ii) **Homogeneous reactions:** The reversible reactions in which only one-phase is present. These are further classified into three types:

(a) When there is no change in the number of molecules, *i.e.*, $\Delta n = 0$.

(b) When there is an increase in the number of molecules, *i.e.*, $\Delta n = +\text{ve}$.

(c) When there is a decrease in the number of molecules, *i.e.*, $\Delta n = -\text{ve}$.

3. Law of chemical equilibrium (Application of law of mass action): Consider the general homogeneous reversible reaction in which equilibrium has been attained at a certain temperature.

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

Rate of forward reaction = Rate of backward reaction

$$k_f[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots = k_b[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots$$

or
$$\frac{\{[B_1]^{n_1}[B_2]^{n_2}[B_3]^{n_3}\ldots\}}{\{[A_1]^{m_1}[A_2]^{m_2}[A_3]^{m_3}\ldots\}} = \frac{k_f}{k_b} = K_c$$

The equilibrium constant, K_c, at a given temperature, is the ratio of rate constants of forward and backward reactions. It is also defined as the ratio between the molar concentrations of the products to the molar concentrations of the reactants with each concentration term raised to the power equal to stoichiometric coefficient in the balanced chemical equation.

The value of equilibrium constant is independent of the following factors;

(i) Initial concentration of reactants.

(ii) The direction from which equilibrium has been attained.

(iii) The presence of a catalyst.

(iv) The presence of inert materials.

The value of equilibrium constant depends upon the following factors:

(i) The mode of representation of the reaction: Consider the reversible reaction,

$$A + B \rightleftharpoons C + D$$

$$K_c = \frac{[C][D]}{[A][B]}$$

The products are made the reactants, *i.e.*, the reaction is reversed:

$$C + D \rightleftharpoons A + B$$

$$K'_c = \frac{[A][B]}{[C][D]}$$

So, $$K'_c = \frac{1}{K_c}$$

(ii) Stoichiometric representation of a chemical equation: The value of equilibrium constant will be numerically different if the reaction can be written with the help of two or more stoichiometric equations.

i.e., $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $\quad K_c = \dfrac{[N_2][O_2]^2}{[NO_2]^2}$

or $NO_2(g) \rightleftharpoons (1/2)N_2(g) + O_2(g)$; $\quad K'_c = \dfrac{[N_2]^{1/2}[O_2]}{[NO_2]}$

Thus, $$K'_c = \sqrt{K_c}$$

(iii) Use of partial pressures: When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature.

$$m_1A_1 + m_2A_2 + m_3A_3 + \ldots \rightleftharpoons n_1B_1 + n_2B_2 + n_3B_3 + \ldots$$

$$K_p = \frac{(p_{B_1})^{n_1}(p_{B_2})^{n_2}(p_{B_3})^{n_3}\ldots}{(p_{A_1})^{m_1}(p_{A_2})^{m_2}(p_{A_3})^{m_3}\ldots}$$

$$K_p = K_c(RT)^{\Delta n}$$

where, Δn = total number of molecules of products − total number of molecules of reactants.

When, $\Delta n = 0$, $K_p = K_c$;
$\Delta n = +\text{ve}$, $K_p > K_c$;
and $\Delta n = -\text{ve}$, $K_p < K_c$;

(iv) Temperature: The value of equilibrium constant changes with temperature. The values of equilibrium constants at two different temperatures are related by the following equation:

$$\log K_2 - \log K_1 = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad T_2 > T_1$$

When, $\Delta H = 0$, *i.e.*, heat of reaction at constant volume is zero,
$K_2 = K_1$

When, $\Delta H = +\text{ve}$, *i.e.*, endothermic reaction,
$K_2 > K_1$

and when, $\Delta H = -\text{ve}$, *i.e.*, exothermic reaction
$K_2 < K_1$

Units of equilibrium constant: Partial pressures are measured in terms of atmospheres. Therefore, units of K_p will be $(\text{atm})^{\Delta n}$. Since, concentrations are measured in terms of moles per litre, the units of K_c are $(\text{mol L}^{-1})^{\Delta n}$.

K_p and K_c will be pure numbers when, $\Delta n = 0$.

4. Equilibrium expressions for some reactions:

(a) $$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Initially	a	b	0
At equilibrium	$(a-x)$	$(b-x)$	$(2x)$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(a-x)(b-x)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{[p_{HI}]^2}{p_{H_2} \times p_{I_2}} = \frac{\dfrac{(2x)^2}{(a+b)^2}P^2}{\left(\dfrac{a-x}{a+b}\cdot P\right)\left(\dfrac{b-x}{a+b}\cdot P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So, $K_c = K_p$

(b) $$2NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

Initially	a	0	0
At equilibrium	$(a-x)$	$x/2$	$x/2$

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2}$$

(c)
$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initially	a	b	0	0
At equil.	$(a-x)$	$(b-x)$	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(a-x)(b-x)}$$

(d) $$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Initially	a	0	0
At equilibrium	$(a-x)$	x	x
Active masses	$\dfrac{(a-x)}{V}$	$\dfrac{x}{V}$	$\dfrac{x}{V}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\dfrac{x}{V} \times \dfrac{x}{V}}{\dfrac{(a-x)}{V}} = \frac{x^2}{(a-x)V}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\dfrac{x}{a+x}\cdot P\right) \times \left(\dfrac{x}{a+x}\cdot P\right)}{\left(\dfrac{a-x}{a+x}\cdot P\right)} = \frac{x^2 P}{(a+x)(a-x)}$$

(e) $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Initially	a	b	0
At equilibrium	$(a-x)$	$(b-3x)$	$2x$
Active masses	$\left(\dfrac{a-x}{V}\right)$	$\left(\dfrac{b-3x}{V}\right)$	$\left(\dfrac{2x}{V}\right)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-3x}{V}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2} \times (p_{H_2})^3} = \frac{\left[\dfrac{2x}{(a+b-2x)}P\right]^2}{\left[\dfrac{(a-x)}{(a+b-2x)}P\right]\left[\dfrac{(b-3x)}{(a+b-2x)}P\right]^3}$$

$$= \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3P^2}$$

5. Activation energies for the forward and backward reactions: Both forward and backward reactions follow the same path and from the same activated complex. However, the activation energies of both reactions are different.

$$\Delta E = E_a\,(f) - E_a\,(b)$$

For exothermic reaction, $E_a\,(f) < E_a\,(b)$, *i.e.*, $\Delta E = -\text{ ve}$

For endothermic reaction, $E_a\,(f) > E_a\,(b)$, *i.e.*, $\Delta E = +\text{ ve}$

Threshold energy = Energy of reactants + Activation energy of forward reaction

Threshold energy = Energy of products + Activation energy of backward reaction

6. Standard free energy change of a reaction and its equilibrium constant are related to each other at temperature *T* by the following relation:

$$\Delta G^\circ = -2.303RT \log K_p$$
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

When, $\Delta G^\circ = -\text{ve}$, the value of equilibrium constant will be large positive quantity and when ΔG° is positive, the value of K is less than 1, *i.e.*, low concentration of products at equilibrium state.

7. Degree of dissociation from density measurements: Degree of dissociation in the case of reversible reactions in which there is increase in the number of molecules can be determined by measuring density of the reaction mixture at equilibrium. Let d be the observed density at a particular temperature when degree of dissociation is x and D be the vapour density when there is no dissociation.

$x = \frac{D-d}{(n-1)d}$; where, n is the number of molecules of products.

8. Heterogeneous equilibria: Law of mass action can also be applied to the heterogeneous system. In such systems the concentrations of pure solids and liquids are not considered in equilibrium expressions.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

$$K_p = \frac{p_{CO} \times p_{H_2}}{p_{H_2O}} \quad \text{or} \quad K_c = \frac{[CO][H_2]}{[H_2O]}$$

i.e., concentration of C(s) is not taken into account.

9. Le Chatelier's principle: It is a qualitative principle which can describe the effect of change in concentration, pressure and temperature on the reversible system whether physical or chemical. It is stated as "If the system at equilibrium is subjected to a change of any one of the factors such as concentration, temperature or pressure, the system adjusts itself in such a way as to annul the effect of that change." The following conclusions have been derived from this principle:

(i) Increase in concentration of any substance favours the reaction in which it is used up.

(ii) High pressure is favourable for the reaction in which there is decrease in volume.

(iii) A rise in temperature favours the endothermic reaction.

Applications of Le Chatelier's Principle

(i) Ice water system (melting of ice):

$$\text{Ice} + \text{Heat} \rightleftharpoons \text{Water}$$

It is an endothermic process and there is decrease in volume. Thus, the favourable conditions for melting of ice are:
(a) High temperature and (b) High pressure.

(ii) Solubility of gases in liquids: When a gas dissolves in a liquid, there is decrease in volume. Thus, increase in pressure will favour the dissolution of a gas in liquid.

(iii) Formation of nitric oxide:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) - 43200 \text{ calorie}$$

In this chemical reaction, there is no change in the number of molecules and heat is absorbed (endothermic). Thus, favourable conditions for greater yields of NO are:

(a) High concentrations of N_2 and O_2,

(b) High temperature and

(c) No effect of pressure and catalyst.

(iv) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22400$ calorie: The reaction involves decrease in number of molecules and evolution of heat (exothermic). The favourable conditions are:

(a) High concentrations of N_2 and H_2,

(b) High pressure and

(c) Low temperature.

To speed up the rate of reaction at low temperature, a suitable catalyst is always employed.

Questions

1. Match List I (Equations) with List II (Type of Processes) and select the correct option:

List-I (Equations)	**List-II (Type of Processes)**
(a) $K_p > Q$	(i) Non-spontaneous
(b) $\Delta G^\circ < RT \log_e Q$	(ii) Equilibrium
(c) $K_p = Q$	(iii) Spontaneous and endothermic
(d) $T > \dfrac{\Delta H}{\Delta S}$	(iv) Spontaneous

(A) a = (i); b = (ii); c = (iii); d = (iv)
(B) a = (iii); b = (iv); c = (ii); d = (i)
(C) a = (iv); b = (i); c = (ii); d = (iii)
(D) a = (ii); b = (i); c = (iv); d = (iii) **[CBSE (PMT) 2010]**

[**Hint:** When $K_p > Q$; rate of forward reaction > rate of backward reaction, *i.e.*, process is spontaneous.

When $\Delta G^\circ < RT \log_e Q$, ΔG° is positive, thus reaction is non spontaneous.

When $K_p = Q$, reaction is at equilibrium.

When $T\Delta S > \Delta H$, ΔG will be negative only when ΔH = +ve, thus is spontaneous and endothermic.]

2. **Matrix-Matching Problems (For IIT Aspirants):**

[A] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p) Unaffected by inert gas addition
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(q) Forward shift by rise in pressure and backward shift by inert gas addition
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(r) Unaffected by increase in pressure
(d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(s) Backward shift by rise in pressure and forward shift by inert gas addition

[B] Match the reactions in the Column-I with the units of equilibrium constant in Column-II:

Column-I	**Column-II**
(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	(p) mol L
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(q) Unitless
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(r) atm
(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(s) $(atm)^{-2}$

[C] Match the reactions of the Column-I with the factors in Column-II:

Column-I	**Column-II**
(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Exothermic)	(p) Forward shift by rise in pressure
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ (Exothermic)	(q) Unaffected by change in pressure
(c) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (Endothermic)	(r) Forward shift by rise in temperature
(d) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ (Endothermic)	(s) Forward shift by lowering the temperature

[D] Match the reactions of the Column-I with the relations in Column-II:

Column-I	**Column-II**
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	(p) $K_p = K_c(RT)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	(q) $K_p = K_c(RT)^2$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r) $K_p = K_c(RT)^{-2}$
(d) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$	(s) $K_p = K_c$

[E] Match the List-I with List-II:

List-I	**List-II**
(a) $Q = K$	(p) Reaction is nearer to completion
(b) $Q < K$	(q) Reaction is not at equilibrium
(c) $Q > K$	(r) Reaction is fast in forward direction
(d) $K >>> 1$	(s) Reaction at equilibrium

[F] Match the List-I with List-II:

List-I (Reaction)	**List-II (K_p/K_c)**
(a) $A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$	(p) $(RT)^{-2}$
(b) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$	(q) $(RT)^0$
(c) $A(s) + \frac{3}{2}B_2(g) \rightleftharpoons AB_3(g)$	(r) $(RT)^{1/2}$
(d) $AB_2(g) \rightleftharpoons AB(g) + \frac{1}{2}B_2(g)$	(s) $(RT)^{-1/2}$

Answers

1. (C) (a = iv); (b = i); (c = ii); (d = iii)
2. [A] (a–p, r); (b–p, r); (c–q); (d–s)
   [B] (a–p, r); (b–p, r); (c–q); (d–s)
   [C] (a–p, s); (b–p, s); (c–q, r); (d–p, r)
   [D] (a–s); (b–r); (c–p); (d–q)
   [E] (a–s); (b–q, r); (c–q); (d–p)
   [F] (a–p); (b–q); (c–s); (d–r)

• PRACTICE PROBLEMS •

1. K_c for the reaction, $NH_3(g) \rightleftharpoons 1/2 N_2(g) + 3/2\, H_2(g)$, at 298 K is 5.2×10^{-5}. What is the value of K_c at 298 K for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)?$$

[**Hint:** K_c' for reaction $1/2\, N_2(g) + 3/2 H_2(g) \rightleftharpoons NH_3$ is $\frac{1}{K_c}$, *i.e.*, $\frac{1}{5.2 \times 10^{-5}}$

K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, will be $= (K_c')^2$

$$= \left[\frac{1}{5.2 \times 10^{-5}}\right]^2 = 3.7 \times 10^8\ ]$$

2. The value of K_p for the reaction,

$$2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g),$$

is 0.035 atm at 400°C, when the partial pressures are expressed in atmosphere. Calculate the value of K_c for the same reaction.
[**Ans.** 6.342×10^{-4} mol L^{-1}]

3. For the reaction,

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g),$$

the equilibrium constant $K_c = 2.52 \times 10^{-2}$ at 27°C; calculate K_p. (Given, $R = 0.082$ litre-atm deg^{-1} mol^{-1})
[**Ans.** 61.99×10^{-2}]

4. If K_p for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, is 1.64×10^{-4} atm^{-2} at 400°C. What will be the equilibrium constant at 500°C, if heat of reaction in this temperature range is – 105185.8 joule?
[**Ans.** 1.44×10^{-5} atm]

5. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = 0.157$ atm at 300 K. Calculate the value of K_c for the same reaction at the same temperature.
[**Ans.** 6.38×10^{-3} mol L^{-1}]

6. For the reaction, $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, the value of K_c is 1.7×10^{12} at 300 K. Calculate the equilibrium constants for the following reactions at 300 K:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

and $$SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$$

[**Ans.** 2.89×10^{24}, 5.88×10^{-13}]

7. Determine K_p for the following reactions:
(a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$;
$K_c = 23.2$ at 600 K
(b) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K_c = 4.62 \times 10^{-3}$ *M* at 298 K
(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$;
$K_c = 2.8 \times 10^2$ M^{-1} at 1000 K
[**Ans.** (a) 23.2 (b) 11.45 kPa (c) 0.0337 kPa]

8. From the following data at 1000 K:

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g); \quad K_1 = 0.329$$
$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g); \quad K_2 = 2.24 \times 10^{22}$$

Calculate the equilibrium constant for the following reaction:

$$2COCl_2(g) + O_2(g) \rightleftharpoons 2CO_2(g) + Cl_2(g)$$

[**Ans.** 2.43×10^{21}]

9. For the reaction, $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, K_p is $32\,(atm)^{-1/2}$ at 800 K and ΔH for the reaction is −187.9 kJ mol^{-1}. Calculate its value at 900 K, if it is assumed that ΔH remains constant over this range of temperature.
[**Ans.** 1.387 $atm^{-1/2}$]

10. The equilibrium constants for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, at 1727°C and 2227°C are 4.08×10^{-4} and 3.6×10^{-3} respectively. Calculate the enthalpy change for the reaction. (Given, $R = 1.987$ cal.)
[**Ans.** 43273 cal]

11. Calculate the equilibrium constant (K_p) for the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, at 1300 K from the following data: $C(s) + 2H_2O(g) \rightleftharpoons CO_2(g) + 2H_2(g)$;
K_p (1300 K) = 3.9 atm

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g);$$

K_p (1300 K) = 0.7 atm
[**Ans.** 1.91 atm]

[**Hint:** $$\frac{[CO]^2}{[CO_2]} = K_{p\,(\text{net})} = \frac{[CO]^2[H_2O]^2}{[H_2]^2[CO_2]^2} \times \frac{[H_2]^2[CO_2]}{[H_2O]^2} = (0.7)^2 \times 3.9\ ]$$

12. The standard equilibrium constant for the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g),$$

is 1.8×10^{-7} at 298 K. Calculate its $\Delta G°$ value.
[**Ans.** 38.49 kJ mol^{-1}]

13. For the equilibrium, $Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$, equilibrium constants are 3.98×10^{-4} and 1.41×10^{-2} respectively at 350 K and 400 K. Calculate the standard enthalpy of decomposition.
[**Ans.** 83.06 kJ/mol]

14. The equilibrium constant for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g),$$

at 715 K is 6.0×10^{-2}. If in a particular reaction, there are 0.25 mol L^{-1} of H_2 and 0.06 mol L^{-1} of NH_3 present, calculate the concentration of N_2 at equilibrium.

[**Ans.** $[N_2] = 3.84$ mol L^{-1}]

15. One mole of H_2O and one mole of CO were heated in a 10 litre closed vessel at 1260 K. At equilibrium, 40% of water was found to react in the equation,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Calculate the equilibrium constant of the reaction.

[**Ans.** 0.44]

[**Hint:** $\underset{(1-0.4)}{H_2O(g)} + \underset{(1-0.4)}{CO(g)} \rightleftharpoons \underset{0.4}{CO_2(g)} + \underset{0.4}{H_2(g)}$

(at equilibrium)]

16. Two moles of PCl_5 were introduced in a 2 litre flask and heated at 600 K to attain equilibrium. PCl_5 was found to be 40% dissociated into PCl_3 and Cl_2. Calculate the value of K_c.

[**Ans.** $K_c = 0.267$ mole L^{-1}]

17. 0.1 mole of PCl_5 is heated in a litre vessel at 533 K. Determine the concentration of various species present at equilibrium, if the equilibrium constant for the dissociation of PCl_5 at 533 K is 0.414.

[**Ans.** $[PCl_5] = 0.0531$ mol L^{-1}; $[PCl_3] = 0.0469$ mol L^{-1}; $[Cl_2] = 0.0469$ mol L^{-1}]

18. At 1000 K, the equilibrium constant, K_c, for the reaction,

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

is equal to 3.04. If 1 mole of CO and 1 mole of Cl_2 are introduced into a 1 litre box at 1000 K, what will be the final concentration of $COCl_2$ at equilibrium?

[**Ans.** $[COCl_2] = 0.568$ mol L^{-1}]

19. Given, that $K_c = 13.7$ at 546 K for

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, calculate what pressure will develop in a 10 litre box at equilibrium at 546 K when 1.00 mole of PCl_5 is injected into the empty box?

[**Ans.** $P = 8.93$ atm]

[**Hint:** First determine degree of dissociation, then evaluate the total pressure by applying, $P = \frac{n}{V} RT$ where, $n = 1 + \alpha$.]

20. In the following reaction,

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

the amounts of H_2, I_2 and HI are 7.8 g, 203.2 g and 1638.4 g respectively at equilibrium at a certain temperature. Calculate the equilibrium constant of the reaction.

[**Ans.** 0.019]

21. Concentrations of two reactants *A* and *B* are 0.8 mol L^{-1} each. On mixing the two, the reaction sets in at a slow rate to form *C* and *D*.

$$A + B \rightleftharpoons C + D$$

At equilibrium, concentration of *C* was found to be 0.60 mol L^{-1}. Calculate the equilibrium constant.

[**Ans.** $K_c = 9$]

22. 15 moles of hydrogen reacting with 5.2 moles of iodine form 10 g mole of hydrogen iodide. Calculate the equilibrium constant of the reaction.

[**Ans.** $K_c = 50$]

23. In the dissociation of HI, it is found that 20% of the acid is dissociated when equilibrium is reached. Calculate the value of K_p for the equilibrium,

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

[**Ans.** $K_p = 1.56 \times 10^{-2}$]

24. The equilibrium constant of the reaction,

$$A + B \rightleftharpoons C + D$$

is unity. What per cent of *A* will be transformed if three moles of *A* are mixed with 5 moles of *B*?

[**Ans.** 62.5%]

[**Hint:** At equilibrium,

$$\underset{(3-x)}{A} + \underset{(5-x)}{B} \rightleftharpoons \underset{x}{C} + \underset{x}{D}$$

Find the value of x. % of *A* transformed $= \frac{x}{3} \times 100$]

25. 2 moles of *A* and 3 moles of *B* are mixed and the reaction is carried at 400°C according to the equation,

$$A + B \rightleftharpoons 2C$$

the equilibrium constant of the reaction is 4. Find the concentration of *C* at equilibrium.

[**Ans.** 2.4 mole]

26. A combination of hydrogen and iodine is carried out by heating 60 mL of hydrogen and 42 mL of iodine in a closed vessel. At equilibrium 28 mL of hydroiodic acid is present in the vessel. Calculate the degree of dissociation of HI.

[**Hint:** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

At equilibrium $(60-14)$ $(42-14)$ 28 mL

$$K_c = \frac{28 \times 28}{46 \times 28} = \frac{14}{23}$$

$$\underset{1-x}{2HI(g)} \rightleftharpoons \underset{x/2}{H_2(g)} + \underset{x/2}{I_2(g)}$$

(x is the degree of [illegible]iation)

$$K'_c = \frac{x/2 \times x/2}{(1-x)^2} =$$ [illegible]

or $$\frac{x}{2(1-x} \quad \overline{\frac{23}{14}} = 1.2817$$

$x = 0.72$]

27. One mole of H_2, 2 moles of I_2 and 3 moles of HI are injected in a one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium when K_c is 45.9?

[**Ans.** $[H_2] = 0.316$ mol L^{-1}, $[I_2] = 1.316$ mol L^{-1}, $[HI] = 4.368$ mol L^{-1}]

[**Hint:** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

At equilibrium $(1-x)$ $(2-x)$ $(3+2x)$

$$K_c = \frac{(3+2x)^2}{(1-x)(2-x)} = 45.9,$$

On solving, $x = 0.684$ mole]

28. Four moles of hydrogen iodide were taken in a 10 litre flask kept at 800 K. When equilibrium was attained, the mixture was found to contain 0.42 mole of iodine. Calculate the equilibrium constant for dissociation of HI.

[**Ans.** $K_c = 1.76 \times 10^{-2}$]

29. The equilibrium constant, K_c, for the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 56.8 at 800 K. When the mixture was analysed, it was found to contain 0.316 mol/L HI at 800 K. What are the concentrations of H_2 and I_2 at equilibrium? (Assume that initial concentrations of H_2 and I_2 were the same.)

[**Ans.** $[H_2] = [I_2] = 0.0419$ mol L^{-1}]

30. At same temperature and under a pressure of 4 atm, PCl_5 is 10% dissociation. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same. **(IIT 1996)**

[**Ans.** 0.96 atm]

31. The reaction of the formation of phosgene gas from CO and Cl_2 is as follows:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

In an experiment, starting with equimolecular CO and Cl_2 in a 250 mL flask, the equilibrium mixture on analysis is found to contain 0.05 mole CO, 0.05 mole Cl_2 and 0.15 mole $COCl_2$. Calculate the equilibrium constant of the reaction.

[**Ans.** $K_c = 15\ \text{mol}^{-1}\text{L}$]

32. At 35°C and 1 atmospheric pressure, N_2O_4 is 27.2% dissociated into NO_2. What is the value of K_p under these conditions?

[**Ans.** $K_p = 0.3195$ atm]

33. Nitrogen and hydrogen are added to a 5 litre flask under pressure. The flask was sealed and heated. The equilibrium mixture contained 19.0 g of ammonia, 0.16 g of hydrogen and 3.4 g of nitrogen. Calculate the equilibrium constant, K_c, of the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

[**Ans.** $K_c = 5.02 \times 10^5\ \text{mol}^{-2}\text{L}^2$]

34. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm pressures respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases. **(IIT 1991)**

[**Hint:** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_p = \frac{(p_{NO_2})^2}{(p_{N_2O_4})} = \frac{(1.1)^2}{0.28} = 4.32 \text{ atm}$$

When the volume is doubled, the pressure becomes half and the system again adjusts to achieve equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$\left(\frac{0.28}{2} - x\right)\left(\frac{1.1}{2} + 2x\right)$$

$$(0.14 - x)\ (0.55 + 2x)$$

$$K_p = \frac{(0.55 + 2x)^2}{(0.14 - x)} = 4.32$$

$$x = 0.045$$

$$p_{N_2O_4} = (0.14 - 0.045) = 0.095 \text{ atm}$$

$$p_{NO_2} = (0.55 + 2 \times 0.045) = 0.64 \text{ atm}]$$

35. At 21.5°C and a total pressure of 0.0787 atm, N_2O_4 is 48.3% dissociated into NO_2. At what total pressure will the per cent dissociation be 10.0%?

[**Ans.** 2.37 atm]

[**Hint:** First calculate the value of K_p and then evaluate the pressure by applying,

$$K_p = \frac{\left(\frac{0.2}{1.1}\right)^2 P^2}{\left(\frac{0.9}{1.1}\right) P} = 0.0959]$$

36. At 3000 K, chlorine gas dissociates into chlorine atoms in an equilibrium reaction for which $K = 0.37$. What is the concentration of chlorine atoms in a vessel that originally contained 1.0 mol L^{-1} of molecular chlorine?

[**Ans.** [Cl] = 0.54 mol L^{-1}]

37. The equilibrium constant K_p for the reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

at 1500°C is 120. If N_2 and O_2 at an initial pressure of 0.25 atm each are maintained at 1500°C till equilibrium is established, calculate the partial pressure of N_2, O_2 and NO in the equilibrium mixture.

[**Ans.** $p_{N_2} = p_{O_2} = 0.04$; $p_{NO} = 0.42$ atm]

38. Find K_p for the following reaction,

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

If sulphuryl chloride decomposes to the extent of 91.2% at 102°C and total pressure 1 atmosphere.

[**Ans.** $K_p = 4.94$ atm]

39. If carbon dioxide is 2% dissociated at 1800°C and 1 atmospheric pressure,

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

Calculate K_p for the reaction.

[**Ans.** $K_p = 4.12 \times 10^{-6}$ atm]

40. At a certain temperature, K_c for the reaction,

$$POCl_3(g) \rightleftharpoons POCl(g) + Cl_2(g)$$

is 0.30. If 0.6 mole of $POCl_3$ is placed in a closed vessel of 3.0 litre capacity at this temperature, what percentage of it will be dissociated when equilibrium is established?

[**Ans.** 68.5%]

41. A reaction carried out by 1 mole of N_2 and 3 moles of H_2 shows at equilibrium the mole fraction of NH_3 as 0.012 at 500°C and total pressure 10 atmosphere; calculate K_p. Also report the pressure at which mole percentage of NH_3 in equilibrium mixture increased to 10.4.

[**Ans.** $K_p = 1.431 \times 10^{-5}\ \text{atm}^{-2}$; $P = 105.41$ atm]

42. The degree of dissociation of N_2O_4 into NO_2 at one atmosphere and 40°C is 0.310. Calculate its K_p at 40°C. Also report degree of dissociation at 10 atmospheric pressure at the same temperature.

[**Ans.** $K_p = 0.425$ atm; degree of dissociation = 0.1025]

43. The vapour density of PCl_5 at 200°C and 252°C are 70.2 and 57.2 respectively at one atmosphere. Calculate its value of dissociation constant at these temperatures.

[**Ans.** $K_p = 0.307, 1.19$]

44. Some solid NH_4HS is placed in a flask containing 0.5 atm of NH_3. What would be the pressures of NH_3 and H_2S when equilibrium is reached?

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g); \quad K_p = 0.11$$

[**Ans.** $NH_3 = 0.83$ atm; $H_2S = 0.33$ atm] **(MLNR 1994)**

[**Hint:** $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

At equilibrium $\qquad x + 0.5 \qquad x$

$$K_p = (x + 0.5)x = 0.11]$$

45. $SnO_2(s) + 2H_2(g) \rightleftharpoons 2H_2O_{(steam)} + Sn(s)$

For the above reaction find K_p, if at 900 K, the equilibrium mixture contains 45% H_2 by volume.

[**Ans.** $K_p = 1.5$]

46. The equilibrium constant for the reaction is 9.40 at 900°C.

$$S_2(g) + C(s) \rightleftharpoons CS_2(g)$$

Calculate the pressure of two gases at equilibrium, when 1.42 atm of S_2 and excess of $C(s)$ come to equilibrium.

[**Ans.** $p_{CS_2} = 1.28$ atm; $p_{S_2} = 0.14$ atm]

47. For the reaction,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$K_p = 1.16$ atm at 800°C. If 20.0 g of $CaCO_3$ were kept in a 10 litre container and heated up to 800°C, what percentage of $CaCO_3$ would remain unreacted at equilibrium?

[**Ans.** 34%]

[**Hint:** $K_p = p_{CO_2} = 1.16$ atm

$$n = \frac{p_{CO_2} \times V}{RT} = \frac{1.16 \times 10}{0.0821 \times 1073} = 0.132 \text{ mol}$$

$$\text{Initial amount of } CaCO_3 = \frac{20.0}{100} = 0.2 \text{ mol}$$

$$\text{Unreacted } CaCO_3 = 0.2 - 0.132 = 0.068 \text{ mol}$$

$$\% \text{ unreacted } CaCO_3 = \frac{0.068}{0.2} \times 100 = 34$$]

48. In the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_p.

[**Ans.** $K_p = 16$ atm]

49. A mixture of 0.373 atm of $NO(g)$ and 0.310 atm of $Cl_2(g)$ is prepared at 500°C. The reaction, $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$, occurs. The total pressure at equilibrium is 0.544 atm. Determine K_p of the reaction.

[**Ans.** $K_p = 50.08 \text{ atm}^{-1}$]

50. For the reaction,

$$3A(g) + B(g) \rightleftharpoons 2C(g)$$

at a given temperature, K_c is 9.0. What must be the volume of a flask if the mixture of 2.0 moles each of A, B and C is obtained at equilibrium?

[**Ans.** $V = 6$ litre]

51. At 700 K hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8. Calculate the amount of H_2, Br_2 and HBr at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of bromine is heated to 700 K. **(IIT 1995)**

[**Hint:** $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

Initial 0.6 0.2

Since, equilibrium constant is very high the reaction will be complete and bromine is consumed.

Thus, 0.2 mole of Br_2 and 0.2 mole of H_2 will be consumed to produce 0.4 mole of HBr. This can be calculated by applying law of mass action.

$$\frac{[HBr]^2}{[H_2][Br_2]} = K \text{ or } \frac{4x^2}{(0.6-x)(0.2-x)} = 5 \times 10^8$$

$$x = 0.6 \text{ or } 0.2$$

The value of x cannot be more than 0.2 as Br_2 is a limiting reactant. Thus, when reaction is complete,

$H_2 = (0.6 - 0.2) = 0.4$ mol; $Br_2 = 0$; HBr = 0.4 mol

At this point some HBr will dissociate.

$$\begin{array}{lccc} & 2HBr(g) & \rightleftharpoons H_2(g) & + \; Br_2(g) \\ \text{At equilibrium} & (0.4 - 2x) & (0.4 + x) & (x) \end{array}$$

$$\frac{(0.4 + x) \times x}{(0.4 - 2x)} = \frac{1}{5 \times 10^8}$$

or $$\frac{0.4x}{0.4} = 2 \times 10^{-10} (\text{since, } x \text{ is very small})$$

or $$x = 2 \times 10^{-10}$$

$[Br_2] = 2 \times 10^{-10}$ mol; $[H_2] = 0.4$ mol; $[HBr] = 0.4$ mol]

52. One mole of H_2, two moles of I_2 and three moles of HI are injected in a 1 litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 490°C? The equilibrium constant for the reaction at 490°C is 45.9.

[**Ans.** $[H_2] = 0.316$; $[I_2] = 1.316$; $[HI] = 4.36$ mol]

53. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows:

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

At equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original total pressure.

[**Ans.** $^{31}/_{27}$]

54. Two solid compounds A and C dissociate into gaseous product at temperature T as follows:

(i) $A(s) \rightleftharpoons B(g) + D(g)$

(ii) $C(s) \rightleftharpoons E(g) + D(g)$

At 20°C, pressure over excess solid A is 50 atm [illegible] that over excess solid C is 68 atm. Find the total pressure [illegible] gases over the solid mixture.

[**Ans.** 84.38 atm]

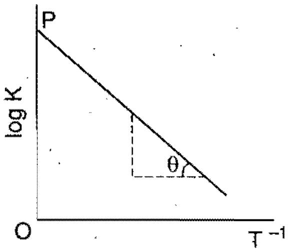
55. Variation of equilibrium constant K with temperature T is given by van't Hoff equation,

$$\log K = \log A - \frac{\Delta H°}{2.303\, RT}$$

A graph between $\log K$ and T^{-1} was a straight line as shown in the figure and having $\theta = \tan^{-1}$ (0.5) and $OP = 10$. Calculate:

(a) $\Delta H°$ (standard heat of reaction) when $T = 298$ K,

(b) A (pre-exponential factor),



(c) Equilibrium constant K at 298 K,

(d) K at 798 K, if $\Delta H°$ is independent of temperature.

[**Ans.** (a) 9.574 J mol^{-1}; (b) $A = 10^{10}$; (c) 9.96×10^9; (d) 9.98×10^9]

[**Hint:** (a) $\log K = \log A - \frac{\Delta H^\circ}{2.303RT}$

It is equation of straight line of the type $y = c + mx$

$$\text{Slope 'm'} = \tan\theta = \frac{\Delta H^\circ}{2.303R}$$

$$0.5 = \frac{\Delta H^\circ}{2.303 \times 8.314}$$

$$\Delta H^\circ = 9.574 \text{ J mol}^{-1}$$

(b) Intercept 'c' = $\log A = 10$

$\therefore$ $A = 10^{10}$

(c) $$\log K = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$K = 9.96 \times 10^9$$

(d) $$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\frac{K_2}{9.96 \times 10^9} = \frac{9.574}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{798}\right)$$

On solving, $K_2 = 9.98 \times 10^9$]

56. When 0.112 mole of NO and 18.22 g of bromine are placed in a 1.00 L reaction vessel and sealed, the mixture is heated to 350 K and the following equilibrium is established:

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

If the equilibrium concentration of nitrosyl bromide is 0.0824 M, what is K_c?

[**Ans.** 106.74]

[**Hint:**

$$\begin{array}{llll} & 2NO(g) + & Br_2(g) \rightleftharpoons & 2NOBr(g); \; n_{Br_2} = \frac{18.22}{160} = 0.1138 \\ t=0 & 0.112 & 0.1138 & 0 \\ t_{eq.} & \left[\frac{0.112 - 2x}{1}\right] & \left[\frac{0.1138 - x}{1}\right] & \frac{2x}{1} \end{array}$$

$$2x = 0.0824$$

$\therefore$ $[NO] = 0.112 - 2x$

$$= 0.112 - 0.0824 = 0.0296\,M$$

$$[Br_2] = 0.1138 - \frac{0.0824}{2} = 0.0726\,M$$

$$K_c = \frac{[NOBr]^2}{[NO]^2[Br_2]} = \frac{[0.0824]^2}{[0.0296]^2[0.0726]} = 106.74\,]$$

57. Solid ammonium carbamate is put into a closed container and allowed to come to equilibrium with the gaseous products at 35°C, the total pressure is found to be 0.30 atmospheres. What is the value of K_p for this reaction at 35°C?

[**Ans.** 4×10^{-3}]

58. K_p for the equilibrium of,

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

at 1000°C is 0.403, if CO(g), at a pressure of 1.0 atm and excess of FeO(s) are placed in a container at 1000°C. What are the pressures of CO(g) and $CO_2(g)$ when the equilibrium is attained?

[**Ans.** $p_{CO} = 0.713$ atm; $p_{CO_2} = 0.287$ atm]

59. A mixture of 1.0 mole of sulphur and 0.2 mole of hydrogen is heated at 90°C in a one litre flask. The equilibrium constant for the formation of hydrogen sulphide, $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ is 6.8×10^{-2}. Calculate the partial pressure of H_2S at equilibrium.

[**Ans.** $p_{H_2S} = 0.397$ atm]

[**Hint:** First determine the initial pressure of H_2 by applying

$$p_0 = \frac{n}{V} \cdot RT = 5.953 \text{ atm}]$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. A reversible reaction is one which:
(a) proceeds in one direction
(b) proceeds in both directions
(c) proceeds spontaneously
(d) all the statements are wrong

2. An example of reversible reaction is:
(a) $Pb(NO_3)_2 + 2NaI = PbI_2 + 2NaNO_3$
(b) $AgNO_3 + HCl = AgCl + HNO_3$
(c) $2Na + 2H_2O = 2NaOH + H_2$
(d) $KNO_3 + NaCl = KCl + NaNO_3$

3. Which one of the following is not a reversible reaction?
(a) $2HI(g) = H_2(g) + I_2(g)$
(b) $PCl_5(g) = PCl_3(g) + Cl_2(g)$
(c) $2KClO_3(s) = 2KCl(s) + 3O_2(g)$
(d) $CaCO_3(s) = CaO(s) + CO_2(g)$

4. Which one is not correct for a reversible reaction?
(a) The reaction is never completed
(b) The reactants are present in the initial stage but after that the reactants and products are always present in the reaction mixture
(c) At equilibrium only products are present
(d) When the reaction is carried out in closed space, it attains equilibrium state after suitable time

5. The law of mass action was proposed by:
(a) Guldberg and Waage (b) Le Chatelier and Braun
(c) Kossel and Lewis (d) van't Hoff

6. The rate at which a substance reacts, depends on its:
(a) active mass (b) molecular mass
(c) equivalent mass (d) total volume

7. Active mass is defined as:
(a) number of g equivalent per unit volume
(b) number of g mol per litre
(c) amount of substance in gram per unit volume
(d) number of g mole in 100 litre

8. 8.50 g of NH_3 is present in 250 mL volume. Its active mass is:
(a) $1.0\,M\,L^{-1}$ (b) $0.5\,M\,L^{-1}$ (c) $1.5\,M\,L^{-1}$ (d) $2.0\,M\,L^{-1}$

9. Theory of 'active mass' indicates that the rate of a chemical reaction is directly proportional to the: **[PET (MP) 1990]**
(a) equilibrium constant (b) properties of reactants
(c) volume of apparatus (d) concentration of reactants

10. The state of equilibrium refers to: **[PMT (Pb.) 1993]**
(a) state of rest (b) dynamic state
(c) stationary state (d) state of inertness

11. In a reversible chemical reaction equilibrium is said to have been established when the:
(a) concentrations of reactants and products are equal
(b) opposing reactions cease
(c) speeds of opposing reactions become equal
(d) temperatures of opposing reactions are equal

12. A chemical reaction, $A \rightleftharpoons B$, is said to be in equilibrium when:
(a) rate of forward reaction is equal to rate of backward reaction
(b) conversion of A to B is only 50% complete
(c) complete conversion of A to B has taken place
(d) only 25% conversion of A to B has taken place

13. The reaction between barium chloride and sodium sulphate goes to completion because:
(a) barium sulphate is almost insoluble
(b) the solubility of barium chloride decreases
(c) lattice energy of barium sulphate is very high
(d) the reaction is irreversible in nature

14. What is the equilibrium constant expression for the reaction,

$$P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)?$$

(Jamia Millia Islamia Engg. Ent. 2007; UPSEE 2007)

(a) $K_c = \dfrac{[P_4O_{10}]}{[P_4]\,[O_2]^5}$ (b) $K_c = \dfrac{[P_4O_{10}]}{5\,[P_4]\,[O_2]}$

(c) $K_c = [O_2]^5$ (d) $K_c = \dfrac{1}{[O_2]^5}$

15. Equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, is correctly given by the expression:

(a) $K_c = \dfrac{[H_2][I_2]}{[HI]}$ (b) $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

(c) $K_c = \dfrac{[HI]}{[H_2][I_2]}$ (d) $K_c = \dfrac{[2HI]}{[H_2][I_2]}$

16. Equilibrium constant for the reaction, $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$, is correctly given by the expression:

(a) $K = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$ (b) $K = \dfrac{[2NOCl]}{[2NO][Cl_2]}$

(c) $K = \dfrac{[NO]^2 + [Cl_2]}{[NOCl]}$ (d) $K = \dfrac{[NO]^2[Cl_2]}{[NOCl]^2}$

17. For the system, $3A + 2B \rightleftharpoons C$, the expression for equilibrium constant is: **[JEE (WB) 2007]**

(a) $\dfrac{[A]^3[B]^2}{[C]}$ (b) $\dfrac{[C]}{[A]^3[B]^2}$ (c) $\dfrac{[A]^2[B]^3}{[C]}$ (d) $\dfrac{[C]}{[A][B]}$

18. The equilibrium constants of the reactions,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

and $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

are K_1 and K_2 respectively. The relationship between K_1 and K_2 is:

(a) $K_1 = K_2$ (b) $K_2^2 = K_1$
(c) $K_1^2 = K_2$ (d) $K_2 = \sqrt{K_1}$

19. The equilibrium constant for the given reaction is 100.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

What is the equilibrium constant for the reaction given below:

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$$

(EAMCET 2009)

(a) 10 (b) 1
(c) 0.1 (d) 0.01

20. For the reaction, $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$, $K_c = 1.8 \times 10^{-6}$ at 185°C. The value of K_c at 185°C for the reaction;

$$NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g) \text{ is:}$$ **(MLNR 1993)**

(a) 0.9×10^6 (b) 1.95×10^{-3}
(c) 1.95×10^3 (d) 7.5×10^2

21. The equilibrium constant for the synthesis of HI at 490°C is 50.0. The value of K for the dissociation of HI will be: **(IIT 1990)**
(a) 0.02 (b) 50.0 (c) 0.50 (d) 0.20

22. Consider the following equilibrium,

$$SO_2(g) + \frac{1}{2}O_2(g) \overset{K_1}{\rightleftharpoons} SO_3(g);$$

$$2SO_3(g) \overset{K_2}{\rightleftharpoons} 2SO_2(g) + O_2(g)$$

What is the relation between K_1 and K_2? **[PET (MP) 1993]**

(a) $K_1 = \dfrac{1}{K_2}$ (b) $K_1 = \dfrac{1}{\sqrt{K_2}}$ (c) $K_1 = K_2$ (d) $K_1 = \dfrac{1}{K_2^2}$

23. For the reaction $AB(g) \rightleftharpoons A(g) + B(g)$, AB is 33%, dissociated at a total pressure of P. Therefore, P is related to K_p by one of the following option : **[AMU (Med.) 2010]**
(a) $P = K_p$ (b) $P = 3K_p$
(c) $P = 4K_p$ (d) $P = 8K_p$

[Hint:

$$\begin{array}{lccc} & AB(g) & \rightleftharpoons A(g) & + B(g) \\ t_0 & 1 & 0 & 0 \\ t_{eq} & 1-\frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{array}$$

$$p_{AB} = \frac{2/3}{4/3} \times p = \frac{p}{2};$$

$$p_A = p_B = \frac{1/3}{4/3} \times p = \frac{p}{4}$$

$$K_p = \frac{\frac{p}{4} \times \frac{p}{4}}{\frac{p}{2}} = \frac{p}{8}$$

$$p = 8K_p\ ]$$

24. For a system, $A + 2B \rightleftharpoons C$, the equilibrium concentrations are $[A] = 0.06$, $[B] = 0.12$ and $[C] = 0.216$. The K_c for the reaction is:
(a) 125 (b) 415
(c) 4×10^{-3} (d) 250

25. The equilibrium concentrations of x, y and yx_2 are 4, 2 and 2 respectively for the equilibrium $2x + y \rightleftharpoons yx_2$. The value of equilibrium constant, K_c is: **(EAMCET 1990)**
(a) 0.625 (b) 6.25 (c) 0.0625 (d) 62.5

26. 4 mole of A are mixed with 4 mole of B when 2 mole of C are formed at equilibrium, according to the reaction,

$$A + B \rightleftharpoons C + D$$

the equilibrium constant is: **(CPMT 1992)**
(a) $\sqrt{2}$ (b) 2 (c) 1 (d) 4

27. If the equilibrium constant of the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.25, the equilibrium constant of $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, under similar conditions, will be:
(a) 4.0 (b) 3.0 (c) 2.0 (d) 1.0

28. HI was heated in a sealed tube at 400°C till the equilibrium was reached. HI was found to be 22% decomposed. The equilibrium constant for dissociation is:
(a) 1.99 (b) 0.0199 (c) 0.0796 (d) 0.282

29. For a reversible reaction if the concentrations of the reactants are doubled at a definite temperature, then equilibrium constant will: **(CPMT 1990; MLNR 1992)**
(a) also be doubled (b) be halved
(c) become one-fourth (d) remain the same

30. In a reversible gaseous system, molar concentrations (active masses) of reactants and products are proportional to:
(a) partial pressure
(b) total pressure
(c) amounts of reactants and products
(d) none of the above

31. At 3000 K, the equilibrium partial pressure of CO_2, CO and O_2 are 0.6, 0.4 and 0.2 atmospheres respectively. K_p for the reaction,

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g) \text{ is :}$$

[BHU (Mains) 2010]
(a) 0.088 (b) 0.0533 (c) 0.133 (d) 0.177

32. Equilibrium constant depends on:
(a) the actual quantities of reactants and products
(b) the presence of a catalyst
(c) temperature
(d) the presence of inert material

33. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant, K_p, changes with:
(a) total pressure
(b) catalyst
(c) the amounts of H_2 and I_2 taken
(d) temperature

34. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
The equilibrium constant of the above reaction is 6.4 at 300 K. If 0.25 mole each of H_2 and I_2 are added to the system, the equilibrium constant will be: **(CET Karnataka 2009)**
(a) 0.8 (b) 3.2 (c) 1.6 (d) 6.4

35. 3.1 mol of $FeCl_3$ and 3.2 mol of NH_4SCN are added to one litre of water. At equilibrium, 3.0 mol of $FeSCN^{2+}$ are formed. The equilibrium constant K_c of the reaction :

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$$

will be : **[BHU (Screening) 2010]**
(a) 6.66×10^{-3} (b) 0.30
(c) 3.30 (d) 150

[Hint:

	Fe^{3+} +	SCN^- $\rightleftharpoons$	$FeSCN^{2+}$
t_0	3.1	3.2	0
$t_{eq.}$	$\frac{0.1}{1}$	$\frac{0.2}{1}$	$\frac{3}{1}$

$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$

$$= \frac{3}{0.1 \times 0.2} = 150]$$

36. K_p and K'_p are the equilibrium constants of the two reactions, given below:

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Therefore, K_p and K'_p are related by **[AMU (PMT) 2009]**
(a) $K_p = K'^2_p$ (b) $K_p = \sqrt{K'_p}$
(c) $K_p = 2K'_p$ (d) $K_p = K'_p$

37. In which of the following equilibrium K_c and K_p are not equal? **[CBSE (PMT) 2010]**
(a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(b) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(d) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

38. Select the correct statement from the following:
(a) equilibrium constant changes with addition of a catalyst
(b) catalyst increases the rate of forward reaction
(c) the ratio of mixture at equilibrium does not change by catalyst
(d) catalysts are active only in solution

39. In which of the following, the reaction proceeds towards completion? **(MLNR 1990)**
(a) $K = 1$ (b) $K = 10^{-2}$
(c) $K = 10$ (d) $K = 10^3$

40. For the following reaction at 250°C, the value of K_c is 26, then the value of K_p at the same temperature will be:
$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ **(MLNR 1990; CBSE 1993)**
(a) 0.57 (b) 0.61 (c) 0.83 (d) 0.91

41. In the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the amounts of PCl_5, PCl_3 and Cl_2 are 2 mole each at equilibrium and the total pressure is 3 atmospheres. The equilibrium constant, K_p, is: **(IIT 1991)**
(a) 1 atm (b) 2 atm (c) 3 atm (d) 1.5 atm

42. In which of the following K_p is less than K_c?
(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

43. For a reversible reaction, the rate constants for the forward and backward reactions are 2.38×10^{-4} and 8.15×10^{-5} respectively. The equilibrium constant for the reaction is:
(a) 0.342 (b) 2.92
(c) 0.292 (d) 3.42

44. The equilibrium constant in a reversible reaction at a given temperature:

(a) depends on the initial concentration of the reactants
(b) depends on the concentration of products at equilibrium
(c) it is not characteristic of the reaction
(d) does not depend on initial concentrations

45. 1.0 g mole of ethyl alcohol and 1.0 g mole of acetic acid are mixed. At equilibrium 0.666 g mole of the ester is present. The value of equilibrium constant is: **[PET (MP) 1993]**

(a) $\frac{1}{4}$ (b) $\frac{1}{2}$ (c) 2 (d) 4

46. The equilibrium constant of the reaction,

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

is 4. If one mole of each of acetic acid and ethyl alcohol are heated in presence of a little concentrated H_2SO_4, at equilibrium the amount of ester present is: **[PET (MP) 1992]**

(a) 1 mole (b) 2 mole
(c) $\frac{2}{3}$ mole (d) $\frac{1}{2}$ mole

47. If different quantities of ethanol and acetic acid are used in the following reversible reaction,

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

the equilibrium constant will have values which will be?

(a) Different in all cases
(b) Same in all cases
(c) Higher in cases where higher concentration of ethanol is used
(d) Higher in cases where higher concentration of acetic acid is used

48. The reaction,

$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

is begun with concentration of A and B both at initial value of 1M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression : **[CBSE (PMT) 2010]**

(a) $[(0.75)^3(0.25)] \div [(1.00)^2(1.00)]$
(b) $[(0.75)^3(0.25)] \div [(0.50)^2(0.75)]$
(c) $[(0.75)^3(0.25)] \div [(0.50)^2(0.25)]$
(d) $[(0.75)^3(0.25)] \div [(0.75)^2(0.25)]$

[**Hint:**

	$2A(g)$	+ $B(g)$	$\rightleftharpoons$	$3C(g)$	+ $D(g)$
t_0	1	1		0	0
$t_{eq.}$	0.50	0.75		0.75	0.25

$$K = \frac{[C]^3[D]}{[A]^2[B]} = \frac{(0.75)^3(0.25)}{(0.50)^2(0.75)}]$$

49. The decomposition of N_2O_4 to NO_2 is carried at 280 K in chloroform. When equilibrium has been established, 0.2 mole of N_2O_4 and 2×10^{-3} mole of NO_2 are present in 2 litre solution. The equilibrium constant for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, is:

(a) 1×10^{-2} (b) 2×10^{-3}
(c) 1×10^{-5} (d) 2×10^{-5}

50. The unit of equilibrium constant, K_c, for the reaction $A + B \rightleftharpoons C$ would be:

(a) mol^{-1} L (b) mol L^{-1} (c) mol L (d) no unit

51. For which of the following reactions does the equilibrium constant depend on the units of concentration?

(a) $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$
(b) $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(c) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(d) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

52. The units of K_p in the following reaction are:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) atm (b) atm^{-2} (c) atm^2 (d) atm^{-1}

53. The equilibrium of formation of phosgene is represented as:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

The reaction is carried out in a 500 mL flask. At equilibrium 0.3 mole of phosgene, 0.1 mole of CO and 0.1 mole of Cl_2 are present. The equilibrium constant of the reaction is:

(a) 30 (b) 15 (c) 5 (d) 3

54. In an equilibrium reaction, for which $\Delta G° = 0$, the equilibrium constant K should be equal to:

(a) zero (b) 10 (c) 1 (d) 2

55. The equilibrium constant K_p for the homogeneous gaseous reaction is 10^{-3}. The standard Gibbs free energy change $\Delta G°$ for the reaction at 27°C (using $R = 2$ cal K^{-1} mol^{-1}) is:

(a) zero (b) − 1.8 kcal
(c) − 4.154 kcal (d) + 4.154 kcal

56. At 500 K, the equilibrium constant for reaction $cis\text{-}C_2H_2Cl_2 \rightleftharpoons trans\text{-}C_2H_2Cl_2$ is 0.6. At the same temperature, the equilibrium constant for the reaction $trans\text{-}C_2H_2Cl_2 \rightleftharpoons cis\text{-}C_2H_2Cl_2$, will be:

(a) 1.67 (b) 0.6 (c) 1.76 (d) 1.64

57. Which one of the following oxides is most stable? The equilibrium constants are given at the same temperature:

(a) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g)$; $K = 1.2 \times 10^{34}$
(b) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$; $K = 3.5 \times 10^{35}$
(c) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $K = 2.2 \times 10^{30}$
(d) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K = 6.71 \times 10^{16}$

58. In a chemical equilibrium, $K_c = K_p$ when: **[CEE (Bihar) 1992]**

(a) the number of molecules entering into a reaction is more than the number of molecules produced
(b) the number of molecules entering into the reaction is equal to the number of molecules produced
(c) the number of molecules entering into the reaction is less to the number of molecules produced
(d) none of the above

59. In a general reaction, $A + B \rightleftharpoons AB$, which value of equilibrium constant most favours the production of AB?

(a) 9.0×10^{-3} (b) 3.5×10^{-3}
(c) 4.0×10^{-7} (d) 4.0×10^{-12}

60. During thermal dissociation of a gas, the vapour density:

(a) remains the same
(b) increases
(c) decreases
(d) increases in some cases and decreases in others

61. The vapour density of fully dissociated NH_4Cl would be:
(a) less than half of the vapour density of pure NH_4Cl
(b) double of the vapour density of pure NH_4Cl
(c) half of the vapour density of pure NH_4Cl
(d) one-third of the vapour density of pure NH_4Cl

62. In the dissociation of $2HI \rightleftharpoons H_2 + I_2$, the degree of dissociation will be affected by:
(a) increase of temperature (b) addition of an inert gas
(c) addition of H_2 and I_2 (d) increase of pressure

63. In lime kilns, the following reversible reaction,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

proceeds to completion because of: **(CPMT 1990)**
(a) high temperature
(b) CO_2 escapes
(c) low temperature
(d) molecular mass of CaO is less than that of $CaCO_3$

64. The equilibrium constant for the reaction,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g), \text{ is:}$$

(a) $K_c = \dfrac{1}{[CO_2]}$ (b) $K_c = [CO_2]$
(c) $K_c = \dfrac{[CaO][CO_2]}{[CaCO_3]}$ (d) $K_c = \dfrac{[CaCO_3]}{[CaO][CO_2]}$

65. For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressure of CO_2 and CO are 2.0 and 4.0 atm, respectively, at equilibrium. The K_p of the reaction is: **(IIT 1992)**
(a) 0.5 (b) 4.0
(c) 32.0 (d) 8.0

66. Iron fillings and water were placed in a 5 litre vessel and sealed. The tank was heated to 1000°C. Upon analysis the tank was found to contain 1.1 g of hydrogen and 42.5 g of water vapour. If the reaction in the tank is represented by,

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

the value of equilibrium constant, K_c, is:
(a) 30 (b) 0.03
(c) 3 (d) 0.003

67. Ammonium hydrogen sulphide is contained in a closed vessel at 313 K when total pressure at equilibrium is found to be 0.8 atm. The value of K_p for the reaction, $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ is:
(a) 0.16 (b) 1.6 (c) 0.016 (d) 16

68. Variation of K with temperature as given by van't Hoff equation can be written as:
(a) $\log \dfrac{K_2}{K_1} = -\dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$
(b) $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$
(c) $\log \dfrac{K_2}{K_1} = -\dfrac{\Delta H}{2.303R}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$
(d) none of the above

69. When any system in equilibrium is subjected to a change in pressure, concentration or temperature, the equilibrium is shifted in the direction which tends to undo the effect of the change. This statement is known as:
(a) First law of thermodynamics
(b) Le Chatelier's principle
(c) Hess's law
(d) Ostwald's law

70. Le Chatelier's principle is applicable to:
(a) only homogeneous chemical reversible reactions
(b) only heterogeneous chemical reversible reactions
(c) only physical equilibria
(d) all systems, chemical or physical, in equilibrium

71. In the melting of ice, which one of the conditions will be more favourable?
(a) High temperature and high pressure
(b) Low temperature and low pressure
(c) Low temperature and high pressure
(d) High temperature and low pressure

72. Solubility of a gas in liquid increases on:
(a) addition of a catalyst (b) decreasing of pressure
(c) increasing of pressure (d) increasing of temperature

73. When KOH is dissolved in water, heat is evolved. If the temperature is raised, the solubility of KOH:
(a) increases (b) decreases
(c) remains the same (d) cannot be predicted

74. The yield of product in the reaction,

$$A_2(g) + 2B(g) \rightleftharpoons C(g) + Q \text{ kJ}$$

would be higher at:
(a) low temperature and high pressure
(b) high temperature and high pressure
(c) low temperature and low pressure
(d) high temperature and low pressure

75. Manufacture of ammonia from the elements is represented by,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 22.4 \text{ kcal}$$

The maximum yield of ammonia will be obtained when the process is made to take place:
(a) at low pressure and high temperature
(b) at low pressure and low temperature
(c) at high pressure and high temperature
(d) at high pressure and low temperature

76. In the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + X$ cal, most favourable conditions of temperature and pressure for greater yield of SO_3 are:
(a) low temperature and low pressure
(b) high temperature and low pressure
(c) high temperature and high pressure
(d) low temperature and high pressure

77. What is the direction of a reversible reaction when one of the products of the reaction is removed?
(a) The reaction moves towards right hand side
(b) The reaction moves towards left hand side
(c) The reaction moves equally on both the sides
(d) The reaction stops

78. In the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93.6$ kJ, the yield of ammonia does not increase when:
(a) pressure is increased
(b) pressure is decreased
(c) temperature is lowered
(d) volume of the reaction vessel is decreased

79. A cylinder provided with a piston has some PCl_5 which is in equilibrium with PCl_3 and Cl_2. The system is compressed with the help of piston. Indicate the correct statement:
(a) some more PCl_5 will decompose
(b) the system remains unaffected
(c) PCl_3 and Cl_2 will combine to form PCl_5
(d) explosion occurs

80. In the manufacture of nitric oxide, the forward reaction is favoured by:
(a) high pressure (b) low pressure
(c) high temperature (d) low temperature

81. The reaction,

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g); \Delta H = -32.7 \text{ kcal}$$

is carried out in a vessel. The equilibrium concentration of C_2H_4 can be increased by:
(a) increasing the temperature
(b) decreasing the pressure
(c) removing some hydrogen
(d) all of these

82. In an exothermic reaction, a 10°C rise in temperature will: **[PMT (Bangalore) 1993]**
(a) decrease the value of equilibrium constant
(b) double the value of equilibrium constant
(c) not produce any change in equilibrium constant
(d) produce some increase in equilibrium constant

83. If K_p for a reaction,

$$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$$

is 0.05 atm at 1000 K, its K_c in terms of R will be:
(a) $20000\,R$ (b) $0.02\,R$ (c) $5\times10^{-5}\,R$ (d) $\dfrac{5\times10^{-5}}{R}$

84. Consider the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ in closed container at equilibrium. What would be the effect of addition of $CaCO_3$ on the equilibrium concentration of CO_2? **(AIIMS 1991)**
(a) Increases
(b) Decreases
(c) Remains unaffected
(d) Data is not sufficient to predict it

85. XY_2 dissociates as:

$$XY_2(g) \rightleftharpoons XY(g) + Y(g)$$

Initial pressure of XY_2 is 600 mm Hg. The total pressure at equilibrium is 800 mm Hg. Assuming volume of system to remain constant, the value of K_p is: **(BHU 1992)**
(a) 50 (b) 100 (c) 200 (d) 400

[Hint: $XY_2(g) \rightleftharpoons XY(g) + Y(g)$
$600 - x \quad x \quad x$
$600 + x = 800$ or $x = 200$]

86. Which of the following reactions will be favoured at low pressure?
(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
(d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

87. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the: **(MLNR 1990)**
(a) amount of solid to decrease
(b) amount of liquid to decrease
(c) temperature to rise
(d) temperature to fall

88. For the reaction:

$$2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$$

two moles each of A and B were taken into a flask. The following must always be true when the system attained equilibrium:
(a) $[A] = [B]$ (b) $[A] < [B]$
(c) $[B] = [C]$ (d) $[A] > [B]$

89. In a vessel containing SO_3, SO_2 and O_2 at equilibrium, some helium gas is introduced so that total pressure increases while temperature and volume remain the same. According to Le Chatelier's principle, the dissociation of SO_3: **(MLNR 1991)**
(a) increases (b) decreases
(c) remains unaltered (d) changes unpredictably

90. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statements is correct?
(a) Concentrations of SO_2Cl_2, SO_2 and Cl_2 do not change
(b) More Cl_2 is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed

91. The vapour density of undecomposed N_2O_4 is 46. When heated, vapour density decreases to 24.5 due to its dissociation to NO_2. The % dissociation of N_2O_4 is:
(a) 40 (b) 57
(c) 67 (d) 87

92. K_p/K_c for the reaction, $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ is:
(a) RT (b) $\dfrac{1}{\sqrt{RT}}$ (c) $\sqrt{RT}$ (d) 1

93. For the reactions,
$A \rightleftharpoons B, K_c = 1$; $B \rightleftharpoons C, K_c = 3$; $C \rightleftharpoons D, K_c = 5$
K_c for the reaction $A \rightleftharpoons D$ is:
(a) 15 (b) 5 (c) 3 (d) 1

[Hint: $\dfrac{[B]}{[A]} = 1$; $\dfrac{[C]}{[B]} = 3$; $\dfrac{[D]}{[C]} = 5$,

Multiplying all the three, $\dfrac{[D]}{[A]} = 1\times3\times5$]

94. The equilibrium constant of the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. If the volume of the container is reduced to one half of its original value, the equilibrium constant will be:
(a) 25 (b) 50
(c) 75 (d) 100

95. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$
The above equilibrium when subjected to pressure: **[PMT (Raj.) 1992]**
(a) remains unaffected
(b) proceeds in the backward direction
(c) proceeds in the forward direction
(d) none of the above

96. Reaction, $A + B \longrightarrow C + D + 38$ kcal has activation energy 20 kcal. Activation energy for the reaction, $C + D \longrightarrow A + B$ is: **[PMT (Pb.) 1993]**

(a) 20 kcal (b) –20 kcal
(c) 18 kcal (d) 58 kcal

97. The equilibrium constant for the reaction,

$$CaSO_4 \cdot 5H_2O(s) \rightleftharpoons CaSO_4 \cdot 3H_2O(s) + 2H_2O(g),$$

is equal to:

(a) $\dfrac{[CaSO_4 \cdot 3H_2O][H_2O]^2}{[CaSO_4 \cdot 5H_2O]}$ (b) $\dfrac{[CaSO_4 \cdot 3H_2O]}{[CaSO_4 \cdot 5H_2O]}$
(c) $[H_2O]^2$ (d) $[H_2O]$

98. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is:

(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

99. The equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 4.0×10^{-4} at 2000 K. In the presence of a catalyst the equilibrium is attained ten times faster. Therefore, the equilibrium constant in presence of the catalyst at 2000 K is: **(MLNR 1994)**

(a) 4×10^{-4}
(b) 40×10^{-4}
(c) 4×10^{-2}
(d) difficult to compute without more data

100. The equilibrium constant for a reaction, $A + B \rightleftharpoons C + D$ is 1×10^{-2} at 298 K and is 2 at 273 K. The chemical process resulting in the formation of C and D is:

(a) exothermic
(b) endothermic
(c) unpredictable
(d) there is no relationship between ΔH and K

101. The equilibrium constant for the reaction, $A + B \rightleftharpoons C + D$ is 2.85 at room temperature and 1.4×10^{-2} at 698 K. This shows that forward reaction is:

(a) exothermic
(b) endothermic
(c) unpredictable
(d) there is no relationship between ΔH and K

102. If E_f and E_r are the activation energies of forward and backward reactions and the reaction is known to be exothermic, then:

(a) $E_f > E_r$
(b) $E_f < E_r$
(c) $E_f = E_r$
(d) no relation can be given between E_f and E_r

103. K_p for a reaction at 25°C is 10 atm. The activation energy for forward and reverse reactions are 12 and 20 kJ/mol respectively. The K_c for the reaction at 40°C will be:

(a) $4.33 \times 10^{-1}\ M$ (b) $3.33 \times 10^{-2}\ M$
(c) $3.33 \times 10^{-1}\ M$ (d) $4.33 \times 10^{-2}\ M$

104. Concentration of pure solid and liquid is not included in the expression of equilibrium constant because:

(a) solid and liquid concentrations are independent of their quantities
(b) solid and liquids react slowly
(c) solid and liquids at equilibrium do not interact with gaseous phase
(d) the molecules of solids and liquids cannot migrate to the gaseous phase

105. For an equilibrium reaction involving gases, the forward reaction is first order while the reverse reaction is second order. The units of K_p for forward equilibrium is:

(a) atm (b) atm^2 (c) atm^{-1} (d) atm^{-2}

106. At temperature T, a compound $AB_2(g)$ dissociates according to the reaction:

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation 'x' which is small as compared to unity. The expression for K_p, in terms of 'x' and total pressure 'P' is

(a) $\dfrac{Px^3}{2}$ (b) $\dfrac{Px^2}{3}$
(c) $\dfrac{Px^3}{3}$ (d) $\dfrac{Px^2}{2}$

107. 40% mixture of 0.2 mole of N_2 and 0.6 mole of H_2 react to give NH_3 according to the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases is:

(a) 4 : 5 (b) 5 : 4
(c) 7 : 10 (d) 8 : 5

108. Two systems,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

and $$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

are simultaneously in equilibrium in a vessel at constant volume. If some $CO(g)$ is introduced in the vessel at constant volume, then at new equilibrium, the concentration of:

(a) PCl_5 is greater (b) PCl_3 remains unchanged
(c) PCl_5 is less (d) Cl_2 is greater

109. For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant K_c at 25°C is 4×10^{-19}; then Ag^+ concentration in a solution which has 0.1 M KCN and 0.03 M $AgNO_3$ is:

(a) 7.5×10^{18} (b) 7.5×10^{-18}
(c) 7.5×10^{19} (d) 7.5×10^{-19}

110. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium:

(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_2$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) decreasing pressure favours reverse reaction

111. For the reaction,

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$$

which one is the correct representation?

(a) $K_p = [p_{H_2O}]^2$ (b) $K_c = [H_2O]^2$
(c) $K_p = K_c(RT)^2$ (d) All of these

112. Which one is the correct representation for,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)?$$

(a) $K_p = \dfrac{[p_{SO_3}]^2}{[p_{SO_2}]^2[p_{O_2}]}$

(b) $K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

(c) $K_p = \dfrac{[n_{SO_3}]^2}{[n_{SO_2}]^2[n_{O_2}]} \times \left[\dfrac{P}{\text{Total mole}}\right]^{-1}$

(d) All of the above

113. For the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$ **(IIT 1991)**

The forward reaction at constant temperature is favoured by:

(a) introducing inert gas at constant volume

(b) introducing chlorine gas at constant volume

(c) introducing an inert gas at constant pressure

(d) none of the above

114. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium, when the flask is heated to 100°C the brown colour deepens and on cooling, the brown colour became less coloured. The change in enthalpy ΔH for the system is: **(KCET 1993)**

(a) negative (b) positive (c) zero (d) not defined

115. Le Chatelier's principle is not applicable to:

(a) $Fe(s) + S(s) \rightleftharpoons FeS(s)$

(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

116. Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase in pressure on the equilibrium $C_{\text{diamond}} \rightleftharpoons C_{\text{graphite}}$:

(a) favours backward reaction

(b) favours forward reaction

(c) has no effect

(d) increases the reaction rate

117. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ in a vessel, after the addition of equal number of moles of N_2 and H_2 equilibrium state is achieved. Which of the following is correct?

(a) $[H_2] = [N_2]$ (b) $[H_2] < [N_2]$

(c) $[H_2] > [N_2]$ (d) $[H_2] > [NH_3]$

118. If pressure is applied to the equilibrium of solid $\rightleftharpoons$ liquid, the melting point of the solid:

(a) will not change

(b) may increase or decrease depending upon its nature

(c) will always increase

(d) will always decrease

119. If concentrations of N_2, H_2 and NH_3 are 1, 2 and 3 respectively, their concentration at equilibrium will be:

	N_2 +	$3H_2 \rightleftharpoons$	$2NH_3$
(a)	$(1-x)$	$(2-3x)$	$2x$
(b)	$(1-x/3)$	$(2-x)$	$2x/3$
(c)	$(1-x)$	$(2-x)$	$(3+x)$
(d)	$(1-x)$	$(2-3x)$	$(3+2x)$

120. A reaction attains equilibrium, when the free energy change is:

(a) zero (b) positive and large

(c) negative and small (d) negative and large

121. If 340 g of a mixture of N_2 and H_2 in the correct ratio gave a 20% yield of NH_3, the mass produced would be:

(a) 16 g (b) 17 g (c) 20 g (d) 68 g

122. If the pressure of N_2 / H_2 mixture in a closed apparatus is 100 atm and 20% of the mixture then reacts, the pressure at the same temperature would be:

(a) 100 (b) 90 (c) 85 (d) 80

123. The equilibrium constants for the reaction, $Br_2 \rightleftharpoons 2Br$, at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is:

(a) endothermic (b) exothermic

(c) fast (d) slow

124. If the concentration of OH^- ions in the reaction:

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq.) + 3OH^-(aq.)$$

is decreased by $\frac{1}{4}$ times, then equilibrium concentration of Fe^{3+} will increase by: **[CBSE (PMT) 2008]**

(a) 64 times (b) 4 times (c) 8 times (d) 16 times

125. K_c for $A + B \rightleftharpoons C + D$ is 10 at 25°C. If a container contains 1, 2, 3 and 4 mol per litre of A, B, C and D respectively at 25°C, the reaction shall:

(a) proceed from left to right (b) proceed from right to left

(c) be at equilibrium (d) none of these

126. In the preparation of CaO from $CaCO_3$ using the equilibrium,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

K_p is expressed as:

$$\log K_p = 7.282 - \frac{8500}{T}$$

For complete decomposition of $CaCO_3$ the temperature in celsius to be used is:

(a) 1167 (b) 894

(c) 8500 (d) 850

127. To the system,

$$LaCl_3(s) + H_2O(g) \rightleftharpoons LaClO(s) + 2HCl(g) - \text{heat}$$

already at equilibrium, more water vapour is added without altering T or V of the system. When equilibrium is re-established, the pressure of water vapour is doubled. The pressure of HCl present in the system increases by a factor of:

(a) 2 (b) $2^{1/2}$ (c) 3 (d) 4

128. For the chemical reaction,

$$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$$

the amount of X_3Y at equilibrium is affected by: **(IIT 1999)**

(a) temperature and pressure

(b) temperature only

(c) pressure only

(d) temperature, pressure and catalyst

129. In a 500 mL capacity vessel CO and Cl_2 are mixed to form $COCl_2$. At equilibrium, it contains 0.2 mole of $COCl_2$ and 0.1 mole of each of CO and Cl_2. The equilibrium constant K_c for reaction, $CO + Cl_2 \rightleftharpoons COCl_2$ is: **(CBSE 1998)**

(a) 5 (b) 10 (c) 15 (d) 20

130. The partial pressures of CH_3OH, CO and H_2 in the equilibrium mixture for the reaction,

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

at 427°C are 2.0, 1.0 and 0.1 atm respectively. The value of K_p for the decomposition of CH_3OH into CO and H_2 is:

(IIT 1999)

(a) 1×10^2 atm (b) 2×10^2 atm^{-1}
(c) 50 atm^2 (d) 5×10^{-3} atm^2

131. 8 mole of a gas AB_3 are introduced into a 1.0 dm^3 vessel. It dissociates as:

$$2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$$

At equilibrium, 2 mole of A_2 are found to be present. The equilibrium constant of the reaction is: **(IIT 1997)**

(a) 2 mol^2 L^{-2} (b) 3 mol^2 L^{-2}
(c) 27 mol^2 L^{-2} (d) 36 mol^2 L^{-2}

132. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction,

$$N_2O_4 \rightleftharpoons 2NO_2$$

is expressed by:

$$K_p = \frac{4x^2P}{(1-x^2)}$$

Where, P = pressure, x = extent of decomposition. Which one of the following statements is true? **[IIT (Screening) 2000]**

(a) K_p increases with increase of P
(b) K_p increases with increase of x
(c) K_p increases with decrease of x
(d) K_p remains constant with change in P and x

133. Consider the reactions,

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g) \qquad K_1$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_2$$

Give the equilibrium constant for the formation of N_2O_4 from N_2 and O_2: **(DCE 2006)**

(a) $\frac{1}{K_1^2} \times \frac{1}{K_2}$ (b) $\frac{1}{2K_1} + \frac{1}{K_2}$ (c) $\sqrt{\frac{1}{K_1K_2}}$ (d) $\frac{K_2}{K_1}$

[Hint: $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g) \; K_1$

$\therefore \quad N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad K = \frac{1}{K_1^2} \qquad$ ... (i)

$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_2$

$\therefore \quad 2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K = \frac{1}{K_2} \qquad$ ... (ii)

Adding eqs. (i) and (ii),

$N_2(g) + 2O_2(g) \rightleftharpoons N_2O_4(g) \qquad K = \frac{1}{K_1^2} \times \frac{1}{K_2}$]

134. Phosphorous pentachloride dissociates as follows:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g).$$

If total pressure at equilibrium is P and the degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be: **(AIEEE 2006)**

(a) $\left(\frac{x}{x+1}\right)P$ (b) $\left(\frac{2x}{1-x}\right)P$ (c) $\left(\frac{x}{x-1}\right)P$ (d) $\left(\frac{x}{1-x}\right)P$

135. At $t = 0$ a vessel (volume 1 litre) contains 1 mole N_2, 3 mole H_2 and 2 mole NH_3. The value of K_c for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 17.5 L^2 mol^{-2}. Then:

(a) total gaseous weight at equilibrium is more than 68 g
(b) total number of moles (gaseous) at equilibrium are more than 6 moles
(c) $\frac{dM}{dt}$ is +ve for $t \in (0, T_{eq.})$ where, M is average molar mass of the reaction mixture
(d) total gaseous weight at equilibrium is less than 68 g

136. A vessel (volume = 2 L) contains 60 g of water gas. When steam is passed through the vessel, the reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$ occurs and equilibrium is attained:

(a) $\frac{n(H_2)}{n(CO)} < 1$ (at equilibrium)
(b) $n(H_2) + n(CO) = 4$ (at any instant)
(c) $\frac{dM}{dt} > 0$ (where, M is average molar mass of gas mixture before the attainment of equilibrium)
(d) $\frac{dM}{dt} < 0$

137. A vessel contains CO_2 and CO with pressures 2 atm and 3 atm respectively at 27°C. At a temperature of 2727°C, the reaction $2CO(g) \rightleftharpoons CO_2(g) + C(s)$ occurs and equilibrium is attained. If the equilibrium pressure is 45 atm, then:

(a) $K_p = 2/9$ atm^{-1}
(b) $p_{CO} : p_{CO_2} = 4:5$ at equilibrium
(c) $K_p = 16$ atm^{-1}
(d) % dissociation of CO = 0.333

138. A vessel (volume 8.2 L) contains $H_2(g)$ at 2 atm pressure. When $H_2S(g)$ at a pressure of 4 atm is introduced into the vessel, the reaction, $8H_2S(g) \rightleftharpoons 8H_2(g) + S_8(s)$ occurs at a temperature of 2000 K. It is found that:

$$\left[\frac{n(H_2)}{n(H_2S)}\right]_{\text{at equilibrium}} = \left[\frac{n(H_2S)}{n(H_2)}\right]_{\text{at } t=0}$$

(a) maximum weight of solid formed is 32 g
(b) maximum weight of solid formed is 0.32 g
(c) $K_p = K_c\,RT$
(d) $K_c = 256$

139. $N_2(g)$ and $H_2(g)$ are taken in a vessel in mass ratio of 7 : 1. The only reaction $N_2 + 2H_2 \rightleftharpoons N_2H_4(g)$ occurs. Pressure due to N_2H_4 at equilibrium is 0.2 times of total pressure 'P'. Then at equilibrium:

(a) partial pressure of $N_2 = 2P/15$
(b) partial pressure of $H_2 = 8P/25$
(c) $2p_{N_2} = p_{H_2}$
(d) $p_{N_2} = 2p_{H_2}$

140. In the equilibrium, $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ at 2000 K and 10 atm pressure, % Cl_2 = % SO_2 = 40 by volume. Then:

(a) $K_p = 2$ atm
(b) $\frac{n(SO_2Cl_2)}{n(SO_2)} = \frac{1}{4}$ at equilibrium
(c) $K_p = 8$ atm
(d) $n(SOCl_2) = n(SO_2) = n(Cl_2)$

141. A 20 litre box contains O_3 and O_2 at equilibrium at 202 K. $K_p = 2 \times 10^{14}$ for $2O_3 \rightleftharpoons 3O_2$. Assume that $p_{O_2} >> p_{O_3}$ and total pressure is 8 atm; the partial pressure of O_3 is:

(a) exactly 1.6×10^{-6} atm
(b) sufficiently less than 1.6×10^{-6} atm

(c) slightly more than 1.6×10^{-6} atm

(d) very slightly less than 1.6×10^{-6} atm

142. For the reactions, $A \rightleftharpoons B, B \rightleftharpoons C$ and $C \rightleftharpoons D$, equilibrium constants are K_1, K_2 and K_3 respectively. What is the value of equilibrium constant for $A \rightleftharpoons D$?

(a) $K_1 + K_2 + K_3$ (b) $K_1 \times K_2 \times K_3$

(c) $K_1K_2/3$ (d) None of these

143. $AO \rightleftharpoons \left(\frac{1}{2}\right) A_2 + \left(\frac{1}{2}\right) O_2; K = 5 \times 10^5$

$BO \rightleftharpoons \left(\frac{1}{2}\right) B_2 + \left(\frac{1}{2}\right) O_2; K = 1.10 \times 10^{12}$

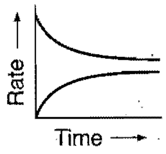
$CO \rightleftharpoons \left(\frac{1}{2}\right) C_2 + \left(\frac{1}{2}\right) O_2; K = 2.3 \times 10^{18}$

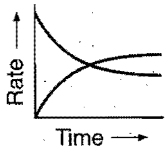
$DO \rightleftharpoons \left(\frac{1}{2}\right) D_2 + \left(\frac{1}{2}\right) O_2; K = 1.4 \times 10^{21}$

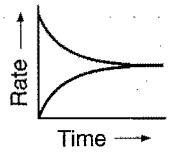
Which oxide is most stable?

(a) AO (b) BO (c) CO (d) DO

144. Which graph will show equilibrium condition?

(a) 

(b) 

(c) 

(d) None of these

145. For the reaction, $N_2 + O_2 \rightleftharpoons 2NO$ equilibrium constant $K_c = 2$. Degrees of dissociation of N_2 and O_2 are:

(a) $\frac{1}{1+\sqrt{2}}, \frac{1}{1-\sqrt{2}}$ (b) $\frac{1}{1-\sqrt{2}}, \frac{1}{1+\sqrt{2}}$

(c) both are $\frac{1}{1+\sqrt{2}}$ (d) $\frac{2}{1+\sqrt{2}}, \frac{2}{1-\sqrt{2}}$

146. $A \rightleftharpoons 2B, K_p$; $C \rightleftharpoons D + E, K_{p'}$. If degrees of dissociation of A and C are same and $K_p = 2K_{p'}$, then the ratio of total pressure p/p' = ?

(a) 1/2 (b) 1/3 (c) 1/4 (d) 2

147. Equilibrium constants for four different reactions are given as: $K_1 = 10^6$, $K_2 = 10^{-4}$, $K_3 = 10$, $K_4 = 1$. Which reaction will take maximum time to attain equilibrium?

(a) $K_1 = 10^6$ (b) $K_2 = 10^{-4}$

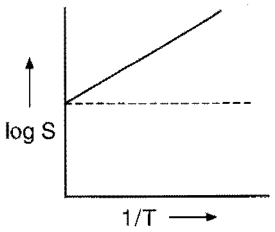
(c) $K_3 = 10$ (d) $K_4 = 1$

148. Solubility of a solute in water is dependent on temperature as given by,

$S = Ae^{-\Delta H/RT}$ where, ΔH = heat of solution

Solute + $H_2O(l) \rightleftharpoons$ Solution; $\Delta H = \pm x$

For a given solution, variation of log S with temperature is shown graphically. Hence, solute is:

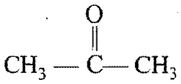


(a) $CuSO_4 \cdot 5H_2O$

(b) NaCl

(c) sucrose

(d) CaO

149. 
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3(g) \rightleftharpoons CH_3-CH_3(g) + CO(g)$

Initial pressure of CH_3COCH_3 is 100 mm. When equilibrium is achieved, the mole fraction of $CO(g)$ is 1/3 hence, K_p is:

(a) 100 mm (b) 50 mm (c) 25 mm (d) 150 mm

150. In which of the following equilibrium, change in the volume of the system does not alter the number of moles? **(AIEEE 2002)**

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(d) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

151. What are the most favourable conditions for the reaction;

$$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g); \Delta H^\circ = -\text{ve}$$

to occur? **[DPMT 2002; JEE (Orissa) 2[illegible]]**

(a) low temp. and high press. (b) low temp. and low press.

(c) high temp. and low press. (d) high temp. and high press.

152. Consider the following reactions in which all the reactants and products are in gaseous state

$$2PQ \rightleftharpoons P_2 + Q_2; \ K_1 = 2.5 \times 10^5$$

$$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR \ ; \ K_2 = 5 \times 10^{-3}$$

The value of K_3 for the equilibrium :

$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$ is : **[PET (Kerala) 2010]**

(a) 2.5×10^{-3} (b) 2.5×10^3

(c) 1.0×10^{-5} (d) 5×10^3

(e) 5×10^{-3}

[Hint:

$$\begin{array}{ll} \frac{1}{2}P_2 + \frac{1}{2}Q_2 \rightleftharpoons PQ & K = \frac{1}{K_1^{1/2}} \\ PQ + \frac{1}{2}R_2 \rightleftharpoons PQR & K_2 \\ \hline \frac{1}{2}P_2 + \frac{1}{2}Q + \frac{1}{2}R_2 \rightleftharpoons PQR & K_3 = \frac{1}{K_1^{1/2}} \times K_2 \\ \hline & = \frac{5 \times 10^{-3}}{(2.5 \times 10^5)^{1/2}} \\ & = 1 \times 10^{-5} \end{array}$$

]

153. Consider the following equilibrium in a closed container,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)? **(IIT 2002)**

(a) neither K_p nor 'α' changes

(b) both K_p and 'α' change

(c) K_p changes but 'α' does not

(d) K_p does not change but 'α' changes

154. For the reaction, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the position of equilibrium can be shifted to the right by: **[PET (MP) 2004]**

(a) doubling the volume

(b) increasing the temperature

(c) addition of equimolar quantities of PCl_3 and PCl_5

(d) addition of Cl_2 at constant volume

155. The most favourable condition for the manufacture of NH_3 is: **[CECE (Bihar) 2004]**

(a) high temperature and high pressure

(b) low temperature and low pressure

(c) high temperature and low pressure

(d) low temperature and high pressure

156. The chemical equilibrium of a reversible reaction is not influenced by: **(KCET 2004)**

(a) catalyst (b) pressure

(c) temperature (d) concentration

157. Which of the following change will shift the reaction in forward direction?

$I_2(g) \rightleftharpoons 2I(g); \Delta H° = +150$ kJ **(AIIMS 2004)**

(a) Increase in total pressure

(b) Increase in temperature

(c) Increase in concentration of I

(d) Decrease in concentration of I_2

158. For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the $\frac{K_p}{K_c}$ is equal to: **(AIEEE 2004)**

(a) $1/RT$ (b) RT (c) $\sqrt{RT}$ (d) 1

159. The equilibrium constant for the reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

at temperature T is 4×10^{-4}.

The value of K_c for the reaction,

$$NO(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$$

at the same temperature is: **(AIEEE 2004)**

(a) 2.5×10^2 (b) 50 (c) 4×10^{-4} (d) 0.02

160. 2 moles of N_2 are mixed with 6 moles of H_2 in a closed vessel of one litre capacity. If 50% N_2 is converted into NH_3 at equilibrium, the value of K_c for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

[PMT (Kerala) 2004]

(a) 4/27 (b) 27/4

(c) 1/27 (d) 27

(e) 9

161. For the reaction, $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$, if the initial concentration of $[H_2] = [CO_2]$ and x mol/litre of H_2 is consumed at equilibrium, the correct expression of K_p is: **[JEE (Orissa) 2005]**

(a) $\frac{x^2}{(1-x)^2}$ (b) $\frac{(1+x)^2}{(1-x)^2}$ (c) $\frac{x^2}{(2+x)^2}$ (d) $\frac{x^2}{1-x^2}$

162. Partial pressure of O_2 in the reaction,

$$2Ag_2O(s) \rightleftharpoons 4Ag(s) + O_2(g)$$

is: **(DCE 2005)**

(a) K_p (b) $\sqrt{K_p}$ (c) $\sqrt[3]{K_p}$ (d) $2K_p$

163. Two moles of PCl_5 are heated in a closed vessel of 2 litre capacity. When the equilibrium is attained 40% of it has been found to be dissociated. What is the value of K_c in mol/dm³? **[PET (Kerala) 2005]**

(a) 0.532 (b) 0.266 (c) 0.133 (d) 0.174

(e) 0.25

[Hint:

$$\begin{array}{llll} & PCl_5(g) & \rightleftharpoons PCl_3(g) & + \; Cl_2(g) \\ t = 0 & 2 & 0 & 0 \\ t_{eq.} & \frac{2-0.8}{2} & \frac{0.8}{2} & \frac{0.8}{2} \end{array}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{0.8}{2} \times \frac{0.8}{2}}{\frac{1.2}{2}} = \frac{0.64}{2.4} = 0.266]$$

164. For the reaction:

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$K_c = 1.8 \times 10^{-6}$ at 184°C

$R = 0.0831$ kJ K^{-1} mol^{-1}

when, K_p and K_c are compared at 184°C it is found that: **(AIEEE 2005)**

(a) K_p is greater than K_c

(b) K_p is less than K_c

(c) $K_p = K_c$

(d) whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

[Hint: $K_p = K_c\,(RT)^{\Delta n}$

$\Delta n = 3 - 2 = 1$

$K_p = K_c\,(RT)^1$

$\therefore \quad K_p > K_c$]

165. $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. If equilibrium pressure is 3 atm for the above reaction; K_p will be: **(DPMT 2005)**

(a) 4 (b) 27 (c) 4/27 (d) 1/27

[Hint: $p_{NH_3} : p_{CO_2} = 2 : 1$

$\therefore \quad p_{NH_3} = 2$ atm; $p_{CO_2} = 1$ atm

$K_p = [p_{NH_3}]^2[p_{CO_2}] = 2^2 \times 1 = 4$]

166. $A + B \rightleftharpoons C + D$. If initially the concentration of A and B are both equal but at equilibrium, concentration of D will be twice of that of A, then what will be the equilibrium constant of the reaction? **[BHU (Pre.) 2005; JIPMER 2006]**

(a) $\frac{4}{9}$ (b) $\frac{9}{4}$ (c) $\frac{1}{9}$ (d) 4

[Hint:

$$\begin{array}{lllll} & A & + \; B & \rightleftharpoons C & + \; D \\ t = 0 & a & a & 0 & 0 \\ t_{eq.} & a - x & a - x & x & x \end{array}$$

$x = 2(a - x)$

$3x = 2a$

$$K = \frac{x \times x}{(a-x)(a-x)} = \frac{x \times x}{\frac{x}{2} \times \frac{x}{2}} = 4]$$

167. 15 moles of H_2 and 5.2 moles of I_2 are mixed and allowed to attain equilibrium at 500°C. At equilibrium, the concentration of HI is found to be 10 moles. The equilibrium constant for the formation of HI is: **(KCET 2005)**

(a) 50 (b) 15 (c) 100 (d) 25

[Hint:

$$\begin{array}{lccc} & H_2 & + \; I_2 & \rightleftharpoons 2HI \\ t=0 & 15 & 5.2 & 0 \\ t_{eq.} & 15-5 & 5.2-5 & 10 \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{100}{10 \times 0.2} = 50]$$

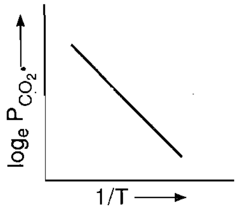
168. For the reaction: $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, K_c at 427°C is 3×10^6 L mol^{-1}. The value of K_p is nearly: **(AIIMS 2005)**

(a) 7.5×10^{-5} (b) 2.5×10^{-5} (c) 2.5×10^{-4} (d) 1.75×10^{-4}

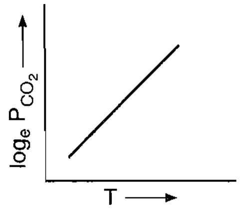
169. For the chemical equilibrium,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

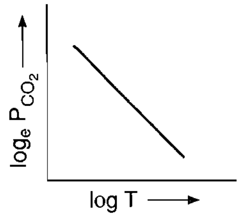
ΔH_r° can be determined from which one of the following plots? **(AIIMS 2005)**



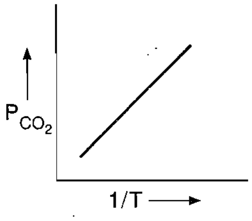
(a)



(b)



(c)



(d)

[Hint: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = P_{CO_2}$$

According to Arrhenius equation:

$$K = Ae^{-\Delta H_r^\circ/RT}$$

$$\log K_p = \log A - \frac{\Delta H_r^\circ}{2.303RT}$$

$$\log P_{CO_2} = \log A - \frac{\Delta H_r^\circ}{2.303R}\frac{1}{T} \quad \text{... (i)}$$

$$Y = C + MX$$

Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.]

170. In gaseous reversible reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) + \text{Heat}$$

If pressure is increased, then the equilibrium constant would be: **[UGET (Manipal, Medical) 2006]**

(a) unchanged
(b) increased
(c) decreased
(d) sometimes increased, sometimes decreased

171. If the equilibrium constant for the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

at 750 K is 49, then the equilibrium constant for the reaction,

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

at the same temperature is: **[PMT (Kerala) 2006]**

(a) 1/49 (b) 49 (c) 7 (d) 49^2
(e) 1/7

172. The equilibrium constant for the reaction,

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

is $K_c = 4.9 \times 10^{-2}$.

The value of K_c for the reaction,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

will be: **(AIEEE 2006)**

(a) 416 (b) 2.40×10^{-3}
(c) 9.8×10^{-2} (d) 4.9×10^{-2}

[Hint: $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$; $K_c = 4.9 \times 10^{-2}$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \qquad K_c = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2$$

$$= 416.5 \approx 416]$$

173. For a reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 721 K, the value of equilibrium constant is 50. If 0.5 mol each of H_2 and I_2 is added to the system, the value of equilibrium constant will be: **[VMMC (Safdarjung) 2006]**

(a) 40 (b) 60 (c) 50 (d) 30

[Hint: Equilibrium constant does not change on adding the reactant.]

174. In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, in a 2 litre flask 0.4 mole of each H_2 and I_2 are taken. At equilibrium 0.5 mole of HI are formed. What will be the value of equilibrium constant K_c? **[PMT (Raj.) 2006]**

(a) 20.2 (b) 25.4 (c) 0.284 (d) 11.1

175. For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the equilibrium constant K_p changes with: **(VITEEE 2007)**

(a) total pressure (b) catalyst
(c) the amount of H_2 and I_2 (d) temperature

176. Given the equilibrium system,

$$NH_4Cl(s) \rightleftharpoons NH_4^+(aq.) + Cl^-(aq.)$$

$$(\Delta H^\circ = +3.5 \text{ kcal/mol})$$

what change will shift the equilibrium to the right? **(VITEEE 2007)**

(a) Decreasing the temperature
(b) Increasing the temperature
(c) Dissolving NaCl crystals in equilibrium mixture
(d) Dissolving NH_4NO_3 crystals in the equilibrium mixture

177. The equilibrium constant (K_p) for the decomposition of gaseous H_2O:

$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$ is related to degree of dissociation (α) at a total pressure P is given by: **[PMT (Kerala) 2007]**

(a) $K_p = \dfrac{\alpha^3 P^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$ (b) $K_p = \dfrac{\alpha^3 P^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(c) $K_p = \dfrac{\alpha^{3/2} P^2}{(1-\alpha)(2+\alpha)^{1/2}}$ (d) $K_p = \dfrac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(e) $K_p = \dfrac{\alpha^2 P}{\sqrt{2}}$

[**Hint:** $H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$

$$\begin{array}{llll} t = 0 & 1 & 0 & 0 \\ t_{eq.} & 1-\alpha & \alpha & \alpha/2 \end{array}$$

$$\Sigma n = 1 - \alpha + \alpha + \frac{\alpha}{2} = 1 + \frac{\alpha}{2} = \left(\frac{2+\alpha}{2}\right)$$

$$K_p = \frac{n_{H_2} \times n_{O_2}^{1/2}}{n_{H_2O}} \times \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

$$= \frac{\alpha \times \left(\frac{\alpha}{2}\right)^{1/2}}{(1-\alpha)} \times \left[\frac{P}{\left(\frac{2+\alpha}{2}\right)}\right]^{1/2}$$

$$= \frac{\alpha^{3/2} P^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}]$$

178. The equilibrium constant for the reaction,

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ is 2×10^{-6} at 185° C

Then, the equilibrium constant for the reaction, $4NO(g) + 2O_2(g) \rightleftharpoons 4NO_2(g)$ at the same temperature would be: **[PET (Kerala) 2007]**

(a) 2.5×10^{-5} (b) 4×10^{-12} (c) 2.5×10^{11} (d) 2×10^6

(e) 5×10^5

179. 1 mole of H_2 and 2 mole of I_2 are taken initially in a 2 L vessel. The number of moles H_2 at equilibrium is 0.2. Then, the number of moles of I_2 and HI at equilibrium are: **[PMT (Raj.) 2007]**

(a) 1.2, 1.6 (b) 1.8, 1.0 (c) 0.4, 2.4 (d) 0.8, 2.0

180. The dissociation equilibrium of a gas AB_2 can be represented as,

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

The degree of dissociation is x and is small as compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is:

(a) $(2K_p/P)^{1/2}$ (b) K_p/P (c) $2K_p/P$ (d) $(2K_p/P)^{1/3}$

[CBSE (PMT) 2008]

[**Hint :** $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

$$\begin{array}{lllll} t_0 & 2 & 0 & 0 & \\ t_{eq.} & 2(1-x) & 2x & x & \text{Total moles} = 2 + x \\ \text{Partial pressure} & \frac{2(1-x)}{2+x} \times P & \frac{2x}{2+x} \times P & \frac{x}{2+x} \times P & \end{array}$$

$$K_p = \frac{p_{AB}^2 \times p_{B_2}}{(p_{AB_2})^2} = \frac{\left[\frac{2}{(2+x)} P\right]^2 \left[\frac{xP}{(2+x)}\right]}{\left[\frac{2(1-x)}{2+x} \times P\right]^2}$$

$$= \frac{4x^3 \times P}{4(2+x)(1-x)^2}$$

$(2+x) \approx 2, (1-x) \approx 1$

$K_p = \dfrac{Px^3}{2}$ $\quad \therefore x = (2K_p/P)^{1/3}$]

181. In which of the following reactions, the concentration of the product is higher than the concentration of reactant at equilibrium ? (K = equilibrium constant) **(AIIMS 2008)**

(a) $A \rightleftharpoons B$; $K = 0.001$ (b) $M \rightleftharpoons N$; $K = 10$

(c) $X \rightleftharpoons Y$; $K = 0.005$ (d) $R \rightleftharpoons P$; $K = 0.01$

182. 1.6 mole of $PCl_5(g)$ is placed in 4 dm^3 closed vessel. When the temperature is raised to 500 K, it decomposes and at equilibrium 1.2 mole of $PCl_5(g)$ remains. What is the K_c value for the decomposition of $PCl_5(g)$ to $PCl_3(g)$ and $Cl_2(g)$ at 500K? [PET (Kerala) 2008]

(a) 0.013 (b) 0.050 (c) 0.033 (d) 0.067

(e) 0.045

183. Consider the following statements regarding chemical equilibrium:

1. For the gaseous reaction, the equilibrium can be established in open vessel.
2. The state of equilibrium is dynamic in nature.
3. If temperature is kept constant, the colour of the reacting system changes with time.

Which of the statements given above is/are correct? (SCRA 2009)

(a) 1 (b) 2 only

(c) 3 only (d) 2 and 3 only

184. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium:

$$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$$

would be : **[CBSE (PMT) 2009]**

(a) 3×10^4 (b) 3×10^5

(c) 3×10^{-5} (d) 3×10^{-4}

[**Hint :** Given

(i) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad K_1 = 1.5 \times 10^{-5}$

(ii) $HCN \rightleftharpoons H^+ + CN^- \quad K_2 = 4.5 \times 10^{-10}$

(iii) $H^+ + CN^- \rightleftharpoons HCN \quad K_3 = \dfrac{1}{K_2} = \dfrac{1}{4.5 \times 10^{-10}}$

Adding (i) and (iii) we get

$$CH_3COOH + CN^- \rightleftharpoons CH_3COO^- + HCN$$

$$K = 1.5 \times 10^{-5} \times \frac{1}{4.5 \times 10^{-10}}$$

$$= 3 \times 10^4]$$

185. One mole of N_2O_4 is heated in a flask with a volume of 0.1 dm^3. At equilibrium, 1.708 mole of NO_2 and 0.146 mole of N_2O_4 were found 134°C. The equilibrium constant will be: (MPPET 2009)

(a) 250 mol dm^{-3} (b) 300 mol dm^{-3}

(c) 200 mol dm^{-3} (d) 230 mol dm^{-3}

186. What is the effect of a tenfold increase in pressure on K_p in the reaction?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

At equilibrium : (EAMCET 2010)

(a) a tenfold increase
(b) a tenfold decrease
(c) no change
(d) equal to K_c

Set–2: The Questions given below may have more than one correct answers

1. Unit of equilibrium constant is:
(a) $(\text{mol/L})^{1-n}$
(b) $(\text{mol/L})^{\Delta n}$
(c) $(\text{atm})^{\Delta n}$
(d) all of these

2. Which is/are correct?
(a) $2.303 \log K = -\Delta H°/RT + \Delta S°/R$
(b) $\Delta G° = -2.303RT \log K$
(c) $-2.303 \log K = -\Delta H°/RT^2 + \Delta S°/R$
(d) $2.303 \log K = (1/RT)(\Delta H° + \Delta S°)$

3. For the reaction, $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, which is correct representation?
(a) $K_p = (p_{CO_2})$
(b) $K_p = K_c(RT)$
(c) $K_c = (CO_2)/1$
(d) All of these

4. $N_2 + O_2 \rightleftharpoons 2NO, K_1; \left(\frac{1}{2}\right) N_2 + \left(\frac{1}{2}\right) O_2 \rightleftharpoons NO, K_2;$

$2NO \rightleftharpoons N_2 + O_2, K_3; NO \rightleftharpoons \left(\frac{1}{2}\right) N_2 + \left(\frac{1}{2}\right) O_2, K_4$

Correct relation(s) between K_1, K_2, K_3 and K_4 is/are:
(a) $K_1 \times K_3 = 1$
(b) $\sqrt{K_1} \times K_4 = 1$
(c) $\sqrt{K_3} \times K_2 = 1$
(d) none of these

5. For the reaction, $N_2O_4 \rightleftharpoons 2NO_2$, if degree of dissociation of N_2O_4 are 25%, 50%, 75% and 100%, the gradation of observed vapour densities is:
(a) $d_1 > d_2 > d_3 > d_4$
(b) $d_4 > d_3 > d_2 > d_1$
(c) $d_1 = d_2 = d_3 = d_4$
(d) none of these

6. The equation, $\alpha = \frac{D-d}{(n-1)d}$ is correctly matched for:
(a) $A \rightleftharpoons nB/2 + nC/3$
(b) $A \rightleftharpoons nB/3 + (2n/3)C$
(c) $A \rightarrow (n/2)B + (n/4)C$
(d) $A \rightleftharpoons (n/2)B + C$

7. For a reaction, $nA \rightleftharpoons A_n$, degree of dissociation when A trimerises is:
(a) $2\left(\frac{d-D}{d}\right)$
(b) $\frac{3}{2}\left(\frac{d-D}{d}\right)$
(c) $\frac{4}{3}\left(\frac{d-D}{d}\right)$
(d) $2\left(\frac{D-d}{d}\right)$

8. For the reaction,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

the forward reaction at constant temperature is favoured by:
(a) introducing an inert gas at constant volume
(b) introducing chlorine gas at constant volume
(c) introducing an inert gas at constant pressure
(d) increasing the volume of the container
(e) introducing PCl_5 at constant volume

9. Which of the following will favour the formation of NH_3 by Haber's process?
(a) Increase of temperature
(b) Increase of pressure
(c) Addition of catalyst
(d) Addition of promoter

10. Which of the following will not affect the value of equilibrium constant of a reaction?
(a) Change in the concentration of the reactants
(b) Change in temperature
(c) Change in pressure
(d) Addition of catalyst

11. Which of the following statements is/are wrong?
(a) At equilibrium, concentrations of reactants and products become constant because the reaction stops
(b) Addition of catalyst speeds up the forward reaction more than the backward reaction
(c) Equilibrium constant of an exothermic reaction decreases with increase of temperature
(d) K_p is always greater than K_c

12. For the gas phase reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6; \quad \Delta H° = -136.8 \text{ kJ mol}^{-1}$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by: **[BHU (Mains) 2008]**
(a) increasing the temperature
(b) decreasing the pressure
(c) removing some H_2
(d) adding some C_2H_6

13. When $NaNO_3$ is heated in a closed vessel oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, which are not correct?
(a) Addition of $NaNO_2$ favours reverse reaction
(b) Addition of $NaNO_3$ favours forward reaction
(c) Increasing temperature favours forward reaction
(d) Increasing pressure favours reverse reaction

14. An increase in temperature increases which of the following?
1. The rate constant of a reaction
2. The ionic product of water
3. The equilibrium constant of an exothermic reaction

Select the correct answer using the code given below: (SCRA 2007)
(a) 1 and 2 only
(b) 1 and 3 only
(c) 2 and 3 only
(d) 1, 2 and 3 only

15. In the following question, more than one answers are correct. Select the correct answer and mark it according to the codes :

Codes : **[BHU (Mains) 2010]**
(a) 1, 2 and 3 are correct
(b) 1 and 2 are correct
(c) 2 and 4 are correct
(d) 1 and 3 are correct

Water gas, an industrial fuel, consisting CO and H_2 in equimolar amounts is obtained by passing steam over red-hot carbon in accordance with the reaction :

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g); \quad \Delta H = +130.5 \text{ kJ}$$

The yield of water gas can be increased by
(1) → Reducing the total presure of the system
(2) → Increasing pressure of steam
(3) → Raising the temperature
(4) → Introducing hot carbon

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions you are required to choose any one of the following four:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).

(b) If both (A) and (R) are correct and (R) is not the correct explanation for (A).

(c) If (A) is correct but (R) is incorrect.

(d) If (A) is incorrect but (R) is correct.

1. (A) K_p can be equal to or less than or even greater than the value of K_c.

   (R) $K_p = K_c\,(RT)^{\Delta n}$

   Relation between K_p and K_c depends on the change in the number of moles of gaseous reactants and products.

2. (A) For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, the equilibrium constant is 'K' then for $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ the equilibrium constant will be $\sqrt{K}$.

   (R) If concentrations are changed to half the equilibrium constant will be halved.

3. (A) A catalyst does not influence the values of equilibrium constant.

   (R) Catalysts influence the rate of both forward and backward reactions equally.

4. (A) The active mass of pure solid and pure liquid is taken unity.

   (R) The active mass of pure solids and liquids depends on density and molecular mass. The density and molecular mass of pure liquids and solids are constant.

5. (A) For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If more Cl_2 is added the equilibrium will shift in backward direction hence, equilibrium constant will decrease.

   (R) Addition of inert gas to the equilibrium mixture at constant volume, does not alter the equilibrium.

6. (A) At equilibrium $\Delta G = 0$

   (R) $\Delta G^\circ = -RT \log_e K_c$ at equilibrium.

7. (A) At equilibrium $\Delta G = 0$

   (R) The Gibbs free energy of reactants and products decreases and become equal at equilibrium.

8. (A) Equilibrium constant of a reaction changes on changing the stoichiometric coefficients of the reaction.

   (R) The reactions : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ and $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$ have same equilibrium constant.

9. (A) The Q_c for the reaction :

   $$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ is } Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

   (R) When $Q_c < K_c$, the reaction is not at equilibrium and it will be fast in backward direction.

10. (A) The equilibrium of $[PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)]$ is not affected by changing the volume of container.

    (R) $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

    Equilibrium constant K_c does not depend on the volume of vessel.

11. (A) The reaction : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ will shift in forward direction by increase in pressure.

    (R) On increasing the pressure, the equilibrium will shift in forward direction.

Answers : OBJECTIVE QUESTIONS

Set–1

1. (b) 2. (d) 3. (c) 4. (c) 5. (a) 6. (a) 7. (b) 8. (d)
9. (d) 10. (b) 11. (c) 12. (a) 13. (d) 14. (d) 15. (b) 16. (a)
17. (b) 18. (c) 19. (c) 20. (d) 21. (a) 22. (b) 23. (d) 24. (d)
25. (c) 26. (c) 27. (a) 28. (b) 29. (d) 30. (a) 31. (a) 32. (c)
33. (d) 34. (d) 35. (d) 36. (b) 37. (d) 38. (c) 39. (d) 40. (b)
41. (a) 42. (c) 43. (b) 44. (d) 45. (d) 46. (c) 47. (b) 48. (b)
49. (c) 50. (a) 51. (d) 52. (b) 53. (b) 54. (c) 55. (d) 56. (a)
57. (d) 58. (b) 59. (a) 60. (c) 61. (c) 62. (a) 63. (b) 64. (b)
65. (d) 66. (d) 67. (a) 68. (c) 69. (b) 70. (d) 71. (a) 72. (c)
73. (b) 74. (a) 75. (d) 76. (d) 77. (a) 78. (b) 79. (c) 80. (c)
81. (d) 82. (a) 83. (d) 84. (c) 85. (b) 86. (c) 87. (a) 88. (b)
89. (c) 90. (a) 91. (d) 92. (b) 93. (a) 94. (b) 95. (b) 96. (d)
97. (c) 98. (b) 99. (a) 100. (a) 101. (a) 102. (b) 103. (c) 104. (a)
105. (a) 106. (a) 107. (a) 108. (c) 109. (b) 110. (c) 111. (d) 112. (d)
113. (c) 114. (b) 115. (a) 116. (a) 117. (b) 118. (b) 119. (d) 120. (a)
121. (d) 122. (b) 123. (a) 124. (a) 125. (a) 126. (b) 127. (b) 128. (a)
129. (b) 130. (d) 131. (c) 132. (d) 133. (a) 134. (a) 135. (c) 136. (b)
137. (b) 138. (d) 139. (c) 140. (c) 141. (d) 142. (b) 143. (d) 144. (c)
145. (c) 146. (a) 147. (b) 148. (d) 149. (b) 150. (a) 151. (a) 152. (c)
153. (d) 154. (d) 155. (d) 156. (a) 157. (b) 158. (a) 159. (b) 160. (a)
161. (a) 162. (a) 163. (b) 164. (a) 165. (a) 166. (d) 167. (a) 168. (d)
169. (a) 170. (a) 171. (e) 172. (a) 173. (c) 174. (d) 175. (d) 176. (b)
177. (d) 178. (c) 179. (a) 180. (d) 181. (b) 182. (c) 183. (d) 184. (a)
185. (c) 186. (c)

Set–2

1. (b, c) 2. (a, b) 3. (d) 4. (a, b, c) 5. (a) 6. (b) 7. (b) 8. (c, d, e)
9. (b, c, d) 10. (a, b, d) 11. (a, b, d) 12. (a, b, c, d) 13. (a, b, d) 14. (a) 15. (a)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (a) 2. (c) 3. (a) 4. (a) 5. (c) 6. (b) 7. (a) 8. (c)
9. (c) 10. (d) 11. (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

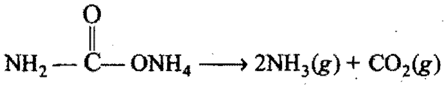
1. Ammonium carbamate when heated to 200°C gives a mixture of NH_3 and CO_2 vapour with a density of 13. What is the degree of dissociation of ammonium carbamate?

[CEE (Kerala) 2004]

(a) $\frac{3}{2}$ (b) $\frac{1}{2}$ (c) 2 (d) 1

(e) $\frac{5}{2}$

[**Hint:**



$$NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-ONH_4 \longrightarrow 2NH_3(g) + CO_2(g)$$

Initial vapour density $D = \frac{\text{Molecular mass}}{2}$

$$= \frac{79}{2} \simeq 39$$

$$\alpha = \frac{D-d}{(n-1)d} = \frac{39-13}{(3-1)\times 13} = \frac{26}{26} = 1$$

here, n = number of moles of product formed by dissociation of 1 mole reactant.]

2. In the heterogeneous equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

what would be the effect of addition of $CaCO_3$ on the equilibrium concentration of CO_2?

(a) Increases (b) Unpredictable

(c) Decreases (d) Remains unaffected

[**Hint:** Gaseous components are not present on both sides, hence, equilibrium will not be affected on addition of $CaCO_3$

$K_p = p_{CO_2}$ = constant (at constant temperature)]

3. For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; if percentage dissociation of N_2O_4 are 25%, 50%, 75% and 100%, then the sequence of observed vapour densities will be:

(a) $d_1 > d_2 > d_3 > d_4$ (b) $d_4 > d_3 > d_2 > d_1$

(c) $d_1 = d_2 = d_3 = d_4$ (d) $(d_1 = d_2) > (d_3 = d_4)$

[**Hint:** Lesser is the percentage dissociation; greater is the vapour density.]

4. In a system:

$$A(s) \rightleftharpoons 2B(g) + 3C(g)$$

if the concentration of C at equilibrium is increased by a factor of 2, it will cause the equilibrium concentration of B to change to:

(a) two times the original value

(b) one half of its original value

(c) $2\sqrt{2}$ times the original value

(d) $\frac{1}{2\sqrt{2}}$ times the original value

5. For the decomposition of $NH_3(g)$ in a sealed tube:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

(a) K_p does not change with pressure

(b) concentration of $H_2(g)$ is less than that of nitrogen

(c) concentration of ammonia does not change with pressure

(d) K_p changes significantly with pressure

6. The equilibrium constant for the decomposition of water,

$$[H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)]$$

is given by:

(a) $K = \frac{\alpha^3 p^{1/2}}{(1-\alpha)(2-\alpha)^{1/2}}$ (b) $K = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(c) $K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$ (d) $K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

7. On heating a mixture of SO_2Cl_2 and CO, two equilibria are simultaneously established:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$
$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

On adding more SO_2 at equilibrium what will happen?

(a) Amount of CO will decrease

(b) Amount of SO_2Cl_2 and $COCl_2$ will increase

(c) Amount of CO will remain unaffected

(d) Amount of SO_2Cl_2 and CO will increase

8. Consider the reactions,

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The addition of an inert gas at constant volume:

(a) will increase the dissociation of PCl_5 as well as N_2O_4

(b) will reduce the dissociation of PCl_5 as well as N_2O_4

(c) will increase the dissociation of PCl_5 and step up the formation of NO_2

(d) will not disturb the equilibrium of the reactions

[**Hint:** At constant volume, inert gas will not affect any of the equilibrium.]

9. Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase of pressure on the equilibrium

$$C\text{ (diamond)} \rightleftharpoons C\text{ (graphite)}$$

(a) favours backward reaction (b) favours forward reaction

(c) has no effect (d) increases the reaction rate

10. A reaction at equilibrium involving 2 moles each of PCl_5, PCl_3 and Cl_2 is maintained at 250°C and a total pressure of 3 atm. The value of K_p is:

(a) 2 (b) 3 (c) 4 (d) 1

[**Hint:**

$$\begin{array}{lccccc} & PCl_5 & \rightleftharpoons & PCl_3 & + & Cl_2 \\ \text{At equilibrium} & 2 & & 2 & & 2 \end{array}$$

$$p_{PCl_5} = \frac{2}{6}\times 3,\ p_{PCl_3} = \frac{2}{6}\times 3,\ p_{Cl_2} = \frac{2}{6}\times 3$$

$$K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{1\times 1}{1} = 1]$$

11. In case of gaseous homogeneous reaction, the active mass of the reactant is given by the expression:

(a) $\frac{RT}{P}$ (b) $\frac{P}{RT}$ (c) $\frac{PV}{RT}$ (d) $\frac{n}{V}RT$

[Hint:

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$\therefore$ Active mass (mol L^{-1}) $= \frac{P}{RT}$]

12. In the dissociation of $I_2(g)$ at 1000 K in a container of 1 litre:

$$I_2(g) \rightleftharpoons 2I^-(g);\ K_c = 10^{-6}$$

Select the correct relation:

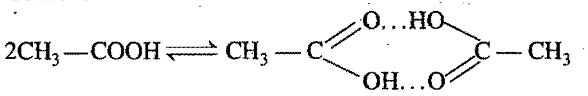
(a) $[I_2] > [I^-]$ (b) $[I_2] < [I^-]$ (c) $[I_2] = [I^-]$ (d) $[I_2] = \frac{1}{2}[I^-]$

[Hint: $K_c = \frac{[I^-]^2}{[I_2]}$

$$10^{-6} = \frac{[I^-]^2}{[I_2]}$$

$\therefore$ $[I_2] > [I^-]$]

13. Acetic acid undergoes dimerisation, when dissolved in benzene



Molecular mass of acetic acid is found 120. Which among the following relation is correct?

(a) $\alpha = 2\left(\frac{D-d}{d}\right)$ (b) $\alpha = 2\left(\frac{D-d}{D}\right)$

(c) $\alpha = 2\left(\frac{d-D}{d}\right)$ (d) $\alpha = \frac{2d}{D-d}$

where, d = Observed vapour density

D = Theoretical vapour density

[Hint: For association of molecule

$$\alpha = \frac{d-D}{d(1-1/n)} = \frac{d-D}{d(1-1/2)}$$

$$= \frac{2(d-D)}{d}]$$

14. The equilibrium:

$$P_4(g) + 6Cl_2(g) \rightleftharpoons 4PCl_3(g)$$

is attained by mixing equal moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium:

(a) $[Cl_2] > [PCl_3]$ (b) $[Cl_2] > [P_4]$

(c) $[P_4] > [Cl_2]$ (d) $[PCl_3] > [P_4]$

15. In the reaction: $A + B \rightleftharpoons 2C + D$. The initial concentration of A and B are 1 M each. The value of K_c is 10^8. What is the equilibrium concentration of A?

(a) 2×10^{-4} M (b) 2×10^{4} M (c) 0.005 M (d) 0.0025 M

16. For the reaction:

$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g);\ K_p = 0.05$ atm at 1000 K

The value of K_c is represented by:

(a) $5\times10^{-4}R$ (b) $\frac{5\times10^{-4}}{R}$ (c) $5\times10^{-5}R$ (d) $\frac{5\times10^{-5}}{R}$

[Hint: $K_p = K_c(RT)^{\Delta n}$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.05}{(1000\times R)^1} = \frac{5\times10^{-5}}{R}]$$

17. Match the List-I (equilibria) with List-II (conditions) and select the correct answer using the options given below:

List-I	List-II
P. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	1. High temperature
Q. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	2. Low temperature
R. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	3. High pressure
	4. Low pressure
	5. Independent of pressure

	P	*Q*	*R*
(a)	1, 3	2, 3	2, 4
(b)	2, 3	1, 4	1, 3
(c)	1, 5	2, 3	2, 4
(d)	2, 4	1, 5	1, 3

18. At constant pressure, the presence of inert gases:

(a) reduces the dissociation of PCl_5

(b) increases the dissociation of PCl_5

(c) does not affect the degree of dissociation of PCl_5

(d) steps up the formation of PCl_5

[Hint: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

On adding inert gas, the equilibrium will shift towards higher volume direction.]

19. Which of the following expressions is correct?

(a) $K_p = K_c\left(\frac{RT}{\Sigma n}\right)^{\Delta n}$ (b) $K_p = K_x\left(\frac{P}{\Sigma n}\right)^{\Delta n}$

(c) $K_p = K_n\left(\frac{P}{\Sigma n}\right)^{\Delta n - 1}$ (d) $K_p = K_c\left(\frac{P}{\Sigma n}\right)^{-\Delta n + 1}$

20. The most stable oxide of nitrogen will be:

(a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g);$ $K = 2.2\times10^{30}$

(b) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g);$ $K = 3.5\times10^{33}$

(c) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g);$ $K = 1.2\times10^{24}$

(d) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g);$ $K = 6.7\times10^{16}$

[Hint: Stability constant $= \frac{1}{K}$

$\therefore$ Smaller is the value of equilibrium constant greater is the stability of oxide.]

21. Equilibrium constant for two complexes are:

A: $K_4[Fe(CN)_6]$ 2.6×10^{37} (for dissociation)

B: $K_3[Fe(CN)_6]$ 1.9×10^{17} (for dissociation)

(a) *A* and *B* are equally stable (b) *A* is more stable than *B*

(c) *B* is more stable than *A* (d) the predictable stability

[Hint: Stability $\propto \frac{1}{\text{Equilibrium constant for dissociation}}$]

22. At the equilibrium of the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the observed molar mass of N_2O_4 is 77.70 g. The percentage dissociation of N_2O_4 is:

(a) 28.4 (b) 46.7 (c) 22.4 (d) 18.4

[Hint: $\alpha = \dfrac{M_0 - M}{(n-1)M}$

$$= \frac{92 - 77.7}{(2-1) \times 77.7} = 0.184$$

% Dissociation = 18.4]

23. Consider the following statements :
In the Haber method of synthesis of ammonia
1. Increase of pressure favours the formation of NH_3
2. Decrease of pressure produces more NH_3
3. Increase of temperature dissociates NH_3
4. Addition of inert gas favours the formation of NH_3
Which of the statements given above are correct?
(SCRA 2009)
(a) 1 and 3 (b) 2 and 4 (c) 1 and 4 (d) 2 and 3

24. For the decomposition of $PCl_5(g)$ in a closed vessel, the degree of dissociation is α at total pressure P.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \quad K_p$$

Which among the following relations is correct?

(a) $\alpha = \sqrt{\dfrac{K_p}{K_p + P}}$ (b) $\alpha = \sqrt{\dfrac{K_p + P}{K_p}}$

(c) $\alpha = \sqrt{K_p + P}$ (d) $\alpha = \dfrac{1}{\sqrt{K_p + P}}$

25. In the decomposition reaction of ammonia:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

2 moles of NH_3 are introduced in the vessel of 1 litre. At equilibrium, 1 mole NH_3 was left, the value of K_c will be:
(a) 0.75 (b) 0.70 (c) 1.75 (d) 1.70

[Hint:

$$\begin{array}{lccc} & 2NH_3(g) & \rightleftharpoons N_2(g) & + 3H_2(g) \\ t=0 & 2 & 0 & 0 \\ t_{eq.} & 1 & 1/2 & 3/2 \end{array}$$

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$= \frac{\frac{1}{2} \times \left(\frac{3}{2}\right)^3}{1^2} = 1.685 \approx 1.7]$$

26. By which of the following relations, the equilibrium constant varies with temperature?

(a) $\ln K_2 - \ln K_1 = \dfrac{\Delta H^\circ}{R} \displaystyle\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$

(b) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R} \displaystyle\int_{1/T_1}^{1/T_2} d\left(\frac{1}{T^2}\right)$

(c) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R} \displaystyle\int_{T_1}^{T_2} d\left(\frac{1}{T}\right)$

(d) $\ln K_2 - \ln K_1 = -\dfrac{\Delta H^\circ}{R} \displaystyle\int_{1/T_2}^{1/T_1} d\left(\frac{1}{T}\right)$

27. For dissociation of a gas N_2O_5 as:

$$N_2O_5(g) \rightleftharpoons 2NO_2(g) + \frac{1}{2} O_2(g);$$

If 'D' is the vapour density of equilibrium mixture and P_0 is the initial pressure of $N_2O_5(g)$, then its equilibrium pressure must not be (M is molecular mass of N_2O_5):

(a) $P_0 \dfrac{(M - 2D)}{3D}$ (b) $\dfrac{P_0 M}{3D - M}$

(c) $\dfrac{P_0 M}{2D}$ (d) $\dfrac{2P_0 D}{M}$

28. $SO_3(g)$ is heated in a closed vessel. An equilibrium:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

is established. The vapour density of the mixture, in which SO_3 is 50% dissociated, is:
(a) 26.5 (b) 35 (c) 42 (d) 55

[Hint: $\alpha = \dfrac{D - d}{(n-1)d}$

$$0.5 = \frac{40 - d}{(2-1)d}$$

$$d = 26.5]$$

29. When $\ln K$ is plotted against $\dfrac{1}{T}$ using the van't Hoff equation, a straight line is expected with a slope equal to:
(a) $\Delta H^\circ/RT$ (b) $-\Delta H^\circ/R$ (c) $\Delta H^\circ/R$ (d) $R/\Delta H^\circ$

30. $AB_2(g)$ dissociates as,

$$AB_2(g) \rightleftharpoons AB(g) + B(g)$$

The initial pressure of AB_2 is 600 mm Hg and total pressure is 800 mm Hg. The equilibrium constant for the reaction will be:
(a) 500 (b) 100 (c) 200 (d) 400

31. For the gaseous reaction,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6,$$

the equilibrium constant has the units:
(a) $mol^2\ dm^{-3}$ (b) $dm^3\ mol^{-1}$ (c) $dm^{-3}\ mol^{-1}$ (d) $mol\ dm^{-3}$

32. The equilibrium constant for the reaction:

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

is 67.8 at 300 K. The equilibrium constant for the dissociation of HBr is:
(a) 0.0147 (b) 67.8 (c) 33.90 (d) 8.349

[Hint: $K_{\text{dissociation}} = \dfrac{1}{K_{\text{formation}}}$]

33. A large positive value of ΔG° corresponds to which of these?
(a) Small positive K (b) Small negative K
(c) Large positive K (d) Large negative K
[Hint: $\Delta G^\circ = -2.303RT \log K_e$]

34. What is ΔG° for the following reaction?

$$\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightleftharpoons NH_3(g); \ K_p = 4.42 \times 10^4 \text{ at } 25^\circ C$$

(a) $-26.5\ kJ\ mol^{-1}$ (b) $-11.5\ kJ\ mol^{-1}$
(c) $-2.2\ kJ\ mol^{-1}$ (d) $-0.97\ kJ\ mol^{-1}$

35. For the following reaction: $K = 1.7 \times 10^7$ at 25°C

$$Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons [Ag(NH_3)_2]^+$$

what is the value of ΔG° in kJ?
(a) −41.2 (b) −17.9 (c) +17.9 (d) +41.2

36. If E°_{cell} for a given reaction is negative, which gives the correct relationships for the values of ΔG° and K_{eq}?
(a) $\Delta G^\circ > 0, K_{eq.} < 1$ (b) $\Delta G^\circ > 0, K_{eq.} > 1$
(c) $\Delta G^\circ < 0, K_{eq.} > 1$ (d) $\Delta G^\circ < 0, K_{eq.} < 1$

37. The free energy of formation of NO is 78 kJ mol^{-1} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K?

$$\frac{1}{2}N_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons NO(g).$$

(a) 8.4×10^{-5} (b) 7.1×10^{-9} (c) 4.2×10^{-10} (d) 1.7×10^{-19}

38. $$2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$$

Given, that the equilibrium constant for the reaction above has a value of 278 at a particular temperature, what is the value of equilibrium constant for the following reaction at same temperature?

$$SO_3(g) \rightleftharpoons SO_2(g)+\frac{1}{2}O_2(g)$$

(a) 1.3×10^{-5} (b) 1.8×10^{-3} (c) 3.6×10^{-3} (d) 6×10^{-2}

39. In which of the following reactions, the increase in volume of the container will favour the formation of products?

(a) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(c) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l)$

(d) $3O_2(g) \rightleftharpoons 2O_3(g)$

40. Consider the reaction, whose $K_c = 33$,

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If 0.1 mol each of SO_2 and NO_2 are placed in 1 L container, what is the concentration of SO_2 at equilibrium?

(a) 0.003 *M* (b) 0.015 *M* (c) 0.085 *M* (d) 0.097 *M*

41.

Reaction	*K*
$\frac{1}{2}N_2(g)+O_2(g) \rightleftharpoons NO_2(g)$	K_1
$2NO_2(g) \rightleftharpoons N_2O_4(g)$	K_2

Using above equations, write down expression for *K* of the following reaction:

$$N_2O_4(g) \rightleftharpoons N_2(g)+\frac{1}{2}O_2(g)$$

(a) K_1K_2 (b) $\frac{K_2^2}{K_1}$ (c) $\frac{1}{K_2K_1^2}$ (d) $\frac{1}{K_1^2K_2}$

42. Cu^{2+} ions react with Fe^{2+} ions according to the following reaction:

$$Cu^{2+} + 2Fe^{2+} \rightleftharpoons Cu + 2Fe^{3+}$$

At equilibrium, the concentration of Cu^{2+} ions is not changed by the addition of:

(a) Cu^{2+} (b) Fe^{2+} (c) Cu (d) Fe^{3+}

43. Consider this equilibrium, for which $\Delta H < 0$,

$$HgO(s) + 4I^-(aq.) + H_2O(l) \rightleftharpoons HgI_4^{2-} + 2OH^-$$

Which changes will increase the equilibrium concentration of HgI_4^{2-}?

I. Increasing the mass of $HgO(s)$ present.

II. Increasing $[I^-]$.

III. Adding 1 *M* HCl.

(a) I only (b) II only

(c) II and III only (d) I, II and III

44. Which of the following do not change the value of *K* for a reaction?

(a) Addition of catalyst

(b) Increase in temperature

(c) Increase in pressure

(d) Removal of one of the products

45. For which of the following reactions at equilibrium at constant temperature doubling the volume will cause a shift to the right?

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

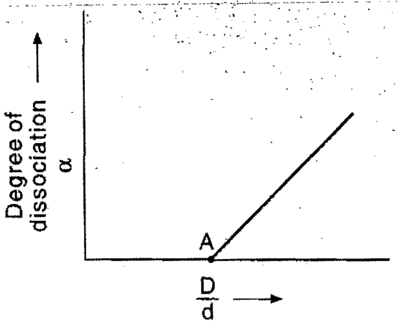
(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(c) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

(d) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

46. In the reaction,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ if *D* and *d* are the vapour densities at initial stage and at equilibrium then what will be the value of $\frac{D}{d}$ at point *A* in the following graph?



(a) 0 (b) 1.5 (c) 1 (d) 0.5

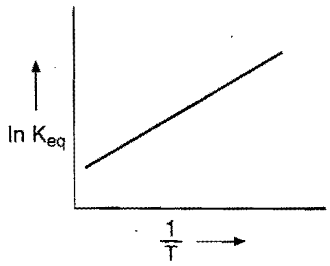
[Hint: $\alpha = \frac{D-d}{(n-1)d}$

For the given reaction, $n = 2$ and $\alpha = 0$ at *A*

$$\therefore \quad \frac{D-d}{(2-1)d} = 0$$

$$\frac{D}{d} = 1]$$

47. A schematic plot of $\ln K_{eq}$ *versus* inverse of temperature for a reaction is shown below:



The reaction must be:

(a) exothermic

(b) endothermic

(c) one with negligible enthalpy change

(d) highly spontaneous at ordinary temperature

[Hint: We know that, $\frac{d \ln K_{eq.}}{dT} = \frac{\Delta H^\circ}{RT^2}$

$$\therefore \qquad \ln K_{eq.} = -\frac{\Delta H^\circ}{RT} + C$$

The plot has positive slope, hence ΔH° will be negative.]

48. The equilibrium:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g),$$

is followed to set-up at 127°C in a closed vessel. The total pressure at equilibrium was 20 atm. The K_c for the reaction is:

(a) $0.092\,M^2$ (b) $0.085\,M^2$

(c) $3.045\,M^2$ (d) none of these

[Hint: $pNH_3 = pH_2S = \frac{20}{2}$ atm

$$K_p = pNH_3 \times pH_2S = 100 \text{ atm}^2$$

$$K_p = K_c\,(RT)^{\Delta n}$$

$$100 = K_c \times (0.0821 \times 400)^2$$

$$K_c = 0.092\,M^2]$$

49. 20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Mixture has the density at equilibrium equal to:

(a) 1.48 g/L (b) 1.84 g/L

(c) 2.25 g/L (d) 3.12 g/L

[Hint: The reaction is:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$n = 2 \text{ and } \alpha = \frac{20}{100} = 0.2$$

$D = 46$, initial vapour density

d = vapour density at equilibrium

$$\alpha = \frac{D-d}{(n-1)d}$$

$$0.2 = \frac{46-d}{(2-1)d}$$

$$d = 38.3$$

Molar mass equilibrium = 2 × 38.3 = 76.6

$Pm = dRT$ Here, d = density of gas mixture

$$d(\text{mix}) = \frac{Pm}{RT} = \frac{1 \times 76.6}{0.0821 \times 300} = 3.12 \text{ g/L}]$$

50. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$; respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is: **(AIEEE 2008)**

(a) 1 : 9 (b) 1 : 36

(c) 1 : 1 (d) 1 : 3

[Hint :

$$\begin{array}{lccccccc} & X & \rightleftharpoons & 2Y & & Z & \rightleftharpoons & P & + & Q \\ t_0 & 1 & & 0 & & 1 & & 0 & & 0 \\ t_{eq.} & 1-\alpha & & 2\alpha & & 1-\alpha & & \alpha & & \alpha \end{array}$$

$$K_{p_1} = \frac{\left[\frac{2\alpha}{1+\alpha}P_1\right]^2}{\left[\frac{1-\alpha}{1+\alpha}P_1\right]} \qquad K_{p_2} = \frac{\left[\frac{\alpha}{1+\alpha}P_2\right]\left[\frac{\alpha}{1+\alpha}P_2\right]}{\left[\frac{1-\alpha}{1+\alpha}P_2\right]}$$

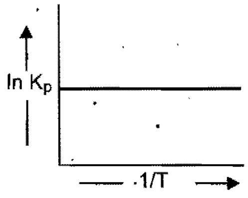
$$= \frac{4\alpha^2 P_1}{1-\alpha^2} \qquad = \frac{\alpha^2 P_2}{1-\alpha^2}$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{4\alpha^2 P_1}{1-\alpha^2} \Big/ \frac{\alpha^2 P_2}{1-\alpha^2}$$

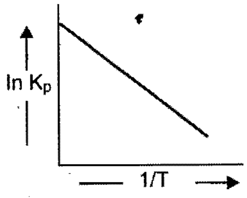
$$\frac{1}{9} = \frac{4P_1}{P_2}$$

$$\frac{P_1}{P_2} = \frac{1}{36}]$$

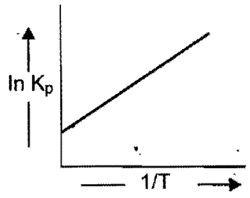
51. Which of the following plots is correct about endothermic reaction ?



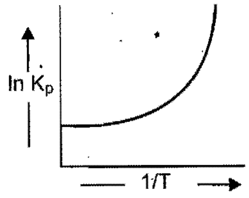
(a)



(b)



(c)



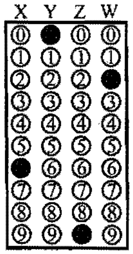
(d)

Answers

1. (d)	**2.** (d)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (b)	**7.** (d)	**8.** (d)
9. (a)	**10.** (d)	**11.** (b)	**12.** (a)	**13.** (c)	**14.** (c)	**15.** (b)	**16.** (d)
17. (c)	**18.** (b)	**19.** (b)	**20.** (d)	**21.** (c)	**22.** (d)	**23.** (a)	**24.** (a)
25. (d)	**26.** (c)	**27.** (a)	**28.** (a)	**29.** (b)	**30.** (b)	**31.** (b)	**32.** (a)
33. (a)	**34.** (a)	**35.** (a)	**36.** (a)	**37.** (a)	**38.** (d)	**39.** (a)	**40.** (b)
41. (d)	**42.** (c)	**43.** (c)	**44.** (a, c, d)	**45.** (a, b)	**46.** (c)	**47.** (a)	**48.** (a)
49. (d)	**50.** (b)	**51.** (b)					

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. For the reaction:
$$AB(g) \rightleftharpoons A(g) + B(g)$$
AB is 33% dissociated at a total pressure of p. Then, $\frac{p}{K_p}$ will be equal to :
2. If the reaction $A \rightleftharpoons B$, has $\Delta G^\circ = 0$, then its equilibrium constant will be equal to :
3. Consider the following reaction
$$A + B \rightleftharpoons E \qquad K_c = 6$$
$$2B + C \rightleftharpoons 2D \qquad K_c = 4$$
What will be the equilibrium constant (K_c) for the following reaction?
$$A + D \rightleftharpoons E + C$$
4. For the equilibrium of the reaction :
$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g) \quad K_p = 81 \text{ atm}^2$$
Total pressure at equilibrium will be x times the pressure of NH_3.
The value of x will be :
5. Mixing 4 moles of A with 4 moles of B forms 2 moles of C at equilibrium, according to the following reaction :
$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$
The value of equilibrium constant is :
6. A reaction at equilibrium involving 2 mol each of PCl_5, PCl_3, Cl_2 is maintained at 250°C and total pressure of 3 atm. The value of K_p is :
7. For the reaction:
$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$
The initial concentrations of A and B are equal. The equilibrium concentration of C is two times the equilibrium concentration of A. The value of equilibrium constant is :
8. $$N_2 + O_2 \rightleftharpoons 2NO; K_1$$
$$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO; K_2$$
$$2NO \rightleftharpoons N_2 + O_2; K_3$$
$$NO \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2; K_4$$
$K_1 \times K_3 = x;\quad \sqrt{K_1} \times K_4 = y;\quad \sqrt{K_3} \times K_2 = z$
What will be the value of xyz?
9. 4.5 moles each of H_2 and I_2 are heated in a sealed 10 L vessel. At equilibrium, 3 mole of HI were found. The equilibrium constant for :
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ is :}$$
10. SO_2Cl_2 and Cl_2 are introduced into a 3 L vessel. Partial pressure of SO_2Cl_2 and Cl_2 at equilibrium are 1 atm and 2 atm respectively. The value of K_p for the following reaction is 10.
$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$
The total pressure in atm at equilibrium would be :

Answers

1. (8) **2.** (1) **3.** (3) **4.** (2) **5.** (1) **6.** (1) **7.** (4) **8.** (1)
9. (1) **10.** (8)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

Phosphorous pentachloride when heated in a sealed tube at 700 K, it undergoes decomposition as,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \quad K_p = 38\,atm$$

vapour density of the mixture is 74.25.

Answer the following questions:

1. The reaction is:
   (a) endothermic
   (b) exothermic
   (c) may be endothermic or exothermic
   (d) unpredictable
2. Percentage dissociation of PCl_5 may be given as:
   (a) 4.04 (b) 40.4 (c) 44.0 (d) 0.404
3. Equilibrium constant K_c for the reaction will be:
   (a) 0.66 *M* (b) 0.56 *M* (c) 0.46 *M* (d) 0.36 *M*
4. If pressure is increased then the equilibrium will:
   (a) be unaffected
   (b) shift in backward direction
   (c) shift in forward direction
   (d) cannot be predicted
5. When inert gas is added to the given reversible process then the equilibrium will:
   (a) be unaffected
   (b) shift in backward direction
   (c) shift in forward direction
   (d) cannot be predicted

• Passage 2

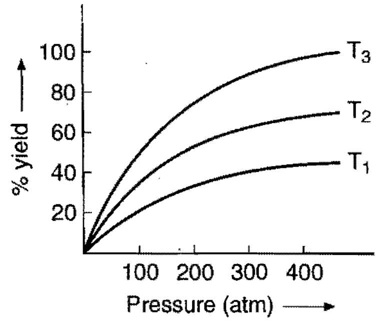
In Haber's process, the ammonia is manufactured according to the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \Delta H^\circ = -(22.4\,kJ)$$

The pressure inside the chamber is maintained at 200 *atm and temperature at* 500°C. *Generally, this reaction is carried out in presence of Fe catalyst.*

Answer the following questions:

1. If K_p for the given reaction is 1.44×10^{-5}, then the value of K_c will be:
   (a) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ mol L^{-1}
   (b) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$ mol L^{-1}
   (c) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ mol L^{-1}
   (d) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$ mol L^{-1}
2. The preparation of ammonia by Haber's process is an exothermic reaction. If the preparation follows the following temperature pressure relationship for its % yield. Then for temperature T_1, T_2 and T_3 the correct option is:



   (a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$
   (c) $T_1 = T_2 = T_3$ (d) nothing could be predicted
   [**Hint:** The % yield will decrease with rise in temperature, since it is exothermic.]
3. 500°C is considered optimum temperature for Haber's process because:
   (a) catalyst has maximum activity at this temperature
   (b) energy required is easily obtained at this temperature
   (c) yield is maximum at this temperature
   (d) rate is fast enough while the yield is also appreciable at this temperature
4. If K_p for the reaction is 1.44×10^{-5}, then the value of K_p for the decomposition of NH_3,
   $$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$
   will be:
   (a) $\sqrt{1.44 \times 10^{-5}}$ (b) $(1.44 \times 10^{-5})^2$
   (c) $\dfrac{1}{1.44 \times 10^{-5}}$ (d) 2.88×10^{-5}
5. 30 litre $H_2(g)$ and 30 litre were taken for the reaction in Haber's process which yields only 50% of the expected ammonia due to reversibility of the reaction. What will be the composition of reaction mixture under the given condition?

	NH_3	N_2	H_2
(a)	20 L	20 L	20 L
(b)	10 L	25 L	15 L
(c)	20 L	10 L	30 L
(d)	20 L	25 L	15 L

• Passage 3

When all the coefficients in a balanced chemical equation are multiplied by a constant factor J, the equilibrium constant (originally K) becomes K^J. Similarly, when balanced equations are added together, the equilibrium constant for the combined process is equal to the product of the equilibrium constants for each step.

Equilibrium constant of the reversed reaction is numerically equal to the reciprocal of the equilibrium constant of the original equation.

$$\text{Unit of } K_p = (atm)^{\Delta n}; \text{ Unit of } K_c = [mol\,L^{-1}]^{\Delta n}$$

Answer the following questions:

1. Consider the reactions:

(i) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$
(ii) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$
(iii) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

Which of the following is correct?

(a) $K_3 = K_1/K_2$ (b) $K_3 = K_1^2/K_2^3$
(c) $K_3 = K_1K_2$ (d) $K_3 = K_1\sqrt{K_2}$

2. The equilibrium constants for the following reactions at 1400 K are given:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g);\ K_1 = 2.1\times10^{-13}$$
$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g); K_2 = 1.4\times10^{-12}$$

Then, the equilibrium constant K for the reaction,

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

is:

(a) 2.04 (b) 20.5 (c) 2.6 (d) 8.4

3. Given: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g); K_1$
$2NO_2(g) \rightleftharpoons N_2O_4(g); K_2$
$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g); K_3$

Which of the following relations is correct?

(a) $K_3 = K_1/K_2$ (b) $K_3 = K_1 \times K_2$
(c) $K_3 = K_1 + K_2$ (d) $K_3 = \frac{K_1}{\sqrt{K_2}}$

4. H_3PO_4 is a tribasic acid, it undergoes ionization as:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-; K_1$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}; K_2$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}; K_3$$

Then, equilibrium constant for the following reaction will be:

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

(a) $K_1K_2K_3$ (b) $\frac{K_1K_2}{K_3}$ (c) $\frac{K_1K_3}{K_2}$ (d) $\frac{K_1K_2}{K_3^2}$

5. Consider the two reactions:

$$XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2HF(g); K_1$$
$$XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g); K_2$$

Then, the equilibrium constant for the following reaction will be:

$$XeO_4(g) + 2HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$$

is given by:

(a) K_1/K_2^2 (b) K_1/K_2 (c) K_1^2/K_2 (d) K_2/K_1

• Passage 4

Mass action ratio or reaction quotient Q for a reaction can be calculated using the law of mass action,

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$
$$Q = \frac{[C][D]}{[A][B]}$$

The value of Q decides whether the reaction is at equilibrium or not.

At equilibrium, $Q = K$
For non-equilibrium process, $Q \neq K$

when $Q > K$, reaction will favour backward direction and when $Q < K$, it will favour forward direction.

Answer the following questions:

1. The reaction quotient Q for:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is given by $Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed in backward direction, when:

(a) $Q = K_c$ (b) $Q < K_c$ (c) $Q > K_c$ (d) $Q = 0$

2. For the reaction:

$$2A + B \rightleftharpoons 3C \quad \text{at 298 K, } K_c = 49$$

A 3L vessel contains 2, 1 and 3 moles of A, B and C respectively. The reaction at the same temperature:

(a) must proceed in forward direction
(b) must proceed in backward direction
(c) must be in equilibrium
(d) cannot be predicted

3. In a reaction mixture containing H_2, N_2 and NH_3 at partial pressure of 2 atm, 1 atm and 3 atm respectively, the value of K_p at 725 K is 4.28×10^{-5} atm^{-2}. In which direction the net reaction will go?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) Forward
(b) Backward
(c) No net reaction
(d) Direction cannot be predicted

4. In the following reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

the equilibrium is not attained. The rate of forward reaction is greater than that of backward reaction. Thus, which of the following is the correct relation between K_p and Q_p?

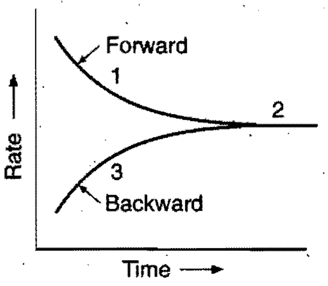
(a) $K_p = Q_p$ (b) $Q_p > K_p$ (c) $Q_p < K_p$ (d) $K_p = Q_p = 1$

5. In the reaction:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

a graph is plotted to show the variation of rate of forward and backward reactions against time:

Which of following is correct?



	$Q > K$	$Q = K$	$Q < K$
(a)	3	2	1
(b)	1	2	3
(c)	2	3	1
(d)	2	1	3

• Passage 5

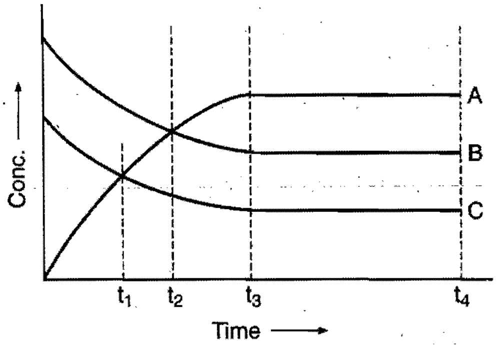
In a reversible chemical reaction, the rate of forward reaction decreases and that of backward reaction increases with the passage of time; at equilibrium the rate of forward and backward reactions become same.

Let us consider the formation of SO_3 in the following reversible reaction:

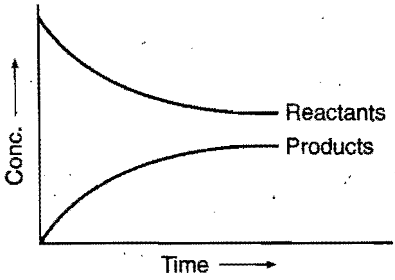
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Following graphs are plotted for this reaction:

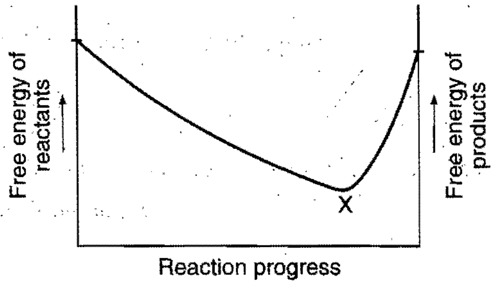
Graph 1



Graph 2



Graph 3



Answer the following questions:

1. In the graph (1), A, B and C respectively are:
   (a) SO_3, SO_2 and O_2 (b) SO_3, O_2 and SO_2
   (c) SO_2, O_2 and SO_3 (d) O_2, SO_2 and SO_3
2. In the graph (1), the equilibrium state is reached at:
   (a) t_1 (b) t_2 (c) t_3 (d) t_4
3. The graph (2) tells us that:
   (a) the reaction is irreversible
   (b) the reaction is reversible
   (c) the reaction is exothermic
   (d) the reaction is endothermic
4. The graph (2) tells us that:
   (a) equilibrium is never achievable
   (b) equilibrium is achieved after the concentrations of reactants and products become equal
   (c) equilibrium is achieved before the concentrations of reactants and products become equal
   (d) none of the above
5. From the graph (3), it can be interpreted that:
   (a) equilibrium is achieved at X
   (b) reaction is nearer to the completion
   (c) $\Delta G = 0$ at X
   (d) all of the above

Answers

Passage 1.	1. (a)	2. (b)	3. (a)	4. (b)	5. (c)
Passage 2.	1. (d)	2. (b)	3. (d)	4. (c)	5. (b)
Passage 3.	1. (c)	2. (d)	3. (b)	4. (a)	5. (d)
Passage 4.	1. (c)	2. (a)	3. (b)	4. (c)	5. (a)
Passage 5.	1. (a)	2. (c)	3. (b)	4. (c)	5. (d)

SELF ASSESSMENT

ASSIGNMENT NO. 9

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. By applying the law of mass action, the equilibrium constant K for the reaction:

$$HA + H_2O \rightleftharpoons H_3^+O + A^- \quad \text{[CET (J\&K) 2007]}$$

(a) $K = \dfrac{[HA][H_2O]}{[H_3O^+][A^-]}$ (b) $K = \dfrac{[H_3^+O][A^-]}{[HA][H_2O]}$

(c) $K = \dfrac{[H_3^+O][H_2O]}{[A^-][HA]}$ (d) $K = \dfrac{[HA][A^-]}{[H_2O][H_3O^+]}$

2. For the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

When temperature increases: **[PMT (Haryana) 2007]**

(a) formation of NH_3 increases

(b) formation of NH_3 decreases

(c) concentration of N_2 decreases

(d) concentration of H_2 decreases

3. For the reaction 1 g mole of $CaCO_3$ is enclosed in 5 L container

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = 1.16$ atm at 1073 K then percentage dissociation of $CaCO_3$ is:

(a) 65% (b) 100% (c) 6.5% (d) zero

4. The activation energy for forward and backward reactions are 50 kJ / mol and 40 kJ / mol respectively. If K_1 and K_2 are the equilibrium constants of reaction at temperature T_1 and T_2 respectively and $T_2 > T_1$ then:

(a) $K_1 < K_2$ (b) $K_1 = K_2$ (c) $K_1 > K_2$ (d) $K_2 = K_1^2$

[**Hint:** $\Delta H = E_f - E_b = 50 - 40 = 10$ kJ / mol. In endothermic reactions, equilibrium constant increases with increase in temperature.]

5. Given, $X(g) \rightleftharpoons nY(g)$.

If degree of dissociation is α, then K_c of the reaction in a vessel of 1 litre is:

(a) $\dfrac{n\alpha^n}{1-\alpha}$ (b) $\dfrac{n\alpha}{1-\alpha}$ (c) $\dfrac{(n\alpha)^n}{1+\alpha}$ (d) $\dfrac{(n\alpha)^n}{1-\alpha}$

6. Consider the following equation in a closed container,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

at a fixed temperature, the volume of the reaction container is halved, for this change, which of the following statement holds true regarding the K_p and degree of dissociation 'α':

(a) neither K_p nor α changes

(b) both K_p and α change

(c) K_p changes but α does not change

(d) K_p does not change but α changes

7. The reaction, $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ is studied in a vessel of one litre at 250° C. The initial concentration of A was $3x$ and that of B was x. At equilibrium, concentration of C was found to be equal to the equilibrium concentration of B. What is the concentration of D at equilibrium:

(a) $\dfrac{x}{2}$ (b) $3x - \dfrac{1}{2}$ (c) $x - \dfrac{x}{2}$ (d) x

SECTION-II

Multiple Answers Type Objective Questions

8. Equilibrium constant does not depend on:

(a) catalyst (b) temperature

(c) pressure (d) inert gas

9. Which of the following reactions have $K_p < K_c$?

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(b) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

(c) $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$

(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

10. Which of the following reactions are not affected by inert gas addition?

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(In a rigid container of constant volume)

(c) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(d) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

11. Which of the following are not affected by pressure change?

(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(b) $2NaNO_2(s) + O_2(g) \rightleftharpoons 2NaNO_3(s)$

(c) $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

(d) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

12. The reaction,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ (Exothermic)}$$

will shift in forward direction by:

(a) adding SO_3 at constant volume

(b) increasing volume of container

(c) adding SO_2 at constant volume

(d) adding inert gas at constant volume

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.

(c) Statement-1 is true; statement-2 is false.

(d) Statement-1 is false; statement-2 is true.

13. **Statement-1:** The value of equilibrium constant depends on the stoichiometry of the equation.

Because

Statement-2: The value of equilibrium constant does not change when the equation is multiplied or divided by a number.

14. **Statement-1:** $K_p = K_c$ for all reactions.

Because

Statement-2: K_p and K_c are interrelated by the equation $K_p = K_c(RT)^{\Delta n}$.

15. **Statement-1:** Catalyst does not change the position of equilibrium.

Because

Statement-2: Catalyst only changes the equilibrium time.

16. **Statement-1:** Free energy of both reactants and products are minimum at equilibrium.

Because

Statement-2: The free energy of reactants and products decreases with passage of time and become equal at equilibrium.

17. **Statement-1:** Addition of inert gases at equilibrium will support the dissociation of PCl_5 at constant temperature.

Because

Statement-2: The addition of inert gas at constant volume will not affect the equilibrium.

SECTION-IV

Matrix-Matching Type Questions

This section contains 4 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in List-I have to be matched with statements (p, q, r and s) in List-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s), then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

18. Match the List-I with List-II:

List-I	List-II
(a) $A(g) \rightleftharpoons B(g) + C(g)$	(p) $\alpha = \sqrt{\frac{K_p}{K_p + 4P}}$
(b) $A_2(g) \rightleftharpoons 2A(g)$	(q) $\alpha = \sqrt{\frac{K_p}{P + K_p}}$
(c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$	(r) $M_{mix} = \frac{M_{reactant}}{1+\alpha}$
(d) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	(s) Forward shift on decreasing the pressure

19. Match the List-I with List-II:

List-I (Mathematical process)	List-II (New equilibrium constant)
(a) Divided by n	(p) K^n
(b) Multiplied by n	(q) $\frac{1}{K}$
(c) Reaction is reversed	(r) $K_1 \times K_2 \times K_3 \times \ldots \times K_n$
(d) n-equations are added	(s) $(K)^{1/n}$

20. Match the List-I with List-II for the following reaction:

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

List-I	List-II
(a) Partial pressure of $NH_4HS(s)$	(p) $p_{NH_3} \times p_{H_2S}$
(b) K_p	(q) $p_{NH_3} + p_{H_2S}$
(c) Total pressure at equilibrium	(r) $(p_{NH_3} \times p_{H_2})(RT)^{-2}$
(d) K_c	(s) Zero

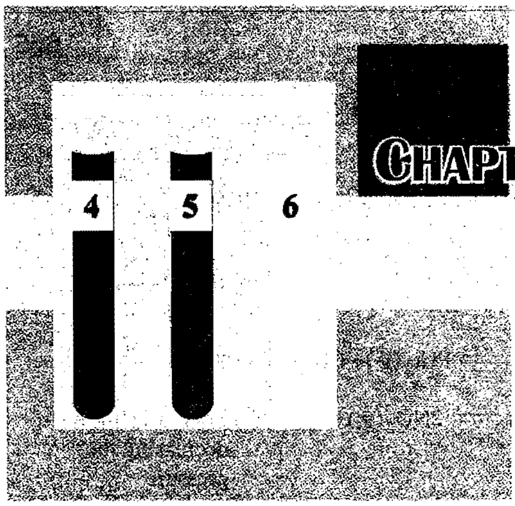
Answers

1. (b) 2. (b) 3. (c) 4. (a) 5. (d) 6. (d) 7. (a) 8. (a, b, d)

9. (b. d) 10. (a, b) 11. (a, b, c) 12. (a, b) 13. (c) 14. (d) 15. (a) 16. (a)

17. (b) 18. (a-q,r,s) (b-p,q,s) (c-q, r,s) (d-p,s) 19. (a-s) (b-p) (c-q) (d-r)

20. (a-s) (b-p) (c-q) (d-r)



CHAPTER 10

IONIC EQUILIBRIUM

10.1 INTRODUCTION

The compounds which give ions either in molten state or in solution are called electrolytes. In the solid state they are bad conductors, but become good conductors either in the molten state or in solution.

There are two types of electrolytes:

(1) Strong electrolytes: These electrolytes are almost completely ionised when dissolved in a polar medium like water. In solution they are excellent conductors, *e.g.*, HNO_3, HCl, KOH, NaOH, etc. Their degree of ionization is high and approaches unity.

(2) Weak electrolytes: These are not completely ionized when dissolved in a polar solvent and they behave as poor conductors of electricity, *e.g.*, CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, etc. Equilibrium between ions and unionised molecules is established in solution; *e.g.*,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

The above equilibrium is termed as ionic equilibrium. Degree of ionization of weak electrolytes is much less than unity.

Degree of ionization 'α' may be defined as a fraction of total number of molecules of an electrolyte which dissociate into ions.

$$\alpha = \frac{\%\text{ ionization}}{100}$$

$$= \frac{\text{Number of molecules dissociated as ions}}{\text{Total number of molecules of electrolyte dissolved}}$$

The following classification of electrolytes is based on their behaviour in a particular solvent, *i.e.*, water.

Solutions (aqueous)

- Conducting (solutions of electrolytes, *i.e.*, acids, bases and salts)
  - Strongly conducting (solns. of strong electrolytes which ionise almost completely in water such as HCl, H_2SO_4, HNO_3, NH_4Cl, NaCl, NaOH, KOH, etc.)
  - Weakly conducting (solutions of weak electrolytes which slightly ionise in water such as CH_3COOH, NH_4OH, H_3PO_4, HCN, etc.)
- Non-conducting (solutions of non-electrolytes such as urea, glucose, sugar, glycerine, etc.)

However, an electrolyte may behave as a strong one in aqueous solution, but it may behave as a weak one in another solvent. For example, sodium chloride behaves as a strong electrolyte and acetic acid as a weak electrolyte when dissolved in water but their conducting abilities are comparable in liquid ammonia solvent.

10.2 OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolytic dissociation, the molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by Ostwald that like chemical equilibrium, **law of mass action** can be applied to such systems also.

Consider a binary electrolyte *AB* which dissociates into A^+ and B^- ions and the equilibrium state is represented by the equation:

	AB	$\rightleftharpoons$	A^+	$+$	B^-
Initially $t = 0$	C		0		0
At equilibrium	$C(1-\alpha)$		$C\alpha$		$C\alpha$

So, dissociation constant may be given as:

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{(1-\alpha)} \qquad \text{... (i)}$$

For very weak electrolytes,

$$\alpha <<< 1, (1-\alpha) \approx 1$$

$$\therefore \quad K = C\alpha^2$$

$$\alpha = \sqrt{K/C} \qquad \text{... (ii)}$$

Concentration of any ion = $C\alpha = \sqrt{CK}$.

From equation (ii), it is clear that degree of ionization increases on dilution.

Thus, **degree of dissociation of a weak electrolyte is proportional to the square root of dilution.**

Limitations of Ostwald's dilution law: The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes. The value of 'α' is determined by conductivity measurements by applying the formula Λ / Λ_∞. The value of 'α' determined at various dilutions of an electrolyte when substituted in eq. (i) gives a constant value of K only in the case of weak electrolytes like CH_3COOH, NH_4OH, etc. The cause of failure of Ostwald's dilution law in the case of strong electrolytes is due to the following factors:

(i) The law is based on the fact that only a portion of the electrolyte is dissociated into ions at ordinary dilution and completely at infinite dilution. Strong electrolytes are almost completely ionised at all dilutions and Λ / Λ_∞ does not give accurate value of 'α'.

(ii) When concentration of the ions is very high, the presence of charges on the ions appreciably affects the equilibrium. Hence, law of mass action in its simple form cannot be strictly applied in the case of strong electrolytes.

SOME SOLVED EXAMPLES

Example 1. *A 0.01 M solution of acetic acid is 5% ionised at 25° C. Calculate its dissociation constant.*

Solution: According to Ostwald's dilution law,

$$K_a = \frac{\alpha^2}{(1-\alpha)V}$$

$$\alpha = 0.05, \quad V = \frac{1}{0.01} = 100 \text{ litre}$$

Hence, $$K_a = \frac{0.05 \times 0.05}{(1-0.05)100} = 2.63 \times 10^{-5}$$

Example 2. *Calculate the H^+ ion concentration of a 0.01 N weak monobasic acid. The value of dissociation constant is 4.0×10^{-10}.*

Solution: $HA \rightleftharpoons H^+ + A^-$

Applying Ostwald's dilution law for a weak acid,

$$\alpha = \sqrt{K_a V}$$

$$K_a = 4.0 \times 10^{-10}, \quad V = \frac{1}{0.01} = 100 \text{ litre}$$

$$\alpha = \sqrt{4 \times 10^{-10} \times 10^2} = 2 \times 10^{-4}$$

Concentration of hydrogen ions

$$= \frac{\alpha}{V} = \frac{2 \times 10^{-4}}{100} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

or concentration of hydrogen ions

$$= \sqrt{CK} = \sqrt{0.01 \times 4 \times 10^{-10}} = 2 \times 10^{-6} \text{ mol L}^{-1}$$

Example 3. *The concentration of H^+ ions in 0.10 M solution of a weak acid is 1.0×10^{-5} mol L^{-1}. Calculate the dissociation constant of the acid.*

Solution:	HA	$\rightleftharpoons$	H^+	$+$	A^-
Initial concentration	0.1		0		0
Equilibrium concentration (mol L^{-1})	$0.1 - 1.0 \times 10^{-5}$		1.0×10^{-5}		1.0×10^{-5}

[HA] can be taken as 0.1 M as 1.0×10^{-5} is very small.

Applying law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{1.0 \times 10^{-5} \times 1.0 \times 10^{-5}}{0.10}$$

$$= 1 \times 10^{-9}$$

Example 4. *What will be the dissociation constant of 0.1N aqueous ammonia solution in terms of degree of dissociation 'α'? What will be the value if the concentration is 0.01N?*

Solution: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

At equilibrium $\quad (1-\alpha) \quad \alpha \quad \alpha$

Since, the solution is 0.1 N,

$$V = \frac{1}{0.1} = 10 \text{ litre}$$

$$[NH_4OH] = \frac{(1-\alpha)}{10}, \; [NH_4^+] = \frac{\alpha}{10} \text{ and } [OH^-] = \frac{\alpha}{10}$$

Applying law of mass action,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{\frac{\alpha}{10} \times \frac{\alpha}{10}}{\frac{1-\alpha}{10}} = \frac{\alpha^2}{10(1-\alpha)}$$

For 0.01 N solution, K_b remains the same at the same temperature but degree of dissociation value becomes different.

Example 5. *A 0.0128 N solution of acetic acid has $\Lambda = 14$ mho equiv^{-1} and $\Lambda_\infty = 391$ mho eq^{-1} at 25°C. Calculate the dissociation constant of the acid.*

Solution: Degree of dissociation,

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{14}{391} = 3.58\times 10^{-2}$$

$$[1-\alpha \longrightarrow 1 \text{ as } \alpha \text{ is very small}]$$

Now applying Ostwald's dilution law,

$$K_a = \frac{\alpha^2}{(1-\alpha)V}$$

$$\alpha = 3.58\times 10^{-2} \quad \text{and} \quad V = \frac{1}{0.0128} \text{ litre}$$

So, $K_a = 3.58\times 10^{-2}\times 3.58\times 10^{-2}\times 0.0128 = 1.64\times 10^{-5}$

10.3 COMMON ION EFFECT

Let AB be the weak electrolyte. Considering its dissociation,

$$AB \rightleftharpoons A^+ + B^-$$

and applying law of mass action, we have

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant, K, has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution, it will increase the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increase, *i.e.*, the equilibrium will shift to the left hand side.

In other words, **the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion.** This is termed as **common ion effect.** Acetic acid is a weak electrolyte and its ionisation is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or NaOH to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH_4^+ or OH^-.

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

SOME SOLVED EXAMPLES

Example 6. *The ionisation constant of HCN is* 4×10^{-10}. *Calculate the concentration of hydrogen ions in* 0.2 *M solution of HCN containing* 1 *mol* L^{-1} *of KCN.*

Solution: The dissociation of HCN is represented as

$$HCN \rightleftharpoons H^+ + CN^-$$

Applying law of mass action,

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \quad \text{or} \quad [H^+] = \frac{K_a\,[HCN]}{[CN^-]}$$

In presence of strong electrolyte, the total CN^- concentration comes from KCN which undergoes complete dissociation. It is further assumed that dissociation of HCN is very-very small and the concentration of HCN can be taken as the concentration of undissociated HCN.

Thus, $[HCN] = 0.2\,M$ and $[CN^-] = 1\,M$

Putting these values in the expression

$$[H^+] = \frac{K_b\,[HCN]}{[CN^-]} = \frac{4\times 10^{-10}\times 0.2}{1} = 8\times 10^{-11} \text{ mol L}^{-1}$$

Note: When KCN is not present, the $[H^+]$ concentration is equal to $\sqrt{CK}$, *i.e.*, $\sqrt{0.2\times 4\times 10^{-10}} = 8.94\times 10^{-6}$ mol L^{-1}. This shows that concentration of H^+ ions falls considerably when KCN is added to HCN solution.

Example 7. *Determine the concentration of hydroxyl ions in* 0.4 *M* NH_4OH *solution having* (*i*) *no ammonium chloride and* (*ii*) 5.35 *g of* NH_4Cl *in a litre of the solution. Ionisation constant of* NH_4OH *is* 1.8×10^{-5}.

Solution: (i) Let 'α' be the degree of dissociation of NH_4OH in absence of NH_4Cl.

$$\alpha = \sqrt{\frac{K_b}{C}}$$

So, $$[OH^-] = C\alpha = \sqrt{K_b C} = \sqrt{1.8\times 10^{-5}\times 0.4}$$

$$= 2.68\times 10^{-3} \text{ mol L}^{-1}$$

(ii) In presence of NH_4Cl,

$$[NH_4^+] = \frac{5.35}{53.5} = 0.1M \quad \text{and} \quad [NH_4OH] = 0.4\,M$$

So, $$[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]} = \frac{1.8\times 10^{-5}\times 0.4}{0.1}$$

$$= 7.2\times 10^{-5} \text{ mol L}^{-1}$$

Example 8. *When* 0.100 *mole of ammonia,* NH_3, *is dissolved in sufficient water to make* 1.0 *L of solution, the solution is found to have a hydroxide ion concentration of* 1.34×10^{-3} *M. Calculate* K_b *for ammonia.*

Solution:

$$\begin{array}{lccc} & NH_3 & +\,H_2O \rightleftharpoons & NH_4^+ \\ \text{At equilibrium} & (0.100 - 1.34\times 10^{-3})\,M & & 1.34\times 10^{-3}\,M \\ & & & +\ OH^- \\ & = 0.09866\,M & & 1.34\times 10^{-3}\,M \end{array}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{1.34\times 10^{-3}\times 1.34\times 10^{-3}}{0.09866} = 1.8199\times 10^{-5}$$

Example 9. K_a *for HA is* 4.9×10^{-8}. *After making the necessary approximation, calculate for its decimolar solution*

(*a*) *% dissociation*

(*b*) H^+ *ion concentration.*

Solution: (a) For a weak electrolyte,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.9\times 10^{-8}}{0.1}} = 7\times 10^{-4}$$

$$\%\,\text{dissociation} = 100\times\alpha = 100\times 7\times 10^{-4}$$
$$= 7\times 10^{-2}$$

(b) $$HA \rightleftharpoons H^+ + A^-$$
$$C(1-\alpha) \qquad C\alpha \qquad C\alpha$$
$$[H^+] = C\times\alpha = 0.1\times 7\times 10^{-4} = 7\times 10^{-5}\ \text{mol L}^{-1}$$

Example 10. *Nicotinic acid ($K_a = 1.4\times 10^{-5}$) is represented by the formula HNiC. Calculate its per cent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2 litre of solution.* **(IIT 1993)**

Solution: Initial concentration of the nicotinic acid $= \frac{0.10}{2} = 0.05\ \text{mol L}^{-1}$

$$HNiC \rightleftharpoons H^+ + NiC^-$$
$$\text{Equilibrium conc.} \quad (0.05-x) \qquad x \qquad x$$

As x is very small, $(0.05-x)$ can be taken as 0.05

$$K_a = \frac{[H^+][NiC^-]}{[HNiC]} = \frac{x\times x}{0.05}$$

or $$x^2 = (0.05)\times(1.4\times 10^{-5})$$

or $$x = 0.83\times 10^{-3}\ \text{mol L}^{-1}$$

$$\%\,\text{dissociation} = \frac{0.83\times 10^{-3}}{0.05}\times 100 = 1.66$$

Alternative method: Let α be the degree of dissociation

$$HNiC \rightleftharpoons H^+ + NiC^-$$
$$\text{At equilibrium} \quad 0.05(1-\alpha) \qquad 0.05\alpha \qquad 0.05\alpha$$
$$K_a = \frac{0.05\alpha\times 0.05\alpha}{0.05(1-\alpha)}$$

As α is very small, $(1-\alpha)\longrightarrow 1$.

So, $$1.4\times 10^{-5} = 0.05\alpha^2$$

or $$\alpha = \sqrt{\frac{1.4\times 10^{-5}}{0.05}} = 1.67\times 10^{-2}$$

$$\text{Per cent dissociation} = 100\times\alpha = 100\times 1.67\times 10^{-2}$$
$$= 1.67$$

Example 11. *At 30°C, the degree of dissociation of 0.066 M HA is 0.0145. What would be the degree of dissociation of 0.02 M solution of the acid at the same temperature?*

Solution: Let the ionisation constant of the acid be K_a. Degree of dissociation at 0.066 M concentration = 0.0145.

Applying $$\alpha = \sqrt{\frac{K_a}{C}}$$

$$0.0145 = \sqrt{\frac{K_a}{0.066}} \qquad \text{... (i)}$$

Let the degree of dissociation of the acid at 0.02 M concentration be α_1.

$$\alpha_1 = \sqrt{\frac{K_a}{0.02}} \qquad \text{... (ii)}$$

Dividing eq. (ii) by eq. (i),

$$\frac{\alpha_1}{0.0145} = \sqrt{\frac{0.066}{0.02}} = 1.8166$$

or $$\alpha_1 = 0.0145\times 1.8166 = 0.0263$$

Example 12. *A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the concentration of S^{2-} and HS^- ions in solution. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.* **(IIT 1992)**

Solution: $$H_2S \rightleftharpoons H^+ + HS^-$$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \qquad \text{... (i)}$$

Further $$HS^- = H^+ + S^{2-}$$

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \qquad \text{... (ii)}$$

Multiplying both the equations

$$K_{a_1}\times K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Due to common ion, the ionisation of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of 0.3 M HCl.

$$[S^{2-}] = \frac{K_{a_1}\times K_{a_2}[H_2S]}{[H^+]^2} = \frac{1.0\times 10^{-7}\times 1.3\times 10^{-13}\times(0.1)}{(0.3)^2}$$
$$= 1.44\times 10^{-20}\ M$$

Putting the value of $[S^{2-}]$ in eq. (ii),

$$1.3\times 10^{-13} = \frac{0.3\times 1.44\times 10^{-20}}{[HS^-]}$$

or $$[HS^-] = \frac{0.3\times 1.44\times 10^{-20}}{1.3\times 10^{-13}} = 3.3\times 10^{-8}\ M$$

Example 13. *What is the H^+ ion concentration of a solution known to contain 0.1g mole of CH_3COONH_4 in one litre of 0.1 M CH_3COOH? Assume effective ionisation of ammonium acetate is 80%. K_a for acetic acid is 1.8×10^{-5}.*

Solution: $$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$(0.1-x) \qquad x \qquad x$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

The solution also contains CH_3COONH_4 which is 80% dissociated, *i.e.*, $\alpha = 0.8$. Thus, the acetate concentration provided by 0.1 M $CH_3COONH_4 = 0.1\times 0.8 = 0.08\,M$

Total $$[CH_3COO^-] = (0.08+x)\,M$$

So, $$K_a = \frac{(0.08+x)x}{(0.1-x)}$$

As x is very small, $(0.1-x)\longrightarrow 0.1$ and neglecting x^2,

$$K_a = \frac{0.08x}{0.1}$$

or $$1.8\times10^{-5}\times0.1=0.08x$$

or $$x=[H^+]=\frac{1.8\times10^{-5}\times0.1}{0.08}=2.25\times10^{-5}\ \text{mol L}^{-1}$$

Example 14. *Ostwald obtained the following table by determining the equivalent conductivities containing one gram equivalent of acetic acid in V litre. If the equivalent conductivity of acetic acid at infinite dilution be* 364, *show that the results are in agreement with Ostwald's law.*

Volume in litre (V)	*Equivalent conductivity*
8	4.34
64	12.09
128	16.99

Solution: Degree of dissociation, $\alpha=\frac{\Lambda_V}{\Lambda_\infty}$

(i) $$\alpha_1=\frac{4.34}{364}=0.0119$$

(ii) $$\alpha_2=\frac{12.09}{364}=0.0332$$

(iii) $$\alpha_3=\frac{16.99}{364}=0.0467$$

Now applying Ostwald's dilution law,

(i) $$K_a=\frac{\alpha_1^2}{V_1}=\frac{0.0119\times0.0119}{8}=1.77\times10^{-5}$$

(ii) $$K_a=\frac{\alpha_2^2}{V_2}=\frac{0.0332\times0.0332}{64}=1.72\times10^{-5}$$

(iii) $$K_a=\frac{\alpha_3^2}{V_3}=\frac{0.0467\times0.0467}{128}=1.70\times10^{-5}$$

The values of K_a are nearly the same which show the validity of Ostwald's dilution law.

Example 15. *Calculate the dissociation constant of* $H_2C_2O_4$ *(oxalic acid) if* 0.02 *M solution is 2% dissociated.*

Solution:
$$\underset{C(1-\alpha)}{H_2C_2O_4} \rightleftharpoons \underset{2C\alpha}{2H^+} + \underset{C\alpha}{C_2O_4^{2-}}$$

$$K_a=\frac{[H^+]^2[C_2O_4^{2-}]}{[H_2C_2O_4]}$$
$$=\frac{(2C\alpha)^2\times(C\alpha)}{C(1-\alpha)}$$
$$=\frac{4C^2\alpha^3}{1-\alpha}\quad[1-\alpha\to1\text{ as }\alpha\text{ is small}]$$
$$=4C^2\alpha^3$$
$$=4\times0.02\times0.02\times(0.02)^3$$
$$=1.28\times10^{-8}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. A monoprotic acid in 0.1 M solution ionizes to 0.001%. Its ionisation constant is:
(a) 1×10^{-3} (b) 1×10^{-6} (c) 1×10^{-8} (d) 1×10^{-11}
[Ans. (d)]
[Hint: $\alpha=\sqrt{\frac{K_a}{C}}$ or $K_a=C\alpha^2=0.1\times\left(\frac{0.001}{100}\right)^2$
$=1\times10^{-11}$]

2. The hydrogen ion concentration in mol/dm^3 in 0.2 M solution of weak acid, HA ($K_a=2\times10^{-5}$) is close to:
(a) 2×10^{-5} (b) 2×10^{-4} (c) 2×10^{-3} (d) 2×10^{-2}
[Ans. (c)]
[Hint: $[H_3O^+]=\sqrt{CK_a}=\sqrt{0.2\times2\times10^{-5}}=2\times10^{-3}$]

3. Autoprotolysis constant of NH_3 is:
(a) $[NH_4^+][NH_3]$ (b) $[NH_2^-][NH_3]$
(c) $[NH_4^+][NH_2^-]$ (d) $\frac{[NH_4^+]}{[NH_2^-]}$
[Ans. (c)]
[Hint: Autoprotolysis of NH_3 takes place as:
$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
∴ Autoprotolysis constant $=[NH_4^+][NH_2^-]$]

4. The degree of ionization of an acid HA is 0.00001 at 0.1 M concentration. Its dissociation constant will be:
(a) 10^{-9} (b) 10^{-8} (c) 10^{-11} (d) 10^{-7}
[Ans. (c)]
[Hint: For monoprotic acid HA:
$K_a=C\alpha^2=0.1\times(10^{-5})^2=10^{-11}$]

5. The first and second dissociation constants of an acid, H_2A, are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be: **(AIEEE 2007)**
(a) 0.2×10^5 (b) 5.0×10^{-5}
(c) 5.0×10^{-15} (d) 5.0×10^{15}
[Ans. (c)]
[Hint: $K_a=K_{a_1}\times K_{a_2}$
$=1\times10^{-5}\times5\times10^{-10}$
$=5\times10^{-15}$]

10.4 SOLUBILITY PRODUCT

If to a given amount of solvent at a particular temperature, a solute is added gradually in increasing amounts, a stage is reached when some of the solute remains undissolved, no matter how long we wait or how vigorously we stir. The solution is then said to be saturated. **A solution which remains in contact with undissolved solute is said to be saturated.** At saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature.

In case, the solute is an electrolyte, its ionisation occurs in solution and degree of dissociation depends on the concentration of dissolved electrolyte at a particular temperature. Thus, in a saturated solution of an electrolyte two equilibria exist and can be represented as:

$$\underset{\text{Solid}}{AB} \rightleftharpoons \underset{\substack{\text{Unionised}\\(\text{Dissolved})}}{AB} \rightleftharpoons \underbrace{A^+ + B^-}_{\text{Ions}}$$

Applying the law of mass action to the ionic equilibrium,

$$\frac{[A^+][B^-]}{[AB]}=K$$

Since, the solution is saturated, the concentration of unionised molecules of the electrolyte is constant at a particular temperature, *i.e.*, $[AB]=K'=$ constant.

Hence, $[A^+][B^-]=K[AB]=KK'=K_s$ (constant)

K_s is termed as the solubility product. It is defined as **the product of the concentration of ions in a saturated solution of an electrolyte at a given temperature.**

Consider, in general, the electrolyte of the type A_xB_y which is dissociated as:

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Applying law of mass action,

$$\frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]}=K$$

When the solution is saturated,

$$[A_xB_y]=K' \text{ (constant)}$$

or $\quad [A^{y+}]^x[B^{x-}]^y=K[A_xB_y]=KK'=K_s$ (constant)

Thus, solubility product is defined as **the product of concentrations of the ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.**

[**Note:** Solubility product is not the ionic product under all conditions but only when the solution is saturated.]

Different Expressions for Solubility Products

(i) Electrolyte of the type *AB*: Its ionisation is represented as:

$$AB \rightleftharpoons A^+ + B^-$$

Thus, $\quad K_s=[A^+][B^-]$

$$\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-; \quad K_s=[\text{Ag}^+][\text{Cl}^-]$$

$$\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}; \quad K_s=[\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

(ii) Electrolyte of the type *AB*$_2$: Its ionisation is represented as:

$$AB_2 \rightleftharpoons A^{2+} + 2B^-$$

Thus, $\quad K_s=[A^{2+}][B^-]^2$

$$\text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-; \quad K_s=[\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{F}^-; \quad K_s=[\text{Ca}^{2+}][\text{F}^-]^2$$

(iii) Electrolyte of the type *A*$_2$*B*: Its ionisation is represented as:

$$A_2B \rightleftharpoons 2A^+ + B^{2-}$$

Thus, $\quad K_s=[A^+]^2[B^{2-}]$

$$\text{Ag}_2\text{CrO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}; \quad K_s=[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$

$$\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}; \quad K_s=[\text{H}^+]^2[\text{S}^{2-}]$$

(iv) Electrolyte of the type *A*$_2$*B*$_3$: Its ionisation is represented as:

$$A_2B_3 \rightleftharpoons 2A^{3+} + 3B^{2-}$$

Thus, $\quad K_s=[A^{3+}]^2[B^{2-}]^3$

$$\text{As}_2\text{S}_3 \rightleftharpoons 2\text{As}^{3+} + 3\text{S}^{2-}; \quad K_s=[\text{As}^{3+}]^2[\text{S}^{2-}]^3$$

$$\text{Sb}_2\text{S}_3 \rightleftharpoons 2\text{Sb}^{3+} + 3\text{S}^{2-}; \quad K_s=[\text{Sb}^{3+}]^2[\text{S}^{2-}]^3$$

(v) Electrolyte of the type *AB*$_3$: Its ionisation is represented as:

$$AB_3 \rightleftharpoons A^{3+} + 3B^-$$

Thus, $\quad K_s=[A^{3+}][B^-]^3$

$$\text{Fe(OH)}_3 \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-; \quad K_s=[\text{Fe}^{3+}][\text{OH}^-]^3$$

$$\text{AlI}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{I}^-; \quad K_s=[\text{Al}^{3+}][\text{I}^-]^3$$

Solubility product of a weak electrolyte: Let degree of ionisation of weak electrolyte A_mB_n be 'α'.

$$\begin{array}{llll} & A_mB_n & \rightleftharpoons mA^{n+} & + nB^{m-} \\ t=0 & S & 0 & 0 \\ t_{\text{eq}} & S-S\alpha & mS\alpha & nS\alpha \end{array}$$

$$K_{\text{sp}}=[A^{n+}]^m[B^{m-}]^n$$

$$=[mS\alpha]^m[nS\alpha]^n$$

$$K_{\text{sp}}=m^m n^n (S\alpha)^{m+n}$$

Criteria of precipitation of an electrolyte: A very useful conclusion is derived from the solubility product concept. No precipitation of the electrolyte occurs if the ionic product is less than the solubility product, *i.e.*, the solution has not reached the saturation stage.

Case I: When $K_{\text{ip}} < K_{\text{sp}}$, then solution is unsaturated in which more solute can be dissolved.

Case II: When $K_{\text{ip}} = K_{\text{sp}}$, then solution is saturated in which no more solute can be dissolved.

Case III: When $K_{\text{ip}} > K_{\text{sp}}$, then solution is supersaturated and precipitation takes place.

When the ionic product exceeds the solubility product, the equilibrium shifts towards left hand side, *i.e.*, increasing the concentration of undissociated molecules of the electrolyte. As the solvent can hold a fixed amount of electrolyte at a definite temperature, the excess of the electrolyte is thrown out from the solution as precipitate.

Thus, for the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product. For example, if equal volumes of 0.02 M AgNO_3 solution and 0.02 M K_2CrO_4 solution are mixed, the precipitation of Ag_2CrO_4 occurs as the ionic product exceeds the solubility product of Ag_2CrO_4 which is 2×10^{-12}.

In the resulting solution,

$$[\text{Ag}^+]=\frac{0.02}{2}=0.01=1\times10^{-2}\ M$$

and $\quad [\text{CrO}_4^{2-}]=\frac{0.02}{2}=0.01=1\times10^{-2}\ M$

Ionic product of $Ag_2CrO_4 = [Ag^+]^2[CrO_4^{2-}]$

$$= (1\times 10^{-2})^2\ (1\times 10^{-2})$$

$$= 1\times 10^{-6}$$

1×10^{-6} is higher than 2×10^{-12} and thus precipitation of Ag_2CrO_4 occurs.

Relationship between Solubility and Solubility Product

Salts like AgI, $BaSO_4$, $PbSO_4$, PbI_2, etc., are ordinarily considered insoluble but they do possess some solubility. These are sparingly soluble electrolytes. A saturated solution of sparingly soluble electrolyte contains a very small amount of the dissolved electrolyte. It is assumed that whole of the dissolved electrolyte is present in the form of ions, *i.e.*, it is completely dissociated.

The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Thus, solubility product, $K_s = [A^{y+}]^x[B^{x-}]^y$

Let 'S' mol litre^{-1} be the solubility of the salt; then

$$A_xB_y \rightleftharpoons \underset{xS}{xA^{y+}} + \underset{yS}{yB^{x-}}$$

So, $$K_s = [xS]^x[yS]^y$$

$$= x^x\cdot y^y(S)^{x+y}$$

(i) 1 : 1 type salts: Examples: AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

Binary electrolyte: $AB \rightleftharpoons \underset{S}{A^+} + \underset{S}{B^-}$

Let solubility of AB be S mol litre^{-1}.

So, $$K_s = [A^+][B^-] = S\times S = S^2$$

or $$S = \sqrt{K_s}$$

(ii) 1 : 2 or 2 : 1 type salts: Examples: Ag_2CO_3, Ag_2CrO_4, $PbCl_2$, CaF_2, etc.

Ternary electrolyte: $AB_2 \rightleftharpoons \underset{S}{A^{2+}} + \underset{2S}{2B^-}$

Let solubility of AB_2 be S mol litre^{-1}.

So, $$K_s = [A^{2+}][B^-]^2 = S\times(2S)^2 = 4S^3$$

or $$S = \sqrt[3]{K_s/4}$$

$$A_2B \rightleftharpoons \underset{2S}{2A^+} + \underset{S}{B^{2-}}$$

Let S be the solubility of A_2B.

$$K_s = [A^+]^2[B^{2-}]$$

$$= (2S)^2(S) = 4S^3$$

or $$S = \sqrt[3]{K_s/4}$$

(iii) 1 : 3 type salts: Examples: AlI_3, $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc.

Quarternary electrolyte: $AB_3 \rightleftharpoons \underset{S}{A^{3+}} + \underset{3S}{3B^-}$

Let S mol litre^{-1} be the solubility of AB_3.

$$K_s = [A^{3+}][B^-]^3 = S\times(3S)^3 = 27S^4$$

or $$S = \sqrt[4]{K_s/27}$$

The presence of common ion affects the solubility of a salt. Let AB be a sparingly soluble salt in solution and $A'B$ be added to it. Let S and S' be the solubilities of the salt AB before and after addition of the electrolyte $A'B$. Let c be the concentration of $A'B$.

Before addition of $A'B$, $K_s = S^2$ ... (i)

After addition of $A'B$, the concentration of A^+ and B^- ions become S' and $(S'+c)$, respectively.

So, $$K_s = S'(S'+c) \quad \text{... (ii)}$$

Equating eqs. (i) and (ii),

$$S^2 = S'(S'+c)$$

Calculation of remaining concentration after precipitation: Sometimes an ion remains after precipitation if it is in excess. Remaining concentration can be determined, *e.g.*,

(i) $$[A^+]_{\text{left}} = \frac{K_{sp}[AB]}{[B^-]}$$

(ii) $$[Ca^{2+}]_{\text{left}} = \frac{K_{sp}[Ca(OH)_2]}{[OH^-]^2}$$

(iii) $$[A^{n+}]^m_{\text{left}} = \frac{K_{sp}[A_mB_n]}{[B^{m-}]^n}$$

Percentage precipitation of an ion

$$= \left[\frac{\text{Initial conc.} - \text{Left conc.}}{\text{Initial conc.}}\right]\times 100$$

Simultaneous Solubility

Solubility of two electrolytes having common ion; when they are dissolved in the same solution, is called **simultaneous solubility**, *e.g.*,

(i) Solubility of AgBr and AgSCN, when dissolved together.
(ii) Solubility of CaF_2 and SrF_2, when dissolved together.
(iii) Solubility of MgF_2 and CaF_2, when dissolved together.

Calculation of simultaneous solubility is divided into two cases:

Case I: When the two electrolytes are almost equally strong (having close solubility product), *e.g.*,

$$AgBr\ (K_{sp} = 5\times 10^{-13});\quad AgSCN\ (K_{sp} = 10^{-12})$$

(See example 26.)

Here, charge balancing concept is applied.

Charge of Ag^+ = Charge of Br^- + Charge of SCN^-

$$[Ag^+] = [Br^-] + [SCN^-]$$

$$(a+b) = a \qquad\qquad b$$

Case II: When solubility products of two electrolytes are not close, *i.e.*, they are not equally strong, *e.g.*,

CaF_2 ($K_{sp} = 3.4 \times 10^{-11}$); SrF_2 ($K_{sp} = 2.9 \times 10^{-9}$)

Most of fluoride ions come of stronger electrolyte.

SOME SOLVED EXAMPLES

Example 16. *The solubility product of silver chloride is 1.5625×10^{-10} at 25°C. Find its solubility in g L^{-1}.*

Solution: Let the solubility of AgCl be S mol litre^{-1}.

$$\underset{}{AgCl} \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{Cl^-}$$

Hence, $S^2 = 1.5625 \times 10^{-10}$

or $S = 1.25 \times 10^{-5}$ mol L^{-1}

Molecular mass of AgCl = (108 + 35.5) = 143.5

So, Solubility in g litre^{-1} = Mol. mass × S

$= 143.5 \times 1.25 \times 10^{-5}$

$= 1.79 \times 10^{-3}$ g L^{-1}

Example 17. *The solubility of $PbSO_4$ in water is 0.038 g L^{-1} at 25°C. Calculate its solubility product at the same temperature.*

Solution: Solubility (S) of $PbSO_4$ in mol L^{-1},

$$= \frac{0.038}{\text{Mol. mass of } PbSO_4} = \frac{0.038}{303} = 1.254 \times 10^{-4}$$

The equilibrium is

$$PbSO_4 \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{S}{SO_4^{2-}}$$

So, $K_s = [Pb^{2+}][SO_4^{2-}] = S \times S = S^2$

or $K_s = 1.254 \times 10^{-4} \times 1.254 \times 10^{-4} = 1.573 \times 10^{-8}$

Example 18. *The concentration of Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20°C is 1.5×10^{-4} mol L^{-1}. Determine the solubility product of Ag_2CrO_4 at 20°C.*

Solution: The equilibrium is:

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

On the basis of this equation, the concentration of CrO_4^{2-} ions will be half of the concentration of Ag^+ ions.

Thus, $[Ag^+] = 1.5 \times 10^{-4}$ M and $[CrO_4^{2-}] = 0.75 \times 10^{-4}$ M

$K_s = [Ag^+]^2[CrO_4^{2-}] = (1.5 \times 10^{-4})^2\ (0.75 \times 10^{-4})$

$= 1.6875 \times 10^{-12}$

Example 19. *The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find out the solubility in (i) pure water and (ii) 0.1 M $BaCl_2$ solution.*

Solution: The equilibrium is:

(i) $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

Let S be the solubility in mol litre^{-1}; then

$K_s = [Ba^{2+}][SO_4^{2-}] = S^2$

or $1.5 \times 10^{-9} = S^2$

So, $S = 3.87 \times 10^{-5}$ mol L^{-1}

(ii) Let S' be the solubility of $BaSO_4$ in 0.1 M $BaCl_2$ solution.

Total Ba^{2+} ions concentration = $(S' + c)$ mol L^{-1}

and SO_4^{2-} ions concentration = S' mol L^{-1}

So, $K_s = (S' + c)\,S' = (S' + 0.1)\,S'$

or $1.5 \times 10^{-9} = (S' + 0.1)\,S'$

or $(S')^2 + 0.1S' = 1.5 \times 10^{-9}$

Neglecting $(S')^2$,

$0.1S' = 1.5 \times 10^{-9}$

or $S' = 1.5 \times 10^{-8}$ mol L^{-1}

Example 20. *The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g L^{-1}. Calculate its solubility in g L^{-1} in 0.02 M $Mg(NO_3)_2$ solution.*

Solution: Solubility of $Mg(OH)_2$ in pure water

$= 9.57 \times 10^{-3}$ g L^{-1}

$$= \frac{9.57 \times 10^{-3}}{\text{Mol. mass}} \text{ mol } L^{-1}$$

$$= \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mol } L^{-1}$$

Further, $Mg(OH)_2 \rightleftharpoons \underset{S}{Mg^{2+}} + \underset{2S}{2OH^-}$

$K_s = [Mg^{2+}][OH^-]^2 = S \times (2S)^2 = 4S^3 = 4 \times (1.65 \times 10^{-4})^3$

$= 17.9685 \times 10^{-12}$

Let S' be solubility of $Mg(OH)_2$ in presence of $Mg(NO_3)_2$

$[Mg^{2+}] = (S' + c) = (S' + 0.02)$

$[OH'] = 2S'$

So, $K_S = (S' + 0.02)(2S')^2$

$17.9685 \times 10^{-12} = 4(S')^2(S' + 0.02)$

$$\frac{17.9685 \times 10^{-12}}{4} = (S')^3 + 0.02(S')^2$$

[neglecting $(S')^3$]

$4.4921 \times 10^{-12} = 0.02(S')^2$

or $(S')^2 = \dfrac{4.4921}{0.02} \times 10^{-12}$

or $S' = 14.9868 \times 10^{-6}$ mol L^{-1}

Solubility of $Mg(OH)_2$ in g litre^{-1} = $S' \times M$

$= 14.9868 \times 10^{-6} \times 58$

$= 8.69 \times 10^{-4}$ g L^{-1}

Example 21. *The solubility product of lead iodide is 1.4×10^{-8}. Calculate its molar solubility in 0.1 M KI solution.*

Solution: Let the solubility of PbI_2 be S. Then,

$$\underset{S}{PbI_2} \rightleftharpoons \underset{S}{Pb^{2+}} + \underset{2S}{2I^-}$$

Potassium iodide is a strong electrolyte and is completely ionised. It shall provide I^- ion concentration = 0.1 M.

$$[Pb^{2+}] = S$$

$$[I^-] = (2S + 0.1)\,M$$

$$K_{sp} = [Pb^{2+}][I^-]^2$$

$$= S \times (2S + 0.1)^2$$

$$= S \times (4S^2 + 0.01 + 0.4S)$$

$$= 4S^3 + 0.01S + 0.4S^2$$

Neglecting S^3 and S^2,

$$1.4 \times 10^{-8} = 0.01S$$

or $$S = \frac{1.4 \times 10^{-8}}{0.01} = 1.4 \times 10^{-6} \text{ mol L}^{-1}$$

Example 22. *The solubility product of lead bromide is* 8×10^{-5}. *If the salt is 80% dissociated in saturated solution, find the solubility of the salt.*

Solution: Let S be the solubility of the salt.

Degree of dissociation of the salt = 0.8.

$$PbBr_2 \rightleftharpoons \underset{0.8S}{Pb^{2+}} + \underset{2 \times 0.8S}{2Br^-}$$

$$K_{sp} = [Pb^{2+}][Br^-]^2$$

$$= (0.8S) \times (1.6S)^2$$

$$= 2.048S^3$$

or $$S^3 = \frac{8 \times 10^{-5}}{2.048} = 3.906 \times 10^{-5}$$

$$S = \sqrt[3]{3.906 \times 10^{-5}} = 3.39 \times 10^{-2} \text{ mol L}^{-1}$$

Mol. mass of $PbBr_2 = 367$

Solubility of $PbBr_2 = 3.39 \times 10^{-2} \times 367 = 12.44 \text{ g L}^{-1}$

Example 23. *A solution has 0.05 M* Mg^{2+} *and 0.05 M* NH_3. *Calculate the concentration of* NH_4Cl *required to prevent the formation of* $Mg(OH)_2$ *in this solution.* K_{sp} *of* $Mg(OH)_2$ $= 9.0 \times 10^{-12}$ *and ionisation constant of* $NH_3 = 1.8 \times 10^{-5}$. **(IIT 1993)**

Solution: The maximum concentration of $[OH^-]$ ions that will precipitate $Mg(OH)_2$ is calculated by applying the equation

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$[OH^-]^2 = \frac{K_{sp}}{[Mg^{2+}]} = \frac{9.0 \times 10^{-12}}{0.05} = 1.8 \times 10^{-10}$$

or $$[OH^-] = 1.34 \times 10^{-5}\,M$$

NH_3 is present in solution in the form of NH_4OH

$$\underset{0.05}{NH_3} + H_2O \rightleftharpoons \underset{0.05}{NH_4OH} \rightleftharpoons NH_4^+ + OH^-$$

The ionisation of NH_4OH is suppressed by the addition of NH_4Cl (Strong electrolyte).

$$K_{NH_3} = K_{NH_4OH} = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

Whole of the concentration of NH_4^+ ions is provided by NH_4Cl.

$$[NH_4^+] = \frac{K_{NH_4OH} \times [NH_4OH]}{[OH^-]}$$

$$= \frac{1.8 \times 10^{-5} \times 0.05}{1.34 \times 10^{-5}} = 0.067\,M$$

i.e., $$[NH_4Cl] = 0.067\,M$$

Example 24. *The solubility product of* $Ag_2C_2O_4$ *at 25°C is* 1.29×10^{-11} $mol^3\ L^{-3}$. *A solution of* $K_2C_2O_4$ *containing 0.1520 mole in 500 mL of water is shaken with excess of* Ag_2CO_3 *till the following equilibrium is reached.*

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. *Assuming the degree of dissociation of* $K_2C_2O_4$ *and* K_2CO_3 *to be equal, calculate the solubility product of* Ag_2CO_3. **(IIT 1991)**

Solution:

	Ag_2CO_3 +	$K_2C_2O_4$	$\rightleftharpoons Ag_2C_2O_4$ +	K_2CO_3
Initial		0.1520 mole		0
At equilibrium		(0.1520 − 0.0358) = 0.1162 mole		0.0358 mole
Concentration		2 × 0.1162 = 0.2324 *M*		2 × 0.0358 = 0.0716 *M*

$$K_{sp}\ Ag_2C_2O_4 = [Ag^+]^2[C_2O_4^{2-}]$$

$$[Ag^+] = \left[\frac{K_{sp}\ Ag_2C_2O_4}{[C_2O_4^{2-}]}\right]^{1/2}$$

$$K_{sp} Ag_2CO_3 = [Ag^+]^2[CO_3^{2-}]$$

$$[Ag^+] = \left[\frac{K_{sp}\ Ag_2CO_3}{[CO_3^{2-}]}\right]^{1/2}$$

So, $$\left[\frac{K_{sp}\ Ag_2C_2O_4}{[C_2O_4^{2-}]}\right]^{1/2} = \left[\frac{K_{sp}\ Ag_2CO_3}{[CO_3^{2-}]}\right]^{1/2}$$

or $$K_{sp}\ Ag_2CO_3 = \frac{K_{sp}\ Ag_2C_2O_4 \times [CO_3^{2-}]}{[C_2O_4^{2-}]}$$

$$= K_{sp}\ Ag_2C_2O_4 \frac{[K_2CO_3]}{[K_2C_2O_4]}$$

$$= 1.29 \times 10^{-11} \times \frac{0.0716}{0.2324} = 3.97 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

Example 25. *20 mL of 0.001 M* $AgNO_3$ *solution is added to 1 litre of 0.002 M* K_2CrO_4 *solution. Will there be any precipitation?* K_{sp} *of* Ag_2CrO_4 *is* 2.4×10^{-12}.

Solution: No. of moles of Ag^+ in 20 mL

$$= \frac{20}{1000} \times 0.001 = 2 \times 10^{-5}$$

No. of moles CrO_4^{2-} in one litre $= 0.002 = 2 \times 10^{-3}$

After mixing, total volume of the solution

$$= 1000 + 20 = 1020 \text{ mL} = 1.02 \text{ L}$$

$$[Ag^+] = \frac{2\times10^{-5}}{1.02} = 1.96\times10^{-5}$$

$$[CrO_4^{2-}] = \frac{2\times10^{-3}}{1.02} = 1.96\times10^{-3}$$

$$\text{Ionic product} = [Ag^+]^2[CrO_4^{2-}]$$

$$= (1.96\times10^{-5})^2\ (1.96\times10^{-3})$$

$$= 7.53\times10^{-13}$$

There will be no precipitation of Ag_2CrO_4 as ionic product is less than solubility product.

Example 26. *Calculate simultaneous solubility of AgCNS and AgBr in a solution of water.* K_{sp} *of AgCNS* $= 1\times10^{-12}$, K_{sp} *of AgBr* $= 5\times10^{-13}$.

Solution: Let the solubility of AgCNS and AgBr in water be a and b respectively.

$$AgCNS \rightleftharpoons \underset{a}{Ag^+} + \underset{a}{CNS^-}$$

$$AgBr \rightleftharpoons \underset{b}{Ag^+} + \underset{b}{Br^-}$$

$$[Ag^+] = a + b, [CNS^-] = a \quad \text{and} \quad [Br^-] = b$$

$$K_{sp} AgCNS = [Ag^+][CNS^-] = a(a+b)$$

$$1\times10^{-12} = a(a+b) \qquad \text{... (i)}$$

$$K_{sp}\ AgBr = [Ag^+][Br^-] = b(a+b)$$

$$5\times10^{-13} = b(a+b) \qquad \text{... (ii)}$$

Dividing eq. (i) by (ii),

$$\frac{1\times10^{-12}}{5\times10^{-13}} = \frac{a}{b}$$

$$2 = \frac{a}{b} \quad \text{or} \quad a = 2b$$

Putting the value of a in eq. (i),

$$6b^2 = 1\times10^{-12}$$

$$b^2 = \frac{1}{6}\times10^{-12}$$

$$b = 4.08\times10^{-7}\ \text{mol L}^{-1}$$

$$a = 2\times4.08\times10^{-7}$$

$$= 8.16\times10^{-7}\ \text{mol L}^{-1}$$

Example 27. *The* K_{sp} *of* $Ca(OH)_2$ *is* 4.42×10^{-5} *at* $25°C$. *500 mL of saturated solution of* $Ca(OH)_2$ *is mixed with equal volume of 0.4 M NaOH. How much* $Ca(OH)_2$ *in mg is precipitated?* (IIT 1992)

Solution: Let S be the solubility of $Ca(OH)_2$ in saturated solution.

$$Ca(OH)_2 \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

$$K_{sp}\ Ca(OH)_2 = [Ca^{2+}][OH^-]^2$$

$$4.42\times10^{-5} = S\times4S^2 = 4S^3$$

$$S = 0.0223\ \text{mol L}^{-1}$$

After mixing the two solutions, the total volume becomes 1 litre.

$$[Ca^{2+}] = \frac{0.0223}{1000}\times500 = 0.01115\ \text{mol L}^{-1}$$

$$[OH^-] = \underset{[\text{From } Ca(OH)_2]}{\frac{0.0223\times2\times500}{1000}} + \underset{(\text{From NaOH})}{\frac{0.4\times500}{1000}} = 0.2223\ \text{mol L}^{-1}$$

Under the high concentration of OH^- ions, some $Ca(OH)_2$ will be precipitated.

$$[Ca^{2+}]_{\text{left}}[OH^-]^2 = K_{sp}$$

$$[Ca^{2+}]_{\text{left}} = \frac{4.42\times10^{-5}}{(0.2223)^2} = 8.94\times10^{-4}\ \text{mol L}^{-1}$$

Moles of $Ca(OH)_2$ precipitated = Moles of Ca^{2+} precipitated

$$= [Ca^{2+}]_{\text{initial}} - [Ca^{2+}]_{\text{left}}$$

$$= 0.01115 - 8.94\times10^{-4}$$

$$= 111.5\times10^{-4} - 8.94\times10^{-4}$$

$$= 102.56\times10^{-4}\ M = 102.56\times10^{-4}\times74\ \text{g}$$

$$= 7589.44\times10^{-4}\ \text{g} = 758.944\ \text{mg}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. The solubility product of sparingly soluble salt Ag_2CrO_4 is 4×10^{-12}. The molar solubility of the salt is:

(a) 1×10^{-4} mol L^{-1} (b) 2×10^{-6} mol L^{-1}

(c) 1×10^{-5} mol L^{-1} (d) 2×10^{-12} mol L^{-1}

[Ans. (a)]

[Hint: $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

If solubility of Ag_2CrO_4 is 'S', then $[Ag^+] = 2S$ and $[CrO_4^{2-}] = S$.

$$K_{sp} = 4S^3$$

$$4\times10^{-12} = 4S^3$$

$$S = 1\times10^{-4}\ M]$$

7. The solubility of $PbSO_4$ at 25°C is 1.1×10^{-4} mol/L. Then its K_{sp} is:

(a) 1.21×10^{-8} (b) 12.1×10^{-6}

(c) 121×10^{-11} (d) 1.21×10^{-10}

[Ans. (a)]

[Hint: $PbSO_4$ is a binary electrolyte, hence its K_{sp} can be calculated as:

$$K_{sp} = S^2 = [1.1\times10^{-4}]^2 = 1.21\times10^{-8}]$$

8. The solubility of CaF_2 ($K_{sp} = 3.4\times10^{-11}$) in 0.1 M solution of NaF would be:

(a) $3.4\times10^{-12}\ M$ (b) $3.4\times10^{-10}\ M$

(c) $3.4\times10^{-9}\ M$ (d) $3.4\times10^{-13}\ M$

[Ans. (c)]

[Hint: $CaF_2 \rightleftharpoons \underset{x}{Ca^{2+}} + \underset{2x}{2F^-}$

$$NaF \longrightarrow \underset{0.1}{Na^+} + \underset{0.1}{F^-}$$

$$[Ca^{2+}] = x, \quad [F^-] = [2x + 0.1] \approx 0.1\,M$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$3.4 \times 10^{-11} = x(0.1)^2$$

$$x = 3.4 \times 10^{-9}\,M]$$

9. The solubility product of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur only when equal volumes of which of the following solutions are mixed ?

(a) $10^{-4}\,M\,Ag^+$ and $10^{-4}\,M\,Cl^-$

(b) $10^{-7}\,M\,Ag^+$ and $10^{-7}\,M\,Cl^-$

(c) $10^{-5}\,M\,Ag^+$ and $10^{-5}\,M\,Cl^-$

(d) $10^{-10}\,M\,Ag^+$ and $10^{-10}\,M\,Cl^-$

[**Ans.** (a)]

[**Hint:** After mixing,

$$[Ag^+] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5}\,M$$

$$[Cl^-] = \frac{1}{2} \times 10^{-4} = 5 \times 10^{-5}\,M$$

$$K_{ip} = [Ag^+][Cl^-] = (5 \times 10^{-5})^2 = 2.5 \times 10^{-9}$$

Since, ionic product is greater than solubility product, hence precipitation will take place.]

10. If x mol L^{-1} is the solubility of $KAl(SO_4)_2$, then K_{sp} is equal to:

(a) x^3 (b) $4x^4$ (c) x^4 (d) $4x^3$

[**Ans.** (b)]

[**Hint:** $KAl(SO_4)_2 \longrightarrow \underset{x}{K^+} + \underset{x}{Al^{3+}} + \underset{2x}{2SO_4^{2-}}$

$$K_{sp} = [K^+][Al^{3+}][SO_4^{2-}]^2$$

$$= x \times x \times (2x)^2 = 4x^4]$$

11. For which of the following sparingly soluble salt, the solubility (S) and solubility product (K_{sp}) are related by the expression:

$$S = \left[\frac{K_{sp}}{4}\right]^{1/3}$$ **[PET (Kerala) 2006]**

(a) $BaSO_4$ (b) $Ca_3(PO_4)_2$ (c) Hg_2Cl_2 (d) Ag_3PO_4

(e) CuS

[**Ans.** (c)]

[**Hint:** $Hg_2Cl_2 \longrightarrow \underset{S}{Hg_2^{2+}} + \underset{2S}{2Cl^-}$ (with S under Hg_2Cl_2)

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = [S][2S]^2 = 4S^3$$

$$S = \left[\frac{K_{sp}}{4}\right]^{1/3}]$$

12. The solubility of Sb_2S_3 in water is 1×10^{-5} mol/L at 298 K. What will be its solubility product? **[PMT (Raj.) 2006]**

(a) 108×10^{-25} (b) 1.0×10^{-25}

(c) 144×10^{-25} (d) 126×10^{-24}

[**Ans.** (a)]

[**Hint:** $\underset{S}{Sb_2S_3} \longrightarrow \underset{2S}{2Sb^{3+}} + \underset{3S}{3S^{2-}}$

$$K_{sp} = [Sb^{3+}]^2[S^{2-}]^3 = [2S]^2[3S]^3 = 108\,S^5$$

$$= 108 \times (10^{-5})^5 = 108 \times 10^{-25}]$$

Applications of Solubility Product

(i) Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ions as:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$HCl \rightleftharpoons H^+ + Cl^-$$

The concentration of Cl^- ions increases considerably in solution due to ionisation of HCl. Hence, the ionic product $[Na^+][Cl^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher fatty acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.

$$\underset{\text{Soap}}{C_nH_{2n+1}COONa} \rightleftharpoons C_nH_{2n+1}COO^- + Na^+$$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Thus, the concentration of Na^+ ions increases considerably on addition of NaCl solution. Hence, the ionic product $[C_nH_{2n+1}COO^-][Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda)

In Solvay's soda process, CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.

$$NH_4OH + CO_2 \longrightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl, NH_4HCO_3 and NaCl.

Thus, baking soda ($NaHCO_3$) can be quantitatively estimated.

(iv) Application of solubility product in quantitative analysis

1. Estimation of barium as barium sulphate: H_2SO_4 as precipitating agent is added to the aqueous solution of $BaCl_2$.

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

Precipitation of $BaSO_4$ takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

2. Estimation of silver as silver chloride: NaCl solution is added to the silver nitrate solution; slight excess of NaCl is added to ensure complete precipitation.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

3. In a similar manner, we estimate lead as lead chromate, calcium as calcium oxalate, etc.

(v) Precipitation of the sulphides of group II and IV

Hydrogen sulphide is a weak electrolyte and is used for the precipitation of various sulphides of group II and IV in qualitative analysis.

It ionises to a small extent in water:

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

Applying law of mass action,

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

The concentration of S^{2-} ions can be decreased by increasing concentration of H^+ ions and it can be increased by decreasing concentration of H^+ ions. In group II, lower concentration of sulphide ions is required as the solubility products of the sulphides of group II are low while higher concentration of sulphide ions is required in group IV as the solubility products of the sulphides of group IV are high. The values of solubility products of various sulphides are given below:

	Metal sulphide	**Solubility product**
Group II	Bi_2S_3	1.6×10^{-72}
	HgS	4×10^{-54}
	CuS	1×10^{-44}
	PbS	5×10^{-29}
	CdS	1.4×10^{-28}
Group IV	CoS	3×10^{-26}
	NiS	1.4×10^{-24}
	ZnS	1.0×10^{-22}
	MnS	1.4×10^{-15}

The concentration of S^{2-} ions in group II is lowered by maintaining acidic medium. In the presence of HCl, the ionisation of H_2S is suppressed due to common ion effect. The concentration is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated. However, CdS has somewhat higher value. For its precipitation, dilution of the solution is done which increases ionisation of H_2S and thereby increasing concentration of S^{2-} ions.

In group IV, higher concentration of S^{2-} ions is needed. This is done by changing the medium from acidic to alkaline. Ammonium hydroxide is added, the OH^- ions furnished by NH_4OH remove H^+ ions from solution in the form of water molecules as,

$$H^+ + OH^- \rightleftharpoons H_2O$$

More of the ionisation of H_2S occurs and, thus, concentration of S^{2-} ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products and they get precipitated.

(vi) Precipitation of III group hydroxides

When NH_4OH is added in presence of NH_4Cl then precipitation of III group hydroxides takes place, *i.e.*, $Al(OH)_3$, $Fe(OH)_3$ and $Cr(OH)_3$ are precipitated. Solubility product of III group hydroxides is less than those of higher group hydroxides.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

NH_4^+ ion furnished by NH_4Cl lowers the ionisation of NH_4OH and hence the concentration of hydroxide ion OH^-. At low concentration of hydroxide ion only III group hydroxides precipitate.

Fractional Precipitation

It is a technique of separating two or more ions from a solution by adding a reagent that precipitates first one ion and then the second.

Let us suppose 0.1 *M* Ba^{2+} and 0.1 *M* Sr^{2+} in aqueous solution. K_2CrO_4 is added as precipitating agent. K_{sp} of $BaCrO_4$ is 1.2×10^{-10} and K_{sp} of $SrCrO_4$ is 3.5×10^{-5}.

$[CrO_4^{2-}]$ concentration required to precipitate $BaCrO_4$

$$= \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = 1.2 \times 10^{-9}$$

$BaCrO_4$ will precipitate first because it requires low concentration of CrO_4^{2-} ions. On addition of chromate ions, $BaCrO_4$ starts precipitating when chromate ion concentration reaches 1.2×10^{-9} *M*. When CrO_4^{2-} ion concentration reaches up to 3.5×10^{-4} *M*, then $SrCrO_4$ also starts precipitating.

Remaining concentration of Ba^{2+} when $SrCrO_4$ starts precipitation

$$= \frac{K_{sp}BaCrO_4}{[CrO_4^{2-}]} = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}} = 3.4 \times 10^{-7}\ M$$

$$\%\ \text{remaining concentration} = \frac{3.4 \times 10^{-7}}{0.1} \times 100$$

$$= 0.00034\%$$

Stability Constant

Let us consider dissociation of the ion $FeBr^+$.

$$FeBr^+ \rightleftharpoons Fe^{2+} + Br^-$$

Dissociation constant for above equilibria may be given as:

$$K_d = \frac{[Fe^{2+}][Br^-]}{[FeBr^+]}$$

Reciprocal of dissociation constant is called stability constant.

$$K_s = \frac{[FeBr^+]}{[Fe^{2+}][Br^-]}$$

Let us consider the formation of complex $K_2Cd(CN)_4$. Complex ion is $Cd(CN)_4^{2-}$ where oxidation state of central metal Cd^{2+} is (+2). Complexing process proceeds in four steps as:

$$Cd^{2+} + CN^- \rightleftharpoons CdCN^+; \qquad K_1 = \frac{[CdCN^+]}{[Cd^{2+}][CN^-]}$$

$$CdCN^+ + CN^- \rightleftharpoons Cd(CN)_2; \qquad K_2 = \frac{[Cd(CN)_2]}{[CdCN^+][CN^-]}$$

$$Cd(CN)_2 + CN^- \rightleftharpoons Cd(CN)_3^-; \qquad K_3 = \frac{[Cd(CN)_3^-]}{[Cd(CN)_2][CN^-]}$$

$$Cd(CN)_3^- + CN^- \rightleftharpoons Cd(CN)_4^{2-}; \qquad K_4 = \frac{[Cd(CN)_4^{2-}]}{[Cd(CN)_3^-][CN^-]}$$

Overall reaction may be given as:

$$Cd^{2+} + 4CN^- \rightleftharpoons [Cd(CN)_4^{2-}]; \qquad K_s = \frac{[Cd(CN)_4^{2-}]}{[Cd^{2+}][CN^-]^4}$$

Here, $K_s = K_1 K_2 K_3 K_4$

Significance of stability constant: Greater will be the value of stability constant more stable will be the complex.

Note: (a) If on addition of a common ion in a salt solution (sparingly soluble), formation of complex ion takes place, then ionisation increases, *i.e.*, equilibrium shifts towards right hand direction to maintain the value of K_{sp} constant. It means, addition of common ion in the case of complex formation increases the solubility of the sparingly soluble salt which is against the concept of common ion effect.

(b) When we add an electrolyte to another electrolyte solution having no common ion, then ionisation of the latter increases.

(c) For a given electrolyte solubility product is always constant at a particular temperature.

Solubility of Metal Hydroxides in Acid Medium

H^+ ion furnished by the medium affects the solubility of metal hydroxide, say $M(OH)_2$, because of neutralization of OH^- ion by H^+ ion.

$$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^-$$

$$K_{sp} \text{ of } M(OH)_2 = [M^{2+}][OH^-]^2$$

$$[M^{2+}] = \frac{K_{sp}}{[OH^-]^2} \qquad \ldots \text{(i)}$$

$$[H^+][OH^-] = K_w = 10^{-14}$$

$$[OH^-]^2 = \frac{10^{-28}}{[H^+]^2} \qquad \ldots \text{(ii)}$$

From eqs. (i) and (ii), we have

$$[M^{2+}] = \frac{K_{sp}[H^+]^2}{10^{-28}}$$

10.5 ACIDS AND BASES

The earliest criteria for the characterisation of acids and bases were the experimentally observed properties of aqueous solutions. An acid* was defined as a substance whose water solution tastes sour, turns blue litmus red, neutralises bases and so on. A substance was a base if its aqueous solution tasted bitter, turns red litmus blue, neutralises acids and so on. **Faraday** termed acids, bases and salts as electrolytes and **Liebig** proposed that acids are compounds containing hydrogen that can be replaced by metals.

Different concepts have been put forth by different investigators to characterise acids and bases but the following are the three important modern concepts of acids and bases:

(1) Arrhenius concept

According to Arrhenius concept, **all substances which give H^+ ions when dissolved in water are called acids while those which ionise in water to furnish OH^- ions are called bases.**

$$HA \rightleftharpoons H^+ + A^- \qquad \text{(Acid)}$$

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{(Base)}$$

Thus, HCl is an acid because it gives H^+ ions in water. Similarly, NaOH is a base as it yields OH^- ions in water.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

Some acids and bases ionise almost completely in solutions and are called strong acids and bases. Others are dissociated to a limited extent in solutions and are termed weak acids and bases. HCl, HNO_3, H_2SO_4, $HClO_4$, etc., are examples of strong acids and NaOH, KOH, $(CH_3)_4NOH$ are strong bases. Every hydrogen compound cannot be regarded as an acid, *e.g.*, CH_4 is not an acid. Similarly, CH_3OH, C_2H_5OH, etc., have OH groups but they are not bases.

Actually free H^+ ions do not exist in water. They combine with solvent molecules, *i.e.*, have strong tendency to get hydrated.

$$HX + H_2O \rightleftharpoons \underset{\text{(Hydronium ion)}}{H_3O^+} + X^-$$

The proton in aqueous solution is generally represented as $H^+(aq.)$. It is now known that almost all the ions are hydrated to more or less extent and it is customary to put (*aq.*) after each ion.

The oxides of many non-metals react with water to form acids and are called acidic oxides or acid anhydrides.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \rightleftharpoons 2H^+(aq.) + CO_3^{2-}(aq.)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \rightleftharpoons 2H^+(aq.) + 2NO_3^-(aq.)$$

Many oxides of metals dissolve in water to form hydroxides. Such oxides are termed basic oxides.

$$Na_2O + H_2O \longrightarrow 2NaOH \rightleftharpoons 2Na^+(aq.) + 2OH^-(aq.)$$

The substance like NH_3 and N_2H_4 act as bases as they react with water to produce OH^- ions.

$$NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+(aq.) + OH^-(aq.)$$

The reaction between an acid and a base is termed neutralisation. According to Arrhenius concept, the neutralisation in aqueous solution involves the reaction between H^+ and OH^- ions or hydronium and OH^- ions. This can be represented as

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

Limitations: (i) For the acidic or basic properties, the presence of water is absolutely necessary. Dry HCl shall not act as an acid. HCl is regarded as an acid only when dissolved in water and not in any other solvent.

(ii) The concept does not explain acidic and basic character of substances in non-aqueous solvents.

(iii) The neutralisation process is limited to those reactions which can occur in aqueous solutions only, although reactions involving salt formation do occur in the absence of solvent.

(iv) It cannot explain the acidic character of certain salts such as $AlCl_3$ in aqueous solution.

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* Acid is a Latin word—*acidus*, meaning sour.

(v) An artificial explanation is required to explain the basic nature of NH_3 and metallic oxides and acidic nature of non-metal oxides.

(2) Bronsted-Lowry concept—The proton-donor-acceptor concept

In 1923, Bronsted and Lowry independently proposed a broader concept of acids and bases. According to Bronsted-Lowry concept **an acid is a substance (molecule or ion) that can donate proton, *i.e.*, a hydrogen ion, H^+, to some other substance and a base is a substance that can accept a proton from an acid.** More simply, an acid is a proton-donor (protogenic) and a base is a proton acceptor (protophilic). Consider the reaction,

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

In this reaction, HCl acts as an acid because it donates a proton to the water molecule. Water, on the other hand, behaves as a base by accepting a proton from the acid.

The dissolution of ammonia in water may be represented as

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In this reaction, H_2O acts as an acid as it donates a proton to NH_3 molecule and NH_3 molecule behaves as a base as it accepts a proton.

When an acid loses a proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a base.

$$\text{Acid} \rightleftharpoons H^+ + \text{Base}$$

The acid and base which differ by a proton are known to form a **conjugate pair.** Consider the following reaction:

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

It involves two conjugate pairs. The acid-base pairs are:

$$\underset{\text{Acid}}{CH_3COOH} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Base}}{CH_3COO^-} \quad \text{and} \quad \underset{\text{Base}}{H_2O} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{\text{Acid}}{H_3O^+}$$

Such pairs of substances which can be formed from one another by loss or gain of a proton are known as **conjugate acid-base pairs.**

If in the above reaction, the acid CH_3COOH is labelled acid$_1$ and its conjugate base, CH_3COO^- as base$_1$. H_2O is labelled as base$_2$ and its conjugate acid H_3O^+ as acid$_2$, the reaction can be written as:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Base}_1 + \text{Acid}_2$$

Thus, any acid-base reaction involves two conjugate pairs, *i.e.*, when an acid reacts with a base, another acid and base are formed. Some more examples are given below:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$
$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$
$$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$
$$HF + CH_3COOH \rightleftharpoons CH_3COOH_2^+ + F^-$$
$$CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$$
$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$
$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Thus, every acid has its conjugate base and every base has its conjugate acid. It is further observed that strong acids have weak conjugate bases while weak acids have strong conjugate bases.

$$\underset{\text{Strong acid}}{HCl} \quad \underset{\text{Weak base}}{Cl^-} \quad \underset{\text{Weak acid}}{CH_3COOH} \quad \underset{\text{Strong base}}{CH_3COO^-}$$

There are certain molecules which have dual character of an acid and a base. These are called **amphiprotic** or **amphoteric.**

Examples are NH_3, H_2O, CH_3COOH, etc.

$$\underset{\text{Acid}}{H_2O} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Base}}{OH^-} \qquad \underset{\text{Acid}}{NH_3} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Base}}{NH_2^-}$$

$$\underset{\text{Base}}{H_2O} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{\text{Acid}}{H_3O^+} \qquad \underset{\text{Base}}{NH_3} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{\text{Acid}}{NH_4^+}$$

The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton.

Acid-base chart containing some common conjugate acid-base pairs

Acid		Conjugate base	
$HClO_4$	(Perchloric acid)	ClO_4^-	(Perchlorate ion)
H_2SO_4	(Sulphuric acid)	HSO_4^-	(Hydrogen sulphate ion)
HCl	(Hydrogen chloride)	Cl^-	(Chloride ion)
HNO_3	(Nitric acid)	NO_3^-	(Nitrate ion)
H_3O^+	(Hydronium ion)	H_2O	(Water)
HSO_4^-	(Hydrogen sulphate ion)	SO_4^{2-}	(Sulphate ion)
H_3PO_4	(Ortho-phosphoric acid)	$H_2PO_4^-$	(Dihydrogen phosphate ion)
CH_3COOH	(Acetic acid)	CH_3COO^-	(Acetate ion)
H_2CO_3	(Carbonic acid)	HCO_3^-	(Hydrogen carbonate ion)
H_2S	(Hydrogen sulphide)	HS^-	(Hydrosulphide ion)
NH_4^+	(Ammonium ion)	NH_3	(Ammonia)
HCN	(Hydrogen cyanide)	CN^-	(Cyanide ion)
C_6H_5OH	(Phenol)	$C_6H_5O^-$	(Phenoxide ion)
H_2O	(Water)	OH^-	(Hydroxide ion)
C_2H_5OH	(Ethyl alcohol)	$C_2H_5O^-$	(Ethoxide ion)
NH_3	(Ammonia)	NH_2^-	(Amide ion)
CH_4	(Methane)	CH_3^-	(Methide ion)

↑ Increasing order of acid strength

Increasing order of basic strength ↓

In acid-base strength series, all acids above H_3O^+ in aqueous solution fall to the strength of H_3O^+. Similarly, the basic strength of bases below OH^- fall to the strength of OH^- in aqueous solution. This is known as **levelling effect.**

The strength of an acid also depends upon the solvent. The acids $HClO_4$, H_2SO_4, HCl and HNO_3 which have nearly the same strength in water will be in the order of $HClO_4 > H_2SO_4 > HCl > HNO_3$ in acetic acid, since, the proton accepting tendency of acetic acid is much weaker than water. So, the real strength of acids can be judged by solvents. On the basis of proton interaction, solvents can be classified into four types:

(i) Protophilic solvents: Solvents which have greater tendency to accept protons, *i.e.*, water, alcohol, liquid ammonia, etc.

(ii) Protogenic solvents: Solvents which have the tendency to produce protons, *i.e.*, water, liquid hydrogen chloride, glacial acetic acid, etc.

(iii) Amphiprotic solvents: Solvents which act both as protophilic or protogenic, *e.g.*, water, ammonia, ethyl alcohol, etc.

(iv) Aprotic solvents: Solvents which neither donate nor accept protons, *e.g.*, benzene, carbon tetrachloride, carbon disulphide, etc.

HCl acts as acid in H_2O, stronger acid in NH_3, weak acid in CH_3COOH, neutral in C_6H_6 and a weak base in HF.

$$\underset{\text{Base}}{HCl} + \underset{\text{Acid}}{HF} \longrightarrow \underset{\text{Acid}}{H_2Cl^+} + \underset{\text{Base}}{F^-}$$

Periodic Variations of Acidic and Basic Properties

(a) Hydracids of the elements of the same period: Consider the hydracids of the elements of II period, *viz.*, CH_4, NH_3, H_2O and HF. These hydrides become increasingly acidic as we move from CH_4 to HF. CH_4 has negligible acidic properties while HF is a fairly stronger acid. The increase in acidic nature is due to the fact that the stability of their conjugate bases increases in the order

$$CH_3^- < NH_2^- < OH^- < F^-$$

The increase in acidic properties is supported by the successive increase in the dissociation constant.

$$CH_4\ (=10^{-58}) < NH_3\ (=10^{-35}) < H_2O\ (=10^{-14}) < HF\ (=10^{-4})$$

(b) Hydracids of the elements of same group: (i) Hydrides of V group elements (NH_3, PH_3, AsH_3, SbH_3 and BiH_3) show basic character which decreases due to increase in size and decrease in electronegativity from N to Bi. There is a decrease in electron density in sp^3-hybrid orbital and thus electron donor capacity decreases.

(ii) Hydracids of VI group elements (H_2O, H_2S, H_2Se and H_2Te) act as weak acids. The strength increases in the order

$$H_2O < H_2S < H_2Se < H_2Te$$

The increasing acidic character reflects decreasing trend in the electron donor capacity of OH^-, HS^-, HSe^- or HTe^- ions.

(iii) Hydracids of VII group elements (HF, HCl, HBr and HI) show acidic nature which increases from HF to HI. This is explained by the fact that bond energies decrease. (H—F = 135 kcal/mol, HCl = 103, HBr = 88 and HI = 71 kcal/mol)

(c) Oxyacids: (i) The acidic character of oxyacids of the same element which is in different oxidation states increases with increase in oxidation number.

$$\overset{+1}{HClO} < \overset{+3}{HClO_2} < \overset{+5}{HClO_3} < \overset{+7}{HClO_4}$$

$$\overset{+4}{H_2SO_3} < \overset{+6}{H_2SO_4};\ \overset{+3}{HNO_2} < \overset{+5}{HNO_3}$$

But this rule fails in oxyacids of phosphorus.

$$H_3PO_2 > H_3PO_3 > H_3PO_4$$

(ii) The acidic character of the oxyacids of different elements which are in the same oxidation state decreases as the atomic number increases. This is due to increase in size and decrease in electronegativity.

$$HClO_4 > HBrO_4 > HIO_4$$

$$H_2SO_3 > H_2SeO_3$$

Limitations: There are number of acid-base reactions in which no proton transfer takes place, *e.g.*,

$$\underset{\text{Acid}_1}{SO_2} + \underset{\text{Base}_2}{SO_2} \rightleftharpoons \underset{\text{Acid}_2}{SO^{2+}} + \underset{\text{Base}_1}{SO_3^{2-}}$$

Thus, the protonic definition cannot be used to explain the reactions occurring in non-protonic solvents such as $COCl_2$, SO_2, N_2O_4, etc.

(3) Lewis concept

This concept was proposed by G.N. Lewis, in 1939. According to this concept, **a base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons.** The acid is also known as electron acceptor or **electrophile** while the base is electron donor or **nucleophile.**

A simple example of an acid-base is the reaction of a proton with hydroxyl ion.

$$\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H^-} = H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H$$

Some other examples are:

$$\underset{\text{Base}}{H_3N:} + \underset{\text{Acid}}{BF_3} = H_3N \rightarrow BF_3$$

$$\underset{\text{Acid}}{H^+} + \underset{\text{Base}}{:NH_3} = [H \leftarrow NH_3]^+$$

$$\underset{\text{Acid}}{BF_3} + \underset{\text{Base}}{[F]^-} = [F \rightarrow BF_3]^+$$

Lewis concept is more general than the Bronsted Lowry concept.

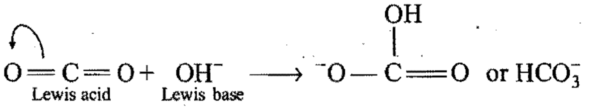
According to Lewis concept, the following species can act as Lewis acids:

(i) Molecules in which the central atom has incomplete octet: All compounds having central atom with less than 8 electrons are Lewis acids, *e.g.*, BF_3, BCl_3, $AlCl_3$, $MgCl_2$, $BeCl_2$, etc.

(ii) Simple cations: All cations are expected to act as Lewis acids since they are deficient in electrons. However, cations such as Na^+, K^+, Ca^{2+}, etc., have a very little tendency to accept electrons, while the cations like H^+, Ag^+, etc., have greater tendency to accept electrons and, therefore, act as Lewis acids.

(iii) Molecules in which the central atom has empty *d*-orbitals: The central atom of the halides such as SiX_4, GeX_4, $TiCl_4$, SnX_4, PX_3, PF_5, SF_4, SeF_4, $TeCl_4$, etc., have vacant *d*-orbitals. These can, therefore, accept an electron pair and act as Lewis acids.

(iv) Molecules having a multiple bond between atoms of dissimilar electronegativity: Typical examples of molecules falling in this class of Lewis acids are CO_2, SO_2 and SO_3. Under the influence of attacking Lewis base, one π-electron pair will be shifted towards the more negative atom.



$$\underset{\text{Lewis acid}}{O{=}C{=}O} + \underset{\text{Lewis base}}{OH^-} \longrightarrow {}^-O-\overset{\overset{\large OH}{|}}{C}{=}O \text{ or } HCO_3^-$$

The following species can act as Lewis bases:

(i) Neutral species having at least one lone pair of electrons: For example, ammonia, amines, alcohols, etc., act as Lewis bases because they contain a pair of electrons.

$$:NH_3, \quad -\ddot{N}H_2, \quad R-\underset{\cdot\cdot}{\ddot{O}}-H$$

(ii) Negatively charged species or anions: For example, chloride, cyanide, hydroxide ions, etc., act as Lewis bases.

$$CN^-, \quad Cl^-, \quad OH^-$$

It may be noted that all Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

Limitations: Since, the strength of the Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

The choice of which definition of acids and bases one wishes to use in a particular instance depends largely on the sort of chemistry that is studied. But Arrhenius concept is perfectly satisfactory and simplest for dealing with reactions in aqueous solutions. It explains satisfactorily the strength of acids and bases in aqueous solutions, neutralisation, salt hydrolysis, etc.

10.6 RELATIVE STRENGTH OF ACIDS AND BASES

According to Arrhenius concept, an acid is a substance which furnishes H^+ ions when dissolved in water. All the acid properties on an acid are due to H^+ ions present in the solution.

The extent to which an acid property is given by an acid is a measure of its strength. The strength of the acid solution does not depend on its concentration but on the number of H^+ ions present. The concentration of H^+ ions depends on the ionisation of an acid in solution. On dilution, the ionisation increases and more of H^+ ions come to solution with the result that the strength of the acid increases. **Thus, strength of the acid increases on dilution while its concentration decreases.** At infinite dilution the dissociation of an acid is nearly complete and all acids are equally strong at infinite dilution.

The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. Thus, to measure the relative strength of the two acids, the measurements of hydrogen ion concentration, *i.e.*, degree of dissociation is made of equinormal solutions of the two acids. Various methods are used for this purpose. Some are described below.

(i) The conductivity method: The degree of dissociation of a weak acid is equal to conductivity ratio $\frac{\Lambda}{\Lambda_\infty}$. Thus, the degrees of dissociation α_1 and α_2 for two equinormal acids are given by:

$$\text{For acid I,} \qquad \alpha_1 = \frac{\Lambda_1}{\Lambda_{\infty_1}}$$

and

$$\text{For acid II,} \qquad \alpha_2 = \frac{\Lambda_2}{\Lambda_{\infty_2}}$$

At infinite dilution, all weak electrolytes have almost the same value of Λ_∞; hence,

$$\Lambda_{\infty_1} = \Lambda_{\infty_2}$$

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \frac{\Lambda_1}{\Lambda_2} = \frac{\dfrac{1000 \times \text{sp. cond. acid I}}{C}}{\dfrac{1000 \times \text{sp. cond. acid II}}{C}}$$

$$= \frac{\text{Sp. cond. acid I}}{\text{Sp. cond. acid II}}$$

The relative strength of two acids is, thus, equal to the ratio of their equivalent conductance or specific conductance of equinormal solutions which can be determined experimentally.

(ii) Comparing dissociation constants: Let K_1 and K_2 be the dissociation constants of two acids and let α_1 and α_2 be their degree of dissociation in equinormal solutions.

Applying Ostwald's dilution law, $\alpha_1 = \sqrt{\frac{K_1}{C}}$ and $\alpha_2 = \sqrt{\frac{K_2}{C}}$

$$\text{Thus,} \qquad \frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}$$

Dissociation constants of some weak acids are given in the table:

Acid-ionization constants at 25°C

Substance	Formula	K_a
Acetic acid	$HC_2H_3O_2$	1.7×10^{-5}
Benzoic acid	$HC_7H_5O_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HCO_3^-	4.8×10^{-11}
Cyanic acid	HOCN	3.5×10^{-4}

Substance	Formula	K_a
Formic acid	$HCHO_2$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulphate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulphide	H_2S HS^-	8.9×10^{-8} 1.2×10^{-13}
Hypochlorous acid	$HClO$	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$H_2C_2O_4$ $HC_2O_4^-$	5.6×10^{-2} 5.1×10^{-5}
Phosphoric acid	H_3PO_4 $H_2PO_4^-$ HPO_4^{2-}	6.9×10^{-3} 6.2×10^{-8} 4.8×10^{-13}
Phosphorous acid	H_2PHO_3 $HPHO_3^-$	1.6×10^{-2} 7.0×10^{-7}
Propionic acid	$HC_3H_5O_2$	1.3×10^{-5}
Pyruvic acid	$HC_3H_3O_3$	1.4×10^{-4}
Sulphurous acid	H_2SO_3 HSO_3^-	1.3×10^{-2} 6.3×10^{-8}

(iii) Thomson thermal method: In this method, heat of neutralisation of two acids is first determined separately with NaOH. Let it be 'x' and 'y' calorie. The one gram equivalent of each of the two acids is mixed and one gram equivalent of NaOH is added. Let the heat evolved in this case be 'z' calorie. The two acids will neutralise a fraction of the base proportional to their relative strength. Suppose n gram equivalent of NaOH is neutralised by acid I and the rest $(1-n)$ by acid II.

$$\text{Total heat evolved, } z = nx + (1-n)y$$

$$= nx + y - ny$$

or

$$z - y = n(x - y)$$

or

$$n = \frac{(z-y)}{(x-y)}$$

So,

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{n}{(1-n)} = \frac{\dfrac{(z-y)}{(x-y)}}{1 - \dfrac{(z-y)}{(x-y)}} = \frac{(z-y)}{(x-z)}$$

Relative strength of bases: A base is a substance which gives OH^- ions when dissolved in water. The strength of the base depends on OH^- ion concentration. The above methods can be used for measuring relative strengths of bases also. In the Thomson thermal method, the two bases and their mixtures will be neutralised by strong acid, say HCl.

The relative strengths of some of the acids are as follows:

(i) $HClO_4 > HBr > HCl > HNO_3 > H_2SO_4 > H_3O^+ > H_2SO_3 > H_2CO_3 > CH_3COOH$

(ii) $HClO_4 > HClO_3 > HClO_2 > HClO$

(iii) $HI > HBr > HCl > HF$

(iv) $HClO_3 > HBrO_3 > HIO_3$

(v) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

(vi) $HCOOH > CH_3COOH > C_2H_5COOH$

The relative strengths of some of the bases are as follows:

(i) $KOH > NaOH > Ca(OH)_2 > NH_4OH$

(ii) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(iii) $(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > (C_2H_5)_3N$

(iv) $NaOH > NH_3 > H_2O$

(v) $NH_3 > NH_2 \cdot NH_2 > NH_2OH$

(vi) $NH_3 > C_5H_5N > C_6H_5NH_2$

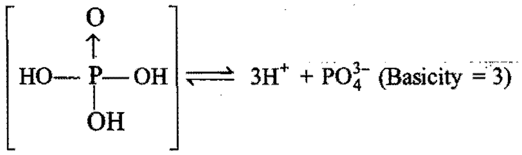
ILLUSTRATIONS OF OBJECTIVE QUESTIONS

13. Which one is correct statement? **(DCE 2007)**

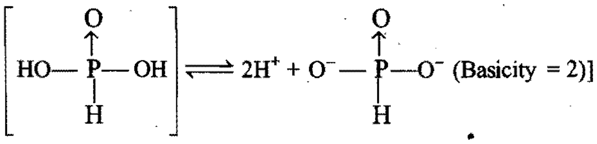
(a) Basicity of H_3PO_4 and H_3PO_3 are 3 and 3 respectively
(b) Acidity of H_3PO_4 and H_3PO_3 are 3 and 3 respectively
(c) Acidity of H_3PO_4 and H_3PO_3 are 3 and 2 respectively
(d) Basicity of H_3PO_4 and H_3PO_3 are 3 and 2 respectively

[Ans. (d)]

[Hint:



$$\left[HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH\right] \rightleftharpoons 3H^+ + PO_4^{3-} \text{ (Basicity = 3)}$$



$$\left[HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{H}{|}}{P}}-OH\right] \rightleftharpoons 2H^+ + O^- - \overset{\overset{O}{\uparrow}}{\underset{\underset{H}{|}}{P}}-O^- \text{ (Basicity = 2)]}$$

14. In the reaction,

$$HC_2O_4^- + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + C_2O_4^{2-}$$

the Bronsted base are: **[PET (Raj.) 2004]**

(a) $PO_4^{3-}, C_2O_4^{2-}$ (b) PO_4^{3-}, HPO_4^{2-}
(c) $HC_2O_4^-, HPO_4^{2-}$ (d) $HC_2O_4^-, C_2O_4^{2-}$

[Ans. (a)]

[Hint: Acid − H^+ = Conjugate base]

15. Conjugate base of HCO_3^- is: **[PET (Raj.) 2005]**

(a) CO_2 (b) H_2CO_3 (c) H_2O (d) CO_3^{2-}

[Ans. (d)]

[Hint: Acid − H^+ = Conjugate base, $HCO_3^- - H^+ = CO_3^{2-}$]

16. Four species are listed below :

(i) HCO_3^- (ii) $H_3\overset{+}{O}$ (iii) HSO_4^- (iv) HSO_3F

Which one of the following is the correct sequence of their acid strength ? **(AIEEE 2008)**

(a) (iii) < (i) < (iv) < (ii) (b) (iv) < (ii) < (iii) < (i)
(c) (ii) < (iii) < (i) < (iv) (d) (i) < (iii) < (ii) < (iv)

[Ans. (d)]

[Hint : $HCO_3^- < HSO_4^- < H_3\overset{+}{O} < HSO_3F$

HSO_3F is super acid and it is most acidic. $H_3\overset{+}{O}$ is more acidic than anions because anions (HCO_3^-, HSO_4^-) do not release H^+ ion easily. HSO_4^- is more acidic than HCO_3^- because sulphur is more electronegative than carbon.]

17. Identify Bronsted-Lowry acids in the reaction given:

$$\underset{(A)}{[Al(H_2O)_6]^{3+}} + \underset{(B)}{HCO_3^-} \rightleftharpoons \underset{(C)}{[Al(H_2O)_5(OH^-)]^{2+}} + \underset{(D)}{H_2CO_3}$$

The correct answer is: [EAMCET (Med.) 2008]

(a) A, C (b) B, D (c) A, D (d) B, C

[**Ans.** (c)]

[**Hint :** $[Al(H_2O)_6]^{3+}$ and H_2CO_3 are proton donor or Bronsted acids]

18. Conjugate base of $H_2PO_4^-$ is: [Comed (Karnataka) 2008]

(a) HPO_4^{2-} (b) PO_4^{3-} (c) H_3PO_4 (d) HPO_4^-

[**Ans.** (a)]

[**Hint :** Acid – H^+ = Conjugate base

$H_2PO_4^- - H^+ = HPO_4^{2-}$]

10.7 ACID-BASE NEUTRALISATION—SALTS

When aqueous solutions of hydrochloric acid and sodium hydroxide are mixed in the proper proportion, a reaction takes place to form sodium chloride and water.

$$HCl(aq.) + NaOH(aq.) \rightleftharpoons \underset{\text{Sodium chloride}}{NaCl(aq.)} + H_2O(l)$$

Such a reaction is termed neutralisation because both acidic (H^+) and basic (OH^-) properties are eliminated during the reaction. The hydrogen ion, which is responsible for the acidic properties, has reacted with the hydroxyl ion which is responsible for the basic properties, producing neutral water. The Na^+ and Cl^- ions have undergone no chemical change and appear in the form of crystalline sodium chloride upon evaporation of the solution. Sodium chloride is an example of the class of compounds called **salts.**

$$H^+(aq.) + Cl^-(aq.) + Na^+(aq.) + OH^-(aq.)$$
$$\rightleftharpoons H_2O(l) + Na^+(aq.) + Cl^-(aq.)$$

or
$$H^+(aq.) + OH^-(aq.) \rightleftharpoons H_2O(l)$$

Thus, the neutralisation of a base with an acid involves the interaction between OH^- and H^+ ions.

Or

The reaction between an acid and a base to form salt and water is termed neutralisation.

The process of neutralisation does not produce the resulting solution always neutral; no doubt it involves the interaction of H^+ and OH^- ions. The nature of the resulting solution depends on the particular acid and a particular base involved in the reaction. The following examples illustrate this point when equivalent amounts of acids and bases are reacted in aqueous solution.

(i) A strong acid plus a strong base gives a neutral solution because both are completely ionised and the reaction goes to completion.

$$H^+ + Cl^- + Na^+ + OH^- \rightleftharpoons H_2O + Na^+ + Cl^-$$

(ii) A strong acid plus a weak base gives an acidic solution as the weak base is not completely ionised. The reaction does not go to completion and there is an excess of hydrogen ions in solution.

$$H^+ + Cl^- + NH_4OH \rightleftharpoons H_2O + NH_4^+ + Cl^-$$

(iii) A weak acid plus a strong base gives a basic solution as the weak acid is not completely ionised. The reaction does not go to completion and there is an excess of hydroxyl ions in solution.

$$CH_3COOH + Na^+ + OH^- \rightleftharpoons H_2O + CH_3COO^- + Na^+$$

(iv) A weak acid plus a weak base gives an acidic or a basic or a neutral solution depending on the relative strength of acid and base. In case, both have equal strength, the resulting solution is neutral in nature.

$$CH_3COOH + NH_4OH \rightleftharpoons H_2O + NH_4^+ + CH_3COO^-$$

Salts: Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid. Salts are ionic compounds. Salts may taste salty, sour, bitter, astringent or sweet or tasteless. Solutions of salts may be acidic, basic or neutral. Fused salts and aqueous solutions of salts conduct electricity and undergo electrolysis. The properties of salts in aqueous solutions are the properties of ions. The salts are generally crystalline solids.

The salts are classified into the following classes:

(i) Simple salts: The salt formed by the neutralisation process, *i.e.*, interaction between acid and base, is termed as simple salt. These are of three types:

(a) Normal salts: The salts formed by the loss of all possible protons (replaceable hydrogen atoms as H^+) are called normal salts. Such a salt does not contain either a replaceable hydrogen or a hydroxyl group.

Examples are: NaCl, $NaNO_3$, K_2SO_4, $Ca_3(PO_4)_2$, Na_3BO_3, Na_2HPO_3 (one H atom is not replaceable as H_3PO_3 is a dibasic acid), NaH_2PO_2 (both H atoms are not replaceable as H_3PO_2 is a monobasic acid), etc.

(b) Acid salts: Salts formed by incomplete neutralisation of poly-basic acids are called acid salts. Such salts still contain one or more replaceable hydrogen atoms. These salts when neutralised by bases form normal salts.

Examples are: $NaHCO_3$, $NaHSO_4$, NaH_2PO_4, Na_2HPO_4, etc.

(c) Basic salts: Salts formed by incomplete neutralisation of polyacidic bases are called basic salts. Such salts still contain one or more hydroxyl groups. These salts when neutralised by acids form normal salts.

Examples are: Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$, $Bi(OH)_2Cl$, etc.

(ii) Double salts: The addition compounds formed by the combination of two simple salts are termed double salts. Such salts are stable in solid state only.

Examples are: Ferrous ammonium sulphate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, Potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and other alums.

Properties: (a) When dissolved in water, it furnishes all the ions present in the simple salts from which it has been constituted.

(b) The solution of double salt shows the properties of the simple salts from which it has been constituted.

(iii) Complex salts: These are formed by combination of simple salts or molecular compounds. These are stable in solid state as well as in solutions.

$$\underbrace{FeSO_4 + 6KCN}_{\text{Simple salt}} \longrightarrow \underset{\text{Complex salt}}{K_4Fe(CN)_6} + K_2SO_4$$

$$\underset{\text{Simple salt}}{CoSO_4} + \underset{\text{Molecular compound}}{6NH_3} \longrightarrow \underset{\text{Complex salt}}{Co(NH_3)_6SO_4}$$

Properties: (a) On dissolving in water, it furnishes a complex ion.

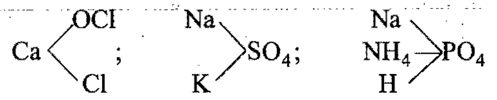
$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + \underset{\text{Complex ion}}{[Fe(CN)_6]^{4-}}$$

$$Cu(NH_3)_4SO_4 \rightleftharpoons \underset{\text{Complex ion}}{[Cu(NH_3)_4]^{2+}} + SO_4^{2-}$$

(b) The properties of the solution are different from the properties of the substances from which it has been constituted.

(iv) Mixed salts: The salt which furnishes more than one cation or more than one anion when dissolved in water is called a mixed salt.

Examples are:



Acidic, Basic and Amphoteric oxides

(i) Non-metal oxides are acidic, they dissolve in water to form acid. These oxides form salt with bases.

e.g., $\left.\begin{array}{l} SO_2, SO_3, P_4O_{10}, CO_2, NO_2, N_2O_5 \\ SiO_2, B_2O_3 \end{array}\right\}$ Non-metal oxides

Some Transition metal oxides are also acidic.

e.g., $CrO_3, MoO_3, WO_3, Mn_2O_7$

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (Carbonic acid)}$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \text{ (Nitrous and nitric acid)}$$

$$P_2O_5 + 3H_2O \longrightarrow \underset{\text{(Phosphoric acid)}}{2H_3PO_4}$$

$$NaOH + SO_3 \longrightarrow \underset{\text{Salt}}{NaHSO_4}$$

$$2KOH + CO_2 \longrightarrow \underset{\text{Salt}}{K_2CO_3} + H_2O$$

(ii) Usually, oxides of highly electropositive metals are basic. These oxides dissolve in water to form base and they form salt with acids.

e.g., $Na_2O, K_2O, MgO, CaO, Sc_2O_3, TiO_2, ZrO_2$

$$Na_2O + H_2O \longrightarrow \underset{\text{(Sodium hydroxide, a base)}}{2NaOH}$$

$$CaO + 2HCl \longrightarrow \underset{\text{Salt}}{CaCl_2} + H_2O$$

$$Mg + H_2SO_4 \longrightarrow \underset{\text{Salt}}{MgSO_4} + H_2O$$

(iii) Oxides of metalloids and less electropositive metals are amphoteric. These oxides form salt with both acids and bases.

e.g., $BeO, Al_2O_3, GeO, SnO, Sb_2O_3, PbO$

ZnO, Cr_2O_3

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$$

10.8 IONIC PRODUCT OF WATER

Pure water is a very weak electrolyte and ionises according to the equation,

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

or $$[H^+][OH^-] = K[H_2O]$$

Since, dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_2O]$, may be regarded as constant. Thus, the product $K[H_2O]$ gives another constant which is designated as K_w. So,

$$[H^+][OH^-] = K_w$$

The constant, K_w, is termed as **ionic product of water.**

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, *i.e.*, the concentration of H^+ and OH^- ions increases with increase in temperature.

Temperature (°C)	Value of K_w
0	0.11×10^{-14}
10	0.31×10^{-14}
25	1.00×10^{-14}
100	7.50×10^{-14}

The value of K_w at 25°C is 1×10^{-14}. Since, pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

$$[H^+] = [OH^-] = x$$

or $$[H^+][OH^-] = x^2 = 1 \times 10^{-14}$$

or $$x = 1 \times 10^{-7}\ M$$

or $$[H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol litre}^{-1}$$

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

When an acid or a base is added to water, the ionic concentration product, $[H^+][OH^-]$, remains constant, *i.e.*, equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases, *i.e.*,

$$[H^+] > [OH^-]; \qquad \text{(Acidic solution)}$$

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,

i.e., $[OH^-] > [H^+]$; (Alkaline or basic solution)

In neutral solution, $[H^+] = [OH^-] = 1 \times 10^{-7}\ M$

In acidic solution, $[H^+] > [OH^-]$

or $\qquad [H^+] > 1 \times 10^{-7}\ M$

and $\qquad [OH^-] < 1 \times 10^{-7}\ M$

In alkaline solution, $\quad [OH^-] > [H^+]$

or $\qquad [OH^-] > 1 \times 10^{-7}\ M$

and $\qquad [H^+] < 1 \times 10^{-7}\ M$

Thus, if the hydrogen ion concentration is more than $1 \times 10^{-7}\ M$, the solution will be acidic in nature and if less than $1 \times 10^{-7}\ M$, the solution will be alkaline.

$[H^+] = 10^{-0} \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6}$ (Acidic)
$[H^+] = \qquad 10^{-7}$ (Neutral)
$[H^+] = 10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8}$ (Alkaline)

We shall have the following table if OH $^-$ ion concentration is taken into account:

$[OH^-] = 10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8}$ (Acidic)
$[OH^-] = \qquad 10^{-7}$ (Neutral)
$[OH^-] = 10^{-0} \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^{-4} \quad 10^{-5} \quad 10^{-6}$ (Alkaline)

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H $^+$ and OH $^-$ ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25° C. If one increases, the other decreases accordingly so that the product remains 1×10^{-14} at 25° C.

If $[H^+] = 10^{-2}\ M$, then $[OH^-] = 10^{-12}\ M$; the product, $[H^+][OH^-] = 10^{-2} \times 10^{-12} = 10^{-14}$; the solution is acidic.

If $[H^+] = 10^{-10}\ M$, then $[OH^-] = 10^{-4}\ M$; the product, $[H^+][OH^-] = 10^{-10} \times 10^{-4} = 10^{-14}$; the solution is alkaline.

10.9 HYDROGEN ION CONCENTRATION—pH SCALE

It is clear from the above discussion that nature of the solution (acidic, alkaline or neutral) can be represented in terms of either hydrogen ion concentration or hydroxyl ion concentration but it is convenient to express acidity or alkalinity of a solution by referring to the concentration of hydrogen ions only. Since, H $^+$ ion concentration can vary within a wide range from 1 mol per litre to about 1.0×10^{-14} mol per litre, a logarithmic notation has been devised by **Sorensen**, in 1909, to simplify the expression of these quantities. The notation used is termed as the pH scale.

The hydrogen ion concentrations are expressed in terms of the numerical value of negative power to which 10 must be raised. This numerical value of negative power was termed as pH, *i.e.*,

$$[H^+] = 10^{-pH}$$

or $\quad \log [H^+] = \log 10^{-pH} = -pH \log 10 = -pH$

or $\quad pH = -\log [H^+]$

or $\quad pH = \log \dfrac{1}{[H^+]}$

pH of a solution is, thus, defined as **the negative logarithm of the concentration (in mol per litre) of hydrogen ions which it contains** or pH of the solution is the **logarithm of the reciprocal of H $^+$ ion concentration.**

Just as pH indicates the hydrogen ion concentration, the pOH represents the hydroxyl ion concentration, *i.e.*,

$$pOH = -\log [OH^-]$$

Considering the relationship,

$$[H^+][OH^-] = K_w = 1 \times 10^{-14}$$

Taking log on both sides, we have

$$\log [H^+] + \log [OH^-] = \log K_w = \log (1 \times 10^{-14})$$

or $\quad -\log [H^+] - \log [OH^-] = -\log K_w = -\log (1 \times 10^{-14})$

or $\quad pH + pOH = pK_w^* = 14$

i.e., sum of pH and pOH is equal to 14 in any aqueous solution at 25° C. The above discussion can be summarised in the following manner:

	$[H^+]$	$[OH^-]$	pH	pOH
Acidic solution	$> 10^{-7}$	$< 10^{-7}$	< 7	> 7
Neutral solution	10^{-7}	10^{-7}	7	7
Basic solution	$< 10^{-7}$	$> 10^{-7}$	> 7	< 7

$[H^+]$	$[OH^-]$	pH	pOH	Nature of solution
10^0	10^{-14}	0	14	Strongly acidic
10^{-2}	10^{-12}	2	12	Acidic
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
10^{-9}	10^{-5}	9	5	Weakly basic
10^{-11}	10^{-3}	11	3	Basic
10^{-14}	10^0	14	0	Strongly basic

The following table shows the pH range for a few common substances:

Substance	pH range	Substance	pH range
Gastric contents	1.0 – 3.0	Milk (cow)	6.3 – 6.6
Soft drinks	2.0 – 4.0	Saliva (human)	6.5 – 7.5
Lemons	2.2 – 2.4	Blood plasma (human)	7.3 – 7.5
Vinegar	2.4 – 3.4	Milk of magnesia	10.5
Apples	2.9 – 3.3	Seawater	8.5
Urine (human)	4.8 – 8.4		

***pK* value:** *p* stands for negative logarithm. Just as H $^+$ and OH $^-$ ion concentrations range over many negative powers of 10, it is convenient to express them as pH or pOH, the dissociation constant (K) values also range over many negative powers of 10 and it is convenient to write them as pK. Thus, pK is the negative logarithm of dissociation constant.

$$pK_a = -\log K_a \qquad \text{and} \qquad pK_b = -\log K_b$$

Weak acids have higher pK_a values. Similarly, weak bases have higher pK_b values.

Any method which can measure the concentration of H^+ ions or OH^- ions in a solution can serve for finding pH value.

Limitations of pH Scale: (i) pH values of the solutions do not give us immediate idea of the relative strengths of the solutions. A solution of pH = 1 has a hydrogen ion concentration 100 times that of a solution of pH = 3 (not three times). A 4×10^{-5} N HCl is twice concentrated of a 2×10^{-5} N HCl solution, but the pH values of these solutions are 4.40 and 4.70 (not double).

(ii) pH value of zero is obtained in 1 N solution of strong acid. In case the concentration is 2 N, 3 N, 10 N, etc. The respective pH values will be negative.

(iii) A solution of an acid having very low concentration, say 10^{-8} N, cannot have pH 8, as shown by pH formula, but the actual pH value will be less than 7.

[**Note:** (i) Normality of strong acid $= [H_3O^+]$

Normality of strong base $= [OH^-]$

$$\therefore \quad pH = -\log[N] \quad \text{for strong acids}$$

$$pOH = -\log[N] \quad \text{for strong bases}$$

(ii) Sometimes, pH of acid comes more than 7 and that of base comes less than 7. It shows that the solution is very dilute; in such cases, H^+ or OH^- contribution from water is also considered, *e.g.*, in 10^{-8} N HCl,

$$[H^+]_{\text{Total}} = [10^{-8}]_{\text{Acid}} + [10^{-7}]_{\text{Water}}$$

$$= 11\times10^{-8}\ M = 1.1\times10^{-7}\ M$$

(iii) **pH of mixture:** Let one litre of an acidic solution of pH 2 be mixed with two litre of other acidic solution of pH 3. The resultant pH of the mixture can be evaluated in the following way:

Sample-1	**Sample-2**
pH = 2	pH = 3
$[H^+] = 10^{-2}\ M$	$[H^+] = 10^{-3}\ M$
$V = 1$ litre	$V = 2$ litre

$$M_1V_1 + M_2V_2 = M_R(V_1+V_2)$$

$$10^{-2}\times1 + 10^{-3}\times2 = M_R(1+2)$$

$$\frac{12\times10^{-3}}{3} = M_R$$

$4\times10^{-3} = M_R$ (Here, M_R = **Resultant molarity**)

$$pH = -\log(4\times10^{-3})$$

(iv) Total concentration of $[H^+]$ or $[H_3^+O]$ in a mixture of **weak acid** and a **strong acid**

$$= \frac{C_2 + \sqrt{C_2^2 + 4K_aC_1}}{2}$$

where, C_1 is the concentration of weak acid (in mol litre^{-1}) having dissociation constant K_a and C_2 is the concentration of strong acid.

(v) Let us consider mixture of two weak acids HA and HB.

$$HA \rightleftharpoons H^+ + A^-$$

$$HB \rightleftharpoons H^+ + B^-$$

On applying charge balance

$$[H^+] = [A^-] + [B^-] + [OH^-]$$

$$= \frac{K_a[HA]}{[H^+]} + \frac{K_b[HB]}{[H^+]} + \frac{K_w}{[H^+]}$$

$$[H^+] = \sqrt{K_a[HA] + K_b[HB] + K_w}$$

$$= \sqrt{CK_a + CK_b + K_w}$$

(vi) Let us consider mixture of two weak bases AOH and BOH with dissociation constant K_1, K_2 and concentration C_1, C_2 respectively

$$[OH^-] = \sqrt{C_1K_1 + C_2K_2 + K_w}$$

10.10 pH OF WEAK ACIDS AND BASES

Weak acids and bases are not completely ionised; an equilibrium is found to have been established between ions and unionised molecules. Let us consider a weak acid of basicity 'n'.

$$\begin{array}{lcccc} & AH_n & \rightleftharpoons & A^{n-} & + \ nH^+ \\ t=0 & C & & 0 & 0 \\ t_{eq} & C(1-\alpha) & & C\alpha & nC\alpha \end{array}$$

$$[H^+] = nC\alpha; \quad \therefore \quad pH = -\log_{10}[nC\alpha] \qquad \dots \text{(i)}$$

For monobasic acid, $n = 1$

$$pH = -\log_{10}[C\alpha] \qquad \dots \text{(ii)}$$

Dissociation constant of acid K_a may be calculated as:

$$K_a = \frac{[A^{n-}][H^+]^n}{[AH_n]} = \frac{[C\alpha][nC\alpha]^n}{C(1-\alpha)}$$

$$= \frac{\alpha[nC\alpha]^n}{(1-\alpha)} \qquad [\text{for weak acids, } \alpha \ll 1$$

$$\therefore (1-\alpha) \approx 1]$$

$$= \alpha[nC\alpha]^n$$

$$nCK_a = nC\alpha[nC\alpha]^n = [nC\alpha]^{(n+1)}$$

$$[nC\alpha] = [nCK_a]^{1/(n+1)}$$

$$[H^+] = [nCK_a]^{1/(n+1)}$$

$$\therefore \quad pH = -\frac{1}{(n+1)}\log_{10}(nCK_a) \qquad \dots \text{(iii)}$$

For monobasic acid, $n = 1$

$$pH = -\log_{10}\sqrt{CK_a} \qquad \dots \text{(iv)}$$

Since, $K_a = \alpha[nC\alpha]^n$

$$\frac{K_a}{\alpha} = (nC\alpha)^n$$

$$[nC\alpha] = \left[\frac{K_a}{\alpha}\right]^{1/n} = [H^+]$$

$$pH = -\frac{1}{n}\log_{10}\left(\frac{K_a}{\alpha}\right) \qquad \dots \text{(v)}$$

For $n = 1$,

$$pH = -\log_{10}\left(\frac{K_a}{\alpha}\right) \qquad \dots \text{(vi)}$$

SOME SOLVED EXAMPLES

Example 28. *The hydrogen ion concentration of a solution is 0.001 M. What will be the hydroxyl ion concentration of solution?*

Solution: We know that, $[H^+][OH^-] = 1.0 \times 10^{-14}$

Given that, $[H^+] = 0.001\,M = 10^{-3}\,M$

So, $$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{10^{-3}} = 10^{-11}\,M$$

Example 29. *What is the pH of the following solutions?*

(a) 10^{-3} *M HCl (b)* 0.0001*M NaOH (c)* 0.0001*M* H_2SO_4

Solution: HCl is a strong electrolyte and is completely ionised.

$$HCl \rightleftharpoons H^+ + Cl^-$$

So, $$[H^+] = 10^{-3}\,M$$

$$pH = -\log[H^+] = -\log(10^{-3}) = 3$$

(b) NaOH is a strong electrolyte and is completely ionised.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

So, $$[OH^+] = 0.0001\,M = 10^{-4}\,M$$

$$pOH = -\log(10^{-4}) = 4$$

As $pH + pOH = 14$

So, $pH + 4 = 14$ or $pH = 10$

Alternative method: $[OH^-] = 10^{-4}\,M$

We know that, $[H^+][OH^-] = 1.0 \times 10^{-14}$

So, $$[H^+] = \frac{1.0 \times 10^{-14}}{10^{-4}} = 10^{-10}\,M$$

$$pH = -\log[H^+] = -\log(10^{-10}) = 10$$

(c) H_2SO_4 is a strong electrolyte and is ionised completely.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

One molecule of H_2SO_4 furnishes $2H^+$ ions.

So, $$[H^+] = 2 \times 10^{-4}\,M$$

$$pH = -\log[H^+]$$
$$= -\log(2 \times 10^{-4}) = 3.70$$

Example 30. *Calculate the pH of the following solutions assuming complete dissociation:*

(a) 0.365 *g* L^{-1} *HCl solution*

(b) 0.001*M* *Ba(OH)*$_2$ *solution.*

Solution: (a) Mole. mass of HCl = 36.5

$$\text{Concentration of HCl} = \frac{0.365}{36.5} = 1.0 \times 10^{-2}\ \text{mol L}^{-1}$$

HCl is a strong electrolyte and is completely ionised.

So, $[H^+] = 1 \times 10^{-2}$ mol L^{-1}

$$pH = -\log[H^+] = -\log(1 \times 10^{-2}) = 2$$

(b) $Ba(OH)_2$ is a strong electrolyte and is completely ionised

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

One molecule on dissociation furnishes 2 OH^- ions.

So, $$[OH^-] = 2 \times 10^{-3}\,M$$

$$pOH = -\log[OH^-]$$
$$= -\log(2 \times 10^{-3}) = 2.7$$

We know that, $pH + pOH = 14$

So, $$pH = (14 - 2.7) = 11.3$$

Example 31. *Find the pH of a* 0.002*N acetic acid solution, if it is 2.3% ionised at a given dilution.*

Solution: Degree of dissociation, $\alpha = \frac{2.3}{100} = 0.023$

Concentration of acetic acid, $C = 0.002\,M$

The equilibrium is,

$$\underset{C(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{CH_3COO^-} + \underset{C\alpha}{H^+}$$

So, $$[H^+] = C\alpha = 0.002 \times 0.023$$
$$= 4.6 \times 10^{-5}\,M$$

$$pH = -\log[H^+]$$
$$= -\log(4.6 \times 10^{-5}) = 4.3372$$

Example 32. *Calculate the pH value of a solution obtained by mixing 50 mL of 0.2 N HCl with 50 mL of 0.1 N NaOH.*

Solution: Number of milli-equivalents of the acid

$$= 50 \times 0.2 = 10$$

Number of milli-equivalents of the base

$$= 50 \times 0.1 = 5$$

Number of milli-equivalents of the acid left after the addition of base

$$= (10 - 5) = 5$$

Total volume of the solution = 50 + 50 = 100 mL

Thus, 5 milli-equivalents of the acid are present in 100 mL of solution.

or 50 milli-equivalents of the acid are present in one litre of solution.

or 0.05 equivalents of the acid are present in one litre of solution.

The acid is monobasic and completely ionised in solution.

$$0.05\,N\ HCl = 0.05\,M\ HCl$$

So, $$[H^+] = 0.05\,M$$

$$pH = -\log[H^+] = -\log 5 \times 10^{-2} = -[\log 5.0 + \log 10^{-2}]$$
$$= -[0.70 - 2] = 1.3$$

Example 33. *What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N HCl, assuming the complete ionisation of the acid and the base?*

Solution: Number of milli-equivalents of NaOH

$$= 800 \times 0.05 = 40$$

Number of milli-equivalents of HCl = 200 × 0.1 = 20

Number of milli-equivalents of NaOH left after the addition of HCl

$$= (40 - 20) = 20$$

Total volume $= (200 + 800)$ mL $= 1000$ mL $= 1$ litre

20 milli-equivalents or 0.02 equivalents of NaOH are present in one litre, *i.e.*,

0.02 N NaOH $= 0.02$ M NaOH (Mono-acidic) and the base is completely ionised.

So, $[OH^-] = 0.02\,M$

or $[OH^-] = 2 \times 10^{-2}\ M$

$$pOH = -\log\,(2 \times 10^{-2}) = 1.7$$

We know that, $pH + pOH = 14$

So, $pH = (14 - 1.7) = 12.3$

Example 34. *What is the hydrogen ion concentration of a solution (i) whose pH is* 12, *(ii) whose pH is* 5.6*?*

Solution:

(i) $pH = -\log\,[H^+]$

or $\log\,[H^+] = -pH = -12$

$$[H^+] = 10^{-12}\ M$$

(ii) $pH = -\log\,[H^+]$

or $\log\,[H^+] = -5.6$

or $[H^+] = 10^{-5.6} = 10^{-6} \times 10^{0.4} = 2.5 \times 10^{-6}\ M$

Example 35. *How many moles of calcium hydroxide must be dissolved to produce* 250 *mL of an aqueous solution of pH* 10.65*? Assume the complete ionisation.*

Solution: We know that,

$$pH + pOH = 14$$

So, $pOH = (14 - 10.65) = 3.35$

$$[OH^-] = 10^{-3.35} = 10^{-4} \times 10^{0.65}$$

$$= 4.47 \times 10^{-4}\ M$$

One molecule of $Ca(OH)_2$ furnishes 2 OH^- ions.

Hence, concentration of

$$Ca(OH)_2 = \frac{4.47 \times 10^{-4}}{2} = 2.235 \times 10^{-4}\ M$$

$$\text{No. of moles in 250 mL} = \frac{2.235 \times 10^{-4}}{4} = 5.58 \times 10^{-5}$$

Example 36. *The pH of* $0.1\,M$ *hydrocyanic acid solution is* 5.2. *What is the value of* K_a *for hydrocyanic acid?*

Solution: $pH = -\log\,[H^+]$

or $\log\,[H^+] = -pH = -5.2$

$$[H^+] = 10^{-5.2} = 10^{-6} \times 10^{0.8}$$

$$= 6.3 \times 10^{-6}\ M$$

$$\text{'}\alpha\text{', degree of dissociation} = \frac{[H^+]}{C} = \frac{6.3 \times 10^{-6}}{0.1} = 6.3 \times 10^{-5}$$

According to Ostwald's formula for weak electrolyte,

$$K_a = \alpha^2 C = 6.3 \times 10^{-5} \times 6.3 \times 10^{-5} \times 0.1$$

$$= 3.69 \times 10^{-10}$$

Example 37. *Calculate the pH of the following solutions:*
(i) 1.0×10^{-8} *M HCl,* *(ii)* 1.0×10^{-8} *M NaOH*

Solution: (i) The neutral water has $[H^+] = 1 \times 10^{-7}\ M$

By adding $1.0 \times 10^{-8}\ M$ HCl, a concentration of $1.0 \times 10^{-8}\ M$ H^+ ions has increased in solution.

Thus, total $[H^+] = (1 \times 10^{-7} + 1 \times 10^{-8})\,M$

$$= (1 \times 10^{-7} + 0.1 \times 10^{-7})\,M$$

$$= 1.1 \times 10^{-7}\ M$$

$$pH = -\log\,(1.1 \times 10^{-7}) = -[\log 1.1 + \log 10^{-7}]$$

$$= -[0.0414 - 7.0] = 6.9586$$

(i) The neutral water has $[OH^-] = 1 \times 10^{-7}\ M$

By adding $1.0 \times 10^{-8}\ M$ NaOH, a concentration of $1.0 \times 10^{-8}\ M$ OH^- ions has increased in solution.

Thus, total $[OH^-] = (1 \times 10^{-7} + 1.0 \times 10^{-8})\,M$

$$= 1.1 \times 10^{-7}\ M$$

$$pOH = -\log 1.1 \times 10^{-7}$$

$$= 6.9586$$

$$pH = (14 - pOH) = (14 - 6.9586) = 7.0414$$

Example 38. *Calculate the* S^{2-} *ion concentration in a saturated solution* $(0.1\,M)$ *of* H_2S *whose pH was adjusted to* 2 *by the addition of HCl.* $(K_a = 1.1 \times 10^{-21})$

Solution: $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_a = \frac{[H^+]^2\,[S^{2-}]}{[H_2S]}$$

or $$[S^{2-}] = \frac{K_a\,[H_2S]}{[H^+]^2}$$

$pH = 2$; So, $[H^+] = 1 \times 10^{-2}\ M$

H_2S is a weak electrolyte, So, $[H_2S] = 0.1\,M$

So, $$[S^{2-}] = \frac{1.1 \times 10^{-21} \times 0.1}{1 \times 10^{-2} \times 1 \times 10^{-2}} = 1.1 \times 10^{-18}\ M$$

Example 39. *What is the hydrogen ion concentration of* 0.1 *N* CH_3COOH *solution? The ionisation constant of* CH_3COOH *is* 1.8×10^{-5}. *What is the pH of the solution?*

(IIT 1993)

Solution: Let the degree of dissociation be 'α'.

CH_3COOH is a weak electrolyte; thus,

$$\alpha^2 C = K_a$$

$$\alpha^2 \times 0.1 = 1.8 \times 10^{-5}$$

or $\alpha = 1.34 \times 10^{-2}$

$$[H^+] = \alpha \cdot C = 1.34 \times 10^{-2} \times 0.1 = 1.34 \times 10^{-3}\ M$$

$$pH = -\log\,[H^+] = -\log 1.34 \times 10^{-3} = 2.8729$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. At 90°C, pure water has $[H_3O^+] = 10^{-6}\ M$. What is the value of K_w at this temperature? **[CBSE (Med.) 2006]**

(a) 10^{-6} (b) 10^{-12} (c) 10^{-13} (d) 10^{-14}

[Ans. (b)]

[Hint: $[H_3O^+] = [OH^-] = 10^{-6}\ M$

$\therefore \quad K_w = [H_3O^+][OH^-] = 10^{-12}$]

20. The pH of 0.5 M aqueous solution of HF ($K_a = 2 \times 10^{-4}$) is:

(a) 2 (b) 4 (c) 6 (d) 10

[Ans. (a)]

[Hint: $[H^+] = \sqrt{CK_a} = \sqrt{0.5 \times 2 \times 10^{-4}} = 10^{-2}\ M$

$pH = -\log_{10}[H^+] = -\log 10^{-2} = 2$]

21. The hydroxyl ion concentration in a solution having pH value 3 will be:

(a) $10^{-11}\ M$ (b) $10^{-7}\ M$ (c) $10^{-3}\ M$ (d) $10^{-14}\ M$

[Ans. (a)]

[Hint: $pH + pOH = 14$

$pOH = 14 - pH = 14 - 3 = 11$

$[OH^-] = 10^{-pOH} = 10^{-11}\ M$]

22. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. The pH of the mixture will be nearly:

(a) 0.76 (b) 1.26 (c) 1.76 (d) 2.26

[Ans. (b)]

[Hint: $pH = 1, [H^+] = 10^{-1}\ M$

$pH = 2, [H^+] = 10^{-2}\ M$

$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$

$10^{-1} \times 50 + 10^{-2} \times 50 = M_R \times 100$

$M_R = 5.5 \times 10^{-2}\ M$

(Resultant molarity of H^+ ions)

$pH = -\log 5.5 \times 10^{-2} = 1.26$]

23. The pH of a solution obtained by mixing 50 mL of 0.4 N HCl and 50 mL of 0.2 N NaOH is:

(a) –log 2 (b) – log 0.2 (c) 1 (d) 2

[Ans. (c)]

[Hint: $N_1V_{1\,\text{acid}} - N_2V_{2\,\text{base}} = N_R(V_1 + V_2)$

$0.4 \times 50 - 0.2 \times 50 = N_R \times 100$

$N_R = 0.1$

$\therefore \quad [H^+] = 0.1\ M$

$pH = -\log[H^+] = -\log 0.1 = 1$]

24. What will be the pH value of 0.05 M $Ba(OH)_2$ solution? **[PMT (Raj.) 2006]**

(a) 12 (b) 13 (c) 1 (d) 12.96

[Ans. (b)]

[Hint: $\underset{0.05\ M}{Ba(OH)_2} \longrightarrow Ba^{2+} + \underset{\substack{2 \times 0.05\ M \\ = 0.1\ M}}{2OH^-}$

$pOH = -\log[OH^-] = -\log 0.1 = 1$

$pH = 14 - 1 = 13$]

25. Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture? **[CBSE (PMT) 2008]**

(a) $3.7 \times 10^{-3} M$ (b) $1.11 \times 10^{-3} M$

(c) $1.11 \times 10^{-4} M$ (d) $3.7 \times 10^{-4} M$

[Ans. (d)]

[Hint: $[H^+] = 10^{-3} M$, $[H^+] = 10^{-4}\ M$, $[H^+] = 10^{-5}\ M$ for the given acids.

$M_{mix}V_{mix} = M_1V_1 + M_2V_2 + M_3V_3$

$M_{mix} \times 3 = 10^{-3} \times 1 + 10^{-4} \times 1 + 10^{-5} \times 1$

$$M_{mix} = \frac{10^{-5}[100 + 10 + 1]}{3} = \frac{111 \times 10^{-5}}{3} = 37 \times 10^{-5}\ M$$

$= 3.7 \times 10^{-4}\ M$]

10.11 BUFFER SOLUTIONS

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is observed that solutions and even pure water (pH = 7) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution.** It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

General Characteristics of a Buffer Solution

(i) It has a definite pH, *i.e.*, it has reserve acidity or alkalinity.

(ii) Its pH does not change on standing for long.

(iii) Its pH does not change on dilution.

(iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

(i) by mixing a weak acid with its salt with a strong base, *e.g.*,
  (a) $CH_3COOH + CH_3COONa$
  (b) Boric acid + Borax
  (c) Phthalic acid + Potassium acid phthalate

(ii) by mixing a weak base with its salt with a strong acid, *e.g.*,
  (a) $NH_4OH + NH_4Cl$
  (b) Glycine + Glycine hydrochloride

(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, *e.g.*, $Na_2HPO_4 + Na_3PO_4$ or a salt of weak acid and a weak base, such as CH_3COONH_4.

The first and second type are also called acidic and basic buffers respectively.

Explanation of Buffer Action

(i) Acidic buffer: Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH_3COOH molecules, CH_3COO^- ions, Na^+ ions, H^+ ions and OH^- ions. Thus, we have the following equilibria in solution:

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \quad \text{(Feebly ionised)}$$

$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^- \quad \text{(Completely ionised)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(Very feebly ionised)}$$

When a drop of strong acid, say HCl, is added, the H^+ ions furnished by HCl combine with CH_3COO^- ions to form feebly ionised CH_3COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H^+ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

Thus, OH^- ions furnished by a base are removed and pH of the solution is practically unaltered.

(ii) Basic buffer: Consider the case of the solution containing NH_4OH and its salt NH_4Cl. The solution will have NH_4OH molecule, NH_4^+ ions, Cl^- ions, OH^- ions and H^+ ions.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad \text{(Feebly ionised)}$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \quad \text{(Completely ionised)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(Very feebly ionised)}$$

When a drop of NaOH is added, the added OH^- ions combine with NH_4^+ ions to form feebly ionised NH_4OH whose ionisation is further suppressed due to common ion effect. Thus, pH is not disturbed considerably.

$$NH_4^+ + \underset{\text{(From strong base)}}{\underset{\uparrow}{OH^-}} \rightleftharpoons NH_4OH$$

When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.

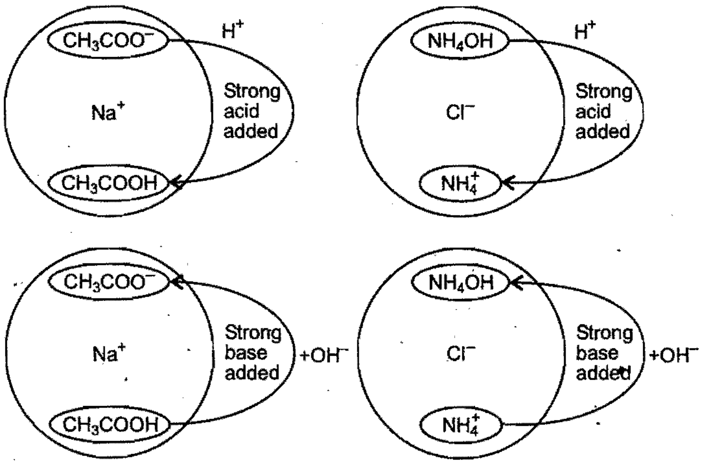
$$NH_4OH + \underset{\text{(From strong acid)}}{\underset{\uparrow}{H^+}} \rightleftharpoons NH_4^+ + H_2O$$

Thus, pH of the buffer is practically unaffected.

Diagramatic Representation of Buffer Action

Acid Buffer $(CH_3COOH + CH_3COONa)$

Base Buffer $(NH_4OH + NH_4Cl)$



Henderson's Equation (pH of a buffer)

(i) Acidic buffer: It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation,

$$HA \rightleftharpoons H^+ + A^-$$

Applying law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{... (i)}$$

or

$$[H^+] = K_a \frac{[HA]}{[A^-]} \quad \text{... (ii)}$$

It can be assumed that concentration of A^- ions from complete ionisation of the salt BA is too large to be compared with concentration of A^- ions from the acid HA.

$$BA \rightleftharpoons B^+ + A^-$$

Thus, $[HA]$ = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $[A^-]$ = Initial concentration of the salt as it is completely ionised.

So, $$[H^+] = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]} \quad \text{... (iii)}$$

Taking logarithm and reversing sign,

$$-\log [H^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

or $$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

or $$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{... (iv)}$$

This is known as **Henderson's equation.**

When $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$, then

$$\text{pH} = 1 + \text{p}K_a$$

and when $\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{10}$, then

$$\text{pH} = \text{p}K_a - 1$$

So, weak acid may be used for preparing buffer solutions having pH values lying within the ranges $\text{p}K_a + 1$ and $\text{p}K_a - 1$. The acetic acid has a $\text{p}K_a$ of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the range 3.8 to 5.8.

(ii) Basic buffer: It consists of a weak base and its salt with strong acid. Ionisation of a weak base, BOH, can be represented by the equation,

$$B\text{OH} \rightleftharpoons B^+ + \text{OH}^-$$

Applying law of mass action,

$$K_b = \frac{[B^+][\text{OH}^-]}{[B\text{OH}]} \qquad \text{... (i)}$$

or

$$[\text{OH}^-] = K_b \frac{[B\text{OH}]}{[B^+]} \qquad \text{... (ii)}$$

As the salt is completely ionised, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.

$$BA \rightleftharpoons B^+ + A^- \quad \text{(Completely ionised)}$$

So,

$$[\text{OH}^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]} \qquad \text{... (iii)}$$

or

$$\text{pOH} = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

or

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \qquad \text{... (iv)}$$

Knowing pOH, pH can be calculated by the application of the formula,

$$\text{pH} + \text{pOH} = 14$$

Buffer capacity: The property of a buffer solution to resist alteration in its pH value is known as **buffer capacity.** It has been found that if the ratio $\frac{[\text{Salt}]}{[\text{Acid}]}$ or $\frac{[\text{Salt}]}{[\text{Base}]}$ is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as **number of moles of acid or base added in one litre of solution as to change the pH by unity,** *i.e.*,

Buffer capacity

$$(\phi) = \frac{\text{No. of moles of acid or base added to 1 litre}}{\text{Change in pH}}$$

or

$$\phi = \frac{\partial b}{\partial(\text{pH})}$$

where, $\partial b \longrightarrow$ number of moles of acid or base added to 1 litre solution and $\partial(\text{pH}) \longrightarrow$ change in pH.

Buffer capacity is maximum:

(i) When [Salt] = [Acid], *i.e.*, $\text{pH} = \text{p}K_a$ for acid buffer

(ii) When [Salt] = [Base], *i.e.*, $\text{pOH} = \text{p}K_b$ for base buffer under above conditions, the buffer is called efficient.

Utility of Buffer Solutions in Analytical Chemistry

Buffers are used:

(i) To determine the pH with the help of indicators.

(ii) For the removal of phosphate ion in the qualitative inorganic analysis after second group using $CH_3COOH + CH_3COONa$ buffer.

(iii) For the precipitation of lead chromate quantitatively in gravimetric analysis, the buffer, $CH_3COOH + CH_3COONa$, is used.

(iv) For precipitation of hydroxides of third group of qualitative analysis, a buffer, $NH_4Cl + NH_4OH$, is used.

(v) A buffer solution of NH_4Cl, NH_4OH and $(NH_4)_2CO_3$ is used for precipitation of carbonates of fifth group in qualitative inorganic analysis.

(vi) The pH of intracellular fluid, blood is naturally maintained. This maintenance of pH is essential to sustain life because, enzyme catalysis is pH sensitive process. The normal pH of blood plasma is 7.4. Following two buffers in the blood help to maintain pH (7.4):

(a) Buffer of carbonic acid (H_2CO_3 and $NaHCO_3$)

(b) Buffer of phosphoric acid ($H_2PO_4^-$, HPO_4^{2-})

Buffers are used in industrial processes such as manufacture of paper, dyes, inks, paints, drugs, etc. Buffers are also employed in agriculture, dairy products and preservation of various types of foods and fruits.

SOME SOLVED EXAMPLES

Example 40. *The pH of a buffer is 4.745. When 0.01 mole of NaOH is added to 1 litre of it, the pH changes to 4.832, calculate its buffer capacity.*

Solution: From definition,

$$\text{Buffer capacity } (\phi) = \frac{\partial b}{\partial[\text{pH}]}$$

$$\partial(\text{pH}) = (4.832 - 4.745) = 0.087; \quad \partial b = 0.01$$

Substituting given values,

$$\phi = \frac{0.01}{0.087} = 0.115$$

Example 41. *Suppose it is required to make a buffer solution of pH = 4, using acetic acid and sodium acetate. How much of sodium acetate is to be added to 1 litre of N/10 acetic acid?*

Dissociation constant of acetic acid $= 1.8 \times 10^{-5}$.

Solution: Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$4 = \log[\text{Salt}] - \log(0.1) - \log 1.8 \times 10^{-5}$$

So, $\log[\text{Salt}] = (4 - 1 - 5 + 0.2552) = \bar{2}.2552$

$$[\text{Salt}] = 0.018 \text{ g mol L}^{-1}$$

The molecular mass of $CH_3COONa = 82$

$$\text{Amount of salt} = 0.018 \times 82 = 1.476 \text{ g}$$

Example 42. *What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing 1M acetic acid and acetate ion? Assume that the total volume is one litre.* (K_a *for* $CH_3COOH = 1.8 \times 10^{-5}$)

Solution: On adding HCl, the free hydrogen ions will combine with CH_3COO^- ions to form CH_3COOH. Thus, the concentration of acetic acid increases while that of CH_3COO^- ions decreases.

$$[CH_3COOH] = (0.2 + 1) = 1.2 \text{ mol litre}^{-1}$$

$$[\text{Salt}] = (1 - 0.2) = 0.8 \text{ mol litre}^{-1}$$

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{0.8}{1.2} - \log 1.8 \times 10^{-5}$$

$$= \log 2 - \log 3 - \log 1.8 \times 10^{-5} = 4.5687$$

Example 43. *20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of solution 4.74. The ionisation constant of acetic acid is* 1.8×10^{-5}.

Solution: No. of moles of NaOH in

$$20 \text{ mL} = \frac{0.2}{1000} \times 20 = 0.004$$

$$\text{No. of moles of acetic acid in } 50 \text{ mL} = \frac{0.2}{1000} \times 50 = 0.01$$

When NaOH is added, CH_3COONa is formed.

$$\underset{1 \text{ mole}}{CH_3COOH} + \underset{1 \text{ mole}}{NaOH} \rightleftharpoons \underset{1 \text{ mole}}{CH_3COONa} + \underset{1 \text{ mole}}{H_2O}$$

No. of moles of CH_3COONa in 70 mL solution = 0.004

No. of moles of CH_3COOH in 70 mL solution

$$= (0.01 - 0.004) = 0.006$$

Applying Henderson's equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{0.004}{0.006} - \log 1.8 \times 10^{-5} = 4.5687$$

On further addition of NaOH, the pH becomes 4.74.

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$= \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log 1.8 \times 10^{-5}$$

$$\text{or } \log \frac{[\text{Salt}]}{[\text{Acid}]} = \text{pH} + \log 1.8 \times 10^{-5} = (4.74 - 4.7448) = -0.0048$$

So,
$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = \bar{1}.9952$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = 0.9891$$

Let 'x' moles of NaOH be added.

$$[\text{Salt}] = (0.004 + x) \text{ mole}$$

$$[\text{Acid}] = (0.006 - x) \text{ mole}$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \frac{0.004 + x}{0.006 - x} = 0.9891$$

or
$$0.004 + x = 0.9891 \times 0.006 - 0.9891x$$

$$x = 0.000972 \text{ mole}$$

Volume of 0.2 M NaOH solution having 0.000972 mole

$$= \frac{1000}{0.2} \times 0.000972 = 4.86 \text{ mL}$$

Example 44. *Calculate the pH of the buffer solution containing 0.15 mole of NH_4OH and 0.25 mole of NH_4Cl. K_b for NH_4OH is* 1.98×10^{-5}.

Solution: Applying the equation,

$$\text{pOH} = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$= \log \frac{0.25}{0.15} - \log 1.8 \times 10^{-5}$$

$$= \log 5 - \log 3 - \log 1.8 \times 10^{-5}$$

$$= 0.6989 - 0.4771 + 4.7448 = 4.966$$

$$\text{pH} = (14 - 4.966) = 9.034$$

Example 45. *What volume of 0.10 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH 4.0? pK_a for formic acid is 3.80.* (IIT 1990)

Solution: Let x mL of 0.10 M sodium formate be added.

$$\text{No. of moles in } x \text{ mL of } 0.10 \, M \text{ sodium formate} = \frac{0.10}{1000} \times x$$

$$\text{No. of moles in } 50 \text{ mL of } 0.05 \, M \text{ formic acid} = \frac{0.05}{1000} \times 50$$

$$\frac{[\text{Sod. formate}]}{[\text{Formic acid}]} = \frac{\frac{0.10 \times x}{1000}}{\frac{0.05 \times 50}{1000}} = \frac{0.10x}{2.5} = 0.04x$$

Applying the equation,

$$\text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} + \text{p}K_a$$

$$4.0 = \log 0.04x + 3.8$$

or
$$x = 39.6 \text{ mL}$$

Example 46. *How many gram moles of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 g formula mass of NaCN? K_a for HCN* $= 4.1 \times 10^{-10}$.

Solution: Let a mole of HCl be added. It will combine with NaCN to form HCN.

$$\underset{a}{NaCN} + \underset{a}{HCl} \longrightarrow NaCl + \underset{a}{HCN}$$

$$[NaCN] = (0.01 - a)$$

$$[HCN] = a$$

Applying the equation,

$$\text{pH} = \log \frac{[NaCN]}{[HCN]} - \log K_a$$

$$8.5 = \log \frac{0.01 - a}{a} - \log 4.1 \times 10^{-10}$$

So, $$\log \frac{(0.01 - a)}{a} = 8.5 + 0.6127 - 10.0 = \bar{1}.1127$$

$$\frac{(0.01 - a)}{a} = 0.1296$$

or $$a = \frac{0.01}{1.1296} = 0.0089 \text{ mole}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

26. The pH of a solution that is 0.1 M NaA and 0.1 M HA $(K_a = 1 \times 10^{-6})$ would be:

(a) 5 (b) 6 (c) 3 (d) 7

[Ans. (b)]

[Hint: $$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log 10^{-6} + \log \frac{0.1}{0.1} = 6]$$

27. pK_a for acetic acid is 4.74. What should be the ratio of concentrations of acetic acid and acetate ions to have a solution with pH 5.74?

(a) 1 : 10 (b) 10 : 1 (c) 1 : 1 (d) 2 : 1

[Ans. (a)]

[Hint: $$\text{pH} = \text{p}K_a + \log \frac{[\text{Acetate ion}]}{[\text{Acetic acid}]}$$

$$5.74 = 4.74 + \log \frac{[\text{Acetate ion}]}{[\text{Acetic acid}]}$$

$$[\text{Acetic acid}] : [\text{Acetate}] = 1 : 10]$$

28. What is the pH of the buffer solution containing 0.15 mol of NH_4OH and 0.25 mol of NH_4Cl? K_b for NH_4OH is 1.98×10^{-5}:

(a) 10 (b) 9 (c) 9.2 (d) 10.2

[Ans. (b)]

[Hint: $$14 - \text{pH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log(1.98 \times 10^{-5}) + \log\left(\frac{0.25}{0.15}\right)$$

$$\text{pH} \approx 9]$$

29. The pH of a buffer solution of 0.1 M CH_3COOH and 0.1 M CH_3COONa is .... $(\text{p}K_a = 4.745)$.

(a) 4.745 (b) 3.745 (c) 5.745 (d) 3.255

[Ans. (a)]

[Hint: $$\text{pH} = \text{p}K_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= 4.745 + \log \frac{0.1}{0.1} = 4.745]$$

30. The pH of a buffer solution prepared by adding 10 mL of 0.1 M CH_3COOH and 20 mL of 0.1 M sodium acetate will be: (Given: pK_a of CH_3COOH = 4.74)

(a) 4.05 (b) 3.04 (c) 5.04 (d) 3.05

[Ans. (c)]

[Hint:

$$\text{Number of moles of } CH_3COOH = \frac{MV}{1000} = \frac{0.1 \times 10}{1000} = 0.001$$

$$\text{Number of moles of } CH_3COONa = \frac{MV}{1000} = \frac{0.1 \times 20}{1000} = 0.002$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.74 + \log\left[\frac{0.002}{0.001}\right] = 5.04]$$

31. 40 mL of 0.1 M ammonium hydroxide is mixed with 20 mL of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution is 4.74.) (AIIMS 2006)

(a) 4.74 (b) 2.26 (c) 9.26 (d) 5

[Ans. (c)]

[Hint: Since, ammonium hydroxide is 50% neutralised, hence

$$[\text{Salt}] = [\text{Base}]$$

$$\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]} = 4.74 + \log_{10} 1 = 4.74$$

$$\text{pH} = 14 - 4.74 = 9.26]$$

32. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA, in which 50% of the acid is ionised, is: (AIEEE 2007)

(a) 7.0 (b) 4.5 (c) 2.5 (d) 9.5

[Ans. (d)]

[Hint: $$\text{pH} = \text{p}K_a + \log_{10} \frac{[A^-]}{[HA]}$$

Since, acid is 50% ionised, hence $[A^-] = [HA]$

or $$\text{pH} = \text{p}K_a + \log 1$$

$$= 4.5$$

$$\text{pOH} = 14 - 4.5 = 9.5]$$

33. pK_a value of acetic acid is 4.75. If the buffer solution contains 0.125 M acetic acid and 0.25 M sodium acetate, the pH of buffer solution is : [Comed (Karnataka) 2008]

(a) 5.05 (b) 5.5 (c) 4.9 (d) 5.75

[Ans. (a)]

[Hint : $$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.75 + \log \frac{0.25}{0.125}$$

$$= 5.05]$$

Example 47. *The dissociation constants for HCOOH and CH_3COOH are 2.1×10^{-4} and 1.8×10^{-5} respectively. Calculate the relative strengths of the acids.*

Solution: The strength of the acid is directly proportional to the square root of the dissociation constant.

$$\text{Strength of the acid} \propto \sqrt{\text{dissociation constant}}$$

Hence, $$\frac{\text{Strength of HCOOH}}{\text{Strength of } CH_3COOH} = \sqrt{\frac{K_{HCOOH}}{K_{CH_3COOH}}}$$

$$= \sqrt{\frac{2.1 \times 10^{-4}}{1.8 \times 10^{-5}}} = 3.415$$

Example 48. *Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.05 mol L^{-1} of NH_4OH and 0.25 mol L^{-1} of NH_4Cl. Calculate the concentration of aluminium and magnesium ions in solution.*

$$K_{sp}\ Al(OH)_3 = 6\times10^{-32};\ K_b\ NH_4OH = 1.8\times10^{-5}$$

$$K_{sp}\ Mg(OH)_2 = 6\times10^{-10}$$

Solution: $$\text{pOH} = \log\frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$-\log[\text{OH}^-] = \log\frac{0.25}{0.05} - \log 1.8\times10^{-5}$$

or $$\log[\text{OH}^-] = \log\frac{1.8\times10^{-5}}{5}$$

$$[\text{OH}^-] = 0.36\times10^{-5}\ \text{mol L}^{-1}$$

$$[\text{Al}^{3+}] = \frac{K_{sp}\ \text{Al(OH)}_3}{[\text{OH}^-]^3} = \frac{6\times10^{-32}}{(0.36\times10^{-5})^3} = 1.29\times10^{-10}\ \text{mol L}^{-1}$$

$$[\text{Mg}^{2+}] = \frac{K_{sp}\ \text{Mg(OH)}_2}{[\text{OH}^-]^2} = \frac{6\times10^{-10}}{(0.36\times10^{-5})^2} = 46.3\ \text{mol L}^{-1}$$

Example 49. *Calculate the pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{2+} ions.* (*K_{sp} $Mg(OH)_2 = 1.0\times10^{-11}$*) **(IIT 1992)**

Solution: $K_{sp}\ \text{Mg(OH)}_2 = 1.0\times10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2$

$$= (0.10)[\text{OH}^-]^2$$

or $$[\text{OH}^-]^2 = \frac{1.0\times10^{-11}}{0.10} = 1\times10^{-10}$$

or $$[\text{OH}^-] = 1\times10^{-5}$$

$$[\text{H}^+] = \frac{1\times10^{-14}}{1\times10^{-5}} = 1\times10^{-9}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1\times10^{-9}) = 9.0$$

Example 50. *An aqueous solution of metal bromide, MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? K_{sp} for $MS = 6.0\times10^{-21}$, conc. of saturated $H_2S = 0.1 M$.*

$K_1 = 10^{-7}$ and $K_2 = 1.3\times10^{-13}$ for H_2S **(IIT 1993)**

Solution: The minimum concentration of S^{2-} ions required to precipitate MS is,

$$[\text{S}^{2-}] = \frac{K_{sp}\ M\text{S}}{[M^{2+}]} = \frac{6.0\times10^{-21}}{0.05} = 1.2\times10^{-19}\ M$$

H_2S ionises in solution in two steps:

$$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-;\ K_1 = 10^{-7}$$

$$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-};\ K_2 = 1.3\times10^{-13}$$

$$\frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = K_1 \quad \text{and} \quad \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = K_2$$

Hence, $$K_1K_2 = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

or $$[\text{H}^+]^2 = \frac{K_1K_2[\text{H}_2\text{S}]}{[\text{S}^{2-}]} = \frac{10^{-7}\times1.3\times10^{-13}\times0.1}{1.2\times10^{-19}}$$

$$= 1.08\times10^{-2}$$

So, $$[\text{H}^+] = 1.04\times10^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.04\times10^{-1}) = 0.98$$

Example 51. *The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.47? K_a for H_2CO_3 in blood is 7.8×10^{-7}.* **(IIT 1993)**

Solution: Let V mL of 5 M NaHCO_3 solution be mixed.

$$\text{Total volume} = (V + 10)\ \text{mL}$$

Conc. of H_2CO_3 and NaHCO_3 in the solution becomes

$$[\text{NaHCO}_3] = \frac{5\times V}{(V+10)}M$$

and $$[\text{H}_2\text{CO}_3] = \frac{2\times10}{(V+10)}M$$

Now applying Henderson's equation,

$$\text{pH} = -\log K_a + \log\frac{[\text{NaHCO}_3]}{[\text{H}_2\text{CO}_3]}$$

$$7.4 = -\log 7.8\times10^{-7} + \log\frac{5\times V}{(V+10)}\times\frac{(V+10)}{2\times10}$$

$$= -\log 7.8\times10^{-7} + \log\frac{V}{4}$$

or $$\log\frac{V}{4} = 7.4 + \log 7.8\times10^{-7}$$

$$V = 78.32\ \text{mL}$$

Example 52. *The pH of 0.05 M aqueous solution of diethylamine is 12. Calculate its K_b.* **(IIT 1993)**

Solution: We know that, $\text{pH} + \text{pOH} = 14$

or $$\text{pOH} = 14 - \text{pH} = 14 - 12 = 2$$

So, $$[\text{OH}^-] = 10^{-2}$$

$$\begin{array}{lcccc} & (\text{C}_2\text{H}_5)_2\text{NH} + \text{H}_2\text{O} & \rightleftharpoons & (\text{C}_2\text{H}_5)_2\text{NH}_2^+ & + \ \text{OH}^- \\ \text{At equilibrium} & (0.05 - x) & & x & x \\ & (0.05 - 0.01) & & 0.01 & 0.01 \end{array}$$

$$K_b = \frac{[(\text{C}_2\text{H}_5)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{C}_2\text{H}_5)_2\text{NH}]} = \frac{0.01\times0.01}{0.04} = 2.5\times10^{-3}$$

Example 53. *100 mL of HCl gas at 25°C and 740 mm pressure were dissolved in one litre of water. Calculate the pH of solution. Given, vapour pressure of H_2O at 25° C is 23.7 mm.*

Solution: Given, $V = 100\ \text{mL} = 0.1\ \text{L}$

$$P = \left(\frac{740 - 23.7}{760}\right)\text{atm} = 0.9425\ \text{atm}$$

$$R = 0.0821$$

$$T = (25 + 273)\ \text{K} = 298\ \text{K}$$

Applying, $$PV = nRT$$

or $$n = \frac{PV}{RT} = \frac{0.9425 \times 0.1}{0.0821 \times 298} = 3.85 \times 10^{-3} \text{ mol}$$

$$\text{Molarity} = \frac{n}{V} = \frac{3.85 \times 10^{-3}}{1} = 3.85 \times 10^{-3}\ M$$

HCl is a strong electrolyte. It is completely dissociated.

So, $$[\text{H}^+] = 3.85 \times 10^{-3}\ M$$

$$\text{pH} = -\log[\text{H}^+] = -\log 3.85 \times 10^{-3} = 2.4146$$

Example 54. *Calculate the* $[Cl^-]$, $[Na^+]$, $[H^+]$, $[OH^-]$ *and pH of the resulting solution obtained by mixing 50 mL of 0.6 N HCl and 50 mL of 0.3 N NaOH.*

Solution:	HCl +	NaOH $\longrightarrow$	NaCl +	H_2O
Milli-equivalents before reaction	50×0.6 = 30	50×0.3 = 15	0	0
Milli-equivalents after reaction	$(30 - 15)$ = 15	0	15	15

$$\text{Total volume} = 50 + 50 = 100 \text{ mL}$$

$$[\text{Cl}^-] = \frac{15+15}{100} = 0.3\,M$$

$$[\text{Na}^+] = \frac{15}{100} = 0.15\,M$$

$$[\text{H}^+] = \frac{15}{100} = 0.15\,M$$

$$[\text{OH}^-] = \frac{10^{-14}}{0.15} = 6.6 \times 10^{-14}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 0.15 = 0.8239$$

Example 55. *What is the pH of a 1.0 M solution of acetic acid? To what volume of one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given,* $K_a = 1.8 \times 10^{-5}$. **(IIT 1990)**

Solution: We know that degree of dissociation,

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$= \sqrt{\frac{1.8 \times 10^{-5}}{1}}$$

$$= 4.2426 \times 10^{-3}$$

$$[\text{H}^+] = C \times \alpha = 1 \times 4.2426 \times 10^{-3}$$

$$= 4.2426 \times 10^{-3} \text{ mol L}^{-1}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 4.2426 \times 10^{-3} = 2.3724$$

So, pH of the acetic acid solution after dilution = 2 × 2.3724

= 4.7448

$$\text{New } [\text{H}^+] = 10^{-4.7448} = 1.8 \times 10^{-5}$$

Let the new concentration be C_0.

$$\underset{\text{At equilibrium } C_0 - 1.8\times10^{-5}}{\text{CH}_3\text{COOH}} \rightleftharpoons \underset{1.8\times10^{-5}}{\text{H}^+} + \underset{1.8\times10^{-5}}{\text{CH}_3\text{COO}^-}$$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{(C_0 - 1.8 \times 10^{-5})} = 1.8 \times 10^{-5}$$

So, $$C_0 = 3.6 \times 10^{-5}$$

Let the new volume be V litre

$$1 \times 1 = 3.6 \times 10^{-5} \times V$$

$$V = \frac{1}{3.6 \times 10^{-5}} = 2.78 \times 10^4 \text{ litre}$$

Example 56. *Calculate the change in pH of one litre buffer solution containing 0.10 mole each of* NH_3 *and* NH_4Cl *upon addition of* (i) 0.02 *mole of dissolved gaseous HCl,* (ii) 0.02 *mole of dissolved NaOH.*

Assume no change in volume (K_b *for* $NH_3 = 1.8 \times 10^{-5}$). **(IIT 1992)**

Solution: pOH of NH_3 and NH_4Cl buffer

$$= -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.1}{0.1} = 4.75$$

$$\text{pH} = (14 - 4.75) = 9.25$$

First case: $$\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}$$

$$[\text{Salt}] = (0.1 + 0.02) = 0.12\,M$$

$$[\text{Base}] = (0.1 - 0.02) = 0.08\,M$$

$$\text{pOH} = -\log K_b + \log \frac{0.12}{0.08}$$

$$= 4.75 + 0.176 = 4.926$$

$$\text{pH} = (14 - 4.926) = 9.074$$

$$\Delta\text{pH} = (9.25 - 9.074) = 0.176 \text{ pH unit}$$

Second case: $$\text{NH}_4\text{Cl} + \text{NaOH} \longrightarrow \text{NH}_3 + \text{NaCl}$$

$$[\text{Salt}] = (0.1 - 0.02) = 0.08\,M$$

$$[\text{Base}] = (0.1 + 0.02) = 0.12\,M$$

$$\text{pOH} = -\log K_b + \log \frac{0.08}{0.12}$$

$$= (4.75 - 0.176) = 4.576$$

$$\text{pH} = (14 - 4.574) = 9.426$$

$$\Delta\text{pH} = (9.426 - 9.25) = 0.176 \text{ pH unit}$$

Example 57. *Saccharin* ($K_a = 2 \times 10^{-12}$) *is a weak acid represented by formula HSac. A* 4×10^{-4} *mole amount of saccharin is dissolved in 200* cm^3 *water of pH* = 3. *Assuming no change in volume, calculate the concentration of* Sac^- *ions in the resulting solution at equilibrium.* **(IIT 1994)**

Solution: Concentration of saccharin

$$= \frac{4 \times 10^{-4}}{200} \times 1000 = 2 \times 10^{-3} \text{ mol L}^{-1}$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3} \text{ mol L}^{-1}$$

$$\underset{[(2\times10^{-3})-x]}{\text{HSac}} \rightleftharpoons \underset{(10^{-3}+x)}{\text{H}^+} + \text{Sac}^-$$

$$K_a = \frac{[\text{H}^+][\text{Sac}^-]}{[\text{HSac}]} = \frac{(10^{-3}+x)[\text{Sac}^-]}{[2\times10^{-3}-x]}$$

$$[\text{Sac}^-] = \frac{2\times10^{-12}\times(2\times10^{-3}-x)}{(10^{-3}+x)}$$

Since, x is very small, it can be neglected.

$$[\text{Sac}^-] = \frac{2\times10^{-12}\times2\times10^{-3}}{10^{-3}} = 4\times10^{-12}\ \text{mol L}^{-1}$$

Example 58. *An aqueous solution contains 10% ammonia by mass and has a density 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. (K_a for $NH_4^+ \approx 5.0\times10^{-10}\ M$)* (IIT 1995)

Solution: Mass of 1 litre solution $= 1000\times0.99$ g

$= 990$ g

NH_3 present in 990 g solution $= 99$ g

1 litre solution contains $= \frac{99}{17} = 5.8$ mole

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x\times x}{(5.8-x)} \approx \frac{x^2}{5.8}$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5.0\times10^{-10}} = 2\times10^{-5}$$

So, $$2\times10^{-5} = \frac{x^2}{5.8}$$

$$x^2 = 2\times10^{-5}\times5.8$$

$$x = 1.078\times10^{-2}\ \text{mol L}^{-1}$$

$$[\text{OH}^-] = x = 1.078\times10^{-2}\ M$$

$$[\text{H}^+] = \frac{10^{-14}}{1.078\times10^{-2}} = 9.27\times10^{-13}\ M$$

Example 59. 0.15 *mole of pyridium chloride has been added into* 500 *cm*^{3} *of* 0.2 *M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume.*

(K_b for pyridine $= 1.5\times10^{-9}\ M$) (IIT 1995)

Solution: Concentration of pyridium chloride

$= 0.15\times2 = 0.3\ M$

$$\text{pOH} = \log\frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$= \log\frac{0.3}{0.2} - \log 1.5\times10^{-9}$$

$$= 9$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9}$$

$$\text{pH} = (14-\text{pOH}) = (14-9) = 5$$

Example 60. *How many moles of acetic acid and sodium acetate each should be dissolved to prepare one litre of* 0.063 *molar buffer solution of pH* 4.5*?*

(K_a for $CH_3COOH = 1.8\times10^{-5}$)

Solution: Applying Henderson's equation,

$$\text{pH} = \log\frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$\log\frac{[\text{Salt}]}{[\text{Acid}]} = 4.5 + \log 1.8\times10^{-5} = -0.2447$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \text{antilog}\ (-0.2447) = 0.5692$$

$$[\text{Salt}] = 0.5692\times[\text{Acid}]$$

Given: $[\text{Acid}] + [\text{Salt}] = 0.063$

$$[\text{Acid}] = \frac{0.063}{1.5692} = 0.040\ \text{mol L}^{-1}$$

$$[\text{Salt}] = (0.063-0.040) = 0.023\ \text{mol L}^{-1}$$

10.12 SALT HYDROLYSIS

Pure water is a weak electrolyte and neutral in nature, *i.e.*, H^+ ion concentration is exactly equal to OH^- ion concentration

$$[\text{H}^+] = [\text{OH}^-]$$

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis.** It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.**

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.

$$M^+ + \text{H}_2\text{O} \rightleftharpoons \underset{\text{Weak base}}{M\text{OH}} + \text{H}^+$$

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.

$$A^- + \text{H}_2\text{O} \rightleftharpoons \underset{\text{Weak acid}}{\text{H}A} + \text{OH}^-$$

The process of hydrolysis is actually the reverse of neutralisation.

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.
Examples: $FeCl_3, CuCl_2, AlCl_3, NH_4Cl, CuSO_4$, etc.

(ii) Salt of a strong base and a weak acid.
Examples: $CH_3COONa, NaCN, NaHCO_3, Na_2CO_3$, etc.

(iii) Salt of a weak acid and a weak base.
Examples: $CH_3COONH_4, (NH_4)_2CO_3, NH_4HCO_3$, etc.

(iv) Salt of a strong acid and a strong base.
Examples: $NaCl, K_2SO_4, NaNO_3, NaBr$, etc.

1. Salt of a strong acid and a weak base

The solution of such a salt is acidic in nature. The cation of the salt which has come from weak base is reactive. It reacts with water to form a weak base and H^+ ions.

$$B^+ + H_2O \rightleftharpoons \underset{\text{Weak base}}{BOH} + H^+$$

Consider, for example, NH_4Cl. It ionises in water completely into NH_4^+ and Cl^- ions. NH_4^+ ions react with water to form a weak base (NH_4OH) and H^+ ions.

$$\underset{C(1-x)}{NH_4^+} + H_2O \rightleftharpoons \underset{Cx}{NH_4OH} + \underset{Cx}{H^+}$$

Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]} = \frac{Cx \cdot Cx}{C(1-x)} = \frac{x^2C}{(1-x)} \qquad \text{... (i)}$$

where, C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-, \; K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{... (ii)}$$

$$H_2O \rightleftharpoons H^+ + OH^-, \; K_w = [H^+][OH^-] \qquad \text{... (iii)}$$

From eqs. (ii) and (iii),

$$\frac{K_w}{K_b} = \frac{[H^+][NH_4OH]}{[NH_4^+]} = K_h \qquad \text{... (iv)}$$

$$[H^+] = \frac{K_h[NH_4^+]}{[NH_4OH]} = \frac{K_w}{K_b} \times \frac{[NH_4^+]}{[NH_4OH]}$$

$$\log [H^+] = \log K_w - \log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$-\text{pH} = -\text{p}K_w + \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{p}K_w - \text{pH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Relation between Hydrolysis Constant and Degree of Hydrolysis

The extent to which hydrolysis proceeds is expressed as degree of hydrolysis and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as h or x.

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Considering again eq. (i),

$$K_h = \frac{x^2C}{(1-x)} \quad \text{or} \quad K_h = \frac{h^2C}{(1-h)}$$

When h is very small $(1-h) \longrightarrow 1$,

$$h^2 = K_h \times \frac{1}{C}$$

or

$$h = \sqrt{\frac{K_h}{C}}$$

$$= \sqrt{\frac{K_w}{K_b \times C}}$$

$$[H^+] = h \times C = \sqrt{\frac{C \times K_w}{K_b}}$$

$$\log [H^+] = \frac{1}{2}\log K_w + \frac{1}{2}\log C - \frac{1}{2}\log K_b$$

$$\text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\log C - \frac{1}{2}\text{p}K_b$$

$$= 7 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log C$$

2. Salt of a weak acid and a strong base

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a weak acid and OH^- ions.

$$A^- + H_2O \rightleftharpoons \underset{\text{Weak acid}}{HA} + OH^-$$

Consider, for example, the salt CH_3COONa. It ionises in water completely to give CH_3COO^- and Na^+ ions. CH_3COO^- ions react with water to form a weak acid, CH_3COOH and OH^- ions.

$$\underset{C(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{Cx}{CH_3COOH} + \underset{Cx}{OH^-}$$

Thus, OH^- ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Cx \times Cx}{C(1-x)} = \frac{Cx^2}{(1-x)} \qquad \text{... (i)}$$

Other equilibria present in the solution are:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+, K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad \text{... (ii)}$$

$$H_2O \rightleftharpoons H^+ + OH^-, K_w = [H^+][OH^-] \qquad \text{... (iii)}$$

From eqs. (ii) and (iii),

$$\frac{K_w}{K_a}=\frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}=K_h \qquad \text{... (iv)}$$

$$[OH^-]=\frac{K_h[CH_3COO^-]}{[CH_3COOH]}=\frac{K_w}{K_a}\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\log[OH^-]=\log K_w-\log K_a+\log\frac{[Salt]}{[Acid]}$$

$$-pOH=-pK_w+pK_a+\log\frac{[Salt]}{[Acid]}$$

$$pK_w-pOH=pK_a+\log\frac{[Salt]}{[Acid]}$$

$$pH=pK_a+\log\frac{[Salt]}{[Acid]}$$

Considering eq. (i) again,

$$K_h=\frac{Cx^2}{(1-x)} \text{ or } K_h=\frac{Ch^2}{(1-h)}$$

When h is very small, $(1-h)\longrightarrow 1$

or $$h^2=\frac{K_h}{C}$$

or $$h=\sqrt{\frac{K_h}{C}}$$

$$[OH^-]=h\times C=\sqrt{CK_h}=\sqrt{\frac{C\times K_w}{K_a}}$$

$$[H^+]=\frac{K_w}{[OH^-]}$$

$$=\frac{K_w}{\sqrt{\frac{C\times K_w}{K_a}}}=\sqrt{\frac{K_a\times K_w}{C}}$$

$$-\log[H^+]=-\frac{1}{2}\log K_w-\frac{1}{2}\log K_a+\frac{1}{2}\log C$$

$$pH=\frac{1}{2}pK_w+\frac{1}{2}pK_a+\frac{1}{2}\log C$$

$$=7+\frac{1}{2}pK_a+\frac{1}{2}\log C$$

3. Salt of a weak acid and a weak base

Maximum hydrolysis occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H^+ and OH^- ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt CH_3COONH_4. It gives CH_3COO^- and NH_4^+ ions in solution. Both react with water.

$$\underset{\text{Weak base}}{NH_4^+ + H_2O \rightleftharpoons NH_4OH} + H^+$$

$$\underset{\text{Weak acid}}{CH_3COO^- + H_2O \rightleftharpoons CH_3COOH} + OH^-$$

Both the reactions occur with same speeds. The solution is neutral.

$$\text{or } \underset{C(1-h)}{CH_3COO^-} + \underset{C(1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{Ch}{CH_3COOH} + \underset{Ch}{NH_4OH}$$

$$K_h=\frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

Other equilibria which exist in solution are:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+, K_a=\frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad \text{... (i)}$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-, \quad K_b=\frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad \text{... (ii)}$$

$$H_2O \rightleftharpoons H^+ + OH^-, \quad K_w=[H^+][OH^-] \qquad \text{... (iii)}$$

From eqs. (i), (ii) and (iii),

$$K_h=\frac{K_w}{K_a\cdot K_b}=\frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \qquad \text{... (iv)}$$

Let C be the concentration and h be the degree of hydrolysis

$$K_h=\frac{h^2}{(1-h)^2}$$

When h is small, $(1-h)\longrightarrow 1$,

$$K_h=h^2$$

$$h=\sqrt{K_h}=\sqrt{\frac{K_w}{K_a\times K_b}}$$

$$[H^+]=K_a\times h$$

$$=K_a\times\sqrt{\frac{K_w}{K_a\times K_b}}$$

$$=\sqrt{\frac{K_a\times K_w}{K_b}}$$

$$-\log[H^+]=-\frac{1}{2}\log K_a-\frac{1}{2}\log K_w+\frac{1}{2}\log K_b$$

$$pH=\frac{1}{2}pK_a+\frac{1}{2}pK_w-\frac{1}{2}pK_b$$

$$=7+\frac{1}{2}pK_a-\frac{1}{2}pK_b$$

When $pK_a=pK_b$, pH = 7, *i.e.*, solution will be neutral in nature.

When $pK_a>pK_b$, the solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case $pK_a<pK_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7.

4. Salt of a strong acid and a strong base

Such a salt, say NaCl, does not undergo hydrolysis as both the ions are not reactive. The solution is thus, neutral in nature.

5. Hydrolysis of amphiprotic anion

Let us consider hydrolysis of amphiprotic anion only, *i.e.*, when counter cation is not hydrolysed example of some salts of this category are $NaHCO_3$, $NaHS$, Na_2HPO_4, NaH_2PO_4.

$$\text{(i) } H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+; \quad K_{a_1} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]}$$

$$\text{(ii) } H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+; \quad K_{a_2} = \frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]}$$

$$\text{(iii) } HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+; \quad K_{a_3} = \frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]}$$

Here, $H_2PO_4^-$ and HPO_4^{2-} are amphiprotic anions, pH after their hydrolysis can be calculated as,

$$\text{pH of } H_2PO_4^- \text{ in aqueous medium} = \frac{pK_{a_1} + pK_{a_2}}{2}$$

$$\text{pH of } HPO_4^{2-} \text{ in aqueous medium} = \frac{pK_{a_2} + pK_{a_3}}{2}$$

Here, $\mathbf{HPO_4^{2-}}$ is conjugate base of $\mathbf{H_2PO_4^-}$ and $\mathbf{H_3PO_4}$ is conjugate acid of $\mathbf{H_2PO_4^-}$.

Similarly, $\mathbf{PO_4^{3-}}$ is conjugate base of $\mathbf{HPO_4^{2-}}$ and $\mathbf{HPO_4^{2-}}$ is conjugate acid of $\mathbf{PO_4^{3-}}$.

(iv) Let us consider amphiprotic bicarbonate anion.

$$\underset{\text{Acid}}{HCO_3^{2-}} + H_2O \rightleftharpoons \underset{\text{Conjugate base}}{CO_3^{2-}} + H_3^+O \quad \text{(Ionization)}$$

$$\underset{\text{Base}}{HCO_3^-} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{H_2CO_3} + OH^- \quad \text{(Hydrolysis)}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; \quad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}; \quad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

pH of HCO_3^- ion after hydrolysis in aqueous medium

$$= \frac{pK_{a_1} + pK_{a_2}}{2}$$

(v) Let us consider the hydrolysis of amphiprotic anion along with cation, *e.g.*, NH_4HCO_3, NH_4HS.

In above examples both cations and anions are derived from weak base and weak acids respectively, hence both will undergo hydrolysis in aqueous medium.

When these salts are dissolved in water, $[H_3O^+]$ concentration can be determined as,

$$[H_3O^+] = \sqrt{K_{a_1}\left[\frac{K_w}{K_b} + K_{a_2}\right]}$$

$$pH = -\log\sqrt{K_{a_1}\left[\frac{K_w}{K_b} + K_{a_2}\right]}$$

Table 10.1 Hydrolysis at a Glance

Salt	Nature	Degree	Hydrolysis Constant	pH
1. NaCl (Strong acid + Strong base)	Neutral	No hydrolysis	—	—
2. CH_3COONa (Weak acid + Strong base)	Basic	$h = \sqrt{\frac{K_w}{CK_a}}$	$K_h = \frac{K_w}{K_a}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
3. NH_4Cl (Strong acid + Weak base)	Acidic	$h = \sqrt{\frac{K_w}{CK_b}}$	$K_h = \frac{K_w}{K_b}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
4. CH_3COONH_4 (Weak acid + Weak base)	*	$h = \sqrt{\frac{K_w}{K_a \times K_b}}$	$K_h = \frac{K_w}{K_a \times K_b}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

*In the case of salt of weak acid and weak base, nature of medium after hydrolysis is decided in the following manner:

(i) If $K_a = K_b$, the medium will be neutral.

(ii) If $K_a > K_b$, the medium will be acidic.

(iii) If $K_a < K_b$, the medium will be basic.

The degree of hydrolysis of salts of weak acids and weak bases is unaffected by dilution because there is no concentration term in the expression of degree of hydrolysis.

[**Note:** Degree of hydrolysis always increases with increase in temperature because at elevated temperature increase in K_w is greater as compared to K_a and K_b.]

SOME SOLVED EXAMPLES

Example 61. *Calculate the degree of hydrolysis and pH of 0.1 M sodium acetate solution. Hydrolysis constant of sodium acetate is* 5.6×10^{-10}.

Solution: $\underset{0.1(1-h)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{(0.1 \times h)}{CH_3COOH} + \underset{(0.1 \times h)}{OH^-}$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{(0.1 \times h)(0.1 \times h)}{0.1(1-h)};$$

$$\because h \text{ is small } (1-h) \longrightarrow 1$$

$$5.6 \times 10^{-10} = 0.1 \times h^2$$

or
$$h^2 = \frac{5.6 \times 10^{-10}}{0.1} = 56 \times 10^{-10}$$

$$h = 7.48 \times 10^{-5}$$

$$[OH^-] = Ch = 0.1 \times 7.48 \times 10^{-5} = 7.48 \times 10^{-6}\ M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{7.48 \times 10^{-6}} = 1.33 \times 10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(1.33 \times 10^{-9}) = 8.88$$

Example 62. *When 0.2 M acetic acid is neutralised with 0.2 M NaOH in 0.5 litre of water the resulting solution is slightly alkaline. Calculate the pH of the resulting solution.* K_a *for* $CH_3COOH = 1.8 \times 10^{-5}$.

Solution: 0.2 M acetic acid will form 0.2 M CH_3COONa in 0.5 litre of water. Hence, concentration of sodium acetate, $[CH_3COONa] = 0.1\,\text{mol L}^{-1}$.

$$\underset{C(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{Cx}{CH_3COOH} + \underset{Cx}{OH^-}$$

$$K_h = \frac{Cx^2}{(1-x)} = Cx^2 \qquad (1-x) \longrightarrow 1$$

$$K_h = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = 5.5\times10^{-10}$$

So, $K_h = Cx^2 = 5.5\times10^{-10}$

or $x^2 = \dfrac{5.5\times10^{-10}}{0.1} = 55\times10^{-10}$

or $x = 7.42\times10^{-5}$

$$[OH^-] = Cx = 7.42\times10^{-5}\times0.1 = 7.42\times10^{-6}\ M$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{7.42\times10^{-6}} = 1.3477\times10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(1.3477\times10^{-9}) = 8.87$$

Example 63. *Calculate the hydrolysis constant for NH_4Cl, pH value and $[OH^-]$ in 0.1 M NH_4Cl solution.*
$(K_{NH_4OH} = 1.75\times10^{-5}, K_w = 1\times10^{-14})$

Solution: We know that, $K_h = \dfrac{K_w}{K_b}$

So, $K_h = \dfrac{1\times10^{-14}}{1.75\times10^{-5}} = 5.7\times10^{-10}$

Hydrolysis of NH_4Cl can be represented as,

$$\underset{C(1-x)}{NH_4^+} + H_2O \rightleftharpoons \underset{Cx}{NH_4OH} + \underset{Cx}{H^+}$$

Thus, $K_h = \dfrac{Cx^2}{(1-x)}$

Neglecting 'x' in denominator,

$$x^2 = \frac{K_h}{C} = \frac{5.7\times10^{-10}}{0.1} = 57\times10^{-10}$$

or $x = 7.55\times10^{-5}$

$$[H^+] = Cx = 0.1\times7.55\times10^{-5} = 7.55\times10^{-6}\ M$$

$$pH = -\log[H^+] = -\log(7.55\times10^{-6}) = 5.12$$

Again, $[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1\times10^{-14}}{7.55\times10^{-6}} = 1.32\times10^{-9}\ M$

Example 64. *Calculate the pH at the equivalence point when a solution of 0.1M acetic acid is titrated with a solution of 0.1M sodium hydroxide.*
K_a for acetic acid $= 1.9\times10^{-5}$ **(IIT 1990)**

Solution: Concentration of sodium acetate $= \dfrac{0.1}{2} = 0.05\ M$ as equal volumes of the acid and the base will be used.

The equilibrium is,

$$\underset{C(1-x)}{CH_3COO^-} + H_2O \rightleftharpoons \underset{Cx}{CH_3COOH} + \underset{Cx}{OH^-}$$

where, x is the degree of hydrolysis, and

$$K_h = \frac{Cx^2}{(1-x)}$$

We know that,

$$K_h = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.9\times10^{-5}} = 5.26\times10^{-10}$$

So, $K_h = Cx^2$ as $(1-x) \longrightarrow 1$

$5.26\times10^{-10} = 0.05\times x^2$

or $x^2 = \dfrac{5.26\times10^{-10}}{0.05} = 1.05\times10^{-8}$

or $x = 1.025\times10^{-4}$

$$[OH^-] = Cx = 1.025\times10^{-4}\times0.05 = 5.125\times10^{-6}\ M$$

$$[H^+] = \frac{1\times10^{-14}}{5.125\times10^{-6}} = 1.95\times10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(1.95\times10^{-9}) = 8.71$$

Example 65. *Calculate the amount of ammonium chloride required to dissolve in 500 mL water to have pH = 4.5. (K_b for NH_4OH is 1.8×10^{-5})*

Solution: $[H^+] = 10^{-pH} = 10^{-4.5} = 10^{-5}$ antilog 0.5
$= 3.162\times10^{-5}\ M$

Let C be the concentration of NH_4Cl

$$\underset{C(1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{Ch}{NH_4OH} + \underset{Ch}{H^+}$$

If h is small, then

$$K_h = Ch^2 \qquad \left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.5\times10^{-10}\right]$$

$$h = \frac{K_h}{Ch} = \frac{K_h}{[H^+]}$$

$$= \frac{5.5\times10^{-10}}{3.162\times10^{-5}} = 1.739\times10^{-5}$$

$$Ch = [H^+]$$

$$C = \frac{[H^+]}{h} = \frac{3.162\times10^{-5}}{1.739\times10^{-5}} = 1.8\ \text{mol L}^{-1}$$

500 mL of water contains $= \dfrac{1.8}{2} = 0.9$ mole

Mass in g $= 0.9\times53.5 = 48.15$ g

Example 66. *Calcium lactate is a salt of a weak organic acid and represented as $Ca(Lac)_2$. A saturated solution of*

$Ca(Lac)_2$ contains 0.13 *mole of this salt in* 0.50 *litre solution. The pOH of this solution is* 5.60. *Assuming a complete dissociation of salt, calculate* K_a *of the lactic acid.* **(IIT 1991)**

Solution:

$$\underset{0.13\times 2\,M}{\mathrm{Ca(Lac)_2}} \rightleftharpoons \mathrm{Ca^{2+}} + \underset{2\times 2\times 0.13\,M}{2\mathrm{Lac^-}}$$

$$\text{At equilibrium}\quad \underset{(0.52-x)}{\mathrm{Lac^-}} + \mathrm{H_2O} \rightleftharpoons \underset{x}{\mathrm{HLac}} + \underset{x}{\mathrm{OH^-}}$$

$$K_h = \frac{x^2}{(0.52-x)} = \frac{x^2}{0.52} \text{ as } x \text{ is small}$$

$$[\mathrm{OH^-}] = 10^{-5.6} = 2.51\times 10^{-6} = x$$

$$K_h = \frac{2.51\times 10^{-6}\times 2.51\times 10^{-6}}{0.52} = 12.12\times 10^{-12}$$

$$K_a = \frac{K_w}{K_h} = \frac{10^{-14}}{12.12\times 10^{-12}} = 8.26\times 10^{-4}$$

Example 67. K_a *for butyric acid is* 2×10^{-5}. *Calculate pH and hydroxyl ion concentration of* 0.2 *M aqueous solution of sodium butyrate.* **(IIT 1994)**

Solution: Butyrate ion hydrolysis in solution into butyric acid and OH^- ions. Let x mole of butyrate ion be hydrolysed.

$$\underset{(0.2-x)}{\mathrm{C_3H_7COO^-}} + \mathrm{H_2O} \rightleftharpoons \underset{x}{\mathrm{C_3H_7COOH}} + \underset{x}{\mathrm{OH^-}}$$

$$K_h = \frac{x^2}{(0.2-x)} = \frac{x^2}{0.2} \quad (x \text{ being small is neglected as compared to } 0.2)$$

So,

$$K_h = \frac{K_w}{K_a}$$

$$\frac{K_w}{K_a} = \frac{x^2}{0.2}$$

$$\frac{10^{-14}}{2\times 10^{-5}} = \frac{x^2}{0.2}$$

or

$$x^2 = 10^{-10} \text{ or } x = 10^{-5} \text{ mol L}^{-1}$$

$$[\mathrm{OH^-}] = 10^{-5}\,M$$

$$[\mathrm{H^+}] = \frac{10^{-14}}{10^{-5}} = 10^{-9}\,M$$

$$\mathrm{pH} = -\log[10^{-9}] = 9$$

Example 68. *Calculate the pH of an aqueous solution of* $1.0M$ *ammonium formate assuming complete dissociation.* pK_a *for formic acid* $= 3.8$ *and* pK_b *of ammonia* $= 4.8$. **(IIT 1995)**

Solution: Ammonium formate is a salt of weak acid and weak base. Hence,

$$\mathrm{pH} = 7 + \frac{1}{2}\mathrm{p}K_a - \frac{1}{2}\mathrm{p}K_b$$

$$= 7 + (1/2)\times 3.8 - (1/2)\times 4.8$$

$$= 7 + 1.9 - 2.4$$

$$= 6.5$$

Example 69. *A certain weak acid has* $K_a = 1.0\times 10^{-4}$. *Calculate the equilibrium constant for its reaction with a strong base.* **(IIT 1991)**

Solution:

$$\underset{\text{Weak}}{\mathrm{H}A} + \underset{\text{Strong}}{B\mathrm{OH}} \rightleftharpoons BA + \mathrm{H_2O}$$

$$\mathrm{H}A + B^+ + \mathrm{OH^-} \rightleftharpoons B^+ + A^- + \mathrm{H_2O}$$

or

$$\mathrm{H}A + \mathrm{OH^-} \rightleftharpoons A^- + \mathrm{H_2O}$$

$$K = \frac{[A^-]}{[\mathrm{H}A][\mathrm{OH^-}]}$$

In the above reaction,

$$K_h = \frac{[\mathrm{H}A][\mathrm{OH^-}]}{[A^-]}$$

So,

$$K = \frac{1}{K_h}$$

We know that,

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.0\times 10^{-4}} = 10^{-10}$$

$$K = \frac{1}{10^{-10}} = 10^{10}$$

Example 70. *Calculate for* 0.01 *N solution of sodium acetate:*

(a) Hydrolysis constant, (b) degree of hydrolysis, (c) pH.
(Given, $K_a = 1.9\times 10^{-5}$*)* **(MLNR 1991)**

Solution: $K_h = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{1.9\times 10^{-5}} = 5.26\times 10^{-10}$

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{5.26\times 10^{-10}}{0.01}} = 2.29\times 10^{-4}$$

$$\mathrm{CH_3COO^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{CH_3COOH} + \underset{Ch}{\mathrm{OH^-}}$$

$$[\mathrm{OH^-}] = C\times h = 0.01\times 2.29\times 10^{-4}$$

$$= 2.29\times 10^{-6}\,M$$

$$[\mathrm{H^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \frac{10^{-14}}{2.29\times 10^{-6}} = 4.37\times 10^{-9}\,M$$

$$\mathrm{pH} = -\log[\mathrm{H^+}] = -\log(4.37\times 10^{-9}) = 8.36$$

Example 71. H_2CO_3 *ionises as,*

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-;\quad K_1 = 4.3\times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-};\quad K_2 = 5.6\times 10^{-11}$$

Calculate the degree of hydrolysis and pH value of 0.12 *M* Na_2CO_3 *solution.*

Solution: $\mathrm{Na_2CO_3}$ is a salt of strong base and weak acid. Thus, $\mathrm{CO_3^{2-}}$ ion is hydrolysed.

$$\underset{0.12(1-h)}{\mathrm{CO_3^{2-}}} + \mathrm{H_2O} \rightleftharpoons \underset{0.12h}{\mathrm{HCO_3^-}} + \underset{0.12h}{\mathrm{OH^-}}$$

$$K_h = h^2 C$$

or $$h^2 = \frac{K_h}{C} = \frac{K_h}{0.12}$$

We know that, $$K_h = \frac{K_w}{K_a} = \frac{K_w}{K_2} = \frac{10^{-14}}{5.6\times10^{-11}} = 1.7857\times10^{-4}$$

So, $$h^2 = \frac{1.7857\times10^{-4}}{0.12} = 14.88\times10^{-4}$$

$$h = 3.85\times10^{-2}$$

$$[OH^-] = C\times h = 0.12\times3.85\times10^{-2}$$

$$= 0.462\times10^{-2} = 4.62\times10^{-3}$$

$$[H^+] = \frac{10^{-14}}{4.62\times10^{-3}} = 2.164\times10^{-12}\ M$$

$$pH = -\log[H^+] = -\log(2.164\times10^{-12}) = 11.665$$

Example 72. *How much must a 0.2 M solution of sodium acetate be diluted at 25°C in order to double the degree of hydrolysis?*

Solution: Let h be the initial degree of hydrolysis

$$K_h = Ch^2 = 0.2\times h^2 \quad \text{... (i)}$$

Let the concentration be C_1 when degree of hydrolysis is $2h$.

$$K_h = C_1(2h)^2 \quad \text{... (ii)}$$

Dividing both the equations,

$$1 = \frac{0.2\times(h^2)}{4C_1\times(h)^2}$$

$$C_1 = \frac{0.2}{4} = 0.05\,M$$

Applying, $$M_1V_1 = M_2V_2$$

$$0.2V_1 = 0.05\times V_2$$

$$V_2 = \frac{0.2}{0.05}V_1 = 4V_1$$

The solution be diluted four times.

Example 73. *Calculate change in pH upon ten-fold dilution of the following solutions:*

(a) 0.1 HCl (b) 0.1 M acetic acid (c) 0.1 M NH_4Cl

$$K_a\ CH_3COOH = 1.8\times10^{-5},\quad K_b\ NH_3 = 1.8\times10^{-5}$$

Solution: (a) HCl is a strong acid. It is completely ionised in solution.

$$HCl \rightleftharpoons H^+ + Cl^-$$

$$[H^+] = 0.1 = 10^{-1}$$

$$pH = -\log[H^+] = -\log(10^{-1}) = 1$$

After dilution, $$[H^+] = 0.01 = 10^{-2}\ M$$

$$pH = -\log[H^+] = -\log 10^{-2} = 2$$

pH change from 1 to 2.

(b) $$\underset{(0.1-x)}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COO^-} + \underset{x}{H^+}$$

(CH_3COOH is a weak acid)

$$\frac{x^2}{0.1} = 1.8\times10^{-5} \text{ or } x^2 = 1.8\times10^{-6} \text{ or } x = 1.34\times10^{-3}$$

$$pH = -\log x = -\log(1.34\times10^{-3}) = 2.87$$

After dilution,

$$\frac{x_1^2}{0.01} = 1.8\times10^{-5} \text{ or } x_1^2 = 18\times10^{-8} \text{ or } x_1 = 4.24\times10^{-4}\ M$$

$$pH = -\log x = -\log 4.24\times10^{-4} = 3.37$$

pH change from 2.87 to 3.37.

(c) NH_4Cl is a salt of weak base and strong acid.

$$\underset{(0.1-h)}{NH_4^+} + H_2O \rightleftharpoons \underset{h}{NH_4OH} + \underset{h}{H^+}$$

$$\frac{h^2}{0.1} = K_h \quad\text{or}\quad h^2 = 0.1\times K_h$$

$$\left[K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} = 5.55\times10^{-10}\right]$$

$$= 0.1\times5.55\times10^{-10}$$

$$h = 7.45\times10^{-6} = [H^+]$$

$$pH = -\log(7.45\times10^{-6}) = 5.128$$

After dilution, $$h^2 = 0.01\times K_h = 0.01\times5.55\times10^{-10}$$

$$h = 2.35\times10^{-6}$$

$$pH = -\log 2.35\times10^{-6} = 5.627$$

pH change from 5.128 to 5.627.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

34. The pH of a solution obtained by mixing 100 mL of 0.2 M CH_3COOH with 100 mL of 0.2 M NaOH would be: (Given: pK_a for CH_3COOH = 4.74)

(a) 4.74 (b) 8.87 (c) 9.10 (d) 8.57

[Ans. (b)]

[Hint: Concentration of salt formed will be 0.1 M.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + 4.74 - 1] = 8.87\ ]$$

35. The pH of 0.02 M $NH_4Cl(aq.)$ (pK_b = 4.73) is equal to:

(a) 3.78 (b) 4.73 (c) 5.48 (d) 7.00

[Ans. (c)]

[Hint: $$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

$$= \frac{1}{2}[14 - 4.73 - \log 0.02]$$

$$= \frac{1}{2}[14 - 4.73 + 1.698] = 5.48\ ]$$

36. pH of 0.05 M $(CH_3COO)_2Ca$ (pK_a = 4.74) is:

(a) 8.72 (b) 8.87 (c) 7 (d) 1.30

[Ans. (b)]

[Hint: $[CH_3COO^-] = 2\times0.05 = 0.1$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + 4.74 + \log 0.1]$$

$$= \frac{1}{2}[14 + 4.74 - 1] = 8.87\ ]$$

37. The degree of hydrolysis of which of the following salt is independent of the concentration of salt solution?

(a) CH_3COONa (b) NH_4Cl
(c) CH_3COONH_4 (d) NaCl

[Ans. (c)]

[Hint: It is the salt of weak acid and weak base, hence its degree of hydrolysis will be independent of concentration.

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}\ ]$$

38. The pH of 1 *M* $PO_4^{3-}(aq.)$ solution will be: (given pK_b of $PO_4^{3-} = 1.62$)

(a) 1.62 (b) 12.38 (c) 13.19 (d) 7

[Ans. (c)]

[Hint: $pK_a = 14 - pK_b = 14 - 1.62 = 12.38$

$$pH = \frac{1}{2}[\ pK_w + pK_a + \log C\ ]$$

$$= \frac{1}{2}[14 + 12.38 + 0] = 13.19\ ]$$

39. For the following equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

calculate the equilibrium constant, if for the equilibrium,

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

the equilibrium constant is 5.5×10^{-10}.

(a) 1.8×10^{-4} (b) 1.8×10^{-5} (c) 1.8×10^{-6} (d) 1.8×10^{-7}

[Ans. (b)]

[Hint: $K_w = K_a \times K_b$

$$10^{-14} = 5.5 \times 10^{-10} \times K_b$$

$$K_b = 1.8 \times 10^{-5}\ ]$$

40. Which of the following expressions is not applicable on the hydrolysis equilibrium? [PET (Raj.) 2004]

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

(a) $K_h = \frac{K_w}{K_a(HCN)}$ (b) $h = \sqrt{\frac{K_h}{C}}$

(c) $pH = \frac{1}{2}pK_a(HCN)$ (d) $(H^+) = \sqrt{\frac{K_w \times K_a}{C}}$

[Ans. (c)]

[Hint: For the salt of weak acid and strong base:

$$pH = \frac{1}{2}[pK_w + pK_a - \log C\ ]$$

41. The pK_a of weak acid H*A* is 4.80 and the pK_b of a weak base *B*OH is 4.78. The pH of an aqueous solution of corresponding salt *BA* will be : (AIEEE 2008)

(a) 9.22 (b) 9.58 (c) 4.79 (d) 7.01

[Ans. (d)]

[Hint: $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

$$= \frac{1}{2}[14 + 4.8 - 4.78] = 7.01\ ]$$

10.13 THEORY OF INDICATORS

An indicator is a substance which is used to determine the end point in a titration. In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colour within a certain pH range. The colour change and the pH range of some common indicators are tabulated below:

Indicator	pH range	Colour change
Methyl orange	3.2 – 4.5	Pink to yellow
Methyl red	4.4 – 6.5	Red to yellow
Litmus	5.5 – 7.5	Red to blue
Phenol red	6.8 – 8.4	Yellow to red
Phenolphthalein	8.3 – 10.5	Colourless to pink

Theory of acid-base indicators: Two theories have been proposed to explain the change of colour of acid-base indicators with change in pH.

1. Ostwald's theory: According to this theory:

(a) The colour change is due to ionisation of the acid-base indicator. The unionised form has different colour than the ionised form.

(b) The ionisation of the indicator is largely affected in acids and bases as it is either a weak acid or a weak base. In case, the indicator is a weak acid, its ionisation is very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. Similarly, if the indicator is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Considering two important indicators phenolphthalein (a weak acid) and methyl orange (a weak base), Ostwald's theory can be illustrated as follows:

Phenolphthalein: It can be represented as HPh. It ionises in solution to a small extent as:

$$\underset{\text{Colourless}}{HPh} \rightleftharpoons H^+ + \underset{\text{Pink}}{Ph^-}$$

Applying law of mass action,

$$K = \frac{[H^+][Ph^-]}{[HPh]}$$

The undissociated molecules of phenolphthalein are colourless while Ph^- ions are pink in colour. In presence of an acid, the ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

Let us derive Henderson's equation for an indicator

$$\underset{\text{'Acid form'}}{HIn} + H_2O \rightleftharpoons H_3^+O + \underset{\text{'Base form'}}{In^-}$$

Conjugate acid-base pair

$$K_{In} = \frac{[In^-][H_3^+O]}{[HIn]}; (K_{In} = \text{Ionization constant of indicator})$$

$$[H_3^+O] = K_{In} \times \frac{[HIn]}{[In^-]}$$

$$pH = -\log_{10}[H_3^+O] = -\log_{10}[K_{In}] - \log_{10}\frac{[HIn]}{[In^-]}$$

$$pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]} \text{ (Henderson's equation for indicator)}$$

At equivalence point;

$$[In^-] = [HIn] \quad \text{and} \quad pH = pK_{In}$$

Methyl orange: It is a very weak base and can be represented as MeOH. It is ionised in solution to give Me^+ and OH^- ions.

$$\underset{\text{Yellow}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

Applying law of mass action,

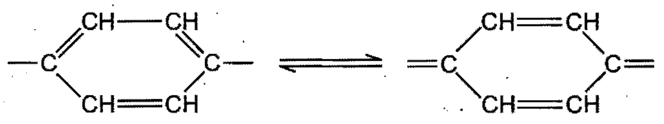
$$K = \frac{[Me^+][OH^-]}{[MeOH]}$$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to left hand side, *i.e.*, the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised methyl orange molecules, *i.e.*, yellow.

This theory also explains the reason why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, *i.e.*, pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why methyl orange is not a suitable indicator for the titration of weak acid with strong base.

2. Quinonoid theory: According to this theory:

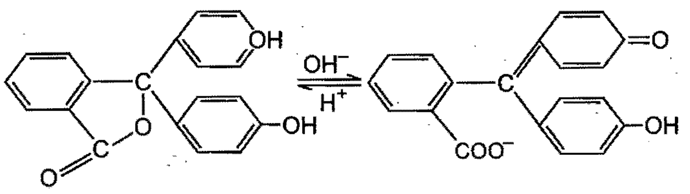
(a) The acid-base indicators exist in two tautomeric forms having different structures. Two forms are in equilibrium. One form is termed **benzenoid form** and the other **quinonoid form.**



(b) The two forms have different colours. The colour change is due to the interconversion of one tautomeric form into other.

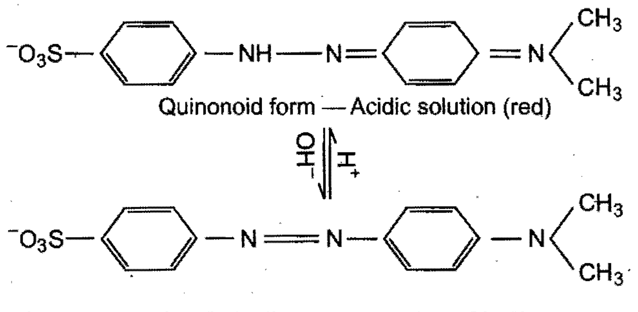
(c) One form mainly exists in acidic medium and the other in alkaline medium.

Thus, during titration the medium changes from acidic to alkaline or *vice-versa*. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Phenolphthalein has benzenoid form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.

Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The colour of benzenoid form is yellow while that of quinonoid form is red.

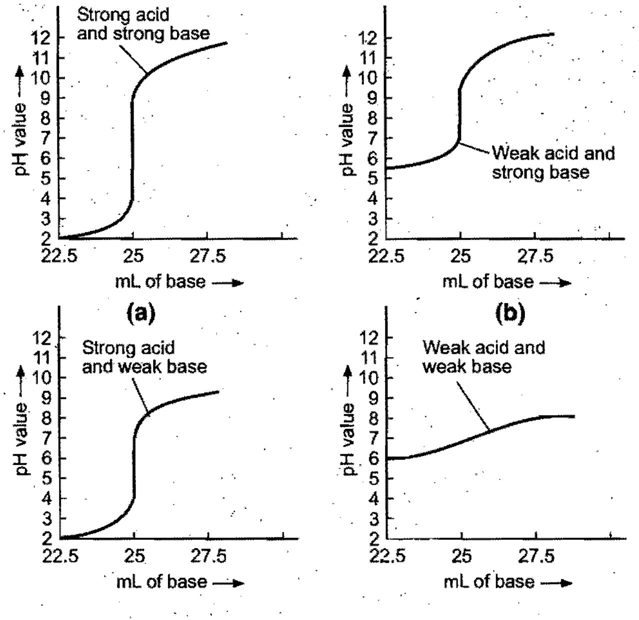


Selection of suitable indicator or choice of indicator

The neutralisation reactions are of the following four types:

(i) A strong acid *versus* a strong base. [Fig. 10.1 (a)]
(ii) A weak acid *versus* a strong base. [Fig. 10.1 (b)]
(iii) A strong acid *versus* a weak base. [Fig. 10.1 (c)]
(iv) A weak acid *versus* a weak base. [Fig. 10.1 (d)]

In order to choose a suitable indicator, it is necessary to understand the pH changes in the above four types of titrations. The change in pH in the vicinity of the equivalence point is most important for this purpose. The curve obtained by plotting pH as ordinate against the volume of alkali added as abscissa is known as neutralisation or titration curve. The titration curves of the above four types of neutralisation reactions are shown in Fig. 10.1 (a), 10.1 (b), 10.1 (c) and 10.1 (d).



(a) (b)

(c) (d)

Fig. 10.1

In each case 25 mL of the acid (*N*/10) has been titrated against a standard solution of a base (*N*/10). Each curve becomes almost vertical for some distance [except curve Fig. 10.1 (d)] and then bends away again. This region of abrupt change in pH indicates the equivalence point. For a particular titration, the indicator should be so selected that it changes its colour within vertical distance of the curve.

(i) Strong acid *vs.* strong base: pH curve of strong acid (say HCl) and strong base (say NaOH) is vertical over almost the pH range 4–10. So, the indicators phenolphthalein (pH range 8.3 to 10.5), methyl red (pH range 4.4–6.5) and methyl orange (pH range 3.2–4.5) are suitable for such a titration.

(ii) Weak acid *vs.* strong base: pH curve of weak acid (say CH_3COOH or oxalic acid) and strong base (say NaOH) is vertical over the approximate pH range 7 to 11. So, phenolphthalein is the suitable indicator for such a titration.

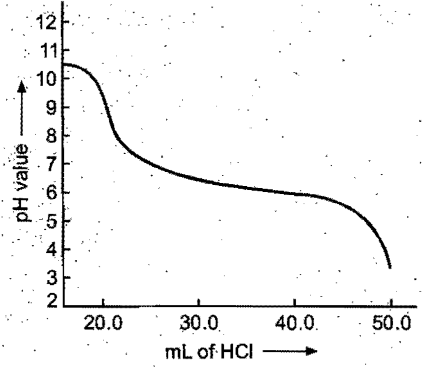


Fig. 10.2

(iii) Strong acid *vs.* weak base: pH curve of strong acid (say HCl or H_2SO_4 or HNO_3) with a weak base (say NH_4OH) is vertical over the pH range of 4 to 7. So, the indicators methyl red and methyl orange are suitable for such a titration.

(iv) Weak acid *vs.* weak base: pH curve of weak acid and weak base indicates that there is no vertical part and hence, no suitable indicator can be used for such a titration.

Titration of soluble carbonate with strong acid.

pH curve of sodium carbonate with HCl shows two inflection points (Fig. 10.2). First inflection point (pH = 8.5) indicates conversion of carbonate into bicarbonate.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

As the inflection point lies in the pH range 8 to 10, phenolphthalein can be used to indicate the above conversion. The second inflection point (pH = 4.3) indicates the following reaction:

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

As the point lies between 3 to 5, methyl orange can be used.

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} litre mol^{-1} sec^{-1}. Calculate rate constant for proton transfer from water to NH_3.* **(IIT 1996)**

Solution: $NH_3 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_4^+ + OH^-; k_b = 3.4 \times 10^{10}$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+; k_a = 5.6 \times 10^{-10}$$

$$K_{Base} = \frac{k_f}{k_b} = \frac{K_w}{K_{Acid}} \quad \text{... (i)}$$

$$K_{Acid} \times K_{Base} = K_w \quad \text{... (ii)}$$

$$\therefore \quad \frac{k_f}{3.4 \times 10^{10}} = \frac{10^{-14}}{5.6 \times 10^{-10}}$$

$$k_f = 6.07 \times 10^5$$

Example 2. *K_a for the acid ionisation constant of Fe^{3+} to $Fe(OH)_2^{2+}$ and H^+ is 6.5×10^{-3}. What is the maximum pH value which could be used so that at least 95% of total Fe^{3+} ion in solution exists free?*

Solution: $Fe^{3+} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+$

$$K = \frac{[Fe(OH)_2]^{2+}[H^+]}{[Fe^{3+}]} = \frac{\frac{5}{100} \times [H^+]}{95/100} = 6.5 \times 10^{-3}$$

$$[H^+] = 0.12\,M$$

$$pH = -\log 0.12 = 0.91$$

Example 3. *K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage hydrolysis in an aqueous solution in which the concentration of Asc^- ions is 0.02 M.* **(IIT 1997)**

Solution:

$$\text{Degree of hydrolysis 'h'} = \sqrt{\frac{K_w}{CK_a}}$$

$$= \sqrt{\frac{10^{-14}}{0.02 \times 5 \times 10^{-5}}} = 10^{-4}$$

$$\% \text{ hydrolysis} = 0.01$$

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 + (-\log 5 \times 10^{-5}) + \log 0.02]$$

$$pH = 8.3$$

$$[H^+] = 5 \times 10^{-9}\,M$$

Example 4. *Determine the number of moles of AgI which may be dissolved in 1 litre of 1 M CN^- solution K_{sp} for AgI and K_c for $Ag(CN)_2^-$ are $1.2 \times 10^{-17}\,M^2$ and $7.1 \times 10^{19}\,M^{-2}$ respectively.* **(IIT 1998)**

Solution: $\mathrm{AgI}(s) \rightleftharpoons \mathrm{Ag}^+ + \mathrm{I}^-$

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{I}^-] = 1.2 \times 10^{-17}$$

$$\mathrm{Ag}^+ + 2\mathrm{CN}^- \rightleftharpoons [\mathrm{Ag(CN)}_2]^-$$

$$K_f = \frac{[\mathrm{Ag(CN)}_2^-]}{[\mathrm{Ag}^+][\mathrm{CN}^-]^2} = 7.1 \times 10^{19}$$

$$K_{\mathrm{eq}} = K_{sp} \times K_f$$

$$= \frac{[\mathrm{Ag(CN)}_2^-][\mathrm{I}^-]}{[\mathrm{CN}^-]^2} = 1.2 \times 10^{-7} \times 7.1 \times 10^{19}$$

$$= 8.52 \times 10^2$$

Let us consider the following equilibrium:

$$\begin{array}{lcccc} & \mathrm{AgI}(s) + & 2\mathrm{CN}^- \rightleftharpoons & [\mathrm{Ag(CN)}_2^-] + & \mathrm{I}^- \\ t=0 & & 1 & 0 & 0 \\ t_{eq} & & 1-2x & x & x \end{array}$$

Let 'x' moles of AgI be dissolved in CN^- solution.

Then,

$$\mathrm{AgI} + 2\mathrm{CN}^- \rightleftharpoons \mathrm{Ag(CN)}_2^- + \mathrm{I}^-$$

$$K_{\mathrm{eq}} = 8.5 \times 10^2 = \frac{x \times x}{(1-2x)^2}$$

$$\frac{x}{1-2x} = 29.2$$

$$x = 0.49 \text{ mole}$$

Example 5. *Given* $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \times 10^{-8}$ *and* K_{sp} *of AgCl is* 1.8×10^{-10} *at* $298\,K$. *Calculate concentration of the complex in* $1\,M$ *aqueous ammonia.* (IIT 1998)

Solution: $\mathrm{AgCl} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{Cl}^-$

On adding ammonia solution, complex formation takes place.

$$\underset{(x-y)}{\mathrm{Ag}^+} + \underset{1}{2\mathrm{NH}_3} \rightleftharpoons \underset{y}{[\mathrm{Ag(NH}_3)_2]^+} \qquad \text{. . . (i)}$$

where, x = solubility of AgCl in NH_3

y = amount of complex formed

$$K_{sp} \text{ of AgCl} = [\mathrm{Ag}^+][\mathrm{Cl}^-]$$

$$1.8 \times 10^{-10} = (x-y) \times x \qquad \text{... (ii)}$$

$$K_c \text{ for equation (i)} = \frac{[\mathrm{Ag(NH}_3)_2]^+}{[\mathrm{Ag}^+][\mathrm{NH}_3]^2}$$

$$\frac{1}{6.2 \times 10^{-8}} = \frac{y}{(x-y)1} \qquad \text{... (iii)}$$

On solving equations (ii) and (iii), we get

$$y = 0.0539\,M$$

Example 6. *An aqueous solution of aniline of concentration 0.24 is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at* 1×10^{-8} *M?* K_a *for* $C_6H_5NH_3^+$ *is* 2.4×10^{-5} *M.* (IIT 1996)

Solution: $\mathrm{C_6H_5NH_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{C_6H_5NH_3^+} + \mathrm{OH}^-$

Thus, $$K_b = \frac{[\mathrm{C_6H_5NH_3^+}][\mathrm{OH}^-]}{[\mathrm{C_6H_5NH_2}]} \qquad \text{... (i)}$$

Also K_b for

$$\mathrm{C_6H_5NH_2} = \frac{K_w}{K_a \text{ for } \mathrm{C_6H_5NH_3^+}} = \frac{10^{-14}}{2.4 \times 10^{-5}} \qquad \text{... (ii)}$$

Since, dissociation of $\mathrm{C_6H_5NH_2}$ occurs in presence of NaOH and thus dissociation of $\mathrm{C_6H_5NH_2}$ will be suppressed.

Thus, $[\mathrm{OH}^-] = ?$; $[\mathrm{C_6H_5NH_2}] = 0.24$; $[\mathrm{C_6H_5NH_3^+}] = 10^{-8}$

Therefore, $$\frac{10^{-14}}{2.4 \times 10^{-5}} = \frac{10^{-8} \times [\mathrm{OH}^-]}{0.24}$$

$$\therefore \quad [\mathrm{OH}^-] = \frac{0.24 \times 10^{-14}}{2.4 \times 10^{-5} \times 10^{-8}} = 0.01$$

$$\therefore \quad [\mathrm{NaOH}] = 0.01\,M$$

Example 7. *A solution contains* 0.05 *mol litre*$^{-1}$ *of* Ba^{2+} *ions and* 0.002 *mol litre*$^{-1}$ *of* Ag^+ *ions. The metals are to be precipitated by addition of chromate ions,* CrO_4^{2-}. *Which ion precipitates first? What percentage of this ion remain in the solution when the second ion begins to precipitate?*

$K_{sp}\ Ag_2CrO_4 = 3 \times 10^{-12}$, $\quad K_{sp}\ BaCrO_4 = 1 \times 10^{-10}$

Solution: $\mathrm{CrO_4^{2-}}$ ion concentration required for precipitation:

For $\mathrm{BaCrO_4}$:

$$[\mathrm{CrO_4^{2-}}] = \frac{K_{sp}\ \mathrm{BaCrO_4}}{[\mathrm{Ba}^{2+}]} = \frac{10^{-10}}{0.05} = 20 \times 10^{-10}\,M$$

For $\mathrm{Ag_2CrO_4}$:

$$[\mathrm{CrO_4^{2-}}] = \frac{K_{sp}\ \mathrm{Ag_2CrO_4}}{[\mathrm{Ag}^+]^2} = \frac{3 \times 10^{-12}}{[0.002]^2} = 0.75 \times 10^{-6}\,M$$

Ba^{2+} will be precipitated first because it requires low concentration of $\mathrm{CrO_4^{2-}}$. Remaining conc. of Ba^{2+} when Ag^+ will start precipitation.

$$[\mathrm{Ba}^{2+}]_{\text{Remaining}} = \frac{K_{sp}\ \mathrm{BaCrO_4}}{[\mathrm{CrO_4^{2-}}]} = \frac{10^{-10}}{0.75 \times 10^{-6}} = 1.33 \times 10^{-4}\,M$$

$$\%\text{of remaining } \mathrm{Ba}^{2+} = \frac{1.33 \times 10^{-4}}{0.05} \times 100 = 0.26\%$$

Example 8. *Calculate pH change which results when* 50 *mL of* 0.1 *M* HNO_3 *is added to each of the following at* 25° *C:*

(*a*) 1.00 *litre of pure water.*

(*b*) 1.00 *litre of a solution containing acetic acid and sodium acetate each of* 0.1 *M concentration.*

Solution:

(a) Molarity after dilution $= M_2$

$$M_1V_1 = M_2V_2$$

$$0.1 \times 50 = M_2 \times 1050$$

$$M_2 = 0.00476$$

$$\text{pH} = -\log(0.00476) = 2.322$$

Change in pH of water $= 7 - 2.322 = 4.68$

(b) $$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4.7447 + \log\frac{0.1}{0.1} = 4.7447$$

Moles of HNO_3 added $= \frac{0.1}{1000} \times 50 = 5 \times 10^{-3}$; it will convert sodium acetate to acetic acid.

$$\text{pH} = 4.7447 + \log\left[\frac{0.1 - 5\times10^{-3}}{0.1 + 5\times10^{-3}}\right] = 4.70123$$

Change in $\text{pH} = 4.7447 - 4.70123 = 0.043$

Example 9. *A certain monoprotic acid (weak) serves as indicator. Assuming that colour change is seen when 1/3rd of the indicator has been converted to ions and that at end point the pH of solution is 6, what is the value of pK_{In}?*

Solution: $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$ (Ionization equilibrium of indicator)

$$\text{pH} = \text{p}K_{\text{In}} + \log_{10}\frac{[\text{In}^-]}{[\text{HIn}]}$$

$$6 = \text{p}K_{\text{In}} + \log_{10}\left[\frac{0.33}{0.67}\right] \quad \text{(1/3rd conversion)}$$

$$\text{p}K_{\text{In}} = 6.307$$

Example 10. *What is the minimum pH of a solution 0.10 M in Mg^{2+} from which $Mg(OH)_2$ will not precipitate? K_{sp} $Mg(OH)_2 = 1.2\times10^{-11}\ M^3$.*

Solution: Given that,

$$K_{sp}\ \text{Mg(OH)}_2 = [\text{Mg}^{2+}][\text{OH}^-]^2$$

$$1.2\times10^{-11} = [0.1][\text{OH}^-]^2$$

$$[\text{OH}^-]^2 = 1.2\times10^{-10}$$

$$[\text{OH}^-] = 1.0954\times10^{-5}\ M$$

$$\text{pOH} = -\log_{10}(1.0954\times10^{-5}) = 4.96$$

$$\text{pH} = 14 - 4.96 = 9.04$$

Thus, at 9.04 pH, precipitation will not take place.

Example 11. *What is the pH of 10^{-7} mol litre^{-1} HCl at 25° C?*

Solution: $$[\text{H}^+] = [\text{H}^+]_{\text{Acid}} + [\text{H}^+]_{\text{Water}}$$

$$= 10^{-7} + 10^{-7} = 2\times10^{-7}\ M$$

$$\text{pH} = -\log(2\times10^{-7}) = 6.70$$

Example 12. *A solution contains 0.1 M Cl^- and 0.001 M CrO_4^{2-}. If solid $AgNO_3$ is gradually added to this solution, which will precipitate first, AgCl or Ag_2CrO_4? Assume that the addition causes no change in volume. Given $K_{sp}\ AgCl = 1.7\times10^{-10}M^2$ and $K_{sp} Ag_2CrO_4 = 1.79\times10^{-12}M^3$.*

What per cent of Cl^- remains in the solution when CrO_4^{2-} starts precipitating?

Solution: Ag^+ ion concentration required for precipitation:

For AgCl:

$$[\text{Ag}^+] = \frac{K_{sp}\ \text{AgCl}}{[\text{Cl}^-]} = \frac{1.7\times10^{-10}}{0.1} = 1.7\times10^{-9}M$$

For Ag_2CrO_4:

$$[\text{Ag}^+]^2 = \frac{K_{sp}\ \text{Ag}_2\text{CrO}_4}{[\text{CrO}_4^{2-}]} = \frac{1.79\times10^{-12}}{[0.001]}$$

$$[\text{Ag}^+] = [1.79\times10^{-9}\ \text{M}^2]^{1/2}$$

$$= 4.23\times10^{-5}M$$

AgCl will precipitate first because it requires low conc. of Ag^+.

$$\text{Remaining conc. of } [\text{Cl}^-] = \frac{K_{sp} \text{ of AgCl}}{[\text{Ag}^+]}$$

$$= \frac{1.7\times10^{-10}}{4.23\times10^{-5}} = 4.01\times10^{-6}M$$

$$\%\ \text{Remaining conc. of } [\text{Cl}^-] = \frac{4.01\times10^{-6}}{0.1}\times100 = 4\times10^{-3}\%$$

Example 13. *25 mL of 0.1 mol dm^{-3} aqueous pyridine ($K_b = 1.7\times10^{-9}$ mol dm^{-3}) is titrated with 0.1 mol dm^{-3} hydrochloric acid. Calculate the pH initially, at equivalence and after 30 cm^3 hydrochloric acid have been added.*

Solution: For salt of weak base and strong acid:

$$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$$

$$\text{p}K_w = 14;\quad \text{p}K_b = -\log_{10} 1.7\times10^{-9} = 8.769;\quad C = 0.05$$

$$\text{pH} = \frac{1}{2}[14 - 8.769 + 1.30102] = 3.27 \quad \text{(pH at equivalence)}$$

5 cc 0.1 M HCl will be considered for pH.

$$\text{Mole of HCl remaining} = \frac{0.1}{1000}\times5 = 5\times10^{-4}$$

$$\text{New molarity} = \frac{5\times10^{-4}}{55}\times1000 = 0.00909\,M$$

$$\text{pH} = -\log[0.00909] = 2.04$$

Example 14. *If very small amount of phenolphthalein is added to 0.15 mol litre^{-1} solution of sodium benzoate, what fraction of the indicator will exist in the coloured form? State any assumption that you make.*

$$K_a\ (\text{Benzoic acid}) = 6.2\times10^{-5},\ K_w\ (H_2O) = 1\times10^{-14},$$

$$K_{In}\ (\text{Phenolphthalein}) = 3.16\times10^{-10}$$

Solution: Formula for pH of salt hydrolysis:

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[14 - \log_{10} 6.2 \times 10^{-5} + \log 0.15]$$

$$= 8.6918$$

Formula for pH of indicator:

$$pH = pK_{In} + \log_{10}\frac{[In^-]}{[HIn]}$$

$$8.6918 = -\log_{10}(3.16 \times 10^{-10}) + \log_{10}\frac{[In^-]}{[HIn]}$$

$0.16 = [In^-]/[HIn] =$ Fraction of indicator in coloured form.

Example 15. *How much NH_3 must be added to 0.004 M Ag^+ solution to prevent the precipitation of AgCl when (Cl^-) reaches 0.001 M? K_{sp} for AgCl is 1.8×10^{-10} and K for $Ag(NH_3)_2^+$ is 5.9×10^{-8}.*

Solution:

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.001} = 1.8 \times 10^{-7}\ M$$

NH_3 is added to keep the conc. of Ag^+ below $1.8 \times 10^{-7}\ M$ to prevent precipitation.

$[Ag(NH_3)_2]^+$ at above limiting condition

$$= 0.004 - 1.8 \times 10^{-7} \approx 0.004\ M$$

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_d = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+}$$

$$5.9 \times 10^{-8} = \frac{[1.8 \times 10^{-7}][NH_3]^2}{[0.004]}$$

$$[NH_3] = 0.036\ M$$

$$[NH_3]_{Total} = [NH_3]_{Free} + [NH_3]_{Complexed}$$

$$= 0.036 + 2 \times 0.004 = 0.044 \text{ mol/litre}$$

Example 16. *Calculate the percentage error in hydronium ion concentration made by neglecting ionization of water in 10^{-6} M NaOH.*

Solution: $[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-6}} = 10^{-8}\ M$

[Neglecting ionization of water]

Consider ionization of water.

$$[H_3O^+] = y \quad [OH^-] = (y + 10^{-6})$$

$$[H_3O^+][OH^-] = K_w = 10^{-14}$$

$$y[y + 10^{-6}] = 10^{-14}$$

$$y^2 + 10^{-6}y - 10^{-14} = 0$$

On solving for y, $y = 9.9 \times 10^{-9}$

$$\%\text{ error} = \frac{10^{-8} - 9.9 \times 10^{-9}}{9.9 \times 10^{-9}} \times 100 = 1\%$$

Example 17. *Determine the silver ion concentration in a 0.2 M solution of $[Ag(NH_3)_2]NO_3$.*

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_{diss.} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

Solution: Let concentration of Ag^+ at equilibrium be 'C' M.

$\therefore$ $[NH_3] = 2C\ M$

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

$$6.8 \times 10^{-8} = \frac{C \times 4C^2}{0.2}$$

$$C = 0.0015\ M$$

Example 18. *The solubility of silver acetate in pure water at 25° C is 8.35 g litre^{-1} and 61.8 g litre^{-1} in an acid solution of pH = 3. Calculate:*

(i) K_{sp} of silver acetate and

(ii) dissociation constant of acetic acid.

Solution: (i) CH_3COOAg (mw) = 167

$$S = \frac{8.35}{167} \text{ mol / litre} = 0.05\ M$$

$$K_{sp} = S^2 = (0.05)^2 = 2.5 \times 10^{-4}\ M$$

(ii) Use expression of salt hydrolysis to calculate K_a.

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$K_a = 1.8 \times 10^{-5}$$

Example 19. *How many moles of NH_3 must be added to 1 litre of a 0.1 M $AgNO_3$ to reduce Ag^+ concentration to 2×10^{-7} M?*

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$

$$K_{diss.} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6.8 \times 10^{-8}$$

Solution: $[Ag(NH_3)_2]^+ \approx 0.1\ M$

$$[Ag^+] = 2 \times 10^{-7}$$

$$K = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+}$$

$$6.8 \times 10^{-8} = \frac{2 \times 10^{-7}[NH_3]^2}{0.1}$$

$$[NH_3] = 0.184\ M$$

It is the concentration of free NH_3.

$$[NH_3]_{Total} = [NH_3]_{Free} + [NH_3]_{Complexed}$$

$$= 0.184 + 2 \times 0.1 = 0.384\ M$$

Example 20. *A buffer of pH 8.50 is prepared from 0.02 mole of KCN. The desired volume of buffer solution is to be 1* *litre. How will you make this buffer by using HCl? What is the change after addition of* 0.5×10^{-4} *mole HCl to* $100\ cm^3$ *and same amount of NaOH in* $100\ cm^3$ *of buffer?* (K_a *HCN* $= 6.2 \times 10^{-10}$)

Solution:

$$\underset{(0.02-x)}{\text{KCN}} + \underset{x}{\text{HCl}} \longrightarrow \underset{x}{\text{KCl}} + \underset{x}{\text{HCN}}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$8.50 = -\log(6.2 \times 10^{-10}) + \log_{10}\left[\frac{0.02-x}{x}\right]$$

$$8.50 = 9.2076 + \log_{10}\left[\frac{0.02-x}{x}\right]$$

$$x = 0.01672$$

(Buffer is prepared by adding 0.01672 mole of HCl in salt KCN.)

Calculation of pH change when HCl is added:

Moles of HCl added in 1 litre buffer $= 0.5 \times 10^{-3}$

HCl will convert more salt into acid.

$$\text{pH} = 9.2076 + \log_{10}\frac{0.00382 - 0.5 \times 10^{-3}}{0.01672 + 0.5 \times 10^{-3}} = 9.4156$$

pH change $= 9.4156 - 8.50 = 0.9156$

Example 21. *What* (H_3O^+) *must be maintained in a saturated* H_2S *solution to precipitate* Pb^{2+}, *but not* Zn^{2+} *from a solution in which each ion is present at a concentration of* $0.01M$? (K_{sp} $H_2S = 1.1 \times 10^{-22}$ *and* K_{sp} *ZnS* $= 1.0 \times 10^{-21}$) **(IIT 2000)**

Solution:

$$K_{sp}\ \text{ZnS} = [\text{Zn}^{2+}][\text{S}^{2-}] = 1.0 \times 10^{-21}$$

or $$0.01 \times [\text{S}^{2-}] = 1.0 \times 10^{-21}$$

or $$[\text{S}^{2-}] = 1.0 \times 10^{-19}$$

To start precipitation of ZnS, the required concentration of sulphide ions is 1.0×10^{-19}.

$$K_{sp}\ \text{H}_2\text{S} = [\text{H}^+]^2[\text{S}^{2-}] = 1.1 \times 10^{-22}$$

or $$[\text{H}^+]^2 = \frac{1.1 \times 10^{-22}}{1.0 \times 10^{-19}} = 1.1 \times 10^{-3}$$

or $$[\text{H}^+] = 0.0331M$$

Thus, the hydrogen ion concentration higher than 0.0331 M will reduce the concentration of sulphide ions which will not allow the precipitation of Zn^{2+} ions as ZnS and under this condition only PbS precipitation occurs.

Example 22. *The average concentration of* SO_2 *in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of* SO_2 *in water at 298 K is 1.3653 mol litre*$^{-1}$ *and the* pK_a *of* H_2SO_3 *is 1.92, estimate the pH of rain on that day.* **(IIT 2000)**

Solution:

$$\text{p}K_a = 1.92$$

$$K_a = \text{antilog}(-1.92) = 0.012$$

$$\begin{array}{llll} & \text{H}_2\text{SO}_3 & \rightleftharpoons\ 2\text{H}^+ & +\ \text{SO}_3^{2-} \\ t=0 & C & 0 & 0 \\ t_{eq} & C - C\alpha & 2C\alpha & C\alpha \end{array}$$

$$K_a = \frac{[\text{H}^+]^2[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3]}$$

$$0.012 = \frac{(2C\alpha)^2 \times C\alpha}{C(1-\alpha)} = \frac{4C^2\alpha^3}{(1-\alpha)} \approx 4C^2\alpha^3$$

$$0.012 = 4 \times (1.3653)^2 \times \alpha^3$$

or $$\alpha = 0.117$$

$$[\text{H}^+] = 2C\alpha = 2 \times 1.3653 \times 0.117 = 0.3194$$

$$\text{pH} = -\log_{10}(0.3194) = 0.495$$

Example 23. 0.16 *g of* N_2H_4 *are dissolved in water and the total volume made up to* 500 *mL. Calculate the percentage of* N_2H_4 *that has reacted with water at this dilution. The* K_b *for* N_2H_4 *is* 4.0×10^{-6} *M.* **(IIT 1998)**

Solution: Concentration of N_2H_4,

$$[\text{N}_2\text{H}_4] = \frac{0.16}{32} \times \frac{1000}{500} = 0.01M$$

$$\begin{array}{lllll} & \text{N}_2\text{H}_4 & +\ \text{H}_2\text{O} \rightleftharpoons & \text{N}_2\text{H}_5^+ & +\ \text{OH}^- \\ \text{At equilibrium} & 1-\alpha & & \alpha & \alpha \end{array}$$

$$K_b = C\alpha^2 \text{ or } \alpha^2 = \frac{K_b}{C} = \frac{4.0 \times 10^{-6}}{0.01} = 4 \times 10^{-4}$$

or $$\alpha = 2 \times 10^{-2}$$

i.e., 2%

Example 24. *What will be the resultant pH when* 200 *mL of an aqueous solution of HCl* (*pH* = 2) *is mixed with* 300 *mL of an aqueous solution of NaOH* (*pH* = 12)? **(IIT 1998)**

Solution: pH of HCl = 2 $\therefore [\text{HCl}] = 10^{-2}\ M$

pH of NaOH = 12 $\therefore [\text{NaOH}] = 10^{-2}\ M$

$$\begin{array}{llll} & \text{HCl} & +\ \text{NaOH} \rightleftharpoons & \text{NaCl} + \text{H}_2\text{O} \\ \text{meq after reaction} & 0 & 100 \times 10^{-2} & \\ & & = 1 & \end{array}$$

$$[\text{OH}^-] \text{ after reaction} = \frac{1}{500} = 2 \times 10^{-3}\ M$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log 2 \times 10^{-3} = 2.7$$

$$\therefore \quad \text{pH} = 14 - 2.7 = 11.3$$

Example 25. 500 *mL of* 0.2 *M aqueous solution of acetic acid is mixed with* 500 *mL of* 0.2 *M HCl at* 25°*C.*

(*a*) *Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.*

(*b*) *If* 6 *g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing.* K_a *for acetic acid is* 1.75×10^{-5} *M.* **(IIT 2002)**

Solution: (a) Conc. of HCl and CH_3COOH after mixing will be 0.1 M.

$$\begin{array}{lllll} & \text{CH}_3\text{COOH} & \rightleftharpoons \text{CH}_3\text{COO}^- & +\ \text{H}^+ & \\ t=0 & 0.1 & 0 & 0.1 & \text{(from HCl)} \\ t_{eq} & 0.1 - x & x & (0.1 + x) & \end{array}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$1.75\times10^{-5}=\frac{x\times(0.1+x)}{(0.1-x)}$$

On approximation, $x\approx1.75\times10^{-5}$

$$[\mathrm{H^+}]=0.1+x\approx0.1\,M$$

$$\mathrm{pH}=-\log[0.1]=1$$

Degree of dissociation of acetic acid $=\dfrac{1.75\times10^{-5}}{0.1}=1.75\times10^{-4}$

(b) Number of moles of NaOH added $=\dfrac{6}{40}=0.15$

$$\begin{array}{lcccccc} & CH_3COOH & + HCl & + NaOH & \rightleftharpoons CH_3COONa & + NaCl & + H_2O \\ t=0 & 0.1 & 0.1 & 0.15 & 0 & 0 & 0 \\ t_{eq} & 0.05 & 0 & 0 & 0.05 & 0 & 0 \end{array}$$

$$\mathrm{pH}=\mathrm{p}K_a+\log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$=-\log1.75\times10^{-5}+\log\frac{0.05}{0.05}=4.757$$

Example 26. *Will the pH of water be same at 4°C and 25°C? Explain.* (IIT 2003)

Solution: We know that,

$$K_w=[\mathrm{H^+}][\mathrm{OH^-}]$$

At 25°C, $[\mathrm{H^+}]=[\mathrm{OH^-}]=1.01\times10^{-7}\,M$

$$\mathrm{pH}=-\log_{10}[\mathrm{H^+}]=-\log_{10}[10^{-7}]=7$$

At 4°C, ionization of water will be less than that at 25°C.

∴ at 25° C $K_w=[\mathrm{H^+}][\mathrm{OH^-}]$ will be less than 10^{-14}. Thus, pH of water will be more than 7 at 4°C.

Example 27. *0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point.* (IIT 2004)

Solution: Neutralization of *HA* with NaOH may be given as,

$$HA+\mathrm{NaOH}\longrightarrow\mathrm{Na}A+\mathrm{H_2O}$$

Concentration of salt will be $\dfrac{0.1}{2}M$, *i.e.*, 0.05 *M*, since volume will be double. pH of the salt after hydrolysis may be calculated as,

$$\mathrm{pH}=\frac{1}{2}[\mathrm{p}K_w+\mathrm{p}K_a+\log C]\qquad\text{... (i)}$$

$$\mathrm{p}K_w=14$$

$$\mathrm{p}K_a=-\log K_a=-\log(5.6\times10^{-6})=5.2518$$

$$\log C=\log0.05=-1.3010$$

Substituting the values of $\mathrm{p}K_w$, $\mathrm{p}K_a$ and $\log C$ in eq. (i) we get,

$$\mathrm{pH}=\frac{1}{2}[14+5.2518-1.3010]=8.9754$$

Example 28. *A solution of acetic acid is 1% ionised. Determine the molar concentration of acetic acid. (ionization constant for acetic acid $=1.8\times10^{-5}$)* [BCECE (Mains) 2006]

Solution: $CH_3COOH\rightleftharpoons CH_3COO^-+H^+$

$$\begin{array}{lccc} t_0 & C & 0 & 0 \\ t_{eq.} & C-C\alpha & C\alpha & C\alpha \end{array}$$

$$K_a=\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}=\frac{C\alpha\times C\alpha}{C-C\alpha}$$

$$=\frac{C\alpha^2}{1-\alpha}\qquad\left(\alpha=\frac{1}{100}=0.01\right)$$

$$1.8\times10^{-5}=\frac{C\times(0.01)^2}{1-0.01}$$

$$1.8\times10^{-5}\approx C\times10^{-4}$$

$$C=0.18\,M$$

Example 29. *A mixture of H_2O and solid AgCl shaken to obtain saturated solution. The solid is filtered and to 100 mL of filtrate, 100 mL of 0.03 M NaBr is added, will a precipitate be formed?* [BCECE (Mains) 2006]

$$K_{sp}\ AgCl=10^{-10},\ K_{sp}\ AgBr=5\times10^{-13}$$

Solution: Let solubility of AgCl is '*S*'

$$\therefore\quad K_{sp}\ \mathrm{AgCl}=S^2$$

$$S=\sqrt{K_{sp}}$$

$$=\sqrt{10^{-10}}=10^{-5}$$

When, 100 mL of both AgCl and NaBr are mixed then, concentration of $\mathrm{Ag^+}$ and $\mathrm{Br^-}$ will be:

$$[\mathrm{Ag^+}]=\frac{100\times10^{-5}}{200}=0.5\times10^{-5}M$$

$$[\mathrm{Br^-}]=\frac{100\times0.03}{200}=0.015\,M$$

Ionic product of AgBr $=0.5\times10^{-5}\times0.015$

$$=7.5\times10^{-8}$$

Since, ionic product of AgBr is greater than its solubility product, hence AgBr will be precipitated.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Strong and weak electrolytes: Electrolytes which ionise almost completely when dissolved in water are termed strong electrolytes while those electrolytes which ionise to small extent are termed as weak electrolytes. The degree of ionisation and electrical conductivity of strong electrolytes have high values while weak electrolytes possess small values. NaOH, HCl, H_2SO_4, $BaCl_2$, KCl, etc., are strong electrolytes while NH_4OH, CH_3COOH, $(NH_4)_2CO_3$, HCN, etc., are weak electrolytes.

Degree of ionisation

$$= \frac{\text{Number of molecules of the electrolyte dissociated into ions}}{\text{Total number of molecules of the electrolyte dissolved}}$$

2. Ostwald's dilution law: A dynamic equilibrium exists between ions and unionised molecules of the electrolyte in solution and law of mass action can be applied to this equilibrium also. Consider a binary electrolyte AB.

$$\begin{array}{lccc} & AB & \rightleftharpoons & A^+ + B^- \\ \text{Initial concentration} & C & & 0 \quad\; 0 \\ \text{Conc. at equilibrium} & C(1-\alpha) & & C\alpha \quad C\alpha \end{array}$$

where, α is the degree of dissociation

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C \times \alpha^2}{(1-\alpha)}$$

K is termed ionisation constant. For a weak electrolyte, the value of α is very small in comparison to 1. Thus, $1-\alpha \to 1$.

$$K = C\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K}{C}} \quad \text{or} \quad \alpha = \sqrt{KV}$$

Where, V is the volume containing one mole of electrolyte.

The degree of dissociation of a weak electrolyte is proportional to the square root of dilution. It increases as V increases and approaches to one at high dilution.

This law holds good for weak electrolytes. In the case of acids, ionisation constant is represented as K_a and in case of bases K_b. Polybasic acids ionise stepwise and each step has its own ionisation constant.

For example, H_3PO_4 ionises in three steps:

Step I: $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $K_1 = \dfrac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$

Step II: $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$; $K_2 = \dfrac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$

Step III: $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$; $K_3 = \dfrac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$

$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$$

$$K = K_1 \times K_2 \times K_3$$

Generally, $K_1 > K_2 > K_3$

3. Common ion effect: The degree of dissociation of a weak electrolyte is suppressed by the presence of another electrolyte (strong) containing a common ion. As a result of common ion effect, the concentration of the ion not in common in two electrolytes decreases.

4. Solubility product: In a saturated solution of an electrolyte, two equilibria exist in solution. It can be represented as:

$$\underset{\text{Solid}}{AB} \rightleftharpoons \underset{\substack{\text{Unionised}\\ \text{(dissolved)}}}{AB} \rightleftharpoons \underbrace{A^+ + B^-}_{\text{Ions}}$$

$$K = \frac{[A^+][B^-]}{[AB]}$$

In saturated solution, the value of $[AB]$ is fixed at a definite temperature.

Thus, $K[AB] = [A^+][B^-] = K_s$ (constant)

K_s is termed solubility product. For a general equation,

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$K_s = [A^{y+}]^x[B^{x-}]^y$$

Thus, solubility product is defined as the product of concentrations of ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte at a given temperature when the solution is saturated.

For the precipitation of an electrolyte, it is necessary that the ionic product must exceed its solubility product.

Relationship between solubility and solubility product: Salts like AgI, $PbSO_4$, $BaSO_4$, PbI_2, etc., which are considered to be insoluble do possess solubility. It is assumed that whole of the dissolved electrolyte is present in the form of ions.

$$A_x \times B_y = \underset{xS}{xA^{y+}} + \underset{yS}{yB^{x-}}$$

Let 'S' mol per litre be solubility of the salt; then

$$K_s = [A^{y+}]^x[B^{x-}]^y$$

$$= (xS)^x(yS)^y$$

$$= x^x y^y (S)^{x+y}$$

(a) 1 : 1 type salts such as AgCl, AgI, $BaSO_4$, $PbSO_4$, etc.

$$K_s = S^2 \quad \text{or} \quad S = \sqrt{K_s}$$

(b) 1 : 2 or 2 : 1 type salts such as Ag_2CO_3, Ag_2CrO_4, PbI_2, CaF_2, etc.

$$K_s = S \times (2S)^2 = 4S^3$$

$$S = \sqrt[3]{\frac{K_s}{4}}$$

(c) 1 : 3 type salts such as AlI_3, $Fe(OH)_3$, etc.

$$K_s = S \times (3S)^3 = 27S^4$$

$$S = \sqrt[4]{\frac{K_s}{27}}$$

The presence of common ion affects the solubility of salt. Let C be the concentration of strong electrolyte containing common ion and new solubility of salt be S'. For an electrolyte, AB,

$$S^2 = K_s = S'(S'+C)$$

Applications of Solubility Product and Common ion Effect

(i) Purification of common salt.
(ii) Salting out of soap.
(iii) Precipitation of the sulphides of group (II) and (IV).
(iv) Precipitation of the hydroxides of group (III).
(v) Using excess of precipitating agent in gravimetric estimations.
(vi) Predicting precipitation in ionic reactions.

5. Acids and Bases: Three important concepts are:

(i) Arrhenius concept: All substances which furnish H^+ ions when dissolved in water are called acids while those which ionise in water to furnish OH^- ions are called bases. Actually free H^+ ions do not exist in water. They combine with water to form hydronium ions (H_3O^+). The reaction between an acid and a base is termed as neutralisation.

All aqueous solutions contain both H^+ and OH^- ions. However, their relative amounts are different in different solutions.

$H^+ > OH^-$ —solution will be acidic
$H^+ < OH^-$ —solution will be basic
$H^+ = OH^-$ —solution will be neutral

(ii) Bronsted-Lowry concept: Any molecule, cation or anion, which provides proton to any other substance is known as an acid and any molecule, cation or anion, which can accept proton from any other substance is known as base. Conjugate acid-base pairs are formed by the loss or gain of a proton.

$$\underset{\text{Acid}}{CH_3COOH} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{Base}}{CH_3COO^-}$$

$$\underset{\text{Base}}{NH_3} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{\text{Acid}}{NH_4^+}$$

In a conjugate pair, if acid is strong, the base will be weak and *vice-versa*. The substances which possess dual nature are termed amphiprotic such as H_2O and NH_3. The acid-base reaction involves two conjugate pairs.

$$\underbrace{\mathrm{Acid}_1 + \underbrace{\mathrm{Base}_2 \rightleftharpoons \mathrm{Acid}_2}_{\text{Conjugate pair}} + \mathrm{Base}_1}_{\text{Conjugate pair}}$$

This concept fails to explain reactions between non-protic acids and bases.

(iii) Lewis concept: A base is defined as a substance which can furnish a pair of electrons to form a coordinate bond whereas an acid is a substance which can accept a pair of electrons, *i.e.*, base is a **nucleophile** and acid is an **electrophile.** All Lewis bases are Bronsted bases but all Lewis acids are not Bronsted acids. All simple cations, molecules whose central atom has incomplete octet, the molecules in which central atom can expand its valence cell and molecules having multiple bonds between atoms of different electronegativities can act as Lewis acids. All simple anions and molecules having one or more lone pairs of electrons can act as Lewis bases.

Arrhenius concept is most simple and explains satisfactorily reactions in aqueous solutions.

6. Relative strength of acids and bases: The extent to which an acid property is given by an acid is a measure of its strength. The strength of the acid solution does not depend on its concentration but on the number of H^+ ions present. On dilution, as the number of H^+ ions increases, the strength of an acid also increases. At infinite dilution, all acids are almost completely ionised and, therefore, tend to be equally strong. The concentration of H^+ ions at all other dilutions of equimolar solutions of the acids may not be equal and depends on their degree of dissociation. The relative strength is generally compared in terms of degree of dissociation of equimolar solutions.

$$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

The strength of the base depends upon OH^- ion concentration.

$$\frac{\text{Strength of base I}}{\text{Strength of base II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

7. Neutralisation: The neutralisation is the interaction of H^+ ions furnished by an acid and OH^- ions furnished by a base or a reaction between acid and base to form salt and water is termed neutralisation.

Salts are regarded as compounds made up of positive and negative ions. The positive part comes from a base and negative part comes from an acid. The salts are generally crystalline solids. These are classified into the following classes:

(i) Simple salts: The salts formed by neutralisation process are of three types:

(a) **Normal salts** are salts formed by the replacement of all replaceable hydrogen atoms at H^+ ions. Examples are NaCl, KNO_3, $CuSO_4$, $FeSO_4$, etc.

(b) **Acid salts** are formed by incomplete neutralisation of polybasic acids. Examples are $NaHCO_3$, $NaHSO_4$, Na_2HPO_4, etc.

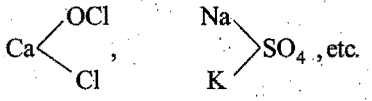
(c) **Basic salts** are salts formed by incomplete neutralisation of polyacidic bases. Examples are: Zn(OH)Cl, Mg(OH)Cl, $Fe(OH)_2Cl$, etc.

(ii) Double salts are the addition compounds formed by combination of two or more simple salts. Such salts are stable in solid state only. Examples are $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, etc. These salts when dissolved in water furnish all the ions present in simple salts.

(iii) Complex salts are the salts formed by combination of simple salts or molecular compounds. These are stable in solid state. On dissolving in water, they furnish at least one complex ion.

Examples are $K_4Fe(CN)_6$, $[Cu(NH_3)_4]SO_4$, etc.

(iv) Mixed salts furnish more than one cation or more than one anion when dissolved in water. Examples are:



$$\mathrm{Ca}\begin{matrix}\mathrm{OCl}\\ \mathrm{Cl}\end{matrix}, \quad \begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\mathrm{SO_4}, \text{ etc.}$$

8. Ionic product of water: Pure water is a weak electrolyte and is very slightly dissociated into hydrogen and hydroxyl ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$[H_2O]$ can be taken as constant.

$$K[H_2O] = [H^+][OH^-] = K_w$$

K_w is constant and known as ionic product of water. Its value is 1×10^{-14} at 25°C. The value increases with increases of temperature. Since, water is neutral, $[H^+]=[OH^-]$

or $$[H^+]=[OH^-]=10^{-7}$$

When $[H^+]>[OH^-]$, the solution is acidic.

Similarly, when $[H^+]<[OH^-]$, the solution is basic in nature. Every aqueous solution, whether acidic, neutral or basic, contains both H^+ and OH^- ions. The product of their concentrations is always 1×10^{-14} at 25° C. If one increases, the other decreases.

$$[H^+]=\frac{K_w}{[OH^-]} \quad \text{and} \quad [OH^-]=\frac{K_w}{[H^+]}$$

9. pH scale: This has been devised by Sorensen in 1909. The negative logarithm of the concentration of hydrogen ions is termed the pH of the solution.

$$pH=-\log[H^+]=\log\frac{1}{[H^+]}$$

pH is thus logarithm of the reciprocal of hydrogen ion concentration.

Similarly, $$pOH=-\log[OH^-]=\log\frac{1}{[OH^-]}$$

$$pH+pOH=14$$

Limitations of pH scale: pH values do not give any immediate idea about the relative strengths of the solution. pH value is zero for 1 *N* solution of strong acid. In case of 2 *N*, 3 *N*, 4 *N*, etc., solutions, pH values are negative. A solution of an acid having very low concentration, say 10^{-8} *N*, cannot have pH 8 as shown by pH formula but the actual pH value will be less than 7.

10. Hydrolysis: It is the interaction of ions of a salt with water to give acidic, basic or neutral solution. It is found in the salts of weak acids and strong bases, in salts of strong acids and weak bases and in salts of weak acids and weak bases. The process of hydrolysis is actually the reverse of neutralisation.

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both acid and base are either strong or weak, the solution is generally neutral in nature.

Salt of a strong acid and a weak base: The solution of such a salt is acidic in nature. The cation of the salt is reactive and reacts with water.

$$\underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{\substack{Ch \\ \text{Weak base}}}{BOH} + \underset{Ch}{H^+}$$

The extent to which hydrolysis proceeds is expressed as degree of hydrolysis. It is denoted as *h* or *x*.

$$h=\frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Let *C* be the concentration of salt and *h* be the degree of hydrolysis.

$$K_h=\frac{[BOH][H^+]}{[B^+]}=\frac{Ch\times Ch}{C(1-h)}=\frac{Ch^2}{(1-h)}\approx Ch^2 \quad (\text{if } h \text{ is small})$$

$$K_h=\frac{K_w}{K_b}$$

$$h=\sqrt{\frac{K_h}{C}}=\sqrt{\frac{K_w}{C\times K_b}}$$

$$=hC=[H^+]=\frac{\sqrt{C\times K_w}}{K_b}$$

$$pH=\tfrac{1}{2}pK_w-\tfrac{1}{2}pK_b-\tfrac{1}{2}\log C$$

11. Summary pH of mixtures of acids and bases:

Let '*x*' meq of acid (H*A*) and '*y*' meq of base (*B*OH) be mixed.

$$\text{meq}=NV\ \text{mL};\ N=M\times\text{acidity or basicity}$$

Case I. Strong acid and strong base

(a) When $x=y$, then there will be complete neutralisation; the solution will then be neutral with pH = 7.

(b) When $x>y$, then acid will remain after neutralisation.

$$\text{meq of remaining acid}=(x-y)$$

$$N_a=\frac{(x-y)}{V\ \text{mL}}$$

$$[H^+]_{\text{Strong acid}}=N_a=\frac{(x-y)}{V\ \text{mL}}$$

$$pH=-\log_{10}\left[\frac{x-y}{V\ \text{mL}}\right]$$

(c) When $y>x$, then base will remain after neutralization.

$$\text{meq of remaining base}=(y-x)$$

$$N_b=\frac{(y-x)}{V\ \text{mL}}$$

$$[OH^-]_{\text{Strong base}}=N_b=\frac{(y-x)}{V\ \text{mL}}$$

$$pOH=-\log_{10}\left[\frac{(y-x)}{V\ \text{mL}}\right]; \qquad pH=14-pOH$$

Case II. Strong base and weak acid

(a) If $x=y$, then after complete neutralisation there will be salt of weak acid and strong base. There will be hydrolysis; pH after hydrolysis may be calculated as:

$$pH=\frac{1}{2}[pK_w+pK_a+\log_{10}C]$$

C = Conc. of salt in mol litre^{-1}.

(b) If $x>y$, then weak acid will be in excess.

$$\text{Weak acid}=(x-y)\ \text{meq}$$

$$\text{Salt}=y\ \text{meq}$$

The resultant solution will be acid buffer; its pH may be calculated as:

$$pH=pK_a+\log\frac{[\text{Salt}]}{[\text{Acid}]}$$

Conc. should be taken in mol litre^{-1}.

(c) When $y > x$, then excess of strong base will remain after neutralisation. Remaining base $= (y - x)$ meq

$$\underset{\text{Strong}}{N_b} = \frac{(y-x)}{V \text{ mL}} = [\text{OH}^-]$$

$$\text{pOH} = -\log_{10}\left[\frac{y-x}{V \text{ mL}}\right]$$

Case III. Strong acid and weak base

(a) When $x = y$, there will be salt formation after complete neutralisation. Salt of weak base and strong base will undergo hydrolysis. pH after hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_a - \log_{10} C]$$

$C =$ Conc. of salt in mol litre^{-1}.

(b) When $x > y$, then strong acid will remain after neutralisation.

Remaining acid $= (x - y)$ meq

$$\underset{\text{Strong}}{N_a} = \frac{(x-y)}{V \text{ mL}} = [\text{H}^+]$$

$$\text{pH} = -\log_{10}\left[\frac{x-y}{V \text{ mL}}\right]$$

(c) When $y > x$, then weak base will remain after salt formation; the resultant mixture will be, therefore, base buffer.

$$14 - \text{pH} = \text{pOH} = \text{p}K_b + \log_{10}\frac{[\text{Salt}]}{[\text{Base}]}$$

Remaining base $= (y - x)$ meq

Salt $= x$ meq

Salt and base conc. should be taken in mol litre^{-1}.

Case IV. Weak acid and weak base

(a) When $x = y$, there will complete neutralisation forming salt of weak acid and weak base. pH after salt hydrolysis may be calculated as:

$$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b]$$

(b) When $x > y$, weak acid will remain after neutralisation; the mixture of weak acid and salt behaves as acid buffer.

(c) When $y > x$, then weak base will remain after salt formation; the mixture thus behaves as base buffer.

12. Acid-base indicators: In acid-base titrations, organic substances (weak acids or weak bases) are generally used as indicators. They change their colours within a certain pH range.

Methyl orange	pH range 3.2 – 4.5	Pink to yellow
Methyl red	pH range 4.4 – 6.5	Red to yellow
Phenolphthalein	pH range 8.3 –10.5	Colourless to pink

Two theories have been proposed to explain the change of colour of these acid-base indicators. These theories are:

(a) Ostwald's theory (b) Quinonoid theory

The suitable indicators for the following titrations are:

(i) Strong acid *versus* strong base—Phenolphthalein, methyl red and methyl orange.

(ii) Weak acid *versus* strong base—Phenolphthalein.

(iii) Strong acid *versus* weak base—Methyl red and methyl orange.

Questions

1. (a) Mention conjugate base of each of the following:
HS^-, H_3O^+, $H_2PO_4^-$, HSO_4^-, HF, CH_3COOH, C_6H_5OH, $HClO_4$, NH_4^+

(b) Mention the conjugate acid of each of the following:
OH^-, CH_3COO^-, Cl^-, CO_3^{2-}, $H_2PO_4^-$, CH_3NH_2, CH_3COOH, NH_2^-

(c) Which of the following behave both as Bronsted acids as well as Bronsted bases?
$H_2O, HCO_3^-, H_2SO_4, H_3PO_4, HS^-, NH_3$

(d) Which is stronger acid in each of the following pairs?
HCl, HI; H_2CO_3, H_2SO_4; H_2O, H_2S; C_6H_5OH, C_2H_5OH; Na^+, K^+

(e) Which is stronger base in each of the following pairs?
OH^-, Cl^-; OH^-, NH_2^-; OH^-, CH_3COO^-; CH_3COO^-, Cl^-; NH_3, CH_3NH_2

(f) Classify the following into acids and bases according to Lewis concept:
S^{2-}, H^+, OH^-, BF_3, Ni^{2+}, NF_3, $AlCl_3$, $SnCl_4$, NH_3, $(CH_3)_2O$

2. Predict whether the following substances will give acidic, basic or neutral solution?

(i)	K_2CO_3	(ii)	NaCl	(iii)	$FeCl_3$
(iv)	$CuSO_4$	(v)	$AlCl_3$	(vi)	NH_4Cl
(vii)	CH_3COONH_4	(viii)	NaCN	(ix)	Na_2S
(x)	$Na_2B_4O_7$				

3. [A] Match the List-I with List-II:

List-I (Salt)	List-II (pH)
(a) Salt of strong acid and strong base	(p) $\frac{1}{2}[pK_w + pK_a - pK_b]$
(b) Salt of weak acid and strong base	(q) $\frac{1}{2}[pK_w + pK_a + \log C]$
(c) Salt of weak base and strong acid	(r) $\frac{1}{2}[pK_w - pK_b - \log C]$
(d) Salt of weak acid and weak base	(s) $\frac{1}{2}pK_w$

[B] Match the List-I with List-II:

List-I (Indicator)	List-II (pH range)
(a) Phenolphthalein	(p) 4.2 – 6.3
(b) Litmus	(q) 3.1 – 4.4
(c) Methyl red	(r) 8.3–10.0
(d) Methyl orange	(s) 5.0–8.0

[C] Match the List-I with List-II:

List-I	List-II
(a) Lewis acid	(p) PH_3
(b) Lewis base	(q) $[Al(H_2O)_5OH]^{2+}$
(c) Conjugate acid	(r) $(CH_3)_3B$
(d) Conjugate base	(s) H_3O^+

4. **Matrix-Matching Problems (For IIT Aspirants):**

[A] Match the List-I with List-II:

List-I	List-II
(a) H_3PO_4	(p) Monobasic
(b) H_3PO_3	(q) Dibasic
(c) H_3PO_2	(r) Tribasic
(d) H_3BO_3	(s) sp^3-hybrid state

[B] Match the List-I with List-II:

List-I (Indicator)	List-II (Types of titration)
(a) Phenolphthalein	(p) NaOH + HCl
(b) Phenol red	(q) $H_2SO_4 + NH_4OH$
(c) Bromo cresol green	(r) $CH_3COOH + NH_4OH$
(d) Methyl orange	(s) $KOH + H_2SO_4$

[C] Match the acid/base in List-I with their nature in List-II:

List-I	List-II
(a) HSO_4^-	(p) Lewis acid
(b) BF_3	(q) Lewis base
(c) NH_3	(r) Bronsted acid
(d) OH^-	(s) Bronsted base

[**Note:** Consider the normal behaviour of species.]

[D] Match the Column-I with Column-II:

Column-I (Salt)	Column-II (Solubility product)
(a) Zirconium phosphate	(p) $27S^4$
(b) Aluminium phosphate	(q) $108S^5$
(c) Calcium phosphate	(r) $6912S^7$
(d) Sodium phosphate	(s) S^2

[E] Match the Column-I with Column-II:

Column-I (Salt)	Column-II (Nature of hydrolysis)
(a) NH_4CN	(p) Only cation hydrolysis
(b) CH_3COONa	(q) Only anion hydrolysis
(c) $NaClO_4$	(r) Both cation and anion hydrolysis
(d) $Fe(NO_3)_2$	(s) No hydrolysis

[F] Match the Column-I with Column-II:

Column-I (Titration)	Column-II (Indicator used)
(a) Strong acid versus strong base	(p) Methyl orange (3 – 4.4)
(b) Weak acid versus strong base	(q) Methyl red (4.3 – 6.3)
(c) Strong acid versus weak base	(r) Phenolphthalein (8–10)
(d) Weak acid versus weak base.	(s) No suitable indicator

Answers

1. (a) S^{2-}, H_2O, HPO_4^{2-}, SO_4^{2-}, F^-, CH_3COO , C_6H_5O , ClO_4^-, NH_3

(b) H_2O, CH_3COOH, HCl, HCO_3^-, H_3PO_4, $CH_3NH_3^+$, $CH_3COOH_2^+$, NH_3

(c) H_2O, HCO_3^-, HS^- and NH_3 behave both as acids and bases.

(d) HI > HCl; $H_2SO_4 > H_2CO_3$; $H_2S > H_2O$;
$C_6H_5OH > C_2H_5OH$; $Na^+ > K^+$

(e) $OH^- > Cl$; $NH_2^- > OH^-$; $OH^- > CH_3COO^-$;
$CH_3COO^- > Cl^-$; $CH_3NH_2 > NH_3$

(f) Lewis acids: H^+, BF_3, Ni^{2+}, $AlCl_3$, $SnCl_4$
Lewis bases: S^{2-}, OH^-, NF_3, NH_3, $(CH_3)_2O$

2. Acidic: $FeCl_3$, $CuSO_4$, $AlCl_3$, NH_4Cl
Basic: K_2CO_3, NaCN, Na_2S, $Na_2B_4O_7$
Neutral: NaCl, CH_3COONH_4

3. [A] (a–s), (b–q), (c–r), (d–p)
[B] (a–r), (b–s), (c–p), (d–q)
[C] (a–r), (b–p), (c–s), (d–q)

4. [A] (a–r, s), (b–q, s), (c–p, s), (d–p)
[B] (a—p, s), (b–r), (c–q), (d–p, s, q)
[C] (a–r, s), (b–p), (c–q, s), (d–q, s)
[D] (a–r), (b–s), (c–q), (d–p)
[E] (a–r), (b–q), (c–s), (d–p)
[F] (a–p, q, r), (b–r), (c–p, q), (d–s)

• PRACTICE PROBLEMS •

1. Calculate the degree of ionisation of 0.1 *M* acetic acid. The dissociation constant of acetic acid is 1.8×10^{-5}.
[Ans. $\alpha = 1.34 \times 10^{-2}$]

2. Calculate the concentration of OH^- ions of 0.01 *M* NH_4OH solution. The equilibrium constant of NH_4OH is 1.8×10^{-5}.
[Ans. 4.24×10^{-4} mol L^{-1}]

3. At 15° C, 0.05 *N* solution of a weak monobasic acid is 3.5% ionised. Calculate the ionisation constant of acid.
[Ans. 6.125×10^{-5}]

4. 0.02 *M* solution of NH_4OH is 3% dissociated. Calculate the dissociation constant of NH_4OH.
[Ans. 1.8×10^{-5}]

5. A solution contains 0.4 *M* CH_3COOH and 0.2 *M* CH_3COONa. Calculate the concentration of H^+ ions. The ionisation constant of acetic acid is 1.8×10^{-5}.
[Ans. 3.6×10^{-5} mol L^{-1}]

6. The dissociation constant of hydrocyanic acid (HCN) is 4×10^{-8}. Calculate the H^+ ion concentration of 0.01 *M* HCN solution.
[2×10^{-5} mol L^{-1}]

7. The degree of dissociation of a weak electrolyte in 0.1 *M* aqueous solution is 0.0114 at 298 K. Calculate the degree of dissociation of the same electrolyte at 298 K in 0.001 *M* solution.
[Ans. 0.114]

8. Calculate K_a for a dibasic acid if its concentration is 0.05 *N* and hydrogen ion concentration is 1×10^{-3} mol L^{-1}.
[Ans. 2×10^{-8}]
[Hint: Conc.= 0.025 *M*, $[H^+] = 2C \times \alpha = 1 \times 10^{-3}$,
i.e., $\alpha = 0.02$, $K_a = 4 \times C^2 \times \alpha^3$]

9. K_a for $HC_2H_3O_2$ is 1.8×10^{-5}. What concentration of the acid must be taken so that it is 1% dissociated?
[Ans. 0.18 mol L^{-1}]

10. Calculate the degree of ionisation and hydroxyl ion concentration in 0.2 *M* NH_3 solution. ($K_b = 1.85 \times 10^{-5}$ at 298 K)
[Ans. $\alpha = 0.962 \times 10^{-2}$, $[OH^-] = 1.924 \times 10^{-3}$ *M*]

11. The dissociation constant of acetic acid at 18° C is 1.8×10^{-5}. Calculate the pH of 0.1 *N* and 0.001 *N* solution of acetic acid.
[Ans. 2.873, 3.726]

12. Calculate the approximate pH of 0.1 *M* aqueous H_2S solution. K_1 and K_2 for H_2S are 1.0×10^{-7} and 1.3×10^{-13} respectively at 25° C.

[**Ans.** pH = 4]

[**Hint:** Second dissociation constant is very small. H^+ ion concentration mainly depends on the first dissociation constant.

$$H_2S \overset{K_1}{\rightleftharpoons} H^+ + HS^-]$$

13. The pH of a soft drink is 4.4. Calculate $[H_3O^+]$ and $[OH^-]$ of the drink.

[**Ans.** 3.98×10^{-5} mol L^{-1}, 2.5×10^{-10} mol L^{-1}]

14. Calculate the pH of a 0.001 *M* solution of $Sr(OH)_2$ assuming it to be completely ionised.

[**Ans.** 11.301]

[**Hint:** $Sr(OH)_2 \rightleftharpoons Sr^{2+} + 2OH^-$;

$[OH^-] = 2 \times 0.001 = 0.002$ *M*]

15. The value of K_w is 9.55×10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

[**Ans.** 6.51]

[**Hint:** $K_w = [H^+][OH^-]$, So, $[H^+] = \sqrt{K_w}$]

16. 9.8 g of H_2SO_4 is present in 500 mL of the solution. Calculate the pH of the solution.

[**Ans.** 0.3979]

17. The pH of a 0.1 *M* solution of an organic acid is 4.0. Calculate the dissociation constant of the acid.

[**Ans.** 1×10^{-7}]

18. Calculate $[H_3O^+]$, $[OH^-]$ and pH of 0.2 *M* solution of HCN. ($K_a = 7.2 \times 10^{-10}$)

[**Ans.** $[H_3O^+] = 1.2 \times 10^{-5}$ mol L^{-1}, $[OH^-] = 8.33 \times 10^{-10}$ mol L^{-1}, pH = 4.92]

19. Calculate pH of 0.002 *M* CH_3COOH if it is 2.3% ionised at this concentration.

[**Ans.** 4.34]

20. Calculate the pH of the solution obtained by mixing 150 mL of 0.2 *M* HCl and 150 mL of 0.1 *M* NaOH.

[**Ans.** 1.30]

21. pH of a 0.1 *M* HCN solution is 5.2. What is the value of K_a for the acid?

[**Ans.** 3.97×10^{-10}]

22. The pH of a solution of $B(OH)_2$ is 10.6. Calculate the solubility and solubility product of hydroxide.

[**Hint:** pOH = 3.4, $[OH^-] = 3.98 \times 10^{-4}$ mol L^{-1}

Solubility = $\frac{1}{2}[OH^-] = 1.99 \times 10^{-4}$ mol L^{-1}

$K_{sp} = [B^+][OH^-]^2 = 3.15 \times 10^{-11}$]

23. Calculate the pH of a solution:

(i) containing 2 g of sodium hydroxide in one litre;

(ii) made by mixing 50 mL of 0.01 *M* $Ba(OH)_2$ solution with 50 mL water.

[**Ans.** (i) pH = 12.7, (ii) pH = 12]

24. What happens to the pH of 500 mL of a solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 mL of 0.1 *M* sodium hydroxide is added?

[**Ans.** pH = 4.7447 and pH will increase]

25. What ratio of acetic acid to sodium acetate concentration is needed to achieve a buffer whose pH is 5.70? The dissociation constant of acetic acid is 1.8×10^{-5}.

[**Ans.** 1 : 9]

26. Find the concentration of H^+, HCO_3^- and CO_3^{2-} in a 0.01 *M* solution of carbonic acid if the pH of the solution is 4.18, $K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$.

[**Ans.** $[H^+] = 6.61 \times 10^{-5}$ *M*, $[HCO_3^-] = 6.73 \times 10^{-5}$ *M*,

$[CO_3^{2-}] = 4.78 \times 10^{-11}$ mol L^{-1}]

[**Hint.** $K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7}$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

$$[H^+] = 6.61 \times 10^{-5}\,M,\ [H_2CO_3] = 0.01\,M$$

$$[HCO_3^-] = 6.73 \times 10^{-5}\,M,\ [CO_3^{2-}] = 4.78 \times 10^{-11} \text{ mol } L^{-1}]$$

27. What will be the pH value of a solution of 500 mL containing 5 g acetic acid and 7.2 g of sodium acetate? $K_a = 1.8 \times 10^{-5}$ at 25° C.

[**Ans.** 4.82]

28. The concentration of HCN and NaCN in a solution is 0.01 *M* each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10}. **(IIT 1991)**

[**Ans.** $[H^+] = 7.2 \times 10^{-10}$ *M*; $[OH^-] = 1.4 \times 10^{-7}$ *M*]

[**Hint:** $\text{pH} = \log \dfrac{[\text{Salt}]}{[\text{Acid}]} - \log K_a = -\log [H^+]$]

29. A buffer solution of pH = 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1.0 *M* NH_4OH solution. ($K_b = 1.8 \times 10^{-5}$) **(MLNR 1991)**

[**Ans.** 1.8 mole]

30. Calculate the amount of $(NH_4)_2SO_4$ which must be added to 500 mL of 0.200 *M* NH_3 to yield a solution of pH 9.35. (K_b for $NH_3 = 1.78 \times 10^{-5}$) **(MLNR 1992)**

[**Ans.** 10.494 g]

31. Calculate the pH of the buffer containing 1.0 mol L^{-1} of weak acid H*A* and 0.1 mol L^{-1} of its sodium salt Na*A* assuming K_a to be 10^{-6}. **(Dhanbad 1993)**

[**Ans.** pH = 5]

32. Calculate K_b for a base whose 0.1 *M* solution has pH of 10.5.

[**Ans.** 10^{-6}]

33. What is the maximum pH of a solution 0.10 *M* in Mg^{2+} from which $Mg(OH)_2$ will not precipitate? Given, $K_{sp}[Mg(OH)_2] = 1.2 \times 10^{-11}$.

[**Ans.** pH = 9.4]

34. A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be the pH of the resulting solution?

[**Ans.** pH = 6.9586]

[**Hint:** pH = 5, $[H^+] = 10^{-5}\,M$. After dilution $= \frac{10^{-5}}{1000} = 10^{-8}\,M$

$$[H^+] = 10^{-8} + 10^{-7}$$
$$= 1.1 \times 10^{-7}$$
$$pH = -\log[H^+] = -\log 1.1 \times 10^{-7} = 6.9586]$$

35. Calculate the pH of the solution obtained by mixing 10 mL of 0.1 M HCl and 40 mL of 0.2 M H_2SO_4.

[**Ans.** pH = 0.4685]

[**Hint:** $[H^+] = \frac{10 \times 0.1 + 40 \times 0.4}{50} = 0.34]$

36. The degree of dissociation of a weak electrolyte in 0.1 M aqueous solution is 0.0114 at 298 K. Calculate the degree of dissociation of the same electrolyte at 298 K in 0.001 M solution.

[**Ans.** 0.114]

[**Hint:** α is proportional to $\sqrt{\frac{1}{C}}$.

$$\frac{\alpha}{\alpha'} = \sqrt{\frac{C'}{C}} = \sqrt{\frac{0.001}{0.1}} = 0.1$$
$$\alpha' = \frac{\alpha}{0.1} = \frac{0.0114}{0.1} = 0.114\,]$$

37. The degree of dissociation of water is 1.8×10^{-9} at 298 K. Calculate the ionisation constant and ionic product of water at 298 K.

[**Hint:** $H_2O \rightleftharpoons H^+ + OH^-$, $[H_2O] = \frac{1000}{18} = 55.56\ \text{mol L}^{-1}$,

$$[H^+] = [OH^-] = C \times \alpha = 55.56 \times 1.8 \times 10^{-9}$$
$$K_a = \frac{[H^+][OH^-]}{[H_2O]} = \frac{55.56 \times 1.8 \times 10^{-9} \times 55.56 \times 1.8 \times 10^{-9}}{55.56}$$
$$= 1.8 \times 10^{-16}$$
$$K_w = [H^+][OH^-] = (55.56 \times 1.8 \times 10^{-9})^2 = 1 \times 10^{-14}\,]$$

38. One litre of a buffer solution is prepared by dissolving 0.6 mole of NH_3 and 0.4 mole of NH_4Cl. What is the pH of the solution? For NH_3, $K_b = 1.8 \times 10^{-5}$.

(i) What is the pH of the buffer after addition of 0.1 mole of HCl?

(ii) What is the pH of the buffer after addition of 0.1 mole of NaOH?

[**Ans.** 9.4314 (i) 9.2553 (ii) 9.6233]

39. One litre of a buffer contains 40 g of NH_4Cl and 20 g of NH_3. Calculate the pH of the solution. $K_b(NH_3) = 1.8 \times 10^{-5}$ at 298 K.

[**Ans.** 9.452]

40. A buffer solution is prepared by mixing 50 mL of 0.5 molar ammonia solution, 40 mL of 0.4 molar NH_4Cl solution and 10 mL of distilled water. Calculate the pH of the buffer. $K_b(NH_3) = 1.8 \times 10^{-8}$ at 298 K.

[**Ans.** 9.45]

[**Hint:** Total volume = 50 + 40 + 10 = 100 mL

$$\text{Molarity of } NH_3 = \frac{0.5 \times 50}{100} = 0.25;$$
$$\text{Molarity of } NH_4Cl = \frac{0.4 \times 40}{100} = 0.16]$$

41. pK_a value of acetic acid is 4.76 at room temperature. How will you obtain buffers of 4.40 and 5.40 pH values from acetic acid and sodium acetate?

[**Ans.** $\frac{\text{Acetate}}{\text{Acid}} = 0.4365$ and $\frac{\text{Acetate}}{\text{Acid}} = 4.364]$

42. Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre and of the other solution containing 1 mole of CH_3COONa + 1 mole of CH_3COOH per litre.

[**Hint:** 1st case: $CH_3COONa + HCl \longrightarrow \underset{\text{1 mole}}{CH_3COOH} + NaCl$

$$pH_1 = -\frac{1}{2}\log K_a$$

2nd case: $pH_2 = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = -\log K_a$

$$\frac{pH_1}{pH_2} = \frac{1}{2}\,]$$

43. Calculate the composition of an acidic buffer solution $(HA + NaA)$ of total molarity 0.29 having pH = 4.4 and $K_a = 1.8 \times 10^{-5}$.

[**Ans.** [Salt] = 0.09 M; [Acid] = 0.20 M]

[**Hint:** $pH = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$

$$= -\log K_a + \log\frac{a}{(0.29 - a)}\,]$$

44. Calculate the pH of a solution obtained by mixing 100 mL of an acid of pH = 3 and 400 mL solution of pH = 1.

[**Ans.** 1.096]

45. The solubility product of AgCl in water is 1.5×10^{-10}. Calculate its solubility in 0.01 M NaCl aqueous solution. (IIT 1995)

[**Ans.** 1.5×10^{-8} mol L^{-1}]

46. Calculate the pH of a 0.02 M aqueous solution of NH_4Cl? Given, $pK_{NH_4OH} = 4.73$.

[**Ans.** 3.78]

47. Determine the pH value of 0.1 M aqueous solution of ammonium cyanide ($pK_a = 9.04$, $pK_b = 4.73$).

[**Ans.** 9.15]

48. Calculate the pH of a 0.2 M solution of strychnine hydrochloride. ($K_b = 1 \times 10^{-7}$)

[**Ans.** 3.8494]

49. The dissociation constants of acetic acid and aniline are 1.8×10^{-5} and 4.2×10^{-10} respectively. What is the degree of hydrolysis of aqueous aniline acetate? What is the pH of the solution?

[**Ans.** 0.5348, pH = 4.684]

50. A weak acid HA after treatment with 12 mL of 0.1 M strong base has a pH of 5. At the end point, the volume of the same base required is 26.6 mL. Calculate the K_a of the acid.

[**Ans.** 8.219×10^{-6}]

[**Hint:** Applying $\underset{\text{Acid}}{M_1V_1} = \underset{\text{Base}}{M_2V_2}$

$$= 26.6 \times 0.1$$

$$= 2.66 \text{ meq.}$$

$$\begin{array}{lcccc} & HA & + BOH & \rightleftharpoons BA & + H_2O \\ & 2.66 & 1.2 & 0 & 0 \\ \text{After the reaction} & 1.46 & 0 & 1.2 & 1.2 \end{array}$$

Applying Henderson's equation,

$$pH = \log \frac{[\text{Salt}]}{[\text{Acid}]} - pK_a \text{]}$$

51. K_a for HCN is 1.4×10^{-9}. Calculate for 0.01 N KCN solution:

(a) degree of hydrolysis

(b) $[OH^-]$ and $[CN^-]$

(c) pH

[**Ans.** (a) 2.67×10^{-2} (b) 2.67×10^{-4}, 9.73×10^{-3} (c) 10.4265]

52. What is the H^+ ion concentration in ammonium acetate solution?

$K_a = 1.8 \times 10^{-5}$, $K_b = 1.8 \times 10^{-5}$ and $K_w = 1.0 \times 10^{-14}$

[**Ans.** 1.0×10^{-7}]

53. A 40 mL sample of 0.1 M solution of nitric acid is added to 20 mL of 0.3 M aqueous ammonia. What is the pH of the resulting solution? Given, K_b for ammonia $= 1.8 \times 10^{-5}$.

[**Ans.** 8.95]

54. Calculate the pH of 0.1 M solution of NH_4OCN. K_b for NH_3 is 1.75×10^{-5} and K_a for HOCN is 3.3×10^{-4}.

[**Ans.** 6.36]

55. Which of the two solutions 0.1 M HCN ($K_a = 4 \times 10^{-10}$) and 0.1 M HF ($K_a = 6.7 \times 10^{-4}$) will have greater degree of ionisation and to what extent?

[**Ans.** HF will have greater degree of dissociation.

$$\frac{\alpha\,(\text{HF})}{\alpha\,(\text{HCN})} = 1294\text{]}$$

56. Calculate the pH of a solution prepared by mixing 100.0 mL of 0.4 M HCl with 100.0 mL of 0.4 M NH_3. Hydrolysis constant of ammonium chloride is 5.6×10^{-10}.

[**Ans.** pH = 4.96]

57. Calculate the per cent hydrolysis in 0.003 M aqueous solution of NaOCN.

(K_a for HOCN $= 3.33 \times 10^{-4}$ M) (IIT 1996)

[**Ans.** 0.01%]

58. What is the $[OH^-]$ in a 0.01 M solution of aniline hydrochloride? K_b for aniline is 4.0×10^{-10}.

[**Ans.** 2.0×10^{-11} M]

[**Hint:** $\underset{(0.01-x)}{C_6H_5NH_3^+} + H_2O \rightleftharpoons \underset{x}{C_6H_5NH_2} + \underset{x}{H_3O^+}$]

59. Calculate the pH of 1.0×10^{-3} M sodium phenolate $NaOC_6H_5$. K_a for C_6H_5OH is 1×10^{-10}.

[**Ans.** pH = 10.43]

[**Hint:** $\underset{(0.001-x)}{C_6H_5O^-} + H_2O \rightleftharpoons \underset{x}{C_6H_5OH} + \underset{x}{OH^-}$

$$K_h = \frac{K_w}{K_a} = 1 \times 10^{-4} = \frac{x^2}{(0.001 - x)}$$

$$x^2 + 1 \times 10^{-4}x - 1 \times 10^{-7} = 0, x = 2.7 \times 10^{-4}, pOH = 3.57]$$

60. The dissociation constants of *m*-nitrobenzoic acid and acetic acid are 36.0×10^{-5} and 1.8×10^{-5} respectively. What are their relative strengths?

[**Ans.** 4.47 : 1]

61. Calculate the degree of hydrolysis of 0.10 solution of KCN. Dissociation constant of HCN $= 7.2 \times 10^{-10}$ at 25° C and $K_w = 1.0 \times 10^{-14}$.

[**Ans.** 1.18×10^{-2}]

62. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M?

(K_a for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$ M) (IIT 1996)

[**Ans.** 0.01 M]

63. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. (IIT 1996)

[**Ans.** pH = 11.5]

64. Calculate the pH of an aqueous solution of 1 M ammonium formate, assuming complete dissociation.

($pK_a = 3.8$, $pK_b = 4.8$) (IIT 1995)

[**Ans.** 6.5]

[**Hint:** Use; $pH = \frac{1}{2}[pK_w - pK_b + pK_a]$]

65. Calculate the hydrolysis constant of the salt containing NO_2^- ions. Given, K_a for $HNO_2 = 4.5 \times 10^{-10}$. (MLNR 1996)

[**Ans.** 2.2×10^{-5}]

66. Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride $[C_6H_5NH_3]Cl$, a salt of aniline and HCl. Calculate the pH of 0.233 M solution of aniline.

[K_b = (aniline) $= 4.6 \times 10^{-10}$]

[**Ans.** 2.64]

67. Calculate the pH of a 0.1 M solution of $AlCl_3$ that dissolves to give hydrated aluminium ion $[Al(H_2O)_6]^{3+}$ in solution. ($K_a = 1.4 \times 10^{-5}$)

[**Ans.** 2.92]

[**Hint:** Consider the equilibrium:

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons H_3O^+ + [Al(H_2O)_5(OH)]^{2+}\text{]}$$

68. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH, when total concentration of buffering reagents is 0.6 mol litre^{-1}, pK_b for $NH_3 = 4.7$, $\log_{10} 2 = 0.30$. (IIT 1997)

[**Ans.** [Salt] = 0.4 M, [Base] = 0.2 M]

69. The solubility product of AgCl in water is 1.5×10^{-10} at 18° C. Calculate its solubility at the same temperature.

[**Ans.** 1.75×10^{-3} g L^{-1}]

70. The solubility product of AgBr is 4×10^{-13} and the concentration of Ag^+ ions in it is 1×10^{-6} mol L^{-1}. What is concentration of Br^- ions?
[**Ans.** 4×10^{-7} mol L^{-1}]

71. A sample of hard water contains 0.005 mole of $CaCl_2$ per litre. What is the minimum concentration of Na_2SO_4 which must be exceeded for removing calcium ions from this water solution? The solubility product of $CaSO_4$ is 2.4×10^{-5}.
[**Ans.** 4.8×10^{-3} mol L^{-1}]

72. Solubility of AgCl at 20° C is 1.435×10^{-5} g L^{-1}. Calculate the solubility product of AgCl.
[**Ans.** 1×10^{-14}]

73. Given, that the solubility product of radium sulphate ($RaSO_4$) is 4×10^{-11}. Calculate its solubility in:
(a) pure water.
(b) 0.10 *M* Na_2SO_4. **(Dhanbad 1992)**
[**Ans.** (a) 6.32×10^{-6} mol L^{-1} (b) 4×10^{-10} mol L^{-1}]

74. Calculate the solubility of AgCl in 0.20 *M* $AgNO_3$. K_{sp} AgCl is 1×10^{-10}.
[**Ans.** 5×10^{-10} mol L^{-1}]

75. The values of K_{sp} for sparingly soluble *AB* and MB_2 are each equal to 4.0×10^{-18}. Which salt is more soluble?
[**Ans.** Solubility $AB = 2 \times 10^{-9}$; Solubility $MB_2 = 1.0 \times 10^{-6}$; MB_2 is more soluble]

76. The solubility of $CaSO_4$ at 25° C is 2.036 g L^{-1} and degree of dissociation of the saturated solution at this temperature is 52.25%. Compute K_{sp} for $CaSO_4$. (Mol. mass of $CaSO_4$ = 136)
[**Ans.** 6.12×10^{-5}]

77. The concentration of the Ag^+ ion in a saturated solution of Ag_2CrO_4 at 20° C is 1.5×10^{-4} mol L^{-1}. Compute the solubility product constant of Ag_2CrO_4 at 20° C.
[**Ans.** 1.7×10^{-12}]

78. K_{sp} AgCl is 2.8×10^{-10} at 25° C. Calculate the solubility of AgCl in (a) pure water (b) 0.1 *M* $AgNO_3$ (c) 0.1 *M* KCl and (d) 0.1 *M* KNO_3. **(MLNR 1994)**
[**Ans.** (a) 1.673×10^{-3} mol L^{-1} (b) 2.8×10^{-9} mol L^{-1} (c) 2.8×10^{-9} mol L^{-1} (d) No common ion is present, so treat it like water 2.8×10^{-9} mol L^{-1}]

79. A solution is saturated with respect to strontium fluoride and strontium carbonate. The fluoride ion concentration in the solution is found to be 3.7×10^{-2} mol L^{-1}. What is the value of $[CO_3^{2-}]$?
K_{sp} $SrF_2 = 7.9 \times 10^{-10}$ and K_{sp} $SrCO_3 = 7.0 \times 10^{-10}$
[**Ans.** 1.2×10^{-3} mol L^{-1}]
[**Hint:** $\frac{K_{sp}\ SrCO_3}{K_{sp}\ SrF_2} = \frac{[Sr^{2+}][CO_3^{2-}]}{[Sr^{2+}][F^-]^2} = \frac{[CO_3^{2-}]}{[F^-]^2}$]

80. A solution contains 0.01 mol L^{-1} of each Pb^{2+} and Zn^{2+} ions. The solution is saturated with H_2S when $[S^{2-}]$ is 1.0×10^{-14} mol L^{-1}. Predict which one of the two ions will be precipitated from the solution? K_{sp} PbS = 2.4×10^{-27} and K_{sp} ZnS = 1.0×10^{-21}.
[**Ans.** Both the ions will be precipitated as ionic products exceed the solubility products of both the sulphides.]

81. An acid type indicator, HIn, differs in colour from its conjugate base In^-. The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in pH of solution to observe a complete colour change? $(K_a = 10^{-5})$ **(IIT 1997)**
[**Ans.** 2]
[**Hint:** For calculation of pH we can use following relation:

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

(i) $pH = 5 + \log_{10} 10 = 6$
(ii) $pH = 5 + \log_{10} 0.1 = 4$
Thus, minimum pH change will be 2.]

82. A sample of AgCl was treated with 5 mL of 1.5 *M* Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g Cl^- per litre. Calculate the solubility product of AgCl. (K_{sp} $Ag_2CO_3 = 8.2 \times 10^{-12}$) **(IIT 1997)**
[**Ans.** K_{sp} AgCl = 1.71×10^{-10}]

83. Calculate the simultaneous solubility of CaF_2 and SrF_2. K_{sp} for the two salts are 4×10^{-11} and 2.8×10^{-9} respectively.
[**Ans.** 1.25×10^{-5} and 8.75×10^{-4}]

84. The solubility product of $Fe(OH)_3$ is 1×10^{-36}. What is the minimum concentration of OH^- ions required to precipitate $Fe(OH)_3$ from 0.001 *M* solution of $FeCl_3$?
[**Ans.** 1×10^{-11} mol L^{-1}]

85. The solubility product of AgCl is 1.5×10^{-10}. Predict whether there will be any precipitation by mixing 50 mL of 0.01 *M* NaCl and 50 mL of 0.01 *M* $AgNO_3$ solution.
[**Ans.** Since, ionic product (2.5×10^{-5}) is greater than solubility product, precipitation will occur.]

86. A solution containing 0.1 *M* Zn^{2+} and 0.01 *M* Cu^{2+} is saturated with H_2S. The S^{2-} concentration is 8.1×10^{-31} *M*. Will ZnS or CuS precipitate?
K_{sp}ZnS = 3.0×10^{-23} and K_{sp}CuS = 8.0×10^{-34}
[**Ans.** CuS precipitates]

87. The precipitate of M_2S_3 is obtained on mixing equal volumes of solutions S_1 having $[M^{3+}] = 4 \times 10^{-5}$ *M* and S_2 having $[S^{2-}] = 2 \times 10^{-3}$ *M*. Calculate its solubility product.
[**Ans.** 4×10^{-17}]
[**Hint:** Let 1 litre of both S_1 and S_2 be mixed; then their concentration in mixture will become half $(M_1V_1 = M_2V_2)$.

$$[M^{3+}] = 2 \times 10^{-4}\ M; [S^{2-}] = 1 \times 10^{-3}$$

$$K_{sp}M_2S_3 = [M^{3+}]^2[S^{2-}]^3$$

$$= [2 \times 10^{-4}]^2[1 \times 10^{-3}]^3 = 4 \times 10^{-17}\ M^5]$$

88. Solubility products (K_{sp}) of two salts *AB* and A_2C are same where, '*A*' is mono cation and *B* and *C* are anions. Calculate the ratio of their solubilities.
[**Ans.** $(16\ K_{sp})^{1/3}$]

[**Hint:** Use; $K_{sp}\ AB = x^2$

$K_{sp}\ A_2C = 4y^3$]

89. Calculate the pH of a solution having 0.1 *M* formic acid and 0.2 *M* HCl. Also find the concentration of all the anions present in the solution.

[**Ans.** pH = 0.6989, $[\text{OH}^-] = 5\times10^{-14}$]

90. Calculate the accurate pH of 5×10^{-3} *M* formic acid solution. K_a (HCOOH) = 2×10^{-4}.

[**Ans.** pH = 3.043]

[**Hint:** Use the quadratic equation:

$$[\text{H}^+]^2 + K_a[\text{H}^+] - CK_a = 0$$

$$[\text{H}^+] = \frac{-K_a + \sqrt{K_a^2 + 4CK_a}}{2} = 9.05\times10^{-4}$$

(On substituting the values of C and K_a)

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$= -\log_{10}[9.05\times10^{-4}]$$

$$= 3.043]$$

91. Calculate the accurate pH of 5×10^{-6} *M* pyridine solution. K_b(pyridine) = 1.5×10^{-9}.

[**Ans.** 7.1215]

[**Hint:** Use; $[\text{OH}^-]^2 = CK_b + K_w$

$$[\text{OH}^-] = \sqrt{5\times10^{-6}\times1.5\times10^{-9} + 10^{-14}}$$

$$= \sqrt{1.75\times10^{-14}}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log\sqrt{1.75\times10^{-14}} = 6.8785$$

$$\text{pH} = 7.1215]$$

92. Ionic product of water (K_w) at two different temperatures 25°C and 50°C are 1.08×10^{-14} and 5.474×10^{-14} respectively. Assuming ΔH of any reaction to be independent of temperature, calculate enthalpy of neutralisation of strong acid with strong base.

[**Ans.** 12.5 kcal]

[**Hint:** Use $\log\dfrac{K_{w_2}}{K_{w_1}} = \dfrac{\Delta H}{2.303\,R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$]

93. The solubility product of PbI_2 is 7.47×10^{-9} at 15°C and 1.39×10^{-8} at 25°C. Calculate the molar heat of solution of PbI_2.

[**Ans.** 44.318 kJ/mol]

[**Hint:** $\log\dfrac{(K_{sp})_2}{(K_{sp})_1} = \dfrac{\Delta H}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$$\log\frac{[1.39\times10^{-8}]}{[7.47\times10^{-9}]} = \frac{\Delta H}{2.303\times8.314}\left(\frac{1}{288} - \frac{1}{298}\right)$$

$$\Delta H = 44318.4\ \text{J} = 44.318\ \text{kJ/mol}]$$

94. Given, a solution of acetic acid. How many times of the acid concentration, acetate salt should be added to obtain a solution with pH = 7?

K_a for dissociation of $\text{CH}_3\text{COOH} = 1.8\times10^{-5}$.

[BCECE (Mains) 2007]

[**Ans.** 1.799×10^2]

OBJECTIVE QUESTIONS

Set–1: Questions with single correct answer

1. A certain weak acid has a dissociation constant of 1×10^{-4}. The equilibrium for its reaction with a strong base is:

(a) 1×10^{-4} (b) 1×10^{-10} (c) 1×10^{10} (d) 1×10^{14}

[**Hint:** $K_h = \dfrac{K_w}{K_a} = \dfrac{1\times10^{-14}}{1\times10^{-4}} = 1\times10^{-10}$;

$$K_{eq} = \frac{1}{K_h} = 1\times10^{10}]$$

2. Which one of the following formulae represents Ostwald's dilution law for a binary electrolyte whose degree of dissociation is 'α' and concentration C?

(a) $K = \dfrac{(1-\alpha)C}{\alpha}$ (b) $K = \dfrac{\alpha^2 C}{(1-\alpha)}$

(c) $K = \dfrac{(1-\alpha)C}{\alpha^2}$ (d) $K = \dfrac{\alpha^2}{(1-\alpha)C}$

3. Which of the following is the correct quadratic form of the Ostwald's dilution law equation? **[CET (J& 2009]**

(a) $\alpha^2C + \alpha K - K = 0$ (b) $\alpha^2C - \alpha K - K = 0$

(c) $\alpha^2C - \alpha K + K = 0$ (d) $\alpha^2C + \alpha K + K = 0$

[**Hint:** According to Ostwald's dilution law :

$$K = \frac{C\alpha^2}{1-\alpha}$$

or $C\alpha^2 + K\alpha - K = 0$]

4. A monoprotic acid in 1.00 *M* solution is 0.001% ionised. The dissociation constant of acid is:

(a) 1.0×10^{-3} (b) 1.0×10^{-6}

(c) 1.0×10^{-8} (d) 1.0×10^{-10}

5. Formic acid is 4.5% dissociated in a 0.1 *N* solution at 20°C. The ionisation constant of formic acid is:

(a) 21×10^{-4} (b) 21

(c) 0.21×10^{-4} (d) 2.1×10^{-4}

6. The fraction of total molecules which is ionised in a solution of an electrolyte is known as:

(a) molecular velocity

(b) order of reaction

(c) degree of ionisation

(d) mole fraction of the electrolyte

97. One litre of water contains 10^{-7} mole of H^+ ions. Degree of ionisation of water is:
(a) $1.8 \times 10^{-7}\%$ (b) $0.8 \times 10^{-9}\%$
(c) $3.6 \times 10^{-9}\%$ (d) $3.6 \times 10^{-7}\%$
[**Hint:** Since, 1 litre of water contains 1000/18 mole, degree of ionisation $= 10^{-7} / \frac{1000}{18}$]

98. The degree of dissociation in a weak electrolyte increases:
(a) on increasing pressure (b) on decreasing dilution
(c) on increasing dilution (d) on increasing concentration

99. Which of the following is the weakest base?
(a) NaOH (b) $Ca(OH)_2$
(c) NH_4OH (d) KOH

100. Acetic acid is a weak electrolyte because:
(a) its molecular mass is high
(b) it is a covalent compound
(c) it is highly unstable
(d) it does not dissociate much or its ionisation is very small

101. When NH_4Cl is added to NH_4OH solution, the dissociation of ammonium hydroxide is reduced. It is due to: [PMT (MP) 1993]
(a) common ion effect (b) hydrolysis
(c) oxidation (d) reduction

102. The addition of HCl will not suppress the ionisation of: [PMT (MP) 1993]
(a) acetic acid (b) sulphuric acid
(c) H_2S (d) benzoic acid

103. H_2S in presence of HCl precipitates second group radicals but not fourth group radicals because:
(a) HCl activates H_2S
(b) HCl decreases concentration of sulphide ions
(c) HCl increases concentration of sulphide ions
(d) sulphides of IV group are unstable in HCl

104. The solubility product of a salt *AB* is 1×10^{-8}. In a solution, in which concentration of *A* is 10^{-3} *M*, *AB* will precipitate when the concentration of *B* will be: [PET (MP) 1990]
(a) 10^{-7} *M* (b) 10^{-4} *M* (c) 10^{-5} *M* (d) 10^{-6} *M*

105. The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 *M* Ba^{2+} ions solution will start on adding H_2SO_4 of concentration:
(a) 10^{-9} *M* (b) 10^{-8} *M*
(c) 10^{-7} *M* (d) 10^{-6} *M*

106. Solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility would be: [UGET (Manipal) 2006]
(a) 1×10^{-27} (b) 1×10^{-3} (c) 1×10^{-7} (d) 1×10^{-2}

107. Which pair will show common ion effect? [PMT (MP) 1990]
(a) $BaCl_2 + Ba(NO_3)_2$ (b) NaCl + HCl
(c) $NH_4OH + NH_4Cl$ (d) AgCN + KCN

108. What is the correct representation of solubility product of Ag_2CrO_4?
(a) $[Ag^+]^2[CrO_4^{2-}]$ (b) $[Ag^+][CrO_4^{2-}]$
(c) $[2Ag^+][CrO_4^{2-}]$ (d) $[2Ag^+]^2[CrO_4^{2-}]$

109. Solubility product of silver bromide 5×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is : (AIEEE 2010)
(a) 6.2×10^{-5} g (b) 5.0×10^{-8} g
(c) 1.2×10^{-10} g (d) 1.2×10^{-9} g

110. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with: [AMU (PMT) 2009]
(a) 10^{-4} *M* $Ag^+ + 10^{-4}$ *M* Cl^-
(b) 10^{-5} *M* $Ag^+ + 10^{-5}$ *M* Cl^-
(c) 10^{-6} *M* $Ag^+ + 10^{-6}$ *M* Cl^-
(d) 10^{-10} *M* $Ag^+ + 10^{-10}$ *M* Cl^-

111. Buffering action of a mixture of CH_3COOH and CH_3COONa is maximum when the ratio of salt to acid is equal to:
(a) 1.0 (b) 100.0 (c) 10.0 (d) 0.1

112. Which hydroxide will have lowest value of solubility product at normal temperature (25°C)? (IIT 1990)
(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

113. The solubility of $Al(OH)_3$ is '*S*' g mol L^{-1}. Its solubility product is:
(a) S^2 (b) S^3 (c) $27S^4$ (d) $27S^3$

114. The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14} at room temperature. If the solution contains Al^{3+} and Zn^{2+} ions, the ion first precipitated by adding NH_4OH is:
(a) Al^{3+} (b) Zn^{2+}
(c) both (d) none of these

115. The solubility product of $CaSO_4$ is 2.4×10^{-5}. When 100 mL of 0.01 *M* $CaCl_2$ and 100 mL of 0.02 *M* Na_2SO_4 are mixed, then:
(a) Na_2SO_4 will precipitate (b) both will precipitate
(c) $CaSO_4$ will precipitate (d) none will precipitate

116. The solubility of AgCl in a solution of common salt is lower than in water. This is due to:
(a) salt effect (b) lowering of solubility effect
(c) common ion effect (d) complex formation

117. The solubility products of AgCl and AgI are 1.1×10^{-10} and 1.6×10^{-16} respectively. If $AgNO_3$ is added drop by drop to the solution containing both chloride and iodide ions, the salt precipitated first is:
(a) AgI (b) $AgNO_3$
(c) AgCl (d) both AgI and AgCl

118. Why is pure NaCl precipitated when HCl gas is passed in saturated solution of NaCl? [PET (MP) 1993]
(a) Impurities dissolve in HCl
(b) The value of $[Na^+]$ and $[Cl^-]$ product becomes smaller than K_{sp} of NaCl
(c) The value of $[Na^+]$ and $[Cl^-]$ product becomes higher than K_{sp} of NaCl
(d) HCl dissolves in water

119. On passing a current of HCl gas in saturated solution of NaCl, the solubility of NaCl:

(a) increases (b) decreases
(c) remains unchanged (d) NaCl decomposes

30. In a saturated solution of electrolytes, the ionic products of their concentration are constant at a particular temperature. This constant for an electrolyte is known as:
(a) ionic product (b) ionisation constant
(c) dissociation constant (d) solubility product

31. On addition of ammonium chloride to a solution of NH_4OH:
(a) dissociation of NH_4OH increases
(b) concentration of OH^- decreases
(c) concentration of OH^- increases
(d) concentration of both NH_4^+ and OH^- increases

32. The solubility product of a salt A_2B is 4×10^{-9}. Its solubility would be: [IIT 1990]
(a) 4×10^{-2} *M* (b) 2×10^{-4} *M*
(c) 1×10^{-4} *M* (d) 1×10^{-3} *M*

33. If the concentration of CrO_4^{2-} ions in a saturated solution of silver chromate is 2×10^{-4}, solubility product of silver chromate will be: [PET (MP) 1992]
(a) 4×10^{-8} (b) 8×10^{-12}
(c) 16×10^{-12} (d) 32×10^{-12}

34. 50% neutralisation of a solution of formic acid ($K_a = 2 \times 10^{-4}$) with NaOH would result in a solution having a hydrogen ion concentration of:
(a) 2×10^{-4} (b) 3.7 (c) 2.7 (d) 1.85

35. The solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility in mol L^{-1} would be:
(a) 1×10^{-3} (b) 1×10^{-9}
(c) 4×10^{-27} (d) 1×10^{-27}

36. Addition of conc. HCl to saturated $BaCl_2$ solution precipitate $BaCl_2$ because: [BHU (Screening) 2010]
(a) at constant temperature the product $[Ba^{2+}][Cl^-]^2$ remains constant in a saturated solution
(b) ionic product of $[Ba^{2+}][Cl^-]$ remains constant in a saturated solution
(c) of common ion effect
(d) it follows Le-Chatelier's principle

37. How many grams of CaC_2O_4 will dissolve in distilled water to make one litre of saturated solution? ($K_{sp} = 2.5 \times 10^{-9}$ and its molecular mass is 128) [PMT (MP) 1993]
(a) 0.0064 g (b) 0.0128 g (c) 0.0032 g (d) 0.0640 g

38. On the addition of a solution containing CrO_4^{2-} ions to the solution of Ba^{2+}, Sr^{2+} and Ca^{2+} ions, the precipitate obtained first will be of: [PET (MP) 1993]
(a) $CaCrO_4$ (b) $SrCrO_4$
(c) $BaCrO_4$ (d) a mixture of all the three

39. Ostwald's dilution law is applicable in the case of the solution of:
(a) NaCl (b) NaOH (c) H_2SO_4 (d) CH_3COOH

40. What will be the solubility of AgCl in a 0.1 *M* NaCl solution? (K_{sp} AgCl $= 1.20 \times 10^{-10}$) [PMT (MP) 1992]
(a) 0.1 *M* (b) 1.2×10^{-4} *M*
(c) 1.2×10^{-9} *M* (d) 1.2×10^{-10} *M*

41. Which of the following metal sulphides has maximum solubility in water?
(a) CdS ($K_{sp} = 36 \times 10^{-30}$) (b) FeS ($K_{sp} = 11 \times 10^{-20}$)
(c) HgS ($K_{sp} = 32 \times 10^{-54}$) (d) ZnS ($K_{sp} = 11 \times 10^{-22}$)

42. The ionisation constant of acetic acid is 1.8×10^{-5}. The concentration at which it will be dissociated to 2%, is:
(a) 1 *M* (b) 0.045 *M* (c) 0.018 *M* (d) 0.45 *M*

43. The solubility of $PbSO_4$ in 0.01 *M* Na_2SO_4 solution is: (K_{sp} for $PbSO_4 = 1.25 \times 10^{-9}$)
(a) 1.25×10^{-7} mol L^{-1} (b) 1.25×10^{-9} mol L^{-1}
(c) 1.25×10^{-10} mol L^{-1} (d) 1.25×10^{-18} mol L^{-1}

44. The value of K_{sp} for $HgCl_2$ is 4×10^{-15}. The concentration of Cl^- ion in its aqueous solution at saturation point is:
(a) 1×10^{-5} *M* (b) 4×10^{-15} *M*
(c) 8×10^{-15} *M* (d) 2×10^{-5} *M*

45. If the solubility of $PbBr_2$ is '*S*' gram mol per litre, considering 80% ionisation, its ionic product is:
(a) $2S^3$ (b) $4S^2$ (c) $4S^3$ (d) $2S^4$

46. If the solubility of M_3N_2 is '*S*' g mol L^{-1}, its solubility product is:
(a) $2S^3$ (b) $8S^4$ (c) $108S^5$ (d) $27S^3$

47. At 30 °C, the solubility of Ag_2CO_3 ($K_{sp} = 8 \times 10^{-12}$) would be greatest in one litre of:
(a) 0.05 *M* Na_2CO_3 (b) 0.05 *M* $AgNO_3$
(c) pure water (d) 0.05 *M* NH_3

48. The following equilibrium exists in aqueous solution;

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

If dilute HCl is added:
(a) the equilibrium constant will increase
(b) the equilibrium constant will decrease
(c) acetate ion concentration will increase
(d) acetate ion concentration will decrease

49. According to Arrhenius concept, base is a substance that:
(a) gives H^+ ions in solution
(b) gives OH^- ions in solution
(c) accepts electrons
(d) donates electrons

50. According to Bronsted-Lowry concept an acid is a substance which:
(a) accepts proton (b) gives an electron pair
(c) gives proton (d) combines with H_3O^+ ions

51. According to Lewis concept, a base is a substance which:
(a) donates an electron pair (b) accepts an electron pair
(c) produces hydronium ions (d) combines with OH^- ions

52. The strength of the acid depends on the:
(a) number of hydrogen atoms present in the molecule
(b) oxygen content
(c) density
(d) concentration of hydrogen ions furnished by ionisation

53. Cl^- ion is the conjugate base of:
(a) HCl (b) HOCl (c) $HClO_3$ (d) $HClO_4$

54. Which one of the following is the strongest acid?
(a) CH_3COOH (b) $CH_2ClCOOH$
(c) $CHCl_2COOH$ (d) CCl_3COOH

55. Number of H^+ ions present in 250 mL of lemon juice of pH = 3 is: **[PMT (Kerala) 2008]**
(a) 1.506×10^{22} (b) 1.506×10^{23}
(c) 1.506×10^{20} (d) 3.012×10^{21}
(e) 2.008×10^{23}
[**Hint:** $[H^+] = 10^{-3}\,M$

$$\text{Number of moles of } H^+ \text{ ions in 250 mL} = \frac{10^{-3}}{4} \times 6.023 \times 10^{23}$$
$$= 1.506 \times 10^{20}\,]$$

56. Conjugate acid of OH^- base is:
(a) H_2 (b) H_2O (c) H^+ (d) H_3O^+

57. Which among the following qualifies as a Lewis acid?
(a) NaF (b) NaCl (c) BF_3 (d) $MgCl_2$

58. Which of the following will qualify as Lewis base?
(a) BCl_3 (b) CH_4 (c) Cl_2 (d) NH_3

59. NH_4^+ ion in an aqueous solution will behave as:
(a) a base (b) an acid
(c) both acid and base (d) neutral

60. In the dissociation of bicarbonate ion, the conjugate base involved is:
(a) CO_3^{2-} (b) CO_2 (c) H_2CO_3 (d) CO

61. Which one of the following is an acidic salt?
(a) $NaHSO_4$ (b) Na_2SO_4 (c) Na_2SO_3 (d) Na_2SO_4

62. The conjugate acid of NH_2^- is:
(a) NH_4^+ (b) NH_3 (c) NH_2OH (d) N_2H_4

63. The correct increasing order of strengths of following acids is:
(a) $H_2SO_4, CH_3COOH, H_2CO_3$
(b) $CH_3COOH, H_2SO_4, H_2CO_3$
(c) $H_2CO_3, CH_3COOH, H_2SO_4$
(d) $CH_3COOH, H_2CO_3, H_2SO_4$

64. The decreasing order of strength of following bases is:
(a) Cl^-, CH_3COO^-, NH_3 (b) CH_3COO^-, NH_3, Cl^-
(c) CH_3COO^-, Cl^-, NH_3 (d) NH_3, CH_3COO^-, Cl^-

65. Which one of the following does not act as a Bronsted acid?
(a) NH_4^+ (b) HCO_3^- (c) HSO_3^- (d) CH_3COO^-

66. Of the given anions, the strongest Bronsted base is:
(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-

67. The compound that is not a Lewis acid is:
(a) $BaCl_2$ (b) $AlCl_3$ (c) BCl_3 (d) $SnCl_4$

68. The dissociation constants of two acids HA_1 and HA_2 are 3.0×10^{-4} and 1.8×10^{-5} respectively. The relative strengths of the acids will be:
(a) 1 : 4 (b) 4 : 1 (c) 1 : 16 (d) 16 : 1

69. In the acid-base relation;
$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+,$$
the conjugate acid of acetic acid is:
(a) Cl^- (b) HCl
(c) $CH_3COOH_2^+$ (d) H_3O^+

70. The numerical value of negative power to which 10 must be raised in order to express hydrogen ion concentration, is equal to:
(a) strength of the solution
(b) pH of the solution
(c) degree of hydrolysis
(d) solubility product of the electrolyte

71. Which one of the following solutions will have pH close to unity? **[IIT 1992; PMT(Kerala) 2008]**
(a) 100 mL of *M*/10 HCl + 100 mL of *M*/10 NaOH
(b) 55 mL of *M*/10 HCl + 45 mL of *M*/10 NaOH
(c) 10 mL of *M*/10 HCl + 90 mL of *M*/10 NaOH
(d) 75 mL of *M*/5 HCl + 25 mL of *M*/5 NaOH
(e) 50 mL of *M*/5 HCl + 50 mL of *M*/5 NaOH
[**Hint:** $M_{\text{mix}} V_{\text{mix}} = M_{\text{HCl}} V_{\text{HCl}} + M_{\text{NaOH}} V_{\text{NaOH}}$

$$M_{\text{mix}}(100) = \frac{1}{5} \times 75 + \frac{1}{5} \times 25 = 20$$
$$M_{\text{mix}} = 0.2$$
$$[H^+] = 0.2\,M$$
$$\text{pH} = -\log 0.2 = 0.7 \approx \text{close to unity}]$$

72. 0.1 *M* acetic acid solution is titrated against 0.1 *M* NaOH solution. What would be the difference in pH between 1/4 and 3/4 stages of neutralisation of acid?
(a) 2 log 3/4 (b) 2 log 1/4 (c) log 1/3 (d) 2 log 3

73. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be:
(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

74. When 10^{-6} mole of a monobasic strong acid is dissolved in one litre of solvent, the pH of the solution is:
(a) 6 (b) 7
(c) less than 6 (d) more than 7

75. When pH of a solution is 2, the hydrogen ion concentration in mol litre^{-1} is:
(a) 1×10^{-12} (b) 1×10^{-2} (c) 1×10^{-7} (d) 1×10^{-4}

76. At 90°C, pure water has $[H_3O^+] = 10^{-6}$ mol litre^{-1}. The value of K_w at 90°C is: **(MLNR 1990)**
(a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}

77. The pH of 10^{-8} molar solution of HCl in water is: **(CPMT 1990; MLNR 1992)**
(a) 8 (b) –8
(c) between 7 and 8 (d) between 6 and 7

78. When pH of 0.001 *M* solution of HCl is:
(a) 1.0 (b) 3 (c) 4.0 (d) 5.0

79. The pH of a solution containing 0.1 *N* NaOH solution is:
(a) 1 (b) 10^{-1} (c) 13 (d) 10^{-13}

80. When 0.4 g of NaOH is dissolved in one litre of solution, the pH of the solution is:
(a) 12 (b) 2 (c) 6 (d) 10

81. The pH of an aqueous solution of a 0.1 M solution of a weak monoprotic acid which is 1% ionised is:
(a) 1 (b) 2 (c) 3 (d) 11

82. The pH of a 0.002 N acetic acid solution if it is 2.3% ionised at this dilution is: ($\log 4.6 = 0.6628$)
(a) 4.3372 (b) 0.4337 (c) 3.4337 (d) 0.6628

83. 0.1 M HCl and 0.1 M H_2SO_4 each of volume 2 mL are mixed and the volume is made up to 6 mL by adding 2 mL of 0.01 N NaCl solution. The pH of the resulting mixture is:
(a) 1.17 (b) 1.0
(c) 0.3 (d) $\log 2 - \log 3$

[**Hint:** Number of millimoles of $H^+ = 0.1 \times 2 + 0.1 \times 2 \times 2 = 0.6$

Concentration of $[H^+] = \frac{0.6}{6} = 0.1$ M

$$pH = -\log[H^+]$$
$$= -\log 0.1 = 1]$$

84. The pH and pOH of 0.1 M aqueous solution of HNO_3 are:
(a) 0, 14 (b) 14, 0 (c) 13, 1 (d) 1, 13

85. The pH of a neutral solution at 50° C is: ($K_w = 10^{-13.26}$ at 50° C)
(a) 7 (b) 6.0 (c) 7.23 (d) 6.63

86. The pH of 0.005 molar aqueous solution of sulphuric acid is approximately:
(a) 0.005 (b) 1 (c) 0.1 (d) 2.0

87. 20 mL of 0.1 N HCl is mixed with 20 mL of 0.1 N KOH solution; the pH of the solution will be:
(a) 0 (b) 2 (c) 7 (d) 9

88. When the pH changes from 4 to 2, the hydrogen ion concentration will increase by a factor:
(a) 2 (b) 1/2 (c) 10^2 (d) $10^{0.5}$

89. 100 mL of 0.2 N HCl is added to 100 mL of 0.18 N NaOH and the whole volume is made one litre. The pH of the resulting solution is:
(a) 1 (b) 2 (c) 3 (d) 4

90. 10 mL of 0.1 N HCl is added to 990 mL solution of NaCl. The pH of the resulting solution is:
(a) zero (b) 3 (c) 7 (d) 10

91. Solutions with reserve acidity and alkalinity are called:
(a) isohydric solutions (b) true solutions
(c) normal solutions (d) buffer solutions

92. A solution which is resistant to changes of pH on dilution, or addition of small amounts of an acid or a base is known as:
(a) buffer solution (b) true solution
(c) isohydric solution (d) ideal solution

93. Which of the following is a buffer solution?
(a) $CH_3COOH + CH_3COONa$
(b) NaCl + NaOH
(c) $HCl + NH_4Cl$
(d) $CH_3COOH + HCl$

94. The hydrogen ion concentration of a buffer solution consisting of a weak acid and its sodium salt is given by:
(a) $[H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]}$ (b) $[H^+] = K_a\,[\text{Salt}]$
(c) $[H^+] = K_a\,[\text{Acid}]$ (d) $[H^+] = K_a \frac{[\text{Salt}]}{[\text{Acid}]}$

95. When a buffer solution of CH_3COOH and CH_3COONa is diluted with water:
(a) CH_3COO^- ion concentration increases
(b) $[H^+]$ ion concentration increases
(c) OH^- ion concentration increases
(d) H^+ ion concentration does not change

96. In a buffer solution consisting of a weak acid and its salt, the ratio of concentration of salt to acid is increased tenfold; then the pH of the solution will:
(a) increase by one (b) increase tenfold
(c) decrease by one (d) decrease tenfold

97. Acetic acid and propionic acid have K_a values 1.75×10^{-5} and 1.3×10^{-5} respectively at a certain temperature. An equimolar solution of a mixture of the two acids is partially neutralised by NaOH. How is the ratio of the contents of acetate and propionate ions related to the K_a values and the molarity?
(a) $\left[\frac{\alpha}{1-\alpha}\right] = \frac{1.75}{1.3} \times \left[\frac{\beta}{1-\beta}\right]$, where, α and β are ionised fractions of the acids
(b) The ratio is unrelated to the K_a values
(c) The ratio is unrelated to the molarity
(d) The ratio is unrelated to the pH of the solution

98. A weak acid of dissociation constant 10^{-5} is being titrated with aqueous NaOH solution. The pH at the point of one-third neutralisation of the acid will be: **[JEE (WB) 2010]**
(a) $5 + \log 2 - \log 3$ (b) $5 - \log 2$
(c) $5 - \log 3$ (d) $5 - \log 6$

[**Hint :** $pK_a = -\log 10^{-5} = 5$

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$= 5 + \log\frac{1/3}{2/3} = 5 - \log 2]$$

99. Which of the following salts when dissolved in water will hydrolyse?
(a) NaCl (b) KCl (c) NH_4Cl (d) Na_2SO_4

100. The aqueous solution of $AlCl_3$ is acidic due to:
(a) cation hydrolysis
(b) anion hydrolysis
(c) hydrolysis of both the ions
(d) dissociation

101. A certain buffer solution contains equal concentration of X^- and H_X. The K_b for X^- is 10^{-10}. The pH of the buffer is:
(a) 4 (b) 7 (c) 10 (d) 14

102. An acidic buffer solution can be prepared by mixing the solutions of:
(a) sodium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium hydroxide
(d) sodium chloride and sodium hydroxide

103. The compound whose aqueous solution has highest pH, is:
(a) NaCl (b) NH_4Cl
(c) CH_3COONH_4 (d) Na_2CO_3

104. The compound whose 0.1 *M* solution basic, is:
(a) ammonium chloride (b) ammonium acetate
(c) ammonium sulphate (d) sodium acetate

105. Aqueous solution of copper sulphate:
(a) turns blue litmus red
(b) turns red litmus blue
(c) does not affect litmus
(d) affects both red and blue litmus

106. When an equivalent of a strong acid is added to one equivalent of a weak base, the resulting solution will be:
(a) neutral (b) acidic
(c) alkaline (d) coloured

107. Indicators used in acid-base titrations are:
(a) strong organic acids
(b) strong organic bases
(c) weak organic acids or weak organic bases
(d) non-electrolytes

108. For the titration between oxalic acid and sodium hydroxide, the indicator used is:
(a) potassium permanganate (b) phenolphthalein
(c) litmus (d) methyl orange

109. Phenolphthalein gives a pink colour in alkaline medium due to the fact that:
(a) it is a coloured compound
(b) it ionises to give coloured ions
(c) it is decomposed by alkali
(d) it forms a complex compound with alkali

110. Which is the best choice for weak base-strong acid titration ? [JEE (Orissa) 2008]
(a) Methyl red (b) Litmus
(c) Phenol red (d) Phenolphthalein

111. Water is:
(a) a base (b) an acid
(c) non-electrolyte (d) an amphiprotic molecule

112. An aqueous solution, whose pH is zero, is:
(a) alkaline (b) neutral
(c) acidic (d) amphoteric

113. 0.1 *N* solution of Na_2CO_3 is being titrated with 0.1 *N* HCl. The best indicator to be used is:
(a) potassium ferricyanide (b) phenolphthalein
(c) methyl red (d) litmus

114. In the reaction, $AlCl_3 + Cl^- = AlCl_4^-$, $AlCl_3$ can be classified as:
(a) a base (b) an acid
(c) a salt (d) none of these

115. Sulphuric acid is a dibasic acid. Hence, it forms:
(a) acidic salt (b) basic and acidic salt
(c) acidic and normal salt (d) double salt

116. The buffer solutions play an important role in:
(a) increasing the pH value (b) decreasing the pH value
(c) keeping the pH constant (d) none of these

117. Which of the following will occur if 1.0 *M* solution of a weak acid is diluted to 0.01 *M* at constant temperature? (AIIMS 1993)
(a) $[H^+]$ will decrease to 0.01 *M*
(b) pH will decrease by 2 units
(c) K_a will increase
(d) Percentage ionisation will increase

118. Which one of the following indicators works in the pH range 8 – 9.8?
(a) Litmus (b) Phenolphthalein
(c) Methyl red (d) Methyl orange

119. What is $[OH^-]$ in the final solution prepared by mixing 20 mL of 0.05 *M* HCl with 30 mL of 0.10 *M* $Ba(OH)_2$? [CBSE (PMT) 2009]
(a) 0.12 *M* (b) 0.10 *M*
(c) 0.40 *M* (d) 0.005 *M*

[**Hint :** $n_{H^+} = \frac{MV}{1000} = \frac{0.05\times 20}{1000} = 10^{-3}$ mol

$$n_{OH^-} = 2\times n_{Ba(OH)_2}$$
$$= 2\times\frac{MV}{1000} = 2\times\frac{0.1\times 30}{1000} = 6\times 10^{-3}\text{ mol}$$

Remaining moles of OH^- after neutralization
$$= 6\times 10^{-3} - 10^{-3}$$
$$= 5\times 10^{-3}\text{ mol}$$

Conc. of $[OH^-] = \frac{n_{OH^-}}{V}\times 1000 = \frac{5\times 10^{-3}}{50}\times 1000 = 0.1M$]

120. The following reaction is known to occur in the human body;
$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
If CO_2 escapes from the system:
(a) pH will decrease
(b) H^+ ion concentration will decrease
(c) H_2CO_3 concentration will be unaltered
(d) the forward reaction will be promoted

121. The pH of human blood is about:
(a) 5.2 (b) 6.3 (c) 7.4 (d) 8.3

122. The dissociation constants of acids H*A*, H*B*, H*C* and H*D* are 2.6×10^{-3}, 5.3×10^{-9}, 1.1×10^{-2} and 7.5×10^{-5} respectively. The weakest acid amongst these acids is:
(a) H*A* (b) H*B* (c) H*C* (d) H*D*

123. The addition of sodium carbonate in pure water causes:
(a) an increase in the hydrogen ion concentration
(b) a decrease in hydroxyl ion concentration
(c) no change in pH
(d) an increase in pH

124. The best indicator for titrating HCl against NH_4OH is:
(a) litmus (b) phenolphthalein
(c) phenol red (d) methyl orange

125. A buffer solution is used in:
(a) preparation of potash alum
(b) the removal of PO_4^{3-} ions
(c) increasing the pH value of a solution
(d) precipitation of $Cr(OH)_3$ from $CrCl_3$

126. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is:
(a) 1.0×10^{-4} (b) 1.0×10^{-10}
(c) 1.0×10^{10} (d) 1.0×10^{-14}

[**Hint:** $HA + BOH \rightleftharpoons BA + H_2O$. The equilibrium constt. $= 1/K_h$ and $K_h = K_w/K_a$]

127. Which one of the following statements is correct?
(a) CH_3COOH is a weak acid
(b) NH_4Cl gives an alkaline solution in water
(c) CH_3COONa gives an acidic solution in water
(d) NH_4OH is a strong base

128. In the hydrolytic equilibrium $A^- + H_2O \rightleftharpoons HA + OH^-$ $K_a = 1.0 \times 10^{-5}$. The degree of hydrolysis of 0.001 M solution of the salt is:
(a) 10^{-3} (b) 10^{-4} (c) 10^{-5} (d) 10^{-6}

129. The pH of an aqueous solution of 0.1 M solution of the salt of a weak base ($K_b = 1.0 \times 10^{-5}$) and a strong acid is:
(a) 4.5 (b) 5.0 (c) 5.5 (d) 6.0

[Hint: First calculate degree of hydrolysis;

$$\alpha^2 C = K_h, K_h = (K_w / K_b), [H^+] = \alpha C]$$

130. The pH of the solution obtained by mixing equal volumes of solution of pH = 5 and pH = 3 of the same electrolyte is:
(a) 3.3 (b) 4.0 (c) 4.5 (d) 2.0

[Hint: $[H^+] = \frac{10^{-3} + 10^{-5}}{2} = \frac{100 \times 10^{-5} + 10^{-5}}{2} = 50.5 \times 10^{-5}$]

131. pK_a values of four acids are given below at 25°C. The strongest acid is: [PMT (MP) 1990]
(a) 2.0 (b) 2.5 (c) 3.0 (d) 4.0

132. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant of the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L mol^{-1} s^{-1}. The rate constant for proton transfer from water to NH_3 is:
(a) 6.07×10^5 s^{-1} (b) 6.07×10^{-10} s^{-1}
(c) 6.07×10^{-5} s^{-1} (d) 6.07×10^{10} s^{-1}

133. The pH of a soft drink is 3.82. The hydrogen ion concentration will be: (given a antilog 0.18 = 1.5) [PET (MP) 1990]
(a) 1.96×10^{-2} mol lit^{-1} (b) 1.96×10^{-5} mol lit^{-1}
(c) 1.5×10^{-4} mol lit^{-1} (d) 1.5×10^{-2} mol lit^{-1}

134. 100 mL of 0.1 M HCl is mixed with 100 mL of 0.01 M HCl. The pH of the resulting solution is:
(a) 2.0 (b) 1.0
(c) 1.26 (d) none of these

135. How many times has a solution of pH 2 higher acidity than a solution of pH 6?
(a) 10,000 (b) 12
(c) 400 (d) 4

136. For a concentrated solution of a weak electrolyte A_xB_y of concentration 'C', the degree of dissociation 'α' is given as: [PET (Kerala) 2008]

(a) $\alpha = \sqrt{K_{eq.}/C(x+y)}$ (b) $\alpha = \sqrt{\frac{C K_{eq.}}{xy}}$

(c) $\alpha = \left[\frac{K_{eq.}}{(C^{x+y-1} x^x y^y)}\right]^{1/x+y}$

(d) $\alpha = \frac{K_{eq.}}{Cxy}$, (e) $\alpha = \frac{K_{eq.}}{C^{xy}}$

[Hint: $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

$$\begin{array}{llll} t_0 & C & 0 & 0 \\ t_{eq.} & C(1-\alpha) & xC\alpha & yC\alpha \end{array}$$

$$K_{eq.} = \frac{(xC\alpha)^x (yC\alpha)^y}{C(1-\alpha)}$$

$$\approx \frac{(xC\alpha)^x (yC\alpha)^y}{C} \quad \because (1-\alpha) \approx 1$$

$$\alpha = \left[\frac{K_{eq.}}{C^{x+y-1} x^x y^y}\right]^{1/x+y}$$]

137. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid;

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid-base pairs is: (IIT 1992)
(a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-)
(b) (HCl, $HC_3COOH_2^+$) and (CH_3COOH, Cl^-)
(c) ($CH_3COOH_2^+$, HCl) and (Cl^-, CH_3COOH)
(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

138. The pH of a 10^{-10} M NaOH solution is: [PMT (Uttarakhand) 2006]
(a) 10 (b) 7.01 (c) 6.99 (d) 4

139. Which of the following is strongest Lewis base?
(a) CH_3^- (b) Ag^+ (c) NH_3 (d) H_2

140. If the solubility of lithium sodium hexafluoro aluminate, $Li_3Na_3(AlF_6)_2$ is 'S' mol L^{-1}, its solubility product is equal to: (CPMT 1992)
(a) S^8 (b) $12S^3$ (c) $18S^3$ (d) $2916S^8$

141. Given that the dissociation constant for water is $K_w = 1 \times 10^{-14}$ mol^2 L^{-2}. The pH of a 0.001 molar KOH solution is: (MLNR 1991)
(a) 10^{-11} (b) 10^{-3} (c) 3 (d) 11

142. Which one of the following solutions will have the highest pH value? (CPMT 1992)
(a) 0.01 M NaOH (b) 0.02 M CH_3COONa
(c) 0.10 M $NaHCO_3$ (d) 0.10 M H_2SO_4

143. In the titration of NH_4OH with HCl, the indicator which cannot be used is:
(a) phenolphthalein
(b) methyl orange
(c) methyl red
(d) both methyl orange and methyl red

144. pH of the buffer containing 0.6 g of acetic acid and 8.2 g of sodium acetate in 1 litre of water is: (pK_a of acetic acid = 4.5)
(a) 7.5 (b) 4.5 (c) 5.5 (d) 6.5

145. At 25°C, the dissociation constants of CH_3COOH and NH_4OH in aqueous solution are almost the same. The pH of a solution of 0.01 N CH_3COOH is 4.0 at 25°C. The pH of 0.01 N NH_4OH solution at the same temperature would be: (IIT 1990)
(a) 3.0 (b) 4.0
(c) 10.0 (d) 10.5

[Hint: $[H^+]$ in CH_3COOH soln. = 10^{-4};
Similarly $[OH^-]$ in NH_4OH soln. = 10^{-4};

So, $[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}$]

146. The dissociation constant of acetic acid is 1.8×10^{-5} and that of ammonium hydroxide is also 1.8×10^{-5} at 25°C. Hence, an aqueous solution of ammonium acetate is:
(a) acidic (b) basic
(c) neutral (d) slightly acidic

147. The concentration of OH^- ions in neutral solution is:
(a) 1×10^{-14} g ions/litre (b) 1×10^{14} g ions/litre
(c) 1×10^{7} g ions/litre (d) 1×10^{-7} g ions/litre

148. 10^{-6} M NaOH is diluted by 100 times. The pH of diluted base is: **[PMT (Pb.) 1993]**
(a) between 6 and 7 (b) between 10 and 11
(c) between 7 and 8 (d) between 5 and 6

149. Ionic dissociation of acetic acid is represented as:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

According to Lowry and Bronsted, the reaction possesses: **[CEE (Bihar) 1992]**
(a) an acid and three bases (b) two acids and two bases
(c) an acid and a base (d) three acids and a base

150. The concept of an acid as an acceptor of a pair of electrons was introduced by:
(a) Lowry (b) Bronsted (c) Arrhenius (d) Lewis

151. The ionic product of water will increase if:
(a) pressure is decreased (b) H^+ ions are added
(c) OH^- ions are added (d) temperature is increased

152. One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH having pK_b of 5 has pH of:
(a) 10 (b) 9 (c) 4 (d) 6

153. An aqueous solution of ferric chloride would be:
(a) acidic (b) neutral (c) basic (d) amphoteric

154. An acid solution of pH 6 is diluted hundred times. The pH of the solution becomes:
(a) 6 (b) 6.95 (c) 4 (d) 8

155. The pH of a solution is 5.0. To this solution sufficient acid is added to decrease the pH to 2.0. The increase in hydrogen ion concentration is: **(CPMT 1990)**
(a) 100 times (b) 10 times (c) 1000 times (d) 2.5 times

156. Conjugate base of HPO_4^{2-} is: **[PMT (MP) 1991]**
(a) PO_4^{3-} (b) $H_2PO_4^-$
(c) H_3PO_4 (d) H_4PO_3

157. The pH of a solution is 2. Its pH is to be changed to 4. Then the H^+ ion concentration of original solution has to be:
(a) halved (b) doubled
(c) increased 100 times (d) decreased 100 times

158. The pH value of 0.1 mol/litre HCl is approximately 1. The approximate pH value of 0.05 mol/litre H_2SO_4 is most likely to be:
(a) 0.05 (b) 0.5
(c) 1 (d) 2

159. The aqueous solution of a salt is alkaline. This shows that the salt is made from: **[PMT (MP) 1991]**
(a) a weak acid and a weak base
(b) a weak acid and a strong base
(c) a strong acid and a strong base
(d) a strong acid and a weak base

160. A semi-normal solution of sodium acetate in water has $[H^+]$:
(a) less than 10^{-7} M (b) greater than 10^{-7} M
(c) equal to 10^{-7} M (d) none of these

161. The most important buffer in the blood consists of:
(a) HCl and Cl^- (b) H_2CO_3 and HCO_3^-
(c) H_2CO_3 and Cl^- (d) HCl and HCO_3^-

162. The pH of a buffer solution containing 25 mL of 1 M CH_3COONa and 25 mL of 1 M CH_3COOH will be appreciably affected by 5 mL of:
(a) 1 M CH_3COOH (b) 5 M HCl
(c) 5 M CH_3COOH (d) 1 M NH_4OH

163. 50 mL of 2 N acetic acid mixed with 10 mL of 1 N sodium acetate solution will have an approximate pH:
(a) 7 (b) 6 (c) 5 (d) 4

164. The solution of which salt in water is acidic?
(a) $Na_2B_4O_7$ (b) $NaHCO_3$ (c) KCl (d) $FeCl_3$

165. Which of the following expressions is not true?
(a) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution
(b) $[H^+] > \sqrt{K_w}$ and $[OH^-] < \sqrt{K_w}$ for an acidic solution
(c) $[H^+] < \sqrt{K_w}$ and $[OH^-] > \sqrt{K_w}$ for an alkaline solution
(d) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures

166. Ammonia gas dissolves in water to give NH_4OH. In this reaction water acts as: **[PMT (MP) 1990]**
(a) an acid (b) a base
(c) a salt (d) a conjugate base

167. What is the decreasing order of strength of the bases OH^-, NH_2^-, $H—C{=}C^-$ and $CH_3CH_2^-$? **(IIT 1993)**
(a) $CH_3CH_2^- > NH_2^- > H—C{\equiv}C^- > OH^-$
(b) $H—C{\equiv}C^- > CH_3—CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H—C{\equiv}C^- > CH_3CH_2^-$
(d) $NH_2^- > H—C{\equiv}C^- > OH^- > CH_3CH_2^-$

168. The best explanation for the solubility of MnS in dil. HCl is that: **(MLNR 1993)**
(a) solubility product of $MnCl_2$ is less than that of MnS
(b) concentration of Mn^{2+} is lowered by the formation of complex ions
(c) concentration of sulphide ions is lowered by oxidation to free sulphur
(d) concentration of sulphide ions is lowered by the formation of weak acid H_2S

169. The correct order of increasing $[H_3O^+]$ in the following aqueous solution is: **(MLNR 1993; AFMC 2009)**
(a) 0.001 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M $NaNO_2$
(b) 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01 M H_2S < 0.01 M H_2SO_4
(c) 0.01 M $NaNO_2$ < 0.01 M NaCl < 0.01 M H_2S < 0.01 M H_2SO_4
(d) 0.01 M H_2S < 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01 M H_2SO_4

170. Which of the following statements/relationships is not correct?
(a) Upon hydrolysis salt of strong base and weak acid gives a solution with pH > 7
(b) $\text{pH} = \log \dfrac{1}{[\text{H}^+]}$
(c) Only at 25° C, the pH of pure water is 7
(d) The value of $\text{p}K_w$ at 25°C is 7

171. Fear and excitement generally cause one to breathe rapidly and it results in the decrease of CO_2 concentration in blood. In what way will it change the pH of the blood? **(IIT 1993)**
(a) pH will decrease (b) pH will increase
(c) No change (d) pH will adjust to 7

172. Nucleophiles are:
(a) Lewis acids (b) Lewis bases
(c) Bronsted acids (d) none of these

173. Electrophiles are:
(a) Lewis acids (b) Lewis bases
(c) Bronsted acids (d) Bronsted bases

174. K_h (hydrolysis constant) of ammonium benzoate can be calculated by the formula:
(a) $\sqrt{\dfrac{K_w}{K_a C}}$ (b) $\sqrt{\dfrac{K_w}{K_a \times K_b}}$ (c) $\sqrt{\dfrac{K_w}{K_b \times C}}$ (d) $\sqrt{\dfrac{K_h}{C}}$

175. The pH of a neutral water is 6.5. Then the temperature of water: **[PET (Kerala) 2007]**
(a) is 25°C
(b) is more than 25°C
(c) is less than 25°C
(d) can be more or less than 25°C
(e) cannot be predicted

176. The buffer capacity of buffer containing acid with $\text{p}K_a = 4.0$ is highest when its pH is equal to:
(a) 6.0 (b) 5.0
(c) 4.0 (d) 3.0

177. K_{sp} (AgCl) > K_{sp} (AgBr) > K_{sp} (AgI). This means that:
(a) AgCl is more ionised than AgBr and AgI
(b) both AgBr and AgI are less soluble than AgCl
(c) AgI is most soluble
(d) AgBr is more soluble than AgCl but less soluble than AgI

178. In the hydrolytic equilibrium;

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$K_b = 1 \times 10^{-5}$. The hydrolysis constant is:
(a) 10^{-5} (b) 10^{-19} (c) 10^{-10} (d) 10^{-9}

179. The solution of a salt of a weak acid and weak base will have pH: ($K_b = 1.0 \times 10^{-6}$ and $K_a = 1.0 \times 10^{-4}$)
(a) 7.0 (b) 8.0
(c) 6 (d) 4.0

180. 0.1 *N* solution of sodium acetate will have pH: ($\text{p}K_a = 4.57$)
(a) 8.78 (b) 11.57
(c) 4.57 (d) 7.0

181. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order: **(IIT 1996)**
ClOH (I) BrOH (II) IOH (III)
(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

182. Which of the following statements is correct?
(a) $\text{p}K_w$ increases with increase of temperature
(b) $\text{p}K_w$ decreases with increase of temperature
(c) $\text{p}K_w = 14$ at all temperatures
(d) $\text{p}K_w = \text{pH}$ at all temperatures

183. For a concentrated solution of a weak electrolyte A_x and B_y, the degree of dissociation is given as:
(a) $\alpha = \sqrt{K_{eq}/c(x+y)}$
(b) $\alpha = \sqrt{K_{eq}c/(xy)}$
(c) $\alpha = (K_{eq}/c^{x+y-1}\, x^x y^y)^{1/(x+y)}$
(d) $\alpha = \sqrt{K_{eq}/xyc}$

184. A solution is saturated with respect to $SrCO_3$ and SrF_2. The $[CO_3^{2-}]$ was found to be $1.2 \times 10^{-3}\ M$. The concentration of F^- in the solution would be:
(a) $1.3 \times 10^{-3}\ M$ (b) $2.6 \times 10^{-2}\ M$
(c) $3.7 \times 10^{-2}\ M$ (d) $5.8 \times 10^{-7}\ M$
(Given: K_{sp} $SrCO_3 = 7.0 \times 10^{-10}\ M^2$,
$K_{sp}(SrF_2) = 7.9 \times 10^{-10}\ M^3$)

185. The solubility of sparingly soluble electrolyte $M_m A_a$ in water is given by the expression:
(a) $S = \left[\dfrac{K_{sp}}{m^m a^a}\right]^{m+a}$ (b) $S = \left[\dfrac{K_{sp}}{m^m a^a}\right]^{1/(m+a)}$
(c) $S = \left[\dfrac{K_{sp}}{m^a a^m}\right]^{m+a}$ (d) $S = \left[\dfrac{K_{sp}}{m^a a^m}\right]^{1/(m+a)}$

186. The solubility of mercurous chloride in water will be given as:
(a) $S = K_{sp}$ (b) $S = K_{sp}/4$
(c) $S = (K_{sp}/4)^{1/2}$ (d) $S = (K_{sp}/4)^{1/3}$

187. In the titration of acetic acid *versus* sodium hydroxide, the pH of the solution at equivalence point (when temperature is 25°C) is:
(a) about 5.5 (b) about 6.5
(c) about 7 (d) about 8.5

188. When K_2O is added to water, the solution is basic because it contains a significant concentration of:
(a) K^+ (b) OH^-
(c) O^{3-} (d) O_2^{2-}

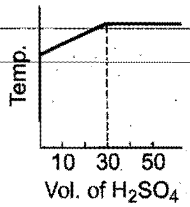
189. The blood buffers are most often involved in stabilizing the pH in presence of metabolically produced:
(a) acids (b) bases
(c) salts (d) none of these

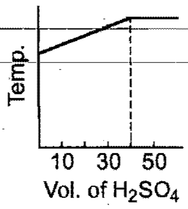
190. The colour of $CuCr_2O_7$ solution in water is green because:
(a) Cu^{2+} ion is green
(b) $Cr_2O_7^{2-}$ ions are green
(c) both the ions are green
(d) Cu^{2+} ion is blue and $Cr_2O_7^{2-}$ ion is yellow

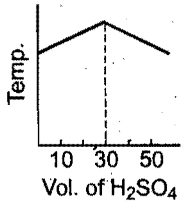
191. An acid with molecular formula $C_7H_6O_3$ forms three types of sodium salts, *i.e.*, $C_7H_5O_3Na$, $C_7H_4O_3Na_2$ and $C_7H_3O_3Na_3$. The basicity of the acid is:
(a) one (b) two (c) three (d) four

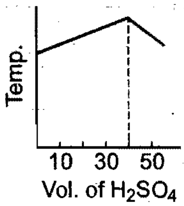
192. If the salts M_2X, QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as:
(a) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$
(b) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
(c) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_3)$
(d) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$

193. In an experiment to determine the enthalpy of neutralization of sodium hydroxide with sulphuric acid, $50\,cm^3$ of 0.4 *M* sodium hydroxide were titrated thermometrically with 0.25 *M* sulphuric acid. Which of the following plots gives the correct representation?

(a)


(b)


(c)


(d)


194. K_{sp} of CuS, Ag_2S and HgS are 10^{-31}, 10^{-44} and 10^{-54} respectively. Select the correct order for their solubility in water: (CBSE 1997)
(a) $Ag_2S > HgS > CuS$ (b) $HgS > CuS > Ag_2S$
(c) $HgS > Ag_2S > CuS$ (d) $Ag_2S > CuS > HgS$
[**Hint:** Solubility of Ag_2S ($4S^3 = K_{sp}$) and for CuS and HgS ($S^2 = K_{sp}$).]

195. If the K_b value in the hydrolysis reaction,

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

is 1.0×10^{-6}, then the hydrolysis constant of the salt would be: (IIT 1998)
(a) 1.0×10^{-6} (b) 1.0×10^{-7} (c) 1×10^{-8} (d) 1.0×10^{-9}

196. The concentration of $[H^+]$ and $[OH^-]$ of a 0.1 *M* aqueous solution of 2% ionised weak acid is: (ionic product of water $= 1 \times 10^{-14}$) (CBSE 1999)
(a) 0.2×10^{-3} *M* and 5×10^{-11} *M*
(b) 1×10^{-3} *M* and 3×10^{-11} *M*
(c) 2×10^{-3} *M* and 5×10^{-12} *M*
(d) 3×10^{-2} *M* and 4×10^{-13} *M*
[**Hint:** $[H^+] = C \times \alpha = 0.1 \times 0.02 = 2 \times 10^{-3}\,M$;
$[OH^-] = \dfrac{K_w}{[H^+]}$]

197. The pH value of decinormal solution of NH_4OH, which is 20% ionised, is: (CBSE [illegible])
(a) 13.30 (b) 14.70 (c) 12.30 (d) 12.95
[**Hint:** $[OH^-] = 0.1 \times 0.2 = 2 \times 10^{-3}$;
$pOH = 1.7\ pH = 14 - pOH$]

198. The pH of 0.1 *M* solution of the following salts increases in the order of: (IIT 1999)
(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

199. A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resists a change in pH yet contains only small concentration of buffering agents. Which one of the following weak acids together with its sodium salt would be best to use? (CBSE 1997)
(a) *m*-chlorobenzoic acid ($pK_a = 3.98$)
(b) *p*-chlorobenzoic acid ($pK_a = 4.41$)
(c) 2,5-dihydroxybenzoic acid ($pK_a = 2.97$)
(d) Acetoacetic acid ($pK_a = 3.58$)

200. Which one does not give a buffer solution?
(a) Ammonia and sodium hydroxide in water
(b) Sodium acetate and acetic acid in water
(c) Ammonia and ammonium chloride in water
(d) Sodium acetate and hydrochloric acid in water

201. Conjugate base of $[Al(H_2O)_3(OH)_3]$ is:
(a) $[Al(H_2O)_3(OH)_2]^+$ (b) $[Al(H_2O)_3(OH)_2O]^-$
(c) $[Al(H_2O)_3(OH)_3]^-$ (d) $[Al(H_2O)_2(OH)_4]^-$

202. The solubility of calcium phosphate in water is *x* mol h^{-1} at 25°C. Its solubility product is equal to: [illegible] 1995
(a) $108x^2$ (b) $36x^3$
(c) $36x^5$ (d) $108x^5$

203. K_{sp} values for silver bromide, silver chloride and silver iodide are $5 \times 10^{-13}\ mol^2\ dm^{-6}$, $2 \times 10^{-10}\ mol^2\ dm^{-6}$ and $8 \times 10^{-17}\ mol^2\ dm^{-6}$ respectively. The order of solubility of these silver salts is : [illegible]
(a) AgCl > AgBr > AgI (b) AgI > AgBr > AgCl
(c) AgCl > AgI > AgBr (d) AgI > AgCl > AgBr

204. In the reaction,

$$I_2 + I^- \longrightarrow I_3^-$$

the Lewis base is: [illegible]
(a) I_2 (b) I^-
(c) I_3^- (d) none of these

205. Which of the following on reaction with H_2S does not produce metallic sulphide? (AIIMS [illegible])
(a) $CdCl_2$ (b) $ZnCl_2$ (c) $CoCl_2$ (d) $CuCl_2$

206. A buffer solution of pH = 9 can be prepared by mixing: (CPMT 2000)
(a) CH_3COONa and CH_3COOH
(b) NaCl and NaOH
(c) NH_4Cl and NH_4OH
(d) KH_2PO_4 and K_2HPO_4

207. Which of the following is the strongest Lewis base? [PMT (MP) [illegible]]
(a) CH_3^- (b) NH_2^- (c) OH^- (d) F^-

208. The monobasic acid among the following is : **(ISAT 2010)**

(a) H_3PO_3 (b) $H_2S_2O_7$
(c) H_3PO_2 (d) $H_4P_2O_7$

209. To Ag_2CrO_4 solution over its own precipitate, CrO_4^{2-} ions are added. This results in: **[MEE (Kerala) 2000]**

(a) increase in Ag^+ concentration
(b) decrease in Ag^+ concentration
(c) increase in solubility product
(d) shifting of Ag^+ ions from the precipitate into the solution

210. Aluminium chloride is: **(KCET 2000)**

(a) Bronsted Lowry acid (b) Arrhenius acid
(c) Lewis acid (d) Lewis base

211. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. The pH of the mixture will be nearly: **[IAS (Prelim.) 1995]**

(a) 0.76 (b) 1.26 (c) 1.76 (d) 2.26

212. The $[Ag^+]$ in a saturated solution of Ag_2CrO_4 is $1.5 \times 10^{-4}\ M$. What is the solubility product of Ag_2CrO_4? **(SCRA 2009)**

(a) $3.375 \times 10^{-12} M^3$ (b) $1.6875 \times 10^{-10} M^3$
(c) $1.6875 \times 10^{-11} M^3$ (d) $1.6875 \times 10^{-12} M^3$

[**Hint :** $Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$

$[Ag^+] = 1.5 \times 10^{-4}\ M \quad \therefore [CrO_4^{2-}] = 0.75 \times 10^{-4}\ M$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$= [1.5 \times 10^{-4}]^2[0.75 \times 10^{-4}]$

$= 1.6875 \times 10^{-12} M^3$]

213. The pH of a buffer containing equal molar concentrations of a weak base and its chloride (K_b for weak base $= 2 \times 10^{-5}$, log 2 = 0.3) is:

(a) 5 (b) 9 (c) 4.7 (d) 9.3

214. The solubility product (K_{sp}) of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur only when equal volumes of solutions of: **[IAS (Prelim.) 1997; PET (MP) 2007]**

(a) $10^{-4}\ M\ Ag^+$ and $10^{-4}\ M\ Cl^-$ are mixed
(b) $10^{-7}\ M\ Ag^+$ and $10^{-7}\ M\ Cl^-$ are mixed
(c) $10^{-5}\ M\ Ag^+$ and $10^{-5}\ M\ Cl^-$ are mixed
(d) $10^{-10}\ M\ Ag^+$ and $10^{-10}\ M\ Cl^-$ are mixed

215. Solid $Ba(NO_3)_2$ is gradually dissolved in a $1 \times 10^{-4}\ M\ Na_2CO_3$ solution. At what concentration of Ba^{2+} will a precipitate begin to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) **(AIEEE 2009)**

(a) $4.1 \times 10^{-5}\ M$ (b) $5.1 \times 10^{-5}\ M$
(c) $8.1 \times 10^{-8}\ M$ (d) $8.1 \times 10^{-7}\ M$

216. How many gram of CaC_2O_4 will dissolve in distilled water to make one litre of unsaturated solution of it? (K_{sp} for $CaC_2O_4 = 2.5 \times 10^{-9}$ mol^2 lit^{-2}) **[PMT (MP) [illegible]]**

(a) 0.0064 g (b) 0.1028 g (c) 0.1280 g (d) 0.2056 g

217. When CO_2 dissolves in water, the following equilibrium is established,

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

for which the equilibrium constant is 3.8×10^{-7} and pH = 6.0. The ratio of $[HCO_3^-]$ to $[CO_2]$ would be:

(a) 3.8×10^{-13} (b) 3.8×10^{-1} (c) 6.0 (d) 13.4

218. pH of a buffer solution decreases by 0.02 units when 0.12 g of acetic acid is added to 250 mL of a buffer solution of acetic acid and potassium acetate at 27°C. The buffer capacity of the solution is: **(EAMCET 2009)**

(a) 0.1 (b) 10 (c) 1 (d) 0.4

219. The dissociation constants of monobasic acids A, B, C and D are 6×10^{-4}, 5×10^{-5}, 3.6×10^{-6} and 7×10^{-10} respectively. The pH values of their 0.1 molar aqueous solutions are in the order:

(a) $A < B < C < D$ (b) $A > B > C > D$
(c) $A = B = C = D$ (d) $A > B < C > D$

220. If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9, then pH in 0.1 M NaA is:

(a) 5 (b) 9 (c) 7 (d) 8

221. If the freezing point of 0.1 molal HA ($aq.$) is – 0.2046°C, then pH of the solution is: $[K_f\ (H_2O) = 1.86°\ mol^{-1}\ kg]$

~~(a) 1 (b) 2 (c) 1.3 (d) 1.7~~

222. ~~% ionisation of weak acid can be calculated as:~~

(a) $100\sqrt{\dfrac{K_a}{c}}$ (b) $\dfrac{100}{1 + 10^{(pK_a - pH)}}$
(c) both correct (d) none is correct

223. Assuming complete ionisation which will have maximum pH?

(a) 0.01 M NH_4Cl (b) 0.01 M $(NH_4)_2SO_4$
(c) 0.01 M $(NH_4)_3PO_4$ (d) equal

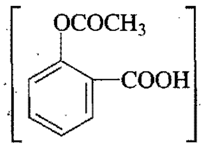
224. $H_2O + H_3PO_4 \rightleftharpoons H_3O^+ + H_2PO_4^-$; $pK_1 = 2.15$

$H_2O + H_2PO_4^- \rightleftharpoons H_3O^+ + HPO_4^{2-}$; $pK_2 = 7.20$

Hence, pH of 0.01 M NaH_2PO_4 is:

(a) 9.35 (b) 4.675 (c) 2.675 (d) 7.350

225. Acetyl salicylic acid



called aspirin is a pain killer with $pK_a = 2$. If two tablets each of 0.09 g mass, containing aspirin are dissolved in 100 mL solution. Its pH will be:

(a) 0.5 (b) 1.0
(c) 0.0 (d) 2.0

226. If ionic product of water is $K_w = 10^{-16}$ at 4°C, then a solution with pH = 7.5 at 4°C will:

(a) turn blue litmus red (b) turn red litmus blue
(c) turn turmeric paper brown (d) be neutral to litmus

227. How do we differentiate between Fe^{3+} and Cr^{3+} in group III? **(AIEEE 2002)**

(a) By taking excess of NH_4OH
(b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration
(d) Both (b) and (c)

228. Which has the highest pH? **[CBSE (PMT) 2002]**

(a) CH_3COOK (b) Na_2CO_3
(c) NH_4Cl (d) $NaNO_3$

229. Water is a: **(KCET 2002)**

(a) protophobic solvent (b) protophilic solvent
(c) amphiprotic solvent (d) aprotic solvent

230. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is: **(AIEEE 2002)**
(a) not a buffer solution with pH < 7
(b) not a buffer solution with pH > 7
(c) a buffer solution with pH < 7
(d) a buffer solution with pH = 7

231. Solution of 0.1 M NH_4OH and 0.1 M NH_4Cl has pH 9.25. Then pK_b of NH_4OH is: **[CBSE (PMT) 2002]**
(a) 9.25 (b) 4.75
(c) 3.75 (d) 8.25

232. Solubility of an MX_2 type electrolyte is 0.5×10^{-4} mol/litre, then K_{sp} of electrolyte is: **[CBSE (PMT) 2002]**
(a) 5×10^{-12} (b) 25×10^{-10}
(c) 1×10^{-13} (d) 5×10^{-13}

233. The concentration of KI and KCl in a certain solution containing both is 0.001 M each. If 20 mL of this solution is added to 20 mL of a saturated solution of AgI in water. What will happen?
(K_{sp} AgCl $= 10^{-10}$; K_{sp} AgI $= 10^{-16}$). **[PET (MP) 2004]**
(a) AgI will be precipitated
(b) AgCl will be precipitated
(c) There will be no precipitate
(d) Both AgCl and AgI will be precipitated

234. Degree of dissociation of NH_4OH in water is 1.8×10^{-5}, then hydrolysis constant of NH_4OH is: **[CECE (Bihar) Pre. 2004]**
(a) 1.8×10^{-5} (b) 1.8×10^{-10}
(c) 5.55×10^{-5} (d) 5.55×10^{-10}

235. What is the pH of 0.01 M glycine solution? For glycine $K_{a_1} = 4.5 \times 10^{-3}$; $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K: **(AIIMS 2004)**
(a) 3.02 (b) 6.94 (c) 7.06 (d) 10.02

236. The rapid change of pH near the stoichiometric point of an acid base titration is the basis of indicator detection. pH of the solution is related to the ratio of the concentrations of the conjugate acid HIn and base In^- forms of the indicator by the expression: **[CBSE (PMT) 2004]**
(a) $\log \frac{[In^-]}{[HIn]} = pK_{In} - pH$ (b) $\log \frac{[HIn]}{[In^-]} = pK_{In} - pH$
(c) $\log \frac{[HIn]}{[In^-]} = pH - pK_{In}$ (d) $\log \frac{[In^-]}{[HIn]} = pH - pK_{In}$

237. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is: **[IIT (S) 2004]**
(a) 0.0001% (b) 0.01% (c) 0.1% (d) 0.15%

238. The molar solubility (in mol litre^{-1}) of a sparingly soluble salt MX_4 is S. The corresponding solubility product K_{sp} is given by the relation: **(AIEEE 2004)**
(a) $S = (K_{sp}/128)^{1/4}$ (b) $S = (218\,K_{sp})^{1/4}$
(c) $S = (256\,K_{sp})^{1/5}$ (d) $S = (K_{sp}/256)^{1/5}$

239. The K_{sp} of $Mg(OH)_2$ is 1×10^{-12}. 0.01 M $Mg(OH)_2$ will precipitate at the limiting pH: **(DPMT 2005)**
(a) 3 (b) 9 (c) 5 (d) 8

[**Hint:** $[Mg^{2+}][OH^-]^2 = 10^{-12}$
$0.01 \times [OH^-]^2 = 10^{-12}$
$[OH^-] = 10^{-5}\,M$
$\therefore [H^+] = 10^{-9}\,M$ and $pH = -\log[10^{-9}] = 9$]

240. The correct expression for the solubility product of $Ca_3(PO_4)_2$ is: **[JEE (Orissa) 2005]**
(a) $108S^5$ (b) $27S^5$ (b) $16S^4$ (d) $81S^4$

241. The solubility product of a salt, having the general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is: **(AIEEE 2005)**
(a) $2 \times 10^{-6}\,M$ (b) $1 \times 10^{-4}\,M$
(c) $1.6 \times 10^{-4}\,M$ (d) $4 \times 10^{-10}\,M$

[**Hint:** It is ternary electrolyte.
$\therefore \quad K_{sp} = 4S^3$
$4 \times 10^{-12} = 4S^3$
$S = 10^{-4}\,M$
$\therefore \quad (M^{2+}) = 10^{-4}\,M$]

242. The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is: **[CBSE (PMT) 2009]**
(a) 5.65×10^{-12} (b) 5.65×10^{-10}
(c) 6.50×10^{-12} (d) 5.65×10^{-13}

[**Hint:** $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.77 \times 10^{-5}}$
$= 5.65 \times 10^{-10}$]

243. The K_a values of formic acid and acetic acid are respectively 1.77×10^{-4} and 1.75×10^{-5}. The ratio of the acid strength of 0.1 M acid is: **[PMT (Kerala) 2005]**
(a) 10 (b) 3.178 (c) 0.3 (d) 0.1
(e) 100

244. Equal volumes of the following Ca^{2+} and F^- solutions are mixed. In which solution will the precipitation occur?

K_{sp} of $CaF_2 = 1.7 \times 10^{-10}$

1. $10^{-2}\,M\,Ca^{2+} + 10^{-5}\,M\,F^-$ 2. $10^{-3}\,M\,Ca^{2+} + 10^{-3}\,M\,F^-$
3. $10^{-4}\,M\,Ca^{2+} + 10^{-2}\,M\,F^-$ 4. $10^{-2}\,M\,Ca^{2+} + 10^{-3}\,M\,F^-$

Select the correct answer using the codes given below: **[PMT (Kerala) 2005]**
(a) in 4 only (b) in 1 and 2 (c) in 3 and 4 (d) in 2, 3 and 4
(e) in all of these

245. Given, pH of a solution A is 3 and it is mixed with another solution B having pH 2. If both are mixed, then the resultant pH of the solution will be: **[BHU (Pre.) 2005]**
(a) 3.2 (b) 1.9 (c) 3.4 (d) 3.5

246. When 10 mL of 0.1 M acetic acid ($pK_a = 5$) is titrated against 10 mL of 0.1 M ammonia solution ($pK_b = 5$), the equivalent point will occur at pH: **(AIIMS 2005)**
(a) 5 (b) 6 (c) 7 (d) 9

247. On adding 0.1 M solution each of Ag^+, Ba^{2+} and Ca^{2+} in an Na_2SO_4 solution, the species first precipitated is: **(DCE 2005)**
(K_{sp} $BaSO_4 = 10^{-11}$, K_{sp} $CaSO_4 = 10^{-6}$, K_{sp} $Ag_2SO_4 = 10^{-5}$)
(a) Ag_2SO_4 (b) $BaSO_4$
(c) $CaSO_4$ (d) all of these

248. When 0.1 mole of CH_3NH_2 (ionization constant, $K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole HCl and the volume is made up to 1 litre, find the $[H^+]$ of resulting solution: **(IIT 2005)**

(a) 8×10^{-2} (b) 2×10^{-11}
(c) 1.23×10^{-4} (d) 8×10^{-11}

[**Hint:**
$$\begin{array}{cccc} CH_3NH_2 + & HCl & \longrightarrow & CH_3NH_3^+Cl^- \\ 0.1\text{ mol} & 0.08\text{ mol} & & 0 \\ 0.02\text{ mol} & 0 & & 0.08 \end{array}$$

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

$$= -\log 5 \times 10^{-4} + \log\frac{0.08}{0.02} = 3.903$$

$$pH = 10.0967$$

$$[H^+] = \text{antilog}[-10.0967] = 8 \times 10^{-11}]$$

249. At 25°C, the dissociation constant of a base BOH is 1×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be: **[CBSE-PMT (Pre.) 2005]**

(a) 10^{-5} mol L^{-1} (b) 10^{-6} mol L^{-1}
(c) 2×10^{-6} mol L^{-1} (d) 10^{-7} mol L^{-1}

[**Hint:** $[OH^-] = \sqrt{CK_b} = \sqrt{0.01 \times 10^{-12}} = 10^{-7}$ mol L^{-1}]

250. Which of the following solutions has pH equal to 10? **[UGET (Manipal) 2006]**

(a) 10^{-4} M KOH (b) 10^{-10} M KOH
(c) 10^{-10} M HCl (d) 10^{-4} M HCl

251. A weak monobasic acid is half neutralised by a strong base. If the pH of the solution is 5.4, its pK_a is: **[JEE (Orissa) 2006]**

(a) 6.8 (b) 2.7 (c) 5.4 (d) 10.8

[**Hint:** [Acid] = [Salt]

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$5.4 = pK_a + \log_{10} 1$$

$$\therefore\ pK_a = 5.4]$$

252. ZnS is not precipitated by passing H_2S in acidic medium but CuS precipitated. The reason for it is: **[JEE (Orissa) 2006]**

(a) K_{sp} CuS << K_{sp} ZnS (b) K_{sp} CuS >> K_{sp} ZnS
(c) K_{sp} CuS = K_{sp} ZnS (d) none of these

253. Solubility product of salt AB is 1×10^{-8} M^2 in a solution, in which the concentration of A^+ ions is 10^{-3} M. The salt will precipitate when the concentration of B^- ions is kept: **(KCET 2006)**

(a) between 10^{-8} M to 10^{-7} M (b) between 10^{-7} M to 10^{-8} M
(c) $> 10^{-5}$ M (d) $< 10^{-8}$ M

254. NaOH(*aq.*), HCl(*aq.*) and NaCl(*aq.*) have concentration of 10^{-3} M each. Their pH will be respectively: **[PMT (Uttarakhand) 2006]**

(a) 10, 6, 2 (b) 11, 3, 7
(c) 10, 3, 7 (d) 10, 4, 7

255. The weak acid, HA, has a K_a of 1.00×10^{-5}. If 0.1 mol of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to: **[CBSE (Med.) 2007]**

(a) 1% (b) 99.9%
(c) 0.1% (d) 99%

[**Hint:**
$$\begin{array}{lccc} & HA & \rightleftharpoons & H^+ & + & A^- \\ t=0 & C & & 0 & & 0 \\ t_{eq.} & C - C\alpha & & C\alpha & & C\alpha \end{array}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{C^2\alpha^2}{C - C\alpha}$$

$$= \frac{C\alpha^2}{1-\alpha} \approx C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.1}} = 10^{-2}$$

% ionisation = $\alpha \times 100 = 1$]

256. At 25° C, the value of pK_b (K_b being the dissociation constant as a base) for NH_3 in aqueous solution is 4.7. What is the pH of 0.1 M aqueous solution of NH_4Cl with 0.01 M NH_3 (approximately)? **(SCRA 2007)**

(a) 8.3 (b) 9 (c) 9.5 (d) 10

[**Hint:** $pOH = pK_b + \log_{10}\frac{[NH_4Cl]}{[NH_4OH]}$

$$= 4.7 + \log\left[\frac{0.1}{0.01}\right] = 5.7$$

$$pH = 14 - 5.7 = 8.3]$$

257. The ionisation of strong electrolytes in acetic acid compared to that in water is: **[CET (J&K) 2007]**

(a) weak, low (b) strong, more
(c) medium, the same (d) no ionisation, 100%

258. By adding a little of acid or base, the change in pH of blood is not significant, because blood: **[PET (Raj.) 2006]**

(a) has iron as a part of molecule
(b) is a body fluid
(c) has serum protein which works as buffer
(d) is easily coagulated

259. 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ ion at equivalence point is: ($K_w = 1 \times 10^{-14}$ at 25°C) **(IIT 2008)**

(a) $3.7 \times 10^{-13} M$ (b) $3.2 \times 10^{-7} M$
(c) $3.2 \times 10^{-2} M$ (d) $2.7 \times 10^{-2} M$

[**Hint:** $1\ BOH + 1HCl \longrightarrow BCl + H_2O$

$$\frac{M_1V_1}{1}\text{ (Base)} = \frac{M_2V_2}{1}\text{ (Acid)}$$

$$\frac{2}{5} \times 2.5 = \frac{2}{15} \times V_2$$

$$V_2 = 7.5\text{ mL}$$

Total volume = 7.5 + 2.5 = 10 mL

Concentration of salt in the mixture :

$$M_1V_1\text{ (Base)} = M_2V_2\text{ (Salt)}$$

$$\frac{2}{5} \times 2.5 = M_2 \times 10$$

$$M_2 = 0.1$$

$$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

$$= \frac{1}{2}[14 - 12 - (-1)] = 1.5$$

$$[H^+] = \text{Antilog}(-1.5) = 0.032\ M]$$

260. Solubility product constants (K_{sp}) of salts of types MX, MX_2, M_3X at temperature T are 4×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol dm^{-3}) of the salts at temperature T are in the order: **(IIT 2008)**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

[**Hint:**

Solubility (S_1) of $MX = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4} M$

Solubility (S_2) of

$$MX_2 = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}} = \left(\frac{3.2 \times 10^{-14}}{4}\right)^{\frac{1}{3}} = 2 \times 10^{-5} M$$

Solubility (S_3) of

$$M_3X = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}} = \left(\frac{2.7 \times 10^{-15}}{27}\right)^{\frac{1}{4}} = 10^{-4} M$$

$\therefore S_1 > S_3 > S_2$]

261. In aqueous solution, the ionization constants for carbonic acid are :

$$K_1 = 4.2 \times 10^{-7} \text{ and } K_2 = 4.8 \times 10^{-11}$$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid : **(AIEEE 2010)**

(a) The concentrations of H^+ and HCO_3^- are approximately equal

(b) The concentration of H^+ is double that of CO_3^{2-}

(c) Concentration of CO_3^{2-} is 0.034 M

(d) The concentration of CO_3^{2-} is greater than that of HCO_3^-

Set-2: The Questions given below may have more than one correct answers

1. For dissociation constant (K) and ionic product (K_w) of water which is correct?

(a) $K > K_w$ (b) $K_w > K$

(c) $K_w = K$ (d) None of these

2. Which is an example of auto protolysis?

(a) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

(b) $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(c) $H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$

(d) All of the above

3. If concentrations of two acids are same, their relative strengths can be compared by:

(a) α_1/α_2 (b) K_1/K_2

(c) $[H^+]_1/[H^+]_2$ (d) $\sqrt{K_1/K_2}$

4. Three bases XOH, YOH and ZOH have pK_b values 2, 3 and 4 respectively; the strongest conjugate acid is:

(a) XOH_2^+ (b) YOH_2^+

(c) ZOH_2^+ (d) all are same

5. Aqueous solution of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is (are): **(IIT 2010)**

(a) HNO_3 and CH_3COOH

(b) KOH and CH_3COONa

(c) HNO_3 and CH_3COONa

(d) CH_3COOH and CH_3COONa

6. Four solutions of NH_4Cl are taken with concentrations 1 M, 0.1 M, 0.01 M and 0.001 M. Their degree of hydrolysis are h_1, h_2, h_3 and h_4. What is the graduation of degree of hydrolysis?

(a) $h_1 > h_2 > h_3 > h_4$ (b) $h_1 = h_2 = h_3 = h_4$

(c) $h_4 > h_3 > h_2 > h_1$ (d) None of these

7. Which has maximum solubility AB, AB_2, AB_3 and AB_4 if K_{sp} for all the salts are 10^{-10} ?

(a) AB (b) AB_2 (c) AB_3 (d) AB_4

8. Dissociation of an indicator can be considered as,

$$HIn \rightleftharpoons H^+ + In^-$$

Colours of HIn and In^- are different. Which statement is correct?

(a) Solution assumes colours of HIn when pH = P_{K-1}

(b) Solution assumes colours of In^- when pH = P_{K+1}

(c) Solution assumes colours of HIn^- when pH = P_{K+1}

(d) Solution assumes colours of In^- when pH = P_{K-1}

9. The % error in $[H^+]$ made by neglecting the ionisation of water in 10^{-6} M NaOH is:

(a) 1% (b) 2% (c) 3% (d) 4%

10. 50 mL $N/10$ NaOH solution is mixed with 50 mL $N/20$ HCl solution. The resulting solution will:

(a) turn phenolphthalein solution pink

(b) turn blue litmus red

(c) turn methyl orange red

(d) $[H^+] < [OH^-]$

11. An acid indicator HIn has $K_a = 3 \times 10^{-5}$, the acid form is red and basic form is blue. Which is correct?

(a) pH = 5 when indicator is 75% red

(b) pH = 4.05 when indicator is 75% red

(c) pH = 5 when indicator is 75% blue

(d) pH = 4.05 when indicator is 75% blue

12. Which of the following will function as buffer? **[IAS (Pre.) 1997]**

(a) NaCl + NaOH (b) Borax + boric acid

(c) $NaH_2PO_4 + NaHPO_4$ (d) $NH_4Cl + NH_4OH$

13. Choose the correct statement(s):

(a) pH of an acidic buffer increases if more salt is added.

(b) pH of a basic buffer decreases if more salt is added.

(c) In a saturated solution, ionic product is equal to its solubility product.

(d) The term solubility product is only for sparingly soluble salts.

14. In the following reaction,

$$\underset{(A)}{[Cu(H_2O)_3(OH)]^+} + \underset{(B)}{[Al(H_2O)_6]^{3+}} \longrightarrow \underset{(C)}{[Cu(H_2O)_4]^{2+}} + \underset{(D)}{[Al(H_2O)_5(OH)]^{2+}} :$$

(a) (A) is an acid and (B) is a base

(b) (A) is a base and (B) is an acid

(c) (*C*) is the conjugate acid of (*A*) and (*D*) is the conjugate base of (*B*)

(d) (*C*) is the conjugate base of (*A*) and (*D*) is the conjugate acid of (*B*)

15. Which among the following will not react with NaOH or which is not acid salt?

(a) NaH_2PO_2 (b) Na_2HPO_3 (c) Na_2HPO_2 (d) $NaHCO_3$

Direction: In the following three questions, more than one of the answers given may be correct. Select the correct answers and mark it according to the codes. [BHU (Med.) 2007]

Codes:

(a) 1, 2 and 3 are correct (b) 1 and 2 are correct

(c) 2 and 4 are correct (d) 1 and 3 are correct

16. If equal volumes of 0.1 *M* HBr and 0.1 *M* KOH are mixed, then which of the following is/are correct about the resulting solution?

(1) $[H_3O^+] = 1.0 \times 10^{-7}$ mol L^{-1}

(2) $[OH^-] = 1.0 \times 10^{-7}$ mol L^{-1}

(3) $[K^+] = 0.05$ mol L^{-1}

(4) $[Br^-] = 0.10$ mol L^{-1}

17. Which of the following solutions will be acidic?

(1) 0.1 *M* $FeSO_4$ (2) 0.1 *M* $(NH_4)_2SO_4$

(3) 0.1 *M* CH_3COONa (4) 0.1 *M* NH_4OH

18. In a buffer solution consisting NaH_2PO_4 and Na_2HPO_4: [BHU (Mains) 2010]

(1) NaH_2PO_4 is acid and Na_2HPO_4 is salt

(2) The pH of solution can be calculated using the relation :

$$pH = pK_2 + \log_{10}\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

(3) The Na_2HPO_4 is acid and NaH_2PO_4 is salt

(4) The pH can not be calculated

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as **'Assertion' (A)** and **'Reason' (R).** While answering these questions you are required to choose any one of the following four responses:

(a) If both (A) and (R) are correct and (R) is the correct explanation for (A).
(b) If both (A) and (R) are correct but (R) is not the correct explanation for (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If both (A) and (R) are incorrect.

1. (A) A very dilute acidic solution of Cd^{2+} and Ni^{2+} gives yellow precipitate of CdS on passing hydrogen sulphide.
(R) Solubility product of CdS is more than that of NiS.

2. (A) In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of the acid required at the equivalence point is twice that of the acid required using phenolphthalein as indicator.
(R) Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3. **(IIT 1991)**

3. (A) The pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.
(R) The ionisation of acetic acid is suppressed by the addition of sodium acetate.

4. (A) In acidic medium, Zn^{2+} is not precipitated by S^{2-} ions.
(R) Common ion effect reduces the concentration of S^{2-} ions to the minimum level.

5. (A) In the acid-base titration involving a strong base and a weak acid, methyl orange can be used as an indicator.
(R) Methyl orange changes its colour in pH range 3 to 5.

6. (A) A mixture of sodium acetate and sodium propionate forms a buffer solution.
(R) A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.

7. (A) When small amount of an acid or base is added to pure water its pH undergoes a change.
(R) Addition of an acid or a base increases the degree of ionisation of water.

8. (A) At 25°C, the pH of $10^{-8}\ M$ HCl is 8.
(R) pH of acidic solution is always below 7 at 25° C.

9. (A) The addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution, will first precipitate AgBr rather than AgCl.
(R) The value of K_{sp} of AgCl $<$ K_{sp} of AgBr. **(AIIMS 2004)**

10. (A) Sb (III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
(R) Concentration of S^{2-} ions in alkaline medium is inadequate for precipitation. **(AIIMS 2004)**

11. (A) Sb_2S_3 is not soluble in yellow ammonium sulphide.
(R) The common ion effect due to S^{2-} ions reduces the solubility of Sb_2S_3. **(AIIMS 2006)**

12. (A) H_2SO_4 acts as a base in presence of $HClO_4$.
(R) Perchloric acid is stronger acid than H_2SO_4.

13. (A) pH of a neutral solution is always 7.
(R) pH of a solution does not depend upon temperature.

14. (A) pH of $10^{-8}\ M$ HCl is not equal to 8.
(R) HCl does not dissociate properly in very dilute solution.

15. (A) If a solution with pH = 2 is diluted to double the volume, the pH of the solution will fall to 1.
(R) pH is inversely proportional to the volume of the solution.

16. (A) If HCl gas is passed through saturated NaCl solution, solid NaCl starts separating out.
(R) HCl decreases the solubility product of NaCl.

17. (A) pH of a buffer changes with temperature.
(R) Ionic product of water (K_w) changes with temperature.

18. (A) $I_2 + I^- \longrightarrow I_3^-$
In above reaction, I_2 is Lewis base.
(R) Electron pair acceptor is Lewis base.

19. (A) Phenolphthalein is used as indicator during the titration of oxalic acid against sodium hydroxide.
(R) The pH range of phenolphthalein is from 8 to 9.6.

20. (A) If K_{sp} is less than K_{ip}, the precipitate is formed.
(R) Solubility product (K_{sp}) is the highest limit of ionic product of electrolyte solutions.

21. (A) H_3PO_3 is a dibasic acid.
(R) There are two hydrogen atoms directly attached to phosphorus. **(AIIMS 2007)**

22. (A) NaCl is precipitated when HCl gas is passed in a saturated solution of NaCl.
(R) HCl is a strong acid. **(AIIMS 2007)**

23. (A) On mixing 500 mL of $10^{-6}\ M$ Ca^{2+} ion and 500 mL of $10^{-6}\ MF^-$ ion, the precipitate of CaF_2 will be obtained. $K_{sp}(CaF_2) = 10^{-18}$.
(R) If K_{sp} is greater than ionic product, precipitate will be obtained. **(AIIMS 2007)**

24. (A) The aqueous solution of CH_3COONa is alkaline in nature.
(R) Acetate ion undergoes an ionic hydrolysis. **(EAMCET 2008)**

25. (A) An aqueous solution of ammonium acetate can act as a buffer.
(R) Acetic acid is a weak acid and NH_4OH is a weak base. **(EAMCET 2010)**

26. (A) $[Al(H_2O)_6]^{3+}$ is a stronger acid than $[Mg(H_2O)_6]^{2+}$.
(R) Size of $[Al(H_2O)_6]^{3+}$ smaller than $[Mg(H_2O)_6]^{2+}$ and possesses more effective nuclear charge. **(AIIMS 2010)**

Answers : OBJECTIVE QUESTIONS

Set–1

1. (c) 2. (b) 3. (a) 4. (d) 5. (d) 6. (c) 7. (a) 8. (c)
9. (c) 10. (d) 11. (a) 12. (b) 13. (b) 14. (b) 15. (d) 16. (b)
17. (c) 18. (a) 19. (d) 20. (a) 21. (a) 22. (d) 23. (c) 24. (a)
25. (c) 26. (c) 27. (a) 28. (c) 29. (b) 30. (d) 31. (b) 32. (d)
33. (d) 34. (c) 35. (a) 36. (c) 37. (a) 38. (c) 39. (d) 40. (c)
41. (b) 42. (b) 43. (a) 44. (d) 45. (a) 46. (c) 47. (d) 48. (d)
49. (b) 50. (c) 51. (a) 52. (d) 53. (a) 54. (d) 55. (c) 56. (b)
57. (c) 58. (d) 59. (b) 60. (a) 61. (a) 62. (b) 63. (c) 64. (d)
65. (d) 66. (a) 67. (a) 68. (b) 69. (c) 70. (b) 71. (d) 72. (d)
73. (d) 74. (a) 75. (b) 76. (b) 77. (d) 78. (b) 79. (c) 80. (a)
81. (c) 82. (a) 83. (b) 84. (d) 85. (d) 86. (d) 87. (c) 88. (c)
89. (b) 90. (b) 91. (d) 92. (a) 93. (a) 94. (a) 95. (d) 96. (a)
97. (a) 98. (b) 99. (c) 100. (a) 101. (a) 102. (a) 103. (d) 104. (d)
105. (a) 106. (b) 107. (c) 108. (b) 109. (b) 110. (a) 111. (d) 112. (c)
113. (c) 114. (b) 115. (c) 116. (c) 117. (d) 118. (b) 119. (b) 120. (b)
121. (c) 122. (b) 123. (d) 124. (d) 125. (b) 126. (c) 127. (a) 128. (a)
129. (b) 130. (a) 131. (a) 132. (a) 133. (c) 134. (c) 135. (a) 136. (c)
137. (d) 138. (b) 139. (a) 140. (d) 141. (d) 142. (c) 143. (a) 144. (b)
145. (c) 146. (c) 147. (d) 148. (c) 149. (b) 150. (d) 151. (d) 152. (a)
153. (a) 154. (b) 155. (c) 156. (a) 157. (d) 158. (c) 159. (b) 160. (a)
161. (b) 162. (b) 163. (d) 164. (d) 165. (d) 166. (a) 167. (a) 168. (d)
169. (c) 170. (d) 171. (b) 172. (b) 173. (a) 174. (b) 175. (b) 176. (c)
177. (b) 178. (d) 179. (c) 180. (a) 181. (a) 182. (b) 183. (c) 184. (c)
185. (b) 186. (d) 187. (d) 188. (b) 189. (a) 190. (d) 191. (c) 192. (a)
193. (b) 194. (d) 195. (c) 196. (c) 197. (c) 198. (b) 199. (c) 200. (a)
201. (d) 202. (d) 203. (a) 204. (b) 205. (c) 206. (c) 207. (d) 208. (c)
209. (b) 210. (c) 211. (b) 212. (d) 213. (d) 214. (a) 215. (b) 216. (a)
217. (b) 218. (d) 219. (d) 220. (b) 221. (b) 222. (c) 223. (c) 224. (b)
225. (d) 226. (a) 227. (d) 228. (b) 229. (c) 230. (a) 231. (b) 232. (d)
233. (a) 234. (d) 235. (c) 236. (c) 237. (b) 238. (d) 239. (b) 240. (a)
241. (b) 242. (b) 243. (b) 244. (d) 245. (b) 246. (c) 247. (a) 248. (d)
249. (d) 250. (a) 251. (c) 252. (a) 253. (c) 254. (b) 255. (a) 256. (a)
257. (a) 258. (c) 259. (c) 260. (d) 261. (b)

Set–2

1. (b) 2. (d) 3. (a, c, d) 4. (c) 5. (c, d) 6. (c) 7. (d) 8. (a, b)
9. (a) 10. (a, d) 11. (b, c) 12. (b, d) 13. (a, b, c) 14. (b, c) 15. (a, b, c) 16. (a)
17. (b) 18. (a)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c) 2. (b) 3. (d) 4. (a) 5. (d) 6. (b) 7. (c) 8. (d)
9. (c) 10. (c) 11. (d) 12. (a) 13. (d) 14. (c) 15. (d) 16. (c)
17. (a) 18. (d) 19. (a) 20. (b) 21. (c) 22. (b) 23. (d) 24. (a)
25. (c) 26. (a)

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

The following questions contain single correct option:

1. The pH value of 10^{-3} M aqueous solution of NaCl is:
(a) 7 (b) 3 (c) 11 (d) 14
[**Hint:** NaCl is the salt of strong acid HCl and strong base NaOH. Its aqueous solution will be neutral with pH equal to seven.]

2. The acidic buffer solution can be prepared by mixing solutions of:
(a) sodium acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
~~(d) sodium chloride and sodium hydroxide~~

3. ~~Hydrolysis constants of two salts KA and KB of weak acids~~ HA and HB are 10^{-8} and 10^{-6}. If the dissociation constant of third acid HC is 10^{-2}. The order of acidic strengths of three acids will be:
(a) $HA > HB > HC$ (b) $HB > HA > HC$
(c) $HC > HA > HB$ (d) $HA = HB = HC$

[**Hint:** $K_a(HA) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$

$K_a(HB) = \frac{K_w}{K_h} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

$K_a(HC) = 10^{-2}$

Greater the value of dissociation constant K_a, more is the acidic strength.]

4. Three sparingly soluble salts that have same solubility products are given below:
I. A_2X II. AX III. AX_3
Their solubilities in a saturated solution will be such that:
(a) III > II > I (b) III > I > II (c) II > III > I (d) II > I > III

[**Hint:** $S = \sqrt{K_{sp}}$ for AX; $S = \left[\frac{K_{sp}}{4}\right]^{1/3}$ for A_2X;

$S = \left[\frac{K_{sp}}{27}\right]^{1/4}$ for AX_3

$\therefore \quad S_{II} > S_I > S_{III}$]

5. Consider the three solutions of 1 M concentration.
1. Sodium acetate (CH_3COONa)
2. Acetic acid + Sodium acetate ($CH_3COOH + CH_3COONa$)
3. Acetic acid (CH_3COOH)

The pH of these solutions will lie in the following sequence:
(a) 3 < 2 < 1 (b) 2 < 1 < 3 (c) 1 < 2 < 3 (d) 3 < 1 < 2

[**Hint:** $\underset{\text{pH} < 7}{CH_3COOH \text{ (Acetic acid)}} < \underset{\text{Buffer}}{(CH_3COOH + CH_3COONa)} < \underset{\substack{\text{pH} > 7 \\ \text{Salt of weak acid} \\ \text{with strong base}}}{CH_3COONa}$]

6. Glycine NH_2CH_2COOH behaves:
(a) as a Bronsted acid
(b) as a Bronsted base
(c) both as an acid and a base
(d) neither as an acid nor as a base

7. Solubility of Hg_2Cl_2 in a solvent is S moles/litre. Its solubility product will be:
(a) $16S^2$ (b) $8S^2$ (c) $16S^4$ (d) $4S^3$
[**Hint:** $Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$]

8. Arrange the following acids in increasing order of their acid strength:
I. $HClO_4$ II. H_2SO_4 III. H_3PO_4
(a) III < II < I (b) I < II < III (c) II < III < I (d) III < I < II

9. Select the anion which is the strongest bronsted base:
(a) ClO_4^- (b) ClO_3^- (c) ClO_2^- (d) ClO^-

[**Hint:** $HClO_4 > HClO_3 > HClO_2 > HClO$
(Decreasing acidic character)

$ClO_4^- < ClO_3^- < ClO_2^- < ClO^-$
(Increasing basic strength)

(Conjugate base of strong acid is weak base)]

10. $M(OH)_x$ has a K_{sp} of 4×10^{-9} and its solubility is 10^{-3} M. The value of x is:
(a) 4 (b) 1 (c) 3 (d) 2

11. What is the maximum possible concentration of Ni^{2+} ions in a solution containing 0.15 M HCl and 0.10 M H_2S? [Given that, $K_{sp}(NiS) = 2 \times 10^{-21}$ and $[S^{2-}]_{H_2S} = 4 \times 10^{-21}$]:
(a) 0.65 M (b) 0.45 M (c) 0.10 M (d) 0.15 M

12. The pH of 10^{-10} M H_2SO_4 will be almost:
(a) 4 (b) 7 (c) 6 (d) 0

13. Solubility of calcium phosphate (molecular mass, M) in water is W g per 100 mL at 25°C. Its solubility product at 25°C will be approximately:
(a) $10^9\left(\frac{W}{M}\right)^5$ (b) $10^7\left(\frac{W}{M}\right)^5$ (c) $10^5\left(\frac{W}{M}\right)^5$ (d) $10^3\left(\frac{W}{M}\right)^5$

[**Hint:** $S = \frac{10W}{M}$ mol litre

K_{sp} of $Ca_3(PO_4)_2 = 108S^5$

$= 108\left(\frac{10W}{M}\right)^5$

$= 10^7\left(\frac{W}{M}\right)^5$ (approximately)]

14. When some amount of sodium acetate is further added to a mixture of acetic acid and sodium acetate, then pH of the solution:

(a) increases
(b) decreases
(c) remains same
(d) none of these can be predicted from given information

[**Hint:** $pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

When the concentration of salt is increased, the value of pH will increase.]

15. When strong base (NaOH) is added to the weak acid (acetic acid, CH_3COOH), then dissociation of acetic acid increases; this effect is known as:

(a) common ion effect (b) reverse ion effect
(c) saltation effect (d) solubility effect

[**Hint:** $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Ionization of acetic acid will increase with the progress of its neutralization. This effect is called reverse ion effect.]

16. In our body, carbon dioxide (CO_2) combines with water (H_2O) to form carbonic acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbonic acid undergoes dissociation as,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

During the physical and mental stress, the rate of respiration increases, which results in the decrease in concentration of CO_2 in the blood. What will be the effect on pH of human blood during the stress?

(a) Decreases (b) Remains same
(c) Increases (d) Cannot be predicted

17. The correct order of basic strength is: **(AIIMS 2007)**

(a) $H_2O < OH^- < CH_3OH < CH_3O^-$
(b) $CH_3OH < H_2O < CH_3O^- < OH^-$
(c) $H_2O < CH_3OH < OH^- < CH_3O^-$
(d) $OH^- < H_2O < CH_3O^- < CH_3OH$

18. Which of the following orders is expected to be correct?

(a) $pK_a(ClCH_2COOH) > pK_a(CH_3COOH) > pK_a(CH_3CH_2COOH)$
(b) $pK_a(ClCH_2COOH) < pK_a(CH_3COOH) < pK_a(CH_3CH_2COOH)$ /
(c) $pK_a(ClCH_2COOH) > pK_a(CH_3COOH) < pK_a(CH_3CH_2COOH)$
(d) $pK_a(ClCH_2COOH) < pK_a(CH_3COOH) > pK_a(CH_3CH_2COOH)$

19. The concentration of H_3^+O ions in pure water is 10^{-6} mol dm^{-3}. The corresponding concentration of OH^- ions will be:

(a) 10^{-14} mol dm^{-3} (b) 10^{-8} mol dm^{-3}
(c) 10^{-6} mol dm^{-3} (d) 10^{-7} mol dm^{-3}

[**Hint:** In water, $[H^+] = [OH^-] = 10^{-6}$ mol dm^{-3}]

20. What will be the pH of a solution formed by mixing 40 cm^3 of 0.1 *M* HCl with 10 cm^3 of 0.45 *M* NaOH?

(a) 10 (b) 8 (c) 5 (d) 12

[**Hint:** Number of moles of HCl $= \frac{MV}{1000} = \frac{0.1 \times 40}{1000} = 0.004$

Number of moles of NaOH $= \frac{MV}{1000} = \frac{0.45 \times 10}{1000} = 0.0045$

Remaining moles of NaOH after neutralization = 0.0005

Molarity of $OH^- = \frac{0.0005}{50} \times 1000 = 0.01M$

$pOH = 2 \quad \therefore \quad pH = 14 - 2 = 12$]

21. In the following reaction:

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

which two substances are Bronsted bases?

(a) CO_3^{2-} and H_3O^+ (b) HCO_3^- and H_3O^+
(c) HCO_3^- and CO_3^{2-} (d) CO_3^{2-} and H_2O

22. Which are strong acids?

I. $HClO_3$ II. H_2SeO_3 III. H_3AsO_4

(a) I only (b) III only
(c) I and III only (d) II and III only

23. $HCOOH \rightleftharpoons HCOO^- + H^+; \quad K_a = 1.7 \times 10^{-4}$

The ionization of formic acid is represented above. Calculate $[H^+]$ of a solution initially containing 0.1 *M* HCOOH and 0.05 *M* HCOONa:

(a) 8.5×10^{-5} *M* (b) 3.4×10^{-4} *M*
(c) 4.1×10^{-3} *M* (d) 1.8×10^{-2} *M*

24. Carbonic acid, H_2CO_3, is a diprotic acid for which $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$. Which solution will produce a pH closest to 9?

(a) 0.1 *M* H_2CO_3
(b) 0.1 *M* Na_2CO_3
(c) 0.1 *M* $NaHCO_3$
(d) 0.1 *M* $NaHCO_3$ and 0.1 *M* Na_2CO_3

25. What is the conjugate acid of HPO_4^{2-}?

(a) H_3PO_4 (b) $H_2PO_4^-$ (c) H_3O^+ (d) PO_4^{3-}

26. What is the K_b of a weak base that produces one OH^- per molecule if a 0.05 *M* solution is 2.5% ionized?

(a) 7.8×10^{-8} (b) 1.6×10^{-6} (c) 3.2×10^{-5} (d) 1.2×10^{-3}

[**Hint:** $K_b = C\alpha^2$

$$= 0.05 \times \left(\frac{2.5}{100}\right)^2 = 3.1 \times 10^{-5}]$$

27. The amount of sodium hydrogen carbonate, $NaHCO_3$, in an antacid tablet is to be determined by dissolving the tablet in water and titrating the resulting solution with hydrochloric acid. Which indicator is the most appropriate for this titration?

Acid	K_a
H_2CO_3	2.5×10^{-4}
HCO_3^-	2.4×10^{-8}

(a) Methyl orange, $pK_{In} = 3.7$
(b) Bromothymol blue, $pK_{In} = 7.0$
(c) Phenolphthalein, $pK_{In} = 9.3$
(d) Alizarin yellow, $pK_{In} = 12.5$

28. If equal volumes of $BaCl_2$ and NaF solutions are mixed, which of these combinations will not give a precipitate?

Substance	K_{sp}
BaF_2	1.7×10^{-7}

(a) 0.004 *M* $BaCl_2$ and 0.02 *M* NaF
(b) 0.010 *M* $BaCl_2$ and 0.015 *M* NaF
(c) 0.015 *M* $BaCl_2$ and 0.010 *M* NaF
(d) 0.020 *M* $BaCl_2$ and 0.002 *M* NaF

[**Hint:** In the mixture of 0.02 M $BaCl_2$ and 0.002 M NaF, the ionic product is less than the solubility product, hence there will be no precipitation of BaF_2.]

29. HCN is a weak acid ($K_a = 6.2 \times 10^{-10}$). NH_4OH is a weak base ($K_b = 1.8 \times 10^{-5}$). A 1 M solution of NH_4CN would be:
(a) strongly acidic (b) weakly acidic
(c) neutral (d) weakly basic
[**Hint:** Since, $K_b > K_a$, hence the medium will be weakly basic.]

30. How many moles of HCOONa must be added to 1 L of 0.1 M HCOOH to prepare a buffer solution with a pH of 3.4?
Given: K_a for HCOOH $= 2 \times 10^{-4}$
(a) 0.01 (b) 0.05 (c) 0.1 (d) 0.2

31. Silver ions are added to the solution with:
$$[Br^-] = [Cl^-] = [CO_3^{2-}] = [AsO_4^{3-}] = 0.1\,M$$
Which compound will precipitate at the lowest $[Ag^+]$?
(a) AgBr ($K_{sp} = 5 \times 10^{-13}$)
(b) AgCl ($K_{sp} = 1.8 \times 10^{-10}$)
(c) Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$)
(d) Ag_3AsO_4 ($K_{sp} = 10^{-22}$)
[**Hint:** In case of AgBr, the ionic product will exceed the solubility product before AgCl, Ag_2CO_3 and Ag_3AsO_4. Thus, AgBr will start precipitation before other salts.]

32. The equilibrium constant for this reaction is approximately 10^{-3}.
$$HPO_4^{2-}(aq.) + HCO_3^-(aq.) \rightleftharpoons H_2PO_4^-(aq.) + CO_3^{2-}(aq.)$$
Which is the strongest conjugate base in this reaction?
(a) $HPO_4^{2-}(aq.)$ (b) $HCO_3^-(aq.)$
(c) $H_2PO_4^-(aq.)$ (d) $CO_3^{2-}(aq.)$
[**Hint:** Conjugate base of weak acid is strong base.]

33. Which mixture forms a buffer when dissolved in 1 L of water?
(a) 0.2 mol NaOH + 0.2 mol HBr
(b) 0.2 mol NaCl + 0.3 mol HCl
(c) 0.4 mol HNO_2 + 0.2 mol NaOH
(d) 0.5 mol NH_3 + 0.5 mol HCl

34. The equilibrium constant for this reaction is 3.6×10^{-7}.
$$OCl^-(aq.) + H_2O(l) \rightleftharpoons HOCl(aq.) + OH^-(aq.)$$
What is K_a for HOCl?
(a) 2.8×10^{-8} (b) 3.6×10^{-7} (c) 6×10^{-4} (d) 2.8×10^{-6}

35. What is the concentration of H^+ in a solution that is prepared by mixing 50 mL of 0.5 M HCl and 200 mL of 0.25 M HCl?
(a) 0.30 M (b) 0.35 M (c) 0.40 M (d) 0.45 M

36. K_a for hydrofluoric acid is 6.9×10^{-4}. What is the equilibrium constant K for the following reaction?
$$F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)$$
(a) 6.9×10^{-11} (b) 1.4×10^{-11} (c) 2.6×10^{-9} (d) 8.3×10^{-6}

37. A solution of 2 M formic acid (HCOOH) is 0.95% ionized. What is the K_a of formic acid?
(a) 1.9×10^{-2} (b) 1.8×10^{-4} (c) 9×10^{-5} (d) 4.5×10^{-5}
[**Hint:** $K_a = C\alpha^2 = 2 \times \left(\frac{0.95}{100}\right)^2$]

38. If 0.1 mol of salt is added to 1 L water, which of these salts is expected to produce the most acidic solution?
(a) $NaC_2H_3O_2$ (b) NH_4NO_3
(c) $CuSO_4$ (d) $AlCl_3$

39. A sample of hard water contains 0.005 mole of calcium chloride per litre. What is the minimum concentration of sodium sulphate which must be added for removing the Ca^{2+} ions from this water sample? K_{sp} of $CaSO_4 = 2.4 \times 10^{-5}$.
(a) 4.8×10^{-2} (b) 4.8×10^{-3}
(c) 2.4×10^{-2} (d) 2.4×10^{-3}

40. Match the List-I and List-II:

	List-I		List-II
(A)	The limits of pH values of buffer solution	(i)	5×10^{-12}
(B)	Concentration of $[H_3O^+]$ in 0.001 M $Ba(OH)_2$	(ii)	Equal
(C)	The buffer capacity of a solution is maximum when concentration of salt to that of acid is	(iii)	10^{-14}
(D)	Ionic product of water is	(iv)	$pK_a \pm 1$

Codes:	A	B	C	D
(a)	iv	ii	i	iii
(b)	iv	i	iii	ii
(c)	i	iv	ii	iii
(d)	iv	i	ii	iii

41. Match the List-I and List-II:

	List-I		List-II
(A)	Degree of ionization of weak electrolytes increases	(i)	Common ion effect
(B)	pH of water decreases on	(ii)	pH = 4
(C)	The solution has hydronium ion concentration of 0.0001 mol/litre	(iii)	Heating
(D)	The addition of NaOH to $Ca(OH)_2$ solution precipitates $Ca(OH)_2$	(iv)	On dilution

Codes:	A	B	C	D
(a)	iv	iii	i	ii
(b)	iii	iv	ii	i
(c)	iv	iii	ii	i
(d)	iv	ii	iii	i

42. Which of the following is not correct about the percentage ionization of BOH ?
(a) $\dfrac{K_w[H^+]}{K_b + K_w}$ (b) $100 \times \sqrt{\dfrac{K_b}{C}}$
(c) $\dfrac{100}{1 + 10^{(pK_b - pOH)}}$ (d) $\dfrac{K_b \times 100}{K_b + OH^-}$

[**Hint:** $BOH \rightleftharpoons B^+ + OH^-$
$$\begin{array}{llll} t_0 & C & 0 & 0 \\ t_{eq.} & C - C\alpha & C\alpha & C\alpha \end{array}$$
$$K_b = \frac{[B^+][OH^-]}{[BOH]} = \frac{C^2\alpha^2}{C(1-\alpha)}$$
$$\approx C\alpha^2 \qquad (\alpha <<< 1)$$

$$\alpha = \sqrt{\frac{K_b}{C}} \quad \% \text{ ionization} = 100 \times \sqrt{\frac{K_b}{C}} \qquad ...(1)$$

$$\alpha = \frac{[B^+]}{[B^+] + [BOH]} = \frac{1}{1 + \frac{[BOH]}{[B^+]}} = \frac{1}{1 + \frac{[OH^-]}{[K_b]}}$$

$$\alpha = \frac{K_b}{K_b + OH^-} \qquad ...(2)$$

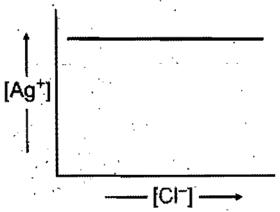
$$\text{Percentage ionization} = \frac{100\,K_b}{K_b + OH^-}$$

$$\alpha = \frac{1}{1 + \frac{[OH^-]}{K_b}} = \frac{1}{1 + \frac{10^{-\text{pOH}}}{10^{-\text{p}K_b}}}$$

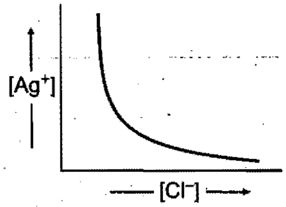
$$\alpha = \frac{1}{1 + 10^{(\text{p}K_b - \text{pOH})}}$$

$$\therefore \text{ Percentage ionization} = \frac{100}{1 + 10^{(\text{p}K_b - \text{pOH})}}]$$

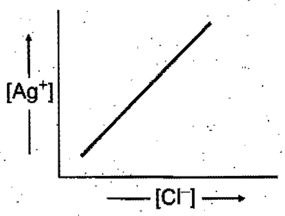
43. When NaCl is added gradually to the saturated solution of AgCl then which of the following plot is correct ?



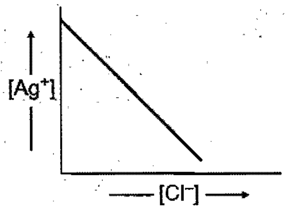
(a)



(b)



(c)



(d)

The following questions may have more than one correct options:

1. Which of the following statements is/are correct about the ionic product of water?
   (a) K (equilibrium constant of water) $< K_w$ (ionic product of water)
   (b) $\text{p}K > \text{p}K_w$
   (c) At 300 K, K_w of water becomes 10^{-12}
   (d) Ionic product of water at 25°C is 10^{-14}

2. Which among the following statements is/are correct?
   (a) $\text{pH} = -\log_{10} (H_3O^+)$
   (b) pH decreases with increase of temperature
   (c) pH cannot be zero, negative or more than 14
   (d) If a solution is diluted ten times, its pH increases by 1

3. Which among the following statements is/are correct?
   (a) pH of 10^{-8} M HCl is equal to 8
   (b) Conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
   (c) pH of 0.1 M NaCl (aqueous solution) $= \frac{1}{2}\text{p}K_w$
   (d) Ionization of water increases with decrease in temperature

4. Let us consider the ionization of HCl in the aqueous solution of CH_3COOH.

   $$CH_3COOH + HCl \rightleftharpoons CH_3COOH_2^+ + Cl^-$$

   Select the correct statement(s) among the following:
   (a) Cl^- is the conjugate base of HCl
   (b) CH_3COOH is the conjugate base of $CH_3COOH_2^+$
   (c) $CH_3COOH_2^+$ is the conjugate base of CH_3COOH
   (d) Cl^- is the conjugate base of CH_3COOH

5. Which among the following species act both as an acid as well as a base?
   (a) SO_4^{2-} (b) HSO_4^-
   (c) PO_4^{3-} (d) NH_3

6. Which among the following salts will give basic solution on hydrolysis? **[PET (MP) 2008]**
   (a) NaH_2PO_4 (b) NH_4Cl
   (c) NaCl (d) K_2CO_3

7. Which among the following represent the conjugate acid/base pairs?
   (a) H_3O^+ / H_2O
   (b) H_2SO_4 / SO_4^{2-}
   (c) HCO_3^- / CO_3^{2-}
   (d) All are conjugate acid/base pairs

8. If you have saturated solution of CaF_2 then:
   (a) $[Ca^{2+}] = \sqrt{K_{sp}}$ (b) $[Ca^{2+}] = 2[F^-]$
   (c) $2[Ca^{2+}] = [F^-]$ (d) $[Ca^{2+}] = [K_{sp/4}]^{1/3}$

9. The relative strength of two weak bases at same concentration may be given as:
   (a) $\frac{K_{b_1}}{K_{b_2}}$ (b) $\frac{[OH^-]_1}{[OH^-]_2}$
   (c) $\frac{\alpha_1}{\alpha_2}$ (d) $\frac{\sqrt{K_{b_1}}}{\sqrt{K_{b_2}}}$

Answers

- **Single correct option**

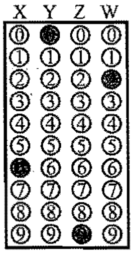
1. (a) **2.** (a) **3.** (c) **4.** (d) **5.** (a) **6.** (c) **7.** (d) **8.** (a)
9. (d) **10.** (d) **11.** (b) **12.** (b) **13.** (b) **14.** (a) **15.** (b) **16.** (c)
17. (c) **18.** (b) **19.** (c) **20.** (d) **21.** (d) **22.** (a) **23.** (b) **24.** (c)
25. (b) **26.** (c) **27.** (a) **28.** (d) **29.** (d) **30.** (b) **31.** (a) **32.** (d)
33. (c) **34.** (a) **35.** (a) **36.** (b) **37.** (b) **38.** (b) **39.** (b) **40.** (d)
41. (c) **42.** (c) **43.** (b)

- **One or more than one correct options**

1. (a, b, c, d) **2.** (a, b, d) **3.** (b, c) **4.** (a, b) **5.** (b, d) **6.** (a, d) **7.** (a, c) **8.** (c, d)
9. (b, c, d)

Integer Answer TYPE QUESTIONS

This section contains 13 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. What will be the pH of 0.1 M CH_3COONH_4? Dissociation constants of CH_3COOH and NH_4OH are $K_a = 1.8 \times 10^{-5}$ and $K_b = 1.8 \times 10^{-5}$ respectively.

2. Ionic product of water is 1×10^{-12}. pH of water will be :

3. Calculate the pH at which an acid indicator HIn with concentration 0.1 M changes its colour. (K_a for HIn $= 1 \times 10^{-5}$)

4. Sum of basicity of H_3PO_4, H_3PO_3, H_3PO_2 is equal to :

5. A given weak acid ($0.01\,M$) has $pK_a = 6$. The pH of this solution is :

6. Solubility product of an electrolyte is $6912S^7$. How many ions will be obtained by the ionization of one molecule of electrolyte?

7. The solubility product of $Mg(OH)_2$ is 5×10^{-19} at 25°C. pH of saturated solution of $Mg(OH)_2$ will be :

8. pH of $10^{-x}\,M$ HCl is 6.9586. The value of x will be :

9. If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9, then the pH of 0.1 M NaA solution will be :

10. Consider the titration of 50 mL of 0.1 M HBr with 0.1 M KOH. Calculate pH after 49 mL of the base has been added to the 50 mL of HBr.

11. The dissociation constant of a substituted benzoic acid at 25°C is 1×10^{-4}. The pH of a 0.01 M solution of its sodium salt is: **(IIT 2009)**

[**Hint :** pH of salt after hydrolysis may be calculated as,

$$\begin{aligned} pH &= \frac{1}{2}[pK_w + pK_a + \log C] \\ &= \frac{1}{2}[14 + (-\log 10^{-4}) + \log 0.01] \\ &= \frac{1}{2}[14 + 4 - 2] = 8 \end{aligned}$$

]

12. The total number of diprotic acids among the following is: H_3PO_4, H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2BO_3, H_3PO_2, H_2CrO_4, H_2SO_3 **(IIT 2010)**

[**Hint :** H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4, H_2SO_3 are diprotic acid.]

13. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is: KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3, NH_4NO_3, LiCN **(IIT 2010)**

[**Hint :** Salts of weak acid and strong base will give basic solution on hydrolysis and will turn red litmus to blue KCN, K_2CO_3 and LiCN are such type of salts.]

Answers

1. (7) **2.** (6) **3.** (5) **4.** (6) **5.** (4) **6.** (7) **7.** (8) **8.** (8)
9. (9) **10.** (3) **11.** (8) **12.** (6) **13.** (3)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

Higher the amount of acid or base used to produce a definite change of pH in a buffer solution, higher will be its buffer capacity. Buffer capacity of solution is maximum under the following conditions:

$$[Salt] = [Acid] \text{ (in acid buffer)}$$
$$[Salt] = [Base] \text{ (in base buffer)}$$

pH of a buffer solution lies in the range given below:

$$pH = pK_a \neq 1$$

In other words, any buffer solution can be used as buffer up to two pH units only, depending upon the value of pK_a or pK_b. A buffer is said to be efficient when $pH = pK_a$ or $pOH = pK_b$.

Answer the following questions:

1. Any buffer can be used as a buffer up to:
   (a) 10 pH units (b) 5 pH units (c) 2 pH units (d) 1 pH unit
2. Which among the following solutions will be the most efficient buffer?
   (a) 0.1 M CH_3COONa + 0.01 M CH_3COOH
   (b) 0.1 M NH_4Cl + 0.1 M NH_4OH
   (c) 0.001 M HCOOH + 0.002 M HCOONa
   (d) All of the above
3. The buffer capacity is equal to:
   (a) $\frac{\Delta n}{\Delta pH}$ (b) $\frac{pH}{\Delta n}$ (c) $\pm 1pK_a$ (d) none of these
4. A buffer of acetic acid ($pK_a \approx 4.8$) with sodium acetate will be, when CH_3COOH and CH_3COONa are present in equivalent amounts has pH limits equal to:
   (a) 0 to 4.8 (b) 3.8 to 5.8 (c) 4.3 to 5.3 (d) 4.8
5. Buffer capacity is maximum when:
   (a) one mole of NH_4Cl is added to two moles of NH_4OH
   (b) one mole of NH_4Cl is added to one mole of NH_4OH
   (c) one mole of NH_4Cl is added to one mole of NaOH
   (d) one mole of NaCl is added to one mole of NaOH
6. A buffer solution is prepared by mixing equal concentration of acid (ionisation constant K_a) and a salt. The pH of buffer is: **[JEE (Orissa) 2008]**
   (a) $pK_a + 7$ (b) $14 - pK_a$ (c) pK_a (d) $pK_a + 1$

• Passage 2

When a salt reacts with water to form acidic or basic solution, the process is called hydrolysis. The pH of salt solution can be calculated using the following relations:

$$pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

(for salt of weak acid and strong base.)

$$pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

(for salt of weak base and strong acid.)

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

(for salt of weak acid and weak base.)

where, 'C' represents the concentration of salt.

When a weak acid or a weak base is not completely neutralized by strong base or strong acid respectively, then formation of buffer takes place. The pH of buffer solution can be calculated using the following relation:

$$pH = pK_a + \log\frac{[Salt]}{[Acid]};\ pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

Answer the following questions using the following data:

$$pK_a = 4.7447, pK_b = 4.7447, pK_w = 14$$

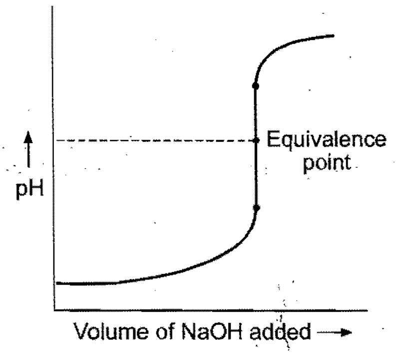
1. When 50 mL of 0.1 M NH_4OH is added to 50 mL of 0.05 M HCl solution, the pH is:
   (a) 1.6021 (b) 12.3979 (c) 4.7447 (d) 9.2553
2. 0.001 M NH_4Cl aqueous solution has pH:
   (a) 6.127 (b) 7.126 (c) 2.167 (d) 1.267
3. 50 mL 0.1 M NaOH is added to 50 mL of 0.1 M CH_3COOH solution, the pH will be:
   (a) 4.7447 (b) 9.2553 (c) 8.7218 (d) 1.6021
4. 1 mole CH_3COOH and 1 mole CH_3COONa are dissolved in water to form 1 litre aqueous solution. The pH of the resulting solution will be:
   (a) 9.2553 (b) 4.7447 (c) 14 (d) 7
5. When 50 mL of 0.1 M NaOH is added to 50 mL of 0.05 M CH_3COOH solution. The pH of the solution is:
   (a) 1.6021 (b) 12.3979 (c) 4.7447 (d) 8.7218

• Passage 3

An acid-base titration consists of the controlled addition of a dissolved base to a dissolved acid (or the reverse). Acid-base react rapidly to neutralize each other. At the equivalence point, enough titrant, the solution being added, has gone into make the chemical amounts of the acid and base exactly equal. The pH of a titration changes every time a drop of titrant is added, but the rate of this change varies enormously. A titration curve, graph of pH as a function of the volume of titrant, displays in detail how the pH changes over the course of an acid-base titration. Significantly, the pH changes most rapidly near the equivalence point. The exact shape of a titration curve depends on the K_a and K_b acid and base.

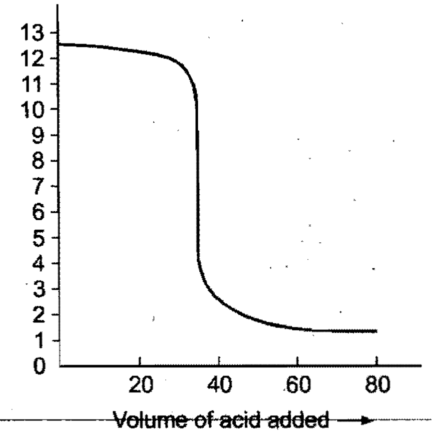
Answer the following questions:

1. The following figure represents titration curve of HCl against NaOH. The pH at equivalence point will be:



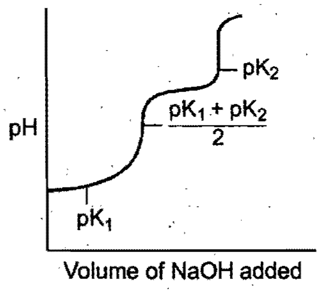
(a) 7 (b) 6 (c) 8 (d) 3

Examine the titration curve below:

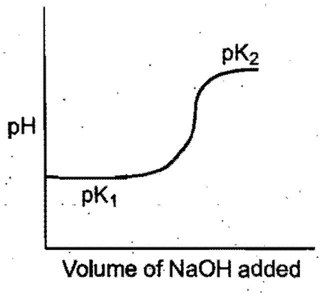


Answer the questions 2, 3 and 4 on the above curve.

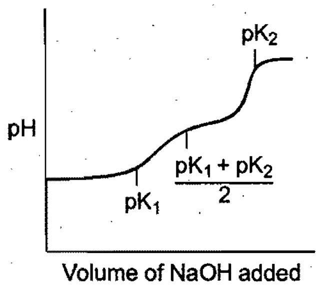
2. Which of the titrations could it represent?
   (a) HCl by KOH (b) RbOH by HBr
   (c) HCl by NaOH (d) NH_3 by HNO_3
3. The suitable indicator for this titration will be:
   (a) bromothymol blue (b) methyl orange
   (c) methyl red (d) all of these
4. The pH at equivalence point is:
   (a) 11 (b) 7 (c) 3 (d) 2
5. Which of the following curves indicates the titration of a weak diprotic acid by NaOH of equivalent strength?



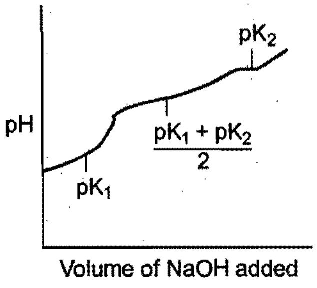
(a)



(b)



(c)



(d)

• Passage 4

Acid rain takes place due to combination of acidic oxides with water. In atmosphere, sulphur dioxide and nitrogen monoxide are oxidised to sulphur trioxide and nitrogen dioxide respectively, which react with water to give sulphuric and nitric acid. The resultant solution so called is acid rain. Sulphur dioxide dissolves in water to form diprotic acid in aqueous solution.

$$SO_2(g) + H_2O(l) \rightleftharpoons HSO_3^- + H^+; K_{a_1} = 10^{-2} M$$

$$HSO_3^- \rightleftharpoons SO_3^{2-} + H^+; \quad K_{a_2} = 10^{-7} M$$

and for equilibrium,

$$SO_2(aq.) + H_2O(l) \rightleftharpoons SO_3^{2-}(aq.) + 2H^+(aq.);$$

$$K_a = K_{a_1} \times K_{a_2} = 10^{-9} \text{ at } 300\,K \text{ at } 27°C$$

Answer the following questions:

1. Which of the following reagents will give white precipitate with the aqueous solution of sulphurous acid?
   (a) NaCl (b) KCl (c) $BaCl_2$ (d) HCl
2. The pH of 0.01 *M* aqueous solution of sodium sulphite will be:
   (a) 8.5 (b) 9 (c) 4.5 (d) 9.5
3. The dominant equilibrium in an aqueous solution of sodium hydrogen sulphite is:
   $$2HSO_3^-(aq.) \rightleftharpoons SO_2(aq.) + SO_3^{2-}(aq.) + H_2O(l)$$
   The equilibrium constant for the above reaction is:
   (a) 10^{-6} (b) 10^{-9} (c) 10^{-5} (d) 10^{-3}
4. Which among the following statements is correct?
   (a) CO_2 gas develops more acidity in rain-water than SO_2
   (b) H_2SO_3 is less acidic than H_2SO_4
   (c) HNO_3 is less acidic than HNO_2
   (d) $SO_2(g)$ is reduced in the atmosphere during thunderstorm

• Passage 5

The product of the concentrations of the ions of an electrolyte raised to power of their coefficients in the balanced chemical equation in the solution at any concentration. Its value is not constant and varies with change in concentration. Ionic product of the saturated solution is called solubility product K_{sp}.

(i) When $K_{ip} = K_{sp}$, the solution is just saturated and no precipitation takes place.

(ii) When $K_{ip} < K_{sp}$, the solution is unsaturated and precipitation will not take place.

(iii) When $K_{ip} > K_{sp}$, the solution is supersaturated and precipitation takes place.

Answer the following questions:

1. The solubility product, K_{sp}, of sparingly soluble salt *MX* at 25°C is 2.5×10^{-9}. The solubility of the salt in mol L^{-1} at this temperature is:
   (a) 1×10^{-14} (b) 5×10^{-8} (c) 1.25×10^{-9} (d) 5×10^{-5}
2. Which of the following is most soluble?
   (a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-70}$) (b) MnS ($K_{sp} = 7 \times 10^{-16}$)
   (c) CuS ($K_{sp} = 8 \times 10^{-37}$) (d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)
3. The concentration of Ag^+ ions in a given saturated solution of AgCl at 25°C is 1.06×10^{-5} g ion per litre. The solubility product of AgCl is:
   (a) 0.353×10^{-10} (b) 0.530×10^{-10}
   (c) 1.12×10^{-10} (d) 2.12×10^{-10}
4. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with:

(a) $10^{-4}\ M\ Ag^+ + 10^{-4}\ M\ Cl^-$
(b) $10^{-5}\ M\ Ag^+ + 10^{-5}\ M\ Cl^-$
(c) $10^{-6}\ M\ Ag^+ + 10^{-6}\ M\ Cl^-$
(d) $10^{-10}\ M\ Ag^+ + 10^{-10}\ M\ Cl^-$

5. When HCl gas is passed through saturated NaCl solution, the ionic product of NaCl is exceeded because of:
(a) increase in Cl^- ion concentration
(b) increase in Na^+ ion concentration
(c) decrease in the NaCl concentration
(d) decrease in Cl^- ion concentration

6. If the solubility of $Li_3Na_3(AlF_6)_2$ is x mol L^{-1}, then its solubility product is equal to:
(a) $12x^3$ (b) $18x^3$ (c) x^8 (d) $2916x^8$

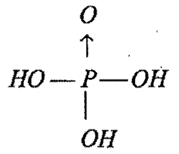
Passage 6

The dissociation of weak electrolyte (weak acid) is expressed in terms of Ostwald dilution law. Stronger is the acid, weaker is its conjugate base. The dissociation constants of an acid (K_a) *and its conjugate base* (K_b) *are related by the given relation:*

$$K_w = K_a \times K_b$$

At 25°C, K_w *(Ionic product of water)* = 10^{-14}.

Phosphoric acid is a weak acid. It is used in fertilizer, food, detergent and toothpaste. Structure of phosphoric acid is:



$$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH \quad (pK_{a_1} = 2.12,\ pK_{a_2} = 7.21,\ pK_{a_3} = 12.32)$$

Aqueous solution of phosphoric acid with a density of 1 g mL^{-1} *containing* 0.05% *by weight of phosphoric acid is used to impart tart taste to many soft drinks.*

Phosphate ion is an interfering radical in qualitative analysis. It should be removed for analysis beyond third group of qualitative analysis.

Answer the following questions:

1. The basicity of phosphoric acid is:
(a) 1 (b) 2 (c) 3 (d) 4

2. The state of hybridization of phosphorous in phosphoric acid is:
(a) sp (b) sp^2 (c) sp^3 (d) sp^3d

3. The removal of PO_4^{3-} in qualitative analysis of basic radicals is made by using a buffer solution of:
(a) HCO_3^- and CO_3^{2-} (b) CH_3COO^- and CH_3COOH
(c) NH_4^+ and NH_4OH (d) none of these

4. What is the molarity of phosphoric acid used in soft drinks?
(a) 5.1×10^{-3} (b) 1.5×10^{-3} (c) 3.1×10^{-3} (d) 2.1×10^{-3}

5. Which among the following relations is correct?
(a) $K_{a_1} < K_{a_2} < K_{a_3}$ (b) $K_{a_1} > K_{a_2} > K_{a_3}$
(c) $K_{a_1} = K_{a_2} = K_{a_3}$ (d) $K_{a_1} > K_{a_3} > K_{a_2}$

6. First ionization of phosphoric acid is:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$
$$pK_{a_1} = 2.21$$

The dissociation constant of conjugate base of H_3PO_4 will be:
(a) 6.45×10^{-9} (b) 1.62×10^{-12}
(c) 3.48×10^{-11} (d) 4.62×10^{-2}

[Hint: $pK_{a_1} = 2.21$

$$K_{a_1} = \text{antilog}(-2.21) = 6.165 \times 10^{-3}$$

$$K_b \text{ (of conjugate base)} = \frac{K_w}{K_{a_1}} = \frac{10^{-14}}{6.165 \times 10^{-3}} = 1.62 \times 10^{-12}$$]

Answers

Passage 1.	1. (c)	2. (b)	3. (a)	4. (b)	5. (b)	6. (c)
Passage 2.	1. (d)	2. (a)	3. (c)	4. (b)	5. (b)	
Passage 3.	1. (a)	2. (b)	3. (d)	4. (b)	5. (a)	
Passage 4.	1. (c)	2. (d)	3. (c)	4. (b)		
Passage 5.	1. (d)	2. (b)	3. (c)	4. (a)	5. (a)	6. (d)
Passage 6.	1. (c)	2. (c)	3. (b)	4. (a)	5. (b)	6. (b)

SELF ASSESSMENT

ASSIGNMENT NO. 10

SECTION-I

Straight Objective Type Questions

This section contains 7 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. When 50 mL of 0.1 M NaOH is mixed with 50 mL of 0.05 M CH_3COOH solution, pH becomes:
(a) 1.602 (b) 12.39
(c) 4.74 (d) 8.72

2. If the degree of dissociation of water at 90°C is 1.28×10^{-8} then the ionisation constant of water at 90°C is:
(a) $7.52 \times 10^{-12}\ M$ (b) $9.07 \times 10^{-15}\ M$
(c) $1.28 \times 10^{-14}\ M$ (d) $1.38 \times 10^{-14}\ M$

3. How much water from 5 litre of $10^{-3}\ M$ HCl should be evaporated to change its pH by 2 units?
(a) 1.5 litre (b) 0.5 litre (c) 2.54 litre (d) 4.95 litre

4. Which among the following cannot exist in an aqueous solution?
(a) NH_4^+ (b) NO_3^-
(c) NO_2^- (d) NH_2^-

5. The pH of an HCl solution is 2. Sufficient water is added to make the pH of new solutions. The hydrogen ion concentration is reduced:
(a) ten fold (b) seven fold
(c) thousand fold (d) hundred fold

6. Consider the following statements:
I. HNO_3 (strong acid) behaves as a base in HF.
II. H_2SO_4 dissociates to a small extent in glacial acetic acid.
III. CH_3COOH (a weak acid) behaves as strong acid in $NH_3(l)$. Select the correct alternate for these statements:
(a) I, II, and III (b) I and III
(c) II and III (d) I and II

7. The solubility of A_2X_5 is x mol dm^{-3}. Its solubility product is:
(a) $36x^6$ (b) $64 \times 10^4\ x^7$
(c) $126x^7$ (d) $1.25 \times 10^4\ x^7$

SECTION-II

Multiple Answers Type Objective Questions

8. During the titration of mixture of NaOH, Na_2CO_3 and an inert substance against hydrochloric acid:
(a) phenolphthalein is used to detect the end point when NaOH is completely neutralized and half of Na_2CO_3 is neutralized
(b) methyl orange is used to detect the final end point
(c) methyl orange is used to detect the first end point
(d) phenolphthalein is used to detect the final end point

9. Solubility product of the hydroxide $M(OH)_2$ is 4×10^{-12}. Select the correct statement(s) among the following:
(a) the pH of its saturated solution will be 10.3
(b) its solubility will decrease in a buffer medium of pH = 9
(c) its solubility will increase in a buffer medium of pH = 1
(d) its solubility is unaffected by pH of the medium

10. Which of the following salt solutions will be basic?
(a) NaCl (b) NaCN (c) K_2CO_3 (d) NH_4NO_3

11. Which of the following salts will not undergo hydrolysis?
(a) NaCl (b) KCl (c) NH_4Cl (d) CH_3COONa

12. Which of the following mixtures will be buffer?
(a) $CH_3COOH + CH_3COONH_4$
(b) HCl + NaCl
(c) Borax + boric acid
(d) $CH_3COOH + CH_3COONa$

SECTION-III

Assertion-Reason Type Questions

This section contains 5 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

13. **Statement-1:** Mixture of CH_3COOH and CH_3COONH_4 is not a buffer solution.

Because

Statement-2: Acid buffer contains the mixture of weak acid and its salt with strong base.

14. **Statement-1:** Addition of NH_4OH to an aqueous solution of $BaCl_2$ in the presence of excess NH_4Cl, precipitates $Ba(OH)_2$.

Because

Statement-2: $Ba(OH)_2$ is soluble in water.

15. **Statement-1:** pH of blood does not change inspite of taking acidic foods.

Because

Statement-2: Blood behaves as buffer solution.

16. **Statement-1:** Borax forms alkaline aqueous solution.

Because

Statement-2: Borax is the salt of a weak acid (H_3BO_3) and a strong base (NaOH).

17. **Statement-1:** When the aqueous solution of CH_3COONH_4 is diluted, then its degree of hydrolysis does not change.

Because

Statement-2: It is the salt of a weak acid and a weak base hence its degree of hydrolysis does not depend on the concentration.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as given:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

18. Match the Column-I with Column-II:

Column-I (Salt solution in water)	**Column-II (Nature of hydrolysis)**
(a) NaCl	(p) Cationic hydrolysis
(b) CH_3COONa	(q) Anionic hydrolysis
(c) NH_4CN	(r) Both cationic and anionic hydrolysis
(d) NH_4Cl	(s) Does not undergo hydrolysis

19. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) H_3PO_2	(p) Dibasic
(b) H_3PO_4	(q) Monobasic
(c) H_3PO_3	(r) Tribasic
(d) H_3BO_3	(s) Aprotic

20. Match the Column-I with Column-II:

Column-I (Salt)	**Column-II (Degree of hydrolysis)**
(a) NH_4Cl	(p) No hydrolysis
(b) NaCl	(q) $h = \sqrt{\frac{K_h}{C}}$
(c) CH_3COONa	(r) $h = \sqrt{\frac{K_w}{CK_b}}$
(d) CH_3COONH_4	(s) $h = \sqrt{K_h}$

Answers

1. (b) **2.** (a) **3.** (a) **4.** (d) **5.** (c) **6.** (a) **7.** (d) **8.** (a, b)

9. (a, b, c) **10.** (b, c) **11.** (a, b) **12.** (c, d) **13.** (d) **14.** (d) **15.** (a) **16.** (a)

17. (a) **18.** (a-s) (b-q) (c-r) (d-p) **19.** (a-q) (b-r) (c-p) (d-q, s) **20.** (a-q, r) (b-p) (c-q) (d-s)

CHAPTER 11

OXIDATION AND REDUCTION

(Redox Reactions)

Several chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed **oxidation-reduction** or **redox reactions.** Redox reactions play a vital role in our daily life. These reactions are accompanied by energy changes in the form of heat, light, electricity, etc. Generation of electricity in batteries, production of heat energy by burning chemical substances, extraction of metals such as sodium, aluminium, iron, etc., manufacture of a number of useful products such as caustic soda, potassium permanganate, etc.; electrodeposition or electroplating are common examples of redox reactions. Before we discuss the application of redox reactions in the production of electricity in different cells and the electrolysis phenomenon, it will be proper to study first the basic concepts of oxidation-reduction. The present chapter deals with the basic fundamentals of oxidation-reduction.

11.1 MOLECULAR AND IONIC EQUATIONS

Consider the reaction between solutions of ferric chloride and stannous chloride. When they are mixed, ferrous chloride and stannic chloride are formed. The chemical change can be represented by the following equation:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

The reactants and products have been written in molecular forms; thus, the equation is termed as **molecular equation.** Since, the reactants and products involved in the chemical change are ionic compounds, these will be present in the form of ions in the solution. So, the above chemical change can be written in the following manner also:

$$2Fe^{3+} + 6Cl^- + Sn^{2+} + 2Cl^- \rightarrow 2Fe^{2+} + 4Cl^- + Sn^{4+} + 4Cl^-$$

or $$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

The ferric ions combine with stannous ions to form ferrous ions and stannic ions. This is an **ionic equation** for the above chemical change.

Ionic equations represent chemical changes in terms of ions which actually undergo reaction. The ions which do not undergo any electronic change during a chemical change are termed **spectator ions.** The spectator ions are not included in the final balanced equations.

The rules to be followed for writing ionic equations are:

(i) All soluble ionic compounds involved in a chemical change are expressed in ionic symbols and covalent substances are written in molecular form. H_2O, NH_3, NO_2, NO, SO_2, CO, CO_2, etc., are expressed in molecular form.

(ii) The ionic compound which is highly insoluble is expressed in molecular form.

(iii) The ions which are common and equal in number on both sides, *i.e.*, spectator ions, are cancelled.

(iv) Besides the atoms, the ionic charges must also be balanced on both the sides.

SOME SOLVED EXAMPLES

Example 1. *Write the following equation in ionic form.*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

Solution: In this equation HCl and $MnCl_2$ are ionic in nature. Writing these compounds in ionic form,

$$MnO_2 + 4H^+ + 4Cl^- = Mn^{2+} + 2Cl^- + 2H_2O + Cl_2$$

$2Cl^-$ ions are common on both sides; so these are cancelled. The desired ionic equation reduces to,

$$MnO_2 + 4H^+ + 2Cl^- = Mn^{2+} + 2H_2O + Cl_2$$

Example 2. *Represent the following equation in ionic form.*

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$

Solution: In this equation except H_2O, all are ionic in nature. Representing these compounds in ionic forms,

$$2K^+ + Cr_2O_7^{2-} + 14H^+ + 7SO_4^{2-} + 6Fe^{2+} + 6SO_4^{2-} \longrightarrow$$

$$6Fe^{3+} + 9SO_4^{2-} + 2Cr^{3+} + 3SO_4^{2-} + 2K^+ + SO_4^{2-} + 7H_2O$$

$2K^+$ ions and $13SO_4^{2-}$ ions are common on both sides, so these are cancelled. The desired ionic equation reduces to,

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} = 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Total charges are equal on both sides; thus, the balanced ionic equation is the same as above.

Example 3. *Write the balanced ionic equation for the reaction of sodium bicarbonate with sulphuric acid.*

Solution: The molecular equation for the chemical change is:

$$NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

$NaHCO_3, H_2SO_4$ and Na_2SO_4 are ionic compounds; so these are written in ionic forms.

$$Na^+ + HCO_3^- + 2H^+ + SO_4^{2-} \longrightarrow 2Na^+ + SO_4^{2-} + H_2O + CO_2$$

Na^+ and SO_4^{2-} ions are spectator ions; hence these shall not appear in the final equation.

$$HCO_3^- + 2H^+ \longrightarrow H_2O + CO_2$$

To make equal charges on both sides, HCO_3^- should have a coefficient 2.

$$2HCO_3^- + 2H^+ \longrightarrow H_2O + CO_2$$

In order to balance the hydrogen and carbon on both sides, the molecules of H_2O and CO_2 should have a coefficient 2 respectively.

$$2HCO_3^- + 2H^+ = 2H_2O + 2CO_2$$

or $$HCO_3^- + H^+ = H_2O + CO_2$$

This is the balanced ionic equation.

Example 4. *Write the following ionic equation in the molecular form if the reactants are chlorides.*

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

Solution: For writing the reactants in molecular forms, the requisite number of chloride ions are added.

$$\underbrace{2Fe^{3+} + 6Cl^-} + \underbrace{Sn^{2+} + 2Cl^-}$$

or $$2FeCl_3 + SnCl_2$$

Similarly $8Cl^-$ ions are added on RHS to neutralise the charges.

$$\underbrace{2Fe^{2+} + 4Cl^-} + \underbrace{Sn^{4+} + 4Cl^-}$$

or $$2FeCl_2 + SnCl_4$$

Thus, the balanced molecular equation is

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

11.2 OXIDATION AND REDUCTION

Early Ideas of Oxidation and Reduction: The term oxidation was first used to describe chemical reactions in which oxygen was added to an element or a compound. The phenomenon of combustion was the earliest example of oxidation. Later on the term oxidation was extended to describe many more reactions which occurred without the use of even oxygen.

Oxidation is a process which involves:

(a) Addition of oxygen:

$2Mg + O_2^* = 2MgO$ (Oxidation of magnesium)

$S + O_2^* = SO_2$ (Oxidation of sulphur)

$2CO + O_2^* = 2CO_2$ (Oxidation of carbon monoxide)

$Na_2SO_3 + H_2O_2^* = Na_2SO_4 + H_2O$ (Oxidation of sodium sulphite)

(b) Removal of hydrogen:

$H_2S + Cl_2^* = 2HCl + S$ (Oxidation of hydrogen sulphide)

$4HI + O_2^* = 2H_2O + 2I_2$ (Oxidation of hydrogen iodide)

$4HCl + MnO_2^* = MnCl_2 + 2H_2O + Cl_2$ (Oxidation of hydrogen chloride)

(c) Addition of an electronegative element:

$Fe + S^* = FeS$ (Oxidation of iron)

$SnCl_2 + Cl_2^* = SnCl_4$ (Oxidation of stannous chloride)

$2Fe + 3F_2^* = 2FeF_3$ (Oxidation of iron)

(d) Removal of an electropositive element:

$2KI + H_2O_2^* = 2KOH + I_2$ (Oxidation of potassium iodide)

$2K_2MnO_4 + Cl_2^* = 2KCl + 2KMnO_4$ (Oxidation of potassium manganate)

$2KI + Cl_2^* = 2KCl + I_2$ (Oxidation of potassium iodide)

A substance which brings oxidation is known as **oxidising agent.** The substances marked with asterisk sign (*) in above equations are oxidising agents.

Reduction is just the reverse of oxidation.

Reduction is a process which involves:

(a) Removal of oxygen:

$CuO + C^* = Cu + CO$ (Reduction of cupric oxide)

$\underset{\text{Steam}}{H_2O} + \underset{\text{Coke}}{C^*} = \underbrace{CO + H_2}_{\text{Water gas}}$ (Reduction of water)

$Fe_3O_4 + 4H_2^* = 3Fe + 4H_2O$ (Reduction of magnetic oxide)

(b) Addition of hydrogen:

$Cl_2 + H_2^* = 2HCl$ (Reduction of chlorine)

$S + H_2^* = H_2S$ (Reduction of sulphur)

$C_2H_4 + H_2^* = C_2H_6$ (Reduction of ethene)

(c) Removal of an electronegative element:

$2HgCl_2 + SnCl_2^* = Hg_2Cl_2 + SnCl_4$ (Reduction of mercuric chloride)

$2FeCl_3 + H_2^* = 2FeCl_2 + 2HCl$ (Reduction of ferric chloride)

$2FeCl_3 + H_2S^* = 2FeCl_2 + 2HCl + S$

(Reduction of ferric chloride)

(d) Addition of an electropositive element:

$HgCl_2 + Hg^* = Hg_2Cl_2$ (Reduction of mercuric chloride)

$CuCl_2 + Cu^* = Cu_2Cl_2$ (Reduction of cupric chloride)

The substance which brings reduction is known as **reducing agent.** The substances marked with asterisk sign (*) in the above equations are reducing agents.

A substance, which undergoes oxidation, acts as a reducing agent while a substance, which undergoes reduction, acts as an oxidising agent.

Mg, S, Cu, Na_2SO_3, H_2S, HI, H_2, C, KI are reducing agents, while O_2, Cl_2, F_2, H_2O_2, MnO_2, $FeCl_3$, $CuCl_2$, Fe_3O_4, CuO, etc., are oxidising agents in the above examples.

All oxidation and reduction reactions are complimentary of one another and occur simultaneously, one cannot take place without the other. No single oxidation and no single reduction process is known. The simultaneous oxidation and reduction reactions are generally termed as redox reactions.

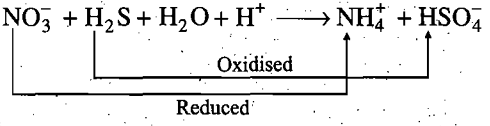
e.g., $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$

In above example iron undergoes reduction from +3 to +2 and tin undergoes oxidation from +2 to +4.

Redox reactions are divided into two main types:

(i) Intermolecular redox: In such redox reactions, one molecule of reactant is oxidised whereas molecule of other reactant is reduced.



e.g., $NO_3^- + H_2S + H_2O + H^+ \longrightarrow NH_4^+ + HSO_4^-$

(ii) Intramolecular redox: One atom of a molecule is oxidised and other atom of same molecule is reduced then it is intramolecular redox reaction.

e.g., $2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$

11.3 MODERN CONCEPT OF OXIDATION AND REDUCTION

According to the modern concept, loss of electrons is oxidation whereas gain of electrons is reduction.

Examples of oxidation reactions are:

$$Na \longrightarrow Na^+ + e$$

$$Zn \longrightarrow Zn^{2+} + 2e$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e$$

$$MnO_4^{2-} \longrightarrow MnO_4^- + e$$

Examples of reduction reactions are:

$$Cl_2 + 2e \longrightarrow 2Cl^-$$

$$S + 2e \longrightarrow S^{2-}$$

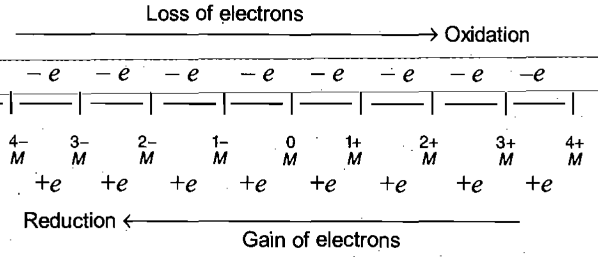
$$Cu^{2+} + 2e \longrightarrow Cu$$

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

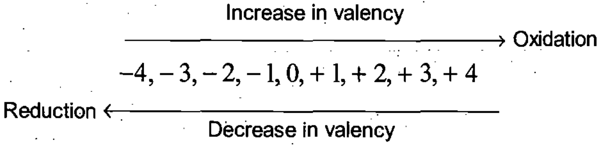
$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O$$

Oxidation and reduction can be represented in a general way as shown below :



In a redox process the valency of the involved species changes. The valency of a reducing agent increases while the valency of an oxidising agent decreases in a redox reaction. The valency of a free element is taken as zero.



When there is no change in valency it means there is no oxidation or reduction, *e.g.*, in

$$\left.\begin{array}{r} BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl \\ BaSO_4 \longrightarrow Ba^{2+} + SO_4^{2-} \end{array}\right\} \text{(No change in valency)}$$

Conclusions

(i) Oxidation is a process in which one or more electrons are lost or valency of the element increases.

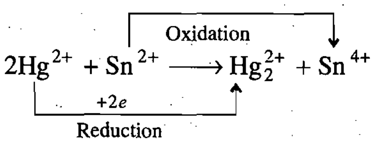
(ii) Reduction is a process in which one or more electrons are gained or valency of the element decreases.

(iii) Oxidising agent is a material which can gain one or more electrons, *i.e.*, valency decreases.

(iv) Reducing agent is a material which can lose one or more electrons, *i.e.*, valency increases.

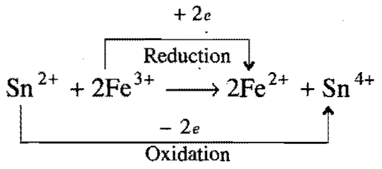
(v) Redox reaction involves two half reactions, one involving loss of electron or electrons (oxidation) and the other involving gain of electron or electrons (reduction).

Examples:



1. $2Hg^{2+} + Sn^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$

2.



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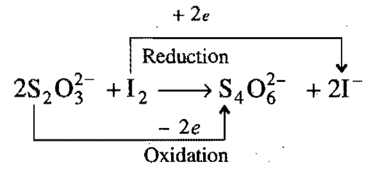


11.4 ION-ELECTRON METHOD FOR BALANCING REDOX REACTIONS

The method for balancing redox reactions by ion electron method was developed by **Jette** and **LaMev** in 1927. It involves the following steps:

(i) Write down the redox reaction in ionic form.

(ii) Split the redox reaction into two half reactions, one for oxidation and the other for reduction.

(iii) Balance each half reaction for the number of atoms of each element. For this purpose:

(a) Balance the atoms other than H and O for each half reaction using simple multiples.

(b) Add water molecules to the side deficient in oxygen and H^+ to the side deficient in hydrogen. This is done in acidic or neutral solutions.

(c) In alkaline solution, for each excess of oxygen, add one water molecule to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, add one OH^- ion for each excess hydrogen on the same side and one water molecule to the other side.

(iv) Add electrons to the side deficient in electrons as to equalise the charge on both sides.

(v) Multiply one or both the half reactions by a suitable number so that the number of electrons become equal in both the equations.

(vi) Add the two balanced half reactions and cancel any term common to both sides.

The following solved problems illustrate the various steps of ion electron method:

Example 5. *Balance the following equations by ion electron method.*

(a) $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

(b) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

(c) $KI + Cl_2 \longrightarrow KCl + I_2$

(d) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

(e) $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Solution: (a) $FeCl_3 + H_2S \longrightarrow FeCl_2 + HCl + S$

Ionic equation, $Fe^{3+} + H_2S \longrightarrow Fe^{2+} + H^+ + S$

1st step. Splitting the redox reaction into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{H_2S \longrightarrow 2H^+ + S} \qquad \underset{\text{(Reduction half reaction)}}{Fe^{3+} \longrightarrow Fe^{2+}}$$

2nd step. Adding electrons to the side deficient in electrons,

$$H_2S \longrightarrow 2H^+ + S + 2e$$

$$Fe^{3+} + e \longrightarrow Fe^{2+}$$

3rd step. Balancing electrons in both the half reactions,

$$H_2S \longrightarrow 2H^+ + S + 2e$$

$$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+}$$

4th step. Adding both the half reactions,

$$H_2S + 2Fe^{3+} \longrightarrow 2H^+ + S + 2Fe^{2+}$$

Converting it into molecular form,

$$H_2S + 2Fe^{3+} + 6Cl^- \longrightarrow 2H^+ + 2Cl^- + S + 2Fe^{2+} + 4Cl^-$$

or $\quad H_2S + 2FeCl_3 \longrightarrow 2HCl + S + 2FeCl_2$

(b) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$

Ionic equation,

$$Cu + H^+ + NO_3^- \longrightarrow Cu^{2+} + NO + H_2O$$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{Cu \longrightarrow Cu^{2+}} \;; \quad \underset{\text{(Reduction half reaction)}}{NO_3^- + H^+ \rightarrow NO + H_2O}$$

2nd step. Adding H^+ ions to the side deficient in hydrogen,

$$Cu \longrightarrow Cu^{2+}; \quad NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$$

3rd step. Adding electrons to the side deficient in electrons,

$$Cu \longrightarrow Cu^{2+} + 2e; \; NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$$

4th step. Balancing electrons in both half reactions,

$$3Cu \longrightarrow 3Cu^{2+} + 6e; \; 2NO_3^- + 8H^+ + 6e \longrightarrow 2NO + 4H_2O$$

5th step. Adding both the half reactions,

$$3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$$

Converting it into molecular form,

$$3Cu + 2NO_3^- + 8H^+ + 6NO_3^- \longrightarrow 3Cu^{2+} + 6NO_3^- + 2NO + 4H_2O$$

or $\quad 3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(c) $\quad KI + Cl_2 \longrightarrow KCl + I_2$

Ionic equation, $I^- + Cl_2 \longrightarrow Cl^- + I_2$

Splitting into two half reactions,

$$\underset{\text{(Oxidation)}}{I^- \longrightarrow I_2}\;; \qquad \underset{\text{(Reduction)}}{Cl_2 \longrightarrow Cl^-}$$

Making number of atoms equal,

$$2I^- \longrightarrow I_2\;; \qquad Cl_2 \longrightarrow 2Cl^-$$

Adding electrons to the sides deficient in electrons,

$$2I^- \longrightarrow I_2 + 2e; \quad Cl_2 + 2e \longrightarrow 2Cl^-.$$

Adding both the half reactions,

$$2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$$

Converting it into molecular form,

$$2K^+ + 2I^- + Cl_2 \longrightarrow I_2 + 2Cl^- + 2K^+$$

or $$2KI + Cl_2 \longrightarrow I_2 + 2KCl$$

(d) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

Ionic equation,

$$MnO_2 + H^+ + Cl^- \longrightarrow Mn^{2+} + H_2O + Cl_2$$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{Cl^- \longrightarrow Cl_2} \quad ; \quad \underset{\text{(Reduction half reaction)}}{MnO_2 + H^+ \longrightarrow Mn^{2+} + H_2O}$$

2nd step. Adding H^+ ions to the side deficient in hydrogen,

$$Cl^- \longrightarrow Cl_2 \quad ; \quad MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O$$

3rd step. Making atoms equal on both sides,

$$2Cl^- \longrightarrow Cl_2 \, ; \quad MnO_2 + 4H^+ \longrightarrow Mn^{2+} + 2H_2O$$

4th step. Adding electrons to the side deficient in electrons,

$$2Cl^- \longrightarrow Cl_2 + 2e$$

$$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O$$

5th step. Adding both the half reactions,

$$2Cl^- + MnO_2 + 4H^+ \longrightarrow Cl_2 + Mn^{2+} + 2H_2O$$

Converting it into molecular form,

$$MnO_2 + 2Cl^- + 4H^+ + 2Cl^- \rightarrow Cl_2 + Mn^{2+} + 2Cl^- + 2H_2O$$

or $$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

(e) $H_2S + HNO_3 \longrightarrow H_2SO_4 + NO_2 + H_2O$

Ionic equation,

$$H_2S + NO_3^- \longrightarrow NO_2 + H_2O$$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{H_2S \longrightarrow SO_4^{2-}} \quad ; \quad \underset{\text{(Reduction half reaction)}}{NO_3^- \longrightarrow NO_2 + H_2O}$$

2nd step. Add water to the side deficient in oxygen,

$$H_2S + 4H_2O \longrightarrow SO_4^{2-} + 10H^+$$

3rd step. Add H^+ ions to the side deficient in hydrogen,

$$NO_3^- + 2H^+ \longrightarrow NO_2 + H_2O$$

4th step. Add electrons to the side deficient in electrons,

$$H_2S + 4H_2O \longrightarrow SO_4^{2-} + 10H^+ + 8e$$

$$NO_3^- + 2H^+ + e \longrightarrow NO_2 + H_2O$$

5th step. Balancing electrons in both the half reactions,

$$H_2S + 4H_2O \longrightarrow SO_4^{2-} + 10H^+ + 8e$$

$$[NO_3^- + 2H^+ + e \longrightarrow NO_2 + H_2O] \times 8$$

6th step. Adding both the half reactions,

$$H_2S + 4H_2O + 8NO_3^- + 6H^+ \longrightarrow SO_4^{2-} + 8NO_2 + 8H_2O$$

or $$H_2S + 8NO_3^- + 6H^+ \longrightarrow SO_4^{2-} + 8NO_2 + 4H_2O$$

Converting it into molecular form,

$$H_2S + 8HNO_3 \longrightarrow H_2SO_4 + 8NO_2 + 4H_2O$$

Example 6. *Balance the following equations by ion electron method:*

(a) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

(b) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$

(c) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$

(d) $Cr_2O_7^{2-} + SO_2 + H^+ \longrightarrow Cr^{3+} + HSO_4^- + H_2O$

(e) $I_2 + OH^- \longrightarrow IO_3^- + I^- + H_2O$

(f) $Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$

Solution:

(a) $MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Reduction half reaction)}}{MnO_4^- + H^+ \longrightarrow Mn^{2+} + H_2O} \, ; \quad \underset{\text{(Oxidation half reaction)}}{Fe^{2+} \longrightarrow Fe^{3+}}$$

2nd step. Adding hydrogen ions to the side deficient in hydrogen,

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

3rd step. Adding electrons to the sides deficient in electrons,

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

4th step. Balancing electrons in both half reactions,

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e$$

5th step. Adding both the half reactions,

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(b) $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$

Splitting into two half reactions,

$$MnO_4^- + H^+ \longrightarrow Mn^{2+} + H_2O; \quad C_2O_4^{2-} \longrightarrow 2CO_2$$

Balanced as in Question (a),

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e$$

Balancing electrons in both half reactions,

$$2[MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O];$$

$$5[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e]$$

Adding both the half reactions,

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(c) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Reduction half reaction)}}{Cr_2O_7^{2-} + H^+ \longrightarrow Cr^{3+} + H_2O} \qquad \underset{\text{(Oxidation half reaction)}}{I^- \longrightarrow I_2}$$

2nd step. Adding hydrogen ions to the side deficient in hydrogen,

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow Cr^{3+} + 7H_2O$$

3rd step. Making atoms equal on both sides,

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O \;;\; 2I^- \longrightarrow I_2$$

4th step. Adding electrons to the sides deficient in electrons,

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \longrightarrow I_2 + 2e$$

5th step. Balancing electrons,

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3[2I^- \longrightarrow I_2 + 2e]$$

6th step. Adding both the half reactions,

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(d) $Cr_2O_7^{2-} + SO_2 + H^+ \longrightarrow Cr^{3+} + HSO_4^- + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Reduction half reaction)}}{Cr_2O_7^{2-} + H^+ \longrightarrow Cr^{3+} + H_2O;} \qquad \underset{\text{(Oxidation half reaction)}}{SO_2 \longrightarrow HSO_4^-}$$

2nd step. Adding H^+ ions to side deficient in hydrogen,

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow Cr^{3+} + 7H_2O$$

3rd step. Adding water to the side deficient in oxygen,

$$SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+$$

4th step. Making atoms equal on both sides,

$$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

5th step. Adding electrons to the sides deficient in electrons,

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O;$$

$$SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e$$

6th step. Balancing electrons in both the half reactions,

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

$$[SO_2 + 2H_2O \longrightarrow HSO_4^- + 3H^+ + 2e] \times 3$$

7th step. Adding both the half reactions,

$$Cr_2O_7^{2-} + 5H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + 3HSO_4^- + H_2O$$

(e) $I_2 + OH^- \longrightarrow IO_3^- + I^- + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{I_2 + OH^- \longrightarrow IO_3^- + H_2O;} \qquad \underset{\text{(Reduction half reaction)}}{I_2 \longrightarrow I^-}$$

2nd step. Adding OH^- ions,

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O$$

3rd step. Adding electrons to the sides deficient in electrons,

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O + 10e;\; I_2 + 2e \longrightarrow 2I^-$$

4th step. Balancing electrons in both the half reactions,

$$I_2 + 12OH^- \longrightarrow 2IO_3^- + 6H_2O + 10e$$

$$5[I_2 + 2e^- \longrightarrow 2I^-]$$

5th step. Adding both the half reactions,

$$6I_2 + 12OH^- \longrightarrow 2IO_3^- + 10I^- + 6H_2O$$

Dividing by 2,

$$3I_2 + 6OH^- \longrightarrow IO_3^- + 5I^- + 3H_2O$$

(f) $Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$

1st step. Splitting into two half reactions,

$$\underset{\text{(Oxidation half reaction)}}{IO_3^- + OH^- \longrightarrow IO_4^- + H_2O\;;} \qquad \underset{\text{(Reduction half reaction)}}{Cl_2 \longrightarrow Cl^-}$$

2nd step. Adding QH^- ions,

$$IO_3^- + 2OH^- \longrightarrow IO_4^- + H_2O$$

3rd step. Adding electrons to the sides deficient in electrons,

$$IO_3^- + 2OH^- \longrightarrow IO_4^- + H_2O + 2e$$

$$Cl_2 + 2e \longrightarrow 2Cl^-$$

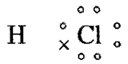
4th step. Adding both the half reactions,

$$IO_3^- + 2OH^- + Cl_2 \longrightarrow IO_4^- + 2Cl^- + H_2O$$

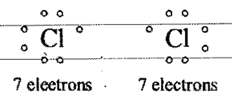
11.5 OXIDATION NUMBER (Oxidation State)

It is defined as **the charge (real or imaginary) which an atom appears to have when it is in combination.** In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion. This is the real charge and is developed by the loss and gain of electron or electrons. For example, in the electrovalent compound, sodium chloride (NaCl), the charge on sodium and chlorine is +1 and −1, respectively. The charges have been developed by the transfer of one electron from Na-atom to Cl-atom. Thus, in NaCl (Na^+Cl^-), the oxidation number of sodium is +1 and that of chlorine is −1.

The oxidation numbers of atoms in covalent compounds can be derived by assigning the electrons of each bond to the more electronegative atom of the bonded atoms. For a molecule of HCl both the electrons of the covalent bond are assigned to the chlorine atom since it is more electronegative than hydrogen.



Thus, chlorine atom has one more electron than the neutral chlorine atom which brings one unit negative charge on chlorine. The oxidation number of chlorine in this compound is –1. The hydrogen atom has lost the only electron possessed by it, thus acquiring one unit positive charge. The oxidation number of hydrogen is, therefore, +1 in this compound. In the case of covalent bond between two identical atoms, *i.e.*, electronegativity difference is zero, the bonding electrons are shared equally between the bonded atoms, *i.e.*, no charge is developed on any of the atoms. Thus, the oxidation numbers of both chlorine atoms are zero in the molecule of chlorine.



[In neutral chlorine atom, 7 electrons are present in the valency shell]

Counting of electrons in this fashion is not convenient in many molecules and therefore the following operational rules are followed which are helpful and convenient in determining the oxidation numbers:

(i) The oxidation number (Ox.no.) of an atom in free elements is zero, no matter how complicated the molecule is, hydrogen in H_2, sulphur in S_8, phosphorus in P_4, oxygen in O_2 or O_3, all have zero value of oxidation numbers.

(ii) The fluorine, which is the most electronegative element, has oxidation number –1 in all of its compounds.

(iii) Oxidation number of oxygen is –2 in all compounds except in peroxides, superoxides and oxygen fluorides. In peroxides (O_2^{2-}), oxygen has oxidation number –1; in superoxides (O_2^-), oxygen has oxidation number $-1/2$; and in OF_2, the oxygen has an oxidation number +2.

(iv) The oxidation number of hydrogen is +1 in all of its compounds except in metallic hydrides like NaH, BaH_2, etc. Hydrogen is in –1 oxidation state in these hydrides.

(v) The oxidation number of an ion is equal to the electrical charge present on it.

(vi) The oxidation number of IA elements (Li, Na, K, Rb, Cs and Fr) is +1 and the oxidation number of IIA elements (Be, Mg, Ca, Sr, Ba and Ra) is +2.

(vii) For complex ions, the algebraic sum of oxidation numbers of all the atoms is equal to the net charge on the ion.

(viii) In the case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecule is zero.

The following solved examples illustrate the application of the above rules for finding out the oxidation number of an element in particular species:

Example 7. *What is the oxidation number of Mn in $KMnO_4$ and of S in $Na_2S_2O_3$?*

Solution: Let the Ox.no. of Mn in $KMnO_4$ be x.

We know that, Ox. no. of K = +1
Ox. no. of O = – 2

$$\begin{aligned} \text{So,}\quad & \text{Ox. no. K} + \text{Ox. no. Mn} + 4(\text{Ox. no. O}) = 0 \\ \text{or}\quad & +1 + x + 4(-2) = 0 \\ \text{or}\quad & +1 + x - 8 = 0 \\ \text{or}\quad & x = +8 - 1 = +7 \end{aligned}$$

Hence, Ox.no. of Mn in $KMnO_4$ is +7.

Similarly, for S in $Na_2S_2O_3$,

$$2(\text{Ox. no. Na}) + 2(\text{Ox. no. S}) + 3(\text{Ox. no. O}) = 0$$
$$2 \times (+1) + 2x + 3(-2) = 0$$
$$x = +2$$

Hence, Ox.no. of S in $Na_2S_2O_3$ = + 2.

Example 8. *What is the oxidation number of Cr in $K_2Cr_2O_7$?* (Ranchi 1996)

Solution: Let the Ox.no. of Cr in $K_2Cr_2O_7$ be x.

We know that, Ox.no. of K = + 1
Ox. no. of O = – 2

$$\begin{aligned} \text{So,}\quad & 2(\text{Ox. no. K}) + 2(\text{Ox. no. Cr}) + 7(\text{Ox. no. O}) = 0 \\ & 2(+1) + 2(x) + 7(-2) = 0 \\ \text{or}\quad & +2 + 2x - 14 = 0 \\ \text{or}\quad & 2x = +14 - 2 = +12 \\ \text{or}\quad & x = +\frac{12}{2} = +6 \end{aligned}$$

Hence, oxidation number of Cr in $K_2Cr_2O_7$ is +6.

Example 9. *What is the oxidation number of Fe in $K_4Fe(CN)_6$?*

Solution: Let the oxidation number of Fe be x.

We know that, Ox.no. of K = +1
Ox. no. of $(CN)^-$ = –1

$$\begin{aligned} \text{So,}\quad & 4(\text{Ox. no. K}) + \text{Ox. no. Fe} + 6(\text{Ox. no. CN}^-) = 0 \\ & 4(+1) + x + 6(-1) = 0 \\ \text{or}\quad & +4 + x - 6 = 0 \\ \text{or}\quad & x = +6 - 4 = +2 \end{aligned}$$

The oxidation number of iron in $K_4Fe(CN)_6$ is +2.

Example 10. *Find the oxidation number of*

(a) S in SO_4^{2-} ion *(b) S in HSO_3^- ion*

(c) Pt in $(PtCl_6)^{2-}$ ion *(d) Mn in $(MnO_4)^-$ ion*

Solution: (a) Let the oxidation number of S be x.

We know that, Ox.no. of O = – 2

$$\begin{aligned} \text{So,}\quad & \text{Ox. no. S} + 4(\text{Ox. no. O}) = -2 \\ \text{or}\quad & x + 4(-2) = -2 \\ \text{or}\quad & x - 8 = -2 \\ \text{or}\quad & x = +8 - 2 = +6 \end{aligned}$$

The oxidation number of S in SO_4^{2-} ion is +6.

(b) Let the oxidation number of S be x in HSO_3^- ion.

We know that, Ox.no. of H = + 1
Ox.no. of O = – 2

$$
\begin{aligned}
\text{So,}\quad & \text{Ox. no. H} + \text{Ox. no. S} + 3(\text{Ox. no. O}) = -1\\
& +1 + x + 3(-2) = -1\\
\text{or}\quad & +1 + x - 6 = -1\\
\text{or}\quad & x - 5 = -1\\
\text{or}\quad & x = +5 - 1 = +4
\end{aligned}
$$

The oxidation number of S in HSO_3^- ion is + 4.

(c) Let oxidation number of Pt be x.

We know that Ox.no. of Cl = − 1.

$$
\begin{aligned}
\text{So,}\quad & \text{Ox. no. Pt} + 6(\text{Ox. no. Cl}) = -2\\
& x + 6(-1) = -2\\
\text{or}\quad & x - 6 = -2\\
\text{or}\quad & x = +6 - 2 = +4
\end{aligned}
$$

The oxidation number of Pt in $[Pt(Cl)_6]^{2-}$ ion is + 4.

(d) Let oxidation number of Mn be x.

We know that, Ox.no. of O = − 2.

$$
\begin{aligned}
\text{So,}\quad & \text{Ox. no. Mn} + 4(\text{Ox. no. O}) = -1\\
& x + 4(-2) = -1\\
\text{or}\quad & x - 8 = -1\\
\text{or}\quad & x = +8 - 1 = +7
\end{aligned}
$$

The oxidation number of Mn in $[MnO_4]^-$ ion is +7.

Example 11. *Which compound amongst the following has the highest oxidation number for Mn?*

$KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3.

Solution:

		Ox.no. of Mn
$KMnO_4$	$+1 + x - 8 = 0$ $x = +7$	$+7$
K_2MnO_4	$+2 + x - 8 = 0$ $x = +6$	$+6$
MnO_2	$x - 4 = 0$ $x = +4$	$+4$
Mn_2O_3	$2x - 6 = 0$ $x = +3$	$+3$

Thus, the highest oxidation number for Mn is in $KMnO_4$.

Sometimes, oxidation numbers have such values which at first sight appear strange. For example, the oxidation number of carbon in cane sugar ($C_{12}H_{22}O_{11}$), glucose ($C_6H_{12}O_6$), dichloromethane, etc., is zero.

Cane sugar ($C_{12}H_{22}O_{11}$)	Glucose ($C_6H_{12}O_6$)
$12 \times x + 22 \times 1 + 11(-2) = 0$	$6 \times x + 12 \times 1 + 6(-2) = 0$
$12x + 22 - 22 = 0$	$6x + 12 - 12 = 0$
So, $x = 0$	So, $x = 0$

Dichloromethane (CH_2Cl_2)

$$
\begin{aligned}
& x + 2 \times 1 + 2(-1) = 0\\
& x + 2 - 2 = 0\\
& \text{So, } x = 0
\end{aligned}
$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Oxidation state of S in SO_4^{2-}: [BCECE (Medical) 2005]

(a) +6 (b) +3
(c) +2 (d) −2

[**Ans.** (a)]

[**Hint:** Let oxidation state of S is x.

$$\therefore \quad x + 4(-2) = -2$$
$$x = +6]$$

2. Arrange the following in the increasing order of oxidation state of Mn: (JCECE 2004)

(i) Mn^{2+} (ii) MnO_2 (iii) $KMnO_4$ (iv) K_2MnO_4

(a) (i) > (ii) > (iii) > (iv) (b) (i) < (ii) < (iv) < (iii)
(c) (ii) < (iii) < (i) < (iv) (d) (iii) < (i) < (iv) < (ii)

[**Ans.** (b)]

[**Hint:** $\underset{(+2)}{Mn^{2+}} < \underset{(+4)}{MnO_2} < \underset{(+6)}{K_2MnO_4} < \underset{(+7)}{KMnO_4}$]

3. Which of the following has least oxidation state of Fe? (JCECE 2004)

(a) $K_3[Fe(OH)_6]$
(b) $K_2[FeO_4]$
(c) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
(d) $[Fe(CN)_6]^{3-}$

[**Ans.** (c)]

[**Hint:** In mohr salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, oxidation state of iron is +2 which is least.

$K_3[Fe(OH)_6]$	$+3 + x - 6 = 0$	$x = +3$
$K_2[FeO_4]$	$+2 + x - 8 = 0$	$x = +6$
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	**+2 state** in $FeSO_4$ ($x - 2 = 0$)	
$Fe(CN)_6^{3-}$	$x - 6 = -3$	$x = +3]$

4. Oxidation state of carbon in HCOOH will be:

(a) +1 (b) +2 (c) − 4 (d) 0

[**Ans.** (b)]

[**Hint:** Let the oxidation state of carbon be x.

$$2 + x - 4 = 0$$
$$x = 2]$$

5. Oxidation states of chlorine in $HClO_4$ and $HClO_3$ are:

(a) +4, +3 (b) +7, +5 (c) +3, +4 (d) +5, +7

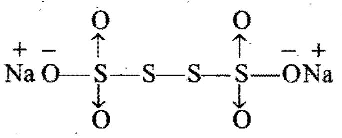
[**Ans.** (b)]

[**Hint:** $HClO_4$: $+1 + x - 8 = 0$, $x = +7$

$HClO_3$: $+1 + x - 6 = 0$, $x = +5$]

11.6 SPECIAL EXAMPLES OF OXIDATION STATE DETERMINATION

1. Oxidation state of sulphur in $Na_2S_4O_6$: It is only average oxidation number of sulphur. Let us see the structure of $Na_2S_4O_6$.



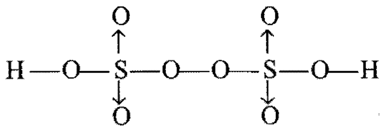
From the structure, it is clear that the sulphur atoms acting as donor atoms have +5 oxidation number (each). On the other hand, the sulphur atom involved in pure covalent bond formation has zero oxidation number.

2. Oxidation number of sulphur in $(CH_3)_2SO$ (dimethyl sulphoxide): Here, oxidation number $O = -2$; oxidation number of each CH_3 group is +1.

$\therefore$ $$+2 + x - 2 = 0 \text{ or } x = 0$$

Thus, sulphur lies in zero oxidation state.

3. Oxidation number of sulphur in perdisulphuric acid $H_2S_2O_8$: It may be done only when the structure is drawn.



$$\mathrm{H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-H}$$

Oxidation number of S = x; oxidation number of H = +1; oxidation number of oxygen in peroxo linkage = −1; oxidation number of other six oxygen atoms = −2 each.

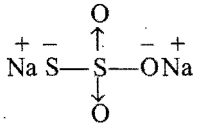
$\therefore$ $$+2 + (-12) + 2x - 2 = 0$$

$\therefore$ $$x = +6 \qquad \text{(oxidation number of sulphur)}$$

4. Oxidation number of sulphur in hypo, $Na_2S_2O_3$: Let the average oxidation number of sulphur be 'x'.

$\therefore$ $$+2 + 2x - 6 = 0 \quad \therefore \quad x = +2$$

Structure of hypo may be drawn as—



$$\mathrm{\overset{+}{Na}\,\overset{-}{S}-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-\overset{-}{O}\overset{+}{Na}}$$

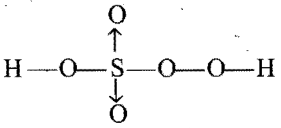
Here, the two sulphur atoms have different oxidation states:

(i) Oxidation number of donor sulphur atom is +5. It gives up four electrons in coordination and one electron in covalent bond formation with oxygen.

(ii) Sulphur, bonded with Na, lies in −1 state since one electron of Na lies towards the sulphur. Electrons of S—S bond are equally shared between two sulphur atoms.

Thus +5 and −1 are two oxidation states of the two sulphur atoms.

5. Oxidation number of sulphur in peroxo monosulphuric acid (H_2SO_5): Let us draw its structure.



$$\mathrm{H-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-H}$$

Here, we have to consider Ox.no. of H = + 1

Ox.no. of oxygen in peroxo linkage = − 1

Ox. no. of rest of oxygen = − 2

$\therefore$ $$+2 + x - 6 - 2 = 0 \text{ or } x = +6$$

Thus, sulphur in H_2SO_5 lies in + 6 oxidation state.

6. Fe in its oxides, FeO, Fe_2O_3 and Fe_3O_4:

In FeO $\longrightarrow x - 2 = 0, x = +2$

In $Fe_2O_3 \longrightarrow 2x - 6 = 0, x = +3$

In $Fe_3O_4 \longrightarrow 3x - 8 = 0, x = +8/3$ (fractional)

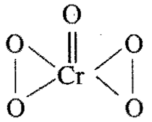
Here, in Fe_3O_4, oxidation number is the average of those in FeO and Fe_2O_3.

$$FeO + Fe_2O_3 = Fe_3O_4$$

Average oxidation number of Fe in

$$Fe_3O_4 = \frac{+2 + 2(+3)}{3} = +\frac{8}{3}$$

7. Oxidation state of chromium in CrO_5: CrO_5 has butterfly structure having two peroxo bonds



Peroxo oxygen has (−1) oxidation state.

Let oxidation state of chromium be 'x'.

$$x + 4(-1) + (-2) = 0$$

$$x = +6$$

8. Oxidation state of chlorine in bleaching powder: Bleaching powder has two chlorine atoms having different oxidation states.

$$Ca^{2+} \quad \underset{\substack{\text{(hypochloride ion)}\\ \text{Chlorine in}\\ +1 \text{ state}}}{(OCl)^-} \quad \underset{\substack{\text{(chloride ion)}\\ \text{Chlorine in}\\ -1 \text{ state}}}{Cl^-}$$

9. Fractional values of oxidation numbers are possible as in $Na_2S_4O_6$, Fe_3O_4, N_3H, etc.

$Na_2S_4O_6$	Fe_3O_4
$2 \times 1 + 4x + 6(-2) = 0$	$3 \times x + 4(-2) = 0$
$2 + 4x - 12 = 0$	$3x - 8 = 0$
$4x = +10$	$3x = 8$
$x = +\frac{10}{4} = +2.5$	$x = +\frac{8}{3}$ or $+2\frac{2}{3}$
Oxidation number of S is + 2.5	Oxidation number of iron is $+2\frac{2}{3}$

N_3H

$$3x + 1 = 0$$

$$3x = -1$$

$$x = -1/3$$

Oxidation number of nitrogen is −1/3

10. Oxidation state of carbon and nitrogen in HCN and HNC: We should take into consideration the following fundamental aspects of bonding while counting the oxidation state of covalently bonded molecules:

(a) Single covalent bond contributes one unit for oxidation number.

(b) Negative oxidation number is assigned to more electronegative atom and positive oxidation number to less electronegative atom.

(c) Coordinate bond is represented by an arrow from donor atom to acceptor atom.

$$\underset{\text{Donor}}{A} \longrightarrow \underset{\text{Acceptor}}{B}$$

If donor atom is less electronegative and acceptor is more, then + 2 state is given to donor and −2 state is given to acceptor.

But it should be noted that if the donor is more electronegative than the acceptor, then contribution of coordinate bond for both atoms regarding oxidation state is neglected, *e.g.,*

(i) $$H—C\equiv N$$

$$+1+a-3=0$$

$$a=+2$$

Carbon is in +2 state and nitrogen is in − 3 state. Each bond contributes −1 state to more electronegative atom.

(ii) $$H—N\equiv C$$

Oxidation state of H = + 1

Oxidation state of nitrogen = (−1) + (−2) + (0) = − 3

Covalent bond with hydrogen contributes (−1) and covalent bond with carbon contributes (−2) and there is zero contribution of coordinate bond. Let the oxidation state of carbon be '*x*'.

$$+1-3+x=0;\ x=+2$$

11. $Fe_{0.94}O$ (Oxidation state of iron is to be determined):

$$0.94x-2=0$$

$$x=2/0.94=200/94$$

12. $NH_2—NH_2$ (Oxidation state of nitrogen is to be determined):

$$2x+4=0$$

$$x=-2$$

13. KI_3 (Oxidation state of iodine is to be determined):

$$+1+3x=0$$

$$x=-1/3$$

KI_3 is mixture of $\overset{+1}{K}\,\overset{-1}{I}$ and $\overset{0}{I_2}$. Thus, two iodine atoms lie in zero state and one lies in −1 state.

14. $Na_2[Fe(CN)_5NO]$: In iron complex NO lies in NO^+ state; thus oxidation state of 'Fe' may be determined as:

$$+2+x-5+1=0$$

$$x=+2$$

15. $[Fe(NO)(H_2O)_5]SO_4$:

$$x+1+5(0)-2=0$$

$$x=+1$$

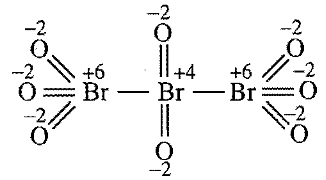
16. NOCl or $Cl—N=O$:

Oxidation state of chlorine = − 1

Oxidation state of oxygen = − 2

Thus, Oxidation state of nitrogen

17. Br_3O_8 (Tribromo octa-oxide):



$$\text{Average oxidation state}=\frac{(+6)+(4)+(+6)}{3}=\frac{16}{3}$$

18. C_3O_2 (Carbon sub-oxide):

$$\overset{-2}{O}=\overset{+2}{C}=\overset{0}{C}=\overset{+2}{C}=\overset{-2}{O}$$

$$\text{Average oxidation state}=\frac{+4}{3}.$$

11.7 OXIDATION NUMBERS (States) IN DIFFERENT TYPES OF ELEMENTS

Zero group elements have zero oxidation number (state) as they do not show chemical activity while other elements have at least two oxidation states: zero when they exist in free state and positive or negative when they exist in compounds. Many elements show different oxidation states in different compounds. In the case of representative elements, the highest positive oxidation number (state) of an element is the same as its group number while the highest negative oxidation state is equal to (8 − group number) with negative sign with a few exceptions.

(i) Alkali metals (IA) show uniformly +1 oxidation state, as they have ns^1 configuration and have only a tendency to lose this electron.

(ii) Alkaline earth metals (IIA) show a common oxidation state of +2 as they have ns^2 configuration.

(iii) Elements of group IIIA have ns^2np^1 outer shell configuration, suggesting +1 and +3 oxidation states corresponding to use of *np* or *ns np* electrons.

(iv) Elements of group IVA have ns^2np^2 outer shell configuration. They show oxidation states +4 (maximum) and − 4 (minimum). However, Sn and Pb show either +2 or +4 oxidation states being metallic in nature.

(v) VB elements have outer shell configuration ns^2np^3. They show oxidation states between +5 and −3.

(vi) The elements of VIA (with the exception of oxygen) show maximum oxidation state +6 and minimum oxidation state −2.

(vii) The elements of VIIA (with the exception of fluorine) show maximum +7 and minimum −1 oxidation state.

(viii) Transition metals exhibit a large number of oxidation states due to involvement of $(n-1)d$ electrons besides *ns* electrons.

The most common oxidation states of the representative elements are shown in the following table:

Group	Outer shell configuration	Common oxidation numbers (states) except zero in free state
IA	ns^1	+ 1
IIA	ns^2	+ 2
IIIA	ns^2np^1	+ 3, + 1
IVA	ns^2np^2	+ 4, + 3, + 2, + 1, − 1, − 2, − 3, − 4
VA	ns^2np^3	+ 5, + 3, + 1, − 1, − 3
VIA	ns^2np^4	+ 6, + 4, + 2, − 2
VIIA	ns^2np^5	+ 7, + 5, + 3, + 1, − 1

11.8 VALENCY AND OXIDATION NUMBER

Valency of an element means the power or capacity of the element to combine with other elements. The valency of an element is numerically equal to the number of hydrogen atoms or chlorine atoms or twice the number of oxygen atoms that combine with one atom of that element. It is also equal to the number of electrons lost or accepted or shared by the atom of an element. In every case valency of an element is a pure number and has no plus or minus sign associated with it, while oxidation number (state) is an arbitrary number which can have positive, negative, zero or even fractional value. For example, in the following compounds of carbon, the oxidation number varies from – 4 to + 4 but valency of carbon is 4 in all the compounds:

Compound	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
Ox.no. of carbon	– 4	–2	0	+2	+4

Thus, valency and oxidation number concepts are different. In some cases (mainly in the case of electrovalent compounds), valency and oxidation number are the same but in other cases they may have different values. Points of difference between the two have been tabulated below:

Valency	Oxidation number
1. It is the combining capacity of the element. No plus or minus sign is attached to it.	Ox.no. is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
2. Valency of an element is usually fixed.	Ox.no. of an element may have different values. It depends on the nature of the compound in which it is present.
3. Valency is always a whole number.	Ox.no. of the element may be a whole number or fractional.
4. Valency of the element is never zero except of noble gases.	Ox.no. of the element may be zero.

Term	Oxidation number
Oxidation	Increases
Reduction	Decreases
Oxidising agent	Decreases
Reducing agent	Increases

Example 12. *In the following reactions, identify the species oxidised, the species reduced, the oxidising agent and the reducing agent:*

(a) $4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$

(b) $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$

(c) $2H^+ + Mg = Mg^{2+} + H_2$

(d) $H_2SO_4 + 2H_2S = 3S + 3H_2O$

Solution: (a) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$

Writing the oxidation numbers on various atoms,

$$\overset{+4\ -2}{MnO_2} + 4\overset{+1\ -1}{HCl} = \overset{+2\ -1}{MnCl_2} + \overset{0}{Cl_2} + 2\overset{+1\ -2}{H_2O}$$

Ox.no. of Mn changes from +4 to +2, *i.e.*, decrease in oxidation number. MnO_2 is thus reduced. It acts as an oxidising agent. Ox.no. of Cl changes from –1 to 0, *i.e.*, increase in oxidation number. HCl is thus oxidised. It acts as a reducing agent.

(b) $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$

Writing the oxidation numbers on various atoms,

$$\overset{+2\ -1}{SnCl_2} + 2\overset{+3\ -1}{FeCl_3} = \overset{+4\ -1}{SnCl_4} + 2\overset{+2\ -1}{FeCl_2}$$

Ox.no. of Sn changes from +2 to +4, *i.e.*, increase in oxidation number. $SnCl_2$ is thus oxidised or it acts as a reducing agent.

Ox.no. of Fe changes from +3 to +2, *i.e.*, decrease in oxidation number. $FeCl_3$ is thus reduced or it acts as an oxidising agent.

(c) $Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$

Writing oxidation numbers of various atoms,

Decrease

$$\overset{0}{Mg} + 2\overset{+1}{H^+} \longrightarrow \overset{(+2)}{Mg^{2+}} + \overset{0}{H_2}$$

Increase

Mg is oxidised, *i.e.*, it acts as a reducing agent. H^+ is reduced, *i.e.*, it acts as an oxidising agent.

(d) $H_2SO_3 + 2H_2S = 3S + 3H_2O$

Writing oxidation numbers on various atoms,

Increase

$$\overset{+1\ +4-2}{H_2SO_3} + 2\overset{+1\ -2}{H_2S} \longrightarrow 3\overset{0}{S} + 3\overset{+1\ -2}{H_2O}$$

Decrease

H_2SO_3 is reduced, *i.e.*, it acts as oxidising agent. H_2S is Oxidised, *i.e.*, it acts as reducing agent.

Example 13. *Which one of the following reactions is a redox reaction?*

(a) $CuSO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$

(b) $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$

(c) $SO_2 + H_2O \longrightarrow H_2SO_3$

(d) $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$

Solution: The reaction in which change in oxidation numbers of some of the atoms takes place is termed as a redox reaction.

(a) $\overset{+2+6-2}{CuSO_4} + 4\overset{-3+1}{NH_3} \longrightarrow [\overset{+2\ -3-1}{Cu(NH_3)_4}]\overset{+6-2}{SO_4}$

No change in oxidation number of any of the atoms.

(b) $\overset{+1\ +6\ -2}{Na_2SO_4} + \overset{+2\ -1}{BaCl_2} \longrightarrow \overset{+2\ +6-2}{BaSO_4} + 2\overset{+1\ -1}{NaCl}$

No change in oxidation number of any one of the atoms.

(c) $\overset{+4-2}{SO_2} + \overset{+1\ -2}{H_2O} \longrightarrow \overset{+1\ +4-2}{H_2SO_3}$

No change in oxidation number of any one of the atoms.

(d) $2\overset{+2+6-2}{CuSO_4} + 4\overset{+1-1}{KI} \longrightarrow \overset{+1\ -1}{Cu_2I_2} + 2\overset{+1\ +6-2}{K_2SO_4} + \overset{0}{I_2}$

Oxidation number of Cu decreases from +2 to +1 and oxidation number of iodine increases from −1 to 0.

Thus, out of the above four reactions, the reaction (d) is a redox reaction.

Example 14. *Explain why HNO_3 acts only as oxidising agent while HNO_2 can act both as a reducing agent and an oxidising agent?*

Solution: Nitrogen can have oxidation numbers from −3 to +5. The oxidation number of nitrogen in HNO_3 is +5. Thus, increase in oxidation number beyond +5 cannot occur. Hence, HNO_3 cannot act as reducing agent. The oxidation number of nitrogen in HNO_3 can only decrease; thus it acts as an oxidising agent. In HNO_2, the oxidation number of nitrogen is +3. Thus, it can increase or decrease within the range −3 to +5. Hence, it can act as an oxidising as well as a reducing agent.

11.9 BALANCING OXIDATION-REDUCTION REACTIONS BY OXIDATION NUMBER METHOD

In a balanced redox reaction, total increase in oxidation number must be equal to the total decrease in oxidation number. This equivalence provides the basis for balancing redox reactions. This method is applicable to both molecular and ionic equations. The general procedure involves the following steps:

(i) Write the skeleton equation (if not given, frame it) representing the chemical change.

(ii) Assign oxidation numbers to the atoms in the equation and find out which atoms are undergoing oxidation and reduction. Write separate equations for the atoms undergoing oxidation and reduction.

(iii) Find the change in oxidation number in each equation. Make the change equal in both the equations by multiplying with suitable integers. Add both the equations.

(iv) Complete the balancing by inspection. First balance those substances which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally balance hydrogen and oxygen by putting H_2O molecules wherever needed.

The final balanced equation should be checked to ensure that there are as many atoms of each element on the right as there are on the left.

(v) In ionic equations the net charges on both sides of the equation must be exactly the same. Use H^+ ion/ions in acidic reactions and OH^- ion/ions in basic reactions to balance the charge and number of hydrogen and oxygen atoms.

The following examples illustrate the above rules:

Example 15. *Balance the following equation by oxidation number method:*

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Solution: Writing the oxidation numbers of all the atoms.

$$\overset{0}{Cu} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+4}{N}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$$

Change in Ox.no. has occurred in copper and nitrogen.

$$\overset{0}{Cu} \longrightarrow \overset{+2}{Cu}(NO_3)_2 \quad \text{... (i)}$$

$$H\overset{+5}{N}O_3 \longrightarrow \overset{+4}{N}O_2 \quad \text{... (ii)}$$

Increase in Ox.no. of copper = 2 units per molecule Cu

Decrease in Ox.no. of nitrogen = 1 unit per molecule HNO_3

To make increase and decrease equal, eq. (ii) is multiplied by 2.

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

Balancing nitrate ions, hydrogen and oxygen, the following equation is obtained:

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

This is the balanced equation.

SOME SOLVED EXAMPLES

Example 16. *Balance the following equation by oxidation number method:*

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 = Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Solution: Writing oxidation numbers of all the atoms.

$$\overset{+2}{K_2}\overset{+6}{Cr_2}\overset{-2}{O_7} + \overset{+2}{Fe}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} = \overset{+3}{Cr_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+3}{Fe_2}(\overset{+6}{S}\overset{-2}{O_4})_3 + \overset{+1}{K_2}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

Change in Ox.no. has occurred in chromium and iron.

$$K_2\overset{+6}{Cr_2}O_7 \longrightarrow \overset{+3}{Cr_2}(SO_4)_3 \quad \text{... (i)}$$

$$\overset{+2}{Fe}SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 \quad \text{... (ii)}$$

Decrease in Ox.no. of Cr per molecule

$$= (2 \times 6 - 2 \times 3) = 6 \text{ units}$$

Increase in Ox.no. of Fe per molecule = 1 unit

Hence, eq. (ii) should be multiplied by 6,

$$K_2Cr_2O_7 + 6FeSO_4 \longrightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3$$

To balance sulphate ions and potassium ions, 7 molecules of H_2SO_4 are needed.

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4$$

To balance hydrogen and oxygen, $7H_2O$ should be added on RHS. Hence, balanced equation is,

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

Example 17. *Balance the following equation by oxidation number method:*

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + H_2O + Cl_2$$

Solution: Writing the oxidation numbers of all the atoms.

$$\overset{+1}{K_2}\overset{+6}{Cr_2}\overset{-2}{O_7} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+1}{K}\overset{-1}{Cl} + \overset{+3}{Cr}\overset{-1}{Cl_3} + \overset{+1}{H_2}\overset{-2}{O} + \overset{0}{Cl_2}$$

The Ox.no. of Cr has decreased while that of chlorine has increased.

$$K_2\overset{+6}{Cr_2}O_7 \longrightarrow 2\overset{+3}{Cr}Cl_3 \quad \text{... (i)}$$

$$H\overset{-1}{Cl} \longrightarrow \overset{0}{Cl} \quad \text{... (ii)}$$

Decrease in Ox.no. of Cr = 6 units per molecule $K_2Cr_2O_7$

Increase in Ox.no. of Cl = 1 unit per molecule HCl

Eq. (ii) is multiplied by 6.

$$K_2Cr_2O_7 + 6HCl \longrightarrow 2CrCl_3 + 3Cl_2$$

To balance chlorine and potassium, 14 molecules of HCl are required.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2CrCl_3 + 3Cl_2 + 2KCl$$

To balance hydrogen and oxygen, $7H_2O$ are added to RHS. Hence, the balanced equation is,

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Example 18. *Balance the following equation by oxidation number method:*

$$NaIO_3 + NaHSO_3 \longrightarrow Na_2SO_4 + NaHSO_4 + I_2 + H_2O$$

Solution: Writing oxidation numbers of all the atoms.

$$\overset{+1}{Na}\,\overset{+5}{I}\,\overset{-2}{O_3} + \overset{+1}{Na}\overset{+1}{H}\,\overset{+4}{S}\,\overset{-2}{O_3} \longrightarrow \overset{+1}{Na_2}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{Na}\overset{+1}{H}\overset{+6}{S}\overset{-2}{O_4} + \overset{0}{I_2} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation no. of I has decreased while that of S has increased.

$$\overset{+5}{NaIO_3} \longrightarrow \overset{0}{I} \qquad \text{... (i)}$$

$$\overset{+4}{NaHSO_3} \longrightarrow \overset{+6}{NaHSO_4} \qquad \text{... (ii)}$$

Decrease in Ox.no. of I = 5 units per molecule $NaIO_3$

Increase in Ox.no. of S = 2 units per molecule $NaHSO_3$

Eq. (i) is multiplied by 2 and eq. (ii) is multiplied by 5 as to make decrease and increase equal.

$$2NaIO_3 + 5NaHSO_3 \longrightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4$$

To balance hydrogen and oxygen, one H_2O molecule should be added on RHS. Hence, the balanced equation is

$$2NaIO_3 + 5NaHSO_3 \rightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4 + H_2O$$

Example 19. *Balance the following equation by oxidation number method:*

$$I_2 + NaOH \longrightarrow NaIO_3 + NaI + H_2O$$

Solution: Writing oxidation numbers of all the atoms,

$$\overset{0}{I_2} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \longrightarrow \overset{+1}{Na}\overset{+5}{I}\overset{-2}{O_3} + \overset{+1}{Na}\overset{-1}{I} + \overset{+1}{H_2}\overset{-2}{O}$$

The Ox.no. of iodine has increased as well as decreased.

$$\overset{0}{I} \longrightarrow \overset{+5}{NaIO_3} \qquad \text{... (i)}$$

$$\overset{0}{I} \longrightarrow \overset{-1}{NaI} \qquad \text{... (ii)}$$

Increase in Ox.no. of I = 5 units per I atom

Decrease in Ox.no. of I = 1 unit per I atom

Eq. (ii) should be multiplied by 5 as to make increase and decrease equal.

$$3I_2 \longrightarrow NaIO_3 + 5NaI$$

To balance Na, 6 molecules of NaOH should be added on LHS.

$$3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI$$

To balance hydrogen and oxygen, $3H_2O$ should be added on RHS. Hence, the balanced equation is

$$3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$$

Example 20. *Balance the following equation by oxidation number method:*

$$PbS + H_2O_2 \longrightarrow PbSO_4 + H_2O$$

Solution: Writing oxidation numbers of all the atoms,

$$\overset{+2}{Pb}\,\overset{-2}{S} + \overset{+1}{H_2}\overset{-1}{O_2} \longrightarrow \overset{+2}{Pb}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation number of S has increased and O has decreased.

$$\overset{-2}{PbS} \longrightarrow \overset{+6}{PbSO_4} \qquad \text{... (i)}$$

$$\overset{-1}{H_2O_2} \longrightarrow \overset{-2}{H_2O} \qquad \text{... (ii)}$$

Increase in Ox.no. of S = 8 units per PbS molecule

Decrease in Ox.no. of O = 1 unit per $\frac{1}{2}$ H_2O_2 molecule

= 2 units per H_2O_2 molecule

Multiplying eq. (ii) by 4 as to make increase and decrease equal.

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

This is the balanced equation.

Example 21. *Balance the following equation by oxidation number method:*

$$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$$

Solution: Writing oxidation numbers of all the atoms,

$$\overset{0}{Zn} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Zn}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{-3}{N}\overset{+1}{H_4}\overset{+5}{N}\overset{-2}{O_3} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation numbers of Zn and N have changed.

$$\overset{0}{Zn} \longrightarrow \overset{+2}{Zn(NO_3)_2} \qquad \text{... (i)}$$

$$\overset{+5}{HNO_3} \longrightarrow \overset{-3}{NH_4NO_3} \qquad \text{... (ii)}$$

Increase in Ox.no. of Zn = 2 units per Zn atom

Decrease in Ox.no. of N = 8 units per HNO_3 molecule

Eq. (i) should be multiplied by 4

$$4Zn + HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3$$

To balance nitrogen, 9 molecules of HNO_3 should be added on LHS.

To balance hydrogen and oxygen, $3H_2O$ molecules should be added on RHS. Hence, the balanced equation is

$$4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Example 22. *Balance the following equation by oxidation number method:*

$$HgS + HCl + HNO_3 \longrightarrow H_2HgCl_4 + NO + S + H_2O$$

Solution: Writing the oxidation numbers of the atoms.

$$\overset{+2}{Hg}\overset{-2}{S} + \overset{+1}{H}\overset{-1}{Cl} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+1}{H_2}\overset{+2}{Hg}\overset{-1}{Cl_4} + \overset{+2}{N}\overset{-2}{O} + \overset{0}{S} + \overset{+1}{H_2}\overset{-2}{O}$$

The oxidation numbers of S and N have changed.

$$\overset{-2}{HgS} \longrightarrow \overset{0}{S} \qquad \text{... (i)}$$

$$\overset{+5}{HNO_3} \longrightarrow \overset{+2}{NO} \qquad \text{... (ii)}$$

Increase in Ox.no. of S = 2 units per HgS molecule

Decrease in Ox. no. of N = 3 units per HNO_3 molecule

Multiplying eq. (i) by 3 and eq. (ii) by 2 as to make increase and decrease equal

$$3HgS + 2HNO_3 \longrightarrow 3S + 2NO$$

Balancing Hg and chlorine,

$$3HgS + 2HNO_3 + 12HCl \longrightarrow 3H_2HgCl_4 + 3S + 2NO$$

To balance hydrogen and oxygen, $4H_2O$ molecules are added on RHS. Hence, the balanced equation is

$$3HgS + 2HNO_3 + 12HCl \rightarrow 3H_2HgCl_4 + 3S + 2NO + 4H_2O$$

Example 23. *Balance the following equation by oxidation number method:*

$$Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$$

Solution: Writing oxidation numbers of all atoms,

$$\overset{0}{Cl_2} + \overset{+5\,-2}{IO_3^-} + \overset{-2\,+1}{OH^-} \longrightarrow \overset{+7\,-2}{IO_4^-} + \overset{-1}{Cl^-} + \overset{+1\,-2}{H_2O}$$

Oxidation numbers of Cl and I have changed.

$$\overset{0}{Cl_2} \longrightarrow 2\overset{-1}{Cl^-} \qquad \text{... (i)}$$

$$\overset{+5}{IO_3^-} \longrightarrow \overset{+7}{IO_4^-} \qquad \text{... (ii)}$$

Decrease in Ox.no. of Cl = 2 units per Cl_2 molecule

Increase in Ox. no. of I = 2 units per IO_3^- molecule

$$Cl_2 + IO_3^- \longrightarrow IO_4^- + 2Cl^-$$

To balance oxygen $2OH^-$ ions be added on LHS and one H_2O molecule on RHS. Hence, the balanced equation is

$$Cl_2 + IO_3^- + 2OH^- \longrightarrow IO_4^- + 2Cl^- + H_2O$$

Example 24. *Balance the following equation by oxidation number method:*

$$Al + KMnO_4 + H_2SO_4 \longrightarrow Al_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O$$

Solution: Writing oxidation numbers of all atoms,

$$\overset{0}{Al} + \overset{+1\,+7\,-2}{KMnO_4} + \overset{+1\,+6\,-2}{H_2SO_4} \longrightarrow \overset{+3\,+6\,-2}{Al_2(SO_4)_3} + \overset{+1\,+6\,-2}{K_2SO_4} + \overset{+2\,+6\,-2}{MnSO_4} + \overset{+1\,-2}{H_2O}$$

The oxidation numbers of Al and Mn have changed

$$\overset{0}{Al} \longrightarrow \overset{+3}{Al_2(SO_4)_3} \qquad \text{... (i)}$$

$$K\overset{+7}{Mn}O_4 \longrightarrow \overset{+2}{Mn}SO_4 \qquad \text{... (ii)}$$

Increase in Ox.no. of Al = 3 units per Al atom

= 6 units per $Al_2(SO_4)_3$ molecule

Decrease in Ox. no. of Mn = 5 units per $KMnO_4$ molecule

Multiply eq. (i) by 10 and eq. (ii) by 6 as to make increase and decrease equal

$$10Al + 6KMnO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4$$

To balance SO_4^{2-} ions, $24H_2SO_4$ molecules be added on LHS.

$$10Al + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4$$

To balance hydrogen and oxygen, 24 H_2O molecules be added on RHS. Hence, the balanced equation is

$$10Al + 6KMnO_4 + 24H_2SO_4 \longrightarrow 5Al_2(SO_4)_3 + 6MnSO_4 + 3K_2SO_4 + 24H_2O$$

11.10 DISPROPORTIONATION AND OXIDATION-REDUCTION

One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised to a higher state and rest of it is reduced to lower state of oxidation. Such a reaction, in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to **disproportionate.**

The following are some of the examples of disproportionation:

Increase

$$\text{(a)}\quad H_2\overset{-1}{O_2} + H_2\overset{-1}{O_2} \longrightarrow H_2\overset{-2}{O} + \overset{0}{O_2}$$

Decrease

Decrease

$$\text{(b)}\quad 4K\overset{+5}{Cl}O_3 \longrightarrow 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$$

Increase

Decrease

$$\text{(c)}\quad 4\overset{0}{P} + 3NaOH + 3H_2O \longrightarrow 3NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$$

Increase

Decrease

$$\text{(d)}\quad 3\overset{0}{Cl_2} + \underset{\text{(conc.)}}{6NaOH} \xrightarrow{\text{Hot}} 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

Increase

(e) Oxidation state of chlorine lies between –1 to +7; thus out of ClO^-, ClO_2^-, ClO_3^-, ClO_4^-; ClO_4^- does not undergo disproportionation because in this oxidation state of chlorine is highest, *i.e.*, +7. Disproportionation of the other oxoanions are:

$$3\overset{+1}{Cl}O^- \longrightarrow 2\overset{-1}{Cl} + \overset{+5}{Cl}O_3^-$$

$$6\overset{+3}{Cl}O_2^- \longrightarrow 4\overset{+5}{Cl}O_3^- + 2\overset{-1}{Cl^-}$$

$$4\overset{+5}{Cl}O_3^- \longrightarrow \overset{-1}{Cl^-} + 3\overset{+7}{Cl}O_4^-$$

Equivalent mass of substance undergoing disproportionation can be calculated by n-factor method:

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{n\text{-factor}}$$

$$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2}$$

Example :

$n = 2$ (loss of two electron)

$$3\overset{+1}{H_3PO_2} \longrightarrow \overset{-3}{PH_3} + 2\overset{+3}{H_3PO_3}$$

$n = 4$ (gain of four electrons)

$$n\text{-factor} = \frac{4 \times 2}{4 + 2} = \frac{4}{3}$$

$$\text{Equivalent mass of } H_3PO_2 = \frac{\text{Molecular mass}}{n\text{-factor}}$$

$$= \frac{m}{4/3} = \frac{3m}{4}$$

11.11 AUTOXIDATION

Turpentine and numerous other unsaturated compounds, phosphorus and certain metals like Zn and Pb can absorb oxygen from the air in presence of water. The water is oxidised to hydrogen peroxide. This phenomenon of formation of H_2O_2 by the oxidation of H_2O is known as **autoxidation.** The substance such as turpentine or phosphorus or lead which can activate the oxygen is called **activator.** The activator is supposed to first combine with oxygen to form an addition compound, which acts as an **autoxidator** and reacts with water or some other acceptor so as to oxidise the latter. For example:

$$\underset{\text{(Activator)}}{Pb} + O_2 \longrightarrow \underset{\text{(Autoxidator)}}{PbO_2}$$

$$PbO_2 + \underset{\text{(Acceptor)}}{H_2O} \longrightarrow PbO + H_2O_2$$

The turpentine or other unsaturated compounds which act as activators are supposed to take-up oxygen molecule at the double bond position to form unstable peroxide called moloxide, which then gives up the oxygen to water molecule or any other acceptor.

$$RCH{=}CHR + O_2 \longrightarrow \underset{\displaystyle O\!-\!O}{RHC\!-\!CHR}$$

$$\underset{\displaystyle O\!-\!O}{RHC\!-\!CHR} + 2H_2O \longrightarrow RCH{=}CHR + 2H_2O_2$$

$$2KI + H_2O_2 \longrightarrow 2KOH + I_2$$

The evolution of iodine from KI solution in presence of turpentine can be confirmed with starch solution which turns blue.

With this concept, the phenomenon of induced oxidation can also be explained. Na_2SO_3 solution is oxidised by air but Na_3AsO_3 solution is not oxidised by air. If mixture of both is taken, it is observed that both are oxidised. This is induced oxidation.

$$Na_2SO_3 + O_2 \longrightarrow \underset{\text{Moloxide}}{Na_2SO_5}$$

$$Na_2SO_5 + Na_3AsO_3 \longrightarrow Na_3AsO_4 + Na_2SO_4$$

$$\overline{Na_2SO_3 + Na_3AsO_3 + O_2 \longrightarrow Na_2SO_4 + Na_3AsO_4}$$

11.12 FORMAL CHARGE

In polyatomic molecule or ion the net charge is possessed by the ion or molecule as a whole and not by particular atom. For certain purpose formal charge (F.C.) is assigned to each atom.

Formal charge (F.C.) on an atom in a Lewis structure = Total number of valence electrons in the free atom (*V*) − Total number of non-bonding (lone pair) electrons (*N*) $-\frac{1}{2}\times$ Total number of bonding (shared electrons) (*B*)

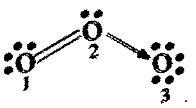
The formal charge of atom in a polyatomic ion/molecule is defined as:

$$F.C. = V - N - \frac{1}{2}B$$

The formal charge is the difference between the number of valence electrons in an isolated (i.e., free) atom and the number of electrons assigned to that atom, in its dot structure.

Let us calculate formal charge on each atom of ozone:

Formal charge at oxygen number 1



$$V = 6, N = 4, B = 4$$

$$F.C. = V - N - \frac{1}{2}B$$

$$= 6 - 4 - \frac{1}{2} \times 4 = 0$$

Formal charge at oxygen number 2

$$V = 6, N = 2, B = 6$$

$$F.C. = V - N - \frac{1}{2}B$$

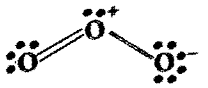
$$= 6 - 2 - \frac{1}{2} \times 6 = 1$$

Formal charge at oxygen number 3

$$V = 6, N = 6, B = 2$$

$$F.C. = 6 - 6 - \frac{1}{2} \times 2 = -1$$

On the basis of formal charge, the structure of ozone may be drawn as,



we must note that formal charges do not indicate real charge separation within the molecule.

Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a compound. The lowest energy structure means the structure with the smallest formal charges on each atom of the compound. Formal charge is based on the concept that electron pairs are shared equally by neighbouring atoms.

Note: (1) A Lewis dot structure for a molecule is preferable when all formal charges are zero.

(2) In a dot structure adjacent formal charges should be zero or of opposite sign.

(3) Among the several Lewis dot structure for same species, the structure with negative formal charges on more electronegative atom is preferred.

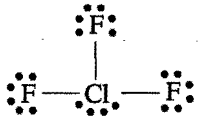
Let us consider thiocyanate:

	Formal charges			Total
	N	C	S	
~~Structure I $(:\ddot{N}=C=\ddot{S}:)^-$~~	~~–1~~	~~0~~	~~0~~	~~–1~~
Structure II $(:\ddot{C}=N=\ddot{S}:)^-$	+1	–2	0	–1
Structure III $(:\ddot{C}=S=\ddot{N}:)^-$	–1	–2	+2	–1

Structure III will be correct structure because each atom has non-zero formal charge in the lowest energy state.

Some illustrations of formal charge calculation:

1.



Formal charge at chlorine:

$$V = 7, N = 4, B = 6$$

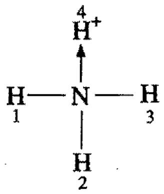
$$\text{F.C.} = 7 - 4 - \frac{1}{2} \times 6 = 0$$

Formal charge at fluorine:

$$V = 7, N = 6, B = 2$$

$$\text{F.C.} = 7 - 6 - \frac{1}{2} \times 2 = 0$$

2.



Formal charge at nitrogen:

$$V = 5, N = 0, B = 8$$

$$\text{F.C.} = 5 - 0 - \frac{1}{2} \times 8 = +1$$

Formal charge at hydrogens 1,2,3:

$$V = 1, N = 0, B = 2$$

$$\text{F.C.} = V - N - \frac{1}{2} \times B$$

$$= 1 - 0 - \frac{1}{2} \times 2 = 0$$

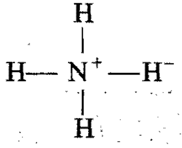
Formal charge at hydrogen number 4:

$$V = 0, N = 0, B = 2$$

$$\text{F.C.} = V - N - \frac{1}{2} \times B$$

$$= 0 - 0 - \frac{1}{2} \times 2 = -1$$

The, structure according to formal charge:



11.13 STOCK NOTATION

~~In the compounds of metals, the oxidation number is represented by the Roman numeral, placed in parenthesis, after the symbol of~~ the metal in the molecular formula. For example:

(i) Cu_2O (Cuprous oxide, oxidation state of copper = +1); its stock notation will be Cu_2(I)O.

(ii) CuO (Cupric oxide, oxidation state of copper = +2); its stock notation will be Cu(II)O.

The stock notation is not used in case of compounds formed by non-metals.

Stock Notation of Some Compounds

Formula of compound	Chemical name of compound	Oxidation state of metal	Stock notation
$HAuCl_4$	Chloroauric acid	Au (+3)	HAu (III) Cl_4
Tl_2O	Thallous oxide	Tl (+1)	Tl_2 (I) O
FeO	Ferrous oxide	Fe (+2)	Fe (II) O
Fe_2O_3	Ferric oxide	Fe (+3)	Fe_2 (III) O_3
Cr_2O_3	Chromic oxide	Cr (+3)	Cr_2 (III) O_3
CuI	Cuprous iodide	Cu (+1)	Cu (I) I
MnO	Mangnese oxide	Mn (+2)	Mn (II) O
MnO_2	Mangnese dioxide	Mn (+4)	Mn (IV) O_2
$K_2Cr_2O_7$	Potassium dichromate	Cr (+6)	Kr Cr_2 (VI) O_7
$KMnO_4$	Potassium permanganate	Mn (+7)	K Mn (VII) O_4
V_2O_5	Vanadium pentoxide	V (+5)	V_2 (V) O_5
$FeSO_4$	Ferrous sulphate	Fe (+2)	Fe_2 (II) SO_4
$Fe_2(SO_4)_3$	Ferric sulphate	Fe (+3)	Fe_2 (III) $(SO_4)_3$
$CuCl_2$	Cupric chloride	Cu (+2)	Cu (II) Cl_2

11.14 STOICHIOMETRY OF REDOX REACTIONS IN SOLUTIONS

Calculations based on chemical equations are known as stoichiometry. A chemical equation is the symbolic representation of a chemical change. It gives the following informations used in solving the numerical problems based on a chemical equation:

(i) It gives the number of moles of the reactants and the products involved in the reaction.

(ii) It gives relative masses of the reactants and products.

(iii) It gives volume of the gaseous reactants and products.

Problems based on chemical equations have also been dealt in Chapter-1. In this section, we will deal with redox reactions only. In the stoichiometry of redox reactions, the chemical equations must be balanced.

Example 25. *Balance the following chemical equation:*

$$H_2O_2 + O_3 \longrightarrow H_2O + O_2$$

Indicating the changes in oxidation numbers of oxygen, find the equivalent weight of H_2O_2 for this reaction. (West Bengal 2005)

Solution: $$\overset{-1}{H_2O_2} + \overset{0}{O_3} \xrightarrow[\text{Oxidised}]{} \overset{-2}{H_2O} + \overset{0}{O_2}$$

Balanced equation will be:

$$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$$

Equivalent mass of $H_2O_2 = \frac{34}{2} = 17$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Molecular and ionic equations: When the reactants and products involved in a chemical change are written in molecular forms in the chemical equation, it is termed as molecular equation. The chemical changes when represented in terms of ions which actually undergo reaction are called ionic equations. The ions which do not undergo any change and equal in number in both reactants and products are termed spectator ions and are not included in the final balanced equations.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3 \quad \text{(Molecular equation)}$$

$$Ag^+ + Cl^- \longrightarrow AgCl \quad \text{(Ionic equation)}$$

[NO_3^- and Na^+ ions are spectator ions.]

2. Oxidation and reduction: Oxidation is a process which involves either of the following:

(i) addition of oxygen,
(ii) removal of hydrogen,
(iii) addition of an electronegative element or group,
(iv) removal of an electropositive element or group,
(v) increase in the valency of an electropositive element,
(vi) loss of one or more electrons by an atom or an ion or a molecule.

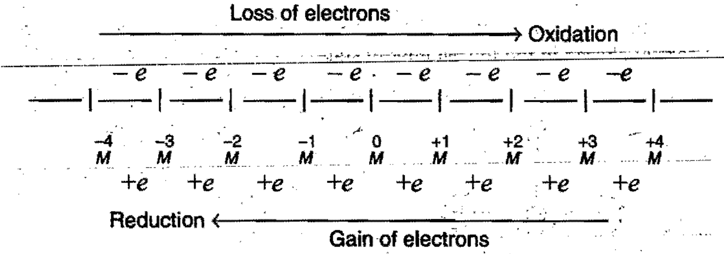
Reduction is just reverse of oxidation. It is a process which involves either of the following:

(i) removal of oxygen,
(ii) addition of hydrogen,
(iii) removal of an electronegative element or group,
(iv) addition of an electropositive element or group,
(v) decrease in the valency of electropositive element,
(vi) gain of one or more electrons by an atom or an ion or a molecule.

A substance which undergoes oxidation or gets oxidised acts as a **reducing agent** while a substance which undergoes reduction or gets reduced acts as an **oxidising agent.**

All oxidation-reduction reactions are complimentary of one another and occur simultaneously. Oxidation-reduction reaction is termed **redox reaction.** The word "redox" includes **red + ox; red** means reduction and **ox** means oxidation. In redox reaction one substance undergoes oxidation and the other substance undergoes reduction, *i.e.*, the reaction between a reducing agent and an oxidising agent is termed as redox reaction.

Any material which is capable of accepting electron or electrons acts as an oxidising agent and the material which loses electron or electrons acts as reducing agents.



3. Ion electron method for balancing redox reaction: The following steps are followed:

(i) Ionic equation of redox reaction is first written.
(ii) The ionic reaction is split into two half reactions, one for oxidation and the other for reduction.
(iii) Each half reaction is balanced for the number of atoms of each element. For this purpose: (a) First of all atoms other than H and O for each half reaction are balanced using simple multiples. (b) In acidic and neutral mediums, H ions are added to the side deficient in hydrogen and water molecules to the side deficient in oxygen. (c) In alkaline medium, for each excess of oxygen atom, one water molecule is added to the same side and two OH^- ions to the other side. If hydrogen is still unbalanced, one OH^- ion is added for each excess of hydrogen on the same side and one water molecule to the other side.
(iv) Electrons are added to the side deficient in electrons as to equalise the charges on both sides of the half reactions.
(v) Electrons are made equal in both the half reactions by multiplying one or both the half reactions by a suitable number.
(vi) Both the balanced half reactions are added and any term common to both sides is cancelled.

4. Oxidation number or oxidation state: It is defined as the charge (real or imaginary) which an atom appears to have when it is in combination. In the case of electrovalent compounds, the oxidation number of an element or radical is the same as the charge on the ion. The following rules are followed in ascertaining the oxidation number in any type of compounds:

- (i) The oxidation number of an atom in free elements is zero no matter how complicated the molecule is.
- (ii) The oxidation number of fluorine is always –1.
- (iii) The oxidation number of oxygen is –2 in all compounds except in peroxides, super oxides and oxygen fluorides.
- (iv) The oxidation number of hydrogen is +1 in all of its compounds except in metallic hydrides. In metallic hydrides, oxidation number of hydrogen is –1.
- (v) The oxidation number of an ion is equal to the electrical charge present on it.
- (vi) The oxidation number of alkali metals is +1 and that of alkaline earth metals is +2.
- (vii) For complex ions, the algebraic sum of oxidation no. of all the atoms is equal to the net charge on the ion.
- (viii) In the case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecules is zero.

Oxidation numbers are quite arbitrary. The values may be positive, negative, zero and even fractional. Many elements show different oxidation numbers in different compounds. In the case of representative elements, the highest oxidation number of an element is the same as its group number while highest negative oxidation number is equal to (8-group number) with negative sign with a few exceptions.

IA elements	+1	VA elements	–3 to +5
IIA elements	+2	VIA elements	–2 to +6
IIIA elements	+3, +1	VIIA elements	–1 to +7
IVA elements	–4 to +4		

The valency and oxidation number concepts are different. In some cases (electrovalent compounds), valency and oxidation number are the same but in other cases they have different values. Valency of an element is usually fixed while oxidation number may have different values.

5. Oxidation and reduction in terms of change in oxidation numbers: Oxidation and reduction are defined on the basis of change in oxidation number.

Oxidation is a process in which an atom undergoes algebraic increase in oxidation number and reduction is a process in which an atom undergoes algebraic decrease in oxidation number. In an oxidising agent, there is always decrease in oxidation number and in reducing agent, there is always increase in oxidation number.

6. Balancing oxidation-reduction reactions by oxidation number method:

- **(i)** The skeleton equation of the chemical change is written.
- **(ii)** Oxidation numbers are assigned to atoms in the equation. The atoms in which change in oxidation number has taken place are selected and two half reactions involving oxidation and reduction are selected.
- **(iii)** Change in oxidation numbers in both the equations is made equal by multiplying with suitable integers and then both the equations are added.
- **(iv)** First of all, those substances are balanced which have undergone change in oxidation number and then other atoms except hydrogen and oxygen. Finally hydrogen and oxygen are balanced.

In ionic equations, the net charges on both sides are made equal. H^+ ions in acidic reactions and OH^- ions in basic reactions are used to balance the charge and number of hydrogen and oxygen atoms.

7. Autoxidation: Certain materials such as turpentine, olefinic compounds, phosphorus, metals like zinc and lead, etc., can absorb oxygen from the air in presence of water and the water is converted to hydrogen peroxide. This phenomenon of formation of H_2O_2 by oxidation of H_2O is known as **autoxidation.** The material which absorbs oxygen and activates it, is called the **activator.** The addition compound of activator and oxygen is termed **autoxidator.** This reacts with water or some other acceptor so as to oxidise the latter.

8. Disproportionation: One and the same substance may act simultaneously as an oxidising agent and as a reducing agent with the result that a part of it gets oxidised and rest of it is reduced. This nature of the change is termed **disproportionation.**

Questions

1. Matrix-Match Type Questions

[A] Match the Column-I with Column-II:

Column-I (Compound)	**Column-II (Oxidation state)**
(a) CrO_5	(p) +6
(b) H_2SO_4	(q) +1
(c) $CaOCl_2$	(r) −1
(d) $(CH_3)_2SO$	(s) 0

[B] Match the Column-I with Column-II:

Column-I (Redox process)	**Column-II (*n*-factor for underlined species)**
~~(a) $\underline{As_2S_3} \rightarrow AsO_3^- + SO_4^{2-}$~~	~~(p) 28~~
(b) $\underline{I_2} \rightarrow I^- + IO_3^-$	(q) 4/3
(c) $\underline{H_3PO_2} \rightarrow PH_3 + 2H_3PO_3$	(r) 1
(d) $\underline{H_3PO_2} + NaOH \rightarrow NaH_2PO_2 + H_2O$	(s) 5/3

[C] Match the Column-I with Column-II:

Column-I (Compound)	**Column-II (Oxidation state of nitrogen)**
(a) Mg_3N_2	(p) −1
(b) NO	(q) +2
(c) $(N_2H_5)_2SO_4$	(r) −2
(d) NH_2OH	(s) −3

[D] Match the Column-I with Column-II:

Column-I (Compound)	**Column-II (Oxidation state of)**
(a) CrO_5	(p) Oxygen is −2
(b) $Na_2S_2O_3$	(q) Oxygen is −1
(c) H_2SO_5	(r) Sulphur is +6
(d) $H_2S_2O_7$	(s) Sulphur is +2

[E] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$	(p) Intermolecular redox reaction
(b) $PbO_2 + H_2O \rightarrow PbO + H_2O_2$	(q) Disproportionation
(c) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$	(r) Intramolecular redox reaction
(d) $Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O$	(s) Metal displacement

2. Indicate which of the substance/ion in the following reactions is an oxidising agent and which is a reducing agent?
   (i) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$
   (ii) $2Mg + SO_2 \longrightarrow 2MgO + S$
   (iii) $2SO_2 + O_2 \longrightarrow 2SO_3$
   (iv) $Ca + Cl_2 \longrightarrow CaCl_2$
   (v) $Sn^{2+} + 2Hg^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$
   (vi) $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$
   (vii) $2I^- + H_2O_2 \longrightarrow 2OH^- + I_2$
   (viii) $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$
   (ix) $SO_2 + 2HNO_3 \longrightarrow H_2SO_4 + 2NO_2$
   (x) $SO_2 + Cl_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$

3. Which substance/ion is oxidised and which substance/ion is reduced in the following reactions?
   (i) $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$
   (ii) $H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S$
   ~~(iii) $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$~~
   ~~(iv) $SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$~~
   (v) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$
   (vi) $3N_2H_4 + 2BrO_3^- \longrightarrow 3N_2 + 2Br^- + 6H_2O$
   (vii) $Cl_2 + SO_3^{2-} + H_2O \longrightarrow 2Cl^- + SO_4^{2-} + 2H^+$
   (viii) $2I^- + Cl_2 \longrightarrow 2Cl^- + I_2$

4. Arrange the following in the order of:
   (a) increasing oxidation number of iodine:
   I_2, HI, HIO_4, ICl
   (b) increasing oxidation number of chlorine:
   Cl_2O_7, Cl_2O, HCl, ClF_3, Cl_2
   (c) increasing oxidation number of nitrogen:
   NH_3, N_3H, N_2O, NO, N_2O_5

5. Find the oxidation number of :
   (i) I in KIO_3
   (ii) P in NaH_2PO_4
   (iii) P in $P_2O_7^{4-}$
   (iv) Fe in $[Fe(CN)_6]^{4-}$
   (v) Ni in $[Ni(CN)_6]^{4-}$
   (vi) S in $H_2S_2O_8$
   (vii) N in NO_3^-
   (viii) S in S_2Cl_2
   (ix) P in $Mg_2P_2O_7$
   (x) Cr in $K_2Cr_2O_7$ (Ranchi 1996)
   (xi) Mn in MnO_4^-
   (xii) Pt in $[PtCl_6]^{2-}$
   (xiii) P in PH_4^+
   (xiv) C in $C_{12}H_{22}O_{11}$
   (xv) Fe in $Na_2[Fe(CN)_5NO]$
   (xvi) Cr in $(NH_4)_2Cr_2O_7$
   (xvii) V in $Rb_4Na[HV_{10}O_{28}]$
   (xviii) Xe in $BaXeO_6$
   (xix) Cl in $Ca(ClO_2)_2$
   (xx) Ni in $Ni(CO)_4$

6. (a) Which compound among the following has the lowest oxidation number of Mn?
$KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3
(b) Which compound among the following has the highest oxidation number of P?
PH_3, H_3PO_2, PCl_3, H_3PO_4
(c) Which compound among the following has the zero oxidation state of carbon?
CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4
(d) Which compound among the following has the lowest oxidation number of chlorine?
$HClO_4$, $HOCl$, ClF_3, $HClO_3$, HCl

Short Answer Type

7. Balance the following equations by ion electron method:

(i) $MnO_4^- + Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$ (acidic medium)

(ii) $MnO_4^- + SnO_2^{2-} + H_2O \longrightarrow MnO_2 + SnO_3^{2-} + OH^-$ (alkaline medium)

(iii) $Cu + NO_3^- + 8H^+ \longrightarrow Cu(NO_3)_2 + NO + H_2O$ (acidic medium)

(iv) $Cl_2 + IO_3^- + OH^- \longrightarrow IO_4^- + Cl^- + H_2O$ (alkaline medium)

(v) $I_2 + NaOH \longrightarrow NaIO_3 + NaI + H_2O$ (alkaline medium)

(vi) $Zn + NO_3^- + OH^- \longrightarrow ZnO_2^{2-} + NH_3 + H_2O$ (alkaline medium)

(vii) $Cr(OH)_3 + ClO^- + OH^- \longrightarrow CrO_4^{2-} + Cl^- + H_2O$

[**Hint:** Half reactions

$$[Cr(OH)_3 + 5OH^- \longrightarrow CrO_4^{2-} + 4H_2O + 3e] \times 2$$
$$[ClO^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-] \times 3$$
$$2Cr(OH)_3 + 4OH^- + 3ClO^- \longrightarrow 2CrO_4^{2-} + 3Cl^- + 5H_2O\ ]$$

(viii) $As_2S_3 + NO_3^- + H^+ + H_2O \longrightarrow H_3AsO_4 + NO + S$

[**Hint:** Half reactions

$$[As_2S_3 + 8H_2O \longrightarrow 2H_3AsO_4 + 3S + 10H^+ + 10e] \times 3$$
$$[NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O] \times 10$$
$$3As_2S_3 + 4H_2O + 10NO_3^- + 10H^+ \longrightarrow 6H_3AsO_4 + 9S + 10NO\ ]$$

(ix) $Zn + H^+ + NO_3^- \longrightarrow Zn^{2+} + NH_4^+ + H_2O$

(x) $P_4 + OH^- + H_2O \longrightarrow H_2PO_2^- + PH_3$

[**Hint:** Half reactions

$$[P_4 + 8OH^- \longrightarrow 4H_2PO_2^- + 4e] \times 3$$
$$P_4 + 12H_2O + 12e \longrightarrow 4PH_3 + 12OH^-$$
$$4P_4 + 12OH^- + 12H_2O \longrightarrow 12H_2PO_2^- + 4PH_3$$
$$\text{or} \quad P_4 + 3OH^- + 3H_2O \longrightarrow 3H_2PO_2^- + PH_3\ ]$$

(xi) $HgS + Cl^- + H^+ + NO_3^- \longrightarrow HgCl_4^{2-} + S + NO + H_2O$

[**Hint:** Half reactions

$$[HgS + 4Cl^- \longrightarrow HgCl_4^{2-} + S + 2e] \times 3$$
$$[NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O] \times 2$$
$$3HgS + 12Cl^- + 2NO_3^- + 8H^+ \longrightarrow 3HgCl_4^{2-} + 3S + 2NO + 4H_2O\ ]$$

(xii) $Co^{2+} + NO_2^- + H^+ \longrightarrow Co^{3+} + NO + H_2O$

(xiii) $CrI_3 + H_2O_2 + OH^- \longrightarrow CrO_4^{2-} + IO_4^- + H_2O$

[**Hint:** Half reactions

$$[CrI_3 + 32OH^- \longrightarrow CrO_4^{2-} + 3IO_4^- + 16H_2O + 27e] \times 2$$
$$[H_2O_2 + 2e \longrightarrow 2OH^-] \times 27$$
$$2CrI_3 + 27H_2O_2 + 10OH^- \longrightarrow 2CrO_4^{2-} + 6IO_4^{2-} + 32H_2O\ ]$$

(xiv) $MnO_4^- + H^+ + H_2O_2 \longrightarrow Mn^{2+} + H_2O + O_2$

[**Hint:** Half reactions

$$[MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$[H_2O_2 \longrightarrow 2H^+ + O_2 + 2e] \times 5$$
$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2\ ]$$

(xv) $C_2H_5OH + I_2 + OH^- \longrightarrow CHI_3 + HCO_2^- + I^- + H_2O$

[**Hint:** Half reactions

$$[C_2H_5OH + \tfrac{3}{2}I_2 + 6OH^- \longrightarrow CHI_3 + HCO_2^- + 5H_2O + 5e] \times 2$$
$$[I_2 + 2e \longrightarrow 2I^-] \times 5$$
$$2C_2H_5OH + 8I_2 + 12OH^- \longrightarrow 2CHI_3 + 2HCO_2^- + 10I^- + 10H_2O$$
$$\text{or} \quad C_2H_5OH + 4I_2 + 6OH^- \longrightarrow CHI_3 + HCO_2^- + 5I^- + 5H_2O\ ]$$

(xvi) $Cr_2O_7^{2-} + H^+ + C_2O_4^{2-} \longrightarrow Cr^{3+} + CO_2 + H_2O$

(xvii) $Ag^+ + AsH_3 + H_2O \longrightarrow H_3AsO_3 + H^+ + Ag$

(xviii) $MnO_2 + OH^- + O_2 \longrightarrow MnO_4^{2-} + H_2O$

[**Hint:** Half reactions

$$[MnO_2 + 4OH^- \longrightarrow MnO_4^{2-} + 2H_2O + 2e] \times 2$$
$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$
$$2MnO_2 + 4OH^- + O_2 \longrightarrow 2MnO_4^{2-} + 2H_2O\ ]$$

8. Balance the following equations by oxidation number method.

(i) $CO + Fe_3O_4 \longrightarrow FeO + CO_2$

(ii) $H_2O_2 + ClO_2 + OH^- \longrightarrow Cl^- + O_2 + H_2O$

(iii) $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow Cr^{3+} + I_2 + H_2O$

(iv) $Cr_2O_7^{2-} + HNO_2 + H^+ \longrightarrow Cr^{3+} + NO_3^- + H_2O$

(v) $KI + H_2SO_4 \longrightarrow K_2SO_4 + I_2 + SO_2 + H_2O$

(vi) $HgS + HCl + HNO_3 \longrightarrow H_2HgI_4 + NO + S + H_2O$

(vii) $[Fe(CN)_6]^{3-} + N_2H_4 + OH^- \rightarrow [Fe(CN)_6]^{4-} + N_2 + H_2O$

[**Hint:** Two half reactions

$$\overset{+3}{[Fe(CN)_6]^{3-}} \longrightarrow \overset{+2}{[Fe(CN)_6]^{4-}}$$

(change in Ox.no. per Fe atom = −1)

$$\overset{-2}{N_2H_4} \longrightarrow \overset{0}{N_2}$$

(change in Ox.no. per N atom = +2)

Total increase = $2 \times (+2) = +4$

$$4[Fe(CN)_6]^{3-} + N_2H_4 \longrightarrow 4[Fe(CN)_6]^{4-} + N_2$$
$$[4Fe(CN)_6]^{3-} + N_2H_4 + 4OH^- \longrightarrow 4[Fe(CN)_6]^{4-} + N_2 + 4H_2O]$$

(viii) $MnO_4^{2-} + H^+ \longrightarrow MnO_2 + MnO_4^- + H_2O$ (IIT 1994)

[**Hint:**

$$\overset{VI}{MnO_4^{2-}} \longrightarrow \overset{IV}{MnO_2}$$
$$[\overset{VI}{MnO_4^{2-}} \longrightarrow \overset{VII}{MnO_4^-}] \times 2$$
$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O]$$

(ix) $HNO_3 + Cu_2O \longrightarrow Cu(NO_3)_2 + NO + H_2O$

(x) $AuCl_4^- + Sn^{2+} + H^+ \longrightarrow Sn^{4+} + AuCl + HCl$

(xi) $S + OH^- \longrightarrow S^{2-} + S_2O_3^{2-}$

[**Hint:** $\overset{0}{S} \longrightarrow S^{2-}$ (decrease of 2)

$2\overset{0}{S} \longrightarrow S_2O_3^{2-}$ (increase of 2 per S atom)]

(xii) $NaClO_3 + KI + HCl \longrightarrow NaCl + KCl + I_2 + H_2O$

(xiii) $PbCrO_4 + H_2SO_4 + FeSO_4 \longrightarrow Fe_2(SO_4)_3 + PbSO_4 + Cr_2(SO_4)_3 + H_2O$

(xiv) $As + HNO_3 \longrightarrow H_3AsO_4 + NO_2 + H_2O$

(xv) $Fe_2(SO_4)_3 + H_2SO_3 + H_2O \longrightarrow FeSO_4 + H_2SO_4$

(xvi) $C_6H_{12}O_6 + H_2SO_4 \longrightarrow CO_2 + SO_2 + H_2O$

9. Balance the following equations:

(i) $Ca_3(PO_4)_2 + SiO_2 + C \longrightarrow CaSiO_3 + P_4 + CO$

(ii) $P_2H_4 \longrightarrow PH_3 + P_4H_2$

[**Hint:** $3 \times [P_2H_4 + 2H^+ + 2e \longrightarrow 2PH_3]$

$2P_2H_4 \longrightarrow P_4H_2 + 6H^+ + 6e$

$5P_2H_4 \longrightarrow 6PH_3 + P_4H_2$]

(iii) $Na_2HAsO_3 + KBrO_3 + HCl \longrightarrow NaCl + KBr + H_3AsO_4$

[**Hint:** $[HAsO_3^{2-} + H_2O \longrightarrow H_3AsO_4 + 2e] \times 3$

$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$

$3HAsO_3^{2-} + BrO_3^- + 6H^+ + 3H_2O \longrightarrow 3H_3AsO_4 + Br^- + 3H_2O$

or $3Na_2HAsO_3 + KBrO_3 + 6HCl \longrightarrow 3H_3AsO_4 + KBr + 6NaCl$]

(iv) $FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$

[**Hint:** Both iron and sulphur in FeS_2 undergo a change in oxidation state.

Increase

$\overset{+2-1}{FeS_2} \longrightarrow \overset{+3}{Fe} + 2\overset{+4}{SO_2}$ Total increase = 10 + 1 = 11

Increase 5 × 2 = 10

$O_2^0 \longrightarrow 2O^{2-}$ Total decrease = 2 × 2 = 4]

(v) $As_2S_5 + HNO_3 \longrightarrow H_3AsO_4 + H_2SO_4 + NO_2 + H_2O$

Increase 5 × 8 = 40

[**Hint:** $As_2\overset{-2}{S_5} + H\overset{+5}{N}O_3 \longrightarrow H_2\overset{+6}{S}O_4 + \overset{+4}{N}O_2$]

Decrease 1 × 1 = 1

(vi) $MnO + PbO_2 + HNO_3 \longrightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$

(vii) $P + NaOH + H_2O \longrightarrow NaH_2PO_2 + PH_3$

Increase 1 × 1 = 1

[**Hint:** $\overset{0}{P} \longrightarrow NaH_2\overset{+1}{P}O_2 + \overset{-3}{P}H_3$]

Decrease 1 × 3 = 3

(viii) $KClO_3 + H_2SO_4 \longrightarrow KHSO_4 + O_2 + ClO_2 + H_2O$

[**Hint:** $[ClO_3^- + 2H^+ + e \longrightarrow ClO_2 + H_2O] \times 2$

$2ClO_3^- \longrightarrow 2ClO_2 + O_2 + 2e$

$4ClO_3^- + 4H^+ \longrightarrow 4ClO_2 + O_2 + 2H_2O$

or $4KClO_3 + 4H_2SO_4 \longrightarrow 4KHSO_4 + 4ClO_2 + O_2 + 2H_2O$]

(ix) $Ag + KCN + O_2 + H_2O \longrightarrow KAg(CN)_2 + KOH$

[**Hint:** $[Ag + 2CN^- \longrightarrow [Ag(CN)_2]^- + e] \times 4$

$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$]

(x) $Ca(OCl)_2 + KI + HCl \longrightarrow CaCl_2 + I_2 + KCl + H_2O$

[**Hint:** $OCl^- + 2H^+ + 2e \longrightarrow Cl^- + H_2O$

$2I^- \longrightarrow I_2 + 2e$

$OCl^- + 2H^+ + 2I^- \longrightarrow Cl^- + I_2 + H_2O$

or $2OCl^- + 4H^+ \longrightarrow 2Cl^- + 2I_2 + 2H_2O$]

---

10. Calculate the oxidation state of underlined:

(a) $Ba_2\underline{Xe}O_2$ (b) $\underline{Ba}Cl_2$ (c) $\underline{C_{12}}H_{22}O_{11}$ (d) $\underline{I}F_7$

(e) $Na_2[\underline{Fe}(CN)_5NO]$ (f) $\underline{Ru}O_4$ (g) $K_2\underline{Ta}F_7$ (h) $Na_2\underline{Mo}O_4$

(i) $\underline{U_2}O_7^{4-}$ (j) C in diamond.

11. Give the oxidation state of underlined:

(a) $\underline{Fe}_3O_4$ (b) $CaO\underline{Cl_2}$ (c) $\underline{N}H_4\underline{N}O_3$

(d) $\underline{N}H_4\underline{N}O_2$ (e) $K\underline{O_2}$ (f) $H_2\underline{S}O_5$

(g) $(CH_3)_2\underline{S}O$ (h) $H_2\underline{S_2}O_8$ (i) $Na_2\underline{S_2}O_3$

(j) $Na_2\underline{S_4}O_6$ (k) $\underline{Cr}O_5$ (l) $\underline{Co}SeO_4$

12. Balance the following equations by ion electron method:

(a) $Zn + BrO_4^- + OH^- + H_2O \longrightarrow [Zn(OH)_4]^{2-} + Br^-$

(b) $MnO_4^{2-} + H_2O \longrightarrow MnO_4^- + OH^- + MnO_2$

(c) $Fe(CN)_6^{4-} + H^+ + MnO_4^- \longrightarrow Fe^{3+} + CO_2 + NO_3^- + Mn^{2+}$

(d) $Cu_3P + Cr_2O_7^{2-} \longrightarrow Cu^{2+} + H_3PO_4 + Cr^{3+}$ (acid medium)

(e) $Hg_2(CN)_2 + Ce^{4+} \longrightarrow CO_3^{2-} + NO_3^- + Hg(OH)_2 + Ce^{3+}$ (basic medium)

(f) $K_3Fe(CN)_6 + Cr_2O_3 + KOH \longrightarrow K_4Fe(CN)_6 + K_2CrO_4 + H_2O$ (basic medium)

(g) $Na_2HAsO_3 + KBrO_3 + HCl \longrightarrow NaCl + KBr + H_3AsO_4$

13. Calculate the oxidation state of vanadium in the following complex compound: $Rb_4Na[HV_{10}O_{28}]$

14. **(a)** Arrange the following compounds in increasing order of oxidation number of manganese:

$MnCl_2, MnO_2, KMnO_4, K_2MnO_4$

(b) Indicate valency and oxidation states of carbon in the following compounds:

$CH_4, CH_3Cl, CH_2Cl_2, CHCl_3, CCl_4$

15. Complete and balance the following compounds:

(a) Acidic solution of Fe^{2+} ion gives a brown ring when it comes in contact with NO_3^- ion. Complete the following reactions of this process:

$[Fe(H_2O)_6]^{2+} + NO_3^- + H^+ \longrightarrow ..... + [Fe(H_2O)_6]^{3+} + H_2O$

$[Fe(H_2O)_6]^{2+} ..... \longrightarrow ..... + H_2O$

(b) $Ca_5(PO_4)_3F + H_2SO_4 + H_2O \xrightarrow{Heat} ..... + 5CaS \cdot 2H_2O + ...$

(c) $Sn + 2KOH + 4H_2O \longrightarrow ..... + ...$ (IIT 1994)

(d) $AlBr_3 + K_2Cr_2O_7 + H_3PO_4 \longrightarrow K_3PO_4 + AlPO_4 + ... + ...$

(e) $K_2Cr_2O_7 + HCl \longrightarrow KCl + ... + ... + H_2O$ (IIT 1992)

(f) $Ag^+ + AsH_3 \longrightarrow H_3AsO_3 + H^+ + ...$

16. Arrange following ions in increasing order of oxidation number of sulphur: $S_4O_6^{2-}, HS^-, HSO_4^-, S_2O_8^{2-}, S_2O_3^{2-}, SO_3^{2-}$

17. Determine equivalent weight of underlined species:

(a) $\underline{NH_4NO_3} \longrightarrow N_2O + 3H_2O$

(b) $\underline{3MnO_2} + 6KOH + KClO_3 \longrightarrow 3K_2MnO_4 + KCl + 3H_2O$

(c) $2HS^- + \underline{4HSO_3^-} \longrightarrow 3S_2O_3^{2-} + 3H_2O$

(d) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + \underline{NaClO_3} + 3H_2O$

(e) $\underline{K_2Cr_2O_7} + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$

18. Which of the following structures is accurate on the basis of formal charge?

(a) $H-C\equiv N:$; (b) $H-N\equiv C:$

[**Hint:** (a) $H-C\equiv N:$

$$\text{F.C.} = V - N - \frac{1}{2}B$$

F.C. at 'H' $= 1 - 0 - \frac{1}{2} \times 2 = 0$

F.C. at 'C' $= 4 - 0 - \frac{1}{2} \times 8 = 0$

F.C. at 'N' $= 5 - 2 - \frac{1}{2} \times 6 = 0$

(b) $H-N\equiv C:$

F.C. at 'H' $= 1 - 0 - \frac{1}{2} \times 2 = 0$

F.C. at 'N' $= 5 - 0 - \frac{1}{2} \times 8 = +1$

F.C. at 'C' $= 4 - 2 - \frac{1}{2} \times 6 = -1$

Structure (a) having zero formal charges at each atom will be accurate.]

19. On the basis of formal charge select the most plausible structure:

(a) H_2NOH or H_2ONH (b) SCN^- or CNS^- or CSN^-

(c) $[:\overset{\bullet\bullet}{N}=N=\overset{\bullet\bullet}{N}:]^-$ or $[:\underset{\bullet\bullet}{\overset{\bullet\bullet}{N}}-N\equiv N:]^-$

(d) NOCl or ONCl

Answers

1. [A] (a — p); (b — p); (c — q, r); (d — s)

[B] (a — p); (b — s); (c — q); (d — r)

[C] (a — s); (b — q); (c — s); (d — p)

[D] (a — p, q); (b — p, s); (c — p, q, r); (d — p, r)

[E] (a — r); (b — p); (c — p, s); (d — q)

2.

	Oxidising agent	Reducing agent
(i)	$FeCl_3$	$SnCl_2$
(ii)	SO_2	Mg
(iii)	O_2	SO_2
(iv)	Cl_2	Ca
(v)	Hg^{2+}	Sn^{2+}
(vi)	Cu^{2+}	I^-
(vii)	H_2O_2	I^-
(viii)	SO_2	H_2S
(ix)	HNO_3	SO_2
(x)	Cl_2	SO_2

3.

	Oxidised	Reduced
(i)	PbS	H_2O_2
(ii)	H_2S	$FeCl_3$
(iii)	HCl	MnO_2
(iv)	$SnCl_2$	$FeCl_3$
(v)	$C_2O_4^{2-}$	MnO_4^-
(vi)	N_2H_4	BrO_3^-
(vii)	SO_3^{2-}	Cl_2
(viii)	I^-	Cl_2

4. (a) $HI(-1), I_2(0), ICl(+1), HIO_4(+7)$

(b) $HCl(-1), Cl_2(0), Cl_2O(+1), ClF_3(+3), Cl_2O_7\ (+7)$

(c) $NH_3(-3), N_3H(-1/3), N_2O(+1), NO(+2), N_2O_5(+5)$.

5. (i) + 5 (ii) + 5 (iii) + 5 (iv) + 2 (v) + 2 (vi) + 6 (one peroxo linkage is present) (vii) + 5 (viii) + 1 (ix) + 5 (x) + 6 (xi) + 7 (xii) + 4 (xiii) −3 (xiv) 0 (zero)(xv) + 3 (xvi) + 6 (xvii) + 5 (xviii) + 8 (xix) +3 (xx) 0 (zero).

6. (a) Mn_2O_3 (b) H_3PO_4 (c) CH_2Cl_2 (d) HCl.

7. (i) $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(ii) $2MnO_4^- + 3SnO_2^{2+} + H_2O \longrightarrow 2MnO_2 + 3SnO_3^{2-} + 2OH^-$

(iii) $3Cu + 2NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$

(iv) $Cl_2 + IO_3^- + 2OH^- \longrightarrow IO_4^- + 2Cl^- + H_2O$

(v) $3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$

(vi) $4Zn + NO_3^- + 7OH^- \longrightarrow 4ZnO_2^{2-} + NH_3 + 2H_2O$

(ix) $4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

(xii) $CO^{2+} + NO_2^- + 2H^+ \longrightarrow CO^{3+} + NO + H_2O$

(xvi) $Cr_2O_7^{2-} + 14H^+ + 3C_2O_4^{2-} \longrightarrow 2Cr^{3+} + 7H_2O + 6CO_2$

(xvii) $AsH_3 + 3H_2O + 6Ag^+ \longrightarrow H_3AsO_3 + 6H^+ + 6Ag$

8. (i) $CO + Fe_3O_4 \longrightarrow 3FeO + CO_2$

(ii) $5H_2O_2 + 2ClO_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O$

(iii) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(iv) $Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$

(v) $2KI + 2H_2SO_4 \longrightarrow K_2SO_4 + I_2 + SO_2 + 2H_2O$

(vi) $3HgS + 12HCl + 2HNO_3 \longrightarrow 3H_2HgCl_4 + 2NO + 3S + 4H_2O$

(ix) $3Cu_2O + 14HNO_3 \longrightarrow 6Cu(NO_3)_2 + 2NO + 7H_2O$

(x) $AuCl_4^- + Sn^{2+} + 3H^+ \longrightarrow AuCl + Sn^{4+} + 3HCl$

(xi) $4S + 6OH^- \longrightarrow 2S^{2-} + S_2O_3^{2-} + 3H_2O$

(xii) $NaClO_3 + 6KI + 6HCl \longrightarrow NaCl + 6KCl + 3I_2 + 3H_2O$

(xiii) $2PbCrO_4 + 6FeSO_4 + 8H_2SO_4 \longrightarrow 2PbSO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$

(xiv) $As + 5HNO_3 \longrightarrow H_3AsO_4 + 5NO_2 + H_2O$

(xv) $Fe_2(SO_4)_3 + H_2SO_3 + H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$

(xvi) $C_6H_{12}O_6 + 12H_2SO_4 \longrightarrow 6CO_2 + 12SO_2 + 18H_2O$

9. (i) $2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + P_4 + 10CO$

(iv) $4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$

(v) $As_2S_5 + 40HNO_3 \longrightarrow 5H_2SO_4 + 2H_3AsO_4 + 40NO_2 + 12H_2O$

(vi) $2MnO + 5PbO_2 + 10HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 4H_2O$

(vii) $4P + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

(ix) $4Ag + 8KCN + O_2 + 2H_2O \longrightarrow 4KAg(CN)_2 + 4KOH$

(x) $Ca(OCl)_2 + 4KI + 4HCl \longrightarrow CaCl_2 + 4KCl + 2I_2 + 2H_2O$

10. (a) 0 (b) +2 (c) 0 (d) +7 (e) 3 (f) +8 (g) +5 (h) +2 (i) +5 (j) 0

OBJECTIVE QUESTIONS

Set–1 : Questions with single correct answer

1. Oxidation is defined as:
(a) loss of electrons (b) gain of electrons
(c) gain of protons (d) loss of protons

2. A reducing agent is a substance which can:
(a) accept electrons (b) donate electrons
(c) accept protons (d) donate protons

3. A redox reaction is:
(a) proton transfer reaction (b) ion combination reaction
(c) a reaction in solution (d) electron transfer reaction

4. Which of the following is not a redox reaction?
(a) Burning of candle (b) Rusting of iron
(c) Dissolving a salt in water (d) Dissolving Zn in dil. H_2SO_4

5. The reaction, $H_2S + H_2O_2 = S + 2H_2O$ manifests:
(a) oxidising action of H_2O_2 (b) reducing nature of H_2O_2
(c) acidic nature of H_2O_2 (d) alkaline nature of H_2O_2

6. The oxidation number of Fe in $K_4Fe(CN)_6$ is: (CBSE 1993; KCET 2008)
(a) + 6 (b) + 4 (c) + 3 (d) + 2

7. In $Ni(CO)_4$, the oxidation state of Ni is:
(a) 4 (b) zero (c) 2 (d) 8

8. Pick the group which does not contain a neutral oxide : (ISAT 2010)
(a) $NO_2, P_4O_{10}, Al_2O_3, NO$ (b) MgO, N_2O_5, SO_3, N_2O
(c) CO_2, SO_3, CaO, XeO_3 (d) $CO, SiO_2, SnO_2, Na_2O_3$

9. Magnesium reacts with acids producing hydrogen and corresponding magnesium salts. In such reactions Mg undergoes:
(a) reduction
(b) oxidation
(c) neither oxidation nor reduction
(d) simple dissolution

10. When P reacts with caustic soda, the products are PH_3 and NaH_2PO_2. The reaction is an example of:
(a) oxidation
(b) reduction
(c) both oxidation and reduction
(d) neutralisation

11. Which of the following reactions is not a redox reaction ? [PET (Raj.) 2008]
(a) $Ag^+ + Cl^- \longrightarrow AgCl$
(b) $Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$
(c) $2Mg(s) + O_2(g) \longrightarrow 2MgO$
(d) $FeO + C \longrightarrow Fe + CO$

12. Which of the following is not a redox change?
(a) $2H_2S + SO_2 = 2H_2O + 3S$
(b) $2BaO + O_2 = 2BaO_2$
(c) $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$
(d) $2KClO_3 = 2KCl + 3O_2$

13. The conversion of $K_2Cr_2O_7$ into $Cr_2(SO_4)_3$ is a process of:
(a) oxidation (b) reduction
(c) decomposition (d) substitution

14. In the reaction, $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, I_2 acts as:
(a) reducing agent
(b) oxidising agent
(c) oxidising as well as reducing agent
(d) none of the above

15. The most common oxidation state of oxygen is –2. This is best explained as due to:
(a) 2 electrons in the outermost shell
(b) 4 electrons in the outermost shell
(c) 6 electrons in the outermost shell
(d) 8 electrons in the outermost shell

16. Select the compound in which chlorine shows oxidation state + 7:
(a) $HClO_4$ (b) $HClO_3$ (c) $HClO_2$ (d) HClO

17. Which one of the following is a reducing agent?
(a) Ozone (b) Chlorine (c) $FeCl_3$ (d) Na_2SO_3

18. The oxidation number of nitrogen in NH_2OH is:
(a) zero (b) +1 (c) –1 (d) –2

19. HBr and HI reduce sulphuric acid. HCl can reduce $KMnO_4$ and HF can reduce:
(a) H_2SO_4 (b) $KMnO_4$
(c) $K_2Cr_2O_7$ (d) none of these

20. One mole of N_2H_4 loses 10 moles of electrons to form a new compound *Y*. Assuming that all nitrogen appear in the new compound, what is the oxidation state of nitrogen? (There is no change in the oxidation state of hydrogen.)
(a) –1 (b) –3 (c) +3 (d) +5

21. The brown ring complex compound is formulated as $[Fe(H_2O)_5(NO)]SO_4$. The oxidation state of iron is: (CET Karnataka 2009)
(a) +1 (b) +2 (c) +3 (d) zero

22. A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of :
(a) sodium atoms (b) sodium hydroxide
(c) sodium amide (d) solvated electrons

23. In which of the following compounds, iron has an oxidation state of +3? (DPMT 2009)

(a) $Fe(NO_3)_2$
(b) FeC_2O_4
(c) $[Fe(H_2O)_6]Cl_3$
(d) $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$

24. When $KMnO_4$ is reduced with oxalic acid in acidic solution, the oxidation number of Mn changes from:
(a) 7 to 2 (b) 7 to 4 (c) 7 to 6 (d) 6 to 2

25. In which of the following reactions the underlined substance is oxidised?
(a) $3Mg + \underline{N_2} + Mg_3N_2$ (b) $2KI + \underline{Br_2} = 2KBr + I_2$
(c) $\underline{CuO} + \overline{H_2} = Cu + H_2O$ (d) $\underline{CO} + \overline{Cl_2} = COCl_2$

26. Of the following elements, which one has the same oxidation state in all of its compounds?
(a) Hydrogen (b) Fluorine (c) Carbon (d) Oxygen

27. When tin(IV) chloride is treated with excess of conc. hydrochloric acid, the complex ion $(SnCl_6)^{2-}$ is formed. The oxidation state of tin in this complex ion is:
(a) +4 (b) zero (c) −2 (d) −4

28. In the following reaction,

$$3Br_2 + 6CO_3^{2-} + 3H_2O = 5Br^- + BrO_3^- + 6HCO_3^-$$

[PMT (MP) 1997]
(a) bromine is oxidised, carbonate is reduced
(b) bromine is reduced, carbonate is oxidised
(c) bromine is neither reduced nor oxidised
(d) bromine is reduced as well as oxidised

29. If an element is in its lowest oxidation state, under proper conditions, it can act as:
(a) a reducing agent
(b) an oxidising agent
(c) oxidising as well as reducing agent
(d) neither oxidising nor reducing agent

30. The oxidation state of phosphorus varies from:
(a) −1 to +1 (b) −3 to +3
(c) −3 to +5 (d) −5 to +1

31. In which of the following reactions no change in valency occurs?
(a) $SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$
(b) $2Na + O_2 \longrightarrow Na_2O_2$
(c) $Cl_2 + 2NaOH \longrightarrow NaClO + NaCl + H_2O$
(d) $AgNO_3 + KCl \longrightarrow AgCl + KNO_3$

32. When SO_2 is passed through an acidified solution of $K_2Cr_2O_7$, then chromium sulphate is formed. Change in oxidation state of Cr is from: (KCET 2008)
(a) +4 to +2 (b) +6 to +3
(c) +7 to +2 (d) +5 to +3

33. In a reaction,
$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + H_2O + SO_2$, H_2SO_4 acts as:
(a) reducing agent (b) oxidising agent
(c) dehydrate (d) none of these

34. Oxidation number of iodine varies from:
(a) −1 to +1 (b) −1 to +7 (c) +3 to +5 (d) −1 to +5

35. Oxidation number of fluorine in F_2O is:
(a) +1 (b) +2 (c) −1 (d) −2

36. In the compounds $KMnO_4$ and $K_2Cr_2O_7$, the highest oxidation state is of the element:
(a) potassium (b) chromium (c) oxygen (d) manganese

37. In a reaction, the oxidation number of an element becomes zero from −1. It is a case of:
(a) oxidation
(b) reduction
(c) neither oxidation nor reduction
(d) both oxidation and reduction

38. $Cl_2 + H_2S \longrightarrow 2HCl + S$,
In the above reaction, oxidation state of chlorine changes from : [PET (Raj.) 2008]
(a) zero to −1 (b) 1 to zero
(c) zero to 1 (d) remains unchanged

39. During electrolysis the reaction at anode is:
(a) oxidation (b) reduction
(c) decomposition (d) none of these

40. Which of the following is a mild oxidising agent?
(a) Ag_2O (b) $KMnO_4$ (c) $K_2Cr_2O_7$ (d) Cl_2

41. The common oxidation state of alkali metals in the combined state is:
(a) +1 (b) +2 (c) −1 (d) −2

42. Carbon is in highest oxidation state in:
(a) CH_3Cl (b) CCl_4 (c) $CHCl_3$ (d) CH_2Cl_2

43. The oxidation number and covalency of sulphur in S_8 is:
(a) +2, 0 (b) 0, 2 (c) 0, 8 (d) 6, 2

44. Addition of iron or zinc to copper sulphate causes precipitation of copper owing to the:
(a) reduction of Cu^{2+} (b) oxidation of Cu^{2+}
(c) hydrolysis of $CuSO_4$ (d) ionisation of $CuSO_4$

45. In a reaction,

$$H_2O\,(steam) + C\,(glowing) = CO + H_2$$

(a) H_2O is the reducing agent
(b) H_2O is the oxidising agent
(c) carbon is the oxidising agent
(d) oxidation-reduction does not occur

46. The oxidation numbers of C in CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 are respectively:
(a) + 4, + 2, 0, −2, −4 (b) + 2, + 4, 0, −4, −2
(c) −4, −2, 0, + 2, + 4 (d) −2, −4, 0, + 4, + 2

47. Which of the following statements is correct?
(a) Oxidation of a substance is followed by reduction of another
(b) Reduction of a substance is followed by oxidation of another
(c) Oxidation and reduction are complementary reactions
(d) It is not necessary that both oxidation and reduction should take place in the same reaction

48. Reduction never involves:
(a) gain of electrons
(b) decrease in oxidation number
(c) loss of electrons
(d) decrease in valency of electropositive component

49. In which of the following reactions has the underlined substance been reduced?
(a) <u>Carbon monoxide</u> + copper oxide ⟶ carbon dioxide + copper
(b) <u>Copper oxide</u> + hydrochloric acid ⟶ copper chloride + water

(c) $\underline{\text{Hydrogen}}$ + iron oxide ⟶ iron + water

(d) $\underline{\text{Steam}}$ + iron ⟶ iron oxide + hydrogen

50. In which of the following reactions, the underlined element has decreased its oxidation number during the reaction?

(a) $\underline{Fe} + CuSO_4 \longrightarrow Cu + FeSO_4$

(b) $\underline{H_2} + Cl_2 \longrightarrow 2HCl$

(c) $\underline{C} + H_2O \longrightarrow CO + H_2$

(d) $\underline{MnO_2} + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

51. If three electrons are lost by a metal ion, M^{3+}, its final oxidation number would be:

(a) zero (b) + 6

(c) + 2 (d) + 4

52. Select the compound in which chlorine is assigned the oxidation number +5:

~~(a) $HClO_4$ (b) $HClO_2$ (c) $HClO_3$ (d) HCl~~

53. ~~In the alumino thermic process, aluminium acts as:~~

(a) an oxidising agent (b) a flux

(c) a reducing agent (d) a solder

54. The strongest reducing agent is:

(a) K (b) Ca (c) Al (d) Zn

55. In the reaction; $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$; Zn undergoes:

(a) oxidation (b) reduction

(c) simple dissolution (d) double decomposition

56. Phosphorus has the oxidation state of +3 in:

(a) ortho phosphoric acid (b) phosphorus acid

(c) meta phosphoric acid (d) pyrophosphoric acid

57. Oxidation number of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively: [CBSE (PMT) 2009]

(a) −3, +6 and +6 (b) +5, +6 and +6

(c) +3, +6 and +5 (d) +5, +3 and +6

58. The conversion of PbO into $Pb(NO_3)_2$ involves:

(a) oxidation

(b) reduction

(c) neither oxidation nor reduction

(d) both oxidation and reduction

59. The highest state of Mn is shown in:

(a) K_2MnO_4 (b) $KMnO_4$ (c) MnO_2 (d) Mn_2O_3

60. In which one of the following changes, there is transfer of five electrons?

(a) $MnO_4^- \longrightarrow Mn^{2+}$ (b) $CrO_4^{2-} \longrightarrow Cr^{3+}$

(c) $MnO_4^- \longrightarrow MnO_2$ (d) $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

61. The oxidation number of phosphorus in $Ba(H_2PO_2)_2$ is: (IIT 1990)

(a) + 3 (b) + 2 (c) + 1 (d) −1

62. The oxidation state of the most electronegative element in the products of the reaction between BaO_2 and H_2SO_4 are: (IIT 1991)

(a) 0 and −1 (b) −1 and −2

(c) −2 and 0 (d) −2 and + 1

63. In the reaction, $4Fe + 3O_2 \longrightarrow 4Fe^{3+} + 6O^{2-}$ which of the following statements is incorrect? (MLNR 1991)

(a) It is a redox reaction

(b) Metallic iron is a reducing agent

(c) Fe^{3+} is an oxidising agent

(d) Metallic iron is reduced to Fe^{2+}

64. Which of the following halide ions is easiest to oxidise?

(a) F^- (b) Cl^- (c) Br^- (d) I^-

65. In the reaction of sodium thiosulphate with I_2 in aqueous medium the equivalent weight of sodium thiosulphate is equal to: [JEE (WB) 2010]

(a) molar mass of sodium thiosulphate

(b) the average molar masses of $Na_2S_2O_3$ and I_2

(c) half the molar mass of sodium thiosulphate

(d) twice of molar mass of sodium thiosulphate

66. The oxidation number of chlorine in HOCl is:

(a) −1 (b) zero (c) + 1 (d) + 2

67. ~~In the reaction, $Cl_2 + OH^- \longrightarrow Cl^- + ClO_4^- + H_2O$, chlorine~~ is:

(a) oxidised

(b) reduced

(c) oxidised as well as reduced

(d) neither oxidised nor reduced

68. The oxidation number of arsenic atom in H_3AsO_4 is:

(a) −1 (b) −3 (c) + 3 (d) + 5

69. In which of the following reactions, hydrogen is acting as an oxidising agent?

(a) With iodine to give hydrogen iodide

(b) With lithium to give lithium hydride

(c) With nitrogen to give ammonia

(d) With sulphur to give hydrogen sulphide

70. In acid medium, the reaction, $MnO_4^- \longrightarrow Mn^{2+}$ is:

(a) oxidation by 3 electrons (b) reduction by 3 electrons

(c) oxidation by 5 electrons (d) reduction by 5 electrons

71. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced equation are: (IIT 1992)

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

72. The oxidation number of Pt in $[Pt(C_2H_4)Cl_3]^-$ is: (MLNR 1993)

(a) + 1 (b) + 2 (c) + 3 (d) + 4

73. Oxidation number of P in $Mg_2P_2O_7$ is:

(a) + 3 (b) + 2 (c) + 5 (d) −3

74. The oxidation number of phosphorus in PO_4^{3-}, P_4O_{10} and $P_2O_7^{4-}$ is: (CPMT 1992)

(a) + 5 (b) + 3 (c) −3 (d) + 2

75. The oxidation state of Cr in $K_2Cr_2O_7$ is: [CEE (Bihar) 1992; AFMC 1993]

(a) + 7 (b) + 6 (c) + 3 (d) + 2

76. Bromine reacts with hot aqueous alkali to give bromide and

bromate. What is the change that is brought about in oxidation state of bromine to bromate?
(a) –1 to + 5 (b) 0 to + 5
(c) –1 to + 7 (d) None of these

77. Which one of the following leads to redox reaction?
(a) $AgNO_3 + HCl$ (b) $KOH + HCl$
(c) $KI + Cl_2$ (d) $NH_3 + HCl$

78. Oxidation number of 'S' in $Na_2S_4O_6$ is: (CBSE 1993)
(a) + 0.5 (b) 2.5 (c) + 4 (d) + 6

79. Which one of the following is not a redox reaction? (AIIMS 1993)
(a) $CaCO_3 \longrightarrow CaO + CO_2$
(b) $2H_2 + O_2 \longrightarrow 2H_2O$
(c) $Na + H_2O \longrightarrow NaOH + \frac{1}{2}H_2$
(d) $MnCl_3 \longrightarrow MnCl_2 + \frac{1}{2}Cl_2$

80. The oxidation number of nitrogen in NO_3^- is:
(a) –1 (b) + 2 (c) + 3 (d) + 5

81. Oxygen has an oxidation state of + 2 in:
(a) H_2O_2 (b) OF_2 (c) SO_2 (d) H_2O

82. When iron is rusted, it is:
(a) oxidised (b) reduced
(c) evaporated (d) decomposed

83. An element, which never has a positive oxidation state in any of its compounds, is:
(a) boron (b) oxygen
(c) chlorine (d) fluorine

84. Starch iodide paper is used to test for the presence of:
(a) iodine (b) iodide ion
(c) oxidising agent (d) reducing agent

85. Which of the acid possesses oxidising, reducing and complex forming properties?
(a) HNO_3 (b) H_2SO_4 (c) HCl (d) HNO_2

86. Which substance is serving as a reducing agent in the following reaction?
$14H^+ + Cr_2O_7^{2-} + 3Ni \longrightarrow 2Cr^{3+} + 7H_2O + 3Ni^{2+}$ (CBSE 1994)
(a) H_2O (b) Ni (c) H^+ (d) $Cr_2O_7^{2-}$

87. The oxidation state of iodine in $H_4IO_6^-$ is:
(a) + 7 (b) –1 (c) + 5 (d) +1

88. Oxidation number of N in NH_4NO_3 is: [PMT (Raj.) 1993]
(a) –3 (b) + 5 (c) –3 and +5 (d) +3 and –5

89. The element, which shows minimum oxidation number in its compounds, is: [PET (Raj.) 1992]
(a) Fe (b) Mn (c) Ca (d) K

90. In which of the following compounds, the oxidation number of iodine is fractional? [PET (Raj.) 1992]
(a) IF_7 (b) I_3^- (c) IF_5 (d) IF_3

91. The missing term in the following equation is:

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + \ldots$$

(a) Sn^{4+} (b) Sn^{3+} (c) Sn^{2+} (d) Sn^+

92. A compound contains atoms A, B and C. The oxidation number of A is + 2, of B is + 5 and of C is –2. The possible formula of the compound is:
(a) ABC_2 (b) $B_2(AC_3)_2$
(c) $A_3(BC_4)_2$ (d) $A_3(B_4C)_2$

93. The correct set of oxidation numbers of nitrogen in ammonium nitrate is: [PET (Raj.) 2007]
(a) – 3, + 3 (b) – 1, + 1 (c) + 1, – 1 (d) – 3, + 5

94. In which of the following pairs, the oxidation states of sulphur and chromium are same? [PET (Raj.) 2007]
(a) SO_3^{2-}, CrO_4^{2-} (b) SO_3, CrO_4^{2-}
(c) SO_2, CrO_4^{2-} (d) SO_2, $Cr_2O_7^{2-}$

95. For the redox reaction, $HgCl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$, the correct coefficients of reactants for the balanced equation are:
(a) 1, 1 (b) 1, 2
(c) 2, 2 (d) 2, 1

96. The value of n in the following equation is:

$$Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$$

[PET (MP) 2008]
(a) 2 (b) 3 (c) 7 (d) 6

97. In the reaction, $8Al + 3Fe_3O_4 \longrightarrow 4Al_2O_3 + 9Fe$, the number of electrons transferred from reductant to oxidant is:
(a) 8 (b) 4 (c) 16 (d) 24

[**Hint:** $8Al \longrightarrow 8Al^{3+} + 24e$
$9Fe^{8/3+} + 24e \longrightarrow 9Fe$]

98. Which of the following examples does not represent disproportionation?
(a) $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
(b) $2H_2O_2 \longrightarrow 2H_2O + O_2$
(c) $4KClO_3 \longrightarrow 3KClO_4 + KCl$
(d) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$

99. Why is the following reaction is not possible?

$$Cr_2O_7^{2-} + Fe^{3+} + H^+ \longrightarrow \ldots + \ldots + \ldots$$

(a) Both $Cr_2O_7^{2-}$ and Fe^{3+} are reducing agents
(b) Both $Cr_2O_7^{2-}$ and Fe^{3+} are oxidising agents
(c) $Cr_2O_7^{2-}$ is a strong oxidising agent while Fe^{3+} is a weak oxidising agent
(d) The solution is acidic in nature

100. Which one of the following statements is not correct?
(a) Oxidation number of S in $(NH_4)_2S_2O_8$ is + 6
(b) Oxidation number of Os in OsO_4 is + 8
(c) Oxidation number of S in H_2SO_5 is + 8
(d) Oxidation number of O in KO_2 is $-\frac{1}{2}$

101. The oxide which cannot act as a reducing agent, is: (CBSE 1995)
(a) SO_2 (b) NO_2
(c) CO_2 (d) ClO_2

102. Coordination number and oxidation number of Cr in $K_3Cr(C_2O_4)_3$ are respectively: (CBSE 1995)
(a) 4 and + 2 (b) 6 and + 3 (c) 3 and –3 (d) 3 and 0

103. In the following reaction,

$$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$$

(a) P is oxidised only
(b) P is reduced only
(c) P is oxidised as well as reduced
(d) none of the above

104. Which reaction does not involve either oxidation nor reduction?
(a) $VO^{2+} \longrightarrow V_2O_3$ (b) $Na \longrightarrow Na^+$
(c) $CrO_4^{2-} \longrightarrow Cr_2O_7^{2-}$ (d) $Zn^{2+} \longrightarrow Zn$

105. In which of the following processes is nitrogen oxidised?
(a) $NH_4^+ \longrightarrow N_2$ (b) $NO_3^- \longrightarrow NO$
(c) $NO_2 \longrightarrow NO_2^-$ (d) $NO_3 \longrightarrow NH_4^+$

106. It is found that V forms a double salt isomorphous with Mohr's salt. The oxidation number of V in this compound is:
(a) + 3 (b) + 2 (c) + 4 (d) − 4

107. How many moles of electrons are involved in the reduction of one mole of MnO_4^- ion in alkaline medium to MnO_3^- ?
(a) 2 (b) 1 (c) 3 (d) 4

108. One mole of N_2H_4 loses 10 moles of electrons to form a new compound *Y*. Assuming that all nitrogen appears in the new compound, what is the oxidation number of nitrogen in *Y* (there is no change in the oxidation state of hydrogen)?
(a) −3 (b) + 3 (c) + 5 (d) + 1

109. Oxidation number of C in HNC is:
(a) + 2 (b) −3 (c) + 3 (d) zero

110. Oxidation number of Fe in $Fe_{0.94}O$ is:
(a) 200 (b) 200/94 (c) 94/200 (d) none of these

111. Oxidation number of Fe in $Na_2[Fe(CN)_5NO]$ is:
(a) + 2 (b) + 1 (c) + 3 (d) −2

112. Oxidation number of Cl in $CaOCl_2$ is:
(a) −1 and + 1 (b) + 2
(c) −2 (d) none of these

113. Equivalent weight of FeC_2O_4 in the change,
$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$ is:
(a) $M/3$ (b) $M/6$ (c) $M/2$ (d) $M/1$

114. Oxidation state of Fe in Fe_3O_8 is: (CBSE 1999)
(a) 3/2 (b) 4/5 (c) 5/4 (d) 8/3

115. In which of the following compounds transition metal has zero oxidation state? (CBSE 1999)
(a) CrO_5 (b) Fe_3O_4 (c) $FeSO_4$ (d) $Fe(CO)_5$

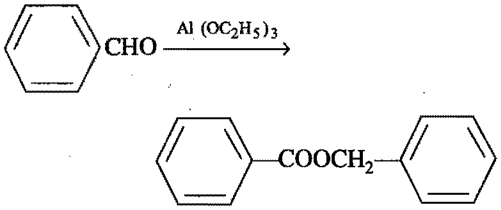
116. The oxidation number of sulphur in S_8, S_2F_2 and H_2S respectively are: (IIT 1999)
(a) 0, +1 and −2 (b) +2, +1 and −2
(c) 0, +1 and +2 (d) −2, +1 and −2

117. The reaction, $3ClO^-(aq.) \rightarrow ClO_3^-(aq.) + 2Cl^-(aq.)$ is an example of: [IIT (S) 2000]
(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction

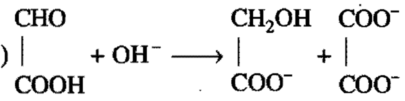
118. The oxidation state of 'S' in $H_2S_2O_8$ is: [PET (MP) 2002; RPMT 2007]
(a) +2 (b) +4 (c) +6 (d) +7

119. Which is not a disproportionation reaction?

(a) 2



(b)



$$\begin{array}{c}CHO\\|\\COOH\end{array} + OH^- \longrightarrow \begin{array}{c}CH_2OH\\|\\COO^-\end{array} + \begin{array}{c}COO^-\\|\\COO^-\end{array}$$

(c) $NaH + H_2O \longrightarrow NaOH + H_2$
(d) All of the above

120. Which of the following is a disproportionation reaction?
(a) $Cu_2O + 2H^+ \longrightarrow Cu + Cu^{2+} + H_2O$
(b) $2CrO_4^2 + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$
(c) $CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + H_2O + CO_2$
(d) $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

121. When $KMnO_4$ acts as an oxidising agent and ultimately forms MnO_4^{2-}, MnO_2, Mn_2O_3 and Mn^{2+}, then the number of electrons transferred in each case respectively is: (AIEEE 2002)
(a) 4, 3, 1, 5 (b) 1, 5, 3, 7
(c) 1, 3, 4, 5 (d) 3, 5, 7, 1

122. Which of the following is a redox reaction: (AIEEE 2002)
(a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$
(b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
(c) $Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$
(d) $Zn + 2AgCN \longrightarrow 2Ag + Zn(CN)_2$

123. For the decolourisation of 1 mole of $KMnO_4$, the no. of moles of H_2O_2 required is: (AIIMS 2004)
(a) $\frac{1}{2}$ (b) $\frac{3}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$

124. In H_2O_2, the oxidation state of oxygen is: (CPMT 2000)
(a) −2 (b) −1 (c) 0 (d) − 4

125. The reaction of $KMnO_4$ and HCl results in:
(a) oxidation of Mn in $KMnO_4$ and production of Cl_2
(b) reduction of Mn in $KMnO_4$ and production of H_2
(c) oxidation of Mn in $KMnO_4$ and production of H_2
(d) reduction of Mn in $KMnO_4$ and production of Cl_2

126. Consider the following reaction,

$$5H_2O_2 + xClO_2 + 2OH^- \longrightarrow x\,Cl^- + y\,O_2 + 6H_2O$$

The reaction is balanced if:
(a) $x = 5, y = 2$ (b) $x = 2, y = 5$
(c) $x = 4, y = 10$ (d) $x = 5, y = 5$

127. In the chemical reaction,

$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$$

(a) water is oxidised (b) electrons are reduced
(c) silver is oxidised (d) silver is reduced
(e) hydrogen is reduced

128. The reaction, $2H_2O(l) \rightarrow 4H^+(aq.) + O_2(g) + 4e^-$ is:
(a) a redox reaction
(b) a hydrolysis reaction
(c) a solvolysis reaction
(d) an oscillatory reaction
(e) an acid catalyst reaction

129. Which of the following molecules can act as an oxidising agent as well as a reducing agent?
(a) H_2S (b) SO_3 (c) H_2O_2 (d) F_2
(e) H_2SO_4

130. Which of the following is not a reducing agent?
(a) SO_2 (b) H_2O_2 (c) CO_2 (d) NO_2

131. Equivalent mass of oxidising agent in the reaction,

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \quad \text{is:}$$

(a) 32 (b) 64 (c) 16 (d) 8

132. A, B and C are three elements forming part of a compound in oxidation states of +2, +5 and –2 respectively. What could be the compound?
(a) $A_2(BC)_2$ (b) $A_2(BC_4)_3$ (c) $A_3(BC_4)_2$ (d) ABC

133. Among the following, identify the species with an atom in +6 oxidation state:
(a) MnO_4^- (b) $Cr(CN)_6^{3-}$ (c) NiF_6^{2-} (d) CrO_2Cl_2

134. On reduction of $KMnO_4$ by oxalic acid in acidic medium, the oxidation number of Mn changes. What is the magnitude of this change?
(a) 7 to 2 (b) 6 to 2 (c) 5 to 2 (d) 7 to 4

135. The oxidation number of iron in Fe_3O_4 is:
(a) +2 (b) +3 (c) 8/3 (d) 2/3

136. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} ions is:
(a) 1/3 (b) 3 (c) 1/6 (d) 6

137. In standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry the equivalent weight of $K_2Cr_2O_7$ is:
(a) molecular weight /2
(b) molecular weight /6
(c) molecular weight /3
(d) same as molecular weight

138. In the balanced chemical reaction,

$$IO_3^- + aI^- + bH^+ \longrightarrow cH_2O + dI_2$$

a, b, c and d respectively correspond to: (AIIMS 2005; AMU 2009)
(a) 5, 6, 3, 3 (b) 5, 3, 6, 3 (c) 3, 5, 3, 6 (d) 5, 6, 5, 5
[Hint: The balanced equation will be:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O]$$

139. In alkaline medium ClO_2 oxidises to H_2O_2 and O_2 and itself gets reduced to Cl^-. How many moles of H_2O_2 are oxidised by 1 mole of ClO_2? (PET 2005)
(a) 1 (b) 1.5 (c) 2.5 (d) 3.5
(e) 5
[Hint: The balanced chemical equation is:

$$2ClO_2 + 5H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O$$

$$2 \text{ mol } ClO_2 \equiv 5 \text{ mol } H_2O_2$$

$$\therefore \quad 1 \text{ mol } ClO_2 \equiv 2.5 \text{ mol } H_2O_2]$$

140. Oxidation number of xenon in $XeOF_2$ is: [CET (J&K) 2005]
(a) zero (b) 2
(c) 4 (d) 3

141. The oxidation number of cobalt in $K[Co(CO)_4]$ is:
(a) +1 (b) +3 (c) –1 (d) –3

142. The oxidation state of iodine in IPO_4 is: [JEE (Orissa) 2005]
(a) +1 (b) +3
(c) +5 (d) +7
[Hint: Let oxidation state of iodine be x
$x - 3 = 0, \ x = +3,$
$\because PO_4^{3-}$ has combined oxidation number –3.]

143. The oxidation state of Cr in $[Cr(NH_3)_4Cl_2]^+$ is:
(a) +3 (b) +2
(c) +1 (d) 0

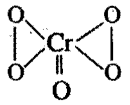
144. Nitrogen forms a variety of compounds in all oxidation states ranging from: [PMT (Himachal) 2006]
(a) –3 to +5 (b) –3 to +3
(c) –3 to +4 (d) –3 to +6

145. In alkaline medium, H_2O_2 reacts with Fe^{3+} and Mn^{2+} separately to give: [JEE (Orissa) 2006]
(a) Fe^{4+} and Mn^{4+} (b) Fe^{2+} and Mn^{2+}
(c) Fe^{2+} and Mn^{4+} (d) Fe^{4+} and Mn^{2+}

[Hint: $$2K_3[\overset{3+}{Fe}(CN)_6] + 2KOH + 2H_2O_2 \longrightarrow 2K_4[\overset{2+}{Fe}(CN)_6] + 2H_2O + O_2$$

$$\overset{2+}{Mn}SO_4 + H_2O_2 \longrightarrow \overset{4+}{Mn}O_2 + H_2SO_4]$$

146. CrO_5 has structure as shown,



The oxidation number of chromium in the above compound is: [PMT (Kerala) 2006; JEE (Orissa) 2008]
(a) +4 (b) +5 (c) +6 (d) +10 (e) 0

147. Which of the following chemical reactions depicts the oxidising behaviour of H_2SO_4? (AIEEE 2006)
(a) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$
(b) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$
(c) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$
(d) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

148. The oxidation numbers of the sulphur atoms in peroxymonosulphuric acid (H_2SO_5) and peroxydisulphuric acid ($H_2S_2O_8$) are respectively : [JEE (J & K) 2009]
(a) + 8 and + 7 (b) + 3 and + 3
(c) + 6 and + 6 (d) + 4 and + 6

149. When phosphorus reacts with caustic soda, the products are PH_3 and NaH_2PO_2. This reaction is an example of: [BHU (Mains) 2007]
(a) oxidation (b) reduction
(c) disproportionation (d) none of these

150. When hydrogen peroxide is added to acidified potassium dichromate, a blue colour is produced due to formation of: [PET (Kerala) 2007]
(a) CrO_3 (b) Cr_2O_3 (c) CrO_5 (d) CrO_4^{2-}
(e) $Cr_2O_7^{2-}$

[**Hint:** $K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + H_2Cr_2O_7$

$[H_2O_2 \longrightarrow H_2O + (O)]4$

$H_2Cr_2O_7 + 4(O) \longrightarrow 2CrO_5 + H_2O$

$\overline{K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow 2CrO_5 + K_2SO_4 + 5H_2O}$]

151. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acid medium will be :
(a) 7.5 moles (b) 0.2 moles (c) 0.6 moles (d) 0.4 moles [CBSE-PMT (Pre) 2008]

[**Hint:** $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2$

Number of moles of MnO_4^- required to oxidise one mole of oxalate $= \frac{2}{5} = 0.4$]

152. Oxidation number of iodine in IO_3^-, IO_4^-, KI and I_2 respectively are : [PMT (Kerala) 2008]
(a) −1, −1, 0, +1 (b) +3, +5, +7, 0
(c) +5, +7, −1, 0 (d) −1, −5, −1, 0
(e) −2, −5, −1, 0

153. In the redox reaction :

$$x\,KMnO_4 + y\,NH_3 \rightarrow KNO_3 + MnO_2 + KOH + H_2O$$

(DPMT 2009)

(a) $x = 4, y = 6$ (b) $x = 3, y = 8$
(c) $x = 8, y = 6$ (d) $x = 8, y = 3$

[**Hint :** Balanced equation is :

$$8KMnO_4 + 3NH_3 \longrightarrow 8MnO_2 + 3KNO_3 + 5KOH + 2H_2O\,]$$

154. The reaction :

$3ClO^- \longrightarrow ClO_3^- + 2Cl^-$ is an example of : (SCRA 2009)

(a) oxidation reaction
(b) reduction reaction
(c) disproportionation reaction
(d) decomposition reaction

155. Which of the following species will not exhibit disproportionation reaction? [AMU (Engg.) 2009]
(a) ClO^- (b) ClO_2^-
(c) ClO_3^- (d) ClO_4^-

156. Which of the following shows nitrogen with its increasing order of oxidation number ? [PMT (Kerala) 2010]
(a) $NO < N_2O < NO_2 < NO_3^- < NH_4^+$
(b) $NH_4^+ < N_2O < NO_2 < NO_3^- < NO$
(c) $NH_4^+ < N_2O < NO < NO_2 < NO_3^-$
(d) $NH_4^+ < NO < N_2O < NO_2 < NO_3^-$

157. Oxidation states of P in $H_4P_2O_5, H_4P_2O_6, H_4P_2O_7$ are respectively : (AIPMT 2010)
(a) +3, +5, +4 (b) +5, +3, +4
(c) +5, +4, +3 (d) +3, +4, +5

Assertion-Reason TYPE QUESTIONS

Set–1

The questions given below consist of an '**Assertion**' **(A)** and '**Reason**' **(R)**. Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. (A) In aqueous solution, SO_2 reacts with H_2S liberating sulphur.
   (R) SO_2 is an effective reducing agent.
2. (A) Fluorine acts as a stronger reducing agent than oxygen.
   (R) Fluorine is more electronegative.
3. (A) $PbCl_2$ is more stable than $PbCl_4$.
   (R) $PbCl_4$ is a powerful oxidising agent.
4. (A) Among halogens fluorine is the.
   (R) Fluorine is the most electronegative element.
5. (A) In the reaction between potassium permanganate and potassium iodide, potassium permanganate act as oxidising agent.
   (R) Oxidation state of manganese changes from +2 to +7 during the reaction.

Set–2

The questions given below consist of two statements each as '**Assertion**' **(A)** and '**Reason**' **(R)**. While answering these questions you are required to choose any one of the following four:

(a) If both (A) and (R) are true, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are true, but (R) is not the correct explanation of (A).
(c) If (A) is true, but (R) is false.
(d) If (A) and (R) are both false.

1. (A) Identification of cathode and anode is done with the help of thermometer.
   (R) Higher is the value of reduction potential, greater would be its reducing power. (AIIMS 1999)
2. (A) Zinc reacts with H_2SO_4 to give H_2 gas but copper does not.
   (R) Zinc has higher reduction potential than copper.
3. (A) Absolute electrode potential can be easily measured by using vacuum tube voltmeter.
   (R) Oxidation or reduction cannot take place alone.
4. (A) Sulphur dioxide and chlorine are both bleaching agents.
   (R) Both are reducing agents. (AIIMS 1994)
5. (A) Hydrogen peroxide acts only as oxidising agent.
   ($H_2O_2 \longrightarrow H_2O + O$)
   (R) All peroxides behave as the oxidising agent only.

6. (A) $HClO_4$ is stronger acid than $HClO_3$.
   (R) Oxidation state of Cl in $HClO_4$ is +VII and in $HClO_3$; it is +V.
7. (A) Oxidation number of Ni in $Ni(CO)_4$ is taken zero.
   (R) The oxidation number of CO has been taken to be zero.
8. (A) Oxidation state of 'H' is +1 in CuH_2 and is −1 in CaH_2.
   (R) Ca is stronger electropositive than hydrogen.
9. (A) Iodine shows oxidation state of +1 and +3 in the compounds ICl and ICl_3 respectively.
   (R) Iodine coming below the halogens F, Cl and Br in the halogen group of elements in the periodic table shows a higher degree of electropositive nature. (SCRA 2007)

Answers : OBJECTIVE QUESTIONS

1. (a)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (c)
9. (b)	**10.** (c)	**11.** (a)	**12.** (c)	**13.** (b)	**14.** (b)	**15.** (c)	**16.** (a)
17. (d)	**18.** (c)	**19.** (d)	**20.** (c)	**21.** (b)	**22.** (d)	**23.** (c)	**24.** (a)
25. (d)	**26.** (b)	**27.** (a)	**28.** (d)	**29.** (a)	**30.** (c)	**31.** (d)	**32.** (b)
33. (b)	**34.** (b)	**35.** (c)	**36.** (d)	**37.** (a)	**38.** (a)	**39.** (a)	**40.** (a)
41. (a)	**42.** (b)	**43.** (b)	**44.** (a)	**45.** (b)	**46.** (c)	**47.** (c)	**48.** (c)
49. (d)	**50.** (d)	**51.** (b)	**52.** (c)	**53.** (c)	**54.** (a)	**55.** (a)	**56.** (b)
57. (b)	**58.** (c)	**59.** (b)	**60.** (a)	**61.** (c)	**62.** (b)	**63.** (d)	**64.** (d)
65. (a)	**66.** (c)	**67.** (c)	**68.** (d)	**69.** (b)	**70.** (d)	**71.** (a)	**72.** (b)
73. (c)	**74.** (a)	**75.** (b)	**76.** (b)	**77.** (c)	**78.** (b)	**79.** (a)	**80.** (d)
81. (b)	**82.** (a)	**83.** (d)	**84.** (c)	**85.** (d)	**86.** (b)	**87.** (a)	**88.** (c)
89. (d)	**90.** (b)	**91.** (a)	**92.** (c)	**93.** (d)	**94.** (b)	**95.** (c)	**96.** (d)
97. (d)	**98.** (a)	**99.** (b)	**100.** (c)	**101.** (c)	**102.** (b)	**103.** (c)	**104.** (c)
105. (a)	**106.** (b)	**107.** (a)	**108.** (b)	**109.** (a)	**110.** (b)	**111.** (a)	**112.** (a)
113. (d)	**114.** (d)	**115.** (d)	**116.** (a)	**117.** (c)	**118.** (c)	**119.** (c)	**120.** (a)
121. (c)	**122.** (c)	**123.** (c)	**124.** (b)	**125.** (d)	**126.** (b)	**127.** (d)	**128.** (a)
129. (c)	**130.** (c)	**131.** (c)	**132.** (c)	**133.** (d)	**134.** (a)	**135.** (c)	**136.** (a)
137. (b)	**138.** (a)	**139.** (c)	**140.** (c)	**141.** (c)	**142.** (b)	**143.** (a)	**144.** (a)
145. (c)	**146.** (c)	**147.** (a)	**148.** (c)	**149.** (c)	**150.** (c)	**151.** (d)	**152.** (c)
153. (d)	**154.** (c)	**155.** (d)	**156.** (c)	**157.** (d)			

Answers : ASSERTION-REASON TYPE QUESTIONS

• Set–1

1. (b)	**2.** (b)	**3.** (b)	**4.** (b)	**5.** (c)

• Set–2

1. (d)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (a)	**8.** (a)
9. (a)							

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

1. Oxidation states of carbon atoms in diamond and graphite are:
(a) +2, +4 (b) +4, +2 (c) – 4, 4 (d) zero, zero

2. Oxidation state(s) of chlorine in $CaOCl_2$ (bleaching powder) is/are:
(a) +1 and –1 (b) +1 only
(c) –1 only (d) none of these

3. Oxidation number of sulphur in S_8, S_2F_2 and H_2S are:
(a) +2, 0, +2 (b) 0, +1, –2 (c) –2, 0, +2 (d) 0, +1, +2

4. The reaction, $H_2S + H_2O_2 \longrightarrow 2H_2O + S$, shows:
(a) acidic nature of H_2O_2 (b) reducing nature of H_2O_2
(c) oxidising action of H_2O_2 (d) alkaline nature of H_2O_2

5. For the redox reaction,
$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O,$$
the correct coefficients of the reactants for the balanced reaction are:

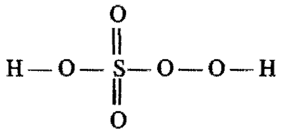
	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	3	12
(c)	15	16	12
(d)	2	16	5

6. Number of moles of $K_2Cr_2O_7$ that can be reduced by 1 mole of Sn^{2+} ions is:
(a) $\frac{1}{3}$ (b) $\frac{3}{2}$ (c) $\frac{5}{6}$ (d) $\frac{6}{5}$
[**Hint:** Balanced equation is:
$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$$
1 mole of $Sn^{2+} \equiv \frac{1}{3}$ mole of $Cr_2O_7^{2-}$]

7. The reaction, $3ClO^-(aq.) \longrightarrow ClO_3^-(aq.) + 2Cl^-(aq.)$, is an example of:
(a) reduction reaction
(b) oxidation reaction
(c) disproportionation reaction
(d) spallation reaction

8. The oxidation states of sulphur in Caro's and Marshall's acid are:
(a) +6, +6 (b) +4, +6 (c) +6, –6 (d) +6, +4
[**Hint:**

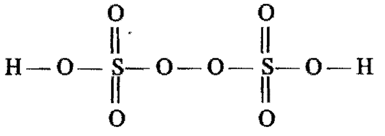
H_2SO_5 **Caro's Acid**



$$H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-H$$

(+6) State

$H_2S_2O_8$ **Marshall's Acid**



$$H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O-H$$

(+6) State

Both these acids have peroxy link.]

9. Which among the following compounds have +6 state with the metal atoms?
(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Cr(CN)_6]^{3-}$ (d) CrO_2Cl_2

10. The oxidation number of nitrogen atoms in NH_4NO_3 are:
(a) +3, +3 (b) +3, –3 (c) –3, +5 (d) –5, +3
[**Hint:** $NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^-$
NH_4^+ $x + 4 = +1$
$x = -3$
NO_3^- $x - 6 = -1$
$x = +5$]

11. In the chemical reaction,
$$K_2Cr_2O_7 + xH_2SO_4 + ySO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + zH_2O$$
the values of x, y and z respectively are:
(a) $x = 1, y = 3, z = 1$ (b) $x = 4, y = 1, z = 4$
(c) $x = 3, y = 2, z = 1$ (d) $x = 2, y = 2, z = 2$

12. In which of the following pairs both members contain peroxy linkage?
(a) $H_2S_2O_8, H_4P_2O_6$ (b) $H_2SO_5, H_4P_2O_7$
(c) $H_2TiO_4, H_4P_2O_8$ (d) S_3O_9, P_4O_7

13. Which of the following agents is the most oxidising?
(a) O_3 (b) $KMnO_4$ (c) H_2O_2 (d) $K_2Cr_2O_7$

14. When methane is burnt in oxygen to produce CO_2 and H_2O, the oxidation number changes by:
(a) –8 (b) zero (c) +8 (d) +4
[**Hint:** $\overset{-4}{C}H_4 + 2O_2 \longrightarrow \overset{+4-4}{C}O_2 + 2H_2O$
Oxidation number change $= +4 - (-4) = +8$]

15. Which of the following has been arranged in order of increasing oxidation number of nitrogen?
(a) $NH_3 < N_2O_5 < NO < N_2$
(b) $NO_2^+ < NO_3^- < NO_2^- < N_3^-$
(c) $NH_4^+ < N_2H_4 < NH_2OH < N_2O$
(d) $NO_2 < NaN_3 < NH_4^+ < N_2O$

16. In the ethylene molecule the two carbon atoms have the oxidation numbers:
(a) –1, –1 (b) –2, –2 (c) –1, –2 (d) +2, –2

17. In which of the following coordination compounds do the transition metals have an oxidation number of +6?
(a) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (b) $[Fe(CO)_5]$
(c) $[(H_2O)_5Cr-O-Cr(H_2O)_5]^{4+}$
(d) $K_2[Cr(CN)_2O_2(O_2)NH_3]$

18. In the redox reaction:
$$xMnO + yPbO_2 + zHNO_3 \longrightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$$
(a) $x = 2, y = 5, z = 10$ (b) $x = 2, y = 7, z = 8$
(c) $x = 2, y = 5, z = 8$ (d) $x = 2, y = 5, z = 5$

19. In the redox reaction:

$x\text{KMnO}_4 + y\text{NH}_3 \longrightarrow \text{KNO}_3 + \text{MnO}_2 + \text{KOH} + \text{H}_2\text{O}$

(a) $x = 4, y = 6$ (b) $x = 8, y = 3$
(c) $x = 8, y = 6$ (d) $x = 3, y = 8$

20. In the ionic equation:

$x\text{CH}_3\text{CH}_2\text{OH} + y\text{I}_2 + z\text{OH}^- \longrightarrow \text{CHI}_3 + \text{HCO}_2^- + \text{I}^- + \text{H}_2\text{O}$

(a) $x = 1, y = 4, z = 6$ (b) $x = 1, y = 6, z = 4$
(c) $x = 1, y = 8, z = 12$ (d) $x = 1, y = 8, z = 8$

21. The oxidation number of Cr is +6 in:

(a) FeCr_2O_4 (b) KCrO_3Cl (c) CrO_5 (d) $[\text{Cr(OH)}_4]^-$

22. The oxidation number of carbon is zero in:

(a) HCHO (b) CH_2Cl_2 (c) $\text{C}_6\text{H}_{12}\text{O}_6$ (d) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

23. Which of the following have been arranged in order of decreasing oxidation number of sulphur?

(a) $\text{H}_2\text{S}_2\text{O}_7 > \text{Na}_2\text{S}_4\text{O}_6 > \text{Na}_2\text{S}_2\text{O}_3 > \text{S}_8$
(b) $\text{SO}^{2+} > \text{SO}_4^{2-} > \text{SO}_3^{2-} > \text{HSO}_4^-$
(c) $\text{H}_2\text{SO}_5 > \text{H}_2\text{SO}_3 > \text{SCl}_2 > \text{H}_2\text{S}$
(d) $\text{H}_2\text{SO}_4 > \text{SO}_2 > \text{H}_2\text{S} > \text{H}_2\text{S}_2\text{O}_8$

24. Oxidation number of carboxylic carbon atom in CH_3COOH is:

(a) +2 (b) +4 (c) +1 (d) +3

25. Which among the following are autoredox reactions?

(a) $\text{P}_4 + \text{OH}^- \longrightarrow \text{H}_2\text{PO}_4^- + \text{PH}_3$
(b) $\text{S}_2\text{O}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{S}$
(c) $\text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$
(d) $\text{AgCl} + \text{NH}_3 \longrightarrow [\text{Ag(NH}_3)_2]\text{Cl}$

26. Oxidation state of nitrogen is incorrectly given for: **[PMT (Pb.) 2006]**

Compound	Oxidation state
(a) $[\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2$	−3
(b) NH_2OH	−1
(c) $(\text{N}_2\text{H}_5)_2\text{SO}_4$	+2
(d) Mg_3N_2	−3

27. Oxidation number of C in HNC is:

(a) +2 (b) −3
(c) +3 (d) zero

[**Hint:** HNC
$+1 - 3 + x = 0$
$x = +2$]

28. Which of the following groups of molecules act both as oxidising agent as well as reducing agent?

(a) $\text{KMnO}_4, \text{O}_3, \text{SO}_3$ (b) $\text{HClO}_4, \text{HNO}_2, \text{H}_2\text{O}_2$
(c) $\text{HNO}_2, \text{SO}_2, \text{H}_2\text{O}_2$ (d) $\text{HNO}_3, \text{SO}_2, \text{H}_2\text{SO}_4$

29. Match the List-I with List-II and select the correct answer from the given Codes:

List-I (Compound)	List-II (Oxidation state of nitrogen)
A. N_2O_5	(i) −2
B. NaN_3	(ii) +5
C. NO	(iii) −1/3
D. N_2H_4	(iv) +2

Codes:	A	B	C	D
(a)	(ii)	(iii)	(iv)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(i)	(ii)	(iii)
(d)	(iii)	(i)	(iv)	(ii)

30. The oxidation state of molybdenum in its oxo complex species $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O}_2)]^{2-}$ is:

(a) 2 (b) 3 (c) 4 (d) 5

31. KMnO_4 is a strong oxidising agent in acid medium. To provide acid medium, H_2SO_4 is used instead of HCl. This is because: **[PMT (Kerala) 2007]**

(a) H_2SO_4 is a stronger acid than HCl
(b) HCl is oxidised by KMnO_4 to Cl_2
(c) H_2SO_4 is a dibasic acid
(d) rate is faster in the presence of H_2SO_4
(e) only H_2SO_4 is completely ionized

32. Which of the following oxides cannot work as a reducing agent? **[PET (Raj.) 2006]**

(a) CO_2 (b) NO_2 (c) SO_2 (d) ClO_2

33. The coordination number and oxidation state of Cr in $\text{K}_3[\text{Cr(C}_2\text{O}_4)_3]$ are respectively: **[PET (Raj.) 2006]**

(a) 3 and +3 (b) 2 and 0
(c) 6 and +3 (d) 4 and +2

34. The reaction, $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$ is an example of : **[JEE (Orissa) 2008]**

(a) disproportionation reaction
(b) neutralisation reaction
(c) double decomposition reaction
(d) pyrolytic reaction

35. Balance the following equation and choose the correct value of sum of coefficients of the products :

$\text{CS}_2 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{S}_2\text{Cl}_2$

(a) 5 (b) 3 (c) 6 (d) 2

36. 6×10^{-3} mole $\text{K}_2\text{Cr}_2\text{O}_7$ reacts completely with 9×10^{-3} mole X^{n+} to give $X\text{O}_3^-$ and Cr^{3+}. The value of 'n' is :

(a) 1 (b) 2 (c) 3 (d) 5

37. Hydrazine reacts with KIO_3 in presence of HCl as;

$\text{N}_2\text{H}_4 + \text{IO}_3^- + 2\text{H}^+ + \text{Cl}^- \longrightarrow \text{ICl} + \text{N}_2 + 3\text{H}_2\text{O}$

The equivalent masses of N_2H_4 and KIO_3 respectively are :

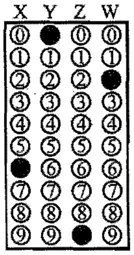
(a) 8, 87 (b) 8, 35.6 (c) 16, 53.5 (d) 8, 53.5

Answers

1. (d) **2.** (a) **3.** (b) **4.** (c) **5.** (a) **6.** (a) **7.** (c) **8.** (a)
9. (d) **10.** (c) **11.** (a) **12.** (c) **13.** (a) **14.** (c) **15.** (c) **16.** (b)
17. (d) **18.** (a) **19.** (b) **20.** (a) **21.** (b, c) **22.** (a, b, c, d) **23.** (a, c) **24.** (d)
25. (a, b, c) **26.** (c) **27.** (a) **28.** (c) **29.** (a) **30.** (b) **31.** (b) **32.** (a)
33. (c) **34.** (a) **35.** (d) **36.** (a) **37.** (d)

Integer Answer TYPE QUESTIONS

This section contains 9 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :

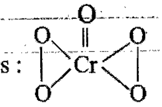


1. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is: **(IIT 2009)**

   [**Hint :** $4KOH + 2MnO_2 + O_2 \longrightarrow 2\overset{+2}{K_2}\overset{+6}{Mn}\overset{-8}{O_4} + 2H_2O$]

2. How many peroxy links are there in CrO_5?

   [**Hint :** Structure of CrO_5 is :



   There are two peroxy links in this molecule.]

3. How many moles of electrons are involved in the conversion of 1 mol $Cr_2O_7^{2-}$ into Cr^{3+} ion?

   $$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

4. In the following reaction, hydrazine is oxidised to N_2

   $$N_2H_4 + OH^- \longrightarrow N_2 + H_2O + e^-$$

   The equivalent mass of N_2H_4 (hydrazine) is:

5. Nitrobenzene ($C_6H_5NO_2$) can be reduced to aniline ($C_6H_5NH_2$) by electrolytic reduction; the equivalent mass of nitrobenzene will be equal to $\left(\frac{\text{molecular mass}}{n}\right)$. The value of n is:

   [**Hint :** $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6[H] \longrightarrow \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$]

6. How many sulphur atoms in $Na_2S_4O_6$ have zero oxidation state?

7. 6×10^{-3} mole $K_2Cr_2O_7$ reacts completely with 9×10^{-3} mole x^{n+} to give XO_3^- and Cr^{3+}. The value of n is:

8. The sum of oxidation number of nitrogen in NH_4NO_3 is :

9. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is: **(IIT 2010)**

   [**Hint :** $Si_6O_{18}^{-12}$ is a cyclic silicate. The value of n will be '3' to balance the charge $Be_nAl_2Si_6O_{18}$

   $$2n + 6 - 12 = 0$$
   $$n = 3$$]

Answers

1. (6)
2. (2)
3. (6)
4. (8)
5. (6)
6. (2)
7. (1)
8. (2)
9. (3)

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Valency and oxidation number are different for an element. Valency of carbon is generally 4, however, the oxidation state may be $-4, -2, 0, +2, -1$, etc. In the compounds containing carbon, hydrogen and oxygen, the oxidation number of carbon can be calculated as:

$$\text{Oxidation number of carbon} = \frac{2n_O - n_H}{n_C}$$

where, n_H, n_O and n_C are number of respective atoms.

Answer the following questions:

1. Which of the following compounds have zero oxidation state at carbon?
   (a) $C_6H_{12}O_6$ (b) HCOOH (c) HCHO (d) CH_4
2. Which of the following oxides of carbon has fractional oxidation state?
   (a) Carbon monoxide (b) Carbon dioxide
   (c) Carbon suboxide (d) All of these
3. Which of the following compounds of carbon has highest oxidation state?
   (a) CH_4 (b) CH_3OH (c) CH_2O (d) HCOOH
4. Oxidation state of carbon in diamond is:
   (a) zero (b) +1 (c) −1 (d) +2
5. In which of the following compounds, the valency of carbon is two?
   (a) Carbenes (b) Allenes (c) Alkenes (d) Ketenes

Passage 2

Oxidation and reduction process involves the transaction of electrons. Loss of electrons is oxidation and the gain of electrons is reduction. It is thus obvious that in a redox reaction, the oxidant is reduced by accepting the electrons and the reductant is oxidised by losing electrons. The reactions in which a species disproportionates into two oxidation states (lower and higher) are called disproportionation reactions. In electrochemical cells, redox reaction is involved, i.e., oxidation takes place at anode and reduction at cathode.

Answer the following questions:

1. The reaction,
   $$Cl_2 \longrightarrow Cl^- + ClO_3^-$$
   is:
   (a) oxidation
   (b) reduction
   (c) disproportionation
   (d) neither oxidation nor reduction
2. Select the correct statement:
   (a) oxidation takes place at anode in electrochemical cell
   (b) reduction takes place at cathode in electrolytic cell
   (c) oxidation takes place at cathode in electrolytic cell
   (d) all are correct
3. In the reaction:
   $$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$
   (a) I_2 is a reducing agent (b) I_2 is an oxidising agent
   (c) $S_2O_3^{2-}$ is a reducing agent (d) $S_2O_3^{2-}$ is an oxidising agent
4. Determine the change in oxidation number of sulphur in H_2S and SO_2 respectively in the following reaction:
   $$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$
   (a) 0, +2 (b) +2, −4 (c) −2, +2 (d) +4, 0
5. Which of the following reactions is/are correctly indicated?

   Oxidant **Reductant**

   (a) $HNO_3 + Cu \longrightarrow Cu^{2+} + NO_2$
   (b) $2Zn + O_2 \longrightarrow ZnO$
   (c) $Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$
   (d) $4Cl_2 + CH_4 \longrightarrow CCl_4 + 4HCl$

Passage 3

Redox reactions are of three types:

(*i*) *Intermolecular redox reactions,*
(*ii*) *Intramolecular redox reactions,*
(*iii*) *Auto redox reactions*
OR
Disproportionation reactions.

Redox reactions are divided into two main types:

(*i*) *Chemical redox reactions,*
(*ii*) *Electrochemical redox reactions which either produce or consume electricity.*

Oxidation and reduction process takes place in a reaction simultaneously.

Answer the following questions:

1. Which of the following is a redox reaction?
   (a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$
   (b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
   (c) $Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$
   (d) $Zn + 2AgCN \longrightarrow 2Ag + Zn(CN)_2$
2. Select the intramolecular redox reaction(s) among the following:
   (a) $2KClO_3 \longrightarrow 2KCl + 3O_2$
   (b) $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$
   (c) $Cl_2 \longrightarrow Cl^- + ClO_3^-$
   (d) $NH_4NO_2 \longrightarrow N_2 + 2H_2O$
3. In which of the following reactions, H_2O_2 acts as reducing agent?
   (a) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$
   (b) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
   (c) $HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$
   (d) $PbO_2 + H_2O_2 \longrightarrow PbO + H_2O + O_2$
4. Which among the following acts as oxidising as well as reducing agent?
   (a) HNO_2 (b) HNO_3 (c) H_2SO_4 (d) $KMnO_4$
5. The value of x in the following reaction,
   $$MnO_4^- + 8H^+ + xe \longrightarrow Mn^{2+} + 4H_2O \text{ is:}$$
   (a) 5 (b) 10 (c) 2 (d) 3

[illegible]

Passage 1.	1. (a, c)	2. (c)	3. (d)	4. (a)	5. (a)
Passage 2.	1. (c)	2. (a, b)	3. (b, c)	4. (b)	5. (a, c, d)
Passage 3.	1. (d)	2. (a, b, d)	3. (a, b, d)	4. (a)	5. (a)

SELF ASSESSMENT

ASSIGNMENT NO. 11

SECTION-I

Straight Objective Type Questions

This section contains 8 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. In the reaction:

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2 \quad \textbf{[PET (MP) 2007]}$$

(a) oxidation of iodide into iodine takes place
(b) reduction of iodine into iodide takes place
(c) both oxidation and reduction of iodine takes place
(d) none of the above

2. The oxidation state of chromium in chromium trioxide is: **[CET (J&K) 2007]**

(a) + 3 (b) + 4 (c) + 5 (d) + 6

3. For the reaction between $KMnO_4$ and H_2O_2, the number of electrons transferred per mol of H_2O_2 is:

(a) one (b) two
(c) three (d) four

4. In the ionic equation,

$$BiO_3^- + 6H^+ + xe^- \longrightarrow Bi^{3+} + 3H_2O$$

the value of x is:

(a) 6 (b) 2
(c) 4 (d) 3

5. In $[Cr(O_2)(NH_3)_4H_2O]Cl_2$, oxidation number of Cr is + 3, then oxygen will be in the form:

(a) dioxo (b) peroxo
(c) superoxo (d) oxo

6. In the reaction, $CrO_5 + SnCl_2 \longrightarrow CrO_4^{2-} + SnCl_4$, the element undergoing oxidation and reduction respectively are:

(a) Cr, Sn (b) Sn, Cr
(c) Sn, O (d) Cl, C

7. Equivalent mass of $KMnO_4$ in acidic, basic and neutral are in the ratio of:

(a) 3 : 5 : 15 (b) 5 : 3 : 1
(c) 5 : 1 : 3 (d) 3 : 15 : 5

8. A compound of Xe and F is found to have 53.5% Xe. What is the oxidation number of Xe in this compound?

(a) – 4 (b) 0
(c) + 4 (d) + 6

SECTION-II

Multiple Answers Type Objective Questions

9. Peroxide ions are present in:

(a) H_2O_2 (b) BaO_2
(c) OF_2 (d) $H_2S_2O_8$

10. The metals undergoing disproportionation are:

(a) Sn (b) Na (c) Cu (d) Ca

11. The non-metals undergoing disproportionation are:

(a) P_4 (b) Cl_2 (c) I_2 (d) F

12. Which of the following can act as oxidising as well as reducing agent?

(a) O_3 (b) HNO_3 (c) SO_2 (d) H_2O_2

13. When Cl_2 reacts with aqueous NaOH in cold condition then oxidation number of chlorine changes from 0 to:

(a) – 1 (b) + 1 (c) – 2 (d) + 2

14. Select those species that can function both as oxidising and also as reducing agent: **[BHU (Mains) 2010]**

(a) KI (b) KI_3 (c) I_2 (d) H_2O_2

15. The species that contain peroxide ions are: **[BHU (Mains) 2010]**

(a) PbO_2 (b) H_2O_2 (c) SrO_2 (d) BaO_2

SECTION-III

Assertion-Reason Type Questions

This section contains 4 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Spectator ions are the species that are present in the solution but do not take part in the reaction.

Because

Statement-2: The phenomena of formation of H_2O_2 by the oxidation of H_2O is known as auto-oxidation.
[**Hint:** $Zn + 2H^+ + 2Cl^- \longrightarrow Zn^{2+} + 2Cl^- + H_2$. Here, Cl^- ion is spectator ion.]

17. Statement-1: Oxidation number of carbon in HCN is + 2.

Because

Statement-2: Carbon always shows an oxidation state of + 4.

18. Statement-1: Bromide ion acts as a reducing agent in the reaction,

$$2MnO_4^- + Br^- + H_2O \longrightarrow 2MnO_2 + BrO_3^- + 2OH^-.$$

Because

Statement-2: Oxidation number of bromine increases from – 1 to + 5.

19. Statement-1: Oxidation number of carbon in HCHO is zero.

Because

Statement-2: HCHO is a covalent organic compound.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as follows:

20. Match the Column-I with Column-II:

Column-I (Chemical species)	**Column-II (Oxidation number of sulphur)**
(a) S	(p) + 6
(b) H_2S	(q) + 1
(c) S_2Cl_2	(r) 0
(d) $H_2S_2O_8$	(s) – 2

21. Match the Column-I with Column-II:

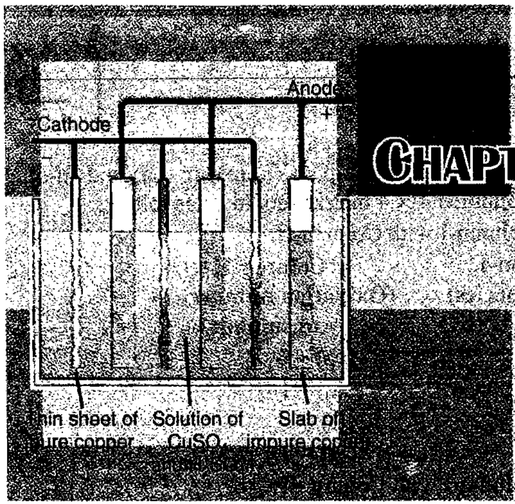
Column-I (Compound)	**Column-II (Oxidation state of sulphur)**
(a) Sulphurus acid (H_2SO_3)	(p) + 5
(b) Peroxy mono sulphuric acid (H_2SO_5)	(q) + 3
(c) Dithionic acid ($H_2S_2O_6$)	(r) + 6
(d) Dithionous acid ($H_2S_2O_4$)	(s) + 4

22. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $O_2^- \longrightarrow O_2 + O_2^{2-}$	(p) Redox reaction
(b) $CrO_4^{2-} + H^+ \longrightarrow$	(q) One of the products has trigonal planar structure
(c) $MnO_4^- + NO_2^- + H^+ \longrightarrow$	(r) dimeric bridged tetrahedral metal ion
(d) $NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s) disproportionation

Answers

1. (a) **2.** (d) **3.** (c) **4.** (b) **5.** (c) **6.** (c) **7.** (d) **8.** (d)
9. (a, b, d) **10.** (a, c) **11.** (a, b, c) **12.** (c, d) **13.** (a, b) **14.** (b, c, d) **15.** (b, c, d) **16.** (b)
17. (c) **18.** (a) **19.** (b) **20.** (a-r) (b-s) (c-q) (d-p) **21.** (a-s) (b-r) (c-p) (d-q)
22. (a-p,s) (b-r) (c-p,q) (d-p)



CHAPTER 12

ELECTROCHEMISTRY

SECTION I : ELECTROLYTES AND ELECTROLYSIS

12.1 INTRODUCTION

Electrochemistry deals with the interactions of electrical energy with chemical species. It is broadly divided into two categories, namely (i) production of chemical change by electrical energy (phenomenon of electrolysis) and (ii) conversion of chemical energy into electrical energy, *i.e.*, generation of electricity by spontaneous redox reactions. In this chapter both of these aspects will be described. All electrochemical reactions involve transfer of electrons and are, therefore, oxidation-reduction (redox) reactions.

Substances which allow the passage of electric current through them are called **electrical conductors** or simply conductors. Those which do not allow the flow of electric current through them are termed **insulators.** Electrical conductors are of two types:

(i) Metallic or electronic conductors: Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as **metallic or electronic conductors.** Metals such as copper, silver, aluminium, etc., non-metals like carbon (graphite—an allotropic form of carbon) and various alloys belong to this class. These materials contain electrons which are relatively free to move. The passage of current through these materials has no observable effect other than a rise in their temperature.

(ii) Electrolytic conductors: Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as **electrolytic conductors.** The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed **electrolytes.**

The substances whose aqueous solutions do not conduct electric current are called **non-electrolytes.** Solutions of cane sugar, glycerine, alcohol, etc., are examples of non-electrolytes.

In order to pass the current through an electrolytic conductor (aqueous solution or fused electrolyte), two rods or plates (metallic conductors) are always needed which are connected with the terminals of a battery. These rods or plates are known as **electrodes.** The electrode through which the current enters the electrolytic solution is called the **anode** (positive electrode) while the electrode through which the current leaves the electrolytic solution is known as **cathode** (negative electrode). The electrolytic solution conducts electricity not by virtue of flow of electrons as in metallic conductors but as a result of movement of charged particles called **ions** towards the respective oppositely charged electrodes. The ions which carry positive charge and move towards cathode are termed **cations** while ions carrying negative charge which move towards anode are called **anions.** When these ions reach the boundary between a metallic and an electrolytic conductor, electrons are being either attached to or removed from the ions. Removal of electrons is termed **oxidation** (de-electronation) which occurs at anode while addition of electrons is called **reduction** (electronation) that takes place at cathode. Hence, flow of electrons through the outer circuit from anode to cathode across the boundary is accompanied by oxidation and reduction.

Distinction between metallic and electrolytic conduction

Metallic conduction	Electrolytic conduction
1. Electric current flows by movement of electrons.	Electric current flows by movement of ions.
2. No chemical change occurs.	Ions are oxidised or reduced at the electrodes.
3. It does not involve the transfer of any matter.	It involves transfer of matter in the form of ions.
4. Ohm's law is followed.	Ohm's law is followed.
5. Resistance increases with increase of temperature.	Resistance decreases with increase of temperature.
6. Faraday's law is not followed.	Faraday's law is followed.

The process of chemical decomposition of an electrolyte by passage of electric current through its solution is called electrolysis.

Or

Chemical change (oxidation and reduction) occurring at electrodes when electric current is passed through electrolytic solution is called electrolysis.

Molecules of an electrolyte when dissolved in water split up into ions, *i.e.*, into cations and anions. On passing current, these ions move towards oppositely charged electrodes. On reaching the electrodes the ions lose their charge either by accepting electrons or losing electrons and thereby deposited at the respective electrodes or undergo a secondary change. For example, when electric current is passed through a solution of hydrochloric acid, the H^+ ions move towards cathode and Cl^- ions move towards anode.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Cathode	Anode
$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$2H \longrightarrow H_2$	$2Cl \longrightarrow Cl_2$
(Reduction)	(Oxidation)

The decomposition of HCl into H_2 and Cl_2 as a result of passage of current is termed electrolysis of HCl. It is, thus, a process in which electric current brings the chemical change.

The device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical change is done is known as **electrolytic cell.** An electrolytic cell consists of a vessel for the electrolytic solution or fused electrolyte and two metallic electrodes immersed in the reaction material which are connected to a source of electric current. The metallic electrodes which do not react with ions or final products are called **inert electrodes.** Inert electrodes are usually used in an electrolytic cell.

12.2 PREFERENTIAL DISCHARGE THEORY

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged at the electrodes simultaneously but certain ions are liberated at the electrodes in preference to others. This is explained by **preferential discharge theory.** It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H^+ ions is lower than Na^+ ions when platinum or most of the other metals* are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^- ions. This can be explained by some examples given below:

(i) Electrolysis of sodium chloride solution

The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- ions due to ionisation of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$2H \longrightarrow H_2$	$2Cl \longrightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

(ii) Electrolysis of copper sulphate solution using platinum electrodes

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$Cu^{2+} + 2e^- \longrightarrow Cu$	$2OH^- \longrightarrow H_2O + O + 2e^-$
	$O + O \longrightarrow O_2$

Copper is discharged at cathode as Cu^{2+} ions have lower discharge potential than H^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, copper is deposited at cathode and oxygen gas is evolved at anode.

(iii) Electrolysis of sodium sulphate solution using inert electrodes

$$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode	At anode
$H^+ + e^- \longrightarrow H$	$2OH^- \longrightarrow H_2O + O + 2e^-$
$2H \longrightarrow H_2$	$O + O \longrightarrow O_2$

Hydrogen is discharged at cathode as H^+ ions have lower discharge potential than Na^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than SO_4^{2-} ions. Thus, hydrogen is evolved at cathode and oxygen is evolved at anode, *i.e.*, the net reaction describes the electrolysis of water. The ions of Na_2SO_4 conduct the current through the solution and take no part in the overall chemical reaction.

---

*When Hg is used as a cathode, Na^+ ions have lower discharge potential than H^+ ions.

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below:

For cations: $K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, H^+, Cu^{2+}, Hg^{2+}, Ag^+$

For anions: $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$

(iv) Electrolysis of copper sulphate solution using copper electrodes

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

At cathode, copper is deposited.

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

At anode, the copper of the electrode is oxidised to Cu^{2+} ions or SO_4^{2-} ions dissolve equivalent amount of copper of the anode.

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

or $$Cu + SO_4^{2-} \longrightarrow CuSO_4 + 2e^-$$

Thus, during electrolysis, copper is transferred from anode to cathode.

(v) Electrolysis of silver nitrate solution using silver electrodes

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

At cathode, silver is deposited.

$$Ag^+ + e^- \longrightarrow Ag$$

At anode, the silver of the electrode is oxidised to Ag^+ ions which go into the solution or NO_3^- ions dissolve equivalent amount of silver of the electrode.

$$Ag \longrightarrow Ag^+ + e^-$$

$$Ag + NO_3^- \longrightarrow AgNO_3 + e^-$$

Table 12.1 Some More Examples of Electrolysis

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified $CuCl_2$ solution	Pt	$Cu^{2+} + 2e^- \longrightarrow Cu$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Molten $PbBr_2$	Pt	$Pb^{2+} + 2e^- \longrightarrow Pb$	$2Br^- \longrightarrow Br_2 + 2e^-$
Sodium chloride solution	Hg	$2Na^+ + 2e^- \longrightarrow 2Na$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Silver nitrate solution	Pt	$Ag^+ + e^- \longrightarrow Ag$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
Sodium nitrate solution	Pt	$2H^+ + 2e^- \longrightarrow H_2$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

12.3 FARADAY'S LAWS OF ELECTROLYSIS

The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented by Faraday in 1834, in the form of laws of electrolysis.

(i) Faraday's first law

When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation:

$$W \propto Q$$

A coulomb is the quantity of charge when a current of one ampere is passed for one second. Thus, amount of charge in coulombs,

$$Q = \text{current in amperes} \times \text{time in seconds}$$
$$= I \times t$$

So, $$W \propto I \times t$$

or $$W = Z \times I \times t$$

where, Z is a constant, known as **electrochemical equivalent,** and is characteristic of the substance deposited.

When a current of one ampere is passed for one second, *i.e.*, one coulomb $(Q = 1)$, then

$$W = Z$$

Thus, **electrochemical equivalent** can be defined as the **mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.** For example, when a charge of one coulomb is passed through silver nitrate solution, the amount of silver deposited is 0.001118 g. This is the value of electrochemical equivalent of silver.

(ii) Faraday's second law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

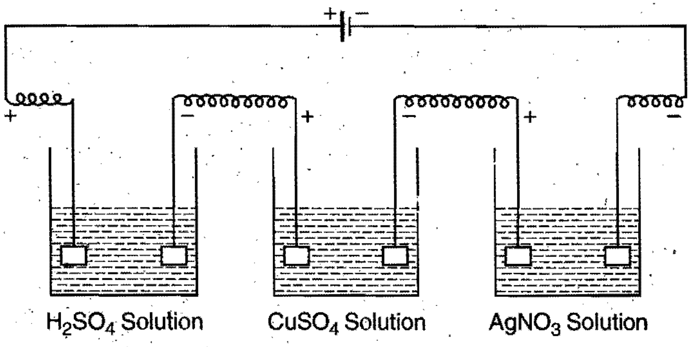


Fig. 12.1 Voltameters arranged in series

The law can be illustrated by passing same quantity of electric current through three voltameters containing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively as shown in Fig. 12.1. In the first voltameter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Mass of copper}} = \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}}$$

or $$\frac{\text{Mass of copper}}{\text{Mass of silver}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

or $$\frac{\text{Mass of silver}}{\text{Mass of hydrogen}} = \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of hydrogen}}$$

It is observed that by passing one coulomb of electric charge,

Hydrogen evolved = 0.00001036 g,

Copper deposited = 0.0003292 g,

and Silver deposited = 0.001118 g

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

$$\text{For hydrogen} = \frac{1}{0.00001036} \approx 96500 \text{ coulomb}$$

$$\text{For copper} = \frac{31.78}{0.0003292} \approx 96500 \text{ coulomb}$$

$$\text{For silver} = \frac{107.88}{0.001118} \approx 96500 \text{ coulomb}$$

This follows that 96500 coulomb of electric charge will deposit one g-equivalent of any substance. 96500 coulomb is termed as one **Faraday** and is denoted by F.

Again according to first law,

$$W = Z \times Q$$

When, $Q = 96500$ coulomb, W becomes gram equivalent mass (E).

Thus, $$E = Z \times 96500$$

or $$Z = \frac{E}{96500}$$

$$\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Fundamental unit of charge: As one g-equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by one g-equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then one mole of these ions will carry a charge of nF coulomb. One g-mole of an ion contains 6.02×10^{23} ions. Then,

$$\text{The charge carried by an ion} = \frac{nF}{6.02 \times 10^{23}} \text{ coulomb}$$

For $n = 1$,

$$\text{The fundamental unit of charge} = \frac{F}{6.02 \times 10^{23}}$$

i.e., $$\frac{96500}{6.02 \times 10^{23}} \approx 1.6 \times 10^{-19} \text{ coulomb}$$

or $$1 \text{ coulomb} {}^{*}= 6.24 \times 10^{18} \text{ electrons}$$

The rate of flowing of electric charge through a conductor is called the electric current.

$$\text{Electric current} = \frac{\text{Electric charge}}{\text{Time}}$$

$$1 \text{ ampere} = \frac{1 \text{ coulomb}}{1 \text{ second}}$$

Volt is a unit of electrical potential difference. It is defined as potential energy per unit charge.

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}} = \frac{1 \text{ newton} \times 1 \text{ metre}}{1 \text{ ampere} \times 1 \text{ second}}$$

$$\begin{aligned} \text{Electrical energy} &= \text{Potential difference} \times \text{Quantity of charge} \\ &= V \times Q \\ &= V \times I \times t \qquad (I = \text{ampere}; t = \text{second}) \\ &= \text{watt-second} \end{aligned}$$

Faraday's Law for Gaseous Electrolytic Product

We know that, $$W = ZQ$$
$$= ZIt$$
$$W = \frac{ItE}{96500} \qquad \text{... (i)}$$

where, $$Z = E/96500$$

Equation (i) is used to calculate the mass of solid substance dissolved or deposited at an electrode.

For the gases, we use

$$V = \frac{ItV_e}{96500} \qquad \text{....(ii)}$$

***Coulomb:** It is the unit of electric charge. It is the amount of charge that moves past any given point in a circuit when a current of 1 ampere is supplied for one second.

1 coulomb = 1 ampere-second

It is also defined as the amount of charge which is required to deposit by electrolysis 0.001118 g of silver from a solution of silver nitrate.

An electron has 1.6×10^{-19} coulomb of negative charge. Hence, one coulomb of charge is carried by 6.24×10^{18} electrons. 1 mole of electrons carry a charge of 96500 coulomb. This quantity of charge is called **Faraday.**

Charge carried by 1 mole of electrons

$$\begin{aligned} &= (6.023 \times 10^{23})(1.6 \times 10^{-19}) \\ &= 96368 \text{ coulomb} \\ &\approx 96500 \text{ coulomb} \end{aligned}$$

where, V = Volume of gas evolved at STP at an electrode

V_e = Equivalent volume

= Volume of gas evolved at an electrode at STP by 1 faraday charge

Illustration

O_2: $M = 32$, $E = 8$

$$\begin{aligned} 32 \text{ g } O_2 &\equiv 22.4 \text{ L at STP} \\ 8 \text{ g } O_2 &\equiv 5.6 \text{ L at STP} \end{aligned} \qquad \begin{bmatrix} M = \text{Molecular mass} \\ E = \text{Equivalent mass} \end{bmatrix}$$

Thus, V_e of $O_2 = 5.6$ L

H_2: $M = 2$, $E = 1$

$$\begin{aligned} 2 \text{ g } H_2 &\equiv 22.4 \text{ L at STP} \\ 1 \text{ g } H_2 &\equiv 11.2 \text{ L at STP} \end{aligned}$$

Thus, V_e of $H_2 = 11.2$ L

Cl_2: $M = 71$, $E = 35.5$

$$\begin{aligned} 71 \text{ g } Cl_2 &\equiv 22.4 \text{ L at STP} \\ 35.5 \text{ g } Cl_2 &\equiv 11.2 \text{ L at STP} \end{aligned}$$

Thus, V_e of $Cl_2 = 11.2$ L

12.4 APPLICATIONS OF ELECTROLYSIS

The phenomenon of electrolysis has wide applications. The important ones are:

(1) Determination of equivalent masses of elements: According to second law of electrolysis when the same quantity of electric current is passed through solutions of salts of two different metals taken in two different cells, the amounts of the metals deposited on the cathodes of the two cells are proportional to their equivalent masses of the respective metals. If the amounts of the metals deposited on the cathodes be W_A and W_B respectively, then

$$\frac{W_A}{W_B} = \frac{\text{Equivalent mass of } A}{\text{Equivalent mass of } B}$$

Knowing the equivalent mass of one metal, the equivalent mass of the other metal can be calculated from the above relationship. The equivalent masses of those non-metals which are evolved at anodes can also be determined by this method.

(2) Electrometallurgy: The metals like sodium, potassium, magnesium, calcium, aluminium, etc., are obtained by electrolysis of fused electrolytes.

Fused electrolyte	Metal isolated
$NaCl + CaCl_2 + KF$	Na
$CaCl_2 + CaF_2$	Ca
Al_2O_3 + cryolite	Al
$MgCl_2$ (35%) + NaCl (50%) + $CaCl_2$ (15%)	Mg
NaOH	Na
$KCl + CaCl_2$	K

(3) Manufacture of non-metals: Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(4) Electro-refining of metals: The metals like copper, silver, gold, aluminium, tin, etc., are refined by electrolysis.

(5) Manufacture of compounds: Compounds like NaOH, KOH, Na_2CO_3, $KClO_3$, white lead, $KMnO_4$, etc., are manufactured by electrolysis.

(6) Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as **electroplating.**

The aims of electroplating are:

(i) To prevent the inferior metal from corrosion.

(ii) To make it more attractive in appearance.

The object to be electroplated is made the cathode and block of the metal to be deposited is made the anode in an electrolytic bath containing a solution of a salt of the anodic metal. On passing electric current in the cell, the metal of the anode dissolves out and is deposited on the cathode-article in the form of a thin film. The following are the requirements for fine coating:

(i) The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.

(ii) The surface of the article should be rough so that the metal deposited sticks permanently.

(iii) The concentration of the electrolyte should be so adjusted as to get smooth coating.

(iv) Current density must be the same throughout.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4$ + dilute H_2SO_4
With silver	Ag	Object	$KAg(CN)_2$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$KAu(CN)_2$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Thickness of Coated Layer

Let the dimensions of metal sheet to be coated be $(a \text{ cm} \times b \text{ cm})$.

Thickness of coated layer = c cm

Volume of coated layer = $(a \times b \times c)$ cm^3

Mass of the deposited substance = volume × density

$$= (a \times b \times c) \times d \text{ g}$$

$$\therefore \quad (a \times b \times c) \times d = \frac{I \times t \times E}{96500}$$

Using above relation we may calculate the thickness of coated layer.

Note: Sometimes radius of atom of deposited metal is given instead of density, *e.g.*,

Radius of silver atom $= 10^{-8}$ cm

Atomic mass of Ag $= 108$

Mass of single silver atom $= \dfrac{108}{6.023 \times 10^{23}}$ g

Volume of single atom $= \dfrac{4}{3} \times \pi R^3$

$$= \frac{4}{3} \times 3.14 \times (10^{-8})^3 \text{ cm}^3$$

$$\text{Density of Ag} = \frac{\text{Mass of single atom}}{\text{Volume of single atom}}$$

$$= \frac{108 / 6.023 \times 10^{23}}{\frac{4}{3} \times 3.14 \times (10^{-8})^3} = 42.82 \text{ g / cm}^3$$

Current Efficiency

Sometimes the ammeter shows false current due to mechanical fault. In this case,

$$\% \text{ current efficiency} = \frac{\text{Actual current}}{\text{Ammeter current}} \times 100$$

[**Note :** The conditions for the operating electrolytic cell are: $\Delta G > 0$ and $E < 0$]

SOME SOLVED EXAMPLES

Example 1. *Find the charge in coulomb on* 1 *g-ion of* N^{3-}.

Solution: Charge on one ion of N^{3-}

$$= 3 \times 1.6 \times 10^{-19} \text{ coulomb}$$

$$\text{one g-ion} = 6.02 \times 10^{23} \text{ ions}$$

Thus, charge on one g-ion of N^{3-}

$$= 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}$$

$$= 2.89 \times 10^5 \text{ coulomb}$$

Example 2. *How much charge is required to reduce* (a) 1 *mole of* Al^{3+} *to Al and* (b) 1 *mole of* MnO_4^- *to* Mn^{2+}*?*

Solution: (a) The reduction reaction is:

$$\underset{1\text{ mole}}{Al^{3+}} + \underset{3\text{ mole}}{3e^-} \longrightarrow Al$$

Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+}.

$$Q = 3 \times F$$

$$= 3 \times 96500 = 289500 \text{ coulomb}$$

(b) The reduction reaction is:

$$\underset{1\text{ mole}}{MnO_4^-} + 8H^+ + \underset{5\text{ mole}}{5e^-} \longrightarrow Mn^{2+} + 4H_2O$$

$$Q = 5 \times F$$

$$= 5 \times 96500 = 482500 \text{ coulomb}$$

Example 3. *How much electric charge is required to oxidise* (a) 1 *mole of* H_2O *to* O_2 *and* (b) 1 *mole of FeO to* Fe_2O_3*?*

Solution: (a) The oxidation reaction is:

$$\underset{1\text{ mole}}{H_2O} \longrightarrow \frac{1}{2} O_2 + 2H^+ + \underset{2\text{ mole}}{2e^-}$$

$$Q = 2 \times F$$

$$= 2 \times 96500 = 193000 \text{ coulomb}$$

(b) The oxidation reaction is:

$$FeO + \frac{1}{2} H_2O \longrightarrow \frac{1}{2} Fe_2O_3 + H^+ + e^-$$

$$Q = F = 96500 \text{ coulomb}$$

Example 4. *Exactly* 0.4 *faraday electric charge is passed through three electrolytic cells in series, first containing* $AgNO_3$, *second* $CuSO_4$ *and third* $FeCl_3$ *solution. How many grams of each metal will be deposited assuming only cathodic reaction in each cell?*

Solution: The cathodic reactions in the cells are respectively,

$$\underset{\substack{1\text{ mole}\\108\text{ g}}}{Ag^+} + \underset{\substack{1\text{ mole}\\1\text{ F}}}{e^-} \longrightarrow Ag$$

$$\underset{\substack{1\text{ mole}\\63.5\text{ g}}}{Cu^{2+}} + \underset{\substack{2\text{ mole}\\2\text{ F}}}{2e^-} \longrightarrow Cu$$

and

$$\underset{\substack{1\text{ mole}\\56\text{ g}}}{Fe^{3+}} + \underset{\substack{3\text{ mole}\\3\text{ F}}}{3e^-} \longrightarrow Fe$$

Hence, $\text{Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$

$$\text{Cu deposited} = \frac{63.5}{2} \times 0.4 = 12.7 \text{ g}$$

and $\text{Fe deposited} = \frac{56}{3} \times 0.4 = 7.47 \text{ g}$

Example 5. *An electric current of* 100 *ampere is passed through a molten liquid of sodium chloride for* 5 *hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.*

Solution: The reaction taking place at anode is:

$$\underset{71.0\text{ g}}{2Cl^-} \longrightarrow \underset{\substack{71.0\text{ g}\\1\text{ mole}}}{Cl_2} + \underset{2 \times 96500\text{ coulomb}}{2e^-}$$

$$Q = I \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60$ coulomb of electric charge

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

Volume of Cl_2 liberated at NTP $= 9.3264 \times 22.4 = 208.91$ L

Example 6. *A* 100 *watt,* 110 *volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What mass of cadmium will be deposited by the current flowing for* 10 *hours?*

Solution: We know that,

$$\text{Watt} = \text{ampere} \times \text{volt}$$

$$100 = \text{ampere} \times 110$$

$$\text{Ampere} = \frac{100}{110}$$

$$\text{Quantity of charge} = \text{ampere} \times \text{second}$$

$$= \frac{100}{110} \times 10 \times 60 \times 60 \text{ coulomb}$$

The cathodic reaction is:

$$\underset{112.4\text{ g}}{Cd^{2+}} + \underset{2 \times 96500\text{ C}}{2e^-} \longrightarrow Cd$$

Mass of cadmium deposited by passing $\frac{100}{110}\times 10\times 60\times 60$ coulomb charge

$$= \frac{112.4}{2\times 96500}\times\frac{100}{110}\times 10\times 60\times 60 = 19.0598 \text{ g}$$

Example 7. *In an electrolysis experiment, a current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold salt and the second cell contains copper sulphate solution. 9.85 g of gold was deposited in the first cell. If the oxidation number of gold is +3, find the amount of copper deposited on the cathode in the second cell. Also calculate the magnitude of the current in ampere.*

Solution: We know that,

$$\frac{\text{Mass of Au deposited}}{\text{Mass of Cu deposited}} = \frac{\text{Eq. mass of Au}}{\text{Eq. mass of Cu}}$$

$$\text{Eq. mass of Au} = \frac{197}{3}\ ;\ \text{Eq. mass of Cu} = \frac{63.5}{2}$$

Mass of copper deposited

$$= 9.85\times\frac{63.5}{2}\times\frac{3}{197}\text{ g} = 4.7625 \text{ g}$$

Let Z be the electrochemical equivalent of Cu.

$$E = Z\times 96500$$

or $$Z = \frac{E}{96500} = \frac{63.5}{2\times 96500}$$

Applying $$W = Z\times I\times t$$

$$t = 5 \text{ hour} = 5\times 3600 \text{ second}$$

$$4.7625 = \frac{63.5}{2\times 96500}\times I\times 5\times 3600$$

or $$I = \frac{4.7625\times 2\times 96500}{63.5\times 5\times 3600} = 0.804 \text{ ampere}$$

Example 8. *How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm^2 with 0.005 mm thick layer? Density of silver is 10.5 g/cm^3.*

Solution: Mass of silver to be deposited

= volume × density

= Area × thickness × density

Given: Area $= 80 \text{ cm}^2$, thickness $= 0.0005$ cm and density $= 10.5 \text{ g/cm}^3$

Mass of silver to be deposited = $80\times 0.0005\times 10.5$

= 0.42 g

Applying to silver $$E = Z\times 96500$$

$$Z = \frac{108}{96500}\text{ g}$$

Let the current be passed for t seconds.

We know that, $$W = Z\times I\times t$$

So, $$0.42 = \frac{108}{96500}\times 3\times t$$

or $$t = \frac{0.42\times 96500}{108\times 3} = 125.09 \text{ second}$$

Example 9. *What current strength in ampere will be required to liberate 10 g of chlorine from sodium chloride solution in one hour?*

Solution: Applying $E = Z\times 96500$ (E for chlorine = 35.5),

$$35.5 = Z\times 96500$$

or $$Z = \frac{35.5}{96500}\text{ g}$$

Now, applying the formula

$$W = Z\times I\times t$$

where, $W = 10$ g, $Z = \frac{35.5}{96500}$, $t = 60\times 60 = 3600$ second

$$I = \frac{10\times 96500}{35.5\times 3600} = 7.55 \text{ ampere}$$

Example 10. 0.2964 *g of copper was deposited on passage of a current of* 0.5 *ampere for* 30 *minutes through a solution of copper sulphate. Calculate the atomic mass of copper.* (1 *faraday* = 96500 *coulomb*)

Solution: Quantity of charge passed

$$= 0.5\times 30\times 60 = 900 \text{ coulomb}$$

900 coulomb deposit copper = 0.2964 g

$$96500 \text{ coulomb deposit copper} = \frac{0.2964}{900}\times 96500 = 31.78 \text{ g}$$

Thus, 31.78 is the equivalent mass of copper.

At. mass = Eq. mass × Valency

= 31.78 × 2 = 63.56

Example 11. 19 *g of molten* $SnCl_2$ *is electrolysed for some time using inert electrodes until* 0.119 *g of Sn is deposited at the cathode. No substance is lost during electrolysis. Find the ratio of the masses of* $SnCl_2 : SnCl_4$ *after electrolysis.*

Solution: The chemical reaction occurring during electrolysis is:

$$\underset{2\times 190\text{ g}}{2SnCl_2} \longrightarrow \underset{261\text{ g}}{SnCl_4} + \underset{119\text{ g}}{Sn}$$

119 g of Sn is deposited by the decomposition of 380 g of $SnCl_2$.

So, 0.119 g of Sn is deposited by the decomposition of

$$\frac{380}{119}\times 0.119 = 0.380 \text{ g of } SnCl_2$$

Remaining amount of $SnCl_2 = (19 - 0.380) = 18.62$ g

380 g of $SnCl_2$ produce = 261 g of $SnCl_4$

So, 0.380 g of $SnCl_2$ produce $= \frac{261}{380} \times 0.380 = 0.261$ g of $SnCl_4$

Thus, the ratio $SnCl_2 : SnCl_4 = \frac{18.62}{0.261}$, *i.e.*, 71.34 : 1

Example 12. *A current of 2.68 ampere is passed for one hour through an aqueous solution of copper sulphate using copper electrodes. Calculate the change in mass of cathode and that of the anode. (At. mass of copper = 63.5)*

Solution: The electrode reactions are:

$$\underset{1\text{ mole}}{Cu^{2+}} + \underset{2 \times 96500\text{ C}}{2e^-} \longrightarrow Cu \text{ (Cathode)}$$

$$Cu \longrightarrow Cu^{2+} + 2e^- \text{ (Anode)}$$

Thus, cathode increases in mass as copper is deposited on it and the anode decreases in mass as copper from it dissolves.

Charge passed through cell = 2.68 × 60 × 60 coulomb

$$\text{Copper deposited or dissolved} = \frac{63.5}{2 \times 96500} \times 2.68 \times 60 \times 60$$
$$= 3.174 \text{ g}$$

Increase in mass of cathode = Decrease in mass of anode
$$= 3.174 \text{ g}$$

Example 13. *An ammeter and a copper voltameter are connected in series through which a constant current flows. The ammeter shows 0.52 ampere. If 0.635 g of copper is deposited in one hour, what is the percentage error of the ammeter? (At. mass of copper = 63.5)*

Solution: The electrode reaction is:

$$\underset{1\text{ mole}}{Cu^{2+}} + \underset{2 \times 96500\text{ C}}{2e^-} \longrightarrow Cu$$

63.5 g of copper deposited by passing charge
$$= 2 \times 96500 \text{ coulomb}$$

0.635 g of copper deposited by passing charge
$$= \frac{2 \times 96500}{63.5} \times 0.653 \text{ coulomb}$$
$$= 2 \times 965 \text{ coulomb}$$
$$= 1930 \text{ coulomb}$$

We know that,

$$Q = I \times t$$
$$1930 = I \times 60 \times 60$$
$$I = \frac{1930}{3600} = 0.536 \text{ ampere}$$

$$\therefore \quad \text{Percentage error} = \frac{(0.536 - 0.52)}{0.536} \times 100 = 2.985$$

Example 14. *A current of 3.7 ampere is passed for 6 hours between platinum electrodes in 0.5 litre of a 2 M solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of electrolysis? What will be the molarity of the solution if nickel electrodes are used? (1F = 96500 coulomb; Ni = 58.7)*

Solution: The electrode reaction is:

$$\underset{1\text{ mole}}{Ni^{2+}} + \underset{2 \times 96500\text{ C}}{2e^-} \longrightarrow Ni$$

Quantity of electric charge passed
$$= 3.7 \times 6 \times 60 \times 60 \text{ coulomb} = 79920 \text{ coulomb}$$

Number of moles of $Ni(NO_3)_2$ decomposed or nickel deposited
$$= \frac{1}{2 \times 96500} \times 79920 = 0.4140$$

Number of moles of $Ni(NO_3)_2$ present before electrolysis
$$= 0.5 \times 2 = 1.0$$

Number of moles of $Ni(NO_3)_2$ present after electrolysis
$$= (1.0 - 0.4140) = 0.586$$

Since, 0.586 moles are present in 0.5 litre,
$$\text{Molarity of the solution} = 2 \times 0.586 = 1.72\, M$$

When nickel electrodes are used, anodic nickel will dissolve and get deposited at the cathode. The molarity of the solution will, thus, remain unaffected.

Example 15. *An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with volume of solution kept at 100 mL and the current at 1.2 amp. Calculate the gases evolved at NTP during the entire electrolysis.*

Solution: 0.4 g of $Cu^{2+} = \frac{0.4}{31.75} = 0.0126$ g - equivalent

At the same time, the oxygen deposited at anode
$$= 0.0126 \text{ g - equivalent}$$
$$= \frac{8}{32} \times 0.0126 = 0.00315 \text{ g-mole}$$

After the complete deposition of copper, the electrolysis will discharge hydrogen at cathode and oxygen at anode.

The amount of charge passed = 1.2 × 7 × 60 = 504 coulomb

$$\text{So, Oxygen liberated} = \frac{1}{96500} \times 504 = 0.00523 \text{ g - equivalent}$$
$$= \frac{8}{32} \times 0.00523 = 0.001307 \text{ g - mole}$$

Hydrogen liberated = 0.00523 g - equivalent
$$= \frac{1}{2} \times 0.00523 = 0.00261 \text{ g - mole}$$

Total gases evolved = (0.00315 + 0.001307 + 0.00261) g - mole
$$= 0.007067 \text{ g - mole}$$

Volume of gases evolved at NTP
$$= 22400 \times 0.007067 \text{ mL}$$
$$= 158.3 \text{ mL}$$

Example 16. *A current of 1.70 ampere is passed through 300 mL of 0.160 M solution of zinc sulphate for 230 seconds with a current efficiency of 90 per cent. Find out the molarity of Zn^{2+} ions after the deposition of zinc. Assume the volume of the solution to remain constant during electrolysis.* **(IIT 1991)**

Solution: Amount of charge passed = 1.70 × 230 coulomb

$$\text{Amount of actual charge passed} = \frac{90}{100} \times 1.70 \times 230$$
$$= 351.9 \text{ coulomb}$$

No. of moles of Zn deposited by passing 351.9 coulomb of charge

$$= \frac{1}{2 \times 96500} \times 351.9 = 0.000182$$

Molarity of Zn^{2+} ions after deposition of zinc

$$= \left[0.160 - \frac{0.000182 \times 1000}{300}\right] M$$
$$= 0.154\, M$$

Example 17. *Calculate the electricity that would be required to reduce* 12.3 *g of nitrobenzene to aniline, if the current efficiency for the process is* 50 *per cent. If the potential drop across the cell is* 3.0 *volt, how much energy will be consumed?* [AIPMT (Mains) 2008]

Solution: The reduction reaction is:

$$\underset{\substack{123\text{ g}\\1\text{ mole}}}{C_6H_5NO_2} + \underset{\substack{6\text{ g}\\3\text{ mole}}}{3H_2} \longrightarrow C_6H_5NH_2 + 2H_2O$$

Hydrogen required for reduction of $\frac{12.3}{123}$ or 0.1 mole of nitrobenzene $= 0.1 \times 3 = 0.3$ mole

Amount of charge required for liberation of 0.3 mole of hydrogen $= 2 \times 96500 \times 0.3 = 57900$ coulomb

Actual amount of charge required as efficiency is 50%

$$= 2 \times 57900 = 115800 \text{ coulomb}$$

$$\text{Energy consumed} = 115800 \times 3.0 = 347400 \text{ J}$$
$$= 347.4 \text{ kJ}$$

Example 18. *An aqueous solution of sodium chloride on electrolysis gives* $H_2(g)$, $Cl_2(g)$ *and NaOH according to the reaction:*

$$2Cl^-(aq.) + 2H_2O \longrightarrow 2OH^-(aq.) + H_2(g) + Cl_2(g)$$

A direct current of 25 *ampere with a current efficiency* 62% *is passed through* 20 *L of NaCl solution* (20% *by mass*). *Write down the reactions taking place at the anode and cathode. How long will it take to produce* 1 *kg of* Cl_2? *What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.* (IIT 1992)

Solution: Reactions at anode and cathode are:

$$2Cl^- \longrightarrow Cl_2 + 2e^- \quad \text{(at anode)}$$
$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad \text{(at cathode)}$$

$$1 \text{ kg of } Cl_2 = \frac{1000}{71.0} = 14.08 \text{ mole}$$

Charge to produce one mole of $Cl_2 = 2 \times 96500$ coulomb

Charge to produce 14.08 mole of $Cl_2 = 2 \times 96500 \times 14.08$ coulomb

$$\text{Effective current} = \frac{62}{100} \times 25.0 = 15.5 \text{ ampere}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{2 \times 96500 \times 14.08}{15.5}$$
$$= 175318.7 \text{ second} = 48.699 \text{ hour}$$

$$OH^- \text{ ions produced} = 2 \times \text{moles of } Cl_2$$
$$= 2 \times 14.08 = 28.16 \text{ mole}$$

$$\text{Molarity} = \frac{\text{Mole}}{\text{Volume}} = \frac{28.16}{20} = 1.408\, M$$

Example 19. *Chromium metal can be plated out from an acidic solution containing* CrO_3 *according to the following reaction:*

$$CrO_3 + 6H^+ + 6e^- \longrightarrow Cr + 3H_2O$$

Calculate the mass of chromium plated out by 24000 *coulomb. How long will it take to plate out* 1.5 *g of chromium using* 12.5 *ampere current?* (IIT 1993)

Solution: $CrO_3 + 6H^+ + \underset{6 \times 96500\text{ C}}{6e^-} \longrightarrow \underset{\substack{1\text{ mole}\\52\text{ g}}}{Cr} + 3H_2O$

Mass of chromium plated out by 24000 coulomb charge

$$= \frac{52}{6 \times 96500} \times 24000 = 2.155 \text{ g}$$

Charge required for plating out 1.5 g of chromium

$$= \frac{6 \times 96500}{52} \times 1.5 = 16701.92 \text{ coulomb}$$

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{16701.92}{12.5} = 1336.15 \text{ second}$$
$$= 22.27 \text{ minute}$$

Example 20. *After electrolysis of a sodium chloride solution with inert electrodes for a certain period of time,* 600 *mL of the solution was left which was found to be* 1 *N in NaOH. During the same period* 31.75 *g of copper was deposited in the copper voltameter in series with the electrolytic cell. Calculate the percentage theoretical yield of NaOH obtained.*

Solution: Equivalent mass of NaOH = 40

$$\text{Amount of NaOH formed} = \frac{40}{1000} \times 600 = 24 \text{ g}$$

31.75 g of Cu = 1 g-equivalent of Cu.

During the same period, 1 g-equivalent of NaOH should have been formed.

$$1 \text{ g-equivalent of NaOH} = 40 \text{ g}$$
$$\% \text{ yield} = \frac{24}{40} \times 100 = 60$$

Example 21. *Peroxy disulphuric acid* ($H_2S_2O_8$) *can be prepared by electrolytic oxidation of* H_2SO_4 *as:*

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$$

Oxygen and hydrogen are by products. In such an electrolysis 9.72 *litre of* H_2 *and* 2.35 *litre of* O_2 *were generated at NTP. What is the mass of peroxy disulphuric acid formed?*

Solution:

Anodic reaction: $2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$

$$2H_2O \longrightarrow 4H^+ + O_2 + 2e^-$$

Cathodic reaction: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

Total equivalent of $H_2S_2O_8$ + equivalent of oxygen

$$= \text{Equivalent of } H_2$$

$$9.72 \text{ litre } H_2 = \frac{9.72}{11.2} = 0.868 \text{ equivalent}$$

$$2.35 \text{ litre } O_2 = \frac{2.35}{5.6} = 0.42 \text{ equivalent}$$

$$\text{Equivalent of } H_2S_2O_8 = (0.868 - 0.420) = 0.448$$

$$\text{Mass of } H_2S_2O_8 = 0.448 \times \frac{194}{2} = 43.456 \text{ g}$$

Example 22. *Cadmium amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. Find how long a current of 5 ampere should be passed in order to prepare 12% Cd-Hg amalgam on a cathode of 2 g mercury. At. mass of Cd = 112.40.*

Solution: 2 g Hg require Cd to prepare 12% amalgam

$$= \frac{12}{88} \times 2 = 0.273 \text{ g}$$

$$\underset{\substack{1 \text{ mole} \\ 112.40 \text{ g}}}{Cd^{2+}} + \underset{2 \times 96500 \text{ C}}{2e^-} \longrightarrow Cd$$

Charge required to deposit 0.273 g of Cd

$$= \frac{2 \times 96500}{112.40} \times 0.273 \text{ coulomb}$$

$$\text{Charge} = \text{ampere} \times \text{second}$$

$$\text{Second} = \frac{2 \times 96500 \times 0.273}{112.40 \times 5} = 93.75$$

Example 23. *Assume that impure copper contains iron, gold and silver as impurities. After passing a current of 140 ampere for 482.5 second, the mass of anode decreased by 22.260 g and the cathode increased in mass by 22.011 g. Estimate the percentage of iron and copper originally present.*

Solution: The increase at the cathode is due to copper only. Hence, there is 22.011 g of copper and rest impurities of iron, gold and silver.

$$\text{Mass of impurities} = (22.260 - 22.011) = 0.249 \text{ g}$$

At anode, only copper and iron are oxidised; the gold and silver collect below anode in the form of anodic mud.

$$\underset{\text{(Copper and iron)}}{M} \longrightarrow M^{2+} + 2e^-$$

$$\text{No. of moles of metal oxidised} = \frac{140 \times 482.5}{2 \times 96500} = 0.35$$

$$\text{No. of moles of copper} = \frac{22.011}{63.5} = 0.3466$$

$$\text{No. of moles of iron} = (0.35 - 0.3466) = 0.0034$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. Amount of energy used in the passage of 1 amp current for 100 sec under a potential of 115 V is:
(a) 20 kJ (b) 11.5 kJ (c) 115 kJ (d) 0.115 kJ
[Ans. (b)]
[Hint: $Q = I \times t = 1 \times 100 = 100$ C
$$\text{Energy} = \text{charge} \times \text{potential} = 100 \times 115 = 11500 \text{ J} = 11.5 \text{ kJ}]$$

2. One litre of 1 M $CuSO_4$ solution is electrolysed. After passing $2F$ charge, the molarity of $CuSO_4$ will be:
(a) $M/2$ (b) $M/4$ (c) M (d) zero
[Ans. (d)]
[Hint: $2F$ charge will deposit 2 equivalent or 1 mole of copper
$$Cu^{2+} + 2e^- \longrightarrow Cu$$
Thus, all the copper from $CuSO_4$ solution will be deposited and molarity of remaining $CuSO_4$ solution will be zero.]

3. The time required to coat a metal surface of 80 cm^2 with 5×10^{-3} cm thick layer of silver (density 1.05 g/cm^3) by passing a current of 3 amp through silver nitrate solution is:
(a) 115 sec (b) 125 sec (c) 135 sec (d) 145 sec
[Ans. (b)]
[Hint:
Mass of silver in coated layer = volume × density
$$= (80 \times 5 \times 10^{-3}) \times 1.05 \text{ g} = 0.42 \text{ g}$$
$$\because \quad W = \frac{ItE}{96500}$$
$$\therefore \quad t = \frac{W \times 96500}{I \times E} = \frac{0.42 \times 96500}{3 \times 108} = 125.09 \text{ sec}]$$

4. 4.5 g of aluminium (At. mass = 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be: **[CBSE (PMT) 2005]**
(a) 44.8 L (b) 22.4 L (c) 11.2 L (d) 5.6 L
[Ans. (d)]
[Hint: Number of equivalents of aluminium deposited
$$= \frac{4.5}{9} = 0.5$$
∴ Number of equivalents of H_2 will also be 0.5.
Volume of H_2 gas at STP = Number of equivalents × Equivalent volume
$$= 0.5 \times 11.2 = 5.6 \text{ L}]$$

5. Cost of electricity for the production of x L H_2 at NTP at cathode is Rs x; then cost of production of x L O_2 at NTP at anode will be : (assume 1 mole of electrons as one unit of electricity)
(a) $2x$ (b) $4x$ (c) $16x$ (d) $32x$
[Ans. (a)]
[Hint: $\dfrac{\text{Volume of } H_2}{\text{Volume of } O_2} = \dfrac{\text{Equivalent volume of } H_2}{\text{Equivalent volume of } O_2}$

$$\frac{x}{\text{Volume of } O_2} = \frac{11.2}{5.6} = 2$$

$$\text{Volume of } O_2 = \frac{x}{2}$$

Thus, $\frac{x}{2}$ L O_2 requires Rs x for its production,

i.e., x L O_2 will require Rs $2x$ for the production.]

6. What current is to be passed for 0.25 sec for deposition of certain weight of metal which is equal to its electrochemical equivalent? **[AMU (Medical) 2006]**

(a) 4 A (b) 100 A (c) 200 A (d) 2 A

[**Ans.** (a)]

[**Hint:**
$$W = ZIt$$
$$\frac{W}{Z} = It$$
$$1 = It = I \times 0.25$$
$$I = 4 \text{ amp.}]$$

7. If the aqueous solutions of the following salts are electrolysed for 1 hour with 10 ampere current, which solution will deposit the maximum mass of the metal at cathode? The atomic weights are: Fe = 56, Zn = 65, Ag = 108, Hf = 178 and W = 184. **[PMT (Kerala) 2006]**

(a) $ZnSO_4$ (b) $FeCl_3$ (c) $HfCl_4$ (d) WCl_6

(e) $AgNO_3$

[**Ans.** (e)]

[**Hint:** Greater is the equivalent mass of the metal more will be the amount deposited at cathode.

Compound	**Equivalent mass of metals**
$ZnSO_4$	$65/2 = 32.5$
$FeCl_3$	$56/3 = 18.66$
$HfCl_4$	$178/4 = 44.5$
WCl_6	$184/6 = 30.66$
$AgNO_3$	$108/1 = 108$

∴ Maximum amount of silver will be deposited at cathode.]

8. When a quantity of electricity is passed through $CuSO_4$ solution, 0.16 g of copper gets deposited. If the same quantity of electricity is passed through acidulated water, then the volume of H_2 liberated at STP will be: (given atomic weight of Cu = 64) **(KCET 2006)**

(a) 4 cm^3 (b) 56 cm^3 (c) 604 cm^3 (d) 8 cm^3

[**Ans.** (b)]

[**Hint:** Number of equivalents of copper deposited $= \frac{0.16}{32} = 0.005$

Volume of H_2 gas at STP $= 11.2 \times 0.005$

$= 0.056 \text{ litre} = 56 \text{ cm}^3$]

9. Number of faraday's required to generate one gram atom of magnesium from molten $MgCl_2$ is: **[PMT (MP) 2007]**

(a) 1 (b) 2 (c) 3 (d) 4

[**Ans.** (b)]

[**Hint:** $Mg^{2+} + 2e^- \longrightarrow Mg$

1 mole of Mg atom requires 2 mole of electrons, *i.e.*, 2 faraday of charge.]

10. A direct current deposits 54 g of silver (Atomic mass = 108) during electrolysis. How much aluminium (Atomic mass = 27) would be deposited from aluminium chloride solution by the same amount of electricity? **[PMT (Kerala) 2008]**

(a) 4.5 g (b) 5.4g (c) 54g (d) 2.7g

(e) 27g

[**Ans.** (a)]

[**Hint:** Equivalent mass of silver = 108

Equivalent mass of aluminium in $(AlCl_3) = \frac{27}{3} = 9$

$$\frac{W_{Ag}}{W_{Al}} = \frac{E_{Ag}}{E_{Al}}$$
$$\frac{54}{W_{Al}} = \frac{108}{9}$$
$$W_{Al} = 4.5 \text{ g}]$$

SECTION II : CONDUCTANCE AND CONDUCTORS

12.5 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as theory of **electrolytic dissociation** or **ionic theory.** The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.

$$AB \longrightarrow A^+ + B^-$$

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$\underset{\text{Electrolyte}}{K_2SO_4} \longrightarrow \underbrace{2K^+ + SO_4^{2-}}_{\text{Ions}}$$

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

$$A^+B^- \longrightarrow A^+ + B^-$$

or
$$A^+B^- + aq. \longrightarrow A^+(aq.) + B^-(aq.)$$

(ii) The process of splitting of the molecules into ions of an electrolyte is called **ionisation.** The fraction of the total number of molecules present in solution as ions is known as **degree of ionisation** or **degree of dissociation.** It is denoted by 'α'

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$$

It has been observed that all electrolytes do not ionise to the same extent. Some are almost completely ionised while others are feebly ionised. The degree of ionisation depends on a number of factors (see 12.6).

(iii) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionised and non-ionised molecules, *i.e.*,

$$AB \rightleftharpoons A^+ + B^-$$

Applying the law of mass action to above equilibrium

$$\frac{[A^+][B^-]}{[AB]} = K$$

K is known as ionisation constant. The electrolytes having high value of K are termed **strong electrolytes** and those having low value of K as **weak electrolytes.**

(iv) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, *i.e.*, electrolysis occurs.

The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

(v) The electrolytic solution is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.

$AB \rightleftharpoons A^+ + B^-$ (Both ions are equal)

$NaCl \rightleftharpoons Na^+ + Cl^-$ (Both ions are equal)

$AB_2 \rightleftharpoons A^{2+} + 2B^-$ (Anions are double that of cations)

$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$ (Anions are double that of cations)

$A_2B \rightleftharpoons 2A^+ + B^{2-}$ (Cations are double that of anions)

$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$ (Cations are double that of anions)

(vi) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.

(vii) The ions act like molecules towards depressing the freezing point, elevating the boiling point, lowering the vapour pressure and establishing the osmotic pressure.

(viii) The conductivity of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.

Evidences in Favour of Ionic Theory

A large number of experimental observations are available which support Arrhenius theory. A few of them are given below:

(i) Ions present in solid electrolytes: X-ray diffraction studies have shown that electrolytes are composed of ions. For example, a crystal of NaCl does not contain NaCl units but Na^+ and Cl^- ions. Each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion in turn is surrounded by six Na^+ ions. The whole system is composed of equal number of Na^+ and Cl^- ions. The ionic compounds behave as good conductors in fused state. It can only be possible if ions are already present in ionic solids.

(ii) Ohm's law applicability: The electrolytic solutions like metallic conductors obey Ohm's law, *i.e.*, the strength of the current flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of the conductor. Mathematically,

$$I = E/R$$

This can only be possible if ions are already present in the solution and no part of the current is used in splitting up the molecules into ions. The current has only directive effect on the ions.

(iii) Ionic reactions: Evidence for the existence of ions in aqueous solutions of electrolytes is furnished by well known reactions in inorganic chemistry. A white precipitate of silver chloride is obtained whenever Ag^+ ions come in contact with chloride ions.

$$Ag^+ + NO_3^- + Na^+ + Cl^- \longrightarrow \underset{\text{ppt.}}{AgCl} + Na^+ + NO_3^-$$

But no precipitation occurs when $AgNO_3$ solution is added to CCl_4, $CHCl_3$ or C_2H_5Cl as these substances being non-electrolytes do not furnish Cl^- ions in solution.

An acid which gives all tests of H^+ ions in aqueous solution, does not give the same tests when dissolved in any organic solvent because no ionisation of the acid occurs in the organic solvent to furnish H^+ ions.

(iv) Heat of neutralization: When one gram-equivalent of a strong acid is neutralized by one gram-equivalent of a strong base, the heat evolved is always the same, *i.e.*, 13.7 kcal. This can be explained on the basis of Arrhenius theory that an acid furnished H^+ ions and base OH^- ions when dissolved in water and the process of neutralisation involves the common reaction.

$$H^+ + OH^- \rightleftharpoons H_2O + 13.7\,\text{kcal}$$

Thus, heat of neutralisation is actually the heat of formation of H_2O from H^+ and OH^- ions.

(v) Abnormal colligative properties: The abnormal behaviour towards colligative properties as observed in the case of electrolytes can be explained on the basis of ionic theory. When an electrolyte is dissolved in water, the number of particles in the solution is always more than the number of molecules actually dissolved due to ionisation. The van't Hoff factor,

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

is always more than one, *i.e.*, $i = 1 + (n-1)\alpha$ where, 'n' is the number of ions produced by the ionisation of one molecule of the electrolyte and 'α' is the degree of ionisation.

(vi) Colour of solutions: The colour of the electrolytes in solution, if any, is due to their ions. The $CuSO_4$ is blue in solution due to the presence of Cu^{2+} ions. Potassium permanganate ($KMnO_4$) is purple in solution due to the presence of MnO_4^- ions.

(vii) Explanation of some other phenomena: Ionic theory provides satisfactory explanations regarding various phenomena such as electrolysis, conductivity, salt hydrolysis, solubility product, etc.

Limitations of Arrhenius Theory

(i) Ostwald's dilution law which is based on Arrhenius theory is not applicable to strong electrolytes.

(ii) Strong electrolytes conduct electricity in fused state, *i. e.*, in absence of water. This is in contradiction of Arrhenius theory according to which the presence of solvent is a must for ionisation.

(iii) Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

12.6 FACTORS PERTAINING TO DEGREE OF IONISATION

The degree of ionisation of an electrolyte in solution depends upon the following factors:

(i) Nature of solute: When the ionisable parts of a molecule of a substance are held more by covalent bonding than by electrovalent bonding, less ions are furnished in solution. Such substances are termed weak electrolytes. H_2S, HCN, NH_4OH, CH_3COOH are examples of this class. NaCl, $Ba(NO_3)_2$, KOH, etc., are strong electrolytes, in which the transfer of electrons seems to be more or less complete, furnish ions immediately when dissolved. Strong electrolytes are almost completely ionised in solution.

(ii) Nature of solvent: The main function of the solvent is to weaken the electrostatic forces of attraction between the two ions and separate them. The force of attraction holding the ions together in any medium is expressed as:

$$F = \frac{1}{K}\frac{q_1 q_2}{r^2}$$

where, K is the dielectric constant of medium.

Any solvent which has high value of dielectric constant has the capacity of separating ions. Water is considered to be the best solvent as it has the highest dielectric constant. The dielectric constants of some of the solvents are given below at 25°C.

Water	Methyl alcohol	Ethyl alcohol	Acetone
81	35	27	21

(iii) Dilution: The extent of ionisation of an electrolyte is inversely proportional to the concentration of its solution. Thus, degree of ionisation increases with the increase of dilution of the solution, *i. e.*, decreasing the concentration of the solution.

(iv) Temperature: The degree of ionisation increases with the increase of temperature. This is due to the fact that at higher temperature molecular speed is increased which overcomes the forces of attraction between the ions.

12.7 ELECTROLYTIC CONDUCTANCE

The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance, *i. e.*,

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{R} \quad \text{... (i)}$$

It is expressed in the unit called reciprocal ohm (ohm^{-1} or mho) or siemens.

Specific Conductance or Conductivity

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a), *i. e.*,

$$R \propto \frac{l}{a} \text{ or } R = \rho\frac{l}{a} \quad \text{... (ii)}$$

where, ρ is called the specific resistance.

If $l = 1$ cm and $a = 1\text{ cm}^2$, then

$$R = \rho \quad \text{... (iii)}$$

The specific resistance is, thus, defined as the resistance of one centimetre cube of a conductor.

The reciprocal of specific resistance is termed the **specific conductance** or it is the conductance of one centimetre cube of a conductor.

It is denoted by the symbol κ. Thus,

$$\kappa = \frac{1}{\rho}, \quad \kappa = \text{kappa—The specific conductance} \quad \text{... (iv)}$$

Specific conductance is also called conductivity.

From eq. (ii), we have

$$\rho = \frac{a}{l}\cdot R \text{ or } \frac{1}{\rho} = \frac{l}{a}\cdot\frac{1}{R}$$

$$\kappa = \frac{l}{a}\times C \qquad \left(\frac{l}{a} = \text{cell constant}\right)$$

or Specific conductance = conductance × cell constant

In the case of electrolytic solutions, the specific conductance is defined as the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimetre apart as shown in Fig. 12.2.

The unit of specific conductance is $\text{ohm}^{-1}\text{ cm}^{-1}$.

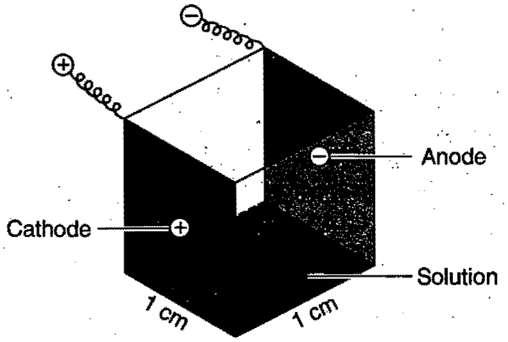


Fig. 12.2 Representation of specific conductance

Equivalent Conductance

One of the factors on which the conductance of an electrolytic solution depends, is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductances.

Equivalent conductance is defined as the conductance of all the ions produced by **one gram-equivalent** of an electrolyte in a given solution. It is denoted by Λ.

To understand the meaning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart, If 1 cm^3 (1 mL)

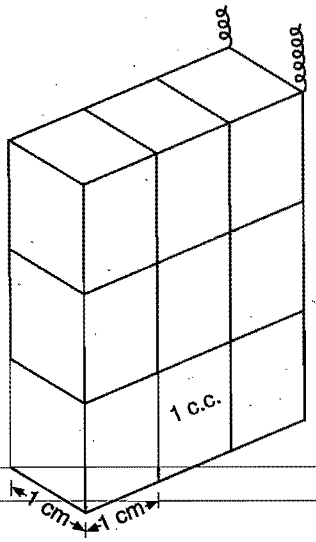


Fig. 12.3

solution containing 1 gram-equivalent of an electrolyte is placed in this container and conductance is measured.

According to definitions,

Conductance = Specific conductance (κ)

= Equivalent conductance (Λ)

If the solution is diluted to say ($9\,\text{cm}^3$) (9 mL), the conductance of the solution will be the same but specific conductance becomes 1/9 th as it contains nine cubes. The conductance is also equal to the equivalent conductance because the solution still has 1 g-equivalent of the electrolyte. This is shown in Fig. 12.3. Thus,

Equivalent conductance $(\Lambda) = 9 \times \kappa$

In general,

$$\Lambda = \kappa \times V \qquad \text{... (v)}$$

where, V is the volume in mL containing 1 g-equivalent of the electrolyte.

In case, if the concentration of the solution is c g-equivalent per litre, then the volume containing 1 g-equivalent of the electrolyte will be $1000/c$.

So, equivalent conductance,

$$\Lambda = \kappa \times \frac{1000}{c} \qquad \text{... (vi)}$$

$$\Lambda = \kappa \times \frac{1000}{N}$$

where, N = normality

The unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$.

Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionisation of **1 g-mole** of an electrolyte when present in V mL of solution. It is denoted by μ.

$$\text{Molar conductance } \mu = \kappa \times V \qquad \text{... (vii)}$$

where, V is the volume in mL containing 1 g-mole of the electrolyte. If c is the concentration of the solution in g-mole per litre, then

$$\mu = \kappa \times \frac{1000}{c}$$

Its unit is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}$$

where,
$$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Measurement of Conductance

It is now known to us that when the solution of an electrolyte is taken between two parallel electrodes of cross-sectional area 'a' and 'l' cm apart, then the specific conductance, κ, should be:

$$\kappa = \frac{l}{a} \cdot \frac{1}{R}$$

Thus, knowing the values of R, l and a, the specific conductance can be measured. The resistance of the solution between two parallel electrodes is determined by using Wheatstone bridge method. The diagram of the apparatus is shown in Fig. 12.4. AB is a uniform wire and X is a sliding contact which moves over it. C is the conductivity cell containing the solution of the electrolyte and S represents the source of alternating current. R is the resistance box and T is a headphone to detect the flow of current. A suitable resistance is taken out from the resistance box and the sliding contact X is moved on the wire to search a point of minimum sound in the headphone. At this point, the bridge is balanced.

$$\frac{\text{Resistance of solution}}{\text{Resistance from resistance box}} = \frac{\text{Resistance } XB}{\text{Resistance } XA} = \frac{\text{Length } XB}{\text{Length } XA}$$

Thus, resistance of solution can be determined. Reciprocal of this resistance gives the conductance of solution.

Direct current (DC) cannot be used because it produces two complications.

(i) Change in the concentration of the solution occurs due to electrolysis which will change the resistance.

(ii) Polarisation at the electrodes sets in which also changes the resistance.

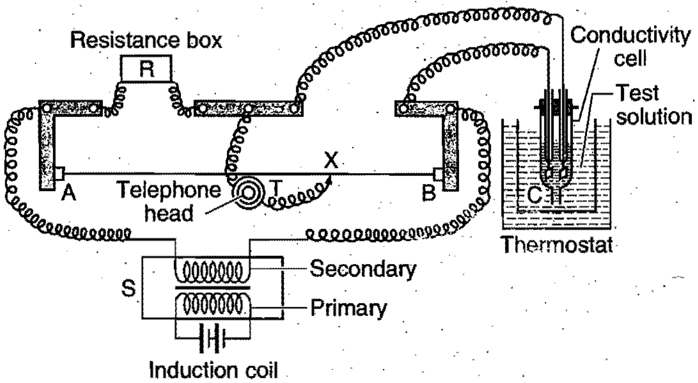


Fig. 12.4 Determination of conductivity

Thus, an alternating current (AC) is used to overcome the above complications.

The solution whose conductance is to be measured is taken in a special type of cell known as conductivity cell. Various types of cells are shown in Fig. 12.5. The electrodes consist of platinum discs coated with finely divided platinum black and welded to platinum wires fused in two glass tubes. The glass tubes contain mercury and are firmly fixed in the cover of cells. Contact with the platinum is made by dipping the copper wires of the circuit in the mercury contained in the tubes. As the conductivity changes with temperature, the cell is usually placed in a constant temperature bath during the experiment. Cells with long paths are used for concentrated solutions and cells with short paths and large electrodes are used for dilute solutions.

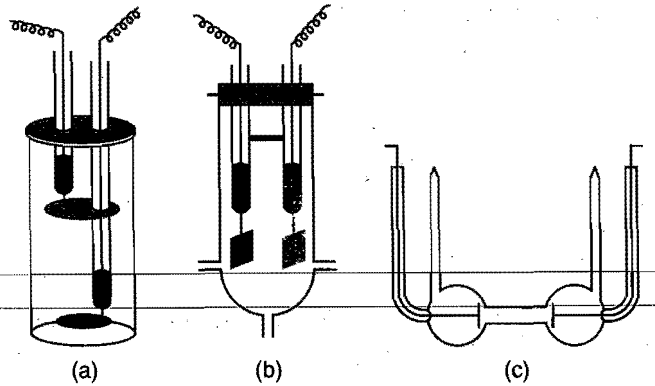

(a) (b) (c)

Fig. 12.5 Conductance cells

Cell Constant

Since, the electrodes are not exactly 1 unit apart and may not possess a surface area of 1 square unit, the measured resistance does not give the specific conductance of the solution. Actual measurements of l and a being inconvenient, an indirect method is employed to determine the value of $\frac{l}{a}$ which is a constant quantity for a particular cell and is known as cell constant. We know that,

$$\frac{\text{Specific conductance}}{\text{Conductance}} = \frac{l}{a} = \text{Cell constant}$$

The resistance of cell, *i.e.*, conductance is measured when filled with a standard solution (say $N/10\,\text{KCl}$ solution) at a given temperature. The standard values of specific conductance of KCl solutions of various concentrations at different temperatures are known. Thus, the cell constant is calculated by using the above equation. The same cell constant applies to a measurement with any other solution.

The determination of specific conductance of an electrolytic solution, thus, consists of two steps:

Step I: Determination of cell constant by using a standard KCl solution of known concentration in the conductivity cell.

Step II: Determination of resistance of the given solution using the same cell. The reciprocal of this gives the value of conductance.

Multiplication of conductance and cell constant gives the value of specific conductance of the solution.

In order to determine equivalent conductance or molar conductance, the concentration of the experimental solution should be known. In conductance measurements, the solutions are always prepared in **conductivity water** which has no conductance due to dissolved impurities. It is prepared by distilling a number of times the distilled water to which a little $KMnO_4$ and KOH have been added in a hard glass distillation assembly. Such water has very low conductance of the order of 4.3×10^{-8} ohm^{-1}. For ordinary purposes, double distilled water may be used.

Effect of Dilution on Equivalent Conductance

The value of equivalent conductance increases with dilution. This is due to the fact that degree of ionisation increases with dilution thereby increasing the total number of ions in solution. Solution which contains large number of ions compared to another solution of the same concentration at the same temperature has more conductance and is said to be **stronger electrolyte.** The one which has relatively small number of ions is called a **weak electrolyte.** The number of ions from an electrolyte depends on the degree of dissociation. The curve (Fig. 12.6) shows the variation of the equivalent conductance of some electrolytes with dilution. It shows that electrolytes behave in two ways on dilution:

(i) Electrolytes like KCl have high value of conductance even at low concentration and there is no rapid increase in their equivalent conductance on dilution. Such electrolytes are termed **strong electrolytes.** In the case of strong electrolytes, there is a tendency for equivalent conductance to approach a limiting value when the concentration approaches zero. When the whole of the electrolyte has ionised, further addition of the water does not bring any change in the value of equivalent conductance. This stage is called infinite dilution. The equivalent conductance has a limiting value at infinite dilution and is represented by Λ_∞.

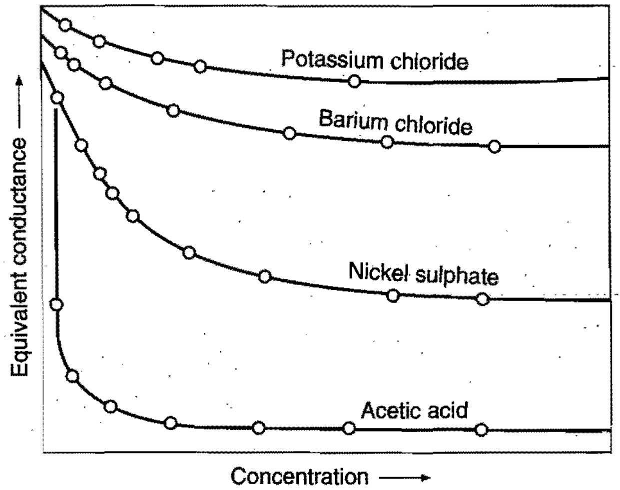


Fig. 12.6 Conductance curve

(ii) Electrolytes like acetic acid have a low value at high concentration and there is a rapid increase in the value of equivalent conductance with dilution. Such electrolytes are termed **weak electrolytes.** There is no indication that a limiting value of equivalent conductance can be attained even when the concentration approaches zero. Thus, graphically, Λ_∞ of weak electrolytes cannot be obtained.

It is thus concluded that equivalent conductance of electrolytes whether strong or weak increases with dilution and reaches to a maximum or limiting value which is termed Λ_∞ (equivalent conductance at infinite dilution). Λ_∞ in the case of strong electrolytes can be obtained by extrapolation of the graph of equivalent conductance to zero concentration but in the case of weak electrolytes it cannot be obtained accurately. An indirect method for obtaining Λ_∞ for weak electrolytes has been given by Kohlrausch.

12.8 KOHLRAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions", *i.e.*, anions and cations. Thus,

$$\Lambda_\infty = \lambda_a + \lambda_c$$

The λ_c and λ_a are called the ionic conductances of cation and anion at infinite dilution respectively. The ionic conductances are proportional to their ionic mobilities. Thus, at infinite dilution,

$$\lambda_c = ku_c$$

and $$\lambda_a = ku_a$$

where, u_c and u_a are ionic mobilities of cation and anion respectively at infinite dilution. The value of k is equal to 96500 C, *i.e.*, one Faraday.

Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte, it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionised at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{\text{Equivalent conductance at a given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

Calculation of absolute ionic mobilities: It has been experimentally found that ionic conductance is directly proportional to ionic mobilities.

$$\lambda_+ \propto u_+$$

$$\lambda_- \propto u_-$$

where, u_+ and u_- are ionic mobilities of cations and anions.

$$\lambda_+ = Fu_+ \quad \text{where, } F = \text{Faraday}$$

$$\lambda_- = Fu_- \qquad = 96500 \text{ coulomb}$$

$$\text{Ionic mobility} = \frac{\text{Ionic velocity}}{\text{Potential gradient}}$$

$$= \frac{\text{Ionic velocity (cm/sec)}}{\text{Potential difference (volt)/electrode separation}}$$

Relation between Equivalent and Molar Conductance at Infinite Dilution

$$\Lambda^\infty = \frac{1}{z^+}\lambda_+^\infty + \frac{1}{z^-}\lambda_-^\infty \quad \text{... (i)}$$

where, z^+ and z^- are corresponding charges on the ions,

e.g., $$\Lambda_{BaCl_2}^\infty = \frac{1}{2}\lambda_{Ba^{2+}}^\infty + \frac{1}{1}\lambda_{Cl^-}^\infty \quad \text{... (ii)}$$

$$\Lambda_{AlCl_3}^\infty = \frac{1}{3}\lambda_{Al^{3+}}^\infty + \frac{1}{1}\lambda_{Cl^-}^\infty \quad \text{... (iii)}$$

$$\Lambda_{Al_2(SO_4)_3}^\infty = \frac{1}{3}\lambda_{Al^{3+}}^\infty + \frac{1}{2}\lambda_{SO_4^{2-}}^\infty \quad \text{... (iv)}$$

Molar Conductance at Infinite Dilution

$$\Lambda_m^\infty \text{ or } \mu^\infty = \text{Molar conductance at infinite dilution}$$

$$= m\lambda_+^\infty + n\lambda_-^\infty$$

where, m and n are number of ions formed.

$$\mu_{Al_2(SO_4)_3}^\infty = 2\lambda_{Al^{3+}}^\infty + 3\lambda_{SO_4^{2-}}^\infty = 6\Lambda_{Al_2(SO_4)_3}^\infty$$

$$\mu_{BaCl_2} = \lambda_{Ba^{2+}}^\infty + 2\lambda_{Cl^-}^\infty = 2\Lambda_{BaCl_2}^\infty$$

12.9 THEORY OF WEAK ELECTROLYTES

(i) Weak electrolytes are not completely ionized when dissolved in a polar medium like water. There exists equilibrium between ions and unionised molecules.

$$AB \rightleftharpoons A^+ + B^-$$

(ii) Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

$$\begin{array}{lccc} & AB & \rightleftharpoons & A^+ \quad + \quad B^- \\ t=0 & C & & 0 \qquad 0 \\ t_{\text{eq.}} & C - C\alpha & & C\alpha \quad C\alpha \end{array}$$

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K = \frac{C\alpha^2}{1-\alpha} \quad \text{... (i)}$$

For weak electrolytes, $\alpha << 1$

$$\therefore \quad (1-\alpha) \approx 1$$

Thus, equation (i) can be written as:

$$K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} \quad \text{... (ii)}$$

From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionisation 'α' increases. At high degree of ionisation both equivalent and molar conductance increase.

(iii) Degree of ionisation can be calculated as:

$$\alpha = \frac{\Lambda_e^C}{\Lambda_e^\infty} = \frac{\Lambda_m^C}{\Lambda_m^\infty} \quad \text{... (iii)}$$

Λ_e^C, Λ_m^C = Equivalent and molar conductance at concentration 'C'

$\Lambda_e^\infty, \Lambda_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Substituting the values of 'α' from eq. (iii) in eq. (i), we get

$$K = \frac{C \times \left(\frac{\Lambda_e^C}{\Lambda_e^\infty}\right)^2}{1 - \frac{\Lambda_e^C}{\Lambda_e^\infty}} = \frac{C(\Lambda_e^C)^2}{\Lambda_e^\infty(\Lambda_e^\infty - \Lambda_e^C)} \quad \text{... (iv)}$$

Similarly,

$$K = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^C)} \quad \ldots \text{(v)}$$

Equations (iv) and (v) are called **Ostwald equations.**

Example 24. *1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.*

Solution: Given, $l = 2.1$ cm, $a = 4.2$ sq cm, $R = 50$ ohm

Specific conductance, $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

or $\kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$

Equivalent conductivity $= \kappa \times V$

V = the volume containing 1 g-equivalent = 1000 mL

So, Equivalent conductivity $= 0.01 \times 1000$

$= 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$

Example 25. *Specific conductance of a decinormal solution of KCl is 0.0112 ohm^{-1} cm^{-1}. The resistance of a cell containing the solution was found to be 56. What is the cell constant?*

Solution: We know that,

Sp. conductance = Cell constant × Conductance

or Cell constant $= \frac{\text{Sp. conductance}}{\text{Conductance}}$

= Sp. conductance × Resistance

$= 0.0112 \times 56 = 0.6272 \text{ cm}^{-1}$

Example 26. *The specific conductivity of 0.02 M KCl solution at 25° C is 2.768×10^{-3} ohm^{-1} cm^{-1}. The resistance of this solution at 25° C when measured with a particular cell was 250.2 ohm. The resistance of 0.01 M $CuSO_4$ solution at 25° C measured with the same cell was 8331 ohm. Calculate the molar conductivity of the copper sulphate solution.*

Solution: Cell constant $= \frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}}$

$= \frac{2.768 \times 10^{-3}}{1/250.2}$

$= 2.768 \times 10^{-3} \times 250.2$

For 0.01 M $CuSO_4$ solution

Sp. conductivity = Cell constant × Conductance

$= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$

Molar conductance = Sp. cond. $\times \frac{1000}{C}$

$$= \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} = 8.312 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example 27. *The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm^{-1} cm^2 eq^{-1}, respectively, at 25° C. Calculate the equivalent conductance of acetic acid at infinite dilution.*

Solution: According to Kohlrausch's law,

$$\Lambda_{\infty CH_3COONa} = \lambda_{CH_3COO^-} + \lambda_{Na^+} = 91.0 \quad \ldots \text{(i)}$$

$$\Lambda_{\infty HCl} = \lambda_{H^+} + \lambda_{Cl^-} = 426.16 \quad \ldots \text{(ii)}$$

$$\Lambda_{\infty NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} = 126.45 \quad \ldots \text{(iii)}$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\lambda_{CH_3COO^-} + \lambda_{Na^+} + \lambda_{H^+} + \lambda_{Cl^-} - \lambda_{Na^+} - \lambda_{Cl^-} = 91.0 + 426.16 - 126.45$$

$$\lambda_{CH_3COO^-} + \lambda_{H^+} = \Lambda_{\infty CH_3COOH} = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Example 28. *The equivalent conductivity of N/10 solution of acetic acid at 25° C is 14.3 ohm^{-1} cm^2 eq^{-1}. Calculate the degree of dissociation of CH_3COOH if $\Lambda_{\infty CH_3COOH}$ is 390.71.*

Solution:

$$\Lambda_{\infty CH_3COOH} = 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

$$\Lambda_{CH_3COOH} = 14.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

Degree of dissociation, $\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{14.3}{390.71}$

$= 0.0366$, *i.e.*, 3.66% dissociated

Example 29. *A decinormal solution of NaCl has specific conductivity equal to 0.0092. If ionic conductances of Na^+ and Cl^- ions at the same temperature are 43.0 and 65.0 ohm^{-1} respectively, calculate the degree of dissociation of NaCl solution.*

Solution: Equivalent conductance of N/10 NaCl solution

Λ_v = Sp. conductivity × dilution

$= 0.0092 \times 10{,}000 = 92 \text{ ohm}^{-1}$

$\Lambda_\infty = \lambda_{Na^+} + \lambda_{Cl^-}$

$= 43.0 + 65.0 = 108 \text{ ohm}^{-1}$

Degree of dissociation, $\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{92}{108} = 0.85$

Example 30. *At 18° C, the conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 mho respectively. If the equivalent conductivity of N/100 solution of NH_4OH is 9.93 mho, calculate the degree of dissociation of NH_4OH at this dilution.*

Solution: $\Lambda_{\infty NH_4Cl} = \lambda_{NH_4^+} + \lambda_{Cl^-} = 129.8 \quad \ldots \text{(i)}$

$$\Lambda_{\infty NaOH} = \lambda_{Na^+} + \lambda_{OH^-} = 217.4 \quad \ldots \text{(ii)}$$

$$\Lambda_{\infty NaCl} = \lambda_{Na^+} + \lambda_{Cl^-} = 108.9 \quad \ldots \text{(iii)}$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\lambda_{NH_4^+} + \lambda_{Cl^-} + \lambda_{Na^+} + \lambda_{OH^-} - \lambda_{Na^+} - \lambda_{Cl^-} =$$

$$\lambda_{NH_4^+} + \lambda_{OH^-} = 129.8 + 217.4 - 108.9$$

$$\Lambda_{\infty NH_4OH} = 238.3 \text{ mho}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{9.93}{238.3} = 0.04167$$

or 4.17 % dissociated.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

11. If the equivalent conductance of 1 M benzoic acid is 12.8 ohm^{-1} cm^2 eq^{-1} and if the conductance of benzoate ion and H^+ ions are 42 and 288.42 ohm^{-1} cm^2 eq^{-1} respectively, its degree of dissociation is: **(DPMT 2005)**

(a) 39% (b) 3.9%

(c) 0.35% (d) 0.039%

[Ans. (b)]

[Hint: $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{12.8}{(42 + 288.42)} = 0.0387$

Percentage dissociation $= 0.0387 \times 100 \approx 3.9\%$]

12. Equivalent conductances of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 ohm^{-1} cm^2 eq^{-1} respectively. The equivalent conductance of CH_3COOH at infinite dilution would be:

(a) 101.38 ohm^{-1} cm^2 eq^{-1} (b) 253.62 ohm^{-1} cm^2 eq^{-1}

(c) 390.71 ohm^{-1} cm^2 eq^{-1} (d) 678.90 ohm^{-1} cm^2 eq^{-1}

[Ans. (c)]

[Hint: $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$

$= 91 + 426.16 - 126.45$

$= 390.71$ ohm^{-1} cm^2 eq^{-1}]

13. The specific conductance of saturated solution of AgCl is found to be 1.86×10^{-6} ohm^{-1} cm^{-1} and that of water is 6×10^{-8} ohm^{-1} cm^{-1}. The solubility of AgCl is ....

Given, $\Lambda^\circ_{AgCl} = 137.2$ ohm^{-1} cm^2 eq^{-1}

(a) $1.7 \times 10^{-3}\, M$ (b) $1.3 \times 10^{-5}\, M$

(c) $1.3 \times 10^{-4}\, M$ (d) $1.3 \times 10^{-6}\, M$

[Ans. (b)]

[Hint: $\kappa_{AgCl} = \kappa_{AgCl\,(Solution)} - \kappa_{H_2O}$

$= 1.86 \times 10^{-6} - 6 \times 10^{-8} = 1.8 \times 10^{-6}$ ohm^{-1} cm^{-1}

$$\Lambda^\circ_{AgCl} = \kappa \times \frac{1000}{S}$$

$$\therefore \quad S = \frac{\kappa \times 1000}{\Lambda^\circ_{AgCl}} = \frac{1.8 \times 10^{-6} \times 1000}{137.2} = 1.31 \times 10^{-5}\, M]$$

14. The specific conductivity of $N/10$ KCl solution at 20°C is 0.0212 ohm^{-1} cm^{-1} and the resistance of the cell containing this solution at 20°C is 55 ohm. The cell constant is:

(a) 4.616 cm^{-1} (b) 1.166 cm^{-1}

(c) 2.173 cm^{-1} (d) 3.324 cm^{-1}

[Ans. (b)]

[Hint: $\kappa = C \times \frac{l}{A}$

$\frac{l}{A} = \kappa \times \frac{1}{C} = \kappa \times R = 0.0212 \times 55 = 1.166$ cm^{-1}]

15. The resistance of 1 N solution of CH_3COOH is 250 ohm; when measured in a cell of cell constant 1.15 cm^{-1}. The equivalent conductance will be:

(a) 4.6 ohm^{-1} cm^2 eq^{-1} (b) 9.2 ohm^{-1} cm^2 eq^{-1}

(c) 18.4 ohm^{-1} cm^2 eq^{-1} (d) 0.023 ohm^{-1} cm^2 eq^{-1}

[Ans. (a)]

[Hint: $\kappa = C \times \frac{l}{A} = \frac{1}{250} \times 1.15 = 4.6 \times 10^{-3}$ ohm^{-1} cm^{-1}

$\Lambda_e = \kappa \times \frac{1000}{N} = 4.6 \times 10^{-3} \times \frac{1000}{1} = 4.6$ ohm^{-1} cm^2 eq^{-1}]

16. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 ohm. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 ohm. The molar conductivity of 0.02 M solution of the electrolyte will be: **(AIEEE 2006)**

(a) 124×10^{-4} S m^2 mol^{-1} (b) 1240×10^{-4} S m^2 mol^{-1}

(c) 1.24×10^{-4} S m^2 mol^{-1} (d) 12.4×10^{-4} S m^2 mol^{-1}

[Ans. (a)]

[Hint:

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

$$1.29 = \frac{1}{100} \times \frac{l}{A}$$

$$\frac{l}{A} = 129 \text{ m}^{-1}$$

$$\Lambda_m = \kappa \times \frac{1000}{M}$$

$$= \left(\frac{1}{R} \times \frac{l}{A}\right) \times \frac{1000}{M}$$

$$= \left(\frac{1}{520} \times 129\right) \times \frac{1000}{0.02} \times 10^{-6}$$

$$= 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}]$$

17. If the molar conductance values of Ca^{2+} and Cl^- at infinite dilution are respectively 118.88×10^{-4} m^2 mho mol^{-1} and 77.33×10^{-4} m^2 mho mol^{-1} then that of $CaCl_2$ is: (in m^2 mho mol^{-1}) **(VITEEE 2007)**

(a) 118.88×10^{-4} (b) 154.66×10^{-4}

(c) 273.54×10^{-4} (d) 196.21×10^{-4}

[Ans. (c)]

[Hint: $\Lambda^\circ_m\ CaCl_2 = \lambda^\circ Ca^{2+} + 2\lambda^\circ Cl^-$

$= (118.88 \times 10^{-4}) + 2(77.33 \times 10^{-4})$

$= 273.54 \times 10^{-4}$ m^2 mho mol^{-1}]

18. The molar conductivities of KCl, NaCl and KNO_3 are 152, 128 and 111 S cm^2 mol^{-1} respectively. What is the molar conductivity of $NaNO_3$? **(VITEEE 2008)**

(a) 101 S cm^2 mol^{-1} (b) 87 S cm^2 mol^{-1}

(c) – 101 S cm^2 mol^{-1} (d) – 391 S cm^2 mol^{-1}

[Ans. (b)]

[Hint: $\Lambda^\circ_{NaNO_3} = \Lambda^\circ_{NaCl} + \Lambda^\circ_{KNO_3} - \Lambda^\circ_{KCl}$

$= 128 + 111 - 152 = 87$ S cm^2 mol^{-1}]

SECTION III : ELECTROCHEMICAL CELL

12.10 ELECTROCHEMICAL CELL

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

(a) Electrolytic cell
(b) Galvanic or voltaic cell

(a) Electrolytic Cell

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

(b) Galvanic or Voltaic Cell

It is a device in which a redox reaction is used to convert chemical energy into electrical energy, *i.e.*, electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called **half-cells.** When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.

12.11 DANIELL CELL

It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current (Fig. 12.7). It consists of two half-cells. The half-cell on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution. The half-cell on the right consists of copper metal electrode in a solution of $CuSO_4$. The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.

When the zinc and copper electrodes are joined by a wire, the following observations are made:

(i) There is a flow of electric current through the external circuit.
(ii) The zinc rod loses its mass while the copper rod gains in mass.
(iii) The concentration of $ZnSO_4$ solution increases while the concentration of copper sulphate solution decreases.
(iv) The solutions in both the compartments remain electrically neutral.

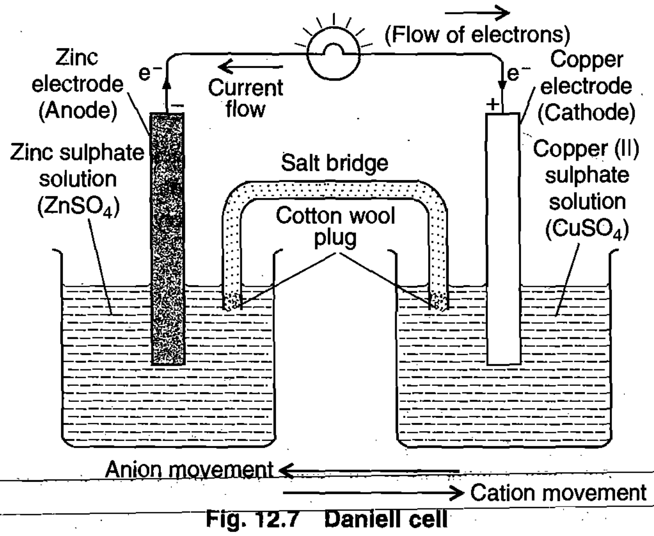


Fig. 12.7 Daniell cell

During the passage of electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidised to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

$$Zn(s) + Cu^{2+}(aq.) \longrightarrow Cu(s) + Zn^{2+}(aq.)$$

Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at copper electrode, reduction takes place; it is the cathode of the cell and is positively charged.

Thus, the above points can be summed up as:

(i) Voltaic or Galvanic cell consists of two **half-cells.** The reactions occurring in half-cells are called **half-cell reactions.** The half-cell in which oxidation occurs is called **oxidation half-cell** and the reaction taking place in it is called **oxidation half-cell reaction.** Similarly, the half-cell in which reduction occurs is called **reduction half-cell** and the reaction taking place in it is called **reduction half-cell reaction.**
(ii) The electrode where oxidation occurs is called anode and the electrode where reduction occurs is termed cathode.
(iii) Electrons flow from anode to cathode in the external circuit.
(iv) Overall ion movement during the operation of the galvanic cell shows that negative ions (anions) move away from cathode where they are present in excess, towards anode, where they are needed to balance the charge of the positive ions (cations) formed. Similarly, cations move away from the anode where they are in excess, towards the cathode, where they balance the anions left in excess.

Example : An $Au(NO_3)_3$ solution containing a gold electrode is connected by means of salt bridge to a $PbCl_2$ solution containing lead electrode. The cell can be correctly represented as,

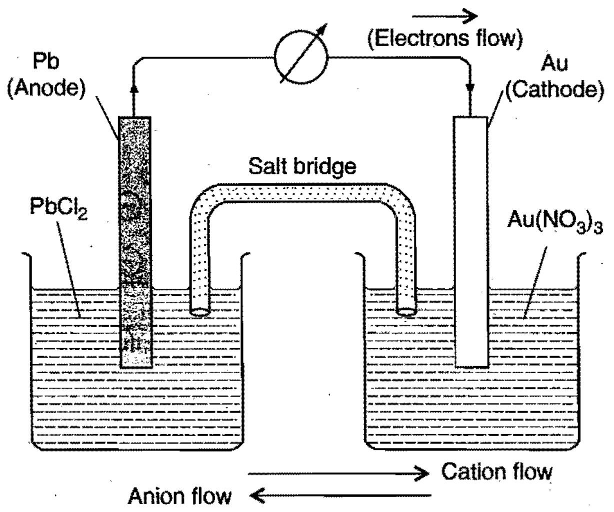


Fig. 12.8

(v) Chemical energy is converted into electrical energy.

(vi) The net reaction is the sum of two half-cell reactions. The reactions in Daniell cell can be represented as:

Oxidation half reaction, $\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq.) + 2e^-$

Reduction half reaction, $\mathrm{Cu}^{2+}(aq.) + 2e^- \longrightarrow \mathrm{Cu}(s)$

Net reaction $\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq.) \longrightarrow \mathrm{Zn}^{2+}(aq.) + \mathrm{Cu}(s)$

Electrode Signs

The signs of the anode and cathode in the voltaic or galvanic cells are opposite to those in the electrolytic cells (Fig. 12.9).

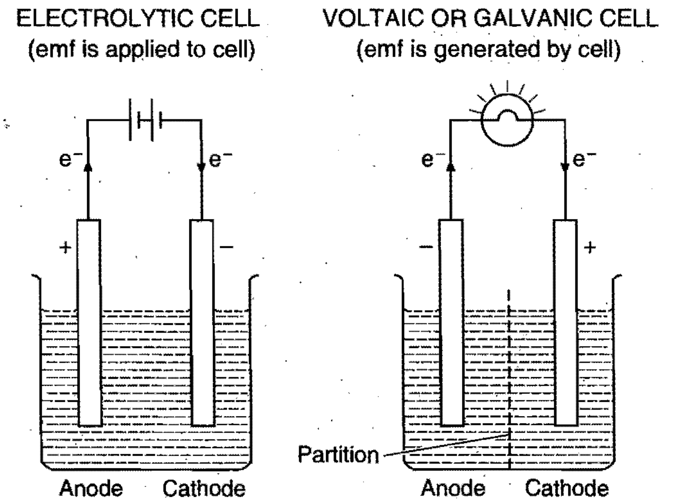


Fig. 12.9

	Electrolytic cell		**Voltaic or Galvanic cell**	
	Anode	**Cathode**	**Anode**	**Cathode**
Sign	+	−	−	+
Electron flow	out	in	out	in
Half reaction	oxidation	reduction	oxidation	reduction

Difference in electrolytic cell and galvanic cell

	Electrolytic cell	**Galvanic cell**
1.	Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
2.	Anode is positive electrode. Cathode is negative electrode.	Anode is negative electrode. Cathode is positive electrode.
3.	Ions are discharged on both the electrodes.	Ions are discharged only on the cathode.
4.	If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
5.	Both the electrodes can be fitted in the same compartment.	The electrodes are fitted in different compartments.

12.12 SALT BRIDGE AND ITS SIGNIFICANCE

Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells. Generally salts like KCl, KNO_3, NH_4NO_3, etc., are used. For the preparation of salt bridge, gelatin or agar-agar is dissolved in a hot concentrated aqueous solution of an inert electrolyte and the solution thus formed is filled in the U-tube. On cooling the solution sets in the form of a gel in the U-tube. The ends of the U-tube are plugged with cotton wool as to minimise diffusion effects. This is used as a salt bridge.

Significance of salt bridge: The following are the functions of the salt bridge:

(i) It connects the solutions of two half-cells and completes the cell circuit.

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.

(iii) It keeps the solutions in two half-cells electrically neutral. In anodic half-cell, positive ions pass into the solution and there shall be accumulation of extra positive charge in the solution around the anode which will prevent the flow of electrons from anode. This does not happen because negative ions are provided by salt bridge. Similarly, in cathodic half-cell, negative ions will accumulate around cathode due to deposition of positive ions by reduction. To neutralise these negative ions, sufficient number of positive ions are provided by salt bridge. Thus, salt bridge maintains electrical neutrality.

(iv) It prevents liquid-liquid junction-potential, *i.e.*, the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \parallel \mathrm{Cu}^{2+} \mid \mathrm{Cu}$$

Salt bridge can be replaced by a porous partition which allows the migration of ions without allowing the solutions to intermix.

12.13 REPRESENTATION OF AN ELECTROCHEMICAL CELL (Galvanic Cell)

The following universally accepted conventions are followed in representing an electrochemical cell:

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \text{ or } \mathrm{Zn};\mathrm{Zn}^{2+}$$

The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example,

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(1\,M) \text{ or } \mathrm{Zn} \mid \mathrm{Zn}^{2+}(0.1\,M)$$

(iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,

$$\mathrm{Cu}^{2+} \mid \mathrm{Cu} \text{ or } \mathrm{Cu}^{2+};\mathrm{Cu} \text{ or } \mathrm{Cu}^{2+}(1\,M) \mid \mathrm{Cu}$$

(iv) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

(v) Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:

$$\overset{-}{\mathrm{Zn}} \mid \mathrm{ZnSO_4}(aq.) \parallel \mathrm{CuSO_4}(aq.) \mid \overset{+}{\mathrm{Cu}}$$

Anode Salt bridge Cathode
Oxidation half-cell Reduction half-cell

or $$\mathrm{Zn} \mid \mathrm{Zn}^{2+} \parallel \mathrm{Cu}^{2+} \mid \mathrm{Cu}$$

or $$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(1\,M) \parallel \mathrm{Cu}^{2+}(1\,M) \mid \mathrm{Cu}$$

12.14 ELECTRODE POTENTIAL

When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential.** For example, when a plate of zinc is placed in a solution having Zn^{2+} ions, it becomes negatively charged with respect to solution and thus a potential difference is set-up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having Cu^{2+} ions, it becomes positively charged with respect to solution. A potential difference is set-up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer at the interface of metal and the solution. The development of negative charge (as on zinc plate) or positive charge (as on copper plate) can be explained in the following manner. When a metal rod is dipped in its salt solution, two changes occur:

$$M(s) \longrightarrow M^{n+}(aq.) + ne^-$$

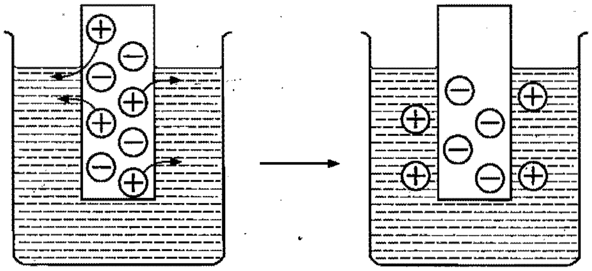


Fig. 12.10 (a)

$$M^{n+}(aq.) + ne^- \longrightarrow M(s)$$

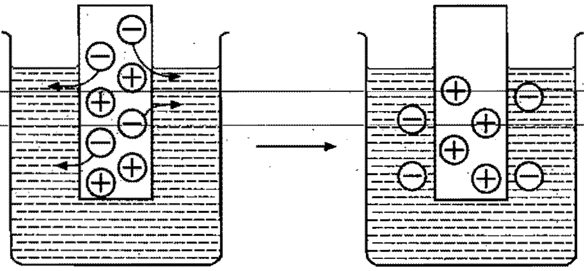


Fig. 12.10 (b)

(a) Oxidation : Metal ions pass from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.

(b) Reduction : Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode.

(i) The conversion of metal atoms into metal ions by the attractive force of polar water molecules.

$$M \longrightarrow M^{n+} + ne^-$$

The metal ions go into the solution and the electrons remain on the metal making it negatively charged. The tendency of the metal to change into ions is known as **electrolytic solution pressure.**

(ii) Metal ions start depositing on the metal surface leading to a positive charge on the metal.

$$M^{n+} + ne^- \longrightarrow M$$

This tendency of the ions is termed **osmotic pressure.**

In the beginning, both these changes occur with different speeds but soon an equilibrium is established.

$$M \rightleftharpoons M^{n+} + ne^-$$

In practice, one effect is greater than the other, if first effect is greater than the second, the metal acquires a negative charge with respect to solution and if the second is greater than the first, it acquires positive charge with respect to solution, thus in both the cases a potential difference is set-up.

The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons, *i.e.*, it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons). The magnitude of potential depends on the following factors:

(i) Nature of the electrode,
(ii) Concentration of the ions in solution,
(iii) Temperature.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

(i) Oxidation potential: When electrode is negatively charged with respect to solution, *i.e.*, it acts as anode. Oxidation occurs.

$$M \longrightarrow M^{n+} + ne^-$$

(ii) Reduction potential: When electrode is positively charged with respect to solution, *i.e.*, it acts as cathode. Reduction occurs.

$$M^{n+} + ne^- \longrightarrow M$$

It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode.** The emf of the resulting cell is measured experimentally. The emf of the cell is equal to the sum of potentials on the two electrodes.

Emf of the cell = $E_{\text{Anode}} + E_{\text{Cathode}}$
= Oxidation potential of anode
+ Reduction potential of cathode

Knowing the value of reference electrode, the value of other electrode can be determined.

12.15 STANDARD ELECTRODE POTENTIAL

In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 *M*) at 25° C (298 K) is called **standard electrode potential.**

According to the IUPAC convention, the reduction potential alone can be called as the electrode potential ($E°$), *i.e.*, the given value of electrode potential can be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential. Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed. Thus,

Standard reduction potential = – Standard oxidation potential

or Standard oxidation potential = – Standard reduction potential

12.16 REFERENCE ELECTRODE (Standard Hydrogen Electrode, SHE or NHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury. The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ion concentration 1 *M*. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. This gives an equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

The temperature of the cell is maintained at 25° C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000... volt.

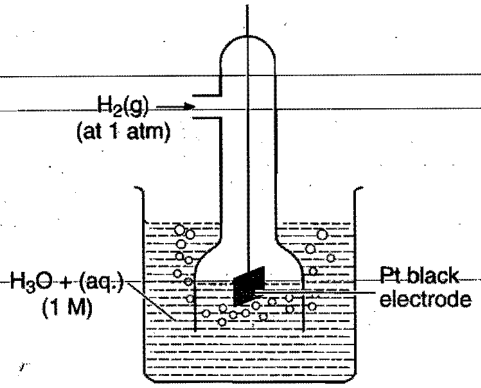


Fig. 12.11 Hydrogen electrode

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	**Electrode potential**
$H_2 \longrightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \longrightarrow H_2$	0.0 V (Cathode)

12.17 MEASUREMENT OF ELECTRODE POTENTIAL

The measurement of electrode potential of a given electrode is made by constituting a voltaic cell, *i.e.*, by connecting it with a standard hydrogen electrode (SHE) through a salt bridge. 1 *M* solution is used in hydrogen half-cell and the temperature is maintained at 25° C. The emf of the cell is measured either by a calibrated potentiometer or by a high resistance voltmeter, *i.e.*, a valve voltmeter. The reading of the voltmeter gives the electrode potential of the electrode in question with respect to the hydrogen electrode. The standard electrode potential of a metal may be determined as it is the potential difference in volt developed in a cell consisting of two electrodes: the pure metal is in contact with a molar solution of one of its ions and the standard hydrogen electrode.

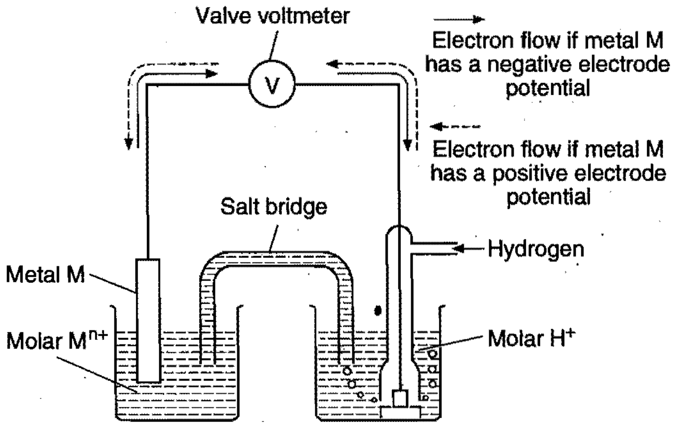


Fig. 12.12

(i) Determination of standard electrode potential of Zn / Zn^{2+} electrode: A zinc rod is dipped in 1 *M* zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge. Both the electrodes are connected with a voltmeter as shown in Fig. 12.13. The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal electrode or the electrons are moving from zinc rod to hydrogen electrode. The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

$$\underset{\text{Anode } (-)}{\underline{Zn \mid Zn^{2+}(aq.)}} \,||\, \underset{\text{Cathode } (+)}{\underline{2H^+(aq.) \mid H_2(g)}}$$

$$\underset{\text{(Oxidation)}}{Zn \longrightarrow Zn^{2+} + 2e^-} \;;\; \underset{\text{(Reduction)}}{2H^+ + 2e^- \longrightarrow H_2\uparrow}$$

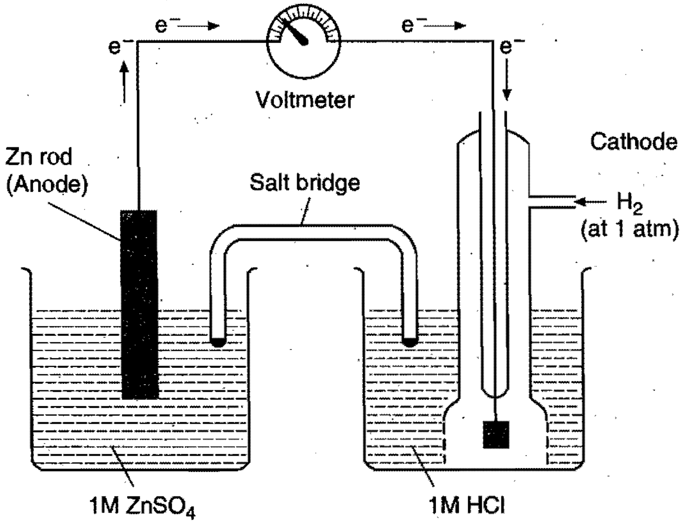


Fig. 12.13 $Zn–H_2$ electrochemical cell

The emf of the cell is 0.76 volt

$$E^\circ_{Cell} = E^\circ_{Anode} + E^\circ_{Cathode}$$

$$0.76 = E^\circ_{Anode} + 0 \text{ or } E^\circ_{Anode} = +0.76\text{ V}$$

As the reaction on the anode is oxidation, *i.e.*,

$$Zn \longrightarrow Zn^{2+} + 2e,$$

E°_{Anode} is the standard oxidation potential of zinc. This potential is given the positive sign.

$$E^\circ_{ox}(Zn / Zn^{2+}) = +0.76\text{ volt}$$

So, standard reduction potential of Zn, *i.e.*, $E^\circ(Zn^{2+} / Zn)$

$$= -E^\circ_{ox} = -(+0.76)$$

$$= -0.76\text{ volt}$$

The emf of such a cell gives the positive value of standard oxidation potential of metal *M*. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.

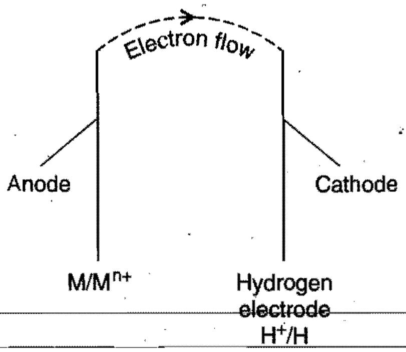


Fig. 12.14

(ii) Determination of standard electrode potential of Cu^{2+} / Cu, electrode: A copper rod is dipped in 1 *M* solution of $CuSO_4$. It is combined with hydrogen electrode through a salt bridge. Both the electrodes are joined through a voltmeter. The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, *i.e.*, the electrons are moving from hydrogen electrode to copper electrode. The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as

$$\underset{\text{Anode } (-)}{H_2(g) \mid 2H^+(aq.)} \,||\, \underset{\text{Cathode } (+)}{Cu^{2+}(aq.) \mid Cu}$$

$$\underset{\text{Oxidation}}{H_2 \longrightarrow 2H^+ + 2e^-} \;;\; \underset{\text{Reduction}}{Cu^{2+} + 2e^- \longrightarrow Cu}$$

The emf of the cell is 0.34 volt.

$$E^\circ_{Cell} = E^\circ_{Anode} + E^\circ_{Cathode}$$

$$0.34 = 0 + E^\circ_{Cathode}$$

Since, the reaction on the cathode is reduction, *i.e.*, $Cu^{2+} + 2e^- \longrightarrow Cu$, $E^\circ_{Cathode}$ is the standard reduction potential of copper. This is given the + ve sign.

E°, *i.e.*, standard reduction potential of $Cu^{2+}/Cu = 0.34$ volt

So, E°_{ox} (standard oxidation potential of copper) = – 0.34 volt

The emf of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

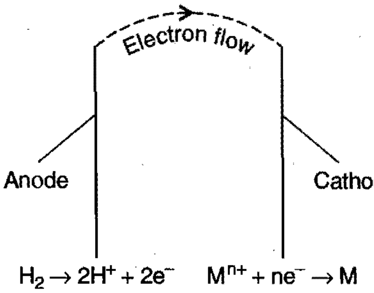


Fig. 12.15

It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode in question with a standard hydrogen electrode and measuring the emf of the cell constituted.

12.18 EMF OF A GALVANIC CELL

Every galvanic or voltaic cell is made up of two half-cells, the oxidation half-cell (anode) and the reduction half-cell (cathode). The potentials of these half-cells are always different. On account of this difference in electrode potentials, the electric current moves from the electrode at higher potential to the electrode at lower potential, *i.e.*, from cathode to anode. The direction of the flow of electrons is from anode to cathode.

$$\text{Anode} \underset{\text{Flow of current}}{\overset{\text{Flow of electrons}}{\rightleftarrows}} \text{Cathode}$$

The difference in potentials of the two half-cells is known as the electromotive force **(emf) of the cell or cell potential.**

The emf of the cell or cell potential can be calculated from the values of electrode potentials of the two half-cells constituting the cell. The following three methods are in use:

(i) When oxidation potential of anode and reduction potential of cathode are taken into account:

$$E^\circ_{\text{cell}} = \text{Oxidation potential of anode} + \text{Reduction potential of cathode}$$
$$= E^\circ_{\text{ox}}\ (\text{anode}) + E^\circ_{\text{red}}\ (\text{cathode})$$

(ii) When reduction potentials of both electrodes are taken into account:

$$E^\circ_{\text{cell}} = \text{Standard Reduction potential of cathode} - \text{Standard Reduction potential of anode}$$
$$= E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$
$$= E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

(iii) When oxidation potentials of both electrodes are taken into account:

$$E^\circ_{\text{cell}} = \text{Oxidation potential of anode} - \text{Oxidation potential of cathode}$$
$$= E^\circ_{\text{ox}}\ (\text{anode}) - E^\circ_{\text{ox}}\ (\text{cathode})$$

Difference between emf and potential difference: The potential difference is the difference between the electrode potentials of the two electrodes of the cell under any condition while emf is the potential generated by a cell when there is zero electron flow, *i.e.*, it draws no current. The points of difference are given ahead:

Emf	Potential difference
1. It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation.
2. It is the maximum voltage that the cell can deliver.	It is always less than the maximum value of voltage which the cell can deliver.
3. It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

12.19 REVERSIBLE AND IRREVERSIBLE CELLS

Daniell cell has the emf value 1.09 volt. If an opposing emf exactly equal to 1.09 volt is applied to the cell, the cell reaction,

$$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$$

stops but if it is increased infinitesimally beyond 1.09 volt, the cell reaction is reversed.

$$Cu + Zn^{2+} \longrightarrow Zn + Cu^{2+}$$

Such a cell is termed a **reversible cell.** Thus, the following are the two main conditions of reversibility:

(i) The chemical reaction of the cell stops when an exactly equal opposing emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the opposing emf is slightly greater than that of the cell.

Any other cell which does not obey the above two conditions is termed as **irreversible.** A cell consisting of zinc and copper electrodes dipped into the solution of sulphuric acid is irreversible. Similarly, the cell

$$Zn \mid H_2SO_4(aq.) \mid Ag$$

is also irreversible because when the external emf is greater than the emf of the cell, the cell reaction,

$$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

is not reversed but the cell reaction becomes

$$2Ag + 2H^+ \longrightarrow 2Ag^+ + H_2$$

12.20 SOME OTHER REFERENCE ELECTRODES

Since, a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as secondary reference electrodes. These are convenient to handle and are prepared easily. Two important secondary reference electrodes are described here.

(i) **Calomel electrode:** It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

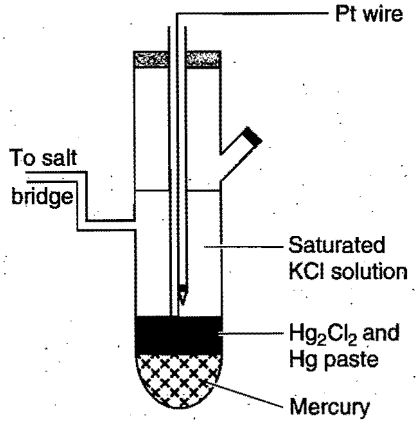


Fig. 12.16 Calomel electrode

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE). The electrode reaction when the electrode acts as cathode is:

$$\frac{1}{2}\mathrm{Hg_2Cl_2} + e^- \rightleftharpoons \mathrm{Hg} + \mathrm{Cl^-}$$

The reduction potentials of the calomel electrodes on hydrogen scale at 298 K are as follows:

Saturated KCl	0.2415 V
1.0 N KCl	0.2800 V
0.1 N KCl	0.3338 V

The electrode potential of any other electrode on hydrogen scale can be measured when it is combined with calomel electrode. The emf of such a cell is measured. From the value of electrode potential of calomel electrode, the electrode potential of the other electrode can be evaluated.

(ii) Silver-silver chloride electrode: This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without inserting liquid junctions.

Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K. The electrode is represented as:

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{Cl^-}$$

The electrode reaction is:

$$\mathrm{AgCl} + e^- \longrightarrow \mathrm{Ag} + \mathrm{Cl^-}$$

12.21 PREDICTION FOR OCCURRENCE OF A REDOX REACTION

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative. The free energy is related to cell emf in the following manner:

$$\Delta G^\circ = -nFE^\circ$$

where, n is the number of electrons involved, F is the value of Faraday and E° is the cell emf. ΔG can be negative if E° is positive.

When E° is positive, the cell reaction is spontaneous and serves as a source of electrical energy.

To predict whether a particular redox reaction will occur or not, write down the redox reaction into two half reactions, one involving oxidation reaction and the other involving reduction reaction. Write the oxidation potential value for oxidation reaction and reduction potential value for reduction reaction. Add these two values, if the algebraic summation gives a positive value, the reaction will occur, otherwise not.

[**Note :** The true conditions for operating voltaic cells are :
$\Delta G < 0,\ E > 0$]

12.22 ELECTRODE AND CELL POTENTIALS—NERNST EQUATION

The electrode potential and the emf of the cell depend upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potentials with concentration of ions in solution can be obtained from thermodynamic considerations. For a general reaction such as

$$m_1A + m_2B + \ldots \rightleftharpoons n_1X + n_2Y + \ldots \qquad \ldots \text{(i)}$$

occurring in the cell, the Gibbs free energy change is given by the equation

$$\Delta G = \Delta G^\circ + 2.303RT\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2}\ldots}{a_A^{m_1} \times a_B^{m_2}\ldots} \qquad \ldots \text{(ii)}$$

where, 'a' represents the activities of reactants and products under a given set of conditions and ΔG° refers to free energy change for the reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction is related to the electrical work that can be obtained from the cell, *i.e.*, $\Delta G = -nFE_{\text{cell}}$ and $\Delta G^\circ = -nFE^\circ$. On substituting these values in eq. (ii), we get

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + 2.303RT\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2}\ldots}{a_A^{m_1} \times a_B^{m_2}\ldots} \qquad \ldots \text{(iii)}$$

or
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF}\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2}\ldots}{a_A^{m_1} \times a_B^{m_2}\ldots} \qquad \ldots \text{(iv)}$$

This equation is known as Nernst equation.

Putting the values of $R = 8.314\ \mathrm{JK^{-1}\ mol^{-1}}$, $T = 298$ K and $F = 96500$ C, eq. (iv) reduces to

$$E = E^\circ - \frac{0.0591}{n}\log_{10}\frac{a_X^{n_1} \times a_Y^{n_2}\ldots}{a_A^{m_1} \times a_B^{m_2}\ldots} \qquad \ldots \text{(v)}$$

$$= E^\circ - \frac{0.0591}{n}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]} \qquad \ldots \text{(vi)}$$

Potential of single electrode (Anode): Consider the general oxidation reaction,

$$M \longrightarrow M^{n+} + ne^-$$

Applying Nernst equation,

$$E_{\text{ox}} = E^{\circ}_{\text{ox}} - \frac{0.0591}{n} \log_{10} \frac{[M^{n+}]}{[M]}$$

where, E_{ox} is the oxidation potential of the electrode (anode), E°_{ox} is the standard oxidation potential of the electrode.

[**Note:** The concentration of pure solids and liquids are taken as unity.]

$$E_{\text{ox}} = E^{\circ}_{\text{ox}} - \frac{0.0591}{n} \log_{10} [M^{n+}]$$

Let us consider a Daniell cell to explain the above equations. The concentrations of the electrolytes are not 1 *M*.

$$\text{Zn}(s) + \text{Cu}^{2+}(aq.) \rightleftharpoons \text{Zn}^{2+}(aq.) + \text{Cu}(s)$$

$$\text{Zn}(s) \mid \text{Zn}^{2+}(aq.) \mid\mid \text{Cu}^{2+}(aq.) \mid \text{Cu}$$

Potential at zinc electrode (Anode)

$$E_{\text{ox}} = E^{\circ}_{\text{ox}} - \frac{0.0591}{n} \log_{10} [\text{Zn}^{2+}]$$

Potential at copper electrode (Cathode)

$$E_{\text{red}} = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log_{10} [\text{Cu}^{2+}]$$

Emf of the cell

$$\begin{aligned} E_{\text{cell}} &= E_{\text{ox}} + E_{\text{red}} \\ &= (E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}}) - \frac{0.0591}{n} \log_{10} \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}}\right] \\ &= E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log_{10} \left[\frac{\text{Zn}^{2+}}{\text{Cu}^{2+}}\right] \end{aligned}$$

The value of $n = 2$ for both zinc and copper.

Let us consider an example, in which the values of *n* for the two ions in the two half-cells are not same. For example, in the cell

$$\text{Cu} \mid \text{Cu}^{2+} \mid\mid \text{Ag}^+ \mid \text{Ag}$$

The cell reaction is:

$$\text{Cu}(s) + 2\text{Ag}^+ \longrightarrow \text{Cu}^{2+} + 2\text{Ag}$$

The two half-cell reactions are:

$$\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$$

$$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$$

The second equation is multiplied by 2 to balance the number of electrons.

$$2\text{Ag}^+ + 2e^- \longrightarrow 2\text{Ag}$$

$$E_{\text{ox}} = E^{\circ}_{\text{ox}} - \frac{0.0591}{2} \log_{10} [\text{Cu}^{2+}]$$

$$E_{\text{red}} = E^{\circ}_{\text{red}} + \frac{0.0591}{2} \log_{10} [\text{Ag}^+]^2$$

$$\begin{aligned} E_{\text{cell}} = E_{\text{ox}} + E_{\text{red}} &= E^{\circ}_{\text{ox}} + E^{\circ}_{\text{red}} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \\ &= E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log_{10} \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \end{aligned}$$

SOME SOLVED EXAMPLES

Example 31. *Construct the cells in which the following reactions are taking place. Which of the electrodes shall act as anode (negative electrode) and which one as cathode (positive electrode)?*

(*a*) $Zn + CuSO_4 = ZnSO_4 + Cu$

(*b*) $Cu + 2AgNO_3 = Cu(NO_3)_2 + 2Ag$

(*c*) $Zn + H_2SO_4 = ZnSO_4 + H_2$

(*d*) $Fe + SnCl_2 = FeCl_2 + Sn$

Solution: It should always be kept in mind that the metal which goes into solution in the form of its ions undergoes oxidation and thus acts as negative electrode (anode) and the element which comes into the free state undergoes reduction and acts as positive electrode (cathode):

(a) In this case Zn is oxidised to Zn^{2+} and thus acts as anode (negative electrode) while Cu^{2+} is reduced to copper and thus acts as cathode (positive electrode). The cell can be represented as

$$\text{Zn} \mid \text{ZnSO}_4 \mid\mid \text{CuSO}_4 \mid \text{Cu}$$

or

$$\underset{\text{Anode }(-)}{\text{Zn} \mid \text{Zn}^{2+}} \mid\mid \underset{\text{Cathode }(+)}{\text{Cu}^{2+} \mid \text{Cu}}$$

(b) In this case Cu is oxidised to Cu^{2+} and Ag^+ is reduced to Ag. The cell can be represented as

$$\text{Cu} \mid \text{Cu(NO}_3)_2 \mid\mid \text{AgNO}_3 \mid \text{Ag}$$

or

$$\underset{\text{Anode }(-)}{\text{Cu} \mid \text{Cu}^{2+}} \mid\mid \underset{\text{Cathode }(+)}{\text{Ag}^+ \mid \text{Ag}}$$

(c) In this case, Zn is oxidised to Zn^{2+} and H^+ is reduced to H_2. The cell can be represented as:

$$\text{Zn} \mid \text{ZnSO}_4 \mid\mid \text{H}_2\text{SO}_4 \mid \text{H}_2(\text{Pt})$$

or

$$\underset{\text{Anode }(-)}{\text{Zn} \mid \text{Zn}^{2+}} \mid\mid \underset{\text{Cathode }(+)}{2\text{H}^+ \mid \text{H}_2(\text{Pt})}$$

(d) Here, Fe is oxidised to Fe^{2+} and Sn^{2+} is reduced to Sn. The cell can be represented as:

$$\text{Fe} \mid \text{FeCl}_2 \mid\mid \text{SnCl}_2 \mid \text{Sn}$$

or

$$\underset{\text{Anode }(-)}{\text{Fe} \mid \text{Fe}^{2+}} \mid\mid \underset{\text{Cathode }(+)}{\text{Sn}^{2+} \mid \text{Sn}}$$

Note : Oxidation potential is $E^{\circ}_{M/M^{n+}}$ while reduction potential is represented as $E^{\circ}_{M^{n+}/M}$. The value of $E^{\circ}_{\text{Zn}/\text{Zn}^{2+}}$ (oxidation potential of Zn) is + 0.76 volt and the value of $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ (reduction potential of copper) is + 0.34 volt. The electrode having lower value of reduction potential acts as an anode while that having higher value of reduction potential acts as cathode.

Example 32. *Consider the reaction,*

$$2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$$

The standard electrode potentials for $Ag^+ \longrightarrow Ag$ *and* $Cd^{2+} \longrightarrow Cd$ *couples are* 0.80 *volt and* – 0.40 *volt respectively.*

(*i*) *What is the standard potential* E° *for this reaction?*

(*ii*) *For the electrochemical cell, in which this reaction takes place which electrode is negative electrode?*

Solution: (i) The half reactions are:

$$2Ag^+ + \underset{\text{(Cathode)}}{\underset{\text{Reduction}}{2e^-}} \longrightarrow 2Ag,$$

$$E^\circ_{Ag^+/Ag} = 0.80 \text{ volt} \qquad \text{(Reduction potential)}$$

$$Cd \longrightarrow \underset{\text{(Anode)}}{\underset{\text{Oxidation}}{Cd^{2+}}} + 2e^-,$$

$$E^\circ_{Cd^{2+}/Cd} = -0.40 \text{ volt} \quad \text{(Reduction potential)}$$

or $E^\circ_{Cd/Cd^{2+}} = +0.40$ volt

$$E^\circ = E^\circ_{Cd/Cd^{2+}} + E^\circ_{Ag^+/Ag} = 0.40 + 0.80 = 1.20 \text{ volt}$$

(ii) The negative electrode is always the electrode whose reduction potential has smaller value or the electrode where oxidation occurs. Thus, Cd electrode is the negative electrode.

Example 33. *Consider the cell,*

$$Zn \,|\, Zn^{2+}(aq.)(1.0M) \,||\, Cu^{2+}(aq.)(1.0M) \,|\, Cu$$

The standard electrode potentials are:

$$Cu^{2+} + 2e^- \longrightarrow Cu(aq.); \qquad E^\circ = 0.350 \text{ volt}$$

$$Zn^{2+} + 2e^- \longrightarrow Zn(aq.); \qquad E^\circ = -0.763 \text{ volt}$$

(*i*) *Write down the cell reaction.*

(*ii*) *Calculate the emf of the cell.*

Solution: (i) Reduction potential of Zn is less than copper, hence Zn acts as anode and copper as cathode.

At anode $Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)

At cathode $Cu^{2+} + 2e^- \longrightarrow Cu$ (Reduction)

Cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(ii) $E^\circ_{cell} = E^\circ_{Zn/Zn^{2+}} + E^\circ_{Cu^{2+}/Cu}$

= Oxi. potential of zinc + Red. potential of copper

$$E^\circ_{Zn^{2+}/Zn} = -0.763 \text{ (Reduction potential)}$$

$$E^\circ_{Zn/Zn^{2+}} = +0.763 \text{ (Oxidation potential)}$$

and $E^\circ_{Cu^{2+}/Cu} = 0.350$ (Reduction potential)

So, $E^\circ_{cell} = 0.763 + 0.350 = 1.113$ volt

Example 34. *Write the electrode reactions and the net cell reactions for the following cells. Which electrode would be the positive terminal in each cell?*

(*a*) $Zn \,|\, Zn^{2+} \,||\, Br^-, Br_2 \,|\, Pt$ (*b*) $Cr \,|\, Cr^{3+} \,||\, I^-, I_2 \,|\, Pt$

(*c*) $Pt \,|\, H_2, H^+ \,||\, Cu^{2+} \,|\, Cu$ (*d*) $Cd \,|\, Cd^{2+} \,||\, Cl^-, AgCl \,|\, Ag$

Solution:

(a) Oxidation half reaction, $Zn \longrightarrow Zn^{2+} + 2e^-$

Reduction half reaction, $Br_2 + 2e^- \longrightarrow 2Br^-$

Net cell reaction $Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^-$

Positive terminal—Cathode Pt

(b) Oxidation half reaction, $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

Reduction half reaction, $[I_2 + 2e^- \longrightarrow 2I^-] \times 3$

Net cell reaction $2Cr + 3I_2 \longrightarrow 2Cr^{3+} + 6I^-$

Positive terminal—Cathode Pt

(c) Oxidation half reaction, $H_2 \longrightarrow 2H^+ + 2e^-$

Reduction half reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction $H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$

Positive terminal—Cathode Cu

(d) Oxidation half reaction, $Cd \longrightarrow Cd^{2+} + 2e^-$

Reduction half reaction,

$$[AgCl + e^- \longrightarrow Ag + Cl^-] \times 2$$

Net cell reaction $Cd + 2AgCl \longrightarrow Cd^{2+} + 2Ag + 2Cl^-$

Positive terminal—Cathode Ag

Example 35. *Will Fe be oxidised to* Fe^{2+} *by reaction with* 1.0 *M HCl?* E° *for* $Fe/Fe^{2+} = +0.44$ *volt.*

Solution: The reaction will occur if Fe is oxidised to Fe^{2+}.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$

Writing two half reactions,

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{Oxidation; } E^\circ_{Fe/Fe^{2+}} = 0.44 \text{ volt}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{Reduction; } E^\circ_{H^+/H} = 0.0 \text{ volt}$$

Adding; emf = 0.44 volt

Since, emf is positive, the reaction shall occur.

Example 36. *The values of* E° *of some of the reactions are given below:*

$$I_2 + 2e^- \longrightarrow 2I^-; \qquad E^\circ = +0.54 \text{ volt}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^-; \qquad E^\circ = +1.36 \text{ volt}$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \qquad E^\circ = +0.76 \text{ volt}$$

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}; \qquad E^\circ = +1.60 \text{ volt}$$

$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}; \qquad E^\circ = +0.15 \text{ volt}$$

On the basis of the above data, answer the following questions:

(*a*) *Whether* Fe^{3+} *oxidises* Ce^{3+} *or not?*

(*b*) *Whether* I_2 *displaces chlorine from KCl?*

(*c*) *Whether the reaction between* $FeCl_3$ *and* $SnCl_2$ *occurs or not?*

Solution: (a) Chemical reaction,

$$Fe^{3+} + Ce^{3+} \longrightarrow Ce^{4+} + Fe^{2+}$$

Two half reactions,

$$Fe^{3+} + e \longrightarrow Fe^{2+}; \quad \text{Reduction; } E^\circ = 0.76 \text{ volt}$$

$$Ce^{3+} \longrightarrow Ce^{4+} + e^-; \quad \underline{\text{Oxidation; } E^\circ_{ox} = -1.60 \text{ volt}}$$

$$\text{Adding; emf} = -0.84 \text{ volt}$$

Since, emf is negative, the reaction does not occur, *i.e.*, Fe^{3+} does not oxidise Ce^{3+}.

(b) Chemical reaction,

$$I_2 + 2KCl = 2KI + Cl_2$$

Half reactions,

$$I_2 + 2e^- \longrightarrow 2I^-; \quad \text{Reduction; } E^\circ = 0.54 \text{ volt}$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-; \quad \underline{\text{Oxidation; } E^\circ_{ox} = -1.36 \text{ volt}}$$

$$\text{Adding; emf} = -0.82 \text{ volt}$$

Since, emf is negative, the reaction does not occur, *i.e.*, I_2 does not displace Cl_2 from KCl.

(c) Chemical reaction,

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

Half reactions,

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \quad \text{Reduction; } E^\circ = 0.76 \text{ volt}$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-; \quad \underline{\text{Oxidation; } E^\circ = -0.15 \text{ volt}}$$

$$\text{Adding; emf} = +0.61 \text{ volt}$$

Since, emf is positive, the reaction will occur.

Example 37. *Calculate the electrode potential at a copper electrode dipped in a* 0.1 *M solution of copper sulphate at* 25° *C. The standard electrode potential of* Cu^{2+}/Cu *system is* 0.34 *volt at* 298 *K.*

Solution: We know that, $E_{red} = E^\circ_{red} + \dfrac{0.0591}{n} \log_{10}[\text{ion}]$

Putting the values of $E^\circ_{red} = 0.34$ V, $n = 2$ and $[Cu^{2+}] = 0.1 M$

$$E_{red} = 0.34 + \frac{0.0591}{2} \log_{10}[0.1]$$

$$= 0.34 + 0.02955 \times (-1)$$

$$= 0.34 - 0.02955 = 0.31045 \text{ volt}$$

Example 38. *What is the single electrode potential of a half-cell for zinc electrode dipping in* 0.01 *M* $ZnSO_4$ *solution at* 25° *C? The standard electrode potential of* Zn/Zn^{2+} *system is* 0.763 *volt at* 25° *C.*

Solution: We know that, $E_{ox} = E^\circ_{ox} - \dfrac{0.0591}{n} \log_{10}[\text{ion}]$

Putting the value of $E^\circ_{ox} = 0.763$ V, $n = 2$ and $[Zn^{2+}] = 0.01$ *M*,

$$E_{ox} = 0.763 - \frac{0.0591}{2} \log_{10}[0.01]$$

$$= 0.763 - 0.02955 \times (-2)$$

$$= (0.763 + 0.0591) \text{ volt} = 0.8221 \text{ volt}$$

Example 39. *The standard oxidation potential of zinc is* 0.76 *volt and of silver is* − 0.80 *volt. Calculate the emf of the cell:*

$$Zn \mid \underset{0.25\,M}{Zn(NO_3)_2} \parallel \underset{0.1\,M}{AgNO_3} \mid Ag$$

at 25° *C.*

Solution: The cell reaction is

$$Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$$

$$E^\circ_{ox} \text{ of Zn} = 0.76 \text{ volt}$$

$$E^\circ_{red} \text{ of Ag} = 0.80 \text{ volt}$$

$$E^\circ_{cell} = E^\circ_{ox} \text{ of Zn} + E^\circ_{red} \text{ of Ag} = 0.76 + 0.80 = 1.56 \text{ volt}$$

We know that, $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n} \log \dfrac{[\text{Products}]}{[\text{Reactants}]}$

$$= E^\circ_{cell} - \frac{0.0591}{2} \log \frac{0.25}{0.1 \times 0.1}$$

$$= 1.56 - \frac{0.0591}{2} \times 1.3979$$

$$= (1.56 - 0.0413) \text{ volt}$$

$$= 1.5187 \text{ volt}$$

Alternative method: First of all, the single electrode potentials of both the electrodes are determined on the basis of given concentrations.

$$E_{ox\,(\text{Zinc})} = E^\circ_{ox} - \frac{0.0591}{2} \log 0.25$$

$$= 0.76 + 0.0177 = 0.7777 \text{ volt}$$

$$E_{red\,(\text{Silver})} = E^\circ_{red} + \frac{0.0591}{1} \log 0.1$$

$$= 0.80 - 0.0591 = 0.7409 \text{ volt}$$

$$E_{cell} = E_{ox\,(\text{Zinc})} + E_{red\,(\text{Silver})}$$

$$= 0.7777 + 0.7409 = 1.5186 \text{ volt}$$

Example 40. *The emf* (E°) *of the following cells are:*

$$Ag \mid Ag^+(1M) \parallel Cu^{2+}(1M) \mid Cu; \quad E^\circ = -0.46 \text{ volt}$$

$$Zn \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu; \quad E^\circ = +1.10 \text{ volt}$$

Calculate the emf of the cell:

$$Zn \mid Zn^{2+}(1M) \parallel Ag^+(1M) \mid Ag$$

Solution: $Zn \mid Zn^{2+}(1M) \parallel Ag^+(1M) \mid Ag$

$$E_{cell} = E_{ox\,(Zn/Zn^{2+})} + E_{red\,(Ag^+/Ag)}$$

With the help of the following two cells, the above equation can be obtained:

$$Ag \mid Ag^+(1M) \parallel Cu^{2+}(1M) \mid Cu; E^\circ = -0.46 \text{ volt}$$

or $Cu \mid Cu^{2+}(1M) \parallel Ag^+(1M) \mid Ag$; E° will be + 0.46 volt or $$+0.46 = E_{\text{ox (Cu/Cu}^{2+})} + E_{\text{red (Ag}^{+}/\text{Ag)}} \quad \text{... (i)}$$

$$\text{Zn} \mid \text{Zn}^{2+}(1\,M) \,||\, \text{Cu}^{2+} \mid \text{Cu};\; E^\circ = +1.10\,\text{volt}$$

$$+1.10 = E_{\text{ox (Zn/Zn}^{2+})} + E_{\text{red (Cu}^{2+}/\text{Cu)}} \quad \text{... (ii)}$$

Adding eqs. (i) and (ii),

$$+1.56 = E_{\text{ox (Cu/Cu}^{2+})} + E_{\text{red (Ag}^{+}/\text{Ag)}} + E_{\text{ox (Zn/Zn}^{2+})} + E_{\text{red (Cu}^{2+}/\text{Cu)}}$$

Since, $E_{\text{ox (Cu/Cu}^{2+})} = -E_{\text{red (Cu}^{2+}/\text{Cu)}}$

So, $$+1.56 = E_{\text{ox (Zn/Zn}^{2+})} + E_{\text{red (Ag}^{+}/\text{Ag)}}$$

Thus, the emf of the following cell is

$$\text{Zn} \mid \text{Zn}^{2+}(1\,M) \,||\, \text{Ag}^{+}(1\,M) \mid \text{Ag is } +1.56\text{ volt}$$

Example 41. *Calculate the emf of the cell.*

$$Mg(s) \mid Mg^{2+}(0.2\,M) \,||\, Ag^{+}(1\times 10^{-3}) \mid Ag$$

$$E^\circ_{Ag^{+}/Ag} = +0.8\,volt,\; E^\circ_{Mg^{2+}/Mg} = -2.37\,volt$$

What will be the effect on emf if concentration of Mg^{2+} ion is decreased to 0.1 M?

Solution: $$E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$

$$= 0.80 - (-2.37) = 3.17\text{ volt}$$

Cell reaction, $\text{Mg} + 2\text{Ag}^{+} \longrightarrow 2\text{Ag} + \text{Mg}^{2+}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{\text{Mg}^{2+}}{[\text{Ag}^{+}]^2}$$

$$= 3.17 - \frac{0.0591}{2}\log\frac{0.2}{[1\times 10^{-3}]^2}$$

$$= 3.17 - 0.1566 = 3.0134\text{ volt}$$

when $\text{Mg}^{2+} = 0.1\,M$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{0.1}{(1\times 10^{-3})^2}$$

$$= (3.17 - 0.1477)\text{ volt}$$

$$= 3.0223\text{ volt}$$

Example 42. *To find the standard potential of M^{3+}/M electrode, the following cell is constituted:*

$$Pt \mid M \mid M^{3+}(0.0018\,mol^{-1}L) \,||\, Ag^{+}(0.01\,mol^{-1}L) \mid Ag$$

The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction $M^{3+} + 3e^{-} \longrightarrow M$. $E^\circ_{Ag^{+}/Ag} = 0.80\,volt$.

Solution: The cell reaction is

$$M + 3\text{Ag}^{+} \longrightarrow 3\text{Ag} + M^{3+}$$

Applying Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{3}\log\frac{[M^{3+}]}{[\text{Ag}^{+}]^3}$$

$$0.42 = E^\circ_{\text{cell}} - \frac{0.0591}{3}\log\frac{(0.0018)}{(0.01)^3} = E^\circ_{\text{cell}} - 0.064$$

$$E^\circ_{\text{cell}} = (0.42 + 0.064) = 0.484\text{ volt}$$

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$

or $$E^\circ_{\text{Anode}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Cell}}$$

$$= (0.80 - 0.484) = 0.32\text{ volt}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

19. The oxidation potential of hydrogen electrode at pH = 10 and $\text{pH}_2 = 1$ atm is:

(a) 0.51 V (b) 0.00 V (c) + 0.59 V (d) 0.059 V

[Ans. (c)]

[Hint: $$E_{\text{ox}} = E^\circ_{\text{ox}} - \frac{0.0591}{n}\log\frac{[\text{H}^{+}]}{\text{pH}_2}$$

$$= 0 - \frac{0.0591}{1}\log\frac{10^{-10}}{1} = 0.59\text{ V}\,]$$

20. The value of equilibrium constant for a feasible cell reaction is:

(a) < 1 (b) = 1 (c) > 1 (d) zero

[Ans. (c)]

[Hint: $K = \text{antilog}\left(\dfrac{nE^\circ}{0.0591}\right)$

For feasible cell, E° is positive; hence from the above equation, $K > 1$ for feasible cell reaction.]

21. E° for the electrochemical cell

$$\text{Zn}(s) \mid \text{Zn}^{2+}\,1\,M\,(aq.) \,||\, \text{Cu}^{2+}\,1\,M\,(aq.) \mid \text{Cu}(s)$$

is 1.10 V at 25°C. The equilibrium constant for the cell reaction,

$$\text{Zn}(s) + \text{Cu}^{2+}(aq.) \rightleftharpoons \text{Zn}^{2+}(aq.) + \text{Cu}(s)$$

will be:

(a) 10^{-37} (b) 10^{37}

(c) 10^{-39} (d) 10^{39}

[Ans. (b)]

[Hint: $$K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$$

$$= \text{antilog}\left[\frac{2\times 1.10}{0.0591}\right] = 1.67\times 10^{37}\,]$$

22. The value of the reaction quotient Q, for the cell

$$\text{Zn}(s) \mid \text{Zn}^{2+}(0.01\,M) \,||\, \text{Ag}^{+}\,(1.25\,M) \mid \text{Ag}(s)$$

is:

(a) 156 (b) 125

(c) 1.25×10^{-2} (d) 6.4×10^{-3}

[Ans. (d)]

[Hint: $\text{Zn}(s) \longrightarrow \text{Zn}^{2+} + 2e^{-}$ (Anodic process)

$2\text{Ag}^{+} + 2e^{-} \longrightarrow 2\text{Ag}(s)$ (Cathodic process)

$\text{Zn}(s) + 2\text{Ag}^{+} \rightleftharpoons 2\text{Ag}(s) + \text{Zn}^{2+}$

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^2} = \frac{0.01}{(1.25)^2} = 6.4\times 10^{-3}\,]$$

23. Calculate the emf of the following concentration cell at 25°C:

$Ag(s) \mid AgNO_3\ (0.01\,M) \parallel AgNO_3\ (0.05\,M) \mid Ag(s)$

(a) − 0.414 V (b) 0.828 V
(c) 0.414 V (d) 0.0414 V

[**Ans.** (d)]

[**Hint:** $E = E^\circ - \frac{0.0591}{n}\log_{10} Q$

($\because E^\circ = 0$ for all concentration cells)

$$= 0 - \frac{0.0591}{1}\log_{10}\left(\frac{0.01}{0.05}\right) = 0.0414\ \text{V}\ ]$$

24. The equilibrium constant of the reaction:

$Cu(s) + 2Ag^+(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$

$E^\circ = 0.46$ V at 298 K is: [CBSE (Med.) 2007]

(a) 2.0×10^{10} (b) 4.0×10^{10}
(c) 4.0×10^{15} (d) 2.4×10^{10}

[**Ans.** (c)]

[**Hint:** $K = \text{antilog}\left[\frac{nE^\circ}{0.059}\right] = \text{antilog}\left[\frac{2 \times 0.46}{0.059}\right]$

$= \text{antilog } 15.593$

$= 3.9 \times 10^{15}$

$\approx 4 \times 10^{15}$]

25. The cell reaction of a cell is:

$Mg(s) + Cu^{2+}(aq.) \rightleftharpoons Cu(s) + Mg^{2+}(aq.)$

If the standard reduction potentials of Mg and Cu are − 2.37 and + 0.34 V respectively. The emf of the cell is: [JEE (WB) 2007]

(a) 2.03 V (b) − 2.03 V (c) + 2.71 V (d) − 2.71 V

[**Ans.** (c)]

[**Hint:** $E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$

$= E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$

$= 0.34 - (-2.37) = +2.71$ V]

26. The equilibrium constant of the following redox reaction at 298 K is 1×10^8

$2Fe^{3+}(aq.) + 2I^-(aq.) \rightleftharpoons 2Fe^{2+}(aq.) + I_2(s)$

If the standard reduction potential of iodine becoming iodide is + 0.54 V. What is the standard reduction potential of Fe^{3+}/Fe^{2+}? [PMT (Kerala) 2008]

(a) + 1.006 V (b) − 1.006 V
(c) + 0.77 V (d) − 0.77 V
(e) − 0.652 V

[Ans. (c)]

[**Hint:** $E^\circ = \frac{0.059}{n}\log_{10} K$

$= \frac{0.059}{2}\log_{10} 10^8 = 0.236$

$E^\circ_{\text{Cell}} = E^\circ_{\text{Reduced species}} - E^\circ_{\text{Oxidised species}}$

$0.236 = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.54$

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{V}$]

12.23 ELECTROCHEMICAL SERIES

By measuring the potentials of various electrodes *versus* standard hydrogen electrode (SHE), a series of standard electrode potentials has been established. When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE. Those with positive E° values for reduction half reactions do in fact act as cathodes *versus* SHE, while those with negative E° values of reduction half reactions behave instead as anodes *versus* SHE. The electrochemical series is shown in the given table:

Standard Aqueous Electrode Potentials at 25° C
'The Electrochemical Series'

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E°, volt
Li	$Li^+ + e^- = Li$	− 3.05
K	$K^+ + e^- = K$	− 2.925
Ca	$Ca^{2+} + 2e^- = Ca$	− 2.87
Na	$Na^+ + e^- = Na$	− 2.714
Mg	$Mg^{2+} + 2e^- = Mg$	− 2.37
Al	$Al^{3+} + 3e^- = Al$	− 1.66
Zn	$Zn^{2+} + 2e^- = Zn$	− 0.7628
Cr	$Cr^{3+} + 3e^- = Cr$	− 0.74
Fe	$Fe^{2+} + 2e^- = Fe$	− 0.44
Cd	$Cd^{2+} + 2e^- = Cd$	− 0.403
Ni	$Ni^{2+} + 2e^- = Ni$	− 0.25
Sn	$Sn^{2+} + 2e^- = Sn$	− 0.14
H_2	$2H^+ + 2e^- = H_2$	0.00
Cu	$Cu^{2+} + 2e^- = Cu$	+ 0.337
I_2	$I_2 + 2e^- = 2I^-$	+ 0.535
Ag	$Ag^+ + e^- = Ag$	+ 0.799
Hg	$Hg^{2+} + 2e^- = Hg$	+ 0.885
Br_2	$Br_2 + 2e^- = 2Br^-$	+ 1.08
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	+ 1.36
Au	$Au^{3+} + 3e^- = Au$	+ 1.50
F_2	$F_2 + 2e^- = 2F^-$	+ 2.87

↓ Increasing tendency to accept electrons
Increasing strength as oxidising agent

↑ Increasing strength as reducing agent
Increasing tendency to lose electrons

Characteristics of Electrochemical Series

(i) The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is − 0.76 volt. When zinc electrode is joined with SHE, it acts as anode (–ve electrode), *i.e.*, oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

(ii) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Applications of Electrochemical Series

(i) Reactivity of metals: The activity of the metal depends on its tendency to lose electron or electrons, *i.e.*, tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active.

The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) Electropositive character of metals: The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups:

(a) Strongly electropositive metals: Metals having standard reduction potential near about –2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) Moderately electropositive metals: Metals having values of reduction potentials between 0.0 and about –2.0 volt are moderately electropositive. Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive metals: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

(iii) Displacement reactions:

(a) To predict whether a given metal will displace another, from its salt solution: A metal higher in the series will displace the metal from its solution which is lower in the series, *i.e.*, **the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential.** A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) Displacement of one non-metal from its salt solution by another non-metal: A non-metal higher in the series (towards bottom side), *i.e.*, having high value of reduction potential will displace another non-metal with lower reduction potential, *i.e.*, occupying position above in the series. The non-metals which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the non-metal having low value of reduction potential. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

$$2I^- \longrightarrow I_2 + 2e^- \qquad \text{(Oxidation)}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^- \qquad \text{(Reduction)}$$

[The activity or electronegative character or oxidising nature of the non-metal increases as the value of reduction potential increases.]

(c) Displacement of hydrogen from dilute acids by metals: The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$$Mn \longrightarrow Mn^{n+} + ne^- \qquad \text{(Oxidation)}$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad \text{(Reduction)}$$

The metal having negative values of reduction potential possess the property of losing electron or electrons.

- **Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.**

The metals which are below hydrogen in electrochemical series like Cu, Hg, Au, Pt, etc., do not evolve hydrogen from dilute acids.

(d) Displacement of hydrogen from water: Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series.

Alkali and alkaline earth metals liberate hydrogen from cold water but Mg, Zn and Fe liberate hydrogen from hot water or steam.

(iv) Reducing power of metals: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. **Thus, reducing nature decreases from top to bottom in the electrochemical series.** The power of the reducing agent increases as the standard reduction potential becomes more and more negative.

Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.

Element	Na	Zn	Fe
Reduction potential	−2.71	− 0.76	− 0.44

$\xrightarrow{\hspace{6em}}$

Reducing nature decreases

Alkali and alkaline earth metals are strong reducing agents.

(v) Oxidising nature of non-metals: Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. **Thus, oxidising nature increases from top to bottom in the electrochemical series.** The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2.

Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2.

Element	I_2	Br_2	Cl_2	F_2
Reduction potential	+ 0.53	+ 1.06	+ 1.36	+ 2.85

$\xrightarrow{\hspace{6em}}$

Oxidising nature increases

Thus, in electrochemical series

Top (Strongest reducing agent)
Highest negative reduction potential
or
(Minimum reduction potential)
Bottom (Strongest oxidising agent)
Highest positive value of reduction potential

Oxidising nature ↓
Reducing nature ↑

(vi) Thermal stability of metallic oxides: The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, *i.e.*, these are decomposed on heating.

$$Ag_2O \xrightarrow{\text{Heat}} 2Ag + \frac{1}{2}O_2$$

$$2HgO \xrightarrow{\text{Heat}} 2Hg + O_2$$

$$\left.\begin{matrix} BaO \\ Na_2O \\ Al_2O_3 \end{matrix}\right] \xrightarrow{\text{Heat}} \text{No decomposition}$$

(vii) Products of electrolysis: In case, two or more types of positive and negative ions are present in solution, during electrolysis certain ions are discharged or liberated at the electrodes in preference to others. **In general, in such competition the ion which is stronger oxidising agent (high value of standard reduction potential) is discharged first at the cathode.** The increasing order of deposition of few cations is:

$$K^+, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}$$

$\xrightarrow{\hspace{20em}}$

Increasing order of deposition

Similarly, the anion which is stronger reducing agent (low value of standard reduction potential) is liberated first at the anode.

The increasing order of discharge of few anions is:

$$SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$$

$\xrightarrow{\hspace{14em}}$

Increasing order of discharge

Thus, when an aqueous solution of NaCl containing Na^+, Cl^-, H^+ and OH^- ions is electrolysed, H^+ ions are discharged at cathode and Cl^- ions at the anode, *i.e.*, H_2 is liberated at cathode and chlorine at anode.

When an aqueous solution of $CuSO_4$ containing Cu^{2+}, SO_4^{2-}, H^+ and OH^- ions is electrolysed, Cu^{2+} ions are discharged at cathode and OH^- ions at the anode.

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(Cathodic reaction)}$$

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \quad \text{(Anodic reaction)}$$

Cu is deposited on cathode while O_2 is liberated at anode.

(viii) Latimer diagram: Redox chemistry of an element can be understand by comparing the standard electrode potentials of the various oxidation states of the element. Latimer diagram showing relative stabilities of different oxidation states are given below :

Acid Medium

$$Fe \xrightarrow{E^\circ_{Fe/Fe^{2+}} = +0.44\text{ V}} Fe^{2+} \xrightarrow{E^\circ_{Fe^{2+}/Fe^{3+}} = -0.77\text{ V}} Fe^{3+}$$

Alkaline Medium

$$Fe \xrightarrow{E^\circ_{Fe/Fe^{2+}} = +0.88\text{ V}} Fe^{2+} \xrightarrow{E^\circ_{Fe^{2+}/Fe^{3+}} = +0.56\text{ V}} Fe^{3+}$$

In acid medium, the positive value of $E^\circ_{Fe/Fe^{2+}}$ indicates that iron will dissolve in acid medium to form Fe^{2+} ion; since $E^\circ_{Fe^{2+}/Fe^{3+}}$ is negative, hence +2 state of iron will be more state than +3 state in acid medium.

When the potential on right of a species is more positive (less negative) than that on the left, then the species will tend to undergo disproportionation.

Example :

Alkaline Medium

$$Cl^- \xrightarrow{E^\circ_{Cl^-/Cl_2} = -1.35\text{ V}} \frac{1}{2}Cl_2 \xrightarrow{E^\circ_{Cl_2/ClO^-} = -0.4\text{ V}} ClO^-$$

Thus, Cl_2 will undergo disproportionation into Cl^- and ClO^- ions in basic medium.

$$Cl_2 + 2OH^- \longrightarrow Cl^- + ClO^- + H_2O$$

(ix) Corrosion of metals: Corrosion is defined as the deterioration of a substance because of its reaction with its environment. This is also defined as the process by which metals have the tendency to go back to their combined state, *i.e.*, reverse of extraction of metals.

Thus, the process of weathering away of the metal due to attack of the atmospheric gases on the surface of the metal *resulting into the formation of compounds such as oxides, sulphates, sulphides, carbonates, etc., is called corrosion.*

The process of corrosion of iron is called rusting. Rust is chemically the hydrated oxide of iron having the formula $Fe_2O_3 \cdot xH_2O$. Other examples of corrosion of metals are tarnishing of silver and those of copper and bronze etc. Corrosion of copper and bronze forms a green coating on the surface. The corrosion of metals, particularly iron, causes damage to buildings, dams, bridges, etc., and we lose a lot of money every year.

Mechanism of Corrosion : Corrosion is a redox process by which metals are oxidised by oxygen in presence of moisture. The mechanism can be understood by taking the example of rusting of iron. The theory of rusting is called **electrochemical theory.** In this theory the process of rusting can be explained on the basis of formation of electrochemical cell on the surface of an iron object.

Rusting of iron involves the following steps :

Step 1 : The water vapours present in contact with iron surface have dissolved CO_2 and O_2 from air.

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(l)$$

Thus, the surface of iron is covered with an aqueous solution of carbonic acid, which undergoes dissociation to a small extent.

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \quad \text{(Ionisation of carbonic acid)}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{(Ionisation of water)}$$

Step 2 : Second step involves oxidation of iron. Oxidation of metal takes place at the point of strain. For example, a steel nail first corrodes at the tip and head. The tip of the nail acts as anode where iron is oxidised to ferrous ion.

$$Fe(s) \longrightarrow Fe^{2+} + 2e^- \quad \text{(Anodic process, oxidation)} \quad \ldots\text{(i)}$$

$$(E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt})$$

Step 3 : The electrons flow along the nail to the areas containing impurities which act as cathode where oxygen (dissolved in water) is reduced to hydroxyl ions.

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-$$

$$\text{(Cathodic process, reduction)}$$

$$(E^\circ_{red} = 1.23 \text{ volt})$$

The process of reduction involves the following two steps :

First of all H^+ ions are reduced to hydrogen atoms.

$$H^+ + e^- \longrightarrow [H] \quad \ldots\text{(ii)}$$

These hydrogen atoms combine with oxygen dissolved in water or from air.

$$4[H] + O_2 \longrightarrow 2H_2O \quad \ldots\text{(iii)}$$

Combining (ii) and (iii), we get

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O(l) \quad \ldots\text{(iv)}$$

$$(E^\circ_{red} = 1.23 \text{ volt})$$

Adding equations (i) and (iv), we get, the overall reactions of microcells established on the surface of iron.

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$(E^\circ_{cell} = 1.67 \text{ volt})$$

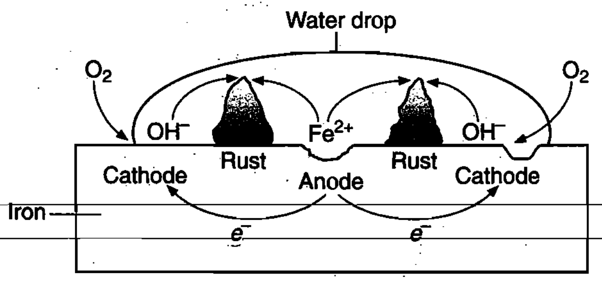
Step 4 : The ferrous ions (Fe^{2+}) formed in the previous step reacts with dissolved oxygen or oxygen from air to form ferric oxide (Fe_2O_3).

$$4Fe^{2+} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+(aq)$$

Hydration of ferric oxide gives rust.

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O$$

The process of rusting may be diagrammatically represented as in Fig. 12.17.



Oxidation : $Fe(s) \longrightarrow Fe^{2+}(aq.) + 2e^-$

Reduction : $O_2 + 4H^+(aq.) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric $4Fe^{2+} + O_2 + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+(aq.)$

Oxidation $Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Rust}}{Fe_2O_3 . xH_2O}$

Fig. 12.17 Rusting of iron

Factors Affecting Corrosion

1. Standard reduction potential : Lesser is the standard reduction potential, greater is the tendency of corrosion. In other words, more is the reactivity of metal, greater is the tendency of corrosion.

2. Strains and corrosion : Corrosion of metals occurs more readily at points of strain, bend, nick and scratches.

3. Impurity of metal and corrosion : Presence of impurity in metals increases the probability of their corrosion. Pure metals, *e.g.*, pure iron does not undergo rusting.

4. Salinity of water and corrosion : If water is saline, it helps in the flow of current in microelectrochemical cells on the surface of iron and hence, increases the process of corrosion.

5. Pollution and corrosion : The acidic oxides like CO_2, SO_2, NO_2 etc., present in air act as catalysts for corrosion. It should be noted that if iron is placed in vacuum, it does not undergo rusting.

Prevention of Rusting : Prevention of rusting is not only important from the point of view of economy but also from the point of view of safety. Prevention of corrosion not only saves money but also prevents accidents due to collapse of bridges and buildings.

Some important methods for preventing corrosion are described below:

1. Using antirust solution : Alkaline phosphate and alkaline chromate solutions are the commonly used antirust solutions. Alkaline phosphates tend to form an insoluble film of iron phosphate on the surface of iron, thereby protecting it from corrosion. In addition, the alkaline nature of an antirust solution decreases the availability of H^+ ions which facilitate the oxidation of Fe to Fe^{2+}. These solutions are used to prevent rusting of radiators of cars and water coolers.

2. Barrier protection : It is one of the simplest methods of preventing corrosion. In this method a barrier or coating is applied to prevent the surface of the metallic object from come in contact with the atmosphere. This can be achieved by the following methods :

(i) Oil paints on the surface of metal prevents its contact with moist air.

(ii) By applying grease or oil on the surface of iron tools and other objects, rusting can be prevented.

(iii) Nichrome (Ni + Cr) plating on the surface of iron also acts as a barrier between metal and atmosphere.

(iv) Bisphenol is an important chemical which can be applied on the surface of the metal to avoid its corrosion.

3. Sacrificial protection : In this method, the surface of iron is coated with a more active metal than iron. This active metal loses electrons, *i.e.*, undergo oxidation in preference to iron and hence, prevents the rusting of iron. So, long as the surface of iron is covered with such metals the corrosion of iron is prevented. If the surface is scratched or the coating is broken, even then the rusting of iron does not start.

Zinc metal is the most stable metal to cover iron surfaces. **The process of coating the iron surface by zinc is called galvanization.** Zinc metal present on the surface of iron forms a thin protective layer of basic zinc carbonate, *i.e.*, $ZnCO_3 \cdot Zn(OH)_2$ due to the reaction between zinc, oxygen, CO_2 and moisture in air.

$$Zn^{2+} + 2e^- \longrightarrow Zn(s); \qquad E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ volt}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \qquad E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt}$$

(Zinc will undergo oxidation in preference to iron.)

Since, standard reduction potential of zinc is less than iron, hence, iron will not undergo corrosion (oxidation) even when the zinc coating is broken due to scratches or some other mechanical stress.

Sometimes an iron surface is coated with tin metal and this process is known as **tinning** or tin plating. This method is not as effective as **galvanization.**

$$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s); \quad E^\circ_{Sn^{2+}/Sn} = -0.14 \text{ volt}$$

$$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s); \quad E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ volt}$$

(Iron will undergo oxidation in preference to tin.)

Tinning is effective in checking the rusting of iron so long as the surface of iron is fully covered by tin. Once the tin coating is broken or scratched then rusting will start because standard reduction potential of iron is less than that of tin.

4. Electrical or Cathodic protection : If a buried steel pipe is connected to an active metal, *i.e.*, highly electropositive metal, say magnesium, a voltaic cell is formed; the active metal is the anode and iron becomes the cathode. Wet soil or moisture forms the electrolyte and the electrode reactions are :

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-; \quad E^\circ_{Mg^{2+}/Mg} = -2.37 \text{ V}$$

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq); \quad E^\circ_{red} = 1.23 \text{ V}$$

Overall: $2Mg(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Mg^{2+} + 4OH^-; \quad E^\circ_{cell} = 3.60 \text{ V}$

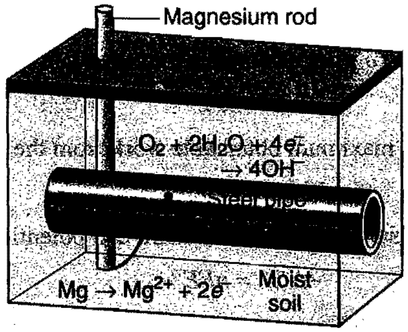


Fig. 12.18 Cathodic protection of a buried steel pipe

As the cathode, the iron containing steel pipe is protected from oxidation. Of course, the magnesium rod is eventually consumed and must be replaced, but this is cheaper than digging up the pipe line. This method is used to prevent the rusting of submarines and base line of oil refineries.

(x) Extraction of metals: A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of Ag and Au by cyanide process. Silver from the solution containing sodium argento cyanide, $NaAg(CN)_2$, can be obtained by the addition of zinc as it is more electropositive than Ag.

$$2NaAg(CN)_2 + Zn \longrightarrow Na_2Zn(CN)_4 + 2Ag$$

Concept of Equilibrium in Electrochemical Cell

In an electrochemical cell a reversible redox process takes place, *e.g.*, in Daniell cell:

$$Zn(s) + Cu^{2+}(aq.) \rightleftharpoons Zn^{2+}(aq.) + Cu(s)$$

(1) At equilibrium mass action ratio becomes equal to equilibrium constant,

i.e., $Q = K_e$

(2) Oxidation potential of anode = − Reduction potential of cathode

i.e., emf = Oxidation potential of anode + Reduction potential of cathode = 0

Cell is fully discharged.

According to Nernst equation:

$$E = E^\circ - \frac{0.0591}{n} \log_{10} Q \text{ at } 25^\circ\text{C}$$

At equilibrium, $E = 0, \ Q = K$

$$0 = E^\circ - \frac{0.0591}{n} \log_{10} K$$

$$K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right]$$

Work done by the Cell

Let n faraday charge be taken out of a cell of emf E; then work done by the cell will be calculated as:

$$\text{Work} = \text{Charge} \times \text{Potential}$$
$$= nFE$$

Work done by the cell is equal to decrease in free energy.

$$-\Delta G = nFE$$

Similarly, maximum obtainable work from the cell will be

$$W_{\max} = nFE^\circ$$

where, E° = standard emf or standard cell potential.

$$-\Delta G^\circ = nFE^\circ$$

The Relationship among K, ΔG° and E° Cell

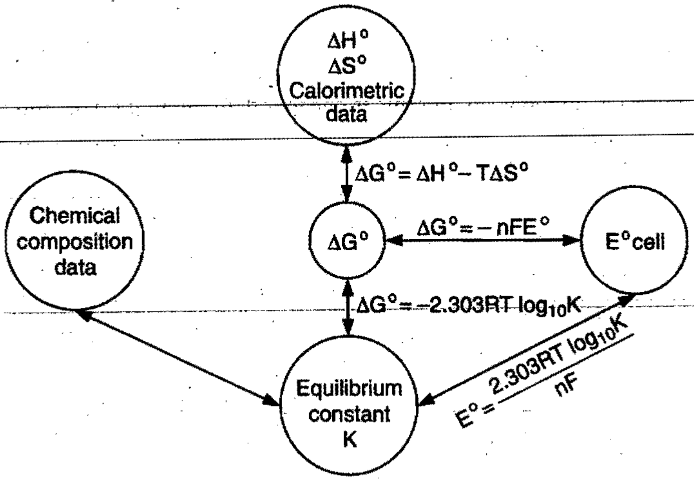


Fig. 12.19

Heat of Reaction in an Electrochemical Cell

Let n faraday charge flows out of a cell of emf E,

Then $$-\Delta G = nFE \quad \text{... (i)}$$

Gibbs-Helmholtz equation from thermodynamics may be given as:

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad \text{... (ii)}$$

From equations (i) and (ii), we get

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_P = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

Here, $\left(\frac{\partial E}{\partial T}\right)_P$ = Temperature coefficient of cell

Case I: When $\left(\frac{\partial E}{\partial T}\right)_P = 0$, then $\Delta H = -nFE$

Case II: When $\left(\frac{\partial E}{\partial T}\right) > 0$, then $nFE > \Delta H$, *i.e.*, process inside the cell is endothermic.

Case III: When $\left(\frac{\partial E}{\partial T}\right) < 0$, then $nFE < \Delta H$, *i.e.*, process inside the cell is exothermic.

12.24 PRIMARY VOLTAIC CELL (The Dry Cell)

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell.

The container of the dry cell is made of zinc which also serves as one of the electrodes. The other electrode is a carbon rod in the centre of the cell. The zinc container is lined with a porous paper. A moist mixture of ammonium chloride, manganese dioxide, zinc chloride and a porous inert filler occupy the space between the paper lined zinc container and the carbon rod. The cell is sealed with a material like wax.

As the cell operates, the zinc is oxidised to Zn^{2+}

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(Anode reaction)}$$

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2 \quad \text{(Cathode reaction)}$$

The cell reaction is

$$Zn + 2NH_4^+ \longrightarrow Zn^{2+} + 2NH_3 + H_2$$

Hydrogen is oxidised by MnO_2 in the cell.

$$2MnO_2 + H_2 \longrightarrow 2MnO(OH)$$

Ammonia produced at cathode combines with zinc ions to form complex ion.

$$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$$

E_{cell} is 1.6 volt.

Alkaline dry cell is similar to ordinary dry cell. It contains potassium hydroxide. The reactions in alkaline dry cell are:

$$Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2e^- \quad \text{(Anode reaction)}$$

$$2MnO_2 + 2H_2O + 2e^- \longrightarrow 2MnO(OH) + 2OH^- \quad \text{(Cathode reaction)}$$

$$Zn + 2MnO_2 + 2H_2O \longrightarrow Zn(OH)_2 + 2MnO(OH) \quad \text{(Overall)}$$

E_{cell} is 1.5 volt.

Button cell : The button cells are usually pallet type flat in construction and look like a button in shape. Owing to their small sizes, they are used in small electronic devices like hearing aids, electronic watches etc. These cells are basically primary cells. Mercuric oxide button cell is the most commonly used button cell. In this cell, zinc anode and mercuric oxide plus carbon paste cathode is used. The electrolyte is a paste of ZnO and KOH.

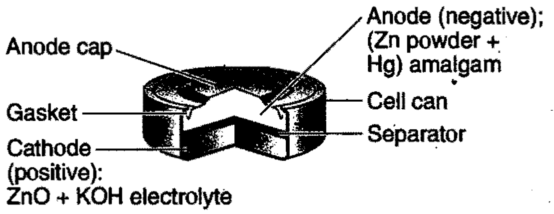


Fig. 12.20

The cell process is given below :

Anode : $$\underset{\text{(Amalgam)}}{Zn} + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

Cathode: $$HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

Overall : $$\underset{\text{Amalgam}}{Zn} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The potential of this cell is approximately 1.35 volt and it remains constant during its life because overall reaction does not involve any ion whose concentration can change during the process.

12.25 SECONDARY VOLTAIC CELL (Lead Storage Battery)

The cell in which original reactants are regenerated by passing direct current from external source, *i.e.*, it is recharged, is called secondary cell. Lead storage battery is the example of this type.

It consists of a group of lead plates bearing compressed spongy lead, alternating with a group of lead plates bearing lead dioxide, PbO_2. These plates are immersed in a solution of about 30% H_2SO_4. When the cell discharges, it operates as a voltaic cell. The spongy lead is oxidised to Pb^{2+} ions and lead plates acquire a negative charge.

$$Pb \longrightarrow Pb^{2+} + 2e^- \qquad \text{(Anode reaction)}$$

Pb^{2+} ions combine with sulphate ions to form insoluble lead sulphate, $PbSO_4$, which begins to coat lead electrode.

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

The electrons are utilised at PbO_2 electrode.

$$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O \qquad \text{(Cathode reaction)}$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

Overall cell reaction is:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

E_{cell} is 2.041 volt.

When a potential slightly greater than the potential of battery is applied, the battery can be recharged.

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$$

After many repeated charge-discharge cycles, some of the lead sulphate falls to the bottom of the container, the sulphuric acid concentration remains low and the battery cannot be recharged fully.

Nickel-Cadmium storage cell : It is also a common storage battery. It is more expensive than the lead storage battery but it is light, therefore, used in calculators, portable power tools, etc.

It is a voltaic cell consisting of an anode of cadmium and a cathode of hydrated nickel oxide on nickel. The electrolyte in the cell is aqueous solution of potassium hydroxide. Electrode processes are given below :

Anode: $$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2 + 2e^-$$

Cathode: $$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$$

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2 + Ni(OH)_2$$

In the recharging of the cell the process is reversed.

$$Cd(OH)_2 + Ni(OH)_2 \longrightarrow Cd(s) + NiO_2(s) + 2H_2O(l)$$

12.26 FUEL CELL

Fuel cells are another means by which chemical energy may be converted into electrical energy. The main disadvantage of a primary cell is that it can deliver current for a short period only. This is due to the fact that the quantity of oxidising agent and reducing agent is limited. But the energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell. The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with an electrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution. Hydrogen is oxidised at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:

Anode $$[H_2(g) + 2OH^-(aq.) \longrightarrow 2H_2O(l) + 2e^-] \times 2$$

Cathode $$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$$

Overall $$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

This type of cells are used in space-crafts. Fuel cells are efficient and pollution free.

Thermodynamic efficiency of fuel cells is the ratio of the electrical free energy to the enthalpy of the reaction.

$$\eta = \frac{\Delta G}{\Delta H}$$

12.27 CONCENTRATION CELLS

If two plates of the same metal are dipped separately into two solutions of the same electrolyte and are connected with a salt bridge, the whole arrangement is found to act as a galvanic cell. In general, there are two types of concentration cells:

(i) Electrode concentration cells: In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressures in the same solution of hydrogen ions constitute a cell of this type.

$$\underset{\text{Anode}}{\underline{\text{Pt, } H_2 \text{ (Pressure } p_1)}} \,|H^+|\, \underset{\text{Cathode}}{\underline{H_2 \text{ (Pressure } p_2) \text{ Pt}}}$$

If $p_1 > p_2$, oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{(p_1)}{(p_2)} \quad \text{at } 25°\text{C}$$

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution.

$$M\,(\text{Hg } C_1)\,|M^{n+}|\,\text{Zn}(\text{Hg } C_2)$$

The emf of the cell is given by the expression

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_1}{C_2} \quad \text{at } 25°\text{C}$$

(ii) Electrolyte concentration cells: In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner:

(C_2 is greater than C_1).

$$M\,|\,M^{n+}(C_1)\,||\,M^{n+}(C_2)\,|\,M$$

or

$$\underset{\text{Anode}}{\underline{\text{Zn}\,|\,\text{Zn}^{2+}(C_1)}}\,||\,\underset{\text{Cathode}}{\underline{\text{Zn}^{2+}(C_2)\,|\,\text{Zn}}}$$

The emf of the cell is given by the following expression:

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_{2\,(\text{RHS})}}{C_{1\,(\text{LHS})}} \quad \text{at } 25°\text{C}$$

The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.

SOME SOLVED EXAMPLES

Example 43. *A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 volt at 25° C. Calculate the concentration of hydrogen ions at the positive electrode.*

Solution: The cell may be represented as

$$\text{Pt}\,|\,H_2\,(1\text{ atm})\,|\,\underset{10^{-6}\,M}{H^+}\,||\,\underset{CM}{H^+}\,|\,H_2\,(1\text{ atm})\,|\,\text{Pt}$$

Anode	Cathode
(–ve)	(+ ve)
$H_2 \rightarrow 2H^+ + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{[H^+]^2_{\text{Cathode}}}{[10^{-6}]^2}$$

$$0.118 = (0.0591) \log \frac{[H^+]}{10^{-6}}$$

$$\log \frac{[H^+]_{\text{Cathode}}}{10^{-6}} = \frac{0.118}{0.0591} = 2$$

$$\frac{[H^+]_{\text{Cathode}}}{10^{-6}} = 10^2$$

$$[H^+]_{\text{Cathode}} = 10^{-6} \times 10^2 = 10^{-4}\,M$$

Example 44. *The emf of the cell*

$Ag\,|\,AgI$ in 0.05 M $KI\,|$ Sol. $NH_4NO_3\,|$ 0.05 M $AgNO_3\,|\,Ag$

is 0.788 volt at 25° C. The activity coefficient of KI and silver nitrate in the above solution is 0.90 each. Calculate (i) the solubility product of AgI and (ii) the solubility of AgI in pure water at 25° C.

Solution: Ag^+ ion concentration on $AgNO_3$ side

$$= 0.9 \times 0.05 = 0.045\,M$$

Similarly I^- ion concentration in 0.05 M KI solution

$$= 0.05 \times 0.9 = 0.045\,M$$

$$E_{\text{cell}} = \frac{0.0591}{1} \log \frac{[Ag^+]_{\text{RHS}}}{[Ag^+]_{\text{LHS}}} = 0.0591 \log \frac{0.045}{[Ag^+]_{\text{LHS}}}$$

or

$$\log \frac{0.045}{[Ag^+]_{\text{LHS}}} = \frac{0.788}{0.0591} = 13.33$$

$$[Ag^+]_{\text{LHS}} = \frac{0.045}{2.138 \times 10^{13}}$$

$$= 2.105 \times 10^{-15}\,M$$

$$\text{Solubility product of AgI} = [Ag^+][I^-]$$

$$= 2.105 \times 10^{-15} \times 0.045$$

$$= 9.472 \times 10^{-17}$$

$$\text{Solubility of AgI} = \sqrt{\text{Solubility product of AgI}}$$

$$= \sqrt{9.472 \times 10^{-17}}$$

$$= 9.732 \times 10^{-9}\text{ g mol L}^{-1}$$

$$= 9.732 \times 10^{-9} \times 143.5\text{ g L}^{-1}$$

$$= 1.396 \times 10^{-6}\text{ g L}^{-1}$$

Example 45. *The observed emf of the cell,*

$Pt\,|\,H_2\,(1\,atm)\,|\,H^+(3 \times 10^{-4}\,M)\,||\,H^+(M_1)\,|\,H_2\,(1\,atm)\,|\,Pt$

is 0.154 V. Calculate the value of M_1 and pH of cathodic solution.

Solution: $E_{\text{cell}} = 0.0591 \log \dfrac{M_1}{3 \times 10^{-4}}$

or

$$\log \frac{M_1}{3 \times 10^{-4}} = \frac{0.154}{0.0591} = 2.6058$$

$$\frac{M_1}{3\times10^{-4}} = 4.034\times10^{2}$$

$$M_1 = 4.034\times10^{2}\times3\times10^{-4}\ M$$

$$= 0.121M$$

$$\text{pH} = -\log[H^+] = -\log 0.121 = 0.917$$

Example 46. *Calculate the emf of the following cell at 25° C:*

$$Pt\ \underset{2\ atm}{H_2}\,|HCl|\,\underset{10\ atm}{H_2}\ Pt$$

Solution:

$$E_{\text{cell}} = \frac{0.0591}{2}\log\frac{p_1}{p_2}$$

$$= \frac{0.0591}{2}\log\frac{2}{10}$$

$$= -\ 0.0206\ \text{volt}$$

Example 47. *In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidised at the anode and O_2 is reduced at the cathode. If 67.2 litre of H_2 at NTP reacts in 15 minute, what is the average current produced? If the entire current is used for electro-deposition of Cu from Cu^{2+}, how many g of Cu are deposited?*

Solution: Reaction at anode of fuel cell,

$$\underset{\substack{1\ \text{mole}\\22.4\ \text{L}}}{H_2(g)} \longrightarrow 2H^+ + \underset{\substack{2\ \text{mole}\\2\ \text{F}}}{2e^-}$$

$$67.2\ \text{L of}\ H_2\ \text{correspond} = \frac{2\times96500}{22.4}\times67.2\ \text{coulomb}$$

$$\text{Time} = 15\times60\ \text{second}$$

$$\text{Average current} = \frac{2\times96500\times67.2}{22.4\times15\times60} = 643.3\ \text{amp}$$

$$\text{Mass of copper deposited by}\ \frac{2\times96500}{22.4}\times67.2\ \text{coulomb}$$

$$= \frac{63.5}{2\times96500}\times\frac{2\times96500\times67.2}{22.4}$$

$$= 190.5\ \text{g}$$

Example 48. *Neglecting the liquid-liquid junction potential, calculate the emf of the following cell at 25° C:*

$$H_2(1\ atm)|\ 0.5\ M\ HCOOH\ ||\ 1M\ CH_3COOH\ |\ (1\ atm)\ H_2$$

K_a for HCOOH and CH_3COOH are 1.77×10^{-4} and 1.8×10^{-5} respectively.

Solution:

$$[H^+]\ \text{in HCOOH} = \sqrt{C\times K_a} = \sqrt{0.5\times1.77\times10^{-4}}$$

$$= 0.9407\times10^{-2}\ M$$

$$[H^+]\ \text{in}\ CH_3COOH = \sqrt{C\times K_a} = \sqrt{1\times1.8\times10^{-5}}$$

$$= 4.2426\times10^{-3}\ M$$

$$E_{\text{cell}} = 0.0591\log\frac{[H^+]_{\text{RHS}}}{[H^+]_{\text{LHS}}} = 0.0591\log\frac{4.2426\times10^{-3}}{0.9407\times10^{-2}}$$

$$= -\ 0.0204\ \text{volt}$$

Example 49. *During the discharge of a lead storage battery, density of H_2SO_4 fell from 1.294 to 1.139 g/mL. Sulphuric acid of density 1.294 is 39% H_2SO_4 by weight and that of density 1.139 g/mL is 20% H_2SO_4 by weight. The battery holds 3.5 litre of the acid and volume remains practically constant during discharge. Calculate ampere-hour of which the battery must have been used. The charging and discharging reactions are:*

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^- \quad (charging)$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O\ (discharging)$$

Solution:

$$\text{Weight of solution before discharge} = 3500\times1.294$$

$$= 4529\ \text{g}$$

$$\text{Weight of}\ H_2SO_4\ \text{before discharge} = \frac{39}{100}\times4529$$

$$= 1766.31\ \text{g}$$

$$\text{Weight of solution after discharge} = 3500\times1.139$$

$$= 3986.5\ \text{g}$$

$$\text{Weight of}\ H_2SO_4\ \text{after discharge} = \frac{20}{100}\times3986.5$$

$$= 797.3\ \text{g}$$

Loss in mass of H_2SO_4 during discharge

$$= 1766.31 - 797.3 = 969.01\ \text{g}$$

Now from first law of electrolysis,

$$W = \frac{Q\times E}{96500}$$

$$969.01 = \frac{Q\times98}{96500}$$

$$Q = 954178.21\ \text{coulomb}$$

$$\text{Ampere-hour} = \frac{\text{Coulomb}}{3600} = \frac{954178.21}{3600}$$

$$= 265.04\ \text{ampere-hour}$$

12.28 COMMERCIAL PRODUCTION OF CHEMICALS

The wide applications of electrolysis have been listed in section 12.4 of this chapter. A large number of chemicals are produced by electrolysis. A few of these are described below:

1. Manufacture of sodium

Sodium is obtained on large scale by two processes:

(i) Castner's process: In this process, electrolysis of fused sodium hydroxide is carried out at 330°C using iron as cathode and nickel as anode.

$$2NaOH \rightleftharpoons 2Na^+ + 2OH^-$$

At cathode: $2Na^+ + 2e \longrightarrow 2Na$

At anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e$

During electrolysis, oxygen and water are produced. Water formed at the anode gets partly evaporated and is partly broken down and hydrogen is discharged at cathode.

$$H_2O \rightleftharpoons H^+ + OH^-$$

At cathode: $2H^+ + 2e \longrightarrow 2H \longrightarrow H_2 \uparrow$

(ii) Down's process: Now-a-days sodium metal is manufactured by this process. It involves the electrolysis of fused sodium chloride containing calcium chloride and potassium fluoride using iron as cathode and graphite as anode at about 600°C (Fig. 12.21).

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At cathode: $Na^+ + e \longrightarrow Na$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

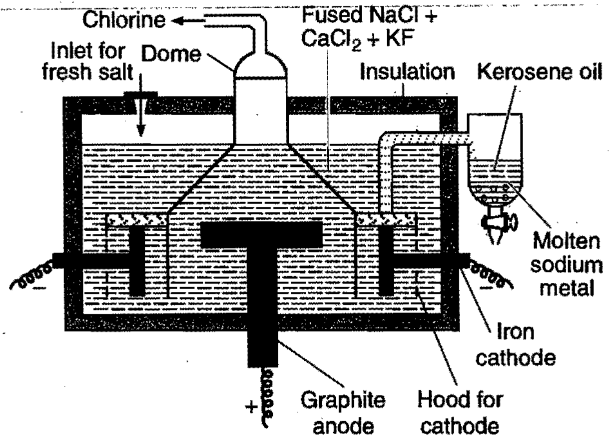


Fig. 12.21 Down's cell for extraction of sodium

The electrolysis of pure NaCl presents the following difficulties:

(a) The fusion temperature of NaCl is high, *i.e.*, 803°C. At this temperature both sodium and chlorine are corrosive.

(b) Sodium forms a metallic fog at this temperature.

To remove above difficulties, the fusion temperature is reduced to 600°C by adding $CaCl_2$ and KF. This is a cheaper method and **chlorine is obtained as a byproduct.** The sodium obtained is of high purity (about 99.5%).

2. Sodium hydroxide (Caustic soda), NaOH

Caustic soda is manufactured by the electrolysis of aqueous solution of sodium chloride in an electrolytic cell.

Principle: A sodium chloride solution contains Na^+, H^+, Cl^- and OH^- ions.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

On passing electricity, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. The discharge potential of H^+ ions is less than Na^+ ions, thus hydrogen ions get discharged easily and hydrogen is liberated. Similarly, at anode Cl^- ions are easily discharged as their discharge potential is less than that of OH^- ions. Cl_2 gas is, therefore, liberated at anode.

The solution on electrolysis becomes richer in Na^+ and OH^- ions.

Since, chlorine reacts with sodium hydroxide solution even in the cold forming sodium chloride and sodium hypochlorite, it is necessary that chlorine should not come in contact with sodium hydroxide during electrolysis.

$$2NaOH + Cl_2 \longrightarrow NaCl + NaClO + H_2O$$

To overcome this problem, the anode is separated from the cathode in the electrolytic cell either by using a porous diaphragm or by using a mercury cathode.

(i) Porous diaphragm process (Nelson cell process): Nelson cell consists of a perforated steel tube lined inside with asbestos. The tube acts as a cathode (Fig. 12.22). It is suspended in a steel tank. A graphite rod dipped in sodium chloride solution serves as anode. On passing electric current, chlorine is liberated at the anode and let out through the outlet. Sodium ions penetrate through the asbestos and reach the cathode where hydrogen and OH^- ions are formed by reduction of water. Sodium ions combine with OH^- ions to form NaOH which is collected in the outer tank while hydrogen is drawn off through the outlet. The steam blown during the process keeps the electrolyte warm and helps to keep perforation clear.

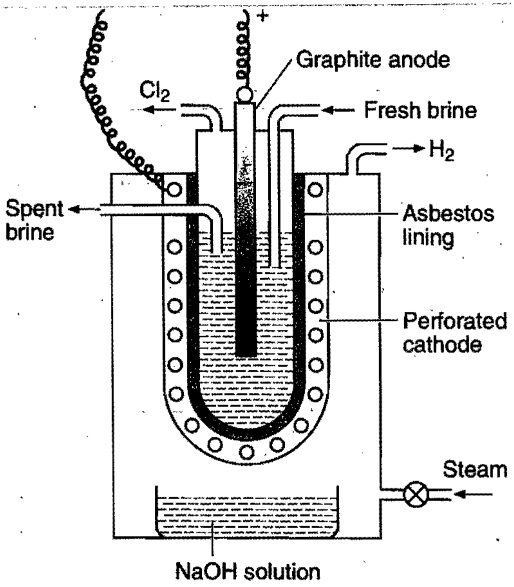


Fig. 12.22 Nelson cell

$$NaCl \rightleftharpoons Na^+ + Cl^- \quad \text{(in solution)}$$

At cathode: $2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$

$$Na^+ + OH^- \rightleftharpoons NaOH$$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$

The solution containing NaOH and NaCl as impurity is taken out and evaporated to dryness.

(ii) Castner-Kellner cell: This is the common cell in which mercury is used as cathode. The advantage of using Hg as a cathode is that the discharge potential of Na^+ ions is less than that of H^+ ions. Na^+ ions get discharged on mercury and the sodium so deposited combines with mercury to form sodium amalgam. The cell consists of a large rectangular trough divided into three compartments by slate partitions which do not touch the bottom of the cell but dipping in mercury as shown in the Fig. 12.23.

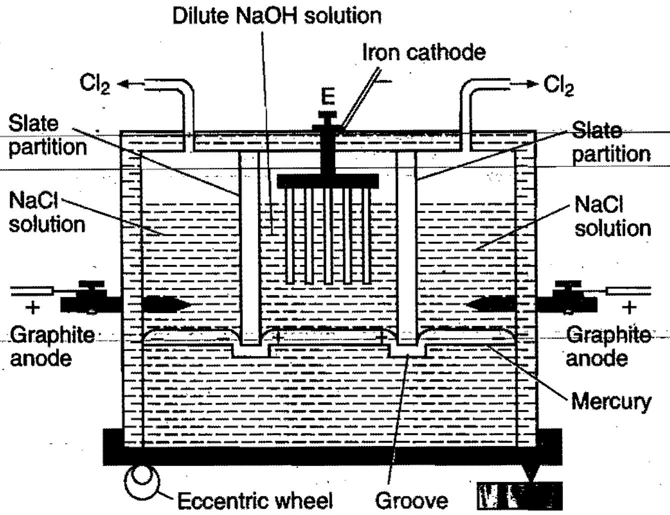


Fig. 12.23 Castner-Kellner cell

The mercury can flow from one compartment into other but the solution kept in one compartment cannot flow into other. Sodium chloride solution is placed in the two outer compartments and a dilute solution of sodium hydroxide in the inner compartment. Two graphite electrodes which act as anodes are fixed in the outer compartments and a series of iron rods fitted in the inner compartment acts as cathode. Mercury in the outer compartments acts as cathode while in the inner compartment it acts as anode by induction. The cell is kept rocking with the help of an eccentric wheel.

When electricity is circulated, sodium chloride in the outer compartments is electrolysed. Chlorine is evolved at the graphite anode while Na^+ ions are discharged at the Hg cathode. The liberated sodium forms amalgam with mercury.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

At anode: $2Cl^- \longrightarrow 2Cl + 2e \longrightarrow Cl_2$

At cathode: $Na^+ + e \longrightarrow Na$

$$Na + Hg \longrightarrow \text{Amalgam}$$

The sodium amalgam thus formed comes in the inner compartment due to rocking. Here, the sodium amalgam acts as the anode and iron rods acts as cathode.

At anode: $\text{Na-amalgam} \longrightarrow Na^+ + Hg + e$

At cathode: $2H_2O + 2e \longrightarrow H_2\uparrow + 2OH^-$

The concentrated solution of sodium hydroxide (about 20%) is taken out from the inner compartment and evaporated to dryness to get solid NaOH.

(iii) Kellner-Solvay cell: This is the modified cell. This cell has no compartments. The flowing mercury as shown in Fig. 12.24 acts as cathode. A number of graphite rods dipping in sodium chloride solution act as anode. A constant level of sodium chloride solution is maintained in the cell. On electrolysis chlorine gas is liberated and Na^+ ions are discharged at cathode (mercury). Sodium discharged dissolves in Hg and forms amalgam. This amalgam flows out in a vessel containing water. Sodium hydroxide is formed with evolution of hydrogen.

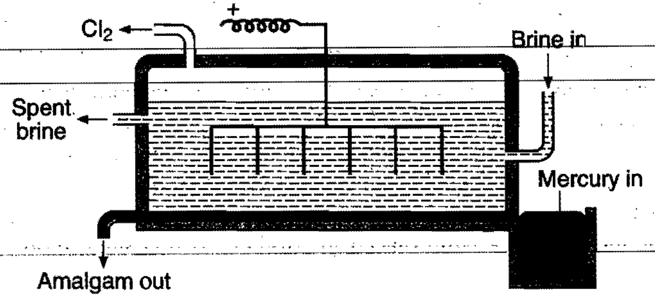


Fig. 12.24 Kellner-Solvay cell

Preparation of pure sodium hydroxide: Commercial sodium hydroxide is purified with the help of alcohol. Sodium hydroxide dissolves in alcohol while impurities like NaCl, Na_2CO_3, Na_2SO_4, etc., remain insoluble. The alcoholic filtrate is distilled. The alcohol distills off while pure solid sodium hydroxide is left behind.

3. Manufacture of aluminium

Aluminium is manufactured from pure bauxite ore by electrolysis. The bauxite ore usually contains impurities such as iron oxide, silica, etc. These impurities are first removed by the application of the following methods in order to get pure alumina, *i. e.*, pure bauxite ore:

(a) Hall's process; (b) Baeyer's process; (c) Serpeck's process.

Electrolytic reduction of pure alumina: The electrolysis of pure alumina faces two difficulties: (i) Pure alumina is a bad conductor of electricity and (ii) The fusion temperature of pure alumina is about 2000°C and at this temperature when the electrolysis is carried of the fused mass, the metal formed vapourises as the boiling point of aluminium is 1800°C.

The above difficulties are overcome by using a mixture containing alumina, cryolite (Na_3AlF_6) and fluorspar (CaF_2) in the ratio of 20 : 60 : 20. The fusion temperature of this mixture is 900°C and it is a good conductor of electricity.

The electrolysis is carried out in an iron box lined inside with gas carbon which acts as cathode. The anode consists of carbon rods which dip in the fused mixture of the electrolyte from above. The fused electrolyte is covered with a layer of coke (Fig. 12.25).

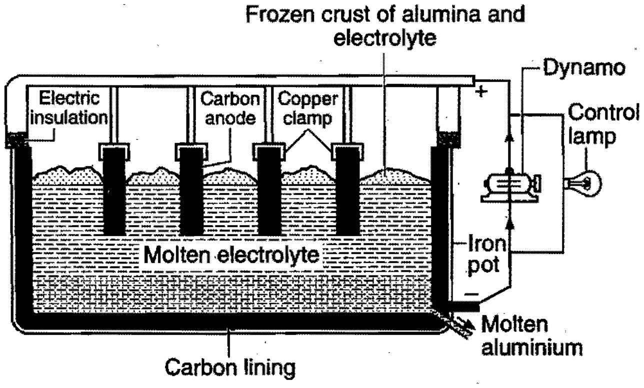


Fig. 12.25

The current passed through the cell serves two purposes: (i) Heating of the electrolyte: The temperature of the cell is automatically maintained at 900 – 950°C. (ii) Electrolysis: On passing current, aluminium is discharged at cathode. Aluminium being heavier than the electrolyte sinks to the bottom and is tapped out periodically from a tapping hole. Oxygen is liberated at anode. It attacks the carbon rods forming CO and CO_2. The process is continuous. When the concentration of the electrolyte decreases, the resistance of the cell increases. This is indicated by the glowing of a lamp placed in parallel. At this stage more of alumina is added.

The exact mechanism of the electrolysis is not yet known. Two concepts have been proposed.

First concept: AlF_3 from cryolite ionises as:

$$AlF_3 \rightleftharpoons Al^{3+} + 3F^-$$

Al^{3+} ions are discharged at cathode and F^- ions at anode.

$$Al^{3+} + 3e \longrightarrow Al \text{ (at cathode)}$$

$$2F^- \longrightarrow F_2 + 2e \text{ (at anode)}$$

The liberated fluorine reacts with alumina to form AlF_3 and O_2. The oxygen attacks the carbon anodes to form CO and CO_2.

$$Al_2O_3 + 3F_2 \longrightarrow 2AlF_3 + \frac{3}{2}O_2$$

$$2C + O_2 \longrightarrow 2CO$$

$$C + O_2 \longrightarrow CO_2$$

Anodes are replaced frequently.

Second concept: Alumina (Al_2O_3) ionises as:

$$Al_2O_3 \rightleftharpoons \underset{\text{Cathode}}{Al^{3+}} + \underset{\text{Anode}}{AlO_3^{3-}}$$

$$Al^{3+} + 3e \longrightarrow Al \text{ (at cathode)}$$

At anode AlO_3^- is oxidised.

$$4AlO_3^{3-} \longrightarrow 2Al_2O_3 + 3O_2 + 12e \text{ (at anode)}$$

Thus, the overall chemical reaction taking place during electrolysis is,

$$2Al_2O_3 \longrightarrow 4Al + 3O_2$$

Aluminium of 99.8% purity is obtained from this process.

Refining of aluminium by Hoope's electrolytic method: Aluminium is further purified by Hoope's process. The electrolytic cell consists of an iron box lined inside with carbon. The cell consists of three layers which differ in specific gravities. The upper layer is of pure aluminium which acts as cathode. The middle layer consists of a mixture of the fluorides of Al, Ba and Na. The lowest layer consists of impure aluminium which acts as anode. The middle layer works as electrolyte.

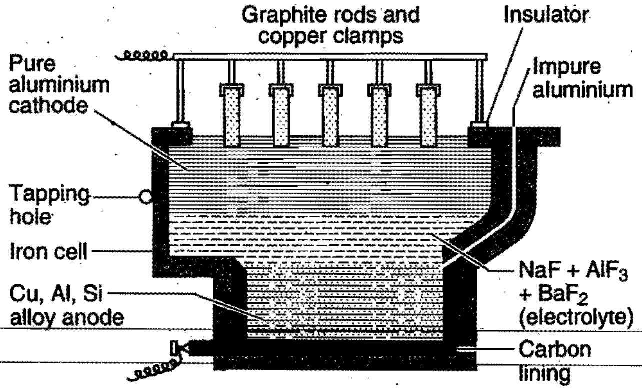


Fig. 12.26

The graphite rods are dipped in pure aluminium and Cu-Al alloy rods at the bottom of impure aluminium work as conductors. On electrolysis, aluminium is deposited at the cathode from the middle layer and an equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while impurities are left behind. Aluminium thus obtained is 99.98%.

4. Isolation of fluorine

Fluorine presented many difficulties in its isolation. It remained a difficult problem in chemistry for many years and after a hard labour of many chemists for about 75 years it could be isolated finally by **Moissan** in 1886. **The reasons for its late discovery were its high reactivity and non-conducting nature of hydrofluoric acid.** Fluorine attacked the material of the vessels used for its isolation. Carbon vessel was attacked with formation of CF_4 and platinum vessel was reduced to chocolate powder. The vessels of other metals were also affected. Platinum and carbon could not be used as electrodes. Another difficulty experienced was that when the electrolysis of aqueous hydrofluoric acid was carried out, hydrogen and oxygen (ozone) were obtained and when anhydrous hydrofluoric acid was tried it was found to be a bad conductor of electricity.

Moissan finally solved the problem and isolated fluorine by the electrolysis of anhydrous hydrofluoric acid in the presence of potassium hydrogen fluoride using Pt-Ir alloy vessel at –23°C. The electrodes used were also of Pt-Ir alloy.

Modern methods of isolation: In modern methods, fluorine is prepared by electrolysis of a fused fluoride (usually potassium hydrogen fluoride, KHF_2). The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite and the fluorine set free contains some carbon tetrafluoride.

Reactions in the electrolytic cell

$$KHF_2 \longrightarrow KF + HF$$

$$\Downarrow$$

$$K^+ + F^-$$

Cathode	Anode
$K^+ + e \rightarrow K$	$F^- \rightarrow F + e$
$K + HF \rightarrow KF + H$	$2F \rightarrow F_2$
$2H \rightarrow H_2$	

The following precautions should be taken in the preparation of fluorine:

(i) The electrolyte must be completely dry. In presence of moisture, the evolved fluorine reacts with moisture to form O_2 and O_3.

(ii) The parts of the apparatus which come in contact with fluorine must be free from oil and grease.

(iii) The vessel in which fluorine is collected should also be absolutely dry.

(iv) The gas must be made free from HF before storing by passing through sodium fluoride (NaF), otherwise HF will attack the vessel.

Note: HF is more corrosive and reactive than fluorine.

Dennis method: The electrolytic cell used in this method consists of a V-shaped copper tube (5 cm in diameter) fitted with copper caps. Graphite electrodes through these caps are sealed and insulated in the tube by bakelite cement which is not affected by fluorine. The cell is covered with an insulating layer of asbestos cement over which is wound a resistance wire for electrical heating. The tube is thickly lagged to prevent the loss of heat.

The electrolyte consists of fused potassium hydrogen fluoride which has already been dried for 48 hours at 130°C. The electrolyte is kept in fused state by electrical heating externally. For electrolysis, a current of 5 ampere and 12 volt is used. On electrolysis fluorine is liberated at anode. To make the liberated fluorine free from HF vapours, it is passed through copper U-tubes containing sodium fluoride.

$$NaF + HF \longrightarrow NaHF_2$$

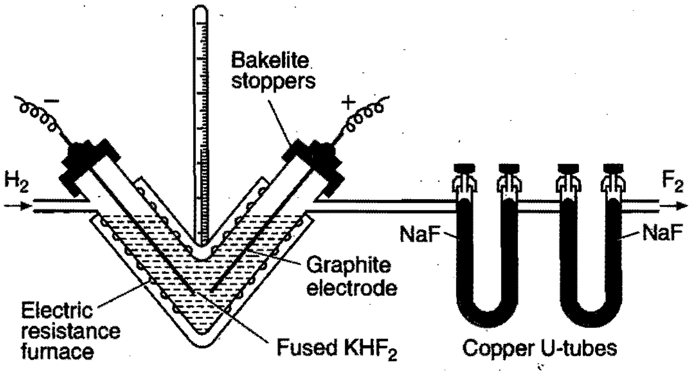


Fig. 12.27

The following difficulty is experienced in this method: The liberated fluorine at anode does not escape fast enough due to narrow exit. The escape is further hindered due to frothing in the electrolyte. There are, thus, chances of mixing of H_2 and F_2 which may result in explosion. To avoid this, a modified apparatus has been devised by Whytlaw-Gray.

Whytlaw-Gray method: It consists of a copper cell wound with resistance wire for electrical heating. The pure graphite anode is enclosed in a copper cylinder which is perforated at the bottom (Fig. 12.28). The electrolysis of fused KHF_2 is carried out in this cell. The escape of fluorine is fast enough and thus no frothing in the electrolyte occurs. There are no chances of mixing of H_2 and F_2 in this cell.

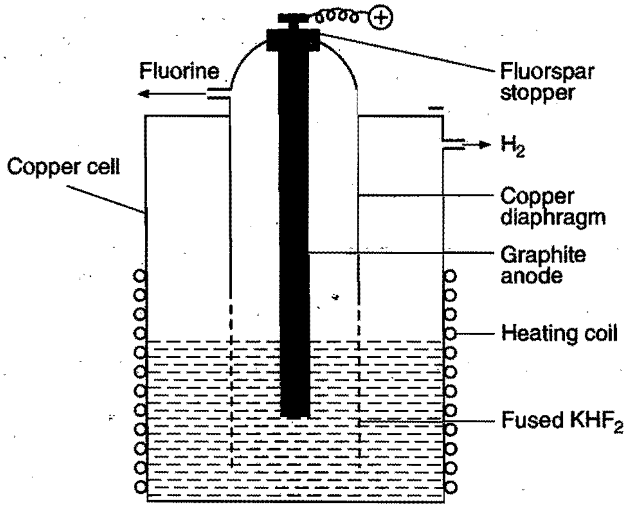


Fig. 12.28

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Anodic oxidation of ammonium hydrogen sulphate produces ammonium persulphate.*

$$NH_4HSO_4 \longrightarrow NH_4SO_4^- + H^+$$

$$2NH_4SO_4^- \longrightarrow (NH_4)_2S_2O_8 + 2e^- \ (Anodic\ oxidation)$$

$$2H^+ + 2e^- \longrightarrow H_2 \ (Cathodic\ reduction)$$

Hydrolysis of ammonium persulphate forms H_2O_2.

$$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow 2NH_4HSO_4 + H_2O_2$$

Current efficiency in electrolytic process is 60%. Calculate the amount of current required to produce 85 g of H_2O_2 per hour. Hydrolysis reaction shows 100% yield.

Solution: Given,

$$\underset{228\,\text{g}}{(\text{NH}_4)_2\text{S}_2\text{O}_8} + \text{H}_2\text{O} \longrightarrow 2\text{NH}_4\text{HSO}_4 + \underset{34\,\text{g}}{\text{H}_2\text{O}_2}$$

$\because$ 34 g H_2O_2 is produced by 228 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$

$\therefore$ 85 g H_2O_2 will be produced by $\frac{228}{24} \times 85$ g $(\text{NH}_4)_2\text{S}_2\text{O}_8$

$$= 570\,\text{g}$$

Equivalent mass of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ may be calculated using the following reaction:

$$2\text{NH}_4\text{SO}_4^- \longrightarrow (\text{NH}_4)_2\text{S}_2\text{O}_8 + 2e$$

$$\text{Equivalent mass of } (\text{NH}_4)_2\text{S}_2\text{O}_8 = \frac{\text{Mol. mass}}{2} = \frac{228}{2} = 114$$

From first law of electrolysis,

$$W = \frac{ItE}{96500}$$

$$570 = \frac{I \times 3600 \times 114}{96500}$$

$$I = 134.0277 \text{ ampere}$$

Given that, current efficiency is 60%, the actual amount of current

$$= \frac{100}{60} \times 134.0277$$

$$= 223.379 \text{ ampere}$$

Example 2. *In a zinc manganese dioxide dry cell, the anode is made up of zinc and cathode of a carbon rod surrounded by a mixture of MnO_2, carbon, NH_4Cl and $ZnCl_2$ in aqueous base.*

The cathodic reaction may be represented as:

$$2MnO_2(s) + Zn^{2+} + 2e^- \longrightarrow ZnMn_2O_4(s)$$

Let there be 8 g MnO_2 in the cathodic compartment. How many days will the dry cell continue to give a current of 4×10^{-3} ampere?

Solution: When MnO_2 will be used up in cathodic process, the dry cell will stop to produce current.

Cathodic process:

$$2\overset{+4}{\text{MnO}_2}(s) + \text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}\overset{+3}{\text{Mn}}_2\text{O}_4$$

$$\text{Equivalent mass of MnO}_2 = \frac{\text{Molecular mass}}{\text{Change in oxidation state}}$$

$$= \frac{87}{1} = 87$$

From first law of electrolysis,

$$W = \frac{ItE}{96500}$$

$$8 = \frac{4 \times 10^{-3} \times t \times 87}{96500}$$

$$t = 2218390.8 \text{ second}$$

$$= \frac{2218390.8}{3600 \times 24} = 25.675 \text{ day}$$

Example 3. *Ten gram of a fairly concentrated solution of cupric sulphate is electrolysed using 0.01 faraday of electricity. Calculate:*

(*i*) *The mass of the resulting solution;*

(*ii*) *The number of equivalents of acid or alkali in the solution.*

Solution: Electrode process during electrolysis of aqueous CuSO_4 may be given as:

$$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu (Cathode)}$$

$$2\text{OH}^- \longrightarrow \text{H}_2\text{O} + \tfrac{1}{2}\text{O}_2 + 2e^- \text{ (Anode)}$$

Mass of copper deposited at cathode by 0.01 faraday charge

$= 0.01 \times 31.75$

$= 0.3175$ g

(Here, 31.75 is the equivalent mass of Cu^{2+}.)

Mass of oxygen evolved by 0.01 faraday charge

$= 0.01 \times 8 = 0.08$ g

Total weight loss from solution $= 0.3175 + 0.08 = 0.3975$ g

Mass of resulting solution $= 10 - 0.3975$

$= 9.6025$ g

After deposition of Cu^{2+} and OH^- ions at the respective electrodes, H_2SO_4 will prevail in the solution. 0.01 faraday of electricity will result in 0.01 equivalent of acid.

Example 4. *A current of 40 microampere is passed through silver nitrate solution for 16 minutes using platinum electrodes. 50% of the cathode is occupied by a single atom thick silver layer. Calculate the total surface area of the cathode if one silver atom occupies 5.5×10^{-16} cm^2 surface area.*

Solution: Mass of silver deposited may be calculated according to Faraday's first law of electrolysis.

$$W = \frac{ItE}{96500}$$

$$= \frac{40 \times 10^{-6} \times 60 \times 16 \times 108}{96500}$$

$$= 42.976 \times 10^{-6} \text{ g}$$

Total number of deposited 'Ag' atoms

$$= \frac{42.976 \times 10^{-6}}{108} \times 6.023 \times 10^{23}$$

$$= 2.3967 \times 10^{17} \text{ atoms}$$

Surface occupied by deposited silver

= number of silver atoms × area occupied by a single atom

$= 2.3967 \times 10^{17} \times 5.5 \times 10^{-16}$

$= 131.818 \text{ cm}^2$

Since, deposited silver occupies 50% of total area of cathode, hence,

Total surface area of cathode $= 2 \times 131.818$

$$= 263.636 \text{ cm}^2$$

Example 5. *A pin of 2 cm length and 0.4 cm diameter was placed in $AgNO_3$ solution through which a 0.2 ampere current was passed for 10 minute to deposit silver on the pin. The pin was used by a surgeon in lachrymal duct operation. The density of silver and electrochemical equivalent are 1.05×10^4 kg m^{-1} and 1.118×10^{-6} kg/coulomb respectively. What is the thickness of silver deposited on the pin? Assume that the tip of the pin contains negligible mass of silver?*

Solution: From Faraday's first law,

$$W = ZIt$$

$$= 1.118 \times 10^{-6} \times 0.2 \times 10 \times 60 = 1.34 \times 10^{-4} \text{ kg}$$

$$V = \frac{W}{d} = \frac{1.34 \times 10^{-4}}{1.05 \times 10^4} = 1.277 \times 10^{-8} \text{ m}^3$$

$$= 1.277 \times 10^{-2} \text{ cm}^3 \quad \text{... (i)}$$

Surface area of pin $= 2\pi rh$

$$= 2 \times 3.14 \times 0.2 \times 2$$

$$= 2.512 \text{ cm}^2$$

Surface area may be treated as that of a rectangle of length 'h' and breadth $2\pi r$. Let the thickness of the coating be 'd' cm. Then

Volume of the occupied metal $= 2.512 \times d \text{ cm}^3$ ... (ii)

From equations (i) and (ii), we get

$$1.277 \times 10^{-2} = 2.512 \times d$$

$$d = 0.5083 \times 10^{-2} \text{ cm}$$

$$= 5.083 \times 10^{-5} \text{ metre}$$

Example 6. *The specific conductivity of a saturated solution of silver chloride is 2.30×10^{-6} mho cm^{-1}, at 25° C. Calculate the solubility of silver chloride at 25° C if $\lambda_{Ag^+} = 61.9$ mho cm^2 mol^{-1} and $\lambda_{Cl^-} = 76.3$ mho cm^2 mol^{-1}.*

Solution: Let the solubility of AgCl be s gram mole per litre

$$\text{Dilution} = \frac{1000}{S}$$

$$\Lambda^{\infty}_{AgCl} = \lambda_{Ag^+} + \lambda_{Cl^-}$$

$$= 61.9 + 76.3$$

$$= 138.2 \text{ mho cm}^2 \text{ mol}^{-1}$$

$$\text{Sp. conductivity} \times \text{dilution} = \Lambda^{\infty}_{AgCl} = 138.2$$

$$2.30 \times 10^{-6} \times \frac{1000}{S} = 138.2$$

$$S = \frac{2.30 \times 10^{-3}}{138.2} = 1.66 \times 10^{-5} \text{ mol per litre}$$

$$= 1.66 \times 10^{-5} \times 143.5 \text{ gL}^{-1}$$

$$= 2.382 \times 10^{-3} \text{ gL}^{-1}$$

Example 7. *Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solutions being taken in the same conductivity cell. If equal volumes of solutions (A) and (B) are mixed, what will be the resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing.*

Solution: Let us suppose κ_1 and κ_2 are the specific conductances of solutions 'A' and 'B' respectively and cell constant is 'y'. We know that,

Specific conductance = Conductance × Cell constant

For (A), $\kappa_1 = \frac{1}{50} \times y$

For (B), $\kappa_2 = \frac{1}{100} \times y$

When equal volumes of (A) and (B) are mixed, the volume becomes double. Then,

$$\text{Specific conductance of mixture} = \frac{\kappa_1 + \kappa_2}{2}$$

$$\therefore \quad \frac{\kappa_1 + \kappa_2}{2} = \frac{1}{R} \times y$$

$$\frac{1}{2}\left[\frac{y}{50} + \frac{y}{100}\right] = \frac{1}{R} \times y$$

$$\frac{1}{100} + \frac{1}{200} = \frac{1}{R}$$

$$R = 200/3 = 66.66 \text{ ohm}$$

Example 8. *A big irregular shaped vessel contained water, specific conductance of which was 2.56×10^{-5} mho cm^{-1}. 500 g of NaCl was then added to the water and the specific conductance after the addition of NaCl was found to be*

3.1×10^{-5} mho cm^{-1}. Find the capacity of the vessel if it was fully filled with water. (Λ^{∞} NaCl $= 149.9$ ohm^{-1} cm^{2} eq^{-1})

Solution: Let us suppose the volume of vessel is V mL

Volume containing 1 equivalent

$$=\frac{\text{Volume}}{\text{Mass / equivalent mass}}$$

$$=\frac{V}{500/58.5}=\frac{V}{8.547}$$

Specific conductance of NaCl

= Specific conductance of NaCl solution − Specific conductance of water

$$=3.1\times10^{-5}-2.56\times10^{-5}$$

$$=0.54\times10^{-5}\ \text{mho cm}^{-1}$$

$\Lambda=\kappa\times$ volume containing 1 equivalent of electrolyte ...(i)

For very dilute solution, when the big vessel is fully filled

$$\Lambda^{\infty}_{\text{NaCl}}=149.9\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

Thus, from eq. (i),

$$149.9=0.54\times10^{-5}\times\frac{V}{8.547}$$

$$V=237258.38\ \text{L}$$

Example 9. *A 0.05 N solution of a salt occupying a volume between two platinum electrodes separated by a distance of 1.72 cm and having an area of 4.5 cm^2 has a resistance of 250 ohm. Calculate the equivalent conductance of the solution.*

Solution:

Specific conductance = conductance × cell constant

$$\kappa=C\times\frac{l}{A}$$

$$=\frac{1}{R}\times\frac{l}{A}$$

$$=\frac{1}{250}\times\frac{1.72}{4.5}$$

$$=1.5288\times10^{-3}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\Lambda_e=\kappa\times\frac{1000}{N}$$

$$=1.5288\times10^{-3}\times\frac{1000}{0.05}$$

$$=30.56\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

Example 10. *At 18° C, the mobilities of NH_4^+ and ClO_4^- ions are 6.6×10^{-4} and 5.7×10^{-4} cm^2 volt^{-1} sec^{-1} at infinite dilution. Calculate the equivalent conductance of ammonium chlorate solution.*

Solution: $\Lambda^{\infty}_{NH_4ClO_4}=\lambda^{\infty}_{NH_4^+}+\lambda^{\infty}_{ClO_4^-}$

$$=(U^{\infty}_{NH_4^+}+U^{\infty}_{ClO_4})F$$

$$=(6.6\times10^{-4}+5.7\times10^{-4})\times96500$$

$$=118.69\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

Example 11. *For the cell reaction,*

$$Mg\,|\,Mg^{2+}(aq.)\,||\,Ag^+(aq.)\,|\,Ag$$

calculate the equilibrium constant at 25° C and maximum work that can be obtained by operating the cell.

$$E^{\circ}_{Mg^{2+}/Mg}=-2.37\ \textit{volt}\ \text{ and }\ E^{\circ}_{Ag^+/Ag}=+0.80\ \textit{volt}$$

Solution: $E^{\circ}_{\text{cell}}=0.80+2.37=3.17$ volt

$$\log K_c=\frac{nE^{\circ}_{\text{cell}}}{0.0591}$$

$$=\frac{2\times3.17}{0.0591}=107.2758$$

$$K_c=1.89\times10^{107}$$

$$-\Delta G=\text{maximum work}$$

$$=nFE^{\circ}=2\times96500\times3.17$$

$$=611810\ \text{J}$$

Example 12. *Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25° C until the equilibrium is reached. If the standard reduction potentials of Zn^{2+}/Zn and Ni^{2+}/Ni are −0.75 and −0.24 volt respectively, find out the concentration of Ni^{2+} ions in solution at equilibrium.* (IIT 1991)

Solution: The reaction to be considered is,

$$\text{Zn}(s)+\text{Ni}^{2+}(aq.)\rightleftharpoons\text{Zn}^{2+}(aq.)+\text{Ni}(s)$$

The cell involving this reaction would be,

$$\text{Zn}(s)\,|\,\text{Zn}^{2+}(aq.)\,||\,\text{Ni}^{2+}(aq.)\,|\,\text{Ni}(s)$$

$$E^{\circ}_{\text{cell}}=-0.24+0.75=0.51\ \text{volt}$$

$$\log K_{\text{eq}}=\frac{nFE^{\circ}}{2.303\,RT}=\frac{nE^{\circ}}{0.0591}=\frac{2\times0.51}{0.0591}=17.25$$

So, $K_{\text{eq}}=1.78\times10^{17}$

Let x be the concentration of Ni^{2+} that have been reduced to nickel at equilibrium.

$$\underset{(1.0-x)}{\text{Zn}(s)+\text{Ni}^{2+}(aq.)}\rightleftharpoons\underset{x}{\text{Zn}^{2+}(aq.)}+\text{Ni}(s)$$

$$K_{\text{eq}}=\frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}=\frac{x}{(1-x)}=1.78\times10^{17}$$

$$x\approx1.0\,M$$

So, $(1-x)=[\text{Ni}^{2+}]=\dfrac{1.0}{1.78\times10^{17}}=5.6\times10^{-18}\ M$

Example 13. *The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt* *respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of* Ag^+ *will the emf of the cell at 25° C be zero if concentration of* Cu^{2+} *is* 0.01 *M?* (IIT 1990)

Solution: Given, $E^\circ_{Cu^{2+}/Cu} = 0.337$ volt and $E^\circ_{Ag^+/Ag} = 0.799$ volt. The standard emf will be positive if Cu / Cu^{2+} is anode and Ag^+ / Ag is cathode. The cell can be represented as:

$$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$$

The cell reaction is,

$$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

$$E^\circ_{cell} = \text{Oxid. potential of anode} + \text{Red. potential of cathode}$$

$$= -0.337 + 0.799$$

$$= 0.462 \text{ volt}$$

Applying the Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

When, $E_{cell} = 0$

$$E^\circ_{cell} = \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

or $$\log \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.462 \times 2}{0.0591} = 15.6345$$

$$\frac{[Cu^{2+}]}{[Ag^+]^2} = 4.3102 \times 10^{15}$$

$$[Ag^+]^2 = \frac{0.01}{4.3102 \times 10^{15}}$$

$$= 0.2320 \times 10^{-17}$$

$$= 2.320 \times 10^{-18}$$

$$[Ag^+] = 1.523 \times 10^{-9}\ M$$

Example 14. *The standard reduction potential for the half- cell having reaction,*

$$NO_3^- (aq.) + 2H^+ (aq.) + e^- \longrightarrow NO_2 (g) + H_2O$$

is 0.78 *volt.*

(*i*) *Calculate the reduction potential in* 8 *M* H^+.

(*ii*) *What will be the reduction potential of the half-cell in a neutral solution?*

Assume all other species to be at unit concentration. (IIT [illegible])

Solution: (i) Applying the formula,

$$E_{red} = E^\circ_{red} + \frac{0.0591}{n} \log [H^+]^2$$

$$= 0.78 + \frac{0.0591}{2} \log 8^2$$

$$= 0.78 + 0.0591 \times 3 \times 0.3010$$

$$= 0.833 \text{ volt}$$

(ii) $$E_{red} = 0.78 + \frac{0.0591}{2} \log (10^{-7})^2$$

[For neutral solution $[H^+] = 10^{-7}\ M$]

$$= 0.78 - 0.0591 \times 7$$

$$= 0.367 \text{ volt}$$

Example 15. *The emf of a cell corresponding to the reaction,*

$$Zn + 2H^+ (aq.) \longrightarrow Zn^{2+}\ (0.1 M) + H_2 (g)\ 1\, atm$$

is 0.28 *volt at* 25° *C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.*

$$E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ volt} \quad \text{and} \quad E^\circ_{H^+/H_2} = 0$$

Solution: $E^\circ_{cell} = 0.76$ volt

Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}][H_2]}{[H^+]^2}$$

$$0.28 = 0.76 - \frac{0.0591}{2} \log \frac{(0.1) \times 1}{[H^+]^2}$$

$$\log \frac{0.1}{[H^+]^2} = \frac{2 \times 0.48}{0.0591}$$

$$\log 0.1 - \log [H^+]^2 = 16.2436 \qquad [\text{Since, } -\log [H^+] = \text{pH}]$$

$$2\, \text{pH} = 16.2436 - \log 0.1$$

$$\text{pH} = \frac{17.2436}{2} = 8.6218$$

Example 16. *Calculate the solubility product constant of AgI from the following values of standard electrode potentials.*

$$E^\circ_{Ag^+/Ag} = 0.80 \text{ volt} \quad \text{and} \quad E^\circ_{I/AgI/Ag} = -0.15 \text{ volt} \quad \text{at } 25^\circ C.$$

Solution: Solubility product of AgI = $[Ag^+][I^-]$

[**Note:** See chapter 10 for solubility product.]

Two half reactions for the cell are:

$$Ag \longrightarrow Ag^+ + e^- \qquad \text{Anode (Oxidation)}$$

$$AgI + e^- \longrightarrow Ag + I^- \qquad \text{Cathode (Reduction)}$$

$$\text{Cell reaction} \qquad AgI \longrightarrow Ag^+ + I^-$$

Applying Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1} \log \frac{[Ag^+][I^-]}{[AgI]}$$

At equilibrium, $E_{cell} = 0$ and $[AgI] = 1$

So, $$\log [Ag^+][I^-] = \frac{E^\circ_{cell}}{0.0591}$$

$$E^\circ_{cell} = -0.80 - 0.15 = -0.95 \text{ volt}$$

$$\log[\mathrm{Ag^+}][\mathrm{I^-}] = -\frac{0.95}{0.0591} = -16.0744$$

Solubility product of AgI $= 8.4 \times 10^{-17}$

Example 17. *The standard reduction potential of Ag^+/Ag electrode at 298K is 0.799 volt. Given for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^-/AgI/Ag$ electrode.* (IIT 1994)

Solution: In the saturated solution of AgI, the half-cell reactions are:

$$\mathrm{AgI} + e^- \longrightarrow \mathrm{Ag} + \mathrm{I^-} \quad \text{Cathode (Reduction)}$$

$$\mathrm{Ag} \longrightarrow \mathrm{Ag^+} + e^- \quad \text{Anode (Oxidation)}$$

$$\text{Cell reaction} \quad \mathrm{AgI} \longrightarrow \mathrm{Ag^+} + \mathrm{I^-}$$

$$E_{\mathrm{Ag^+/Ag}} = E^\circ_{\mathrm{Ag^+/Ag}} + 0.0591 \log[\mathrm{Ag^+}]$$

$$[\mathrm{Ag^+}][\mathrm{I^-}] = K_{sp}(\mathrm{AgI}) = [\mathrm{Ag^+}]^2 = [\mathrm{I^-}]^2$$

So, $[\mathrm{Ag^+}]^2 = 8.7 \times 10^{-17}$

$$[\mathrm{Ag^+}] = \sqrt{8.7 \times 10^{-17}} = 9.3 \times 10^{-9}$$

Substituting the value of $E^\circ_{\mathrm{Ag^+/Ag}}$ and $[\mathrm{Ag^+}]$ in the above equation.

$$\begin{aligned} E_{\mathrm{Ag^+/Ag}} &= 0.799 - 0.0591 \log(9.3 \times 10^{-9}) \\ &= 0.324 \text{ volt} \\ E^\circ_{\text{cell}} &= 0.0591 \log K_{sp}(\mathrm{AgI}) \\ &= 0.0591 \log(8.7 \times 10^{-17}) \\ &= -0.95 \text{ volt} \end{aligned}$$

$$E^\circ_{\text{cell}} = \text{Oxid. pot. of anode} + \text{Red. pot. of cathode}$$

$$\begin{aligned} \text{Red. pot. of cathode } E^\circ_{\mathrm{I^-/AgI/Ag}} &= -0.95 - (-0.799) \\ &= -0.95 + 0.799 \\ &= -0.151 \text{ volt} \end{aligned}$$

Example 18. *Calculate the pH of the following half-cells solutions:*

(*a*) $PtH_2(1\,atm) | H^+ (HCl)$; $E = 0.25$ *volt*

(*b*) $PtH_2(1\,atm) | H^+ (H_2SO_4)$; $E = 0.3$ *volt*

Solution: (a) $\mathrm{H_2} \longrightarrow 2\mathrm{H^+} + 2e$

$$E_{\mathrm{H_2/H^+}} = E^\circ_{\mathrm{H_2/H^+}} - \frac{0.0591}{2} \log \frac{[\mathrm{H^+}]^2}{P_{\mathrm{H_2}}}$$

$$= 0.0 - 0.0591 \log \frac{[\mathrm{H^+}]}{1}$$

$$0.25 = 0.0591\,\mathrm{pH}$$

$$\mathrm{pH} = \frac{0.25}{0.0591} = 4.23$$

(b)
$$E_{\mathrm{H_2/H^+}} = E^\circ_{\mathrm{H_2/H^+}} - \frac{0.0591}{2} \log \frac{[\mathrm{H^+}]^2}{P_{\mathrm{H_2}}}$$

$$= 0.0 - 0.0591 \log \frac{[\mathrm{H^+}]}{1}$$

$$0.3 = 0.0591\,\mathrm{pH}$$

$$\mathrm{pH} = \frac{0.3}{0.0591} = 5.076$$

Example 19. *The emf of the cells obtained by combining zinc and copper electrodes of the Daniell cell with calomel electrodes are 1.083 volt and – 0.018 volt respectively at 25°C. If the reduction potential of normal calomel electrode is + 0.28 volt, find the emf of the Daniell cell.*

Solution: For the cell Zn electrode || Calomel electrode

E_{cell} = Oxid. pot. of Zn electrode + Red. pot. of calomel electrode

So, oxid. pot. of Zn electrode = 1.083 – 0.28 = 0.803 volt

For the cell,

Cu electrode || Calomel electrode

E_{cell} = Oxid. pot. of Cu electrode + Red. pot. of calomel electrode

So, oxid. pot. of Cu electrode = – 0.018 – 0.28 = – 0.298 volt

For the Daniell cell,

Zn electrode || Cu electrode

E_{cell} = Oxid. pot. of Zn electrode + Red. pot. of copper electrode

= 0.803 + 0.298 = 1.101 volt

Example 20. *The Edison storage cell is represented as:*

$$Fe(s) | FeO(s) | KOH(aq.) | Ni_2O_3(s) | Ni(s)$$

The half-cell reactions are:

$$Ni_2O_3(s) + H_2O(l) + 2e^- \longrightarrow 2NiO(s) + 2OH^-; \quad E^\circ = +0.40\,volt$$

$$FeO(s) + H_2O(l) + 2e^- \longrightarrow Fe(s) + 2OH^-; \quad E^\circ = -0.87\,volt$$

(*a*) *What is the cell reaction?*

(*b*) *What is the emf of the cell? How does it depend on the concentration of KOH?*

(*c*) *What is the maximum amount of energy that can be obtained from one mole of Ni_2O_3?* (IIT 1994)

Solution: Actual half reactions are:

$$\mathrm{Fe} + 2\mathrm{OH^-} \longrightarrow \mathrm{FeO} + \mathrm{H_2O} + 2e^- \quad \text{Anode (Oxidation)}$$

$$\mathrm{Ni_2O_3} + \mathrm{H_2O} + 2e^- \longrightarrow 2\mathrm{NiO} + 2\mathrm{OH^-} \quad \text{Cathode (Reduction)}$$

Thus, the cell reaction is:

(a) $\mathrm{Fe} + \mathrm{Ni_2O_3} \longrightarrow \mathrm{FeO} + 2\mathrm{NiO}$

(b) $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{2} \log \dfrac{[\mathrm{NiO}]^2[\mathrm{FeO}]}{[\mathrm{Fe}][\mathrm{Ni_2O_3}]} = E^\circ_{\text{cell}}$

$$\left[\text{Since, } \frac{[\text{NiO}]^2[\text{FeO}]}{[\text{Fe}][\text{Ni}_2\text{O}_3]} = 1 \text{ as all are solids}\right]$$

$$= 0.87 + 0.40 = 1.27 \text{ volt}$$

The emf of the cell is independent of KOH concentration.

(c) Maximum amount of electrical energy

$$= nFE^\circ$$

$$= 2 \times 96500 \times 1.27$$

$$= 245.11 \text{ kJ}$$

Example 21. *The normal oxidation potential of zinc referred to the standard hydrogen electrode is 0.76 volt and that of copper is – 0.34 volt at 25° C. When excess of zinc is added to a solution of copper sulphate, the zinc displaces copper till equilibrium is reached. What is the ratio of concentration of Zn^{2+} to Cu^{2+} ions at equilibrium?*

Solution: The reaction is,

$$\text{Zn} + \text{CuSO}_4 \longrightarrow \text{Cu} + \text{ZnSO}_4$$

or

$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Cu} + \text{Zn}^{2+}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

At equilibrium, $E_{\text{cell}} = 0$

$$E^\circ_{\text{cell}} = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

or

$$\log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{2 \times E^\circ_{\text{cell}}}{0.0591}$$

$$(E^\circ_{\text{cell}} = 0.76 + 0.34 = 1.10 \text{ volt})$$

$$= \frac{2 \times 1.10}{0.0591} = 37.225$$

$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.679 \times 10^{37} : 1$$

Example 22. *An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25° C. Calculate $E^\circ_{Hg_2^{2+}/Hg}$ assuming that the only reaction that occurs is*

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$$

(Given, $E_{Fe^{3+}/Fe^{2+}} = 0.77$ volt). (IIT 1995)

Solution:

$$\begin{array}{lcccc} & 2\text{Hg} + & 2\text{Fe}^{3+} \longrightarrow & \text{Hg}_2^{2+} + & 2\text{Fe}^{2+} \\ \text{At equilibrium, excess} & & \dfrac{10^{-3} \times 5}{100} & \dfrac{10^{-3} \times 95}{2 \times 100} & \dfrac{10^{-3} \times 95}{100} \end{array}$$

At equilibrium, $E_{\text{cell}} = 0$

$$0 = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Hg}_2^{2+}][\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

$$= (E^\circ_{\text{Hg}/\text{Hg}_2^{2+}} + E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}) - \frac{0.0591}{2} \log \frac{\left(\dfrac{10^{-3} \times 95}{2 \times 100}\right)\left(\dfrac{10^{-3} \times 95}{100}\right)^2}{\left(\dfrac{10^{-3} \times 5}{100}\right)^2}$$

$$E^\circ_{\text{Hg}/\text{Hg}_2^{2+}} = -0.77 + \frac{0.0591}{2} \log \frac{(95)^3 \times 10^{-5}}{25 \times 2}$$

$$= -(0.77 + 0.0226)$$

$$= -0.7926 \text{ volt}$$

$$E^\circ_{\text{Hg}_2^{2+}/\text{Hg}} = +0.7926 \text{ volt}$$

Example 23. *Prove that for two half reactions having potentials E_1 and E_2 which are combined to yield a third half reaction, having a potential E_3,*

$$E_3 = \frac{n_1 E_1 + n_2 E_2}{n_3}$$

Solution:

$$\Delta G_3 = \Delta G_1 + \Delta G_2$$

$$-n_3 FE_3 = -n_1 FE_1 - n_2 FE_2$$

or

$$n_3 E_3 = n_1 E_1 + n_2 E_2$$

or

$$E_3 = \frac{n_1 E_1 + n_2 E_2}{n_3}$$

Example 24. *What is the standard potential of the Tl^{3+}/Tl electrode?*

$$Tl^{3+} + 2e^- \longrightarrow Tl^+; \quad E^\circ = 1.26 \text{ volt}$$

$$Tl^+ + e^- \longrightarrow Tl; \quad E^\circ = -0.336 \text{ volt}$$

Solution:

$$\text{Tl}^{3+} + 2e^- \longrightarrow \text{Tl}^+; \quad nFE^\circ = 2 \times 1.26 \times F = 2.52F$$

$$\text{Tl}^+ + e^- \longrightarrow \text{Tl}; \quad nFE^\circ = 1 \times (-0.336) \times F = -0.336F$$

Adding

$$\text{Tl}^{3+} + 3e^- \longrightarrow \text{Tl}; \quad E^\circ = \frac{2.52F - 0.336F}{nF} = \frac{2.184}{3}$$

$$= 0.728 \text{ volt}$$

Example 25. *Calculate the minimum mass of NaOH required to be added in RHS to consume all the H^+ present in RHS of the cell of emf + 0.701 volt at 25° C before its use. Also report the emf of the cell after addition of NaOH.*

$$\underset{}{Zn} \mid \underset{0.1\,M}{Zn^{2+}} \parallel \underset{1\,litre}{HCl} \mid \underset{1\,atm}{Pt(H_2 g)}; \quad E^\circ_{Zn/Zn^{2+}} = 0.760\,V$$

Solution: The cell reaction is,

$$\text{Zn} + 2\text{H}^+ \longrightarrow \text{Zn}^{2+} + \text{H}_2$$

Applying Nernst equation,

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$0.701 = 0.760 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

So, $$\log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = \frac{0.0591 \times 2}{0.0591} = 2$$

or $$\frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} = 10^2$$

$$[\text{H}^+]^2 = \frac{0.1}{10^2} = 10^{-3}$$

$$[\text{H}^+] = 0.0316 \text{ mol L}^{-1}$$

Thus, 0.0316 mol/litre of NaOH is required to neutralise H^+ ions.

$$\text{Mass of NaOH} = 0.0316 \times \text{Mol. mass of NaOH}$$
$$= 0.0316 \times 40 = 1.264 \text{ g}$$

After addition of NaOH, the solution becomes neutral, *i.e.*, the concentration of H^+ ions in cathodic solution becomes 10^{-7}.

Applying again Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$= 0.760 - \frac{0.0591}{2} \log \frac{0.1}{(10^{-7})^2} = 0.3759 \text{ volt}$$

Example 26. *For the galvanic cell,*

$$Ag \mid AgCl(s), KCl\,(0.2\,M) \parallel KBr\,(0.001\,M), AgBr(s) \mid Ag$$

Calculate the emf generated and assign correct polarity to each electrode for the spontaneous process after taking into account the cell reaction at 25° C.

Given, $K_{sp\,AgCl} = 2.8 \times 10^{-10}$; $K_{sp\,AgBr} = 3.3 \times 10^{-13}$ **(IIT 1992)**

Solution:

$$E_{\text{cell}} = E_{\text{Oxid. pot. LHS electrode}} + E_{\text{Red. pot. RHS electrode}}$$

$$= E^\circ_{\text{Oxid. pot. Ag/Ag}^+} - 0.0591 \log [\text{Ag}^+]_{\text{LHS}} + E^\circ_{\text{Red. pot. Ag}^+/\text{Ag}} + 0.0591 \log [\text{Ag}^+]_{\text{RHS}}$$

$$= 0.0591 \log \frac{[\text{Ag}^+]_{\text{RHS}}}{[\text{Ag}^+]_{\text{LHS}}} \quad \left[\text{Since, } E^\circ_{\text{Ag/Ag}^+} + E^\circ_{\text{Ag}^+/\text{Ag}} = 0\right]$$

$$= 0.0591 \log \frac{\dfrac{K_{\text{sp AgBr}}}{[\text{Br}^-]}}{\dfrac{K_{\text{sp AgCl}}}{[\text{Cl}^-]}}$$

$$= 0.0591 \log \frac{3.3 \times 10^{-13}}{0.001} \times \frac{0.2}{2.8 \times 10^{-10}}$$

$$= -\,0.0371 \text{ volt}$$

The cell potential is negative; therefore, the cell reaction is non-spontaneous. For spontaneous reaction emf should be positive. Therefore, the correct cell reaction is

$$\underset{\text{Anode}}{\text{Ag} \mid \text{AgBr}; \text{KBr}} \parallel \underset{\text{Cathode}}{\text{KCl, AgCl}} \mid \text{Ag}$$

Example 27. *The following electrochemical cell has been set-up,*

$$Pt(1) \mid Fe^{3+}, Fe^{2+}\,(a = 1) \parallel Ce^{4+}, Ce^{3+}\,(a = 1) Pt(2)$$

$$E^\circ(Fe^{3+}/Fe^{2+}) = 0.77\ V;\ E^\circ(Ce^{4+}/Ce^{3+}) = 1.61 V$$

If an ammeter is connected between the two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time? **(IIT 2000)**

Solution: Current will flow from higher reduction potential electrode to lower reduction potential electrode, *i.e.*, from Pt(2) electrode to Pt(1) electrode.

$$E^\circ_{\text{cell}} = 1.61 - 0.77 = 0.84 \text{ volt}$$

Example 28. *Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.* **(IIT 2000)**

Solution: Number of faraday passed through the aqueous solution of $CuSO_4$

$$= \frac{I \times t}{96500} = \frac{(2 \times 10^{-3}) \times 16 \times 60}{96500} = 1.98 \times 10^{-5}$$

Thus, number of equivalents of $CuSO_4$ involved in electrolysis from 1 litre solution

$$= 4 \times 1.98 \times 10^{-5} = 7.92 \times 10^{-5}$$

Since, after electrolysis, the absorbance reduces to 50% hence, initial number of equivalents of $CuSO_4$ per litre

$$= 2 \times 7.92 \times 10^{-5}$$
$$= 1.584 \times 10^{-4}$$

or Normality of $CuSO_4$ solution $= 1.584 \times 10^{-4}\ N$.

Example 29. *A silver electrode is immersed in saturated* $Ag_2SO_4(aq.)$. *The potential difference between silver and the standard hydrogen electrode is found to be 0.711 V. Determine* $K_{sp}(Ag_2SO_4)$. *(Given,* $E^\circ_{Ag^+/Ag} = 0.799 V$ *)* **(IIT 2000)**

Solution: The cell may be represented as:

$$\text{Pt}(\text{H}_2\ 1\text{atm}) \mid \text{H}^+(1\,M) \parallel \text{Ag}^+(\text{salt}) \mid \text{Ag}(s)$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{H}^+/\text{H}_2}$$

$$= 0.799 - 0 = 0.799 \text{ V}$$

Given, emf of the cell = 0.711 V

$$H_2 + 2Ag^+ \longrightarrow 2Ag + 2H^+$$

$$Q = \frac{[Ag]^2[H^+]^2}{[H_2][Ag^+]^2} = \frac{1^2 \times 1^2}{1 \times [Ag^+]^2} = \frac{1}{[Ag^+]^2}$$

Applying Nernst equation,

$$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$

or $$0.711 = 0.799 - \frac{0.0591}{2}\log_{10}\frac{1}{[Ag^+]^2}$$

$$[Ag^+] = 0.03243 \text{ mol L}^{-1}$$

$$Ag_2SO_4 \rightleftharpoons \underset{0.03243}{2Ag^+} + \underset{0.016215}{SO_4^{2-}}$$

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (0.03243)^2 \times (0.016215) = 1.705 \times 10^{-5}.$$

Example 30. *Calculate the equilibrium constant for the reaction,*

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Ce^{3+} + Fe^{3+}$$

Given, $E^\circ_{Ce^{4+}/Ce^{3+}} = 1.44\ V$ *and* $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.68\ V$

[IIT (July) 1997]

Solution: $$E^\circ_{cell} = \frac{0.059}{1}\log K_c$$

$$E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe^{3+}} + E^\circ_{Ce^{4+}/Ce^{3+}}$$

$$= -0.68 + 1.44 = 0.76\text{ V}$$

$$\log_{10} K_c = \frac{0.76}{0.059} = 12.8814$$

$$K_c = 7.6 \times 10^{12}$$

Example 31. *Find the solubility product of a saturated solution of* Ag_2CrO_4 *in water at 298 K if the emf of the cell*

$$Ag \mid Ag^+ \text{ (satd. } Ag_2CrO_4 \text{ soln.)} \parallel Ag^+ (0.1\,M) \mid Ag$$

is 0.164 V at 298 K. (IIT 1998)

Solution: $$E_{cell} = \frac{0.059}{1}\log\frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}}$$

$$0.164 = \frac{0.059}{1}\log\frac{0.1}{[Ag^+]_{LHS}}$$

or $$[Ag^+]_{LHS} = 1.66 \times 10^{-4}\ M$$

So, $$[CrO_4^{2-}] = \frac{1.66 \times 10^{-4}}{2}$$

$$K_{sp(Ag_2CrO_4)} = [Ag^+]^2[CrO_4^{2-}]$$

$$= (1.66 \times 10^{-4})^2\left(\frac{1.66 \times 10^{-4}}{2}\right)$$

$$= 2.287 \times 10^{-12} \text{ mol}^3 \text{ L}^{-3}$$

Example 32. *The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 25°C*

$$PtH_2(g) \mid HCl(aq.) \parallel AgCl(s) \mid Ag(s)$$

(*i*) *Write cell reaction.*

(*ii*) *Calculate* ΔH° *and* ΔS° *for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.*

(*iii*) *Calculate the solubility of AgCl in water at 25°C. Given the standard reduction potential of the* Ag^+/Ag *couple is 0.80 volt at 25°C.* (IIT 2001)

Solution: (i) Electrode process:

$$\tfrac{1}{2}H_2 \longrightarrow H^+ + e^- \qquad \text{(Anode)}$$

$$AgCl + e^- \longrightarrow Ag + Cl^- \qquad \text{(Cathode)}$$

$$\tfrac{1}{2}H_2 + AgCl \rightleftharpoons H^+ + Ag + Cl^-$$

(ii) We know that, $\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$

$$-22195 = \Delta H^\circ - 288 \times \Delta S^\circ$$

$$-20265 = \Delta H^\circ - 308 \times \Delta S^\circ$$

On solving, $\Delta S^\circ = -96.5\text{ J}, \Delta H^\circ = 49.987\text{ kJ}$

(iii) $$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$

At equilibrium, $E = 0, Q = K = [Ag^+][Cl^-]$

$$0 = (0.8 - 0.22) + \frac{0.0591}{1}\log K_{sp}$$

$$\frac{(-0.8 + 0.22)}{0.0591} = \log K_{sp}$$

$$K_{sp} = 1.47 \times 10^{-10}$$

Solubility, $$S = \sqrt{K_{sp}}$$

$$= \sqrt{1.47 \times 10^{-10}} = 1.21 \times 10^{-5}\ M$$

Example 33. *Two students use same stock solution of* $ZnSO_4$ *and a solution of* $CuSO_4$*. The emf of one cell is 0.03 V higher than that of other. The concentration of* $CuSO_4$ *in the cell with higher emf value is 0.5 M. Find out the concentration of* $CuSO_4$ *in the other cell.* $\left(\frac{2.303\,RT}{F} = 0.06\right)$ (IIT 2003)

Solution: **Student I.**

$$Zn(s) \mid ZnSO_4\ (C_1) \parallel 0.5\,M\ CuSO_4 \mid Cu(s)$$

$$E_1 = E^\circ - \frac{0.06}{2}\log\frac{C_1}{0.5} \qquad \text{. . . (i)}$$

Student II. $Zn(s) \mid ZnSO_4(C_1) \parallel CuSO_4\ (C_2) \mid Cu(s)$

$$E_2 = E^\circ - \frac{0.06}{2}\log\frac{C_1}{C_2} \qquad \text{. . . (ii)}$$

$$E_1 - E_2 = \frac{0.06}{2}\left[\log\frac{C_1}{C_2} - \log\frac{C_1}{0.5}\right]$$

$$0.03 = \frac{0.06}{2}\left[\log\left(\frac{0.5}{C_2}\right)\right]$$

$$1 = \log\frac{0.5}{C_2}$$

$$C_2 = 0.05\,M$$

Example 34. *Find the equilibrium constant for the reaction,*

$$In^{2+} + Cu^{2+} \rightleftharpoons In^{3+} + Cu^{+} \text{ at } 298\,K$$

Given: $E_{Cu^{2+}/Cu^{+}} = 0.15\,V;\ E^{\circ}_{In^{2+}/In^{+}} = -0.4$ *volt*

$E^{\circ}_{In^{3+}/In^{+}} = -0.42$ *volt* (IIT 2004)

Solution: The given reversible reaction can be obtained as,

$$\mathrm{Cu}^{2+} + e^- \longrightarrow \mathrm{Cu}^{+}; \quad \Delta G^{\circ} = -0.15F \quad \because \Delta G^{\circ} = -nFE^{\circ}$$

$$\mathrm{In}^{2+} + e^- \longrightarrow \mathrm{In}^{+}; \quad \Delta G^{\circ} = +0.40F$$

$$\mathrm{In}^{+} \longrightarrow \mathrm{In}^{3+} + 2e^-; \Delta G^{\circ} = -0.84F$$

$$\mathrm{Cu}^{2+} + \mathrm{In}^{2+} \rightleftharpoons \mathrm{In}^{3+} + \mathrm{Cu}^{+}; \quad \Delta G^{\circ} = -0.59\,F$$

$$-nFE^{\circ} = -0.59\,F$$

$$E^{\circ} = 0.59 \text{ volt}$$

Equilibrium constant can be calculated as,

$$K = \text{antilog}\left[\frac{nE^{\circ}}{0.059}\right]$$

$$= \text{antilog}\left[\frac{1 \times 0.59}{0.059}\right] = 10^{10}$$

Example 35. *In which direction can the reaction,*

$$2Hg\,(l) + 2Ag^{+}(aq.) \rightleftharpoons 2Ag(s) + Hg_2^{2+}(aq.)$$

proceed spontaneously at the following concentrations of the ions participating in the reactions (i) and (ii)?

(*i*) $[Ag^{+}] = 10^{-4}\ mol\,L^{-1}$ *and* $[Hg_2^{2+}] = 10^{-1}\ mol\,L^{-1}$

(*ii*) $[Ag^{+}] = 10^{-1}\ mol\,L^{-1}$ *and* $[Hg_2^{2+}] = 10^{-4}\ mol\,L^{-1}$

Given: $E^{\circ}_{Hg_2^{2+}/Hg} = 0.79\,V;\ E^{\circ}_{Ag^{+}/Ag} = 0.80\,V$

[CBSE (Mains) Medical 2006]

Solution: (i) $Q = \dfrac{[\mathrm{Hg}_2^{2+}]}{[\mathrm{Ag}^{+}]^2} = \dfrac{10^{-1}}{[10^{-4}]^2} = 10^{7}$

$$E^{\circ} = E^{\circ}_{\mathrm{Ag^{+}/Ag}} - E^{\circ}_{\mathrm{Hg_2^{2+}/Hg}}$$

$$= 0.80 - 0.79 = 0.01\,\mathrm{V}$$

$$E = E^{\circ} - \frac{0.059}{n}\log Q$$

$$= 0.01 - \frac{0.059}{2}\log 10^{7}$$

$$= -0.1965\,\mathrm{V}$$

Negative value shows that the reaction will proceed from right to left, *i.e.*, in backward direction.

(ii) $Q = \dfrac{[\mathrm{Hg}_2^{2+}]}{[\mathrm{Ag}^{+}]^2} = \dfrac{10^{-4}}{[10^{-1}]^2} = 10^{-2}$

$$n = 2$$

$$E^{\circ} = 0.01 \text{ volt}$$

$$E = E^{\circ} - \frac{0.059}{n}\log_{10} Q$$

$$= 0.01 - \frac{0.059}{2}\log_{10} 10^{-2}$$

$$= 0.01 + 0.059\,\mathrm{V}$$

$$= 0.069\,\mathrm{V}$$

Since, the value of cell potential is positive, the reaction will proceed spontaneously in forward direction.

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. **Electrochemistry** is a branch of physical chemistry which deals with the relationship between chemical energy and electrical energy and how one can be converted into another. The subject is divided into two categories: (i) use of electrical energy to produce chemical changes (electrolysis) and (ii) conversion of chemical energy into electrical energy (production of electricity by spontaneous redox reactions).

2. **Conductors** are the substances which allow the passage of electric current through them. Those which do not allow the flow of electric current through them are called **insulators.** Conductors are of two types:

(a) Metallic or electronic conductors are those which remain unchanged as current flows through them. These conductors transfer electric current by transfer of electrons without transfer of matter. Metals such as Cu, Ag, Al, Pt, etc., non- metals like carbon (graphite) and various alloys belong to this class.

(b) Electrolytic conductors are the conductors like aqueous solutions of acids, bases and salts or substance in molten state which allow the flow of electric current with chemical decomposition. These conductors are termed as **electrolytes.** The substances whose aqueous solutions do not conduct electric current are called **non-electrolytes.**

To pass the current through an electrolytic conductor, two metallic rods or plates are required. These are termed **electrodes.** The electrode which is connected with the positive terminal of battery or through which electric current enters the solution is termed **anode** and the electrode which is connected with negative terminal of battery or through which electric current leaves the solution is termed **cathode.** Actually the anode is the electrode where oxidation occurs and the cathode is the electrode where reduction takes place.

3. **Electrolysis** is the process of chemical decomposition of an electrolyte by passage of electric current through its aqueous solution or molten state. Molecules of the electrolyte when dissolved in water split up into cations and anions. On passing electric current these ions move towards their respective electrodes. On reaching electrodes these ions lose their charge either by losing or accepting electrons and thereby deposited at the respective electrodes or undergo a secondary change. The device in which electrolysis is carried out is known as **electrolytic cell.**

4. **Preferential discharge theory:** If more than one type of ion is attracted towards a particular electrode, then the ion discharged is the one which requires least energy.

The decreasing order of the discharge potential or the increasing order of deposition for the cations and anions is as follows:

Cations : $K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}$.

Anions : $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$.

5. **Faraday's laws of electrolysis:** These present the relationship between the quantity of electric charge and the amount of the substance deposited at the electrode. These were given by Faraday in 1834.

(i) First law: When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge which flows through the electrolyte.

Mathematically, $$W \propto Q$$

or $$W = ZQ = Z \times I \times t$$

where, Z is a constant, known as electrochemical equivalent, I is the current in amperes and t is the time in seconds. When $Q = 1$ coulomb or one ampere of current is passed for 1 second, $W = Z$. Z is thus the mass of the substance deposited by one coulomb.

(ii) Second law: When the same quantity of current is passed through different electrolytes, the masses of different substances deposited on the electrodes will be in the ratio of their equivalent masses. For example, if same quantity of current is passed through copper sulphate and silver nitrate solutions, then

$$\frac{\text{Mass of copper deposited}}{\text{Mass of silver deposited}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

One gram equivalent of any substance is deposited by passing same amount of charge, *i.e.*, 96500 coulomb (1 faraday).

$$E = Z \times 96500$$

or $$Z = \frac{E}{96500}$$

$$\text{The charge carried by an ion} = \frac{nF}{6.02 \times 10^{23}} \text{ coulomb}$$

When, $n = 1$,

$$\text{The fundamental unit of charge} = \frac{F}{6.02 \times 10^{23}} = \frac{96500}{6.02 \times 10^{23}}$$

$$= 1.6 \times 10^{-19} \text{ coulomb}$$

$$1 \text{ coulomb} = 6.24 \times 10^{18} \text{ electrons}$$

Charge on one mole of electrons

$$= 6.02 \times 10^{23} \times 1.6 \times 10^{-19}$$

$$\approx 96500 \text{ coulomb}$$

Applications of electrolysis: (i) Determination of equivalent masses of elements (ii) Electrometallurgy (iii) Manufacture of non-metals (iv) Electroplating of metal (v) Manufacture of compounds (vi) Electroplating—The process of coating an inferior metal with a superior metal by electrolysis.

6. **Arrhenius theory of electrolytic dissociation:** It was put forward by Arrhenius in 1884 to explain the properties of electrolytic solutions. The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles called ions. The ion carrying positive charge is called **cation** and the ion carrying negative charge is called **anion.**

$$AB \rightleftharpoons A^+ \text{ (cation)} + B^- \text{ (anion)}$$

(ii) The process of splitting of the molecules of the electrolyte into ions is called **ionisation.** The fraction of the total number of molecules present in solution as ions is known as **degree of ionisation.**

It is denoted by 'α'.

$$\alpha = \frac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules dissolved}}$$

The degree of ionisation depends upon: (a) Nature of solute (b) Nature of solvent (c) Dilution and temperature.

(iii) Ions present in solution constantly reunite to form neutral molecules; thus, there is a state of dynamic equilibrium between ionised and unionised molecules.

$$AB \rightleftharpoons A^+ + B^-$$

$$\frac{[A^+][B^-]}{[AB]} = K \text{ (ionisation constant)}$$

(iv) The ions are discharged always in equivalent amounts when current is passed through electrolytic solution no matter what their relative speeds are.

(v) The electrolytic solution is always neutral in nature as the total charge on cations is equal to the total charge on anions. However, it is not necessary that the number of cations and anions should be always equal.

(vi) The properties of electrolytes in solution are the properties of ions present in the solution.

(vii) The ions act as molecules for colligative properties.

(viii) The conductivity of the solution depends on the nature and number of ions.

Evidences in favour of Arrhenius theory: (i) Ohm's law applicability: No part of the current is used in splitting up the molecules into ions. (ii) X-ray studies have shown that ions are present in solid electrolytes. The ionic compounds in molten state behave as good conductors. (iii) Ionic reactions are observed in the case of electrolytes. (iv) Constant value of heat of neutralisation. (v) Abnormal colligative properties in the case of electrolytes. (vi) Colour of compounds in solution. (vii) This theory explains satisfactorily various phenomena such as electrolysis, conductivity, salt hydrolysis, etc.

7. **Conductivity** is the property of the conductor which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance.

$$\text{Conductivity} = \frac{1}{\text{Resistance}} = \frac{1}{R}$$

It is expressed as ohm^{-1} or mho.

Specific conductivity is defined as the reciprocal of specific resistance, *i.e.*, it is the conductance of 1 cm^3 of a conductor. It is represented by the symbol κ.

$$\kappa = \frac{1}{\rho} = \frac{l}{a} \times \text{conductivity}$$

where, l = distance between electrodes and a = area of cross-section of electrode.

In the case of electrolytic solutions, specific conductance is the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimetre. The units of specific conductance are $\text{ohm}^{-1}\ \text{cm}^{-1}$. The ratio of l/a is called **cell constant.**

Equivalent conductance: Conductivity of a solution containing 1g equivalent of the electrolyte. It is denoted by 'Λ'. If the concentration of solution is C g equivalent per litre, then

$$\Lambda = \kappa \frac{1000}{C}$$

or $$\Lambda = \kappa \times V$$

where, V is the volume in mL containing 1g equivalent of the electrolyte. The unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$.

Molar conductance: Conductance of a solution containing 1 g mole of an electrolyte. If V is volume in mL containing 1g mole, then

$$\text{Molar conductance, } \mu = \kappa \times V$$

If C is the concentration of the solution in g mole per litre, then

$$\mu = \kappa \times \frac{1000}{C}$$

Its unit is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

$$\text{Equivalent conductance} = \frac{\text{Molar conductance}}{n}$$

where, $$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

8. **Kohlrausch's law:** At infinite dilution, each ion makes a definite contribution towards equivalent conductance of the electrolyte. The value of equivalent conductance at infinite dilution for any electrolyte is the sum of conductances at infinite dilution of its constituent ions. Thus,

$$\Lambda_\infty = \Lambda_a + \Lambda_c$$

Λ_a and Λ_c are called the ionic conductances of anion and cation at infinite dilution respectively. It can be used to determine degree of dissociation.

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{\text{Equivalent conductance at given concentration}}{\text{Equivalent conductance at infinite dilution}}$$

9. **Galvanic or Voltaic or Electrochemical cell:** It is the device in which chemical energy is converted into electrical energy. In this cell a redox reaction is carried out in an indirect manner and the decrease in free energy during the chemical process appears as electrical energy.

The common galvanic cell, dry cell and the lead storage battery are the devices for converting chemical energy into electrical energy. Daniell cell is the typical example of galvanic cell. It consists of two half-cells, one containing zinc electrode dipping in solution of zinc sulphate (1 M) and another containing copper electrode dipping in solution of copper sulphate (1 M). Zinc electrode acts as anode. At this electrode oxidation occurs. $Zn \rightarrow Zn^{2+} + 2e^-$. Copper electrode acts as cathode. At this electrode reduction occurs, $Cu^{2+} + 2e^- \rightarrow Cu$. When the two half-cells are connected by a salt bridge and the metal electrodes are joined externally, the electrons from zinc electrode (–ve electrode) move towards copper electrode (+ve electrode), *i.e.*, current flows from cathode to anode. The cell reaction is:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Salt-bridge allows the flow of current by completing the circuit and maintains electrical neutrality. It also prevents liquid-liquid junction potential.

A galvanic cell is represented in the following manner:

Salt-bridge

LHS	RHS
Anode (–ve)	Cathode (+ve)
$Zn \mid Zn^{2+}\ (1\ M)$	$Cu^{2+}\ (1\ M) \mid Cu$
Oxidation half-cell	Reduction half-cell
$Zn \rightarrow Zn^{2+} + 2e^-$	$Cu^{2+} + 2e^- = Cu$

10. **Electrode potential:** When a metal is placed in a solution of its ions, the metal either acquires a positive charge or negative charge with respect to solution. On account of this a definite potential is developed between the metal and the solution. This potential difference is termed **electrode potential.** The magnitude of potential depends on the nature of electrode, concentration of ions and temperature. It is a measure of the tendency of the metal to lose or gain electrons or a measure of the relative tendency to undergo oxidation or reduction. Depending on the nature of the metal electrode, the electrode potential is of two types:

(i) Oxidation potential: When electrode is negatively charged with respect to solution, *i.e.*, oxidation occurs and the electrode acts as anode

$$M \rightarrow M^{n+} + ne^-$$

(ii) Reduction potential: When electrode is positively charged with respect to solution, *i.e.*, reduction occurs and the electrode acts as cathode,

$$M^{n+} + ne^- \rightarrow M$$

Standard electrode potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 *M*) at 25°C is called standard electrode potential.

It is not possible to measure the absolute value of single electrode potential directly. Only difference in potential of two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as **reference electrode.** The emf of the resulting cell is measured experimentally.

$$\text{Emf of the cell} = E_{\text{Anode}} + E_{\text{Cathode}}$$

$$= \text{Oxid. pot. of anode} + \text{Red. pot. of cathode}$$

Knowing the value of reference electrode, the value of other electrode can be determined.

Standard reduction potential = – (Standard oxidation potential)

Standard oxidation potential = – (Standard reduction potential)

11. Reference electrode (Standard hydrogen electrode, SHE): It is a primary standard electrode. It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with outer circuit through mercury. The platinum strip and glass tube is surrounded by another glass tube which has an inlet for hydrogen gas and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in acid solution which has H^+ ion concentration 1 *M*. Pure hydrogen gas is circulated at 1 atmospheric pressure. The temperature of the cell is maintained at 25°C. By international agreement, the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000... volt. This electrode can act as cathode or anode with respect to other electrode.

The electrode whose electrode potential is to be determined is connected with SHE and emf of such a cell is determined which is taken as the electrode potential of the given electrode. The metal electrode which acts as anode with respect to hydrogen electrode, the **oxidation potential** of the electrode is given positive sign and the metal electrode which acts as cathode with respect to hydrogen electrode, the reduction potential is given the positive sign.

12. Emf of a cell: The difference in potentials of two half-cells is known as the emf of the cell.

$$E^\circ_{\text{Cell}} = \text{Red. pot. cathode} - \text{Red. pot. anode } (E^\circ_{\text{right}} - E^\circ_{\text{left}})$$

$$= \text{Red. pot. cathode} + \text{Oxid. pot. anode}$$

$$= \text{Oxid. potential anode} - \text{Oxid. potential cathode}$$

13. Some more reference electrodes: Since, a hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes which are known as **secondary** reference electrodes. These are convenient to handle and prepared easily. Calomel electrode and silver-silver chloride are used as reference electrodes. The potentials of these electrodes are fixed on hydrogen scale but their values depend on strong electrolyte concentration.

14. Reversible and irreversible cells: A cell is said to be reversible if the following two conditions are fulfilled:

(i) The chemical reaction of the cell stops when an exactly equal external emf is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external emf is slightly higher than that of the cell.

Any other cell which does not obey the above two conditions is termed as irreversible. Daniell cell is reversible but $Zn\,|\,H_2SO_4\,|\,Ag$ cell is irreversible in nature.

15. Prediction for occurrence of a redox reaction: Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative.

$\Delta G^\circ = -nFE^\circ$ where, '*n*' is the number of electrons involved, *F* is the value of faraday and E° is the cell emf. ΔG° can be negative if E° is positive.

When E° is positive, the cell reaction will be spontaneous and serves as a source of electrical energy.

16. Nernst equation: The potential of an electrode changes with the change in concentration of ions in solution in contact with the electrode. Increase in concentration of cations results in an increase of reduction potential of an electrode.

Consider $M^{n+} + ne^- \rightarrow M$

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{2.303RT}{nF}\log\frac{[\text{reduced form}]}{[\text{oxidised form}]}$$

At 25°C, $\dfrac{2.303RT}{F} = 0.0591$

and the concentration of metal is unity.

$$E_{\text{red}} = E^\circ_{\text{red}} + \frac{0.0591}{n}\log[M^{n+}]$$

Similarly, consider the electrode where oxidation occurs.

$$M \rightarrow M^{n+} + ne^-$$

$$E_{\text{oxid.}} = E^\circ_{\text{oxid.}} - \frac{0.0591}{n}\log[M^{n+}]$$

Cell potential depends on the potential of anode and cathode.

$$E_{\text{Cell}} = E_{\text{Anode}} + E_{\text{Cathode}}$$

$$= \text{Oxid. pot. of anode} - \text{Red. pot. of cathode}$$

$$= E^\circ_{\text{oxid.}} - \frac{0.0591}{n}\log[\text{Anodic ion conc.}]$$

$$+ E^\circ_{\text{red}} - \frac{0.0591}{n}\log[\text{Cathodic ion conc.}]$$

$$= E^\circ_{\text{oxid.}} + E^\circ_{\text{red}} - \frac{0.0591}{n}\log\frac{[\text{Anodic ion conc.}]}{[\text{Cathodic ion conc.}]}$$

$$= E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

or

$$= E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{ion}]_{\text{LHS}}}{[\text{ion}]_{\text{RHS}}}$$

17. Electrochemical series: When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the electrochemical or activity series of the elements.

Characteristics of Electrochemical Series

(i) The negative sign of reduction potential indicates that an electrode when joined with SHE acts as anode. Similarly the positive sign of reduction potential indicates that the electrode joined with SHE acts as cathode.

(ii) The substances which act as stronger reducing agents than hydrogen are placed above hydrogen in series. All those which have positive values of reduction potentials and placed below hydrogen are weaker reducing agents than hydrogen.

(iii) The substances which are stronger oxidising agents are placed below hydrogen in the series.

(iv) The metals at the top have the tendency to lose electrons readily. The activity of metals decreases from top to bottom while that of non-metals increases from top to bottom.

(v) A metal higher in the series will displace the metal from its solution which is lower in the series.

(vi) A non-metal higher in the series (towards bottom side) having high value of reduction potential will displace another non-metal with lower reduction potential.

(vii) The metals occupying top positions in the series readily liberate hydrogen from dilute acids.

(viii) Iron and metals above iron are capable of liberating hydrogen from water.

(ix) The oxides of metals having low reduction potentials are thermally stable while the oxides of metals having high reduction potentials are thermally not stable.

18. Relation between emf and equilibrium constant:

$$\Delta G^\circ = -2.303RT \log K$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

So,

$$nFE^\circ_{\text{cell}} = 2.303\,RT \log K$$

$$E^\circ_{\text{cell}} = \frac{2.303RT}{nF} \log K$$

$$= \frac{0.0591}{n} \log K \qquad (T = 298\text{ K})$$

19. Primary cells are those which have definite life and become dead over a time. These cannot be recharged. Examples are dry cell, mercury cell, etc.

Secondary cells are the cells which can be recharged by passing direct current through them. Lead storage battery and nickel-cadmium cell are examples of secondary cells. Lead storage battery consists of spongy lead as anode, a grid of lead packed with PbO_2 as cathode and an aqueous solution of H_2SO_4 (38% by mass or 20% H_2SO_4 of specific gravity 2.15) as electrolyte.

Reaction during discharging	**Reaction during charging**
$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$ Voltage 2.0 volt. The concentration of H_2SO_4 decreases during discharging.	$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

Name of cell	**Anode**	**Cathode**	**Electrolyte used**
Dry cell	Zn	Graphite	MnO_2 + C (around cathode) $NH_4Cl + ZnCl_2$ (around anode)
Mercury cell	Zn	Graphite	HgO + KOH (moist)
Lead storage battery	Pb	PbO_2	H_2SO_4 (38% by mass)
Lithium battery	Li	Metal sulphide	$LiClO_4$ in organic solvent
Ni-Cad cell	Cd	NiO	KOH solution
Fuel cell (H_2-O_2)	Porous carbon (with catalyst)	Porous carbon (with catalyst)	Conc. NaOH or KOH (*aq.*)

20. Fuel cell: The cells which convert chemical energy of fuels directly into electrical energy are known as fuel cells. One of such cells is fuel cell (H_2-O_2) in which electrical energy is generated by the use of H_2 and O_2. In fuel cell NaOH is used as an electrolyte and hydrogen gas is diffused at the anode made of porous carbon. At the cathode oxygen is diffused through a porous carbon. The following chemical reactions occur:

(i) At anode, $$H_2 \rightarrow 2H$$

$$2H + 2OH^- \rightarrow 2H_2O + 2e^-$$

(ii) At cathode, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Net cell reaction $2H_2 + O_2 \rightarrow 2H_2O + \text{energy}$

Fuel cells are quite efficient, and free from pollution. These are used in spacecrafts.

21. Concentration cells: If two plates of the same metal are dipped separately into two solutions of the same electrolyte and are connected with a salt bridge, the whole arrangement is found to acts as galvanic cell. Such cells are known as concentration cells. These are of two types:

(i) Electrode concentration cells

$$\text{Pt, } H_2 \text{ (pressure } p_1) \mid H^+ \mid H_2 \text{ (pressure } p_2), \text{ Pt}$$

If $p_1 > p_2$ oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{(p_1)}{(p_2)} \text{ at } 25°\text{C}$$

(ii) Electrolyte concentration cells

$$M \mid M^{n+}(C_1) \parallel M^{n+}(C_2) \mid M$$

$$Zn \mid Zn^{n+}(C_1) \parallel Zn^{n+}(C_2) \mid Zn$$

C_2 is higher than C_1.

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1} \text{ at } 25°\text{C}$$

Questions

1. Match the List-I with List-II and List-III:

List-I (Quantity)	**List-II (Symbol)**	**List-III (Unit)**
(a) Conductivity	(p) Λ_m	(u) mho cm^{-1}
(b) Cell constant	(q) κ	(v) cm^{-1}
(c) Molar conductance	(r) Λ_e	(w) $ohm^{-1}\ cm^2\ mol^{-1}$
(d) Equivalent conductance	(s) l/A	(x) $ohm^{-1}\ cm^2\ eq^{-1}$

2. Match the salts in the Column-I with their use in Column-II:

Column-I	**Column-II**
(a) Hg_2Cl_2	(p) Salt bridge
(b) Agar-agar	(q) Calomel electrode
(c) 0.1 N KCl	(r) Used in ice cream
(d) Quinhydrone	(s) Redox electrode

3. Match the Column-I with Column-II:

Column-I (Term)	**Column-II (Relation)**
(a) α (Degree of ionisation)	(p) λ^+/Λ
(b) t_+ (Transport number)	(q) Λ_m^c/Λ_m^0
(c) Fraction of a mole undergoing ionization	(r) $U^+/U^+ + U^-$
(d) NaCl	(s) Λ_e^c/Λ_e^0
	(t) $\Lambda_m = \Lambda_e$

4. Match the physical quantities in the List-I with their units in List-II:

List-I	**List-II**
(a) Resistance	(p) ohm
(b) Resistivity	(q) volt amp^{-1}
(c) Conductivity	(r) ohm m
(d) Specific conductance	(s) $ohm^{-1}\ m^{-1}$

5. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Specific conductance, κ	(p) $\Lambda_m^c / \Lambda_m^\circ$
(b) Molar conductance, Λ_m	(q) Decreases with dilution
(c) Resistance of electrolyte solution R	(r) Increases with dilution
(d) Degree of ionization of weak electrolyte, α	(s) Increases with increase in the distance between parallel plates

6. Match Column-I with Column-II:

Column-I (Combination of half-cell reactions)	**Column-II (Potential of overall process)**
(a) $6OH^- + Br^- \rightleftharpoons BrO_3^- + 3H_2O + 6e^-$ $E° = -0.61$ V $2OH^- + Br^- \rightleftharpoons BrO^- + H_2O + 2e^-$ $E° = -0.76$ V $4OH^- + BrO^- \rightleftharpoons BrO_3^- + 2H_2O + 4e^-$ $E° = ?$	(p) $E° = 0.56$ V
(b) $H_2SO_3 + 4H^+ + 4e^- \rightleftharpoons S + 3H_2O$ $E° = 0.45$ V $SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3 + H_2O$ $E° = 0.17$ V $SO_4^{2-} + 8H^+ + 6e^- \rightleftharpoons S + 4H_2O$ $E° = ?$	(q) $E° = -0.535$V
(c) $ClO_3^- + 6H^+ + 6e^- \rightleftharpoons Cl^- + 3H_2O$ $E° = +1.45$ V $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ $E° = +1.36$ V $ClO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}Cl_2 + 3H_2O$ $E° = ?$	(r) $E° = +0.36$ V
(d) $Zn^{2+}_{(aq)} + 2e \longrightarrow Zn(s)$ $E° = -0.76$ V $Ag^+ + e^- \longrightarrow Ag(s)$ $E° = +0.80$ V $Zn(s) + 2Ag^+ \rightleftharpoons Zn^{2+}(aq) + 2Ag(s)$ $E° = ?$	(s) $E° = +1.47$ V

7. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Concentration cell	(p) Fe is oxidised by Ni_2O_3
(b) Edison cell	(q) Zinc anode
(c) Mercury cell	(r) HgO cathode
(d) Dry cell	(s) $E° = 0$

8. Match the Column-I with Column-II:

Column-I (Electrode)	**Column-II (Type)**
(a) Calomel	(p) Reference
(b) Glass	(q) Redox
(c) Hydrogen	(r) Membrane
(d) Quinhydrone	(s) Gas

9. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Kohlrausch law	(p) $\Lambda_m / \Lambda^\circ_m$
(b) Λ_m	(q) $\frac{1}{R} \times \frac{1}{A}$
(c) κ (kappa)	(r) $\Lambda^\circ_m Ca_3(PO_4)_2 = 3\lambda^\circ Ca^{2+} + 2\lambda^\circ PO_4^{3-}$
(d) α	(s) $\kappa \times \frac{1000}{M}$

10. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $E^\circ = 0$	(p) Cell is discharged
(b) $E = 0$	(q) $Q = K$
(c) $\Delta G = 0$	(r) 96500 coulomb
(d) 1 Faraday	(s) 1 mol electrons
	(t) Concentration cell

Answers

1. (a—q, u), (b—s, v), (c—p, w), (d—r, x)
2. (a—q), (b—p, r), (c—p), (d—s)
3. (a—q, s), (b—p, r), (c—q, s), (d—t)
4. (a—p, q), (b—r), (c—s), (d—s)
5. (a—q), (b—r), (c—q, s), (d—p, r)
6. (a—q), (b—r), (c—s), (d—p)
7. (a—s), (b—p), (c—q, r), (d—q)
8. (a—p), (b—r), (c—s), (d—q)
9. (a—r), (b—s), (c—q), (d—p)
10. (a—t), (b—p, q), (c—p, q), (d—r, s)

• PRACTICE PROBLEMS •

1. How many coulombs are required for the following reductions?

(i) 1 mole of Ag^+ ions to Ag

(ii) 1 mole of Cu^{2+} ions to Cu

(iii) 1 mole of MnO_4^- ions to MnO_4^{2-}

[**Ans.** (i) 96500 coulomb (ii) 193000 coulomb (iii) 96500 coulomb]

2. How many faradays are needed to reduce 2 gram-mole of Cu^{2+} to Cu metal?

[**Ans.** 4 faraday]

3. How many faradays are released when 12.7 g of copper metal is changed into copper ions?

[**Ans.** 0.4 faraday]

[**Hint:** $\underset{\substack{1\text{ mole}\\63.5}}{Cu} \longrightarrow Cu^{2+} + \underset{\substack{2\text{ mole}\\2F}}{2e^-}$]

4. Calculate the number of coulombs required to deposit 40.5 g Al when the electrode reaction is:

$$Al^{3+} + 3e^- \longrightarrow Al$$

[**Ans.** 4.34×10^5 coulomb]

5. Calculate the number of coulombs required to deposit 50 g of silver at cathode from silver nitrate solution.
(Atomic mass of silver = 108)

[**Ans.** 44675.9 coulomb]

6. How much electric charge is required to produce 20.0 g of calcium from molten $CaCl_2$?

[**Ans.** 96500 coulomb]

7. If 3 faradays of electricity are passed through an iron (II) bromide solution, how many grams of iron metal will be deposited? (At. mass of iron = 56)

[**Ans.** 84 g]

8. A certain quantity of electricity deposits 0.54 g of Ag from silver nitrate solution. What volume of hydrogen will be liberated by the same quantity of electricity at 27°C and 750 mm of Hg pressure?

[**Hint:** $\dfrac{\text{Mass of } H_2}{\text{Mass of Ag}} = \dfrac{\text{Eq. mass of } H_2}{\text{Eq. mass of Ag}}$

$$\text{Mass of } H_2 = \frac{1 \times 0.54}{108} = 0.005 \text{ g}$$

$$\text{Volume of } H_2 = \frac{0.005 \times 0.0821 \times 300 \times 760}{2 \times 750} \quad \left(V = \frac{w}{M} \cdot \frac{RT}{P}\right)$$

$$= 0.06234 \text{ litre}$$]

9. In the electrolysis of an aqueous cupric bromide solution, how many grams of bromine are formed on passing a current of 1 ampere for 16 minutes and 5 seconds? Write the anode and the cathode half reactions.

[**Ans.** 0.80 g; cathode reaction $Cu^{2+} + 2e^- \longrightarrow Cu$;
anode reaction $2Br^- \longrightarrow Br_2 + 2e^-$]

10. A current of 1.5 amperes is passed through a solution of a salt of a bivalent metal for 30 minutes. Increase in mass of cathode is 0.8898 g. Find the atomic mass of the metal.

[**Ans.** 63.6]

11. A lead storage battery is discharged in which the following electrode reaction takes place:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(l) \longrightarrow 2PbSO_4 + 2H_2O$$

The original volume in electrolyte is 1 litre. During discharge the concentration of H_2SO_4 changes from 34.6% by weight (density 1.261 g/mL) to 27% by weight. How many faradays have left the anodic half-cell? Water produced during electrolysis is used up.

[**Ans.** 1.254 faraday]

12. The chemical reaction given below:

$$Cl_2(g) + SO_2(g) + 2H_2O(l) \longrightarrow 2Cl^-(aq.) + 3H^+(aq.) + HSO_4^-(aq.)$$

proceeds readily in aqueous acid solution.

(i) Give the half-cell reactions.

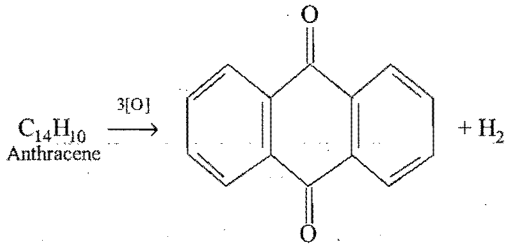
(ii) If a fully charged cell initially held 1 mole of Cl_2, for how many days could it sustain a current of 0.05 ampere, assuming the cell becomes non-operative when 90% of initial Cl_2 has been used up?

[**Ans.** 40.2 days]

13. A current of 80 microampere is passed through a solution of $AgNO_3$ for 32 minutes using platinum electrodes. A uniform single atom thick layer is deposited covering 86% of the cathode surface. If total surface area of cathode is 601.7 cm^2, calculate the area covered by one Ag atom.

[**Ans.** 5.4×10^{-16} cm^2]

14. Anthracene can be electrolytically oxidised to anthraquinone.



Anthraquinone

What mass of anthraquinone can be produced by the passage of 1 ampere current for an hour at 100% efficiency?

[**Ans.** 1.2932 g]

15. Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^6 coulomb per second at an appropriate voltage. How much time would it take to electrolyse the lake?

[**Ans.** 1.9 million year]

16. How many grams of H_2 and O_2 are produced during the electrolysis of water by a 1.30 ampere current for 5 hours? What volumes of dry gases are produced at NTP?

[**Ans.** 0.242 g H_2; 1.94 g O_2; 2.72 litre H_2; 1.36 litre O_2]

17. How many coulombs of electricity would be required to reduce the iron in 36.0 g of potassium hexacyano ferrate(III), $K_3Fe(CN)_6$, to metallic iron?
[**Ans.** 3.17×10^4 coulomb]
[**Hint:** Iron in the complex is Fe^{3+}.

$$\underset{1\text{ mole}}{K_3Fe(CN)_6} + \underset{3 \times 96500\text{ C}}{3e^-} \longrightarrow 3K^+ + 6CN^- + Fe\ ]$$

18. What current strength in ampere will be required to liberate 5 g of iodine from potassium iodide solution in 30 minutes?
[**Ans.** 2.11 ampere]

19. The mass of copper deposited from a solution of copper sulphate by a uniform current of 0.25 ampere flowing for one hour is 0.295 g. Find the equivalent mass of copper. (1 faraday = 96500 coulomb)
[**Ans.** 31.75]

20. The solution of a salt of a metal of atomic mass 112 was electrolysed for 15 minutes with a current of 1.5 ampere. The mass of the metal deposited was 0.788 g. Find the valency of the metal.
[**Ans.** 2]

21. If a monovalent metal ion carries 1.6×10^{-19} coulomb of electricity, what is the amount of electricity carried by one gram molecular mass of the metal ions?
[**Ans.** 9.6336×10^4 coulomb]

22. Calculate approximately how much current is necessary to produce oxygen gas at the rate of 1 mL per second?
[**Ans.** 17.23 ampere]
[**Hint:** 1 g-equivalent of oxygen or $\frac{22400}{4}$ mL is liberated by 96500 coulomb.]

23. 0.5 faraday of electricity was required to deposit all the copper in 500 mL of a copper sulphate solution. What is the normality of the copper sulphate solution?
[**Ans.** Normality = 1 *N*]

24. Copper is deposited at an electrode according to the reaction $Cu^{2+} \xrightarrow{+2e^-} Cu$. When a current of 1.34 ampere was passed through a solution of copper sulphate for 10 hours, 15.885 g of copper was deposited.
(i) How many coulombs of electricity were passed through the solution?
(ii) How many moles of copper were deposited?
(iii) How many coulombs are required for the deposition of 1 mole of copper?
(iv) If the charge on an electron is 1.6×10^{-19} coulomb, calculate the value of Avogadro's number.
[**Ans.** (i) 482.40 coulomb (ii) 0.25 mol (iii) 2×96500 coulomb (iv) 6.03×10^{23}]

25. Calculate the mass and volume at NTP of hydrogen and chlorine that will be formed by passing 10,000 coulomb of charge through an aqueous solution of potassium chloride. The cell reaction is:

$$2KCl + 2HOH \longrightarrow 2KOH + Cl_2 + H_2$$

[**Ans.** 0.1036 g H_2, volume 1.063 litre; 3.678 g Cl_2, volume 1.1603 litre]

26. Three electrolytic cells *A*, *B* and *C* containing electrolytes zinc sulphate, silver nitrate and copper sulphate respectively, were connected in series. A steady current of 1.50 ampere was passed through them until 1.45 g of silver was deposited at the cathode of cell *B*. How long did the current flow? What masses of copper and zinc were deposited?
(At. mass: Cu = 63.5, Zn = 65.4, Ag = 107.8)
[**Ans.** 865 second; 0.427 g Cu; 0.44 g Zn]

27. An electric current passing for 6 minutes through a dilute H_2SO_4 solution gave 40 mL of the electrolytic gas ($H_2 + O_2$) measured at NTP. What was the average value of current?
[**Ans.** 0.638 ampere]
[**Hint:** 96500 coulomb give 11.2 litre of H_2 and 5.6 litre of O_2, *i.e.*, 16.8 litre of electrolytic gas at NTP.]

28. The same quantity of electricity that liberated 2.158 g silver was passed through a solution of a gold salt and 1.314 g of gold was deposited. The equivalent mass of silver is 107.9. Calculate the equivalent mass of gold. What is the oxidation state of gold in this gold salt? (At. mass of gold = 197)
[**Ans.** Eq. mass = 65.7; Oxidation state = 3]

29. Calculate the volume of Cl_2 at NTP produced during electrolysis of $MgCl_2$ which produces 6.50 g Mg. (At. mass of Mg = 24.3)
[**Ans.** 5.99 litre]

30. How long does it take to deposit 100 g of Al from an electrolytic cell containing Al_2O_3 using a current of 125 ampere?
[**Ans.** 8577.8 second]

31. 10g fairly concentrated solution of $CuSO_4$ is electrolysed using 1.01 faraday of electricity. Calculate the mass of the resulting solution.
[**Ans.** 9.6025 g]

32. The density of copper is 8.94 g mL^{-1}. Find out the number of coulombs needed to plate an area $10 \times 10\ cm^2$ to a thickness of 10^{-2} cm using $CuSO_4$ solution as electrolyte. (At. mass of Cu = 63.6)
[**Ans.** 27129.2 coulomb]

33. What mass of Ag (At. mass 108) could be plated on a spoon from electrolysis of $AgNO_3$ solution by one ampere current for 10 minutes? (Dhanbad 1990)
[**Ans.** 0.6715 g]

34. If a current of 0.3 ampere is drawn from a Daniell cell for 1 hour, what would be the change in mass of electrodes? (At. mass of Cu = 63.5 and Zn = 65.37)
[**Ans.** 0.356 g Cu deposited, 0.366 g of Zn dissolves]

35. An element *A* (At. mass 112) and an element *B* (At. mass 27) form chlorides. Solutions of these chlorides are electrolysed separately and it is found that when the same quantity of electricity is passed, 5.6 g of *A* was deposited while in the other cell only 0.9 g of *B* was deposited. What is the valency of *A* if the valency of *B* is 3? (Dhanbad 1991)
[**Ans.** 2]

36. How many coulombs must be applied to a cell for the electrolytic production of 245 g $NaClO_4$ from $NaClO_3$. The anode efficiency for the desired reaction is 60%.
[**Ans.** 6.43×10^5 coulomb]

37. Calculate the mass of Hg_2Cl_2 which can be prepared by the reduction of mercury(II) ions in the presence of chloride ions by the passage of 5.0 ampere current for 3.0 hours.

[**Ans.** 132.34 g]

[**Hint:** $\underset{}{2Hg^{2+}} + 2Cl^- + \underset{2\,F}{2e^-} \longrightarrow \underset{1\text{ mole}}{Hg_2Cl_2}$]

38. How long will it take for a uniform current of 6.0 ampere to deposit 78.0 g gold from a solution of $AuCl_4^-$? What mass of chlorine gas will be formed simultaneously at the anode in the electrolytic cell?

[**Ans.** 19104 second; chlorine liberated = 42.17 g]

[**Hint:** $AuCl_4^- + \underset{3\,F}{3e^-} \longrightarrow \underset{1\text{ mole}}{Au} + 4Cl^-$ (Cathode)

$2Cl^- \longrightarrow \underset{1\text{ mole}}{Cl_2} + \underset{2\,F}{2e^-}$ (Anode)]

39. How long will it take 5 ampere of current to deposit 2 g of copper from a solution of copper sulphate?
(Given, CE of copper = 32, F = 96500 coulomb)
(Ranchi 1996)

[**Ans.** 20.1 minute]

40. The amount of lactic acid, $HC_3H_5O_3$, produced in a sample of muscle tissue was analysed by reaction with hydroxide ion. Hydroxide ion was produced in the sample mixture by electrolysis. The cathode reaction was,

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$$

Hydroxide ion reacts with lactic acid as soon as it is produced. The end point of the reaction is detected with an acid-base indicator. It required 115 seconds for a current of 15.6 mA to reach end point. How many grams of lactic acid (a monoprotic acid) were present in the sample?

[**Ans.** 1.674×10^{-3} g]

[**Hint:** No. of moles of lactic acid = No. of moles of OH^- used
= No. of faraday used in electrolysis

$$\text{Number of faraday used} = \frac{I \times t}{96500} = \frac{15.6 \times 10^{-3} \times 115}{96500}$$
$$= 1.86 \times 10^{-5}$$

Mass of lactic acid = Number of moles × Molecular mass

$$= 1.86 \times 10^{-5} \times 90$$
$$= 1.674 \times 10^{-3}\text{ g}]$$

41. In what direction, can the reaction:

$$2NaCl + Fe_2(SO_4)_3 \rightleftharpoons 2FeSO_4 + Cl_2 + Na_2SO_4$$

proceed spontaneously?

(Given: $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V}$; $E^\circ_{Cl^-/Cl_2} = 1.36\text{ V}$)
(BCECE 2005)

[**Ans.** Forward]

42. How many faradays of electricity will be required to completely electrolyse one mole of molten Al_2O_3 to produce Al metal and O_2 gas? **|JEE (West Bengal) 2005|**

[**Ans.** 3 F]

43. The resistance of 0.01 N solution at 25°C is 200 ohm. Cell constant of the conductivity cell is unity. Calculate the equivalent conductance of the solution.

[**Ans.** $500\text{ ohm}^{-1}\text{ cm}^2\text{ eq}^{-1}$]

44. A conductivity cell was filled with 0.01 M solution of KCl which was known to have a specific conductivity of 0.1413 $\text{ohm}^{-1}\text{ m}^{-1}$ at 298 K. Its measured resistance at 298 K was 94.3 ohm. When the cell was filled with 0.02 M $AgNO_3$ solution, its resistance was 50.3 ohm. Calculate (i) cell constant and (ii) the specific conductance of $AgNO_3$ solution.

[**Ans.** 13.32 m^{-1}; $2.648 \times 10^{-1}\text{ ohm}^{-1}\text{ m}^{-1}$]

45. A conductance cell was calibrated by filling it with a 0.02 M solution of potassium chloride. (specific conductance $= 0.2768\text{ ohm}^{-1}\text{ m}^{-1}$) and measuring the resistance at 298 K which was found to be 457.3 ohm. The cell was then filled with a calcium chloride solution containing 0.555 g of $CaCl_2$ per litre. The measured resistance was 1050 ohm. Calculate the molar conductivity of $CaCl_2$ solution.

[**Ans.** $0.0241\text{ mho m}^2\text{ mol}^{-1}$]

[**Hint:** Determine cell constant with KCl data. Its value is 126.6 m^{-1}.

$$\text{Sp. cond. of } CaCl_2 \text{ soln.} = \text{Cell const.} \times \frac{1}{\text{Resistance}}$$
$$= 126.6 \times \frac{1}{1050} = 0.1206\text{ ohm}^{-1}\text{ m}^{-1}$$
$$\text{Molar conductance} = \frac{\text{Sp. cond.}}{\text{Conc.}}$$
$$\text{Conc.} = \frac{0.555}{111.0} = 0.005\text{ mol dm}^{-3} = 5\text{ mol m}^{-3}]$$

46. The molar conductivities at infinite dilution of KCl, KNO_3 and $AgNO_3$ at 298 K are $0.01499\text{ mho m}^2\text{ mol}^{-1}$, $0.01250\text{ mho m}^2\text{ mol}^{-1}$ and $0.01334\text{ mho m}^2\text{ mol}^{-1}$ respectively. What is the molar conductivity of AgCl at infinite dilution at this temperature?

[**Ans.** $0.01383\text{ mho m}^2\text{ mol}^{-1}$]

47. The electrodes in a conductivity cell have area $1.2 \times 10^{-4}\text{ m}^2$ and they are fixed 3×10^{-3} m apart. A solution containing 200 g equivalent of the electrolyte per m^3 of the solution has a resistance of 60 ohm at 298 K. Calculate the equivalent conductivity of the solution.

[**Ans.** $2.09 \times 10^{-2}\text{ mho m}^2\text{ eq}^{-1}$]

48. The molar conductivities of NH_4^+ ion and Cl^- ion are 73.5 $\text{mho cm}^2\text{ mol}^{-1}$ and $76.2\text{ mho cm}^2\text{ mol}^{-1}$ respectively. The specific conductivity of 0.1 M NH_4Cl is $1.288 \times 10^{-2}\text{ mho cm}^{-1}$. What is the dissociation constant of NH_4Cl?

[**Ans.** 0.86]

49. The specific conductivity of a saturated solution of silver chloride at 18°C is 1.24×10^{-6} mho after subtracting that of water. Ionic conductances at infinite dilution of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively. Calculate the solubility of silver chloride in gram per litre.

[**Ans.** 1.494×10^{-3} g per litre]

50. Given:

$$\lambda^{\infty}\,[\tfrac{1}{2}\,Mg^{2+}] = 53.06\ ohm^{-1}\ cm^2\ mol^{-1}$$
$$\lambda^{\infty}\,[\tfrac{1}{2}\,SO_4^{2-}] = 80\ ohm^{-1}\ cm^2\ mol^{-1}$$
$$\lambda^{\infty}\,[\tfrac{1}{3}\,Al^{3+}] = 63\ ohm^{-1}\ cm^2\ mol^{-1}$$

Calculate the values of $\Lambda_m^{\infty}\,[Al_2(SO_4)_3]$ and $\Lambda^{\infty}\,[MgSO_4]$.

[**Ans.** 858 $ohm^{-1}\ cm^2\ mol^{-1}$, 266.12 $ohm^{-1}\ cm^2\ mol^{-1}$]

51. Hydrofluoric acid is a weak acid. At 25°C, the molar conductivity of 0.002 M HF is 176.2 $ohm^{-1}\ cm^2\ mol^{-1}$. If its $\Lambda_m^{\infty} = 405.2\ ohm^{-1}\ cm^2\ mol^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.

[**Ans.** $\alpha = 0.435, K = 6.7 \times 10^{-4}$]

52. For mercury at 0°C specific conductance,

$$\kappa = 1.062963 \times 10^6\ S/m.$$

(a) If the resistance of a cell containing mercury is 0.243166 ohm, what is the cell constant of the cell?

(b) If the same cell is filled with KCl solution at 0°C, the resistance of the cell is 3.966×10^4 ohm. What is the conductivity of KCl solution?

(c) If the average cross-sectional area of the cell is 0.9643 mm^2, what is the effective distance between the electrodes?

[**Ans.** (a) 2.58476×10^5 S/m; (b) 6.517 S/m; (c) 0.2492 m]

53. The mobility of the NH_4^+ ions is $7.623 \times 10^{-8}\ m^2/Vs$. Calculate:

(a) the molar conductivity of NH_4^+ ion;

(b) velocity of the ion if 15 volt are applied across the electrodes 25 cm apart.

[**Ans.** (a) $73.55 \times 10^{-4}\ S\ m^2/mol$; (b) 4.574 μm/s]

54. Construct electric cells for the following reactions:

(a) $Fe + Cu^{2+} \longrightarrow Cu + Fe^{2+}$

(b) $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$

(c) $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(d) $Cd + I_2 \longrightarrow Cd^{2+} + 2I^-$

(e) $2Fe^{3+} + 2Cl^- \longrightarrow 2Fe^{2+} + Cl_2$

[**Ans.** (a) $Fe \mid Fe^{2+} \parallel Cu^{2+} \mid Cu$

(b) $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$

(c) $Pt \mid Fe^{2+}, Fe^{3+} \parallel H^+, Cr_2O_7^{2-}, Cr^{3+} \mid Pt$

(d) $Cd \mid Cd^{2+} \parallel I^-, I_2 \mid Pt$

(e) $Pt \mid Cl_2, Cl^- \parallel Fe^{3+}, Fe^{2+} \mid Pt$]

55. Predict whether the following reaction will occur spontaneously or not:

$$Co^{2+} + Sn \longrightarrow Co + Sn^{2+}$$

$E^{\circ}_{Co/Co^{2+}} = 0.277$ volt and $E^{\circ}_{Sn/Sn^{2+}} = 0.136$ volt

[**Ans.** No; E°_{cell} is negative = – 0.141 volt]

56. An iron wire is immersed in a solution containing $ZnSO_4$ and $NiSO_4$. Predict giving reasons which of the following reactions is likely to proceed?

(i) Iron reduces Zn^{2+} ions (ii) Iron reduces Ni^{2+} ions.

Given: $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ volt; $E^{\circ}_{Fe^{2+}/Fe} = -0.44$ volt and $E^{\circ}_{Ni^{2+}/Ni} = -0.25$ volt.

[**Ans.** Iron reduces Ni^{2+} ions as the E°_{cell} in this case has positive value.]

57. Can a solution of 1 M $CuSO_4$ be stored in a vessel made of nickel metal?

Given: $E^{\circ}_{(Ni^{2+};\,Ni)} = -0.25$ volt

$E^{\circ}_{(Cu^{2+};\,Cu)} = 0.34$ volt

Ans. No; The reaction takes place between $CuSO_4$ and nickel s E°_{cell} is positive.]

58. Answer whether, under standard conditions, the following reactions are possible or not:

(i) Will copper reduce Ag^+ to Ag? Given: $E^{\circ}_{Ag^+/Ag} = 0.799$ volt; $E^{\circ}_{Cu^{2+}/Cu} = -0.337$ volt

(ii) Will Fe^{3+} be reduced to Fe^{2+} by Sn^{2+} ion? Given:

$Fe^{3+} \mid Fe^{2+} = 0.771$ volt;

$Sn^{2+} \mid Sn^{4+} = -0.250$ volt

(iii) Would you use a silver spoon to stir a solution of $Cu(NO_3)_2$?

[**Ans.** (i) Yes, E°_{cell} $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$ is positive (+ 0.462 volt)

(ii) Yes, E°_{cell} $Pt \mid Sn^{4+}, Sn^{2+} \parallel Fe^{3+}, Fe^{2+} \mid Pt$ is positive (+0.621 volt)

(iii) Yes, the reaction does not occur.]

59. The electrode potentials of two half reactions are as follows:

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $E^{\circ} = +0.76$ volt

$Ce^{4+} + e^- \longrightarrow Ce^{3+}$; $E^{\circ} = +1.60$ volt

Giving reason, describe if Ce^{3+} can be oxidised by Fe^{3+}.

[**Hint:** $Ce^{3+} + Fe^{3+} \longrightarrow Ce^{4+} + Fe^{2+}$

$Ce^{3+} \longrightarrow Ce^{4+} + e^-$ (oxidation); $E^{\circ} = -1.60$ volt

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (reduction); $E^{\circ} = +0.76$ volt

Adding both, E° of the reaction = – 0.84 volt

The oxidation of Ce^{3+} by Fe^{3+} is not possible.]

60. Calculate the standard reduction potential of Ni^{2+}/Ni electrode when the emf of the cell

$$Ni \mid Ni^{2+}\,(1\,M) \parallel Cu^{2+}\,(1\,M) \mid Cu$$

is 0.59 volt and $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ volt

[**Ans.** – 0.25 volt]

61. Calculate the half-cell potential at 298 K for the reaction,

$$Zn^{2+} + 2e^- \longrightarrow Zn$$

if $[Zn^{2+}] = 0.1\,M$ and $E^{\circ} = -0.76$ volt.

[**Ans.** – 0.789 volt]

62. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution. Calculate the emf of the cell at 25°C. Write the chemical equations for the electrode reactions and represent the cell. (Given: $E^{\circ}_{Zn^{2+}/Zn} = -0.76$ volt and $E^{\circ}_{Pb^{2+}/Pb} = -0.13$ volt)

[**Ans.** $Zn \longrightarrow Zn^{2+} + 2e^-$, $\quad Pb^{2+} + 2e^- \longrightarrow Pb$

$$Zn \mid \underset{0.1\,M}{Zn^{2+}} \parallel \underset{0.02\,M}{Pb^{2+}} \mid Pb$$

$E^\circ_{cell} = 0.63$ volt $\quad E_{cell} = 0.609$ volt]

63. Calculate the cell potential of the cell at 25°C having the cell reaction:

$$2Ag^+ + Cu \rightleftharpoons 2Ag + Cu^{2+}$$

(Given that, $[Ag^+] = 1.0 \times 10^{-3}\,M$,

$[Cu^{2+}] = 1.0 \times 10^{-4}\,M$, $E^\circ_{cell} = 0.46$ volt)

[**Ans.** 0.40 volt]

64. Calculate the E and E° of the cell

$$Ni \mid Ni^{2+} \parallel Cu^{2+} \mid Cu$$

from the following half-cell reactions:

$Ni^{2+} + 2e^- \longrightarrow Ni$; $\quad E^\circ = -0.25$ volt

$Cu^{2+} + 2e^- \longrightarrow Cu$; $\quad E^\circ = +0.34$ volt

(Given: $[Ni^{2+}] = 1\,M$ and $[Cu^{2+}] = 10^{-3}\,M$)

[**Ans.** $E^\circ_{cell} = 0.59$ volt; $E_{cell} = 0.5015$ volt]

65. Use E° values to calculate ΔG° for the reaction

$$Fe^{2+} + Ag^+ \longrightarrow Fe^{3+} + Ag$$

$E^\circ_{Ag^+/Ag} = 0.80$ volt and $E^\circ_{Pt/Fe^{3+}, Fe^{2+}} = 0.77$ volt

[**Ans.** -2895 J]

[**Hint:** $E^\circ_{cell} = 0.03$ volt, $\Delta G^\circ = -nFE^\circ_{cell}$]

66. A piece of zinc metal is dipped in a 0.1 M solution of zinc salt. The salt is dissociated to the extent of 20%. Calculate the electrode potential of Zn^{2+}/Zn.

(Given: $E^\circ_{Zn^{2+}/Zn} = -0.76$ volt.)

[**Ans.** -0.8102 volt]

[**Hint:** $[Zn^{2+}] = 0.1 \times 0.2 = 0.02\,M$

$Zn^{2+} + 2e^- \longrightarrow Zn$ (Reduction)

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} + \frac{0.0591}{2}\log_{10}[Zn^{2+}]\,]$$

67. Estimate the concentration limit beyond which the half-cell potential of $Cu^{2+} \mid Cu$ will be zero.

$$E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ volt}$$

[**Ans.** 3.1×10^{-12} mol L^{-1}]

[**Hint:** $E^\circ_{Cu^{2+}/Cu} = \frac{0.0591}{2}\log[Cu^{2+}]$]

68. Calculate equilibrium constant for the following reaction:

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

$E^\circ_{Zn/Zn^{2+}} = 0.765$ volt; $\quad E^\circ_{Cu^{2+}/Cu} = 0.347$ volt

[**Ans.** 1.862×10^{37}]

69. For the cell reaction,

$$Ni \mid Ni^{2+} \parallel Ag^+ \mid Ag$$

Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by the operation of this cell?

[**Ans.** 3.98×10^{35}, Max. work = 202650 J]

70. Calculate the emf of the cell

$$Cr \mid Cr^{3+}\,(0.1\,M) \parallel Fe^{2+}\,(0.01\,M) \mid Fe$$

(Given: $E^\circ_{Cr^{3+}/Cr} = -0.75$ volt; $E^\circ_{Fe^{2+}/Fe} = -0.45$ volt)

[**Ans.** 0.261 volt]

71. Calculate the equilibrium constant for the reaction,

$$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow 2Ag(s) + Zn^{2+}(aq.) + 2OH^-(aq.)$$

when $E^\circ_{cell} = 1.11$ at 298 K.

[**Ans.** $K_c = 3.499 \times 10^{37}$]

72. The standard reduction potential of $Ag^+ \mid Ag$ electrode is 0.80 volt. Calculate the standard electrode potential of $Cl^- \mid AgCl \mid Ag$ at 25°C. Given solubility product, $K_{sp}(AgCl) = 1.8 \times 10^{-10}$.

[**Hint:** Apply

$E^\circ_{cell} = 0.0591 \times \log[Ag^+][Cl^-] = 0.0591 \log K_{sp}(AgCl)$

$E^\circ_{cell} = -0.576$ volt

E°_{cell} = Oxid. pot. anode + Red. pot. cathode

Red. pot. cathode $[Cl^- \mid AgCl \mid Ag] = -0.576 - (-0.80)$

$= -0.576 + 0.80 = 0.224$ volt]

73. Derive Nernst equation for the cell.

$$Ni(s) \mid Ni^{2+}\,(aq.\ 0.1\,M) \parallel Ag^+\,(aq.\ 0.1\,M) \mid Ag(s)$$

and also find its cell potential. Given:

$E^\circ_{Ag^+/Ag} = 0.80$ volt and $E^\circ_{Ni^{2+}/Ni} = -0.25$ volt

[**Hint:** Cell reaction,

$Ni + 2Ag^+ \longrightarrow 2Ag + Ni^{2+}$; $\quad E^\circ_{cell} = 1.05$ volt

Nernst equation, $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$

$\doteq (1.05 - 0.0295)$ volt

$= 1.02$ volt]

74. Determine the equilibrium constant of the following reaction at 298 K:

$$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$

(Given: $E^\circ_{Sn^{4+}/Sn^{2+}} = 0.15$ volt, $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ volt)

[**Ans.** $K = 1.0 \times 10^{21}$]

[**Hint:** Calculate E°_{cell}. The value is 0.621 volt.

Apply $E^\circ_{cell} = \frac{0.0591}{2}\log K$]

75. The zinc-silver oxide cell is used in hearing aids and electric watches. From the following data:

$Zn^{2+} + 2e^- \longrightarrow Zn$; $\quad E^\circ = -0.76$ volt

$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$; $\quad E^\circ = 0.334$ volt

Answer the following:

(a) Construct the cell and what will be its emf?

(b) What is its cell reaction and what will be ΔG° value of this cell reaction?

(c) Name the species which undergo oxidation and reduction when the cell is in operation.

[**Ans.** (a) Cell $Zn \mid Zn^{2+} \parallel OH^- \mid Ag_2O \mid Ag$

$E^\circ_{cell} = 1.104$ volt

(b) Cell reaction,

$$Ag_2O + H_2O + Zn \longrightarrow 2Ag + Zn^{2+} + 2OH^-$$

$$\Delta G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 1.104 = -213072 \text{ J}$$

(c) Zinc is oxidised to Zn^{2+} and Ag_2O is reduced to Ag.]

76. An excess of Hg was added to 10^{-3} *M* acidified solution of Fe^{3+} ions. It was found that only 4.6% of the ions remained as Fe^{3+} at equilibrium at 25°C. Calculate E° for $2Hg / Hg_2^{2+}$ at 25°C for

$$2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$$

[**Ans.** -0.7912 volt]

77. The emf of the cell,

$$Ag \mid AgI \ (0.05) \ M \ KI \parallel (0.05) \ M \ AgNO_3 \mid Ag$$

is 0.788 volt. Calculate the solubility product of AgI.

[**Ans.** 1.10×10^{-16}]

78. At equimolar concentrations of Fe^{2+} and Fe^{3+}, what must $[Ag^+]$ be so that the voltage of the galvanic cell made from Ag^+/Ag and Fe^{3+}/Fe^{2+} electrodes equals zero? The reaction is $Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$. Determine the equilibrium constant at 25°C for the reaction. (Given: $E^\circ_{Ag^+/Ag} = 0.799$ volt and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$ volt)

[**Hint:** $E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe^{3+}} + E^\circ_{Ag^+/Ag}$

$$= -0.771 + 0.799 = 0.028 \text{ volt}$$

At equilibrium, $E_{cell} = 0$

$$0 = E^\circ_{cell} - \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]}$$

$$= E^\circ_{cell} - 0.0591 \log \frac{1}{[Ag^+]}$$

$$[Ag^+] = 0.34$$

$$\log K = \frac{nE^\circ}{0.0591}$$

$$K = 3.0]$$

79. Using Nernst equation for the cell reaction,

$$Pb + Sn^{2+} \longrightarrow Pb^{2+} + Sn$$

Calculate the ratio $\frac{[Pb^{2+}]}{[Sn^{2+}]}$ for which $E_{cell} = 0$.

(Given: $E^\circ_{Pb/Pb^{2+}} = 0.13$ volt and $E^\circ_{Sn^{2+}/Sn} = -0.14$ volt)

[**Ans.** $\frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.5$]

80. Determine the potential of a Daniell cell, initially containing 1.00 L each of 1.0 *M* copper(II) ion and 1.0 *M* zinc(II) ion, after passage of 10^5 coulomb charge. The E° of the Daniell cell is 1.10 volt.

[**Ans.** 1.09 volt]

[**Hint:** By passage of 10^5 coulomb charge, zinc ion concentration increases by 0.518 mole while copper ion concentration decreases by 0.518 mole.

Thus, $[Zn^{2+}] = 1.518 \, M$ and $[Cu^{2+}] = 0.482 \, M$

(Now apply Nernst equation)]

81. Calculate the standard potential for the reaction,

$$Hg_2Cl_2 + Cl_2 \longrightarrow 2Hg^{2+} + 4Cl^-$$

(Given:

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-; \quad E^\circ = 0.270 \text{ volt}$$

$$Hg_2^{2+} \longrightarrow 2Hg^{2+} + 2e^-; \quad E^\circ = -0.92 \text{ volt}$$

$$2Hg \longrightarrow Hg_2^{2+} + 2e^-; \quad E^\circ = -0.79 \text{ volt}$$

$$Cl_2 + 2e^- \longrightarrow 2Cl^-; \quad E^\circ = 1.36 \text{ volt})$$

Ans. -0.08 volt]

[**Hint:** First determine E° for

$$Hg_2Cl_2 \longrightarrow 2Hg^{2+} + 2Cl^- + 2e^- \text{ electrode.}$$

It comes to -1.44 volt.

This electrode is now coupled with $Cl_2 + 2e^- \longrightarrow 2Cl^-$ electrode.]

82. Given:

$$Cu^{2+} + e^- \longrightarrow Cu^+; \quad E^\circ = 0.15 \text{ volt}$$

$$Cu^+ + e^- \longrightarrow Cu; \quad E^\circ = 0.5 \text{ volt}$$

Calculate potential for $Cu^{2+} + 2e^- \longrightarrow Cu$.

[**Ans.** 0.325 volt]

83. What is the standard electrode potential for the electrode MnO_4^-/MnO_2 in solution?

(Given: $E^\circ_{MnO_4^-/Mn^{2+}} = 1.51$ volt, $E^\circ_{MnO_2/Mn^{2+}} = 1.23$ volt)

[**Ans.** 1.7 volt]

[**Hint:**

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O; \ E^\circ = 1.51 \text{ volt}$$

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O; \ E^\circ = 1.23 \text{ volt}$$

Subtracting

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O; \ E^\circ = ?$$

$$E^\circ = \frac{5 \times 1.51 - 2 \times 1.23}{3} = \frac{7.55 - 2.46}{3} = \frac{5.09}{3} = 1.70 \text{ volt}]$$

84. What ratio of Pb^{2+} to Sn^{2+} concentration is needed to reverse the following cell reaction?

$$Sn(s) + Pb^{2+}(aq.) \longrightarrow Sn^{2+}(aq.) + Pb(s)$$

$$E^\circ_{Sn^{2+}/Sn} = -0.136 \text{ volt} \quad \text{and} \quad E^\circ_{Pb^{2+}/Pb} = -0.126 \text{ volt}$$

[**Ans.** $\frac{[Pb^{2+}]}{[Sn^{2+}]} < 0.458$]

85. For the cell $Mg \mid Mg^{2+} \parallel Ag^+ \mid Ag$, calculate the equilibrium constant at 25°C and the maximum work that can be obtained during the operation of the cell.

(Given: $E^\circ_{Mg/Mg^{2+}} = 2.37$ volt and $E^\circ_{Ag^{2+}/Ag} = 0.80$ volt)

[**Ans.** $K = 2.86 \times 10^{107}$; $W_{max} = 6.118 \times 10^5$ J]

86. Determine the potential for the cell:

$$\text{Pt} \mid \text{Fe}^{2}, \text{Fe}^{3+} \parallel \text{Cr}_2\text{O}_7^{2-}, \text{Cr}^{3+}, \text{H}^+ \mid \text{Pt}$$

in which $[\text{Fe}^{2+}]$ and $[\text{Fe}^{3+}]$ are $0.5M$ and $0.75M$ respectively and $[\text{Cr}_2\text{O}_7^{2-}]$, $[\text{Cr}^{3+}]$ and $[\text{H}^+]$ are $2M$, $4M$ and $1M$ respectively. Given:

$$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}; \qquad E° = 0.770 \text{ volt}$$

$$14\text{H}^+ + 6e^- + \text{Cr}_2\text{O}_7^{2-} = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}; \qquad E° = 1.35 \text{ volt}$$

[**Ans.** 0.56 volt]

87. For the measurement of the solubility product of AgCl the following cell is constructed:

$$\text{Ag} \mid \text{AgCl} \parallel \text{KCl}\ (0.1\ M) \parallel \text{AgNO}_3\ (0.1\ M) \mid \text{Ag}$$

The emf of the cell is 0.45 volt. In the cell, KCl is dissociated to the extent of 83% and AgNO_3 is dissociated to the extent of 86%. Calculate the solubility product of AgCl at 298 K.

[**Ans.** 1.735×10^{-10}]

[**Hint:** $E_{\text{cell}} = E°_{\text{cell}} - 0.0591 \log \dfrac{[\text{Ag}^+]_{\text{Anode}}}{[\text{Ag}^+]_{\text{Cathode}}}$]

88. Excess of AgCl is added to 0.1 M solution of KBr at 298 K. Calculate the equilibrium concentrations of Br^- and Cl^- ions.

$$E°_{\text{Cl}^-/\text{AgCl}/\text{Ag}} = 0.222 \text{ volt} \quad E°_{\text{Br}^-/\text{AgBr}/\text{Ag}} = 0.095 \text{ volt}$$

[**Ans.** $[\text{Cl}^-] = 0.09929 \text{ mol L}^{-1}$, $[\text{Br}^-] = 0.00071 \text{ mol L}^{-1}$]

[**Hint:** $\underset{}{\text{AgCl}} + \underset{(0.1-x)}{\text{Br}^-} \rightleftharpoons \text{AgBr} + \underset{x}{\text{Cl}^-}$

At equilibrium

Apply $\log K = \dfrac{E°_{\text{cell}}}{0.0591}$

or $\log \dfrac{x}{(0.1-x)} = \dfrac{E°_{\text{cell}}}{0.0591}$]

89. The emf of the cell $\text{Cu} \mid \underset{a\,=\,0.1}{\text{CuSO}_4} \parallel \underset{x}{\text{CuSO}_4} \mid \text{Cu}$ is -0.03 V at 25°C. Calculate the activity of copper sulphate solution in the right hand side electrode.

[**Ans.** $0.009616 \text{ mol L}^{-1}$]

[**Hint:** Apply $E = (E°_{\text{Cu}} - E°_{\text{Cu}}) - \dfrac{0.0591}{2} \log \dfrac{0.1}{x}$]

90. The cell, $\text{Pt} \mid \text{H}_2\ (1 \text{ atm}) \parallel \text{H}^+\ (\text{pH} = x) \mid$ normal calomel electrode, has an emf of 0.67 volt as 25°C. Calculate the pH of the solution. The oxidation potential of calomel electrode on the hydrogen scale is -0.28 volt.

[**Ans.** pH = 6.61]

91. The emf of the cell,

$$\text{Ag} \mid \text{AgI}, \text{KI}\ (0.05\ M) \parallel \text{AgNO}_3\ (0.05\ M) \mid \text{Ag}$$

is 0.788 volt. Calculate the solubility product of AgI.

[**Ans.** 1.101×10^{-16}]

92. The standard reduction potential for Cu^{2+}/Cu is + 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of Cu(OH)_2 is 1.0×10^{-19}.

[**Ans.** -0.22 V] **(IIT 1996)**

93. Calculate the potential of a cell in which H electrode is immersed in a solution of pH 3.5 and in a solution of pH 10.7.

[**Ans.** 0.4255 volt]

94. Calculate the emf of the cell,

$$\text{Cl}_2\ (1 \text{ atm}) \mid \text{NaCl}\ (aq.) \mid \text{Cl}_2\ (0.1 \text{ atm})$$

[**Ans.** -0.0295 volt]

95. The standard free energy change for the reaction,

$$\text{H}_2(g) + 2\text{AgCl}(s) \longrightarrow 2\text{Ag}(s) + 2\text{H}^+(aq.) + 2\text{Cl}^-(aq.)$$

is $-10.26 \text{ kcal mol}^{-1}$ at 25°C. A cell using the above reaction is operated at 25°C under $P_{\text{H}_2} = 1$ atm, $[\text{H}^+]$ and $[\text{Cl}^-] = 0.1$. Calculate the emf of the cell.

[**Ans.** 0.340 volt]

96. For the reaction, $\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}$. $E°$ is -0.036 volt and the standard electrode potential for $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$ is 0.771 volt. Calculate the $E°$ for $\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$.

[**Ans.** -0.4395 volt]

97. The standard reduction potential at 25°C of the reaction $2\text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2 + 2\text{OH}^-$ is -0.8277 volt. Calculate the equilibrium constant for the reaction,

$$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \text{ at } 25°\text{C}$$

[**Ans.** $\approx 10^{14}$]

[**Hint:**

$$\text{H}_2\text{O} + e^- \longrightarrow \tfrac{1}{2}\text{H}_2 + \text{OH}^- \text{ (Cathode)}; \quad E° = -0.8277 \text{ volt}$$

$$\text{H}_2\text{O} + \tfrac{1}{2}\text{H}_2 \longrightarrow \text{H}_3\text{O}^+ + e^- \quad \text{(Anode)}; \quad E° = 0$$

$E°$ for the cell = -0.8277 volt

Apply now $E° = \dfrac{0.0591}{n} [\log K]$ $(n = 1)$]

98. Calculate the emf of the following cell:

$$\text{Pt(H}_2\ 1 \text{ atm}) \mid \text{CH}_3\text{CH}_2\text{COOH}\ (0.15\ M) \parallel 0.01\ M\ \text{NH}_4\text{OH} \mid \text{H}_2\ (1 \text{ atm})\ \text{Pt}$$

K_a for $\text{CH}_3\text{CH}_2\text{COOH} = 1.4 \times 10^{-5}$

K_b for $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$

[**Ans.** -0.4603 volt]

[**Hint:** $[\text{H}^+]$ in $\text{CH}_3\text{CH}_2\text{COOH} = \sqrt{C \times K_a} = \sqrt{0.15 \times 1.4 \times 10^{-5}}$
$= 1.449 \times 10^{-3}$

$[\text{OH}^-]$ in $\text{NH}_4\text{OH} = \sqrt{C \times K_b} = \sqrt{0.01 \times 1.8 \times 10^{-5}} = 0.4242 \times 10^{-3}$

$$[\text{H}^+] \text{ in NH}_4\text{OH} = \frac{10^{-14}}{0.4242 \times 10^{-3}} = 2.3573 \times 10^{-11}$$

$$E_{\text{cell}} = 0.0591 \log \frac{[\text{H}^+]_{\text{RHS}}}{[\text{H}^+]_{\text{LHS}}}$$]

99. Calculate equilibrium constant for

$$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$$

at 298 K from the following information:

$$\text{I}_2(aq.) + 2e^- \longrightarrow 2\text{I}^-; \qquad E° = 0.6197 \text{ volt}$$

$$\text{I}_3^- + 2e^- \longrightarrow 3\text{I}^-; \qquad E° = 0.5355 \text{ volt}$$

[**Ans.** 706.9]

[**Hint:**

$$\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-; \qquad E° = 0.6197 \text{ volt}$$

$$3\text{I}^- \longrightarrow \text{I}_3^- + 2e^-; \quad E° = -0.5355 \text{ volt}$$

$$\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-; \qquad E° = 0.6197 - 0.5355$$

$$= 0.0842 \text{ volt}$$

$$K = \text{antilog}\left[\frac{nE^\circ}{0.0591}\right] = \text{antilog}\left[\frac{2 \times 0.0842}{0.0591}\right] = 706.9]$$

100. A lead storage battery has initially 200 g of lead and 200 g of PbO_2, plus excess H_2SO_4. How long could this cell deliver a current of 10 amp, without recharging, if it was possible to operate it so that the reaction goes to completion?

[**Ans.** 4.48 hour]

101. $Zn(s) + 2AgCl(s) \rightleftharpoons ZnCl_2\ (0.555\ M) + 2Ag(s)$

$$E_{0^\circ C} = 1.015 \text{ volt} \left(\frac{dE}{dT}\right)_P = -4.02 \times 10^{-4} \text{ volt per degree.}$$

Find $\Delta G, \Delta S$.

[**Ans.** $\Delta G = -195.895$ kJ, $\Delta S = -18.55$ cal]

[**Hint:** We know that,

$$\Delta H = nF\left[T\left(\frac{dE}{dT}\right)_P - E\right]$$

$$= 2 \times 96500\,[-273 \times 4.02 \times 10^{-4} - 1.015]$$

$$= -217075.98 \text{ joule} = -217.075 \text{ kJ}$$

$$\Delta G = -nFE = -2 \times 96500 \times 1.015 = -195895 \text{ J}$$

$$= -195.895 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S$$

$$-195.895 = -217.075 - 273 \times \Delta S$$

$$\Delta S = -0.07758 \text{ kJ} = -77.58 \text{ J} = -18.55 \text{ cal}]$$

102. Calculate the equilibrium constant for the reaction,

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$

The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+}/Fe^{2+} and I_3^-/I^- couples. (IIT 1998)

[**Ans.** 6.26×10^7]

103. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as the per reaction,

$$Mn^{2+}(aq.) + 2H_2O \longrightarrow MnO_2 + 2H^+(aq.) + H_2$$

Passing a current of 27 A for 24 hours gives one kg of MnO_2. What is the value of current efficiency? Write the reactions taking place at the cathode and at the anode. [IIT (May) 1997]

[**Hint:** Apply $w = \dfrac{E \times i \times t}{96500}$

$$1000 = \frac{87 \times i \times 24 \times 60 \times 60}{2 \times 96500}$$

$$i = 25.6 \text{ ampere}$$

$$\text{Current efficiency} = \frac{25.6}{27.0} \times 100 = 94.8\%$$

Reactions:

Anode: $Mn^{2+} \longrightarrow Mn^{4+} + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$]

104. Calculate the number of kWh of electricity is necessary to produce 1 metric ton (1000 kg) of aluminium by Hall process in a cell operating at 15 V.

[**Ans.** 4.47×10^4 kWh]

105. What will be the value of Λ for a 0.001 M aqueous NH_3 solution?

$K_b = 1.6 \times 10^{-5}$ and $\Lambda_0 = 2.38 \times 10^{-2}$ ohm^{-1} m^2 mol^{-1}

[**Ans.** 2.998×10^{-3} ohm^{-1} cm^2 mol^{-1}]

[**Hint:**

$$K_b = C\alpha^2$$

$$1.6 \times 10^{-5} = 0.001 \times \alpha^2$$

$$\alpha = 0.126$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty};$$

(Λ_m^c = molar conductance at concentration 'c' and Λ_m^∞ = molar conductance at infinite dilution)

$$0.126 = \frac{\Lambda_m^c}{2.38 \times 10^{-2}}$$

$$\Lambda_m^c = 2.998 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}]$$

106. A weak monobasic acid is 5% dissociated in 0.01 mol dm^{-3} solution. The limiting molar conductivity at infinite dilution is 4.00×10^{-2} ohm^{-1} m^2 mol^{-1}. Calculate the conductivity of a 0.05 mol dm^{-3} solution of the acid.

[**Ans.** 8.92×10^{-4} ohm^{-1} cm^2 mol^{-1}]

[**Hint:** Dissociation constant of acid $K_a = C\alpha^2$

$$= 0.01 \times (0.05)^2$$

$$= 2.5 \times 10^{-5}$$

$$K_a = C\alpha^2$$

$$2.5 \times 10^{-5} = 0.05 \times \alpha^2$$

$$\alpha = 0.0223$$

We know that, $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^\infty}$

$$0.0223 = \frac{\Lambda_m^c}{4 \times 10^{-2}}$$

$$\Lambda_m^c = 8.92 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}]$$

107. 1.05 g of a lead ore containing impurity of Ag was dissolved in quantity of HNO_3 and the volume was made 350 mL. A Ag electrode was dipped in the solution and E_{cell} of,

$$Pt(H_2) \mid H^+(1\,M) \parallel Ag^+ \mid Ag$$

was 0.503 V at 298 K. Calculate % of lead in the ore.

$$E^\circ_{Ag^+/Ag} = 0.80 \text{ V}$$

[**Ans.** 0.0339%]

[**Hint:** Anode $\frac{1}{2}H_2(g) \longrightarrow H^+(1\,M) + e^-$

Cathode $Ag^+(x) + e^- \longrightarrow Ag(s)$

$$\frac{1}{2}H_2(g) + Ag^+(x) \rightleftharpoons Ag(s) + H^+(1\,M) \qquad (n = 1)$$

$$E^\circ = 0.80 - 0 = 0.80 \text{ volt}$$

$$Q = \frac{[H^+]}{[Ag^+]} = \frac{1}{x}$$

$$E = E^\circ - \frac{0.0591}{n}\log_{10} Q$$

$$0.503 = 0.80 - \frac{0.0591}{1}\log_{10}\left(\frac{1}{x}\right)$$

$$x = 9.43 \times 10^{-6}\ M$$

Number of moles of Ag^+ in 350 mL

$$= \frac{MV}{1000} = \frac{9.43 \times 10^{-6} \times 350}{1000}$$

$$= 3.3 \times 10^{-6}$$

$$\text{Mass of Ag} = 3.3 \times 10^{-6} \times 108 = 3.56 \times 10^{-4}\ \text{g}$$

$$\%\ \text{Ag in the ore} = \frac{3.56 \times 10^{-4}}{1.05} \times 100 = 0.0339\%]$$

108. Calculate E° of the following half-cell reaction at 298 K:

$$Ag(NH_3)_2^+ + e^- \longrightarrow Ag + 2NH_3$$

$$Ag^+ + e^- \longrightarrow Ag; \qquad E^\circ_{Ag^+/Ag} = 0.80\ V$$

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3; \qquad K = 6 \times 10^{-8}$$

[**Ans.** 0.373 volt]

[**Hint:** Anode $Ag(s) \longrightarrow Ag^+ + e^-$; $E^\circ = 0.80$ volt

Cathode $[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag(s) + 2NH_3$; $E^\circ = v$ volt

$$\overline{Ag(s) + [Ag(NH_3)_2]^+ \rightleftharpoons Ag(s) + Ag^+ + 2NH_3}$$

$$Q = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2]^+} = 6 \times 10^{-8} \qquad (n = 1)$$

$$E^\circ_{\text{cell}} = (v - 0.80)$$

At equilibrium, $E = 0$

$$\therefore \quad E = E^\circ - \frac{0.0591}{n} \log Q$$

$$0 = (v - 0.80) - \frac{0.0591}{1} \log (6 \times 10^{-8})$$

$$v = 0.373\ \text{volt}]$$

OBJECTIVE QUESTIONS

Set-1: Questions with single correct answer

1. An electrolyte is a substance which:
(a) conducts electricity
(b) decomposes on heating
(c) is acidic in nature
(d) when dissolved in water, dissociates into ions

2. The theory of ionisation was presented by:
(a) Faraday (b) Arrhenius (c) Ostwald (d) Rutherford

3. Dissociation of an electrolyte in water into negative and positive ions is called:
(a) ionisation (b) electrolysis
(c) decomposition (d) hydrolysis

4. Degree of ionisation is equal to:
(a) total number of moles of the electrolyte present in solution
(b) total number of moles of the electrolyte dissociated into ions
(c) number of moles dissociated /total number of moles dissolved
(d) total number of moles dissolved/number of moles dissociated

5. Conductivity of aqueous solution of an electrolyte depends on:
(a) molecular mass of the electrolyte
(b) boiling point of solvent
(c) degree of ionisation
(d) volume of the solvent

6. Degree of ionisation does not depend on:
(a) nature of the solvent
(b) nature of the electrolyte
(c) dilution
(d) molecular mass of the electrolyte

7. Substances which give good conducting aqueous solution are called:
(a) weak electrolytes (b) strong electrolytes
(c) non-electrolytes (d) catalysts

8. The number of ions given by one molecule of $K_4Fe(CN)_6$ after complete dissociation is:
(a) 5 (b) 11 (c) 2 (d) 10

9. The amount of electricity required to produce one mole of copper from copper sulphate solution will be : **(VITEEE 2008)**
(a) 1 faraday (b) 2.33 faraday
(c) 2 faraday (d) 1.33 faraday

[**Hint :** $Cu^{2+} + 2e^- \longrightarrow Cu\ (s)$

1 mole copper requires 2 mole electron, *i.e.*, 2 faraday charge.]

10. The process in which chemical change occurs on passing electricity is termed:
(a) ionisation (b) neutralisation
(c) electrolysis (d) hydrolysis

11. Which of the following condition is correct for operation of electrolytic cell?
(a) $\Delta G = 0, E = 0$ (b) $\Delta G < 0, E > 0$
(c) $\Delta G > 0, E < 0$ (d) $\Delta G > 0, E > 0$

12. Which one is the correct equation that represents the first law of electrolysis?
(a) $mZ = ct$ (b) $m = cZt$ (c) $mc = Zt$ (d) $c = mZt$

13. When one coulomb of electricity is passed through an electrolytic solution, the mass deposited on the electrode is equal to:
(a) equivalent weight (b) molecular weight
(c) electrochemical equivalent (d) one gram

14. One faraday is equal to:
(a) 9650 coulomb (b) 10,000 coulomb
(c) 19640 coulomb (d) 96500 coulomb

15. When one faraday of electric current is passed, the mass deposited is equal to:
(a) one gram equivalent (b) one gram mole
(c) electrochemical equivalent (d) half gram equivalent

16. On passing one faraday of electricity through a dilute solution of an acid, the volume of hydrogen obtained at NTP is:
(a) 22400 mL (b) 1120 mL
(c) 2240 mL (d) 11200 mL

17. *w* g of copper is deposited in a copper voltameter when an electric current of 2 ampere is passed for 2 hours. If one ampere of electric current is passed for 4 hours in the same voltameter, copper deposited will be:
(a) w (b) $w/2$ (c) $w/4$ (d) $2w$

18. Copper sulphate solution is electrolysed between two platinum electrodes. A current is passed until 1.6 g of oxygen is liberated at anode. The amount of copper deposited at the cathode during the same period is:
(a) 6.36 g (b) 63.6 g (c) 12.7 g (d) 3.2 g

19. When electricity is passed through a solution of $AlCl_3$, 13.5 g of Al is discharged. The amount of charge passed is:
(a) 1.5 F (b) 0.5 F (c) 1.0 F (d) 2.0 F

20. When the same electric current is passed through the solution of different electrolytes in series, the amounts of elements deposited on the electrodes are in the ratio of their:
(a) atomic numbers (b) atomic masses
(c) specific gravities (d) equivalent masses

21. Faraday's laws of electrolysis are related to:
(a) atomic number of the cation
(b) atomic number of the anion
(c) equivalent mass of the electrolyte
(d) speed of the cation

22. The specific conductance of a 0.01 *M* solution of KCl is 0.0014 ohm^{-1} cm^{-1} at 25°C. Its equivalent conductance is:
(a) 14 (b) 140 (c) 1.4 (d) 0.14

23. The equivalent conductivity of 0.1 *N* CH_3COOH at 25°C is 80 and at infinite dilution 400 ohm^{-1}. The degree of dissociation of CH_3COOH is:
(a) 1 (b) 0.2 (c) 0.1 (d) 0.5

24. The number of electrons involved when one faraday of electricity is passed through an electrolytic solution is:
(a) 96500 (b) 8×10^{6} (c) 12×10^{16} (d) 6×10^{23}

25. One faraday of charge was passed through the electrolytic cells placed in series containing solutions of Ag^+, Ni^{2+} and Cr^{3+} respectively. The amount of Ag (At. mass 108), Ni (At. mass 59) and Cr (At. mass 52) deposited will be:

	Ag	Ni	Cr
(a)	108 g	29.5 g	17.5 g
(b)	108 g	59.0 g	52.0 g
(c)	108 g	108.0 g	108.0 g
(d)	108 g	117.5 g	166.0 g

26. One faraday of electricity will liberate one gram mole of the metal from the solution of:
(a) $BaCl_2$ (b) $CuSO_4$
(c) $AlCl_3$ (d) NaCl

27. Strong electrolytes are those which:
(a) dissolve readily in water
(b) conduct electricity
(c) dissociate into ions even at high concentration
(d) dissociate into ions at high dilution

28. The extent of ionisation increases:
(a) with increase in concentration of the electrolyte
(b) on decreasing temperature of solution
(c) on addition of excess of water
(d) on stirring the solution vigorously

29. Molten sodium chloride conducts electricity due to the presence of:
(a) free electrons (b) free ions
(c) free molecules (d) free atoms of Na and Cl

30. When NaCl is dissolved in water, the sodium ion is:
(a) oxidised (b) reduced
(c) hydrolysed (d) hydrated

31. A solution of sodium sulphate in water is electrolysed using platinum electrodes. The products at cathode and anode are respectively:
(a) H_2, O_2 (b) O_2, H_2
(c) O_2, Na (d) O_2, SO_2

32. The electric conduction of a salt solution in water depends on the:
(a) shape of molecules (b) size of its molecules
(c) size of solvent molecules (d) extent of its ionisation

33. In electroplating, the article to be electroplated serves as:
(a) cathode (b) electrolyte
(c) anode (d) conductor

34. The amount of electricity that can deposit 108 g of silver from silver nitrate solution is: **(AFMC 1993)**
(a) 1 ampere (b) 1 coulomb
(c) 1 faraday (d) 2 ampere

35. A certain current liberated 0.504 g of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in $CuSO_4$ solution?
(a) 12.7 g (b) 15.9 g (c) 31.8 g (d) 63.5 g

36. If the specific resistance of a solution of concentration *C* g equivalent $litre^{-1}$ is *R*, then its equivalent conductance is:
(a) $\frac{100R}{C}$ (b) $\frac{RC}{1000}$ (c) $\frac{1000}{RC}$ (d) $\frac{C}{1000R}$

37. If the specific conductance and conductance of a solution are same, then its cell constant is equal to:
(a) 1 (b) 0 (c) 10 (d) 100

38. On increasing the dilution, the specific conductance: **(Jiwaji 1990)**
(a) increases (b) decreases
(c) remains constant (d) none of these

39. The distance between two electrodes of a cell is 2.5 cm and area of each electrode is 5 cm^2. The cell constant is: **(Jabalpur 1990)**
(a) 2 (b) 12.5 (c) 7.5 (d) 0.5

40. At 25°C, the molar conductances at infinite dilution for the strong electrolytes NaOH, NaCl and $BaCl_2$ are 248×10^{-4}, 126×10^{-4} and 280×10^{-4} $Sm^2\ mol^{-1}$ respectively. $\Lambda^{\circ}_{m}Ba(OH)_2$ in $S\ m^2\ mol^{-1}$: **(EAMCET 2009)**
(a) 52.4×10^{-4} (b) 524×10^{-4}
(c) 402×10^{-4} (d) 262×10^{-4}

[**Hint :** $\Lambda^{\circ}_{m}Ba(OH)_2 = \Lambda^{\circ}_{m}BaCl_2 + 2\Lambda^{\circ}_{m}NaOH - 2\Lambda^{\circ}_{m}NaCl$
$= 280\times10^{-4} + 2\times248\times10^{-4} - 2\times126\times10^{-4}$
$= 524\times10^{-4} S\ m^2\ mol^{-1}$]

41. The electrochemical cell stops working after some time because : **(VITEEE 2008)**
(a) electrode potential of both the electrodes becomes zero
(b) electrode potential of both the electrodes becomes equal
(c) one of the electrodes is eaten away
(d) the cell reaction gets reversed

42. Which reaction will take place at cathode when fused calcium chloride is electrolysed?
(a) $Ca^{2+} + 2e^- \longrightarrow Ca$ (b) $Cl^- \longrightarrow Cl + e^-$
(c) $Ca^{2+} - 2e^- \longrightarrow Ca$ (d) $Cl^- - e^- \longrightarrow Cl$

43. In electrolysis oxidation takes place at:
(a) both the electrodes (b) cathode
(c) anode (d) in the solution

44. The equation representing the process by which standard reduction potential of zinc can be defined is:
(a) $Zn^{2+}(s) + 2e^- \longrightarrow Zn$
(b) $Zn(g) \longrightarrow Zn^{2+}(g) + 2e^-$
(c) $Zn^{2+}(g) + 2e^- \longrightarrow Zn$
(d) $Zn^{2+}(aq.) + 2e^- \longrightarrow Zn(s)$

45. The measured potential for,

$$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$$

does not depend upon:
(a) raising the temperature
(b) increasing the concentration of Mg^{2+} ions
(c) making the magnesium plate bigger
(d) purity of magnesium plate

46. All cells do not contain:
(a) an anode (b) a cathode
(c) ions (d) a porous partition

47. When lead accumulator is charged, it is:
(a) an electrolytic cell (b) a galvanic cell
(c) a Daniell cell (d) none of these

48. The standard electrode potentials for the reactions,

$$Ag^+(aq.) + e^- \longrightarrow Ag(s)$$
$$Sn^{2+}(aq.) + 2e^- \longrightarrow Sn(s)$$

at 25°C are 0.80 volt and – 0.14 volt respectively. The emf of the cell,

$$Sn \mid Sn^{2+}(1\,M) \parallel Ag^+(1\,M) \mid Ag$$

is:
(a) 0.66 volt (b) 0.80 volt (c) 1.08 volt (d) 0.94 volt

49. The cathodic reaction in electrolysis of dilute H_2SO_4 with platinum electrode is:
(a) oxidation
(b) reduction
(c) both oxidation and reduction
(d) neutralization

50. Strongest reducing agent is:
(a) K (b) Mg (c) Al (d) I

51. The metal oxide which decomposes on heating, is:
(a) ZnO (b) HgO (c) Al_2O_3 (d) CuO

52. The reaction, $\frac{1}{2}H_2(g) + AgCl(s) = H^+(aq.) + Cl^-(aq.) + Ag(s)$ occurs in the galvanic cell: **(AFMC 2009)**
(a) $Ag \mid AgCl(s) \mid KCl\ (soln.) \parallel AgNO_3\ (soln.) \mid Ag$
(b) $Pt \mid H_2(g) \mid HCl\ (soln.) \parallel AgNO_3\ (soln.) \mid Ag$
(c) $Pt \mid H_2(g) \mid HCl\ (soln.) \parallel AgCl(s) \mid Ag$
(d) $Pt \mid H_2(g) \mid KCl\ (soln.) \parallel AgCl(s) \mid Ag$

53. The standard oxidation potentials, E°, for the half reactions are as,

$$Zn \longrightarrow Zn^{2+} + 2e^-; \quad E^\circ = +0.76 \text{ volt}$$
$$Fe \longrightarrow Fe^{2+} + 2e^-; \quad E^\circ = +0.41 \text{ volt}$$

The emf of the cell, $Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$ is:
[CET (Karnataka) 2009]
(a) + 0.35 volt (b) – 0.35 volt
(c) +1.17 volt (d) –1.17 volt

54. The standard reduction potentials at 25°C for the following half reactions are given against each;

$$Zn^{2+}(aq.) + 2e^- \rightleftharpoons Zn(s); \quad -0.762$$
$$Cr^{3+}(aq.) + 3e^- \rightleftharpoons Cr(s); \quad -0.740$$
$$2H^+ + 2e^- \rightleftharpoons H_2(g); \quad 0.00$$
$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}; \quad 0.77$$

Which is the strongest reducing agent? **(VITEEE 2007)**
(a) Zn (b) Cr
(c) $H_2(g)$ (d) $Fe^{2+}(aq.)$

55. Hydrogen gas will not reduce heated:
(a) cupric oxide (b) ferric oxide
(c) stannic oxide (d) aluminium oxide

56. A solution containing one mole per litre of each $Cu(NO_3)_2$; $AgNO_3$; $Hg_2(NO_3)_2$ and $Mg(NO_3)_2$ is being electrolysed by using inert electrodes. The values of standard electrode potentials (reduction potentials) are $Ag/Ag^+ = 0.80$ volt, $2Hg/H_2^{2+} = 0.79$ volt, $Cu/Cu^{2+} = +0.24$ volt, $Mg/Mg^{2+} = -2.37$ volt. With increasing voltage, the sequence of deposition of metals on the cathode will be:
[PMT (Kerala) 2004]
(a) Ag, Hg, Cu (b) Cu, Hg, Ag
(c) Ag, Hg, Cu, Mg (d) Mg, Cu, Hg, Ag

57. Four colourless salt solutions are placed in separate test tubes and a strip of copper is dipped in each. Which solution finally turns blue?
(a) $Pb(NO_3)_2$ (b) $AgNO_3$ (c) $Zn(NO_3)_2$ (d) $Cd(NO_3)_2$

58. Red hot carbon will remove oxygen from the oxide *XO* and *YO* but not from *ZO*. *Y* will remove oxygen from *XO*. Use this evidence to deduce the order of activity of the three metals *X*, *Y* and *Z* putting the most active first:
(a) *XYZ* (b) *ZYX* (c) *YXZ* (d) *ZXY*

59. Which of the following metals does not give the following reaction?

$$M + \text{Water} \longrightarrow \text{Oxide or hydroxide} + H_2$$

(a) Iron (b) Sodium (c) Mercury (d) Magnesium

60. Which is the best reducing agent?

(a) F^- (b) Cl^- (c) Br^- (d) I^-

61. If a spoon of copper metal is placed in a solution of ferrous sulphate:

(a) Cu will precipitate out
(b) iron will precipitate
(c) Cu and Fe will precipitate
(d) no reaction will take place

62. Among Na, Hg, S, Pt and graphite, which can be used as electrodes in electrolytic cells having aqueous solutions?

(a) Hg and Pt (b) Hg, Pt and graphite
(c) Na and S (d) Na, Hg and S

63. The most reactive metal among the following is:

(a) Al (b) Ni (c) Pb (d) Cu

64. Which of the following metals is most readily corroded in moist air?

(a) Copper (b) Iron
(c) Silver (d) Nickel

65. Which one will liberate Br_2 from KBr?

(a) HI (b) I_2 (c) Cl_2 (d) SO_2

66. Which one of the following is not the correct representation?

(a) E°_{cell} = Red. pot. of cathode + Oxid. pot. of anode
(b) E°_{cell} = Red. pot. of cathode − Oxid. pot. of anode
(c) E°_{cell} = Red. pot. of cathode − Red. pot. of anode
(d) E°_{cell} = Oxid. pot. of cathode + Oxid. pot. of anode

67. Which of the following represents the potential of silver wire dipped into 0.1 M $AgNO_3$ solution at 25°C ?

(a) $E^\circ_{red.}$ (b) $(E^\circ_{red.} + 0.059)$
(c) $(E^\circ_{oxid.} - 0.059)$ (d) $(E^\circ_{red.} - 0.059)$

68. If the solution of the $CuSO_4$ in which copper rod is immersed is diluted to 10 times, the electrode potential:

(a) increases by 0.030 volt (b) decreases by 0.030 volt
(c) increases by 0.059 volt (d) decreases by 0.0059 volt

69. A solution of Cu(II) sulphate is reacted with KCl and KI. In which case will the Cu^{2+} be reduced to Cu^+?

(a) In both the cases
(b) When reacted with KCl
(c) When reacted with KI
(d) In both the cases but in presence of H^+

70. From the electrochemical series, it can be concluded that:

(a) Zn^{2+} will liberate H_2 from 1 M HCl
(b) Ag metal reacts spontaneously with Zn^{2+}
(c) Zn metal will liberate H_2 from 1 M HCl
(d) Ag metal will liberate H_2 from 1 M HCl

71. The potential of a hydrogen electrode at pH = 1 is:

(a) 0.059 volt (b) 0 volt
(c) −0.059 volt (d) 0.59 volt

72. Which is not true for a standard hydrogen electrode?

(a) The hydrogen ion concentration is 1 M
(b) Temperature is 25°C
(c) Pressure of hydrogen is 1 atmosphere
(d) It contains a metallic conductor which does not absorb hydrogen

73. The electrode potential becomes equal to standard electrode potential when reactants and products ratio is:

(a) equal to 1 (b) greater than 1
(c) less than 1 (d) none of these

74. For the half-cell reaction,

$$Au^{3+} + 3e^- \longrightarrow Au$$

the value of n used in Nernst equation is:

(a) 3 (b) 2 (c) 1 (d) 3 × 96500

75. When a piece of sodium metal is dropped in water, a reaction takes place to yield hydrogen because:

(a) sodium loses electrons
(b) sodium acts as an oxidising agent
(c) water loses electrons
(d) water acts as a reducing agent

76. Which one is the wrong statement about electrochemical series?

(a) Active metals have negative reduction potentials
(b) Active non-metals have positive reduction potentials
(c) Metals above hydrogen liberate hydrogen from acids
(d) Metals below hydrogen are strong reducing agents

77. The reduction potential values are given below:

$Al^{3+}/Al = -1.67$ volt, $Mg^{2+}/Mg = -2.34$ volt,
$Cu^{2+}/Cu = +0.34$ volt, $I_2/2I^- = +0.53$ volt.

Which one is the best reducing agent?

(a) Al (b) Mg
(c) Cu (d) I_2

78. From the values given in question No. 77, which one is the best oxidising agent?

(a) Al (b) Mg (c) I_2 (d) Cu

79. When iron is rusted, it is:

(a) reduced (b) oxidised
(c) evaporated (d) decomposed

80. Galvanization of iron denotes coating with:

(a) Cu (b) Sn (c) Zn (d) Al

81. The standard electrode potentials of four elements A, B, C and D are −3.05, 1.66, −0.40 and 0.80 volt. The highest chemical activity will be shown by:

(a) A (b) B (c) C (d) D

82. Which of the following methods does not liberate hydrogen?

(a) Zn + H_2SO_4 (dil.) (b) Mg + H_2SO_4 (dil.)
(c) Cu + H_2SO_4 (dil.) (d) Zn + HCl (dil.)

83. A depolarizer used in dry cell is:

(a) ammonium chloride (b) manganese dioxide
(c) potassium oxide (d) sodium phosphate

84. The oxide which can be reduced by hydrogen is:

(a) Na_2O (b) CaO (c) K_2O (d) CuO

85. The reference electrode is made from which of the following?

(a) $ZnCl_2$ (b) $CuSO_4$ (c) Hg_2Cl_2 (d) $HgCl_2$

86. Given, standard electrode potentials;

$$Fe^{3+} + 3e^- \longrightarrow Fe; \qquad E° = -0.036 \text{ volt}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe; \qquad E° = -0.440 \text{ volt}$$

The standard electrode potential $E°$ for $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ is: **[AMU (Medical) 2007; AIEEE 2009]**

(a) − 0.476 volt (b) − 0.404 volt

(c) 0.440 volt (d) − 0.772 volt

[**Hint:** Apply $\Delta G = -nFE$

$Fe^{2+} + 2e^- \longrightarrow Fe \ \Delta G = -2 \times F \times (-0.440 \text{ V}) = 0.88F$ ...(i)

$Fe^{3+} + 3e^- \longrightarrow Fe \ \Delta G = -3 \times F \times (-0.036) = 0.108F$ ...(ii)

Subtracting eq. (i) from eq. (ii),

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}; \qquad \Delta G = 0.108F - 0.880F$$
$$= -0.772F$$

$$E° \text{ for the reaction} = -\frac{\Delta G}{nF} = -\frac{(-0.772F)}{1 \times F} = 0.772 \text{ volt}]$$

87. K, Ca and Li metals may be arranged in the decreasing order of their standard electrode potentials as:

(a) K, Ca and Li (b) Li, K and Ca

(c) Li, Ca and K (d) Ca, Li and K

88. In a galvanic cell energy changes occur like:

(a) chemical energy ⟶ electrical energy

(b) electrical energy ⟶ chemical energy

(c) chemical energy ⟶ internal energy

(d) internal energy ⟶ electrical energy

89. The reaction is spontaneous if the cell potential is:

(a) positive (b) negative

(c) zero (d) infinite

90. Is the reaction, $2Al + 3Fe^{2+} \rightleftharpoons 2Al^{3+} + 2Fe$ possible?

(a) No, because standard oxidation potential of Al < Fe

(b) Yes, because standard oxidation potential of Al > Fe

(c) Cannot be predicted

(d) Yes, because aluminium is a strong oxidising agent

91. In an experimental set-up for the measurement of emf of a half-cell using a reference electrode and a salt bridge, when the salt bridge is removed, the voltage:

(a) does not change (b) increases to maximum

(c) decreases half the value (d) drops to zero

92. More electronegative elements have:

(a) negative reduction potential

(b) tendency to lose electrons

(c) positive reduction potential

(d) positive oxidation potential

93. Which metal will be deposited in the galvanic cell?

$$Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$$

(a) Cu (b) Ag

(c) Both (d) None of these

94. In the cell $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$, the negative electrode is:

(a) Cu (b) Cu^{2+} (c) Zn (d) Zn^{2+}

95. Which of the following gains electrons more easily?

(a) Na^+ (b) Zn^{2+}

(c) Al^{3+} (d) H^+

96. The potential of a hydrogen electrode at pH 10 is:

(a) 0.51 volt (b) 0 volt

(c) − 0.591 volt (d) 0.059 volt

97. The emf of the cell,

$$Ni \mid Ni^{2+} (1.0\,M) \parallel Ag^+ (1.0\,M) \mid Ag$$

($E°$ for $Ni^{2+}/Ni = -0.25$ volt, $E°$ for $Ag^+/Ag = 0.80$ volt) is given by:

(a) $-0.25 + 0.80 = 0.55$ volt

(b) $-0.25 - (+0.80) = -1.05$ volt

(c) $0 + 0.80 - (-0.25) = +1.05$ volt

(d) $-0.80 - (-0.25) = -0.55$ volt

98. The reaction for the cell,

$$Zn \mid Zn^{2+} (1.0\,M) \parallel Cd^{2+} (1.0\,M) \mid Cd$$

is:

(a) $Cd \longrightarrow Cd^{2+} + 2e^-$

(b) $Zn^{2+} \longrightarrow Zn - 2e^-$

(c) $Cd + Zn^{2+} \longrightarrow Cd^{2+} + Zn$

(d) $Zn + Cd^{2+} \longrightarrow Cd + Zn^{2+}$

99. The position of some metals in the electrochemical series in decreasing electropositive character is given as Mg > Al > Zn > Cu > Ag. What will happen if a copper spoon is used to stir a solution of aluminium nitrate?

(a) The spoon will get coated with aluminium

(b) An alloy of aluminium and copper is formed

(c) The solution becomes blue

(d) There is no reaction

100. The half-cell reaction is the one that:

(a) takes place at one electrode

(b) consumes half a unit of electricity

(c) involves half a mole of electrolyte

(d) goes half way to completion

Which Nernst equation is true to find out the potential of non-standard electrochemical cell from the following ?

$$Fe(s) \mid Fe^{2+} (xM) \parallel I^- (aq.) \mid I_2(s)\ (Pt)$$

[CET (Gujarat) 2008]

(a) $E_{cell} = E^\circ_{cell} - \frac{0.592}{n} \log_{10} [Fe^{2+}][I^-]^2$

(b) $E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log_{10} [Fe^{2+}][I^-]^2$

(c) $E_{cell} = E^\circ_{cell} - \frac{0.0592}{n} \log_{10} [Fe^{2+}][I^-]$

(d) $E_{cell} = E^\circ_{cell} - \frac{0.0592}{nF} \log_{10} \frac{[Fe^{2+}][I^-]^2}{[Fe][I_2]}$

102. During the electrolysis of fused NaCl, which reaction occurs at anode?

(a) Chloride ions are oxidised

(b) Sodium ions are oxidised

(c) Chloride ions are reduced

(d) Sodium ions are reduced

103. $E°(Ni^{2+}/Ni) = -0.25$ volt, $E°(Au^{3+}/Au) = 1.50$ volt. The emf of the voltaic cell,

$$Ni \mid Ni^{2+}\ (1.0\ M) \parallel Au^{3+}\ (1.0\ M) \mid Au$$

is:

(a) 1.25 volt (b) −1.75 volt (c) 1.75 volt (d) 4.0 volt

104. Which of the following does not occur at cathode?

(a) $Ag^+ \longrightarrow Ag - e^-$ (b) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

(c) $Cu^{2+} + 2e^- \longrightarrow Cu$ (d) $2H^+ \longrightarrow H_2 - 2e^-$

105. The strong oxidising agent has:

(a) high value of reduction potential

(b) high value of oxidation potential

(c) low value of reduction potential

(d) high tendency to lose electrons

106. The passage of electricity in the Daniell cell when Zn and Cu electrodes are connected is from:

(a) Cu to Zn in the cell

(b) Cu to Zn outside the cell

(c) Zn to Cu outside the cell

(d) Zn to Cu in the cell

107. Which of the following can be used as an electrode?

(a) A glass rod (b) A wooden stick

(c) A nail (d) A soda straw

108. H^+ ions are reduced at platinum electrode prior to:

(a) Zn^{2+} (b) Cu^{2+} (c) Ag^+ (d) I_2

109. Which of the following statements is wrong?

(a) F_2 is the strongest oxidising agent as its reduction potential is high

(b) Li is the weakest reducing agent as its reduction potential is low

(c) Li is the strongest reducing agent as its oxidation potential is high

(d) F^- ion does not show reducing property

110. Out of Cu, Ag, Fe and Zn, the metal which can displace all others from their salt solution is:

(a) Ag (b) Cu (c) Fe (d) Zn

111. When the electric current is passed through a cell having an electrolyte, the positive ions move towards cathode and negative ions towards the anode. If the cathode is pulled out of the solution:

(a) the positive and negative ions will move towards anode

(b) the positive ions will start moving towards the anode while negative ions will stop moving

(c) the negative ions will continue to move towards anode while positive ions will stop moving

(d) the positive and negative ions will start moving randomly

112. The oxidation potentials of Zn, Cu, Ag, H_2 and Ni are 0.76, − 0.34, − 0.80, 0 and 0.25 volt respectively. Which of the following reactions will provide maximum voltage? **[PET (Kerala) 2007]**

(a) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

(b) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$

(c) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$

(d) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

(e) $Zn(s) + 2H^+(aq.) \rightleftharpoons Zn^{2+}(aq.) + H_2(g)$

113. Which one of the following will increase the voltage of the cell?

$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$

(a) Increase in the size of silver rod

(b) Increase in the concentration of Sn^{2+} ions

(c) Increase in the concentration of Ag^+ ions

(d) None of the above

114. A chemist wants to produce $Cl_2(g)$ from molten NaCl. How many grams could be produced if he uses a steady current of 2 ampere for 2.5 minutes?

(a) 3.55 g (b) 1.775 g (c) 0.110 g (d) 0.1775 g

115. In the electrolysis of $CuCl_2$ solution, the mass of cathode increased by 6.4 g. What occurred at copper anode?

(a) 0.224 litre of Cl_2 was liberated

(b) 1.12 litre of oxygen was liberated

(c) 0.05 mole Cu^{2+} passed into the solution

(d) 0.1 mole Cu^{2+} passed into the solution

116. Consider the reaction,

$$Cl_2(g) + 2Br^-(aq.) \longrightarrow 2Cl^-(aq.) + Br_2$$

The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01\ M$ and Cl_2 gas is at 1 atm pressure, will be: (E° for the above reaction is 0.29 volt)

(a) 0.54 volt (b) 0.35 volt (c) 0.24 volt (d) − 0.29 volt

117. If λ°_c, λ°_a and λ° refer to equivalent conductance of a cation, an anion and equivalent conductance of the salt at infinite dilution, then according to Kohlrausch's law:

(a) $\lambda^\circ = \lambda^\circ_c + \lambda^\circ_a$ (b) $\lambda^\circ = \lambda^\circ_c - \lambda^\circ_a$

(c) $\lambda^\circ = \lambda^\circ_a - \lambda^\circ_c$ (d) $\lambda^\circ = \lambda^\circ_c / \lambda^\circ_a$

118. How much silver will be obtained by that quantity of current which displaces 5.6 litre of H_2? **[PMT (Pb.) 1993]**

(a) 54 g (b) 13.5 g (c) 20 g (d) 108 g

119. The specific conductance of a salt of 0.01 M concentration is 1.061×10^{-4}. Molar conductance of the same solution will be: **[PMT (Pb.) 1993]**

(a) 1.061×10^{-4} (b) 1.061 (c) 10.61 (d) 106.1

120. What is the number of coulombs required for the conversion of one mole of MnO_4^- to one mole of Mn^{2+}? **[MBBS (Orissa) 1993]**

(a) 5 × 96500 (b) 3 × 96500 (c) 96500 (d) 9650

121. Which of the following solutions of NaCl will have the highest specific conductance?

(a) 0.001 N (b) 0.1 N (c) 0.01 N (d) 1.0 N

122. The equivalent conductance of a 1 N solution of an electrolyte is nearly:

(a) 10^3 times its specific conductance

(b) 10^{-3} times its specific conductance

(c) 100 times its specific conductance

(d) the same as its specific conductance

123. Zinc is coated over iron to prevent rusting of iron because:

(a) it is cheaper than iron (b) $E^\circ_{(Zn^{2+}/Zn)} = E^\circ_{(Fe^{2+}/Fe)}$

(c) $E^\circ_{(Zn^{2+}/Zn)} < E^\circ_{(Fe^{2+}/Fe)}$ (d) $E^\circ_{(Zn^{2+}/Zn)} > E^\circ_{(Fe^{2+}/Fe)}$

124. Free energy change (ΔG) is related to the emf of the cell (E)

(a) $E = -nF\,\Delta G$ (b) $\Delta G = -nFE$

(c) $\Delta G = -\frac{RT}{n} F \log E$ (d) $\Delta G = -\frac{nF}{RT} \log E$

125. The standard reduction potentials at 25°C of Li^+/Li, Ba^{2+}/Ba, Na^+/Na and Mg^{2+}/Mg are – 3.05, – 2.73, – 2.71 and – 2.37 volt respectively. Which one of the following is the strongest oxidising agent?

(a) Na^+ (b) Li^+

(c) Ba^{2+} (d) Mg^{2+}

126. Three faradays of electricity was passed through an aqueous solution of iron(II) bromide. The mass of iron metal (At. mass 56) deposited at the cathode is: **(EAMCET 1991)**

(a) 56 g (b) 84 g (c) 112 g (d) 168 g

127. The standard electrode potentials of Zn, Ag and Cu are – 0.76, 0.80 and 0.34 volt respectively; then:

(a) Ag can oxidise Zn and Cu

(b) Ag can reduce Zn^{2+} and Cu^{2+}

(c) Zn can reduce Ag^+ and Cu^{2+}

(d) Cu can oxidise Zn and Ag

128. The standard emf for the cell reaction,

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

is 1.10 volt at 25°C. The emf for the cell reaction when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used at 25°C is: **(MLNR 1994)**

(a) 1.10 volt (b) 0.110 volt

(c) – 1.10 volt (d) – 0.110 volt

129. Three mole of electrons are passed through three solutions in succession containing $AgNO_3$, $CuSO_4$ and $AuCl_3$ respectively. The ratio of amounts of cations reduced at cathode will be:

(a) 1 : 2 : 3 (b) 2 : 1 : 3

(c) 3 : 2 : 1 (d) 6 : 3 : 2

130. In the electrolysis of an aqueous solution of NaOH, 2.8 litre of oxygen gas at NTP was liberated at anode. How much of hydrogen gas was liberated at cathode?

(a) 2.8 litre (b) 5.6 litre

(c) 11.2 litre (d) 22.4 litre

131. Two half-cells have potentials – 0.44 and 0.799 volt respectively. These two are coupled to make a galvanic cell. Which of the following will be true?

(a) Electrode of half-cell potential – 0.44 V will act as anode

(b) Electrode of half-cell potential – 0.44 V will act as cathode

(c) Electrode of half-cell potential 0.799 V will act as anode

(d) Electrode of half-cell potential – 0.44 V will act as a positive terminal

132. When a lead storage battery is charged:

(a) PbO_2 dissolves

(b) the lead electrode becomes coated with lead sulphate

(c) sulphuric acid is regenerated

(d) the amount of acid decreases

133. An example of a simple fuel cell is:

(a) lead storage battery (b) $H_2 — O_2$ cell

(c) Daniell cell (d) Lechlanche cell

134. For the cell reaction,

$$Mg(s) + 2Ag^+(aq.) \rightleftharpoons Mg^{2+}(aq.) + 2Ag(s).$$

E°_{cell} is +3.17 V at 298 K. The value of E_{cell}, ΔG° and Q at Ag^+ and Mg^{2+} concentrations of 0.001 M and 0.02 M respectively are: **(ISAT 2010)**

(a) 3.04 V, –605.8 kJ mol^{-1}, 20000

(b) 3.04 V, 611.8 kJ mol^{-1}, 20000

(c) 3.13 V, –604 kJ mol^{-1}, 20

(d) 3.04 V, –611.8 kJ, 20000

[**Hint:** $E^\circ = +3.17$ V, $n = 2$

$$Q = \frac{[Mg^{2+}]}{[Ag^+]^2} = \frac{0.02}{[0.001]^2} = 20000$$

$$\Delta G^\circ = -nFE^\circ$$
$$= -2 \times 96500 \times 3.17$$
$$= -611.8 \text{ kJ}$$
$$E = E^\circ - \frac{0.059}{n} \log_{10} Q$$
$$= 3.17 - \frac{0.059}{2} \log(20000)$$
$$= +3.04 \text{ V}]$$

135. Which of the following statements is correct?

(a) The temperature coefficient of electrolytic conductance is positive

(b) The temperature coefficient of electrolytic resistance is negative

(c) The resistance of an electrolyte decreases with decreasing temperature

(d) The resistance of electrolytic conductors is independent of temperature

136. Kohlrausch's law states that at: **[CBSE (PMT) 2008]**

(a) infinite dilution, each ion makes definite contribution to conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

(b) infinite dilution, each ion makes definite contribution to the equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

(c) finite dilution, each ion makes definite contribution to the equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte

(d) infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte

137. Which one of the following conditions will increase the voltage of the cell represented by the equation?

$Cu(s) + 2Ag^+(aq.) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$ **(KCET 2006)**

(a) Increase in the dimension of Cu electrode

(b) Increase in the dimension of Ag electrode

(c) Increase in the concentration of Cu^{2+} ion

(d) Increase in the concentration of Ag^+ ion

[**Hint:** Cell voltage will increase, either by increasing the concentration of Cu^{2+} ion or by decreasing the concentration of Ag^+.

$$Q = \frac{[Cu^{2+}]}{[Ag^+]}$$

Lesser is the value of Q, greater is the cell voltage.]

138. Which of the following reactions occurs at cathode during charging of storage battery? **(MGIMS 2007)**

(a) $Pb^{2+} + 2e^- \longrightarrow Pb$

(b) $Pb \longrightarrow Pb^{2+} + 2e^-$

(c) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

(d) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_2^{2-} + 2e^-$

139. The amount of silver deposited on passing 2F of electricity through aqueous solution of $AgNO_3$ is: **(MHT-CET 2007)**

(a) 54 g (b) 108 g (c) 216 g (d) 324 g

140. Statements:

(i) Unit of specific conductivity is $ohm^{-1}\ cm^{-1}$.

(ii) Specific conductivity of strong electrolytes decreases on dilution.

(iii) The amount of an ion discharged during electrolysis does not depend upon resistance.

(iv) The unit of electrochemical equivalence is g/coulomb.

(a) All are correct

(b) All are wrong

(c) Only (i), (ii) and (iv) are correct

(d) Only (ii), (iii) and (iv) are correct

141. Which among the following expressions is/are not correct?

(a) $\mu^\infty = \gamma_+ \lambda_+^\infty + \gamma_- \lambda_-^\infty$

(b) $\lambda^\infty = \frac{1}{n^+}\lambda_+^\infty + \frac{1}{n_-}\lambda_-^\infty$

(c) $\lambda_{cation}^\infty = \mu_{cation}^\infty \times$ faraday

(d) $\lambda_{anion}^\infty = \mu_{cation}^\infty \times$ faraday

142. For the electrochemical cell, $M\,|\,M^+\,||\,X^-\,|\,X$, $E^\circ_{M^+/M} = 0.44$ V and $E^\circ_{X/X^-} = 0.33$ V. From this data we can deduce that: **[IIT (Screening) 2000]**

(a) $M + X \longrightarrow M^+ + X^-$ is the spontaneous reaction

(b) $M^+ + X^- \longrightarrow M + X$ is the spontaneous reaction

(c) $E_{cell} = 0.77$ V

(d) $E_{cell} = -0.77$ V

143. For the cell reaction,

$$\underset{(C_1)}{Cu^{2+}(aq.)} + Zn(s) \longrightarrow \underset{(C_2)}{Zn^{2+}(aq.)} + Cu(s)$$

the change in free energy (ΔG) at a given temperature is a function of: **(CBSE 1998)**

(a) $\ln C_1$ (b) $\ln\left(\frac{C_2}{C_1}\right)$

(c) $\ln(C_1 + C_2)$ (d) $\ln C_2$

144. The standard reduction potential values of three metallic cations X, Y and Z are 0.52, –3.03 and –1.18 V respectively. The order of reducing powers of the corresponding metals is: **(IIT 1998)**

(a) $Y > Z > X$ (b) $X > Y > Z$

(c) $Z > Y > X$ (d) $Z > X > Y$

145. A gas 'X' at 1 atm is bubbled through a solution containing a mixture of 1 $M\ Y^-$ and 1 $M\ Z^-$ at 25°C. If the reduction potential of $Z > Y > X$, then: **(IIT 1999)**

(a) Y will oxidise X and not Z

(b) Y will oxidise Z and not X

(c) Y will oxidise both Z and X

(d) Y will reduce both X and Z

146. The number of coulombs required for the deposition of 107.87 g of silver is: **[PMT (MP) 1998]**

(a) 48250 (b) 10000 (c) 96500 (d) 19300

147. At 25°C, the standard emf of a cell having reaction involving two electrons change is found to be 0.295 V. The equilibrium constant of the reaction is: **(IIT 1999)**

(a) 29.5×10^{-2} (b) 10

(c) 1×10^{10} (d) 29.5×10^{10}

148. The emf of the cell in which the following reaction,

$$Zn(s) + Ni^{2+}\ (0.1\ M) \longrightarrow Zn^{2+}\ (1.0\ M) + Ni(s)$$

occurs, is found to 0.5105 V at 298 K. The standard emf of the cell is: **(IIT 1998)**

(a) 0.4810 V (b) 0.5696 V

(c) – 0.5105 V (d) 0.5400 V

[Hint: $E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{1}{0.1}$]

149. The molar conductances of NaCl, HCl and CH_3COONa at infinite dilution are 126.45, 426.16 and 91 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. The molar conductance of CH_3COOH at infinite dilution is: **[CBSE 1997; DCE 2009]**

(a) 201.28 $ohm^{-1}\ cm^2\ mol^{-1}$ (b) 390.71 $ohm^{-1}\ cm^2\ mol^{-1}$

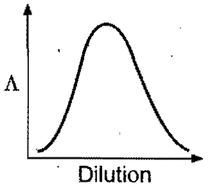
(c) 698.28 $ohm^{-1}\ cm^2\ mol^{-1}$ (d) 540.48 $ohm^{-1}\ cm^2\ mol^{-1}$

150. The specific conductance of a 0.1 N KCl solution at 23°C is 0.0112 $ohm^{-1}\ cm^{-1}$. The resistance of the cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be: **(CBSE 1999)**

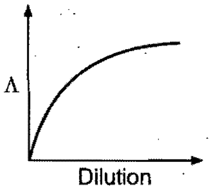
(a) 0.142 cm^{-1} (b) 0.918 cm^{-1}

(c) 1.12 cm^{-1} (d) 0.616 cm^{-1}

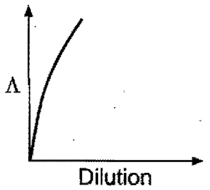
151. Which of the following plots represents correctly variation of equivalent conductance (Λ) with dilution for a strong electrolyte?



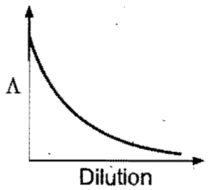
(a)



(b)



(c)



(d)

152. The standard reduction potential for Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are 0.337 V and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half cell is: **[AMU (PMT) 2009; CBSE (PMT) 2009]**

(a) 0.184 V (b) 0.827 V
(c) 0.521 V (d) 0.490 V

153. Solubility of a sparingly soluble salt S, specific conductance κ and the equivalent conductance Λ_0 are related as: **[IAS (Pre.) 1997]**

(a) $S = \frac{1000}{\kappa}\Lambda_0$ (b) $S = \kappa\Lambda_0$
(c) $S = \frac{\kappa}{1000\Lambda_0}$ (d) $S = \frac{1000\kappa}{\Lambda_0}$

154. $2Ag^{+}(aq.) + Cu(s) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$
($E^{\circ}_{cell} = +0.46$ V)
Which change will increase potential the most?

(a) Doubling the $[Ag^{+}]$
(b) Halving the $[Cu^{2+}]$
(c) Doubling the size of Cu electrode
(d) Halving the size of Ag electrode

155. As a lead storage battery is charged: **[PMT (MP) 1993, 2000]**

(a) lead dioxide dissolves
(b) sulphuric acid is regenerated
(c) lead electrode becomes coated with lead sulphate
(d) the concentration of sulphuric acid decreases

156. In the electrochemical reaction,

$$2Fe^{3+} + Zn \longrightarrow Zn^{2+} + 2Fe^{2+}$$

increasing the concentration of Fe^{2+}: **[CEE (Kerala) 2000]**

(a) increases the cell emf
(b) increases the current flow
(c) decreases the cell emf
(d) alters the pH of the solution

157. In the cell reaction,

$$Cu(s) + 2Ag^{+}(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s).$$

$E^{\circ}_{cell} = 0.46$ V. By doubling the concentration of Cu^{2+}, E°_{cell} is: **[MEE (Kerala) 2000]**

(a) doubled
(b) halved
(c) increased but less than double
(d) decreased by a small fraction

158. The conductivity of 0.01 mol/dm^3 aqueous acetic acid at 300 K is 19.5×10^{-5} ohm^{-1} cm^{-1} and the limiting molar conductivity of acetic acid at the same temperature is 390 ohm^{-1} cm^2 mol^{-1}. The degree of dissociation of acetic acid is: **[IAS (Pre.) 1995]**

(a) 0.5 (b) 0.05 (c) 5×10^{-3} (d) 5×10^{-7}

159. The ionization constant of a weak electrolyte is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is 19.6 s cm^2 eq^{-1}. The equivalent conductance of the electrolyte at infinite dilution (in s cm^2 eq^{-1}) will be: **[IAS (Pre.) 1998]**

(a) 250 (b) 196
(c) 392 (d) 384

160. What is the amount of chlorine evolved when 2 ampere of current is passed for 30 minutes in an aqueous solution of NaCl? **(BHU 1998; AIIMS 1999)**

(a) 66 g (b) 1.32 g
(c) 33 g (d) 99 g

161. When 9.65 coulomb of electricity is passed through a solution of silver nitrate (Atomic mass of Ag = 108 g mol^{-1}), the amount of silver deposited is: **(KCET 2000)**

(a) 16.2 mg (b) 21.2 mg
(c) 10.8 mg (d) 6.4 mg

162. The quantity of electricity needed to deposit 127.08 g of copper is: **[CET (Pb.) 2000; PET (MP) 2004]**

(a) 1 faraday (b) 4 coulomb
(c) 4 faraday (d) 1 ampere

163. The charge required to deposit 9 g of Al from Al^{3+} solution is (At. wt. of Al = 27.0): **[MEE (Kerala) 2000]**

(a) 3216.3 C (b) 96500 C (c) 9650 C (d) 32163 C

164. The emf of the cell $Ni|Ni^{2+}(1.0\,M)\,||\,Au^{3+}(1.0\,M)|Au$ is (E° for $Ni^{2+}|Ni = -0.25$ V; E° for $Au^{3+}|Au = 1.5$ V): **[CET (Pb.) 2000; PMT (MP) 20[illegible]]**

(a) +1.25 V (b) +1.75 V (c) −1.25 V (d) −1.75 V

165. For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46 V at 25°C. The value of standard Gibbs energy, ΔG° will be :
($F = 96500$ C mol^{-1}) **(AIPMT 2010)**

(a) −89 kJ (b) −89 J
(c) −44.5 kJ (d) −98 kJ

166. In electrolysis of NaCl when Pt electrode is taken then H_2 is liberated at cathode while with Hg cathode it forms sodium amalgam: **[CBSE (PMT) 2002]**

(a) Hg is more inert than Pt
(b) more voltage is required to reduce H^{+} at Hg than at Pt
(c) Na is dissolved in Hg while it does not dissolve in Pt
(d) concentration of H^{+} ions is larger when Pt electrode is taken

167. Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because: **[CBSE (PMT) 2002]**

(a) Zn acts as oxidising agent when reacts with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) in electrochemical series, Zn is above hydrogen
(d) NO_3^{-} is reduced in preference to hydronium ion

168. A current is passed through two voltameters connected in series. The first voltameter contains XSO_4 $(aq.)$ while the second voltameter contains Y_2SO_4 $(aq.)$. The relative atomic masses of X and Y are in the ratio 2 : 1. The ratio of the mass of X liberated to the mass of Y liberated is:

(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) none of these

169. Which of the following reactions is possible at anode? **(AIEEE 2002)**

(a) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^{+}$
(b) $F_2 \longrightarrow 2F^{-}$
(c) $\frac{1}{2}O_2 + 2H^{+} \longrightarrow H_2O$
(d) None of the above

170. When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are: **(AIEEE 2002)**

	Cathode	**Anode**
(a)	Pure zinc	Pure copper
(b)	Impure sample	Pure copper
(c)	Impure zinc	Impure sample
(d)	Pure copper	Impure sample

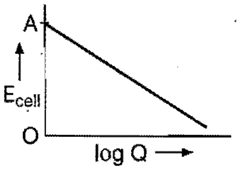
171. Conductivity (Unit Siemen's 'S') is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is: **(AIEEE 2002)**

(a) $S\ \text{m mol}^{-1}$ (b) $S\ \text{m}^2\ \text{mol}^{-1}$

(c) $S^{-2}\ \text{m}^2\ \text{mol}$ (d) $S^2\ \text{m}^2\ \text{mol}^{-2}$

172. $Zn(s) + Cu^{2+}(aq.) \rightleftharpoons Cu(s) + Zn^{2+}(aq.)$

Reaction quotient $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$, variation E_{cell} with Q is of the ne with $OA = 1.10$ volt. $E_{\text{cell}} = 1.1591$ volt when:



(a) $[Cu^{2+}]/[Zn^{2+}] = 0.01$ (b) $[Zn^{2+}]/[Cu^{2+}] = 0.01$

$[Zn^{2+}]/[Cu^{2+}] = 0.1$ (d) $[Zn^{2+}]/[Cu^{2+}] = 1$

173. In which of the following cells will the emf be independent of the activity of the chloride ions?

(a) $Zn\ |\ ZnCl_2(aq.)\ |\ Pt(Cl_2)$

(b) $Zn\ |\ ZnCl_2(aq.)\ ||\ KCl(aq.)\ |\ AgCl(s), Ag(s)$

(c) $Ag, AgCl(s)\ |\ KCl(aq.)\ |\ Pt(Cl_2)$

(d) $Hg, Hg_2Cl_2(s)\ |\ KCl(aq.)\ ||\ AgNO_3(aq.)\ |\ Ag(s)$

174. Standard electrode potential data are useful for understanding the suitability of an oxidant in a redox titration. Some half-cell reactions and their standard potentials are given below:

$MnO_4^-(aq.) + 8H^+(aq.) + 5e^- \longrightarrow Mn^{2+}(aq.) + 4H_2O(l);$ $E° = 1.51$ volt

$Cr_2O_7^{2-}(aq.) + 14H^+(aq.) + 6e^- \longrightarrow 2Cr^{3+}(aq.) + 7H_2O(l);$ $E° = 1.38$ volt

$Fe^{3+}(aq.) + e^- \longrightarrow Fe^{2+}(aq.);$ $E° = 0.77$ volt

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq.);$ $E° = 1.40$ volt

Identify the only incorrect statement regarding the quantitative estimation of aqueous $Fe(NO_3)_2$: **(IIT 2002)**

(a) MnO_4^- can be used in aqueous HCl

(b) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(c) MnO_4^- can be used in aqueous H_2SO_4

(d) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

175. The standard reduction potential $E°$, for the half reaction are:

$Zn \longrightarrow Zn^{2+} + 2e^-;$ $E° = 0.76$ V

$Cu \longrightarrow Cu^{2+} + 2e^-;$ $E° = 0.34$ V

The emf for the cell reaction, $Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$ is: **[Bihar CECE (Pre.) 2004]**

(a) 0.42 V (b) − 0.42 V

(c) − 1.1 V (d) + 1.1 V

176. In a galvanic cell, the electrons flow from: **(KCET 2004)**

(a) anode to cathode through the solution

(b) cathode to anode through the solution

(c) anode to cathode through the external circuit

(d) cathode to anode through the external circuit

177. The standard emf of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be:
Given: $F = 96500\ \text{C mol}^{-1}$; $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ **[CBSE (PMT) 2004; AIEEE 2004]**

(a) 2×10^{11} (b) 4×10^{12}

(c) 1×10^2 (d) 1×10^{10}

178. The emf of the cell,

$Zn\ |\ Zn^{2+}\ (0.01\ M)\ ||\ Fe^{2+}\ (0.001\ M)\ |\ Fe$

at 298 K is 0.2905 V then the value of equilibrium constant for the cell reaction is: **[IIT (S) 2004]**

(a) $e^{0.32/0.0295}$ (b) $10^{0.32/0.0295}$

(c) $10^{0.26/0.0295}$ (d) $10^{0.32/0.0591}$

179. The standard emf of the following electrodes are;

$$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\ \text{V};\ E^\circ_{Sn^{2+}/Sn} = -0.14\ \text{V}$$

under standard conditions, the potential for the reaction,

$Sn(s) + 2Fe^{3+}(aq.) \longrightarrow 2Fe^{2+}(aq.) + Sn^{2+}(aq.)$ is: **(AIEEE 2004)**

(a) 1.68 V (b) 1.40 V (c) 0.91 V (d) 0.63 V

180. The highest electrical conductivity of the following aqueous solutions is of: **(AIEEE 2005)**

(a) 0.1 M acetic acid (b) 0.1 M chloroacetic acid

(c) 0.1 M fluoroacetic acid (d) 0.1 M difluoroacetic acid

181. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (Atomic mass = 27 amu; 1 faraday = 96500 coulomb). The cathode reaction is:

$$Al^{3+} + 3e^- \longrightarrow Al$$

To prepare 5.12 kg of aluminium metal by this method we would require: **(AIEEE 2005)**

(a) 5.49×10^7 C of electricity (b) 1.83×10^7 C of electricity

(c) 5.49×10^4 C of electricity (d) 5.49×10^{10} C of electricity

182. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are: **(AIEEE 2005)**

(a) Sn and Ag (b) Pb and Zn

(c) Ag and Au (d) Fe and Ni

183. When an acid cell is charged, then: **(AFMC 2005)**

(a) voltage of the cell increases

(b) electrolyte of the cell dilutes

(c) resistance of the cell increases

(d) none of the above

184. How many coulombs of electricity are required for the reduction of 1 mole of MnO_4^- to Mn^{2+}? **[PMT (Kerala) 2005]**

(a) 96500 C (b) 1.93×10^5 C

(c) 4.83×10^5 C (d) 9.65×10^6 C

(e) 5.62×10^5 C

185. The standard electrode potential of Ag^+/Ag is + 0.80 V and of Cu^{2+}/Cu is + 0.34 V. These electrodes are connected through a salt bridge and if: **[PET (Kerala) 2005]**

(a) copper electrode acts as cathode, then E°_{cell} is + 0.46 volt

(b) silver electrode acts as anode, then E°_{cell} is – 0.34 volt

(c) copper electrode acts as anode, then E°_{cell} is + 0.46 volt

(d) silver electrode acts as cathode, then E°_{cell} is – 0.34 volt

(e) silver electrode acts as anode, then E°_{cell} is + 1.14 volt

186. The half-cell reaction for the corrosion,

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O; \quad E^\circ = 1.23 \text{ V}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s); \quad E^\circ = -0.44 \text{ V}$$

Find the ΔG° (in kJ) for the overall reaction: **[IIT (S) 2005]**

(a) – 76 kJ (b) – 322 kJ (c) – 161 kJ (d) – 152 kJ

[Hint:

$$Fe(s) \longrightarrow Fe^{2+} + 2e^-; \quad \Delta G_1^\circ$$

$$2H^+ + 2e^- + \frac{1}{2}O_2 \longrightarrow H_2O(l); \quad \Delta G_2^\circ$$

$$\underline{\overline{Fe(s) + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O; \ \Delta G_3^\circ}}$$

Applying $\Delta G_1^\circ + \Delta G_2^\circ = \Delta G_3^\circ$

$$\begin{aligned}\Delta G_3^\circ &= (-2F \times 0.44) + (-2F \times 1.23)\\ &= (-2 \times 96500 \times 0.44) + (-2 \times 96500 \times 1.23)\\ &= -322310 \text{ J} = -322 \text{ kJ}]\end{aligned}$$

187. What is the cell reaction occurring in Daniell cell (galvanic cell)? **[CET (J&K) 2006]**

(a) $Cu(s) + ZnSO_4(aq.) \longrightarrow CuSO_4(aq.) + Zn(s)$

(b) $Zn(s) + CuSO_4(aq.) \longrightarrow Cu(s) + ZnSO_4(aq.)$

(c) $Ni(s) + ZnSO_4(aq.) \longrightarrow NiSO_4(aq.) + Zn(s)$

(d) $2Na(s) + CdSO_4(aq.) \longrightarrow Na_2SO_4(aq.) + Cd(s)$

188. What are the units of equivalent conductivity of a solution? **[CET (J&K) 2006]**

(a) mho cm^{-1} (b) ohm cm^{-1} g $equiv^{-1}$

(c) mho cm^{-2} g $equiv^{-1}$ (d) mho cm^2 g $equiv^{-1}$

189. The amount of copper deposited by one faraday current will be maximum in an acidic solution of one litre of: **[PMT (Kerala) 2006]**

(a) 1 M Cu_2Cl_2 (b) 2 M $Cu(NO_3)_2$

(c) 5 M $CuSO_4$ (d) 5 M $Cu_3(PO_4)_2$

(e) 10 M CuF_2

[Hint: Greater is the equivalent mass, more is the amount deposited by 1 F charge.]

190. The reduction potential values of M, N and O are +2.46 V, – 1.13 V, – 3.13 V respectively. Which of the following orders is correct regarding their reducing property? **[JEE (Orissa) 2006]**

(a) $O > N > M$ (b) $O > M > N$

(c) $M > N > O$ (d) $M > O > N$

191. The molar conductivities of Λ°_{NaOAc} and Λ°_{HCl} at infinite dilution in water at 25°C are 91 and 426.2 S cm^2 mol^{-1} respectively. To calculate, Λ°_{HOAc}, the additional value required is: **(AIEEE 2006)**

(a) $\Lambda^\circ_{H_2O}$ (b) Λ°_{KCl}

(c) Λ°_{NaOH} (d) Λ°_{NaCl}

[Hint: $\Lambda^\circ_{HOAc} = \Lambda^\circ_{NaOAc} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$]

192. The equivalent conductances at infinite dilution of HCl and NaCl are 426.15 and 126.15 mho cm^2 g eq^{-1} respectively. It can be said that the mobility of: **[CET (Gujarat) 2006]**

(a) H^+ ions is much more than that of Cl^- ions

(b) Cl^- ions is much more than that of H^+ ions

(c) H^+ ions is much more than that of Na^+ ions

(d) Na^+ ions is much more than that of H^+ ions

193. The tendencies of the electrodes made up of Cu, Zn and Ag to release electrons when dipped in their respective salt solutions decrease in the order: **(VITEEE 2006)**

(a) Zn > Ag > Cu (b) Cu > Zn > Ag

(c) Zn > Cu > Ag (d) Ag > Cu > Zn

194. The electrode reaction that takes place at the anode of CH_4 — O_2 fuel cell is: **(VITEEE 2006)**

(a) $2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O$

(b) $CH_4 + 2H_2O \longrightarrow CO_2 + 8H^+ + 8e^-$

(c) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

(d) $2H^+ + 2e^- \longrightarrow H_2$

195. The cell,

$$Zn(s) | Zn^{2+} (1\,M \| Cu^{2+} (1\,M) | Cu(s) \ (E^\circ_{cell} = +1.10 \text{ V})$$

was allowed to be completely discharged at 298K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is: **(AIEEE 2007)**

(a) 9.65×10^4 (b) antilog (24.08)

(c) 37.3 (d) $10^{37.3}$

[Hint:

$$E = E^\circ - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$0 = 1.10 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3$$

$$\therefore \quad \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}]$$

196. The efficiency of a cell is given by: **[CBSE (Med.) 2007]**

(a) $\frac{\Delta G}{\Delta S}$ (b) $\frac{\Delta G}{\Delta H}$

(c) $\frac{\Delta S}{\Delta G}$ (d) $\frac{\Delta H}{\Delta G}$

197. An electric current of 1 amp is passed through acidulated water for 160 minutes and 50 seconds. What is the volume of the hydrogen liberated at the anode (as reduced to NTP)? **(SCRA 2007)**

(a) 1.12 litre (b) 2.24 litre (c) 11.2 litre (d) 22.4 litre

[**Hint:** $V = \frac{I + V_e}{96500}$

$= \frac{1 \times 9650 \times 11.2}{96500} = 1.12$ litre]

198. The resistance of $N/10$ solution is found to be 2.5×10^3 ohm. The equivalent conductance of the solution is (cell constant $= 1.25\ \text{cm}^{-1}$): **[PMT (Kerala) 2007]**

(a) $2.5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$ (b) $5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

(c) $2.5\ \text{ohm}^{-1}\ \text{cm}^{-2}\ \text{equiv}^{-1}$ (d) $5\ \text{ohm}^{-1}\ \text{cm}^{-2}\ \text{equiv}^{-1}$

(e) $1.25\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

199. For strong electrolytes, the plot of molar conductance *versus* $\sqrt{C}$ is: **(VITEEE 2007)**

(a) parabolic (b) linear

(c) sinusoidal (d) circular

200. How long (in hours) must a current of 5 ampere be maintained to electroplate 60 g of calcium from molten $CaCl_2$? **(VITEEE 2007)**

(a) 27 hours (b) 8.3 hours (c) 11 hours (d) 16 hours

201. Emf of hydrogen electrode in term of pH is (at 1 atm pressure): **(MHT-CET 2007)**

(a) $E_{H_2} = \frac{RT}{F} \times \text{pH}$ (b) $E_{H_2} = \frac{RT}{F} \frac{1}{\text{pH}}$

(c) $E_{H_2} = \frac{2.303RT}{F}\text{pH}$ (d) $E_{H_2} = -0.0591\,\text{pH}$

202. The rusting of iron is catalysed by which of the following? **(MGIMS 2007)**

(a) Fe (b) O_2 (c) Zn (d) H^+

203. On the basis of $E°$ values, the strongest oxidising agent is :

$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^-$ $E° = -0.35$ V

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $E° = -0.77$ V

[CBSE (PMT) 2008]

(a) Fe^{3+} (b) $[Fe(CN)_6]^{3-}$

(c) $[Fe(CN)_6]^{4-}$ (d) Fe^{2+}

204. Given $E^\circ_{Cr^{3+}/Cr} = -0.72\ \text{V}, E^\circ_{Fe^{2+}/Fe} = -0.42$ V

The potential for the cell, $Cr|Cr^{3+}(0.1M)\,||\,Fe^{2+}(0.01M)|Fe$ is: **(AIEEE 2008)**

(a) – 0.26 V (b) 0.26 V (c) 0.339 V (d) – 0.339 V

[**Hint:** $E^\circ_{\text{cell}} = -0.42 - (-0.72) = +0.30$ V

$2Cr(s) + 3Fe^{2+}(0.01M) \rightleftharpoons 2Cr^{3+}(0.1M) + 3Fe(s)$

$$Q = \frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} = \frac{[0.1]^2}{[0.01]^2} = 10^4$$

According to Nernst equation,

$$E = E° - \frac{0.059}{n}\log_{10} Q$$

$$= 0.30 - \frac{0.059}{6}\log 10^4 \qquad (\because\ n = 6)$$

$= 0.261$ V]

205. Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli ampere current. The time required to liberate 0.01 mole of H_2 gas at the cathode is: (1 faraday = 96500 C mol^{-1}) **(IIT 2008)**

(a) 9.65×10^4 sec (b) 19.3×10^4 sec

(c) 28.95×10^4 sec (d) 38.6×10^4 sec

[**Hint:** Mass of 0.01 mol H_2 = 0.02 g

$$W = \frac{ItE}{96500}$$

$$0.02 = \frac{10 \times 10^{-3} \times t \times 1}{96500}$$

$t = 19.3 \times 10^4$ sec]

206. The emf of a cell containing sodium/copper electrodes is 3.05 V, if the electrode potential of copper electrode is + 0.34 V, the electrode potential of sodium is: **[Comed (Karnataka) 2008]**

(a) – 2.71 V (b) + 2.71 V (c) – 3.71 V (d) + 3.71 V

207. What is the number of moles of oxygen gas evolved by electrolysis of 180 g of water? **(SCRA 2009)**

(a) 2.5 (b) 5.0 (c) 7.5 (d) 10.0

208. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2;\ \Delta_rG = +966\ \text{kJ mol}^{-1}$$

The potential difference needed for the electrolytic reduction of Al_2O_3 at 500°C is at least : **(AIEEE 2010)**

(a) 2.5 V (b) 5.0 V (c) 4.5 V (d) 3.0 V

[**Hint:** In the given reaction,

$$\frac{2}{3}[2Al^{3+}] + 4e \longrightarrow \frac{4}{3}Al \quad (n = 4)$$

$\therefore$ $\Delta G = -nFE$

$$E = -\frac{\Delta G}{nF} = -\frac{966 \times 1000}{4 \times 96500}$$

$= -2.5$ V]

Set–2: The questions given below may have more than one correct answers

1. What is the difference between galvanic cell and electrolytic cell?
   (a) In galvanic cell, electrical energy is produced while in electrolytic cell electrical energy is consumed
   (b) In galvanic cell, anode is (–)ve while in electrolytic cell anode is (+)ve
   (c) In galvanic cell, cathode is (+)ve while in electrolytic cell anode is (–)ve
   (d) All are correct

2. $Ag\,|\,Ag^+, KI\,||\,AgI\,|\,Ag$ emf is E, then K_{sp} of AgI is given as:

   (a) $K_{sp} = \frac{nF}{2.303RT}\log E°$ (b) $\ln K_{sp} = nF\left[\frac{\delta E°}{\delta T} - E°\right]$

   (c) $\ln K_{sp} = \frac{nF}{E°}$ (d) $\log K_{sp} = \frac{nFE°}{2.303RT}$

3. A hydrogen electrode is placed in a buffer solution of acetic acid and sodium acetate in the ratio $y : x$ and $x : y$ has

electrode potential values E_1 and E_2 volts respectively. pK_a value for acetic acid is:

(a) $\frac{E_1 + E_2}{0.118}$ (b) $\frac{E_2 - E_1}{0.118}$

(c) $\frac{-(E_1 + E_2)}{0.118}$ (d) $\frac{E_1 - E_2}{0.118}$

(E_1 and E_2 are oxidation potentials)

4. For which electrolyte $\alpha = \frac{\lambda_v}{\lambda_\infty}$ doesn't hold good?

(a) CH_3OH (b) $HClO_4$

(c) HCOOH (d) $NaNH_2$

5. The main factors which affect corrosion are:

(a) position of metal in electrochemical series

(b) presence of CO_2 in water

(c) presence of impurities in metal

(d) presence of protective coating

6. Which is correct about silver plating?

(a) Anode—pure Ag

(b) Cathode—object to be electroplated

(c) Electrolyte—$Na[Ag(CN)_2]$

(d) Electrolyte—$AgNO_3$

7. Lead storage battery contains:

(a) Pb rod as anode

(b) Pb rod as cathode

(c) Pb plates coated with PbO_2 act as cathode

(d) electrolyte is H_2SO_4

8. During the electrolysis of $AgNO_3$ (using Pt electrodes) concentration around cathode as well as anode falls from $4M$ to $3M$. What will happen if this happened with Ag electrodes?

(a) Result will remain same

(b) Concentration around cathode will fall from $4M$ to $3M$ but around anode will increase from $4M$ to $5M$

(c) Reverse of statement (b)

(d) Concentration increases from $4M$ to $5M$ on both the electrodes

9. Emf of the cell $Pt \cdot H_2$ (1 atm) | $H^+(aq.)$ || AgCl|Ag is 0.27 V and 0.26 V at 25°C and 35°C. Heat of reaction occurring inside the cell at 25°C is:

(a) – 54.8 kJ (b) 26.05 kJ

(c) – 26.05 kJ (d) + 54.8 kJ

10. Given that,

$$Ni^{2+}/Ni = 0.25\ V,\ \ Cu^{2+}/Cu = 0.34\ V,$$
$$Ag^{+}/Ag = 0.80\ V \ \text{ and }\ Zn^{2+}/Zn = -0.76\ V$$

which of the following reactions under standard condition will not take place in the specified direction?

(a) $Ni^{2+}(aq.) + Cu(s) \longrightarrow Ni(s) + Cu^{2+}(aq.)$

(b) $Cu(s) + 2Ag^{+}(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s)$

(c) $Cu(s) + 2H^{+}(aq.) \longrightarrow Cu^{2+}(aq.) + H_2(g)$

(d) $Zn(s) + 2H^{+}(aq.) \longrightarrow Zn^{2+}(aq.) + 3H_2(g)$

11. Which of the following statements is/are correct?

(a) One faraday is the charge carried by one mole of electrons

(b) If same quantity of electricity flows through the solutions of 0.1 M $AgNO_3$ and 0.1 M $CuSO_4$ solutions, same weight of silver and copper will be deposited

(c) Electrochemical equivalent has the units of grams per coulomb

(d) Passage of one faraday of electricity produces one gram equivalent of the substance at the electrode

12. Which of the following statements is/are not correct?

(a) Zn-Cu cell is called Daniell cell

(b) Rust is Fe_2O_3

(c) Saline water slows down rusting

(d) Pure metals undergo corrosion faster than impure metals

13. In electrolysis of very dilute NaOH solution using platinum electrodes:

(a) H_2 is evolved at cathode

(b) H_2 is produced at anode

(c) Na is obtained at cathode

(d) O_2 is produced at anode

14. We observe blue colour if:

(a) Cu electrode is placed in the $AgNO_3$ solution

(b) Cu electrode is placed in the $ZnSO_4$ solution

(c) Cu electrode is placed in the dil. HNO_3

(d) Cu electrode is placed in dil. H_2SO_4

15. In which of the following cell (s); $E_{cell} = E^{\circ}_{cell}$?

(a) $Cu(s) \mid Cu^{2+}(0.01\ M) \parallel Ag^{+}(0.1\ M) \mid Ag(s)$

(b) $Pt(H_2) \mid pH = 1 \parallel Zn^{2+}(0.01\ M) \mid Zn(s)$

(c) $Pt(H_2) \mid pH = 1 \parallel Zn^{2+}(1\ M) \mid Zn(s)$

(d) $Pt(H_2) \mid H^{+} = 0.01\ M \parallel Zn^{2+}(0.01\ M) \mid Zn(s)$

16. Rusting on the surface of iron involves:

(a) $Fe(s) \longrightarrow Fe^{2+}(aq.) + 2e^-$ (at anodic site)

(b) $O_2(g) + 4H^{+}(aq.) + 4e^- \longrightarrow 2H_2O(l)$ (at cathodic site)

(c) $4Fe^{2+}(aq.) + O_2(g) + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^{+}$

(d) $Fe_2O_3(s) + xH_2O(l) \longrightarrow Fe_2O_3 \cdot xH_2O$

17. Fuel cell involves following reaction(s):

(a) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$ (at cathode)

(b) $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq.)$ (at anode)

(c) $2H_2(g) + 4OH^-(aq.) \longrightarrow 4H_2O(l) + 4e^-$ (at anode)

(d) $2H_2(g) + 4OH^-(aq.) \longrightarrow 4H_2O(l) + 4e^-$ (at cathode)

18. In the following question, more than one of the answers given may be correct. Select the correct answers and mark it according to the code:

Codes : **[BHU (Mains) 2008]**

(a) 1, 2 and 3 are correct (b) 1 and 2 are correct

(c) 2 and 4 are correct (d) 1 and 3 are correct

[**Hint :** In a cell $Zn(s) \mid Zn^{2+} \parallel H^{+} \mid H_2(Pt)$; the addition of H_2SO_4 to the cathode compartment, will:

1. decrease E
2. increase E
3. shift equilibrium to left
4. shift equilibrium to right]

19. For the reduction of NO_3^- in an aqueous solution, $E°$ is 0.96 V. Values of $E°$ for some metal ions are given below :

$$V^{2+}_{(aq)} + 2e^- \longrightarrow V \qquad E° = -1.19\text{ V}$$
$$Fe^{3+}_{(aq)} + 3e^- \longrightarrow Fe \qquad E° = -0.04\text{ V}$$
$$Au^{3+}_{(aq)} + 3e^- \longrightarrow Au \qquad E° = +1.40\text{ V}$$
$$Hg^{2+}_{(aq)} + 2e^- \longrightarrow Hg \qquad E° = +0.86\text{ V}$$

The pair(s) of metal that is(are) oxidised by NO_3^- in aqueous solution is(are) : **(IIT 2009)**

(a) V and Hg (b) Hg and Fe
(c) Fe and Au (d) Fe and V

[**Hint :** $E^\circ_{M^{n+}/M}$ for V, Fe and Hg are lower than that of NO_3^-, so, NO_3^- will oxidise V, Fe and Hg.]

Assertion-Reason TYPE QUESTIONS

The questions given below consist of an **'Assertion' (A)** and **'Reason' (R)**. Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. (A) When acidified zinc sulphate solution is electrolysed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.
(R) The electrode potential of zinc is more negative than hydrogen as the over voltage for the hydrogen evolution on zinc is quite large.

2. (A) In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.
(R) The molecular weights of silver and copper are different. **(AIIMS 1996)**

3. (A) Equivalent conductance of all electrolytes decreases with increasing concentration.
(R) Lesser number of ions are available per gram equivalent at higher concentration. **(AIIMS 1999)**

4. (A) Zinc displaces copper from copper sulphate solution.
(R) The $E°$ is Zn of – 0.76 volt and that of copper is +0.34 volt. **(AIIMS 1999)**

5. (A) An electrochemical cell can be set-up only if the redox reaction is spontaneous.
(R) A reaction is spontaneous if free energy change is negative.

6. (A) If an aqueous solution of NaCl is electrolysed, the product obtained at the cathode is H_2 gas and not Na.
(R) Gases are liberated faster than the metals.

7. (A) Specific conductance decreases with dilution whereas equivalent conductance increases.
(R) On dilution, number of ions per cc decreases but total number of ions increases considerably.

8. (A) The cell constant of a cell depends upon the nature of the material of the electrodes.
(R) The observed conductance of a solution depends upon the nature of the material of the electrodes.

9. (A) The ratio of specific conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.
(R) Specific conductivity decreases with dilution whereas observed conductance increases with dilution.

10. (A) Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.
(R) Kohlrausch's law helps to find the molar conductivity of a weak electrolyte at infinite dilution.

11. (A) One coulomb of electric charge deposits weight equal to the electrochemical equivalent of the substance.
(R) One faraday deposits one mole of the substance.

12. (A) If standard reduction potential for the reaction, $Ag^+ + e^- \longrightarrow Ag$ is 0.80 volt, then for the reaction, $2Ag^+ + 2e^- \longrightarrow 2Ag$, it will be 1.60 volt.
(R) If concentration of Ag^+ ions is doubled, the electrode potential is also doubled.

13. (A) Gold chloride ($AuCl_3$) solution cannot be stored in a vessel made of copper, iron, nickel, chromium, zinc or tin.
(R) Gold is very precious metal.

14. (A) In the Daniell cell, if concentrations of Cu^{2+} and Zn^{2+} ions are doubled, the emf of the cell will be doubled.
(R) If the concentration of ions in contact with the metals is doubled, the electrode potential is doubled.

15. (A) $H_2 + O_2$ fuel cell gives a constant voltage throughout its life.
(R) In this fuel cell, H_2 reacts with OH^- ions, yet the overall concentration of OH^- ions does not change.

16. (A) Presence of CO_2 in the air accelerates corrosion.
(R) CO_2 is a poisonous gas.

17. (A) For the Daniell cell, $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ with $E_{cell} = 1.1$ volt, the application of opposite potential greater than 1.1 V results into flow of electrons from cathode to anode.
(R) Zn is deposited at anode and Cu is dissolved at cathode. **(AIIMS 2006)**

18. (A) A current of 96.5 ampere is passed into aqueous $AgNO_3$ solution for 100 second. The weight of silver deposited is 10.8 g. (Atomic weight of Ag = 108)
(R) The mass of a substance deposited during the electrolysis of an electrolyte is inversely proportional to the quantity of electricity passing through the electrolyte. **[EAMCET (Engg.) 2006]**

19. (A) According to Kohlrausch's law, the molar conductance of a strong electrolyte at infinite dilution is sum of molar conductivities of its ions.
(R) The current carried by cation and anion is always equal. **(AIIMS 2007)**

20. (A) The cell potential of mercury cell is 1.35 V, which remains constant.
(R) In mercury cell, the electrolyte is a paste of KOH and ZnO. **(AIIMS 2008)**

Answers : OBJECTIVE QUESTIONS

- **Set–1**

1. (d)	**2.** (b)	**3.** (a)	**4.** (c)	**5.** (c)	**6.** (d)	**7.** (b)	**8.** (a)
9. (c)	**10.** (c)	**11.** (c)	**12.** (b)	**13.** (c)	**14.** (d)	**15.** (a)	**16.** (d)
17. (a)	**18.** (a)	**19.** (a)	**20.** (d)	**21.** (c)	**22.** (b)	**23.** (b)	**24.** (d)
25. (a)	**26.** (d)	**27.** (c)	**28.** (c)	**29.** (b)	**30.** (d)	**31.** (a)	**32.** (d)
33. (a)	**34.** (c)	**35.** (b)	**36.** (c)	**37.** (a)	**38.** (b)	**39.** (d)	**40.** (b)
41. (b)	**42.** (a)	**43.** (c)	**44.** (d)	**45.** (c)	**46.** (d)	**47.** (d)	**48.** (d)
49. (d)	**50.** (a)	**51.** (b)	**52.** (c)	**53.** (a)	**54.** (a)	**55.** (d)	**56.** (a)
57. (b)	**58.** (b)	**59.** (c)	**60.** (d)	**61.** (d)	**62.** (b)	**63.** (a)	**64.** (b)
65. (c)	**66.** (b)	**67.** (d)	**68.** (b)	**69.** (c)	**70.** (c)	**71.** (c)	**72.** (d)
73. (a)	**74.** (a)	**75.** (a)	**76.** (d)	**77.** (b)	**78.** (c)	**79.** (b)	**80.** (c)
81. (a)	**82.** (c)	**83.** (b)	**84.** (d)	**85.** (c)	**86.** (d)	**87.** (b)	**88.** (a)
89. (a)	**90.** (b)	**91.** (d)	**92.** (c)	**93.** (b)	**94.** (c)	**95.** (d)	**96.** (c)
97. (c)	**98.** (d)	**99.** (d)	**100.** (a)	**101.** (b)	**102.** (a)	**103.** (c)	**104.** (b)
105. (a)	**106.** (b)	**107.** (c)	**108.** (a)	**109.** (b)	**110.** (d)	**111.** (d)	**112.** (b)
113. (c)	**114.** (c)	**115.** (d)	**116.** (b)	**117.** (a)	**118.** (a)	**119.** (c)	**120.** (a)
121. (d)	**122.** (a)	**123.** (c)	**124.** (b)	**125.** (d)	**126.** (b)	**127.** (c)	**128.** (a)
129. (d)	**130.** (b)	**131.** (a)	**132.** (c)	**133.** (b)	**134.** (d)	**135.** (d)	**136.** (a)
137. (d)	**138.** (a)	**139.** (c)	**140.** (a)	**141.** (d)	**142.** (b)	**143.** (b)	**144.** (a)
145. (a)	**146.** (c)	**147.** (c)	**148.** (d)	**149.** (b)	**150.** (d)	**151.** (b)	**152.** (c)
153. (d)	**154.** (a)	**155.** (b)	**156.** (c)	**157.** (d)	**158.** (b)	**159.** (c)	**160.** (b)
161. (c)	**162.** (c)	**163.** (b)	**164.** (b)	**165.** (b)	**166.** (b)	**167.** (d)	**168.** (a)
169. (a)	**170.** (d)	**171.** (a)	**172.** (b)	**173.** (c)	**174.** (a)	**175.** (d)	**176.** (c)
177. (d)	**178.** (b)	**179.** (c)	**180.** (d)	**181.** (a)	**182.** (c)	**183.** (a)	**184.** (c)
185. (c)	**186.** (b)	**187.** (b)	**188.** (d)	**189.** (a)	**190.** (a)	**191.** (d)	**192.** (c)
193. (c)	**194.** (b)	**195.** (d)	**196.** (b)	**197.** (a)	**198.** (b)	**199.** (b)	**200.** (d)
201. (d)	**202.** (d)	**203.** (a)	**204.** (b)	**205.** (b)	**206.** (a)	**207.** (b)	**208.** (a)

- **Set–2**

1. (d)	**2.** (d)	**3.** (a)	**4.** (b)	**5.** (a, b, c, d)	**6.** (a, b, c)	**7.** (a, c, d)	**8.** (b)
9. (a)	**10.** (a, c)	**11.** (a, c, d)	**12.** (b, c, d)	**13.** (a, d)	**14.** (a, c)	**15.** (a, b)	**16.** (a, b, c, d)
17. (a, c)	**18.** (c)	**19.** (a, b, d)					

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (a)	**2.** (b)	**3.** (c)	**4.** (a)	**5.** (b)	**6.** (c)	**7.** (c)	**8.** (d)
9. (b)	**10.** (b)	**11.** (c)	**12.** (d)	**13.** (b)	**14.** (d)	**15.** (a)	**16.** (c)
17. (b)	**18.** (c)	**19.** (c)	**20.** (b)				

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. When aluminium oxide (Al_2O_3) is electrolysed for the production of aluminium metal. For a given quantity of electricity, the number of moles of aluminium obtained if the volume of O_2 gas obtained is 201.6 litre measured at NTP, is:
(a) 9 (b) 6 (c) 12 (d) 4.5

[**Hint:** Number of equivalents of oxygen $= \frac{201.6}{5.6} = 36$

(Equivalent volume of oxygen = 5.6 litre at NTP)

$\therefore$ Number of equivalents of Al = 36

Mass of aluminium $= 36 \times 9$ g

Number of moles of aluminium $= \frac{36 \times 9}{27} = 12$]

2. A smuggler could not carry gold by depositing iron on the gold surface since:
(a) gold is denser
(b) iron rusts
(c) gold has higher reduction potential than iron
(d) gold has lower reduction potential than iron

3. On electrolysis, which of the following does not give out oxygen?
(a) Acidic water using Pt electrode
(b) Fused NaOH using Pt electrode
(c) Dilute H_2SO_4 using Pt electrode
(d) Dilute H_2SO_4 using Cu electrode

4. During electrolysis of a solution of $AgNO_3$, 9650 coulomb of charge pass through the electrolytic cell; the mass of silver deposited on the cathode will be:
(a) 21.6 g (b) 108 g (c) 10.8 g (d) 1.08 g

5. An electrolytic cell contains a solution of Ag_2SO_4 and has platinum electrodes. A current is passed until 1.6 g of O_2 has been liberated at anode. The amount of silver deposited at cathode will be:
(a) 108 g (b) 1.6 g (c) 0.8 g (d) 21.60 g

[**Hint:** Number of equivalents of oxygen $= \frac{1.6}{8} = 0.2$

$\therefore$ Number of equivalents of Ag deposited = 0.2

Mass of Ag deposited $= 0.2 \times 108 = 21.6$ g]

6. In the process of electroplating, *m* g of silver is deposited when 4 ampere of current flows for 2 minutes. The amount (in g) of silver deposited by 6 ampere of current flowing for 40 seconds will be:
(a) $4m$ (b) $\frac{m}{2}$ (c) $\frac{4m}{3}$ (d) $3m$

[**Hint:**
$$\frac{W_1}{W_2} = \frac{Q_1}{Q_2}$$
$$\frac{W_1}{W_2} = \frac{I_1 \times t_1}{I_2 \times t_2}$$
$$\frac{m}{W_2} = \frac{4 \times 2 \times 60}{6 \times 40}$$
$$W_2 = \frac{m}{2} \text{ g}]$$

7. If four moles of electrons are transferred from anode to cathode in an experiment on electrolysis of water, then total volume of the two gases produced at STP will be:
(a) 224 L (b) 72.6 L (c) 67.2 L (d) 89.4 L

[**Hint:** Equivalent volume of H_2 = 11.2 L

Equivalent volume of O_2 = 5.6 L

Volume of H_2 and O_2 evolved by 4 moles electrons or 4 faraday charge $= 4 \times 11.2 + 4 \times 5.6 = 67.2$ L]

8. When one faraday of electricity is passed through three electrolytic cells containing Ag^+, Ni^{2+} and Cr^{3+} ions respectively, the deposited Ag (At. mass = 108), Ni (At. mass = 59) and Cr (At. mass = 52) are:

	Ag	Ni	Cr
(a)	108 g	29.5 g	17.3 g
(b)	108 g	59 g	52 g
(c)	108 g	108 g	17.3 g
(d)	108 g	29.5 g	166 g

[**Hint:** Equivalent mass of Ag $= \frac{108}{1} = 108$

Equivalent mass of Ni $= \frac{59}{2} = 29.5$

Equivalent mass of Cr $= \frac{52}{3} = 17.3$

$\therefore$ Amount of these metals deposited by 1 faraday charge will be: 108 g Ag, 29.5 g Ni and 17.3 g Cr respectively.]

9. Which of the following reactions occur at the cathode during the charging of lead storage battery?
(a) $Pb^{2+} + 2e^- \longrightarrow Pb$
(b) $Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$
(c) $Pb \longrightarrow Pb^{2+} + 2e^-$
(d) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

10. A current of 2.6 amp was passed through $CuSO_4$ solution for 6 minutes and 20 seconds. The amount of copper deposited is:
(a) 0.3175 g (b) 0.0031 g (c) 6.35 g (d) 3.175 g

[**Hint:** $W = \frac{ItE}{96500} = \frac{2.6 \times 380 \times 31.75}{96500} \approx 0.32$ g]

11. In the electrolysis of fused salt, the weight of the substance deposited on an electrode will not depend on:
(a) temperature of the bath
(b) current intensity
(c) time of electrolysis
(d) electrochemical equivalent of the ions

12. When an aqueous solution of sodium chloride is electrolysed using platinum electrodes, the ions discharged at the electrodes are:

(a) sodium and hydrogen (b) sodium and chloride
(c) hydrogen and chloride (d) hydroxyl and chloride

13. How many coulombs are required for the oxidation of 1 mole of H_2O_2 to O_2?
(a) 9.65×10^4 C (b) 93000 C
(c) 1.93×10^5 C (d) 19.3×10^2 C

[**Hint:** $H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$

$$1 \text{ mol } H_2O_2 \equiv 2 \text{ mol } e^-$$
$$\equiv 2 \times 96500 \text{ C}$$
$$\equiv 193000 \text{ C}$$
$$= 1.93 \times 10^5 \text{ C}]$$

14. A current of 2 amp when passed for 5 hours through a molten salt deposits 22.2 g of metal of atomic mass 177. The oxidation state of the metal in the metal salt is:
(a) +1 (b) +2 (c) +3 (d) +4

[**Hint:** $W = \frac{ItE}{96500}$

$$E = \frac{W \times 96500}{It} = \frac{22.2 \times 96500}{2 \times 5 \times 3600} = 59.5$$

$$\text{Equivalent mass} = \frac{\text{Atomic mass}}{\text{Oxidation state}}$$

$$59.5 = \frac{177}{n}$$

$\therefore$ $n \approx 3$]

15. When water is electrolysed, hydrogen and oxygen gases are produced. If 1.008 g of H_2 is liberated at cathode, what mass of O_2 is formed at the anode?
(a) 32 g (b) 16 g (c) 8 g (d) 4 g

[**Hint:** $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

$$\frac{1.008}{W_2} = \frac{1.008}{8}$$

$\therefore$ $W_2 = 8$ g

where, E_1 and E_2 are equivalent mass of hydrogen and oxygen respectively.]

16. The cell potential (E) and the free energy change (ΔG) accompanying an electrochemical reaction are related by:
(a) $\Delta G = nF \log E$ (b) $\Delta G = nFE$
(c) $-\Delta G = nFE$ (d) $-\Delta G = nF \log E$

17. The units of conductivity are:
(a) siemens^{-1} cm^{-1} (b) siemens cm
(c) siemens cm^{-1} (d) siemens cm^{-2} mol^{-1}

18. The calomel electrode used as a reference electrode contains:
(a) PbO_2-$PbSO_4$ mixture (b) $HgCl_2$
(c) Hg_2Cl_2 (d) $ZnCl_2$

19. KCl is used in salt bridge because:
(a) it forms a good jelly with agar-agar
(b) it is a strong electrolyte
(c) it is a good conductor of electricity
(d) the transference number of K^+ and Cl^- ions are almost equal

[**Hint:** Only those electrolytes are used in salt bridge whose ions have same transference number in agar-agar gel.]

20. The increase in the equivalent conductance of a salt solution on dilution is due to increase in the:
(a) attraction between the ions
(b) degree of ionization of the salt
(c) molecular attraction
(d) association of the salt

21. When 96500 coulombs of electricity are passed through nickel sulphate solution, the amount of nickel deposited will be:
(a) 1 mol (b) 0.5 mol (c) 0.1 mol (d) 2 mol

[**Hint:** 1 faraday deposits 1 equivalent of nickel.
1 equivalent of Ni = 1/2 mole of nickel.]

22. $Al^{3+}(aq.) + 3e^- \longrightarrow Al(s); \; E° = -1.66$ V
$Cu^{2+}(aq.) + 2e^- \longrightarrow Cu(s); \; E° = +0.34$ V

What voltage is produced under standard conditions by combining the half reactions with these standard electrode potentials?
(a) 1.32 V (b) 2.00 V (c) 2.30 V (d) 4.34 V

[**Hint:** The cell will be:

$$Al(s) \,|\, Al^{3+}(aq.) \,||\, Cu^{2+}(aq.) \,|\, Cu(s)$$

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$
$$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Al^{3+}/Al}$$
$$= +0.34 - (-1.66) = +2.00 \text{ V}]$$

23. For which of these oxidation/reduction pairs will the reduction potential vary with pH?
I. AmO_2^{2+} / AmO_2^+ II. AmO_2^{2+} / Am^{4+} III. Am^{4+} / Am^{2+}
(a) I only (b) II only
(c) I and II only (d) I, II and III

[**Hint:** $4H^+ + AmO_2^{2+} + 2e^- \longrightarrow Am^{4+} + 2H_2O$
It includes H^+ ions; hence the electrode potential depends on pH.]

24. $2Ag^+(aq.) + Cu(s) \rightleftharpoons Cu^{2+}(aq.) + 2Ag(s)$
The standard potential $E°$ for this reaction is 0.46 V. Which change will increase the potential the most?
(a) Doubling the $[Ag^+]$
(b) Halving the $[Cu^{2+}]$
(c) Doubling the size of the Cu(s) electrode
(d) Decreasing the size of the Ag electrode by one-half

25. $10Cl^-(aq.) + 2MnO_4^-(aq.) + 16H^+(aq.) \rightleftharpoons 5Cl_2(g) + 2Mn^{2+}(aq.) + 8H_2O(l)$
The value of $E°$ for this reaction is 0.15 V. What is the value of the equilibrium constant (K) for this reaction?
(a) 2.4×10^{25} (b) 4.9×10^{12} (c) 1.2×10^5 (d) 3.4×10^2

[**Hint:** $K = \text{antilog}\left[\frac{nE^\circ}{0.059}\right]$

$$= \text{antilog}\left[\frac{10 \times 0.15}{0.059}\right]$$
$$\approx 2.4 \times 10^{25}]$$

26. What takes place when zinc metal is added to an aqueous solution containing magnesium nitrate and silver nitrate?

1. Zn is oxidised 2. Mg^{2+} is reduced

3. Ag^+ is reduced 4. No reaction takes place

(a) 1 and 2 only (b) 1 and 3 only

(c) 1, 2 and 3 only (d) 4 only

27. In the galvanizing process, iron is coated with zinc. The resulting chemical protection is most similar to that provided when:

(a) a magnesium bar is connected to an iron pipe

(b) an iron can is plated with tin

(c) copper pipes are connected using lead solder

(d) a copper pipe is covered with epoxy paint

28. What is the sign of $\Delta G°$ and the value of K for an electrochemical cell for which $E^\circ_{cell} = 0.80\,V$?

	$\Delta G°$	K
(a)	–	> 1
(b)	+	> 1
(c)	+	< 1
(d)	–	< 1

29. Consider a voltaic cell based on these half-cells:

$$Ag^+(aq.) + e^- \longrightarrow Ag(s); \; E° = +0.80\,V$$

$$Cd^{2+}(aq.) + 2e^- \longrightarrow Cd(s); \; E° = -0.40\,V$$

Identify the anode and give the voltage of this cell under standard conditions.

(a) Ag; $E_{cell} = 0.40\,V$ (b) Ag; $E_{cell} = 2.00\,V$

(c) Cd; $E_{cell} = 1.20\,V$ (d) Cd; $E_{cell} = 2.00\,V$

[**Hint:** Anode has lower standard reduction potential; thus Cd will be considered as anode.

$$E^\circ_{Cell} = E_{Cathode} - E_{Anode}$$

$$= E_{Ag^+/Ag} - E^\circ_{Cd^{2+}/Cd}$$

$$= 0.80 - (-0.40) = 1.20\,V\,]$$

30. If the E°_{cell} for a given reaction has a negative value, which gives the correct relationships for the values of $\Delta G°$ and K_{eq}?

(a) $\Delta G° > 0$; $K_{eq} < 1$ (b) $\Delta G° > 0$; $K_{eq} > 1$

(c) $\Delta G° < 0$; $K_{eq} > 1$ (d) $\Delta G° < 0$; $K_{eq} < 1$

31. Which of the following solutions is used as an anti-rusting solution?

(a) Na_2SO_4 (b) Na_3PO_4 (c) Na_3BO_3 (d) Na_2S

32. The pressure of hydrogen gas is increased from 1 atm to 100 atm. Keeping the H^+ (1 M) constant, the voltage of the hydrogen half-cell at 25°C will be:

(a) 0.059 V (b) 0.59 V (c) 0.0295 V (d) 0.118 V

33. Efficiency of the following cell is 84%.

$$A(s) + B^{2+}(aq.) \rightleftharpoons A^{2+}(aq.) + B(s); \; \Delta H = -285\,kJ$$

Then the standard electrode potential of the cell will be:

(a) 1.20 V (b) 2.40 V (c) 1.10 V (d) 1.24 V

[**Hint:** Efficiency $= \dfrac{\Delta G°}{\Delta H°} = \dfrac{-nFE°}{\Delta H°}$

$$0.84 = -\frac{2 \times E° \times 96500}{-285 \times 1000}$$

$$E° = +1.24\,V\,]$$

34. A chemical reaction will be spontaneous if:

(a) E°_{cell} is positive (b) $\Delta G°$ is negative

(c) reaction quotient, $Q < K$ (d) E°_{oxid} is negative

35. Match the List-I with List-II :

	List-I (Electrode)		**List-II (Type)**
1.	Calomel	(A)	Reference
2.	Glass	(B)	Redox
3.	Hydrogen	(C)	Membrane
4.	Quinhydrone	(D)	Gas

Codes:

(a)	1–A	2–C	3–D	4–B
(b)	1–B	2–A	3–D	4–C
(c)	1–C	2–B	3–A	4–D
(d)	1–D	2–A	3–C	4–B

36. The conductivity of saturated solution of $BaSO_4$ is 3.06×10^{-6} mho cm^{-1} and its equivalent conductance is 1.53 mho cm^2 eq^{-1}. The K_{sp} for $BaSO_4$ will be:

(a) $4 \times 10^{-12}\,M$ (b) $4 \times 10^{6}\,M$

(c) $4 \times 10^{-12}\,M^2$ (d) $4 \times 10^{-6}\,M^2$

37. The standard reduction potential of hydrogen is zero because:

(a) it is assumed

(b) hydrogen is easiest to oxidise

(c) hydrogen has single electron

(d) hydrogen is electronegative

In the following three questions, three statements I, II and III are given. Mark:

(a) if all the statements are correct

(b) if II and III are correct

(c) if I and III are correct

(d) if only II is correct **[BHU (Mains) 2007]**

38. I. Conductance of electrolyte solution increases with temperature.

II. Resistivity is reciprocal of molar conductivity of electrolyte.

III. Cell constant has unit cm^{-1}.

(a) (b) (c) (d)

39. I. The conductivity of molten NaCl is due to movement of Na^+ and Cl^- ions.

II. Solid NaCl is also conductor of electricity.

III. Molten sodium is a good conductor because of mobile electrons.

(a) (b) (c) (d)

40. I. Cathode is –ve terminal both in electrochemical and electrolytic cells.

II. Reduction occurs at cathode both in galvanic as well as electrolytic cells.

III. Chemical charge in electrolytic cell is non-spontaneous.

(a) (b) (c) (d)

41. In an experiment, 0.04 F was passed through 400 mL of a 1 *M* solution of NaCl. What would be the pH of the solution after the electrolysis? **[PMT (Kerala) 2007]**
(a) 8 (b) 10 (c) 13 (d) 6
(e) 9

[**Hint:** Electrolysis of *aq.* NaCl gives hydrogen gas at cathode and oxygen gas at anode, the electrolyte solution contains NaOH after electrolysis.

Number of equivalents of NaOH formed = 0.04

$$\text{Normality,}\quad N = \frac{0.04 \times 1000}{400} = 0.1$$

$$[OH^-] = 0.1M$$

$$pOH = 1 \qquad \therefore\ pH = 13]$$

42. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 mL. A silver electrode was dipped in the solution and the emf of the cell set-up $Pt(s), H_2(g) | H^+ (1M) || Ag^+ (aq.) | Ag(s)$ was 0.62 V. If E°_{cell} is 0.80 V, what is the percentage of Ag in the alloy?
(At 25°C, $RT/F = 0.06$) **[PET (Kerala) 2007]**
(a) 25 (b) 2.50 (c) 10 (d) 1
(e) 50

[**Hint:** Overall cell reaction is:

$$H_2(g) + 2Ag^+ \rightleftharpoons 2Ag(s) + 2H^+(aq.)$$

$$E = E^\circ - \frac{0.06 \times 2.303}{2} \log \frac{[H^+]^2}{[Ag^+]^2\, pH_2}$$

$$0.62 = 0.80 + \frac{2 \times 0.06 \times 2.303}{2} \log [Ag^+]$$

$$[Ag^+] = 0.05\, M$$

Number of moles of Ag^+ in 100 mL

$$= \frac{MV}{1000} = \frac{0.05 \times 100}{1000} = 0.005$$

Mass of silver = 0.005 × 108 g

$$\text{Percentage of Ag in 1.08 g of alloy} = \frac{0.005 \times 108 \times 100}{1.08} = 50\%]$$

43. Select the correct statements about dry cell:
(a) It is also called Leclanche cell
(b) It is also called Daniell cell
(c) Electrolyte used is moist paste of NH_4Cl and $ZnCl_2$
(d) Cathodic process is:

$$2MnO_2(s) + 2NH_4^+(aq.) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$$

44. Given the standard oxidation potentials,

$$Fe \xrightarrow{+0.4\ V} Fe^{2+}(aq.) \xrightarrow{-0.8\ V} Fe^{3+}(aq.)$$

$$Fe \xrightarrow{+0.9\ V} Fe(OH)_2 \xrightarrow{0.6\ V} Fe(OH)_3$$

It is easier to oxidise Fe^{2+} to Fe^{3+} in:
(a) acid medium
(b) alkaline medium
(c) neutral medium
(d) both in acidic and alkaline mediums

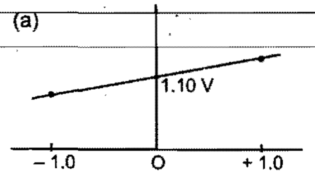
[**Hint:** $E^\circ_{Fe^{2+}/Fe^{3+}}$ is positive in alkaline solution, therefore, it is easier to oxidise Fe^{2+} to Fe^{3+} in alkaline medium.]

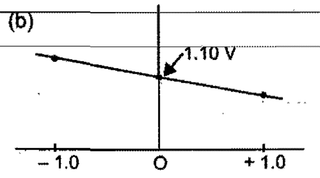
45. Dipping iron article into a strongly alkaline solution of sodium phosphate: **(VITEEE 2008)**
(a) does not affect the article
(b) forms $Fe_2O_3 \cdot xH_2O$ on the surface
(c) forms iron phosphate film
(d) forms ferric hydroxide

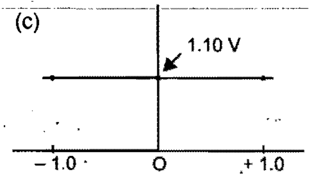
46. For the redox process,

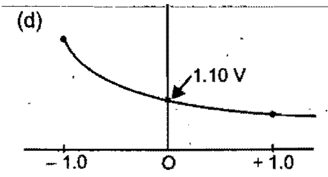
$$Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)\ E^\circ_{cell} = +1.10\ V$$

which graph correctly represents E_{cell} (*Y*-axis) as a function of $\log \frac{[Zn^{2+}]}{[Cu^{2+}]}$ (*X*-axis)?









47. A fuel cell involves combustion of the butane at 1 atm and 298 K

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$$

$$\Delta G^\circ = -2746\ \text{kJ/mol}$$

what is E° of a cell ?
(a) + 4.74 V (b) + 0.547 V (c) + 1.09 V (d) + 4.37 V

[**Hint :** In the reaction

$$\overset{-10}{C_4}\overset{+10}{H_{10}}(g) + \frac{13}{2}O_2(g) \longrightarrow 4\overset{+4}{C}\overset{-4}{O_2}(g) + 5H_2O(l)$$

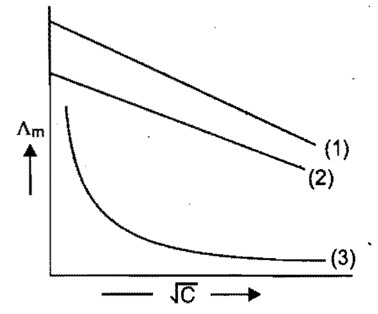
Change in oxidation number of carbon = + 16 – (– 10) = + 26

∴ Number of electrons involved in cell process will be 26.

$$E^\circ = \frac{-\Delta G^\circ}{nF} = -\frac{(-2746) \times 1000}{26 \times 96500}$$

$$= +1.09\ V]$$

48. Molar conductance Λ_m is plotted agains $\sqrt{C}$ (mol litre^{-1}) for three electrolytes (NaCl, HCl, NH_4OH)



which of the following is correct ?

	1	2	3
(a)	NaCl	HCl	NH_4OH
(b)	HCl	NaCl	NH_4OH
(c)	NH_4OH	NaCl	HCl
(d)	NH_4OH	HCl	NaCl

49. In the concentration cell

$$\mathrm{Pt(H_2)}\left|\begin{matrix}HA\ (0.1\,M)\\ \mathrm{Na}A\ (1M)\end{matrix}\right|\left|\begin{matrix}HA\ (1\,M)\\ \mathrm{Na}A\ (1M)\end{matrix}\right|\mathrm{(H_2)\ Pt}$$

(pK_a of $HA = 4$)
Cell potential will be:
(a) 0.03 V (b) 0.06 V (c) – 0.06 V (d) – 0.03 V

[**Hint :** $E_{cell} = \frac{0.0591}{1}\log_{10}\frac{[H^+]\text{ Cathode}}{[H^+]\text{ Anode}}$

$$E_{cell} = 0.06\,[\text{pH Anode} - \text{pH Cathode}] \qquad ...(1)$$

$$\text{pH Anode} = pK_a + \log\overline{[HA]} = 4 + \log\frac{0.1}{1} = 3$$

$$\text{pH Cathode} = 4 \ \text{(from eq. 1)}$$

$$E_{cell} = -\,0.06\text{ V}]$$

50. In the following process of disproportionation:

$$\underset{\text{Chlorate ion}}{2ClO_3^-} \rightleftharpoons ClO_2^- + \underset{\text{Per chlorate ion}}{ClO_4^-} \qquad E^\circ_{ClO_4^-/ClO_3^-} = +\,0.36\text{ V} \qquad E^\circ_{ClO_3^-/ClO_2^-} = +\,0.33\text{ V}$$

Initial concentration of chlorate ion was 0.1 *M*. The equilibrium concentration of per chlorate ion will be :
(a) 0.19 V (b) 0.1 *M* (c) 0.024 *M* (d) 0.019 *M*

[**Hint :**

$$ClO_3^-(aq.) + H_2O(l) \longrightarrow ClO_4^-(aq.) + 2H^+(aq.) + 2e^-$$
$$2H^+ + ClO_3^-(aq.) + 2e^- \longrightarrow ClO_2^-(aq.) + H_2O(l)$$
$$2ClO_3^-(aq.) \rightleftharpoons ClO_2^-(aq.) + ClO_4^-(aq.)$$

$$E^\circ_{cell} = 0.33 - 0.36 = -\,0.03\text{ V}$$

$$E = E^\circ - \frac{0.059}{n}\log Q$$

At equilibrium, $E = 0,\quad n = 2,\quad Q = K$

$$0 = -\,0.03 - \frac{0.059}{2}\log K$$

$$\log K = -\,1$$

$$K = \frac{1}{10} \qquad ...(1)$$

$$\begin{array}{llll} & 2ClO_3^-(aq.) \rightleftharpoons & ClO_2^-(aq.) + & ClO_4^-(aq.) \\ t_0 & 0.1 & 0 & 0 \\ t_{eq.} & 0.1 - 2x & x & x \end{array}$$

$$K = \frac{x \times x}{(0.1 - 2x)^2} = \frac{1}{10}$$

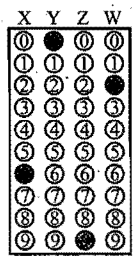
$$x = 0.019]$$

Answers

1. (c)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (c)	**8.** (a)
9. (d)	**10.** (a)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (c)	**16.** (c)
17. (c)	**18.** (c)	**19.** (d)	**20.** (b)	**21.** (b)	**22.** (b)	**23.** (b)	**24.** (a)
25. (a)	**26.** (b)	**27.** (a)	**28.** (a)	**29.** (c)	**30.** (a)	**31.** (b)	**32.** (d)
33. (d)	**34.** (a, b, c, d)	**35.** (a)	**36.** (d)	**37.** (a)	**38.** (c)	**39.** (c)	**40.** (b)
41. (c)	**42.** (e)	**43.** (a, c, d)	**44.** (b)	**45.** (c)	**46.** (b)	**47.** (c)	**48.** (b)
49. (c)	**50.** (d)						

Integer Answer TYPE QUESTIONS

This section contains 10 questions. The answer to each of the questions is a single digit integer, ranging from 0 to 9. If the correct answers to question numbers X, Y, Z and W (say) are 6, 0, 9 and 2 respectively, then the correct darkening of bubbles will look like the given figure :



1. How many grams of water will be electrolysed by 96500 coulomb charge?
2. Number of faradays required to convert 1 mole of $Cr_2O_7^{2-}$ into Cr^{3+} ions is :
3. At what pH the potential of hydrogen electrode will be 0.059 V?
4. The ratio of $\left(\frac{\Lambda_m}{\Lambda_e}\right)$ for $Ca_3(PO_4)_2$ will be equal to :
5. $I_2(s)/I^-$ (0.1 M) half-cell is connected to $H^+(aq)/(H_2$ 1 atm) Pt half-cell and its cell potential is found to be 0.7714 V. If $E^\circ_{I_2/I^-} = 0.535$ V, the pH of H^+/H_2 half-cell will be :
6. If an aqueous solution of NaCl is electrolysed using platinum electrode by a current of 5 amp, then what volume of Cl_2 gas in litres at STP will be produced?
7. Charge of 6.24×10^{18} electrons will be (in coulomb) :
8. A current of 2 ~~amp when~~ passed for 5 hour through a molten salt deposits 22.2 g of metal of atomic mass 177. The positive oxidation state of the metal in the metal salt is :
9. $$Cr(s) \mid Cr^{3+} \parallel Fe^{2+} \mid Fe(s)$$
   In above cell, the value of n in the Nernst equation:
   i.e., $E = E^\circ - \frac{0.059}{n}\log_{10} Q$ will be :
10. In the Nernst Equation,
    $$E = E^\circ - \frac{2.303RT}{nF}\log_{10} Q$$
    Q will be equal to the equilibrium constant K_C, when the cell potential E is equal to :

Answers

1. (9) 2. (6) 3. (1) 4. (6) 5. (3) 6. (7) 7. (1) 8. (3)
9. (6) 10. (0)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

In a lead storage battery, Pb (anode) and PbO_2 (cathode) are used. Concentrated H_2SO_4 is used as electrolyte. The battery holds 3.5 litre acid with it. In the discharge process, the density of acid fell from 1.294 to 1.139 g/mL. The sulphuric acid of density 1.294 g mL^{-1} is 39% by mass and that of density 1.139 g/mL is 20% by mass.

Answer the following questions:

1. Equivalent mass of sulphuric acid in lead storage battery is:
   (a) 49 (b) 98
   (c) 24.5 (d) none of these
2. Normalities of sulphuric acid before and after discharge are:
   (a) 5.15, 2.32 (b) 2.32, 5.15 (c) 5.15, 5.15 (d) 2.32, 2.32
3. The number of ampere-hours for which the battery must have been used is:
   (a) 26504 amp-hrs (b) 2650.4 amp-hrs
   (c) 265.04 amp-hrs (d) 26.504 amp-hrs
4. The amount of charge which the battery must have been used is:
   (a) 9.88 F (b) 8.98 F (c) 8.89 F (d) 7.88 F
5. Which of the following takes place in discharge process at anode?
   (a) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$
   (b) $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$
   (c) $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$
   (d) $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

• Passage 2

Electrolysis is the process in which electrical energy is converted to chemical energy. In electrolytic cell, oxidation takes place at anode and reduction at cathode. Electrode process depends on the electrode taken for electrolysis. Amount of substance liberated at an electrode is directly proportional to the amount of charge passed through it. The mass of substance liberated at electrode is calculated using the following relation:

$$m = \frac{ItE}{96500}$$

Here, E represents the equivalent mass and 96500 C is called the Faraday constant. Faraday (96500 C) is the charge of 1 mole electron, i.e., 6.023×10^{23} electrons; it is used to liberate one gram equivalent of the substance.

Answer the following questions:

1. The platinum electrodes were immersed in a solution of cupric sulphate ($CuSO_4$) and electric current is passed through the solution. After sometime, it was observed that the colour of copper sulphate disappeared with evolution of a gas at the electrode. The colourless solution contains:
   (a) platinum sulphate (b) copper nitrate
   (c) copper sulphate (d) sulphuric acid
2. The passage of current liberates H_2 at cathode and Cl_2 at anode. The solution is:
   (a) copper chloride in water (b) NaCl in water
   (c) mercuric chloride in water (d) $AuCl_3$ in water
3. On electrolysis of dilute sulphuric acid using platinum electrodes, the product obtained at the anode will be:
   (a) hydrogen (b) oxygen
   (c) hydrogen sulphide (d) sulphur oxide
4. How many faradays are required to reduce 1 mol BrO_3^- to Br^-?
   (a) 3 (b) 5 (c) 6 (d) 4
5. Calculate the volume of gas liberated at the anode at STP during the electrolysis of a $CuSO_4$ solution by a current of 1 A passed for 16 minutes and 5 seconds:
   (a) 224 mL (b) 56 mL (c) 112 mL (d) 448 mL

[**Hint:** At anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

(Oxygen gas is evolved)

Equivalent volume V_e of oxygen = 5.6 litre

$$\therefore \quad V = \frac{ItV_e}{96500} = \frac{1 \times 965 \times 5.6 \times 10^3}{96500} = 56 \text{ mL}]$$

6. The quantity of electricity required to liberate 112 cc hydrogen at S.T.P from acidified water is: **[Comed (Karnataka) 2008]**
   (a) 965 C (b) 9650 C (c) 96500 C (d) 4825 C

• Passage 3

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:

$$M(s) \mid M^+ (aq.\ 0.05 \text{ molar}) \parallel M^+ (aq;\ 1 \text{ molar}) \mid M(s)$$

For the above electrolytic cell, the magnitude of the cell potential $|E_{cell}| = 70$ mV.

Answer the following questions:

1. For the above cell
   (a) $E_{cell} < 0$; $\Delta G > 0$ (b) $E_{cell} > 0$; $\Delta G < 0$
   (c) $E_{cell} < 0$; $\Delta G^\circ > 0$ (d) $E_{cell} > 0$; $\Delta G^\circ < 0$
2. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be:
   (a) 35 mV (b) 70 mV
   (c) 140 mV (d) 700 mV **[IIT 2010]**

[**Hint:** 1 (b) Electrolyte concentration cell will be spontaneous when the concentration in cathodic half cell is greater than that of anodic half cell. Thus, the given cell is spontaneous hence

$$\Delta G < 0, \ E_{cell} > 0$$

2. (c) $E^\circ_{cell} = 0$, for every concentration cell

$$E = 0 - \frac{0.059}{n}\log\frac{[M^+]_{anode}}{[M^+]_{cathode}}$$

$$= -\frac{0.059}{1}\log[0.0025]$$

$$= +153 \text{ mV}$$

It is close to 140 mV.]

• Passage 4

The driving force ΔG diminishes to zero on the way to equilibrium, just as in any other spontaneous process. Both ΔG and the corresponding cell potential $\left(E = -\frac{\Delta G}{nF}\right)$ are zero when the redox reaction comes to equilibrium. The Nernst equation for the redox process of the cell may be given as:

$$E = E^\circ - \frac{0.059}{n}\log Q$$

The key to the relationship is the standard cell potential E°, derived from the standard free energy change as:

$$E^\circ = -\frac{\Delta G^\circ}{nF}$$

At equilibrium, the Nernst equation is given as:

$$E^\circ = \frac{0.059}{n}\log K$$

Answer the following questions:

1. On the basis of information available for the reaction:

$$\frac{4}{3}\text{Al} + \text{O}_2 \longrightarrow \frac{2}{3}\text{Al}_2\text{O}_3;\ \Delta G = -827\ \text{kJ / mol of O}_2$$

the minimum emf required to carry out an electrolysis of Al_2O_3 is:
(Given: 1 F = 96500 C)
(a) 2.14 V (b) 4.28 V (c) 6.42 V (d) 8.56 V
[Hint: $\text{Al} \longrightarrow \text{Al}^{3+} + 3e^-$

$$\frac{4}{3}\text{ mol Al} \equiv \frac{4}{3}\times 3\text{ mol } e^-$$

$$\equiv 4\text{ mol } e^-$$

i.e., $n = 4$

$$\Delta G = -nFE$$

$$-827\times 1000 = -4\times 96500\times E$$

$$E = 2.14\text{ V}$$]

2. The equilibrium constant K_c will be equal to Q, when:
(a) $E = E^\circ$ (b) $RT/nF = 1$
(c) $E = 0$ (d) $E^\circ = 1$

3. The nature of graph of E°_{cell} against $\log K_c$ is a/an:
(a) straight line (b) parabola
(c) hyperbola (d) elliptical curve

4. The equilibrium constant K_c for the reaction:
$\text{Cu}(s) + 2\text{Ag}^+(aq.) \rightleftharpoons \text{Cu}^{2+}(aq.) + 2\text{Ag}(s)$ $(E^\circ_{\text{cell}} = 0.46\text{ V})$
will be:
(a) antilog 15.6 (b) antilog 2.5
(c) antilog 1.5 (d) antilog 12.2

5. E for the electrochemical cell,
$\text{Zn}(s) \mid \text{Zn}^{2+}(1\,M)\ aq. \parallel \text{Cu}^{2+}(1\,M)\ aq. \mid \text{Cu}(s)$ is 1.10 volt at 25°C.
The equilibrium constant for the cell reaction:

$$\text{Zn}(s) + \text{Cu}^{2+}(aq.) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}(aq.)$$

will be:
(a) 10^{-37} (b) 10^{37} (c) 10^{-39} (d) 10^{39}

• Passage 5

Conductors allow the passage of electric current through them. Metallic and electrolytic are the two types of conductors. Current carriers in metallic and electrolytic conductors are free electrons and free ions respectively. Specific conductance or conductivity of the electrolyte solution is given by the following relation:

$$\kappa = c\times\frac{l}{A}$$

where, $c = 1/R$ is the conductance and l/A is the cell constant. Molar conductance (Λ_m) and equivalence conductance (Λ_e) of an electrolyte solution are calculated using the following similar relations:

$$\Lambda_m = \kappa\times\frac{1000}{M}$$

$$\Lambda_e = \kappa\times\frac{1000}{N}$$

where, M and N are the molarity and normality of the solution respectively. Molar conductance of strong electrolyte depends on concentration:

$$\Lambda_m = \Lambda^\circ_m - b\sqrt{c}$$

where, Λ°_m = molar conductance at infinite dilution
c = concentration of the solution
b = constant

The degrees of dissociation of weak electrolytes are calculated as:

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{\Lambda_e}{\Lambda^\circ_e}$$

Answer the following questions:

1. Which of the following decreases on dilution of electrolyte solution?
(a) Equivalent conductance (b) Molar conductance
(c) Specific conductance (d) Conductance

2. The correct order of equivalent conductances at infinite dilution of LiCl, NaCl and KCl is:
(a) LiCl > NaCl > KCl (b) KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl (d) LiCl > KCl > NaCl

3. For which of the following electrolytic solutions Λ_m and Λ_e are equal?
(a) $BaCl_2$ (b) KCl (c) $Al_2(SO_4)_3$ (d) $CaCl_2$

4. The conductance of a solution of an electrolyte is equal to that of its specific conductance. The cell constant of the conductivity cell is equal to:
(a) resistance (b) faraday
(c) zero (d) unity

5. Which of the following equality holds good for the strong electrolytes?
(a) $\Lambda = \Lambda^\circ$ as $c \to 1$ (b) $\Lambda = \Lambda^\circ$ as $c \to 0$
(c) $\Lambda = \Lambda^\circ$ as $c \to \infty$ (d) $\Lambda = \Lambda^\circ$ as $c \to \sqrt{b}$

• Passage 6

At infinite dilution, when the dissociation of electrolyte is complete, each ion makes a definite contribution towards the molar conductance of electrolyte, irrespective of the nature of the other ion with which it is associated.

The molar conductance of an electrolyte at infinite dilution can be expressed as the sum of the contributions from its individual ions.

$$A_xB_y \longrightarrow xA^{y+} + yB^{x-}$$

$$\Lambda_m^\circ(A_xB_y) = x\lambda^\circ_{A^{y+}} + y\lambda^\circ_{B^{x-}}$$

where, x and y are the number of cations and anions respectively.

The degree of ionisation 'α' of weak electrolyte can be calculated as:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Answer the following questions:

1. The ionic conductances of Al^{3+} and SO_4^{2-} ions at infinite dilution are x and y ohm^{-1} cm^2 mol^{-1} respectively. If Kohlrausch's law is valid, then molar conductance of aluminium sulphate at infinite dilution will be:
(a) $3x + 2y$ (b) $3y + 2x$ (c) $2x + 2y$ (d) $3x + 3y$
2. The molar conductances at infinite dilution for electrolytes BA and CA are 140 and 120 ohm^{-1} cm^2 mol^{-1}. If the molar conductance at infinite dilution of BX is 198 ohm^{-1} cm^2 mol^{-1}, then at infinite dilution, the molar conductance of CX is:
(a) 178 (b) 198 (c) 218 (d) 130
[**Hint:** $\Lambda^\circ_{CX} = \Lambda^\circ_{CA} + \Lambda^\circ_{BX} - \Lambda^\circ_{AB}$
$= 120 + 198 - 140 = 178$]
3. The molar conductance of 0.001 M acetic acid is 50 ohm^{-1} cm^2 mol^{-1}. The maximum value of molar conductance of acetic acid is 250 ohm^{-1} cm^2 mol^{-1}. What is the degree of dissociation (α) of acetic acid?
(a) 0.5 (b) 0.2 (c) 0.3 (d) 0.4
4. Which of the following solutions will have highest value of the molar conductance of CH_3COOH?
(a) 1 M CH_3COOH (b) 0.5 M CH_3COOH
(c) 0.3 M CH_3COOH (d) 0.1 M CH_3COOH
5. The unit of molar conductance of an electrolyte solution will be:
(a) ohm^{-1} cm^2 mol^{-1} (b) mho cm^2 mol^{-1}
(c) S cm^2 mol^{-1} (d) ohm^{-1} cm^{-1} mol^{-1}

• Passage 7

The potential associated with each electrode is known as electrode potential. If the concentration of each species taking part in the electrode reaction is unity (if any appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298 K, then the potential of each electrode is said to be the standard electrode potential. By convention, the standard electrode potential of hydrogen electrode is 0.0 volt. The electrode potential value for each electrode process is a measure of relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple. The metal with greater positive value of standard reduction potential forms the oxide of greater thermal stability.

Answer the following questions:

1. Given the standard reduction potentials,
$E^\circ_{K^+/K} = -2.93$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V, $E^\circ_{Hg^{2+}/Hg} = 0.79$ V
$E^\circ_{Mg^{2+}/Mg} = -2.37$ V, $E^\circ_{Cr^{3+}/Cr} = -0.74$ V.
The correct increasing order of reducing power is:
(a) K > Mg > Cr > Hg > Ag (b) Ag > Hg > Cr > Mg > K
(c) Mg > K > Cr > Hg > Ag (d) Cr > Hg > K > Mg > Ag
2. Which of the following oxides will be thermally most stable?
(a) ZnO (b) MgO (c) Cu_2O (d) Ag_2O
3. Which of the following reactions is not correct?
(a) $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$
(b) $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$
(c) $Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$
(d) $Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2$
4. Which of the following couples will have highest value of emf ?
(a) $Mg \mid Mg^{2+} \parallel Ag^+ / Ag$ (b) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$
(c) $Zn \mid Zn^{2+} \parallel Ag^+ / Ag$ (d) $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$
5. Which of the following metals will not displace hydrogen from water?
(a) Mg (b) Zn (c) Sn (d) Ag

• Passage 8

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (Atomic mass : Na = 23; Hg = 200; 1 Faraday = 96500 coulombs). **(IIT 2007)**

Answer the following questions:

1. The total number of moles of chlorine gas evolved is:
(a) 0.5 (b) 1.0 (c) 2.0 (d) 3.0
[**Hint:** Number of moles of NaCl $= \frac{MV}{1000} = \frac{4 \times 500}{1000} = 2$
$$2Cl^- \longrightarrow Cl_2 + 2e^-$$
2 mol Cl^- ions give 1 mol Cl_2]
2. If the cathode is a Hg electrode, the maximum weight (in g) of amalgam formed from this solution is:
(a) 200 (b) 225 (c) 400 (d) 446
[**Hint:** Electrolysis gives 2 mol sodium at cathode. Thus, amalgam (Na / Hg) will contain 2 mol of each sodium and Hg.
Mass of amalgam $= 2 \times 200 + 2 \times 23 = 446$]
3. The total charge (in coulombs) required for complete electrolysis is:
(a) 24125 (b) 48250 (c) 96500 (d) 193000
[**Hint:** 2 mol electrons will be required, therefore, required charge will be 2 faraday or 193000 coulombs.]

Answers

Passage 1.	1. (b)	2. (a)	3. (c)	4. (a)	5. (c)	
Passage 2.	1. (d)	2. (b)	3. (b)	4. (c)	5. (b)	6. (a)
Passage 3.	1. (b)	2. (b)	3. (a)	4. (d)	5. (a)	
Passage 4.	1. (a)	2. (c)	3. (a)	4. (a)	5. (b)	
Passage 5.	1. (c)	2. (b)	3. (b)	4. (d)	5. (b)	
Passage 6.	1. (b)	2. (a)	3. (b)	4. (d)	5. (a, b, c)	
Passage 7.	1. (a)	2. (d)	3. (d)	4. (a)	5. (d)	
Passage 8.	1. (b)	2. (d)	3. (d)			

SELF ASSESSMENT

ASSIGNMENT NO. 12

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. The specific conductance (κ) of an electrolyte of $0.1N$ concentration is related to equivalent conductance (Λ_e) by the following formula: **[CET (J&K) 2007]**

(a) $\Lambda_e = \kappa$ (b) $\Lambda_e = 10\kappa$
(c) $\Lambda_e = 100\kappa$ (d) $\Lambda_e = 10000\kappa$

2. The standard E°_{red} values of A, B and C are $+0.68$ V, -2.54 V, -0.50 V respectively. The order of their reducing power is: **(MHT-CET 2007)**

(a) $A > B > C$ (b) $A > C > B$ (c) $C > B > A$ (d) $B > C > A$

3. In the electrochemical reaction,

$$2Fe^{3+} + Zn \longrightarrow Zn^{2+} + 2Fe^{2+},$$

increasing the concentration of Fe^{2+}: **[JEE (WB) 2007]**

(a) increasing the cell emf
(b) increasing the current flow
(c) decrease the cell emf
(d) alter the pH of the solution

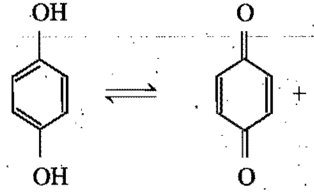
4. Fully charged lead storage battery contains 1.5 L of 5 M H_2SO_4. If 2.5 amp of current is taken from the cell for 965 minutes, then what will be the molarity of remaining H_2SO_4? Assume that volume of battery fluid to be constant:

(a) 4 M (b) 3.5 M (c) 2 M (d) 4.25 M

5. In a hydrogen-oxygen, 67.2 litre of H_2 at STP is used in 15 minutes. What is the average current produced?

(a) 549.4 amp (b) 643.33 amp
(c) 965 amp (d) 129.8 amp

6. The cell reaction involving quinhydrone electrode is:



$+ \ 2H^+ + 2e^-;\ E^\circ = 1.30$ volt

What will be the electrode potential at pH = 3 ?

(a) 1.48 V (b) 1.20 V (c) 1.10 V (d) 1.30 V

[Hint: $E = E^\circ - \dfrac{0.0591}{2}\log[H^+]^2$

$= 1.30 + 0.0591 \times 3 = 1.48$ V]

7. The standard reduction potential E° for OCl^- / Cl^- and for $Cl^- / 1/2Cl_2$ are 0.86 V and -1.10 volt respectively. The E° value of $OCl^- / 1/2Cl_2$ will be:

(a) $+1.96$ V (b) -1.96 V (c) $+0.24$ V (d) -0.24 V

[Hint:

$$OCl^- + H_2O + e^- \longrightarrow Cl^- + 2OH^- \qquad E^\circ_{\text{red}} = 0.86 \text{ V}$$

$$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^- \qquad E^\circ_{\text{oxi.}} = -1.10 \text{ V}$$

$$OCl^- + H_2O \longrightarrow \frac{1}{2}Cl_2 + 2OH^- \qquad E^\circ = 0.86 + (-1.10)$$

$= -0.24$ V]

8. The standard reduction potential for the following two reactions are given:

$AgCl + e^- \longrightarrow Ag(s) + Cl^-(aq.);\quad E^\circ = 0.22$ V ...(i)
$Ag^+(aq.) + e^- \longrightarrow Ag(s) \quad E^\circ = 0.80$ V ...(ii)

The solubility product of AgCl under standard condition will be:

(a) $1.613 \times 10^{-5}\ M^2$ (b) $1.535 \times 10^{-8}\ M^2$
(c) $3.213 \times 10^{-10}\ M^2$ (d) $1.535 \times 10^{-10}\ M^2$

[**Hint:** From eqs. (i) and (ii),

$AgCl(s) \rightleftharpoons Ag^+ + Cl^-; E^\circ = 0.22 - 0.80 = -0.58$ V

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log [Ag^+][Cl^-]$$

$$0 = -0.58 - \frac{0.0591}{2} \log [Ag^+][Cl^-]$$

$$K_{sp} = [Ag^+].[Cl^-] = 1.535 \times 10^{-10} M^2]$$

9. The equilibrium constant for the reaction,

$$Cu(s) + Cu^{2+}(aq.) \rightleftharpoons 2Cu^+(aq.)$$

$E^\circ_{Cu^{2+}/Cu} = 0.34$ V $\quad E^\circ_{Cu^{2+}/Cu} = 0.15$ V

(Given: log 3.72 = 0.571)

(a) 3.72×10^{-6} (b) 3.72×10^{-5}

(c) 3.72×10^{-7} (d) 3.72×10^{-8}

10. Cations absorb 6.023×10^{22} electrons for their reduction. How many equivalents of the ion are reduced?

(a) 0.1 (b) 0.01 (c) 0.001 (d) 0.0001

SECTION-II

Multiple Answers Type Objective Questions

11. In an electrolytic cell:

(a) anode is positively charged

(b) cathode is negatively charged

(c) oxidation takes place at anode

(d) reduction takes place at cathode

12. One gram equivalent of a substance is liberated at an electrode by:

(a) 6.023×10^{23} electrons

(b) 96500 C

(c) 1 amp current for 1 second

(d) 1 amp current for 96500 sec

13. If 9 gm H_2O is electrolysed completely with the current of 50% efficiency then:

(a) 96500 charge is required

(b) 2×96500 C charge is required

(c) 5.6 L of O_2 at STP will be formed

(d) 11.2 L of O_2 at STP will be formed

14. A galvanic cell involves the following reaction:

$Zn(s) + 2Ag^+(aq.) \rightleftharpoons Zn^{2+}(aq.) + 2Ag(s)$

Select the correct statements among the following:

(a) Zinc is negatively charged

(b) The given redox process is spontaneous

(c) $Ag^+ + e^- \longrightarrow Ag$, takes place at anode

(d) $Zn(s) \longrightarrow Zn^{2+} + 2e^-$, takes place at cathode

15. Given that,

$$E^\circ_{Ni^{2+}/Ni} = -0.25 \text{ V}, \; E^\circ_{Cu^{2+}/Cu} = +0.34 \text{ V}$$

$$E^\circ_{Ag^+/Ag} = +0.80 \text{ V} \; E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$$

Which of the following redox processes will not take place in specified direction?

(a) $Ni^{2+}(aq.) + Cu(s) \longrightarrow Ni(s) + Cu^{2+}(aq.)$

(b) $Cu(s) + 2Ag^+(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s)$

(c) $Cu(s) + 2H^+(aq.) \longrightarrow Cu^{2+}(aq.) + H_2(g)$

(d) $Zn(s) + 2H^+(aq.) \longrightarrow Zn^{2+}(aq.) + H_2(g)$

SECTION-III

Assertion-Reason Type Questions

This section contains 6 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.

(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.

(c) Statement-1 is true; statement-2 is false.

(d) Statement-1 is false; statement-2 is true.

16. Statement-1: During the electrolysis of water, two faraday of charge will produce a total of 33.6 litre of gases at STP at electrodes.

Because

Statement-2: In the electrolysis of water, two faraday of charge will produce half mole of H_2 gas and one fourth mole of O_2 gas.

17. Statement-1: Aqueous solution of $CuSO_4$ turns colourless on complete electrolysis using platinum electrode.

Because

Statement-2: $CuSO_4$ is converted to $Cu(OH)_2$ on electrolysis.

18. Statement-1: Sodium ions are discharged at a mercury cathode in preference to hydrogen ion.

Because

Statement-2: Na^+ is stronger reducing agent than H^+.

19. Statement-1: KCl and NH_4Cl cannot be used in salt bridge of a cell containing Ag^+, Hg_2^{2+} and Tl^+ ions.

Because

Statement-2: Cell will be destroyed due to precipitation of metal chlorides.

20. Statement-1: The voltage of mercury cell remains constant for its life time.

Because

Statement-2: Overall cell reaction does not involve any ion.

21. Statement-1: In alkaline version of dry cell, NH_4Cl is replaced by KOH.

Because

Statement-2: Zinc container does not undergo corrosion in alkaline medium.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correct bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	ⓠ	ⓡ	●
b	ⓟ	●	●	ⓢ
c	●	●	ⓡ	ⓢ
d	ⓟ	ⓠ	ⓡ	●

22. Match the Column-I with Column-II:

Column-I	Column-II
(a) Nickel-Cadmium cell	(p) Used in auto vehicles
(b) Lithium battery	(q) Secondary cell
(c) $H_2 - O_2$ cell	(r) Fuel cell
(d) Lead storage battery	(s) Used in Apollo space craft

23. Match the Column-I with Column-II:

Column-I	Column-II
(a) Specific conductance, κ	(p) $\Lambda_m^c / \Lambda_m^\circ$
(b) Molar conductance, Λ_m	(q) Decreases with dilution
(c) Resistance of electrolyte solution, R	(r) Increases with dilution
(d) Degree of ionization of weak electrolyte, α	(s) Increases with increase in the distance between parallel plates

24. Match the Column-I with Column-II:

Column-I	Column-II
(a) Concentration cell	(p) Fe is oxidised by Ni_2O_3
(b) Edison cell	(q) Zinc anode
(c) Mercury cell	(r) HgO cathode
(d) Dry cell	(s) $E^\circ = 0$

SECTION-V

Linked Comprehension Type Questions

Redox reactions play a pivotal role in chemistry and biology. The values of standard redox potential (E°) of two half-cells reactions decide which way the reaction is expected to proceed. A simple example is a Daniell cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.

$I_2 + 2e^- \longrightarrow 2I^-$; $E^\circ = 0.54$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$; $E^\circ = 1.36$

$Mn^{3+} + e^- \longrightarrow Mn^{2+}$; $E^\circ = 1.50$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $E^\circ = 0.77$

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$; $E^\circ = 1.23$ **(IIT 2007)**

Answer the following questions:

25. Among the following, identify the correct statement:
(a) Chloride ion is oxidised by O_2
(b) Fe^{2+} is oxidised by iodine
(c) Iodide ion is oxidised by chlorine
(d) Mn^{2+} is oxidised by chlorine
[**Hint:** Species with greater reduction potential, oxidises other with lower reduction potential.]

26. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because:
(a) O_2 oxidises Mn^{2+} to Mn^{3+}
(b) O_2 oxidises both Mn^{2+} and Fe^{2+}
(c) Fe^{3+} oxidises H_2O to O_2
(d) Mn^{3+} oxidises H_2O to O_2
[**Hint:** Mn^{3+} oxidises H_2O to O_2 because the standard reduction potential of ($Mn^{3+} \longrightarrow Mn^{2+}$) is greater than that of ($O_2 \longrightarrow H_2O$).]

Answers

1. (d) **2.** (d) **3.** (c) **4.** (a) **5.** (b) **6.** (a) **7.** (d) **8.** (b)
9. (c) **10.** (a) **11.** (a, b, c, d) **12.** (a, b, d) **13.** (b, c) **14.** (a, b) **15.** (a, c) **16.** (c)
17. (c) **18.** (b) **19.** (a) **20.** (a) **21.** (a) **22.** (a-q) (b-q) (c-r,s) (d-p,q)
23. (a-q) (b-r) (c-q,s) (d-p,r) **24.** (a-s) (b-p) (c-q,r) (d-q) **25.** (c) **26.** (d)

CHAPTER 13

ADSORPTION AND CATALYSIS

ADSORPTION

13.1 INTRODUCTION

There are several examples which reveal the fact that the surface of a solid (or liquid) has a tendency to attract and retain the molecules of other immiscible phase with which it is brought into contact. These molecules remain only at the surface and do not go deeper into the bulk. **This tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed adsorption.** The molecular species or substance which concentrates or accumulates at the surface is termed **adsorbate** and the material on whose surface the adsorption has taken place is called **adsorbent.**

Adsorption is essentially a **surface phenomenon** and solids, particularly in finely divided state, have large surface area and, therefore, show this property to a much larger extent than liquids. Charcoal, silica gel, alumina gel, clay, Fuller's earth, colloids, metals in finely divided state, etc., act as good **adsorbents.**

The adsorption of gases on metal surfaces is called occlusion.

Examples of Adsorption

(i) If a gas like Cl_2, NH_3 or SO_2 is enclosed in presence of powdered charcoal in a closed vessel, it is observed that the pressure of the gas decreases. The gas molecules concentrate at the surface of the charcoal, *i.e.*, gases are adsorbed at the surface.

(ii) In a solution of an organic dye say methylene blue, when animal charcoal is added and the solution is well shaken, it is found that the filtrate obtained after filtration is colourless. The molecules of the dye, thus, concentrate on the surface of charcoal, *i.e.*, solute molecules from solution are adsorbed.

(iii) Water solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by animal charcoal.

(iv) The air becomes dry, *i.e.*, loses moisture in presence of silica gel. Molecules of water concentrate on the surface of gel, *i.e.*, are adsorbed.

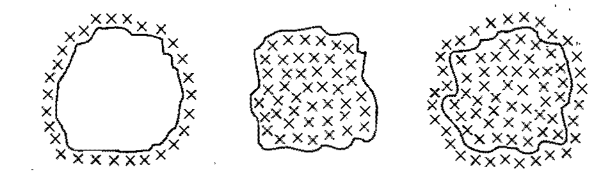
It is clear from the above examples that solid surfaces can hold the gas molecules, liquid molecules and also solid molecules by virtue of adsorption. **The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.**

13.2 DISTINCTION BETWEEN ADSORPTION AND ABSORPTION

There are two similar sounding terms adsorption and absorption. Both the terms have different meanings. In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to go deep inside the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid or liquid. For example, when a chalk stick is dipped in ink, the surface attains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick it is found that it is white from inside. Water vapours are absorbed by anhydrous calcium chloride while these are adsorbed by silica gel. **In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.**

Both adsorption and absorption take place simultaneously. **Mc Bain** introduced a general term **sorption** to describe both the

Note: Rate of adsorption is high at the beginning and then decreases till equilibrium is attained. On the other hand, rate of absorption remains same throughout the process.



Adsorption Absorption Sorption

Fig. 13.1

processes. However, adsorption is instantaneous, *i.e.*, a fast process while absorption is a slow process, *e.g.*,

(i) If silica gel is placed in a vessel containing water vapours, the latter are adsorbed on the former. On the other hand, if anhydrous $CaCl_2$ is kept in place of silica gel, absorption takes place as the water vapours are uniformly distributed in $CaCl_2$ to form hydrated calcium chloride ($CaCl_2 \cdot 2H_2O$).

(ii) Dyes get adsorbed as well as absorbed in the cotton fibres, *i.e.*, sorption takes place.

13.3 MECHANISM OF ADSORPTION

Adsorption is due to the fact that the surface particles of the adsorbent are in different state than the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface.

The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure. This shows that with increase of surface area, the unbalanced attractive forces of the surface are also increased.

Another important factor regarding adsorption is the **heat of adsorption.** During adsorption, there is always decrease in residual forces of the surface, *i.e.*, there is decrease in surface energy which appears as heat. **Adsorption, therefore, is invariably accompanied by evolution of heat,** *i.e.*, it is an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules becomes restricted. This amounts to decrease in the entropy of the gas after adsorption, *i.e.*, ΔS is negative. **Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system.** For a process to be instantaneous, the thermodynamic requirement is that ΔG must be negative, *i.e.*, there is decrease in free energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $-T\Delta S$ is positive.

Thus, in an adsorption process, which is spontaneous,

ΔS is negative,

ΔH is also sufficiently negative,

and as a combination of these two factors,

ΔG is negative.

ΔH becomes less and less negative as adsorption proceeds further and further. Ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. This is the state at which equilibrium is attained.

13.4 TYPES OF ADSORPTION
(Adsorption of Gases)

There are two main types of adsorption of gases on solids.

If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as physical adsorption or physisorption. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption** or **chemisorption.** The chemical bonds may be covalent or ionic in nature. Chemisorption has a rather high energy of activation and is, therefore, often referred to as **activated adsorption.** Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, hydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.

Some of the important characteristics of both types of adsorption are described below:

1. Characteristics of physical adsorption

(i) Lack of specificity: The surface of an adsorbent does not show very strong attraction for a particular gas as the van der Waals' forces are universal.

(ii) Nature of gas: The amount of gas adsorbed by a solid depends on the nature of gas. In general, more easily liquefiable gases (*i.e.*, higher critical temperatures) are readily adsorbed as van der Waals' forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs 380 mL of sulphur dioxide (critical temp. 157° C), 16 mL of methane (critical temp. − 83° C) and 4.5 mL of hydrogen (critical temp. −240° C).

Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Volume adsorbed (c.c.)	4.5	8	9.3	16.2	48	72	181	380
Critical temperature (K)	33	126	134	190	304	324	406	430

(iii) Reversible nature: Physical adsorption of a gas by a solid is generally reversible. The gas adsorbed can be removed by reversing the conditions of temperature and pressure. Thus,

$$\text{Gas} \rightleftharpoons \text{Gas/ Solid} + \text{Heat}$$

More of gas is adsorbed when pressure is increased as the volume of the gas decreases (Le-Chatelier's principle) and it can be removed by decreasing pressure.

Since, the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le-Chatelier's principle). As the activation energy in the physical adsorption is more or less zero, the rate of adsorption is not affected even at low temperature.

(iv) Surface area of adsorbent: The extent of adsorption increases with increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

(v) Heat of adsorption: No doubt, physical adsorption is an exothermic process but its heat of adsorption is quite low

(20 – 40 kJ mol^{-1} or about 5 kcal mol^{-1}) since the attraction between gas molecules and solid surface is due to weak van der Waals' forces.

2. Characteristics of chemisorption

(i) High specificity: Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals with unpaired *d*-orbitals leading to hydride formation.

(ii) Nature of gas: Chemisorption will occur if there is some possibility of chemical action between the gas and the solid adsorbent.

(iii) Irreversibility: As chemisorption involves compound formation, it is commonly irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperature on account of high energy of activation. Like most chemical changes, it often increases with rise of temperature. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.

High pressure is favourable for chemisorption.

(iv) Surface area: Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.

(v) Heat of adsorption: Heat of adsorption is high enough (40–400 kJ/mol) as chemisorption involves bond formation.

Comparison of physisorption and chemisorption

	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemisorption.
5.	Heat of adsorption is low.	Heat of adsorption is high.
6.	Low temperature is favourable. It decreases with increase of temperature.	High temperature is favourable. It increases with increase of temperature.
7.	No appreciable activation energy is involved.	High activation energy is involved.
8.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does not cause desorption.
9.	It depends on the surface area. It increases with increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
10.	It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

Adsorption of N_2 on the Surface of Iron

Nature of adsorption of nitrogen on the surface of iron depends on the temperature. At 83 K, nitrogen is physisorbed on iron surface as N_2 molecules. The degree of adsorption decreases rapidly as the temperature increases. At room temperature, there is no adsorption of N_2 on iron. When temperature is further increased up to 773 K and above, then nitrogen is chemisorbed on the iron surface as nitrogen atom.

Activation of Adsorption

Adsorbing power of an adsorbent can be increased by a number of ways. Some important methods are described below:

(i) Metallic adsorbents are activated by rubbing the surface.

(ii) Activity of adsorbent can be increased by taking it in powdered state because in the powdered state the surface area is maximum.

(iii) Adsorbing power of adsorbent can be increased by heating with superheated steam. For example, the charcoal is activated by heating between 650 K and 1330 K in vacuum, air or superheated steam.

13.5 ADSORPTION ISOTHERMS

The variation of the amount of the gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve. This curve is termed as **adsorption isotherm** at the particular temperature.

Freundlich adsorption isotherm: Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

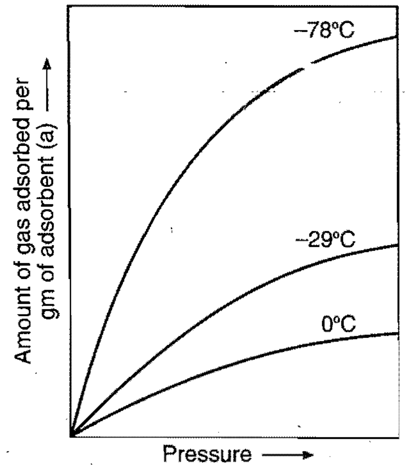


Fig. 13.2 Adsorption isotherm

$$\frac{x}{m} = k \cdot P^{1/n} \qquad \ldots (i)$$

where '*x*' is the mass of the gas adsorbed on a mass '*m*' of the adsorbent at a pressure *P*. *k* and *n* are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve when mass of the gas adsorbed per gram of the adsorbent is plotted against the pressure (Fig. 13.2). These curves indicate that at a fixed pressure, there is decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of equation (i),

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P \qquad \text{. . . (ii)}$$

This is the equation of a straight line. The validity of Freundlich isotherm can be verified by plotting $\log \frac{x}{m}$ on y-axis (ordinate) and $\log P$ on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not [Fig. 13.3(a)]. The slope of the straight line gives the value of $1/n$.

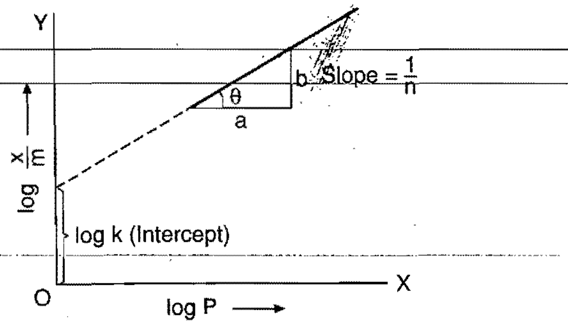


Fig. 13.3 (a) Freundlich isotherm

$$\tan \theta = \frac{b}{a} = \frac{1}{n}$$

The intercept on the y-axis gives the value of $\log k$.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $1/n$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (i) holds good over a limited range of pressure.

When $1/n = 0$, $x/m =$ constant which shows that adsorption is independent of pressure. When, $1/n = 1$, $x/m = kP$, *i.e.*, $x/m \propto P$. The adsorption varies directly with pressure. See graph in Fig. 13.3(b).

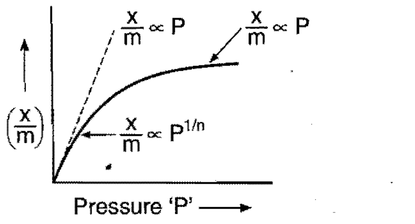


Fig. 13.3(b)

Both the above conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

Shortcomings of Freundlich adsorption isotherm:

(i) Concept of Freundlich adsorption is purely empirical.

(ii) It does not consider the role of surface area of adsorbent in the process of adsorption.

(iii) It is unable to explain, why the degree of adsorption is constant at higher pressure.

(iv) It is applicable for only physical adsorption because it considers multimolecular layer of adsorption.

The Freundlich adsorption isotherm was modified by Langmuir in 1916.

Langmuir adsorption isotherm: Langmuir (1916) derived a simple adsorption isotherm. He postulated the following theory of adsorption:

(i) Gases form unimolecular layer of adsorption on the surface of adsorbate.

(ii) Gases undergoing adsorption behave ideally.

(iii) Adjacent adsorbed molecules do not interact. In other words, adsorption of a gas molecule at a particular site is independent, whether the neighbouring sites are adsorbed or not.

(iv) Dynamic equilibrium exists on the surface of adsorbent, *i.e.*, two opposite processes take place simultaneously on the surface of adsorbent.

(a) Adsorption or condensation of gas molecules on the surface of solid or adsorbent.

(b) Desorption or evaporation of gas molecules from the surface of adsorbent.

At the stage of adsorption equilibrium, the rate of adsorption becomes equal to the rate of desorption.

Let us derive mathematical relation of adsorption isotherm. Let θ is the fraction of surface area of adsorbent covered by the gas molecules, then $(1-\theta)$ will be the fraction of surface area base which is available for adsorption. Rate of adsorption depends on the fraction of surface area base and the pressure of gas on the surface of adsorbent.

$$\text{Rate of adsorption} = k_1 (1-\theta)P \qquad \text{. . . (i)}$$

Rate of desorption is directly proportional to the fraction of surface area of adsorbent occupied.

$$\text{Rate of desorption} = k_2\theta \qquad \text{. . . (ii)}$$

At equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

$$k_1 (1-\theta)P = k_2\theta$$

$$\theta = \frac{k_1 P}{k_2 + k_1 P}$$

$$\theta = \frac{(k_1/k_2)P}{1+\left(\frac{k_1}{k_2}\right)P} = \frac{KP}{1+KP}$$

where, $K = \frac{k_1}{k_2} = \text{constant}$

According to Langmuir, the degree of adsorption is directly proportional to the θ, *i.e.*, fraction of surface area occupied.

$$\frac{x}{m} \propto \theta = \frac{k\,KP}{1+KP} = \frac{K'P}{1+KP} \qquad \text{. . . (iii)}$$

where, $K' = kK$

Equation (iii) can be rearranged as:

$$\frac{P}{(x/m)} = \frac{1}{K'} + \left(\frac{K}{K'}\right)P$$

It is of the form $y = c + mx$, *i.e.*, equation of straight line but not passing through origin. By plotting $\frac{P}{(x/m)}$ against 'P' we get a straight line.

Slope of the line $AB = \frac{K}{K'} = \tan\theta$

Intercept of the line $= \frac{1}{K'} =$ length OA

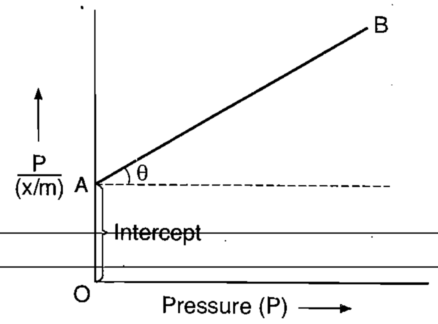


Fig. 13.3(c) Plot of Langmuir adsorption isotherm

Interpretation of Langmuir adsorption isotherm: Let us consider the mathematical relation

$$\frac{x}{m} = \frac{K'P}{1+KP}$$

Case I. When pressure is very high then $1 + KP \approx KP$

$$\therefore \quad \frac{x}{m} = \frac{K'P}{KP} = \text{constant}$$

Thus, at high pressure, the degree of adsorption approaches a limiting value.

Case II. When pressure is low then $1 + KP \approx 1$

$$\therefore \quad \frac{x}{m} = K'P$$

Thus, degree of adsorption is directly proportional to pressure.

Case III. When pressure is moderate then expression is of the form $\frac{x}{m} = KP^{1/n}$; where, $\frac{1}{n}$ lies between 0 and 1.

Alternatively,

If Langmuir adsorption isotherm is expressed as:

$$\frac{x}{m} = \frac{aP}{1+bP} \quad \text{...(i)}$$

then,

$$\frac{P}{(x/m)} = \frac{1}{a} + \frac{b}{a}P \quad \text{...(ii)}$$

Thus, a plot of $\frac{P}{(x/m)}$ against will be a straight line with slope $\frac{b}{a}$ and intercept $\frac{1}{a}$.

Equation (i) may also be taken as:

$$\frac{m}{x} = \frac{b}{a} + \frac{1}{a} \times \frac{1}{P}$$

When, $\left(\frac{m}{x}\right)$ is plotted against $\frac{1}{P}$, we get straight line with slope $\left(\frac{1}{a}\right)$ and intercept $\left(\frac{b}{a}\right)$.

13.6 ADSORPTION FROM SOLUTION PHASE

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. The litmus solution when shaken with charcoal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of magneson. The colour is due to adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

(i) The extent of adsorption decreases with the increase of temperature.

(ii) The extent of adsorption increases with the increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute in solution.

(iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

When the concentration of adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption. If the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with the difference that instead of pressure, concentration of the solution is taken into account, *i.e.*,

$$\frac{x}{m} = kC^{1/n}$$

(C is the equilibrium concentration, *i.e.*, when adsorption is complete.)

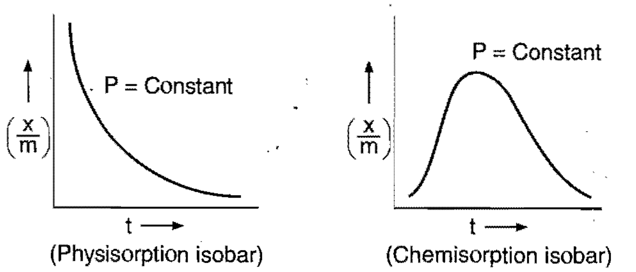
On taking logarithm of the above equation, we have

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C$$

Plotting $\log x/m$ against $\log C$ a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial concentration and final concentration gives the value of x. Using the above equation, validity of Freundlich isotherm can be established.

13.7 ADSORPTION ISOBARS AND ISOSTERE

A graph drawn between degree of adsorption (x/m) and temperature 't' at a constant pressure of adsorbate gas is known as adsorption isobar.



(Physisorption isobar) (Chemisorption isobar)

Fig. 13.4

Adsorption isobars of physical and chemical adsorptions show an important difference and this difference is helpful in distinguishing these two types of adsorption.

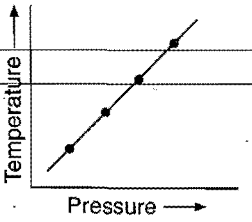


Fig. 13.5

Adsorption Isostere: Degree of adsorption depends on temperature as well as on pressure. When temperature increases, the extent of adsorption decreases. A linear relationship should exist between temperature and pressure with a certain amount of adsorption. *The plot of temperature versus pressure for a given amount of adsorption is called adsorption isostere.*

Preferential Adsorption OR Competing Adsorption

Whenever a mixture is allowed to come in contact with a particular adsorbent under the same conditions, the more strongly adsorbable adsorbate is adsorbed to a greater extent irrespective of its amount present. A preferentially adsorbable adsorbate can displace a weakly adsorbed substance from the surface of the adsorbent.

Determination of Surface Area of Adsorbent

If V litre of a gas is adsorbed at temperature T and pressure 'P' then number of gas molecules adsorbed will be:

$$\text{Number of molecules} = \left(\frac{PV}{RT}\right) \times 6.023 \times 10^{23} \quad \ldots\text{(i)}$$

If monomolecular layer of adsorption is formed then:

Surface area of adsorbent

= Number of molecules × Area of cross-section of a molecule

Area of cross section of molecule is usually determined from the density of the liquefied or solidified adsorbate.

$$\text{Volume of gas molecule} = \frac{M}{\rho \times 6.023 \times 10^{23}}$$

$$\frac{4}{3}\pi r^3 = \frac{M}{\rho N_A}$$

$$r = \left[\frac{3}{4\pi}\frac{M}{\rho N_A}\right]^{1/3}$$

$$\text{Area of cross-section} = \pi r^2 = \pi\left[\frac{3}{4\pi}\frac{M}{\rho N_A}\right]^{2/3}$$

13.8 APPLICATIONS OF ADSORPTION

The phenomenon of adsorption finds a number of applications. Important ones are given here:

1. **Production of high vacuum:** A bulb of charcoal cooled in liquid air is connected to a vessel which has already been exhausted as far as possible by a vacuum pump. The remaining traces of air are adsorbed by the charcoal. This results in a very high vacuum.

2. **Gas masks:** Gas mask is a device which consists of activated charcoal or a mixture or adsorbents. This apparatus is used to adsorb poisonous gases and thus purify the air for breathing.

3. **Humidity control:** Silica and aluminium gels are used as adsorbents for removing moisture. These gels are used for controlling humidity of rooms. Silica gel is also used in desiccators.

4. **Removal of colouring matter from solution:** Animal charcoal removes colours of solutions by adsorbing coloured impurities. Animal charcoal is used as decolouriser in the manufacture of cane sugar.

5. **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts affects the rate of reaction between the reactants. The reaction proceeds more rapidly after adsorption. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

6. **Separation of inert gases:** Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

7. **Softening of hard water:** The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate). Ca^{2+} and Mg^{2+} ions, which are responsible for hardness, get adsorbed on zeolite, exchanging sodium ions.

$$Na_2Al_2Si_2O_8 + CaCl_2 \longrightarrow CaAl_2Si_2O_8 + 2NaCl$$

The exhausted zeolite is regenerated with 10% of sodium chloride solution.

$$CaAl_2Si_2O_8 + 2NaCl \longrightarrow Na_2Al_2Si_2O_8 + CaCl_2$$

8. **Deionisation of water:** Water can be deionised by removing all dissolved salts with the help of cation and anion-exchanger resin. Cation-exchanger is an organic synthetic resin such as polystyrene containing a macroanion ($R—SO_3^-$) which has adsorbed H^+ ions. A resin containing a basic group ($—N^+R_3$) which has adsorbed OH^- ions acts as anion-exchanger. The water containing dissolved salts is first passed through cation-exchanger and then through anion-exchanger. The cation-exchanger removes the cations by exchange with H^+ ions while anion-exchanger removes the anions by exchange with OH^- ions:

$$\underset{\text{Cation-exchanger}}{R^- - - - H^+} + Na^+ \longrightarrow R^- - - - Na^+ + H^+$$

$$\underset{\text{Anion-exchanger}}{R^+ - - - OH^-} + Cl^- \longrightarrow R^+ - - - Cl^- + OH^-$$

The H^+ and OH^- ions thus produced react with each other to form water molecules.

$$H^+ + OH^- \longrightarrow H_2O$$

9. In curing diseases: A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and heat them.

10. Cleaning agents: Soaps and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently the dirt is removed from the cloth.

11. Froth floatation process: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method. The finely divided ore is added to water containing pine oil and foaming agent. The air is bubbled through the mixture. The foam formed rises to the surface on which mineral particles wetted with oil are adsorbed while earthy matter settles down at the bottom.

12. Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. In the case of precipitation titrations (for example $AgNO_3$ *versus* NaCl) the indicator is adsorbed at the end point producing a characteristic colour on the precipitate.

13. Chromatographic analysis: The phenomenon of adsorption has given an excellent technique of analysis known as chromatographic analysis. The technique finds a number of applications in analytical and industrial fields.

14. Surfactants: Surfactants work as emulsifier in the manufacture of emulsion. The emulsifiers work on the principle of adsorption.

15. Adsorption and kinetics: Many reactions that occur on a metal surface are of zero-order, *e.g.*, decomposition of N_2O on platinum surface. It is because the rate determining step occurs on the surface itself. Once the surface of adsorbent gets covered by the reactant, the rate of reaction becomes independent of concentration of the reactant.

CATALYSIS

13.9 INTRODUCTION

Potassium chlorate when strongly heated decomposes slowly giving oxygen. The decomposition occurs in the temperature range of 380–600°C.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerable lower temperature range, *i.e.*, 200–360°C at a much accelerated rate. The manganese dioxide added remains unchanged with regard to its mass and composition.

In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance. The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by **Berzelius,** in 1835. He suggested the name **catalyst,** for such substances.

Substances which thus alter the velocity of a reaction, themselves remaining chemically and quantitatively unchanged after the reaction, are known as **catalysts** and the phenomenon is known as **catalysis.** Ostwald (1895), defined a catalyst as: *a substance which changes the reaction rate without affecting the overall energetics of the reaction.*

13.10 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Catalytic reactions can be broadly divided into two groups:

1. Homogeneous catalysis: When the reactants and the catalyst are in the same phase, *i.e.*, solid, liquid or gas, the catalysis is said to be **homogeneous.** The following are some of the examples of homogeneous catalysis:

(i) Oxidation of sulphur dioxide into sulphur trioxide with oxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

The reactants sulphur dioxide and oxygen are in gaseous state. The catalyst nitric oxide is also in gaseous state, *i.e.,* all are in the same phase.

(ii) Hydrolysis of methyl acetate is catalysed by H^+ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(l) + CH_3OH(l)^*$$

Both the reactants and catalyst are in the same phase.

(iii) Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{Solution}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6(l)} + \underset{\text{Fructose}}{C_6H_{12}O_6(l)}}_{\text{Solution}}$$

Both the reactants and the catalyst are in the same phase.

2. Heterogeneous catalysis: The catalytic process in which the reactants and the catalyst are in different phases is known as **heterogeneous catalysis.** Some of the examples of heterogeneous catalysis are given below:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of platinum metal or vanadium pentoxide as catalyst in the contact process for the manufacture of sulphuric acid.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactants are in gaseous state while the catalyst is in solid state.

(ii) Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in Haber process.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

The reactants are in gaseous state while the catalyst is in solid state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze as a catalyst in Ostwald's process.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

---

*(l) represents liquid or solution in chemical reactions.

The reactants are in gaseous state while the catalyst is in the solid state.

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{Vegetable oils }(l) + H_2(g) \xrightarrow{\text{Ni}(s)} \text{Vanaspati ghee}(s)$$

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in solid state.

13.11 TYPES OF CATALYSIS

Catalytic reactions are of the following types:

1. Positive catalysis: When the rate of reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and the phenomenon as **positive catalysis.**

Examples of positive catalysis:

(i) Decomposition of H_2O_2 in presence of colloidal platinum.

$$2H_2O_2(l) \xrightarrow{\text{Pt}} 2H_2O(l) + O_2(g)$$

(ii) Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3(s) \xrightarrow[270°C]{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

(iii) Oxidation of ammonia in presence of platinum gauze.

$$4NH_3(g) + 5O_2(g) \xrightarrow[300°C]{\text{Pt}(s)} 4NO(g) + 6H_2O(g)$$

(iv) Oxidation of sulphur dioxide in presence of nitric oxide.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(v) Oxidation of sulphur dioxide in presence of platinized asbestos or vanadium pentoxide.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{or Pt}(s)]{V_2O_5(s)} 2SO_3(g)$$

(vi) Oxidation of hydrochloric acid into chlorine by Deacon's process in presence of $CuCl_2$.

$$4HCl(g) + O_2(g) \xrightarrow[450°C]{CuCl_2(s)} 2Cl_2(g) + 2H_2O(g)$$

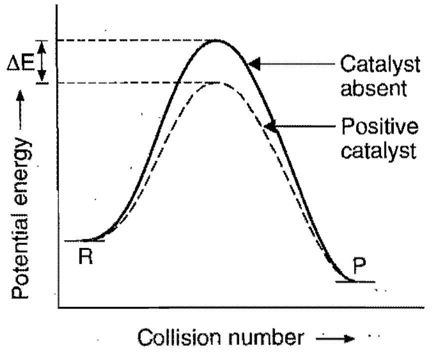


Fig. 13.6

(vii) Hydrogenation of vegetable oil in presence of nickel.

$$\text{Vegetable oil}(l) + H_2(g) \xrightarrow{\text{Ni}(s)} \text{Vanaspati ghee}(s)$$

(viii) Synthesis of ammonia by Haber process in presence of a mixture of iron and molybdenum.

$$N_2(g) + 3H_2(g) \xrightarrow[450\text{-}500°C]{\text{Fe}(s)} 2NH_3(g)$$

(ix) Manufacture of methyl alcohol in presence of ZnO/Cr_2O_3.

$$CO(g) + 2H_2(g) \xrightarrow[Cr_2O_3(s)]{ZnO(s),\ 250°C} CH_3OH(g)$$

(x) Formation of methane in presence of nickel.

$$CO(g) + 3H_2(g) \xrightarrow{\text{Ni}(s)} CH_4(g) + H_2O(g)$$

Positive catalyst increases the rate by lowering activation energy of reaction. Catalyst changes the mechanism by changing the intermediate, *i.e.*, an intermediate of low energy is formed. It increases the rate by converting some inactive molecules into active ones.

From chemical kinetics:

$$\frac{k_p}{k_a} = e^{\Delta E/RT}$$

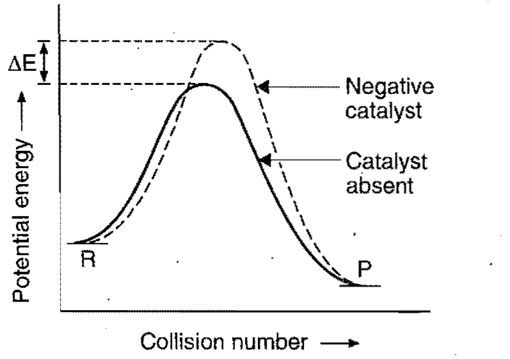
where, k_p = rate constant in presence of catalyst, k_a = rate constant in absence of catalyst.

ΔE = Lowering of activation energy

$$\log_e\left(\frac{k_p}{k_a}\right) = \frac{\Delta E}{RT}$$

$$\frac{k_p}{k_a} = \text{antilog}\left[\frac{\Delta E}{2.303\,RT}\right]$$

2. Negative catalysis: There are certain substances which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalysts** or **inhibitors** and the phenomenon is known as **negative catalysis.**



ΔE = Increased activation energy

Fig. 13.7

Examples of negative catalysis:

(i) The oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3(s) + O_2(g) \xrightarrow{\text{Alcohol}(l)} 2Na_2SO_4(s)$$

Alcohol acts as a negative catalyst.

(ii) The decomposition of hydrogen peroxide decreases in presence of glycerine. Thus, in this reaction glycerine acts as a negative catalyst.

$$2H_2O_2(l) \xrightarrow{\text{Glycerine}(l)} 2H_2O(l) + O_2(g)$$

(iii) The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{\text{Alcohol}(l)} 2COCl_2(g) + 2HCl(g)$$

(iv) The oxidation of benzaldehyde is retarded if some diphenyl amine is added. It acts as a negative catalyst.

$$2C_6H_5CHO(l) + O_2(g) \xrightarrow{\text{Diphenyl amine}(l)} 2C_6H_5COOH(l)$$

(v) Tetraethyl lead (TEL) acts as an antiknocking agent in the case of petrol. Thus, it decreases knocking of petrol and acts as a negative catalyst.

(vi) Addition of small amount of acetanilide shows slow decomposition of hydrogen peroxide.

Negative catalysts decrease the rate by increasing the activation energy of reaction. Mechanism is altered by altering the intermediate; the new intermediate lies at high energy state.

3. Autocatalysis: In certain reactions, one of the products acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existence, the reaction rate increases. This type of phenomenon, in which one of the products itself acts as a catalyst, is known as **autocatalysis.**

Examples of autocatalysis:

(i) The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of Mn^{2+} ions which are formed during reaction. Thus, Mn^{2+} ions act as autocatalyst.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

(ii) When nitric acid is poured on copper, the reaction is very slow in the beginning; gradually the reaction becomes faster due to the formation of nitrous acid during the reaction which acts as an autocatalyst.

(iii) In hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to the formation of acetic acid which acts as an autocatalyst in this reaction.

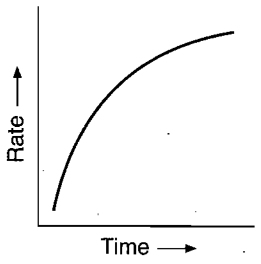


Fig. 13.8

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

In the case of homogeneous autocatalytic reactions, rate increases with passage of time because in such cases rate of reaction is directly proportional to concentration of catalyst, *e.g.*,

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\,\underset{\text{Reactant}}{[CH_3COOC_2H_5]}\,\underset{\text{Catalyst}}{[CH_3COOH]}$$

4. Induced catalysis: When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as **induced catalysis.**

Examples of induced catalysis:

(i) Sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4$$

$$Na_3AsO_3 + \frac{1}{2}O_2 \longrightarrow Na_3AsO_4$$

(ii) The reduction of mercuric chloride ($HgCl_2$) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and mercuric chloride, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

13.12 CHARACTERISTICS OF CATALYSIS

The following are the characteristics which are common to most of the catalytic reactions:

(i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction: The amount of the catalyst found at the completion of the reaction is the same as taken at the start of the reaction. There is also no change in its composition. However, it is observed that in some cases the physical state may change. For example, manganese dioxide used in the granular form as a catalyst in the decomposition of $KClO_3$ is left as a fine powder at the completion of the reaction.

(ii) A small quantity of the catalyst is generally sufficient to catalyse almost unlimited reaction: For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyse 10^8 litre of hydrogen peroxide. One mole of Cu^{2+} in 10^6 litre can catalyse the oxidation of sodium sulphite by atmospheric oxygen.

However, in some reactions the rate of the reaction is proportional to the concentration of the catalyst. For the acid and alkaline hydrolysis of an ester, the rate of reaction is proportional to the concentration of H^+ or OH^- ions.

$$RCOOR'(l) + H_2O(l) \xrightarrow[OH^-]{H^+ \text{ or}} RCOOH(l) + R'OH(l)$$

In Friedel-Crafts reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene.

$$C_6H_6(l) + C_2H_5Cl(l) \xrightarrow{AlCl_3(s)} C_6H_5C_2H_5(l) + HCl(l)$$

It is also observed that in certain heterogeneous reactions, the rate of reaction increases with the increase of area of the catalytic surface.

(iii) The catalyst cannot initiate the reaction: The function of a catalyst is to alter the speed of the reaction rather than to start it. The reaction in presence of a positive catalyst adopts some alternative path which requires less amount of activation energy.

However, there are certain instances where it is observed that the reaction cannot be started in absence of a catalyst. For example, there is no reaction between H_2 and O_2 at room temperature but the reaction occurs very readily in presence of platinum black.

$$2H_2(g)+O_2(g)\xrightarrow{\text{Room temp.}}\text{No reaction}$$

$$2H_2(g)+O_2(g)\xrightarrow{\text{Pt black}}2H_2O(g)$$

Similarly, combination of dry chlorine with dry hydrogen is not possible unless water vapours are added. Water vapours which act as a catalyst might be thought to start the reaction.

$$H_2(g)+Cl_2(g)\xrightarrow{\text{Water vapour}}2HCl(g)$$

The concept is still disputed.

(iv) The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reactions. Different catalysts for the same reactants may form different products. Manganese dioxide which acts as a catalyst for the decomposition of potassium chlorate fails to catalyse the decomposition of potassium perchlorate. Ethanol yields ethene when passed over alumina but in presence of hot copper, acetaldehyde is formed.

$$C_2H_5OH(l)\xrightarrow{Al_2O_3}C_2H_4(g)+H_2O(g)\ \text{(Dehydration)}$$

$$C_2H_5OH(l)\xrightarrow{Cu}CH_3CHO(g)+H_2(g)\ \text{(Dehydrogenation)}$$

Similarly, in the case of formic acid, different products are formed using Cu or Al_2O_3 as catalysts.

$$HCOOH(l)\xrightarrow{Cu}CO_2(g)+H_2(g)\ \text{(Dehydrogenation)}$$

$$HCOOH(l)\xrightarrow{Al_2O_3}CO(g)+H_2O(g)\ \text{(Dehydration)}$$

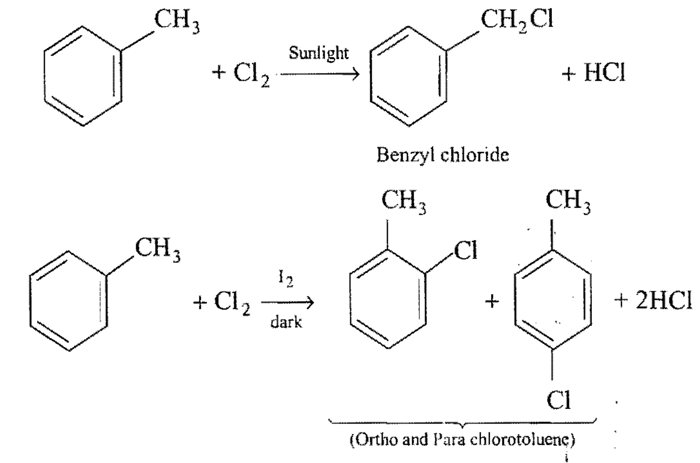
Carbon monoxide and hydrogen combine to form CH_4, CH_3OH, HCHO depending on the nature of the catalyst used.

$$CO(g)+3H_2(g)\xrightarrow{Ni}CH_4(g)+H_2O$$

$$CO(g)+2H_2\xrightarrow{ZnO+Cr_2O_3}CH_3OH$$

$$CO(g)+H_2(g)\xrightarrow{Cu}HCHO$$

Sometimes catalyst may alter the reaction product:



Enzymes have also specific action. However, transition metals like Fe, Co, Ni, Pt, Pd, etc., can catalyse reactions of various types.

(v) The catalyst cannot change the position of equilibrium: In the case of reversible reactions, the concentrations of the products and reactants cannot be affected by the catalyst if the equilibrium has been established. However, the use of a catalyst can help to achieve the equilibrium state in lesser time as forward and backward reactions are influenced to the same extent by the catalyst.

Let us consider a reversible reaction,

$$A+BC\rightleftharpoons AB+C$$

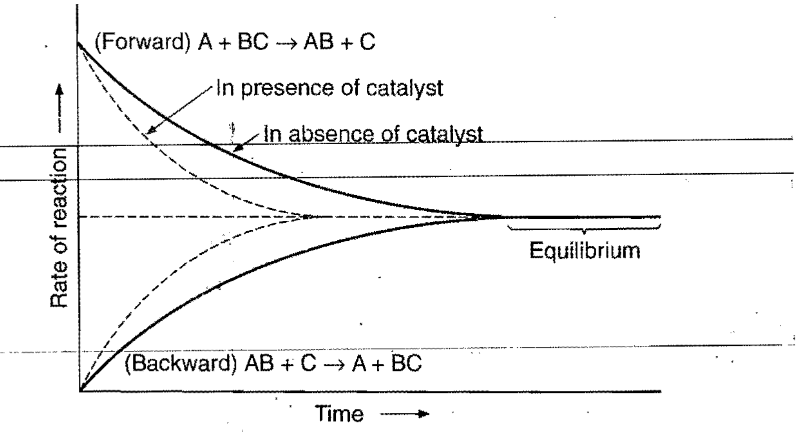


Fig. 13.9 Equilibrium state and catalyst

(vi) Catalytic promoters: Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency, are called as **promoters** or **activators.** Some examples of the promoters are given below:

(a) In the Haber process for the synthesis of ammonia, traces of molybdenum increase the activity of finely divided iron which acts as a catalyst. Oxides of aluminium and thorium are also used as promoter in this reaction.

(b) In the manufacture of methyl alcohol from water gas ($CO+H_2$), chromic oxide (Cr_2O_3) is used as a promoter with the catalyst zinc oxide (ZnO).

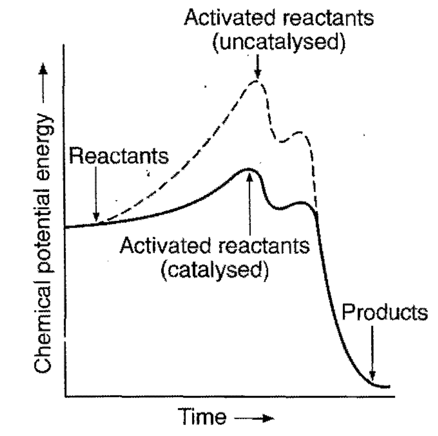


Fig. 13.10

(c) In the hydrogenation of oils, the activity of the catalyst nickel increases on adding small amount of copper and tellurium.

(vii) Catalytic poisons: Substances which destroy the activity of the catalyst by their presence are known as **catalytic poisons.** Some of the examples are:

(a) The presence of traces of arsenious oxide (As_2O_3) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

(b) The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber process.

(c) The platinum catalyst used in the oxidation of hydrogen is poisoned by CO.

The poisoning of a catalyst is probably due to the preferential adsorption of poison on the surface of the catalyst, thus reducing the space available for the adsorption of reacting molecules.

(viii) Change of temperature alters the rate of catalytic reaction as it does for the same reaction in absence of a catalyst: By increasing the temperature, there is an increase in the catalytic power of a catalyst but after a certain temperature its power begins to decrease. A catalyst has, thus, a particular temperature at which its catalytic activity is maximum. This temperature is termed as **optimum temperature.**

However, in the case of colloidal solutions acting as catalysts, the catalytic activity decreases by the rise of temperature as it may cause coagulation of the colloidal solution.

(ix) A positive catalyst lowers the activation energy: According to collision theory, a reaction occurs on account of effective collisions between the reacting molecules. For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (E_a). Under this condition, molecules after collision form an activated complex which dissociates to yield the product molecules.

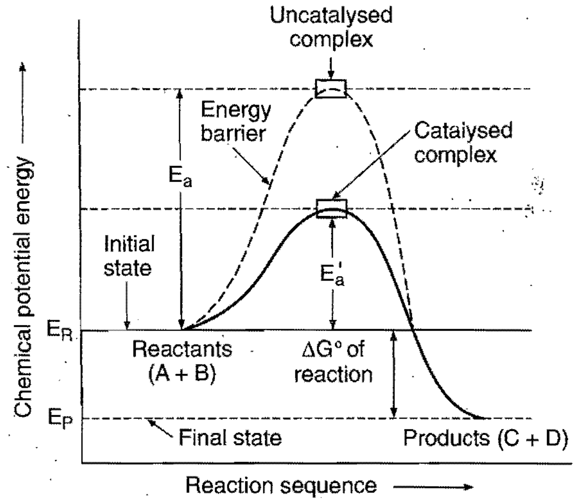


Fig. 13.11 (a)

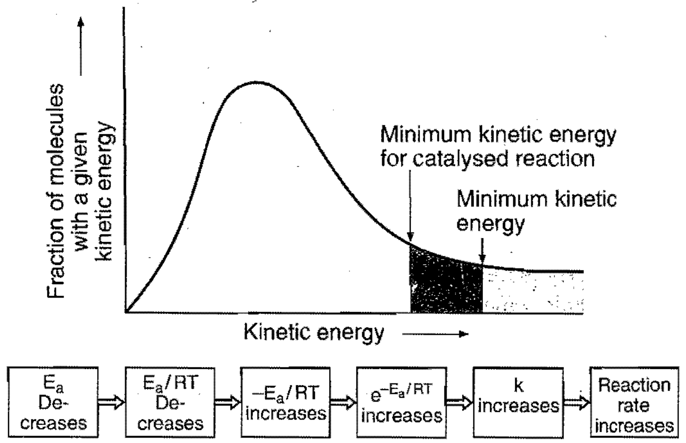


Fig. 13.11 (b) Lowering of energy barrier by the catalyst

The catalyst provides a new pathway involving lower amount of activation energy. Thus, larger number of effective collisions occur in the presence of a catalyst in comparison to effective collisions at the same temperature in absence of a catalyst. Hence, the presence of a catalyst makes the reaction to go faster.

Fig. 13.11 (a) shows that activation energy, E_a, in absence of a catalyst is higher than the activation energy, E'_a, in presence of a catalyst. E_R and E_P represent the average energies of reactants and products. The difference gives the value of ΔG, *i.e.*,

$$\Delta G = E_R - E_P$$

13.13 THEORIES OF CATALYSIS

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis as catalytic reactions are of varied nature. However, two broad theories of catalytic action have been proposed. First theory known as **intermediate compound formation theory** explains successfully the homogeneous catalysis while second theory termed as **adsorption theory** explains the heterogeneous catalysis.

1. Intermediate compound formation theory: This theory was proposed by **Clement** and **Desormes** in 1806.

According to this theory, **the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.**

For example, a reaction of the type

$$A + B \overset{K}{=} AB$$

which occurs in presence of a catalyst K, may take place as,

$$A + \underset{\text{Catalyst}}{K} = \underset{\substack{\text{Intermediate}\\\text{compound}}}{AK} \qquad \text{(Slow reaction)}$$

$$AK + B = \underset{\text{Product}}{AB} + \underset{\text{Catalyst}}{K} \qquad \text{(Fast reaction)}$$

$$\text{Rate} = K'[A][K \text{ catalyst}]$$

Many catalytic reactions can be explained on the basis of this theory:

(i) The catalytic oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process probably takes place as:

$$\underset{\text{Catalyst}}{2NO} + O_2 \longrightarrow \underset{\text{Intermediate product}}{2NO_2}$$

$$NO_2 + SO_2 \longrightarrow \underset{\text{Product}}{SO_3} + \underset{\text{Catalyst}}{NO}$$

(ii) The catalytic action of manganese dioxide on the decomposition of $KClO_3$ was proposed by McLeod. The reaction probably takes place as follows:

$$2MnO_2 + 2KClO_3 \longrightarrow 2KMnO_4 + Cl_2 + O_2$$

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

$$K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2$$

$$\overline{2KClO_3 + [2MnO_2] \longrightarrow 2KCl + 3O_2 + [2MnO_2]}$$

The reaction accounts for the fact that oxygen given out is often contaminated with a little of chlorine.

(iii) The formation of methyl benzene (toluene) from benzene and methyl chloride in presence of a catalyst anhydrous aluminium chloride can be explained in the following way:

$$\underset{\text{Catalyst}}{AlCl_3} + CH_3Cl \longrightarrow \underset{\text{Intermediate compound}}{(CH_3)^+(AlCl_4)^-}$$

$$C_6H_6 + (CH_3)^+(AlCl_4)^- \longrightarrow \underbrace{C_6H_5CH_3 + HCl}_{\text{Products}} + \underset{\text{Catalyst}}{AlCl_3}$$

(iv) The formation of diethyl ether from ethyl alcohol using sulphuric acid as a catalyst can be explained as:

$$C_2H_5OH + \underset{\text{Catalyst}}{H_2SO_4} \longrightarrow \underset{\text{Intermediate compound}}{C_2H_5HSO_4}$$

$$C_2H_5HSO_4 + HOC_2H_5 \longrightarrow \underset{\text{Product}}{C_2H_5OC_2H_5} + \underset{\text{Catalyst}}{H_2SO_4}$$

(v) The decomposition of acetaldehyde which occurs as follows,

$$CH_3CHO \xrightarrow{I_2} CH_4 + CO$$

can be explained as shown below:

$$CH_3CHO + \underset{\text{Catalyst}}{I_2} \longrightarrow \underset{\text{Intermediate}}{CH_3I} + HI + CO$$

$$CH_3I + HI \longrightarrow CH_4 + I_2$$

$$\overline{CH_3CHO \longrightarrow CH_4 + CO}$$

This theory explains why a catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. The scope of this theory is, however, limited as the formation of intermediate compound is possible in the case of homogeneous catalysis only. It also fails to explain the action of catalytic promoters, catalytic poisons and action of finely divided catalysts.

(vi) Variable oxidation state of transition metals makes them efficient catalysts. For example, Fe^{3+} catalyses the reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$$

The catalytic action can be explained as,

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

2. Adsorption theory: This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when a catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. The increased concentration of the reactants on the surface influences the rate of reaction (law of mass action). Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of the catalyst which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst.

Adsorption is broadly of two types: physical and chemical. The chemical adsorption is specific and involves chemical combination on the surface of the catalyst. The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

(i) Diffusion of reactants to the surface of the catalyst.

(ii) Some form of association between the catalyst surface and the reactants occurs. This is assumed to be adsorption.

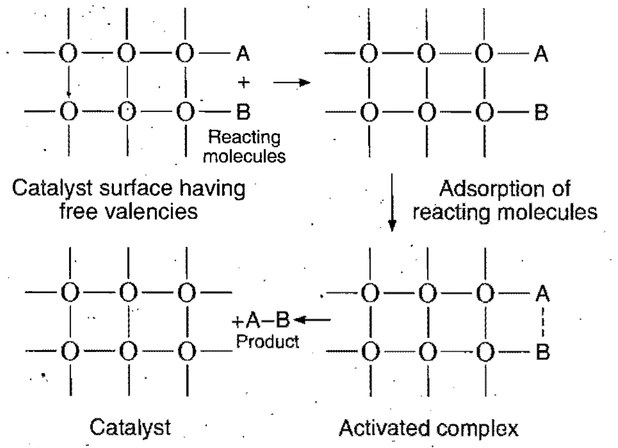


Fig. 13.12 Adsorption of reacting molecules, formation of activated complex and adsorption of products

(iii) Occurrence of chemical reaction on the catalyst surface.

(iv) Desorption of reaction products away from the catalyst surface.

(v) Diffusion of reaction products away from the catalyst surface.

The catalyst surface is a seat of chemical forces of attraction. There are free valencies on the surface of a catalyst. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react and new molecules so formed may evaporate leaving the way for the fresh reactant molecules (Fig. 13.12).

In case, free valencies are responsible for the catalytic activity, it follows that with the increase of these valencies on the surface of a catalyst, the catalytic activity will be greatly enhanced. The free valencies can be increased in the following two ways:

(a) Sub-division of the catalyst,

(b) Rough surface of the catalyst.

(a) Sub-division of the catalyst: The number of free valencies increases on disintegration. Finely powdered or colloidal catalyst particles having large surface area are very rich in free valencies.

Actually, it is observed that finely divided nickel and colloidal platinum act as efficient catalysts.

(b) Rough surface of the catalyst: There are a number of active spots in the form of edges, corners, cracks and peaks on a rough surface. They give rise to an increase in number of free valencies. These active spots enhance the adsorption and thereby increase the catalytic efficiency of the catalyst.

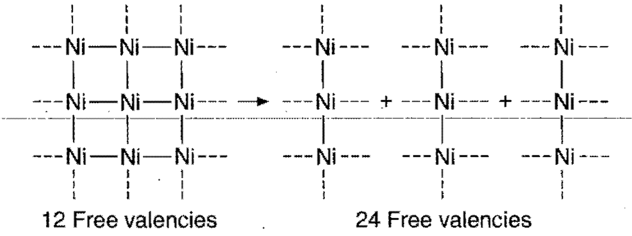


Fig. 13.13 Increase in number of free valencies

The adsorption theory explains the following facts of heterogeneous catalysis:

(i) The surface of the catalyst is used again and again due to alternate adsorption and desorption. **Thus, a small quantity of a catalyst can catalyse large amounts of reactants.**

(ii) Chemical adsorption depends on the nature of the adsorbent and adsorbate. Hence, catalysts are specific in action.

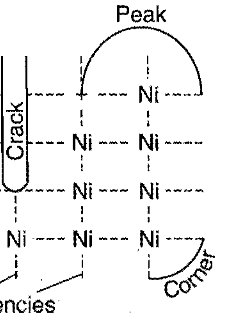


Fig. 13.14

(iii) Desorption leaves the catalytic surface unchanged. Thus, the catalyst at the end of reaction remains same in mass and composition.

(iv) The energy of adsorption compensates the activation energy of the reacting molecules to some extent. Thus, the reactions occur at faster rate.

(v) Greater efficiency of the catalyst in finely divided state and rough surface.

(vi) It adequately explains the poisoning of catalysts. The poisons are preferentially adsorbed at the active centres of the catalyst. This effect reduces the free valencies for the reacting molecules and, thus, the catalytic activity decreases.

(vii) Promoters are responsible for increasing the roughness of the surface of a catalyst. This effect increases the free valencies for the reacting molecules and, thus, the catalytic activity of the catalyst is increased.

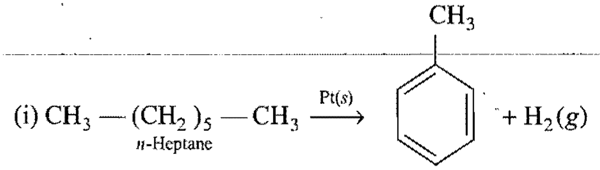
Activity and Selectivity of Heterogeneous Catalysis

Activity is the ability of a catalyst to accelerate chemical reactions. In certain cases the activity can be as high as 10^{10}, *i.e.*, the catalysed reaction is 10^{10} times faster than the uncatalysed reaction.

$$H_2(g) + O_2(g) \longrightarrow \text{No reaction}$$

$$2H_2(g) + O_2(g) \xrightarrow[\Delta]{\text{Pt}} 2H_2O(g)$$

Selectivity of a catalyst is its ability to direct the reaction in such a way as to yield particular products excluding others, *e.g.*,



n-Heptane is catalysed by Pt to toluene.

(ii) Propylene and oxygen selectively give acrolein over bismuth molybdate as catalyst.

$$CH_3-CH=CH_2+O_2 \xrightarrow[\text{BiMoO}_4]{\text{Bismuth molybdate}} \underset{\text{Acrolein}}{CH_2=CH-CHO} + H_2O$$

(iii) Acetylene on hydrogenation in presence of Pt or Ni or Pd catalyst gives ethane.

$$H-C\equiv C-H+2H_2(g) \xrightarrow{\text{Pt/Pd/Ni}} \underset{\text{Ethane}}{CH_3-CH_3}$$

Hydrogenation of acetylene in presence of Lindlar's catalyst gives ethylene.

$$H-C\equiv C-H+H_2 \xrightarrow[\text{Sulphur or quinoline}]{\text{Pd-BaSO}_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

13.14 ACID-BASE CATALYSIS

Generally, homogeneous catalysis in solution is brought about by acids and bases. On the basis of studies done by Arrhenius and Ostwald in the hydrolysis of esters and nitrites, it was established that in acid-base catalysis, it is the hydrogen ion or hydroxyl ion which acts as catalyst.

Examples of acid-base catalysis:

(i) Hydrolysis of an ester:

$$CH_3COOC_2H_5(l)+H_2O(l) \xrightarrow[\text{OH}^-]{\text{H}^+\text{ or}} CH_3COOH(l)+C_2H_5OH(l)$$

(ii) Inversion of cane sugar:

$$C_{12}H_{22}O_{11}(l)+H_2O(l) \xrightarrow{\text{H}^+} C_6H_{12}O_6(l)+C_6H_{12}O_6(l)$$

(iii) Conversion of acetone into diacetone alcohol:

$$CH_3COCH_3(l) + CH_3COCH_3(l) \xrightarrow{OH^-} CH_3COCH_2 \cdot C(CH_3)_2OH(l)$$

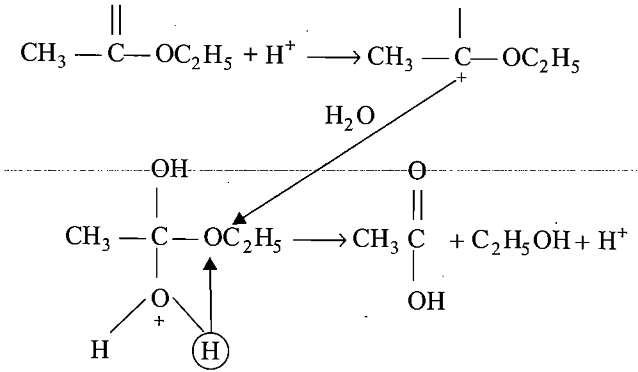
(iv) Decomposition of nitramide:

$$NH_2 \cdot NO_2(l) \xrightarrow{OH^-} N_2O(g) + H_2O(l)$$

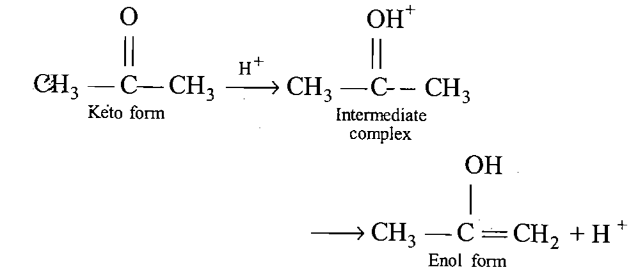
The recent work has shown that all substances which have a tendency to lose or to gain protons can show catalytic activity, *i.e.,* all Bronsted acids and bases act as acid-base catalysts.

Mechanism of Acid-Base Catalysis

(a) In acid catalysis, the proton given by Bronsted acid forms an intermediate complex with the reactant which then reacts to give back the proton (H^+). For example, the hydrolysis of ester occurs in the following manner:



The mechanism of keto-enol tautomerism of acetone is:



$$\underset{\text{Keto form}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{H^+} \underset{\substack{\text{Intermediate}\\\text{complex}}}{CH_3-\overset{\overset{\displaystyle OH^+}{\|}}{C}-CH_3} \longrightarrow \underset{\text{Enol form}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2} + H^+$$

(b) In base catalysed hydrolysis, the OH^- ion or any Bronsted base accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the OH^- or Bronsted base. In presence of OH^- ions, the decomposition of nitroamine can be shown as:

$$NH_2NO_2 + OH^- \longrightarrow \begin{array}{c} NHNO_2^- \\ \downarrow \\ N_2O + OH^- \end{array} + H_2O$$

or in presence of CH_3COO^- ions,

$$NH_2NO_2 + CH_3COO^- \longrightarrow \begin{array}{c} NHNO_2^- \\ \downarrow \\ N_2O + OH^- \end{array} + CH_3COOH$$

$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

13.15 ENZYME CATALYSIS

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. Enzymes are actually high molecular mass protein molecules. Enzymes form colloidal solutions in water and are very effective catalysts. They catalyse numerous reactions, especially those connected with natural processes. Numerous reactions occur in the bodies of animals and plants to maintain the life process. These reactions are catalysed by enzymes. The enzymes are thus termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis.**

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme catalysis:

(i) Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(l)} + \underset{\text{Fructose}}{C_6H_{12}O_6(l)}$$

(ii) Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(l)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(l)} + 2CO_2(g)$$

(iii) Conversion of starch into maltose: The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n(l)} + nH_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(l)}$$

(iv) Conversion of maltose into glucose: The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(l)}$$

(v) Decomposition of urea into ammonia and carbon dioxide: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2(l) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3(g) + CO_2(l)$$

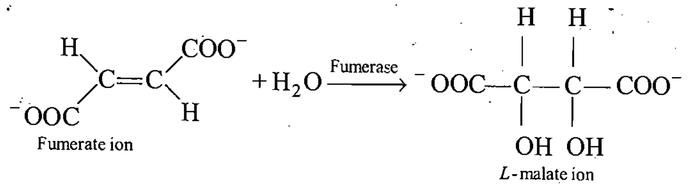
(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreas trypsin converts proteins into amino acids by hydrolysis.

(vii) Conversion of ethyl alcohol into acetic acid: The *Mycoderma aceti* enzyme converts dilute solutions of alcohol into acetic acid and water.

$$C_2H_5OH(l) + O_2(g) \xrightarrow{\textit{Mycoderma aceti}} CH_3COOH(l) + H_2O(l)$$

(viii) Conversion of milk into curd: It is an enzymatic reaction brought about by *lactic bacilli* enzyme present in curds.

(ix) The enzyme **fumerase** catalyses the hydration process of fumerate ion.



This reaction shows selectivity of enzymes because fumerase enzyme is unable to catalyse '*Cis*' isomer, *i.e.*, malate ion.

(x) In our body, the enzyme **carbonic anhydrase** catalyses the following reaction:

$$CO_2(aq.) + H_2O(l) \rightleftharpoons H^+(aq.) + HCO_3^-(aq.)$$

Forward process takes place when CO_2 goes to tissues from blood, whereas backward process takes place when CO_2 gas is released from the blood to the lungs.

Carbonic anhydrase has very high efficiency, one molecule of it catalyses 10^6 substrate molecules.

(xi) Lysozyme is found in the tear of our eyes. It protects our eyes from bacteria. It breaks down the cell wall of bacteria and then it ruptures due to endo-osmosis.

(xii) Nitrogenase enzyme is found in the bacteria of the root nodules of leguminous plants such as peas and beans. It catalyses the nitrogen fixation, *i.e.*, conversion of N_2 from atmosphere to the NH_3 in the soil.

Table 13.1 gives the summary of some important enzymatic reactions:

Table 13.1 Some enzymatic reactions

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose ⟶ Glucose and fructose
2.	Zymase	Yeast	Glucose ⟶ Ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch ⟶ Maltose
4.	Maltase	Yeast	Maltose ⟶ Glucose
5.	Urease	Soyabean	Urea ⟶ Ammonia and carbon dioxide
6.	Pepsin	Stomach	Proteins ⟶ Amino acids
7.	Trypsin	Intestine	Proteins ⟶ Amino acids
8.	Amylase	Saliva	Starch ⟶ Glucose
9.	*Lactic bacilli*	Curd	Fermentation of milk
10.	*Mycoderma aceti*	Vinegar	Ethyl alcohol ⟶ Acetic acid
11.	Lipase	Castor seed	Fat ⟶ Glycerol
12.	Ptylin	Saliva	Starch ⟶ Sugar

Characteristics of Enzyme Catalysis

Enzyme catalysis is intermediate between homogeneous and heterogeneous catalysis. In general, it is similar to inorganic heterogeneous catalysis and sometimes it is called microheterogeneous catalysis. However, it is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

(i) Most efficient catalysts: The enzyme-catalysed reactions are very fast in comparison to the reactions catalysed by inorganic substances. This is due to the fact that activation energy of a reaction in presence of an enzyme is low. One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) High specific nature: Each enzyme is specific for a given reaction, *i.e.*, one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse any other amide, not even methyl urea.

(iii) Temperature dependence: The rate of an enzyme reaction depends on the temperature. The enzyme activity rises rapidly with temperature and becomes maximum at a definite temperature, called the **optimum temperature.** Beyond the optimum temperature, the enzyme activity decreases and ultimately becomes zero. The enzyme activity is destroyed at about 70° C. The optimum temperature of enzyme reactions occurring in the human body is 37° C. At higher temperatures (fever), the enzyme activity becomes less. The favourable temperature range for enzymatic activity is 25–37 ° C.

(iv) pH dependence: The rate of an enzyme-catalysed reaction varies with pH of the system. The enzyme activity is maximum at a particular pH called optimum pH. The optimum pH of enzyme reactions occurring in human body is 7.4. The favourable pH range for enzymatic reactions is 5–7.

Activity of enzyme decreases above and below the optimum pH. Effect of pH on enzymatic rate may reflect denaturation.

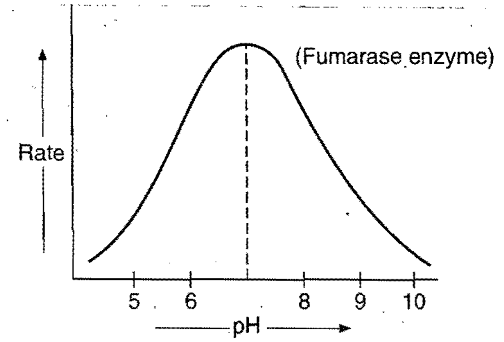


Fig. 13.15

(v) No effect on equilibrium state: Like ordinary catalysts, enzymes cannot disturb the final state of equilibrium of a reversible reaction.

(vi) Colloidal nature: Enzymes form colloidal solutions in water. Their efficiency is retarded in presence of large quantities of electrolytes. Enzymes are destroyed by ultraviolet rays.

(vii) Activators or coenzymes: The enzymatic activity is increased in the presence of certain substances, known as **coenzymes.** It has been observed that when a small non-protein

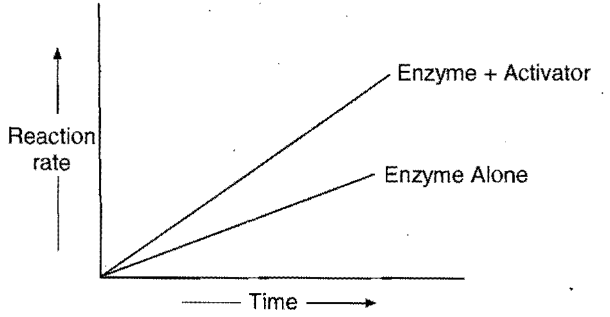


Fig. 13.16 Effect of activators on the rate of enzyme catalysis

(vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably.

Activators are generally metal ions such as $Na^+, Mn^{2+}, Co^{2+}, Cu^{2+}$, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride, *i.e.*, Na^+ ions are catalytically very active.

(viii) Inhibitors and poisons: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes.

The use of many drugs is related to their action as enzyme inhibitors in the body.

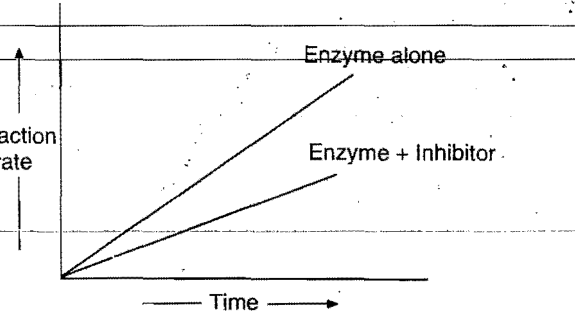


Fig. 13.17 Effect of inhibitor on the rate of enzyme catalysis

Mechanism of enzyme catalysis: There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $—NH_2$, —COOH, —SH, —OH, etc. These are actually the active centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

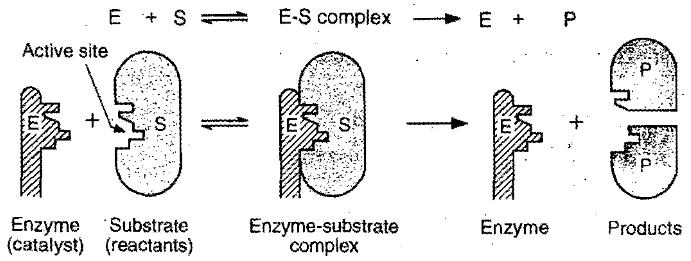


Fig. 13.18

Michaelis and Menten suggested the following mechanism for enzyme catalysis:

Step 1. Binding of enzyme to substrate to form an activated complex,

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

Step 2. Product formation in the activated complex,

$$ES \xrightarrow{k_2} EP$$

Step 3. Decomposition of *EP* into products and enzyme again, $EP \longrightarrow P + E$

This mechanism accounts for the high specificity of enzymatic reactions.

The rate of enzyme catalysed reaction is given by:

$$\text{rate} = k_2[ES] = \frac{k_2[E][S]}{K_m + [S]} \text{...(i) (Michaelis-Menten equation)}$$

K_m = Michaelis- Menten constant

$[S]$ = Concentration of substrate

$[E]$ = Concentration of enzyme

Case I. When, $[S] >>> K_m$, then K_m can be neglected.

$\therefore$ Rate $= k_2[E]$ and the reaction belongs to first order. The rate law may be given as,

$$r_{\max} = k_2[E] \qquad \text{...(ii)}$$

Dividing eq. (i) by (ii)

$$\frac{r}{r_{\max}} = \frac{[S]}{[S] + K_m}$$

when, $K_m = [S], r = \frac{1}{2} r_{\max}$

Case II. When, $[S] <<< K_m$, then reaction will be of second order.

$$\text{Rate} = \frac{k_2}{K_m}[E][S] \qquad \text{(Second order rate law)}$$

Enzyme kinetics may be graphically represented as :

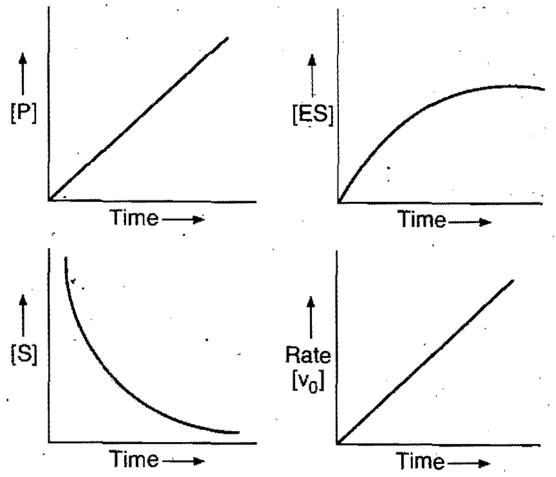


Fig. 13.19 Variation with time in enzyme catalysis

Competitive Enzyme Kinetics

Enzyme X and enzyme Y catalyse the same reaction and exhibit v_0 (rate) versus [S] curves shown ahead :

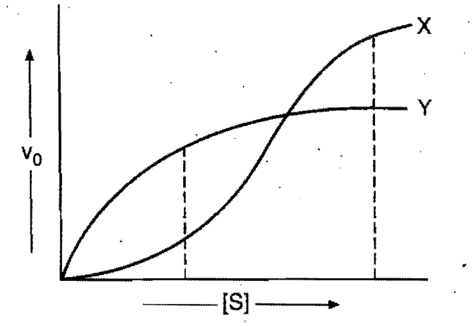


Fig. 13.20

At low substrate concentration, enzyme Y will be more efficient because activation energy will be low, in the presence of enzyme (Y). At high substrate concentration, enzyme X will be more efficient.

13.16 CATALYSTS IN INDUSTRY

Some of the important technical catalytic processes are listed in table 13.2 as to give an idea about the utility of catalysts in industries.

Table 13.2 Some Industrial Catalytic Processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Finely divided iron. Molybdenum as promoter. Conditions: 200 atmospheric pressure and 450–500°C temperature.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(l)$	Platinised asbestos Temperature 300°C.
3. Lead chamber process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$	Nitric oxide.
4. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7(l)}$ $H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$	Platinised asbestos or vanadium pentoxide (V_2O_5). Temperature 400 – 450°C.
5. Deacon process for the manufacture of chlorine. $4HCl(g) + O_2(g) \longrightarrow 2H_2O(l) + 2Cl_2(g)$	Cupric chloride ($CuCl_2$). Temperature 500°C.
6. Bosch process for the manufacture of hydrogen. $\underbrace{CO + H_2}_{\text{Water gas}} + H_2O(l) \longrightarrow CO_2(g) + 2H_2(g)$	Ferric oxide (Fe_2O_3) + chromic oxide as a promoter. Temperature 400–600°C.
7. Synthesis of methanol. $CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$	Zinc oxide (ZnO) + chromic oxide as a promoter. Pressure 200 atmospheres and temperature 250°C
8. Hydrogenation of vegetable oils. $Oil(l) + H_2(g) \longrightarrow$ Vanaspati ghee(s)	Nickel (finely divided). Temperature 150 –200°C. High pressure
9. Manufacture of ethyl alcohol by fermentation of molasses (sugar solution). $C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{\text{Invertase}} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$ $C_6H_{12}O_6(l) \xrightarrow{\text{Zymase}} 2C_2H_5OH(l) + 2CO_2(g)$	Invertase enzyme and zymase (yeast) enzyme Temperature 25–30°C. Conversion occurs in 2 or 3 days.
10. Manufacture of ethyl alcohol from starch. (a) Starch $\xrightarrow{\text{Diastase}}$ Maltose (b) Maltose $\xrightarrow{\text{Maltase}}$ Glucose $\xrightarrow{\text{Zymase}}$ Alcohol	Germinated barley (diastase enzyme) Temperature 50 – 60°C. Yeast (maltase and zymase enzymes). Temperature 25–30°C.
11. Manufacture of acetic acid from ethyl alcohol. $C_2H_5OH(l) + O_2(g) \longrightarrow CH_3COOH(l) + H_2O(l)$	*Mycoderma aceti.* Temperature 25–30°C.
12. Bergius process for the synthesis of petrol from coal. Coal + $H_2(g) \longrightarrow$ Mix. of hydrocarbons	Ferric oxide (Fe_2O_3) Temperature 475°C. Pressure 200 atmosphere.
13. Polymerisation of ethene to polythene. $\underset{\text{Ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{Polythene}}{\left[\!-CH_2-CH_2-\!\right]_n}$	$TiCl_4$ and Al R_3 (Ziegler Natta Catalyst)

13.17 ZEOLITES

Zeolites are naturally occurring or synthetic microporous aluminosilicates of general formula:

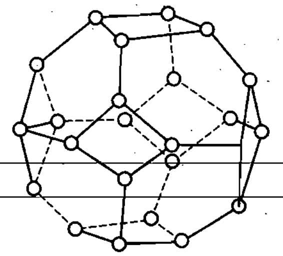
$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y]m\cdot H_2O$$

where, $M = Na^+, K^+$ or Ca^{2+} like metals

n = valency of metal cation

m = molecules of water of crystallization

Zeolite may be considered as open structure of silica in which trivalent aluminium has been substituted in a fraction $x/(x+y)$ of tetravalent sites occupied by silicon atoms. Since a substitution of an atom of silicon by aluminium generates one negative charge on the aluminosilicate frame work, substitution of x atoms generates x negative charge on the aluminosilicate framework. This charge is neutralised by the exchangeable cations M of valency n. The void spaces which can be greater than 50% of the volume are occupied by 'm' molecules of water in the unit cell. Zeolite is derived from the Greek language which means 'boiling stone' because the water trapped in void spaces boils off when the naturally occurring zeolite stone is heated. Building block of zeolite is truncated octahedron (Cubo-octahedron). This structure is called β-cage or sodalite cage.



Truncated octahedron.

Stoichiometric formulae of some well known **zeolites** are:

(i) Faujasite (natural) $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]250H_2O$

(ii) Gemelinite $Na_2Ca(AlO_2)_2(SiO_2)_4\cdot 6H_2O$

(iii) Zeolite sieve of molecular porosity-5 (ZSM-5)

$$H_x[(AlO_2)_x(SiO_2)_{96-x}].16H_2O$$

(iv) Erionite $Na_2K_2CaMg(AlO_2)_2(SiO_2)_2.6H_2O$

Shape selectivity of zeolite: Zeolite is the most widely studied shape selective catalyst. Shape selectivity of zeolite depends upon pore structure of the catalyst, pore size generally varies between 260 pm to 740 pm. Such catalysts are highly specific, it is because molecules of only a particular size and shape can enter these pores and get adsorbed. Shape selectivity of ZSM-5 in the conversion of alcohols into hydrocarbons are given in following table. The table gives the percentage of different hydrocarbons in the mixtures of hydrocarbons obtained from two different alcohols, *i.e.*, CH_3OH (methyl alcohol) and $nC_7H_{15}OH$ (*n*-heptyl alcohol).

Product	**Starting with CH_3OH (%)**	**Starting with $C_7H_{15}OH$ (%)**
Methane	1.0	0.0
Ethane	0.6	0.3
Isobutane	18.7	19.3
n-butane	5.6	11.0
Iso-pentane	7.8	8.7
Benzene	1.7	3.4
Toluene	10.5	14.3
Xylene	17.2	11.6

Persorption : It is a special type of sorption, introduced by Mc Bain. Persorption is the process in which the molecules like H_2O, CH_3OH, C_2H_5OH are adsorbed in the internal cavity of zeolite or chabazite $(CaAl_2Si_4O_{12}\cdot 6H_2O)$.

Phase transfer catalyst: Substrate dissolved in organic layer and an anionic reagent dissolved in the aqueous layer are brought together by a catalyst. The catalyst transports the anion into the organic phase where reaction takes place with the substrate.

Quaternary ammonium and phosphonium salts with their unique ability to dissolve in both aqueous and organic liquids are the most suitable phase transfer catalysts.

13.18 AUTOMOBILE CATALYTIC CONVERTER

Automobile exhaust systems are being designed with built in catalytic converters. This system contains two types of heterogeneous catalyst, powdered noble metals and powdered transition metal oxides. They catalyze the oxidation of unburned hydrocarbon fuel and of partial combustion products such as carbon monoxide.

$$\underset{\text{Iso-octane}}{2C_8H_{18}} + 25O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 16CO_2(g) + 18H_2O(g)$$

$$2CO(g) + O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 2CO_2(g)$$

The same catalysts also catalyze another reaction, the decomposition of nitrogen oxide NO, into harmless N_2 and O_2.

$$2NO(g) \xrightarrow[\text{NiO}]{\text{Pt}} N_2(g) + O_2(g)$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Adsorption: It is a tendency of accumulation of molecular species at the surface of a solid or liquid. The molecular species which accumulates is termed **adsorbate** and the material on whose surface adsorption has taken place is called **adsorbent.** The process of removing an adsorbed substance from the surface of the adsorbent is called **desorption.**

2. Distinction between adsorption and absorption: In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the adsorbent. In adsorption, the concentration of the adsorbate increases on the surface only while in absorption, the concentration is uniform throughout the bulk of adsorbent. Both adsorption and absorption take place simultaneously and the process is termed **sorption.** However, adsorption is instantaneous while absorption is a slow process.

3. Physical adsorption or physisorption: If the forces of attraction existing between adsorbate and adsorbent are van der Waals' forces, the adsorption is called **physical adsorption** or **physisorption.** In general, more easily liquefiable gases are readily adsorbed near their critical temperatures. It is generally reversible. It occurs readily at low temperature and decreases with increasing temperature. The extent of adsorption increases with increase of surface area and increase of pressure. Heat of adsorption is quite low (20– 40 kJ mol^{-1} or about 5 kcal mol^{-1}).

4. Chemisorption: If the forces of attraction between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is termed **chemisorption** or **Langmuir adsorption.** This type of adsorption is highly specific and commonly irreversible in nature. It is slow at low temperature but increases with rise of temperature on account of high energy of activation. High pressure is favourable for chemisorption. Heat of adsorption is high (40– 400 kJ mol^{-1} or 10–100 kcal mol^{-1}). It also increases with increase of surface area.

5. Adsorption isotherms: The curve showing the variation of the amount of adsorbate at a particular temperature with pressure or concentration is termed **adsorption isotherm.**

Freundlich adsorption isotherm: Freundlich, in 1909, gave an empirical relationship between the quantity of adsorbate adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship is expressed by the following equation:

$$\frac{x}{m} = k \cdot P^{1/n}$$

where, x is the mass of gas adsorbed, m is the mass of adsorbent, P is the pressure of gas and k, n are constants. Another form of equation is:

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

This is the equation of a straight line. The slope of the straight line gives the value of $\frac{1}{n}$ and the intercept on the y-axis gives the value of log k.

6. Adsorption from solution phase: Solids can adsorb solutes from solutions also. Litmus solution becomes colourless when shaken with charcoal. Similarly, when a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by charcoal. In such cases, the following observations have been made:

(i) The extent of adsorption decreases with the rise of temperature.

(ii) The extent of adsorption increases with the surface area of the adsorbent.

(iii) The extent of adsorption depends upon the concentration of the solute in solution.

$$\frac{x}{m} = kC^{1/n}$$

or $$\log \frac{x}{m} = \log k + \frac{1}{n} \log C$$

7. Applications of adsorption: Important applications of adsorption are:

(i) Production of high vacuum.

(ii) Gas masks—It is a device which consists of activated charcoal. This is used to adsorb poisonous gases.

(iii) Humidity control—Silica gel and aluminium gel are used for this purpose.

(iv) Removal of colouring matter from solutions—Animal charcoal is used for decolorising cane sugar.

(v) Heterogeneous catalysis (vi) Separation of inert gases by coconut charcoal (vii) Softening of hard water (viii) De-ionising of water (ix) Cleaning agents (x) Froth floatation process (xi) Adsorption indicators (xii) Chromatographic analysis (xiii) In medicines.

8. Catalysis: Substances which alter the velocity of a reaction by mere presence, without undergoing any change in mass and composition, are termed catalysts and the phenomenon is known as catalysis. Catalytic reactions are broadly divided into two groups: (i) Homogeneous catalysis (ii) Heterogeneous catalysis. When the reactants and catalyst are in the same phase, the catalysis is said to be **homogeneous catalysis.**

Examples: $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(l) + CH_3OH(l)$$

$$C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$$

(ii) Those catalytic reactions in which the physical state of reactants is different from the catalysts are termed heterogeneous catalysis.

Examples: $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

$$N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

$$4HCl(g) + O_2(g) \xrightarrow{Cu_2Cl_2(s)} 2H_2O(g) + 2Cl_2(g)$$

9. Types of catalysis:

(i) Positive catalysis: When the rate of reaction is accelerated by a foreign substance, it is said to be a positive catalyst and the phenomenon is positive catalysis.

(ii) Negative catalysis: The substance which when added to the reaction mixture, retards the reaction rate is termed negative catalyst and the phenomenon is known as negative catalysis.

(iii) Autocatalysis: In certain reactions, one of the products acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existence, the reaction rate increases.

(iv) Induced catalysis: When one reaction influences the rate of another reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

10. Characteristics of catalysis: The following are the characteristics which are common to most of the catalytic reactions:

(i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(ii) A small quantity of the catalyst is generally sufficient to catalyse almost an unlimited reaction.

(iii) A catalyst cannot initiate the reaction.

(iv) The catalyst is generally specific in nature.

(v) The catalyst cannot change the position of equilibrium in a reversible reaction. However, it can help to achieve the equilibrium state in lesser time.

(vi) Substances which themselves are not catalysts but when mixed in small quantities with the catalysts enhance their efficiency are called as **promoters** or **activators.**

(vii) Substances which destroy the activity of a catalyst by their presence are known as **catalytic poisons.**

(viii) A catalyst has a particular temperature at which its activity is maximum. This temperature is termed as **optimum temperature.**

(ix) A positive catalyst lowers the activation energy and provides a new pathway involving lower amount of activation energy.

11. Theories of catalysis: Two broad theories of catalytic action have been proposed:

(i) Intermediate compound formation theory: This was proposed by Clement and Desormes in 1806. According to this theory, the catalyst first forms an intermediate with one of the reactants, which being unstable combines with other reactants to form the desired product and the catalyst is regenerated.

$$A + K \text{ (catalyst)} = AK \text{ (intermediate)}$$

$$AK + B = AB + K$$

The scope of this theory is limited as the formation of intermediate is not possible in the case of many reactions.

It also fails to explain the action of promoters and poisons.

(ii) Adsorption theory: The catalytic activity is localised on the surface of a catalyst. The molecules of the reactants are adsorbed on the surface of the catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction (law of mass action). There are free valencies on the surface which are responsible for loose chemical combination of the reactants with the catalyst. If different molecules are adsorbed side by side, they may react readily and new molecules are formed which evaporate leaving the way for the fresh reactant molecules. The free valencies can be increased in two ways:

(a) Sub-division of the catalyst,

(b) Rough surface of the catalyst.

Adsorption theory is a better theory as it can explain a number of characteristics of the catalyst, especially a heterogeneous catalyst.

12. Enzyme catalysis: Enzymes are complex nitrogenous organic compounds of high molecular masses produced by living plants and animals. Enzymes are protein molecules, form colloidal solutions in water and catalyse numerous reactions especially connected with natural processes. The enzymes are also termed as **biochemical catalysts** and the phenomenon is known as biochemical catalysis.

The catalytic activity of enzymes is perhaps the greatest of all the catalysts. Their activity is also due to their capacity to lower the activation energy for a reaction. Each enzyme can catalyse a specific reaction. The enzyme reactions are sensitive to temperature and pH. Generally, the optimum temperature varies between 290–300 K and the favourable pH range is 5–7.

Questions

1. **Matrix Matching Problems (For IIT Aspirants):**

[A] Match the reactions of Column-I with the catalysts in Column-II:

Column-I (Reaction)	**Column-II (Catalyst)**
(a) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$	(p) Al_2O_3
(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	(q) Pt
(c) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$	(r) V_2O_5
(d) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	(s) MnO_2

[B] Match the reaction in List-I with the catalysts in List-II and types of catalysis in List-III:

List-I	**List-II**	**List-III**
(a) Oxidation of SO_2 to SO_3 in lead chamber process	(p) NO	(u) Positive catalyst
(b) Synthesis of methanol from CO and H_2	(q) Pt	(v) Poisoned by CO
(c) Oxidation of CO to CO_2	(r) V_2O_5	(w) Heterogeneous
(d) Oxidation of NH_3 to NO in Ostwald's process	(s) Rh	(x) Homogeneous

[C] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) ZSM-5	(p) $Na_2K_2CaMg(AlO_2)_2(SiO_2)_2 \cdot 6H_2O$
(b) Erionite	(q) Catalyst to convert alcohol to gasoline (petrol)
(c) Gemelinite	(r) $Na_2Ca(AlO_2)_2(SiO_2)_4 \cdot 6H_2O$
(d) Cavity size 550 pm	(s) $H_x[(AlO_2)_x(SiO_2)_{96-x}] \cdot 16H_2O$

[D] Match the List-I with List-II:

List-I	**List-II**
(a) Mo	(p) Promotor
(b) Cu	(q) Negative catalyst
(c) TEL	(r) Decomposition of hydrogen peroxide
(d) Glycerine	(s) Haber process

[E] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Removal of water by silica gel	(p) Absorption
(b) Removal of water by anhydrous $CaCl_2$	(q) Adsorption
(c) Surface phenomena	(r) Evaporation of liquid
(d) Bulk phenomena	(s) Boiling of liquid

[F] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $BaSO_4$	(p) Inhibitor for decomposition of H_2O_2
(b) Acetamide	(q) Catalyst
(c) Zeolite	(r) Removes hardness of water
(d) Nickel	(s) Poison for Pd in Lindlar's catalyst

[G] Match the phenomena in Column-I with example in Column-II:

Column-I	**Column-II**
(a) Persorption	(p) H_2 on Ni surface
(b) Sorption	(q) CH_3OH in chabazite
(c) Negative adsorption	(r) NH_3 in H_2O
(d) Occlusion	(s) Dil. NaCl on blood charcoal

Answers

1. [A] (a—s); (b—q, r); (c—q); (d—p).
[B] (a—p—x, u); (b—q, s—v, u); (c—p—x, u); (d—q—u, v, w).
[C] (a—q, s); (b—p); (c—r); (d—s).
[D] (a—p, s); (b—p); (c—q); (d—r).
[E] (a—q); (b—p); (c—q, r); (d—p, s).
[F] (a—s); (b—p); (c—q, r); (d—q).
[G] (a—q); (b—r); (c—s); (d—p).

• PRACTICE PROBLEMS •

1. Show that the maximum enzyme catalysed reaction rate will occur for

$$[\mathrm{H^+}]_{\text{opt}} = \sqrt{k_1 k_2}$$

The general pH control enzyme catalysed reaction is

$$E\mathrm{H}_2^{2+} \rightleftharpoons E\mathrm{H}^+ \rightleftharpoons E$$

Only $E\mathrm{H}^+$ is capable for binding substrate and catalysing the desired reaction;

$$k_1 = \frac{[E\mathrm{H}^+][\mathrm{H}^+]}{[E\mathrm{H}_2^{2+}]}; \quad k_2 = \frac{[E][\mathrm{H}^+]}{[E\mathrm{H}^+]}$$

[**Hint:** $k_1 k_2 = \dfrac{[E]\,[\mathrm{H}^+]^2}{[E\mathrm{H}_2^{2+}]}$

In pH control it may be considered that $[E] \approx [E\mathrm{H}_2^{2+}]$, *i.e.*, enzyme combines almost completely with H^+ ions.

Thus, $k_1 k_2 \approx [\mathrm{H}^+]^2; [\mathrm{H}^+] = \sqrt{k_1 k_2}$]

2. The rate of decomposition of acetaldehyde into methane and CO in the presence of I_2 at 800 K follows the rate law

$$\text{Rate} = k\,[CH_3CHO][I_2]$$

The decomposition is believed to go by a two steps mechanism:

$$CH_3CHO + I_2 \longrightarrow CH_3I + HI + CO$$

$$CH_3I + HI \longrightarrow CH_4 + I_2$$

What is the catalyst for the reaction? Which of the two steps is a slower one?

[**Ans.** I_2 is catalyst; first step is slow.]

3. A solution of palmitic acid ($M = 256$) in benzene contains 4.24 g acid per litre. When this solution is dropped on the water surface, benzene evaporates and palmitic acid forms monomolecular film of the solid type. If we wish to cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area occupied by one palmitic acid molecule may be taken to be 2.1×10^{-20} m^2.

[**Ans.** 0.0239 cm^3]

[**Hint:** V litre volume of solution taken.

$$W = (4.24 \times V)\ \text{g}$$

$$\text{Number of atoms} = \frac{W}{\text{Atomic mass}} \times \text{Avogadro's number}$$

$$= \frac{4.24V}{256} \times 6.023 \times 10^{23}$$

$$\text{Area} = 500 \times 10^{-4}\ \text{m}^2 = \left[\frac{4.24V}{256} \times 6.023 \times 10^{23}\right] \times 21 \times 10^{-20}$$

$$V = 0.0000239\ \text{litre} = 0.0239\ \text{cm}^3]$$

4. Give the mechanism of the following reactions:

(a) In lead chamber process, NO(g) is used as catalyst in the oxidation of SO_2 to SO_3.

(b) NO(g) catalyses the decomposition ozone to oxy

(c) Ozone layer depletion by Freon or Teflon.

[**Hint:** (a) $2NO(g) + O_2(g) \longrightarrow \underset{\text{Intermediate}}{2NO_2}$

$$2NO_2(g) + 2SO_2(g) \longrightarrow 2SO_3(g) + 2NO(g)$$

OR

$$SO_2(g) + H_2O + NO_2(g) \longrightarrow \underset{\text{Intermediate}}{H_2SNO_5}$$

$$H_2SNO_5 \longrightarrow H_2SO_4 + NO(g)$$

(b) $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

$$2O_3(g) \longrightarrow 3O_2(g) \quad \text{(Overall reaction)}$$

(c) Chlorine atoms furnished by freon and teflon act as a catalyst in the decomposition of ozone in the ozone layer.

$$O_3 \xrightarrow{\text{Sunlight}} O_2 + [O]$$

$$O_3 + Cl \longrightarrow O_2 + OCl$$

$$OCl + O \longrightarrow Cl + O_2\ ]$$

5. One gram of charcoal adsorbs 100 mL of 0.5 M CH_3COOH to form a mono-layer and thereby the molarity of acetic acid is reduced to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.01×10^2 m^2/gm. **(IIT 2003)**

[**Hint:** Number of moles of acetic acid initially present

$$= \frac{MV}{1000} = \frac{0.5 \times 100}{1000} = 0.05$$

Number of moles of acetic acid left

$$= \frac{MV}{1000} = \frac{0.49 \times 100}{1000} = 0.049$$

Number of moles of acetic acid adsorbed

$$= 0.05 - 0.049 = 0.001\ \text{mol}$$

Number of molecules of acid adsorbed

$$= 0.001 \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$$

Area occupied by single molecule of acetic acid

$$= \frac{\text{Total area}}{\text{Number of molecules adsorbed}}$$

$$= \frac{3.01 \times 10^2}{6.023 \times 10^{20}}$$

$$= 5 \times 10^{-19}\ \text{m}^2]$$

OBJECTIVE QUESTIONS

[illegible]: Questions with single correct answer

1. Adsorption is the phenomenon in which a substance:
   (a) accumulates on the surface of the other substance
   (b) goes into the body of the other substance
   (c) remains close to the other substance
   (d) oxidises or reduces the other substance
2. Physical adsorption is appreciable at:
   (a) higher temperature (b) lower temperature
   (c) room temperature (d) 100° C
3. The rate of chemisorption:
   (a) decreases with increase of pressure
   (b) is independent of pressure
   (c) is maximum at one atmospheric pressure
   (d) increases with increase of pressure
4. A poisonous gas is adsorbed at activated charcoal. The activated charcoal is:
   (a) absorber (b) adsorbate
   (c) adsorbent (d) absorbate
5. Chromatography is a technique based on:
   (a) solubilities of solute
   (b) adsorption of solute
   (c) chemical adsorption followed by dispersion
   (d) differential adsorption of different constituents of a mixture
6. Which of the following is not a characteristic of chemisorption?
   (a) Adsorption is irreversible
   (b) ΔH is of the order of 400 kJ
   (c) Adsorption is specific
   (d) Adsorption increases with increase of surface area
7. In the Freundlich adsorption isotherm equation :
   $\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log P$, the value of '$n$' is: **[CET (J&K) 2009]**
   (a) any value from 0 to 1
   (b) a negative integer
   (c) a positive integer
   (d) a positive or negative fractional number
8. Which of the following is not the application of adsorption?
   (a) De-ionisation of water
   (b) Gas masks
   (c) Hygroscopic nature of $CaCl_2$
   (d) Heterogeneous catalysis
9. Which one of the following is not a correct statement?
   (a) Physical adsorption is reversible in nature
   (b) Physical adsorption involves van der Waals' forces
   (c) Rate of physical adsorption increases with increase of pressure on the adsorbate
   (d) High activation energy is involved
10. Which one of the following is the correct statement?
    (a) Chemisorption is reversible in nature
    (b) Chemisorption is high at low temperature
    (c) Chemisorption depends on the nature of gas
    (d) Chemisorption does not involve activation energy
11. A catalyst is a substance which:
    (a) increases the equilibrium concentration of the product
    (b) changes the equilibrium constant of the reaction
    (c) shortens the time to reach equilibrium
    (d) supplies energy to the reaction
12. A catalyst:
    (a) increases the free energy change in the reaction
    (b) decreases the free energy change in the reaction
    (c) does not increase or decrease the free energy change in the reaction
    (d) can either decrease or increase the free energy change depending on what catalyst we use
13. Which of the following statements is more correct?
    (a) A catalyst only accelerates the rate of a chemical reaction
    (b) A catalyst can retard the rate of a chemical reaction
    (c) A catalyst can control the speed of a reaction
    (d) A catalyst alters the speed of a reaction
14. A catalyst is a substance which: **[JEE (WB) 2008]**
    (a) increases the equilibrium constant of the reaction
    (b) increases the equilibrium concentration of products
    (c) does not alter the reaction mechanism
    (d) changes the activation energy of the reaction
15. Which of the following reactions is an example for homogeneous catalysis? **[CET (J&K) 2006]**
    (a) $2H_2O_2(l) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$
    (b) $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$
    (c) $2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$
    (d) $H_2(g) + C_2H_4(g) \xrightarrow{Ni(s)} C_2H_6(g)$
16. The substance which decreases the rate of a chemical reaction is called:
    (a) inhibitor (b) poison (c) moderator (d) promoter
17. The decomposition of hydrogen peroxide can be slowed down by the addition of a small amount of acetamide. The latter acts as:
    (a) inhibitor (b) promoter (c) moderator (d) poison
18. The temperature at which the catalytic activity of the catalyst is maximum, is called:
    (a) critical temperature (b) room temperature
    (c) absolute temperature (d) optimum temperature
19. Efficiency of the catalyst depends on its:
    (a) molecular weight (b) number of free valencies
    (c) physical state (d) amount used
20. Which of the following types of metals make the most efficient catalysts?

(a) Transition metals (b) Alkali metals
(c) Alkaline earth metals (d) Radioactive metals

21. Enzymes are made up of: **[CG (PET & PMT) 2007]**
(a) edible proteins
(b) proteins with specific structure
(c) nitrogen containing carbohydrate
(d) carbohydrates

22. In lead chamber process, which one of the following oxides is used as a catalyst?
(a) NO (b) NO_2 (c) N_2O_3 (d) N_2O_5

23. Enzymes are:
(a) substances made by chemists to activate washing powders
(b) catalysts found in organisms
(c) synthetic catalysts
(d) very active vegetative catalysts

24. Alcoholic fermentation is brought about by the action of:
(a) yeast (b) CO_2 (c) O_2 (d) CO

25. Glucose or fructose is converted into C_2H_5OH in the presence of:
(a) invertase (b) diastase (c) maltase (d) zymase

26. The name catalysis was given by:
(a) Rutherford (b) Langmuir
(c) Graham (d) Berzelius

27. In the reaction, $KMnO_4 + H_2SO_4 + H_2C_2O_4 \longrightarrow$ Products, Mn^{2+} ions act as:
(a) positive catalyst (b) negative catalyst
(c) autocatalyst (d) enzyme catalyst

28. In the Haber process of synthesis of NH_3:
(a) Mo acts as a catalyst and Fe as a promoter
(b) Fe acts as a catalyst and Mo as a promoter
(c) Fe acts as inhibitor and Mo as a catalyst
(d) Fe acts as promoter and Mo as autocatalyst

29. TEL minimises the knocking effect when mixed with petrol. It acts as:
(a) positive catalyst (b) negative catalyst
(c) autocatalyst (d) induced catalyst

30. Edges and peaks are more effective in a catalyst because:
(a) they have more free valencies
(b) they have limited number of atoms
(c) they have limited number of molecules
(d) none of the above

31. Hydrolysis of starch involves the use of the enzyme:
(a) maltase (b) zymase
(c) invertase (d) diastase

32. Which of the following statements is incorrect?
(a) Enzymes exist in colloidal state
(b) Enzymes are catalysts
(c) Enzymes can catalyse any reaction
(d) Urease is an enzyme

33. Which of the following catalysts is used in Friedel-Crafts reaction for preparation of toluene from benzene?
(a) Anhydrous aluminium chloride
(b) Nickel
(c) Platinum (d) Palladium

34. Platinised asbestos is used as a catalyst in the manufacture of H_2SO_4. It is an example of:
(a) homogeneous catalyst (b) heterogeneous catalyst
(c) autocatalyst (d) induced catalyst

35. The catalyst used in the manufacture of sulphuric acid by contact process is:
(a) Al_2O_3 (b) Cr_2O_3 (c) V_2O_5 (d) MnO_2

36. The formation of diethyl ether from ethanol is catalysed by:
(a) H_2SO_4 (b) Al_2O_3 (c) Cu (d) Ni

37. Which of the following catalysts is sensitive to temperature changes?
(a) Fe (b) Pt (c) Ni (d) Enzyme

38. The catalyst used in the Deacon's process for the manufacture of chlorine is:
(a) Pt (b) $CuCl_2$ (c) V_2O_5 (d) Fe

39. A catalytic poison renders the catalyst ineffective because: **(IIT 1991)**
(a) it is preferentially adsorbed on the catalyst
(b) it adsorbs the molecules of the reactants
(c) it combines chemically with the catalyst
(d) it combines with one of the reactants

40. A finely divided state of the catalyst is more efficient because in this state:
(a) more surface area is available
(b) more energy is stored in the catalyst
(c) positive charge is acquired
(d) negative charge is acquired

41. The catalyst used in the hydrogenation of oils is:
(a) V_2O_5 (b) Fe (c) Ni (d) Pt

42. Which of the following statements is not true? **(MLNR 1993)**
(a) The action of a catalyst is specific
(b) The catalyst does not alter the equilibrium
(c) A small amount of catalyst is sufficient to catalyse large amounts of reactants
(d) The catalyst initiates the reaction

43. The catalyst used in the manufacture of hydrogen by Bosch's process is:
(a) Fe_2O_3 (b) Cr_2O_3
(c) $Fe_2O_3 + Cr_2O_3$ (d) Cu

44. The catalyst used for olefin polymerisation is: **[JEE (WB) 2009]**
(a) Ziegler-Natta catalyst (b) Wilkinson catalyst
(c) Raney nickel catalyst (d) Merifield resin

45. The modern theory of catalysis is based on:
(a) active masses (b) atomic or molecular weights
(c) size of the particles (d) number of free valencies

46. According to adsorption theory of catalysis, the reaction rate increases, because:
(a) adsorption produces heat which increases the rate of reaction
(b) in the process of adsorption, the kinetic energy of the molecules increases
(c) the concentration of reactants at the active centres becomes high due to adsorption
(d) the activation energy of the reaction becomes high due to adsorption

47. Which one of the following statements is false?
(a) Enzymes are highly specific
(b) Enzymes increase activation energy
(c) Enzymes require optimum temperature
(d) Enzymes require optimum pH

48. An example of an autocatalytic reaction is:
(a) hydrogenation of oils
(b) decomposition of nitroglycerine
(c) oxidation of Na_3AsO_3 in presence of Na_2SO_3
(d) thermal decomposition of $KClO_3$ in presence of MnO_2

49. Enzyme catalysis is an example of:
(a) autocatalysis (b) heterogeneous catalysis
(c) homogeneous catalysis (d) induced catalysis

50. The biocatalysts are:
(a) enzymes (b) minerals
(c) plants (d) all proteins

51. Which one of the following statements is incorrect in the case of heterogeneous catalyst? **(CPMT 1990)**
(a) The catalyst lowers the energy of activation
(b) The catalyst actually forms a compound with the reactant
(c) The surface of the catalyst plays a very important role
(d) There is no change in the energy of activation

52. Regarding criteria of catalysis which one of the following statements is not true? **(CPMT 1990)**
(a) The catalyst is unchanged chemically during the reaction
(b) A small quantity of catalyst is often sufficient to bring about a considerable amount of the reaction
(c) In reversible reaction, the catalyst alters the equilibrium position
(d) The catalyst accelerates the rate of reaction

53. In which of the following processes, a catalyst is not used?
(a) Haber's process (b) Deacon's process
(c) Solvay process (d) Lead chamber process

54. The effect of a catalyst in a chemical reaction is to change the:
(a) activation energy (b) equilibrium concentration
(c) heat of reaction (d) final products

55. Protons accelerate the hydrolysis of esters. This is an example of:
(a) a promoter (b) a heterogeneous catalyst
(c) an acid-base catalyst (d) an autocatalyst

56. In the Ostwald's process for the manufacture of HNO_3, the catalyst used is:
(a) Fe (b) Pt
(c) V_2O_5 (d) Mo

57. The efficiency of an enzyme in catalysing a reaction is due to its capacity:
(a) to form a strong enzyme substrate complex
(b) to decrease the bond energies in the substrate molecule
(c) to change the shape of the substrate molecule
(d) to lower the activation energy of the reaction

58. The enzymes are killed:
(a) at a very high temperature
(b) during the chemical reaction
(c) at low temperature
(d) under atmospheric pressure

59. The enzyme ptyalin used for digestion of food is present in:
(a) saliva (b) blood
(c) intestine (d) adrenal glands

60. Which of the following acts as a negative catalyst?
(a) Lead tetraethyl as antiknock compound
(b) Glycerol in decomposition of H_2O_2
(c) Ethanol in the oxidation of chloroform
(d) All of the above

61. Which of the following types of materials act as effective catalysts?
(a) Alkali metals (b) Transition metals
(c) Alkaline earth metals (d) Radioactive metals

62. In which of the following reactions is a catalyst required?
(a) $S + O_2 \longrightarrow SO_2$ (b) $C + O_2 \longrightarrow CO_2$
(c) $2SO_2 + O_2 \longrightarrow 2SO_3$ (d) All of these

63. Which is not the characteristic of a catalyst? **(AFMC 1992)**
(a) It changes the equilibrium point
(b) It initiates the reaction
(c) It alters the rate of reaction
(d) It increases the average KE of molecules

64. In chemical reaction, the catalyst: **(AFMC 1993)**
(a) alters the amount of products
(b) lowers the activation energy
(c) decreases ΔH of forward reaction
(d) increases ΔH of forward reaction

65. Which statement is not correct? **[PMT (MP) 1993]**
(a) Physical adsorption is due to van der Waals' forces
(b) Physical adsorption decreases at high temperature and low pressure
(c) Physical adsorption is reversible
(d) Adsorption energy for chemical adsorption is generally lesser than that for physical adsorption

66. In the adsorption of oxalic acid by activated charcoal, the activated charcoal is known as:
(a) adsorbent (b) adsorbate
(c) absorber (d) none of these

67. Which can adsorb larger volume of hydrogen gas?
(a) Colloidal solution of palladium
(b) Finely divided nickel
(c) Finely divided platinum
(d) Colloidal $Fe(OH)_3$

68. Platinum is used as a catalyst in:
(a) oxidation of ammonia to form nitric acid
(b) hardening of oils
(c) production of synthetic rubber
(d) synthesis of methanol

69. Hydrolysis of cane sugar is catalysed by:
(a) H^+ (b) mineral acids
(c) enzymes (d) all of these

70. $KClO_3$ on heating decomposes into KCl and O_2. If some MnO_2 is added the reaction goes much faster because:
(a) MnO_2 decomposes to give oxygen
(b) MnO_2 provides heat by reacting
(c) better contact is provided by MnO_2
(d) MnO_2 acts as catalyst

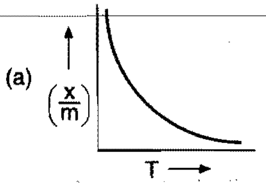
71. Which acts as poison for Pd-charcoal in Lindlar's catalyst?
(a) $BaSO_4$ (b) Quinoline
(c) Both (a) and (b) (d) None of these

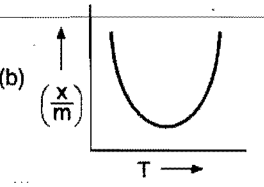
72. The inhibitors:
(a) retard the rate of a chemical reaction
(b) stop a chemical reaction immediately
(c) are reducing agents
(d) do not allow the reaction to proceed

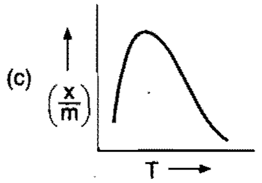
73. The catalyst used in the manufacture of nitric acid by Ostwald's process is:
(a) Mo (b) Pt (c) V_2O_5 (d) Fe

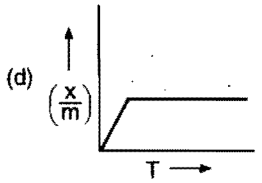
74. Which is an example of autocatalysis?
(a) Hydrolysis of methyl acetate
(b) Decomposition of TNG
(c) Oxidation of oxalic acid by $KMnO_4$
(d) All of the above

75. Which plot is the adsorption isobar for chemisorption?

(a)


(b)


(c)


(d)


76. In the titration between oxalic acid and acidified potassium permanganate, the manganous salt formed during the reaction catalyses the reaction. The manganous salt acts as:
(a) promoter (b) positive catalyst
(c) autocatalyst (d) none of these

77. Adsorption is accompanied by:
(a) decrease in entropy of the system
(b) decrease in enthalpy of the system
(c) $T\Delta S$ for the process is negative
(d) all of the above

78. Consider the following statements:
1. Zeolites are aluminosilicates.
2. Aluminium can occupy two adjacent sites in zeolites.
Which of the following statements is correct? **(SCRA 2009)**
(a) 1 only (b) 2 only
(c) both 1 and 2 (d) neither 1 nor 2

79. Zeolites are used as catalyst in:
(a) petrochemical industries during cracking
(b) the preparation of H_2SO_4
(c) the hydrolysis of ester
(d) all of the above

80. Choose the correct statement for chemical adsorption: **[CET (Gujarat) 2006]**
(a) Value of adsorption enthalpy is above -20 kJ mol^{-1}
(b) van der Waals' forces exist between adsorbent and adsorbate
(c) Usually monomolecular layer is formed on adsorbent
(d) Multimolecular layer may be formed on adsorbent

81. The function of zymase is to: **(AIIMS 1992)**
(a) change starch into sugar
(b) ferment glucose to alcohol and carbon dioxide
(c) change malt sugar into glucose
(d) change starch into malt sugar and dextrin

82. Which of the following relations is/are correct? **(AIIMS 1995)**
(i) x/m = constant (at high pressure)
(ii) x/m = constant × $P^{1/n}$ (at intermediate pressure)
(iii) x/m = constant × P^n (at low pressure)
(a) All are correct (b) All are wrong
(c) (i) and (ii) are correct (d) (iii) is correct

83. The principle(s) involved in chromatographic operation is/are: **(AIIMS 1996)**
(a) adsorption (b) absorption
(c) partition (d) none of these

84. The function of enzymes in the living system is to: **(CBSE 1997)**
(a) transport oxygen
(b) provide immunity
(c) catalyse biochemical reaction
(d) provide energy

85. Which one of the following is a shape selective catalyst?
(a) V_2O_5 (b) Cr_2O_3
(c) Hydrated zeolites (d) ZSM-5

86. The process which is catalysed by one of the products is called: **(DPMT 1999)**
(a) acid-based catalyst (b) autocatalyst
(c) negative catalyst (d) positive catalyst

87. The heats of adsorption in physisorption lie in the range (kJ/mol):
(a) 40–400 (b) 40–100 (c) 10–400 (d) 1–10

88. In physical adsorption, the forces associated are: **[CET (Haryana) 2000]**
(a) ionic (b) covalent
(c) van der Waals' (d) H-bonding

89. In Ziegler-Natta polymerisation of ethylene, the active species are:
(a) $AlCl_3$ (b) EtA
(c) CH_2CH_2 (d) Ti^{3+}
(e) $TiCl_4$

90. ZSM-5 converts:
(a) alcohol to petrol (b) benzene to toluene
(c) toluene to benzene (d) heptane to toluene

91. A catalyst increases the rate of reaction by: **(CPMT 1999)**
(a) decreasing enthalpy
(b) decreasing internal energy

(c) decreasing activation energy
(d) increasing activation energy

92. The role of a catalyst in a reversible reaction is to: **(EAMCET 1999)**
(a) increase the rate of forward reaction
(b) decrease the rate of backward reaction
(c) alter the equilibrium constant of a reaction
(d) allow the equilibrium to be achieved quickly

93. A catalyst in finely divided state is more efficient because in this state:
(a) it has got large activation energy
(b) it can react with one reactant more effectively
(c) it has large surface area
(d) all of the above

94. In case of autocatalysis: **(KCET 2002)**
(a) reactant catalyses
(b) heat produced in the reaction catalyses
(c) product catalyses
(d) solvent catalyses

95. Which of the following statements is false? **(KCET 2002)**
(a) Increase of pressure increases the amount of adsorption
(b) Increase of temperature may decrease the amount of adsorption
(c) The adsorption may be monolayered or multilayered
(d) Particle size of the adsorbent will not affect the amount of adsorption

96. Rate of physi-sorption increases with: **(IIT 2003)**
(a) decrease in temperature (b) increase in temperature
(c) decrease in pressure (d) decrease in surface area

97. Which of the following characteristics is not correct for physical adsorption? **(AIEEE 2003)**
(a) Adsorption increases with increase in temperature
(b) Adsorption is spontaneous
(c) Both enthalpy and entropy of adsorption are negative
(d) Adsorption on solid is reversible

98. According to adsorption theory of catalysis, the speed of reaction increases because: **(CBSE 2003)**
(a) the concentration of the reactant molecules at the active centres of catalyst becomes high due to adsorption
(b) in the process of adsorption, the activation energy of the molecules becomes large
(c) adsorption produces heat which increases the speed of the reaction
(d) adsorption lowers the activation energy of the reaction

99. The chemical equilibrium of a reversible reaction is not influenced by: **(KCET 2004)**
(a) catalyst (b) pressure
(c) temperature (d) concentration

100. Identify the gas which is readily adsorbed by activated charcoal: **(KCET 2004)**
(a) N_2 (b) H_2 (c) O_2 (d) SO_2

101. Pick out the one which does not belong to the family of enzymes: **(KCET 2004)**
(a) lipase (b) pepsin (c) ptylin (d) cellulose

102. Which one of the following statements about zeolite is false? **[CBSE (PMT) 2004]**
(a) They are used as cation exchanger
(b) They have open structure which enables them to take up small molecules
(c) Zeolites are aluminosilicates having a three dimensional network
(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites

103. Adsorption of gases on solid surface is generally exothermic because: **[IIT (S) 2004]**
(a) enthalpy is positive (b) entropy decreases
(c) entropy increases (d) free energy increases

104. Identify the correct statement regarding enzymes. **(AIEEE 2004)**
(a) Enzymes are specific biological catalysts that can normally function at very high temperature ($T \approx 1000$ K)
(b) Enzymes are normally heterogeneous catalysts that are very specific in action
(c) Enzymes are specific biological catalysts that cannot be poisoned
(d) Enzymes are specific biological catalysts that possess well defined active site

105. The extent of adsorption of a gas on a solid depends on: **(KCET 2005)**
(a) nature of the gas (b) pressure of the gas
(c) temperature of the gas (d) all are correct

106. The conversion of maltose to glucose is possible by the enzyme: **(AFMC 2005)**
(a) zymase (b) lactase
(c) maltase (d) diastase

107. Which of the following is true in respect of adsorption? **[PET (Kerala) 2006]**
(a) $\Delta G < 0; \Delta S > 0; \Delta H < 0$ (b) $\Delta G < 0; \Delta S < 0; \Delta H < 0$
(c) $\Delta G > 0; \Delta S > 0; \Delta H < 0$ (d) $\Delta G < 0; \Delta S < 0; \Delta H > 0$
(e) $\Delta G > 0; \Delta S > 0; \Delta H > 0$

108. If x/m is the mass of adsorbate adsorbed per unit mass of adsorbent, P is the pressure of the adsorbate gas, a and b are constants, which of the following represents **"Langmuir adsorption isotherm"?** **[PET (Kerala) 2006]**
(a) $\log\left(\frac{x}{m}\right) = \log\left(\frac{a}{b}\right) + \frac{1}{a}\log P$
(b) $\frac{x}{m} = \frac{b}{a} + \frac{1}{aP}$ (c) $\frac{x}{m} = \frac{1+bP}{aP}$
(d) $\frac{1}{(x/m)} = \frac{a}{b} + \frac{P}{a}$ (e) $\frac{1}{(x/m)} = \frac{b}{a} + \frac{1}{aP}$

109. The efficiency of an enzyme to catalyse a reaction is due to its capacity to: **[PMT (Kerala) 2006]**
(a) reduce the activation energy of the reaction
(b) form strong enzyme-substrate complex
(c) decrease the bond energy of all substrate molecules
(d) increase the free energy of the catalyst-substrate reaction
(e) alter the substrate geometry to fit into the shape of the enzyme molecule

110. Although, nitrogen does not adsorb on a surface at room temperature, it adsorbs on the surface at 83 K. Which one of the following statements is correct? **[PMT (HP) 2006]**

(a) At 83 K, there is formation of monomolecular layer
(b) At 83 K, there is formation of multimolecular layers
(c) At 83 K, nitrogen molecules are held by chemical bonds
(d) At 83 K, nitrogen is adsorbed as atoms

111. What is the equation form of Langmuir adsorption isotherm under high pressure? **[CET (Gujarat) 2006]**

(a) $\frac{x}{m}=\frac{a}{b}$ (b) $\frac{x}{m}=aP$ (c) $\frac{x}{m}=\frac{1}{aP}$ (d) $\frac{x}{m}=\frac{b}{a}$

[**Hint:** Langmuir adsorption isotherm may be given as:

$$\frac{x}{m}=\frac{aP}{a+bP}$$

~~At high pressure, $a+bP \approx bP$~~

$$\therefore \quad \frac{x}{m}=\frac{aP}{bP}$$

$$\frac{x}{m}=\frac{a}{b}\ ]$$

112. Freundlich adsorption isotherm is: **[MHT-CET 2007; DCE 2009]**

(a) $\frac{x}{m}=KP^{1/n}$ (b) $x=mKP^{1/n}$
(c) $\frac{x}{m}=KP^{-n}$ (d) all of these

113. Which of the following statements is incorrect regarding physisorption? **(AIEEE 2009)**

(a) It occurs because of van der Waals' forces
(b) More easily liquefiable gases are adsorbed readily
(c) Under high pressure it results into multimolecular layer on adsorbent surface
(d) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive

114. Active charcoal is a good catalyst because: **[Jamia Millia Islamia (Engg.) 2006]**

(a) it is made of carbon atoms
(b) it is very reactive
(c) it has more adsorption power
(d) it has inert nature towards reagent

115. According to the adsorption theory of catalysis, the speed of reaction increases because: **(AIIMS 2007)**

(a) adsorption produces heat which increases the speed of the reaction
(b) adsorption lowers the activation energy of the reaction
(c) the concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
(d) in the process of adsorption, the activation energy of the molecules becomes large

116. The Langmuir adsorption isotherm is deduced using the assumption: **[CBSE (Med.) 2007]**

(a) the adsorption sites are equivalent in their ability to adsorb the particles
~~(b) the heat of adsorption varies with coverage~~
~~(c) the adsorbed molecules interact with each other~~
(d) the adsorption takes place in multilayers

117. The efficiency of enzyme catalysis is due to its capacity to: **[PET (Kerala) 2007]**

(a) form a strong enzyme-substrate complex
(b) change the shape of the substrate
~~(c) lower the activation energy of the reaction~~
(d) form a colloidal solution in water
(e) decrease the bond energies in substrate molecules

118. Which type of phenomenon is used when coloured dye is removed from solution of sugar by charcoal ? **[CET (Gujarat) 2008]**

(a) Absorption
(b) Adsorption
(c) Absorption and adsorption both
(d) None of the above

119. Shape selective catalysis is a reaction catalysed by : **[PMT (Kerala) 2008]**

(a) zeolites (b) enzymes
(c) platinum (d) Ziegler-Natta catalyst
(e) acids or bases

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as '**Assertion**' **(A)** and '**Reason**' **(R).** While answering these questions you are required to choose any one of the following four responses:

(a) If both (A) and (R) are true and (R) is the correct explanation of (A).
(b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) and (R) are both incorrect.

1. (A) A catalyst does not alter the equilibrium constant of the reaction.
(R) The catalyst forms a complex with the reactants and provides an alternate path with the lower energy of activation for the reaction; the forward and backward reactions are affected to the same extent. **(AIIMS 2010)**

2. (A) Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas in presence of alkali, it is a reaction of second order.
(R) Acid only acts as a catalyst whereas alkali acts as one of the reactants.

3. (A) In chemisorption, adsorption keeps on increasing with temperature.
(R) Heat keeps on providing more and more activation energy.

4. (A) A reaction cannot become fast by itself unless a catalyst is added.
(R) A catalyst always increases the speed of a reaction.

5. (A) A catalyst speeds up a reaction but doesn't participate in its mechanism.
(R) A catalyst provides an alternative path of lower activation energy to the reactants.

6. (A) Fruit formation process shows increase in rate with passage of time.
   (R) Hydrolysis of ester is a homogeneous autocatalytic reaction.
7. (A) A catalyst speeds up the process without participating in its mechanism.
   (R) A catalyst provides an alternative path of lower activation energy to the reactants.
8. (A) Catalysts are always transition metals.
   (R) Transition metals have a variable oxidation state.
9. (A) The mass of nickel catalyst recovered after being used in the hydrogenation of an oil is less than the mass of nickel added to the reaction.
   (R) Catalyst take part in the reaction but are recovered in the end.
10. (A) All enzymes are proteins, but all proteins are not enzymes.
   (R) Enzymes are biocatalysts and posses a stable configuration having active sites.
11. (A) The reaction of oxalic acid with acidified $KMnO_4$ is first slow and then proceeds with faster speed.
   (R) Acidified $KMnO_4$ is a strong oxidising agent.
12. (A) For adsorption ΔG, ΔS and ΔH all have negative values.
   (R) Adsorption is a spontaneous process accompanied by decrease in randomness.
13. (A) A gas with higher critical temperature is adsorbed more than a gas with lower critical temperature.
   (R) Higher critical temperature implies that the gas is more easily liquefiable.
14. (A) Physical adsorption of molecules on the surface requires activation energy.
   (R) Because the bonds of adsorbed molecules are broken. **(AIIMS 1994)**
15. (A) Activity of an enzyme is pH dependent.
   (R) Changes in pH affect the solubility of the enzyme in water. **(AIIMS 2003)**
16. (A) Alcohols are dehydrated to hydrocarbons in presence of acidic zeolite.
   (R) Zeolites are porous catalyst. **(AIIMS 2004)**
17. (A) ZSM-5 is used as a catalyst in petrochemical industries.
   (R) Zeolites are three-dimensional network silicates in which some silicon atoms are replaced by aluminium atoms.
18. (A) A catalyst increases the rate of a reaction.
   (R) In presence of a catalyst, the activation energy of the reaction increases. **[EAMCET (Engg.) 2007]**

   [**Hint:** A negative catalyst may increase the activation energy of reaction.]
19. (A) NO is used as a homogeneous catalyst for oxidation of CO.

$$2CO + O_2 \longrightarrow 2CO_2$$

   (R) NO increases the rate of oxidation.

Answers : OBJECTIVE QUESTIONS

1. (a)	2. (b)	3. (d)	4. (c)	5. (d)	6. (b)	7. (a)	8. (c)
9. (d)	10. (c)	11. (c)	12. (c)	13. (d)	14. (d)	15. (c)	16. (a)
17. (a)	18. (d)	19. (b)	20. (a)	21. (b)	22. (a)	23. (b)	24. (a)
25. (d)	26. (d)	27. (c)	28. (b)	29. (b)	30. (a)	31. (d)	32. (c)
33. (a)	34. (b)	35. (c)	36. (a)	37. (d)	38. (b)	39. (a)	40. (a)
41. (c)	42. (d)	43. (c)	44. (a)	45. (d)	46. (c)	47. (b)	48. (b)
49. (b)	50. (a)	51. (d)	52. (c)	53. (c)	54. (a)	55. (c)	56. (b)
57. (d)	58. (a)	59. (a)	60. (d)	61. (b)	62. (c)	63. (b)	64. (b)
65. (d)	66. (a)	67. (a)	68. (a)	69. (d)	70. (d)	71. (c)	72. (a)
73. (b)	74. (d)	75. (c)	76. (c)	77. (d)	78. (a)	79. (a)	80. (c)
81. (b)	82. (c)	83. (a)	84. (c)	85. (d)	86. (b)	87. (c)	88. (c)
89. (d)	90. (a)	91. (c)	92. (d)	93. (c)	94. (c)	95. (d)	96. (a)
97. (a)	98. (a)	99. (a)	100. (d)	101. (d)	102. (d)	103. (b)	104. (b)
105. (d)	106. (c)	107. (b)	108. (c)	109. (a)	110. (b)	111. (a)	112. (d)
113. (d)	114. (c)	115. (b)	116. (a)	117. (c)	118. (b)	119. (a)	

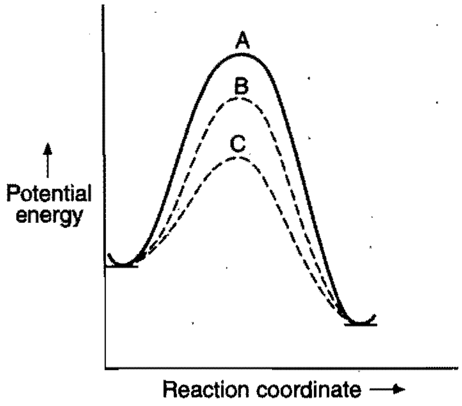
Answers : ASSERTION-REASON TYPE QUESTIONS

1. (a)	2. (a)	3. (d)	4. (d)	5. (d)	6. (a)	7. (d)	8. (b)
9. (b)	10. (b)	11. (b)	12. (a)	13. (b)	14. (d)	15. (b)	16. (b)
17. (b)	18. (b)	19. (b)					

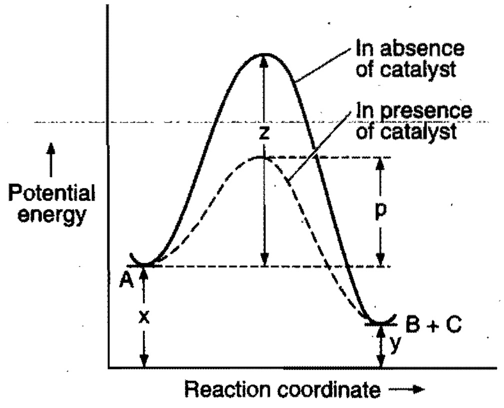
BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

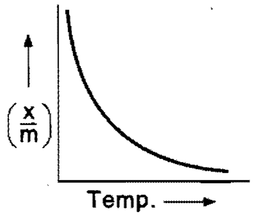
1. In presence of a catalyst, the activation energy is lowered by 3 kcal at 27°C. Hence, the rate of reaction will increase by:
   (a) 32 times (b) 243 times (c) 2 times (d) 148 times
   [**Hint:** $$\frac{\text{Rate in presence of catalyst}}{\text{Rate in absence of catalyst}} = \text{Antilog}\left[\frac{\Delta E}{2.303RT}\right]$$
   $$= \text{Antilog}\left[\frac{3000}{2.303 \times 2 \times 300}\right]$$]
2. According to the adsorption theory of catalysis, the rate of reaction increases because:
   (a) adsorption lowers the activation energy of the reaction
   (b) concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
   (c) adsorption produces heat which increases the rate of reaction
   (d) adsorption increases the activation energy of the reaction
3. Which of the following characteristics is not correct for physical adsorption?
   (a) Adsorption is spontaneous
   (b) ΔH and ΔS are negative
   (c) It is reversible in nature
   (d) Degree of adsorption increases with temperature
4. Freundlich adsorption isotherm gives a straight line on plotting:
   (a) $\frac{x}{m}$ vs. P (b) $\log\left(\frac{x}{m}\right)$ vs. P
   (c) $\log\left(\frac{x}{m}\right)$ vs. $\log P$ (d) $\frac{x}{m}$ vs. $\frac{1}{P}$
5. Adsorption is an exothermic process. The amount of substance adsorbed should: **(DPMT 2009)**
   (a) increase with decrease in temperature
   (b) increase with increase in temperature
   (c) decrease with decrease in temperature
   (d) decrease with increase in temperature
6. In homogeneous catalytic reactions, there are three alternative paths A, B and C (shown in the figure). Which one of the following indicates the relative ease with which the reaction can take place?



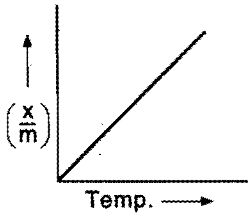
   (a) $A > B > C$ (b) $C > B > A$ (c) $B > C > A$ (d) $A = B = C$
   [**Hint:** Activation energy in the different paths lies in the following sequence: $C < B < A$.
   Lesser is the activation energy, greater is the ease with which the reaction can take place.
   $\therefore C > B > A$ (Decreasing ease with which the reaction can take place.)]
7. For the reaction ($A \longrightarrow B + C$); the energy profile diagram is given in the figure.



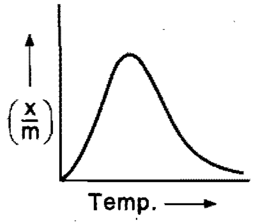
   The decrease in energy of activation in presence of catalyst is:
   (a) z (b) $z - p$ (c) $y - z$ (d) $z - x$
8. Which of the following represents physical adsorption?



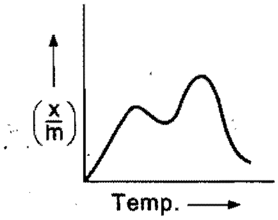
(a)



(b)



(c)



(d)

9. The colloidal system consisting of a liquid adsorbate in a solid adsorbent is termed as:
   (a) aerosol (b) foam
   (c) emulsion (d) gel

10. Which can adsorb a larger volume of hydrogen gas?
(a) Colloidal solution of palladium
(b) Finely divided nickel
(c) Finely divided platinum
(d) Colloidal $Fe(OH)_3$

11. Which is false for a catalyst?
(a) A catalyst can initiate a reaction
(b) It does not alter the position of equilibrium in a reversible reaction
(c) A catalyst remains unchanged in quality and composition at the end of reaction
(d) Catalysts are sometimes very specific in reaction

12. The curve showing the variation of pressure with temperature for a given amount of adsorption is called:
(a) adsorption isobar (b) adsorption isotherm
(c) adsorption isostere (d) adsorption isochore

13. Which of the following statements is incorrect?
(a) Adsorption always leads to a decrease in enthalpy and entropy of the system
(b) Adsorption arises due to unsaturation of valence forces of atoms or molecules on the surface
(c) Adsorption increases with rise in temperature
(d) Adsorption decreases the surface energy

14. Which of the following gas molecules have maximum value of enthalpy of physisorption?
(a) C_2H_6 (b) Ne (c) H_2O (d) H_2
[**Hint:** Since, H_2O can be liquefied easily, hence it will have the maximum enthalpy of physisorption.]

15. Which of the following gases is adsorbed most by activated charcoal? **[AMU (Med.) 2010]**
(a) CO_2 (b) N_2 (c) CH_4 (d) H_2
[**Hint:** CO_2 is an easily liquefiable gas, hence it is adsorbed most by charcoal.]

16. Which of the following factors are responsible for the increase in the rate of a surface catalysed reaction? **[PMT (Kerala) 2006]**
I. A catalyst provides proper orientation for the reactant molecules to react
II. Heat of adsorption of reactants on a catalyst helps reactant molecules to overcome activation energy
III. The catalyst increases the activation energy of the reaction
IV. Adsorption increases the local concentration of reactant molecules on the surface of the catalyst
Select the correct answer using the codes given below:
(a) I and II (b) I and III (c) II and IV (d) I, II and III
(e) I, II and IV

17. In Langmuir's model of adsorption of a gas on a solid surface: **(AIEEE 2006)**
(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
(b) the adsorption at a single site on the surface may involve multiple molecules at the same time
(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

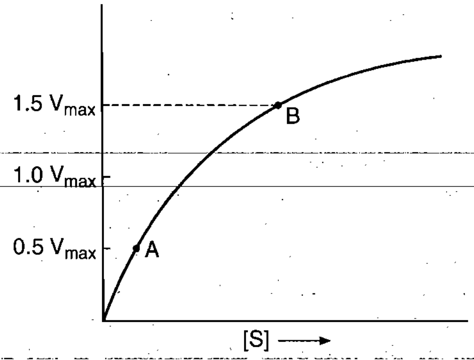
18. An enzyme $[E]$ is combined with the substrate $[S]$ as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} P + E$$

The overall reaction rate is given by:

$$\text{Rate} = \frac{V_{\max}[S]}{K_m + [S]}$$ and the rate of reaction varies with substrate concentration as:



The order of reaction at point A is:
(a) one (b) two (c) three (d) zero

19. Which type of graph gives straight line in Langmuir adsorption isotherm ? **[CET (Gujarat) 2008]**
(a) $\frac{x}{m} \rightarrow \frac{1}{P}$ (b) $\frac{m}{x} \rightarrow \frac{1}{P}$
(c) $\log\left(\frac{x}{m}\right) \rightarrow \frac{1}{P}$ (d) $\log\left(\frac{x}{m}\right) \rightarrow P$

20. Plot of $\log\left(\frac{x}{m}\right)$ against $\log P$ is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be : ($\log 5 = 0.6990$) **[PET (Kerala) 2008]**
(a) 1 g (b) 2 g (c) 3 g (d) 5 g
(e) 2.5 g
[**Hint :** According to Freundlich Adsorption Isotherm :

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log P$$

When $\log\left(\frac{x}{m}\right)$ is plotted against $\log P$, we get straight line of slope $(1/n)$ and intercept $(\log k)$.

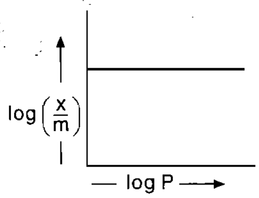
$$\frac{1}{n} = \tan 45° = 1$$

$$\log k = \log 10 = 1$$

$$\frac{x}{m} = k\,(P)^{1/n} = 10\,(0.5)^1 = 5$$

When $m = 1\,\text{g}$, $x = 5\,\text{g}$]

21. Following graphs will be true when :
(a) $P = 0$ (b) $P = 1$
(c) $\frac{1}{n} = 0$ (d) $\frac{1}{n} = \infty$



Answers

1. (d)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (b)	**8.** (a)
9. (d)	**10.** (a)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (a)	**16.** (e)
17. (c)	**18.** (a)	**19.** (b)	**20.** (d)	**21.** (c)			

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Only the surface atoms in an adsorbent, play an active role in adsorption. These atoms possess some residual forces like van der Waals' forces and chemical forces.

In the process of adsorption, weak adsorbate is substituted by strong adsorbate. Activated charcoal used in gas mask is already exposed to the atmospheric air, so the gases and water vapours in air are adsorbed on its surface. When the mask is exposed to chlorine atmosphere, the gases are displaced by chlorine. Porous and finely powdered solids, e.g., charcoal and Fuller's earth adsorb more as compared to the hard non-porous material. It is due to this property that the powdered charcoal is used in gas masks. In general, easily liquefiable gases like CO_2, NH_3, Cl_2 and SO_2, etc., are adsorbed to a greater extent than the elemental gases, e.g., H_2, N_2, O_2, He, etc.

Answer the following questions:

1. Gas masks work on the principle of:
   (a) physical adsorption
   (b) chemical adsorption
   (c) both physical and chemical adsorptions
   (d) absorption
2. Which of the following gases will be most easily adsorbed by the charcoal in the gas mask?
   (a) H_2 (b) O_2 (c) N_2 (d) SO_2
3. Gas mask contains:
   (a) charcoal granules (b) powdered charcoal
   (c) calcium carbonate (d) Fuller's earth
4. Which of the following gas molecules has maximum value of enthalpy of physisorption in a gas mask?
   (a) C_2H_6 (b) Ne (c) H_2O (d) H_2
5. Which of the following gases will substitute O_2 from adsorbed charcoal?
   (a) H_2 (b) N_2 (c) Ar (d) Cl_2

Passage 2

Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a multimolecular layer on the surface of adsorbent. In such cases, the degree of adsorption varies linearly with pressure but at high pressure, it becomes independent of pressure.

The relation of Freundlich adsorption isotherm is:

$$\frac{x}{m} = kP^{1/n}$$

where, k and n are constants.

Langmuir adsorption isotherm is obeyed by the adsorption where the adsorbate forms only a unimolecular adsorbed layer. The mathematical relation of Langmuir adsorption isotherm is:

$$\frac{x}{m} = \frac{aP}{1+bP}$$

Select whether the following statements are true or false:

1. When $\log\left(\frac{x}{m}\right)$ is plotted against $\log P$, we get a straight line with slope $(1/n)$.
   (a) True (b) False
2. The degree of adsorption (x/m) at low pressure will be:
   $$\frac{x}{m} = a$$
   (a) True (b) False
3. When $\left(\frac{m}{x}\right)$ is plotted against $\frac{1}{P}$, we get a straight line with slope $(1/a)$ and intercept (b/a).
   (a) True (b) False
4. In the mathematical relation of Freundlich adsorption isotherm, the value of $(1/n)$ is $0 \le \frac{1}{n} \le 1$.
   (a) True (b) False
5. Freundlich adsorption isotherm is valid for chemisorption.
   (a) True (b) False

Answers

Passage 1.	**1.** (c)	**2.** (d)	**3.** (b)	**4.** (c)	**5.** (d)
Passage 2.	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (b)

SELF ASSESSMENT

ASSIGNMENT NO. 13

SECTION-I

Straight Objective Type Questions

This section contains 8 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. At high pressure, Langmuir adsorption isotherm takes the form:

(a) $\frac{x}{m} = \frac{aP}{1+bP}$ (b) $\frac{x}{m} = \frac{a}{b}$

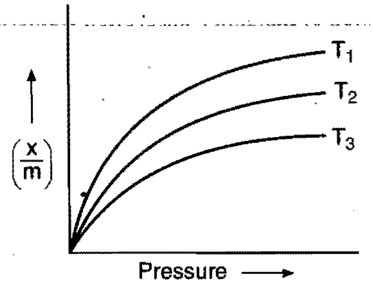
(c) $\frac{x}{m} = aP$ (d) $\frac{m}{x} = \frac{b}{a} + \frac{1}{aP}$

2. Which of the following is used to adsorb water?

(a) Silica gel (b) Anhydrous $CaCl_2$

(c) Coal (d) Coke

3. Select the correct option for the following graph:



(a) $T_1 > T_2 > T_3$ (b) $T_1 = T_2 = T_3$

(c) $T_1 < T_2 < T_3$ (d) $T_1 > T_2 < T_3$

4. Which of the following substances adsorbs H_2 gas most strongly?

(a) Platinum black (b) Nickel powder

(c) Activated charcoal (d) Silica gel

5. The order of volume of gases NH_3, CO_2 and CH_4 adsorbed by one gram of charcoal at 298 K is:

(a) $CH_4 > CO_2 > NH_3$ (b) $NH_3 > CH_4 > CO_2$

(c) $NH_3 > CO_2 > CH_4$ (d) $CO_2 > NH_3 > CH_4$

6. Activated charcoal is prepared by:

(a) adding $Ba_3(PO_4)_2$ to charcoal

(b) treatment with conc. HNO_3

(c) heating charcoal with steam to make it more porous

(d) adding silica to charcoal

7. In the manufacture of H_2SO_4 by contact process the presence of AS_2O_3 acts as:

(a) catalytic promoter (b) induced catalyst

(c) catalytic poison (d) autocatalyst

8. In Rosenmund reactions, presence of $BaSO_4$ acts as .... for Pd.

(a) promoter (b) moderator

(c) inhibitor (d) poison

SECTION-II

Multiple Answers Type Objective Questions

9. Which of the following are correct about a catalyst?

(a) It participates in the reaction but is recovered at last

(b) It does not affect ΔG

(c) It does not affect ΔH

(d) It alters the mechanism of reaction

10. Which of the following statements are correct?

(a) Physical adsorption is of multimolecular layer

(b) Degree of chemical adsorption increases with increase in temperature

(c) Adsorption increases the surface energy

(d) Sometimes solvent is adsorbed in preference to solute

11. Which of the following are zeolites?

(a) Granite (b) Faujasite

(c) Natrolite (d) Thomisite

12. Which of the following act as negative catalysts?

(a) Ethanol in oxidation of chloroform

(b) Tetra ethyl lead used as antiknocking agent

(c) Glycerol in the decomposition of H_2O_2

(d) Fe in the formation of ammonia by Haber's process

13. Select the correct statements about enzymes:

(a) Enzymes are biological catalysts found in organisms

(b) All enzymes are proteins

(c) Enzymes can catalyse any reaction

(d) Enzymes' activity is optimum at 27° C

SECTION-III

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s) (b-q,r), (c-p,q) and (d-s), then the correctly bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

14. Match the Column-I with Column-II:

Column-I (Process)	**Column-II (Catalyst)**
(a) Cracking of hydrocarbons	(p) Ni
(b) Ostwald's process	(q) NO
(c) Sulphuric acid manufacture	(r) Pt
(d) Catalytic converter	(s) NiO

15. Match the Column-I with Column-II:

Column-I (Catalyst)	**Column-II (Process)**
(a) Ni	(p) Cracking of hydrocarbons
(b) $AlCl_3$	(q) Fischer-Tropsch process
(c) Co/Al_2O_3	(r) Hydrogenation of oil
(d) Zeolite	(s) Friedel-Crafts reaction

16. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Chemisorption	(p) Exothermic
(b) Physisorption	(q) Endothermic
(c) Desorption	(r) Removal of adsorbed substance
(d) Activation of adsorbent	(s) Specific

Answers

1. (b) **2.** (a) **3.** (c) **4.** (a) **5.** (c) **6.** (c) **7.** (c) **8.** (d)
9. (a, b, c, d) **10.** (a, b, d) **11.** (b, c, d) **12.** (a, b, c) **13.** (a, b, d) **14.** (a-r) (b-r) (c-q, r) (d-p, s)
15. (a-r) (b-s) (c-q) (d-p) **16.** (a-p, s) (b-p), (c-q, r) (d-q)

CHAPTER 14

VOLUMETRIC ANALYSIS

Volumetric analysis is a method of quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution whose concentration or strength is to be determined. By knowing the volume of the known solution, the concentration of the solution under investigation can be calculated. Volumetric analysis is also termed as **titrimetric analysis.**

14.1 IMPORTANT TERMED USED IN VOLUMETRIC ANALYSIS

(i) Titration: The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as **titration.** Thus, a titration involves two solutions:

(a) Unknown solution and (b) Known solution or standard solution.

(ii) Titrant: The reagent or substance whose solution is employed to estimate the concentration of unknown solution is termed **titrant.** There are two types of reagents or titrants:

(a) Primary titrants: These reagents can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid, potassium dichromate, silver nitrate, copper sulphate, ferrous ammonium sulphate, sodium thiosulphates, etc., are the examples of primary titrants.

(b) Secondary titrants: These reagents cannot accurately weighed and their solutions are to be standardised before use. Sodium hydroxide, potassium hydroxide, hydrochloric acid, sulphuric acid, iodine, potassium permanganate, etc., are the examples of secondary titrants.

(iii) Standard solution: The solution of exactly known concentration of the titrant is called the standard solution.

(iv) Titrate: The solution consisting the substance to be estimated is termed unknown solution. The substance is termed **titrate.**

(v) Equivalence point: The point at which the reagent (titrant) and the substance (titrate) under investigation are chemically equivalent is termed **equivalence point or stoichiometric end point** or **simply end point.**

(vi) Indicator: It is the auxiliary substance used for physical (visual) detection of the completion of titration or detection of end point is termed as indicator. Indicators show change in colour or turbidity at the stage of completion of titration.

14.2 CONCENTRATION REPRESENTATION OF SOLUTION

1. Concentration Representation in Physical Units

(a) Strength of solution: Number of grams of solute dissolved per litre of solution is called strength of solution.

(b) Parts Per Million (ppm): Number of grams of solute dissolved per 10^6 grams of solvent is called concentration of solution in the unit of Parts Per Million (ppm). This unit is used to represent hardness of water and concentration of very dilute solutions.

(c) Percentage by mass: Number of grams of solute dissolved per 100 grams of solution is called percentage by mass.

(d) Percentage by volume: Number of millilitres of solute per 100 mL of solution is called percentage by volume.

For example, if 25 mL ethyl alcohol is diluted with water to make 100 mL solution then the solution thus obtained is 25% ethyl alcohol by volume.

(e) Percentage mass by volume: Number of grams of solute present per 100 mL of solution is called percentage mass by volume.

For example, let 25 g glucose is dissolved in water to make 100 mL solution then the solution is 25% glucose mass by volume.

2. Concentration Representation in Chemical Units

(a) Normality: Number of gram equivalents of solute dissolved per litre of solution is called the normality of the solution. It is denoted by N and it can be calculated as,

$$N = \frac{w_B \times 1000}{E_B \times V} \qquad \text{... (i)}$$

where, w_B = mass of solute in grams

E_B = gram equivalent mass of solute

V = volume of solution in mL

Another relation for calculation of normality is

$$N = \frac{x \times d \times 10}{E_B} \quad \text{... (ii)}$$

where, d = density of solution is g/mL

x = percentage by mass of solute

Symbol	Normality	Physical significance
(i) N	Normal solution, *i.e.*, Normality = 1	1 g equivalent of solute per litre of solution
(ii) $0.1\ N$ or $\frac{N}{10}$	Decinormal solution, *i.e.*, Normality = 0.1	0.1 g equivalent of solute per litre of solution
(iii) $0.01\ N$ or $\frac{N}{100}$	Centinormal solution, *i.e.*, Normality = 0.01	0.01 g equivalent of solute per litre of solution
(iv) $0.001\ N$ or $\frac{N}{1000}$	Millinormal solution, *i.e.*, Normality = 0.001	0.001 g equivalent of solute per litre of solution
(v) $0.5\ N$ or $\frac{N}{2}$	Seminormal solution, *i.e.*, Normality = 0.5	0.5 g equivalent of solute per litre of solution

Note: If normality of a solution is given then number of equivalents of solute in a definite volume of solution may be calculated easily.

$$\text{Number of equivalents of solute} = \frac{N \times V}{1000}$$

where, V = volume of solution in mL.

(b) Molarity: Number of moles of solute dissolved per litre of solution is called molarity. It is denoted by 'M'. It may be calculated using the following relations:

$$M = \frac{w_B \times 1000}{m_B \times V} \quad \text{... (i)}$$

or

$$M = \frac{x \times d \times 10}{m_B} \quad \text{... (ii)}$$

where, w_B = mass of solute in grams

m_B = gram molecular mass of solute

x = percentage by mass of solute

d = density of solution in g mL^{-1}

In the problems of volumetric analysis, concept of molarity is very useful. Let us consider an equation of the following type :

$$n_1 A + n_2 B \longrightarrow m_1 C + m_2 D$$

Let molar of A and B are M_1 and M_2 respectively, then

$$\frac{M_1 V_1}{n_1}(A) = \frac{M_2 V_2}{n_2}(B)$$

(c) Molality: Number of moles of solute dissolved per 1000 g (per kg) of solvent is called molality of solution. It is denoted by 'm'. It can be calculated as,

$$m = \frac{w_B \times 1000}{m_B \times w_A}$$

where, w_B = mass of solute in grams

m_B = gram molecular mass of solute

[illegible] = mass of solvent in grams

Principle of Volumetric Analysis

Volumetric analysis is based on the **principle of equivalence.** According to this principle, substances combine together in the ratio of their equivalent masses.

Let x g of a compound 'A' completely react with y g of another compound 'B'.

Then, $$\frac{\text{Equivalent mass of '}A\text{'}}{\text{Equivalent mass of '}B\text{'}} = \frac{x}{y}$$

$$\frac{x}{\text{Equivalent mass of '}A\text{'}} = \frac{y}{\text{Equivalent mass of '}B\text{'}}$$

Number of gram equivalents of 'A' = Number of gram equivalents of 'B'

Thus, **one gram equivalent of a substance 'A' completely reacts with one gram equivalent of another substance 'B'.**

According to the principle of equivalence,

Number of gram equivalents of A

= No. of gram equivalents of B

$$\text{Number of gram equivalents of } A = \frac{N_A \times V_A}{1000};$$

where, V_A = volume of A in mL

$$\text{Number of gram equivalents of } B = \frac{N_B \times V_B}{1000};$$

where, V_B = volume of B in mL

$$\therefore \quad \frac{N_A \times V_A}{1000} = \frac{N_B \times V_B}{1000}$$

$$N_A \times V_A = N_B \times V_B$$

The above equation is called normality equation and it is very useful in numerical calculations of volumetric analysis.

14.3 CLASSIFICATION OF REACTIONS INVOLVED IN VOLUMETRIC ANALYSIS

1. Neutralisation Reactions

The reaction in which acids and bases react to form salt is called neutralisation.

e.g., $$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$H^+_{(acid)} + OH^-_{(base)} \longrightarrow H_2O\text{(feebly ionised)}$$

The titration based on neutralisation is called acidimetry or alkalimetry.

2. Oxidation-Reduction Reactions

The reactions involving simultaneous loss and gain of electrons among the reacting species are called oxidation-reduction or redox reactions, *e.g.*, let us consider oxidation of ferrous sulphate (Fe^{2+} ion) by potassium permanganate (MnO_4^- ion) in acidic medium.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \text{(Gain of electrons or reduction)}$$

$$5 \times [Fe^{2+} \longrightarrow Fe^{3+} + e^-] \quad \text{(Loss of electrons or oxidation)}$$

$$\overline{MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O}$$

In the given reaction, MnO_4^- acts as oxidising agent and Fe^{2+} acts as reducing agent.

The titrations involving redox reactions are called redox titrations. These titrations are also called according to the reagent used in the titration, *e.g.*, iodometric, iodimetric, cerimetric, permanganometric and dichromometric titrations.

3. Precipitation Reaction

A chemical reaction in which cations and anions combine to form a compound of very low solubility (in the form of residue or precipitate), is called precipitation.

e.g., $BaCl_2 + Na_2SO_4 \longrightarrow \underset{\text{(White precipitate)}}{BaSO_4} + 2NaCl$

$$AgNO_3 + NaCl \longrightarrow \underset{\text{(White precipitate)}}{AgCl} + NaNO_3$$

The titrations involving precipitation reactions are called **precipitation titrations.**

4. Complex Formation Reactions

These are ion combination reactions in which a soluble slightly dissociated complex ion or compound is formed. Complex compounds retain their identity in the solution and have the properties of the constituent ions and molecules.

e.g., $CuSO_4 + 4NH_3 \longrightarrow \underset{\text{(Complex compound)}}{[Cu(NH_3)_4]SO_4}$

$$AgNO_3 + 2KCN \longrightarrow \underset{\text{(Complex compound)}}{K[Ag(CN)_2]} + KNO_3$$

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{(Complex compound)}}{Cu_2[Fe(CN)_6]} + 2K_2SO_4$$

The titrations involving complex formation reactions are called **complexometric titrations.**

14.4 CALCULATION OF EQUIVALENT MASS OF DIFFERENT SUBSTANCES

The equivalent mass of a substance is defined as the number of parts by mass of it which combine with or displace 1.0078 parts by mass of hydrogen, 8 parts by mass of oxygen and 35.5 parts by mass of chlorine.

The equivalent mass of a substance expressed in grams is called **gram equivalent mass.**

The equivalent mass of a substance is not constant. It depends upon the reaction in which the substance is participating. A compound may have different equivalent mass in different chemical reactions and under different experimental conditions.

(A) Equivalent Mass of an Acid

It is the mass of an acid in grams which contains 1.0078 g of replaceable H^+ ions or it is the mass of acid which contains one mole of replaceable H^+ ions. It may be calculated as:

$$\text{Equivalent mass of acid} = \frac{\text{Molecular mass of acid}}{\text{Basicity of acid}}$$

Basicity of acid = number of replaceable hydrogen atoms present in one molecule of acid

Acid	Basicity	Molecular mass	Equivalent mass
HNO_3	1	63	$\frac{63}{1} = 63$
HCl	1	36.5	$\frac{36.5}{1} = 36.5$
CH_3COOH	1	60	$\frac{60}{1} = 60$
H_3PO_2	1	66	$\frac{66}{1} = 66$
H_2SO_4	2	98	$\frac{98}{2} = 49$
$\underset{\text{COOH}}{\overset{\text{COOH}}{\vert}} \cdot 2H_2O$	2	126	$\frac{126}{2} = 63$
H_3PO_3	2	82	$\frac{82}{2} = 41$

Note: Phosphoric acid may act as monobasic or dibasic or tribasic acid, *e.g.*,

(i) $H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

Here, phosphoric acid acts as monobasic acid.

$$\therefore \text{ Equivalent mass of } H_3PO_4 = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{1} = 98$$

(ii) $H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + 2H_2O$

Here, Basicity of $H_3PO_4 = 2$

$$\text{Equivalent mass of } H_3PO_4 = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{2} = 49$$

(iii) $H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$

Here, Basicity of $H_3PO_4 = 3$

$$\text{Equivalent mass of } H_3PO_4 = \frac{\text{Molecular mass}}{\text{Basicity}} = \frac{98}{3} = 32.66$$

(B) Equivalent Mass of a Base

It is the mass of the base which contains one mole of replaceable OH^- ions in a molecule.

$$\text{Equivalent mass of base} = \frac{\text{Molecular mass of base}}{\text{Acidity of the base}}$$

Acidity of base = Number of replaceable OH^- ions present in one molecule of the base

or

It is the mass of a base which completely reacts with one gram equivalent mass of an acid, *e.g.*, $$\underset{74\,g}{Ca(OH)_2} + \underset{73\,g}{2HCl} \longrightarrow CaCl_2 + 2H_2O$$

$$= 2\text{ g equivalent of HCl}$$

2 gram equivalent of HCl reacts with 74 g $Ca(OH)_2$

$\therefore$ 1 gram equivalent of HCl will react with 37 g $Ca(OH)_2$

Thus, equivalent mass of $Ca(OH)_2 = 37$

Base	Acidity	Molecular mass	Equivalent mass
NaOH	1	40	40/1 = 40
KOH	1	56	56/1 = 56
$Ca(OH)_2$	2	74	74/2 = 37
NH_4OH	1	35	35/1 = 35

(C) Equivalent Mass of Salt

Let us consider a salt of weak acid (H_2CO_3) and strong base (NaOH). This salt undergoes hydrolysis in water to form basic solution.

$$Na_2CO_3 + 2H_2O \rightleftharpoons H_2CO_3 + 2Na^+ + 2OH^-$$

Such salts react with mineral acids like HCl

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

In the above reaction one mole of Na_2CO_3 reacts with 2 equivalents of HCl

$$\therefore \text{ Equivalent mass of } Na_2CO_3 = \frac{\text{Molecular mass of } Na_2CO_3}{2}$$

$$= \frac{106}{2} = 53$$

Thus, *mass of the salt which reacts with one gram equivalent of acid or base is called its equivalent mass, e.g.*,

(i) $$\underset{1\text{ mol}}{NH_4Cl} + \underset{1\text{ g equivalent}}{NaOH} \longrightarrow NH_3 + NaCl + H_2O$$

$$\text{Equivalent mass of } NH_4Cl = \frac{\text{Molecular mass of } NH_4Cl}{1}$$

(ii) $$\underset{1\text{ mol}}{AgNO_3} + \underset{1\text{ g equivalent}}{HCl} \longrightarrow AgCl + HNO_3$$

$$\text{Equivalent mass of } AgNO_3 = \frac{\text{Molecular mass of } AgNO_3}{1}$$

Alternatively,

$$\text{Equivalent mass of salt} = \frac{\text{Molecular mass of salt}}{\text{Total positive or negative valency}}$$

Salt	Valency	Equivalent mass
NaCl	1	molecular mass/1
$CaCl_2$	2	molecular mass/2
$Ca_3(PO_4)_2$	6	molecular mass/6
$AlCl_3$	3	molecular mass/3

(D) Equivalent Mass of an Oxidising Agent

(a) Available oxygen concept: The mass of oxidising agent which contains 8 g of available oxygen (*i.e.*, the oxygen which can be used for oxidation) is called the equivalent mass of oxidising agent.

Examples:

(i) $$\underset{294.2\,g}{K_2Cr_2O_7} + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \underset{\substack{3\times 16\,g\\ = 48\,g}}{3[O]}$$

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{294.2}{48} \times 8 = 49.03$$

(ii) Equivalent mass of $KMnO_4$: Potassium permanganate is a powerful oxidising agent in acid, base and in neutral medium.

(1) Acid medium:

$$\underset{2\times 158\,g}{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + \underset{5\times 16\,g}{5[O]}$$

~~80 g oxygen is furnished by 316 g $KMnO_4$~~

~~$\therefore$ 8 g oxygen is furnished by 31.6 g $KMnO_4$~~

i.e., equivalent mass of $KMnO_4$ in acidic medium is 31.6.

(2) Neutral medium:

$$\underset{2\times 158\,g}{2KMnO_4} + H_2O \longrightarrow 2MnO_2 + 2KOH + \underset{3\times 16\,g}{3[O]}$$

$$\text{Equivalent mass of } KMnO_4 = \frac{316}{48} \times 8 = 52.66$$

(3) Alkaline medium:

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

$$2 \times 158\text{ g } KMnO_4 \equiv 16\text{ g 'O'}$$

$$\text{Equivalent mass of } KMnO_4 = \frac{316}{16} \times 8 = 158$$

(b) Electron concept:

Equivalent mass of oxidising agent

$$= \frac{\text{Molecular mass of oxidising agent}}{\text{Number of electrons gained by one molecule}}$$

Examples: (i) Equivalent mass of potassium dichromate:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Molecular mass}}{6} = \frac{294}{6} = 49$$

(ii) Equivalent mass of $KMnO_4$ in acid medium:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$\text{Equivalent mass of } KMnO_4 = \frac{\text{Molecular mass}}{5} = \frac{158}{5} = 31.6$$

Similarly, equivalent mass of $KMnO_4$ in neutral and alkaline medium can be calculated.

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-} \qquad \text{(Neutral medium)}$$

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \text{ (Alkaline medium)}$$

(c) Oxidation number concept:

Equivalent mass of oxidising agent

$$= \frac{\text{Molecular mass of oxidising agent}}{\text{Total change in oxidation number per molecule of oxidising agent}}$$

Examples:

(i) Equivalent mass of $K_2Cr_2O_7$:

$$\overset{+2}{K_2}\,\underline{\overset{+12}{Cr_2}}\,\overset{-14}{O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \underline{\overset{+6}{Cr}}_2\overset{-6}{(SO_4)_3} + 4H_2O + 3[O]$$

Change in oxidation number of chromium = 12 − 6 = 6

$$\text{Equivalent mass of } K_2Cr_2O_7 = \frac{\text{Molecular mass}}{6} = \frac{294}{6} = 49$$

(ii) Equivalent mass of $KMnO_4$ in acid medium:

$$2\overset{+1}{K}\,\underline{\overset{+7}{Mn}}\,\overset{-8}{O_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\underline{\overset{+2}{Mn}}\,\overset{-2}{SO_4} + 3H_2O + 5[O]$$

Change in oxidation number of manganese = 7 − 2 = 5

Equivalent mass of $KMnO_4$

$$= \frac{\text{Molecular mass}}{5} = \frac{158}{5} = 31.6$$

(E) Equivalent Mass of a Reducing Agent

(a) Available oxygen concept: The amount of reducing agent in gram which reacts with 8 g of available oxygen is called gram equivalent mass of reducing agent.

Examples:

(i) Oxalic acid:

$$\underset{1\ \text{mol}\ (126\ \text{g})}{\begin{array}{c}\text{COOH}\\ |\\ \text{COOH}\end{array}} \cdot 2H_2O + \underset{16\ \text{g}}{[O]} \longrightarrow 2CO_2 + 3H_2O$$

$$\text{Equivalent mass of oxalic acid} = \frac{126}{16} \times 8 = 63$$

(ii) Ferrous sulphate:

$$\underset{2\ \text{mol}\ (2\times 152\ \text{g})}{2FeSO_4} + H_2SO_4 + \underset{16\ \text{g}}{[O]} \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$\text{Equivalent mass of ferrous sulphate} = \frac{2\times 152}{16} \times 8 = 152$$

Similarly, equivalent mass of Mohr salt can be determined.

$$2\ \text{mol}\ FeSO_4(NH_4)_2SO_4 \cdot 6H_2O \equiv 1 \text{ gram atom of oxygen}$$

$$\therefore \text{Equivalent mass of Mohr salt} = \frac{392 \times 2 \times 8}{16} = 392$$

(b) Electron loss concept:

Equivalent mass of a reducing agent

$$= \frac{\text{Molecular mass}}{\text{Number of electrons lost by one molecule}}$$

Example: Ferrous ammonium sulphate (Mohr salt). Oxidation of Mohr salt involves the following ionic reaction:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Equivalent mass = Molecular mass

(c) Oxidation number concept:

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{Total change in oxidation number of the oxidised element per molecule}}$$

The oxidation number of iron in ferrous salt is +2 while the oxidation number of iron in ferric salt is +3. The change in oxidation number per atom of iron is 1, *i.e.*, one unit.

∴ Equivalent mass of ferrous ammonium sulphate

$$= \frac{\text{Molecular mass}}{1} = \frac{392}{1} = 392$$

SOME SOLVED EXAMPLES

Example 1. *When hydrogen gas was passed over 8.08 g of heated metal oxide, it was completely reduced and 1.8 g of water was formed:*

(a) What is weight of oxygen in the metal oxide?

(b) What is the equivalent mass of the metal?

Solution: (a) When hot metal oxide is treated with hydrogen, 1.8 g water is formed.

18 g H_2O contains 16 g oxygen.

Thus, 1.8 g H_2O will contain 1.6 g oxygen.

(b) Equivalent mass may be defined as weight of the metal that combines with 8 parts of oxygen to form its oxide.

Mass of metal in its oxide = 8.08 − 1.6
= 6.48 g

∵ 1.6 g oxygen combines with 6.48 g of metal

$$\therefore 8 \text{ g oxygen will combine with} = \frac{6.48}{1.6} \times 8 \text{ g of metal} = 32.4 \text{ g}$$

Thus, equivalent mass of metal = 32.4

Example 2. *SO_2 is oxidised to SO_4^{2-} in acid medium. Calculate equivalent mass of SO_2.*

Solution: $\overset{+4}{S}O_2(g) + 2H_2O \longrightarrow \overset{+2}{H_2}\overset{+6}{S}\overset{-8}{O_4} + 2H^+ + 2e^-$

Change in oxidation number of sulphur = 6 − 4 = 2

$$\text{Equivalent mass of } SO_2 = \frac{\text{Molecular mass}}{2} = \frac{64}{2} = 32$$

Example 3. *What is the equivalent mass of:*

(a) H_3PO_4 when neutralised to HPO_4^{2-}

(b) $HClO_4$

(c) $NaIO_3$ when reduced to I^-

(d) $NaIO_3$ when reduced to I_2

(e) $Al(OH)_3$.

Solution: (a) Molecular mass of $H_3PO_4 = (3 + 31 + 64) = 98$ g. H_3PO_4 when neutralised to HPO_4^{2-}, two H^+ ions have been replaced.

$$\text{Thus, eq. mass} = \frac{\text{Mol. mass}}{\text{No. of replaceable hydrogen atoms}} = \frac{98}{2} = 49.0 \text{ g}$$

(b) $HClO_4$ molecule contains one replaceable hydrogen atom.

$$\text{Thus, eq. mass} = \frac{\text{Mol. mass}}{1} = \frac{100.5}{1} = 100.5$$

(c) $NaIO_3 \longrightarrow I^-$

Oxidation no. $+5$ $\quad -1$

Change in oxidation number = 6

Mol. mass of $NaIO_3 = (23 + 127 + 48) = 198$ g

$$\text{Eq. mass of } NaIO_3 = \frac{\text{Mol. mass}}{\text{Change in O.N.}} = \frac{198}{6} = 33.0$$

(d) $NaIO_3 \longrightarrow I_2$

Oxidation no. $+5$ $\quad 0$

Change in oxidation number = 5

$$\text{Eq. mass of } NaIO_3 = \frac{198}{5} = 39.6$$

(e) The acidity of $Al(OH)_3$ is 3.

$$\text{Eq. mass of } Al(OH)_3 = \frac{\text{Mol. mass}}{\text{Acidity}} = \frac{78}{3} = 26.0 \text{ g}$$

Example 4. *Calculate the number of millimoles and milliequivalents of $Cr_2O_7^{2-}$ ions in acid medium when 100 mL of 0.01 M $Cr_2O_7^{2-}$ is reduced to Cr^{3+} by Fe^{2+}.*

Solution: $\underset{1\text{ mol}}{Cr_2O_7^{2-}} + 14H^+ + \underset{6\text{ mol}}{6e^-} \longrightarrow 2Cr^{3+} + 7H_2O$

$$\therefore \quad 0.01\,M\ Cr_2O_7^{2-} \equiv 0.06\,N\ Cr_2O_7^{2-}$$

Number of millimoles $= M \times V = 0.01 \times 100 = 1$

Number of milliequivalents $= N \times V = 0.06 \times 100 = 6$

Example 5. *Give the relation between molecular mass (M) and equivalent mass (E) of the underlined species in the following reactions:*

(*a*) $\underline{H_3PO_4} + Ca(OH)_2 \longrightarrow CaHPO_4 + 2H_2O$

(*b*) $\underline{H_2O_2} + MnO_4^- \longrightarrow Mn^{2+} + O_2 + H_2O$

(*c*) $\underline{4H_3PO_3} \longrightarrow 3H_3PO_4 + PH_3$

(*d*) $\underline{HC{\equiv}CH} + 2Na \longrightarrow NaC{\equiv}CNa + H_2$

Solution: (a) $\underline{H_3PO_4} + Ca(OH)_2 \longrightarrow CaHPO_4 + 2H_2O$

Basicity of $H_3PO_4 = 2$

$$\therefore \text{ Equivalent mass of } H_3PO_4(E) = \frac{\text{Molecular mass }(M)}{2}$$

(b) $\underline{\overset{+2}{H_2}\,\overset{-2}{O_2}} \longrightarrow \overset{0}{O_2}$

Change in oxidation number of $H_2O_2 = 2$

$$\therefore \text{ Equivalent mass of } H_2O_2\ (E) = \frac{\text{Molecular mass }(M)}{2}$$

(c) $\underline{\overset{+3}{H_3}\ \overset{+3}{P}\,\overset{-6}{O_3}} \longrightarrow \overset{+3}{H_3}\ \overset{+5}{P}\,\overset{-8}{O_4}$

Change in oxidation number of 'P' = 2

$$\therefore \text{ Equivalent mass } (E_1) = \frac{\text{Molecular mass }(M)}{2}$$

$$\overset{+3}{H_3}\ \overset{+3}{P}\,\overset{-6}{O_3} \longrightarrow \overset{-3}{P}\,\overset{+3}{H_3}$$

Change in oxidation number of 'P' $= +3 - (-3) = +6$

$$\text{Equivalent mass } (E_2) = \frac{\text{Molecular mass }(M)}{6}$$

Overall equivalent mass $= E_1 + E_2$

$$= \frac{M}{2} + \frac{M}{6} = \frac{4M}{6} = \frac{2M}{3}$$

(d) $\underline{H{-}C{\equiv}C{-}H} + 2Na \longrightarrow NaC{\equiv}CNa + H_2$

Basicity of acetylene = 2

$$\therefore \quad \text{Equivalent mass } (E) = \frac{\text{Molecular mass }(M)}{2}$$

Example 6. *Determine the number of g equivalents of solute in (a) 100 mL of 5 N HCl (b) 250 mL of 0.1 N Na_2CO_3.*

Solution : We know that

Number of g equivalents = Normality × Vol. of solution (litres)

(a) Number of g equivalents of HCl $= 5 \times \dfrac{100}{1000} = 0.5$

(b) Number of g equivalents of $Na_2CO_3 = 0.1 \times \dfrac{250}{1000}$

$= 0.025$

Example 7. *What volumes of 12 N HCl and 3 N HCl must be mixed to form one litre 6 N HCl?*

Solution: Let x mL of 12 N HCl and y mL of 3 N HCl be mixed to form one litre 6 N HCl.

So, $\quad x + y = 1000 \quad$ ... (i)

Applying the formula $N_1V_1 + N_2V_2 = N_3V_3$,

$N_1 = 12\,N, V_1 = x, N_2 = 3\,N, V_2 = y, N_3 = 6\,N, V_3 = 1000$

So, $\quad 12x + 3y = 6 \times 1000 \quad$ ... (ii)

Putting the value of $y = (1000 - x)$ from eq. (i) in eq. (ii),

$$12x + 3(1000 - x) = 6000$$

or $\quad 12x - 3x + 3000 = 6000$

or $\quad 9x = 3000$

$$x = \frac{3000}{9} = 333.3 \text{ mL}$$

So, $\quad y = (1000 - x) = (1000 - 333.3) = 666.7$ mL

i.e., 333.3 mL 12 N HCl and 666.7 mL 3 N HCl are mixed.

Example 8. (*a*) *What is the normality of a 96 per cent solution of H_2SO_4 of specific gravity 1.84?*

(*b*) *How many mL of 96 per cent sulphuric acid solution is necessary to prepare one litre 0.1 N H_2SO_4?*

(*c*) *To what volume should 10 mL of 96 per cent H_2SO_4 be diluted to prepare 2 N solution?*

Solution: Mass of 1 litre of H_2SO_4 solution

= Vol. × Density

$= 1000 \times 1.84 = 1840$ g

Mass of H_2SO_4 present in one litre 96% H_2SO_4 solution

$$= \frac{96}{100} \times 1840 = 1766.4 \text{ g}$$

Strength of H_2SO_4 solution $= 1766.4$ g/L

(a) $\text{Normality} = \frac{\text{Strength}}{\text{Eq. mass}} = \frac{1766.4}{49} = 36.05\ N$

(b) Let the volume taken be V_1 mL

Applying $N_1V_1 = N_2V_2$

$N_1 = 36.05N, \quad V_1 = ?, \quad N_2 = \frac{N}{10}, \quad V_2 = 1000 \text{ mL}$

$$36.05 \times V_1 = \frac{1}{10} \times 1000$$

So, $V_1 = \frac{1000}{36.05 \times 10} = 2.77 \text{ mL}$

i.e., 2.77 mL of H_2SO_4 is diluted to one litre.

(c) $\underset{\text{Before dilution}}{N_BV_B} = \underset{\text{After dilution}}{N_AV_A}$

$$10 \times 36.05 = V_A \times 2$$

$$V_A = 180.25 \text{ mL}$$

i.e., 10 mL of given H_2SO_4 is diluted to 180.25 mL.

Example 9. *250 mL of x M solution and 500 mL of y M solution of a solute A are mixed and diluted to 2 litre to produce a final concentration of 1.6 M.*

If $x : y = 5 : 4$, calculate x and y.

Solution: We know that,

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$x \times 250 + y \times 500 = 1.6(2000)$$

$$x + 2y = 1.6 \times 8$$

$$x + 2y = 12.8$$

$$\frac{x}{y} + 2 = \frac{12.8}{y}$$

$$\frac{5}{4} + 2 = \frac{12.8}{y}$$

$$\frac{13}{4} = \frac{12.8}{y}$$

$$y = \frac{12.8 \times 4}{13} = 3.94$$

Similarly, $x = 4.92$

Example 10. *2.68×10^{-3} mol of a solution containing an ion A^{n+} required 1.6×10^{-3} mol of MnO_4^- for oxidation of A^{n+} to AO_3^- ion in acid medium. What is the value of n?*

Solution: A^{n+} is oxidised to AO_3^-

Change in oxidation number $= 5(\text{in } AO_3^-) - n(\text{in } A^{n+})$

$= 5 - n$ ... (i)

2.68×10^{-3} mol of A^{n+} ion react with 1.6×10^{-3} mol of MnO_4^- ions

$\therefore$ 1 mol of A^{n+} ion will react with $\frac{1.6 \times 10^{-3}}{2.68 \times 10^{-3}}$ mol of MnO_4^- ions

$= 0.579$ mol of MnO_4^- ions

$$2K\overset{+7}{Mn}O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2\overset{+2}{Mn}SO_4 + 3H_2O + 5[O]$$

Number of equivalents of MnO_4^- used in oxidation of A^{n+} to $AO_3^- = 0.597 \times 5 = 2.985 \approx 3$

Thus, from equation (i), $5 - n = 3$

$n = 2$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. An element X having equivalent mass E forms a general oxide X_mO_n, its atomic mass should be:

(a) $\frac{2En}{m}$ (b) $2mEn$ (c) $\frac{E}{n}$ (d) $\frac{ME}{2n}$

[**Ans.** (a)]

[**Hint:** Amount of X that combines with 8 g of oxygen,

i.e., $E = \frac{m \times \text{Atomic mass}}{n \times 2}$

$\therefore$ $\text{Atomic mass} = \frac{2En}{m}$]

2. In the reaction,

$$FeS_2 + KMnO_4 + H^+ \longrightarrow Fe^{3+} + SO_2 + Mn^{2+} + H_2O$$

the equivalent mass of FeS_2 would be equal to:

(a) molar mass (b) $\frac{\text{molar mass}}{10}$

(c) $\frac{\text{molar mass}}{11}$ (d) $\frac{\text{molar mass}}{13}$

[**Ans.** (c)]

[**Hint:** $Fe^{2+} \longrightarrow Fe^{3+} + e^-$; $S_2^{2-} \longrightarrow 2S^{4+} + 10e^-$

$\therefore$ $FeS_2 \longrightarrow 2S^{4+} + Fe^{3+} + 11e^-$

Equivalent mass of $FeS_2 = \frac{\text{Molar mass}}{11}$]

3. The equivalent mass of H_3BO_3 in its reaction with NaOH to form $Na_2B_4O_7$ is equal to:

(a) molar mass/4 (b) molar mass/3

(c) molar mass/2 (d) molar mass

[**Ans.** (d)]

[**Hint:** Boric acid is a monobasic acid.

Hence, Equivalent mass = Molar mass]

4. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, if molecular masses of NH_3 and N_2 are M_1 and M_2, their equivalent masses are E_1 and E_2, then $(E_1 - E_2)$ is:

(a) $\frac{2M_1 - M_2}{6}$ (b) $M_1 - M_2$

(c) $3M_1 - M_2$ (d) $M_1 - 3M_2$

[**Ans.** (a)]

[**Hint:** Equivalent mass of N_2, *i.e.*, $E_2 = \frac{M_2}{6}$

Equivalent mass of NH_3, *i.e.*, $E_1 = \frac{M_1}{3}$

Then, $E_1 - E_2 = \frac{M_1}{3} - \frac{M_2}{6} = \frac{2M_1 - M_2}{6}$]

5. X g metal gave Y g of its oxide. Hence, equivalent mass of the metal is:

(a) $\left(\frac{X}{Y-X}\right)\times 8$ (b) $\left(\frac{Y-X}{X}\right)\times 8$

(c) $\left(\frac{Y+X}{X}\right)\times 8$ (d) $\frac{X}{Y}\times 8$

[**Ans.** (a)]

[**Hint:** Mass of oxygen in the oxide = $(Y-X)$

$\therefore$ 8 g oxygen will combine with $\frac{X}{Y-X}\times 8$ g metal.

$$\therefore \qquad E=\left(\frac{X}{Y-X}\right)\times 8]$$

6. $KMnO_4$ (m.w. = 158) oxidises oxalic acid in acid medium to CO_2 and water as follows:

$$5C_2O_4^{2-}+2MnO_4^-+16H^+\rightarrow 10CO_2+2Mn^{2+}+8H_2O$$

What is the equivalent weight of $KMnO_4$? **[CET (J&K) 2006]**

(a) 158 (b) 31.6 (c) 39.5 (d) 79

[**Ans.** (b)]

[**Hint:** MnO_4^- $\longrightarrow$ Mn^{2+}

(Oxidation number of Mn = + 7) (Oxidation number of Mn = + 2)

$$\text{Equivalent mass of } KMnO_4=\frac{\text{Molecular mass}}{\text{Change in oxidation number}}$$

$$=\frac{158}{5}=31.6]$$

7. The formula mass of Mohr's salt is 392. The iron present in it is oxidised by $KMnO_4$ in acid medium. The equivalent mass of Mohr's salt is:

(a) 392 (b) 31.6 (c) 278 (d) 156

[**Ans.** (a)]

[**Hint:** Formula of Mohr's salt: $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$

Oxidation of Fe^{2+} ions take place as:

$$5Fe^{2+}+MnO_4^-+8H^+\longrightarrow 5Fe^{3+}+Mn^{2+}+4H_2O$$

Change in oxidation number of Fe = + 3 − (+2) = + 1

$$\text{Equivalent mass of Mohr's salt}=\frac{\text{Molecular mass}}{\text{Change in oxidation number}}$$

$$=\frac{392}{1}=392]$$

8. In a redox reaction, dichromate ion ($Cr_2O_7^{2-}$) is reduced to Cr^{3+} ion, the equivalent mass of $K_2Cr_2O_7$ in this reaction is: **(EAMCET 2007)**

(a) $\frac{\text{molecular mass}}{3}$ (b) $\frac{\text{molecular mass}}{6}$

(c) $\frac{\text{molecular mass}}{1}$ (d) $\frac{\text{molecular mass}}{2}$

[**Ans.** (b)]

[**Hint:** $Cr_2O_7^{2-}+14H^++6e^-\longrightarrow 2Cr^{3+}+7H_2O$

Change in oxidation number = 6

$$\therefore \text{Equivalent mass}=\frac{\text{Molecular mass}}{6}]$$

14.5 ACID-BASE TITRATIONS

The determination of concentration of bases by titration with a standard acid is called **acidimetry** and the determination of concentration of acids by titration with a standard base is called **alkalimetry.**

The substances which give different colours with acids and bases are called acid-base indicators. These indicators are used in the visual detection of the equivalence point in acid-base titrations. The acid-base indicators are also called pH indicators because their colour change according to pH of the solution.

pH Range of Indicators

Indicators	pH range	Colour of indicator	
		Acid medium	Basic medium
Methyl orange	3.1 – 4.4	Red	Orange
Bromo phenol blue	3 – 4.6	Yellow	Blue
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5 – 8	Red	Blue
Bromo-thymol blue	6 – 7.6	Yellow	Blue
Phenol red	8.3 – 10	Colourless	Pink
Thymol phthalein	8.3 – 10.5	Colourless	Blue

In the selection of indicator for a titration, following two informations are taken into consideration:

(i) pH range of indicator.

(ii) pH change near the equivalence point in the titration.

The indicator whose pH range is included in the pH change of the solution near the equivalence point, is taken as suitable indicator for the titration.

(i) Strong acid-strong base titration: In the titration of HCl with NaOH, the equivalence point lies in the pH change of 4 –10. Thus, methyl orange, methyl red and phenolphthalein will be suitable indicators.

(ii) Weak acid-strong base titration: In the titration of CH_3COOH with NaOH the equivalence point lies between 7.5 and 10. Hence, phenolphthalein (8.3–10) will be the suitable indicator.

(iii) Weak base-strong acid titration: In the titration of NH_4OH (weak base) against HCl (strong acid), the pH at equivalence point is about 6.5 and 4. Thus, methyl orange (3.1–4.4) or methyl red (4.2–6.3) will be suitable indicators.

(iv) Weak acid-weak base titration: In the titration of a weak acid (CH_3COOH) with weak base (NH_4OH) the pH at the equivalence point is about 7, *i. e.*, lies between 6.5 and 7.5 but no sharp change in pH is observed in these titrations. Thus, no simple indicator can be employed for the detection of the equivalence point.

(v) Titration of a salt of a weak acid and a strong base with strong acid:

$$\underset{\text{Weak acid}}{H_2CO_3}+\underset{\text{Strong base}}{2NaOH}\longrightarrow Na_2CO_3+2H_2O$$

Na_2CO_3 when titrated with HCl, the following two stages are involved:

$$Na_2CO_3+HCl\longrightarrow NaHCO_3+NaCl \qquad \text{(First stage)}$$

pH = 8.3, near equivalence point

$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3$ (Second stage)
pH = 4, near equivalence point

For first stage, phenolphthalein and for second stage, methyl orange will be the suitable indicator.

14.6 TITRATION OF MIXTURE OF NaOH, Na_2CO_3 AND $NaHCO_3$ BY STRONG ACID LIKE HCl

In this titration the following indicators are mainly used:

(i) Phenolphthalein (weak organic acid): It shows colour change in the pH range (8–10).

(ii) Methyl orange (weak organic base): It shows colour change in the pH range (3.1–4.4). Due to lower pH range, it indicates complete neutralisation of whole of the base.

S.No.	Base	Phenolphthalein	Methyl orange
1.	NaOH	Shows complete neutralisation, $NaOH + HCl \rightarrow NaCl + H_2O$	Shows complete neutralisation, $NaOH + HCl \rightarrow NaCl + H_2O$
2.	Na_2CO_3	Shows half neutralisation due to following reaction: $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	Shows complete neutralisation, $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
3.	$NaHCO_3$	Shows no reaction	Show complete reaction, $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

Let for complete neutralisation of Na_2CO_3, $NaHCO_3$ and NaOH, x, y and z mL of standard HCl are required. The titration of the mixture may be carried by two methods as summarised below:

Mixture	Volume of HCl used with		Volume of HCl used	
	Phenolphthalein from beginning	Methyl orange from beginning	Phenolphthalein from beginning	Methyl orange after first end point
1. NaOH + Na_2CO_3	$z + (x/2)$	$(x + z)$	$z + \frac{x}{2}$	$x/2$ (for remaining 50% Na_2CO_3)
2. NaOH + $NaHCO_3$	$z + 0$	$(z + y)$	$(z + 0)$	y (for 100% remaining $NaHCO_3$)
3. Na_2CO_3 + $NaHCO_3$	$(x/2) + 0$	$(x + y)$	$(x/2) + 0$	$(x/2) + y$ (for remaining 50% of Na_2CO_3 and 100% $NaHCO_3$ are indicated)

SOME SOLVED EXAMPLES

Example 11. *What is the strength in g per litre of a solution of sulphuric acid, 12 mL of which neutralise 15 mL of N/10 sodium hydroxide solution?*

Solution: Applying $\underset{\text{(NaOH)}}{N_1V_1} = \underset{(H_2SO_4)}{N_2V_2}$

$$\frac{1}{10} \times 15 = N_2 \times 12$$

$$N_2 = \frac{15}{10 \times 12} = 0.125$$

Normality × Eq. mass = Strength (g/L)

Strength = 0.125 × 49 = 6.125 g/L

Example 12. *4.9 g of H_2SO_4 is present in 100 mL of the solution. What is the molarity of the solution? Calculate its normality also.*

Solution: Strength (g/L) of $H_2SO_4 = \frac{4.9}{100} \times 1000 = 49$

$$\text{Molarity} = \frac{\text{Strength}}{\text{Mol. mass}} = \frac{49}{98} = 0.5\,M$$

Normality = n × Molarity

$$n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2$$

Normality = 2 × 0.5 = 1.0

Hence, the H_2SO_4 solution is 1 N.

Example 13. *25 mL of N/10 caustic soda solution exactly neutralises 20 mL of an acid solution containing 7.875 g of acid per litre. Calculate the equivalent mass of the acid.*

Solution: $\underset{\text{(NaOH)}}{N_1V_1} = \underset{\text{(Acid)}}{N_2V_2}$

$$\frac{1}{10} \times 25 = N_2 \times 20$$

$$N_2 = \frac{25}{10 \times 20} = 0.125$$

Strength = Normality × Eq. mass

$$\text{Eq. mass of the acid} = \frac{7.875}{0.125} = 63.00$$

Example 14. *150 mL of N/10 HCl is required to react completely with 1.0 g of a sample of limestone. Calculate the percentage purity of calcium carbonate.*

Solution: $150\text{ mL}\,\frac{N}{10}\text{ HCl} \equiv 150\text{ mL}\,\frac{N}{10}\,CaCO_3$

$$\underset{\text{Mol. mass}}{CaCO_3} + \underset{\text{2g eq.}}{2HCl} \longrightarrow CaCl_2 + H_2O + CO_2$$

$$\text{Eq. mass of } CaCO_3 = \frac{40 + 12 + 48}{2} = \frac{100}{2} = 50$$

Mass of $CaCO_3$ present in 150 mL $N/10$ solution,

$$\left[N \times E \times \frac{V}{1000}\right] = 50 \times \frac{1}{10} \times \frac{150}{1000} = 0.75\text{ g}$$

$$\text{Purity} = \frac{0.75}{1} \times 100 = 75\%$$

Example 15. *0.63 g of dibasic acid was dissolved in water. The volume of the solution was made 100 mL. 20 mL of this acid solution required 10 mL $\frac{N}{5}$ NaOH solution. What is the equivalent mass and molecular mass of the acid?*

Solution: $$\underset{\text{(Acid)}}{N_1V_1} \equiv \underset{\text{(NaOH)}}{N_2V_2}$$

$$N_1 \times 20 = \frac{1}{5} \times 10$$

$$N_1 = \frac{1}{5} \times \frac{10}{20} = \frac{1}{10}$$

Strength of the acid solution = Eq. mass of the acid × Normality

$$= E \times \frac{1}{10} = \frac{E}{10}\ \text{g/L}$$

Mass of acid in 100 mL of the solution $= \frac{E}{10} \times \frac{100}{1000} = \frac{E}{100}$

Mass of acid in 100 mL of the solution = 0.63 g (given)

So, $\frac{E}{100} = 0.63$ or $E = 63$

Mol. mass = Basicity × Eq. mass

$= 2 \times 63 = 126$

Example 16. *10.875 g of a mixture of NaCl and Na_2CO_3 was dissolved in water and the volume made up to 250 mL, 20 mL of this solution required 75.5 mL of $\frac{N}{10}$ H_2SO_4. Find out the percentage composition of the mixture.*

Solution: Only Na_2CO_3 will react with H_2SO_4.

Applying $$\underset{(Na_2CO_3)}{N_1V_1} \equiv \underset{(H_2SO_4)}{N_2V_2}$$

$$N_1 \times 20 = 75.5 \times \frac{1}{10}$$

$$N_1 = \frac{75.5}{20 \times 10} = 0.3775$$

$$\underset{\text{1 mol. mass}}{Na_2CO_3} + \underset{\text{2g eq.}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O + CO_2$$

Eq. mass of $Na_2CO_3 = \frac{106}{2} = 53$

Mass of Na_2CO_3 present in 250 mL 0.3775 *N* solution

$$= \frac{N \times E \times V}{1000} = \frac{0.3775 \times 53 \times 250}{1000}$$

$$= 5.0018\ \text{g}$$

Mass of NaCl = (10.875 − 5.0018) = 5.8732 g

$$Na_2CO_3 = \frac{5.0018}{10.875} \times 100 = 45.99\%$$

$$NaCl = \frac{5.8732}{10.875} \times 100 = 54.0\%$$

Example 17. *A quantity of ammonium chloride was heated with 100 mL of 0.8 N NaOH solution till the reaction was complete. The excess of NaOH was neutralised with 12.5 mL of 0.75 N H_2SO_4. Calculate the quantity of ammonium chloride.*

Solution:

12.5 mL of 0.75 *N* H_2SO_4 ≡ 12.5 mL of 0.75 *N* NaOH

12.5 mL of 0.75 *N* NaOH ≡ 11.72 mL of 0.8 *N* NaOH

NaOH solution used by NH_4Cl

= (100 − 11.72) mL of 0.8 N NaOH

= 88.28 mL of 0.8 *N* NaOH

≡ 88.28 mL of 0.8 *N* NH_4Cl

Mass of NH_4Cl present in 88.28 mL of 0.8 *N* NH_4Cl solution

$$= \frac{N \times E \times V}{1000} = \frac{0.8 \times 53.5 \times 88.28}{1000} = 3.7783\ \text{g}$$

[Eq. mass of NH_4Cl = 53.5]

Example 18. *A sample of $Na_2CO_3 \cdot H_2O$ weighing 0.62 g is added to 100 mL of 0.1 N sulphuric acid. Will the resulting solution be acidic, basic or neutral? (At. mass H = 1, C = 12, O = 16, Na = 23, S = 32)*

Solution: Mass of $Na_2CO_3 \cdot H_2O$ = 0.62 g

$$\text{No. of g equivalents} = \frac{\text{Mass}}{\text{Eq. mass}} = \frac{0.62}{62} = 0.01$$

[Eq. mass of $Na_2CO_3 \cdot H_2O = \frac{124}{2} = 62$]

No. of g equivalents of H_2SO_4 in 100 mL $= \frac{0.1}{1000} \times 100$

$$= \frac{0.1}{10} = 0.01$$

Both the substances are present in same equivalent; they will completely neutralise each other and hence, the resulting solution will be neutral.

Example 19. *A solution containing 4.2 g of KOH and $Ca(OH)_2$ is neutralised by an acid. If it consumes 0.1 g equivalents of the acid, calculate the composition of the sample.*

Solution: Let mass of KOH be present in mixture = *a* g

and Mass of $Ca(OH)_2$ = (4.2 − *a*) g

Eq. mass of KOH = 56; Eq. mass of $Ca(OH)_2 = \frac{74}{2} = 37$

g equivalent of KOH + g equivalent of $Ca(OH)_2$

= g equivalent of the acid

$$\frac{a}{56} + \frac{(4.2 - a)}{37} = 0.1$$

or $37a - 56a = 0.1 \times 56 \times 37 - 4.2 \times 56$

or $19a = 28$

$$a = \frac{28}{19} = 1.47$$

Mass of KOH in the sample = 1.47 g

Percentage of KOH = 35

and Percentage of $Ca(OH)_2$ = 100 − 35 = 65

Example 20. *40 mL of HCl is exactly neutralised by 20 mL of NaOH solution. The resulting neutral solution is evaporated to dryness and the residue is found to have a mass of 0.117 g. Calculate the normality of the HCl and NaOH.*

Solution: $$\underset{\substack{36.5\\ \text{1g eq.}}}{HCl} + \underset{\substack{40\\ \text{1g eq.}}}{NaOH} \longrightarrow \underset{\substack{58.5\\ \text{1g eq.}}}{NaCl} + H_2O$$

$$\text{Mass of NaCl obtained} = 0.117\text{ g}$$

$$\text{Eq. mass of NaCl} = 58.5$$

$$\text{No. of g equivalents of NaCl} = \frac{0.117}{58.5} = 0.002$$

Thus, 0.002 g eq. of HCl will react with 0.002 g eq. of NaOH to form 0.002 g eq. NaCl.

$$\text{Normality of HCl} = \frac{0.002}{40} \times 1000 = 0.05\,N$$

$$\text{Normality of NaOH} = \frac{0.002}{20} \times 1000 = 0.10\,N$$

Example 21. *1.03 g mixture of sodium carbonate and calcium carbonate require 20 mL N HCl for complete neutralisation. Calculate the percentage of sodium carbonate and calcium carbonate in the given mixture.*

Solution: $\underset{106}{Na_2CO_3} + \underset{2\times 36.5}{2HCl} \longrightarrow 2NaCl + H_2O + CO_2$

$$\begin{array}{lll} \text{Eq. mass} & 53 & 36.5 \\ & 1\text{ g eq.} & 1\text{ g eq.} \end{array}$$

$$\underset{100}{CaCO_3} + \underset{2\times 36.5}{2HCl} \longrightarrow CaCl_2 + H_2O + CO_2$$

$$\begin{array}{lll} \text{Eq. mass} & 50 & 36.5 \\ & 1\text{ g eq.} & 1\text{ g eq.} \end{array}$$

Let x g $CaCO_3$ be present in the mixture.

$$\text{Mass of } Na_2CO_3 \text{ in the mixture} = (1.03 - x)\text{ g}$$

$$\text{No. of g equivalents of } CaCO_3 = \frac{x}{50}$$

$$\text{No. of g equivalents of } Na_2CO_3 = \frac{(1.03 - x)}{53}$$

$$\text{No. of g equivalents in 20 mL } N \text{ HCl} = \frac{\text{Normality} \times \text{Vol.}}{1000} = \frac{1 \times 20}{1000} = \frac{1}{50}$$

At equivalence point,

No. of g equivalents of $CaCO_3$ + No. of g equivalents of Na_2CO_3 = No. of gram equivalents of HCl

$$\frac{x}{50} + \frac{1.03 - x}{53} = \frac{1}{50}$$

or

$$x = 0.50$$

$$CaCO_3 = 0.50\text{ g}, \quad \%\,CaCO_3 = \frac{0.50}{1.03} \times 100 = 48.54$$

$$Na_2CO_3 = 0.53\text{ g}, \%\,Na_2CO_3 = \frac{0.53}{1.03} \times 100 = 51.46$$

Example 22. *1.325 g of anhydrous sodium carbonate are dissolved in water and the solution made up to 250 mL. On titration 25 mL of this solution neutralise 20 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid solution to make it exactly N/12?*

Solution: $\text{Eq. mass of } Na_2CO_3 = \frac{\text{Mol. mass}}{2} = \frac{106}{2} = 53$

250 mL of the sodium carbonate solution contains = 1.325 g

1000 mL of the sodium carbonate solution contains

$$= \frac{1.325\text{ g}}{250} \times 1000 = 5.300\text{ g}$$

$$\text{Normality of } Na_2CO_3 \text{ solution} = \frac{\text{Strength (g/L)}}{\text{Eq. mass}} = \frac{5.30}{53} = \frac{1}{10}\,N$$

Applying $\underset{(Na_2CO_3)}{N_1V_1} \equiv \underset{(H_2SO_4)}{N_2V_2}$

$$\frac{1}{10} \times 25 = N_2 \times 20$$

$$N_2 = \frac{25}{10 \times 20} = \frac{1}{8}$$

Applying $\underset{\text{(Before dilution)}}{N_BV_B} \equiv \underset{\text{(After dilution)}}{N_AV_A}$

$$\frac{1}{8} \times 450 = \frac{1}{12} \times V_A$$

$$V_A = \frac{450 \times 12}{8} = 675\text{ mL}$$

Water to be added for dilution = (675 − 450) = 225 mL

Example 23. *A sample of sodium carbonate contains sodium sulphate also. 1.5 g of the sample is dissolved in water and volume raised to 250 mL. 25 mL of this solution requires 20 mL of $\frac{N}{10}$ H_2SO_4 solution for neutralisation. Calculate the percentage of sodium carbonate in the sample.*

Solution: Only Na_2CO_3 will react with H_2SO_4.

Applying $\underset{(Na_2CO_3)}{N_1V_1} = \underset{(H_2SO_4)}{N_2V_2}$

$$N_1 \times 25 = 20 \times \frac{1}{10}$$

$$N_1 = \frac{20}{25 \times 10} = 0.08$$

$$\text{Eq. mass of } Na_2CO_3 = \frac{\text{Mol. mass}}{2} = \frac{106}{2} = 53$$

Mass of Na_2CO_3 present in 250 mL 0.08 N solution

$$= \frac{N \times E \times V}{1000} = \frac{0.08 \times 53 \times 250}{1000} = 1.06\text{ g}$$

$$\text{Percentage of } Na_2CO_3 \text{ in the mixture} = \frac{1.06}{1.50} \times 100 = 70.67$$

Example 24. *In a sample of sodium carbonate some sodium sulphate is also mixed. 1.25 g of this sample is dissolved and the volume made up to 250 mL. 25 mL of this solution neutralises 20 mL of $\frac{N}{10}$ sulphuric acid. Calculate the percentage of sodium carbonate in the sample.*

Solution: 25 mL of sample solution neutralises

$$= 20 \text{ mL } \frac{N}{10} H_2SO_4$$

250 mL of sample solution will neutralise

$$= 200 \text{ mL } \frac{N}{10} H_2SO_4$$

$$200 \text{ mL } \frac{N}{10} H_2SO_4 \equiv 200 \text{ mL } \frac{N}{10} Na_2CO_3 \text{ solution}$$

$$\text{Amount of } Na_2CO_3 \text{ present} = \frac{E \times N \times V}{1000}$$

$$= \frac{53 \times 200}{10 \times 1000} = 1.06$$

$$\% \text{ of } Na_2CO_3 \text{ in the sample} = \frac{1.06}{1.25} \times 100 = 84.8$$

Example 25. *1.725 g of a metal carbonate is mixed with 300 mL of $\frac{N}{10}$ HCl. 10 mL of $\frac{N}{2}$ sodium hydroxide were required to neutralise excess of the acid. Calculate the equivalent mass of the metal carbonate.*

Solution: 10 mL of $\frac{N}{2}$ NaOH solution

$$= 10 \text{ mL of } \frac{N}{2} \text{ HCl solution}$$

$$\equiv 50 \text{ mL of } \frac{N}{10} \text{ HCl solution}$$

$$\text{Volume of } \frac{N}{10} \text{ HCl used for neutralisation} = 300 - 50 = 250 \text{ mL}$$

$$250 \text{ mL of } \frac{N}{10} \text{ HCl} \equiv 250 \text{ mL of } \frac{N}{10} \text{ metal carbonate solution}$$

Let the equivalent mass of metal carbonate be E.
Mass of metal carbonate present in solution

$$= \frac{N \times E \times V}{1000} = 1.725$$

$$= \frac{1 \times E \times 250}{10 \times 1000} = 1.725$$

$$= \frac{E}{40} = 1.725$$

$$E = 40 \times 1.725 = 69$$

Example 26. *1.575 g of oxalic acid $(COOH)_2 \cdot xH_2O$ are dissolved in water and the volume made up to 250 mL. On titration 16.68 mL of this solution requires 25 mL of $\frac{N}{15}$ NaOH solution for complete neutralisation. Calculate x.*

Solution:

$$25 \text{ mL of } \frac{N}{15} \text{ NaOH solution} \equiv 25 \text{ mL of } \frac{N}{15} \text{ oxalic acid solution}$$

$$\text{Mass of oxalic acid present in 25 mL of } \frac{N}{15} \text{ oxalic acid solution}$$

$$= \frac{N \times E \times V}{1000} = \frac{1 \times (90 + 18x) \times 25}{15 \times 2 \times 1000}$$

$$= \frac{(90 + 18x)}{1200} \text{ g}$$

Actually $\frac{(90+18x)}{1200}$ g oxalic acid is present in 16.68 mL solution.

250 mL of the solution contains oxalic acid

$$= \frac{(90 + 18x) \times 250}{1200 \times 16.68} = 1.575 \text{ (given)}$$

$$\text{or} \quad 90 + 18x = \frac{1.575 \times 1200 \times 16.68}{250} = 126$$

$$\text{or} \quad 18x = 126 - 90 = 36$$

$$x = 2$$

Example 27. *25 mL of a mixture of NaOH and Na_2CO_3 when titrated with N/10 HCl using phenolphthalein indicator required 25 mL HCl. The same volume of mixture when titrated with N/10 HCl using methyl orange indicator required 30 mL of HCl. Calculate the amount of Na_2CO_3 and NaOH in one litre of this mixture.*

Solution: When phenolphthalein is the indicator, whole of NaOH has been neutralised and carbonate converted into bicarbonate, *i.e.*,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

So, 25 mL $\frac{N}{10}$ HCl ≡ NaOH + 1/2 Na_2CO_3 present in 25 mL of mixture

In another titration when methyl orange is the indicator, whole of NaOH has been neutralised and carbonate converted into carbonic acid, *i.e.*,

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2CO_3$$

$$30 \text{ mL } \frac{N}{10} \text{ HCl} \equiv NaOH + Na_2CO_3 \text{ present in 25 mL of mixture}$$

Hence,

$$(30 - 25) \text{ mL } \frac{N}{10} \text{ HCl} \equiv \frac{1}{2} Na_2CO_3 \text{ present in 25 mL of mixture}$$

Hence,

$$10 \text{ mL } \frac{N}{10} \text{ HCl} \equiv Na_2CO_3 \text{ present in 25 mL of mixture}$$

$$\equiv 10 \text{ mL } \frac{N}{10} Na_2CO_3 \text{ solution}$$

$$\text{Amount of } Na_2CO_3 = \frac{53 \times 10}{10 \times 1000} = 0.053 \text{ g}$$

This amount of Na_2CO_3 is present in 25 mL of mixture.

The amount present in one litre of mixture

$$= \frac{0.053}{25} \times 1000 = 2.12 \text{ g}$$

$$(30-10)\,\text{mL}\,\frac{N}{10}\,\text{HCl} \equiv \text{NaOH present in 25 mL mixture}$$

$$\equiv 20\ \text{mL}\ \frac{N}{10}\ \text{NaOH}$$

$$\text{Amount of NaOH in 25 mL of mixture} = \frac{40 \times 20}{10 \times 1000} = 0.08\ \text{g}$$

$$\text{The amount present in one litre of mixture} = \frac{0.08}{25} \times 1000 = 3.20\ \text{g}$$

Example 28. *25 mL of a mixture of* $NaOH + Na_2CO_3$, *when titrated with* $\frac{N}{10}$ *HCl using phenolphthalein indicator required 25 mL HCl to decolourise phenolphthalein. At this stage methyl orange was added and addition of acid was continued. The second end point was reached after further addition of 5 mL of the acid. Calculate the amount of* Na_2CO_3 *and NaOH in one litre of the solution.*

Solution: Between first and second end points,

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2CO_3$$

$$5\ \text{mL}\ \frac{N}{10}\ \text{HCl} \equiv \frac{1}{2}\ Na_2CO_3 \text{ present in 25 mL of a mixture}$$

$$\text{or } 10\ \text{mL}\ \frac{N}{10}\ \text{HCl} \equiv Na_2CO_3 \text{ present in 25 mL of a mixture}$$

$$\equiv 10\ \text{mL}\ \frac{N}{10}\ Na_2CO_3 = 0.053\ \text{g}\ Na_2CO_3$$

$$\text{Amount of } Na_2CO_3 \text{ in one litre of mixture} = \frac{0.053}{25} \times 1000$$

$$= 2.12\ \text{g}$$

$$(25-5)\,\text{mL}\,\frac{N}{10}\,\text{HCl} \equiv \text{NaOH present in 25 mL of mixture}$$

$$\equiv 25\ \text{mL}\ \frac{N}{10}\ \text{NaOH}$$

$$\equiv 0.08\ \text{g NaOH}$$

$$\text{Amount of NaOH in one litre of mixture} = \frac{0.08}{25} \times 1000$$

$$= 3.2\ \text{g}$$

Example 29. *A solution contains* Na_2CO_3 *and* $NaHCO_3$. *10 mL of the solution required 2.5 mL of 0.1 M* H_2SO_4 *for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M* H_2SO_4 *was required. Calculate the amount of* Na_2CO_3 *and* $NaHCO_3$ *in one litre of the solution.*

Solution: 2.5 mL of 0.1 M H_2SO_4 = 2.5 mL of 0.2 N H_2SO_4

$$= \frac{1}{2}\ Na_2CO_3 \text{ present in 10 mL of mixture}$$

So,

5 mL of 0.2 N H_2SO_4 = Na_2CO_3 present in 10 mL of mixture

$$\equiv 5\ \text{mL of } 0.2\ N\ Na_2CO_3$$

$$\equiv \frac{0.2 \times 53}{1000} \times 5 = 0.053\ \text{g}$$

$$\text{Amount of } Na_2CO_3 = \frac{0.053}{10} \times 1000 = 5.3\ \text{g/L of mixture}$$

Between first and second end points,

= 2.5 mL of 0.2 M H_2SO_4 used

= 2.5 mL of 0.4 N H_2SO_4 used

= 5 mL of 0.2 N H_2SO_4 used

$$\equiv \frac{1}{2}\ Na_2CO_3 + NaHCO_3 \text{ present in 10 mL of mixture}$$

$$(5-2.5)\,\text{mL}\ 0.2\ N\ H_2SO_4$$

$$\equiv NaHCO_3 \text{ present in 10 mL of mixture}$$

$$\equiv 2.5\ \text{mL}\ 0.2\ N\ NaHCO_3$$

$$\equiv \frac{0.2 \times 84}{1000} \times 2.5 = 0.042\ \text{g}$$

$$\text{Amount of } NaHCO_3 = \frac{0.042}{10} \times 1000 = 4.20\ \text{g/L of mixture.}$$

Example 30. *Calculate the normality of a solution obtained by mixing 100 mL* $\frac{N}{10}$ H_2SO_4, *50 mL* $\frac{N}{2}$ HNO_3 *and 25 mL* $\frac{N}{5}$ *HCl solutions.*

Solution: Let the final normality be N.

Total volume = (100 + 50 + 25) = 175 mL

So,
$$175 \times N = \underset{(H_2SO_4)}{N_1V_1} + \underset{(HNO_3)}{N_2V_2} + \underset{(HCl)}{N_3V_3}$$

$$= \left(100 \times \frac{1}{10}\right) + \left(50 \times \frac{1}{2}\right) + \left(25 \times \frac{1}{5}\right)$$

$$= (10 + 25 + 5) = 40$$

$$N = \frac{40}{175} = 0.2286$$

Hence, normality of solution = 0.2286 N

Example 31. *0.5 g of fuming* H_2SO_4 *(oleum) is diluted with water. This solution is completely neutralised by 26.7 mL of 0.4 N NaOH. Find the percentage of free* SO_3 *in the sample solution.*

Solution: Oleum consists of SO_3 and H_2SO_4.

Let the mass of SO_3 in the given sample of oleum be = x g

Mass of H_2SO_4 in the given sample of oleum = $(0.5 - x)$ g

$$\text{Eq. mass of } SO_3 = \frac{80}{2} = 40$$

$$\text{No. of g equivalents of } SO_3 = \frac{x}{40}$$

$$[2NaOH + SO_3 \longrightarrow Na_2SO_4 + H_2O$$
$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O]$$

$$\text{Eq. mass of } H_2SO_4 = \frac{98}{2} = 49$$

$$\text{No. of g equivalents of } H_2SO_4 = \frac{(0.5 - x)}{49}$$

$$\text{Total no. of g equivalents} = \frac{x}{40} + \frac{(0.5-x)}{49}$$

26.7 mL of 0.4 N NaOH contain no. of equivalents of NaOH

$$= \frac{0.4}{1000} \times 26.7$$

At equivalence point,

$$\text{No. of g equivalents of NaOH} = \frac{x}{40} + \frac{(0.5-x)}{49}$$

So, $$\frac{0.4 \times 26.7}{1000} = \frac{49x + (40 \times 0.5 - 40x)}{40 \times 49}$$

$$x = \frac{0.9328}{9} = 0.1036$$

$$\text{Hence, \% of free } SO_3 = \frac{0.1036}{0.5} \times 100$$

$$= 20.72$$

Example 32. *0.789 g of crystalline barium hydroxide is dissolved in water. For the neutralisation of this solution, 20 mL of* $\frac{N}{4}$ *HNO_3 is required. How many molecules of water are present in one g mole of this base? ($Ba = 137.4$, $O = 16$, $N = 14$, $H = 1$)*

Solution: Let the molecular formula be $Ba(OH)_2 \cdot xH_2O$

$$\text{Mol. mass of } Ba(OH)_2 \cdot xH_2O = 137.4 + (2 \times 16) + 2 \times 1 + 18x$$

$$= 171.4 + 18x$$

$$\text{Eq. mass of } Ba(OH)_2 \cdot xH_2O = \frac{171.4 + 18x}{2}$$

$$20 \text{ mL } \frac{N}{4} HNO_3 \equiv 20 \text{ mL } \frac{N}{4} Ba(OH)_2 \cdot xH_2O$$

$$\text{Amount of } Ba(OH)_2 \cdot xH_2O = \frac{(171.4 + 18x)}{2 \times 4} \times \frac{20}{1000}$$

$$= \frac{171.4 + 18x}{400} \text{ g}$$

$$\text{Amount of } Ba(OH)_2 \cdot xH_2O = 0.789 \text{ g}$$

Hence, $$\frac{171.4 + 18x}{400} = 0.789$$

or $$171.4 + 18x = 0.789 \times 400$$

$$x = \frac{144.2}{18} = 8.01 \approx 8$$

Thus, 8 g moles of water molecules are present in one g mole of the base.

Example 33. *A piece of aluminium weighing 2.7 g is heated with 75 mL of H_2SO_4 (sp. gr. 1.18, containing 24.7% H_2SO_4 by mass). After the metal is carefully dissolved, the solution is diluted to 400 mL. Calculate the molarity of the free H_2SO_4 in the resulting solution.*

Solution: $$\text{Mass of } H_2SO_4 = \frac{24.7}{100} \times 75 \times 1.18$$

$$= 21.8595 \text{ g}$$

$$\text{Reaction}: \quad \underset{2 \times 27}{2Al} + \underset{3 \times 98}{3H_2SO_4} \longrightarrow Al_2(SO_4)_3 + 3H_2$$

H_2SO_4 required for dissolving 2.7 g Al

$$= \frac{3 \times 98}{2 \times 27} \times 2.7 = 14.7 \text{ g}$$

H_2SO_4 left unreacted = (21.895 − 14.7) g = 7.1595 g

7.1595 g H_2SO_4 is present in 400 mL

$$\text{Amt. of } H_2SO_4 \text{ present in one litre} = \frac{7.1595}{400} \times 1000 \text{ g}$$

$$= 17.898 \text{ g}$$

$$\text{No. of g moles of } H_2SO_4 = \frac{17.898}{98} = 0.1826$$

Hence, molarity of $H_2SO_4 = 0.1826\ M$

Example 34. *0.50 g of a mixture of K_2CO_3 and Li_2CO_3 requires 30 mL of a 0.25 N HCl solution for neutralisation. What is the percentage composition of the mixture?*

Solution: $$\begin{array}{lcccl} & K_2CO_3 & + & 2HCl & \longrightarrow 2KCl + H_2O + CO_2 \\ & 138 & & 2 \times 36.5 & \\ \text{Eq. mass} & 69 & & 36.5 & \end{array}$$

$$\begin{array}{lcccl} & Li_2CO_3 & + & 2HCl & \longrightarrow 2LiCl + H_2O + CO_2 \\ & 74 & & 2 \times 36.5 & \\ \text{Eq. mass} & 37 & & 36.5 & \end{array}$$

Let x g of K_2CO_3 be present in the mixture.

$$\text{Mass of } Li_2CO_3 = (0.50 - x)$$

$$\text{No. of g equivalents of } K_2CO_3 = \frac{x}{69}$$

$$\text{No. of g equivalents of } Li_2CO_3 = \frac{(0.50 - x)}{37}$$

No. of g equivalents in 30 mL of 0.25 N HCl

$$= \frac{\text{Normality} \times \text{Volume}}{1000} = \frac{0.25 \times 30}{1000}$$

$$= \frac{3}{400}$$

At equivalence point,

$$\frac{x}{69} + \frac{(0.50 - x)}{37} = \frac{3}{400}$$

So, $$x = 0.48$$

$$K_2CO_3 = 0.48 \text{ g; or } 96\%$$

$$Li_2CO_3 = 0.02 \text{ g; or } 4\%$$

Example 35. *5 mL of 8 N nitric acid, 4.8 mL of 5 N hydrochloric acid and a certain volume of 17 M sulphuric acid are mixed together and made up to 2 litres. Thirty mL of this acid mixture exactly neutralise 42.9 mL of sodium carbonate solution containing one gram of $Na_2CO_3 \cdot 10H_2O$ in 100 mL of water. Calculate the amount in grams of the sulphate ions in solution.*

Solution: Molecular mass of $Na_2CO_3 \cdot 10H_2O = 286$

$$\text{Equivalent mass of } Na_2CO_3 \cdot 10H_2O = \frac{286}{2} = 143$$

100 mL solution of sodium carbonate contains = 1 g
1000 mL solution of sodium carbonate contains = 10 g

$$\text{Normality of the solution} = \frac{10}{143}$$

Applying the formula,
Normality of acid solution × its volume
= Normality of sodium carbonate solution × its volume,

$$\text{Normality of the acid solution} = \frac{10 \times 42.9}{143 \times 30} = 0.1$$

Let V mL be the volume of H_2SO_4 taken.

$$8 \times 5 + 4.8 \times 5 + 34 \times V = 0.1 \times 2000$$

$$V = 4 \text{ mL}$$

$$\text{Amount of } SO_4^{2-} = \frac{\text{Normality} \times \text{Eq. mass} \times \text{Volume}}{1000}$$

$$= \frac{34 \times 48 \times 4}{1000} = 6.528 \text{ g}$$

Example 36. *2.26 g of an ammonium salt were treated with 100 mL of normal NaOH solution and boiled till no more of ammonia gas was given off. The excess of NaOH solution left over required 60 mL normal sulphuric acid. Calculate the percentage of ammonia in the salt.*

Solution: 60 mL normal $H_2SO_4 \equiv$ 60 mL normal NaOH

Thus, (100 − 60) mL normal NaOH were consumed by ammonium salt.

So, 40 mL normal NaOH ≡ 40 mL normal NH_3

Amount of NH_3 in 40 mL normal NH_3

$$= \frac{\text{Eq. mass of } NH_3 \times 40}{1000}$$

$$= \frac{17 \times 40}{1000} = 0.68$$

$$\text{So, \% of ammonia in the ammonium salt} = \frac{0.68}{2.26} \times 100$$

$$= 30.09$$

Example 37. *10 mL of a solution containing sulphuric acid and hydrochloric acid required 16 mL $\frac{N}{8}$ caustic soda solution for neutralisation. On adding excess of barium chloride to 20 mL of the same solution of the mixture of the two acids it gives 0.3501 g barium sulphate. What is the amount of hydrochloric acid per litre in the mixture of acids? (Ba = 137.4, S = 32, O = 16, Cl = 35.5)*

Solution: Mol. mass of $BaSO_4$ = (137.4 + 32 + 64) = 233.4

$$\underset{98\text{ g}}{H_2SO_4} + BaCl_2 \longrightarrow \underset{233.4\text{ g}}{BaSO_4} + 2HCl$$

233.4 g of $BaSO_4$ is obtained from = 98 g of H_2SO_4

$$0.3501 \text{ g of } BaSO_4 \text{ is obtained from} = \frac{98}{233.4} \times 0.3501$$

$$= 0.147 \text{ g of } H_2SO_4$$

20 mL of acid mixture contains 0.147 g of H_2SO_4

So, 10 mL of acid mixture contains 0.0735 g of H_2SO_4

Amount of NaOH in 16 mL $\frac{N}{8}$ NaOH solution

$$= \frac{E \times N \times V}{1000}$$

$$= \frac{40 \times 16}{8 \times 1000} = 0.08 \text{ g}$$

$$\underset{98\text{ g}}{H_2SO_4} + \underset{2 \times 40 = 80\text{ g}}{2NaOH} \longrightarrow Na_2SO_4 + 2H_2O$$

Thus, 98 g of H_2SO_4 require = 80 g of NaOH

$$0.0735 \text{ g of } H_2SO_4 \text{ will require} = \frac{80}{98} \times 0.0735 \text{ g of NaOH}$$

$$= 0.06 \text{ g of NaOH}$$

Let the amount of HCl in 10 mL acid mixture be = x g

$$\underset{36.5\text{ g}}{HCl} + \underset{40\text{ g}}{NaOH} \longrightarrow NaCl + H_2O$$

36.5 g HCl require = 40 g of NaOH

$$x \text{ g HCl will require} = \frac{40}{36.5} x \text{ g of NaOH}$$

$$= 1.0958x \text{ g of NaOH}$$

$$1.0958x + 0.06 = 0.08$$

$$x = \frac{(0.08 - 0.06)}{1.0958} = 0.01825 \text{ g}$$

Amount of HCl present in one litre of the acid solution

$$= \frac{0.01825 \times 1000}{10} = 1.825$$

Example 38. *A small amount of $CaCO_3$ completely neutralises 525 mL of 0.1 N HCl and no acid is left in the end. After converting all calcium chloride to $CaSO_4$, how much plaster of Paris can be obtained?* **(Dhanbad 1991)**

Solution:

525 mL of 0.1 N HCl = 525 mL of 0.1 N $CaCl_2$
= 525 mL of 0.1 N plaster of Paris

$$\text{Molecular mass of plaster of Paris} = CaSO_4 \cdot \tfrac{1}{2} H_2O = 145$$

$$\text{Equivalent mass of plaster of Paris} = \frac{145}{2} = 72.5$$

Mass of plaster of Paris in 525 mL of 0.1 N solution

$$= \frac{N \times E \times V}{1000} = \frac{0.1 \times 72.5 \times 525}{1000}$$

$$= 3.806 \text{ g}$$

Example 39. *25 mL of 0.107 M H_3PO_4 was titrated with 0.115 M solution of NaOH to the end point identified by indicator bromocresol green. This required 23.1 mL. The titration was repeated using phenolphthalein as indicator. This time 25 mL of 0.107 M H_3PO_4 required 46.2 mL of the 0.115 M NaOH. What is the coefficient 'n' in the following reaction?*

$$H_3PO_4 + nOH^- \longrightarrow [H_{3-n}PO_4]^{n-} + nH_2O$$

Solution: Number of milliequivalents of H_3PO_4

$$= 25 \times 0.107 \times n$$
$$= 2.675 \times n$$

In first titration: Number of milliequivalents of OH^- used

$$= 23.1 \times 0.115 \times 1 = 2.66$$

(Acidity of NaOH = 1)

In second titration: Number of milliequivalents of OH^- used

$$= 46.2 \times 0.115 \times 1 = 5.313$$

$\therefore$ In first titration: $2.675 \times n = 2.66$

i.e., $n = 1$

$\therefore$ In second titration: $2.675 \times n = 5.313$

$$n = 2$$

Example 40. *11.2 g carbon reacts completely with 19.63 litre O_2 at NTP. The cooled gases are passed through 2 litre of 2.5 N NaOH solution. Calculate concentration of remaining NaOH and Na_2CO_3 in solution. (CO does not react with NaOH under these conditions.)*

Solution: Let x moles of carbon be converted into CO and y moles of carbon be converted into CO_2.

$$\underset{x}{C} + \underset{x/2}{\tfrac{1}{2}O_2} \longrightarrow CO$$

$$\underset{y}{C} + \underset{y}{O_2} \longrightarrow CO_2$$

Total volume of oxygen used $= \frac{x}{2} \times 22.4 + y \times 22.4$

$$= 19.63$$

$$11.2x + 22.4y = 19.63 \qquad \text{... (i)}$$

$$x + y = \frac{11.2}{12};\ i.e., 12x + 12y = 11.2 \qquad \text{... (ii)}$$

Solving eqs. (i) and (ii), we get

$$x = 0.11,\ y = 0.82$$

Number of moles of CO_2 formed = 0.82

Number of milliequivalents of NaOH solution through which CO_2 is massed $= N \times V = 2.5 \times 2000 = 5000$

Number of milliequivalents of CO_2 passed $= 0.82 \times 2 \times 1000$

$$= 1640$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Number of milliequivalents of $Na_2CO_3 = 1640$

$$N_{Na_2CO_3} = \frac{1640}{2000} = 0.82$$

Number of milliequivalents of remaining NaOH

$$= 5000 - 1640 = 3360$$

Normality of remaining NaOH $= \frac{3360}{2000} = 1.68$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

9. How many grams of $NaHCO_3$ are required to neutralise 1 mL of 0.0902 N vinegar?

(a) 8.4×10^{-3} g (b) 1.5×10^{-3} g

(c) 0.758×10^{-3} g (d) 1.07×10^{-3} g

[Ans. (c)]

[Hint: Number of equivalents of $NaHCO_3$

$$= \text{Number of equivalents of acid}$$
$$= \frac{NV}{1000} = \frac{0.0902 \times 1}{1000}$$

Mass of $NaHCO_3 = \frac{0.0902 \times 1 \times 84}{1000}$

$$= 0.758 \times 10^{-3}\ \text{g}]$$

10. 0.7 g of $Na_2CO_3 \cdot xH_2O$ was dissolved in water and the volume made up to 100 mL, 20 mL of it required 19.8 mL of $\frac{N}{10}$ HCl for complete neutralisation. The value of x is:

(a) 7 (b) 3

(c) 2 (d) 5

[Ans. (c)]

[Hint: Number of milliequivalents of $Na_2CO_3 \cdot xH_2O$ in 20 mL

$$= 19.8 \times \frac{1}{10}$$
$$= 1.98$$

$\therefore$ Number of milliequivalents in 100 mL $= 1.98 \times 5 = 9.9$

$$\frac{\text{Mass}}{\text{Equivalent mass}} \times 1000 = 9.9$$

$$\frac{0.7}{M/2} \times 1000 = 9.9$$

$$M = 141.40$$

(Molar mass of $Na_2CO_3 \cdot xH_2O$)

$$106 + 18x = 141.40$$
$$x = 2]$$

11. Calculate the equivalent mass of Na_2CO_3 when it is titrated against HCl in presence of phenolphthalein.

(a) 106 (b) 53

(c) 26.5 (d) 212

[Ans. (a)]

[Hint: The reaction involved is,

$$Na_2CO_3 + HCl \longrightarrow NaCl + NaHCO_3$$

Equivalent mass of $Na_2CO_3 = \frac{106}{1} = 106]$

12. 1 mol H_2SO_4 will exactly neutralise:

(a) 2 mol of ammonia (b) 1 mol of $Ba(OH)_2$

(c) 0.5 mol of $Ba(OH)_2$ (d) 2 mol of KOH

[Ans. (a, b, d)]

[Hint: $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$$Ba(OH)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2H_2O$$
$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O]$$

13. Which of the following gives equivalent mass of Na_2CO_3 when titrated against HCl in the presence of methyl orange?

(a) 5.3 (b) 53
(c) 10.6 (d) 106
[**Ans.** (b)]

[**Hint:** $Na_2CO_3 + 2HCl \xrightarrow{\text{Methyl orange}} 2NaCl + H_2O + CO_2$
Equivalent mass = molecular mass/2 = 106/2 = 53]

14.7 REDOX TITRATIONS

Oxidimetry: The determination of the strength of a solution of a reducing agent by titration with a standard solution of an oxidising agent is called oxidimetry.

Reductimetry: The determination of the strength of a solution of an oxidising agent by titration with standard solution of reducing agent is called reductimetry.

(Species) Oxidising Agent (OA) Or Reducing Agent (RA)	Reaction involved	Change in oxidation number Or Number of electrons involved	Equivalent mass
MnO_4^- (Acidic medium OA)	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	5	M.w./5
MnO_4^- (Neutral medium OA)	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	3	M.w./3
MnO_4^- (Basic medium OA)	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	1	M.w./1
H_2O_2 (OA)	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	2	M.w./2
H_2O_2 (RA)	$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	2	M.w./2
$S_2O_3^{2-}$ (RA)	$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$	1 (per molecule)	M.w./1
Cl_2 (OA) (Obtained from bleaching powder)	$Cl_2 + 2e^- \rightarrow 2Cl^-$	2	M.w./2
$Cr_2O_7^{2-}$ (OA)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	6	M.w./6
MnO_2 (OA)	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+}$	2	M.w./2
Fe^{2+} (RA)	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	1	M.w./1

Equivalent Mass of Substance Undergoing Disproportionation

Let us consider, disproportionation of H_3PO_2.

$$3H_3\overset{+1}{P}O_2 \longrightarrow 2H_3\overset{+3}{P}O_3 + \overset{-3}{P}H_3$$

−2*e* oxidation

$+4e^-$

Reduction

$$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{4 \times 2}{4+2} = \frac{4}{3}$$

$$\text{Equivalent mass of } H_3PO_2 = \frac{\text{Molecular mass}}{n\text{-factor}} = \frac{m}{4/3} = \frac{3m}{4}$$

14.8 IODOMETRIC AND IODIMETRIC TITRATIONS

(Titrating solution is $Na_2S_2O_3 \cdot 5H_2O$ called hypo.)

(i) *Estimation of* I_2:

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Eq. mass of $Na_2S_2O_3 \cdot 5H_2O$ = M. w./1

(ii) *Estimation of* $CuSO_4$:

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

Eq. mass of $CuSO_4$ = M. w./1

(iii) *Estimation of* MnO_2 *present in pyrolusite:*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

or $$MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$$

$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$$

Eq. mass of MnO_2 = M. w./2

(iv) *Estimation of available chlorine in bleaching powder:*

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

Eq. mass of $CaOCl_2$ = M. w./2

(v) *Estimation of* H_2O_2:

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$$

Eq. mass of H_2O_2 = M. w./2

(vi) *Estimation of ozone:*

$$O_3 + 6I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Eq. mass of O_3 = M. w./6

(vii) *Estimation of* $Cr_2O_7^{2-}$:

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

Eq. mass of $Cr_2O_7^{2-}$ = M. w./6

(viii) *Estimation of* ClO^-:

$$ClO^- + 2I^- + 2H^+ \longrightarrow H_2O + Cl^- + I_2$$

Eq. mass of ClO^- = M. w./2

(ix) *Estimation of* IO_3^-:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Eq. mass of IO_3^- = M. w./5

SOME SOLVED EXAMPLES

Example 41. *0.5 g of an oxalate was dissolved in water and the solution made to 100 mL. On titration 10 mL of this solution required 15 mL of* $\frac{N}{20}$ *$KMnO_4$. Calculate the percentage of oxalate in the sample.*

Solution:

$$15 \text{ mL } \frac{N}{20} KMnO_4 = 10 \times \text{Normality of oxalate solution.}$$

$$\text{Normality of oxalate solution} = \frac{15}{10} \times \frac{1}{20} = \frac{3}{40}$$

Strength of oxalate solution = Normality × Eq. mass of oxalate

$$= \frac{3}{40} \times 44 = 3.3 \text{ g/L} \quad \left[\text{Eq. mass of } C_2O_4^{2-} = \frac{88}{2} = 44\right]$$

$$\text{Amount of oxalate in 100 mL solution} = \frac{3.3}{1000} \times 100 = 0.33 \text{ g}$$

$$\% \text{ of oxalate} = \frac{0.33}{0.5} \times 100 = 66.0$$

Example 42. *How many mL of a 0.05 M $KMnO_4$ solution are required to oxidise 2.0 g of $FeSO_4$ in a dilute solution (acidic)?*

Solution:

$$\underset{10 \times 151.8}{10FeSO_4} + \underset{2 \times 158}{2KMnO_4} + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

10×151.8 g of $FeSO_4$ require $KMnO_4 = 2 \times 158$ g

$$2 \text{ g of } FeSO_4 \text{ will require } KMnO_4 = \frac{2 \times 158 \times 2}{10 \times 151.8} \text{ g}$$

Suppose, V mL of $KMnO_4$ solution (0.05 M) is required.

$$\text{Amount of } KMnO_4 \text{ in this solution} = \frac{158 \times 0.05}{1000} \times V$$

Thus,

$$\frac{158 \times 0.05 \times V}{1000} = \frac{2 \times 158 \times 2}{10 \times 151.8}$$

$$V = 52.7 \text{ mL}$$

Example 43. *5.5 g of a mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ required 5.4 mL of 0.1 N $KMnO_4$ solution for complete oxidation. Calculate the gram mole of hydrated ferric sulphate in the mixture.*

(At. mass $H = 1, O = 16, S = 32, Fe = 56$)

Solution: Only $FeSO_4 \cdot 7H_2O$ will be oxidised by $KMnO_4$.

$$\text{Mol. mass of } FeSO_4 \cdot 7H_2O = 278$$

As the conversion involves one electron,

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-,$$

$$\text{The eq. mass of } FeSO_4 \cdot 7H_2O = \frac{278}{1} = 278$$

5.4 mL of 0.1 N $KMnO_4$

$\equiv$ 5.4 mL of 0.1 N $FeSO_4 \cdot 7H_2O$ solution

$$\text{Amount of } FeSO_4 \cdot 7H_2O = \frac{0.1 \times 278}{1000} \times 5.4 = 0.15 \text{ g}$$

Amount of $Fe_2(SO_4)_3 \cdot 9H_2O = (5.5 - 0.15) = 5.35$ g

Mol. mass of $Fe_2(SO_4)_3 \cdot 9H_2O = 562$

$$\text{No. of g moles of } Fe_2(SO_4)_3 \cdot 9H_2O = \frac{\text{Mass}}{\text{Mol. mass}}$$

$$= \frac{5.35}{562} = 0.00952$$

$$= 9.52 \times 10^{-3}$$

Example 44. *0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required 100 cm³ of 0.15 N sodium thiosulphate solution for titration. Find the per cent amount of each in the mixture.* (IIT 1995)

Solution: Let 'a' g of $K_2Cr_2O_7$ be present in the mixture.

$$\text{Mass of } KMnO_4 = (0.5 - a) \text{ g}$$

$$\text{Eq. mass of } K_2Cr_2O_7 = \frac{\text{Mol. mass}}{6} = \frac{294}{6} = 49.0$$

$$\text{Eq. mass of } KMnO_4 = \frac{\text{Mol. mass}}{5} = \frac{158}{5} = 31.6$$

$$\text{No. of equivalents of } K_2Cr_2O_7 = \frac{a}{49.0}$$

$$\text{No. of equivalents of } KMnO_4 = \frac{(0.5 - a)}{31.6}$$

No. of equivalents of $Na_2S_2O_3$ in 100 cm³ of 0.15 N solution

$$= \frac{100 \times 0.15}{1000} = 0.015$$

Equivalents of $K_2Cr_2O_7$ + Equivalents of $KMnO_4$

$\equiv$ Equivalents of iodine

$\equiv$ Equivalents of $Na_2S_2O_3$

$$\frac{a}{49.0} + \frac{(0.5 - a)}{31.6} = 0.015$$

$$17.4a = 1.274$$

$$a = 0.0732$$

$$\% \text{ of } K_2Cr_2O_7 = \frac{0.0732 \times 100}{0.5} = 14.64$$

$$\% \text{ of } KMnO_4 = 85.36$$

Example 45. *Calculate the percentage of available chlorine in a given sample of bleaching powder from the following data:*

3.55 g of bleaching powder when treated with acetic acid and xcess of KI liberated iodine which required 60 mL of 0.5 N odium thiosulphate solution.

Solution: $60 \text{ mL } 0.5\,N\ Na_2S_2O_3 \equiv 60 \text{ mL } 0.5\,N\ I_2$

$$\equiv 60 \text{ mL } 0.5\,N\ Cl_2$$

$$\text{Amount of chlorine} = \frac{35.5 \times 0.5}{1000} \times 60 = 1.065 \text{ g}$$

$$\% \text{ available chlorine} = \frac{1.065}{3.55} \times 100 = 30.0$$

Example 46. *0.261 g of a sample of pyrolusite was heated with excess of HCl and the chlorine evolved was passed in a solution of KI. The liberated iodine required 90 mL $\frac{N}{30}$ $Na_2S_2O_3$. Calculate the percentage of MnO_2 in the sample.*

Solution: $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

$$2KI + Cl_2 \longrightarrow 2KCl + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$90 \text{ mL } \frac{N}{30}\, Na_2S_2O_3 \equiv 90 \text{ mL } \frac{N}{30}\, I_2$$

$$\equiv 90 \text{ mL } \frac{N}{30}\, Cl_2$$

$$\equiv 90 \text{ mL } \frac{N}{30}\, MnO_2$$

$$\text{Eq. mass of } MnO_2 = \frac{\text{Mol. mass}}{2} = \frac{87}{2}$$

[Since, change in O.N. is from 4 to 2]

$$\text{Amount of } MnO_2 = \frac{87}{2 \times 30} \times \frac{90}{1000} = 0.1305 \text{ g}$$

$$\% \text{ of } MnO_2 = \frac{0.1305}{0.261} \times 100 = 50$$

Example 47. (*i*) *What is the mass of sodium bromate and molarity of the solution necessary to prepare 85.4 mL of 0.672 N solution when the half reaction is,*

$$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$$

(*ii*) *What would be the mass as well as molarity if the half cell reaction is,*

$$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$$

Solution:

(i) Molecular mass of $NaBrO_3 = 23 + 80 + (3 \times 16) = 151$

Each bromate ion takes-up 6 electrons; therefore,

$$\text{Eq. mass of } NaBrO_3 = \frac{\text{Mol. mass}}{6} = \frac{151}{6}$$

Amount of $NaBrO_3$ in 85.5 mL 0.672 N solution

$$= \frac{0.672}{1000} \times \frac{151}{6} \times 85.5 = 1.446 \text{ g}$$

$$\text{Molarity} = \frac{\text{Normality}}{n} = \frac{0.672}{6} = 0.112\,M$$

(ii) Each bromate ion takes-up 5 electrons; therefore,

$$\text{Eq. mass of } NaBrO_3 = \frac{\text{Mol. mass}}{5} = \frac{151}{5}$$

Amount of $NaBrO_3$ in 85.5 mL 0.672 N solution

$$= \frac{151}{5} \times \frac{0.672}{1000} \times 85.5$$

$$= 1.7352 \text{ g}$$

$$\text{Molarity} = \frac{\text{Normality}}{n} = \frac{0.672}{5} = 0.1344\,M$$

Example 48. *50 mL of an aqueous solution of H_2O_2 was treated with an excess of KI solution and dilute H_2SO_4. The liberated iodine required 20 mL 0.1 N $Na_2S_2O_3$ solution for complete interaction. Calculate the concentration of H_2O_2 in g/L.*

Solution: $H_2O_2 + 2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + I_2$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$\text{Eq. mass } H_2O_2 = \frac{34}{2} = 17$$

$$20 \text{ mL } 0.1\,N\ Na_2S_2O_3 = 20 \text{ mL } 0.1\,N\ I_2 \text{ solution}$$

$$\equiv 20 \text{ mL } 0.1\,N\ H_2O_2 \text{ solution}$$

Amount of H_2O_2 in 50 mL *aq.* solution

$$= \frac{0.1 \times 17}{1000} \times 20 = 0.034 \text{ g}$$

$$\text{Concentration in g/L} = \frac{0.034}{50} \times 1000 = 0.68$$

Example 49. *0.124 g of iron wire was dissolved in dilute H_2SO_4 in oxygen free atmosphere and the resultant solution was titrated against 0.09672 N solution of $KMnO_4$. The titre value was 22.90 mL. Calculate the percentage purity of iron wire.*

Solution:

$$22.90 \text{ mL } 0.09672\,N\ KMnO_4 \equiv 22.90 \text{ mL } 0.09672\,N\ FeSO_4$$

$$\text{Amount of } FeSO_4 \text{ in the solution} = \frac{0.09672 \times 152 \times 22.90}{1000}$$

$$= 0.3366 \text{ g}$$

$$\text{Amount of iron in 0.3366 g of } FeSO_4 = \frac{56}{152} \times 0.3366$$

$$= 0.124 \text{ g}$$

Thus, $\text{percentage} = \frac{0.124}{0.124} \times 100 = 100$

The iron wire is 100% pure.

Example 50. *A sample of hydrazine sulphate ($N_2H_6SO_4$) was dissolved in 100 mL of water. 10 mL of this solution was* *reacted with excess of $FeCl_3$ solution and warmed to complete the reaction. Ferrous ion formed was estimated and it required 20 mL of $\frac{M}{50}$ $KMnO_4$. Estimate the amount of hydrazine sulphate in one litre of solution.*

Reactions: $4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Solution: $20\text{ mL}\ \frac{M}{50}\ \text{KMnO}_4 = 20\text{ mL}\ \frac{N}{10}\ \text{KMnO}_4$

$$\left[\text{Equivalent mass of KMnO}_4 = \frac{\text{Molecular mass}}{5}\right]$$

$$20\text{ mL}\ \frac{N}{10}\ \text{KMnO}_4 \equiv 20\text{ mL}\ \frac{N}{10}\ \text{Ferrous ion}$$

$$\equiv 20\text{ mL}\ \frac{N}{10}\ \text{FeCl}_3$$

$$\equiv 20\text{ mL}\ \frac{N}{10}\ \text{N}_2\text{H}_6\text{SO}_4$$

$$\text{Eq. mass N}_2\text{H}_6\text{SO}_4 = \frac{\text{Mol. mass}}{4} = \frac{130}{4} = 32.5$$

[Since, change in O.N. ($\text{N}_2\text{H}_4 \rightarrow \text{N}_2$) per molecule = 4]

Amount of hydrazine sulphate in 10 mL of solution

$$= \frac{1}{10} \times \frac{32.5}{1000} \times 20 = 0.065\text{ g}$$

Amount of hydrazine sulphate in one litre of solution

$$= \frac{0.065}{10} \times 1000 = 6.50\text{ g}$$

Example 51. *0.1 M $KMnO_4$ is used for the following titration. What volume of the solution in mL will be required to react with 0.158 g of $Na_2S_2O_3$?*

$$S_2O_3^{2-} + MnO_4^- + H_2O \longrightarrow MnO_2(s) + SO_4^{2-} + OH^-$$

(not balanced) (MLNR 1992)

Solution: $\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{SO}_4^{2-}$

Change in oxidation number of sulphur per molecule of $\text{S}_2\text{O}_3^{2-} = 2 \times (6 - 2) = 8$

Change in oxidation number of Mn per molecule of MnO_4^- $= 7 - 4 = 3$

$$\text{No. of moles in 0.158 g of Na}_2\text{S}_2\text{O}_3 = \frac{0.158}{158} = 1 \times 10^{-3}$$

$$\text{No. of equivalents} = 8 \times 10^{-3}$$

Normality of 0.1 M KMnO_4 solution $= 0.1 \times 3 = 0.3$

Let V mL of volume of KMnO_4 be required; then

$$\frac{V}{1000} \times 0.3 = 8 \times 10^{-3}$$

or $$V = \frac{8}{0.3} \times 10^{-3} \times 10^3$$

$$= 26.7\text{ mL}$$

Example 52. *25 mL of H_2O_2 solution were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N $Na_2S_2O_3$ for titration. Calculate the strength of H_2O_2 in terms of normality, percentage and volume.* (MLNR 1996)

Solution: 20 mL of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$

$$= 20\text{ mL of 0.1 } N\ \text{I}_2 \text{ solution}$$

$$= 20\text{ mL of 0.1 } N\ \text{H}_2\text{O}_2 \text{ solution}$$

$$\equiv 25\text{ mL of 0.08 } N\ \text{H}_2\text{O}_2 \text{ solution}$$

$$\text{Mass of H}_2\text{O}_2 \text{ in 100 mL solution} = \frac{0.08 \times 17 \times 100}{1000} = 0.136\text{ g}$$

$$\% = 0.136$$

68 g H_2O_2 evolve oxygen at NTP = 22400 mL

0.00136 g H_2O_2 evolve oxygen at NTP

$$= \frac{22400}{68} \times 0.00136 = 0.448$$

The solution is of 0.448 volume.

Example 53. *0.804 g sample of iron ore was dissolved in acid. Iron was reduced to +2 state and it required 47.2 mL of 0.112 N $KMnO_4$ solution for titration. Calculate the percentage of iron and Fe_3O_4 in the ore.*

Solution: The titration involves the conversion of ferrous into ferric.

$$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$$

47.2 mL of 0.112 N KMnO_4 ≡ 47.2 mL of 0.112 N Fe^{2+} ions

$$= \frac{47.2 \times 0.112 \times 55.5}{1000} = 0.2934$$

Mass of iron = 0.2934 g

$$\text{\% of iron in the ore} = \frac{0.2934}{0.804} \times 100 = 36.49$$

$$\underset{(3\times 55.5)}{3\text{Fe}} \longrightarrow \underset{(3\times 55.5 + 64)}{\text{Fe}_3\text{O}_4}$$

3×55.5 g of iron form 230.5 g of Fe_3O_4.

$$\text{0.2934 g of iron will form} = \frac{230.5}{166.5} \times 0.2934 = 0.406\text{ g}$$

$$\text{\% of Fe}_3\text{O}_4 \text{ in the ore} = \frac{0.406}{0.804} \times 100 = 50.5$$

Example 54. *An equal volume of a reducing agent is treated separately with 1 M $KMnO_4$ in acid, neutral and alkaline media. The volume of $KMnO_4$ required are 20 mL in acid, 33.4 mL in neutral and 100 mL in alkaline media. Find out the oxidation state of manganese in each reaction product. Give the balanced equations for all the three half reactions. Find out the volume of 1 M $K_2Cr_2O_7$ consumed, if the same volume of the reducing agent is treated in acid medium.*

Solution: Let N_1, N_2 and N_3 be the normalities of $1\,M$ $KMnO_4$ solution in acid, neutral and alkaline mediums, respectively.

$$20\,\text{mL}\ N_1 \equiv 33.4\,\text{mL}\ N_2 \equiv 100\,\text{mL}\ N_3$$

In acidic medium, the half reaction is:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

$$1\,M\ KMnO_4 = 5\,N\ KMnO_4$$

Thus, from above relation,

$$N_2 = \frac{20}{33.4} \times N_1 = \frac{20}{33.4} \times 5\,N = 3\,N$$

and $$N_3 = \frac{20}{100} \times N_1 = \frac{20}{100} \times 5\,N = 1\,N$$

The equations in the three media are:

$$MnO_4^- + 5e^- \xrightarrow{\text{Acid}} Mn^{2+}$$

$$MnO_4^- + 3e^- \xrightarrow{\text{Neutral}} Mn^{4+}$$

$$MnO_4^- + e^- \xrightarrow{\text{Alkaline}} Mn^{6+}$$

The balanced equations are:

$$MnO_4^- + 8H^+ + 5e^- \xrightarrow{\text{Acid}} Mn^{2+} + 4H_2O$$

$$MnO_4^- + 2H_2O + 3e^- \xrightarrow{\text{Neutral}} MnO_2 + 4OH^-$$

$$MnO_4^- + e^- \xrightarrow{\text{Alkaline}} MnO_4^{2-}$$

The balanced equation in the case of acidified $K_2Cr_2O_7$ solution can be written as:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 3Cr^{3+} + 7H_2O$$

$$1\,M\ K_2Cr_2O_7 = 6\,N\ K_2Cr_2O_7$$

The volume required for the titration of the same volume of reducing agent with acidified $K_2Cr_2O_7$ solution as follows:

$$20\ \text{mL}\ 5\,N\ KMnO_4 \equiv V\ 6\,N\ K_2Cr_2O_7$$

$$V = \frac{20 \times 5}{6} = 16.66\,\text{mL}$$

Example 55. *1.6 g of pyrolusite ore was treated with $50\,cm^3$ of $1.0\,N$ oxalic acid and some sulphuric acid. The oxalic acid left undecomposed was raised to $250\,cm^3$ in a flask. $25\,cm^3$ of this solution when titrated with $0.1\,N$ $KMnO_4$ required $32\,cm^3$ of the solution. Find the percentage of pure MnO_2 in the sample and also the percentage of available oxygen.* (IIT 1996)

Solution: $25\ cm^3$ of undecomposed oxalic acid required

$$= 32\ cm^3\ 0.1\,N\ KMnO_4\ \text{solution}$$

Thus, $250\,cm^3$ of undecomposed oxalic acid required

$$= 320\ cm^3\ 0.1\,N\ KMnO_4\ \text{solution}$$

$$\equiv 32\ cm^3\ 1\,N\ KMnO_4\ \text{solution}$$

$$= 32\ cm^3\ 1\,N\ \text{oxalic acid solution}$$

Oxalic acid used by pyrolusite

$$= (50 - 32)\ cm^3\ 1\,N\ \text{solution}$$

$$= 18\ cm^3\ 1\,N\ \text{solution}$$

$$\equiv 18\ cm^3\ 1\,N\ MnO_2\ \text{solution}$$

$$\text{Mass of } MnO_2 = \frac{N \times E \times V}{1000} = \frac{1 \times 18 \times 87}{1000 \times 2} = 0.783\ \text{g}$$

$$\text{Percentage of } MnO_2 = \frac{0.783}{1.6} \times 100 = 48.9$$

$$\underset{87\,\text{g}}{MnO_2} \longrightarrow MnO + \overset{16\,\text{g}}{O}$$

$$\text{Oxygen given by } 0.783\ \text{g}\ MnO_2 = \frac{16}{87} \times 0.783 = 0.144\ \text{g}$$

$$\%\ \text{of available oxygen} = \frac{0.144}{1.6} \times 100 = 9.0$$

Example 56. *A mixture of $H_2C_2O_4$ and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made up to one litre. 10 mL of this solution required 3.0 mL of $0.1\,N$ NaOH solution for complete neutralisation. In another experiment 10 mL of same solution in hot dilute H_2SO_4 medium required 4 mL of $0.1\,N$ $KMnO_4$ for complete neutralisation. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture.* (IIT 1990)

Solution: Let mass of $H_2C_2O_4$ present in the mixture be $= a$ g in 1 litre

and mass of $NaHC_2O_4$ present in the mixture be $= b$ g in 1 litre

For acid-base reaction

$$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$$

$$\text{Eq. mass of } H_2C_2O_4 = \frac{\text{Mol. mass}}{2} = \frac{90}{2} = 45$$

$$NaHC_2O_4 + NaOH \longrightarrow Na_2C_2O_4 + H_2O$$

$$\text{Eq. mass of } NaHC_2O_4 = \frac{\text{Mol. mass}}{1} = 112$$

Now,

$$\underset{\text{in 10 mL solution}}{\text{Equivalents of } H_2C_2O_4} + \underset{\text{in 10 mL solution}}{\text{Equivalents of } NaHC_2O_4} = \frac{3 \times 0.1}{1000}$$

$$\frac{a \times 10}{45 \times 1000} + \frac{b \times 10}{112 \times 1000} = \frac{3 \times 0.1}{1000}$$

or $$112a + 45b = \frac{3 \times 0.1 \times 45 \times 112}{10} = 151.2 \qquad \text{... (i)}$$

For redox reaction

$$\text{Eq. mass of } H_2C_2O_4 = \frac{90}{2} = 45;$$

$$\text{Eq. mass of } NaHC_2O_4 = \frac{112}{2} = 56$$

(Change in oxidation number of carbon per molecule = 2; $C_2^{3+} \longrightarrow 2C^{4+}$)

Now,

$$\underset{\text{in 10 mL solution}}{\text{Equivalents of } H_2C_2O_4} + \underset{\text{in 10 mL solution}}{\text{Equivalents of } NaHC_2O_4} = \frac{4 \times 0.1}{1000}$$

$$\frac{a \times 10}{45 \times 1000} + \frac{b \times 10}{56 \times 1000} = \frac{4 \times 0.1}{1000}$$

or $$56a + 45b = 100.8 \qquad \text{... (ii)}$$

Solving equations (i) and (ii),

$$a = 0.9 \text{ g} \quad \text{and} \quad b = 1.12 \text{ g}$$

Example 57. *A 3.0 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted to Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 mL. A 20 mL of the dilute solution requires 11.0 mL of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 mL of the diluted solution after complete extraction of iodine requires 12.8 mL of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for oxidation of Fe^{2+}. Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample.* **(IIT 1996)**

Solution: Fe_3O_4 is an equimolar mixture of Fe_2O_3 and FeO. Thus, the sample contains Fe_2O_3, FeO and impurities. The amount of iodine liberated depends on the amount of Fe_2O_3 and the entire iron is converted into Fe^{2+}.

$$Fe_3O_4 + 2KI + H_2SO_4 \longrightarrow 3FeO + H_2O + K_2SO_4 + I_2$$

$$Fe_2O_3 + KI + H_2SO_4 \longrightarrow 2FeO + H_2O + K_2SO_4 + I_2$$

$$\begin{aligned} 5 \times 11.0 \text{ mL of } 0.5\,M\,Na_2S_2O_3 &\equiv 55.0 \text{ mL of } 0.5\,N\,Na_2S_2O_3 \text{ soln.} \\ &\equiv 55.0 \text{ mL of } 0.5\,N\,I_2 \text{ soln.} \\ &\equiv 55.0 \text{ mL of } 0.5\,N\,Fe_2O_3 \text{ soln.} \\ &= 27.5 \times 10^{-3} \text{ equivalent } Fe_2O_3 \text{ soln.} \\ &= 13.75 \times 10^{-3} \text{ moles } Fe_2O_3 \end{aligned}$$

$$\begin{aligned} 2 \times 12.8 \text{ mL of } 0.25\,M\,KMnO_4 \text{ soln.} & \\ &\equiv 25.6 \text{ mL of } 1.25\,N\,KMnO_4 \text{ soln.} \\ &\equiv 25.6 \text{ mL of } 1.25\,N \text{ FeO soln.} \\ &= 32.0 \times 10^{-3} \text{ equivalent FeO} \\ &= 32.0 \times 10^{-3} \text{ moles FeO} \end{aligned}$$

$$\text{Moles of FeO in } Fe_3O_4 = 0.032 - 0.0275 = 0.0045$$

$$\text{Mass of } Fe_3O_4 = 0.0045 \times 232 = 1.044 \text{ g}$$

Moles of Fe_2O_3 existing separately

$$= 0.01375 - 0.0045 = 0.00925$$

$$\text{Mass of } Fe_2O_3 = 0.00925 \times 160 = 1.48 \text{ g}$$

$$\%\ Fe_3O_4 = \frac{1.044}{3} \times 100 = 34.8$$

$$\%\ Fe_2O_3 = \frac{1.48}{3} \times 100 = 49.33$$

Example 58. *Hydroxylamine reduces iron (III) according to the equation,*

$$2NH_2OH + 4Fe^{3+} \longrightarrow N_2O(g)\uparrow + H_2O + 4Fe^{2+} + 4H^+$$

Iron (II) thus produced is estimated by titration with a standard permanganate solution. The reaction is:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

A 10 mL sample of hydroxylamine solution was diluted to one litre. 50 mL of this diluted solution was boiled with excess of iron (III) solution. The resulting solution required 12 mL of 0.02 M $KMnO_4$ solution for complete oxidation of iron (II). Calculate the mass of hydroxylamine in one litre of the original solution.

Solution:

$$\begin{aligned} 12 \text{ mL of } 0.02\,M\,KMnO_4 &\equiv 12 \text{ mL of } 0.1\,N\,KMnO_4 \\ &\equiv 12 \text{ mL of } 0.1\,N\,Fe^{2+} \\ &\equiv 12 \text{ mL of } 0.1\,N\,NH_2OH \end{aligned}$$

$$\text{Eq. mass of } NH_2OH = \frac{\text{Mol. mass}}{2} = \frac{33}{2} = 16.5$$

Mass of NH_2OH in 12 mL of 0.1 N NH_2OH soln.

$$= \frac{N \times E \times V}{1000} = \frac{0.1 \times 16.5 \times 12}{1000} = 0.0198 \text{ g}$$

50 mL of diluted solution contains NH_2OH = 0.0198 g

1000 mL of diluted solution contains NH_2OH

$$= \frac{0.0198}{50} \times 1000 = 0.396 \text{ g}$$

10 mL of original solution contains NH_2OH = 0.396 g

1000 mL of original solution contains NH_2OH

$$= 100 \times 0.396 = 39.6 \text{ g}$$

Example 59. *0.56 g of limestone was treated with oxalic acid to give CaC_2O_4. The precipitate decolourised 45 mL of 0.2 N $KMnO_4$ in acid solution. Calculate the % of CaO in limestone.*

Solution:

$$\begin{aligned} 45 \text{ mL of } 0.2\,N\,KMnO_4 &= 45 \text{ mL of } 0.2\,N\,CaC_2O_4 \\ &= 45 \text{ mL of } 0.2\,N\,CaCO_3 \\ &= 45 \text{ mL of } 0.2\,N \text{ CaO} \end{aligned}$$

$$\text{Mass of CaO} = \frac{N \times E \times V}{1000} = \frac{0.2 \times 28 \times 45}{1000} = 0.252 \text{ g}$$

$$\%\text{ of CaO in limestone} = \frac{0.252}{0.56} \times 100 = 45$$

Example 60. *A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 mL oxidant. The resulting solution is neutralised by Na_2CO_3, acidified with dilute acetic acid and titrated with excess of KI. The liberated iodine required 11.3 mL of 0.05 M $Na_2S_2O_3$ for complete reduction. Find out the mole ratio of Cu^{2+} and $C_2O_4^{2-}$ in the compound.* **(IIT 1991)**

Solution: **1st case:** Only $C_2O_4^{2-}$ ions are oxidised by $KMnO_4$ solution.

$$\text{Normality of } KMnO_4 \text{ solution} = 0.02 \times 5 = 0.1\,N$$

$$22.6 \text{ mL of } 0.1\,N\,KMnO_4 = 22.6 \text{ mL of } 0.1\,N\,C_2O_4^{2-} \text{ soln.}$$

Mass of $C_2O_4^{2-}$ ions in the solution $= \dfrac{N\times E\times V}{1000} = \dfrac{N\times M\times V}{1000\times 2}$

No. of moles of $C_2O_4^{2-}$ ions in the solution $= \dfrac{N\times M\times V}{1000\times 2\times M}$

$$= \frac{N\times V}{2000}$$

$$= \frac{0.1\times 22.6}{2000}$$

$$= 11.3\times 10^{-4}$$

2nd case: Only Cu^{2+} ions are reduced by KI and iodine liberated is neutralised by $Na_2S_2O_3$ solution.

$$11.3 \text{ mL of } 0.05\,M\ Na_2S_2O_3 \equiv 11.3 \text{ mL of } 0.05\,N\ Na_2S_2O_3$$

$$= 11.3 \text{ mL of } 0.05\,N\ I_2$$

$$= 11.3 \text{ mL of } 0.05\,N\ Cu^{2+}$$

Mass of Cu^{2+} ions in the solution $= \dfrac{N\times E\times V}{1000} = \dfrac{N\times M\times V}{1000}$

No. of moles of Cu^{2+} ions in the solution $= \dfrac{N\times M\times V}{1000\times M}$

$$= \frac{N\times V}{1000}$$

$$= \frac{0.05\times 11.3}{1000}$$

$$= 5.65\times 10^{-4}$$

Molar ratio of $\dfrac{Cu^{2+}}{C_2O_4^{2-}} = \dfrac{5.65\times 10^{-4}}{11.3\times 10^{-4}} = \dfrac{1}{2}$

Example 61. *12 g of an impure sample of arsenious oxide was dissolved in water containing 7.5 g of sodium bicarbonate and the resulting solution was diluted to 250 mL. 25 mL of this solution was completely oxidised by 22.4 mL of a solution of iodine. 25 mL of this iodine solution reacted with same volume of a solution containing 24.8 g of sodium thiosulphate solution ($Na_2S_2O_3\cdot 5H_2O$) in one litre. Calculate the percentage of arsenious oxide in the sample. (Atomic mass of As = 75)* (IIT 1999)

Solution: Normality of $Na_2S_2O_3$ soln. $= \dfrac{24.8}{248} = 0.1\,N$

Applying $N_1V_1 = N_2V_2$

Volume of As_2O_3 soln. in $NaHCO_3$ × Normality of this soln.

= Volume of iodine soln. × Normality of iodine soln.

$$25\times N_1 = 22.4\times 0.1$$

$$\therefore \quad N_1 = \frac{22.4\times 0.1}{25}$$

Amt. of As_2O_3 present in 250 mL of the solution

$$= N_1 \times \frac{\text{Equivalent mass of } As_2O_3}{1000}\times 250$$

$$= \frac{22.4\times 0.1}{25}\times\frac{198}{4}\times\frac{250}{1000} = 1.1088 \text{ g}$$

Percentage of $As_2O_3 = \dfrac{1.1088}{12}\times 100 = 9.24$

Example 62. *Hydrogen peroxide solution (20 mL) reacts quantitatively with a solution of $KMnO_4$ (20 mL) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolourised by 10 mL of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 mL of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2.* (IIT 2001)

Solution:

$$\text{(i)}\ \underset{\substack{\text{ppt.}\\ \text{1 mole}}}{MnO_2} + \underset{\text{1 mole}}{Na_2C_2O_4} + 2H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4 + 2CO_2 + 2H_2O$$

$$\text{mM of } MnO_2 = \text{mM of } Na_2C_2O_4 = 10\times 0.2 = 2$$

$$\text{(ii)}\ \underset{\text{2 mole}}{2\,KMnO_4} + 3MnSO_4 + 2H_2O \longrightarrow \underset{\substack{\text{ppt.}\\ \text{5 mole}}}{5MnO_2} + K_2SO_4 + 2H_2O$$

$$\text{mM of } KMnO_4 = \text{mM of } MnO_2 \times \frac{2}{5} = 2\times\frac{2}{5} = \frac{4}{5}$$

$$\text{(iii)}\ \underset{\text{2 mole}}{2KMnO_4} + 3H_2SO_4 + \underset{\text{5 mole}}{5H_2O_2} \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$\therefore \quad \text{mM of } H_2O_2 = \text{mM of } KMnO_4 \times \frac{5}{2} = \frac{4}{5}\times\frac{5}{2} = 2$$

$$\therefore \quad M\times 20 = 2$$

$$\text{or} \quad M_{H_2O_2} = \frac{2}{20} = 0.1\,M$$

Example 63. *The Mn_3O_4 formed on strong heating of a sample of $MnSO_4\cdot 4H_2O$ was dissolved in 100 cm^3 of 0.1 N $FeSO_4$ containing dilute H_2SO_4. The resulting solution reacted completely with 50 cm^3 of $KMnO_4$ solution. 25 cm^3 of this $KMnO_4$ solution requires 30 cm^3 of 0.1 N $FeSO_4$ solution for complete reaction. Calculate the amount of $MnSO_4\cdot 4H_2O$ in the sample.* (IIT 2001)

Solution: $MnSO_4\cdot 4H_2O \xrightarrow{\text{Heat}} Mn_3O_4$

Mn_3O_4 is dissolved in ferrous sulphate solution and is reduced from $Mn^{(8/3)+}$ to Mn^{2+}. The excess of $FeSO_4$ is estimated by doing titration with $KMnO_4$ solution. The normality of $KMnO_4$ solution is determined by another ferrous sulphate solution.

For normality of $KMnO_4$ solution:

$$25\times N = 30\times 0.1$$

$$N = \frac{30\times 0.1}{25} = \frac{3}{25}$$

Let the volume of unreacted $FeSO_4$ solution be V mL

$$V \text{ mL of } 0.1\,N\ \mathrm{FeSO_4} = 50 \text{ mL of } \frac{3}{25}\,N\ \mathrm{KMnO_4}$$

or
$$V = \frac{50\times 3}{0.1\times 25} = 60 \text{ mL}$$

$$\therefore \text{Volume of } \mathrm{FeSO_4} \text{ used for } \mathrm{Mn_3O_4} = (100-60)\text{ mL} = 40 \text{ mL}$$

$$40 \text{ mL of } 0.1\,N\ \mathrm{FeSO_4} \equiv 40 \text{ mL of } 0.1\,N\ \mathrm{Mn_3O_4} \equiv 40 \text{ mL of } 0.1\,N\ \mathrm{MnSO_4\cdot 4H_2O}$$

$$\text{Mass of } \mathrm{MnSO_4\cdot 4H_2O} = \frac{E\times 0.1\times 40}{1000} = \frac{E}{250}\text{ g}$$

Equivalent mass of

$$\mathrm{MnSO_4\cdot 4H_2O} = \frac{M}{\left(\frac{8}{3}-2\right)} = \frac{3M}{2} = \frac{3\times 223}{2}$$

$$\therefore \text{Mass of } \mathrm{MnSO_4\cdot 4H_2O} = \frac{3\times 223}{2\times 250} = 1.338 \text{ g}$$

Example 64. *0.96 g of hydrogen iodide was heated to 450°C till the equilibrium was reached. It was then quickly cooled and the amount of iodine liberated required 15.7 cc of N/10 sodium thiosulphate. Calculate the percentage of hydrogen iodide dissociated at 450°C.*

Solution: Reactions involved

$$2\mathrm{HI} \rightleftharpoons \mathrm{H_2} + \mathrm{I_2}$$

$$\mathrm{I_2} + 2\mathrm{Na_2S_2O_3} \rightarrow 2\mathrm{NaI} + \mathrm{Na_2S_4O_6}$$

$$1 \text{ mole } \mathrm{I_2} \equiv 2 \text{ mole hypo}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{Molecular mass (158)}} = \frac{E\times N\times V}{1000\times 158}$$

where, E, N and V are equivalent weight, normality and volume of hypo used.

$$E = 158, N = 1/10, V = 15.7$$

$$\because \quad \text{No. of moles of } \mathrm{Na_2S_2O_3} = \frac{158\times 1/10\times 15.7}{1000\times 158} = 1.57\times 10^{-3} \text{ mole}$$

Moles of $\mathrm{I_2}$ produced by decomposition of HI

$$= \frac{1}{2} \text{ mole of } \mathrm{Na_2S_2O_3}$$

$$= \frac{1}{2}\times 1.57\times 10^{-3} = 0.785\times 10^{-3} \text{ mole} \quad \text{... (i)}$$

$$\text{Moles of HI} = \frac{\text{Mass}}{\text{M.w.}} = \frac{0.96}{128} = 7.5\times 10^{-3}$$

$$\begin{array}{llll} & \mathrm{HI} \rightleftharpoons & \frac{1}{2}\mathrm{H_2} & + \frac{1}{2}\mathrm{I_2} \\ \text{At } t = 0 & C & 0 & 0 \\ \text{At equilibrium} & C(1-\alpha) & \frac{C\alpha}{2} & \frac{C\alpha}{2} \end{array}$$

where, $C = 7.5\times 10^{-3}$, α = degree of dissociation

$$\text{Moles of } \mathrm{I_2} = \frac{C\alpha}{2} = \frac{7.5\times 10^{-3}\alpha}{2} \quad \text{... (ii)}$$

Equating eqs. (i) and (ii), we get

$$\frac{7.5\times 10^{-3}\alpha}{2} = 0.785\times 10^{-3}$$

$$\alpha = 0.209$$

$$\%\text{ dissociation of HI} = \text{Degree of dissociation}\times 100 = 0.209\times 100 = 20.9\%$$

Example 65. *50 mL sample of ozonised oxygen at NTP was passed through a solution of potassium iodide. The liberated iodine required 15 mL of 0.08 N $Na_2S_2O_3$ solution for complete titration. Calculate the volume of ozone at NTP in the given sample.*

Solution: Reactions involved may be given as:

$$2\mathrm{KI} + \mathrm{H_2O} + \mathrm{O_3} \longrightarrow 2\mathrm{KOH} + \mathrm{I_2} + \mathrm{O_2}\uparrow$$

$$\mathrm{I_2} + 2\mathrm{Na_2S_2O_3} \longrightarrow 2\mathrm{NaI} + \mathrm{Na_2S_4O_6}$$

$$1 \text{ mole } \mathrm{O_3} = 2 \text{ mole } \mathrm{Na_2S_2O_3} \quad \text{... (i)}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{Molecular mass (158)}} = \frac{E\times N\times V}{1000\times 158}$$

where, $E_{\mathrm{Na_2S_2O_3}} = 158, N = 0.08, V = 15$

$$\therefore \quad \text{No. of moles of hypo} = \frac{158\times 0.08\times 15}{1000\times 158} = 1.2\times 10^{-3}$$

$$\text{No. of moles of } \mathrm{O_3} = \frac{1}{2} \text{ mole of hypo} \quad \text{[from eq. (i)]}$$

$$= \frac{1}{2}\times 1.2\times 10^{-3}$$

$$= 6\times 10^{-4} \text{ mole}$$

$$\text{Volume of } \mathrm{O_3} \text{ at NTP} = \text{No. of moles}\times 22400 = 6\times 10^{-4}\times 22400 = 13.44 \text{ mL at NTP}$$

Example 66. *10 mL of a potassium dichromate solution liberates iodine from potassium iodide solution. When the iodine was titrated with hypo solution (N/20), the titre value was 15 mL. Find the concentration of dichromate solution in g per litre.*

Solution: The reactions involved may be given as

$$\mathrm{Cr_2O_7^{2-}} + 6\mathrm{I^-} + 14\mathrm{H^+} \longrightarrow 2\mathrm{Cr^{3+}} + 3\mathrm{I_2} + 7\mathrm{H_2O}$$

$$3[\mathrm{I_2} + 2\mathrm{Na_2S_2O_3}] \longrightarrow 3[2\mathrm{NaI} + \mathrm{Na_2S_4O_6}]$$

$$1 \text{ mole } \mathrm{K_2Cr_2O_7} \equiv 6 \text{ moles of } \mathrm{Na_2S_2O_3} \quad \text{... (i)}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{M.w. (158)}} = \frac{E\times N\times V}{1000\times 158}$$

$$= \frac{158 \times 1/20 \times 15}{1000 \times 158}$$

$$= 7.5 \times 10^{-4} \text{ mole}$$

$$\text{No. of moles of } K_2Cr_2O_7 = \frac{1}{6}[\text{No. of moles of } Na_2S_2O_3]$$

$$= 1.25 \times 10^{-4} \text{ mole}$$

$$\text{Mass of } K_2Cr_2O_7 \text{ in 10 mL solution} = 1.25 \times 10^{-4} \times 294$$

$$= 0.03675 \text{ g}$$

$$\text{Weight of } K_2Cr_2O_7 \text{ in 10 mL solution} = 3.675 \text{ g/L}$$

Example 67. *1.5 g of sample of impure potassium dichromate was dissolved in water and made up to 500 mL solution. 25 mL of this solution required iodometrically 24 mL of a sodium thiosulphate solution. 26 mL of this sodium thiosulphate solution required 25 mL of N/20 solution of pure potassium dichromate. Find the percentage purity of impure sample of potassium dichromate.*

Solution: Normality of sodium thiosulphate solution may be determined as:

$$N_1V_1(Na_2S_2O_3) = N_2V_2 \text{ (pure } K_2Cr_2O_7)$$

$$N_1 \times 26 = 25 \times \frac{1}{20}$$

$$N_1 = 0.048 \text{ (hypo)}$$

The reaction involved may be given as:

$$Cr_2O_7^{2-} + 6I^- + 4H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$3[I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6]$$

$$1 \text{ mole } K_2Cr_2O_7 \equiv 6 \text{ mole } Na_2S_2O_3 \qquad \text{... (i)}$$

25 mL of solution of $K_2Cr_2O_7$ is treated by 24 mL of 0.048 *N* hypo

$\therefore$ 500 mL of solution will be titrated by 480 mL of 0.048 *N* hypo

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{M.w. (158)}} = \frac{E \times N \times V}{1000 \times 158}$$

$$= \frac{158 \times 0.048 \times 480}{1000 \times 158}$$

$$= 0.02304 \text{ mole}$$

$$\text{No. of moles of } K_2Cr_2O_7 = \frac{1}{6}[\text{No. of moles of hypo}]$$

$$= \frac{1}{6}[0.02304] = 3.84 \times 10^{-3}$$

$$\text{Mass of } K_2Cr_2O_7 = 3.84 \times 10^{-3} \times 294$$

$$= 1.12896$$

$$\% \text{ purity} = \frac{1.12896}{1.5} \times 100 = 75.26\%$$

Example 68. *5 g of a sample of brass were dissolved in 1 litre dil. H_2SO_4. 20 mL of this solution were mixed with KI and liberated iodine required 20 mL of 0.0327 N hypo solution for titration. Calculate the amount of copper in the alloy.*

Solution: When brass is extracted with concentrated H_2SO_4, it gives copper sulphate.

$$2[Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O]$$

$$2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + 2CuI_2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

$$2 \text{ mole Cu} \equiv 1 \text{ mole } I_2 \equiv 2 \text{ mole hypo}$$

20 mL of solution reacts with 20 mL of 0.0327 *N* hypo

$\therefore$ 1000 mL of solution will react with 1000 mL of 0.0327 *N* hypo

$$\text{No. of moles of hypo used} = \frac{\text{Mass}}{\text{Molecular mass (158)}}$$

$$= \frac{E \times N \times V}{1000 \times 158}$$

where, $E = 158$, $N = 0.0327$ given, $V = 1000$ mL

$$\therefore \text{ No. of moles of hypo used} = \frac{158 \times 0.0327 \times 1000}{1000 \times 158}$$

$$= 0.0327$$

$$\text{No. of moles of Cu} = \text{No. of moles of hypo}$$

$$= 0.0327 \text{ mole}$$

$$\text{Mass of copper in brass} = 0.0327 \times 63.5 = 2.07645$$

$$\% \text{ of copper in brass} = \frac{2.07645}{5} \times 100$$

$$= 41.529\%$$

Example 69. *An excess KI solution is mixed in a solution of $K_2Cr_2O_7$ and liberated iodine required 72 mL of 0.05 N $Na_2S_2O_3$ for complete reaction. How many grams of $K_2Cr_2O_7$ were present in the solution of $K_2Cr_2O_7$? The reaction occurs as:*

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

Solution: The reaction involved may be given as:

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

$$3[I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6]$$

$$1 \text{ mole } K_2Cr_2O_7 = 6 \text{ mole } Na_2S_2O_3 \qquad \text{... (i)}$$

$$\text{No. of moles of hypo} = \frac{\text{Mass}}{\text{M.w. (158)}} = \frac{E \times N \times V}{1000 \times 158}$$

$$N_{Na_2S_2O_3} = \frac{158 \times 0.05 \times 72}{1000 \times 58} = 3.6 \times 10^{-3}$$

$$\text{No. of moles of } K_2Cr_2O_7 = \frac{1}{6}[\text{No. of moles of } Na_2S_2O_3]$$

$$= \frac{1}{6}[3.6\times 10^{-3}] = 6\times 10^{-4} \text{ mole}$$

Mass of $K_2Cr_2O_7$ in the given solution

$$= \text{No. of moles} \times \text{Molecular weight}$$

$$= 6\times 10^{-4}\times 294 = 0.1764$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

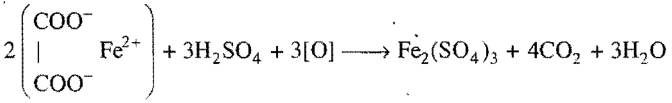
14. How many moles of MnO_4^- ions will react with 1 mole of ferrous oxalate in acid medium?

(a) 1/5 (b) 2/5 (c) 3/5 (d) 5/3

[Ans. (c)]

[Hint:

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$



$$2\left(\begin{array}{l}COO^-\\ |\qquad Fe^{2+}\\ COO^-\end{array}\right) + 3H_2SO_4 + 3[O] \longrightarrow Fe_2(SO_4)_3 + 4CO_2 + 3H_2O$$

$$\therefore \quad 6 \text{ mole } KMnO_4 \equiv 10 \text{ mole } FeC_2O_4$$

$\therefore$ 1 mole FeC_2O_4 will react with $\frac{3}{5}$ mole of $KMnO_4$]

15. The molecular mass of $K_2Cr_2O_7$ is 294 amu. It acts as oxidising agent in a redox titration. Its equivalent mass in acid medium will be:

(a) 294 (b) 49 (c) 147 (d) 74

[Ans. (b)]

[Hint: $\overset{+12}{K_2Cr_2O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \overset{+6}{Cr_2(SO_4)_3} + 4H_2O + 3[O]$

Change in oxidation number = 6

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{6} = \frac{294}{6} = 49]$$

16. In acid medium, both $KMnO_4$ and $K_2Cr_2O_7$ act as oxidising agents. Which among the following is correct about the oxidising behaviour?

(a) $KMnO_4 > K_2Cr_2O_7$ (b) $KMnO_4 < K_2Cr_2O_7$

(c) $KMnO_4 = K_2Cr_2O_7$ (d) Cannot be predicted

[Ans. (a)]

[Hint:

$$2\overset{+7}{KMnO_4} + 3H_2SO_4 \rightarrow K_2SO_4 + 2\overset{+2}{MnSO_4} + 3H_2O + 5[O]$$

Change in oxidation number = 10

$$\overset{+12}{K_2Cr_2O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \overset{+6}{Cr_2(SO_4)_3} + 4H_2O + 3[O]$$

Change in oxidation number = 6]

17. $KMnO_4$ reacts with oxalic acid according to the equation,

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Here, 20 mL of 0.1 *M* $KMnO_4$ is equivalent to:

(a) 120 mL of 0.25 *M* $H_2C_2O_4$

(b) 150 mL of 0.1 *M* $H_2C_2O_4$

(c) 50 mL of 0.1 *M* $H_2C_2O_4$

(d) 50 mL of 0.2 *M* $H_2C_2O_4$

[Ans. (c)]

[Hint: $\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(H_2C_2O_4)$

$$\frac{0.1\times 20}{2} = \frac{M_2V_2}{5}$$

$$M_2V_2 = 5$$

It is possible in the option (c).]

18. A solution of H_2O_2 is titrated against a solution of $KMnO_4$. The reaction is:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

If it requires 46.9 mL of 0.145 *M* $KMnO_4$ to oxidise 20 g of H_2O_2, the mass percentage of H_2O_2 in this solution is:

(a) 2.9 (b) 29 (c) 21 (d) 4.9

[Ans. (a)]

[Hint: Number of moles of $KMnO_4 = \frac{MV}{1000} = \frac{0.145\times 46.9}{1000}$

$$= 6.8\times 10^{-3}$$

Number of moles of $H_2O_2 = 6.8\times 10^{-3}\times 2.5 = 0.017$

$$\text{Mass of } H_2O_2 = 0.017\times 34 = 0.578$$

$$\text{Mass \% of } H_2O_2 = \frac{0.578}{20}\times 100 \approx 2.9]$$

19. In an oxidation-reduction, MnO_4^- ion is converted to Mn^{2+}, what is the number of equivalents of $KMnO_4$ (mol. wt. = 158) present in 250 mL of 0.04 *M* $KMnO_4$ solution ?

(CPMT 2008)

(a) 0.02 (b) 0.05 (c) 0.04 (d) 0.07

[Ans. (b)]

[Hint : In redox-reaction :

$$8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

Change in oxidation state of $MnO_4^- = (+7) - (+2) = +5$

$$\therefore \quad N_{KMnO_4} = M_{KMnO_4}\times 5$$

$$= 0.04\times 5 = 0.20$$

$$\text{Number of equivalents} = \frac{NV}{1000} = \frac{0.2\times 250}{1000} = 0.05\,]$$

20. The strength of 10 volume of H_2O_2 solution is :

(AMU Engg. 2009)

(a) 10 (b) 68 (c) 60.70 (d) 30.36

[Ans. (d)]

[Hint : 10 volume H_2O_2 means, 1 litre of H_2O_2 will give 10 litre oxygen at STP.

$$\underset{68\text{ g}}{2H_2O_2} \longrightarrow 2H_2O + \underset{22.4\text{ L at STP}}{O_2}$$

$\because$ 22.4 L O_2 is obtained at STP from 68 g H_2O_2

$\therefore$ 10 L O_2 is obtained at STP from $\frac{68}{22.4}\times 10$ g H_2O_2

$$= 30.36\text{ g}$$

Thus, strength of H_2O_2 = 30.36 g/L.]

Questions

1. Calculate the equivalent mass of underlined species:
   (i) $Na_2SO_3 + \underline{Na_2CrO_4} \rightarrow Na_2SO_4 + Cr(OH)_3$
   (ii) $Fe_3O_4 + \underline{KMnO_4} \rightarrow Fe_2O_3 + MnO_2$
   (iii) $\underline{2Na_2S_2O_3} + I_2 \rightarrow Na_2S_4O_6 + 2NaI$
   (iv) $\underline{As_2S_3} + 10NO_3^- + 4H^+ \rightarrow 10NO_2 + 2AsO_4^{3-} + 3S + 2H_2O$
   (v) $\underline{H_3PO_3} \rightarrow H_3PO_4 + PH_3$
   (vi) $\underline{5SO_2} + 2KMnO_4 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$
2. 12 mL of 0.25 *N* sulphuric acid is neutralised with 15 mL of sodium hydroxide solution on titration. Calculate the normality of sodium hydroxide solution.
3. What will be the volume of *N*/10 solution of oxalic acid obtained by dissolving 63 g of oxalic acid?
4. If 1.26 g of oxalic acid is dissolved in 250 mL of solution, find its normality. The equivalent mass of oxalic acid is 63.
5. (a) 50 mL of 0.2 *N* $KMnO_4$ is required for complete oxidation of 0.45 g of anhydrous oxalic acid. Calculate the normality of oxalic acid solution.
   (b) In the titration of Fe^{2+} ions with $KMnO_4$ in acid medium, why is dilute H_2SO_4 used and not dilute HCl? [CBSE (Mains) 2005]

   [**Hint:** The reaction involved in the titration is:
   $$10FeSO_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$
   If HCl is taken in place of H_2SO_4, then HCl will be oxidised to Cl_2.]
6. 30 mL of sodium carbonate solution is mixed with 20 mL of 0.8 *N* sulphuric acid. The resultant solution needed 20 mL of 0.7 *N* hydrochloric acid solution for complete neutralisation. Determine the strength of the sodium carbonate in gram per litre. (Take sodium carbonate to be anhydrous.)
7. 0.25 g of an oxalate salt was dissolved in 100 mL of water. 10 mL of this solution required 8 mL of *N*/20 $KMnO_4$ for its oxidation. Calculate the percentage of oxalate in the salt.
8. 1.13 g of an ammonium sulphate were treated with 50 mL of normal NaOH solution and boiled till no more ammonia was given off. The excess of the alkali solution left over was titrated with normal H_2SO_4. The volume required was 30 mL. Find out the percentage of NH_3 in the salt.
9. The normality of the mixture of HCl and H_2SO_4 solution is *N*/5. 0.287 g of AgCl is obtained when 20 mL of this solution is treated with excess of $AgNO_3$. Calculate the percentage of both the acids in the mixture.
10. 1.17 g of an impure sample of oxalic acid was dissolved and made up to 200 mL with water. 10 mL of this solution in acid medium required 8.5 mL of a solution of potassium permanganate containing 3.16 g per litre of oxidation. Calculate the percentage purity of oxalic acid.
11. What amount of silver chloride will be obtained when 20 mL *N*/20 HCl is made to react with excess of $AgNO_3$?
12. 1.0 g carbonate of a metal was dissolved in 50 mL *N*/2 HCl solution. The resulting liquid required 25 mL of *N*/5 NaOH solution to neutralise it completely. Calculate the equivalent mass of the metal carbonate.
13. 0.35 g of a metal was dissolved in 50 mL *N*-acid. The whole solution then required 20.85 mL of normal alkaline solution to neutralise the excess of the acid. Calculate the equivalent mass of the metal.
14. 2.650 g of anhydrous sodium carbonate are dissolved in water and the solution made up to 500 mL. On titration 50 mL of this solution neutralises 50 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid as to make it exactly *N*/12 ?
15. Two acids *A* and *B* are titrated separately each time with 25 mL of *N* Na_2CO_3 solution and require 10 mL and 40 mL respectively for complete neutralisation. What volume of *A* and *B* would you mix to produce one litre of normal acid solution?
16. 1.64 g of a mixture of calcium carbonate and magnesium carbonate were dissolved in 50 mL of 0.8 *N* hydrochloric acid. The excess of the acid required 16 mL *N*/4 sodium hydroxide solution for neutralisation. Find out the percentage composition of the mixture of two carbonates.
17. 30 mL of *N*/10 HCl are required to neutralise 50 mL of a sodium carbonate solution. How many mL of water must be added to 30 mL of this solution so that the solution obtained may have a concentration equal to *N*/50?
18. 2.65 g of diacidic base was dissolved in water and made up to 500 mL. 20 mL of this solution completely neutralised 12 mL of *N*/6 HCl. Find out the equivalent mass and molecular mass of the base.
19. In a sample of sodium carbonate, some sodium sulphate is mixed. 2.50 g of this sample is dissolved and the volume made up to 500 mL. 25 mL of this solution neutralises 20 mL of *N*/10 sulphuric acid. Calculate the percentage of sodium carbonate in the sample.
20. Some amount of NH_4Cl was boiled with 50 mL of 0.75 *N* NaOH solution till the reaction was complete. After the completion of the reaction, 10 mL of 0.75 *N* H_2SO_4 were required for the neutralisation of the remaining NaOH. Calculate the amount of NH_4Cl taken.
21. 25 mL of a mixed solution of sodium carbonate and sodium bicarbonate required 10 mL of *N*/20 HCl when titrated in the presence of phenolphthalein but 25 mL of the same when titrated separately in presence of methyl orange required 25 mL of *N*/10 HCl. Calculate the amount of anhydrous sodium carbonate and bicarbonate in grams per litre of the solution.
22. 4 g of a mixture of NaCl and Na_2CO_3 were dissolved in water and volume made up to 250 mL. 15 mL of this solution required 50 mL of *N*/10 HCl for complete neutralisation. Calculate the percentage composition of the original mixture.
23. 40 mL of a mixture of Na_2CO_3 and NaOH when titrated against *N*/10 HCl, the end point with phenolphthalein was reached at 25 mL of HCl and at this stage methyl orange was added, the quantity of acid further required for second end point was 5 mL. Calculate the amount of Na_2CO_3 and NaOH in g/L of the solution.

24. Find out the percentage of oxalate in a given sample of an oxalate salt of which when 0.3 g were dissolved in 100 mL of water required 90 mL of *N*/20 $KMnO_4$ solution for complete oxidation.

25. A 1.0 g sample of H_2O_2 solution containing '*x*' per cent by weight requires *x* mL of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of the $KMnO_4$ solution.

26. 25 g of a sample of ferrous sulphate was dissolved in water containing dilute H_2SO_4 and the volume made up to one litre. 25 mL of this solution required 20 mL of *N*/10 $KMnO_4$ solution for complete oxidation. Calculate the percentage of $FeSO_4 \cdot 7H_2O$ in the sample.

27. A sample of KCl is contaminated with NaCl. 4.176 g of the sample is dissolved in distilled water and the solution is made to 500 mL. 25 mL of the above solution required 27.50 mL of a solution of silver nitrate (normality factor 0.115) to react completely with it. Calculate the percentage contamination of the sample.

28. The saponification number of fat or oil is defined as the number of mg of KOH required to saponify 1 g oil or fat. A sample of peanut oil weighing 1.5763 g is added to 25 mL of 0.421 *M* KOH. After saponification is complete, 8.46 mL of 0.2732 *M* H_2SO_4 is needed to neutralise excess of KOH. What is the saponification number of peanut oil?

29. 500 mL of 2 *M* HCl, 100 mL of 2 *M* H_2SO_4 and one gram equivalent of monoacidic alkali are mixed together. 30 mL of this solution required 20 mL of $Na_2CO_3 \cdot xH_2O$ solution obtained by dissolving 143 g $Na_2CO_3 \cdot xH_2O$ in one litre solution. Calculate the water of crystallisation of $Na_2CO_3 \cdot xH_2O$.

30. 1 g of the complex $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ was passed through a cation exchanger to produce HCl. The acid liberated was diluted to 1 litre. What is the normality of this acid solution?

31. 5.0 g of bleaching powder was suspended in water and volume made up to half a litre. 20 mL of this suspension when acidified with acetic acid and treated with excess of KI solution liberated iodine which required 20 mL of a decinormal hypo solution for titration. Calculate percentage of available chlorine in bleaching powder. (IIT 1990)

32. To a solution of excess of KI in dilute H_2SO_4, 25 mL of an unknown solution of $KMnO_4$ were added. The liberated iodine was exactly reduced by 42.5 mL of *N*/10 $Na_2S_2O_3$ solution. Calculate the concentration of $KMnO_4$ solution.

33. In 20 mL of a solution of HCl, 3 g of $CaCO_3$ were dissolved, 0.5 g of $CaCO_3$ being left undissolved. Find out the strength of this solution in terms of (i) normality and (ii) g/L. Find the volume of this acid which would be required to make 1 litre of normal solution of this acid.

34. 1.0 litre of a solution contains 5.3 g of Na_2CO_3 and 8 g of NaOH. 20 mL of this solution are taken and titrated against *N*/10 HCl using separately (a) methyl orange as an indicator and (b) phenolphthalein as an indicator. What will be the titre values in these two cases?

35. To 20 mL of a copper solution after necessary treatment were added excess of KI and the liberated iodine required 11.2 mL decinormal solution of hypo. Express the strength of the original solution in grams of copper per litre of the solution.

36. 0.28 g of a commercial sample of $K_2Cr_2O_7$ was dissolved in water. Excess of KI was added to it along with dilute H_2SO_4. Iodine liberated was then titrated against sodium thiosulphate solution containing 24.82 g of $Na_2S_2O_3 \cdot 5H_2O$ per litre. The thiosulphate solution required was 50 mL. Find the percentage purity of the sample of $K_2Cr_2O_7$.

37. A mixture containing KCl and NaCl was dissolved and total halide was determined by titration with silver nitrate. A sample weighing 0.3250 g required 51 mL of 0.1 *N* solution. Calculate the percentage of each salt in the sample.

38. 1.355 g of pyrolusite sample are added to 50 mL of 1 *N* oxalic acid solution containing sulphuric acid. After the reaction is completed, the contents are transferred to a measuring flask and the volume made up to 200 mL. 20 mL of this solution is titrated against $KMnO_4$ solution whose strength is 2 g/L and 31.6 mL of $KMnO_4$ solution are required. Calculate the percentage purity in the given sample of pyrolusite.

39. 0.5 g of bleaching powder was suspended in water an excess of KI added. On acidifying with dilute H_2SO_4 iodine was liberated which required 50 mL of *N*/10 hyposolution. Calculate the percentage of available chlorine in bleaching powder.

40. Calculate the number of oxalic acid molecules in 100 mL of 0.02 *N* oxalic acid solution. (IIT 1991)

[**Hint :** Molarity $= \frac{0.02}{2} = 0.01\,M$

No. of molecules in one molar solution $= 6.02 \times 10^{23}$

No. of molecules in 100 mL of 0.01 *M* oxalic acid solution

$$= \frac{0.01 \times 6.02 \times 10^{23}}{1000} \times 100 = 6.02 \times 10^{20}]$$

41. 1.26 g of a dibasic acid were dissolved in water and made up to 200 mL. 20 mL of this solution were completely neutralised by 10 mL of *N*/5 caustic soda solution. Calculate the equivalent mass and molecular mass of the acid.

42. 3.0 g of a sample of impure ammonium chloride were boiled with excess of caustic soda solution. Ammonia gas so evolved was passed into 120 mL of *N*/2 H_2SO_4. 28 mL of *N*/2 NaOH were required to neutralise residual acid. Calculate the percentage of purity of the given sample of ammonium chloride.

[**Hint :** $(120 - 28)$ mL *N*/2 $H_2SO_4 \equiv 92$ mL *N*/2 NH_4Cl]

43. 2.20 g of an ammonium salt were boiled with 75 mL of *N* NaOH till the emission of ammonia gas ceased. The excess of unused NaOH solution required 70 mL of *N*/2 sulphuric acid for neutralisation. Calculate the percentage of ammonia in the salt.

44. 3.45 g of a metallic carbonate were mixed with 240 mL of *N*/4 HCl. The excess acid was neutralised by 50 mL of *N*/5 KOH solution. Calculate the equivalent mass of the metal.

Hint : Equivalent mass of metal carbonate

$$= \frac{3.45 \times 4 \times 1000}{200} = 69$$

Equivalent mass of metal = 69 − Eq. mass of carbonate

$$= (69 - 30) = 39]$$

45. (a) 2 g of a metal carbonate were dissolved in 50 mL of *N* HCl. 100 mL of 0.1 *N* NaOH were required to neutralise the resultant solution. Calculate the equivalent mass of the metal carbonate.

(b) How much water should be added to 75 mL of 3 *N* HCl to make it a normal solution?

46. Upon mixing 45.0 mL of 0.25 *M* lead nitrate solution with 25 mL of 0.1 *M* chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble. **(IIT 1993)**

[**Hint :** The reaction is:

$$\underset{3\text{ mole}}{3Pb(NO_3)_2} + \underset{1\text{ mole}}{Cr_2(SO_4)_3} \longrightarrow \underset{3\text{ mole}}{3PbSO_4} + \underset{2\text{ mole}}{2Cr(NO_3)_3}$$

$$\text{No. of moles of } Pb(NO_3)_2 = 45 \times 10^{-3} \times 0.25$$
$$= 11.25 \times 10^{-3} \text{ mole}$$

$$\text{No. of moles of } Cr_2(SO_4)_3 = 25 \times 10^{-3} \times 0.1 = 2.5 \times 10^{-3} \text{ mole}$$

Thus, $Cr_2(SO_4)_3$ has limiting concentration. It shall be consumed fully and the number of moles of lead sulphate produced will be

$$= 3 \times 2.5 \times 10^{-3} = 7.5 \times 10^{-3} \text{ mole}$$

$$\text{No. of moles of lead nitrate left} = 11.25 \times 10^{-3} - 7.5 \times 10^{-3}$$
$$= 3.75 \times 10^{-3} \text{ mole}$$

$$\text{Total volume} = (45.0 + 25.0) = 70 \text{ mL or } 70 \times 10^{-3} \text{ litre}$$

$$\text{Molarity} = \frac{3.75 \times 10^{-3}}{70 \times 10^{-3}} = 0.0536\,M$$

$$\text{No. of moles of } Cr(NO_3)_3 \text{ formed} = 2 \times 2.5 \times 10^{-3} = 5 \times 10^{-3} \text{ mole}$$

$$\text{Molarity} = \frac{5 \times 10^{-3}}{70 \times 10^{-3}} = 0.0714\,M$$

$Pb(NO_3)_2$ and $Cr(NO_3)_3$ will be present in solution in ionic form.

Thus, $[Pb^{2+}] = 0.0536\,M$

$[Cr^{3+}] = 0.0714\,M$

$[NO_3^-] = (2 \times 0.0536) + (3 \times 0.0714)$

$= 0.3214\,M$]

47. A sample of hydrazine sulphate ($N_2H_6SO_4$) were dissolved in 250 mL of water. 10 mL of this solution was reacted with excess of ferric chloride solution and warmed to complete the reaction. Ferrous ions formed were estimated and it required 10 mL of 0.04 *M* potassium permanganate solution. Estimate the amount of hydrazine sulphate dissolved in 250 mL of the solution. Reactions:

$$4Fe^{3+} + N_2H_4 \longrightarrow N_2 + 4Fe^{2+} + 4H^+$$
$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(MLNR 1993)

[**Hint :** See example 50]

48. In an ore the only oxidisable material is Sn^{2+}. This ore is titrated with a dichromate solution containing 2.5 g $K_2Cr_2O_7$ in 0.50 litre. A 0.40 g of sample of the ore required 10.0 cm^3 of the titrant to reach equivalent point. Calculate the percentage of tin in ore. (K = 39.1, Cr = 52, Sn = 118.7) **(IIT 1993)**

[**Hint :** Mol. mass of $K_2Cr_2O_7 = 2 \times 39.1 + 2 \times 52 + 7 \times 16$

$$= 78.2 + 104.0 + 112.0$$
$$= 294.2$$

$$\text{Eq. mass of } K_2Cr_2O_7 = \frac{294.2}{6} = 49.03$$

$$\text{Normality of } K_2Cr_2O_7 \text{ solution} = \frac{2.5}{49.03} \times \frac{1000}{500} = \frac{5}{49.03}\,N$$

$$10 \text{ mL } \frac{5}{49.03}\,N\ K_2Cr_2O_7 \equiv 10 \text{ mL } \frac{5}{49.03}\,N \text{ stannous ion}$$

$$\text{Eq. mass of } Sn^{2+} = \frac{118.7}{2} = 59.35$$

$$\text{Amount of Sn in the sample} = \frac{5}{49.03} \times \frac{59.35}{1000} \times 10$$
$$= 0.0605 \text{ g}$$

$$\text{Percentage of Sn in the ore} = \frac{0.0605}{0.40} \times 100 = 51]$$

49. 2.26 g of impure ammonium chloride were boiled with 100 mL of *N* NaOH solution till no more ammonia was given off. The excess of NaOH solution left over required 30 mL 2 *N* H_2SO_4 for neutralisation. Calculate the percentage purity of the salt.

(H = 1; N = 14; O = 16; Na = 23; S = 32; Cl = 35.5)

50. Metallic tin in the presence of HCl is oxidised by $K_2Cr_2O_7$ solution to stannic chloride. What volume of decinormal dichromate solution would be reduced by 1 g of Sn? **(MLNR 1994)**

[**Hint :**

$$\underset{3\times118.7\text{ g}}{3Sn} + \underset{2\times294\text{ g}}{2K_2Cr_2O_7} + 28HCl \longrightarrow 3SnCl_4 + 4KCl + 4CrCl_3 + 14H_2O$$

$$K_2Cr_2O_7 \text{ required for 1 g of Sn} = \frac{2 \times 294}{3 \times 118.7} = 1.65 \text{ g}]$$

51. A 0.5 g sample containing MnO_2 is treated with HCl liberating Cl_2. The Cl_2 is passed into a solution of KI and 30.0 cm^3 of 0.1 *M* $Na_2S_2O_3$ are required to titrate the liberated iodine. Calculate the percentage of MnO_2 in the sample. **(IIT 1994)**

[**Hint:** $30.0 \text{ mL } 0.1\,M\,Na_2S_2O_3 \equiv 30.0 \text{ mL } 0.1\,N\ Na_2S_2O_3$

$$\equiv 30.0 \text{ mL } 0.1\,N\ I_2$$
$$\equiv 30.0 \text{ mL } 0.1\,N\ Cl_2$$
$$\equiv 30.0 \text{ mL } 0.1\,N\ MnO_2$$

$$\text{Amount of } MnO_2 \text{ present} = \frac{N \times E \times V}{1000}$$
$$= \frac{1}{10} \times \frac{87}{2} \times \frac{30}{1000}$$

$$\%\ MnO_2 = \frac{87 \times 30 \times 100}{10 \times 2 \times 1000 \times 0.5} = 26.1]$$

52. 3.2 g of a mixture of calcium carbonate and sodium chloride was dissolved in 100 mL of 1.02 *N* HCl. After the reaction the solution was filtered and after separating the precipitate the volume was raised to 200 mL. 20 mL of this solution required 25 mL *N*/5 caustic soda solution for neutralisation. Find out the percentage of calcium carbonate in the mixture.

53. 4 g of a mixture of Na_2SO_4 and anhydrous Na_2CO_3 were dissolved in pure water and volume made up to 250 mL. 20 mL of this solution required 25 mL of *N*/5 H_2SO_4 for complete neutralisation. Calculate the percentage composition of the mixture.

54. A 1.2 g mixture of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 cm^3 of a solution. 20 cm^3 of this solution required 40 cm^3 of 0.1 *N* HCl for neutralisation. Calculate the mass of Na_2CO_3 and K_2CO_3 in the mixture. **(IIT 1997)**

55. One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 mL of $M/10$ sodium thiosulphate solution for titration. What is the weight per cent of ozone in the mixture? Ultraviolet radiation of wavelength 300 nm can decompose ozone. Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?

[Hint: Let the total moles of O_2 and O_3 in the mixture be n.

Applying $PV = nRT$

$$1 \times 1 = n \times 0.0821 \times 273$$

$$n = 0.044 \text{ mole.}$$

$$\text{Moles of } O_3 = \text{moles of } I_2 = 1/2 \text{ moles of } Na_2S_2O_3$$

$$= \frac{1}{2} \times \frac{1}{10} \times \frac{40}{1000} = 0.002 \text{ moles}$$

Moles of O_2 in the mixture = 0.044 − 0.002 = 0.042 moles

Mass of $O_2 = 0.042 \times 32 = 1.344$ g

Mass of $O_3 = 0.002 \times 48 = 0.096$ g

$$\% \ O_3 = \frac{0.096}{1.44} \times 100 = 6.67$$

No. of photons required to decompose 0.002 moles of ozone

$$= 0.002 \times 6.02 \times 10^{23} = 1.204 \times 10^{21}]$$

56. 20 mL of a solution containing 0.2 g of impure sample of H_2O_2 reacts with 0.316 g of $KMnO_4$ (acidic). Calculate:
   (a) Purity of H_2O_2
   (b) Volume of dry O_2 evolved at 27° C and 750 mm pressure.

57. Five gram of copper alloy was dissolved in one litre of dilute H_2SO_4. 20 mL of this solution was titrated iodometrically and it required 20 mL of a hypo solution. 20 mL of $K_2Cr_2O_7$ which contained 2.4 g per litre, in presence of H_2SO_4 and excess of KI, required 30 mL of the same hypo solution. Calculate the % purity of copper in the alloy.

58. How many millilitres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate?

[Hint : $N_1V_1 = N_2V_2$

N_1 = Normality of $H_2SO_4 = 0.5 \times 2 = 1 \ N$

V_1 = Vol. of H_2SO_4

N_2 = Normality of copper (II) carbonate $= \dfrac{0.5 \times 2}{123.5} \ N$

V_2 = Volume of copper (II) carbonate = 1000 mL

Thus, $$1.0 \times V_1 = \frac{0.5 \times 2}{123.5} \times 1000$$

or $$V_1 = 8.09 \text{ mL}]$$

59. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated iodine consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

[Hint : $2KIO_3 + 10KI + 12HCl \longrightarrow 12KCl + 6I_2 + 6H_2O$

$$[2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6] \times 6$$

$$\underset{\text{2 moles}}{2KIO_3} + 10KI + \underset{\text{12 moles}}{12Na_2S_2O_3} + 12HCl \longrightarrow 12KCl + 12NaI + 6Na_2S_4O_6 + 6H_2O$$

No. of moles of $KIO_3 = \dfrac{0.10}{214}$

No. of moles of $Na_2S_2O_3$ required for $\dfrac{0.10}{214}$ moles of KIO_3

$$= \frac{12}{2} \times \frac{0.10}{214} = \frac{0.60}{214}$$

$$\text{Molarity of } Na_2S_2O_3 = \frac{0.6}{214} \times \frac{1000}{45} = 0.0623 \ M]$$

60. Gastric juice contains 3 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day, how many antacid tablets each containing 400 mL of $Al(OH)_3$ are needed to neutralise all the HCl produced in one day?

61. Zinc can be determined volumetrically by the precipitation reactions,

$$3Zn^{2+} + 2K_4[Fe(CN)_6] \longrightarrow K_2Zn_3[Fe(CN)_6] + 6K^+$$

A sample of Zn ore weighing 1.5432 g was prepared for reaction and required 34.68 mL of 0.1043 M $K_4[Fe(CN)_6]$ for titration. What is percentage of zinc in the ore?

62. A mixture of KOH and Na_2CO_3 solution required 15 mL of $N/20$ HCl using phenolphthalein as indicator. The same amount of alkali mixture when titrated using methyl orange as indicator required 25 mL of same acid. Calculate amount of KOH and Na_2CO_3 present in solution.

63. 1000 mL O_2 at NTP was passed through Siemen's ozonizer so that the volume is reduced to 888 mL at same condition. Ozonized oxygen is passed through KI solution. Liberated I_2 was titrated with 0.05 N hypo. Calculate volume of hypo used.

64. 30 mL of $K_2Cr_2O_7$ liberated iodine from KI solution when the iodine was titrated with hypo solution ($N/20$), the titre value was 45 mL. Find the concentration of $K_2Cr_2O_7$ in g per litre.

65. Excess of KI and dil. H_2SO_4 were mixed in 50 mL H_2O_2. The liberated I_2 required 20 mL of 0.1 N $Na_2S_2O_3$. Find out the strength of H_2O_2 in g per litre.

66. 25 mL H_2O_2 were added to excess of acidified solution of KI. The iodine so liberated required 20 mL of 0.1 N sodium thiosulphate for titration. Calculate the strength in terms of normality, percentage and volume.

67. Cl_2 gas can be produced in the lab by the reaction,

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

If a 6.13 g sample that is 96% $K_2Cr_2O_7$ is allowed to react with 320 mL of HCl solution having density 1.15 g/mL and containing 30% by mass of HCl, what mass of Cl_2 is generated?

68. What is the weight in gram of available O_2 per litre from a solution of H_2O_2, 10 mL of which when titrated with $N/20$ $KMnO_4$ solution required 25 mL for the reaction?

$$2KMnO_4 + 5H_2O_2 + 4H_2SO_4 \longrightarrow 5O_2 + 8H_2O + 2KHSO_4 + 2MnSO_4$$

69. A quantity of $KMnO_4$ was boiled with HCl and the gas evolved was led into a solution of KI. When the reaction was complete, the I_2 liberated was titrated with a solution of hypo containing 124 g of $Na_2S_2O_3 \cdot 5H_2O$ per litre. It was found that exactly 60 mL were required to decolourise the solution of I_2. What weight of $KMnO_4$ was used?

70. 0.5 g of a sample of bleaching powder was suspended in water and excess KI is added. On acidifying with dil. H_2SO_4, I_2 was liberated which required 50 mL of $N/10$ hypo ($Na_2S_2O_3 \cdot 5H_2O$). Calculate the percentage of available Cl_2 in bleaching powder.

71. 1.2 g of a sample of $CaOCl_2$ were suspended in water made up to 100 mL. 25 mL of this solution was treated with KI and the I_2 liberated corresponded to 10 mL of $N/25$ hypo. Calculate the percentage of Cl_2 available in $CaOCl_2$.

72. 1.6 g of pyrolusite was treated with 60 mL of normal oxalic acid and some H_2SO_4. The oxalic acid left undecomposed was made up to 250 mL, 25 mL of this solution required 32 mL of 0.1 N potassium permanganate ($KMnO_4$). Calculate the percentage of pure MnO_2 in pyrolusite.

73. A sample of pyrolusite weighing 0.5 g is distilled with conc. HCl. The evolved Cl_2 when passed through a solution of KI liberates sufficient I_2 to react with 125 mL of $N/12.5$ hypo ($Na_2S_2O_3 \cdot 5H_2O$). Calculate the percentage of MnO_2 in pyrolusite.

74. The iodide content of a solution was determined by titration with sodium thiosulphate crystalline containing 11.2% impurity. Calculate the normality of iodide ion solution in 250 mL of the iodide solution required 20 mL hypo (42 g hypo is dissolved in 1 litre).

75. The formula weight of an acid is 82. In a titration, 100 cm^3 of a solution of this acid containing 39.0 g of the acid per litre were completely neutralised by 95.0 cm^3 of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid? (IIT 2000)

[**Hint :** Normality of NaOH = 1

$$\text{Normality of acid} = \frac{1 \times 95}{100} = 0.95$$

Let the eq. mass of the acid be E.

$$\therefore \quad \frac{39}{E} = 0.95 \text{ or } E = 41\ ; \qquad \text{Basicity} = \frac{82}{41} = 2]$$

76. 20 mL of a solution containing ferrous sulphate and ferric sulphate acidified with H_2SO_4 is reduced by metallic zinc. The solution required 27.4 mL of 0.1 N solution of $K_2Cr_2O_7$ for oxidation. However before reduction with zinc, 20 mL of same solution required 17.96 mL of same $K_2Cr_2O_7$. Calculate the mass of $FeSO_4$ and $Fe_2(SO_4)_3$ per litre of the solution.

[**Hint :** After reduction $Fe_2(SO_4)_3$ is also reduced to $FeSO_4$ and titration gives total concentration of $FeSO_4$ and $Fe_2(SO_4)_3$. Titration before reduction gives only $FeSO_4$.

Milli equiv. of $K_2Cr_2O_7$ after reduction $= 27.4 \times 0.1 = 2.740$
Milli equiv. of $K_2Cr_2O_7$ before reduction $= 17.96 \times 0.1 = 1.796$
Milli equiv. of $Fe_2(SO_4)_3$ in 20 mL = 0.944
Milli equiv. of $FeSO_4$ in 20 mL = 1.796

$$\therefore \quad FeSO_4\ (gL^{-1}) = \frac{1.796}{1000} \times \text{Eq. mass} \times 40$$
$$= \frac{1.796}{1000} \times 152 \times 40 = 10.92$$
$$Fe_2(SO_4)_3\ (gL^{-1}) = \frac{0.944}{1000} \times \text{Eq. mass} \times 40$$
$$= \frac{0.944}{1000} \times 200 \times 40 = 7.55]$$

77. 3.0 g of pyrolusite ore were treated with 20 g of pure ferrous ammonium sulphate (Mol. mass = 392 g mol^{-1}) and dilute H_2SO_4. After the reaction, the solution was diluted to 500 mL. 50 mL of diluted solution required 10 mL of 0.1 N $K_2Cr_2O_7$ solution. Calculate the % of pure MnO_2 in pyrolusite.

[**Hint:** MnO_2 present in pyrolusite oxidises ferrous ammonium sulphate into ferric ammonium sulphate, *i.e.*, $Fe^{2+} \longrightarrow Fe^{3+}$. Unreacted ferrous ammonium sulphate is estimated by potassium dichromate solution.

$$MnO_2 + 2Fe^{2+} + 4H^+ \longrightarrow Mn^{2+} + 2H_2O + 2Fe^{3+}$$
$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

50 mL diluted ferrous ammonium sulphate solution

$$= 10 \text{ mL of } 0.1\ N\ K_2Cr_2O_7$$

500 mL diluted ferrous ammonium sulphate solution

$$= 10 \times 10 \text{ mL of } 0.1\ N\ K_2Cr_2O_7$$
$$= 100 \text{ mL of } 0.1\ N \text{ FeAS}$$
$$= \frac{0.1 \times 392}{1000} \times 100 = 3.92 \text{ g}$$

$$\text{Used FeAS} = (20 - 3.92) = 16.08 \text{ g}$$

$$MnO_2 \text{ present in pyrolusite} = \frac{87}{392 \times 2} \times 16.08 = 1.784 \text{ g}$$

$$\text{Percentage of pure } MnO_2 = \frac{1.784}{3.0} \times 100 = 59.4\%]$$

Answers

1. (i) 54; (ii) 52.66; (iii) 158; (iv) M.w./10; (v) 41; (vi) 32
2. 0.2 N **3.** 10 L **4.** 0.08 N
5. (a) 0.2 N **6.** 45 g/L **7.** 70.4%
8. 30%
9. HCl = 42.69, H_2SO_4 = 57.31 **10.** 91.54%
11. 0.1435 g **12.** 50.0 **13.** 12
14. Vol. of water = 225 mL
15. Vol. of A = 200 mL, Vol. of B = 800 mL
16. $CaCO_3$ = 48.78%, $MgCO_3$ = 51.22%
17. 60 mL **18.** 53, 106 **19.** Na_2CO_3 = 84.8%
20. 1.605 g **21.** Na_2CO_3 = 2.12 g/L, $NaHCO_3$ = 0.84 g/L
22. NaCl = 33.75%, Na_2CO_3 = 66.25%
23. NaOH = 2.0 g/L, Na_2CO_3 = 1.325 g/L
24. 66% **25.** 0.6 N **26.** 88.96%
27. Contamination percentage 46.95%
28. 209.8 **29.** $10H_2O$ **30.** 0.0075 N
31. 35.5% **32.** 5.372 g/L **33.** 91.25 g/L, 2.5 N, 400 mL

34. With phenolphthalein 50 mL, with methyl orange 60 mL
35. 3.528 g/L **36.** 87.5%
37. NaCl 61.81%; KCl 38.19% **38.** 96.31%
39. 35.5% **41.** 63, 126 **42.** 82%
43. 30.90 **45.** (a) 50, (b) 150 mL
47. 1.625 g **49.** 94.7% **50.** 337 mL
52. 81.25%
53. Na_2CO_3 = 82.8%; Na_2SO_4 = 17.2%
54. Na_2CO_3 = 0.5962; K_2CO_3 = 0.6038
56. % H_2O_2 = 85; Vol. O_2 = 124.79 mL
57. 41.52% **60.** 14 **61.** 22.85
62. Na_2CO_3 = 0.053 g; KOH = 0.014 g
63. 400 mL **64.** 3.675 g **65.** 0.68 g
66. N = 0.08, V = 0.448
67. 4.263 **68.** 2 g **69.** 0.9486 g
70. 35.5% **71.** 4.7% **72.** 76.125%
73. 87% **74.** 0.024 **77.** 59.4%

OBJECTIVE QUESTIONS

Set–1 : Questions with single correct answer

1. A normal solution:
(a) contains one gram equivalent mass of the substance in one litre solution
(b) contains one gram molecular mass of the substance in one litre solution
(c) contains one gram equivalent mass of the substance in 100 mL of the solution
(d) is that whose concentration is known

2. Which one of the following is a standard solution?
(a) It contains one gram equivalent mass of the substance in one litre solution
(b) Its strength is accurately known
(c) Its strength is to be determined
(d) A solution which has been prepared from pure substance

3. The molecular mass of H_3PO_3 is 82. Its equivalent mass, if it is completely neutralised, is:
(a) 82 (b) 27.3 (c) 41 (d) 246

4. The molecular mass of Mohr's salt, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, is 392. Its equivalent mass is:
(a) 196 (b) 39.2 (c) 98.0 (d) 392

5. According to the following equation,
$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$
the equivalent mass of $K_2Cr_2O_7$ is:
(a) mol. mass/3 (b) mol. mass/6
(c) mol. mass (d) mol. mass/12

6. Amount of oxalic acid required to prepare 250 mL of $N/10$ solution (Mol. mass of oxalic acid = 126) is:
(a) 1.5759 g (b) 3.15 g (c) 15.75 g (d) 63.0 g

7. Normality of 2% H_2SO_4 solution by volume is nearly:
(a) 2 (b) 4 (c) 0.2 (d) 0.4

8. The molecular mass of $KMnO_4$ is M. Its equivalent mass in acidic medium will be:
(a) M (b) $M/2$ (c) $M/5$ (d) $M/4$

9. When $KMnO_4$ is reduced with oxalic acid in acidic medium, the oxidation number of Mn changes from:
(a) 7 to 4 (b) 6 to 4 (c) 7 to 2 (d) 4 to 2

10. For the half cell reaction,

$$2BrO_3^- + 12H^+ + 10e \longrightarrow Br_2 + 6H_2O$$

the equivalent mass of sodium bromate is:
(a) equal to its mol. mass (b) 1/3 of its mol. mass
(c) 1/6 of its mol. mass (d) 1/5 of its mol. mass

11. In the reaction,

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

equivalent mass of iodine is:
(a) equal to its molecular mass
(b) 1/2 the molecular mass
(c) 1/4 the molecular mass
(d) twice the molecular mass

12. A molal solution is one that contains one mole of the solute in:
(a) 1000 g of the solvent (b) one litre of the solvent
(c) one litre of the solution (d) 22.4 litre of the solvent

13. In alkaline conditions, $KMnO_4$ reacts as follows,

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Therefore, its equivalent mass will be:
(a) 31.6 (b) 52.7 (c) 72.0 (d) 158.0

14. 0.1 N solution of Na_2CO_3 is being titrated with 0.1 N HCl, the best indicator to be used is:
(a) potassium ferricyanide (b) phenolphthalein
(c) methyl orange (d) litmus

15. For the preparation of a litre of $N/10$ solution of H_2SO_4, we need:
(a) 9.8 g (b) 4.9 g (c) 10 g (d) 98 g

16. Molecular mass of a tribasic acid is M. Its equivalent mass will be:
(a) $M/3$ (b) $3\,M$ (c) $M/2$ (d) $2\,M$

17. A solution containing Fe^{2+} ions is titrated with $KMnO_4$ solution. Indicator used will be:
(a) phenolphthalein (b) methyl orange
(c) litmus (d) none of these

18. If 200 mL of $N/10$ HCl were added to 1 g calcium carbonate, what would remain after the reaction?
(a) $CaCO_3$ (b) HCl
(c) Neither of the two (d) Part of both

19. How many mL of 1 M H_2SO_4 acid solution is required to neutralise 10 mL of 1 M NaOH?
(a) 5 mL (b) 2.5 mL
(c) 10 mL (d) 20 mL

20. 200 mL of 3 N HCl were mixed with 200 mL of 6 N H_2SO_4 solution. The final normality of H_2SO_4 in the resultant solution will be:
(a) 9 N (b) 3 N (c) 6 N (d) 2 N

21. The volume of water to be added to 400 mL of $N/8$ HCl to make it exactly $N/12$, is:
(a) 400 mL (b) 300 mL
(c) 200 mL (d) 100 mL

22. 100 mL of 0.3 N HCl were mixed with 200 mL of 0.6 N H_2SO_4 solution. The final normality of acid was:
(a) 0.4 N (b) 0.5 N (c) 0.6 N (d) 0.9 N

23. The M mass of NaOH is 40.50 mL of a solution containing 2 g of NaOH in 500 mL will require for complete neutralisation:
(a) 10 mL decinormal HCl (b) 20 mL decinormal HCl
(c) 50 mL decinormal HCl (d) 25 mL decinormal HCl

24. 50 g of a sample of NaOH required for complete neutralisation, 1 litre N HCl. What is the percentage purity of NaOH?
(a) 80 (b) 70 (c) 60 (d) 50

25. Weight of iodine required to oxidise 500 mL N $Na_2S_2O_3$ solution, is:
(a) 6.35 g (b) 63.5 g (c) 127 g (d) 254 g

26. 25 mL N $K_2Cr_2O_7$ acidified solution will liberate . . . iodine from KI solution.
(a) 0.3175 g (b) 3.175 g (c) 31.75 g (d) 317.5 g

27. The indicator used in iodometric titrations is:
(a) phenolphthalein (b) litmus
(c) potassium iodide (d) starch

28. Which of the following acids is added in the titration of oxalic acid and potassium permanganate?
(a) HNO_3 (b) HCl
(c) CH_3COOH (d) H_2SO_4

29. In the titration of $K_2Cr_2O_7$ iodometrically, near the end point the colour of the solution becomes:
(a) green (b) red (c) yellow (d) blue

30. In the titration of ferrous ammonium sulphate and potassium dichromate, the external indicator used is:
(a) KCNS (b) NH_4CNS
(c) $K_3Fe(CN)_6$ (d) $K_4Fe(CN)_6$

31. 0.1 N solution of a dibasic acid can be prepared by dissolving 0.45 g of the acid in water and diluting to 100 mL. The molecular mass of the acid is:
(a) 45 (b) 90 (c) 135 (d) 180

32. 100 mL of 0.2 N HCl solution is added to 100 mL of 0.2 N $AgNO_3$ solution. The molarity of nitrate ions in the resulting mixture will be:
(a) 0.05 M (b) 0.5 M (c) 0.1 M (d) 0.2 M

33. In an experiment, 20 mL of a decinormal HCl solution was added to 15 mL of a decinormal $AgNO_3$ solution. AgCl was precipitated out and excess of acid was titrated with N/20 NaOH solution. The volume of NaOH required was:
(a) 10 mL (b) 20 mL (c) 30 mL (d) 5 mL

34. Iodine solution is prepared by dissolving iodine in:
(a) NaOH (b) Na_2CO_3 (c) H_2O (d) KI

35. Which one of the following is not a primary standard?
(a) Oxalic acid (b) Sodium thiosulphate
(c) Sodium hydroxide (d) Potassium dichromate

36. Which one of the following is a primary standard?
(a) $KMnO_4$ (b) $CuSO_4 \cdot 5H_2O$
(c) I_2 (d) H_2SO_4

37. When 10 mL of 10 M solution of H_2SO_4 and 100 mL of 1 M solution of NaOH are mixed, the resulting solution will be:
(a) acidic (b) neutral
(c) alkaline (d) cannot be predicted

38. 1.0 g of a metal carbonate neutralises 200 mL of 0.1 N HCl. The equivalent mass of the metal will be:
(a) 50 (b) 40 (c) 20 (d) 100

39. The normality of a 26% mass/volume solution of ammonia (density 0.885 g/mL) is approximately:
(a) 1.5 (b) 4.0 (c) 0.4 (d) 15.3

40. The molarity of pure water is:
(a) 18 M (b) 50.0 M (c) 55.6 M (d) 100 M

41. 5.0 g of H_2O_2 is present in 100 mL of the solution. The molecular mass of H_2O_2 is 34. The molarity of the solution is:
(a) 1.5 M (b) 0.15 M (c) 3.0 M (d) 50 M

42. 2 N solution of sodium carbonate is equivalent to a solution of strength:
(a) 106 g per 100 mL (b) 53 g per 100 mL
(c) 10.6 g per 100 mL (d) 5.3 g per 100 mL

43. Which one of these solutions has the highest normality?
(a) 8 g KOH per 100 mL (b) 0.5 M H_2SO_4
(c) 6 g of NaOH per 100 mL (d) N H_3PO_4

44. 1 g of a metal required 50 mL of 0.5 N HCl to dissolve it. The equivalent mass of the metal is:
(a) 25 (b) 50 (c) 20 (d) 40

45. What volume of CO_2 at NTP will be liberated by the action of 100 mL of 0.2 N HCl on $CaCO_3$?
(a) 112 mL (b) 224 mL (c) 448 mL (d) 120 mL

46. The equivalent mass of phosphoric acid (H_3PO_4) is 49. It behaves as . . . acid.
(a) monobasic (b) dibasic
(c) tribasic (d) tetrabasic

47. The normality of 10% (mass/volume) acetic acid is:
(a) 1 N (b) 10 N (c) 1.7 N (d) 0.83 N

48. Equivalent mass of $KMnO_4$, when it is converted to $MnSO_4$, is: [illegible]
(a) M/5 (b) M/3 (c) M/6 (d) M/2

49. How many grams of CH_3OH would have to be added to water to prepare 150 mL of a solution that is 2.0 M CH_3OH? [illegible]
(a) 9.6 (b) 2.4 (c) 9.6×10^3 (d) 4.3×10^2

50. On dissolving 1 mole of each of the following acids in one litre water, the acid which does not give a solution of strength 1 N is: [illegible]
(a) HCl (b) $HClO_4$ (c) HNO_3 (d) H_3PO_4

51. 0.16 g a dibasic acid required 25 mL of decinormal NaOH solution for complete neutralisation. The molecular mass of the acid is: [illegible]
(a) 32 (b) 64 (c) 128 (d) 256

52. 5 mL of N HCl, 20 mL of N/2 H_2SO_4 and 30 mL of N/3 HNO_3 are mixed together and volume made to one litre. The normality of the resulting solution is: [illegible]
(a) N/5 (b) N/10
(c) N/20 (d) N/40

53. The equivalent mass of $MnSO_4$ is half its molecular mass when it is converted to:
(a) Mn_2O_3 (b) MnO_2
(c) MnO_4^- (d) MnO_4^{2-}

54. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced reaction are: [illegible]

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

55. 100 mL solution consists 4 g caustic soda. The normality of the solution is: [illegible]
(a) 1.0 (b) 0.1 (c) 0.5 (d) 4.0

56. The amount of a caustic soda required for complete neutralisation of 100 mL 0.1 N HCl is: [PMT (MP) 1994]
(a) 4.0 g (b) 0.04 g (c) 0.4 g (d) 2.0 g

57. What volume of $N/2$ and $N/10$ HCl should be taken in order to make a 2 litre solution of $N/5$ strength?
(a) 0.5 litre $N/2$ HCl and 1.5 litre of $N/10$ HCl
(b) 1 litre $N/2$ HCl and 1 litre $N/10$ HCl
(c) 1.5 litre $N/2$ HCl and 0.5 litre $N/10$ HCl
(d) 0.7 litre $N/2$ HCl and 1.3 litre $N/10$ HCl

58. The molar concentration of the chloride ion in the solution obtained by mixing 300 mL of 3.0 M NaCl and 200 mL of 4.0 M solution of $BaCl_2$ is:
(a) 1.6 M (b) 1.8 M (c) 5.0 M (d) 0.5 M

59. The normality of 0.3 M phosphorous acid (H_3PO_3) is: [illegible]
(a) 0.1 (b) 0.9 (c) 0.3 (d) 0.6

60. A 100 mL solution of 0.1 N HCl was titrated with 0.2 N NaOH solution. The titration was discontinued after adding 30 mL of NaOH solution. The titration was completed by adding 0.25 N KOH solution. The volume of KOH required for completing the titration is: [illegible]
(a) 70 mL (b) 32 mL (c) 35 mL (d) 16 mL

61. An aqueous solution of 6.3 g of oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is: [illegible]
(a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL

62. In order to prepare one litre normal solution of $KMnO_4$, how many grams of $KMnO_4$ are required if the solution is to be used in acid medium for oxidation? [illegible]
(a) 158 g (b) 31.6 g (c) 62 g (d) 790 g

63. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. Equivalent weight of the metal is: [illegible]
(a) 33.25 (b) 3.325 (c) 12 (d) 20

64. Phosphoric acid H_3PO_4 can be neutralised to:
(a) HPO_4^{2-} (b) PO_4^{3-} (c) $H_2PO_4^-$ (d) HPO_3^{2-}

65. 'a' g KHC_2O_4 required to reduce 100 mL of 0.02 M $KMnO_4$ in acid medium and 'b' g KHC_2O_4 neutralises 100 mL of 0.05 M $Ca(OH)_2$ then :
(a) $a = b$ (b) $2a = b$
(c) $a = 2b$ (d) none of these

66. Which of the following statements is /are true about H_3PO_2?
(a) It is a tribasic acid
(b) One mole of it is neutralised by 0.5 mole of $Ca(OH)_2$
(c) NaH_2PO_2 is acidic salt
(d) It disproportionates to H_3PO_3 and PH_3 on heating

67. Mixture of 1 mole BaF_2 and 2 mole H_2SO_4 can be neutralised by:
(a) 1 mole KOH (b) 2 mole $Ca(OH)_2$
(c) 4 mole NaOH (d) 2 mole KOH

68. $28\,NO_3^- + 3As_2S_3 + 4H_2O \rightarrow 6AsO_4^{3-} + 28NO + 9SO_4^{2-} + 8H^+$.
What will be the equivalent mass of As_2S_3 in above reaction?
(a) $\frac{\text{M. wt.}}{2}$ (b) $\frac{\text{M. wt.}}{4}$ (c) $\frac{\text{M. wt.}}{24}$ (d) $\frac{\text{M. wt.}}{28}$

69. The number of moles of $KMnO_4$ that will need to react completely with one mole of ferrous oxalate in acidic solution is: [IIT (July) 1997]
(a) 2/5 (b) 3/5 (c) 4/5 (d) 1

70. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is: [IIT (July) 1997]
(a) 2/5 (b) 3/5 (c) 4/5 (d) 1

71. The equivalent weight of KIO_3 in the reaction,

$$2Cr(OH)_3 + OH^- + KIO_3 \longrightarrow 2CrO_4^{2-} + 5H_2O + KI \text{ is:}$$

[PET (MP) 2003]
(a) molecular weight (b) $\frac{\text{molecular weight}}{3}$
(c) $\frac{\text{molecular weight}}{6}$ (d) $\frac{\text{molecular weight}}{2}$

72. In the reaction,

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

equivalent weight of iodine will be equal to: [PMT (MP) 2004]
(a) 4/6 of molecular weight
(b) molecular weight
(c) 2/9 of molecular weight
(d) twice the molecular weight

73. The volume of a concentrated H_2SO_4, mixed with 0.5 N KOH to prepare 150 cm^3 of 0.2 N KOH. Solution is: (KCET 2004)
(a) 50 cm^3 (b) 60 cm^3 (c) 70 cm^3 (d) 80 cm^3

74. For the decolorisation of 1 mole of $KMnO_4$, the number of moles of H_2O_2 required is: (AIIMS 2004)
(a) 1/2 (b) 3/2 (c) 5/2 (d) 7/2

75. The product of oxidation of I^- with MnO_4^- in alkaline medium is: [IIT (S) 2004]
(a) IO_3^- (b) I_2 (c) IO^- (d) IO_4^-

76. Volume of 0.1 M $K_2Cr_2O_7$ required to oxidise 35 mL of 0.5 M $FeSO_4$ solution is: [illegible]
(a) 29.2 mL (b) 17.5 mL
(c) 175 mL (d) 145 mL

77. A commercial sample of H_2O_2 is labelled 10 volume. Its percentage strength is nearly: [illegible]
(a) 1% (b) 3% (c) 10% (d) 90%

78. 50 mL of 10 N H_2SO_4, 25 mL of 12 N HCl and 40 mL of 5 N HNO_3 are mixed and the volume of the mixture is made 1000 mL by adding water. The normality of the resulting solution will be: [illegible]
(a) 1 N (b) 2 N (c) 3 N (d) 4 N
(e) 9 N

[**Hint:** $N_1V_1 + N_2V_2 + N_3V_3 = N_R \times V_R$
$10 \times 50 + 12 \times 25 + 5 \times 40 = N_R \times 1000$
$500 + 300 + 200 = N_R \times 1000$
$N_R = 1$ (Resultant normality)]

79. Acidified $KMnO_4$ oxidizes oxalic acid to CO_2. What is the volume (in litre) of 10^{-4} M $KMnO_4$ required to completely oxidize 0.5 litre of 10^{-2} M oxalic acid in acid medium? [illegible]
(a) 125 (b) 1250 (c) 200 (d) 20

[**Hint:** $2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}COOH\\ |\\ COOH\end{matrix} \longrightarrow K_2SO_4$
$+ 2MnSO_4 + 10CO_2 + 8H_2O$

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}\begin{pmatrix}COOH\\ |\\ COOH\end{pmatrix}$$

$$\frac{10^{-4} \times V_1}{2} = \frac{10^{-2} \times 0.5}{5}$$

$$V_1 = 20 \text{ L}]$$

80. The concentration of oxalic acid is 'x' mol litre^{-1}. 40 mL of this solution reacts with 16 mL of 0.05 M acidified $KMnO_4$. What is the pH of 'x' M oxalic acid solution?
(Assume that oxalic acid dissociates completely.)
[EAMCET (Engg.) 2006]

(a) 1.3 (b) 1.699 (c) 1 (d) 2

[**Hint:** $2KMnO_4 + 3H_2SO_4 + 5\begin{matrix}COOH\\ |\\ COOH\end{matrix} \longrightarrow K_2SO_4 + 2MnSO_4$
$+ 8H_2O + 10CO_2$

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}\begin{pmatrix}COOH\\ |\\ COOH\end{pmatrix}$$

$$\frac{0.05 \times 16}{2} = \frac{x \times 40}{5}$$

$$x = 0.05\ M$$

$$[H^+] = 2 \times 0.05 = 0.1\ M$$

$$pH = -\log(H^+) = -\log(0.1) = 1]$$

81. Consider the titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is: (IIT 2007)

(a) 3 (b) 4 (c) 5 (d) 6

[**Hint:** $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
1 mole of dichromate oxidises six moles of ferrous ion present in Mohr's salt]

82. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is:
[CBSE (Med.) 2007]

(a) $\frac{4}{5}$ (b) $\frac{2}{5}$ (c) 1 (d) $\frac{3}{5}$

[**Hint:** The redox reaction is:
$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$
1 mole SO_3^{2-} will be oxidised by $\frac{2}{5}$ mol of MnO_4^-]

83. For the reaction between $KMnO_4$ and H_2O_2, the number of electrons transferred per mole of H_2O_2 is:
[PMT (Haryana) 2007]

(a) one (b) two (c) three (d) four

84. Number of moles of $K_2Cr_2O_7$ reduced by one mole of Sn^{2+} is:
[PMT (Raj.) 2007]

(a) 1/3 (b) 3 (c) 1/6 (d) 6

85. The formula mass of Mohr's salt is 392. The iron present in it is oxidised by $KMnO_4$ in acid medium. The equivalent mass of Mohr's salt is: [Indraprasth (Engg.) 2007]

(a) 392 (b) 31.6 (c) 278 (d) 156

86. To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorus acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is: [Jamia Millia Islamia (Engg.) 200

(a) 10 mL (b) 20 mL (c) 40 mL (d) 60 mL

[**Hint:** $H_3PO_3 + 2KOH \longrightarrow K_2HPO_3 + 2H_2O$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$\frac{0.1 \times 20}{1} = \frac{0.1 \times V_2}{2}$$

$$V_2 = 40 \text{ mL}]$$

87. 10 cm^3 of 0.1 N monobasic acid requires 15 cm^3 of sodium hydroxide solution whose normality is :

(a) 0.066 N (b) 0.66 N (c) 1.5 N (d) 0.15 N
(KCET 2008)

[**Hint :** $N_1V_1 = N_2V_2$

$$0.1 \times 10 = N_2 \times 15$$

$$N_2 = 0.066]$$

88. Amount of oxalic acid present in solution can be oxidised by its titration with $KMnO_4$ solution in the presence of H_2SO_4. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl: (AIEEE 2008)

(a) oxidises oxalic acid to carbon dioxide and water
(b) gets oxidised by oxalic acid to chlorine
(c) Furnishes H^+ ions in addition to those from oxalic acid
(d) reduces permanganate to Mn^{2+}

89. How many moles of acidified $FeSO_4$ can be completely oxidised by one mole of $KMnO_4$? [BHU (Mains) 2008]

(a) 10 (b) 5 (c) 6 (d) 2

[**Hint:** $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$[2FeSO_4 + H_2SO_4 + [O] \rightarrow Fe_2(SO_4)_3 + H_2O] \times 5$

$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4$
$+ 5Fe_2(SO_4)_3 + 8H_2O$

---

2 mole $KMnO_4 \equiv 10$ mole $FeSO_4$
1 mole $KMnO_4 \equiv 5$ mole $FeSO_4$]

90. In the titration of nitric acid against potassium carbonate, the indicator used is : [Comed (Karnataka) 20

(a) methyl orange (b) self indicator
(c) phenolphthalein (d) diphenylamine

91. In transforming 0.01 mole of PbS to $PbSO_4$, the volume of 10 volume H_2O_2 required will be : [JEE (WB) 20

(a) 11.2 mL (b) 22.4 mL (c) 33.6 mL (d) 44.8 mL

[**Hint :** $PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$

0.04 mole of H_2O_2 is required to react with 0.01 mole PbS.
Molarity of H_2O_2 may be calculated as,

Volume strength = Molarity × 11.2

$$10 = M \times 11.2$$

$$M = 0.892$$

$$\text{Number of moles} = \frac{MV}{1000}$$

$$0.04 = \frac{0.892 \times V}{1000}$$

$$V = 44.8 \text{ mL}]$$

92. A solution containing Na_2CO_3 and NaOH requires 300 mL of 0.1 *N* HCl using phenolphthalein as an indicator. Methyl orange is then added to above titrated solution when a further 25 mL of 0.2 *N* HCl is required. The amount of NaOH present in the original solution is:

(a) 0.5 g (b) 1 g (c) 2 g (d) 4 g

[**Hint** : 300 mL HCl of 0.1 *N* neutralises entire amount of NaOH and 1/2 of Na_2CO_3. Remaining 1/2 of Na_2CO_3 is neutralised by 25 mL of 0.2 *N* HCl, *i.e.*, 50 mL of 0.1 *N* HCl.

Thus, 250 mL of 0.1 *N* HCl is required to neutralise NaOH completely.

$$\begin{aligned} N_1V_1(\text{NaOH}) &= N_2V_2(\text{HCl}) \\ &= 0.1 \times 250 \\ &= 25 \\ W_{\text{NaOH}} &= \frac{ENV}{1000} = \frac{40 \times 25}{1000} = 1\text{ g}\,] \end{aligned}$$

93. Ceric ammonium sulphate and potassium permanganate are used as oxidising agents in acidic medium for oxidation of ferrous ammonium sulphate to ferric sulphate. The ratio of number of moles of ceric ammonium sulphate required per mole of ferrous ammonium sulphate to the number of moles of $KMnO_4$ required per mole of ferrous ammonium sulphate is:

(a) 5.0 (b) 0.2 (c) 0.6 (d) 2.0

[**Hint** : Oxidation of ferrous ammonium sulphate by $KMnO_4$ is :

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \longrightarrow$$
$$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + 68H_2O$$

$\therefore$ 1 mole of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ consumes 1/5 mole of $KMnO_4$.

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+}$$

$$\text{Required ratio} = \frac{1}{1/5} = 5.0\,]$$

94. One kilogram of sea water sample contains 6 mg of dissolved O_2. The concentration of O_2 in the sample in ppm is:

(a) 0.6 (b) 6.0 (c) 60.0 (d) 16.0
(e) 32.0

[**Hint** : 1 kg water $\equiv 10^6$ mg:
10^6 mg water contains 6 mg O_2
$\therefore$ Concentration of O_2 is 6 ppm.]

95. The estimation of available chlorine in bleaching powder is done by:

(a) Acid-base titration (b) Permanganometric titration
(c) Iodimetric titration (d) Iodometric titration

96. What volume of 0.1 M H_2SO_4 is required in litres to neutralize completely 1 litre of a solution containing 20 g of NaOH?

(a) 5.0 (b) 0.5 (c) 2.5 (d) 10.0

[**Hint** : $M_{\text{NaOH}} = \dfrac{w_B \times 1000}{m_B \times V} = \dfrac{20 \times 1000}{40 \times 1000} = 0.5$

Reaction : $H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{2}$$
$$0.1 \times V_1 = \frac{0.5 \times 1}{2}$$
$$V_1 = 2.5\text{ L}]$$

Assertion-Reason TYPE QUESTIONS

The questions given below consist of an **'Assertion' (A)** and **'Reason' (R).** Use the following keys to choose the appropriate answer:

(a) If both (A) and (R) are correct, and (R) is the correct explanation of (A).
(b) If both (A) and (R) are correct, but (R) is not the correct explanation of (A).
(c) If (A) is correct, but (R) is incorrect.
(d) If (A) is incorrect, but (R) is correct.

1. (A) H_3PO_3 is a dibasic acid.
(R) Two H-atoms are directly attached to phosphorus '*P*'.

2. (A) Equivalent mass of $KMnO_4$ is equal to one-fifth of its molecular mass when it acts as an oxidising agent in acidic medium.
(R) Oxidation number of Mn in $KMnO_4$ is +7.

3. (A) 5 *M* HCl solution is diluted 10 times, its molarity becomes 50.
(R) On dilution, molarity of the solution decreases.

4. (A) In the reaction, $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$; I_2 is oxidised.
(R) During oxidation, loss of electron takes place.

5. (A) In the titration of HCl against NaOH, phenolphthalein is used as suitable indicator.
(R) Phenolphthalein is pink coloured in basic medium.

6. (A) Concentration of H_2O_2 is expressed in volume.
(R) Volume strength of H_2O_2 = Normality × 5.6.

7. (A) Iodimetric titrations are redox titrations.
(R) The iodine solution acts as an oxidising agent.

8. (A) Starch is used as absorption indicator in iodometric and iodimetric titrations.
(R) Starch forms iodostarch complex with iodine, which is blue coloured.

9. (A) H_3BO_3 is monobasic Lewis acid but its salt Na_3BO_3 exists.
(R) H_3BO_3 reacts with NaOH to give Na_3BO_3.
[Hint $H_3BO_3 + NaOH \longrightarrow NaB(OH)_4$
$3C_2H_5OH + H_3BO_3 \longrightarrow (C_2H_5)_3BO_3 + 3H_2O$
$(C_2H_5)_3BO_3 + 3NaOH \longrightarrow Na_3BO_3 + 3C_2H_5OH$]

10. (A) Equivalent weight of a base = $\dfrac{\text{Molecular weight}}{\text{Acidity}}$
(R) Acidity is the number of replaceable hydrogen atoms in one molecule of the base.

Answers : OBJECTIVE QUESTIONS

1. (a)	2. (b)	3. (c)	4. (d)	5. (b)	6. (a)	7. (d)	8. (c)
9. (c)	10. (d)	11. (b)	12. (a)	13. (d)	14. (c)	15. (b)	16. (a)
17. (d)	18. (c)	19. (a)	20. (b)	21. (c)	22. (b)	23. (c)	24. (a)
25. (b)	26. (b)	27. (d)	28. (d)	29. (a)	30. (c)	31. (b)	32. (c)
33. (a)	34. (d)	35. (c)	36. (b)	37. (a)	38. (a)	39. (d)	40. (c)
41. (a)	42. (c)	43. (c)	44. (d)	45. (b)	46. (b)	47. (c)	48. (a)
49. (a)	50. (d)	51. (c)	52. (d)	53. (b)	54. (a)	55. (a)	56. (c)
57. (a)	58. (c)	59. (d)	60. (d)	61. (a)	62. (b)	63. (a)	64. (a, b, c)
65. (b)	66. (b, d)	67. (b, c)	68. (d)	69. (b)	70. (a)	71. (c)	72. (b)
73. (b)	74. (c)	75. (a)	76. (a)	77. (b)	78. (a)	79. (d)	80. (c)
81. (d)	82. (b)	83. (c)	84. (a)	85. (a)	86. (c)	87. (a)	88. (d)
89. (b)	90. (c)	91. (d)	92. (b)	93. (a)	94. (b)	95. (d)	96. (c)

Answers : ASSERTION-REASON TYPE QUESTIONS

1. (c)	2. (b)	3. (d)	4. (d)	5. (b)	6. (b)	7. (a)	8. (a)
9. (c)	10. (c)						

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

1. The value of n in the equation,

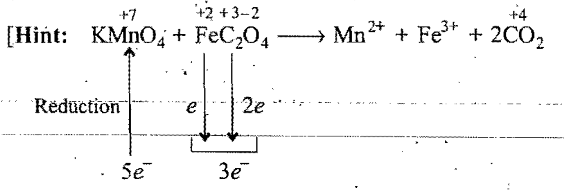
$$Cr_2O_7^{2-} + 14H^+ + ne^- \longrightarrow 2Cr^{3+} + 7H_2O$$

is:

(a) 2 (b) 3 (c) 4 (d) 6

2. The number of moles of acidified $KMnO_4$ required to oxidise one mole of ferrous oxalate (FeC_2O_4) is:

(a) 5 (b) 3 (c) 0.6 (d) 1.5



[**Hint:** $\overset{+7}{KMnO_4} + \overset{+2\ +3-2}{FeC_2O_4} \longrightarrow Mn^{2+} + Fe^{3+} + 2\overset{+4}{CO_2}$

∴ 5 mole $FeC_2O_4 \equiv 3$ mole $KMnO_4$

1 mole $FeC_2O_4 \equiv 0.6$ mole $KMnO_4$]

3. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of the solution required 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. Then the amount of Na_2CO_3 and $NaHCO_3$ in 1 litre of the solution is:

(a) 5.3 g and 4.2 g (b) 3.3 g and 6.2 g

(c) 4.2 g and 5.3 g (d) 6.2 g and 3.3 g

4. V_1 mL of NaOH of normality x and V_2 mL of $Ba(OH)_2$ of normality y are together sufficient to neutralize exactly 100 mL of 0.1 N HCl. If $V_1 : V_2 = 1 : 4$ and if $x : y = 4 : 1$, what fraction of the acid is neutralised by $Ba(OH)_2$?

(a) 0.5 (b) 0.33 (c) 0.67 (d) 0.25

5. A 0.518 g sample of limestone is dissolved in HCl and then the calcium is precipitated as CaC_2O_4. After filtering and washing the precipitate, it requires 40 mL of 0.25 N $KMnO_4$ solution acidified with H_2SO_4 to titrate it as,

$$MnO_4^- + H^+ + C_2O_4^{2-} \longrightarrow CO_2 + Mn^{2+} + 2H_2O$$

The percentage of CaO in the sample is:

(a) 54% (b) 27.1% (c) 42% (d) 84%

[**Hint:** Number of milliequivalents of CaC_2O_4, $KMnO_4$ and CaO will be same.

$$40 \times 0.25 = W / \frac{56}{2} \times 1000$$

$$W = 0.28 \text{ g (Mass of CaO)}$$

$$\% \text{ CaO} = \frac{0.28}{0.518} \times 100 = 54\%]$$

6. When 40 mL of 0.1 N HCl and 20 mL of 0.1 M H_2SO_4 are mixed together, the normality of the mixture will be:

(a) $\frac{1}{5}N$ (b) $\frac{2}{15}N$ (c) $\frac{15}{2}N$ (d) $\frac{5}{1}N$

[**Hint:** $N_1V_1 + N_2V_2 = N_R(V_1 + V_2)$

$$0.1 \times 40 + 0.2 \times 20 = N_R(60)$$

$$N_R = \frac{8}{60} = \frac{2}{15}\ ]$$

7. What is the normality of 0.3 M H_3PO_4 when it undergoes the reaction as?

$$H_3PO_4 + 2OH^- \longrightarrow HPO_3^{2-} + 2H_2O$$

(a) 0.3 N (b) 0.15 N (c) 0.60 N (d) 0.90 N

8. In the mixture of ($NaHCO_3 + Na_2CO_3$), volume of HCl required is x mL with phenolphthalein indicator and y mL with methyl orange indicator in same titration. Hence, volume of HCl for complete reaction of Na_2CO_3 is:

(a) $2x$ (b) y (c) $x/2$ (d) $(y - x)$

[**Hint:** In presence of phenolphthalein, 50% Na_2CO_3 is neutralised whereas $NaHCO_3$ remains unaffected. In presence of methyl orange, both Na_2CO_3 and $NaHCO_3$ will be 100% neutralised.

Let volume of HCl for complete reaction of $Na_2CO_3 = V_1$ mL and volume of HCl for complete reaction of $NaHCO_3 = V_2$ mL. With phenolphthalein, 50% Na_2CO_3 will be neutralized.

∴ $$\frac{V_1}{2} = x,\ V_1 = 2x]$$

9. 40 mL of 0.05 M $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (sesquicarbonate) is titrated against 0.05 M HCl. x mL of HCl is used when phenolphthalein is the indicator and y mL HCl is used when methyl orange is the indicator in two separate titrations; hence $(y - x)$ is:

(a) 80 mL (b) 30 mL

(c) 120 mL (d) none of these

10. Equivalent mass of H_3PO_2 when it disproportionates into PH_3 and H_3PO_3 is (Molecular mass = M):

(a) M (b) $\frac{M}{2}$ (c) $\frac{M}{4}$ (d) $\frac{3M}{4}$

[**Hint:** $H_3\overset{+1}{P}O_2 \longrightarrow H_3\overset{+3}{P}O_3$; Eq. wt. $= \frac{M}{2}$

(Change in oxidation number = 2)

$$H_3\overset{+1}{P}O_2 \longrightarrow \overset{-3}{P}H_3;\ \text{Eq. wt.} = \frac{M}{4}$$

(Change in oxidation number = 4)

The equivalent mass of H_3PO_2 in the process of disproportionation $= \frac{M}{2} + \frac{M}{4} = \frac{3M}{4}$]

11. The reagent commonly used to determine hardness of water titrimetrically is:

(a) oxalic acid (b) disodium salt of EDTA

(c) sodium citrate (d) sodium thiosulphate

12. The equivalent mass of sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) in the reaction,

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

is:

(a) 248 (b) 124 (c) 596 (d) 62

13. If 100 mL of the acid is neutralised by 100 mL of 4 M NaOH, the purity of concentrated HCl (sp. gravity = 1.2) is:

(a) 12% (b) 98% (c) 73% (d) 43%

14. 2 moles of $FeSO_4$ are oxidised by x moles of $KMnO_4$ in acid medium into ferric sulphate. 3 moles of ferric oxalate are oxidised by y moles of $K_2Cr_2O_7$ in acid medium. The value of (x/y) is:

(a) 6/5 (b) 2/15 (c) 18/5 (d) 3/5

15. What volume of 0.05 M $Cr_2O_7^{2-}$ in acid medium is needed for complete oxidation of 200 mL of 0.6 M FeC_2O_4 solution?

(a) 0.6 L (b) 1.2 L (c) 2.4 L (d) 3.6 L

16. $KMnO_4$ reacts with oxalic acid according to the reaction:

$$2KMnO_4 + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Then, 20 mL of 0.1 M $KMnO_4$ is equivalent to:

(a) 30 mL of 0.5 M $C_2H_2O_4$ (oxalic acid)
(b) 50 mL of 0.1 M $C_2H_2O_4$ (oxalic acid)
(c) 20 mL of 0.5 M $C_2H_2O_4$ (oxalic acid)
(d) 10 mL of 0.1 M $C_2H_2O_4$ (oxalic acid)

[**Hint:** $\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(H_2C_2O_4)$

$$\frac{0.1 \times 20}{2} = \frac{M_2V_2}{5}$$

$$M_2V_2 = 5$$

(It is possible in case of b.)]

17. Potassium permanganate is titrated against ferrous ammonium sulphate in acidic medium; the equivalent mass of potassium permanganate is:

(a) $\frac{\text{molecular mass}}{3}$ (b) $\frac{\text{molecular mass}}{5}$
(c) $\frac{\text{molecular mass}}{2}$ (d) $\frac{\text{molecular mass}}{10}$

[**Hint:** The ionic reaction involved in titration is:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Since, a molecule of $KMnO_4$ accepts 5 electrons in acid medium, its equivalent mass will be $\left(\frac{\text{molecular mass}}{5}\right)$.]

18. Number of moles of $K_2Cr_2O_7$ that can be reduced by 1 mole of Sn^{2+} ions is:

(a) 1/3 (b) 3/2 (c) 5/6 (d) 6/5

[**Hint:** The redox reaction is:

$$Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 3Sn^{4+}$$

$\therefore$ 1 mole of Sn^{2+} will reduce 1/3 mole of $K_2Cr_2O_7$]

19. Potassium permanganate acts as an oxidising agent in acidic, alkaline as well as neutral media. Which among the following statements is incorrect?

(a) $N = M/5$ (in acid medium)
(b) $N = M/3$ (in alkaline medium)
(c) $N = M/3$ (in neutral medium)
(d) $N = M$ (in alkaline medium)

20. The number of equivalents of $Na_2S_2O_3$ required for the volumetric estimation of one equivalent of Cu^{2+} is:

(a) 1/3 (b) 1 (c) 3/2 (d) 2/3

[**Hint:** Number of equivalents of reacting species in a chemical reaction are same.]

21. The equivalent mass of $MnSO_4$ becomes half of its molecular mass when it is converted into:

(a) MnO_4^- (b) MnO_2 or Mn_3O_4
(c) MnO_4^{2-} (d) $Mn_2O_4^{2-}$

[**Hint:** When $\overset{(+2)}{Mn}SO_4$ is converted to $\overset{(+4)}{Mn}O_2$, the oxidation number changes by 2, thus

$$\text{Equivalent mass of } MnSO_4 = \frac{\text{Molecular mass}}{2}]$$

22. A solution of 10 mL of $\frac{M}{10}$ $FeSO_4$ was titrated with $KMnO_4$ solution in acidic medium; the amount of $KMnO_4$ used will be:

(a) 10 mL of 0.5 M (b) 10 mL of 0.1 M
(c) 10 mL of 0.02 M (d) 5 mL of 0.1 M

[**Hint:** The involved reaction is:

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

$$\frac{M_1V_1}{n_1}(KMnO_4) = \frac{M_2V_2}{n_2}(FeSO_4)$$

$$\frac{M_1V_1}{2} = \frac{0.1 \times 10}{10}$$

$M_1V_1 = 0.2$ which is possible in (c)]

23. Among the following reactions, used in titrations, select the reaction(s) in which the chlorine is oxidised:

1. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$
2. $2KI + Cl_2 \longrightarrow 2KCl + I_2$
3. $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$
4. $CrO_2Cl_2 + 2NaOH \longrightarrow Na_2CrO_4 + 2HCl$

(a) reactions 2, 3 and 4 (b) reaction 1 only
(c) reactions 1 and 3 (d) reaction 4 only
(e) reactions 2 and 4

24. Oxalic acid dihydrate, $H_2C_2O_4 \cdot 2H_2O(s)$ is often used as a primary reagent to standardise sodium hydroxide solution. Which of these facts are reasons to choose this substance as a primary standard?

I. It is diprotic.
II. It is a stable compound that can be weighed directly in air.
III. It is available in pure form.

(a) III only (b) I and II only
(c) II and III only (d) I, II and III

25. A 20 mL sample of a $Ba(OH)_2$ solution is titrated with 0.245 M HCl. If 27.15 mL of HCl is required, what is the molarity of the $Ba(OH)_2$ solution?

(a) 0.166 M (b) 0.180 M (c) 0.333 M (d) 0.666 M

26. A solution of which substance can best be used as both titrant and its own indicator in an oxidation-reduction titration?

(a) I_2 (b) NaOCl (c) $K_2Cr_2O_7$ (d) $KMnO_4$

27. A 0.2 g sample of benzoic acid, C_6H_5COOH, is titrated with a 0.120 M $Ba(OH)_2$ solution. What volume of the $Ba(OH)_2$ solution is required to reach the equivalence point?

Substance	Molar mass
C_6H_5COOH	122.1 g mol^{-1}

(a) 6.82 mL (b) 13.6 mL (c) 17.6 mL (d) 35.2 mL

28. What mass of magnesium hydroxide is required to neutralise 125 mL of 0.136 M HCl solution?

Substance	Molar mass
$Mg(OH)_2$	58.33 g mol^{-1}

(a) 0.248 g (b) 0.496 g (c) 0.992 g (d) 1.98 g

29. In the titration of $K_2Cr_2O_7$ and $FeSO_4$, the following data is obtained: V_1 mL of $1M_1$ $K_2Cr_2O_7$ requires V_2 mL of $1M_2$ $FeSO_4$. Which of the following relations is true for the above titration?

(a) $6M_1V_1 = M_2V_2$ (b) $M_1V_1 = 6M_2V_2$
(c) $M_1V_1 = M_2V_2$ (d) $3M_1V_1 = 4M_2V_2$

[Hint:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

$$\frac{M_1V_1}{n_1}(K_2Cr_2O_7) = \frac{M_2V_2}{n_2}(FeSO_4)$$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{6}$$

$$6M_1V_1 = M_2V_2\,]$$

30. When 20 mL of $\frac{M}{10}$ NaOH are added to 10 mL of $\frac{M}{10}$ HCl, the resulting solution will:

(a) turn blue litmus red
(b) turn phenolphthalein solution pink
(c) turn methyl orange red
(d) have no effect on either red or blue litmus

31. A sample of coconut oil weighing 1.5763 g is mixed with 25 mL of 0.4210 M KOH. Some KOH is used in saponification of coconut oil. After the saponification is complete, 8.46 mL of 0.2732 M H_2SO_4 is required to neutralize excess KOH. The saponification number of peanut oil is:

(a) 209.6 (b) 98.9 (c) 108.9 (d) 218.9

[Hint: Number of milliequivalent of KOH added

$$= 25 \times 0.421 = 10.525$$

Number of milliequivalents left unreacted

= Number of milliequivalents of H_2SO_4 used

$= 8.46 \times 0.2732 \times 2 = 4.623$ (Here, basicity of $H_2SO_4 = 2$)

Number of milliequivalents of KOH used by oil

$$= 10.525 - 4.623 = 5.902$$

$$\text{Mass of KOH used} = \frac{5.902 \times 56}{1000} = 0.3305 \text{ g} = 330.5 \text{ mg}$$

Saponification number = Mass of KOH in mg used by 1 g oil or fat

$$= \frac{0.3305 \times 1000}{1.5763} = 209.6\,]$$

32. 12.5 mL of a solution containing 6 g of a dibasic acid in one litre was found to be neutralized by 10 mL of a decinormal solution of NaOH. The molecular mass of the acid is:

(a) 110 (b) 75 (c) 120 (d) 150

[Hint: N_1V_1 (acid) $= N_2V_2$ (base)

$$N_1 \times 12.5 = \frac{1}{10} \times 10$$

$$N_1 = \frac{1}{12.5}$$

$$\text{Strength} = N \times Ew$$

$$6 = \frac{1}{12.5} \times Ew$$

$$Ew = 75$$

Molar mass = Equivalent mass × Basicity

$$= 75 \times 2 = 150\,]$$

33. 20 mL of 0.1 M H_3BO_3 solution on complete neutralisation requires x mL of 0.05 M NaOH solution. The value of x will be:

(a) 20 mL (b) 40 mL (c) 120 mL (d) 80 mL

[Hint: Boric acid is monobasic acid.

$$H_3BO_3 + NaOH \longrightarrow Na[B(OH)_4]$$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

$$\frac{0.1 \times 20}{1} = \frac{0.05 \times x}{1}$$

$$x = 40 \text{ mL}\,]$$

34. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is:

(a) acetamide (b) benzamide (c) urea (d) thiourea

[Hint: $H_2SO_4 + 2KOH \longrightarrow K_2SO_4 + 2H_2O$

$$\frac{M_1V_1}{1}(\text{excess } H_2SO_4) = \frac{M_2V_2}{2}(KOH)$$

$$\frac{0.1 \times V_1}{1} = \frac{0.5 \times 20}{2}$$

$$V_1 = 50 \text{ mL}$$

Volume of sulphuric acid used up to absorb $NH_3 = 50$ mL

$$\%N = \frac{2.8 \times MV}{W} = \frac{2.8 \times 0.1 \times 50}{0.3} = 46.6$$

Thus, the organic compound will be urea, which has 46.6% nitrogen.]

35. A solution contains Na_2CO_3 and $NaHCO_3$; 10 mL of this solution required 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein indicator. Methyl orange is added after first end point, further titration required 2.5 mL of 0.2 M H_2SO_4. The amount of Na_2CO_3 and $NaHCO_3$ in 1 litre of the solution is:

(a) 5.3 g and 4.2 g (b) 3.3 g and 6.2 g
(c) 4.2 g and 5.3 g (d) 6.2 g and 3.3 g

36. MnO_4^- ions are reduced in acidic condition to Mn^{2+} ions whereas they are reduced in neutral condition to MnO_2. The oxidation of 25 mL of a solution X containing Fe^{2+} ions required in acidic condition, 20 mL of a solution Y containing MnO_4^- ions. What volume of solution Y would be required to oxidise 25 mL of solution X containing Fe^{2+} ions in neutral condition ?

(a) 11.4 mL (b) 12 mL
(c) 33.3 mL (d) 35 mL
(e) 25 mL

[**Hint :**

Acid medium

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{5}$$

$$\frac{M_1 \times 20}{1} = \frac{M_2 \times 25}{5}$$

$$M_1 = \frac{M_2}{4} \qquad \text{...(i)}$$

Neutral medium

$$MnO_4^- + 3Fe^{2+} + 4H^+ \longrightarrow MnO_2 + 3Fe^{3+} + 2H_2O$$

$$\frac{M_1V_1}{1} = \frac{M_2V_2}{3}$$

$$\left(\frac{M_2}{4}\right) \times V_1 = \frac{M_2 \times 25}{3}$$

$$V_1 = 33.3 \text{ mL}]$$

Answers

1. (d)	**2.** (c)	**3.** (a)	**4.** (a)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (a)
9. (a)	**10.** (d)	**11.** (b)	**12.** (a)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (b)
17. (b)	**18.** (a)	**19.** (b)	**20.** (b)	**21.** (b)	**22.** (c)	**23.** (c)	**24.** (c)
25. (a)	**26.** (d)	**27.** (a)	**28.** (b)	**29.** (a)	**30.** (b)	**31.** (a)	**32.** (d)
33. (b)	**34.** (c)	**35.** (a)	**36.** (c)				

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Pyrolusite, MnO_2, is the main ore from which manganese is produced. The manganese content of the ore may be determined by reducing the MnO_2 under acetic conditions to Mn^{2+} with the oxalate ion, $C_2O_4^{2-}$, the oxalate ion being oxidised to carbon dioxide during the reaction. The analytical determination is carried out by adding a known excess volume of oxalate solution to a suspension of the pyrolusite and digesting the mixture on a hot water bath until all the MnO_2 has been reduced. The excess, unreacted oxalate solution is then titrated with standardised potassium permanganate, $KMnO_4$ solution after which the manganese content of the ore can be calculated.

A student prepared a standard solution of sodium oxalate by weighing 3.2 g of the dry anhydrous salt, dissolving it in distilled water and making the solution up to 500 mL. 25 mL of the oxalate solution required 24.76 mL of $KMnO_4$ solution.

Answer the following questions:

1. What is the equivalent mass of MnO_2 in the present titration?
   (a) $\frac{M.w.}{1}$ (b) $\frac{M.w.}{2}$ (c) $\frac{M.w.}{3}$ (d) $\frac{2M.w.}{3}$
2. How many moles of $C_2O_4^{2-}$ ions will be oxidised by 1 mole MnO_4^-?
   (a) 1/2 (b) 3/2 (c) 5/2 (d) 7/2
3. Molarity of the sodium oxalate solution is ....
   (a) 0.04776 (b) 0.07446 (c) 0.06447 (d) 0.07644
4. What is the molarity of $KMnO_4$ solution?
   (a) 0.04776 (b) 0.01929 (c) 0.038 (d) 0.028
5. Role of $KMnO_4$ in the given titration can be described as:
   (a) oxidising agent
   (b) reducing agent
   (c) indicator
   (d) oxidising agent and indicator

Passage 2

For a series of indicators the following colours and pH range over which colour change takes place are as follows:

Indicator	**Colour change over pH range**	
U	*yellow to blue*	(*pH* 0 *to* 1.6)
V	*red to yellow*	(*pH* 2.8 *to* 4.1)
W	*red to yellow*	(*pH* 4.2 *to* 5.8)
X	*yellow to blue*	(*pH* 6.0 *to* 7.7)
Y	*colourless to red*	(*pH* 8.2 *to* 10)

Answer the following questions:

1. Indicator *V* could be used to find the equivalence point for 0.1 *M* acetic acid and 0.1 *M* ammonium hydroxide solution:
   (a) True (b) False
2. Indicator *Y* could be used to distinguish between the solutions of ammonium chloride and sodium acetate solution:
   (a) True (b) False
3. Indicator *X* could be used to distinguish between the solutions of ammonium chloride and sodium acetate solution:
   (a) True (b) False
4. Indicator *W* would be suitable for use in the determination of the concentration of acetic acid in white vinegar by base titration:
   (a) True (b) False
5. Indicator *U* could be used to distinguish between 0.1 *M* and 0.01 *M* solution of sulphuric acid:
   (a) True (b) False

Passage 3

Chemists work with standardised solution, a solution whose concentration is known. The requirements to standardise the solution are:

1. *the volume of the solution.*
2. *the number of moles of solute in that volume.*

A primary standard solution is used in determining the molarity of a solution. To find the molarity of HCl, 0.317 g of Na_2CO_3, the primary standard dissolved in water, is used in titrating the solution of HCl. 22.9 mL of acid are required to neutralise the sodium carbonate. This is the needed volume (first requirement). The stoichiometric equation is used to know the second requirement.

$$2HCl(aq.) + Na_2CO_3(aq.) \longrightarrow 2NaCl + H_2O + CO_2 \uparrow$$

Answer the following questions:

1. What is the molarity of HCl in the above case?
   (a) 0.261 *M* (b) 0.522 *M* (c) 0.1 *M* (d) 1 *M*
2. Equivalent mass of Na_2CO_3 in the above equation will be:
   (a) 106 (b) 53 (c) 26.5 (d) 13.25
3. The suitable indicator in the above titration will be:
   (a) phenolphthalein (b) methyl orange
   (c) litmus (d) bromothymol blue
4. Solution of Na_2CO_3 in water will be:
   (a) acidic (b) neutral
   (c) basic (d) cannot be predicted
5. What fraction of Na_2CO_3 will be neutralised by HCl in presence of phenolphthalein indicator?
   (a) 1/3 (b) 2/3 (c) 1/2 (d) 1/4

Passage 4

0.5 g bleaching powder was suspended in water and excess KI is added. On acidifying with dil. H_2SO_4, I_2 was liberated which required 50 mL of N/10 hypo ($Na_2S_2O_3 \cdot 5H_2O$) in presence of starch. The reactions involved are:

I. $CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$
II. $2KI + Cl_2 \longrightarrow 2KCl + I_2$
III. $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Answer the following questions:

1. In the reaction (I), which one is reduced?
   (a) $CaOCl_2$ (b) H_2SO_4
   (c) Both (d) None of these

2. In the given titration, starch acts as:
   (a) oxidising agent (b) indicator
   (c) reducing agent (d) catalyst
3. In reaction (II), Cl_2 acts as:
   (a) reducing agent
   (b) oxidising agent
   (c) indicator
   (d) both oxidising agent and indicator
4. Percentage of available chlorine in bleaching powder is:
   (a) 35.5% (b) 71%
   (c) 17.25% (d) 50%
5. Starch forms iodo-starch complex in the given titration. The colour of the complex will be:
   (a) green (b) blue
   (c) pale yellow (d) milky white

• Passage 5

Hypo is the common name of sodium thiosulphate, with molecular formula $Na_2S_2O_3$. It is used as intermediate in iodometric as well as in iodimetric titrations.

Iodine and chlorine react with hypo in different ways as follows:

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

$$Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + Cl^- + S$$

Suppose, 50 mL of 0.01 M $Na_2S_2O_3$ solution and 5×10^{-4} mol of Cl_2 are allowed to react according to the above equation. Hypo is also used in photography to dissolve AgBr, forming a complex compound.

$$2Na_2S_2O_3 + AgBr \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

Answer the following questions:

1. The balanced chemical reaction with Cl_2 is:
   (a) $Cl_2 + 2Na_2S_2O_3 \longrightarrow 2NaCl + Na_2S_4O_6$
   (b) $Cl_2 + H_2O + Na_2S_2O_3 \longrightarrow Na_2SO_4 + 2HCl + S$
   (c) $Cl_2(g) + S_2O_3^{2-} \longrightarrow SO_4^{2-} + S + Cl^-$
   (d) none of the above
2. Number of moles of $S_2O_3^{2-}$ present in the sample is:
   (a) 0.0005 (b) 0.01
   (c) 0.0025 (d) 0.02
3. What is the molarity of Na_2SO_4 formed in the reaction between $Na_2S_2O_3$ and Cl_2?
   (a) 0.08 *M* (b) 0.04 *M*
   (c) 0.02 *M* (d) 0.01 *M*
4. The process of photography, in which $Na_2S_2O_3$ is used, is called:
   (a) developing (b) image fixing
   (c) tonning (d) all of these
5. Oxidation state of silver in $Na_3[Ag(S_2O_3)_2]$ is:
   (a) 0 (b) +1
   (c) +2 (d) −1

• Passage 6

Equivalent mass of a substance may be calculated as,

$$\textit{Equivalent mass} = \frac{\textit{Molecular mass}}{\textit{n-factor}} = \frac{\textit{Atomic mass}}{\textit{n-factor}}$$

n-factor = Basicity of acid or acidity of base
n-factor = Number of moles of electrons gained or lost per mole of oxidising or reducing agents
n-factor = Total positive or negative valency of a salt
n-factor = Valency of an ion.

Concept of n-factor is very important for redox as well as for non-redox reactions :

Answer the following questions:

1. When $KMnO_4$ is titrated against ferrous ammonium sulphate in acid medium then equivalent mass of $KMnO_4$ will be:
   (a) $\frac{\text{Molecular mass}}{10}$ (b) $\frac{\text{Molecular mass}}{5}$
   (c) $\frac{\text{Molecular mass}}{3}$ (d) $\frac{\text{Molecular mass}}{2}$

   [Hint:
   $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ n-factor = 5]
2. Equivalent mass of ferrous oxalate FeC_2O_4 in the following reaction is:
   $$FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2$$
   (a) $\frac{\text{Molecular mass}}{1}$ (b) $\frac{\text{Molecular mass}}{2}$
   (c) $\frac{\text{Molecular mass}}{3}$ (d) $\frac{\text{Molecular mass}}{4}$

   [Hint : $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
   $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$
   $FeC_2O_4 \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$ n-factor = 3]
3. Equivalent mass of H_3PO_2 when it undergoes disproportionation to PH_3 and H_3PO_3 will be:
   (a) M.w./2 (b) M.w./4 (c) M.w./24 (d) 3M.w./4

   [Hint: $H_3PO_2 + 4H^+ + 4e^- \longrightarrow PH_3 + 2H_2O$ $n_1 = 4$
   $H_3PO_2 + H_2O \longrightarrow H_3PO_3 + 2H^+ + 2e^-$ $n_2 = 2$
   $$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{2 \times 4}{2 + 4} = \frac{8}{6} = \frac{4}{3}$$
   $$\text{E.w.} = \text{M.w.}/\frac{4}{3} = \frac{3\,\text{M.w.}}{4}\;]$$
4. BrO_3^- ion reacts with Br^- to form Br_2, in acid medium. The equivalent mass of Br_2 in this reaction is:
   (a) $\frac{4\text{M.w.}}{6}$ (b) $\frac{3\text{M.w.}}{5}$ (c) $\frac{5\text{M.w.}}{3}$ (d) $\frac{5\text{M.w.}}{8}$

   [Hint : $2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O$ $n_1 = 10$
   $2Br^- \longrightarrow Br_2 + 6e^-$ $n_2 = 2$
   $$n\text{-factor} = \frac{n_1 \times n_2}{n_1 + n_2} = \frac{10 \times 2}{10 + 2} = \frac{20}{12} = \frac{5}{3}$$
   $$\text{E.w.} = \frac{\text{M.w.}}{5/3} = \frac{3\text{M.w.}}{5}\;]$$

Answers

Passage 1.	1. (b)	2. (c)	3. (a)	4. (b)	5. (d)
Passage 2.	1. (b)	2. (b)	3. (a)	4. (b)	5. (b)
Passage 3.	1. (a)	2. (b)	3. (b)	4. (c)	5. (c)
Passage 4.	1. (d)	2. (b)	3. (b)	4. (a)	5. (b)
Passage 5.	1. (b)	2. (a)	3. (d)	4. (b)	5. (b)
Passage 6.	1. (b)	2. (c)	3. (d)	4. (b)	

SELF ASSESSMENT

ASSIGNMENT NO. 14

SECTION-I

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. For decolorisation of 1 mole of $KMnO_4$, the moles of H_2O_2 required is: (AIEEE 2007)

(a) $\frac{1}{2}$ (b) $\frac{3}{2}$ (c) $\frac{5}{2}$ (d) $\frac{7}{2}$

2. If equal volume of 1 M $KMnO_4$ and 1 M $K_2Cr_2O_7$ solutions are allowed to oxidise Fe^{2+} to Fe^{3+} in acidic medium, then Fe^{2+} will be oxidised: [illegible]

(a) more by $KMnO_4$ (b) more by $K_2Cr_2O_7$
(c) equal in both cases (d) cannot be determined

3. MnO_2 on reaction with conc. HCl liberates chlorine; the liberated chlorine on treatment with aqueous KI gives iodine. The iodine is neutralized by 40 mL of 0.1 N hypo solution. The reaction is:

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

The amount of MnO_2 used in the reaction is:

(a) 10 g (b) 0.174 g (c) 1.74 g (d) 0.0174 g

4. 1.520 g of hydroxide of a metal on ignition gave 0.995 g of oxide. The equivalent mass of metal is:

(a) 1.52 (b) 0.995 (c) 190 (d) 9

5. Identify the incorrect statement regarding the volumetric estimation of $FeSO_4$:

(a) $KMnO_4$ can be used in aqueous HCl
(b) $K_2Cr_2O_7$ can be used in aqueous HCl
(c) $KMnO_4$ can be used in aqueous H_2SO_4
(d) $K_2Cr_2O_7$ can be used in aqueous H_2SO_4

6. When one gram mole of $KMnO_4$ is mixed with hydrochloric acid then, the volume of chlorine gas liberated at NTP will be:

(a) 11.2 litre (b) 22.4 litre (c) 56 litre (d) 44.8 litre

[**Hint:** The reaction between $KMnO_4$ and HCl may be given as:
$$2MnO_4^- + 10Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O]$$

7. 0.7 g of $Na_2CO_3.xH_2O$ was dissolved in water to make 100 mL solution, 20 mL of this solution required 19.8 mL of 0.1 N HCl for complete neutralisation. The value of x is:

(a) 5 (b) 2
(c) 3 (d) 4

8. 0.5 g of impure ammonium chloride was heated with caustic soda solution to evolve ammonia gas, the gas is absorbed in 150 mL of $N/5$ H_2SO_4 solution. Excess sulphuric acid required 20 mL of 1 N NaOH for complete neutralization. The percentage of NH_3 in the ammonium chloride is:

(a) 68% (b) 34% (c) 48% (d) 17%

9. One mole of a mixture of CO and CO_2 requires exactly 20 g of NaOH to convert all the CO_2 into Na_2CO_3. How many more grams of NaOH would it require for conversion into Na_2CO_3 if the mixture (one mole) is completely oxidised to CO_2?

(a) 60 g (b) 80 g (c) 40 g (d) 20 g

10. 0.1 litre of 0.01 M $KMnO_4$ is used by 100 mL of H_2O_2 in acidic medium. Volume of same $KMnO_4$ required in alkaline medium to oxidise 0.1 litre of some H_2O_2 will be:

(a) $\frac{100}{3}$ mL (b) $\frac{500}{3}$ mL (c) $\frac{300}{5}$ mL (d) $\frac{400}{3}$ mL

SECTION-II

Multiple Answers Type Objective Questions

11. One mole of acidic $KMnO_4$ reacts with:

(a) $\frac{5}{3}$ mol of FeC_2O_4 (b) $\frac{5}{2}$ mol of SO_2
(c) 4 mol of FeS (d) 1 mol of H_2SO_4

12. Boric acid (H_3BO_3) is:

(a) tribasic (b) dibasic (c) monobasic (d) aprotic

13. 0.6 mol $K_2Cr_2O_7$, in acid medium can oxidise:

(a) 3.6 mol $FeSO_4$ to $Fe_2(SO_4)_3$
(b) 0.1 mol $FeSO_4$ to $Fe_2(SO_4)_3$
(c) 0.05 mol of Sn^{2+} to Sn^{4+}
(d) 1.8 mol of Sn^{2+} to Sn^{4+}

14. Which of the following statement(s) is/are correct?

(a) H_2SO_4 and H_3PO_3 both are dibasic
(b) H_3BO_3 and H_3PO_4 both are tribasic
(c) H_3BO_3 and H_3PO_2 both are monobasic
(d) HNO_3 and HCl both are monobasic

15. In the titration of CH_3COOH against NaOH, we cannot use the:

(a) methyl orange (b) methyl red
(c) phenolphthalein (d) bromothymol blue

SECTION-III

Assertion-Reason Type Questions

This section contains 3 questions. Each question contains **Statement-1** (Assertion) and **Statement-2** (Reason). Each question has following 4 choices (a), (b), (c) and (d), out of which only one is correct.

(a) Statement-1 is true; statement-2 is true; statement-2 is a correct explanation for statement-1.
(b) Statement-1 is true; statement-2 is true; statement-2 is not a correct explanation for statement-1.
(c) Statement-1 is true; statement-2 is false.
(d) Statement-1 is false; statement-2 is true.

16. **Statement-1:** Equivalent mass of H_3PO_2 is equal to its molecular mass.

Because

Statement-2: H_3PO_2 is a monobasic acid.

17. **Statement-1:** When Na_2CO_3 is titrated against HCl in presence of phenolphthalein indicator, it is converted to NaCl.

Because

Statement-2: Phenolphthalein shows colour change in the pH range of (3.5 — 4.6).

18. **Statement-1:** 1 mol of H_2SO_4 is neutralised by 2 mol of NaOH; however, 1 equivalent of H_2SO_4 is neutralised by 1 equivalent of NaOH.

Because

Statement-2: Equivalent mass of H_2SO_4 is half of its molecular mass, however, the equivalent mass of NaOH is equal to its molecular mass.

SECTION-IV

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbles as illustrated in the following examples:

If the correct matches are (a-p,s); (b-q,r); (c-p,q) and (d-s); then correctly bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

Match the Column-I with Column-II:

[EAMCET (Med.) 2007]

Column-I	Column-II
(a) 10 volume H_2O_2	(p) Perhydrol
(b) 20 volume H_2O_2	(q) 5.358 N
(c) 30 volume H_2O_2	(r) 1.785 M
(d) 100 volume H_2O_2	(s) 3.03%

20. Match the Column-I with Column-II:

Column-I (Acid)	Column-II (Information)
(a) CH_3COOH	(p) Tribasic (E_w = M.w./3)
(b) H_3PO_4	(q) Dibasic reducing
(c) H_2SO_4	(r) Dibasic (E_w = M.w./2)
(d) H_3PO_3	(s) Monobasic (E_w = M.w.)

21. Match the Column-I with Column-II:

Column-I (Reaction)	Column-II (Equivalent mass of reactant)
(a) $NH_3 \longrightarrow NO_3^-$	(p) M.w./20
(b) $Fe_2S_3 \longrightarrow FeSO_4 + SO_2$	(q) M.w./2
(c) $CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$	(r) M.w./8
(d) $CuS \longrightarrow CuSO_4$	(s) 50

Answers

1. (c)	**2.** (a)	**3.** (b)	**4.** (d)	**5.** (a)	**6.** (c)	**7.** (b)	**8.** (b)
9. (a)	**10.** (b)	**11.** (a, b)	**12.** (c, d)	**13.** (a, d)	**14.** (a, c, d)	**15.** (a, b, d)	
16. (a)	**17.** (c)	**18.** (b)	**19.** (a-s) (b-r) (c-q) (d-p)		**20.** (a-s) (b-p) (c-r) (d-q,r)		
21. (a-r) (b-p) (c-q,s) (d-r)							

CHAPTER 15

STOICHIOMETRY

(Chemical Formulae and Equations)

In the discovery of a new chemical compound, the first question to answer is, what is the formula of the compound? The answer begins with stoichiometric calculation and analysis of the compound.

The percentage composition of a compound leads directly to its empirical formula. An **empirical formula** or simplest formula for a compound is the formula of a substance written with the smallest integer (whole number) subscripts.

The molecular formula of a compound is a multiple of its empirical formula.

$$\text{Molecular mass} = n \times \text{empirical formula mass.}$$

The calculations of empirical and molecular formulae are dealt in the very first chapter of this book.

Stoichiometry: Quantitative Relations in Chemical Reactions

Stoichiometry is the calculation of the quantities of reactants and products involved in a chemical reaction.

It is based on the chemical equation and on the relationship between mass and moles.

A chemical equation can be interpreted as follows:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\text{1 molecule } N_2 + \text{3 molecules } H_2 \longrightarrow \text{2 molecules } NH_3$$

(Molecular interpretation)

$1 \text{ mol } N_2 + 3 \text{ mol } H_2 \longrightarrow 2 \text{ mol } NH_3$ (Molar interpretation)

$28 \text{ g } N_2 + 6 \text{ g } H_2 \longrightarrow 34 \text{ g } NH_3$ (Mass interpretation)

$1 \text{ vol. } N_2 + 3 \text{ vol. } H_2 \longrightarrow 2 \text{ vol. } NH_3$ (Volume interpretation)

Thus, calculations based on chemical equations are divided into four types:

(i) Calculations based on mole-mole relationship.
(ii) Calculations based on mass-mass relationship.
(iii) Calculations based on mass-volume relationship.
(iv) Calculations based on volume-volume relationship.

(i) Calculations based on mole-mole relationship

In such calculations, number of moles of reactants are given and those of products required. Conversely, if number of moles of products are given, then number of moles of reactants are required.

SOME SOLVED EXAMPLES

Example 1. *Oxygen is prepared by catalytic decomposition of potassium chlorate ($KClO_3$). Decomposition of potassium chlorate gives potassium chloride (KCl) and oxygen (O_2). How many moles and how many grams of $KClO_3$ are required to produce 2.4 mole O_2?*

Solution: Decomposition of $KClO_3$ takes place as,

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

$$2 \text{ mole of } KClO_3 \equiv 3 \text{ mole of } O_2$$

$\because$ 3 mole O_2 formed by 2 mole $KClO_3$

$\therefore$ 2.4 mole O_2 will be formed by $\left(\frac{2}{3} \times 2.4\right)$ mole $KClO_3$

$$= 1.6 \text{ mole of } KClO_3$$

$$\text{Mass of } KClO_3 = \text{Number of moles} \times \text{Molar mass}$$

$$= 1.6 \times 122.5 = 196 \text{ g}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

1. One mole of calcium phosphide on reaction with excess of water gives:
(a) three moles of phosphine
(b) one mole of phosphoric acid
(c) two moles of phosphine
(d) one mole of P_2O_5
[**Ans.** (c)]
[**Hint:** $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$
$1 \text{ mole of } Ca_3P_2 \equiv 2 \text{ mole of } PH_3$]

2. $Mg(OH)_2$ in the form of milk of magnesia is used to neutralize excess stomach acid. How many moles of stomach acid can be neutralized by 1 g of $Mg(OH)_2$? (Molar mass of $Mg(OH)_2$ = 58.33)

(a) 0.0171 (b) 0.0343 (c) 0.686 (d) 1.25

[Ans. (b)]

[Hint: $Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$

Number of moles of stomach acid neutralized

$$= 2 \times \text{number of moles of } Mg(OH)_2$$

$$= 2 \times \frac{1}{58.33} = 0.0343]$$

3. When a mixture of 10 moles of SO_2 and 16 moles of O_2 were passed over a catalyst, 8 moles of SO_3 were formed at equilibrium. The number of moles of SO_2 and O_2 remaining unreacted were:

(a) 2, 12 (b) 12, 2 (c) 3, 10 (d) 10, 3

[Ans. (a)]

[Hint:

$$\begin{array}{lccccc} & 2SO_2(g) & + & O_2(g) & \rightleftharpoons & 2SO_3(g) \\ t = 0 & 10 & & 16 & & 0 \\ t_{eq.} & (10-2x) & & (16-x) & & 2x \end{array}$$

$$2x = 8, \quad i.e., \quad x = 4$$

$\therefore$ Remaining $SO_2 = 10 - 8 = 2$ mol

Remaining $O_2 = 16 - 4 = 12$ mol]

4. Calcium carbonate decomposes on heating according to the following equation:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

How many moles of CO_2 will be obtained by decomposition of 50 g $CaCO_3$?

(a) $\frac{3}{2}$ (b) $\frac{5}{2}$ (c) $\frac{1}{2}$ (d) 1

[Ans. (c)]

[Hint:

Number of moles of CO_2 = Number of moles of $CaCO_3$

$$= \frac{\text{Mass}}{\text{Molar mass}} = \frac{50}{100} = \frac{1}{2}\ ]$$

5. Sulphur trioxide is prepared by the following two reactions:

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

How many grams of SO_3 are produced from 1 mole of S_8?

(a) 1280 (b) 640 (c) 960 (d) 320

[Ans. (b)]

[Hint: From the given reaction, it is clear that 1 mole of S_8 will give 8 moles of SO_3.

Mass of SO_3 formed = Number of moles × Molar mass

$$= 8 \times 80 = 640 \text{ g}]$$

(ii) Calculations based on mass-mass relationship

In making necessary calculations, following steps are followed:

(a) Write down the balanced chemical equation.

(b) Write down the theoretical amount of reactants and products involved in the reaction.

(c) Calculate the unknown amount of substance using unitary method.

SOME SOLVED EXAMPLES

Example 2. *Calculate the mass of (CaO) that can be prepared by heating 200 kg of limestone $CaCO_3$ which is 95% pure.*

Solution: Amount of pure $CaCO_3 = \frac{95}{100} \times 200 = 190$ kg

$$= 190000 \text{ g}$$

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

$$1 \text{ mole } CaCO_3 \equiv 1 \text{ mole } CaO$$

$$100 \text{ g } CaCO_3 \equiv 56 \text{ g } CaO$$

$\because$ 100 g $CaCO_3$ give 56 g CaO

$\therefore$ 190000 g $CaCO_3$ will give $\frac{56}{100} \times 190000$ g CaO

$$= 106400 \text{ g} = 106.4 \text{ kg}$$

Example 3. *Chlorine is prepared in the laboratory by treating manganese dioxide (MnO_2) with aqueous hydrochloric acid according to the reaction,*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

How many grams of HCl will react with 5 g MnO_2?

Solution: 1 mole of MnO_2 reacts with 4 mole of HCl

or 87 g MnO_2 reacts with 146 g HCl

$\therefore$ 5 g MnO_2 will react with $\frac{146}{87} \times 5$ g HCl = 8.39 g HCl

Example 4. *How many grams of oxygen are required to burn completely 570 g of octane?*

Solution: Balanced equation,

$$\underset{\substack{2 \text{ mol} \\ 2 \times 114}}{2C_8H_{18}} + \underset{\substack{25 \text{ mol} \\ 25 \times 32}}{25O_2} \longrightarrow 16CO_2 + 18H_2O$$

First method: For burning 2 × 114 g of octane, oxygen required

$$= 25 \times 32 \text{ g}$$

For burning 1 g of octane, oxygen required $= \frac{25 \times 32}{2 \times 114}$ g

Thus, for burning 570 g of octane, oxygen required

$$= \frac{25 \times 32}{2 \times 114} \times 570 \text{ g} = 2000 \text{ g}$$

Mole method: Number of moles of octane in 570 grams

$$= \frac{570}{114} = 5.0$$

For burning 2.0 moles of octane, oxygen required

$$= 25 \text{ mol} = 25 \times 32 \text{ g}$$

For burning 5 moles of octane, oxygen required

$$= \frac{25 \times 32}{2.0} \times 5.0 \text{ g} = 2000 \text{ g}$$

Proportion method: Let x g of oxygen be required for burning 570.0 g of octane. It is known that 2 × 114 g of the octane require 25 × 32 g of oxygen; then, the proportion,

$$\frac{25\times 32\text{ g oxygen}}{2\times 114\text{ g octane}}=\frac{x}{570.0\text{ g octane}}$$

$$\therefore \qquad x=\frac{25\times 32\times 570}{2\times 114}=2000\text{ g}$$

Example 5. *Calculate the number of grams of magnesium chloride that could be obtained from 17.0 g of HCl when HCl is reacted with an excess of magnesium oxide.*

Solution: Balanced equation,

$$\underset{1\text{ mol}}{\text{MgO}}+\underset{\substack{2\text{ mol}\\(2\times 36.5)\text{g}\\=73\text{ g}}}{2\text{HCl}}\longrightarrow\underset{\substack{1\text{ mol}\\(24+71)\text{g}\\=95\text{ g}}}{\text{MgCl}_2}+\underset{1\text{ mol}}{\text{H}_2\text{O}}$$

$$73\text{ g of HCl produce MgCl}_2=95\text{ g}$$

$$1\text{ g of HCl produce MgCl}_2=\frac{95}{73}\text{ g}$$

$$17\text{ g of HCl will produce MgCl}_2=\frac{95}{73}\times 17\text{ g}=22.12\text{ g}$$

Example 6. *How many kilograms of pure H_2SO_4 could be obtained from 1 kg of iron pyrites (FeS_2) according to the following reactions?*

$$4FeS_2+11O_2\longrightarrow 2Fe_2O_3+8SO_2$$

$$2SO_2+O_2\longrightarrow 2SO_3$$

$$SO_3+H_2O\longrightarrow H_2SO_4$$

Solution: Final balanced equation,

$$\underset{\substack{4\text{ mol}\\4\times 120\text{g}}}{4\text{FeS}_2}+15\text{O}_2+8\text{H}_2\text{O}\longrightarrow 2\text{Fe}_2\text{O}_3+\underset{\substack{8\text{ mol}\\8\times 98\text{g}}}{8\text{H}_2\text{SO}_4}$$

$$4\times 120\text{ g of FeS}_2\text{ yield H}_2\text{SO}_4=8\times 98\text{ g}$$

$$1000\text{ g of FeS}_2\text{ will yield H}_2\text{SO}_4=\frac{8\times 98}{4\times 120}\times 1000$$

$$=1.63\text{ kg}$$

Limiting reagent: *Limiting reactant or reagent is the reactant that is entirely consumed when a reaction goes to completion.* Other reactants which are not completely consumed in the reaction are called excess reactants.

OR

The reactant which gives least amount of product on being completely consumed is called limiting reactant.

Example 7. *If 20 g of $CaCO_3$ is treated with 20 g of HCl, how many grams of CO_2 can be generated according to the following equation?*

$$CaCO_3(s)+2HCl(aq.)\longrightarrow CaCl_2(aq.)+H_2O(l)+CO_2(g)$$

Solution:

$$\underset{\substack{1\text{ mol}\\100\text{ g}}}{\text{CaCO}_3(s)}+\underset{\substack{2\text{ mol}\\73\text{g}}}{2\text{HCl}(aq.)}\longrightarrow\text{CaCl}_2(aq.)+\text{H}_2\text{O}(l)+\underset{\substack{1\text{ mol}\\44\text{g}}}{\text{CO}_2(g)}$$

Let $\text{CaCO}_3(s)$ be completely consumed in the reaction.

$$\because\ 100\text{ g CaCO}_3\text{ give }44\text{ g CO}_2$$

$$\therefore\ 20\text{ g CaCO}_3\text{ will give }\frac{44}{100}\times 20\text{ g CO}_2=8.8\text{ g CO}_2$$

Let HCl be completely consumed.

$$\because\ 73\text{ g HCl give }44\text{ g CO}_2$$

$$\therefore\ 20\text{ g HCl will give }\frac{44}{73}\times 20\text{ g CO}_2=12.054\text{ g CO}_2$$

Since, CaCO_3 gives least amount of product CO_2, hence, CaCO_3 is limiting reactant. Amount of CO_2 formed will be 8.8 g.

Example 8. *100 g sample of calcium carbonate is reacted with 70 g of orthophosphoric acid. Calculate:*

(*a*) *the number of grams of calcium phosphate that could be produced.*

(*b*) *the number of grams of excess reagent that will remain unreacted.*

Solution: (a) The balanced equation is:

$$\underset{\substack{3\text{ mol}\\3(40+12+48)\\=300\text{ g}}}{3\text{CaCO}_3}+\underset{\substack{2\text{ mol}\\2(3+31+64)\\=196\text{ g}}}{2\text{H}_3\text{PO}_4}\longrightarrow\underset{\substack{1\text{ mol}\\(3\times 40+2\times 95)\\=310\text{ g}}}{\text{Ca}_3(\text{PO}_4)_2}+3\text{CO}_2+3\text{H}_2\text{O}$$

$$300\text{ g of CaCO}_3\text{ produce Ca}_3(\text{PO}_4)_2=310\text{ g or 1 mol}$$

100 g of CaCO_3 would produce

$$\text{Ca}_3(\text{PO}_4)_2=\frac{310}{300}\times 100$$

$$=103\text{ g}$$

$$=0.33\text{ mol}$$

$$196\text{ g of H}_3\text{PO}_4\text{ produce Ca}_3(\text{PO}_4)_2=310\text{ g or 1 mol}$$

$$70\text{ g of H}_3\text{PO}_4\text{ would produce Ca}_3(\text{PO}_4)_2=\frac{310}{196}\times 70$$

$$=110.7\text{ g or 0.356 mol}$$

The above values suggest that CaCO_3 is the limiting reagent. Hence, calcium phosphate formed is 103 g or 0.33 mole.

(b) For producing 103 g of $\text{Ca}_3(\text{PO}_4)_2$, H_3PO_4 required will be

$$=\frac{196}{310}\times 103=65.12\text{ g}$$

$$\text{Mass of remaining H}_3\text{PO}_4=(70-65.12)=4.88\text{ g}$$

Example 9. *1 g of Mg is burnt in a closed vessel which contains 0.5 g of O_2:*

(*i*) *Which reactant is left in excess?*

(*ii*) *Find the mass of the excess reactant.*

Solution: (i) The balanced equation is:

$$\underset{\substack{2\times 24\\=48\text{ g}}}{2\text{Mg}}+\underset{\substack{2\times 16\\=32\text{ g}}}{\text{O}_2}\longrightarrow\underset{\substack{2(24+16)\\=80\text{ g}}}{2\text{MgO}}$$

$$48\text{ g of Mg require oxygen}=32\text{ g}$$

1 g of Mg requires oxygen $= \frac{32}{48} = 0.66$ g

But only 0.5 g oxygen is available. Hence, O_2 is a limiting agent and a part of magnesium will not burn.

$\therefore$ Magnesium will be left in excess.

(ii) 32 g of O_2 react with magnesium = 48 g

0.5 g of O_2 will react with magnesium $= \frac{48}{32} \times 0.5 = 0.75$ g

Hence, the mass of excess magnesium

$$= (1.0 - 0.75) = 0.25 \text{ g}$$

Example 10. *The reaction,*

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

is carried out by taking 24 g of carbon and 96 g O_2. Find out:

(*a*) *Which reactant is left in excess?*

(*b*) *How much of it is left?*

(*c*) *How many moles of CO are formed?*

(*d*) *How many grams of other reactant should be taken so that nothing is left at the end of the reaction?*

Solution: $\underset{\substack{2\text{ mol}\\24\text{ g}}}{2C(s)} + \underset{\substack{1\text{ mol}\\32\text{ g}}}{O_2(g)} \longrightarrow \underset{\substack{2\text{ mol}\\56\text{ g}}}{2CO(g)}$

Let carbon be completely consumed.

24 g carbon give 56 g CO

Let O_2 is completely consumed.

$\because$ 32 g O_2 give 56 g CO

$\therefore$ 96 g O_2 will give $\frac{56}{32} \times 96$ g CO = 168 g CO

Since, carbon gives least amount of product, *i.e.*, 56 g CO or 2 mole CO, hence carbon will be the limiting reactant.

$\therefore$ Excess reactant is O_2.

Amount of O_2 used = 56 − 24 = 32 g

Amount of O_2 left = 96 − 32 = 64 g

32 g O_2 react with 24 g carbon

$\therefore$ 96 g O_2 will react with 72 g carbon.

Thus, carbon should be taken 72 g so that nothing is left at the end of the reaction.

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

6. 0.5 mole $BaCl_2$ is mixed with 0.2 mole Na_3PO_4; the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is:

(a) 0.7 (b) 0.5 (c) 0.2 (d) 0.1

[**Ans.** (d)]

[**Hint:** $3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6NaCl$

Number of moles of $Ba_3(PO_4)_2$ formed by $BaCl_2$

$$= \frac{1}{3} \times 0.5 = 0.166$$

Number of moles of $Ba_3(PO_4)_2$ formed by 0.2 mole Na_3PO_4

$$= \frac{1}{2} \times 0.2 = 0.1$$

Thus, Na_3PO_4 will be limiting and actual amount of product will be 0.1 mole.]

7. In the following reaction:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$$

when 1 mole ammonia and 1 mole of O_2 are mixed, then the number of moles of NO formed will be:

(a) 0.8 (b) 0.7 (c) 0.6 (d) 0.5

[**Ans.** (a)]

[**Hint:** 1 mole of NH_3 (on complete reaction) gives 1 mole NO. Similarly, 1 mole of O_2 (on complete reaction) gives $\frac{4}{5}$, *i.e.*, 0.8 mole NO. Thus, O_2 will be limiting reactant and actual amount of NO formed in the reaction will be 0.8 mole.]

8. 30 g Mg and 30 g O_2 are reacted and the residual mixture contains:

(a) 60 g of MgO only

(b) 40 g of MgO and 20 g of O_2

(c) 45 g of MgO and 15 g of O_2

(d) 50 g of MgO and 10 g of O_2

[**Ans.** (d)]

[**Hint:** $\underset{\substack{2\text{ mol}\\2\times24\text{ g}}}{2Mg(s)} + \underset{\substack{1\text{ mol}\\1\times32\text{ g}}}{O_2(g)} \longrightarrow \underset{\substack{2\text{ mol}\\2\times40\text{ g}}}{2MgO(g)}$

30 g Mg gives $\left(\frac{80}{48} \times 30\right)$ g MgO on complete reaction,

i.e., 30 g Mg ≡ 50 g MgO

30 g O_2 gives $\left(\frac{80}{32} \times 30\right)$ g MgO on complete reaction,

i.e., 30 g O_2 ≡ 75 g MgO

$\therefore$ Mg is limiting reactant and MgO formed in the reaction will be 50 g.

Unreacted amount of O_2 = 30 − 20 = 10 g

$\therefore$ Mixture contains 50 g MgO and 10 g O_2.]

9. 254 g of iodine and 142 g of chlorine are made to react completely to give a mixture of ICl and ICl_3. How many moles of each are formed?

(a) 0.1 mole of ICl and 0.1 mole of ICl_3

(b) 1 mole of ICl and 1 mole of ICl_3

(c) 0.5 mole of ICl and 0.1 mole of ICl_3

(d) 0.5 mole of ICl and 1 mole of ICl_3

[**Ans.** (b)]

[**Hint:** Both reactants are completely consumed, hence, both are limiting.

$$I_2 + 2Cl_2 \longrightarrow ICl + ICl_3$$

254 g or 1 mole I_2 and 142 g or 2 mole Cl_2 will react to give 1 mole ICl and 1 mole ICl_3.]

10. Magnesium hydroxide, $Mg(OH)_2$ is the white milky substance in milk of magnesia. What mass of $Mg(OH)_2$ is formed when 15 mL of 0.18 *M* NaOH are combined with 12 mL of 0.14 *M* $MgCl_2$? The molar mass of $Mg(OH)_2$ is 58.3 g mol^{-1}.

(a) 0.079 g (b) 0.097 g (c) 0.16 g (d) 0.31 g

[**Ans.** (a)]

[**Hint:**
$$n_{MgCl_2} = \frac{MV}{1000} = \frac{12 \times 0.14}{1000} = 1.68 \times 10^{-3}$$
$$n_{NaOH} = \frac{15 \times 0.18}{1000} = 2.7 \times 10^{-3}$$

NaOH will be limiting reagent because on complete consumption, NaOH gives least amount of $Mg(OH)_2$.

$$\text{Mass of } Mg(OH)_2 = \frac{1}{2} \times 2.7 \times 10^{-3} \times 58.3 = 0.079 \text{ g}]$$

Calculations involving per cent yield

In general, when a reaction is carried out in the laboratory we do not obtain actually the theoretical amount of the product. The amount of the product that is actually obtained is called the actual yield. Knowing the actual yield and theoretical yield the per cent yield can be calculated by the given formula:

$$\text{Per cent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Example 11. *For the reaction,*

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

1.23 g of CaO is reacted with excess of hydrochloric acid and 1.85 g of $CaCl_2$ is formed. What is the per cent yield?

Solution: The balanced equation is:

$$\underset{\substack{1\text{ mol}\\56\text{ g}}}{CaO} + 2HCl \longrightarrow \underset{\substack{1\text{ mol}\\111\text{ g}}}{CaCl_2} + H_2O$$

$$56 \text{ g of CaO produce } CaCl_2 = 111 \text{ g}$$
$$1.23 \text{ g of CaO produce } CaCl_2 = \frac{111}{56} \times 1.23 = 2.43 \text{ g}$$

Thus, Theoretical yield = 2.43 g

Actual yield = 1.85 g

$$\text{Per cent yield} = \frac{1.85}{2.43} \times 100 = 76.1$$

Calculations involving per cent purity

Depending upon the mass of the product, the equivalent amount of the reactant present can be determined with the help of a chemical equation. Knowing the actual amount of the reactant taken and the amount calculated with the help of a chemical equation the percentage purity can be determined.

Example 12. *Chlorine evolved by the reaction of 45.31 g of pyrolusite (impure) and excess of HCl is found to combine completely with the hydrogen produced by the reaction of 10 g of magnesium and excess of dilute hydrochloric acid. Find the percentage of purity of MnO_2 in the given pyrolusite.*

Solution:
$$\underset{24\text{ g}}{Mg} + \underset{(2\times 36.5)\text{ g}}{2HCl} \longrightarrow MgCl_2 + \underset{2\text{ g}}{H_2}$$
$$\underset{87\text{ g}}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{71\text{ g}}{Cl_2} + 2H_2O$$
$$\underset{2\text{ g}}{H_2} + \underset{71\text{ g}}{Cl_2} \longrightarrow 2HCl$$

2 g of hydrogen obtained by using 24 g of Mg will combine completely with 71 g of chlorine produced from 87 g of pure MnO_2.

Thus, when 10 g of Mg are used,

$$\text{the mass of the pure } MnO_2 \text{ required is} = \frac{87}{24} \times 10 = 36.25 \text{ g}$$

So, 45.31 g of pyrolusite contain MnO_2 (pure) = 36.25 g

$\therefore$ 100 g of pyrolusite contain MnO_2 (pure)

$$= \frac{36.25}{45.31} \times 100 = 80.00 \text{ g}$$

$\therefore$ Percentage of purity = 80.00

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

11.
$$\underset{\substack{\text{Salicylic acid}\\(138.12\text{ g mol}^{-1})}}{C_7H_6O_3} + \underset{\substack{\text{Acetic anhydride}\\(102.09\text{ g mol}^{-1})}}{C_4H_6O_3} \longrightarrow \underset{\substack{\text{Aspirin}\\(180.15\text{ g mol}^{-1})}}{C_9H_8O_4} + \underset{\substack{\text{Acetic acid}\\(60.05\text{ g mol}^{-1})}}{C_2H_4O_2}$$

What is the percentage yield if 0.85 g of aspirin formed in the reaction of 1 g of salicylic acid with excess of acetic anhydride?

(a) 65% (b) 77% (c) 85% (d) 91%

[**Ans.** (a)]

[**Hint:** Mass of aspirin (theoretical) formed from 1 g salicylic acid $= \frac{180.15}{138.12} = 1.304$g

$$\% \text{ yield} = \frac{\text{Actual amount of product}}{\text{Theoretical amount of product}} \times 100$$
$$= \frac{0.85}{1.304} \times 100 \approx 65\%]$$

12. A sample of impure silver (1.5 g) is heated with sulphur to form Ag_2S. The mass of Ag_2S formed was 0.124 g. What was the percentage yield of silver sulphide?

(a) 6.41% (b) 7.20% (c) 8.27% (d) 10.8%

[**Ans.** (b)]

[**Hint:**
$$\underset{\substack{2\text{ mol}\\2\times 108 = 216\text{ g}}}{2Ag} + S \longrightarrow \underset{\substack{1\text{ mol}\\248\text{ g}}}{Ag_2S}$$

Amount of Ag_2S that can be formed from 1.5 g silver

$$= \frac{248}{216} \times 1.5 = 1.722 \text{ g}$$
$$\% \text{ yield of } Ag_2S = \frac{0.124}{1.722} \times 100 = 7.2\,]$$

13. Magnetite, Fe_3O_4, can be converted into metallic iron by heating with carbon monoxide as represented by this equation:

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

How many kilogram of Fe_3O_4 must be processed in this way to obtain 5 kg iron; if the process is 85% efficient? (Molar mass of Fe_3O_4 is 232 g mol^{-1}.)

(a) 6.92 kg (b) 8.12 kg (c) 20.8 kg (d) 24.4 kg

[**Ans.** (b)]

[**Hint:** 1 mole Fe_3O_4 (232 g) = 3 mole Fe (168 g)

$$\text{Amount of } Fe_3O_4 \text{ required for 5 kg iron} = \frac{232}{168} \times 5 \text{ kg}$$
$$= 6.904 \text{ kg}$$

Since, efficiency of the reaction is 85%, hence, the actual required amount of Fe_3O_4 will be

$$= \frac{100 \times 6.904}{85} \text{ kg, } i.e., = 8.12 \text{ kg}]$$

14. Iodobenzene is prepared from aniline ($C_6H_5NH_2$) in a two step process as shown here:

$$C_6H_5NH_2 + HNO_2 + HCl \longrightarrow C_6H_5N_2^+Cl^- + 2H_2O$$

$$C_6H_5N_2^+Cl^- + KI \longrightarrow C_6H_5I + N_2 + KCl$$

In an actual preparation, 9.30 g of aniline was converted to 12.32 g of iodobenzene. The percentage yield of iodobenzene is:

(a) 8% (b) 50%
(c) 75% (d) 80%

[Ans. (d)]

[Hint: 1 mole of $C_6H_5NH_2$ (123 g) ≡ 1 mole of C_6H_5I (204 g)

$\therefore$ 9.3 g aniline will give $= \left(\frac{204}{123} \times 9.3\right)$ g iodobenzene

$= 15.424$ g iodobenzene

$$\% \text{ yield} = \frac{\text{Actual amount of product}}{\text{Calculated amount of product}} \times 100$$

$$= \frac{12.32}{15.424} \times 100 \approx 80\%]$$

15. Benzamide can be prepared by the action of concentrated ammonia upon benzoyl chloride.

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + 2NH_3 \longrightarrow \underset{\text{Benzamide}}{C_6H_5CONH_2} + NH_4Cl$$

In one such experiment, 65 cc of concentrated ammonia (in excess) was reacted with 15 g of benzoyl chloride to give 11.1 g of pure benzamide. Molar masses: benzoyl chloride (141); benzamide (121). The percentage yield of benzamide is:

(a) $\frac{11.1}{15} \times 100$ (b) $\frac{(15 - 11.1)}{15} \times 100$
(c) $\frac{11.1}{65} \times 100$ (d) $\frac{121}{141} \times 100$
(e) $\frac{11.1 \times 141}{121 \times 15} \times 100$

[Ans. (e)]

[Hint: Amount of benzamide from 15 g benzoyl chloride $= \frac{121}{141} \times 15$ g

Actual amount of benzamide formed = 11.1 g

$$\% \text{ yield} = \frac{\text{Actual amount of product}}{\text{Calculated amount of product}} \times 100$$

$$= \frac{11.1 \times 100}{\left(\frac{121}{141} \times 15\right)} = \frac{11.1 \times 141}{121 \times 15} \times 100]$$

Analysis of mixtures: In such problems, one of the components is supposed to be x g and the other will be the difference from the total. Balanced chemical equations for the reactions of both the components are now written and the total amount of the common product produced by the components of the mixture is calculated. It is equated with the data given and the unknown factors are, thus, worked out.

SOME SOLVED EXAMPLES

Example 13. *A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the mass of the residue was constant. If the loss in mass is 28.0 per cent, find the amount of lead nitrate and sodium nitrate in the mixture.* (IIT 1990)

Solution: Let the amount of $NaNO_3$ in the mixture be $= x$ g

$\therefore$ The amount of $Pb(NO_3)_2$ in the mixture $= (5.0 - x)$ g

$$\underset{(2 \times 85)\text{ g}}{2NaNO_3} \xrightarrow{\text{Heat}} 2NaNO_2 + \underset{32\text{ g}}{O_2}$$

$$\underset{\substack{(2 \times 331)\text{ g} \\ 662\text{ g}}}{2Pb(NO_3)_2} \xrightarrow{\text{Heat}} 2PbO + \underbrace{\underset{(4 \times 46)\text{ g}}{4NO_2} + \underset{32\text{ g}}{O_2}}_{216\text{ g}}$$

170 g of $NaNO_3$ evolve oxygen = 32 g

x g of $NaNO_3$ evolve oxygen $= \frac{32}{170} \times x$ g

662 g of $Pb(NO_3)_2$ evolve gases = 216 g

$(50 - x)$ g of $Pb(NO_3)_2$ evolve gases $= \frac{216}{662} \times (5.0 - x)$ g

$$\text{Total loss} = \frac{32}{170} \times x + \frac{216}{662} \times (5.0 - x)$$

$$\text{Loss given in the problem} = \frac{28}{100} \times 5 = 1.4 \text{ g}$$

$$\therefore \quad \frac{32}{170}x + \frac{216}{662}(5.0 - x) = 1.4$$

On solving, $x = 1.676$ g

Thus, Mass of $NaNO_3$ = 1.676 g

Mass of $Pb(NO_3)_2 = (5.0 - 1.676)$ g $= 3.324$ g

Example 14. *3.68 g of a mixture of calcium carbonate and magnesium carbonate when heated strongly leaves 1.92 g of a white residue. Find the percentage composition of the mixture.*

Solution: Let x g of $CaCO_3$ be present in the mixture.

The mass of $MgCO_3$ in the mixture $= (3.68 - x)$ g.

$$\underset{100\text{ g}}{CaCO_3} \xrightarrow{\text{Heat}} \underset{56\text{ g}}{CaO} + CO_2$$

$$\underset{84\text{ g}}{MgCO_3} \xrightarrow{\text{Heat}} \underset{40\text{ g}}{MgO} + CO_2$$

$$\therefore \quad \frac{56 \times x}{100} + \frac{40 \times (3.68 - x)}{84} = 1.92$$

On solving, $x = 2$

$$\text{Percentage of } CaCO_3 = \frac{2}{3.68} \times 100 = 54.35\%$$

$$\text{Percentage of } MgCO_3 = 100 - 54.35 = 45.65\%$$

Example 15. *0.5 g of a mixture of K_2CO_3 and Li_2CO_3 required 30 mL of 0.25 N HCl solution for neutralization. What is the percentage composition of the mixture?*

Solution: Let the amount of K_2CO_3 be 'x' g.

$$\therefore \quad \text{Amount of } Li_2CO_3 = (0.5 - x)\text{ g}$$

$$\text{Number of equivalents} = \frac{x}{138/2} + \frac{(0.5-x)}{74/2} \qquad \ldots\text{(i)}$$

Number of equivalents of HCl used

$$= \frac{NV}{1000} = \frac{0.25 \times 30}{1000} = 7.5 \times 10^{-3} \qquad \ldots\text{(ii)}$$

Comparing eqs. (i) and (ii), we get

$$x = 0.48\text{ g}$$

$$\therefore \quad \text{Mass of } K_2CO_3 = 0.48\text{ g}$$

$$\text{Mass of } Li_2CO_3 = 0.02\text{ g}$$

$$\%\, K_2CO_3 = \frac{0.48}{0.5} \times 100 = 96$$

$$\%\, Li_2CO_3 = \frac{0.02}{0.5} \times 100 = 4$$

(iii) Calculations based on mass-volume relationship

In such calculations, masses of reactants are given and volume of the product is required and *vice-versa.*

1 mole of a gas occupies 22.4 litre volume at STP mass of a gas can be related to volume according to the following gas equation:

$$PV = nRT$$

$$PV = \frac{w}{m} RT$$

Example 16. *What volume of $NH_3(g)$ at 27° C and 1 atm pressure will be obtained by thermal decomposition of 26.25 g NH_4Cl?*

Solution: Ammonium chloride undergoes decomposition as;

$$\underset{\substack{1\text{ mol}\\53.5\text{ g}}}{NH_4Cl(s)} \longrightarrow \underset{\substack{1\text{ mol}\\1\text{ mol}}}{NH_3(g)} + HCl(g)$$

$\because$ 53.5 g NH_4Cl give 1 mol NH_3

$\therefore$ 26.25 g NH_4Cl will give $\frac{1}{53.5} \times 26.25$ mole NH_3

$$= 0.5\text{ mole}$$

$$PV = nRT$$

$$1 \times V = 0.5 \times 0.0821 \times 300$$

$$V = 12.315\text{ litre}$$

Example 17. *What quantity of copper(II) oxide will react with 2.80 litre of hydrogen at NTP?*

Solution: The balanced equation is:

$$\underset{\substack{1\text{ mol}\\79.5\text{ g}}}{CuO} + \underset{\substack{1\text{ mol}\\22.4\text{ litre at NTP}}}{H_2} \longrightarrow Cu + H_2O$$

22.4 litre of hydrogen at NTP reduce CuO = 79.5 g

2.80 litre of hydrogen at NTP will reduce CuO

$$= \frac{79.5}{22.4} \times 2.80\text{ g} = 9.95\text{ g}$$

Example 18. *Calculate the volume of carbon dioxide at NTP evolved by strong heating of 20 g calcium carbonate.*

Solution: The balanced equation is:

$$\underset{\substack{1\text{ mol}\\100\text{ g}}}{CaCO_3} \longrightarrow CaO + \underset{\substack{1\text{ mol}\\= 22.4\text{ litre at NTP}}}{CO_2}$$

100 g of $CaCO_3$ evolve carbon dioxide = 22.4 litre

20 g $CaCO_3$ will evolve carbon dioxide

$$= \frac{22.4}{100} \times 20 = 4.48\text{ litre}$$

Example 19. *Calculate the volume of hydrogen liberated at 27° C and 760 mm pressure by treating 1.2 g of magnesium with excess of hydrochloric acid.*

Solution: The balanced equation is:

$$\underset{\substack{1\text{ mol}\\24\text{ g}}}{Mg} + 2HCl \longrightarrow MgCl_2 + \underset{\substack{1\text{ mol}\\22.4\text{ litre at NTP}}}{H_2}$$

24 g of Mg liberate hydrogen = 22.4 litre

1.2 g Mg will liberate hydrogen $= \frac{22.4}{24} \times 1.2 = 1.12$ litre

Volume of hydrogen under given condition can be calculated by applying

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P_1 = 760$ mm $\qquad P_2 = 760$ mm

$T_1 = 273$ K $\qquad T_2 = (27 + 273) = 300$ K

$V_1 = 1.12$ litre $\qquad V_2 = ?$

$$V_2 = \frac{760 \times 1.12}{273} \times \frac{300}{760} = 1.2308\text{ litre}$$

Example 20. *A solid mixture (5 g) consisting of lead nitrate and sodium nitrate was heated below 600° C until the weight of the residue is constant. If the loss in weight is 28%, find the amount of lead nitrate and sodium nitrate in the mixture.*

(IIT 1990)

Solution: Loss in weight is due to formation of NO_2 and O_2 gases (weight loss $= \frac{5}{100} \times 28 = 1.4$ g).

$$\underset{x\text{ g}}{Pb(NO_3)_2} \longrightarrow \underset{(x-y)\text{ g}}{PbO} + \underbrace{NO_2 + O_2}_{y\text{ g}}$$

$$\underset{(5-x)}{NaNO_3} \longrightarrow \underset{(3.6-x+y)}{NaNO_2} + \underset{(1.4-y)}{\tfrac{1}{2}O_2}$$

Number of moles of $Pb(NO_3)_2$ = Number of moles of PbO

$$\frac{x}{331} = \frac{(x-y)}{223} \qquad \ldots(i)$$

∵ M.w. $Pb(NO_3)_2 = 331$, M.w. $PbO = 223$

Number of moles of $NaNO_3$ = Number of moles of $NaNO_2$

$$\frac{5-x}{85} = \frac{3.6-x+y}{69} \qquad \ldots(ii)$$

Solving eqs. (i) and (ii), we get

$$\text{Mass of } Pb(NO_3)_2 = x = 3.3246 \text{ g}$$

$$\text{Mass of } NaNO_3 = 5 - 3.3246 = 1.6754 \text{ g}$$

(iv) Calculations based on volume-volume relationship

These calculations are based on two laws:

(i) Avogadro's law (ii) Gay-Lussac's law

For example:

$$\underset{\substack{1\text{ mol}\\ 1\times 22.4\text{ L}}}{N_2(g)} + \underset{\substack{3\text{ mol}\\ 3\times 22.4\text{ L}}}{3H_2(g)} \longrightarrow \underset{\substack{2\text{ mol}\\ 2\times 22.4\text{ L}}}{2NH_3(g)} \quad \text{(Avogadro's law)}$$

(under similar conditions of temperature and pressure, equal moles of gases occupy equal volumes)

$$\underset{1\text{ vol.}}{N_2(g)} + \underset{3\text{ vol.}}{3H_2(g)} \longrightarrow \underset{2\text{ vol.}}{2NH_3(g)}$$

under similar conditions, ratio of coefficients by mole is equal to ratio of coefficient by volume.

Example 21. *1 litre mixture of CO and CO_2 is taken. This is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. The volumes are measured under the same conditions. Find the composition of mixture by volume.*

Solution: Let there be x mL CO in the mixture, hence, there will be $(1000-x)$ mL CO_2. The reaction of CO_2 with red hot charcoal may be given as,

$$\underset{\substack{1\text{ vol.}\\ (1000-x)}}{CO_2(g)} + C(s) \longrightarrow \underset{\substack{2\text{ vol.}\\ 2(1000-x)}}{2CO(g)}$$

Total volume of the gas becomes $= x + 2(1000-x)$

$$x + 2000 - 2x = 1600$$

$$x = 400 \text{ mL}$$

∴ Volume of CO = 400 mL and volume of CO_2 = 600 mL

Example 22. *What volume of air containing 21% oxygen by volume is required to completely burn 1 kg of carbon containing 100% combustible substances?*

Solution: Combustion of carbon may be given as,

$$\underset{\substack{1\text{ mol}\\ 12\text{ g}}}{C(s)} + \underset{\substack{1\text{ mol}\\ 1\text{ mol}}}{O_2(g)} \longrightarrow CO_2(g)$$

∵ 12 g carbon requires 1 mole O_2 for complete combustion

∴ 1000 g carbon will require $\frac{1}{12} \times 1000$ mole O_2 for combustion, *i.e.*, 83.33 mole O_2

Volume of O_2 at NTP $= 83.33 \times 22.4$ litre $= 1866.592$ litre

∵ 21 litre O_2 is present in 100 litre air

∴ 1866.592 litre O_2 will be present in $\frac{100}{21} \times 1866.592$ litre O_2

$$= 8888.5 \text{ litre} = 8.8885 \times 10^3 \text{ litre}$$

Example 23. *What volume of oxygen gas at NTP is necessary for complete combustion of 20 litre of propane measured at 27° C and 760 mm pressure?*

Solution: The balanced equation is:

$$\underset{\substack{1\text{ vol.}\\ 1\text{ litre}}}{C_3H_8} + \underset{\substack{5\text{ vol.}\\ 5\text{ litre}}}{5O_2} \longrightarrow 3CO_2 + 4H_2O$$

1 litre of propane requires = 5 litre of oxygen

20 litre of propane will require $= 5 \times 20 = 100$ litre of oxygen at 760 mm pressure and 27° C.

This volume will be converted to NTP conditions.

Given conditions	NTP conditions
$P_1 = 760$ mm	$P_2 = 760$ mm
$V_1 = 100$ litre	$V_2 = ?$
$T_1 = 27 + 273 = 300$ K	$T_2 = 273$

Applying $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{760 \times 100}{300} \times \frac{273}{760} = 91.0 \text{ litre}$$

Example 24. *One litre of oxygen at NTP is allowed to react with three times of carbon monoxide at NTP. Calculate the volume of each gas found after the reaction.*

Solution: The desired equation is:

$$\underset{2\text{ vol.}}{2CO} + \underset{1\text{ vol.}}{O_2} \longrightarrow \underset{2\text{ vol.}}{2CO_2}$$

1 vol. of O_2 reacts with 2 vol. of CO

or 1 litre of O_2 reacts with 2 litre of CO

Thus, 1 litre of CO remains unreacted.

1 vol. of O_2 produces CO_2 = 2 vol.

or 1 litre of O_2 will produce CO_2 = 2 litre

Thus, gaseous mixture after the reaction consists

Volume of CO = 1 litre

Volume of CO_2 = 2 litre

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

16. 10 litre of O_2 gas is reacted with 30 litre of CO gas at STP. The volumes of each gas present at the end of reaction are: **[CMC (Vellore) 2008]**

(a) CO (10 litre), CO_2 (20 litre)
(b) O_2 (10 litre), CO (30 litre)
(c) CO (20 litre), CO_2 (10 litre)
(d) O_2 (10 litre), CO_2 (20 litre)
(e) O_2 (10 litre), CO (10 litre)

[**Ans.** (a)]

[**Hint:**
$$\begin{array}{lccc} & CO(g) & +\ \frac{1}{2}O_2(g) \longrightarrow & CO_2(g) \\ t=0 & 30\ L & 10\ L & 0 \\ \text{After reaction} & (30-20)L & 0 & 20\ L] \end{array}$$

17. When 10 g of 90% pure limestone is heated, the volume of CO_2 (in litre) liberated at STP is: **[JEE (WB) 2007]**

(a) 22.4 litre (b) 2.24 litre
(c) 20.16 litre (d) 2.016 litre

[**Ans.** (d)]

[**Hint:** Mass of $CaCO_3$ in the sample $= 10 \times \frac{90}{100} = 9$ g

$$\begin{array}{ccc} CaCO_3(s) \longrightarrow & CaO(s) + & CO_2(g) \\ 1\ \text{mol} & & 1\ \text{mol} \\ 100\ \text{g} & & 22.4\ \text{L} \end{array}$$

9 gm $CaCO_3$ will give $\left(\frac{22.4}{100} \times 9\right)$ litre of CO_2, *i.e.*, 2.016 litre of CO_2 .]

18. 100 mL of PH_3 on heating forms P_4 and H_2, volume changes in the reaction is: **(DPMT 2009)**

(a) an increase of 50 mL (b) an increase of 100 mL
(c) an increase of 150 mL (d) a decrease of 50 mL

[**Ans.** (a)]

[**Hint:** $\underset{\substack{4\ \text{mol} \\ 4\ \text{mL}}}{4PH_3(g)} \longrightarrow P_4(s) + \underset{\substack{6\ \text{mol} \\ 6\ \text{mL}}}{6H_2(g)}$

volume of H_2 produced by 100 mL PH_3 $= \frac{6}{4} \times 100 = 150$ mL

Thus, there is increase of 50 mL.]

MISCELLANEOUS NUMERICAL EXAMPLES

Example 1. *Calculate the weight of CaO required to remove the hardness of* 1000000 *litre of water containing* 1.62 g *of* $CaCO_3$ *per litre.*

Solution: Mass of $Ca(HCO_3)_2$ in the water

$$= 1.62 \times 1000000$$
$$= 1620000\ \text{g} = 1620\ \text{kg}$$

Reaction involved in the removal of hardness may be given as,

$$\underset{162\ \text{kg}}{Ca(HCO_3)_2} + \underset{56\ \text{kg}}{CaO} \longrightarrow 2CaCO_3 + H_2O$$

∵ 162 kg $Ca(HCO_3)_2$ require 56 kg CaO.

∴ 1620 kg $Ca(HCO_3)_2$ will require 560 kg CaO.

Example 2. *A mixture in which the mole ratio of* H_2 *and* O_2 *is* 2 : 1 *is used to prepare water by the reaction,*

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The total pressure in the container is 0.8 *atm at* 20° C *before the reaction. Determine the final pressure at* 120° C *after reaction assuming* 80% *yield of water.* **(IIT 1999)**

Solution: $p_{H_2} = \frac{2}{3} \times 0.8 = 0.533$ atm

$$p_{O_2} = \frac{1}{3} \times 0.8 = 0.266\ \text{atm}$$

$$\begin{array}{lccc} & 2H_2\quad + & O_2 \quad\longrightarrow & 2H_2O \\ t=0 & 0.533 & 0.266 & 0 \\ \text{After the reaction} & \frac{0.533 \times 20}{100} & \frac{0.266 \times 20}{100} & \frac{0.533 \times 80}{100} \\ & = 0.1066 & = 0.0533 & = 0.4264 \end{array}$$

Total pressure $= 0.1066 + 0.0533 + 0.4264 = 0.5863$ atm

Using Gay-Lussac's law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{0.5863}{293} = \frac{P_2}{393}$$
$$P_2 = 0.7864\ \text{atm}$$

Example 3. *An impure sample of calcium carbonate contains* 80% *pure calcium carbonate.* 25 g *of the impure sample reacted with excess of hydrochloric acid. Calculate the volume of carbon dioxide at NTP obtained from this sample.*

Solution: 100 g of impure calcium carbonate contain

$$= 80\ \text{g pure calcium carbonate}$$

25 g of impure calcium carbonate sample contain

$$= \frac{80}{100} \times 25$$
$$= 20\ \text{g pure calcium carbonate}$$

The desired equation is:

$$\underset{\substack{1\ \text{mol} \\ 100\ \text{g}}}{CaCO_3} + 2HCl \longrightarrow CaCl_2 + \underset{\substack{22.4\ \text{litre} \\ \text{at NTP}}}{CO_2} + H_2O$$

100 g pure $CaCO_3$ liberate = 22.4 litre CO_2

20 g pure $CaCO_3$ liberate $= \frac{22.4}{100} \times 20$

$$= 4.48\ \text{litre } CO_2$$

Example 4. *The weight of* 1 *litre sample of ozonised oxygen at NTP was found to be* 1.5 g. *When* 100 mL *of this mixture at NTP were treated with turpentine oil, the volume was reduced to* 90 mL. *Hence, calculate the molecular weight of ozone.*

Solution: Volume of ozone

= volume absorbed in turpentine oil
= 10 mL

Volume of oxygen = 90 mL

Mass of 100 mL mixture $= \frac{10}{22400} \times M + \frac{90}{22400} \times 32 = 0.15$

On solving, we get $M = 48$

∴ Molecular mass of ozone = 48

Example 5. *A mixture of $NaHCO_3$ and Na_2CO_3 weighed 1.0235 g. The dissolved mixture was reacted with excess of $Ba(OH)_2$ to form 2.1028 g $BaCO_3$, by the following reactions:*

$$Na_2CO_3 + Ba(OH)_2 \longrightarrow BaCO_3 + 2NaOH$$

$$NaHCO_3 + Ba(OH)_2 \longrightarrow BaCO_3 + NaOH + H_2O$$

What was the percentage of $NaHCO_3$ in the original mixture?

Solution: Let x g of $NaHCO_3$ be present in the mixture.

Mass of Na_2CO_3 in the mixture $= (1.0235 - x)$ g

$$\text{Number of moles of } NaHCO_3 = \frac{x}{84}$$

$$\text{Number of moles of } Na_2CO_3 = \frac{(1.0235 - x)}{106}$$

Number of moles of $BaCO_3$

$$= \text{Number of moles of } NaHCO_3 + \text{Number of moles of } Na_2CO_3$$

$$\frac{2.1028}{197} = \frac{x}{84} + \frac{(1.0235 - x)}{106}$$

$\therefore$ $x = 0.4122$

Amount of $NaHCO_3$ = 0.4122 g

$$\text{Percentage of } NaHCO_3 = \frac{0.4122}{1.0235} \times 100 = 40.27$$

Example 6. *A mixture of ethane and ethene occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_6 and C_2H_4 in the mixture.* **(IIT 1995)**

Solution: Volume of the mixture at NTP

$$= \frac{40 \times 1}{400} \times \frac{273}{1} = 27.3 \text{ litre}$$

Let the volume of ethane = x litre

Volume of ethene = $(273 - x)$ litre

Balanced equations:

$$\underset{1\text{ vol.}}{C_2H_6} + \underset{7/2\text{ vol.}}{7/2\,O_2} \longrightarrow 2CO_2 + 3H_2O$$

$$\underset{1\text{ vol.}}{C_2H_4} + \underset{3\text{ vol.}}{3O_2} \longrightarrow 2CO_2 + 2H_2O$$

Total volume of oxygen required for complete combustion of the mixture is:

$$\left[\frac{7}{2}x + (27.3 - x) \times 3\right] \text{litre}$$

or

$$\left[\frac{7x + (27.3 - x) \times 6}{2}\right] \text{litre}$$

$$\text{Mass of oxygen} = \left[\frac{7x + (27.3 - x) \times 6}{2}\right] \times \frac{32}{22.4}$$

$$130 = (x + 163.8) \times \frac{16}{22.4}$$

$\therefore$ $x = 18.2$

$$\text{Hence, mole fraction of ethane} = \frac{18.2}{27.3} \times 100 = 66.66$$

Mole fraction of ethene = 33.34

Example 7. *A mixture of HCOOH and $H_2C_2O_4$ is heated with concentrated H_2SO_4. The gas produced is collected and on treating with KOH solution, the volume of the gas decreases by 1/6th. Calculate the molar ratio of the two acids in the original mixture.* **(IIT 1990)**

Solution:

$$\underset{1\text{ mol}}{HCOOH} \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} \underset{1\text{ mol}}{CO} + H_2O$$

$$\underset{1\text{ mol}}{H_2C_2O_4} \xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4} \underset{1\text{ mol}}{CO} + \underset{1\text{ mol}}{CO_2} + H_2O$$

Let a moles of HCOOH and b moles of $H_2C_2O_4$ be present in the original mixture.

Moles of CO formed = $a + b$

Moles of CO_2 formed = b

Total moles of gases = $a + b + b = a + 2b$

CO_2 is absorbed by KOH and the volume reduces by 1/6th.

$$\text{Moles of } CO_2 = \frac{a + 2b}{6}$$

or $$b = \frac{a + 2b}{6}$$

or $$a = 4b$$

or $$\frac{a}{b} = 4$$

or $$a : b = 4 : 1$$

Example 8. *3.6 g mixture of sodium chloride and potassium chloride is dissolved in water. The solution is treated with excess of silver nitrate solution. 7.74 g of silver chloride is obtained. Find the percentage of sodium chloride and potassium chloride in the mixture.*

Solution: The balanced equation between NaCl and $AgNO_3$ is:

$$\underset{\substack{1\text{ mol}\\58.5\text{ g}}}{NaCl} + AgNO_3 \longrightarrow \underset{\substack{1\text{ mol}\\143.5\text{ g}}}{AgCl} + NaNO_3$$

Let x g of NaCl be present in the mixture.

58.5 g NaCl produce = 143.5 g AgCl

$$x \text{ g NaCl will produce} = \frac{143.5}{58.5} \times x \text{ g AgCl}$$

The balanced equation between KCl and $AgNO_3$ is:

$$\underset{\substack{1\text{ mol}\\74.5\text{ g}}}{KCl} + AgNO_3 \longrightarrow \underset{\substack{1\text{ mol}\\143.5\text{ g}}}{AgCl} + KNO_3$$

KCl present in the mixture = $(3.60 - x)$ g

74.5 g of Cl produce = 143.5 g of AgCl

$$(3.6 - x) \text{ g of KCl will produce} = \frac{143.5}{74.5} \times (3.6 - x) \text{ g of AgCl}$$

$$\text{Thus, } \frac{143.5}{58.5}x + \frac{143.5}{74.5}(3.6 - x) = 7.74$$

$$x = 1.54$$

$$\% \text{ of NaCl} = \frac{1.54}{3.60} \times 100 = 42.7$$

$$\% \text{ of KCl} = \frac{(3.60 - 1.54)}{3.60} \times 100 = 57.3$$

Example 9. *5 g of K_2SO_4 were dissolved in 250 mL of solution. How many mL of this solution should be used so that 1.2 g of $BaSO_4$ may be precipitated from $BaCl_2$ solution?*

Solution: The desired equation is:

$$BaCl_2 + \underset{\substack{2\times 39+32+64\\ =174\,g}}{K_2SO_4} \longrightarrow \underset{\substack{137+32+64\\ =233\,g}}{BaSO_4} + 2KCl$$

233 g of $BaSO_4$ obtained from 174 g of K_2SO_4

1.2 g of $BaSO_4$ will be obtained from $\frac{174}{233} \times 1.2$

$$= 0.8961 \text{ g of } K_2SO_4$$

5 g of K_2SO_4 are present in 250 mL of solution

So, 0.8961 g of K_2SO_4 will be present in $\frac{250}{5} \times 0.8961$

$$= 44.8 \text{ mL of solution}$$

Example 10. *A 2.00 g of sample containing Na_2CO_3 and $NaHCO_3$ loses 0.248 g when heated to 300° C, the temperature at which $NaHCO_3$ decomposes into Na_2CO_3, CO_2 and steam. What is the percentage of Na_2CO_3 in the mixture?*

Solution: $$\underset{168\,g}{2NaHCO_3} \longrightarrow Na_2CO_3 + \underbrace{\underset{44}{CO_2} + \underset{18}{H_2O}}_{62\,g}$$

The loss comes due to evolution of CO_2 and steam.

62 g loss occurs when the quantity of $NaHCO_3$ is 168 g.

0.248 g loss will occur when the quantity of $NaHCO_3$

$$= \frac{168}{62} \times 0.248 = 0.672 \text{ g}$$

Quantity of Na_2CO_3 in the sample $= (2.0 - 0.672) = 1.328$ g

$$\% \text{ of } Na_2CO_3 = \frac{1.328}{2} \times 100 = 66.4$$

Example 11. *A 1.00 g sample of $KClO_3$ was heated under such conditions that a part of it was decomposed according to the equation,*

$$2KClO_3 \longrightarrow 2KCl + 3O_2 \qquad \ldots (i)$$

and the remaining underwent change according to the equation,

$$4KClO_3 \longrightarrow 3KClO_4 + KCl \qquad \ldots (ii)$$

If the amount of oxygen evolved was 146.8 mL at STP, calculate the percentage by mass of $KClO_4$ in the residue.

Solution: $$\underset{\substack{2(39+35.5+48)\\ 245\,g}}{2KClO_3} \longrightarrow \underset{\substack{2(39+35.5)\\ 149\,g}}{2KCl} + \underset{\substack{3\times 22.4 \text{ litre}\\ 67.2 \text{ litre}}}{3O_2}$$

67.2 litre of oxygen evolved from 245 g of $KClO_3$

0.1468 litre of oxygen will be evolved $= \frac{245}{67.2} \times 0.1468$

$$= 0.5352 \text{ g of } KClO_3$$

Hence, $KClO_3$ left for eq. (ii) reaction,

$$(1.00 - 0.5352) = 0.4648 \text{ g}$$

245 g $KClO_3$ will yield KCl = 149 g

0.5352 g $KClO_3$ will yield KCl $= \frac{149}{245} \times 0.5352 \text{ g} = 0.3254$ g

Considering eq. (ii),

$$\underset{\substack{4(39+35.5+48)\\ 490\,g}}{4KClO_3} \longrightarrow \underset{\substack{3(39+35.5+64)\\ 415.5\,g}}{3KClO_4} + \underset{\substack{(39+35.5)\\ 74.5\,g}}{KCl}$$

490 g of $KClO_3$ yield = 415.5 g of $KClO_4$

0.4648 g of $KClO_3$ will yield $= \frac{415.5}{490} \times 0.4648$

$$= 0.3941 \text{ g of } KClO_4$$

490 g $KClO_3$ yield = 74.5 g of KCl

0.4648 g of $KClO_3$ will yield $= \frac{74.5}{490} \times 0.4648$

$$= 0.0707 \text{ g of KCl}$$

Total mass of residue = 0.3254 + 0.3941 + 0.0707

$$= 0.7902 \text{ g}$$

$$\% \ KClO_4 = \frac{0.3941}{0.7902} \times 100 = 49.8$$

Example 12. *A mixture of FeO and Fe_3O_4 when heated in air to a constant weight gains 5% in its mass. Find the composition of the initial mixture.*

Solution: Let the % of FeO in the mixture be $= x$

So, % of Fe_3O_4 in the mixture $= (100 - x)$

FeO on heating is converted into Fe_2O_3.

$$\underset{288\,g}{4FeO} + O_2 \longrightarrow \underset{320\,g}{2Fe_2O_3}$$

288 g of FeO yield = 320 g of Fe_2O_3

x g of FeO will yield $= \frac{320}{288} x$ g of Fe_2O_3

$$\underset{464\,g}{2Fe_3O_4} + \frac{1}{2} O_2 \longrightarrow \underset{480\,g}{3Fe_2O_3}$$

464 g of Fe_3O_4 yield = 480 g of Fe_2O_3

$(100 - x)$ g of Fe_2O_3 will yield $= \frac{480}{464}(100 - x)$ of Fe_2O_3

$$\text{Total } Fe_2O_3 = \frac{320}{288} x + \frac{480}{464}(100 - x)$$

According to the question,

$$\frac{320}{288} x + \frac{480}{464}(100 - x) = 105$$

$$x = 20.2$$

So, percentage of FeO = 20.2

and percentage of $Fe_3O_4 = 79.8$

Example 13. *A mixture in which the mole ratio of H_2 and O_2 is 2 : 1, is used to prepare water by the reaction:*

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

The total pressure in the container is 0.8 atm at 20° C before the reaction. Determine the final pressure at 120° C after the reaction, assuming 80% yield of water. **(IIT 1999)**

Solution: The given reaction is:

$$\begin{array}{lccc} & 2H_2(g) & + \; O_2(g) \longrightarrow & 2H_2O(g) \\ \text{Initial moles} & 2n & n & 0 \\ \text{Final moles} & (2n-2x) & (n-x) & 2x \end{array}$$

$$\%\ \text{yield} = 80$$

$$\therefore \quad \frac{2x}{2n} \times 100 = 80$$

$$x = 0.8\,n$$

After the reaction,

Number of moles of $H_2 = 2n - 2 \times 0.8n = 0.4n$

Number of moles of $O_2 = 0.2n$

Number of moles of $H_2O = 1.6n$

$$\text{Total moles} = 0.4n + 0.2n + 1.6n = 2.2n$$

Initial state: $PV = nRT$

$$0.8 \times V = 3n \times R \times 293 \qquad \ldots(i)$$

After the reaction, $P \times V = 2.2n \times R \times 393$ ...(ii)

Solving eqs. (i) and (ii), we get

$$P = 0.787 \text{ atm}$$

Questions

1. 500 mL of 0.25 *M* Na_2SO_4 solution is added to an aqueous solution of 15 g of $BaCl_2$ resulting in the formation of a white precipitate of insoluble $BaSO_4$. How many moles and how many grams of $BaSO_4$ are formed?
2. Zinc and hydrochloric acid react according to the reaction:
$$Zn(s) + 2HCl(aq.) \longrightarrow ZnCl_2(aq.) + H_2(g)$$
If 0.3 mole Zn are added to hydrochloric acid containing 0.52 mole HCl, how many moles of H_2 are produced?
3. Calcium carbonate reacts with aqueous HCl to give $CaCl_2$ and CO_2 according to the reaction:
$$CaCO_3(s) + 2HCl(aq.) \longrightarrow CaCl_2(aq.) + H_2O + CO_2(g)$$
What mass of $CaCO_3$ is required to react completely with 25 mL of 0.75 *M* HCl?
4. Calculate the mass of iron which will be converted into its oxide by the action of 18 g of steam. **(MLNR 1996)**
5. How much potassium chlorate is needed to obtain 2.4 litre oxygen at NTP?
6. Calculate the volume of carbon dioxide obtained at NTP by heating 8.4 g of sodium bicarbonate.
7. Calculate the volume of air needed for the combustion of 1 kg of carbon.
[**Hint:** 100 parts of air contain 21 parts of oxygen by volume.]
8. How many grams of oxygen will be formed by the action of 12 g of sodium peroxide on water? Calculate also the volume of the gas at NTP.
9. A gaseous compound of carbon and nitrogen containing 53.8% by weight of nitrogen was found to have a vapour density of 25.8. What is the molecular formula of the compound?
10. Calculate the weight of lime (CaO) that can be obtained by heating 200 kg of limestone which is 93% pure.
11. How many moles of impure potassium chlorate of 75% purity are required to produce 48 g of oxygen?
12. What weight of zinc will react with dil. sulphuric acid to liberate 1000 mL of hydrogen at 27°C and 750 mm pressure?
13. 1.2 g sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 mL solution. 20 mL of this solution required 40 mL of 0.1 *N* HCl for complete neutralization. Calculate the weight of Na_2CO_3 in the mixture. If another 20 mL of this solution is treated with excess of $BaCl_2$, what will be the weight of the precipitate? **(IIT 1997)**
14. Calculate the volume of air containing 21% by volume of oxygen at NTP required to convert 294 mL of SO_2 into SO_3 under the same conditions.
15. 4 g of an impure sample of $CaCO_3$ on treatment with excess HCl produce 0.88 g CO_2. What is the per cent purity of $CaCO_3$ sample?
16. What weight of AgCl will be precipitated when a solution containing 4.77 g of NaCl is added to a solution of 5.77 g of $AgNO_3$?
[**Hint:** $AgNO_3$ is a limiting reagent in this problem.]
17. 1.0 g of an alloy of aluminium and magnesium is treated with excess of dil. HCl. The evolved hydrogen collected over mercury at 0°C has a volume of 1.20 litre at 0.29 atm pressure. Calculate the percentage composition of the alloy.
18. How much iron can be theoretically obtained by the reduction of 1.0 kg of Fe_2O_3? (At. wt. of Fe = 56)
19. 34 g of pure H_2O_2 is decomposed. Calculate the mass and volume at NTP of oxygen that will be evolved.
20. Find the percentage composition of iron and magnesium, 5.0 g, which when dissolved in acid, gave 2.81 litre of H_2 at NTP.
21. Equal weights of Hg and iodine are allowed to react completely to form a mixture of mercurous iodide and mercuric iodide. Calculate the ratio of the masses of mercurous and mercuric iodides formed. (Hg = 201, I = 117)
[**Hint:** $\underset{201\text{ g}}{Hg} + \underset{254\text{ g}}{I_2} \longrightarrow \underset{455\text{ g}}{HgI_2}$;

$$\underset{402\text{ g}}{2\text{Hg}} + \underset{254\text{ g}}{\text{I}_2} \longrightarrow \underset{656\text{ g}}{\text{Hg}_2\text{I}_2}$$

Let the wt. of Hg_2I_2 formed be x and HgI_2 formed be y.

In the case of $Hg_2I_2, Hg = \frac{402}{656}x, I_2 = \frac{254}{656}x$

In the case of HgI_2, $Hg = \frac{201}{455}y, I_2 = \frac{254}{455}y$

So, $$\frac{402}{656}x + \frac{201}{455}y = \frac{254}{656}x + \frac{254}{455}y$$

From this equation, x/y can be calculated.]

22. A mixture of NaI and NaCl gave with sulphuric acid, Na_2SO_4 equal in mass to the original mixture taken. Find the percentage composition of the mixture.

23. A mixture of calcium and magnesium carbonates weighing 1.4 g was strongly heated until no further loss of weight was perceived. The residue weighed 0.76 g. What percentage of $MgCO_3$ was present in the mixture?

Answers

1. 0.072 mol, 16.8 g
2. 0.26
3. $CaCO_3$ = 0.94 g
4. 42 g
5. 8.75 g
6. 1.12 L
7. 8890 L
8. 2.462 g; 1.723 L
9. C_2N_2
10. 104.16 kg
11. 1.33 mol
12. 2.245 g of zinc
13. Na_2CO_3 = 0.5962 g, K_2CO_3 = 0.6038 g, $BaCO_3$ = 0.394 g
14. 700 mL
15. 50%
16. AgCl = 4.87 g
17. Al = 54.87%, Mg = 45.13%
18. 700 g
19. 16 g; 11.2 litre
20. Fe = 69.60%, Mg = 30.40%
21. 0.513 : 1
22. NaI = 28.86%, NaCl = 71.14%
23. 20.45%

OBJECTIVE QUESTIONS

Set–1 : Questions with single correct answer

1. The formula which represents the simple ratio of atoms in a compound is called:
(a) empirical formula (b) molecular formula
(c) structural formula (d) rational formula

2. The empirical formula of a compound is CH. Its molecular weight is 78. The molecular formula of the compound will be:
(a) C_2H_2 (b) C_3H_3 (c) C_4H_4 (d) C_6H_6

3. An organic compound on analysis gave C = 5.45%, H = 9.1% by mass. Its empirical formula is:
(a) CHO_2 (b) CH_2O (c) C_2H_4O (d) C_3H_4O

4. The chloride of a metal has the formula MCl_3. The formula of its phosphate will be:
(a) M_2PO_4 (b) MPO_4 (c) M_3PO_4 (d) $M(PO_4)_2$

5. The formula of chloric acid is $HClO_3$. The formula for calcium chlorate is:
(a) $CaClO_3$ (b) $Ca(ClO_3)_2$
(c) Ca_2ClO_3 (d) $Ca(ClO_3)_3$

6. An element A is tetravalent and another element B is divalent. The formula of the compound formed from these elements will be:
(a) A_2B (b) AB (c) AB_2 (d) A_2B_3

7. A compound of aluminium and chlorine is composed of 9.0 g Al for every 35.5 g of chlorine. The empirical formula of the compound is:
(a) $AlCl$ (b) $AlCl_2$ (c) $AlCl_4$ (d) $AlCl_3$

8. Two elements A (At. mass = 75) and B (At. mass = 16) combine to yield a compound. The % by mass of A in the compound was found to be 75.08. The formula of the compound is: (MLNR 1991)
(a) A_2B (b) AB (c) AB_2 (d) A_2B_3

9. On analysis, a certain compound was found to contain iodine and oxygen in the ratio of 254 : 80. The formula of the compound is: (At. mass I = 127, O = 16)
(a) IO (b) I_2O (c) I_5O_2 (d) I_2O_5

10. The haemoglobin from red corpuscles of most mammals contains approximately 0.33% of iron by weight. The molecular weight of haemoglobin is 67,200. The number of iron atoms in each molecule of haemoglobin is:
(a) 1 (b) 2 (c) 3 (d) 4

11. 24.9 g of sodium thiosulphate (Mol. mass = 249) is weighed by a chemist. The moles of sodium thiosulphate he has weighed, are:
(a) $\frac{1}{10}$ (b) $\frac{1}{5}$ (c) $\frac{1}{2}$ (d) 1

12. The mass of sulphuric acid needed for dissolving 3 g magnesium carbonate is:
(a) 3.5 g (b) 7.0 g (c) 1.7 g (d) 17.0 g

13. 10 mL of a solution of H_2O_2 liberated 0.5 g of iodine from KI solution. The percentage of H_2O_2 in the solution is:
(a) 0.27 g (b) 0.67 g (c) 0.47 g (d) 0.87 g

14. The mass of CO_2 obtained when 60 g of calcium carbonate is treated with excess of hydrochloric acid is:
(a) 30.0 g (b) 15.0 g (c) 13.2 g (d) 26.4 g

15. The % loss in mass after heating a pure sample of potassium chlorate (Mol. mass = 122.5) will be:
(a) 12.25 (b) 24.50 (c) 39.17 (d) 49.0

16. The volume of oxygen required for complete oxidation of 2.0 litre methane at NTP is:
(a) 2 litre (b) 4 litre (c) 1 litre (d) 3 litre

17. 3 volumes of hydrogen are required to combine with one volume of nitrogen to form 2 volumes of ammonia. When 1 mole of hydrogen is allowed to react with the mole of nitrogen, the two gases:
(a) do not combine
(b) combine and both the gases are used up completely
(c) 2/3 mole of nitrogen remains unreacted
(d) some hydrogen remains uncombined

18. The percentage of nitrogen in urea is about:
(a) 38.4 (b) 46.6 (c) 59.1 (d) 61.3

19. If a mixture containing 3 moles of hydrogen and 1 mole of nitrogen is converted completely into ammonia, the ratio of initial and final volumes under the same temperature and pressure would be:
(a) 3 : 1 (b) 1 : 3 (c) 2 : 1 (d) 1 : 2

20. The mass of residue left after strongly heating 1.38 g of silver carbonate will be:
(a) 1.16 g (b) 1.33 g (c) 2.66 g (d) 1.08 g

21. The mass of oxygen with which 13.5 g of aluminium will completely react is:
(a) 4 g (b) 8 g (c) 12 g (d) 16 g

22. 1.6 g of an organic compound on combustion gave 4.4 g carbon dioxide. The % of carbon in the organic compound is:
(a) 30 (b) 45 (c) 60 (d) 75

23. At NTP, 10 litre of hydrogen sulphide gas reacted with 10 litre of sulphur dioxide gas. The volume of gas, after the reaction is complete, would be:
(a) 5 litre (b) 10 litre (c) 15 litre (d) 20 litre

24. A substance contains 0.25% iron by weight. The molecular mass of the substance is 89600. The number of iron atoms per molecule of the substance is:
(a) 5 (b) 4 (c) 3 (d) 2

25. The minimum amount of hydrogen required to reduce 7.95 g of CuO (Mol. mass = 79.5) will be:
(a) 2 g (b) 4 g
(c) 2240 mL at NTP (d) 22400 mL at NTP

26. 2.0 g mixture of sodium carbonate and sodium bicarbonate on heating to constant mass gave 224 mL of CO_2 at NTP. The % mass of sodium bicarbonate in the mixture is:
(a) 50 (b) 54 (c) 80 (d) 84

27. What volume of hydrogen at NTP will be liberated when 3.25 g of zinc completely dissolve in dilute HCl? (At. mass of Zn = 65)
(a) 1.12 litre (b) 11.20 litre
(c) 2.24 litre (d) 22.40 litre

28. The volume of oxygen at NTP evolved when 1.70 g of sodium nitrate is heated to a constant mass is:
(a) 0.112 litre (b) 0.224 litre (c) 22.4 litre (d) 11.2 litre

29. 50 g limestone is heated. The quantity of quicklime produced is:
(a) 56 g (b) 28 g (c) 14 g (d) 10 g

30. Assuming that petrol is octane (C_8H_{18}) and has a density of 0.8 g mL^{-1}, 1.425 litre of petrol on combustion will consume:
(a) 100 mole of oxygen (b) 124 mole of oxygen
(c) 150 mole of oxygen (d) 175 mole of oxygen

31. 1 mole of calcium phosphide on reaction with excess of water gives: **(IIT 1999)**
(a) 1 mole of phosphine
(b) 2 mole of phosphine
(c) 2 mole of phosphoric acid
(d) 1 mole of phosphorus pentoxide

32. Assuming fully decomposed, the volume of CO_2 released at STP on heating 9.85 g of $BaCO_3$ will be: (Atomic mass of Ba = 137) **[CBSE (PMT) 2004]**
(a) 0.84 L (b) 2.24 L (c) 4.06 L (d) 1.12 L

33. MnO_4^{2-} (1 mole) in neutral aqueous medium disproportionates to: **(AIIMS 2003)**
(a) 2/3 mole MnO_4^- and 1/3 mole MnO_2
(b) 1/3 mole MnO_4^- and 2/3 mole MnO_2
(c) 1/3 mole Mn_2O_7 and 1/3 mole MnO_2
(d) 2/3 mole Mn_2O_7 and 1/3 mole of MnO_2

34. 56 g of nitrogen and 8 g of hydrogen gas are heated in a closed vessel. At equilibrium 34 g of ammonia are present. The equilibrium number of moles of nitrogen, hydrogen and ammonia are respectively: **(KCET 2004)**
(a) 1, 2, 2 (b) 2, 2, 1 (c) 1, 1, 2 (d) 2, 1, 2

35. If 30 mL of H_2 and 20 mL of O_2 reacts to form H_2O, what is left at the end of the reaction? **(AFMC 200**
(a) 10 mL of H_2 (b) 5 mL of H_2
(c) 10 mL of O_2 (d) 5 mL of O_2

[**Hint:** $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$]

	$H_2(g)$	$O_2(g)$	$H_2O(g)$
Initially	30	20	0
After the reaction	0	(20 – 15)	30

36. For the formation of 3.65 g of hydrogen chloride gas, what volumes of hydrogen gas and chlorine gas are required at NTP conditions? **[PMT (Kerala) 2005]**
(a) 1.12 L, 1.12 L (b) 1.12 L, 2.24 L
(c) 3.65 L, 1.83 L (d) 1 L, 1 L

37. An alkaloid contains 17.28% of nitrogen and its molecular mass is 162. The number of nitrogen atoms present in one molecule of alkaloid is: **[PMT (Kerala) 2005]**
(a) five (b) four (c) three (d) two

38. *x* gm of $CaCO_3$ was completely burnt in air. The weight of the solid residue formed is 28 g. What is the value of '*x*' in grams? **(EAMCET 2005)**
(a) 44 (b) 200 (c) 150 (d) 50

39. Sodium bicarbonate on heating decomposes to form sodium carbonate, CO_2 and water. If 0.2 mole of sodium bicarbonate is completely decomposed, how many mole of sodium carbonate is formed? **[CET (J&K) 2006; SCRA 2009]**
(a) 0.1 (b) 0.2 (c) 0.05 (d) 0.025
[**Hint:** The reaction involved is :

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(l)\,]$$

40. One mole of acidified $K_2Cr_2O_7$ on reaction with excess of KI will liberate . . . . moles of I_2. **[PET (Kerala) 2006]**
(a) 6 (b) 1 (c) 7 (d) 3
[**Hint:** $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$]

41. The decomposition of a certain mass of $CaCO_3$ gave 11.2 dm^3 of CO_2 gas at STP. The mass of KOH required to completely neutralise the gas is: **[KCET 2006; Indraprastha (Engg.) 2007]**
(a) 56 g (b) 28 g (c) 42 g (d) 20 g

42. At *T* K, 100 litre of dry oxygen is present in a sealed container. It is subjected to silent electric discharge, till the volumes of oxygen and ozone become equal. What is the volume (in litre) of ozone formed at *T* K? **[EAMCET (Engg.) 2006]**
(a) 50 L (b) 60 L (c) 30 L (d) 40 L
[**Hint:**

	$3O_2$	$\longrightarrow 2O_3$
$t = 0$	100	0
After the reaction	$100 - 3x$	$2x$

$\because$ $100 - 3x = 2x$ or $x = 20$
$\therefore$ Volume of ozone $= 2x = 40$ L]

43. In the reaction,
$2Al(s) + 6HCl(aq.) \longrightarrow 2Al^{3+}(aq.) + 6Cl^-(aq.) + 3H_2(g)$: **(AIEEE 2007)**
(a) 11.2 L $H_2(g)$ at STP is produced for every mole of $HCl(aq.)$ consumed
(b) 6 L $HCl(aq.)$ is consumed for every 3 L $H_2(g)$ produced
(c) 33.6 L $H_2(g)$ is produced regardless of temperature and pressure for every mole of Al that reacts
(d) 67.2 L $H_2(g)$ at STP is produced for every mole of Al that reacts

44. The weight of iron which will be converted into its oxide (Fe_3O_4) by the action of 18 g of steam on it will be: (Atomic mass of Fe = 56) **[CMC (Vellore) 2007]**
(a) 168 g (b) 84 g (c) 42 g (d) 21 g
[**Hint:** $3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g)$

$3Fe(s)$	$4H_2O(g)$
3 mol	4 mol
3×56	4×18
= 168 g	= 72 g

$\because$ 72 g steam reacts with 168 g of iron
$\therefore$ 18 g steam will react with 42 g of iron.]

45. Match the following :

List-I	List-II (at STP)
(A) 10 g $CaCO_3 \xrightarrow[\text{Decomposition}]{\Delta}$	(i) 0.224 L CO_2
(B) 1.06 g $Na_2CO_3 \xrightarrow{\text{Excess HCl}}$	(ii) 4.48 L CO_2
	(iii) 0.448 L CO_2
(C) 2.4 g C $\xrightarrow[\text{Combustion}]{\text{Excess } O_2}$	(iv) 2.24 L CO_2
(D) 0.56 g CO $\xrightarrow[\text{Combustion}]{\text{Excess } O_2}$	(v) 22.4 L CO_2

The correct match is: [EAMCET (Engg.) 2008]

	A	B	C	D
(a)	(iv)	(i)	(ii)	(iii)
(b)	(v)	(i)	(ii)	(iii)
(c)	(iv)	(i)	(iii)	(ii)
(d)	(i)	(iv)	(ii)	(iii)

[**Hint:** (A) $$\underset{\substack{100\text{ g}\\10\text{ g}}}{CaCO_3} \xrightarrow{\Delta} CaO + \underset{\substack{22.4\text{ L}\\2.24\text{ L}}}{CO_2}$$

(B) $$\underset{\substack{1\text{ mol }(106\text{ g})\\1.06\text{ g}}}{Na_2CO_3} + 2HCl \longrightarrow 2NaCl + H_2O + \underset{\substack{22.4\text{ L}\\0.224\text{ L}}}{CO_2}$$

(C) $$\underset{\substack{12\text{ g}\\2.4\text{ g}}}{C} + O_2 \longrightarrow \underset{\substack{22.4\text{ L}\\4.48\text{ L}}}{CO_2}$$

(D) $$\underset{\substack{28\text{ g}\\0.56\text{ g}}}{CO} + \frac{1}{2}O_2 \longrightarrow \underset{\substack{22.4\text{ L}\\0.448\text{ L}}}{CO_2}\ ]$$

46. $Fe^{2+} \longrightarrow Fe^{3+} + e^-$, $MnO_4^- + 5e^- \longrightarrow Mn^{2+}$, the ratio of stoichiometric coefficient of Fe^{2+} and MnO_4^- is: (DPMT 2008)

(a) 1 : 5 (b) 5 : 1 (c) 2 : 3 (d) 6 : 1

47. What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely 1L of propane gas (C_3H_8) measured under the same conditions ? [CBSE-PMT (Pre.) 2008]

(a) 5 L (b) 10 L (c) 7 L (d) 6 L

[**Hint:** $$\underset{\substack{1\text{ vol.}\\1\text{ L}}}{C_3H_8(g)} + \underset{\substack{5\text{ vol.}\\5\text{ L}}}{5O_2(g)} \longrightarrow \underset{\substack{3\text{ vol.}\\3\text{ L}}}{3CO_2(g)} + \underset{\substack{4\text{ vol.}\\4\text{ L}}}{4H_2O(g)}\ ]$$

48. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g PbO and 3.2 g HCl ? [CBSE-PMT (Pre.) 2008]

(a) 0.011 (b) 0.029 (c) 0.044 (d) 0.333

[**Hint:** $n_{PbO} = \frac{6.5}{224} = 0.029$; $n_{HCl} = \frac{3.2}{36.5} = 0.087$

The reaction is,

$$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$

PbO will be limiting reagent because on complete consumption, it gives least amount of product, *i.e.*, 0.029 mol $PbCl_2$.]

49. 1 mole of methylamine on reaction with nitrous acid gives at NTP:

(a) 1 litre of nitrogen (b) 22.4 litre of nitrogen
(c) 11.2 litre of nitrogen (d) 5.6 litre of nitrogen

[**Hint:** $$\underset{1\text{ mol}}{CH_3{-}NH_2} + HONO \longrightarrow CH_3{-}OH + \underset{\substack{22.4\text{ litre}\\\text{at STP}}}{N_2} + H_2O]$$

50. The value of 'n' in the reaction :

$$Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$$

will be : [PET (MP) 2008]

(a) 2 (b) 3 (c) 6 (d) 7

51. In the complex with formula $MCl_3 \cdot 4H_2O$, the coordination number of the metal M is six and there is no molecule of hydration in it. The volume of 0.1 M $AgNO_3$ solution needed to precipitate the free chloride ions in 200 mL of 0.01 M solution of the complex is: [PMT (Kerala) 2008]

(a) 40 mL (b) 20 mL (c) 60 mL (d) 80 mL

[**Hint:** The complex will be $[M(H_2O)_4Cl_2]Cl$, the complex will have free chloride ion concentration of (0.01 M).

$$1\,Cl^- + 1AgNO_3 \longrightarrow AgCl + NO_3^-$$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2} \text{ or } \frac{0.01 \times 200}{1} = \frac{0.1 \times V_2}{1}$$

$$V_2 = 20 \text{ mL}\ ]$$

52. 1.5 g $CdCl_2$ was found to contain 0.9 g Cd. Calculate the atomic weight of Cd. [EAMCET (Engg.) 2009]

(a) 118 (b) 112 (c) 106.5 (d) 53.25

[**Hint:** ∵ 0.6 g chlorine combines with 0.9 g Cd

∴ 71 g chlorine will combine with $\frac{0.9}{0.6} \times 71$ g Cd, *i.e*, 106.5 g Cd

∴ Atomic weight of Cd = 106.5]

53. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be : (AIPMT 2009)

(a) 1 mol (b) 2 mol (c) 3 mol (d) 4 mol

[**Hint:** 10 g H_2, *i.e.*, 5 mol is mixed with 64 g O_2, *i.e.*, 2 mol

$$\underset{2\text{ mol}}{2H_2(g)} + \underset{1\text{ mol}}{O_2(g)} \longrightarrow \underset{2\text{ mol}}{2H_2O(g)}$$

Case I : **Let H_2 is completely consumed**

∵ 2 mol H_2 gives 2 mol H_2O

∴ 5 mol H_2 gives 5 mol H_2O

Case II : **Let O_2 is completely consumed**

∵ 1 mol O_2 gives 2 mol H_2O

∴ 2 mol O_2 gives 4 mol H_2O

Since O_2 gives least amount of product on complete consumption hence it is limiting reagent and amount of H_2O formed will be 4 mol.]

54. In an experiment, 4 g of M_2O_x oxide was reduced to 2.8 g of the metal. If the atomic mass of the metal is 56 g mol^{-1}, the number of oxygen atoms in the oxide is: (AFMC 2010)

(a) 1 (b) 2 (c) 3 (d) 4

55. A vessel fitted with a weightless, frictionless piston of 0.025 m^2 area contains conc. HCl. The piston moved 1 m outward when 0.075 kg of iron fillings were added at 300 K. The solution left behind was found to contain Fe(II). The approximate purity of the iron sample is: (ISAT 2010)

(a) 50% (b) 75% (c) 90% (d) 40%

[**Hint:** Volume of H_2 gas produced = 0.025 × 1 = 0.025 m^3

= 25 L

$$PV = nRT$$

$$1 \times 25 = n \times 0.082 \times 300$$

$$n_{H_2} = 1.016$$

The reaction involved is :

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow$$

Thus, number of moles of iron will be 1.016.

i.e., Mas iron is 1.016 × 56 *i.e.*, 56.896 g

$$\% \text{ purity of iron sample} = \frac{56.896}{75} \times 100 \approx 75\%]$$

56. The reaction of calcium with water is represented by the equation:

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2\uparrow$$

What volume of H_2 at STP would be liberated when 8 g of calcium completely reacts with water? **(AIIMS 2010)**

(a) 0.2 cm^3 (b) 0.4 cm^3 (c) 224 cm^3 (d) 4480 cm^3

57. What volume of hydrogen will be liberated at NTP by the reaction of Zn on 50 mL dilute H_2SO_4 of specific gravity 1.3 and having purity 40%? **[BHU (Mains) 2010]**

(a) 3.5 litre (b) 8.25 litre (c) 6.74 litre (d) 5.94 litre

[Hint: Mass of $H_2SO_4 = \frac{50 \times 1.3 \times 40}{100} = 26$ g

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Volume of H_2 at NTP $= \frac{22.4}{98} \times 26 = 5.94$ litre]

Answers : OBJECTIVE QUESTIONS

1. (a)	**2.** (d)	**3.** (c)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (d)	**8.** (b)
9. (d)	**10.** (d)	**11.** (a)	**12.** (a)	**13.** (b)	**14.** (d)	**15.** (c)	**16.** (b)
17. (c)	**18.** (b)	**19.** (c)	**20.** (d)	**21.** (c)	**22.** (d)	**23.** (a)	**24.** (b)
25. (c)	**26.** (d)	**27.** (a)	**28.** (b)	**29.** (b)	**30.** (a)	**31.** (b)	**32.** (d)
33. (a)	**34.** (c)	**35.** (d)	**36.** (a)	**37.** (d)	**38.** (d)	**39.** (a)	**40.** (d)
41. (b)	**42.** (d)	**43.** (c)	**44.** (c)	**45.** (a)	**46.** (b)	**47.** (a)	**48.** (b)
49. (b)	**50.** (c)	**51.** (b)	**52.** (c)	**53.** (d)	**54.** (c)	**55.** (b)	**56.** (d)
57. (d)							

BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS for IIT ASPIRANTS

The following questions contain single correct option:

1. What mass of $Mg(OH)_2$ is required to neutralize 125 mL of 0.136 M hydrochloric acid solution?
Molar mass of $Mg(OH)_2 = 58.33\text{ g mol}^{-1}$.
(a) 0.248 g (b) 0.496 g (c) 0.992 g (d) 1.98 g
[Hint: $Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$

$$\text{Number of moles of HCl} = \frac{MV}{1000} = \frac{0.136 \times 125}{1000} = 0.017$$

2 mole HCl is neutralized by 58.33 g of $Mg(OH)_2$

$$\therefore 0.017 \text{ mole HCl will be neutralized by } \frac{58.33}{2} \times 0.017 \text{ g of } Mg(OH)_2 = 0.496 \text{ g}]$$

2. Calculate the mass of ammonia that can be produced from the decomposition of a sample of $(NH_4)_2PtCl_6$ containing 0.1 g Pt: Molar mass of $(NH_4)_2PtCl_6$ is 443.9 g mol^{-1}.
(a) 0.0811 g (b) 0.0766 g (c) 0.0175 g (d) 0.00766 g

3. Consider the following data:

Element	**Atomic mass**
A	12.01
B	35.5

A and B combine to form new substance X. If 4 moles of B combine with 1 mole of A to give 1 mole of X, then weight of one mole of X is:
(a) 154 g (b) 74 g (c) 47.5 g (d) 166 g
[Hint: $A + 4B \longrightarrow X$

Molar mass of $X = 12.01 + 4 \times 35.5 = 154\text{ g mol}^{-1}$]

4. Chlorine can be prepared by reacting HCl with MnO_2. The reaction is represented by this equation:

$$MnO_2(s) + 4HCl(aq.) \longrightarrow Cl_2(g) + MnCl_2(aq.) + 2H_2O(l)$$

Assuming the reaction goes to completion, what mass of concentrated HCl solution (36% HCl by mass) is needed to produce 2.5 g of Cl_2?
(a) 5.15 g (b) 14.3 g (c) 19.4 g (d) 26.4 g

5. What volume of 3 M Na_2SO_4 must be added to 25 mL of 1 M $BaCl_2$ to produce 5 g $BaSO_4$?
(a) 7.2 mL (b) 8.3 mL (c) 10 mL (d) 14 mL
[Hint: $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2NaCl$

$$\text{Number of moles of } BaSO_4 = \frac{\text{Mass}}{\text{Molar mass}} = \frac{5}{233} = 0.0215$$

Number of moles of Na_2SO_4 needed = 0.0215

$$\frac{MV}{1000} = 0.0215$$

$$\frac{3 \times V}{1000} = 0.0215$$

$$V = 7.2 \text{ mL}]$$

6. When $FeCl_3$ is ignited in an atmosphere of pure oxygen, this reaction takes place:

$$4FeCl_3(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s) + 6Cl_2(g)$$

If 3 moles of $FeCl_3$ are ignited in the presence of 2 moles of O_2 gas, how much of which reagent is present in excess and therefore, remains unreacted?
(a) 0.33 mole $FeCl_3$ remains unreacted
(b) 0.67 mole $FeCl_3$ remains unreacted
(c) 0.25 mole O_2 remains unreacted
(d) 0.50 mole O_2 remains unreacted

7. A self-contained breathing apparatus uses potassium superoxide, KO_2, to convert the carbon dioxide and water in exhaled air into oxygen, as shown by the equation:

$$4KO_2(s) + 2H_2O(g) + 4CO_2(g) \longrightarrow 4KHCO_3(s) + 3O_2(g)$$

How many molecules of oxygen gas will be produced from 0.0468 g of carbon dioxide that is exhaled in a typical breath?
(a) 4.8×10^{20} (b) 6.4×10^{20} (c) 8.5×10^{20} (d) 1.9×10^{21}
[Hint: $\because$ 4 mole CO_2 gives 3 mole O_2

$$\therefore \left(\frac{0.0468}{44}\right) \text{ mole } CO_2 \text{ will give } \frac{3}{4} \times \frac{0.0468}{44} \text{ mole } O_2 = 7.977 \times 10^{-4} \text{ mol}$$

$$\text{Number of molecules of } O_2 = 7.977 \times 10^{-4} \times 6.023 \times 10^{23} = 4.8 \times 10^{20}]$$

8. Antimony reacts with chlorine according to this equation:

$$2Sb + 3Cl_2 \rightleftharpoons 2SbCl_3$$

How many grams of $SbCl_3$ can be prepared if 0.012 mole of antimony are reacted with 0.02 mole of chlorine? The molar mass of $SbCl_3$ equals 228.2 g mol^{-1}.
(a) 1.52 g (b) 1.83 g (c) 2.74 g (d) 4.56 g

9. A gaseous mixture of propane and butane of volume 3 L on complete combustion produces 10 L of CO_2 under standard conditions of temperature and pressure. The ratio of volumes of propane to butane is:
(a) 1 : 2 (b) 2 : 1 (c) 3 : 2 (d) 3 : 1

10. What amount of silver will be obtained on thermal decomposition of 2.76 g of silver carbonate, Ag_2CO_3 (276 amu)?
(a) 2.16 g (b) 0.216 g (c) 216 g (d) 21.6 g

11. $PH_3(g)$ decomposes on heating to produce phosphorous and hydrogen. The change in volume when 100 mL of such gas decomposed is:
(a) +50 mL (b) +500 mL (c) −50 mL (d) −500 mL
[Hint: $4PH_3(g) \xrightarrow{\text{Heat}} P_4(s) + 6H_2(g)$

Volume of H_2 formed by decomposition of 100 mL PH_3

$$= \frac{6}{4} \times 100 = 150 \text{ mL}$$

Thus, change in volume = (150 − 100) = 50 mL]

12. What amount of $BaSO_4$ can be obtained on mixing 0.5 mole $BaCl_2$ with 1 mole of H_2SO_4?
(a) 0.5 mol (b) 0.15 mol (c) 0.1 mol (d) 0.2 mol
[Hint:

$$\begin{array}{lccccc} & BaCl_2 & + \; H_2SO_4 & \longrightarrow & BaSO_4 & + \; 2HCl \,] \\ \text{Initially} & 0.5 & 1 & & 0 & 0 \\ \text{After the reaction} & 0 & (1-0.5) & & 0.5 & 2 \times 0.5 \end{array}$$

13. In the reaction,

$$CrO_5 + H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + H_2O + O_2$$

one mole of CrO_5 will liberate how many moles of O_2?

(a) 5/2 (b) 5/4
(c) 9/2 (d) None of these

14. Calcium carbonate decomposes on heating according to the equation;

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

At STP, the volume of CO_2 obtained by thermal decomposition of 50 g of $CaCO_3$ will be:

(a) 22.4 litre (b) 44 litre (c) 11.2 litre (d) 1 litre

15. The volume in litre of CO_2 liberated at STP when 10 g of 90% pure limestone is heated completely, is:

(a) 22.4 L (b) 2.24 L (c) 20.16 L (d) 2.016 L

[Hint: $\underset{\substack{\text{1 mole}\\ \text{(100 g)}}}{CaCO_3} \longrightarrow CaO + \underset{\text{22.4 litre at STP}}{CO_2(g)}$

$\because$ 100 g $CaCO_3 \equiv$ 22.4 L CO_2 at STP

$\therefore$ 9 g $CaCO_3 \equiv \dfrac{22.4}{100} \times 9$ L CO_2 at STP

= 2.016 L CO_2 at STP]

16. A metal oxide has the formula Z_2O_3. It can be reduced by hydrogen to give free metal and water. 0.1596 g of the metal requires 6 mg of hydrogen for complete reduction. The atomic mass of the metal is:

(a) 27.9 g mol^{-1} (b) 159.6 g mol^{-1}
(c) 79.8 g mol^{-1} (d) 55.8 g mol^{-1}

[Hint: $Z_2O_3 + 3H_2(g) \longrightarrow 2Z + 3H_2O$

$\because$ 6 g H_2 gives 2 mole Z

$\therefore$ 6×10^{-3} g H_2 will give 0.002 mole Z

$$\text{Number of moles} = \frac{\text{Mass}}{\text{Molar mass}}$$

$$0.002 = \frac{0.1596}{\text{Molar mass}}$$

$\therefore$ $\text{Molar mass} = \dfrac{0.1596}{0.002} = 79.8 \text{ g mol}^{-1}$]

17. 10 g $CaCO_3$ is completely decomposed to X and CaO. X is passed into an aqueous solution containing one mole of sodium carbonate. What is the number of moles of sodium bicarbonate formed?
[Molar mass: $CaCO_3$(100); Na_2CO_3(106); $NaHCO_3$(84)].

(a) 0.2 (b) 0.1 (c) 0.01 (d) 10

18. Chlorine gas can be produced by reacting sulphuric acid with a mixture of MnO_2 and NaCl. The reaction follows the equation:

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + Cl_2 + 2H_2O$$

What volume of chlorine can be produced from 1 g of sodium chloride under standard conditions of temperature and pressure?

(a) 1.915 L (b) 19.15 L (c) 20.22 L (d) 0.191 L

[Hint: 2 mole NaCl (117 g) $\equiv$ 1 mole Cl_2 (22.4 L at STP)

$\therefore$ 1 g NaCl will give $= \dfrac{22.4}{117}$ L Cl_2 at STP

= 0.191 L Cl_2 at STP]

19. 1 mole of a gaseous aliphatic compound $C_nH_{3n}O_m$ is completely burnt in an excess of oxygen. The contraction in volume is:

(a) $\left(1 + \frac{1}{2}n - \frac{3}{4}m\right)$ (b) $\left(1 + \frac{3}{4}n - \frac{1}{4}m\right)$
(c) $\left(1 - \frac{1}{2}n - \frac{3}{4}m\right)$ (d) $\left(1 + \frac{3}{4}n - \frac{1}{2}m\right)$

20. A mixture of CH_4 and C_2H_4 was completely burnt in an excess of oxygen, yielding equal volumes of CO_2 and steam. Calculate the percentages of the compounds in the original mixture:

(a) 25% CH_4 and 75% C_2H_4 (b) 30% CH_4 and 70% C_2H_4
(c) 75% CH_4 and 25% C_2H_4 (d) 50% CH_4 and 50% C_2H_4

21. When same amount of zinc is treated separately with excess of H_2SO_4 and NaOH, the ratio of volumes of H_2 evolved is:

(a) 1 : 1 (b) 1 : 2 (c) 2 : 1 (d) 9 : 4

[Hint: $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$]

22. 10 mole of SO_2 and 15 mole of O_2 were passed over a catalyst to produce 8 mole of SO_3. The ratio of SO_2 and SO_3 moles in mixture is:

(a) 5/4 (b) 1/4 (c) 1/2 (d) 3/4

[Hint:
$$\begin{array}{llll} & SO_2(g) + & \frac{1}{2}O_2(g) \xrightarrow{\text{Catalyst}} & SO_3(g) \\ t = 0 & 10 & 15 & 0 \\ \text{Final} & 10 - x & 15 - \frac{x}{2} & x \end{array}$$

$x = 8$

$\therefore$ $n_{SO_2} = 10 - x = 2, n_{SO_3} = 8$

$\dfrac{n_{SO_2}}{n_{SO_3}} = \dfrac{2}{8} = \dfrac{1}{4}$]

23. $HgCl_2 + 4KI \longrightarrow K_2[HgI_4] + 2KCl$

1 mole each of Hg^{2+} and I^- will fc [illegible] ow many moles of HgI_4^{2-}?

(a) 1 mol (b) 0.5 mol (c) 0.25 mol (d) 2 mol

24. 25 mL of 0.15 M $Pb(NO_3)_2$ reacts completely with 20 mL of $Al_2(SO_4)_3$. The molar concentration of $Al_2(SO_4)_3$ will be:

$$3Pb(NO_3)_2(aq.) + Al_2(SO_4)_3(aq.) \longrightarrow 3PbSO_4(s) + 2Al(NO_3)_3(aq.)$$

(a) 0.0625 M (b) 0.0242 M
(c) 0.1875 M (d) 0.2346 M

[Hint: $\dfrac{M_1V_1}{n_1} Pb(NO_3)_2 = \dfrac{M_2V_2}{n_2} Al_2(SO_4)_3$

$$\frac{0.15 \times 25}{3} = \frac{M_2 \times 20}{1}$$

$M_2 = 0.0625$]

25. In the reaction,

$$2NH_3(g) + 5F_2 \longrightarrow N_2F_4 + 6HF$$

3.56 g N_2F_4 is obtained by mixing 2 g NH_3 and 8 g F_2. The percentage yield of the production is:

(a) 81.28% (b) 71.2% (c) 68% (d) 79%

[Hint: $\underset{34\text{ g}}{2NH_3(g)} + \underset{190\text{ g}}{5F_2} \longrightarrow \underset{104\text{ g}}{N_2F_4} + 6HF$

Amount of N_2F_4 formed by 2 g $NH_3 = \dfrac{104}{34} \times 2 = 6.12$ g

Amount of N_2F_4 formed by 8 g $F_2 = \frac{104}{190} \times 8 = 4.38$ g

N_2F_4 will be limiting and actual amount of product is 3.56 g

$$\therefore \quad \% \text{ yield} = \frac{\text{Actual amount of product}}{\text{Calculated amount of product}} \times 100$$

$$= \frac{3.56}{4.38} \times 100$$

$$= 81.28\% \,]$$

The following questions may have more than one correct options:

1. 1.5 g of oxygen is produced by heating $KClO_3$. How much KCl is produced in the reaction?
(a) 4.15×10^{-2} mol (b) 4.33 g
(c) 1.78×10^{-2} mol (d) 1.33 g

2. Calculate the amount of lime that can be produced by heating 100 g of 90% pure limestone:
(a) 50.4 g (b) 0.98 mol (c) 0.9 mol (d) 56 g
[**Hint:** $\underset{100\text{ g}}{CaCO_3} \longrightarrow \underset{56\text{ g}}{CaO} + CO_2$

$$100 \text{ g } CaCO_3 \equiv 56 \text{ g } CaO$$

$$\therefore \quad 90 \text{ g } CaCO_3 \equiv \frac{56}{100} \times 90 \text{ g CaO, } i.e., 50.4 \text{ g CaO}$$

$$\text{Number of moles of CaO} = \frac{50.4}{56} = 0.9]$$

3. In an experiment, the following four gases were produced. 11.2 L of which two gases at STP will weigh 14 g?
(a) N_2O (b) NO_2 (c) N_2 (d) CO

4. 2 mole of CO_2 is required to prepare:
(a) 336 g of $NaHCO_3$ (b) 168 g of $NaHCO_3$
(c) 462 g of $Ca(HCO_3)_2$ (d) 162 g of $Ca(HCO_3)_2$

5. 8.7 g of pure MnO_2 is heated with an excess of HCl and the gas evolved is passed into a solution of KI. Calculate the amount of the iodine liberated (Mn = 55, Cl = 35.5, I = 127):
(a) 0.1 mol (b) 25.4 g
(c) 15.4 g (d) 7.7 g

6. 100 mL of gaseous mixture containing CO, CO_2 and O_2 was sparked; there was contraction of 80 mL volume when the mixture was passed through aqueous caustic potash KOH. The composition of initial gaseous mixture will be respectively:
(a) 20 mL, 70 mL, 10 mL (b) 50 mL, 30 mL, 20 mL
(c) 30 mL, 50 mL, 20 mL (d) 30 mL, 60 mL, 10 mL
[**Hint :** (d) $CO + \frac{1}{2}O_2 \longrightarrow CO_2$

10 mL O_2 will give 20 mL CO_2 in above reaction. Thus, total volume of CO_2 will be 80 mL which will be absorbed in caustic potash KOH.

Similarly in (c) option, 30 mL CO_2 will be formed on sparking.

$$\underset{\substack{30\text{ mL}\\(\text{Limiting})}}{CO} + \frac{1}{2}O_2 \longrightarrow \underset{30\text{ mL}}{CO_2}$$

Total volume of CO_2 will be 80 mL]

7. SO_2 gas is slowly passed through an aqueous suspension containing 12 g $CaSO_3$ till the milkiness just disappears, what amount of SO_2 would be required? [BHU (Mains) 2010]
(a) 12.8 g (b) 6.4 g (c) 0.2 mole (d) 0.1 mole
[**Hint :** The reaction involved is

$$\underset{\substack{\text{milky}\\1\text{ mol}\\120\text{ g}}}{CaSO_3} + H_2O + \underset{\substack{1\text{ mol}\\64\text{ g}}}{SO_2} \longrightarrow \underset{\text{colourless}}{Ca(HSO_3)_2}$$

12 g $CaSO_3$ will react with 6.4 g SO_2 or 0.1 mol SO_2.]

Answers

- **Single correct option**

1. (b) **2.** (c) **3.** (a) **4.** (b) **5.** (a) **6.** (a) **7.** (a) **8.** (c)
9. (b) **10.** (a) **11.** (a) **12.** (a) **13.** (d) **14.** (c) **15.** (d) **16.** (c)
17. (a) **18.** (d) **19.** (d) **20.** (d) **21.** (a) **22.** (b) **23.** (c) **24.** (a)
25. (a)

- **One or more than one correct options**

1. (c, d) **2.** (a, c) **3.** (c, d) **4.** (b, d) **5.** (a, b) **6.** (c, d) **7.** (b, d)

LINKED COMPREHENSION TYPE QUESTIONS

• Passage 1

In a reaction vessel, 100 g H_2 *and* 100 g Cl_2 *are mixed and suitable conditions are provided for the following reaction:*

$$H_2(g) + Cl_2(g) \xrightarrow{?} 2HCl(g)$$

Quantum yield of this reaction is $\phi = 10^5$.

Answer the following questions:

1. Select the correct statement(s) for the above reaction:
(a) Presence of light is required for this reaction
(b) It is a chain reaction
(c) Catalyst is required
(d) All of the above

2. The limiting reagent in this reaction will be:
(a) H_2 (b) Cl_2
(c) both (d) cannot be predicted

3. The actual amount of HCl formed in this reaction is:
(a) 102.8 g (b) 73 g
(c) 36.5 g (d) 142 g

4. The amount of excess reactant remaining is:
(a) 50 g (b) 97.2 g
(c) 46 g (d) 64 g

5. The amount of HCl formed (at 90% yield) will be:
(a) 36.8 g (b) 62.5 g
(c) 80 g (d) 92.53 g

• Passage 2

Dissolved oxygen in water is determined by using a redox reaction. Following equations describe the procedure:

$$\text{I. } 2Mn^{2+}(aq.) + 4OH^-(aq.) + O_2(g) \longrightarrow 2MnO_2(s) + 2H_2O(l)$$

$$\text{II. } MnO_2(s) + 2I^-(aq.) + 4H^+(aq.) \longrightarrow Mn^{2+}(aq.) + I_2(aq.) + 2H_2O(l)$$

$$\text{III. } 2S_2O_3^{2-}(aq.) + I_2(aq.) \longrightarrow S_4O_6^{2-}(aq.) + 2I^-(aq.)$$

Answer the following questions:

1. How many moles of $S_2O_3^{2-}$ are equivalent to each mole of O_2?
(a) 0.5 (b) 1 (c) 2 (d) 4

2. What amount of I_2 will be liberated from 8 g dissolved oxygen?
(a) 127 g (b) 254 g (c) 504 g (d) 1008 g

3. If 3×10^{-3} moles O_2 is dissolved per litre of water, then what will be the molarity of I^- produced in the given reaction?
(a) $3 \times 10^{-3}\ M$ (b) $4 \times 3 \times 10^{-3}\ M$
(c) $2 \times 3 \times 10^{-3}\ M$ (d) $\frac{1}{2} \times 3 \times 10^{-3}\ M$

4. Number of which two chemical species will be same in the given procedure?
(a) MnO_2 (b) I_2 (c) I^- (d) $S_2O_3^{2-}$

5. 8 mg dissolved oxygen will consume:
(a) 5×10^{-4} mol Mn^{2+} (b) 2.5×10^{-4} mol Mn^{2+}
(c) 10^{-3} mol Mn^{2+} (d) 2 mol Mn^{2+}

Answers

Passage 1.	**1.** (a, b)	**2.**)	**3.** (a)	**4.** (b)	**5.** (d)
Passage 2.	**1.** (d)	**2.** [illegible]	**3.** (b)	**4.** (a)	**5.** (a)

SELF ASSESSMENT

ASSIGNMENT NO. 15

Straight Objective Type Questions

This section contains 10 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. An oxide of iodine contains 25.4 g of iodine for 8 g of oxygen. Its molecular formula will be:

(a) I_2O_3 (b) I_2O (c) I_2O_5 (d) I_2O_7

2. 2 g H_2 and 1 g O_2 are allowed to react according to following equation:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Amount of H_2O formed in the reaction will be:

(a) 3 g (b) 1.125 g

(c) 4.5 g (d) 2.50 g

3. 20 cc of CO_2 gas is passed over red hot coke. The volume of carbon monoxide evolved is:

(a) 10 cc (b) 20 cc (c) 30 cc (d) 40 cc

4. In the Haber process:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

30 L of H_2 and 30 L of N_2 were taken for reaction which yielded only 50% of expected product. What will be the composition of the gaseous mixture in the end ?

(a) 20 L NH_3, 25 L N_2 and 20 L H_2

(b) 10 L NH_3, 25 L N_2 and 15 L H_2

(c) 20 L NH_3, 10 L N_2 and 30 L H_2

(d) 20 L NH_3, 25 L N_2 and 15 L H_2

5. $KMnO_4$ reacts with oxalic acid according to the equation:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

20 mL of 0.1 *M* $KMnO_4$ will react with:

(a) 120 mL of 0.25 *M* oxalic acid

(b) 150 mL of 0.1 *M* oxalic acid

(c) 50 mL of 0.1 *M* oxalic acid

(d) 50 mL of 0.2 *M* oxalic acid

6. Orthoboric acid, on heating, decomposes in two ways:

$$\text{(I) } H_3BO_3 \longrightarrow HBO_2 + H_2O$$
$$\text{(II) } H_3BO_3 \longrightarrow B_2O_3 + H_2O$$

If 9 moles of H_3BO_3 decomposes by (I) pathway and remaining by (II) pathway. If total 11 moles of water are formed, then the number of moles of B_2O_3 formed is:

(a) 6 (b) 5 (c) 3 (d) 2

7. 2 moles of H_2S and 11.2 L of SO_2 at NTP react to give *x* mole of sulphur. The value of '*x*' will be:

Reaction: $SO_2(g) + 2H_2S(g) \longrightarrow 3S + 2H_2O$

(a) 1.5 (b) 3 (c) 11.2 (d) 6

8. A sample of argentite ore contains 1.34% of Ag_2S by mass. How many grams of this ore would give 1 g of Ag on extraction?

(a) 134 g (b) 108 g (c) 85.7 g (d) 74.6 g

9. What mass of HNO_3 is needed to convert 5 g of iodine into iodic acid according to the reaction?

$$I_2 + HNO_3 \longrightarrow HIO_3 + NO_2 + H_2O$$

(a) 12.4 g (b) 24.8 g (c) 0.248 g (d) 49.6 g

10. $$KI + I_2 + HNO_3 \longrightarrow HIO_3 + KIO_3 + NO_2$$

If 3 moles of KI and 2 moles of I_2 are mixed with excess HNO_3, then volume of NO_2 gas evolved at NTP is:

(a) 716.8 litre (b) 1075.2 litre

(c) 44.8 litre (d) 67.2 litre

11. The decomposition of certain mass of $CaCO_3$ gave 11.2 dm^3 of CO_2 gas at STP. The mass of KOH required to completely neutralise the gas is : **[BHU (Screening) 2010]**

(a) 56 g (b) 28 g (c) 42 g (d) 20 g

Answers

1. (c) **2.** (b) **3.** (d) **4.** (b) **5.** (c) **6.** (d) **7.** (a) **8.** (c)

9. (a) **10.** (a) **11.** (a)

SPONTANEOUS ASSESSMENT SECTION

MODULE–1

IIT Entrance Test Paper

There are 59 questions in this module.

(1) Q. 1 – 20. *Have single correct answer.*
(2) Q. 21 – 30. *Have more than one correct answers.*
(3) Q. 31 – 35. *True/false problems.*
(4) Q. 36 – 40. *Statement/explanation problems.*
(5) Q. 41 – 48. *Thought type/comprehensive problems.*
(6) Q. 49 – 53. *Multiple true/false problems.*
(7) Q. 54 – 58. *True or false type questions.*
(8) Q. 59. *Matching type question.*

1. Kinetic energy of 0.3 mole of 'He' gas in a container of maximum capacity of 4 litre at 5 atm, must be: ($R = 0.0821$ atm litre $\text{mol}^{-1}\ \text{K}^{-1}$)

(a) 30 atm litre (b) 100 atm litre
(c) 9 atm litre (d) 11.11 atm litre

[**Hint:** $PV = \frac{1}{3} mnc^2$

$$\frac{3}{2} PV = \frac{1}{2} mnc^2 = \text{KE}$$

$$\text{KE} = \frac{3}{2} PV = \frac{3}{2} \times 5 \times 4 = 30 \text{ atm litre}]$$

2. What will be the maximum spin multiplicity for 4*d*- orbital?

(a) 4 (b) 6 (c) 5 (d) 10

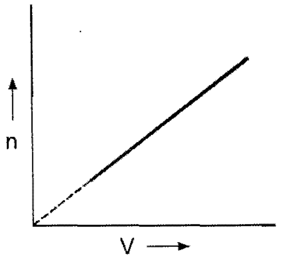
[**Hint:** Spin multiplicity $= 2\Sigma\, s + 1$

$$= 2 \times 5 \times \frac{1}{2} + 1 = 6]$$

3. Number of 'He' atoms in 52 amu sample is:

(a) $2 \times 6.023 \times 10^{23}$ (b) 13
(c) 4 (d) $4 \times 6.023 \times 10^{23}$

4. For a given one mole of ideal gas kept at 6.5 atm in a container of capacity 2.463 litre. The Avogadro proportionality constant for the hypothesis is: (see figure)



(a) 0.406 (b) 2.46
(c) 22.4 (d) none of

[**Hint:** $PV = nRT$

$$6.5 \times 2.463 = 1 \times 0.0821 \times T$$

$$T = 195 \text{ K}$$

$$V = n\left[\frac{RT}{P}\right]$$

Avogadro proportionality constt. $= \frac{RT}{P} = \frac{0.0821 \times 195}{6.5} = 2.461]$

5. $A(s) \rightleftharpoons B(g) + C(g)$. Total pressure at time of equilibrium is 40 atmosphere. If all the contents of this reactor have been shifted to another reactor of double capacity, then the total equilibrium pressure in the new reactor will be: (in atmosphere)

(a) 20 (b) 40 (c) 400 (d) 1600

[**Hint:** Since, gaseous species are not present on both sides, hence the equilibrium will not shift.]

6. Gadolinium-153 is used in the detection of osteoporosis disease of bones. Half life of gadolinium-153 is 500 days. After how many days, on an average, the nuclide can be considered absent from the body of patients?

(a) 500 days (b) 1000 days
(c) Infinite (d) 350 days

[**Hint:** The radioactive element will disappear from the body of patient after infinite time.]

7. Amount of energy required to excite an electron of an atom from the lower energy state to its next higher energy state is defined as:

(a) ionization potential (b) electron affinity
(c) critical potential (d) reduction potential

8. Consider the values for $\Delta H°$ (in kJ mol^{-1}) and for $\Delta S°$ (in J $\text{mol}^{-1}\ \text{K}^{-1}$) given for four different reactions. For which reaction will $\Delta G°$ increase the most (becoming more positive), when the temperature is increased from 0°C to 25°C?

(a) $\Delta H° = 50, \Delta S° = 50$ (b) $\Delta H° = 90, \Delta S° = 20$
(c) $\Delta H° = -20, \Delta S° = -50$ (d) $\Delta H° = -90, \Delta S° = -20$
(e) None of these

9. The energy of the orbitals decreases in the order:

(a) $s > p > sp^3 > sp > sp^2$ (b) $p > sp^3 > sp^2 > sp > s$
(c) $sp^3 > sp^2 > sp > s > p$ (d) $s > sp > sp^2 > sp^3 > p$
(e) none of these

[**Hint:** Greater the percentage of '*p*' character, more is the energy of the orbital.]

10. These are the first eight ionization energies for a particular neutral atom. All values are expressed in MJ mol^{-1}. How many valence electrons do/does this atom possess?

1st	2nd	3rd	4th	5th	6th	7th	8th
1.31	3.39	5.30	7.47	10.99	13.33	71.33	84.01

(a) 1 (b) 2 (c) 4 (d) 6
(e) None of these

11. Consider the reaction:

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The rate law for this reaction is,

$$\text{Rate} = k\,[H_2][NO]^2$$

Under what conditions could these steps represent the mechanism?

Step 1. $2NO \rightleftharpoons N_2O_2$

Step 2. $N_2O_2 + H_2 \longrightarrow N_2O + H_2O$

Step 3. $N_2O + H_2 \longrightarrow N_2 + H_2O$

(a) These steps cannot be the mechanism under any circumstances
(b) These steps could be the mechanism if step 1 is the slowest step
(c) These steps could be the mechanism if step 2 is the slowest step
(d) These steps could be the mechanism if step 3 is the slowest step
(e) None of the above

12. Match the following:

1. Energy of ground state of He^+	(i) -6.04 eV
2. Potential energy of 1st orbit of H-atom	(ii) -27.2 eV
3. Kinetic energy of 2nd excited state of He^+	(iii) 8.7×10^{-18} J
4. Ionisation potential of He^+	(iv) -54.4 eV

(a) 1–(i); 2–(ii); 3–(iii); 4–(iv)
(b) 1–(iv); 2–(iii); 3–(ii); 4–(i)
(c) 1–(iv); 2–(ii); 3–(i); 4–(iii)
(d) 1–(ii); 2–(iii); 3–(i); 4–(iv)

13. If electrons are transited from n_2 excited state to n_1 excited state, then number of lines observed in the spectrum will be:

(a) $\frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$ (b) $\frac{(n_1 - n_2)(n_2 - n_1 + 1)}{2}$
(c) $\frac{(n_2 + n_1)(n_1 + n_2 + 1)}{2}$ (d) $2(n_1 - n_2)(n_1 + n_2 - 1)^2$

14. When an electron is transited from $2E$ to E energy level, the wavelength of photon produced is λ_1. In making electronic transition from $\frac{4}{3}E$ to E level, the wavelength λ_2 is:

(a) $\lambda_2 = \lambda_1$ (b) $\lambda_2 = \frac{3\lambda_1}{4}$ (c) $\lambda_2 = 3\lambda_1$ (d) $\lambda_2 = \frac{4\lambda_1}{3}$

15. Completely filled orbitals have special stability and are spherically symmetrical like d^{10}, p^6, f^{14}, etc. The species among Cl^-, Ar and N_3^- which have such orbitals are:

(a) Cl^-, Ar (b) N_3^-, Cl^-
(c) Ar, N_3^- (d) Ar, Cl^-, N_3^-

16. An atom has x energy levels; then total number of lines in the emission spectrum will be:

(a) $1 + 2 + 3 + \ldots + (x + 1)$
(b) $1 + 2 + 3 + \ldots + x^2$
(c) $1 + 2 + 3 + \ldots + x$
(d) $1 + 2 + 3 + \ldots + (x - 1)$

17. Carbon atom has electronic configuration, $C = 1s^2$, $2s^2$ and $2p^2$. The spin multiplicity of carbon atom is:

(a) 3 (b) 2 (c) 1 (d) 4

18. An electron moves around protons (nucleus) in a circle of radius r. Assuming that the uncertainty of momentum of electron is of the same order as the momentum itself, the momentum of the electron will be:

(a) $\frac{h}{4\pi r}$ (b) $\frac{h}{2\pi r}$ (c) $4\pi hr$ (d) $2\pi hr$

19. The oxidation state of iron in sodium nitroprusside is:

(a) –3 or –2 (b) +3 or –3 (c) +2 or –2 (d) –2 or –3

20. The oxidation state of sodium in sodium amalgam is:

(a) +1 (b) –1 (c) zero (d) +2

Question 21 *to* 30 *have more than one correct answers:*

21. The substance(s) which can act as oxidising as well as reducing agent is/are:

(a) H_2O_2 (b) O_3
(c) $NH_2 — NH_2$ (d) HNO_3

22. Which of the following statements is/are correct?

(a) The electronic configuration of Cr is [Ar] $3d^5 4s^1$
(b) The magnetic quantum number may have negative value
(c) In silver, 23 electrons have a spin of one type and 24 of the opposite type
(d) The oxidation state of hydrogen in NH_3 is +3

23. Which of the following statement(s) about wave function ψ of an electron is/are correct?

(a) ψ has no physical significance
(b) ψ^2 represents the probability of finding electrons
(c) $\psi\psi^* = \psi^2 = |\psi|^2$
(d) ψ is continuous, definite, finite and single valued

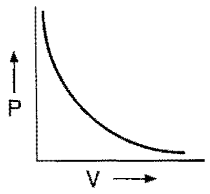
24. Loss of a β-particle is equivalent to:

(a) increase in number of protons by one
(b) decrease in number of neutrons by one
(c) change in atomic mass by one unit
(d) none of the above

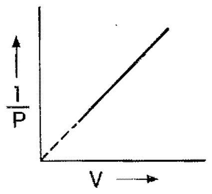
25. The maximum velocity of liquid molecules up to which its flow is streamline is called critical velocity. The critical velocity of a liquid depends upon:

(a) coefficient of viscosity (b) radius of the tube
(c) density of the liquid (d) mass of the tube

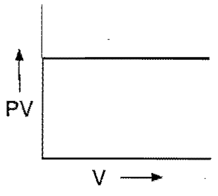
26. Which of the following curves represent(s) Boyle's law?



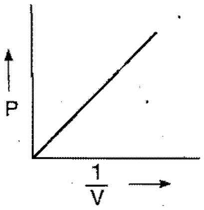
(a)



(b)



(c)



(d)

27. Which of the following set(s) of compounds is/are used as semipermeable membrane?
(a) Calcium phosphate, cellulose nitrate
(b) Calcium phosphate, copper ferrocyanide
(c) Cellulose nitrate, copper ferrocyanide
(d) Copper ferrocyanide, copper sulphate

28. For exact determination of molecular mass:
(a) solute must be volatile
(b) solution must be very dilute
(c) solvent must be non-volatile
(d) solute must not be dissociated or associated

29. For the reaction to be spontaneous:
(a) ΔS should be positive
(b) $(\Delta H - T\Delta S)$ should be negative
(c) $(\Delta H + T\Delta S)$ should be negative
(d) ΔH should be negative

30. When a colloidal solution X is converted into two different solutions Y and Z, the osmotic pressures of Y and Z were found to be respectively higher and lower than X. This indicates that:
(a) X is a colloidal solution and Y is suspension
(b) X is a colloidal solution and Z is true solution
(c) X is colloidal solution and Z is suspension
(d) X is a colloidal solution and Y is true solution

In the following questions (31–35), indicate 'a' if the statement is true and 'b' if the statement is false:

31. The plot of PV *versus* P at constant temperature is a straight line passing through origin.

32. Bohr model could not explain the fine line spectrum of hydrogen.

33. $_{21}$Sc and Cr^{3+} are isoelectronic, hence they have same electronic configuration.

34. van't Hoff factor is equal to unity if the solute undergoes 100% dissociation.

35. A mixture of ideal gas is cooled up to liquid helium temperature (4.22 K) to form an ideal solution.

*In each of the following questions, a **Statement (S)** and **Explanation (E)** are given. Choose the correct answer from the codes a, b, c and d given for each question:*

(*a*) ***S** is correct but **E** is wrong.*
(*b*) ***S** is wrong but **E** is correct.*
(*c*) *Both **S** and **E** are correct and **E** is the correct explanation of **S**.*
(*d*) *Both **S** and **E** are correct but **E** is not correct explanation of **S**.*

36. (S) All Arrhenius acids are also Bronsted acids.
(E) All Bronsted bases are also Lewis bases.

37. (S) 1 amu equals to 1.66×10^{-24} g.
(E) 1.66×10^{-24} g equals 1/12th mass of ^{12}C atom.

38. (S) Spectral lines are not observed for $2p_x - 2p_z$ transition.
(E) p_x, p_y and p_z are three-fold degenerate orbitals.

39. (S) Compressibility factor (Z) for non-ideal gas is always greater than unity.
(E) Non-ideal gases exert less pressure compared to ideal gases under identical conditions.

40. (S) If in zero order reaction, the concentration of the reactant is doubled, the half life period is also doubled.
(E) For a zero order reaction, the rate of reaction is independent of initial concentration.

When 2 g non-volatile solute is dissolved in 100 g of benzene, the vapour pressure of benzene at 20°C is lowered from 74.66 mm to 74.01 mm.

Answer the following questions:

41. Mole fraction of benzene in the solution will be:
(a) 0.89 (b) 0.69 (c) 0.99 (d) 0.79

42. The molar mass of solute will be:
(a) 200 (b) 277.624 (c) 177.624 (d) 350

43. Molecular formula of solute may be:
(a) $C_{14}H_{10}$ (b) $C_{12}H_{26}$ (c) $C_{14}H_{30}$ (d) $C_{14}H_{28}$

44. If the solute is a hydrocarbon containing 94.4% carbon, then the number of moles of carbon in 1 mol of it will be:
(a) 12 (b) 10 (c) 16 (d) 14

45. Molality of solution will be:
(a) 0.013 (b) 0.06 (c) 0.23 (d) 0.05

The age of articles of organic origin can be estimated by radiocarbon dating. The radio-isotope carbon-14 is produced continuously in the upper atmosphere as the nitrogen atoms capture cosmic ray neutrons.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

The ^{14}C atoms react with oxygen molecules to form $^{14}CO_2$. $^{14}CO_2$ is absorbed by the plants in photosynthesis. Carbon-14 decays with a half life of 5730 years.

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$$

After death, the plant no longer carries out photosynthesis, so it no longer takes-up $^{14}CO_2$. Other organisms that consume plants for food stop doing so at death. The emission from ^{14}C in dead tissue then decreases with the passage of time. The activity per gram of carbon is a measure of the length of time elapsed since death. The carbon-14 technique is useful only for dating objects for a limited period of time.

Answer the following questions:

46. Which one is correct?
(a) Carbon dating is predicted only for wood not older than 60000 years.
(b) Carbon dating is predicted only for wood not older than 600 years.
(c) Age of any older wood can be predicted by the radio carbon dating.
(d) Radio carbon dating is used only for wooden objects.

47. A piece of wood taken from a cave dwelling in New Mexico is found to have a carbon-14 activity (per gram of carbon) only 0.636 times that of wood cut today. Estimate the age of the wood:
(a) 7430 yr (b) 3740 yr (c) 4370 yr (d) 7340 yr

48. In carbon dating:
(a) the decay rate of ${}^{14}_{6}C$ is studied
(b) the rate of accumulation of ${}^{14}_{6}C$ is studied
(c) the rate of decay of ${}^{12}_{6}C$ is studied
(d) the rate of formation of ${}^{13}_{6}C$ is studied

In each of the following questions, three statements I, II, III are given. Mark:
(*a*) *if all the statements are correct*
(*b*) *if II and III are correct*
(*c*) *if I and III are correct*
(*d*) *if only II is correct*

49. In CrO_5:
(I) Oxidation number of Cr is +6.
(II) Four oxygen atoms are involved in peroxy linkage.
(III) Only one oxygen atom has –2 state.

50. (I) The conductance of molten NaCl is due to movement of Na^+ and Cl^- ions.
(II) Molten NaCl is a good conductor due to mobility of free electrons.
(III) Solid NaCl is a bad conductor of electricity.

51. (I) Resistance of metals increases on heating.
(II) Unit of cell constant is cm^{-1}.
(III) Specific conductance decreases on dilution.

52. (I) Oxidation number is same as formal charge.
(II) The numerical value of oxidation number and valency may differ.
(III) Absolute value of electrode potential cannot be determined.

53. (I) Cathode is –ve terminal in both electrolytic and electrochemical cells.
(II) Reduction occurs at cathode, both in electrolytic and electrochemical cells.
(III) Chemical change in electrolytic cell is non- spontaneous.

Predict whether the following statements are True or False:

54. At Curie point, ferromagnetic solid changes to paramagnetic solid.
(a) True (b) False (c) cannot be predicted

55. pH of 10^{-10} M HCl is 10.
(a) True (b) False (c) cannot be predicted

56. Specific conductance of electrolyte solution decreases on dilution.
(a) True (b) False (c) cannot be predicted

57. 3*s*-orbital has 2 nodes, inclusive of radial and angular nodes.
(a) True (b) False (c) cannot be predicted

58. Conductance of LiCl is greater than NaCl at infinite dilution.
(a) True (b) False (c) cannot be predicted

59. [A] Match the Column-I with Column-II. Choose the correct one from the alternatives (a), (b), (c) and (d).

Column-I	**Column-II**
P. Wilkinson catalyst	I. *trans*-$IrCl(CO)(PPh_3)_2$
Q. Speier catalyst	II. Hydrosilylation
R. Water gas shift catalyst	III. $RhCl(PPh_3)_3$
S. Zeolite ZSM-5 catalyst	IV. Synthetic gasoline
	V. Hydroformylation
	VI. Zinc-copper oxide

(a)	(b)	(c)	(d)
P–III	P–I	P–V	P–III
Q–II	Q–V	Q–II	Q–VI
R–VI	R–III	R–VI	R–IV
S–IV	S–IV	S–IV	S–II

[B] Match the Column-I with Column-II. Choose the correct one from the alternatives (a), (b), (c) and (d).

Column-I	**Column-II**
P. Low temperature	I. $\frac{a}{V^2}$
Q. Mean speed	II. Maxwellian distribution
R. Internal pressure	III. b
S. Excluded volume	IV. Adiabatic demagnetisation
	V. $\left(a+\frac{b}{V^2}\right)$

(a)	(b)	(c)	(d)
P–IV	P–V	P–I	P–IV
Q–II	Q–IV	Q–II	Q–V
R–I	R–II	R–III	R–III
S–III	S–III	S–IV	S–II

Answers

1. (a)	**2.** (b)	**3.** (b)	**4.** (b)	**5.** (b)	**6.** (c)	**7.** (c)	**8.** (c)
9. (b)	**10.** (d)	**11.** (c)	**12.** (c)	**13.** (a)	**14.** (c)	**15.** (a)	**16.** (d)
17. (a)	**18.** (a)	**19.** (b)	**20.** (c)	**21.** (a, b, c)	**22.** (a, b, c)	**23.** (a, b, c, d)	**24.** (a, b)
25. (a, b, c)	**26.** (a, b, c, d)	**27.** (a, b, c)	**28.** (b, d)	**29.** (a, b)	**30.** (c, d)	**31.** (b)	**32.** (a)
33. (b)	**34.** (b)	**35.** (b)	**36.** (a)	**37.** (a)	**38.** (a)	**39.** (b)	**40.** (d)
41. (c)	**42.** (c)	**43.** (a)	**44.** (d)	**45.** (a)	**46.** (a)	**47.** (b)	**48.** (a)
49. (a)	**50.** (c)	**51.** (a)	**52.** (b)	**53.** (d)	**54.** (a)	**55.** (b)	**56.** (a)
57. (a)	**58.** (b)	**59.** (A–d), (B–a)					

MODULE–2

IIT Entrance Test Paper

Following questions have single correct option:

1. The frequency of de Broglie wave associated with a microscopic particle of mass 10^{-27} gm is 2.5×10^4 MHz, then the velocity of the particle will be:
(a) 4.08 km/s (b) 5.81 km/s
(c) 17.32 km/s (d) 1.22 km/s

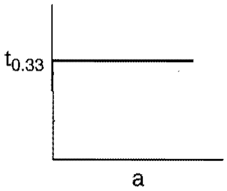
2. The total number of nodes for 4*d*-orbital will be:
(a) 2 (b) 3 (c) 0 (d) 1

3. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ + heat. The activation energy for the forward as well as backward reaction is decreased by 100 J, then the equilibrium amount of NH_3 will:
(a) increase (b) decrease
(c) remain constant (d) cannot be predicted

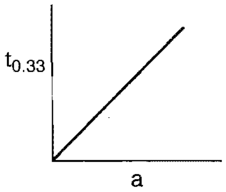
4. During *K*-electron capture mainly:
(a) γ-rays are emitted (b) β-particles are emitted
(c) positron are emitted (d) X-rays are emitted

5. The magnetic moment of an iron compound is 5.918 BM, then the oxidation state of iron in this compound will be:
(a) 0 (b) 1 (c) 2 (d) 3

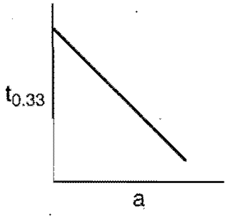
6. Which of the following graphs represents a first order reaction?



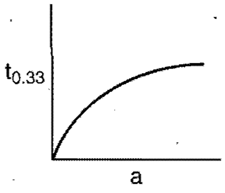
(a)



(b)



(c)



(d)

7. For the reaction,

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l); \quad \Delta U = -2810 \text{ kJ/mol}$$

ΔH in kJ/mol is:
(a) 845 (b) −890 (c) −2810 (d) −2864

8. The standard emf of the cell, set-up from the reaction,

$$2Cu^+(aq.) \rightleftharpoons Cu(s) + Cu^{2+}(aq.)$$

is 0.36 V at 298 K. The standard free energy in kJ/mol for this reaction is:
(a) − 34.73 (b) − 69.46 (c) − 3473 (d) − 6946

9. When the reaction is first order in *A* and zero order in *B*, rate constant is:
(a) $\left\{-\frac{1}{t[A]_0}\right\} \ln \frac{[A]_0}{[A]_t}$ (b) $\left(-\frac{1}{t}\right) \ln \frac{[A]_0}{[A]_t}$
(c) $\frac{1}{t} \ln \frac{[A]_0}{[A]_t}$ (d) $\frac{1}{t[A]_0} \ln \frac{[A]_0}{[A]_t}$

10. A hypothetical reaction, $2X + Y_2 \longrightarrow 2XY$ follows the mechanism:

$$X + X \rightleftharpoons X_2 \quad \text{(fast)}$$
$$X_2 + Y_2 \rightleftharpoons 2XY \quad \text{(slow)}$$

then the order of reaction is:
(a) 1 (b) 2 (c) 3 (d) undefined

11. The inversion of cane sugar in aqueous acidic medium is a reaction of:
(a) zero order (b) first order
(c) second order (d) third order

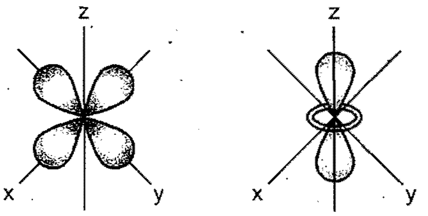
12. Which of the following belongs to, *e.g.*, (double grade) orbitals?
(a) d_{xy}, d_{yz} (b) d_{yz}, d_{zx}
(c) d_{xy}, d_{zx} (d) $d_{x^2-y^2}, d_{z^2}$

13. Which among the following is correct about the energy sequence (in case of H-atom)?
(a) $3s < 3p < 3d$ (b) $3s = 3p = 3d$
(c) $3s > 3p > 3d$ (d) $3s > 3p < 3d$

14. If the equivalent weight of an element is 32, then the percentage of oxygen in its oxide is:
(a) 16 (b) 40 (c) 32 (d) 20

15. Which of the following statements are true?
(a) For gases, in general, viscosity increases with increase in temperature.
(b) For liquids, viscosity varies directly with pressure.
(c) For gases, viscosity is independent of pressure.
(d) All of the above are true.
(e) None of the above

16. The following figures show the angular probability distribution of:



(a) d_{xy} and d_{yz} orbitals (b) $d_{x^2-y^2}$ and d_{z^2} orbitals
(c) d_{xy} and d_{xz} orbitals (d) none of these

17. The equation $E = h\nu$ indicates that:
(a) photons have both particle and wave nature
(b) photons are waves
(c) photons are stream of particles
(d) no such inference can be drawn from the given equation

18. In which of the following conditions, the density of N_2 is maximum?
(a) STP (b) 273 K and 2 atm
(c) 546 K and 1 atm (d) 546 K and 2 atm

19. A sample of natural gas contains 85% CH_4 and 15% C_2H_6. What is the molecular mass of the mixture?
(a) 16.6 (b) 26.6 (c) 30.6 (d) 20.6

20. Match the List-I and List-II:

	List-I	List-II
(A)	The limits of pH values of buffer solution.	(i) 5×10^{-12}
(B)	The $[H_3O]^+$ concentration in 0.001 M $Ba(OH)_2$ solution.	(ii) Equal
(C)	The buffer capacity of a solution is maximum when conc. of salt to that acid is:	(iii) 1st order reaction
(D)	Hydrolysis of ethyl acetate in acidic solution.	(iv) $pK_a \pm 1$

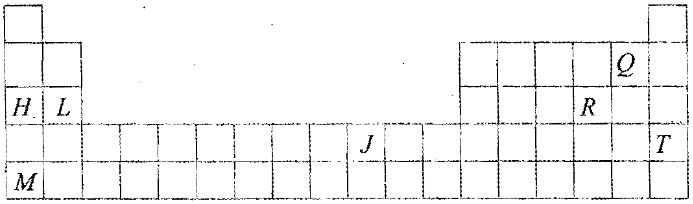
Codes:	(A)	(B)	(C)	(D)
(a)	iv	ii	i	iii
(b)	iv	i	iii	ii
(c)	i	iv	ii	iii
(d)	iv	i	ii	iii

21. Match the List-I and List-II:

	List-I	List-II
(A)	Rate constant has the same unit as the rate of reaction.	(i) One
(B)	Reactions having apparent molecularity more than three.	(ii) Zero order reaction
(C)	Reactions having molecularity two but order of reaction is one.	(iii) Complex reaction
(D)	For a reaction, $A \rightarrow B$, the rate of reaction doubles as the concentration of A is doubled.	(iv) Pseudo unimolecular reaction

Codes:	(A)	(B)	(C)	(D)
(a)	ii	iv	iii	i
(b)	ii	iii	iv	i
(c)	iii	ii	iv	i
(d)	ii	iv	i	iii

The diagram below shows part of the skeleton of the periodic table in which elements are indicated by letters which are not their usual symbols.



Select whether the following statements are True or False:
True (*a*) *False* (*b*)

22. The greatest ionic character of compounds formed by reaction of pairs of the listed elements would be exhibited by the compound with the formula, M_2Q.

23. The J^{2+} ion is coloured and has an electronic configuration of $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^7$.

24. The carbonate of compound H is insoluble in water.

25. Element R is a gas at room temperature.

26. Element T is an inert gas with an electronic configuration $1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6$.

20 cm^3 of a gaseous element X reacts with excess of an element Y to form 40 cm^3 of a gaseous compound of X and Y. All volumes are measured under the same conditions of temperature and pressure.

Select whether the following statements are True or False.
True (*a*) *False* (*b*)

27. Molecule of X contains at least two atoms of X.

28. The formula of the compound formed is XY.

29. Molecules of X cannot consist of more than two atoms.

30. X is less dense than the compound of X and Y.

31. Y is less dense than the compound of X and Y.

Assertion-Reason Type Questions:

In the questions 32 to 36, statements are given for ***Assertion(A)*** *and* ***Reason (R)****. Choose the correct answers from the codes given below:*

(*a*) *Both (A) and (R) are correct and (R) is the correct explanation of (A).*
(*b*) *Both (A) and (R) are correct but (R) is not the correct explanation of (A).*
(*c*) *(R) is correct but (A) is wrong.*
(*d*) *(A) is correct but (R) is wrong.*

32. (A) In hydrogen spectrum (6569 Å) line is observed in Balmar series.
(R) Balmar lines are found in ultraviolet region.

33. (A) All Arrhenius acids are also Bronsted acids.
(R) All Bronsted bases are also Lewis bases.

34. (A) All p-orbitals are directional.
(R) p-orbitals are oriented along axes.

35. (A) 0.1 M NaCl + 0.05 M HCl solution on mixing in equal volume forms a buffer solution.
(R) The solution is a mixture of salt and acid thus act as a buffer.

36. (A) Number of revolution per second by an electron is same in all shells.
(R) Orbital frequency $= \dfrac{v}{2\pi r}$.

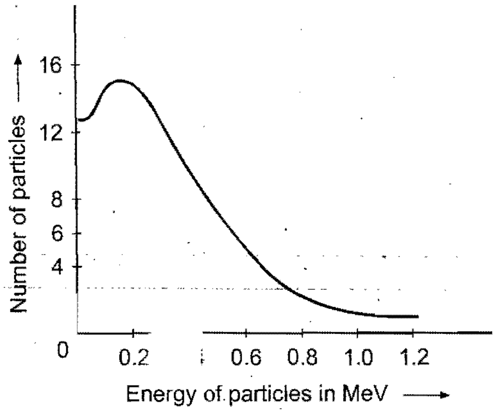
Questions with more than one correct options:

37. The substance(s) which can act as oxidising as well as reducing agent is/are:
(a) H_2O_2 (b) O_3
(c) $NH_2 - NH_2$ (d) HNO_3

38. Which of the following statement(s) is/are correct?
(a) The electronic configuration of Cr is [Ar] $3d^5, 4s^1$.
(b) The magnetic quantum number may have a negative value.
(c) In silver, 23 electrons have clockwise spin and 24 electrons have anticlockwise spin.
(d) The oxidation number of N in N_3H is –3.

39. Loss of a β-particle is equivalent to:
(a) increase in number of protons by one
(b) decrease in number of neutrons by one
(c) change in atomic mass by one unit
(d) none of the above

40. Following curve shows the energy spectrum of β-particles in the figure:



The curve indicates:
(a) β-rays spectrum is continuous
(b) different β-particles (emitted) have different energies
(c) the energy spectrum of β-particles of all the elements is the same
(d) no β-particle has energy more than 1 MeV

41. Maximum velocity of a liquid up to which its flow is stream line is called critical velocity. The critical velocity of a liquid depends upon:
(a) coefficient of viscosity (b) radius of the tube
(c) density of the liquid (d) mass of the tube

42. When a liquid solidifies, generally, there is:
(a) decrease in enthalpy (b) decrease in entropy
(c) increase in enthalpy (d) increase in entropy

43. Which of the following set(s) of chemical compounds is/are used as semipermeable membrane?
(a) calcium phosphate, cellulose nitrate
(b) calcium phosphate, copper ferrocyanide
(c) cellulose nitrate, copper ferrocyanide
(d) copper ferrocyanide, copper sulphate

44. For the depression in freezing point. The correct statement(s) is/are:
(a) The vapour pressure of pure solvent is more than that of solution.
(b) The vapour pressure of pure solvent is less than that of solution.
(c) Only solute molecules solidify at the freezing point.
(d) Only solvent molecules solidify at the freezing point.

45. For exact determination of molecular mass:
(a) solute must be volatile
(b) solution must be very dilute
(c) solution must be of similar components
(d) solute must not be dissociated or associated

46. Match the Column-I with Column-II:

	Column-I		Column-II
(a)	de Broglie equation	(p)	$\lambda = \frac{h}{p}$
(b)	Lyman series	(q)	$\lambda = \frac{h}{\sqrt{2Em}}$
(c)	Wavelength associated with particle of mass *m*	(r)	Transition from higher shell to *K*-shell
(d)	6.6×10^{-19} J energy per photon	(s)	Ultraviolet radiation

(a)	ⓟ	ⓠ	ⓡ	ⓢ
(b)	ⓟ	ⓠ	ⓡ	ⓢ
(c)	ⓟ	ⓠ	ⓡ	ⓢ
(d)	ⓟ	ⓠ	ⓡ	ⓢ

47. Match the Column-I with Column-II:

	Column-I		Column-II
(a)	Mn	(p)	Radius ratio (0.732–1)
(b)	Body-centred cubic	(q)	Hexagonal close-packed
(c)	ABC ABC ABC	(r)	Packing (0.68)
(d)	Be	(s)	Number of constituent units in one unit cell (1)

(a)	ⓟ	ⓠ	ⓡ	ⓢ
(b)	ⓟ	ⓠ	ⓡ	ⓢ
(c)	ⓟ	ⓠ	ⓡ	ⓢ
(d)	ⓟ	ⓠ	ⓡ	ⓢ

48. 75.2 g of C_6H_5COOH is dissolved in a kg of benzene to lower its freezing point by 7 K. K_f for benzene is 14 K kg mol^{-1}. Calculate the percentage association when it forms a dimer.

●	●	⓪	⓪
①	①	①	①
②	②	②	②
③	③	●	③
④	④	④	④
⑤	⑤	⑤	⑤
⑥	⑥	⑥	⑥
⑦	⑦	⑦	⑦
⑧	⑧	⑧	⑧
⑨	⑨	⑨	⑨

[**Hint:** $\Delta T = i \times K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$$7 = i \times 14 \times \frac{75.2 \times 1000}{122 \times 1000}$$

$$i = 0.81$$

$$\alpha = \frac{1-i}{1-1/n} = \frac{1-0.81}{1-1/2} = 0.38$$

Percentage association = $\alpha \times 100 = 38$]

49. A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 L to 12 L. During this process, it absorbs 600 J heat from its surroundings. Calculate the decrease in the internal energy of the system in joule.

●	⓪	⓪	⓪
①	①	●	①
②	②	②	②
③	③	③	●
④	●	④	④
⑤	⑤	⑤	⑤
⑥	⑥	⑥	⑥
⑦	⑦	⑦	⑦
⑧	⑧	⑧	⑧
⑨	⑨	⑨	⑨

[**Hint:** $q = 600\,\text{J}, \Delta V = 12 - 2 = 10\,\text{L}, P = 1\,\text{atm}$

$$w = -P\Delta V = -1 \times 10 \times 101.3 = -1013\,\text{J}$$

$$\Delta U = q + w = 600 - 1013 = -413\,\text{J}]$$

Predict whether the following statements are True/False:

50. For mixing of two ideal gases at 25°C and 1 atm, $\Delta G_{\text{mix}} = 0$.
(a) True (b) False

51. For mixing of two ideal gases at 25°C and 1 atm, $\Delta S_{\text{mix}} = 0$.
(a) True (b) False

52. Isobaric thermal coefficient of an ideal gas is 'R'.
(a) True (b) False

53. The criterion for the spontaneity of a process is $\Delta S_{\text{system}} > 0$.
(a) True (b) False

54. The radioactive element undergoes complete decay in twice of half life.
(a) True (b) False

Answers

1. (a) **2.** (b) **3.** (c) **4.** (d) **5.** (d) **6.** (b) **7.** (c) **8.** (a)
9. (c) **10.** (c) **11.** (b) **12.** (d) **13.** (b) **14.** (c) **15.** (a) **16.** (b)
17. (d) **18.** (b) **19.** (a) **20.** (d) **21.** (b) **22.** (b) **23.** (b) **24.** (b)
25. (b) **26.** (a) **27.** (b) **28.** (a) **29.** (b) **30.** (b) **31.** (b) **32.** (d)
33. (d) **34.** (a) **35.** (b) **36.** (c) **37.** (a, b, c) **38.** (a, b, c) **39.** (a, b) **40.** (a, b)
41. (a, b, c) **42.** (a, b) **43.** (a, b, c) **44.** (a, d) **45.** (b, d) **46.** (a-p,q) (b-r,s) (c-p,q) (d-r,s)
47. (a-s, (b-p,r) (c-q) (d-q) **50.** (a) **51.** (b) **52.** (a) **53.** (b) **54.** (b)

IIT ENTRANCE TEST PAPERS

TEST SERIES I

SECTION-I

REASONING APTITUDE (For IIT & AIIMS Aspirants)

The questions given below (1 to 10) consist of an **'Assertion'** (A) in column (1) and **'Reason'** (R) in column (2). Use the following keys to choose the appropriate answer:

(a) If both assertion and reason are correct and reason is the correct explanation of the assertion.
(b) If both assertion and reason are correct but reason is not correct explanation of the assertion.
(c) If assertion is correct but reason is incorrect.
(d) If assertion is incorrect but reason is correct.

Assertion (Column 1)	**Reason (Column 2)**
1. Noble gases can be liquefied.	Attractive forces can exist between non-polar molecules.
2. Boiling point of a solvent increases when a non-volatile solute is dissolved in it.	The boiling point of a liquid is the temperature at which vapour pressure of a liquid equals the vapour pressure of the atmosphere.
3. A mixture of sodium acetate and sodium propionate forms a buffer solution.	A buffer solution reacts with small quantities of hydrogen or hydroxyl ions and keeps the pH almost same.
4. The pressure of a fixed amount of an ideal gas is proportional to its temperature at constant volume.	Ideal gas molecules neither attract nor repel each other.
5. In a radioactive disintegration, an electron is emitted by the nucleus.	Electrons are always present inside the nucleus.
6. The ratio C_P/C_V for a diatomic gas is more than that for a monoatomic gas.	The molecules of a monoatomic gas have less degrees of freedom than those of a diatomic gas.
7. Many endothermic reactions that are not spontaneous at room temperature, become spontaneous at high temperature.	Entropy of the system increases with increase in temperature.
8. No two electrons in an atom can have the same values of four quantum numbers.	No two electrons in an atom can be simultaneously in the same shell, subshell, orbitals and have same spin.
9. In radioactive disintegrations, $_2He^4$ nuclei can come out of the nucleus but lighter $_2He^3$ cannot.	Binding energy of $_2He^3$ is more than that of $_2He^4$.
10. A crystal having fcc structure is more closely packed than a crystal having bcc structure.	Packing fraction for fcc structure is double than that of bcc structure.

SECTION-II

SELECT CORRECT ALTERNATIVE AMONG THE GIVEN OPTIONS (For AIEEE & Medical Entrance Aspirants)

11. Pick out the pair in which the energy change of one is reverse of the energy change in the other:
(1) radio (2) fluorescent lamp (3) toaster (4) photoelectric cell
(a) 1 and 2 (b) 2 and 3 (c) 2 and 4 (d) 3 and 4

12. Consider the following statements about first order reaction:
(1) The rate of reaction is directly proportional to the concentration of the reactant.
(2) Its half life period is always constant.
(3) Concentration of reactant falls exponentially.
(4) It has low activation energy.
Of these statements:
(a) 1, 3 and 4 are correct (b) 1, 2 and 4 are correct
(c) 1, 2 and 3 are correct (d) 2, 3 and 4 are correct

13. Which one of the following is the correct order of energies of $3p$, $3d$, $4s$ and $4p$ orbitals as per Aufbau principle?
(a) $3p < 3d < 4s < 4p$ (b) $3p < 4s < 3d < 4p$
(c) $3d < 4s < 4p < 3p$ (d) $3d < 3p < 4p < 4s$

14. In the emission line spectra of hydrogen atom, how many lines can be accounted for by all possible electron transitions between five lowest energy levels within the atom?
(a) 4 (b) 5 (c) 10 (d) 20

15. In a closed container at 1 atm pressure, 2 mole of $SO_2(g)$ and 1 mole of $O_2(g)$ were allowed to react to form $SO_3(g)$ under the influence of a catalyst. The following reaction occurred:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

At equilibrium it was found that 50% of $SO_2(g)$ was converted to $SO_3(g)$. The partial pressure of $O_2(g)$ at equilibrium will be:
(a) 0.66 atm (b) 0.493 atm (c) 0.33 atm (d) 0.2 atm

16. The electronic configuration $1s^2, 2s^2 2p^5, 3s^1$ describes which one of the following?
(a) An excited state of fluorine atom
(b) The ground state of neon
(c) The excited state of O^{2-}
(d) The ground state of fluoride ion F^-

17. When acetone and chloroform are mixed, hydrogen bonding takes place between them; such a liquid pair will cause:
(a) positive deviation from Raoult's law
(b) negative deviation from Raoult's law
(c) no deviation from Raoult's law
(d) cannot be predicted

18. A maxima or minima obtained in the temperature. Composition curve of a mixture of two liquids indicates:
(a) that the liquids are immiscible with one another
(b) that the liquids are partially miscible at the maximum or minimum
(c) an azeotropic mixture
(d) a eutectic formation

19. The electrode reactions for charging of a lead battery are:

$$PbSO_4 + 2e \longrightarrow Pb + SO_4^{2-}$$

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e$$

The electrolyte in the battery is an aqueous solution of H_2SO_4. After this battery has been charged:

(a) the sulphuric acid will be more concentrated
(b) the sulphuric acid will be less concentrated
(c) the concentration of H_2SO_4 will be unchanged
(d) H_2SO_4 will have been completely decomposed

20. At 291 K, the molar conductivity at infinite dilution of NH_4Cl, NaOH, NaCl are 129.8, 217.4, 108.9 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. If the molar conductivity of centinormal solution of NH_4OH is 9.33 $ohm^{-1}\ cm^2\ mol^{-1}$, what is the percentage dissociation of NH_4OH at this dilution?

(a) 0.392 (b) 39.2 (c) 3.92 (d) 0.039

21. Through molten $AlCl_3$, a charge equal to the charge of 1 mole N^{3-} was passed. Volume of Cl_2 evolved at anode will be:

(a) 22.4 litre (b) 67.2 litre (c) 33.6 litre (d) 11.2 litre

22. The rate constant of a reaction will be equal to pre-exponential factor when:

(a) temperature in centigrade is zero
(b) absolute temperature is zero
(c) absolute temperature is infinity
(d) no suitable answer

23. The energy levels of A, B and C of certain atoms correspond to increasing values of energy, *i.e.*,

$$E_A < E_B < E_C$$

If λ_1, λ_2 and λ_3 are wavelengths C to B, B to A and C to A respectively; which of the following relation is correct?

(a) $\lambda_3 = \lambda_1 + \lambda_2$ (b) $\lambda_3 = \lambda_1\lambda_2/(\lambda_1 + \lambda_2)$
(c) $\lambda_1 + \lambda_2 + \lambda_3 = 0$ (d) $\lambda_3^2 = \lambda_1^2 + \lambda_2^2$

24. A stationary hydrogen atom emits a photon corresponding to the first line of Lyman series. What velocity does the atom acquire?

(a) 3.25 m/sec (b) 2.35 m/sec
(c) 3.52 m/sec (d) 5.23 m/sec

25. Which of the following transitions is not allowed in the normal electronic spectrum of an atom?

(a) $2p \to 1s$ (b) $3d \to 2p$ (c) $5p \to 3s$ (d) $2s \to 1s$

26. How many spectral lines can be observed when an excited electron returns from 7th to 2nd shell?

(a) 10 (b) 15 (c) 20 (d) 14

27. Two lines of Balmer series of hydrogen are 486.1 and 410.2 nm. If the difference of wave numbers of these lines corresponds to the wave number of a line in the series, to which of following series does the line belong?

(a) Brackett (b) Paschen (c) Pfund (d) Humphrey

28. For a third order reaction, half life is given as:

(a) $t_{1/2} \propto \frac{1}{a}$ (b) $t_{1/2} \propto \frac{1}{a^2}$ (c) $t_{1/2} \propto a^2$ (d) $t_{1/2} \propto a$

29. What specific name can be given to the following sequence of steps?

$$Hg + h\nu \longrightarrow Hg^*$$

$$Hg^* + H_2 \longrightarrow Hg + H_2^*$$

$$H_2^* \longrightarrow 2H$$

(a) Photosensitization (b) Photosorption
(c) Phosphorescence (d) Chemiluminescence

30. If the tetrahedral sites in a ccp array of negative ions (B) were half filled with cations (A), the empirical formula of the compound will be:

(a) A_2B_3 (b) A_2B (c) AB_2 (d) AB

31. An electron in the p-orbital has an orbital angular momentum of:

(a) $\sqrt{2}\,h$ (b) $\frac{\sqrt{2}h}{2\pi}$ (c) $\frac{h}{\pi}$ (d) $\frac{h}{2\pi}$

32. An electron of velocity 'v' is found to have a certain value of de Broglie wavelength. The velocity to be possessed by a neutron to have the same de Broglie wavelength is:

(a) $1840v$ (b) $v/1840$ (c) v (d) $1840/v$

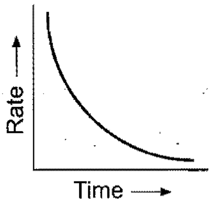
33. van't Hoff factor for a dilute aqueous solution of HCN is 1.00002. The percentage degree of dissociation of the acid is:

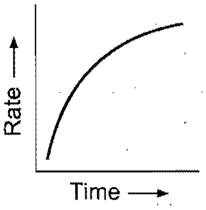
(a) 2×10^{-5} (b) 1×10^{-5} (c) 2×10^{-3} (d) 1×10^{-3}

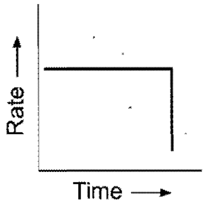
34. The average life of a radioactive element is 10 minute. In 10 minute what percentage of a radioactive element will decay?

(a) 50% (b) 63.21% (c) 75% (d) 100%

35. Which of the following corresponds to zero order reaction?

(a)


(b)


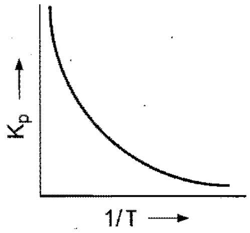
(c)


(d) None of these

36. The equilibrium constant K_p for the reaction,

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

is found to vary with temperature in the diagram as shown:



(a) The reaction is exothermic in forward reaction
(b) The equilibrium mixture contains a high proportion of Z at higher pressure
(c) The equilibrium mixture contains a high proportion of Z at high temperature
(d) The equilibrium is unaffected by addition of inert gas

37. Helium was discovered in sun's atmosphere by analysing:

(a) Mayer hoff bands (b) Fraunhofer lines
(c) spectrum (d) spectrometer

38. For an ideal solution of miscible components:

$$\Delta S_{mix} = -R\ \Sigma\ n_2 \log x_1$$

(a) ΔS_{mix} is a negative quantity
(b) ΔS_{mix} is a positive quantity
(c) ΔS_{mix} is zero
(d) ΔS_{mix} is sometimes negative and sometimes positive

39. Specific conductance of a conductivity solution:

(a) increases with dilution
(b) decreases with dilution

(c) is independent of concentration
(d) depends upon the cell constant

40. In the oxide of a compound 'A', oxide ions are arranged in hexagonal close packing and A^{3+} ions occupy two-thirds of the octahedral voids. What is the formula of corundum?
(a) AO (b) A_2O (c) A_2O_3 (d) AO_2

41. Spinel structure is shown by:
(a) $MgAl_2O_4$ (b) $ZnAl_2O_4$ (c) $MgFe_2O_4$ (d) all of these

42. Which of the following atomic orbitals does not have the four lobes lying symmetrically between the axial directions?
(a) $3d_{xy}$ (b) $3d_{xz}$ (c) $3d_{yz}$ (d) $3d_{x^2-y^2}$

43. The degree of dissociation (α) of a weak electrolyte A_xB_y is related to van't Hoff factor 'i' by expression:
(a) $\alpha = \dfrac{i-1}{x+y-1}$ (b) $\alpha = \dfrac{i-1}{x+y+1}$
(c) $\alpha = \dfrac{x+y-1}{i-1}$ (d) $\alpha = \dfrac{x+y+1}{i-1}$

44. The solubility of mercurous chloride in water will be given as:
(a) $S = K_{sp}$ (b) $S = K_{sp}/4$
(c) $S = (K_{sp}/4)^{1/2}$ (d) $S = (K_{sp}/4)^{1/3}$

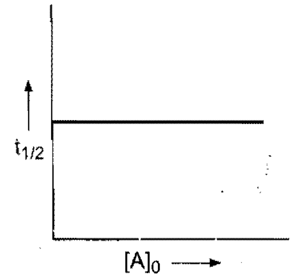
45. The activation energies of two reactions are E_{a_1} and E_{a_2}. If the temperature of the reacting systems is increased from T_1 to T_2, predict which of the following alternatives is correct?
(a) $\dfrac{k_1'}{k_1} = \dfrac{k_2'}{k_2}$ (b) $\dfrac{k_1'}{k_1} > \dfrac{k_2'}{k_2}$
(c) $\dfrac{k_1'}{k_1} < \dfrac{k_2'}{k_2}$ (d) $\dfrac{k_1'}{k_1} < 2\dfrac{k_2'}{k_2}$
where, k_1' and k_2' are rate constants at higher temperature.

46. In a cubic unit cell, seven of the eight corners are occupied by atoms 'A' and centres of faces are occupied by atoms 'B'. The general formula of the compound is:
(a) A_7B_6 (b) A_7B_{12} (c) A_7B_{24} (d) $A_{24}B_7$

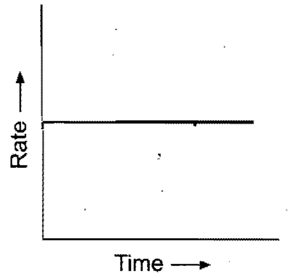
47. The rate law of a reaction of 'A' and 'B',

$$\text{rate} = k[A]^n[B]^m$$

may be determined by plotting $t_{1/2}$ *versus* $[A]_0$ (plot 1) and rate *versus* time for 'B' (plot 2).



(plot 1)



(plot 2)

The rate law superscripts, 'n' and 'm' are:
(a) 0, 0 (b) 0, 1 (c) 1, 0 (d) 1, 1

48. For 1*s*-orbital of hydrogen, the radial electron probability has a maximum value at:
(a) 0.1 Å (b) 0.40 Å (c) 0.53 Å (d) 2.1 Å

49. Which of the following expressions correctly represents the relationship between average kinetic energy of CO and N_2 molecules at the same temperature?
(a) $E_{CO} > E_{N_2}$
(b) $E_{CO} < E_{N_2}$
(c) $E_{CO} = E_{N_2}$
(d) Cannot be predicted unless volumes of the gases are given

50. On the basis of Hardy-Schulze rule, which of the following sequences represents the coagulating power of cations?
(a) $Ba^{2+} > Al^{3+} > Na^+$ (b) $Ba^{2+} > Na^+ > Al^{3+}$
(c) $Al^{3+} > Na^+ > Ba^{2+}$ (d) $Al^{3+} > Ba^{2+} > Na^+$

51. Adiabatic expansion of an ideal gas is accompanied by:
(a) increase in temperature
(b) decrease in ΔS
(c) decrease in ΔE
(d) no change in any one of the above properties

52. For a cyclic process, which of the following is not true?
(a) $W = 0$ (b) $\Delta E = 0$ (c) $\Delta H = 0$ (d) $\Delta G = 0$

53. Radius of nucleus is related to the mass number 'A' by:
(a) $R = R_0A^{1/2}$ (b) $R = R_0A$
(c) $R = R_0A^2$ (d) $R = R_0A^{1/3}$

54. A catalyst:
(a) increases the average kinetic energy of molecules
(b) increases the activation energy
(c) alters the reaction mechanism
(d) increases the frequency of collisions of reacting species

55. A chemist wishes to prepare a buffer solution of pH = 3.85 that efficiently resists changes in pH yet contains only small concentration of the buffering agents. Which one of the following weak acids together with its sodium salt would be best to use?
(a) *m*-chlorobenzoic acid ($pK_a = 3.98$)
(b) *p*-chlorocinnamic acid ($pK_a = 4.41$)
(c) 2,5-hydroxybenzoic acid ($pK_a = 2.97$)
(d) Aceto-acetic acid ($pK_a = 3.58$)

56. For coordination number 4, the geometry that is not possible is:
(a) trigonal planar (b) tetrahedral
(c) irregular tetrahedral (d) trigonal pyramidal

57. The rate constant, the activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3 \times 10^{-4}\ sec^{-1}$, 104.4 kJ mol^{-1} and $6 \times 10^{14}\ sec^{-1}$ respectively. The value of rate constant as $T \to \infty$ is:
(a) $2 \times 10^{18}\ s^{-1}$ (b) $6 \times 10^{14}\ s^{-1}$
(c) infinity (d) $3.6 \times 10^{30}\ s^{-1}$

58. Emission of one 'α' and two 'β' particles successively from an element forms:
(a) isotope of parent element (b) isobar of parent element
(c) isotone of parent element (d) isomer of parent element

59. Fraction of the total volume occupied by atoms in a simple cube is:
(a) $\dfrac{\pi}{2}$ (b) $\dfrac{\sqrt{3}\pi}{8}$ (c) $\dfrac{\sqrt{2}\pi}{6}$ (d) $\dfrac{\pi}{6}$

60. Which of the following statements is wrong?
(a) Crystalline solids are optically anisotropic
(b) Glass is amorphous solid
(c) There are 14 Bravais lattices
(d) There are only 10 crystal symmetries

61. Which of the following pairs is correctly matched?

	Experimental observation	**Phenomenon**
(a)	X-ray spectra	Charge on the nucleus
(b)	α-particle scattering	Quantized electron orbit
(c)	Emission spectra	Quantization of energy
(d)	The photoelectric effect	The nuclear atom

62. Arrangement of the following group of orbitals in which they fill with electrons:

$$(5f, 6p, 4p, 6s, 4d, 4f)$$

(a) $4p, 4d, 6s, 4f, 6p, 5f$ (b) $6s, 4d, 4f, 5f, 4p, 6p$
(c) $6s, 4p, 4d, 4f, 5f, 6p$ (d) $4d, 4p, 4f, 5f, 6s, 6p$

63. π° meson is exchanged between:
(a) proton and neutron
(b) proton and proton
(c) neutron and neutron
(d) may be between two protons or two neutrons

64. If nucleons in an excited state fall to a lower energy level, energy is emitted as:
(a) α-rays (b) β-rays (c) γ-rays (d) X-rays

65. Minimum amount of energy required to remove a proton is approximately:
(a) 2 MeV (b) 4 MeV (c) 6 MeV (d) 8 MeV

66. Mark the incorrect statement:
(a) Semiconductors are basically insulator
(b) In metal crystal conduction occurs because molecular orbitals extend over the whole crystal and there is no energy gap between filled and unfilled molecular orbital
(c) Mobile electrons account for high thermal and electrical conduction of metals
(d) When a metal is heated with a non-metal, the resulting compound is never an ionic compound

67. Given:
(i) $NH_3(g) + 3Cl_2(g) \longrightarrow NCl_3(g) + 3HCl(g)$; ΔH_1
(ii) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; ΔH_2
(iii) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; ΔH_3

Express the enthalpy of formation of $NCl_3(g)$ (ΔH_f) in terms of ΔH_1, ΔH_2 and ΔH_3:

(a) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} + \frac{3}{2}\Delta H_3$

(b) $\Delta H_f = \Delta H_1 + \frac{1}{2}\Delta H_2 - \frac{3}{2}\Delta H_3$

(c) $\Delta H_f = \Delta H_1 - \frac{1}{2}\Delta H_2 - \frac{3}{2}\Delta H_3$

(d) $\Delta H_f = \Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{3}{2}\Delta H_3$

68. A spontaneous process may be defined as:
(a) a process which is exothermic and evolves a lot of heat
(b) a process which is slow and reversible
(c) a process which takes place only in presence of a catalyst
(d) a process that occurs without any input from the surroundings

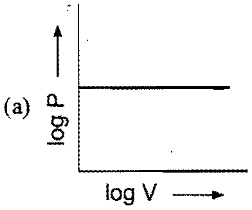
69. In the sequence of reaction,

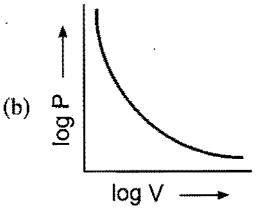
$$L \xrightarrow{k_1} M \xrightarrow{k_2} N \xrightarrow{k_3} O$$

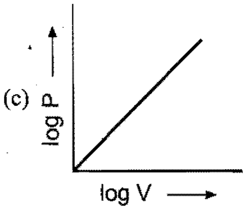
$$k_3 > k_2 > k_1$$

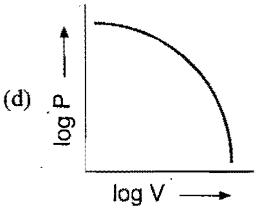
The rate determining step of the reaction is:
(a) $L \longrightarrow M$ (b) $M \longrightarrow N$ (c) $N \longrightarrow O$ (d) $L \longrightarrow O$

70. The plot of log V against log P at constant temperature for a fixed mass of gas is:

(a)


(b)


(c)


(d)


71. When mercuric iodide is added to aqueous solution of KI:
(a) freezing point is raised
(b) freezing point does not change
(c) freezing point is lowered
(d) boiling point does not change

72. The van der Waals' constant 'b' for water vapour is 0.03 litre mol^{-1}. The radius of water vapour molecule is:
(a) 1.448 cm (b) 1.448 Å (c) 1.448 pm (d) 1.448 nm

73. For a reaction $A \begin{matrix} \nearrow^{k_1} C \\ \searrow_{k_2} B \end{matrix}$, the overall rate constant is related to individual rate constants by:
(a) $k = k_1 - k_2$ (b) k_1/k_2 (c) k_1k_2 (d) $k_1 + k_2$

74. N_2O_5 decomposes to N_2O_4 and O_2 as:

$$N_2O_5 \longrightarrow N_2O_4 + \tfrac{1}{2}O_2$$

The pressure P_t at any stage is related to p_0 and 'x', the fraction of dissociation, as:

(a) p_0 (b) $(1 + \frac{1}{2}x)\,p_0$
(c) $1 - \frac{3}{2}p_0$ (d) $\frac{3}{2}xp_0$

SECTION III

MULTIPLE CHOICE QUESTIONS (For IIT, AIIMS and BHU Medical Entrance)

This section includes those questions in which two or more options may be correct. Few of them have single correct choice.

75. An ideal gas:
(a) has no intermolecular attraction
(b) molecules do not collide with each other
(c) the product of P and V is constant at a fixed temperature for definite mass
(d) can be liquefied easily

76. Extensive properties among the following is/are:
(a) refractive index (b) volume
(c) density (d) mass

77. Which of the following statements regarding equilibrium is /are true?
(a) Equilibrium constant varies with temperature
(b) Equilibrium constant varies with catalyst
(c) The reaction stops when the equilibrium is reached
(d) The equilibrium constant depends on the concentration of reactants

78. When mercuric iodide is added to aqueous KI solution:
(a) freezing point is raised (b) osmotic pressure is raised
(c) boiling point is elevated (d) vapour pressure is raised

79. The correct statements are:
(a) Smoke is carbon dispersed in air
(b) Butter is water dispersed in fat
(c) Greater is the valency of ion more will be its coagulating power
(d) More is the gold number of a lyophobic sol, more is protecting power

80. Select the correct statements among the following:
(a) Order can be zero.
(b) Order cannot have fractional value.
(c) Order is a theoretical quantity.
(d) Order is equal to molecularity for decomposition of N_2O_5 giving N_2O_4 and O_2.

81. Rate law for a chemical reaction is:

$$\text{Rate} = k[A]^{1/2}[B]^1$$

Choose the correct options among the following:
(a) Order of the reaction is 3/2.
(b) Unit of its rate constant is $\text{litre}^{1/2}\ \text{mol}^{-1/2}\ \text{sec}^{-1}$.
(c) Unit of rate is $\text{mol litre}^{-1}\ \text{sec}^{-1}$.
(d) Its molecularity is always 3.

82. Liquid benzene burns in oxygen according to:

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

If density of liquid benzene is 0.88 g/cc, what volume of O_2 at STP is needed to complete the combustion of 39 cc of liquid benzene?
(a) 11.2 litre (b) 74 litre (c) $0.074\ m^3$ (d) $37\ dm^3$

83. For the reaction;

$$N_2H_4(l) + 2H_2O_2(l) \longrightarrow N_2(g) + 4H_2O(g)$$

heats of formation of N_2H_4, H_2O_2, H_2O are 12, − 45 and −57.8 kcal mol^{-1}. Internal energy change for this reaction is/are at 298 K:
(a) $-153.2\ \text{kcal mol}^{-1}$ (b) $-641.142\ \text{kJ mol}^{-1}$
(c) $-24.8\ \text{kcal mol}^{-1}$ (d) $-309\ \text{kcal mol}^{-1}$

84. Which of the following electrolytes have same osmotic pressure as that of 0.1 *M* KCl?
(a) 0.1 *M* HCl (b) 0.1 *M* NaCl
(c) 0.1 *M* CsCl (d) None of these

85. Select the correct statements about the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\quad \Delta H = -22.4\ \text{kcal mol}^{-1}$$

(a) Increase in pressure will favour forward reaction.
(b) Addition of inert gas forms more NH_3.
(c) At low temperature, there is forward shift.
(d) Catalyst will increase the amount of NH_3.

86. Which among the following is/are correct about penetrating power?
(a) α-rays are less penetrating than β-rays.
(b) β-rays are less penetrating than γ-rays.
(c) α, β, γ rays have equal penetrating power.
(d) γ-rays are most penetrating.

87. Select the natural series among the following:
(a) $(4n + 1)$ (b) $(4n + 2)$ (c) $4n$ (d) $(4n + 3)$

88. Select the correct conclusion(s) about average life:
(a) Average life = 1/λ
(b) Average life = $1.44 \times t_{1/2}$
(c) The time in which 63.2% element decays is called average life
(d) None of the above

89. Which of the following statements are correct?
(a) 1 faraday is the charge of 1 mole electron.
(b) 1 faraday is used to deposit 1 g equivalent of a substance.
(c) 5.6 litre O_2 will be evolved at STP by 1 faraday charge.
(d) 11.2 litre Cl_2 will be evolved at STP by 1 faraday charge.

90. Select the species having zero oxidation state at the underlined elements:
(a) $(CH_3)_2\underline{S}O$ (b) $\underline{C}_{12}H_{22}O_{11}$ (c) $H_2\underline{S}_2O_3$ (d) $\underline{N}_2H_4$

91.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

'α' is the degree of dissociation of PCl_5 at equilibrium pressure '*P*'. Which among the following is the correct expression for degree of dissociation of 'α'?
(a) $\alpha = \sqrt{\dfrac{K_p}{P + K_p}}$ (b) $\alpha = \sqrt{\dfrac{P + K_p}{K_p}}$
(c) $\alpha = \sqrt{K_p P}$ (d) $\alpha = \sqrt{P/K_p}$

92. In Wilson Cloud Chamber, the track is formed by:
(a) α-rays (b) β-rays (c) γ-rays (d) all of these

93. Select the correct relation:
(a) $N_0 = N \cdot 10^{\lambda t/2.303}$ (b) $N_0 = Ne^{\lambda t}$
(c) $N_0 = N \dfrac{\lambda}{10^{2.303t}}$ (d) $N = N_0 e^{-\lambda t}$

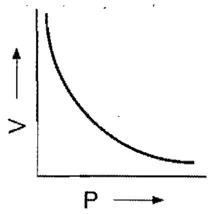
94. For the first order reaction, $t_{99\%} = x \times t_{90\%}$, the value of '*x*' will be:
(a) 10 (b) 6 (c) 3 (d) 2

95. Which among the following has same kinetic energy as O_2 gas at NTP?
(a) H_2 (b) N_2 (c) CO_2 (d) None of these

96. Which among the following is correct about γ-rays?
(a) High energy electrons
(b) Low energy electrons
(c) High energy electromagnetic waves
(d) High energy positrons

97. The RMS speed at NTP of a gas can be calculated from the expression:
(a) $\sqrt{3P/d}$ (b) $\sqrt{3PV/M}$ (c) $\sqrt{3RT/M}$ (d) $\sqrt{3d/P}$

98. The graph representing Boyle's law is(are):

(a)


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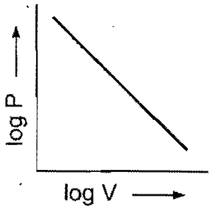

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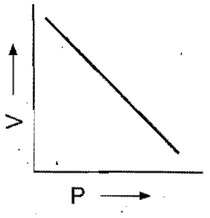
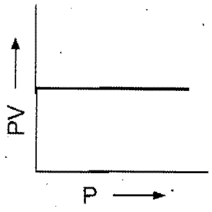


(d)


99. For diatomic molecules; the correct relation is/are:
(a) $C_P = \frac{7}{2}R$ (b) $C_V = \frac{5}{2}R$ (c) $\gamma = 1.4$ (d) $C_P = \frac{3}{2}R$

100. Which of the following aqueous solutions produce the same osmotic pressure?
(a) 0.1 M NaCl solution
(b) 0.1 M glucose solution
(c) 0.6 g urea in 100 mL solution
(d) 1.0 g of a non-electrolyte solute in 50 mL solution (Molar mass = 200)

Answers with Hints for Selected Questions

SECTION I

1. (b) **2.** (b) **3.** (b) **4.** (b) **5.** (c)

6. (d) Degree of freedom = $3n$
where, n = no. of atoms in the molecule.

7. (b) At high temperature, $T\,\Delta S > \Delta H$

$$\therefore \quad \Delta G = \Delta H - T\Delta S = -\text{ ve}$$

and process will be spontaneous.

8. (a)

9. (c) Binding energy has no role in emission of α-particle. n/p ratio determines the mode of emission.

$$4\,[{}_1\text{H}^1\,] \longrightarrow {}_2\text{He}^4 + 2\,[{}_{+1}e^0\,] + \text{Energy}$$

10. (c) Packing fraction (fcc) = 74%
Packing fraction (bcc) = 67.9%

SECTION II

11. (c)

12. (c) Rate = $k\,[A]^1$ (for first order)

$$t_{1/2} = \frac{0.693}{k} = \text{constant}$$

13. (b) Lower the value of $(n + l)$, lesser is the energy of orbital.

14. (c) No. of lines = $\dfrac{(n_2 - n_1)\,(n_2 - n_1 + 1)}{2}$

n_2 = higher shell
n_1 = lower shell

15. (d) $p_A = x_A \times p = \frac{1}{2} \times 1 = 0.5$ atm, $x_A = \frac{1}{2}$ = mole fraction of O_2.

16. (c)

17. (b) Greater is the intermolecular force on mixing, more negative will be the deviation $p < p_A^0 x_A + p_B^0 x_B$
Experimental vapour pressure will be less than calculated vapour pressure.

18. (c) Non-ideal solutions form low or high boiling azeotrope, hence, maxima and minima in the curve are obtained.

19. (a)

20. (c) $\Lambda_m^\infty \text{ NH}_4\text{OH} = \Lambda_m^\infty \text{ NH}_4\text{Cl} + \Lambda_m^\infty \text{ NaOH} - \Lambda_m^\infty \text{ NaCl}$

$$= 129.8 + 217.4 - 108.9$$

$$= 238.3 \text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{9.33}{238.3} = 0.03915$$

% Ionization = 3.92

21. (c)

22. (c) $k = Ae^{-E_a/RT}$ When $T = \infty$, $k = Ae^0 = A$

23. (b) $\dfrac{hc}{\lambda_3} = \dfrac{hc}{\lambda_1} + \dfrac{hc}{\lambda_2}$

$$\frac{1}{\lambda_3} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\lambda_3 = \frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}$$

24. (a) **25.** (d)

26. (b) $n_2 = 7, \quad n_1 = 2$

$$\text{No. of lines} = \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$

$$= \frac{(7-2)(7-2+1)}{2}$$

$$= \frac{5 \times 6}{2} = 15$$

27. (c) The difference fall in far infrared series.

28. (b) $t_{1/2} \propto \dfrac{1}{a^{n-1}}$, where, n = order of reaction.

29. (a)

30. (d) Number of 'B' atoms = n
Number of tetrahedral void = $2n$
Number of 'A' atoms = $\dfrac{2n}{2} = n$

$$A : B = n : n = 1 : 1$$

Formula = AB

31. (b) Orbital angular momentum = $\sqrt{l\,(l+1)}\,\dfrac{h}{2\pi}$

$l = 1$ for 'p' subshell.

32. (b)

33. (c) $\alpha = \dfrac{i-1}{n-1}$, $\quad n = 2$ for HCN

$$\alpha = \frac{1.00002 - 1}{2 - 1} = 0.00002$$

% dissociation = 0.002

34. (b)

35. (c) Rate of zero order reaction is constant.

36. (b) **37.** (b) (b)

39. (b) Number of ion per unit volume decreases on dilution

40. (c)

41. (d) AB_2O_4 has spinel structure.

42. (d) **43.** (a)

44. (d) $\underset{S}{\text{Hg}_2\text{Cl}_2} \longrightarrow \underset{S}{\text{Hg}_2^{2+}} + \underset{2S}{2\text{Cl}^-}$

$$K_{sp} = [\text{Hg}_2^{2+}\,][\text{Cl}^-\,]^2 = [S\,][2S]^2 = 4S^3$$

45. (b) Use the relation,

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

When $\quad E_{a_1} > E_{a_2}$

$$\frac{k_2}{k_1} > \frac{k_2'}{k_1'} \quad \text{or} \quad \frac{k_1'}{k_1} \quad \frac{k'}{k_2}$$

46. (c)

47. (c) $t_{1/2}$ of first order reaction is constant (plot 1).

$$t_{1/2} = \frac{0.693}{R}$$

Rate of zero order reaction is constant (plot 2).

$$\text{Rate} = k\,[A]^0$$

48. (c) **49.** (c) **50.** (d)

51. (c) Adiabatic expansion results into decrease in internal energy and temperature of system.

52. (d) **53.** (d)

54. (c) Catalyst forms new intermediate of either low or high activation energy.

55. (a)

56. (a) Either square planar or tetrahedral geometry is possible.

57. (b) **58.** (a) **59.** (d) **60.** (d)

61. (c) In emission spectra quantum of electromagnetic radiations are released.

62. (a) **63.** (d)

64. (c) γ-rays are evolved due to secondary effect of α, β emission.

65. (a) **66.** (d) **67.** (b) **68.** (d)

69. (a) Slowest step is $L \xrightarrow{k_1} M$; it will be rate determining.

70. (b)

71. (a) $HgI_2 + 2KI \longrightarrow K_2[HgI_4]$

Nessler's reagent $K_2[HgI_4]$ is formed which lowers the overall number of particles in the solution. Thus, on mixing the two components freezing point will be raised.

72. (b) $b = 4NV' = 4N\left(\frac{4}{3}\pi r^3\right)$

V' = volume occupied by single molecule.

73. (d)

74. (b)

$$\begin{array}{lccc} & N_2O_5(g) & \longrightarrow N_2O_4(g) + & (\tfrac{1}{2})\,O_2(g) \\ t=0 & p_0 & 0 & 0 \\ \text{At } `t\text{'} & p_0(1-x) & p_0x & p_0x/2 \end{array}$$

$$P_t = p_0(1-x) + p_0\,x + \frac{p_0\,x}{2} = p_0\left(1 + \frac{x}{2}\right)$$

SECTION III

75. (a, c) **76.** (b, d) **77.** (a, b)

78. (a, d) KI reacts with HgI_2 to form Nessler's reagent. Number of particles are lowered.

$$2KI + HgI_2 \longrightarrow K_2[HgI_4]$$

79. (a, b, c) **80.** (a, d) **81.** (a, b, c) **82.** (b, c)

83. (a, b)

84. (a, b, c) van't Hoff factor will be same for the given electrolytes.

85. (a, b, c) **86.** (a, b, d) **87.** (b, c, d) **88.** (a, b, c)

89. (a, b, c, d) **90.** (a, b) **91.** (a) **92.** (a, b)

93. (a, b, d) **94.** (d) **95.** (a, b, c) **96.** (c)

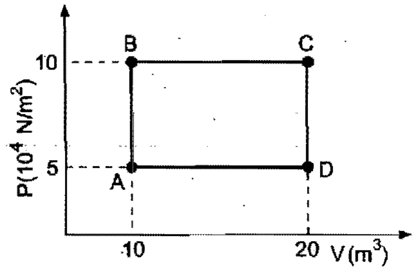
97. (a, b, c) **98.** (a, b, d) **99.** (a, b, c) **100.** (b, c, d)

IIT ENTRANCE TEST PAPERS

TEST SERIES II

(Graphical Aptitude)

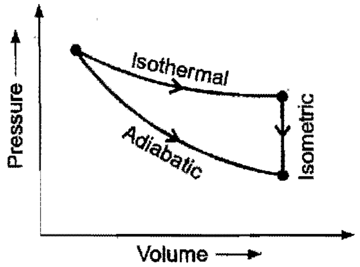
1. A sample of 2 kg of helium (assumed ideal) is taken through the process *ABC* and another sample of 2 kg of the same gas is taken through the process *ADC*. Then the temperature of the states *A* and *B* are: (Given, $R = 8.3$ joules/mol K)



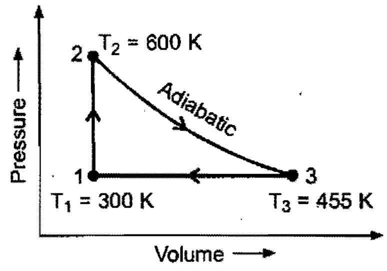
(a) $T_A = 120.5\text{ K}, T_B = 120.5\text{ K}$
(b) $T_A = 241\text{ K}, T_B = 241\text{ K}$
(c) $T_A = 120.5\text{ K}, T_B = 241\text{ K}$
(d) $T_A = 241\text{ K}, T_B = 482\text{ K}$

2. An ideal diatomic gas is caused to pass through a cycle shown on the $P-V$ diagram in figure, where $V_2 = 3.00\,V_1$. If P_1, V_1 and T_1 specify the state 1, then the temperature of the state 3 is:

(a) $(T_1/3)^{1.4}$ (b) $T_1/3^{1.4}$
(c) $T_1/3^{0.4}$ (d) cannot be determined

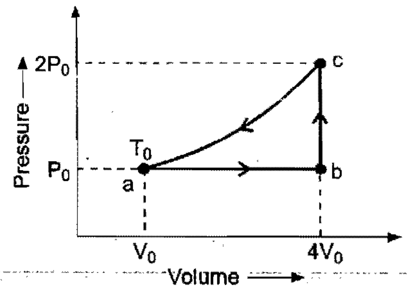


3. A heat engine carries one mole of an ideal monoatomic gas around the cycle as shown in the figure. Process 1 → 2 takes place at constant volume, process 2 → 3 is adiabatic and process 3 → 1 takes place at constant pressure. Then the amount of heat added in the process 1 → 2 is:



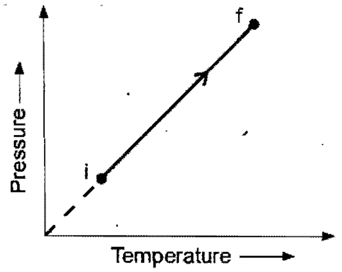
(a) 3740 J (b) −3740 J (c) 1810 J (d) 3220 J

4. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then the change in the internal energy in expanding the gas from *a* to *c* along the path *abc* is:



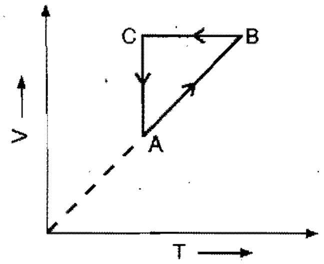
(a) $3P_0V_0$ (b) $6RT_0$ (c) $4.5RT_0$ (d) $10.5RT_0$

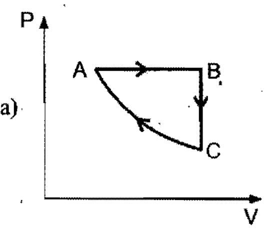
5. A thermodynamic system consists of a cylinder-piston arrangement with ideal gas in it. It goes from the state *i* to the state *f* as shown in the figure. The work done by the gas during the process:

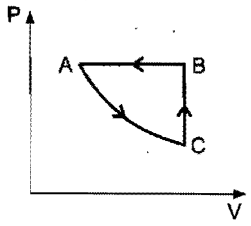


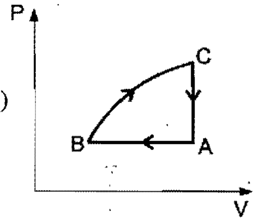
(a) is zero (b) is negative
(c) is positive (d) nothing can be predicted

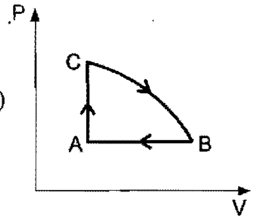
6. A cyclic process *ABCA* is shown in a $V-T$ diagram. The corresponding $P-V$ diagram is:



(a)


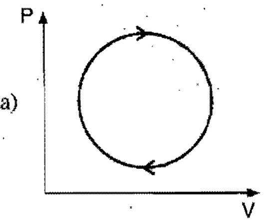
(b)


(c)


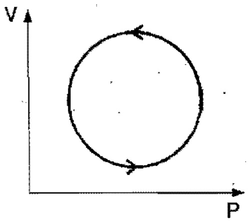
(d)


7. The following are the $P-V$ diagrams for cyclic processes for a gas. In which of these processes heat is not absorbed by the gas?

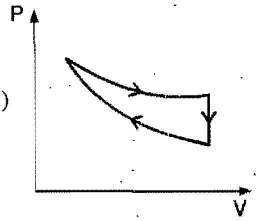
(a)



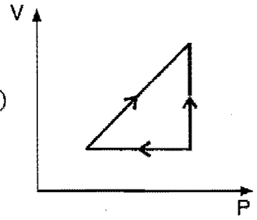
(b)



(c)

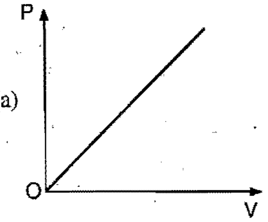


(d)

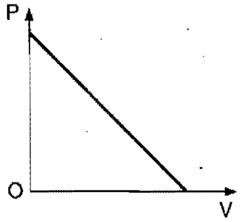


8. The graph between P and V at constant temperature should look like:

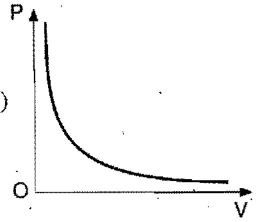
(a)



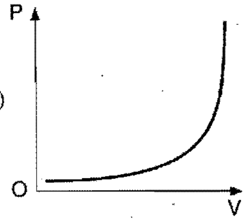
(b)



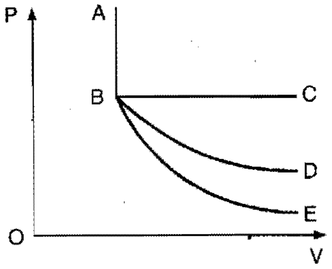
(c)



(d)

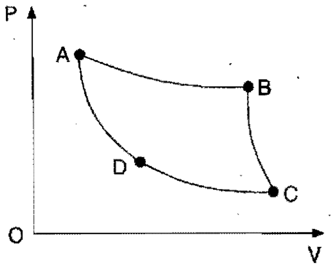


9. In $P-V$ diagram shown below:



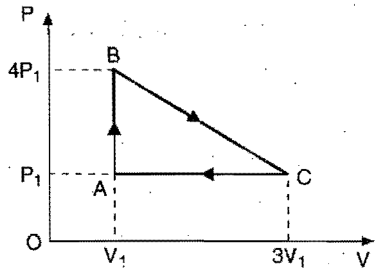
(a) AB represents adiabatic process
(b) AB represents isothermal process
(c) AB represents isobaric process
(d) AB represents isochoric process

10. The pressure-volume graph of an ideal gas cycle is shown below. The adiabatic process is described by:



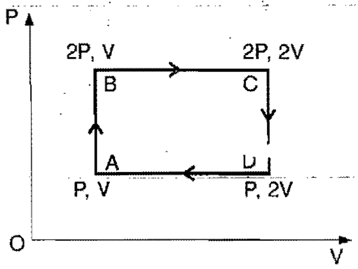
(a) AB and BC (b) AB and CD
(c) AD and BC (d) BC and CD

11. An ideal gas is taken around the cycle $ABCA$ shown in $P-V$ diagram. The net work done by the gas during the cycle is equal to: (BHU 1994)



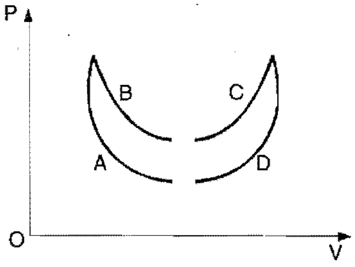
(a) $12P_1V_1$ (b) $6P_1V_1$ (c) $3P_1V_1$ (d) P_1V_1

12. An ideal monoatomic gas is taken round the cycle $ABCDA$ as shown in figure. The work done during cycle is:



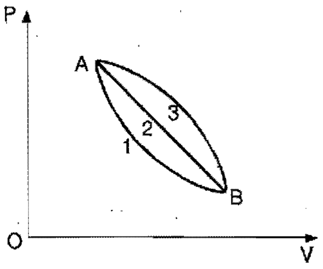
(a) PV (b) $2PV$ (c) $\frac{1}{2}PV$ (d) zero

13. Four curves A, B, C and D are drawn in figure for a given amount of gas. The curve which represents adiabatic and isothermal changes are:



(a) C and D respectively (b) D and C respectively
(c) A and B respectively (d) B and A respectively

14. A given mass of gas expands from the state A to the state B by three paths 1, 2 and 3 as shown in the figure. If W_1, W_2 and W_3 respectively be the work done by the gas along three paths then: (CPMT 1992)

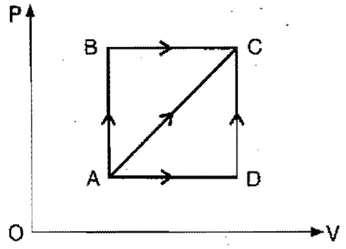


(a) $W_1 > W_2 > W_3$ (b) $W_1 < W_2 < W_3$
(c) $W_1 = W_2 = W_3$ (d) $W_1 < W_2$; $W_1 < W_3$

15. A thermodynamic process is shown in the following figure. The pressure and volumes corresponding to some points in the figure are:

$P_A = 3\times10^4\text{Pa}, V_A = 2\times10^{-3}\ \text{m}^3$;

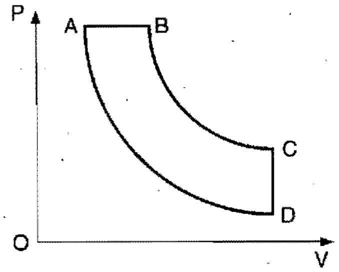
$P_B = 8\times10^4\text{Pa}, V_D = 5\times10^{-3}\ \text{m}^3$



In process AB, 600 J of heat is added to the system and in the process BC, 200 J of heat is added to the system. The change in internal energy of the system in the process AC would be: **(CBSE 1992)**

(a) 560 J (b) 800 J (c) 600 J (d) 640 J

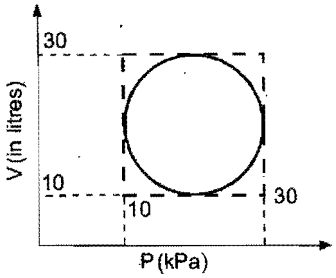
16. In the pressure-volume diagram given below, the isochoric, isothermal, isobaric and isoentropic parts respectively are:



(a) BA, AD, DC, CB (b) DC, CB, BA, AD

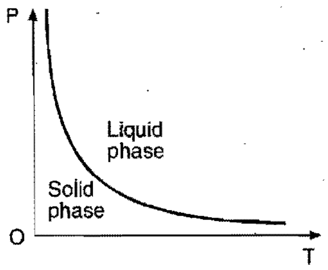
(c) AB, BC, CD, DA (d) CD, DA, AB, BC

17. Heat energy absorbed by a system in going through a cyclic process shown in figure is: **(AIIMS 1995)**



(a) $10^7\pi$ J (b) $10^4\pi$ J (c) $10^2\pi$ J (d) $10^{-3}\pi$ J

18. The pressure-temperature ($P-T$) phase diagram shown below corresponds to the: **[CEE (Haryana) 1996]**



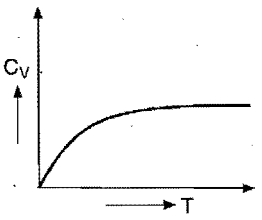
(a) Curve of fusion of solids that expand on solidification

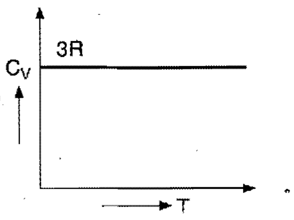
(b) Curve of sublimation of solids that directly go over to the vapour phase

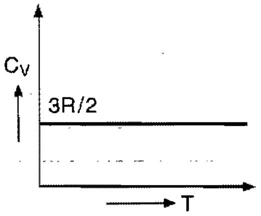
(c) Curve of fusion of solids that contract on solidification

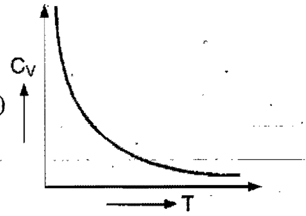
(d) Curve of fusion of solids that do not change in volume upon solidification

19. Graph of specific heat at constant volume for a monoatomic gas is:

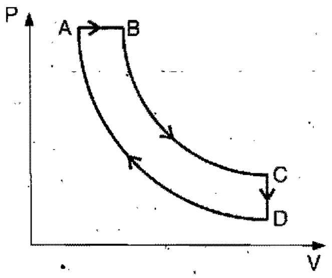
(a)


(b)


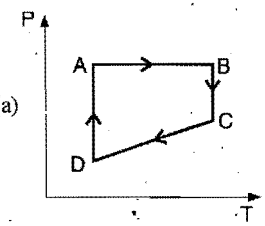
(c)


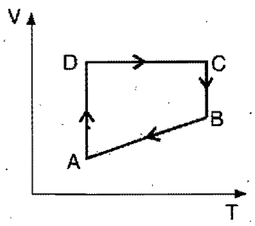
(d)


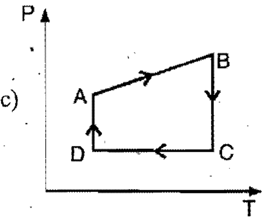
20.

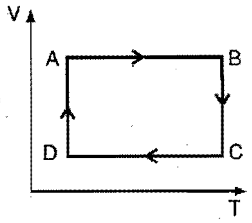


A cyclic process $ABCD$ is shown in the $P-V$ diagram. Which of the following curves represents the same process?

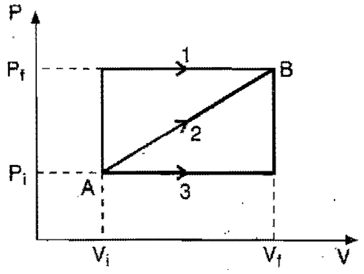
(a)


(b)


(c)


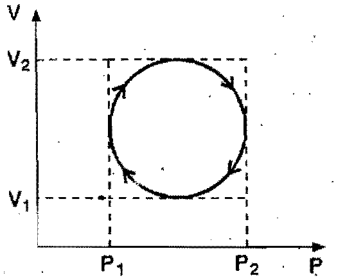
(d)


21. A system is taken from state A to B through three different paths 1, 2 and 3. The work done is maximum in: **(CPMT 1997)**



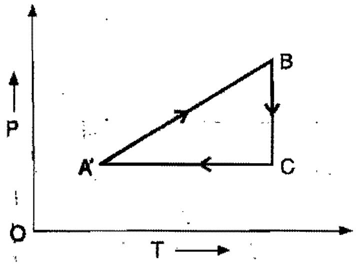
(a) process 1 (b) process 2
(c) process 3 (d) equal in all processes

22. In the cyclic process shown on $P-V$ diagram, the magnitude of the work done is:

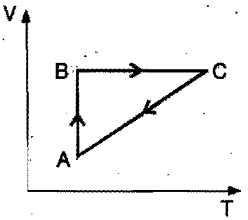


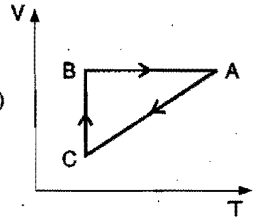
(a) $\pi\left(\frac{P_2-P_1}{2}\right)^2$ (b) $\pi\left(\frac{V_2-V_1}{2}\right)^2$
(c) $\frac{\pi}{4}(P_2-P_1)(V_2-V_1)$ (d) $\pi(P_2V_2 = P_1V_1)$

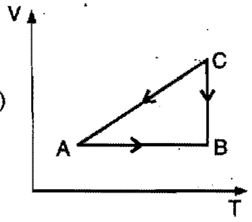
23. A cyclic process is shown in the $P-T$ diagram:

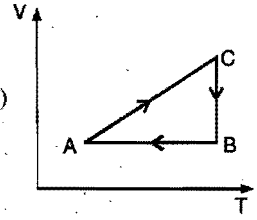


Which of the curves shows the same process on a $V-T$ diagram?

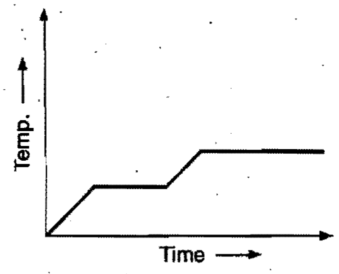
(a)


(b)


(c)


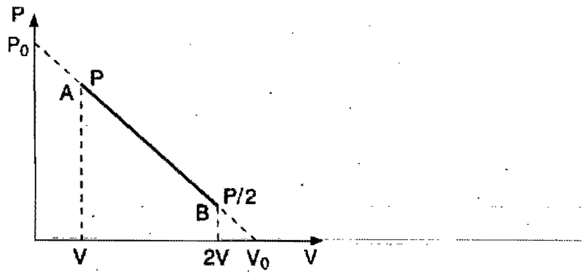
(d)


24. Heat is supplied to a certain homogeneous sample of matter, at a uniform rate. Its temperature is plotted against time, as shown. Which of the following conclusions can be drawn?



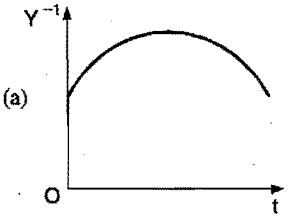
(a) Its specific heat capacity is greater in the solid state than in the liquid state.
(b) Its specific heat capacity is smaller in the solid state than in the liquid stat.
(c) Its latent heat of vaporization is greater than its latent heat of fusion.
(d) Its latent heat of vaporization is smaller than its latent heat of fusion.

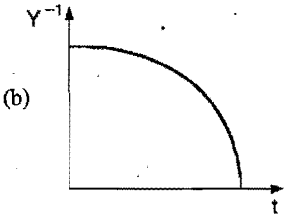
25. An ideal gas is taken from the state A (pressure P, volume V) to the state B (pressure $P/2$, volume $2V$) along a straight line path in the $P-V$ diagram. Select the wrong statement from the following:

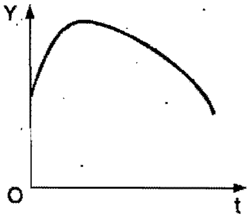


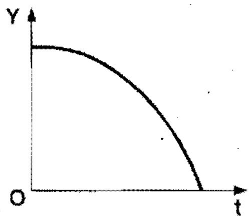
(a) The work done by the gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along the isotherm
(b) In the $T-V$ diagram, the path AB becomes a part of parabola
(c) In the $P-T$ diagram, the path AB becomes a part of hyperbola
(d) In going from A to B, the temperature T of the gas first increases to a maximum value and then decreases

26. The radioactive nucleus of an element X decays to a stable nucleus of element Y. A graph of the rate of formation of Y against time would look like:

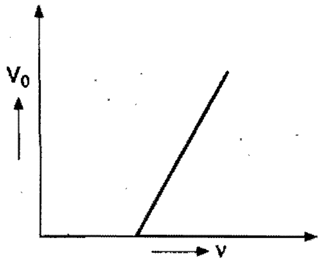
(a)


(b)


(c)


(d)


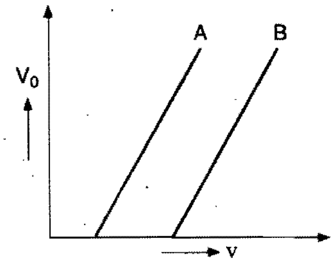
27. In photoelectric effect the slope of straight line graph between stopping potential (V_0) and frequency of incident light (ν) gives:



(a) charge on electron
(b) work function of emitter

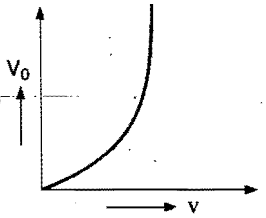
(c) Planck's constant
(d) ratio of Planck's constant to charge on electron

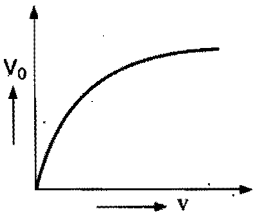
28. The sloping potential as a function of frequency of incident radiation is plotted for two different photoelectric surfaces A and B. The graphs show that the work function of A is:

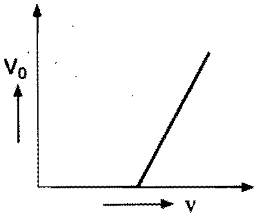


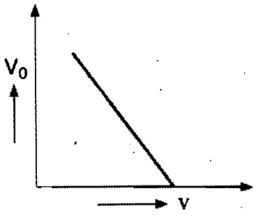
(a) greater than that of B
(b) smaller than that of B
(c) same as that of B
(d) ~~such that~~ no comparison can be done from given graphs

29. Which of the following is the graph between the frequency (ν) of the incident radiations and the stopping potential?

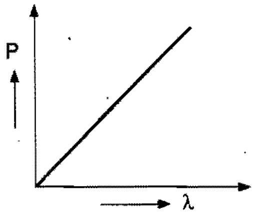
(a) 

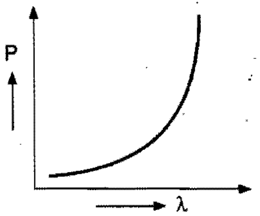
(b) 

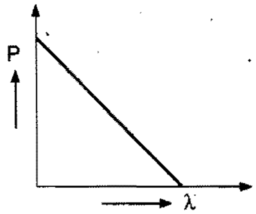
(c) 

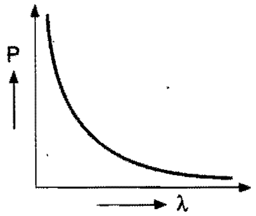
(d) 

30. Which of the following figures represents the variations of particle momentum and associated de Broglie wavelength?

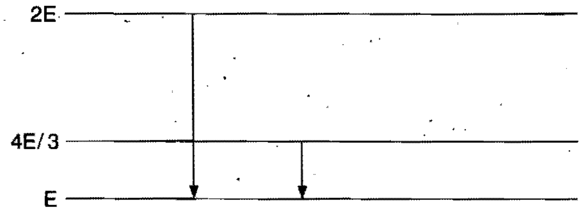
(a) 

(b) 

(c) 

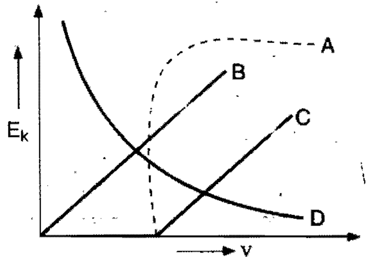
(d) 

31. The given figure indicates the energy levels of a certain atom. When the system moves from $2E$ level to E, a photon of wavelength λ is emitted. The wavelength of photon produced during the transition from level $4E/3$ to level E is:



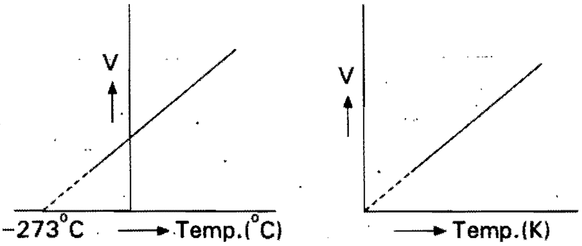
(a) $\lambda/3$ (b) $3\lambda/4$ (c) $4\lambda/3$ (d) 3λ

32. The maximum kinetic energy (E_k) of the photoelectron varies with frequency (ν) of the incident light as shown by the curve:



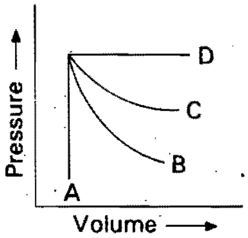
(a) A (b) B (c) C (d) D

33. The following graphs illustrate:



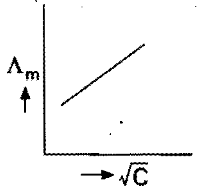
(a) Dalton's law (b) Charles' law
(c) Boyle's law (d) Gay-Lussac's law

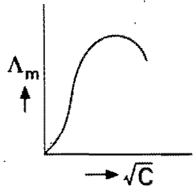
34. In the following graph:

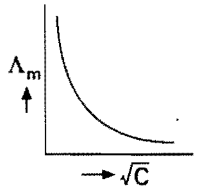


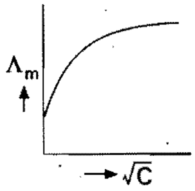
(a) 'A' represents isochoric process
(b) 'B' represents adiabatic process
(c) 'C' represents isothermal process
(d) 'D' represents isobaric process

35. The variation of Λ_m of acetic acid with concentration is correctly represented by:

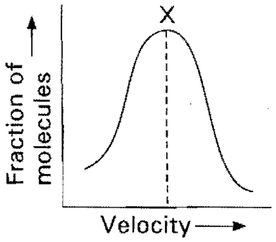
(a) 

(b) 

(c) 

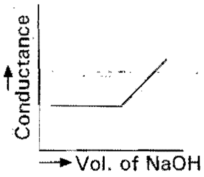
(d) 

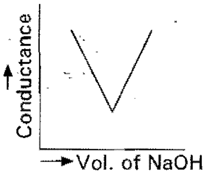
36. Distribution of fraction of molecules with velocity is represented in the figure. Velocity corresponding to X is:

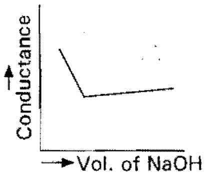


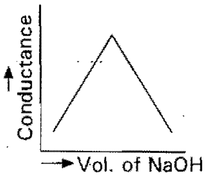
(a) $\sqrt{\frac{2RT}{M}}$ (b) $\sqrt{\frac{3RT}{M}}$ (c) $\sqrt{\frac{8RT}{\pi M}}$ (d) none of these

37. CH_3COOH is neutralized by NaOH. Conductometric titration curve will be of the type:

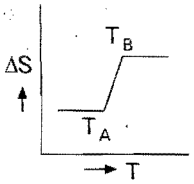
(a)


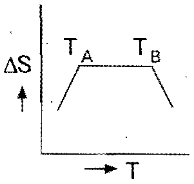
(b)


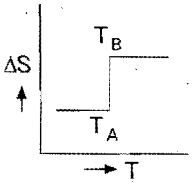
(c)


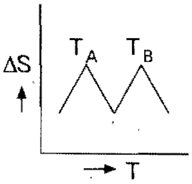
(d)


38. If for a given substance, T_B is the m.pt. and T_A is the freezing point, then correct variation of entropy by graph between entropy change (ΔS) and temperature is:

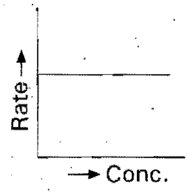
(a)


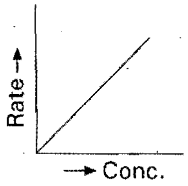
(b)


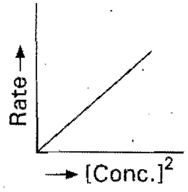
(c)


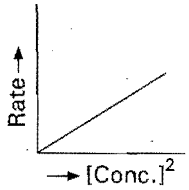
(d)


39. Which of the following represents zero order reaction?

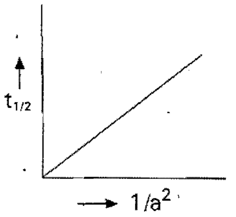
(a)


(b)


(c)


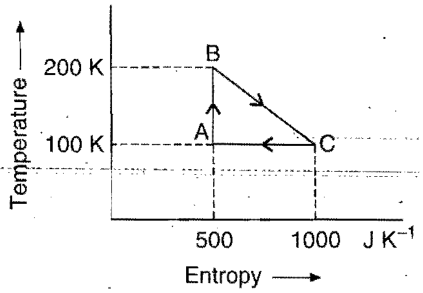
(d)


40. This graph represents:



(a) first order reaction (b) zero order reaction
(c) second order reaction (d) third order reaction

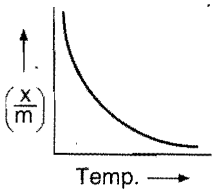
41. The efficiency of the reversible cycle shown in the given figure is:

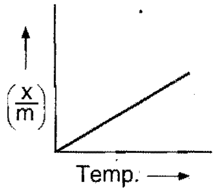


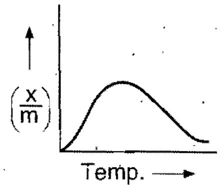
(a) 33.33% (b) 56% (c) 66% (d) 16.7%

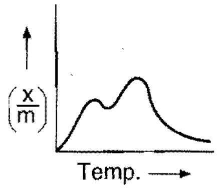
[Hint: $\text{Efficiency} = \frac{\text{Area bounded by the curve}}{\text{Total area under the line BC}} \times 100$]

42. Which of the following curves represents the chemical adsorption?

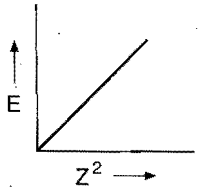
(a)


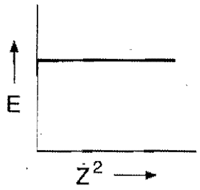
(b)


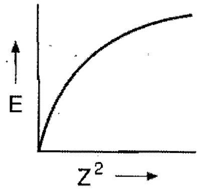
(c)


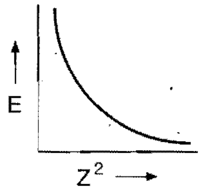
(d)


43. Energy of electron varies with atomic number as the following curve/line:

(a)


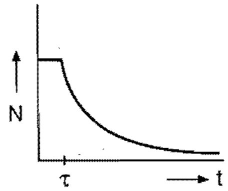
(b)


(c)


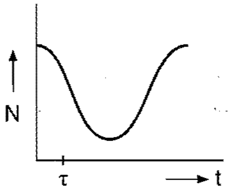
(d)


[**Hint:** $E = -\frac{Z^2}{n^2} \times 13.6 \text{ eV}, E \propto \frac{1}{Z^2}$; therefore, E will decrease exponentially with increase in Z^2.]

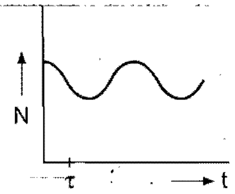
44. A radioactive sample consists of two distinct species having equal number of atoms initially. The mean life of one of the species τ and that of the other is 5τ. The decay products in both the cases are stable. A plot is made of total number of radioactive nuclei as the function of time. Which of the following figures best represents the form of this plot?



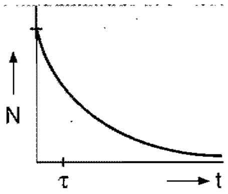
(a)



(b)



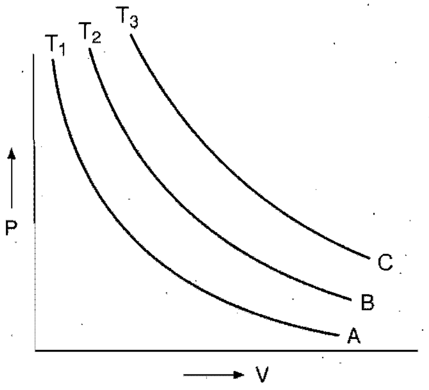
(c)



(d)

[**Hint:** The activity will decay spontaneously with passage of time.]

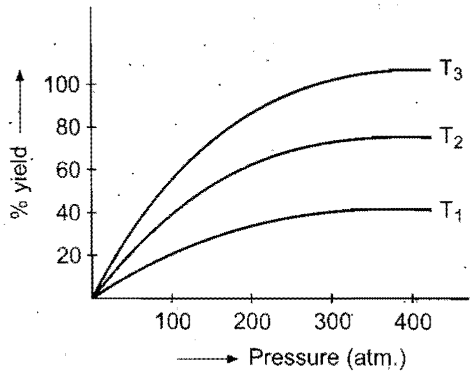
45. In following isothermal graphs A, B and C at temperatures T_1, T_2 and T_3; the correct order of temperatures will be:



(a) $T_1 > T_2 > T_3$ (b) $T_1 > T_3 > T_2$
(c) $T_3 > T_2 > T_1$ (d) $T_3 > T_1 > T_2$

46. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H° = -22.4 \text{ kJ mol}^{-1}$. Percentage yield of the reaction against pressure is plotted at three different temperatures T_1, T_2 and T_3, then:

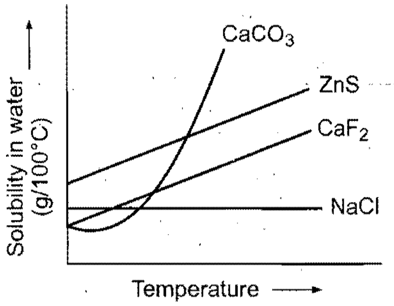
(a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$
(c) $T_1 = T_2 = T_3$ (d) none of these



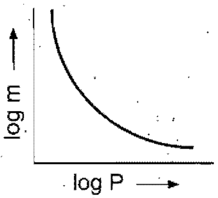
[**Hint:** Reaction is exothermic; hence, the reaction will shift in forward direction to give better yield.

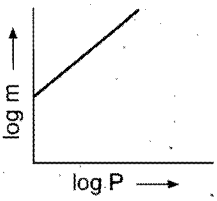
$\therefore \xrightarrow[\text{Decreasing yield of reaction}]{T_1 > T_2 > T_3}$]

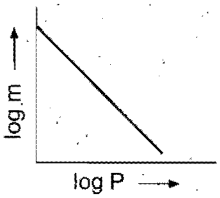
47. From the given graph, predict the compound which would be most easily purified by recrystallisation from aqueous solution:
(a) ZnS
(b) $CaCO_3$
(c) CaF_2
(d) NaCl

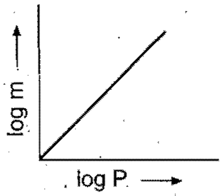


48. Which of the following curves represents the Henry's law?

(a)


(b)


(c)


(d)


Answers

1. (c)	**2.** (c)	**3.** (a)	**4.** (d)	**5.** (a)	**6.** (a)	**7.** (d)	**8.** (a)
9. (c)	**10.** (d)	**11.** (c)	**12.** (c)	**13.** (c)	**14.** (b)	**15.** (b)	**16.** (d)
17. (c)	**18.** (a)	**19.** (c)	**20.** (c)	**21.** (d)	**22.** (b)	**23.** (c)	**24.** (c)
25. (c)	**26.** (c)	**27.** (d)	**28.** (b)	**29.** (c)	**30.** (d)	**31.** (d)	**32.** (c)
33. (b)	**34.** (a, b, c, d)		**35.** (c)	**36.** (a)	**37.** (a)	**38.** (a)	**39.** (a)
40. (d)	**41.** (a)	**42.** (c)	**43.** (d)	**44.** (d)	**45.** (d)	**46.** (b)	**47.** (d)
48. (b)							

TEST OF MATCHING APTITUDE

TEST SERIES III

1. Match the List-I with List-II and pick up the correct matching from the codes given below:

List-I	List-II
A. $\left(\frac{\partial E}{\partial V}\right)_T = 0$	1. Isothermal process
B. $W = -\Delta E$	2. $-nFE°$
C. $\Delta E = 0$	3. Adiabatic reaction
D. $\Delta G°$	4. van der Waals' gas
E. $\left(\frac{\partial T}{\partial P}\right)_H \neq 0$	5. Ideal gas

Codes:

(a)	A–2	B–1	C–4	D–5	E–3
(b)	A–2	B–5	C–1	D–4	E–3
(c)	A–3	B–1	C–2	D–5	E–4
(d)	A–5	B–4	C–1	D–2	E–3
(e)	A–5	B–3	C–1	D–2	E–4

2. Match the Column-I with Column-II:

Column-I	Column-II
(I). $^{40}_{20}\text{Ca}$	1. Unstable, α-emitter
(II). $^{133}_{53}\text{I}$	2. Unstable, β-emitter
(III). $^{121}_{53}\text{I}$	3. Unstable, positron emitter
(IV). $^{232}_{90}\text{Th}$	4. Stable

Codes:

(a)	I–1	II–2	III–3	IV–4
(b)	I–4	II–3	III–2	IV–1
(c)	I–4	II–2	III–3	IV–1
(d)	I–4	II–3	III–1	IV–2

3. Match the List-I with List-II and select the correct answer using the options given below the lists:

List-I (Electrochemical parameter)	List-II (Units)
(I). Ionic mobility	1. cm^{-1}
(II). Cell constant	2. $\text{ohm}^{-1}\ \text{cm}^{-1}$
(III). Specific conductance	3. $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$
(IV). Molar conductance	4. $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$

Codes:

(a)	I–4	II–1	III–2	IV–3
(b)	I–2	II–3	III–4	IV–1
(c)	I–3	II–1	III–2	IV–4
(d)	I–1	II–2	III–3	IV–4

4. Match the Column-I with Column-II and select the correct answer using the sequences given below:

Column-I (Compounds)	Column-II (Oxidation state of nitrogen)
A. NaN_3	1. +5
B. N_2H_4	2. +1
C. NH_2OH	3. $-1/3$
D. N_2O_5	4. -2

Codes:

	A	B	C	D
(a)	3	4	2	1
(b)	4	3	1	2
(c)	3	4	1	2
(d)	4	3	2	1

5. Match the Column-I with Column-II and pick up the correct alternate:

Column-I	Column-II
(I). For spontaneous reaction	A. $\Sigma(\text{BE})_R - \Sigma(\text{BE})_P$
(II). For endothermic reaction	B. $\Delta H = \Delta E$
(III). Bond dissociation energy	C. $\Delta G = -$ ve
(IV). For solids and liquids in a thermochemical reaction	D. $\Sigma H_P > \Sigma H_R$

Codes:

(a)	I – C	II–A	III–D	IV–B
(b)	I – B	II–D	III–A	IV– C
(c)	I – C	II–D	III–B	IV–A
(d)	I – C	II–D	III–A	IV–B

6. Match the Column-I with Column-II and pick up the correct answer:

Column-I	Column-II
(I). Nickel	A. Conversion of alcohol to gasoline
(II). ZSM-5	B. Alkylation of benzene
(III). SiO_2	C. Hydrogenation of oil

Codes:

(a)	I – C	II–A	III–B
(b)	I – A	II–B	III– C
(c)	I – C	II–B	III–A
(d)	I – B	II– C	III–B

7. Match the List-I (enzymes) with List-II (metals) and select the correct answer using the codes given below the lists:

List-I	List-II
A. Nitrogenase	1. Cu
B. Cytochrome oxidase	2. Mo
C. Cytochrome-C	3. Zn
D. Carboxypeptidase	4. Fe

Codes:

	A	B	C	D
(a)	1	2	4	3
(b)	2	1	3	4
(c)	2	1	4	3
(d)	1	2	3	4

8. Match the Column-I with Column-II and select the correct answer:

Column-I	Column-II
(I). Curie	A. 10^6 dis sec^{-1}
(II). Rutherford	B. 3.7×10^{10} dis sec^{-1}
(III). Becquerel	C. 1 dis sec^{-1}

Codes:

(a)	I–B	II–A	III–C
(b)	I–B	II–C	III–A
(c)	I–A	II–B	III–C
(d)	I–C	II–B	III–A

9. Match the List-I with List-II:

List-I	List-II
(I). $\Delta H = q_P$	1. $\Delta S^\circ = 0$
(II). Kirchhoff's equation	2. State function
(III). $H^+(aq.)$	3. Path function
(IV). Spontaneous process	4. $\Delta G > 0$
	5. $\Delta S^\circ_{Total} > 0$
	6. $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$

Codes:

	(I)	(II)	(III)	(IV)
(a)	1	2	4	5
(b)	5	4	3	6
(c)	2	6	1	5
(d)	6	2	5	1

10. Match the List-I with List-II:

List-I	List-II
(I). Mixing of two ideal gases	1. $\Delta G_{mix} = 0$
(II). Criterion for irreversibility	2. $1/P$
(III). Isobaric thermal coefficient of an ideal gas	3. $1/T$
(IV). Joule-Thomson effect	4. $\Delta S_{Total} > 0$
	5. $\Delta G_{mix} < 0$
	6. $\Delta H = 0$

Codes:

	(I)	(II)	(III)	(IV)
(a)	1	2	4	5
(b)	5	4	3	6
(c)	2	6	1	5
(d)	6	2	5	1

11. Match the List-I with List-II:

List-I	List-II
(I). Translational kinetic energy	1. $\frac{3}{2}P$
(II). Rotational kinetic energy of CO_2	2. 15/13
(III). Translational kinetic energy per unit volume	3. 7/5
(IV). γ for CO_2 at very high temperature	4. Function of T only
	5. RT
	6. $\frac{3}{2}RT$

Codes:

	(I)	(II)	(III)	(IV)
(a)	2	4	5	1
(b)	4	5	1	2
(c)	5	6	2	3
(d)	6	1	3	4

12. Match the Column-X with Column-Y:

Column-X (Colloids)	Column-Y (Classification)
(I). Rain cloud	A. Sol
(II). Milk of magnesia	B. Aerosol
(III). Soap suds	C. Gel
(IV). Butter	D. Foam

Codes:

	(I)	(II)	(III)	(IV)
(a)	A	B	C	D
(b)	A	C	B	D
(c)	B	A	D	C
(d)	B	A	C	D

13. Match the List-I with List-II and select the correct answer from given codes:

List-I (Spectrum)	List-II (Region)
A. Lyman	1. Ultraviolet
B. Paschen	2. Visible
C. Balmer	3. Near infrared
D. Pfund	4. Far infrared

Codes:

	A	B	C	D
(a)	1	3	2	4
(b)	1	2	3	4
(c)	4	3	2	1
(d)	1	2	4	3

14. Match the List-I with List-II and select the correct answer:

List-I	List-II
A. Critical temperature	1. a/Rb
B. Boyle temperature	2. $2a/Rb$
C. Inversion temperature	3. T/T_c
D. Reduced temperature	4. $8a/27Rb$

Codes:

	A	B	C	D
(a)	4	1	2	3
(b)	2	1	4	3
(c)	4	3	2	1
(d)	2	3	1	4

15. Match the List-I, List-II and List-III and select the answer from the given codes:

List-I (Order)	List-II (Unit of rate constant)	List-III (Relation between half life and initial concentration)
A. Zero	(i) $L^2\ mol^{-2}\ s^{-1}$	1. $t_{1/2} = \text{Constant}$
B. First	(ii) $L\ mol^{-1}\ s^{-1}$	2. $t_{1/2} \propto \frac{1}{a}$
C. Second	(iii) s^{-1}	3. $t_{1/2} \propto a$
D. Third	(iv) $mol\ L^{-1}\ s^{-1}$	4. $t_{1/2} \propto \frac{1}{a^2}$

Codes:

	A	B	C	D
(a)	i–2	ii–4	iii–3	iv–1
(b)	i–4	iv–3	ii–2	iii–1
(c)	iv–3	iii–1	ii–2	i–4
(d)	ii–2	i–1	iii–3	iv–4

16. Match the List-I (solutions of salts) with List-II (pH of the solutions) and select the correct answer using the codes given below the lists:

List-I	**List-II**
A. Weak acid and strong base	1. $\frac{1}{2}\,pK_w$
B. Strong acid and weak base	2. $\frac{1}{2}[pK_w - pK_b + pK_a]$
C. Weak acid and weak base	3. $\frac{1}{2}[pK_w - pK_b - \log c]$
D. Strong acid and strong base	4. $\frac{1}{2}[pK_w + pK_a + \log c]$

Codes:

	A	B	C	D
(a)	4	3	2	1
(b)	1	2	3	4
(c)	2	3	4	1
(d)	3	2	1	4

17. Match the List-I with List-II and choose the correct answer from the codes:

List-I (Electrolyte)	**List-II (Solubility product)**
A. Bi_2S_3	1. $4s^3$
B. $Al(OH)_3$	2. $27s^4$
C. CdS	3. $108s^5$
D. CaF_2	4. s^2

Codes:

	A	B	C	D
(a)	1	2	3	4
(b)	2	3	1	4
(c)	4	3	2	1
(d)	3	2	4	1

18. Match the following combinations of electrical units with their terms as single unit:

Electrical unit	**Single unit**
(I). ampere-second	A. coulomb
(II). volt-ampere	B. ohm
(III). volt-ampere^{-1}	C. ampere
(IV). watt/ampere ohm	D. watt
(V). joule /ampere second	E. volt

Codes:

	A	B	C	D	E
(a)	I	III	IV	II	V
(b)	I	II	III	IV	V
(c)	V	IV	III	II	I
(d)	I	V	IV	II	III

19. Match the List-I with List-II and select the correct answer from the given codes:

List-I (Thermodynamic properties)	**List-II (Relation)**
A. Free energy change of a reaction (ΔG)	1. $-RT \log K$
B. Standard enthalpy change (ΔH°) of a reaction	2. $RT^2\left(\frac{d \ln K}{dT}\right)_P$
C. Standard entropy change (ΔS°)	3. $-nFE$
D. Standard free energy change (ΔG°)	4. $-\left(\frac{d\,\Delta G}{dT}\right)_P$

Codes:

	A	B	C	D
(a)	3	2	4	1
(b)	1	2	3	4
(c)	4	3	2	1
(d)	2	3	1	4

20. Match the List-I, List-II and List-III:

List-I	**List-II**	**List-III**
A. $\Delta G > 0$	X. $\Delta S > 0$	1. Non-spontaneous
B. $\Delta G < 0$	Y. $\Delta S < 0$	2. Spontaneous
C. $\Delta G = 0$	Z. $\Delta S = 0$	3. Equilibrium

Select the correct answer from the following codes:

	A	B	C
(a)	(Y, 1)	(X, 2)	(Z, 3)
(b)	(X, 2)	(Y, 3)	(Z, 1)
(c)	(X, 3)	(Y, 1)	(Z, 2)
(d)	(Y, 1)	(X, 3)	(Z, 2)

21. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Spontaneous process	(p) $\Delta H = -$ ve
(b) Heat flow from high temperature of system towards low temperature of surroundings	(q) $\Delta G = +$ ve
(c) Exergonic process	(r) $\Delta S_{\text{Total}} = +$ ve
(d) Increase in the randomness of system by heating	(s) $\Delta G = -$ ve

(a)	ⓟ	ⓠ	ⓡ	ⓢ
(b)	ⓟ	ⓠ	ⓡ	ⓢ
(c)	ⓟ	ⓠ	ⓡ	ⓢ
(d)	ⓟ	ⓠ	ⓡ	ⓢ

22. Match the items of Column-I with the items of Column-II:

Column-I (Metal)	**Column-II (Packing/coordination number)**
(a) Na	(p) ccp
(b) Cu	(q) bcc
(c) Au	(r) 12
(d) K	(s) 8

23. Match the Column-I with Column-II and Column-III:

l = Edge length of unit cell;

r = Radius of spherical constituent unit

Column-I	**Column-II**	**Column-III**
(a) Simple cubic unit cell	(p) $l\sqrt{3} = 4r$	(u) 74% occupied space
(b) Face-centred cubic unit cell	(q) $l = 2r$	(v) 67.98% occupied space
(c) Body-centred cubic unit cell	(r) $l\sqrt{2} = 4r$	(w) 52.33% occupied space

24. Match the List-I with List-II:

List-I	**List-II**
(a) Silicon doped with phosphorus	(p) Acceptor level above valence bond
(b) Metal excess non-stoichiometry in NaCl	(q) n-type semiconductor
(c) Ge doped with Ga	(r) Donor level just below the conduction band
(d) Anion vacancy with trapped electron	(s) F-centre

25. Match the solids in List-I with their properties in List-II:

List-I	List-II
(a) MnO	(p) Ferromagnetic solid
(b) ZnO	(q) Antiferromagnetic solid
(c) CrO_2	(r) Zero magnetic moment
(d) TiO	(s) Attracted in magnetic field

26. Match the List-I with List-II:

List-I	List-II
(a) The highest temperature at which liquid CO_2 exists	(p) $\frac{V_{\text{real}}}{V_{\text{ideal}}}$
(b) $8a/27Rb$	(q) Critical temperature
(c) Compressibility factor $Z = 3/8$ at	(r) Ideal gas
(d) Compressibility factor $Z = 1$ for	(s) 30.98° C

27. Match the physical properties of Column-I with their values in Column-II:

Column-I	Column-II
(a) SATP	(p) 1 bar/1 atm
(b) Temperature in STP	(q) 99.6° C
(c) Pressure in NTP	(r) 273.15 K
(d) Standard boiling point of water	(s) 298.15 K

SATP $\longrightarrow$ Standard ambient temperature and pressure
STP $\longrightarrow$ Standard temperature and pressure
NTP $\longrightarrow$ Normal temperature and pressure

28. Match the quantities in Column-I with their units in Column-II:

Column-I	Column-II
(a) Coefficient of viscosity	(p) L mol^{-1}
(b) van der Waals' constant '*b*'	(q) N s m^{-2}
(c) Molar volume of gas at STP = 22.4 ...	(r) Pas
(d) van der Waals' constant '*a*'	(s) L^2 atm mol^{-2}

29. Match the temperature in List-I with its value in List-II:

List-I	List-II
(a) Critical temperature	(p) a/Rb
(b) Boyle's temperature	(q) θ
(c) 1/2 [Inversion temperature]	(r) T/T_c
(d) Reduced temperature	(s) $8a/27Rb$

30. Match the items of Column-I with its proportional term in the items of Column-II:

Column-I	Column-II
(a) Kinetic energy	(p) Mole fraction
(b) Partial pressure of a gas	(q) Density
(c) Rate of diffusion	(r) Molar mass
(d) Vapour pressure of a liquid	(s) Absolute temperature

31. Match the List-I with List-II and List-III:

List-I (Solids)	List-II (Unit cell)	List-III (Coordination number)
(a) Rock salt	(p) Face-centred cubic, anion in tetrahedral void	(w) 6
(b) Fluorite	(q) Face-centred cubic, cation in octahedral void	(x) Cation (8), anion (4)
(c) AgI, ZnS	(r) Face-centred cubic, cation in alternate tetrahedral void	(y) Cation (4), anion (8)
(d) Na_2O	(s) Face-centred cubic, cation in tetrahedral void	(z) Cation (4), anion (4)

Answers

1. (e) **2.** (c) **3.** (a) **4.** (a) **5.** (d) **6.** (a) **7.** (b) **8.** (a)
9. (c) **10.** (b) **11.** (d) **12.** (c) **13.** (a) **14.** (a) **15.** (c) **16.** (a)
17. (d) **18.** (a) **19.** (a) **20.** (a) **21.** (a-r,s) (b-p,r,s) (c-q) (d-q,r)
22. (a-q,s) (b-p,r) (c-p,r) (d-q,s) **23.** (a-q-w) (b-r-u) (c-p-v)
24. (a-q,r) (b-s) (c-p) (d-s) **25.** (a-q,r) (b-r) (c-p,s) (d-s) **26.** (a-q,s) (b-q) (c-p,q) (d-r) **27.** (a-p,s) (b-r) (c-p) (d-q)
28. (a-q,r) (b-p) (c-p) (d-s) **29.** (a-s) (b-p) (c-p) (d-q,r) **30.** (a-s) (b-p,s) (c-q,r) (d-p,s)
31. (a-q-w) (b-p-x) (c-r-z) (d-s-y)

TEST OF REASONING APTITUDE

TEST SERIES IV

REASON AND ASSERTION

(For IIT & AIIMS Aspirants)

In each of the following questions, a statement of **Assertion (A)** is given followed by corresponding statement of **Reason (R)** just below it. Mark the correct answer as:

(a) Both (R) and (A) are true and reason is the correct explanation of assertion.
(b) Both (R) and (A) are true but reason is not correct explanation of assertion.
(c) Assertion (A) is true but reason (R) is false.
(d) Assertion (A) and reason (R) both are false.
(e) Assertion (A) is false but reason (R) is true.

1. (A) CH_4 and CO_2 have the value of Z (compressibility factor) less than one.
(R) $Z < 1$ is due to repulsive forces among the molecules.

2. (A) More is the value of van der Waals' constant 'a', greater is the tendency of liquefaction.
(R) 'a' measures the magnitude of force of attraction among the molecules.

3. (A) Crystalline solids are anisotropic.
(R) Crystalline solids are not as closely packed as amorphous solids.

4. (A) Antiferromagnetic substances possess zero magnetic moment.
(R) MnO is an antiferromagnetic substance.

5. (A) Isotonic solutions do not show osmosis.
(R) Isotonic solutions have equal osmotic pressure.

6. (A) In a gaseous reaction, K_c is unitless when $\Delta n = 0$.
(R) Unit of $K_c = (\text{mol L}^{-1})^{\Delta n}$.

7. (A) Strength of acidic character of oxyacids lies in the following sequence:

$$HClO_4 > HBrO_4 > HIO_4$$

(R) Greater is the oxidation state of a halogen, more is the acidic character of its oxyacid.

8. (A) The molecularity of the following reaction is 2

$$H_2 + Br_2 \longrightarrow 2HBr$$

(R) The order of reaction is 3/2.

9. (A) Half-life of a first order reaction is independent of the initial concentration of reactant.
(R) $t_{1/2}$ (first order) $= \dfrac{\tau}{1.44}$
where, τ = average life.

10. (A) For the reaction,

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

$\Delta H > \Delta U$.
(R) The enthalpy change is always greater than internal energy change.

11. (A) $^{20}N_e$ and $^{22}N_e$ are isotones.
(R) Noble gases do not exist as isotopes as they are not reactive.

12. (A) $3d_{z^2}$ orbital is spherically symmetrical.
(R) $3d_{z^2}$ orbital is the only d-orbital which is spherical in shape.

13. (A) The kinetic energy of the photoelectron ejected increases with increase in intensity of incident radiation.
(R) Increase in intensity of incident light increases the rate of emission.

14. (A) $^{133}_{56}Be + e^- \longrightarrow\, ^{133}_{55}Cs + X\text{-ray}$
It is a process of K-electron capture.
(R) The atomic number decreases by one unit as a result of K-capture.

15. (A) Vapour pressure is a colligative property.
(R) Colligative property depends on the number of solute particles dissolved in the solution.

16. (A) Entropy decreases when an egg is boiled.
(R) It is solidified due to denaturation of albumin.

17. (A) 1 faraday = 96,500 coulomb.
It is a charge of 1 mole electrons.
(R) 1 faraday charge liberates one gram equivalent of substance at an electrode.

18. (A) The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm.
(R) Its resistivity is equal to 76.234 ohm-cm.

19. (A) If water is heated to 350 K, then pOH will increase to 8.
(R) K_w increases with increase in temperature.

20. (A) Magnetic quantum number can have the value $0, \ldots, (n-1)$.
(R) Magnetic quantum number specifies the number of orbitals.

Answers

1. (a) **2.** (a) **3.** (c) **4.** (b) **5.** (a) **6.** (a) **7.** (b) **8.** (b)
9. (a) **10.** (c) **11.** (d) **12.** (d) **13.** (e) **14.** (b) **15.** (e) **16.** (a)
17. (b) **18.** (c) **19.** (e) **20.** (e)

LOGARITHMS

x	0	1	2	3	4	5	6	7	8	9	Mean differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	5	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Contd.......

LOGARITHMS

x	0	1	2	3	4	5	6	7	8	9	Mean differences								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

x	0	1	2	3	4	5	6	7	8	9	Mean differences								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	1	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	1	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	1	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	1	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	3
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	3
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	3
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	3
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	2	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	2	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	2	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	2	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	2	2	2	3	3	4
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	2	2	2	3	3	4
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	2	2	2	3	3	4
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	2	2	2	3	3	4
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	4
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	4
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	2	3	3	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	2	3	3	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	1	1	2	2	3	3	4	4	5
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	4	4	5	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	4	4	5	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	4	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	5
.43	2692	2698	2704	2711	2716	2723	2729	2735	2742	2748	1	1	2	2	3	4	4	5	5
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	2	3	4	4	5	5
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	6	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	6	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	6	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS

x	0	1	2	3	4	5	6	7	8	9	Mean differences								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	6
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	6	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	6	6	7
.53	3338	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	6	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	2	3	4	5	6	6	7
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	4	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	5	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	7	8	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	4	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	10	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	8	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	2	4	5	6	7	8	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	10	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	6	7	8	10	11	13
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	8	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	10	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	14
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	6	8	10	11	13	14
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	14	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	15
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	13	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	5	7	9	11	13	14	16
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	10	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	11	13	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	13	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	18	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	15	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	21