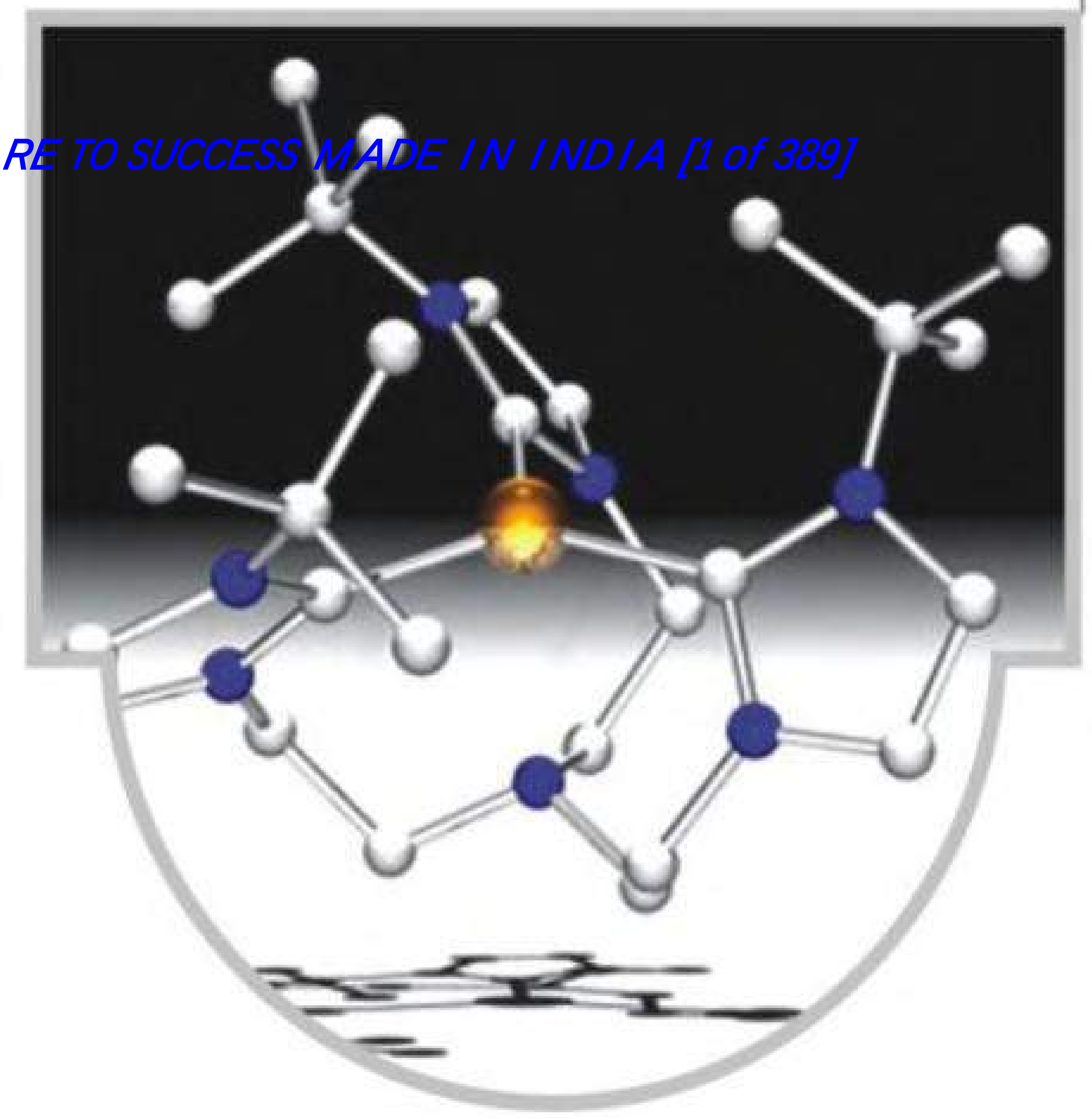

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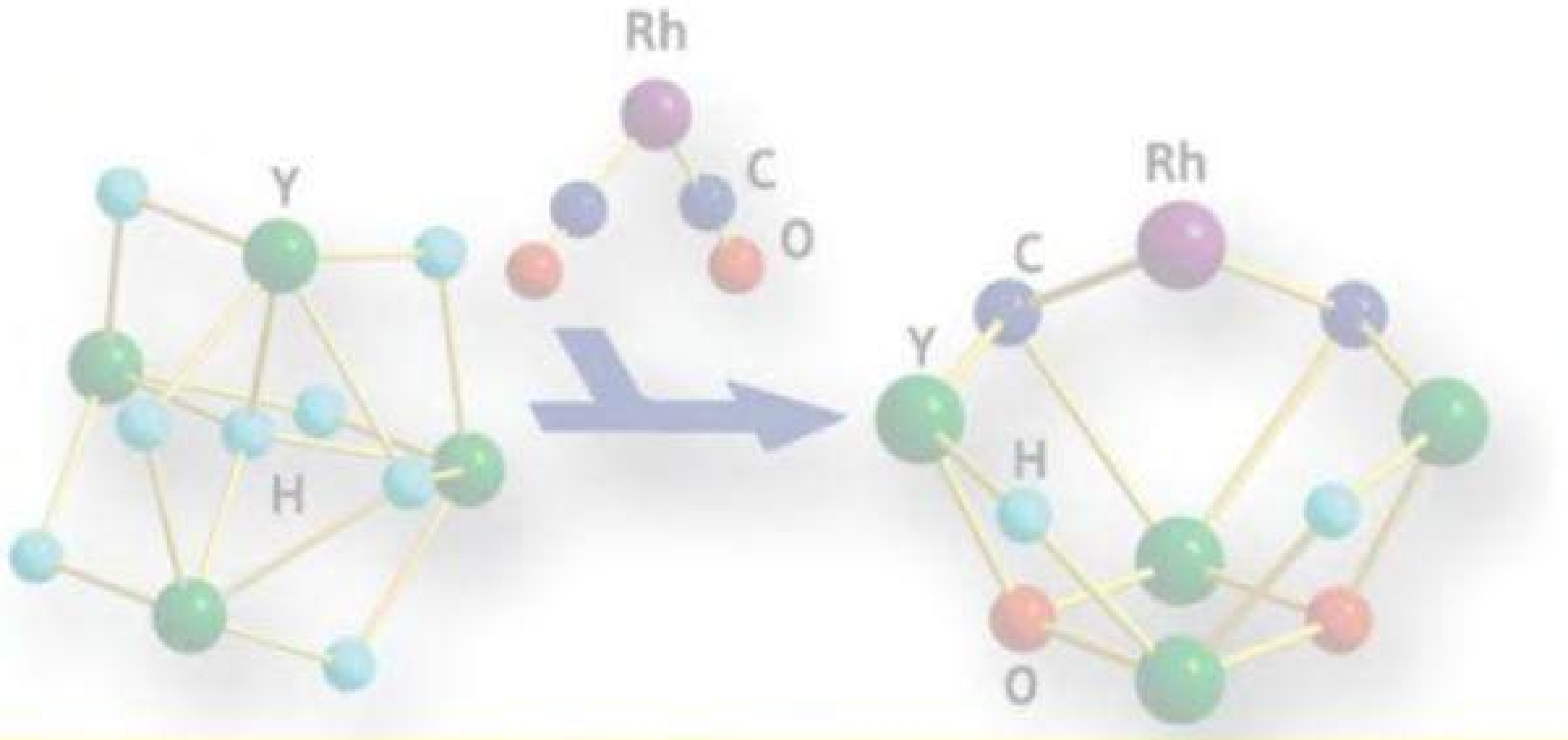

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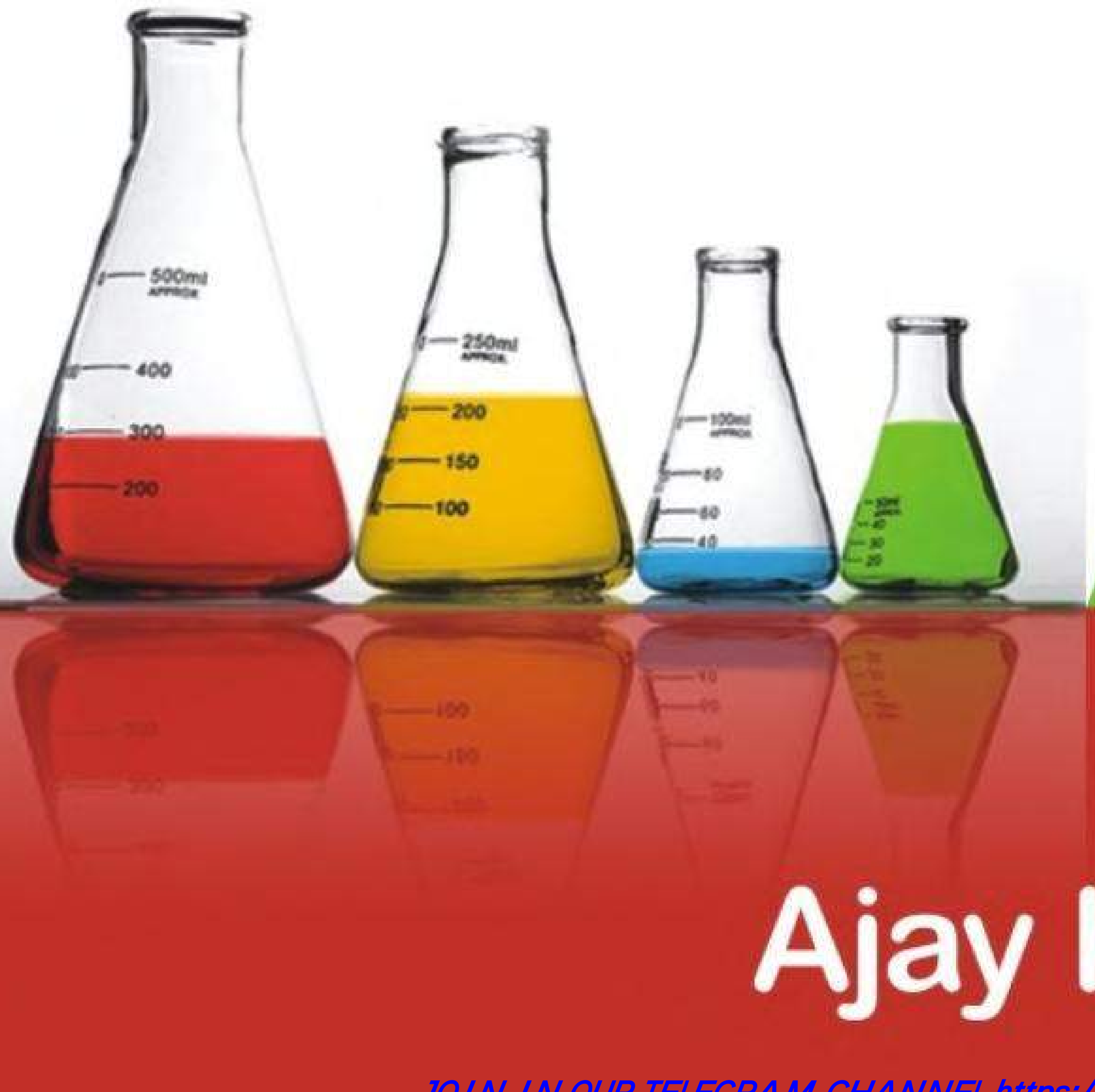

Ajay Kumar

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Numerical Chemistry

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Colligative Properties

CHAPTER 1

Stoichiometry

Basic Concepts in Chemistry

The branch of chemistry which contains the fundamental concepts and relationship between chemical identities is called as stoichiometry. In this unit following facts are discussed.

(A) Laws of Chemical Combinations
(B) Significant Figures
(C) Scientific Notations
(D) Mole Concepts
(E) Atomic and Molecular Mass
(F) Equivalent Concepts
(G) Limiting Reagent
(H) Concentration Units
(I) Volumetric Analysis
(J) Concept of H_2O_2 Solution
(K) Concept of Oleum
(L) Hardness of Water

Laws of Chemical Combinations

Law of Conservation of Mass (Lavoisier)

It states that the mass of reactants before reaction and the mass of products and reactants (if left) are equal.

i.e. $A + B \rightarrow \text{Products}$

It shows that mass of reactants A and B before reaction is equal to mass of products formed and mass of reactant if remain, after reaction

Law of Constant Composition or Definite Proportions (Proust)

It states that mass ratio of the elements in a compound is always fixed and it is independent of the method by which it is formed, e.q. Mass ratio of Hydrogen and Oxygen in H_2O is 2 : 16 or 1 : 8 (It is fixed).

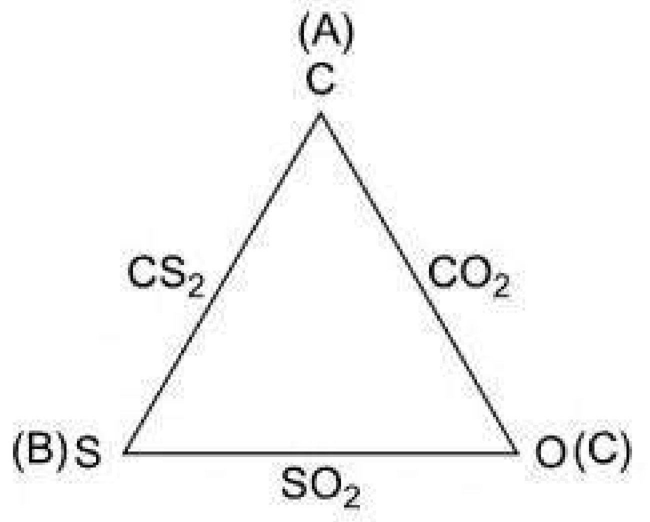
Law of Multiple Proportions (Dalton)

It states that weight of different elements which combine with fixed weight of other element, bear a simple ratio. e.q. The weight of oxygen that combine with 14 parts by weight of Nitrogen in NO, NO_2, N_2O_3, N_2O_4 and N_2O_5 are 8, 16, 24, 32 and 40 i.e. in the ratio 1 : 2 : 3 : 4 : 5.

Law of Reciprocal Proportion (Ritcher)

It states that weights of two elements *A* and *B* which combine separately with a fixed weight of third element *C*, are either the same or in simple ratio of *A* and *B*.

e.q.



Mass ratio of C:S in $CS_2 = 12 : 64$

Mass ratio of C&O in $CO_2 = 12 : 32$

$\therefore$ Mass ratio of S:O in $SO_2 = 32 : 32 = 1 : 1$

Law of gaseous volume (Gay-Lussac)

It states that if gases reactants combined to form the gaseous products their mole ratio is simply expressed in terms of volume ratio. *e.q.*

$$\underset{(g)}{H_2} + \underset{(g)}{Cl_2} \rightarrow 2\,\underset{(g)}{HCl}$$

The ratio of the volume of H_2, Cl_2 and HCl are 1 : 1 : 2 respectively.

Significant Figures

The Significant Figures are the digits which are known accurately and one extra digit which is known in accurately e.q.

0012 has 2 significant figure
1002 has 4 significant figure
10.0 has 2 significant figure
7500 has 4 significant figure
6.023×10^{23} has 4 significant figure

Scientific Notations

In Scientific Notation, digits are written in terms of digit having decimal after a digit and other terms are written in power of 10. e.q.

1232 is written as 1.232×10^3
6023 is written as 6.023×10^3
0.001 is written as 1.0×10^{-3}

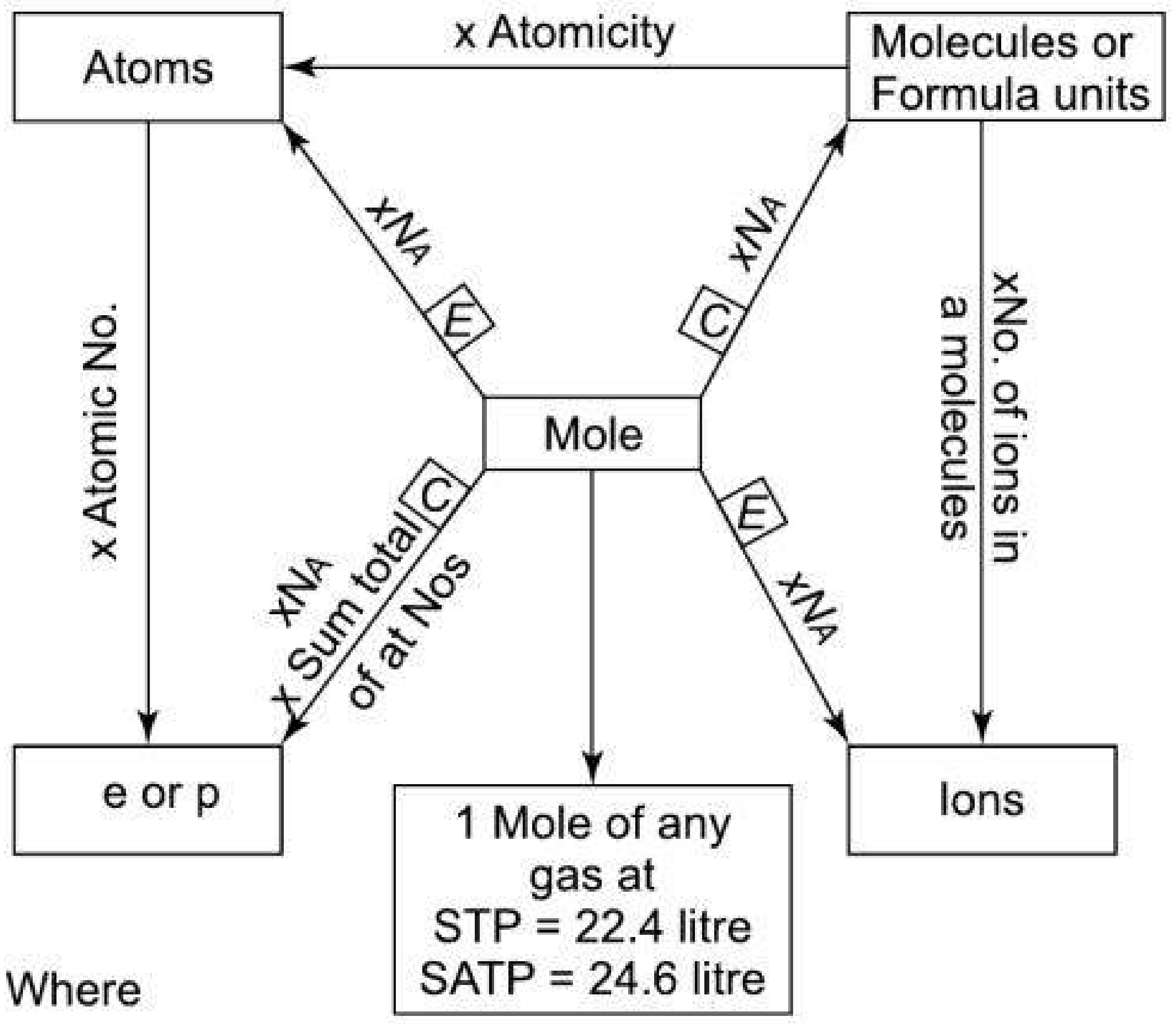
Mole Concepts

"Mole" literary mean "Collection of identities". It is the unit of amount of substance. One mole is that amount of substance which contains Avogadro's Number (6.02×10^{23}) of its smallest part.

$$\underset{\text{(For elements)}}{\text{No. of mole}} = \frac{\text{Given Mass (in gm)}}{\text{Atomic Mass}} = \frac{\text{No. of atoms given}}{N_A}$$

$$\underset{\text{(For compounds)}}{\text{No. of mole}} = \frac{\text{Given Mass in gm.}}{\text{Molecular Mass}} = \frac{\text{No. of molecules}}{N_A}$$

Conversion of Mole into Atoms, Ions, Molecules, Electrons, Protons or Neutrons



Where

E = Element *C* = Compound (ionic or covalent)
N_A = Avogadro's No. (6.02×10^{23}) *e* = No. of electrons
p = No. of protons

Gram-Atom: One gm-atom is equivalent to one mole of that element. e.q.

6gm of carbon = 6/12 gm-atom = 0.5 gm-atom.

Loschmidt Number: It is the no. of particles in 1 cm^3 of a gas at STP (2.688×10^{19})

Equivalent Mass

It is that mass of an element which either combine or displace by 1 part by mass of Hydrogen, 8 parts by mass of oxygen, 35.5 parts by mass of chlorine, 80 parts by mass of bromine etc.

$$\text{Equivalent Mass} = \frac{\text{Atomic or Molecular Mass}}{n-\text{factor}}$$

$$E_{\text{element}} = \frac{\text{Atomic Mass}}{\text{Valency}} \quad \text{e.q. } E_{\text{Al}} = \frac{27}{3} = 9$$

$$E_{\text{compound}} = \frac{\text{Molecular Mass}}{\text{Total charge on cation or anion part}}$$

$$\text{e.g. } E_{\text{CaCO}_3} = \frac{100}{2} = 50$$

$$E_{\text{ions}} = \frac{\text{Ionic Mass}}{\text{Charge}} \qquad \text{e.g. } E_{\text{CO}_3^{2-}} = \frac{60}{2} = 30.$$

$$E_{\text{oxidising or reducing agent}} = \frac{\text{Molecular Mass}}{n - \text{factor}}$$

$$\text{e.g. } E_{\text{KMnO}_4}(\text{H}^+ \text{ medium}) = \frac{158}{5} \quad \left(\text{MnO}_4^- \to \text{Mn}^{2+}\right)$$

$$= 31.6$$

$$E_{\text{KMnO}_4}(\text{OH}^- \text{ medium}) = \frac{158}{1} = 158$$

$$\left(\text{MnO}_4^- \to \text{MnO}_4^{2-}\right)$$

$$E_{\text{KMnO}_4}(\text{Neutral medium}) = \frac{158}{3} = 52.66$$

$$\left(\text{MnO}_4^- \to \text{MnO}_2\right)$$

$$E_{\text{Acid}} = \frac{\text{Molecular Mass}}{\text{Basicity}}$$

$$\text{e.g. } E_{\text{H}_2\text{SO}_4} = \frac{98}{2},\ E_{\text{H}_3\text{PO}_4} = \frac{98}{3},\ E_{\text{H}_3\text{PO}_3} = \frac{82}{2}$$

$$E_{\text{Base}} = \frac{\text{Molecular Mass}}{\text{Acidity}}$$

$$\text{e.g. } E_{\text{Al(OH)}_3} = \frac{71}{3},\ E_{\text{Ca (OH)}_2} = \frac{74}{2}$$

Methods of Calculating Equivalent Mass

(a) H_2 Displacement Method

$$E_{\text{element}} = \frac{W_{\text{element in gm}}}{W_{\text{Hydrogen}}} \times 1.008$$

$$= \frac{W_{\text{element in gm}}}{V_{\text{H}_2 \text{ gas at STP in litre}}} \times 11.2$$

(b) Oxide Formation Method

$$E_{\text{element}} = \frac{W_{\text{element in gm}}}{W_{\text{oxygen required}}} \times 8$$

$$= \frac{W_{\text{element in gm}}}{V_{\text{O}_2 \text{ gm at STP}}} \times 5.6$$

(c) Halide Formation Method

$$E_{\text{element}} = \frac{W_{\text{element in gm}}}{W_{\text{halogen required}}} \times E_{\text{halogen}}$$

(d) Double Decomposition method

$$\frac{W_{\text{compound I}}}{W_{\text{compound II}}} = \frac{E_{\text{compound I}}}{E_{\text{compound II}}}$$

$$\text{e.g. } \frac{W_{\text{CaCO}_3}}{W_{\text{CaO}}} = \frac{E_{\text{CaCO}_3}}{E_{\text{CaO}}} = \frac{E_{\text{Ca}^{2+}} + E_{\text{CO}_3^{2-}}}{E_{\text{Ca}^{2+}} + E_{\text{O}^{2-}}}$$

$$= \frac{E_{\text{Ca}^{2+}} + 30}{E_{\text{Ca}^{2+}} + 8}$$

(e) Law of Isomorphism

$$\frac{W_{\text{metal in compound I}}}{W_{\substack{\text{metal in compound II which} \\ \text{reacts with same mass of an} \\ \text{ion as in compound I}}}} = \frac{E_{\text{M in compound I}}}{E_{\text{M in compound II}}}$$

(F) Atomic Mass

It is the relative number which state how much times an atom of that element is heavier than that of $\frac{1}{12}$ th part of an atom of C^{12}. (Either it is unit less or expressed in a.m.u)

$$1 \text{ a.m.u} = 1.66054 \times 10^{-24} \text{ gm}$$
$$= 1.66054 \times 10^{-27} \text{ kg.}$$

Methods of determining Atomic Mass

(a) Dulong and Petit's Method

Atomic Mass (approx.) × Specific heat $\simeq 6.4$.

This law is only applicable for the solid elements which do not have allotropes. e.g. *B*, *C*, Be, Li, etc.

Exact atomic Mass = Eq. Mass × valency.

(b) Vapour Density Method

$$\text{Atomic Mass} = \text{Eq. Mass} \times \text{Valency}$$

$$\text{Valency} = \frac{\text{Molar Mass}}{\text{Equivalent Mass}}$$

or $$\text{Valency} = \frac{2 \times \text{Vapour density}}{\text{Equivalent Mass}}$$

(c) Law of Isomorphism

For two isomorphous compounds:

$$\frac{W_{\text{Metal in compound I}}}{W_{\substack{\text{Metal in compound II} \\ \text{that reacts with same mass} \\ \text{of anion as in compound I}}}} = \frac{\text{Atomic Mass of metal in compound I}}{\text{Atomic Mass of metal in compound II}}$$

Molecular Mass: It is the relative mass of one molecule of a compound which state that a molecule is how much times heavier than that of $\frac{1}{12}$th part of an atom of C^{12}.

Methods of determining molecular Mass

(a) Vapour Density Method

(For volatile substance)

$$\text{Molecular Mass} = 2 \times \text{Vapour density}$$

Where vapour density is determined by Duma's method or victor-Meyer's method.

(b) Diffusion Method

According to Graham's law

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Where r_1 = rate of diffusion of gas having molecular mass M_1

r_2 = rate of diffusion of gas having molecular mass M_2.

GMM (Gram Molecular Mass): Molecular mass expressed in gm is called gram-molecular mass (No. of molecules in one GMM = 6.02×10^{23})

Limiting Reagent

The reactant which consume or react completely during a chemical reaction is called Limiting Reagent. Any calculation for the product/s must be on the basis of Limiting Reagent. Let us consider a chemical reaction:

Let us suppose the formation of H_2O

	H_2 (g)	$+ \frac{1}{2} O_2$ (g) $\rightarrow$	H_2O (liq)
Mole (B.R)	1	0.5	0
Mass (B.R)	2	16	0

It means 2 gm H_2 reacts with 16 gm O_2 to form 18 gm H_2O. If both H_2 and O_2 are given in equal amount, it is oxygen which react completely and hence it is limiting reagent in that instance and H_2 behavs as excess reagent.

Concentration Units

Molarity (M)

It is the number of moles of solute per litre of solution.

$$M = \frac{W_{\text{Solute}} \times 1000}{M_{\text{Solute}} \times V_{\text{solution in ml}}}$$

Molality (m)

It is the number of moles of solute per kg. of solvent.

$$M = \frac{W_{\text{Solute}} \times 1000}{M_{\text{Solute}} \times W_{\text{Solvent in gm}}}$$

Relation between M and m

$$M = \frac{d}{\frac{M_{\text{Solute}}}{1000} + \frac{1}{m}}$$

where M_{Solute} = Molecular Mass of solute

d = density of solvent

Normality (N)

It is the number of equivalents of solute per litre of solution.

$$N = \frac{W_{\text{Solute}} \times 1000}{E_{\text{Solute}} \times V_{\text{Solution in ml}}}$$

Relation between Normality and Molarity

Normality = Molarity × (Molar Mass/Eq. Mass)

$$N = nM$$

Where n = factor or it is the number which divided by mol. mass to obtain equivalent mass. of that species

Percentage Strength

- % by mass $(W/W) = \dfrac{W_{\text{Solute}} \times 100}{W_{\text{Solution}}}$

  i.e. both solute and solution are expressed in mass.
- % by volume $(V/V) = \dfrac{V_{\text{Solute}} \times 100}{V_{\text{Solution}}}$

  i.e. both solute and solution are expressed in volume
- % by weight-volume $(W/V) = \dfrac{W_{\text{Solute}} \times 100}{V_{\text{Solution}}}$

  i.e. solute is expressed in mass while solution is expressed in volume.

Mole Fraction

The fractional mole of either solute or solvent per mole of solution.

$$\underset{(X_{\text{Solute}})}{\text{Mole fraction of solute}} = \frac{\text{Mole of Solute}}{\text{Mole of Solution}}$$

Mole fraction of solvent

$$(X_{\text{solvent}}) = \frac{\text{Mole of Solvent}}{\text{Mole of Solution}}$$

For a binary system $X_{\text{solute}} + X_{\text{solvent}} = 1$.

$$\frac{X_{\text{solute}}}{X_{\text{solvent}}} = \frac{\text{Mole of Solute}}{\text{Mole of Solvent}}$$

Formality (F)

The number of formula units per litre of solution.

$$F = \frac{W_{\text{solute}} \times 1000}{\text{Formula Mass of solute} \times V_{\text{solution in ml}}}$$

Formula mass is only for ionic compound.

Ionic Strength

The strength of a solution when two or more ionic compounds are mixed together is called Ionic Strength of that solution it is calculated as

$$\text{Ionic Strength} = \frac{1}{2}\Sigma MZ^2$$

(Where M = Molarity and Z = Valency).

Volumetric Analysis

It is the quantitative analysis by measuring volume of the reacting substance, on the basis of neutralisation (seen by using indicators).

Titration

The process by which the strength of the unknown solution is determined with the help of a standard solution, is called Titration.

(a) Acidimetry: To find out the strength of acid with the help of standard base is called acidimetry.

(b) Alkalimetry: To find out the strength of alkali with the help of standard acid is called alkalimetry.

Types of Titration

(a) Acid-Base Titration
  (i) Strong Acid Vs Strong Base
  (ii) Strong Acid Vs Weak Base
  (iii) Weak Acid Vs Strong Base
  (iv) Weak Acid Vs Weak base
(b) Redox Titration
  (i) Permagnetometry
  (ii) Dichrometry
  (iii) Iodometry
  (iv) Iodimetry
(c) Precipitation Titration
(d) Gravimetric Titration
(e) Potentiometric Titration.

Law of equivalence

Whenever a substance react or to which extent it react, with another substance, the equivalent of both the substances are the same.

i.e. $N_1V_1 = N_2V_2$.
No. of Gram Equivalent = $N \times V$ in litre
No. of milli equivalent (m.eq.) = $N \times V$ in cm^3.

$$W_{\text{substance in gm}} = \frac{\text{m.eq.}}{100} \times E_{\text{substance}}$$

Strength of solutions or Mixtures

(a) When a number of acids or bases are added.

$$N_m V_m = N_1V_1 + N_2V_2 + N_3V_3 + \cdots$$

Where $V_m = V_1 + V_2 + V_3 + \cdots$ (Total volume)

N_m = Normality of mixture

(b) When acids and bases are mixed together

$$N_m V_m = (N_1V_1 + N_2V_2 + \cdots) - \left(N_1^1V_1^1 + N_2^1V_2^1 + \cdots\right)$$

Where $N_1\ N_2 \cdots$ are normalities of acid or base having volume V_1, V_2 $\cdots$ respectively N_1^1, N_2^1 $\cdots$ are the normalities of base or acid having volume $V_1^1, V_2^1 \cdots$ respectively.

Double Indicator Titration

Whenever two alkali mixtures such as Na_2CO_3 and $NaHCO_3$ or NaOH and Na_2CO_3 or NaOH and $NaHCO_3$ are mixed and their composition is determined by using methyl orange or phenolphthalein indicator, the only fact you have to remember is that phenolphthalein changed its colour as soon as CO_2 or SO_2 starts forming during a reaction. But methyl orange shows complete neutralisation, e.q. Neutralisation of NaOH and Na_2CO_3 mixture by HCl is shown as follows:

(a) $NaOH + HCl \rightarrow NaCl + H_2O$

(b) $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

(c) $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

Methyl orange colour change is due to complete Neutralisation by *a*, *b* and *c*. But phenolphthalein colour change is due to only *a* and *b*.

Concepts of H_2O_2 Solution

H_2O_2 decomposes to give O_2 gas as

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The part of O_2 gas at STP is produced by the decomposition of one part of H_2O_2 in called volume strength of H_2O_2. It is represented by 'V' in inverted comma such as '5V', '10V', etc.

$$\text{Percent strength of } H_2O_2 = \frac{17}{56} \times \text{Volume strength}$$

$$\text{Volume Strength} = 5.6 \times \text{Normality}$$

$$\text{Volume Strength} = 11.2 \times \text{Molarity}$$

Concept of Oleum

Oleum is $H_2S_2O_7$ i.e. $H_2SO_4 + SO_3$ i.e. when SO_3 gas is saturated in H_2SO_4 solution, it is called oleum. Its percentage in terms of H_2SO_4 is always more than 100 %. The extra % is the mass of H_2O needed in order to react with SO_3 to form H_2SO_4 by the reaction

	SO_3	+	H_2O	$\rightarrow$	H_2SO_4
Mole →	1		1		1
Mass →	80 gm		18 gm		98 gm.

For example: 109 % oleum means 9 gm H_2O is required to react with 40 gm SO_3 to form H_2SO_4. Hence % of free SO_3 = 40 and H_2SO_4 (%) in oleum is 60.

Hardness of Water

- If water does not produce or produce a little-bit froth, with soap, then water is called hard.
- Hardness of water are two types. Temporary and Permanent. Temporary hardness is due to presence of bicarbonates of Ca and Mg while permanent hardness is due to presence of solute chlorides and sulphates of Ca ang Mg.
- Hardness is expressed in term of $CaCO_3$ i.e. no. of parts of $CaCO_3$ present per million parts by weight of H_2O (10^6 parts)

$$\text{Hardness in ppm} = \frac{\text{Mass of } CaCO_3}{10^6 \text{ gm of } H_2O}$$

IIT WINDOW–I

➤ Solved Numerical Problems

➤ Example 1.1

10 gm of a metal form 12 gm of its oxide on heating in air. Calculate the equivalent mass of that metal.?

➤ Solution

$$E_{\text{Metal}} = \frac{W_{\text{Metal}}}{W_{O_2}} \times 8$$

$$= \frac{10 \times 8}{(12 - 10)} = \frac{10 \times 8}{2} = 40 \textbf{ Ans.}$$

➤ Example 1.2

How much volume of water is required to dilute 500 ml. of $\frac{N}{2}$ HCl into decinormal?

➤ Solution

For dilution of any solution m.eq. of the solution in both the cases are the same. i.e

$$N_1 V_1 = N_2 V_2$$

$$\frac{1}{2} \times 500 = \frac{1}{10} \times V_2 \Rightarrow V_2 = 2500 \text{ cm}^3.$$

Hence volume of water added

$= (2500 - 500) = 2000$ ml or cm^3 **Ans.**

➤ Example 1.3

Calculate the no. of mole, molecules, atoms and electrons in 3.0 gm of C_2H_6.?

➤ Solution

No. of mole of C_2H_6 $= \frac{3}{-30} = 0.1$ mole

No. of molecules $= 0.1 \times 6.02 \times 10^{23}$
$= 6.02 \times 10^{22}$ molecules.

No. of atoms $= 0.1 \times 6.02 \times 10^{23} \times 8$
$= 4.816 \times 10^{23}$ atoms.

No. of electrons $= 0.1 \times 6.02 \times 10^{23} \times 18$
$= 10.836 \times 10^{23}$ electrons.

➤ Example 1.4

How many atoms, ions and electrons are present in 1.06 gm of Na_2CO_3?

➤ Solution

Mass of Na_2CO_3 given
$= 1.06$ gm

Molecular Mass of Na_2CO_3
$= 23 \times 2 + 12 + 16 \times 3$
$= 106$

No. of mole of $Na_2CO_3 = \frac{1.06}{106} = 0.01$ mole

Na_2CO_3 ionises as

$$Na_2CO_3 = 2\,Na^+ + CO_3^{2-}$$

No. of formula units of Na_2CO_3
$= 0.01 \times 6.02 \times 10^{23}$
$= 6.02 \times 10^{21}$

No. of atoms (Total)
$= 6.02 \times 10^{21} \times 6$
$= 3.612 \times 10^{22}$

No. of total ions $= 6.02 \times 10^{21} \times 3$
(cations & anions)
$= 18.069 \times 10^{21}$ **Ans.**

➤ Example 1.5

From 200 mg of CO_2, 10^{21} molecules of CO_2 are removed. Calculate the no. of mole of CO_2 left behind.?

➤ Solution

$$\text{Total mole of } CO_2 = \frac{200 \times 10^{-3}}{44.0}$$

$$= 4.545 \times 10^{-3}$$

$$\text{Mole of } CO_2 \text{ left} = 4.545 \times 10^{-3} - \frac{10^{21}}{6.02 \times 10^{23}}$$

$$= 4.545 \times 10^{-3} - 1.66 \times 10^{-3}$$

$$= 2.885 \times 10^{-3} \text{ mole } \textbf{Ans.}$$

➤ Example 1.6

Calculate the equivalent Mass of FeS in the following reaction.?

$$FeS + O_2 \xrightarrow{\Delta} Fe_2O_3 + SO_2$$

➤ Solution

In order to calculate equivalent mass of a substance, Let us calculate the no. of overall electrons required as

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$S^{2-} \rightarrow S^{+4} + 6e^-$$

$$\overline{FeS \rightarrow Fe^{3+} + S^{+4} + 7e^-}$$

$$\text{Thus, } E_{Fes} = \frac{\text{Mol. Mass}}{7} \textbf{ Ans.}$$

➤ Example 1.7

Calculate the equivalent Mass of $KMnO_4$ if following change is observed.?

$$3\ MnO_4^- \rightarrow Mn^{2+} + 2\ MnO_2$$

➤ Solution

It is a disproportion reaction hence equivalent mass is calculated by calculating the overall change in oxidation state per molecule.

Change in Oxidation State

$$= |1 \times 2 - 1 \times 7| + |2 \times 4 - 2 \times 7|$$

$$= |2 - 7| + |8 - 14| = 5 + 6 = 11$$

$$\therefore \quad \text{Change in O.S per molecule} = \frac{11}{3}$$

$$\therefore \quad E_{MnO_4^-} \text{ in this reaction} = \frac{M}{\frac{11}{3}} = \frac{3M}{11}$$

(Where M = Mol. Mass of $KMnO_4$)

➤ Example 1.8

Calculate the strenght of 20 'V' H_2O_2 in gm/litre.

➤ Solution

20 'V' H_2O_2 means '1' part H_2O_2 produce 20 parts 'O_2' at S.T.P.

As, $E_{H_2O_2} = \frac{34}{2} = 17.$

Using equation, volume strength

$= 5.6 \times N$

$$= 5.6 \times \frac{\text{strength in gm / litre}}{\text{Eq. Mass.}}$$

$\therefore$ strength in gm/litre = 60.86 **Ans.**

➤ Example 1.9

18.0 gm glucose present in 198 gm of its syrup having density 1.05 gm/m^3. Calculate molarity (M) molality (m) and mole fraction of solute.?

➤ Solution

Glucose ($C_6H_{12}O_6$) = 180

$$\text{Molarity } (M) = \frac{W_{\text{Glucose}} \times 1000}{M_{\text{Glucose}} \times V_{\text{Solution}}}$$

$$M = \frac{18 \times 1000 \times 1.05}{180 \times 198}$$

$$= 0.53 \text{ M}$$

$$\text{Molality } (m) = \frac{W_{\text{Glucose}} \times 1000}{M_{\text{Glucose}} \times W_{\text{Solvent}}}$$

$$= \frac{18 \times 1000}{180 \times (198 - 18)}$$

$$= 0.55 \text{ m}$$

Mole Fraction of Glucose

$$= \frac{n_{\text{Glucose}}}{n_{\text{Glucose}} + n_{H_2O}}$$

$$= \frac{\frac{18}{180}}{\frac{18}{180} + \frac{180}{18}} = \frac{0.1}{0.1 + 10}$$

$= 0.00990$ **Ans.**

➤ Example 1.10

What is the molarity of water at 4°C? **(IIT, 2003)**

➤ Solution

As we know water has density 1 gm ml^{-1} (Maximum) at 4°C.

$$\text{Molarity } (M) = \frac{W_{\text{Solute}} \times 1000}{M_{\text{Solute}} \times V_{\text{Solution}}}$$

$$\Rightarrow \quad M = \frac{1000 \times 1000}{18 \times 1000} = 55.56 \text{ mole L}^{-1} \textbf{ Ans.}$$

➤ Example 1.11

A plant virus is found to consists of uniform cylindrical particles of 150 A° in diameter and 5000 A° long. The specific volume of the virus is 0.75 cm^3/gm. If the virus is considered to be a single particle, find its molor mass. **(IIT, 1999)**

➤ Solution

Since the virus is cylindrical its volume = $\pi r^2 l$

$$= 3.14 \times \left(\frac{150}{2} \times 10^{-8}\right)^2 \times 5000 \times 10^{-8} \text{ cm}^3$$

$$= 8.8312 \times 10^{-17}\ \text{cm}^3$$

$$\text{Mass of one virus} = \frac{8.83 \times 10^{-17} \times 1}{0.75}\ \text{gm}$$

$$= 1.18 \times 10^{-16}\ \text{gm}$$

∴ Molecular Mass of Virus

$$= 1.18 \times 10^{-16} \times 6.023 \times 10^{23}$$

$$= 7.107 \times 10^{7}\ \text{gm mole}^{-1}$$ **Ans.**

➤ Example 1.12

If 200 gm of 20 % and 300 gm of 25 % solution of HCl are mixed together. Calculate the composition of mixture in terms of mass.?

➤ Solution

Mass percent means mass of solute per 100 gm of solution.

$$W_{\text{HCl}} \text{ in 20 \% solution} = \frac{20 \times 200}{100} = 40 \text{ gm}$$

$$W_{\text{HCl}} \text{ in 25 \% solution} = \frac{25 \times 300}{100} = 75 \text{ gm}$$

$$\text{Total } W_{\text{HCl}} = 40 + 75 = 115 \text{ gm}$$

Total Mass of Solution = 200 + 300 = 500.

$$\text{Mass \% in the mixture} = \frac{175}{500} \times 100$$

$$= 23\ \%$$ **Ans.**

➤ Example 1.13

Calculate the percentage of Fe^{2+} and Fe^{3+} in $Fe_{0.94}O$. (A non-stoichiometric oxide).

➤ Solution

Let overall oxidation state of Fe in $Fe_{0.94}O$ is x. Then

$$0.94 \times x - 2 = 0 \Rightarrow x = \frac{2}{0.94}$$

Again suppose the % of Fe^{2+} is x' and hence % of Fe^{3+} is $100 - x'$

Thus,

$$\frac{2}{0.94} \times 100 = x' \times 2 + (100 - x') \times 3$$

$$\Rightarrow \qquad x' = 87.21$$

∴ % of Fe^{2+} = 87.21

and % of Fe^{3+} = 100 – 87.21 = 12.786 **Ans.**

➤ Example 1.14

20 gm of a mixture of Na_2CO_3 and $CaCO_3$ is heated to a constant mass 1.5 gm. Calculate the composition of mixture?

➤ Solution

Since Na_2CO_3 does not decompose on heating, it is only $CaCO_3$ that decomposes as

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)\uparrow$$

And loss of mass is due to loss of CO_2 gas.

$$\underset{100}{CaCO_3} \xrightarrow{\Delta} \underset{56}{CaO} + \underset{44}{CO_2}$$

∴ 44 gm CO_2 ≡ 100 gm $CaCO_3$

$$\therefore \quad 0.5 \text{ gm } CO_2 \equiv \frac{100}{44} \times 0.5 = 1.136 \text{ gm}$$

$\text{Mass of}_{CaCO_3} = 1.136$ gm and $\text{Mass of}_{Na_2CO_3} = 0.864$ gm

➤ Example 1.15

6.0 gm sample of $CaCO_3$ reacts with 20 gm solution of HCl having 20% by mass of HCl (density = 1.10 gm/ml). Calculate percentage purity of $CaCO_3$ sample.?

➤ Solution

$$V_{\text{HCl solution}} = \frac{20}{1.1} = 18.18 \text{ cm}^3$$

$$N_{\text{HCl}} = \frac{W_{\text{HCl}} \times 1000}{M_{\text{HCl}} \times V_{\text{HCl}}} = \frac{4 \times 1000}{36.5 \times 18.18}$$

(Since 20 % of 20 gm = 4 gm.)

M.eq. of HCl ≡ M.eq. of $CaCO_3$

$$= \frac{4 \times 1000}{36.5 \times 18.18} \times 18.18 = 109.6$$

$$W_{CaCO_3} = \frac{M\text{.eq. of } CaCO_3}{1000} \times E_{CaCO_3}$$

$$= \frac{109.6}{1000} \times \frac{100}{2} = 5.48 \text{ gm}$$

$$\% \text{ Purity of sample} = \frac{5.48}{6} \times 100 = 91.33\ \%$$

➤ Example 1.16

100 cm^3 $\frac{M}{2}$ HCl, 200 cm^3 $\frac{M}{5}$ H_2SO_4, 200 cm^3 $\frac{M}{10}$ NaOH and 100 cm^3 $\frac{M}{2}$ $Ca(OH)_2$ are mixed together.

Calculate the normality of mixture and its nature?

➤ Solution

HCl ($N = M$), H_2SO_4 ($N = 2$ M)

NaOH ($N = M$) and $Ca(OH)_2$ ($N = 2$ M).

$$V_m N_m = (V_1 N_1 + V_2 N_2 + \cdots) - \left(V_1^1 N_1^1 + V_2^1 N_2^1 + \cdots\right)$$

Where $V_m = (V_1 + V_2 + \cdots) + \left(V_1^1 N_2^1 + \cdots\right)$

$$600\, N_m = \overset{\text{Acid}}{\left(100 \times \frac{1}{2} + 200 \times \frac{2}{5}\right)} - \overset{\text{Base}}{\left(200 \times \frac{1}{10} + 100 \times 1\right)}$$

$$= (50 + 80) - (20 + 100)$$

$$= 130 - 120 = 10$$

$$N_m = \frac{10}{600} = \frac{1}{60}$$

Since M.eq. of Acid is more, the nature of solution is acidic. **Ans.**

➤ Example 1.17

105 cm^3 $FeSO_4$ solution reacts with 150 cm^3 of $\frac{M}{2}$ $KMnO_4$ solution in acidic medium. Calculate the strength of $FeSO_4$ in gm litre^{-1}.

[Fe = 56, S = 32, O = 16]

➤ Solution

For $KMnO_4$ (acid medium), $N = 5M$ $\left(\because E = \frac{M}{5}\right)$

M.eq. of $FeSO_4$ is equal to M.eq. of $KMnO_4$.

$\therefore$ M.eq. of $KMnO_4$

$$= N \times V \text{ in ml}$$

$$= \frac{1}{10} \times 150 = 15$$

$$\equiv \text{M.eq. of } FeSO_4$$

$$W_{FeSO_4} = \frac{\text{M.eq.}}{1000} \times E_{FeSO_4}$$

$$W_{FeSO_4} = \frac{15}{1000} \times \frac{152}{1}$$ (Since Fe^{2+} is converted into Fe^{3+}, hence $E = \frac{M}{1}$)

$$W_{FeSO_4} = 2.28 \text{ gm}$$

$\therefore$ Strength in gm litre^{-1} = 21.71 **Ans.**

➤ Example 1.18

110 cm^3 of $K_2Cr_2O_7$ solution having molarity $\frac{M}{2}$ reacts with sufficient amount of HCl solution to liberate Cl_2 gas along with other products. Calculate the volume of Cl_2 gas at STP liberates.?

➤ Solution

$E_{K_2Cr_2O_7}$ in acidic medium = $\frac{M}{6}$

Hence $N = 6M$.

M.eq. of $K_2Cr_2O_7$ = M.eq. of Cl_2

$$\frac{1}{12} \times 110 = \text{M.eq. of } Cl_2$$

Volume of Cl_2 gas at STP

$$= \frac{110 \times 35.5 \times 22.4}{12 \times 1000 \times 71} = 0.1026 \text{ litre}$$ **Ans.**

➤ Example 1.19

50 ml of a mixture of NaOH and Na_2CO_3 diluted to 200 ml, 25 ml of this solution require 12 ml $\frac{N}{10}$ HCl

(a) 2 mole (b) 1 mole
(c) 0.5 mole (d) 0.25 mole

7. An ionic compound is represented by the formula M_xN_y, the total no. of ions formed is equal to

(a) M^{x+} (b) M^{y+}
(c) M^{x+y} (d) $x + y$

8. A sentence contains 35 alphabets and written in a line. One page contain 35 lines. The mass of carbon needed to write this page if one alphabet contains 10^{16} carbon atoms is approximately

(a) 2.44×10^{2} gm (b) 2.44×10^{-2} gm
(c) 2.44×10^{-3} gm (d) 2.44×10^{-4} gm

9. A sample of lime stone have 75 % purity. If 5 gm sample is used, the no. of CaO formula units present is:

(a) 6.02×10^{23} (b) 6.02×10^{22}
(c) 4×10^{22} (d) 4×10^{23}

10. If 10^{22} molecules of CH_4 is effused out from a vessel in which 16.0 gm CH_4 is taken, the no. of molecules of CH_4 in the vessel is:

(a) 6.02×10^{1} (b) 60.2×10^{1}
(c) 59.2×10^{22} (d) 59.2

11. If a person inhale 10^{20} oxygen atom per sec. The volume of oxygen gas (O_2) inhaled by the person in a day at STP is:

(a) 16.06 litre (b) 16.06×10^{-5} litre
(c) 16.06×10^{-2} litre (d) 16.06×10^{1} litre

12. The density of CCl_4 vapour in gm/L at STP will be

(a) 3.425 (b) 6.875
(c) 10.252 (d) 4.575

13. If air contains 21 % O_2 by volume. The number of atoms of oxygen per litre of air at STP is:

(a) 3.8×10^{23} (b) 0.38×10^{23}
(c) 38×10^{23} (d) None of these

14. How many moles of electrons weigh one kilogram

(a) 6.02×10^{23}

(b) $\dfrac{1}{9.108} \times 10^{31}$

(c) $\dfrac{6.02}{9.108} \times 10^{54}$

(d) $\dfrac{1}{9.108 \times 6.022} \times 10^{8}$ **[IIT, 2002]**

15. The number of atoms of Na in 5 a.m.u of it is? [Na = 23]

(a) 23 (b) 5
(c) 5/23 (d) 23/5

16. The number of electrons present in 5.6 litre of H_2 gas at S.T.P. is?

(a) 6.02×10^{23} (b) 3.012×10^{23}
(c) 12.04×10^{23} (d) 3.0×10^{10}

17. The total cationic charge in coulomb present in 46 gm of Al_2O_3 is?

(a) 26.07×10^{4} C (b) 2.607×10^{4} C
(c) 260.7×10^{4} C (d) 2.6×10^{8} C

18. The number of O_2 molecule and its volume at S.T.P in 50.6 gm of hydrated sodium carbonate ore:

(a) 6.926×10^{23}, 22.4 litre
(b) 5.92×10^{21}, 25.76 litre
(c) 6.926×10^{23}, 25.76 litre
(d) 5.92×10^{21}, 22.4 litre

19. The volume of CO_2 contains the same no. of molecules as in 5 gm of CH_4 is:

(a) 5 litre of CO_2 (b) 7 litre of CO_2
(c) 9 litre of CO_2 (d) 3 litre of CO_2

20. 10.0 gm of CO on buring in air gives the product which have the number of nucleons

(a) 9.47×10^{23} (b) 94.7×10^{23}
(c) 947×10^{23} (d) None

HINTS AND SOLUTIONS: IIT WINDOW–II

➤ Multiple Choice Question (with one correct option)

1. No. of atoms in 10 gm $CaCO_3$

$$= \frac{10}{100} \times 6.02 \times 10^{23} \times 5$$

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

No. of atoms in 2.24 litre of CO_2

$= \frac{2.24}{22.4} \times 6.02 \times 10^{23} \times 3$

$= 1.86 \times 10^{23}$ atoms

No. of atoms in 2 mole of H_2
$= 2 \times 6.02 \times 10^{23} \times 2$
$= 12.08 \times 10^{23}$ atoms

No. of atoms in 5 gm-atom of
$Na_2CO_3 = 5 \times 6.02 \times 10^{23} \times 6$
$= 18.07 \times 10^{24}$ atoms

2. No. of gm-atom (mole) of Na $= \frac{2 \times 10^{23}}{6.02 \times 10^{23}}$

$= 0.33$

3. No. of molecules in 0.1 mole of $CO_2 = 0.1 \times N_A$
$= 0.1\ N_A$

No. of molecules in 11.2 litre of CO_2 at STP

$= \frac{11.2}{22.4} \times N_A = 0.5\ N_A$

No. of molecules in 22 gm $CO_2 = \frac{22}{44} \times N_A$

$= 0.5\ N_A$

No. of molecules in 22.4×10^3 ml CO_2 at STP

$= \frac{22.4 \times 10^3}{2.24 \times 10^4}\ N_A = N_A$

4. No. of molecules in 1.6 gm $CH_4 = \frac{1.6}{16} \times N_A$

$= 0.1\ N_A$

No. of molecules in 22.4 litre of CH_4 at S.T.P

$= \frac{22.4}{22.4} N_A = N_A$

No. of molecules in 2-gm-mole of CH_4
$= 2N_A$

No. of molecules in 22400 cm^3 CH_4 at S.T.P.

$= \frac{22400}{22400} N_A = N_A$

5. Mass of H_2O = Volume × density $= 0.06 \times 1$
$= 0.06$ gm/ml.

No. of molecules of $H_2O = \frac{0.06}{18} \times N_A$

$= 3.33 \times 10^{-3} \times 6.02 \times 10^{23}$
$= 2 \times 10^{21}$

6. $2Al + 3/2O_2 \rightarrow Al_2O_3$
2 mole — 1 mole
2×27 gm — $2 \times 27 + 16 \times 3$
$\therefore$ 27 gm Al $\equiv 0.5$ mole of Al_2O_3

7. $M_xN_y = xM^{y+} + yN^{x-}$
Total no. of ions $= x + y$.

8. Total No. of alphabets in a page $= 35 \times 35$
$= 1225$

Total No. of carbon atoms $= 1225 \times 10^{16}$ atoms

Mass of carbon $= \frac{1225 \times 10^{16}}{6.02 \times 10^{23}} \times 12$ gm

$= 2.44 \times 10^{-4}$ gm

9. Mass of pure CaO in the sample $= \frac{5 \times 75}{100}$

$= 3.75$ gm

No. of formula units $= \frac{3.75}{56} \times N_A$

$= 0.4 \times 10^{23}$

10. 16.0 gm $CH_4 = 6.02 \times 10^{23}$ molecules of CH_4
No. of CH_4 molecules left $= 6.02 \times 10^{23} - 10^{22}$
$= 10^{22}(6.02 \times 10^{-1})$
$= 59.2 \times 10^{22}$

11. No. of oxygen atom inhaled per day
$= 10^{20} \times 60 \times 60 \times 24$ atoms
No of molecules of O_2 gas

$= 10^{20} \times 60 \times 60 \times 24 \times \frac{1}{2}$

$= 4.32 \times 10^{24}$ molecules
Volume of O_2 gas at STP

$= \frac{4.32 \times 10^{24}}{6.02 \times 10^{23}} \times 22.4$ litre

$= 16.04 \times 10^{1}$ litre.

12. density $= \frac{\text{Mass}}{\text{Volume}} = \frac{12 + 35.5 \times 4}{22.4}$

$= 6.875$ gm/litre

13. Volume of O_2 per litre of air $= 0.71$ litre

No. of 'O' atom per litre

$= \frac{0.71}{22.4} \times 6.02 \times 10^{23} \times 2$

$= 0.38 \times 10^{23}$

14. Mass of 1 electron = 9.108×10^{-31} kg

$$\Rightarrow 9.108 \times 10^{-31}\text{ kg} = \frac{1}{6.023 \times 10^{23}} \text{ mole of electron}$$

$$\therefore 1\text{ kg} = \frac{1}{6.023 \times 9.108 \times 10^{23} \times 10^{-31}} \text{ mole of } e^-$$

$$= \frac{10^8}{6.023 \times 9.108} \text{ mole of } e^-$$

15. 1 amu = one twelfth the mass of one atom of C^{12}

Na has atomic mass 23 i.e. one atom of Na weighs 23 amu.

$\therefore$ No. of atoms in 5 amu = 5/23 atom

16. No. of electrons in 5.6 litre of H_2 at S.T.P

$$= \frac{5.6}{22.4} \times 6.023 \times 10^{23} \times 2$$

(Since 1 molecule of $H_2 = Ze^-$)

$$= 3.012 \times 10^{23}$$

17. $Al_2O_3 = 27 \times 2 + 16 \times 3 = 102$

Total cationic charge

$$= \frac{46}{102} \times 6.02 \times 10^{23} \times 2 \times 3 \times 1.6 \times 10^{-19}$$

$$= 26.07 \times 10^4 \text{ coulomb.}$$

18. Hydrated Sodium Carbonate = $Na_2CO_3 \cdot 10H_2O$

Its molecular mass = 106 + 180 = 286

$$\therefore \quad \text{No. of mole} = \frac{50.6}{286}$$

$\therefore$ No. of O_2 molecule in the above mole

$$= \frac{50.6}{286} \times 6.02 \times 10^{23} \times \frac{13}{2} \text{ molecules}$$

$= 6.926 \times 10^{23}$ molecules

Volume of O_2 gas of S.T.P

$$= \frac{6.926 \times 10^{23}}{6.02 \times 10^{23}} \times 22.4 \text{ litre}$$

$= 25.76$ litre

19. No. of molecules in 5 gm CH_4

$$= \frac{5}{16} \times 6.02 \times 10^{23}$$

$$\therefore \quad \frac{5}{16} \times 6.02 \times 10^{23} \text{ molecules of } CO_2$$

$$= \frac{5 \times 6.02 \times 10^{23}}{16 \times 6.02 \times 10^{23}} \times 22.4 \text{ litre of } CO_2$$

$= 7$ litre of CO_2

20.
$$\begin{array}{lcccc} CO & + & \frac{1}{2}O_2 & \rightarrow & CO_2 \\ 1\text{ mole} & & & & 1\text{ mole} \\ 28\text{ gm} & & & & 44\text{ gm} \end{array}$$

$$10\text{ gm CO} = \frac{44}{28} \times 10 \text{ gm } CO_2$$

$$= \frac{44 \times 10}{28 \times 44} \text{ mole } CO_2$$

$$= \frac{44 \times 10}{28 \times 44} \times 6.02\ 10^{23} \text{ molecules of } CO_2$$

$$= \frac{44 \times 10 \times 6.02 \times 10^{23}}{28 \times 44} \times 44 \text{ nucleons}$$

$= 94.647 \times 10^{23}$ nucleons

(Total *n* and *p* which are present in the nucleus are called nucleons.)

➤ (B) ON EQUIVALENT CONCEPT

1. Equivalent mass of a metal, *x* gm of which reacts with 1-gm-equivalent of an acid is?

   (a) 1 (b) *x*/2
   (c) 2*x* (d) *x*

2. An element (*x*) having equivalent mass '*E*' forms a general oxide $X_m O_n$. The atomic mass of an element should be?

   (a) $\frac{2E_n}{n}$ (b) $2mE_n$
   (c) E/n (d) $\frac{ME}{2n}$

3. 5.0 gm of a metal reacts with oxygen to form 5.6 gm of its oxide. The eq. Mass of metal is?

   (a) 33.33 (b) 66.66
   (c) 99.99 (d) 44.44

4. 8.6 gm of an element when treated with excess of acid produce 1900 ml of H_2 gas at S.T.P. The equivalent mass of metal is?

   (a) 48.69 (b) 58.69
   (c) 50.69 (d) 56.69

5. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, if molecular mass of NH_3 and N_2 are M_1 and M_2, their equivalent masses are E_1 and E_2 respectively, then $E_1 - E_2$ is:

(a) $\frac{2M_1 - M_2}{6}$ (b) $M_1 - M_2$

(c) $3M_1 - M_2$ (d) $M_1 - 3M_2$

6. In the reaction

$FeS_2 + KMnO_4 + H^+ \rightarrow Fe^{3+} + SO_2 + Mn^{2+} + H_2O$

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) $\frac{\text{Molar Mass}}{13}$

7. Equivalent mass of *S* in SCl_2 is 16. What is the equivalent weight of *S* in S_2Cl_2 (S = 32, Cl = 35.5)

(a) 16 (b) 32

(c) 8 (d) 64

8. The equivalent weight of $MnSO_4$ is half of its molecular weight when it is converted to:

(a) Mn_2O_3 (b) MnO_2

(c) MnO_4 (d) MnO_4^{2-}

[IIT, 1988]

9. 14.2 gm of M_2CO_3 on heating produce 8.6 gm of MO. The equivalent mass of M is

(a) 25.78 (b) 21.23

(c) 27.9 (d) 32.5

10. 0.65 gm Zn treated with H_2SO_4 to form its sulphate with the liberation of H_2 gas. The $ZnSO_4$ on strong heating produce 0.81 gm of its oxide. The equivalent mass of Zn is:

(a) 65 (b) 32.5

(c) 16.25 (d) 36

11. The ratio of the equivalent mass of $KMnO_4$ in acidic and alkaline medium is

(a) 1 (b) $\frac{1}{5}$

(c) $\frac{1}{4}$ (d) $\frac{1}{8}$

12. The equivalent Mass of MnO_4^- in the following reaction is:

$$3MnO_4 \rightarrow 2Mn^{2+} + MnO_2$$

(a) $\frac{3\,M}{13}$ (b) $\frac{3\,M}{11}$

(c) $\frac{13\,M}{3}$ (d) $\frac{M}{11}$

13. The equivalent mass of H_3BO_3 in its reaction with NaOH to from $Na_2B_4O_7$ is equal to

(a) M/4 (b) M/3

(c) M/2 (d) M

14. 6.35 gm of Cu is displaced by a metal (2.9 gm) when added in its sulphate solution. If equivalent mass of Cu is 31.5, The equivalent mass of metal is:

(a) 19.5 (b) 14.4

(c) 24.8 (d) 20.5

15. 2 gm metal '*X*' on reaction with sufficient Acid produce 1120 cm^3 H_2 gas at STP. Its equivalent mass is:

(a) 10 (b) 20

(c) 30 (d) 40

HINTS AND SOLUTIONS: ON EQUIVALENT CONCEPT

1. That mass of metal is called equivalent mass which reacts with 1-gm-equivalent of an acid.

2. As we know,

Equivalent Mass of $X = \frac{\text{Atomic Mass}}{\text{Valency}}$

$\Rightarrow \quad E = \frac{\text{Atomic Mass}}{n}$

$\Rightarrow$ Atomic Mass = En.

Since oxygen have valency 2, hence $m = 2$

$\Rightarrow \quad En = \frac{2\,En}{m}$

3. Equivalent Mass

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

$= \frac{5}{0.6} \times 8 = 66.66$

4. Equivalent Mass

$$= \frac{\text{Mass of metal}}{\text{Vol. of } H_2 \text{ gas at S.T.P.(litre)}} \times 11.2$$

$$= \frac{8.6}{1.9} \times 11.2 = 50.69$$

5. $E_1(NH_3) = \frac{M_1}{3}, E_2(N_2) = \frac{M_2}{6}$

$$E_1 - E_2 = \frac{M_1}{3} - \frac{M_2}{6} = \frac{2M_1 - M_2}{6}$$

6.

$$\begin{array}{l} Fe_2 + \rightarrow Fe^{3+} + e \\ (S_2)^{-2} \rightarrow 2S^{4+} + 10e^- \\ \hline FeS_2 \rightarrow Fe^{3+} + 2S^{4+} + 11e^- \end{array}$$

$\therefore \quad E_{FeS_2} = \frac{M}{11}$ (M = Molar Mass of FeS_2)

7. In SCl_2,
One mole of S combine with 2 mole of Cl and
1 equivalent of $S \equiv$ 1 mole of Cl
$\therefore \quad E_{Cl} = 1 \times 35.5 = 35.5$
In S_2Cl_2
2 mole of Cl $\equiv$ 2 mole of S
1 equivalent of Cl $\equiv$ 1 mole of S
$E_s = 1 \times 32 = 32$

8. $MnSO_4^{2+} \rightarrow MnO_2^{+4}$

Change in oxidation state of Mn = 2

$$\therefore \quad E_{MnSO_4} = \frac{M}{2}$$

9. $\frac{\text{Wt. of } M_2CO_3}{\text{Wt. of MO}} = \frac{E_{M_2CO_3}}{E_{MO}}$

$$\frac{14.2}{8.6} = \frac{E_M + 30}{E_M + 8}$$

$$\Rightarrow \quad E_m = 25.78$$

10. $\frac{W_{Zn}}{E_{Zn}} = \frac{W_{ZnO}}{E_{Zn} + E_{O^{2-}}} \Rightarrow \frac{0.65}{E_{Zn}} = \frac{0.81}{E_{Zn} + 8}$

$$\Rightarrow \quad E_{Zn} = 32.5$$

11. $E_{KMnO_4}(\text{acidic}) = \frac{\text{Mol. Mass}}{5}$

$$E_{KMnO_4}(\text{alkaline}) = \frac{\text{Mol. Mass}}{1}$$

$$\therefore \quad \frac{E_{KMnO_4}(\text{acidic})}{E_{KMnO_4}(\text{Alkaline})} = \frac{1}{5}$$

12. $3\,MnO_4^- \rightarrow 2\,Mn^{2+} + MnO_2$

$$\begin{aligned} \text{Change in O.S.} &= |2\times2 - 2\times7| + |1\times4 - 1\times7| \\ &= |4-14| + |4-7| \\ &= 10 + 3 = 13 \end{aligned}$$

Change in O.S per molecule = $\frac{13}{3}$

$$\therefore \quad E_{MnO_4^-} = \frac{3\,M}{13}$$

13. $4H_3^{+3}BO_3 + 2NaOH \rightarrow Na_2B_4^{+3}O_7 + 7H_2O$

Change in O.S of Beron is not observed hence

$$E_{H_3BO_3} = \frac{M}{1}$$

14. $\frac{W_{Cu}}{W_{Metal}} = \frac{E_{Cu}}{E_{metal}}$

$$\Rightarrow \frac{6.35}{2.9} = \frac{31.5}{E_{Metal}}$$

$$\Rightarrow E_{metal} = \frac{31.5 \times 2.9}{6.35} \simeq 14.4.$$

15. E_{Metal}

$$= \frac{\text{Mass of metal}}{\text{Vol. of } H_2 \text{ gas at STP(in ml)}} \times 11200$$

$$= \frac{2}{1120} \times 11200 = 20$$

➤ (C) ON Atomic and Molecular Mass

1. 30 gm of an oxide of divalent metal is converted to its chloride completely. The mass of chloride is found to be 5.0 gm. The atomic mass of metal is?

(a) 33.25	(b) 66.5
(c) 99.75	(d) 40.25

2. 2.492 gm of ZnO is produced when 2 gm pure Zn metal is oxidised in air. If the atomic mass of oxygen is 16, What will the atomic mass of Zn?

(a) 63.0	(b) 65.0
(c) 64.0	(d) 66.0

3. Chlorine exist in two isotopic forms Cl^{35} and Cl^{37}. The ratio of the percentage of Cl^{35} and Cl^{37} is? [If average atomic Mass is given as 35.5 a.m.u.]

(a) 1 : 1 (b) 2 : 1
(c) 3 : 1 (d) 4 : 5

4. 216.0 gm of metal oxide when reduced by carbon produce metal along with a poisoneous gas which on passing through ammonical cuprous chloride, the rise in mass observed is 28.0 gm. What is the atomic mass of metal?

(a) 64.0 (b) 200.0
(c) 216.0 (d) 244.0

5. 2.6 gm of metal when treated with 1120 cm^3 O_2 at S.T.P. and the product when passed through alkaline pyragallol solution, its mass increases by 0.5 gm. The Atomic Mass of metal is?

(a) 41.6 (b) 36.5
(c) 35.5 (d) 40.5

6. 5.6 gm of iron is oxidised by 4.4 gm of CO_2 in a closed retort at 450°C into Fe^{2+} and a poisoneous gas is released. If atomic mass of oxygen is 16 the atomic mass of Fe is:

(a) 28 (b) 32
(c) 56 (d) 58

7. Vapour density of a chloride of non metal is 104.25. The non metal is a member of 15th group. The non metal is?

(a) N (b) P
(c) As (d) Sb

8. M_2S and Hg_2S are isomorphous with each other and the percentage of *S* in both the compounds are respectively 20 and 8 % respectively. If atomic Mass of Hg is 200.0, atomic mass of '*M*' is:

(a) 72.52 (b) 61.28
(c) 168.6 (d) 69.56

9. 5 gm of a pure metal produce 5.8 gm of its oxide on heating in air. If the specific heat of metal is 0.06 cal/gm. Its exact atomic mass would be:

(a) 106.66 (b) 50
(c) 100 (d) 90

10. Two elements A and B combine to form two compounds A_2B_3 and AB_3. If 0.2 mole of both the compound weighs 20 gm and 15.0 gm respectively. The atomic mass of A and B are:

(a) 40 & 25 (b) 25 & 16.66
(c) 25.2 & 16.0 (d) 20.22 & 18.0

11. 0.5 gm of a gas have volume 250 cm^3 at 600 mm of Hg at 300 k. Its molecular mass would be:

(a) 48.2 (b) 62.4
(c) 56.28 (d) 72.2

12. Duma's bulb is filled with a compound at 27°C and 720 mm of Hg weighs 0.5 gm. The molecular mass of compound is

(a) 92.0 (b) 108
(c) 118 (d) 120

13. 0.607 gm of a silver salt of tribasic acid is reduced to 0.370 gm pure silver. The molecular mass of acid would be: (Ag = 108)

[AIEEE '08]

(a) 210.0 (b) 180.0
(c) 192.0 (d) 160.0

14. 0.15 gm of a volatile compound taken in a Victor-Meyer apparatus and it displaces 40 cm^3 of air measured at 27°C and 720 mm of Hg. if aq. tension at 27° C is 10 mm Hg, the molecular mass of compound is:

(a) 198.8 (b) 160.2
(c) 140.6 (d) 98.8

15. Chlorophyll contains 0.025 % Mg by mass. Then the probable molecular mass of chlorophyll is: (If one molecule of chlorophyll contain one Mg atom).

(a) 96000 (b) 56000
(c) 25000 (d) 12696

HINTS AND SOLUTIONS: ON ATOMIC AND MOLECULAR MASS

1. $$\frac{W_{\mathrm{MO}}}{W_{\mathrm{MCl_2}}} = \frac{E_{\mathrm{M}} + E_{\mathrm{O^{2-}}}}{E_{\mathrm{M}} + E_{\mathrm{Cl^-}}}$$

$$\Rightarrow \frac{3.0}{5.0} = \frac{E_M + 8}{E_M + 35.5} \Rightarrow E_{\mathrm{m}} = 33.25$$

$$\text{Atomic Mass} = \text{Eq. Mass} \times \text{Valency}$$
$$= 33.25 \times 2 = 66.5$$

2. $$\frac{W_{\text{Zn}}}{W_{\text{Oxygen}}} = \frac{\text{Atomic Mass of Zn}}{\text{Atomic Mass of oxygen}}$$

$$= \frac{2.0}{0.492} = \frac{x}{16} \Rightarrow \quad x = 65.04$$

Atomic Mass of Zn = 65.04

3. Let % of $Cl^{35} = x$, $\therefore$ % of $Cl^{37} = 100 - x$

Then $100 \times 35.5 = x \times 35 + (100 - x)\,37$

$\Rightarrow \quad x = 75\ \%$

% of Cl^{35} = 75, & % of Cl^{37} = 25

$$\therefore \quad \frac{\%\,Cl^{35}}{\%\,Cl^{37}} = \frac{75}{25} = 3$$

4. CO is absorbed in ammonical Cu_2Cl_2 solution and increase in mass is the mass of CO.

$\therefore$ Mass of CO = 28 gm

$\therefore$ Mass of oxygen in it = 16 gm

$$\therefore \quad \frac{W_{\text{Metal oxide}}}{W_{\text{Oxygen}}} = \frac{\text{Atomic Mass of Metal}}{\text{Atomic Mass of oxygen}}$$

$$\Rightarrow \quad \frac{216 - 16}{16} = \frac{\text{Atomic Mass of Metal}}{16}$$

$\Rightarrow$ Atomic Mass of metal = 200.0

5. The increase of mass of alkaline pyragallol is due to absorption of on reacted O_2 gas.

$$\text{Total Mass of } O_2 = \frac{32 \times 1120}{22400} = 1.5 \text{ gm}$$

Mass of O_2 reacted with metal = 1.5 – 0.5
= 1.0 gm

$$\frac{W_{\text{metal}}}{W_{O_2}} = \frac{\text{Atomic Mass of metal}}{\text{Atomic Mass of } O_2}$$

$$\Rightarrow \quad \frac{2.6}{1.0} = \frac{\text{Atomic Mass of metal}}{16}$$

$$\Rightarrow \quad \text{Atomic Mass of metal} = \frac{16 \times 2.6}{1.0}$$

$$= 41.6$$

6.

	Fe	+	CO_2	→	FeO	+	CO
Given	5.6		4.4		7.2		

$$\text{Eq. Mass of Fe} = \frac{5.6}{1.6} \times 8 = 28$$

$\therefore$ Atomic Mass of Fe = 2 × 28 = 56

[Since change in O.S of Fe = 2]

7. Since non metal is a member of 15th group, it means its valency is either 3 or 5 and Molecular Mass is twice of V.D. so, it must be 208.5 gm/mole. It is possible only when valency is 5.

MCl_5 = Atomic Mass of $M + 5 \times 35.5$

$\Rightarrow \quad 208.5$ = Atomic Mass of $M + 5 \times 35.5$

Atomic Mass = 31. (It must be *P*).

8. For Isomorphous compounds

$$\frac{\text{Wt. of Metal in compound Ist}}{\begin{array}{l}\text{Wt. of mental in compound IInd}\\ \text{that reacts with same mass of anion as in Ist}\end{array}}$$

$$= \frac{\text{At. Mass of metal I}}{\text{At. Mass of metal II}}$$

$$\Rightarrow \quad \frac{92}{32} = \frac{200}{\text{Atomic Mass of metal '}M\text{'}}$$

$$\Rightarrow \quad \text{Atomic Mass of metal '}M\text{'} = \frac{200 \times 32}{92}$$

$$= 69.56$$

9. $$\text{Approx. at mass} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.06} = 106.66$$

$$E_{\text{metal}} = \frac{5}{0.8} \times 8 = 50.$$

$$\therefore \quad \text{Valency} = \frac{106.66}{50} \simeq 2$$

Exact at mass = Eq. Mass × Valency
= 50 × 2 = 100

10. According to question,

$$2x + 3y = 20 \times 5$$

$$x + 3y = 15 \times 5$$

$$\Rightarrow \quad x = 25 \text{ and } y = 16.66$$

When x = Atomic Mass of A, y = Atomic Mass of B.

11. use $$PV = \frac{W}{M} RT.$$

$$\Rightarrow \quad M = \frac{W}{PV} RT$$

$$= \frac{0.5 \times 00821 \times 300}{\frac{600}{760} \times \frac{250}{1000}}$$

$\simeq$ 62.4. **Ans.**

12. As we know

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$\therefore$ Volume of vapour at S.T.P

$$= \frac{720 \times 120 \times 273}{300 \times 760}$$

$= 103.45 \text{ cm}^3$

Since $103.45 \text{ cm}^3 \equiv 0.5$ gm

$$\therefore \quad 22400 \text{ cm}^3 \equiv \frac{0.5 \times 22400}{103.45}$$

$$= 108.26 \text{ gm/mole}$$

13. $$\frac{M_{\text{silver}}}{\text{Atomic Mass of Ag}} = \frac{3 \times S_{\text{silver salt}}}{\text{Mol. Mass of salt}}$$

$$\Rightarrow \quad \frac{0.37}{108} = \frac{3 \times 0.607}{\text{Mol. Mass of Ag salt}}$$

$\Rightarrow$ Mol. Mass of silver salt = 531.0

$\therefore$ Mol. Mass of tribasic acid = 531 – 324 + 3 = 210.

14. Press of dry gas = (720 – 10) = 710 m.m. of Hg

Volume of air at STP is calculated by $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\Rightarrow \quad V_1 = \frac{P_2V_2 \times T_1}{T_2 \times P_1} = \frac{710 \times 40 \times 273}{300 \times 760}$$

$= 34 \text{ cm}^3$

$34 \text{ cm}^3 \simeq 0.15$ gm volalite substance

$$\therefore \quad 22400 \text{ cm}^3 \equiv \frac{0.15 \times 22400}{34} = 98.8$$ **Ans.**

15. Chlorophyll contain 0.025 % Mg by Mass

0.025 gm Mg ≡ 100 gm chlorophyll

$$24 \text{ gm Mg} \equiv \frac{100 \times 24}{0.025} = 96000 \text{ gm}$$

Molecular Mass = 96000 gm/mole

➤ (D) On Volumetric Analysis

1. The volume of H_2O added in order to convert 50 cm^3 of $\frac{N}{2}$ H_2SO_4 solution into decinormal is:

(a) 200 cm^3 (b) 250 cm^3
(c) 100 cm^3 (d) 50 cm^3

2. Fuming HNO_3 have specific gravity 1.90 and it is 92 % pure by mass. The volume of this sample HNO_3 required to prepare 250 ml $\frac{N}{5}$ solution is:

(a) 2.5 cm^3 (b) 2.0 cm^3
(c) 1.8 cm^3 (d) 1.5 cm^3

3. Molarity of 560 gm pure H_2O at 4° C is:

(a) 40 (b) 4
(c) 55.5 (d) 44.5

4. The mole fraction of solute in 1 molal aqueous solution is:

(a) 0.0176 (b) 1.8
(c) 0.05 (d) 0.92

5. 0.7 g of $Na_2CO_3 \cdot xH_2O$ is dissolved in 100 cm^3 of H_2O, 5.0 cm^3 of which required 19.8 ml of 0.1 N HCl. The value of x is?

(a) 4 (b) 3
(c) 2 (d) 1

6. 100 cm^3 M/2 H_2SO_4, 200 ml $\frac{M}{5}$ HNO_3 and 100 cm^3 of $\frac{M}{5}$ HCl are mixed together. The normality of mixture is:

(a) 0.5 (b) 0.2
(c) 0.3 (d) 0.4

7. 200 ml $\frac{M}{2}$ HNO_3, 100 ml $\frac{M}{1}$ NaOH, 200 ml $\frac{M}{5}$ HCl are mixed together. The normality and the nature of mixture is:

(a) 0.28, basic (b) 0.28, acidic
(c) 0.32, acidic (d) 0.32, basic

8. The mass of 60% HCl required for the neutralisation of 10L of 0.1MKOH is:

(a) 60.8 g (b) 21.9 gi
(c) 100 gu (d) 219 gn

9. 50 ml of 10 N H_2SO_4, 25 ml of 12 N HCl and 40 ml of SN HNO_3 were mixed together and the volume of mixture was made up to 1000 ml by adding water. The normality of resulting solution is:

(a) 1 N (b) 2 N
(c) 3 N (d) 4 N

10. The normality of a solution of a mixture containing HCl and H_2SO_4 is N/5. 20 ml of this solution reacts with excess of $AgNO_3$ solution to give 0.287 gm of AgCl. The normality of HCl solution is:

(a) 0.10 (b) 0.20
(c) 0.15 (d) 0.50

11. A solution mixture containing 0.5 M $CaSO_4$, 0.2 M $MgCl_2$ and 0.4 M $Al_2(SO_4)_3$. The total ionic strength is:

(a) 8.3 (b) 9.3
(c) 10.3 (d) None of these

12. An aqueous solution of 6.3 g. Oxallic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely to neutralise 10 ml of this solution is: **[IIT, 2001]**

(a) 40 ml (b) 20 ml
(c) 10 ml (d) 4 ml

13. How many moles of electron weighs 1 kg.

(a) 6.023×10^{23}

(b) $\dfrac{1}{9.108} \times 10^{23}$ (c) $\dfrac{6.023 \times 10^{54}}{9.108}$

(d) $\dfrac{1}{9.108 \times 6.023} \times 10^{8}$

14. 100 ml 0.1 M $KMnO_4$ solution neutralises 50 ml $FeSO_4$ solution in acidic medium. The mass of $FeSO_4$ is: [Fe = 56, S = 32, O = 16]

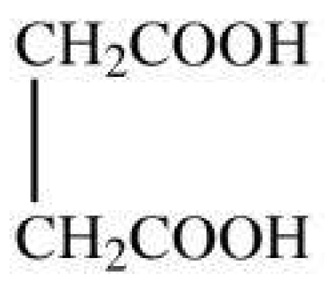
(a) 5 gm (b) 6.2 gm
(c) 7.6 gm (d) 8.6 gm

15. One gm Zn sample is dissolved in 250 ml 0.1 N H_2SO_4 solution and the excess of H_2SO_4 is neutralised by 100 ml $\frac{N}{50}$ NaOH solution. The % purity of sample is:

(a) 25 % (b) 50 %
(c) 75 % (d) 90 %

16. 100 ml a dibasic acid contains 2.94 gm acid 25 ml of this solution requires 15 ml normal NaOH for neutralisation using methyl orange as an indicator. The acid would be:

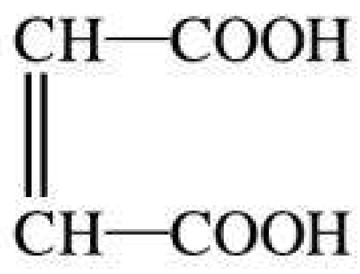
(a) HCOOH

(b)


$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$

(c)


$\begin{array}{l} COOH \\ | \\ COOH \end{array}$

(d)


$\begin{array}{l} CH{-}COOH \\ \| \\ CH{-}COOH \end{array}$

17. How many litre of conc. HCl of specific gravity 1.2 gm/ml containing 40% by strength HCl will be required to prepare 2 litre of $\frac{N}{10}$ solution?

(a) 0.125 litre (b) 0.1825 litre
(c) 0.525 litre (d) 0.25 litre

18. 1.25 gm of a sample of bleaching powder is dissolved in 250 cm^3 of H_2O and 25 ml of this solution reacts with KI solution. The Iodine liberated requires 12.5 cm^3 of $\frac{N}{25}$ hypo solution. The % of available chlorine in the sample of bleaching powder is:

(a) 5.68 % (b) 10.25
(c) 14.2 % (d) 16.8 %

19. The no. of moles of $KMnO_4$ that will needed to react completely with one mole of ferrous oxalate in acidic solution is? **[IIT, 1997]**

(a) 3/5 (b) 2/5
(c) 4/5 (d) 1

20. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ions in acidic solution is **[IIT, 1997]**

(a) 2/5 (b) 3/5
(c) 4/5 (d) 1

HINTS AND SOLUTIONS: ON VOLUMETRIC ANALYSIS

1. From the law of equivalence
We have $V_1N_1 = V_2N_2$

$$50 \times \frac{1}{2} = V_2 \times \frac{1}{10}$$

$$V_2 = 250 \text{ cm}^3$$

Volume of H_2O added $= 250 - 50 = 200 \text{ cm}^3$

2. HNO_3 sample is 92% pure

i.e. 100 gm sample contain 92 gm HNO_3

i.e. $\frac{100}{1.90}$ cm^3 sample contain 92 gm HNO_3

$$N_{HNO_3 \text{ sample}} = \frac{92 \times 1000}{63 \times 100} \times 1.90 = 27.75$$

From law of equivalence,

We have $N_1V_1 = N_2V_2$

$$27.75 \times V_1 = \frac{1}{5} \times 250 \Rightarrow \quad V_1 = \frac{50}{27.75}$$

$$= 1.80 \text{ cm}^3$$

3. $M = \dfrac{W \times 1000}{\text{Mol. Mass} \times \text{Volume}}$

$= \dfrac{560 \times 1000}{18 \times 560}$ (Since 560 gm H_2O = 560 cm^3 because density = 1 gm/cm)^3.

$= 55.5$

4. 1 molal means 1 mole solute in 1 kg of solvent

Mole fraction of solvent $(X_{\text{solvent}}) = \dfrac{\frac{1000}{18}}{\frac{1000}{18} + 1}$

$= 0.9823$

$\therefore$ Mole fraction of solute $= 1 - 0.9823$

$= 0.0176$

5. M.eq of HCl (100 ml) $= 5 \times 19.8 \times 0.1 = 9.9$

$$W_{Na_2CO_3} = \frac{9.9}{1000} \times 53 = 0.5247 \text{ gm}$$

$\Rightarrow$ 0.5247 gm $Na_2CO_3 \equiv 0.1753$ gm H_2O

$\Rightarrow$ 106 gm $Na_2CO_3 \equiv 35.4$ gm H_2O. $\simeq$ 2 mole

$\therefore \quad x = 2.$

6. M.eq. of the mixture is the sum total of the m.eq. of all the acids.

$$V_mN_m = V_1N_1 + V_2N_2 + V_3N_3$$

$$\Rightarrow \quad 400\, N_m = 100 \times 1 + 200 \times \frac{1}{5} + 100 \times \frac{1}{5}$$

$$\Rightarrow \quad N_m = \frac{160}{400} \Rightarrow N_m = 0.4$$

7. $V_mN_m = V_1N_1 + V_2N_2 - V_3N_3$

$$500\, N_m = (200 \times 1 + 200 \times \frac{1}{5}) - 100 \times 1$$

$$= 240 - 100 = 140$$

$$N_m = \frac{140}{500} = 0.28$$

Since M.eq. of Acid is more than M.eq. of base. Thus, solution is acidic

8. M.eq. of KOH $= 10{,}000 \times 0.1 = 1{,}000$

$\therefore \quad \equiv$ m.eq. of HCl

$$\therefore \quad W_{HCl} = \frac{1000}{1000} \times 36.5 = 36.5 \text{ gm pure.}$$

60 gm pure sample $\equiv$ 100 gm sample HCl

$\therefore$ 36.5 gm pure sample $\equiv \dfrac{100}{60} \times 36.5$ gm sample HCl $\equiv 60.8$ gm

9. $N_mV_m = N_1V_1 + N_2V_2 + N_3V_3$

$$N_m \times 115 = 50 \times 10 + 25 \times 12 + 40 \times 5$$

$$N_m = 8.70$$

Again this solution vol. made up to 1000 ml.

$\therefore \quad N_1V_1 = N_2V_2$

$$8.7 \times 115 = N_2 \times 1000 \Rightarrow N_2 = \frac{8.7 \times 115}{1000}$$

$$\simeq 1.$$

10. m.eq. of acid $= 20 \times \dfrac{1}{5} = 4$

$$\text{m.eq. of AgCl} = \frac{0.287 \times 1000}{143.5} = 2.$$

$\Rightarrow$ 2 meq. of acid is not of nutralised ie. HCl.

$\Rightarrow$ 2 meq. of HCl = Volume of HCl × N

$= 20 \times \text{N}$

$$\Rightarrow \quad \text{N} = \frac{2}{20} = \frac{1}{10} = 0.1.$$

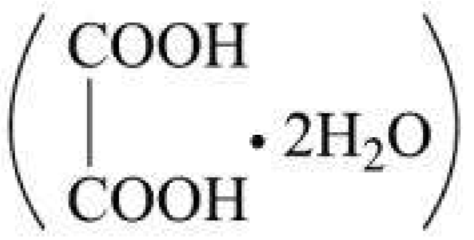
11. Ionic Strength (u) = $\frac{1}{2}\ \Sigma CZ^2$

Where C is constant and Z is valency.

$$u = \frac{1}{2}\left(0.5\times 2^2+0.5\times 2^2\right)+\left(0.2\times 2^2+0.2\times 1^2\right)+\left(1.2\times 3^2+1.2\times 2^2\right)$$

$$= \frac{1}{2}(4+1+10.8+4.8) = 10.3$$

12. Mol. for of oxalic acid dihydrate



$$\left(\begin{array}{l}\text{COOH}\\ |\\ \text{COOH}\end{array}\cdot 2H_2O\right) = 126$$

$E_{\text{Oxalic acid}} = 63$

M.eq. of oxalic acid ≡ M.eq. of NaOH

$\Rightarrow\ N_1\times V_1 = N_2\times V_2$

$\Rightarrow\ \frac{6.3\times 1000}{63\times 250}\times 10 = 0.1\times V_2$

$\Rightarrow V_2 = 40$ ml.

13. $M_{\text{electron}} = 9.108\times 10^{-31}$ kg

$\therefore\ 1$ kg electron $= \frac{1}{9.108\times 10^{-31}}$ electron

$= \frac{1}{9.108\times 10^{-31}}\times\frac{1}{6.023\times 10^{23}}$ mole electron

$= \frac{10^8}{9.108\times 6.023}$ mole electron

14. E_{KMnO_4} in acid medium $= \frac{\text{Molecular Mass}}{5}$

$\therefore\ N = 5M$

$N_{KMnO_4} = 5\times 0.1 = 0.5$

M.eq. of $KMnO_4$ ≡ M.eq. of $FeSO_4$

$\Rightarrow\ 100\times 0.5 = 50$ m.eq.

$\Rightarrow\ N_{FeSO_4}\times V_{FeSO_4} = 50 \Rightarrow\ N_{FeSO_4} = \frac{50}{50}$

$= 1$

$W_{FeSO_4} = \frac{50}{1000}\times\frac{\text{Mol. Mass }(FeSO_4)}{1}$

(Since Fe^{2+} changes into Fe^{3+}).

$= \frac{50}{1000}\times 152 = 7.6$ gm

15. M.eq. of $H_2SO_4 = 250\times 0.1 = 25$

M.eq. of NaOH $= 100\times\frac{1}{50} = 2$

M.eq. of H_2SO_4 reacted with Zinc $= 25 - 2 = 23$

$$W_{Zn} = \frac{\text{m.eq.}}{1000}\times E_{Zn}$$

$$= \frac{23}{1000}\times\frac{65}{2} = 0.7475 \text{ gm}$$

% Purity $= \frac{0.7475}{1}\times 100 = 74.75$ %

16. M.eq. of NaOH (100 ml) $= 4\times 15\times 1 = 60$

M.eq. of NaOH = M.eq. of oxalic acid

$W_{\text{oxalic acid}} = \frac{\text{m.e}}{1000}\times\frac{M_{\text{oxalic acid}}}{2}$

$\Rightarrow\ 2.94 = \frac{60}{1000}\times\frac{M_{\text{oxalic acid}}}{2}$

$\Rightarrow\ M_{\text{oxalic acid}} = \frac{2.94\times 2\times 1000}{60} = 98$

17. For dilution $N_1V_1 = N_2V_2$

$\frac{40}{36.5}\times V_1 = \frac{1}{10}\times 2\ \Rightarrow\ V_1 = \frac{2}{10}\times\frac{36.5}{40}$

$= 0.1825$ litre

18. M.eq. of all the reacting components are the same.

Thus, m.eq. of available chlorine ≡ m.eq. of iodine

≡ m.eq. of hypo solution

$\equiv \frac{1}{25}\times 12.5 = 0.5$

m.eq. of available Cl_2 in 250 ml

$= \frac{0.5\times 250}{25} = 5$

$$W_{Cl_2} = \frac{5}{1000} \times 35.5 = 0.1775 \text{ gm}$$

$$\therefore \quad \% \text{ of available } Cl_2 = \frac{0.1775}{1.25} \times 100$$

$$= 14.2 \ \%$$

19. 6 $KMnO_4$ +24 H_2SO_4 + 10 FeC_2O_4 → 3 K_2SO_4 + 6 $MnSO_4$ + 5 $Fe_2[SO_4]_3$ + 24 H_2O + 10 CO_2.

$\therefore$ No. of mole of $KMnO_4$ per mole of FeS_2O_4 = 315.

20. 2 $KMnO_4$ + 5H_2SO_3 → K_2SO_4 + 2$MnSO_4$ + 3H_2O + 2H_2SO_4

$\therefore$ No. of mole of $KMnO_4$ per mole of H_2SO_3 = 215.

➤ (E) ON Chemical Calculations

1. The volume of air (21 % O_2 by volume) required to burn completely 2.5 gm of acetylene gas is:

(a) 25.6 litre (b) 42.5 litre
(c) 51.4 litre (d) 60.2 litre

2. 5 gm each of H_2 and Cl_2 reacts together to form maximum HCl of mass:

(a) 5 gm HCl (b) 5.14 gm HCl
(c) 10 gm HCl (d) 25 gm HCl

3. The mass of HNO_3 needed to convert 5 gm of Iodine into Iodic acid according to the reaction

$$I_2 + HNO_3 \rightarrow HIO_3 + NO_2 + H_2O$$

(a) 12.4 gm (b) 24.8 gm
(c) 0.248 gm (d) 4.96 gm

4. NH_3 gas is passed through 50 ml of H_2O at 4°C till saturation. The density of solution now decreases to 0.8 gm/ml and if NH_3 is 40 % by mass in solution. Its volume will be:

(a) 104 ml (b) 102 ml
(c) 50 ml (d) 90 ml.

5. Assuming that petrol is octane having density 0.8 gm/ml 1.425 litre of petrol on combustion will consume:

(a) 0.50 mole of O_2 (b) 0.1 mole of O_2
(c) 0.125 mole of O_2 (d) 0.2 mole of O_2

6. The percentage by volume of C_3H_8 in the mixture of C_3H_8, CH_4 and CO is 36.5. The volume of CO_2 produced when 100 ml of the mixture is burnt in excess of oxygen is:

(a) 17.3 ml (b) 173 ml
(c) 346 ml (d) 86.5 ml

7. The mixture of N_2 and H_2 is caused to react in a closed container to form NH_3. If two mole of each components are persent after reaction. The mole of N_2 and H_2 originally present is respectively are?

(a) 3 and 4 (b) 3 and 5
(c) 3 and 6 (d) 4 and 5

8. Equal weights of Zn and Iodine are mixed together and Iodine is completely converted to Zinc iodide. The fraction of the original Zinc remains unreacted is: [Zn = 65]

(a) 0.746 (b) 0.256
(c) 0.529 (d) 0.488

9. If the yield of chloroform obtainable from acetone and bleaching powder is 75 %. What is the weight of acetone required for producing 30 gm chloroform?

(a) 40 gm (b) 19.4 gm
(c) 10.92 gm (d) 14.5 gm

10. If 0.5 mole of $BaCl_2$ is mixed with 0.2 mole of Na_3PO_4 solution. The maximum mole $(Ba_3(PO_4))_2$ that can be formed is

(a) 0.7 (b) 0.5
(c) 0.3 (d) 0.1

11. The ratio of amounts of H_2S needed to precipitate all the metal ions from 100 ml of 1 M NO_3 Ag and 100 ml 1 M $CuSO_4$ is

(a) 1 : 2 (b) 2 : 1
(c) Zero (d) Infinity

12. A partially dried clay mineral contains 8% H_2O. The original sample contained 12% H_2O and 45% silica. The% of silica in the partially dried sample is nearly:

(a) 50 % (b) 49 %
(c) 55 % (d) 47 %

13. '*X*' gm Ag was dissolved in HNO_3 and the solution was treated with excess of NaCl, 2.87 gm of AgCl was precipitated. The value of *x* is:

(a) 1.08 gm (b) 2.16 gm
(c) 2.70 gm (d) 1.62 gm

$\Rightarrow$ 119.5 gm chloroform $\equiv$ 58 gm CH_3COCH_3

75 % product formed $\equiv$ 30 gm $CHCl_3$

Since 75% $CHCl_3$ = 30 gm

$\therefore$ 100 % $CHCl_3$ = 40 gm

Since 119.5 gm $CHCl_3 \equiv$ 58 gm acetone

$$\therefore \quad 40 \text{ gm } CHCl_3 \equiv \frac{58 \times 40}{119.5} = 19.4 \text{ gm}$$

10. $3BaCl_2 + 2Na_3PO_4 = 6NaCl + Ba_3(PO_4)_2$

	$3BaCl_2$	$2Na_3PO_4$	$6NaCl$	$Ba_3(PO_4)_2$
Initially	3	2	6	1
Given mole	0.5	0.2		

Thus Na_3PO_4 is limiting reagent

Hence Mole of $Ba_3(PO_4)_2$ formed = 0.1

11. $2AgNO_3 + H_2S \rightarrow Ag_2S\downarrow + 2HNO_3$

$CuSO_4 + H_2S \rightarrow CuS\downarrow + H_2SO_4$

Thus ratio of precipitate formed by same mole of $AgNO_3$ and $CuSO_4$ is 1 : 2.

12. Clay contains silica, H_2O and impurities

	% of silica	% of H_2O	% of Impurities
dried clay	x	8 %	$92 - x$
original clay	45 %	12 %	43 %

The mass ratio of silica and impurities remain constant throughout, hence,

$$\frac{x}{45} = \frac{92 - x}{43}$$

$$x = 47 \text{ \%}$$

13. During the reaction mass of Ag remain constant throughout

$$\text{Thus mass of silver in AgCl} = \frac{108}{143.5} \times 2.87 = 2.16 \text{ gm}$$

➤ (F) ON H_2O_2, Oleum, Water of Crystallisation, Hardness, etc

1. 0.2 gm sample of H_2O_2 required 10 ml of (N) $KMnO_4$ in a titration in presence of H_2SO_4. The purity of H_2O_2 is:

(a) 25 % (b) 85 %
(c) 65 % (d) 95 %

2. The volume strength of 1.5 N H_2O_2 solution is:

(a) 4.8 (b) 8.4
(c) 3.0 (d) 8.0

3. A Commercial bottle of H_2O_2 is labelled as '20 V'. Its Molarity is:

(a) 1.785 (b) 1.587
(c) 1.23 (d) 1.03

4. The strength of H_2O_2 solution which is labelled as '10 V' in the bottle is:

(a) 15.18 (b) 30.36
(c) 15.28 (d) 10.28

5. The ratio of H_2SO_4 prepared by free SO_3 and H_2SO_4 present initially in 109 % oleum is:

(a) 0.726 (b) 0.816
(c) 0.521 (d) 0.92

6. If 5 litre of H_2O_2 produces 50 litres of O_2 at S.T.P. H_2O_2 is?

(a) '50V' (b) '10V'
(c) '5V' (d) '250V'

7. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^- with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water. If 1000 kg of this water is treated with the amount of CaO. (Calculated above). What will be the concentration above (in ppm) of residual Ca^{2+} ion. **[IIT, 1997]**

(a) 20 ppm (b) 40 ppm
(c) 60 ppm (d) 80 ppm

8. 10 ml of hydrocarbon gas burnt in air and on cooling volume. is reduced by 30 ml. When passed through KOH, a further 30 ml volume. decrease is observed. The molecular formula of hydrocarbon is:

(a) C_2H_6 (b) C_3H_8
(c) C_3H_6 (d) C_2H_2

9. The amount of CO needed per kg of Ni in Mond's process given below is

$$Ni + 4\,CO \rightarrow Ni(CO)_4 \qquad [Ni = 58]$$

(a) 1.93 kg (b) 1.52 kg
(c) 1.22 kg (d) 1.0 kg

10. CS_2 and Cl_2 in the mass ratio 1 : 2 are allowed to react according to

$$CS_2 + 3\,Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

The fraction of it left behind is?

(a) 0.358 (b) 0.287
(c) 0.208 (d) 0.576

Fraction of CS_2 left $= 1 - 0.713$
$= 0.287$

IIT WINDOW–III

MCQ Multiple Answer

1. 4.4 gm of CO_2 contains:
- (a) 1 mole of CO_2
- (b) 0.1 mole of CO_2
- (c) 6.02×10^{22} molecules of CO_2
- (d) 0.1 gm-mole of CO_2.

2. In the reaction:

$$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$$

- (a) Equivalent Mass of FeS_2 = M/11 (M = Mol. Mass of FeS_2)
- (b) Molar ratio of FeS_2, Fe_2O_3 and SO_2 is 4 : 2 : 8 respectively.
- (c) Oxidation state of iron in FeS_2 is +2.
- (d) Equivalent Mass of SO_2 is M/3 (M = Molar Mass of SO_2).

3. 5 gm each of H_2 and O_2 combine to form H_2O.
- (a) 5. gm H_2O (maximum) will be formed
- (b) 5.6 gm H_2O (maximum) will be formed
- (c) O_2 behave as limiting reagent
- (d) H_2 behave as limiting reagent

4. Loschmidt number is equal to:
- (a) the number of particles in 1 cm^3 of a gas at STP
- (b) the number of particles in 22.4 litre of a gas at STP
- (c) 6.02×10^{19} particles
- (d) 2.688×10^{19} particles

5. 100 ml of $\frac{N}{10}$ HCl, 200 ml of $\frac{N}{5}$ HNO_3 and 300 ml of $\frac{N}{10}$ NaOH are mixed together. The resulting mixture has:
- (a) normality equal to 1/30
- (b) Acidic in nature
- (c) 30 m.eq.of alkali neutralises 30 m.eg. of acid
- (d) 50 m.eq. of acid remain unreacted.

6. 1 gm Mg sample is treated with 125 ml 0.1 N HCl and the excess of HCl is neutralised by 50 ml 0.5 N NaOH completely. The correct statement is/are:
- (a) Mass of Mg present in the sample is 0.12 gm
- (b) Mass of Mg sample unreacted is 0.88 gm
- (c) % of Mg present in the sample is 12 %
- (d) Mass of impurities present in the sample is 0.88 gm.

7. 1 g $Na_2CO_3\,x\,H_2O$ is dissolved in 50 ml of 1M HCl. The excess acid required for neutralisation is 86 cm^3 N/2 $Ca(OH)_2$. The correct statement is/are:
- (a) Water of crystallisation of washing soda is 10.
- (b) M.eq. of HCl used for washing soda = 7
- (c) M.eq. of HCl used for $Ca(OH)_2$ = 43
- (d) Total M.eq. of HCl = 50.

8. x gm of Na_2CO_3 and NaOH mixture is dissolved in 100 ml H_2O. 25 ml of this solution requires 20 ml of 0.05 N HCl for colour change. If methyl orange is taken 25 ml mixture requires 25 ml 0.05 N HCl. The correct statement is/are:
- (a) 0.02 gm NaOH in the mixture.
- (b) 0.02 gm Na_2CO_3 is the mixture.
- (c) 0.0265 gm Na_2CO_3 is the mixture.
- (d) 0.0565 gm Mixture is given.

9. 20 ml of a mixture of C_3H_8 and CO when burnt in oxygen produce 40 ml gas. The correct statement is/are
- (a) 15 ml CO in the mixture
- (b) 10 ml C_3H_8 in the mixture
- (c) 10 ml CO in the mixture
- (d) 5 ml CO in the mixture

10. 5 gm of a mixture of Ca and Mg reacts with sufficient N_2 to form compound which on hydrolysis produce 0.1444 mole of NH_3 gas. Choose the correct statement/statements.
- (a) Mass of Ca in the mixture is 2 gm
- (b) Mass of Al in the mixture is 3 gm
- (c) Mole of Ca in the mixture is 10 gm
- (d) Mole of Al in the mixture is 0.111.

atm pressure. Calculate the composition of the alloy (Al = 27, Mg = 24)?

14. Dry hydrogen was passed over 1.58 gm of red hot copper oxide till it is completely reduced to 1.26 gm copper. If in this process 0.36 gm of H_2O is formed. What will be the equivalent weight of Cu and O.?

15. Calculate the equivalent Mass of the compounds underlined in the following equations.

(a) $FeS_2 + KMnO_4 + H^+ \rightarrow Fe^{3+} + SO_2 + Mn^{2+} + H_2O$.

(b) $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

➤ (D) ON VOLUMETRIC ANALYSIS

16. Calculate the strength in gm/litre of a solution of H_2SO_4, 12 cm^3 of which neutralises 15 cm^3 of decinormal NaOH solution.?

17. 100 gm of a sample of HCl solution of relative density 1.17 contains 33.4 gm of HCl. What volume of this HCl solution will be required to neutralise exactly 5 litres of decinormal NaOH solution.?

18. One gm-atom of Ca was burnt in excess of oxygen and the oxide was dissolved in water to make a 1-litre solution. Calculate normality of alkaline solution.?

19. A metal weighing 0.43 gm was dissolved in 50 ml of (N) H_2SO_4. The unreacted H_2SO_4 required 14.2 ml of (N) NaOH for neutralisation. Find out the equivalent weight of the metal.?

20. 4.35 g of a mixture of NaCl and Na_2CO_3 was dissolved in 100 cm^3 of H_2O, 20 ml of which was neutralised by 75.5 ml of $\frac{N}{10}$ solution of H_2SO_4. Calculate the percentage of NaCl and Na_2CO_3 in the mixture.?

21. You are given a 2.198 gm sample containing a mixture of XO and X_2O_3. It requires 0.015 mole $K_2Cr_2O_7$ to oxidise the sample completely to form XO_4^- and Cr^{3+}. If 0.0187 mole of XO_4^- is formed what is the atomic mass of X?

22. 3.68 gm of a mixture of $CaCO_3$ and Na_2CO_3 on reaction with 1000 ml of $\frac{N}{10}$ HCl solution produces 1.76 gm of CO_2. Calculate the % of each components in the mixture.?

23. 100 ml of 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 remaining titration was completed by adding 0.25 N KOH solution. Calculate the volume of KOH required.?

24. 100 ml of 0.6 N. H_2SO_4 and 200 ml of 0.3 N HCl were mixed together. What will be the normality of the resulting solution?

25. Calculate the normality of a mixture obtained by mixture 100 ml of 0.2 M H_2SO_4 with 100 ml of 0.2 M NaOH.?

➤ (E) ON WATER OF CRYSTALLISATION AND DOUBLE INDICATORS

26. 500 ml of 2 M HCl, 100 ml of 2 M H_2SO_4 and one-gm-equivalent of a monoacidic alkali are mixed together, 30 ml of this solution required 20 ml of 143 gm $Na_2CO_3{\cdot}xH_2O$ in one litre solution. Calculate water of Crystallisation of $Na_2CO_3xH_2O$?

27. In a mixture of $NaHCO_3$ and Na_2CO_3, volume of a given HCl required is x ml with phenolphthalein indicator and y ml is required with methyl orange indicator. Calculate volume of HCl for complete neutralisation of $NaHCO_3$ in the mixture.?

28. A solution contains Na_2CO_3 and NaOH. 25 ml of this mixture require 19.5 ml of 0.005 N HCl for the end point, when phenolphthalein is used as indicator if methyl orange is used as indicator, then 25 ml of solution mixture requires 25.9 ml of the same HCl for end point. Calculate the strength of Na_2CO_3 is the mixture.?

29. A mixture of Na_2CO_3 and $NaHCO_3$ (8 gm) dissolved in 1 litre water. 25 ml of this solution require 32 ml of decinormal HCl using methyl orange as an indicator and 12 ml decinormal HCl when phenolphthalein is used as an indicator. Calculate the strength of $NaHCO_3$ and Na_2CO_3 in the mixture.?

30. 50 ml of a mixture solution containing NaOH and Na_2CO_3 is taken. 5 ml of this solution when titrated with $\frac{N}{5}$ HCl require 12 ml for neutralisation when phenolphthalein is taken. A further drop of methyl orange is added in the same solution and titrated with the same HCl requires 4 ml. Calculate the % strength of NaOH and Na_2CO_3 in the mixture solution.?

HINTS AND SOLUTIONS: IIT-WINDOW IV

1. $E_{Ca} = \frac{\text{Wt. of metal}}{\text{Wt. of oxygen}} \times 8 = \frac{1.35}{0.53} \times 8 = 20.38$

Atomic Mass = 2 × 20.38 ≈ 40.75 **Ans.**

2. **Ans.** 24

3. $E_M = \frac{0.165}{0.835} \times 35.5 = 7.0$

Molecular Mass = 85 × 2 = 170

According to question $MClx = 170$

$7 \times x + 35.5\, x = 170$

$\Rightarrow \quad 42.5\, x = 170 \Rightarrow \quad x = 4$

$\therefore$ Valency = 4

Atomic Mass of Metal = 7 × 4 = 28

4. $\frac{\text{Mass of Cu in } Cu_2S}{\text{Mass of Ag that reacts with same mass of S as in Cu}}$

$= \frac{\text{Atomic Mass of Cu}}{\text{Atomic Mass of Ag}}$

$\frac{79.86}{135.53} = \frac{63.5}{x} \Rightarrow \quad x = 107.76$ **Ans.**

5. 1 mole of $A_2B_3 = \frac{15.9}{0.15} = 106$

1 mole of $AB_2 = \frac{9.3}{0.15} = 62$

We have $2x + 3y = 106 \Rightarrow \quad x = 26$

and $x + 2y = 62 \quad\quad y = 18$

6. No. of mole of $N_2 = \frac{84}{28} = 3$

No. of mole of gas is also 3.

Hence its molecular mass = $\frac{96}{3} = 32$

7. In Fe_3O_4, mole of iron = 3.

1.5 mole Fe ≡ 116 gm Fe_3O_4

3 mole Fe ≡ 232 gm Fe_3O_4

Mol. Mass of Fe_3O_4 = 232 gm.

8. 0.497 gm Ag ≡ 0.701 gm of its salt

$\therefore \quad 216 \text{ gm Ag} \equiv \frac{0.71}{0.497} \times 216 = 304.65 \text{ gm}$

Hence Mol. Mass of Acid = 304.65 – 216 + 2(dibasic)

= 90.65 **Ans.**

9. Mole of Pt = $\frac{0.262}{195}$

$\Rightarrow \quad \frac{0.262}{195}$ mole Pt ≡ 0.80 gm base

$\therefore \quad 1 \text{ mole Pt} \equiv \frac{0.80 \times 195}{0.262}$ gm base

= 595.4 **Ans.**

10. By using

$PV = nRT$

$$\left(\frac{740-18}{760}\right)\left(\frac{49.4}{1000}\right) = \frac{0.168}{M} \times 0.082 \times 293$$

$\Rightarrow \quad M = 86.113$

11. **Ans.** 32

12. Mass ratio is equal to equivalent ratio if valency is the same.

$$\frac{M_{Ca}}{M_{Zn}} = \frac{E_{Ca}}{E_{Zn}} \Rightarrow \frac{1.60}{2.60} = \frac{x}{32.6}$$

$\Rightarrow \quad x = 20.06$ **Ans.**

13. Let Mass of Al = x gm

Mass of Mg = $1 - x$ gm

$$Al + 3HCl \rightarrow AlCl_3 + \frac{3}{2}H_2$$

1 mole 1.5 mole

27 gm Al ≡ 1.5 × 22.4 litre of H_2 at STP

$x \text{ gm Al} \equiv \frac{1.5 \times 22.4 \times x}{27}$, litre of H_2.

Similarly

$$Mg + 2\,HCl \rightarrow MgCl_2 + H_2$$

together and made up to 2 litre. 30 ml of this acid mixture exactly neutralises 42.9 ml of Na_2CO_3 solution containing 1 gm Na_2CO_3 10 H_2O in 100 ml of H_2O. Calculate the amount of sulphate ion in gm present in solution.? **[IIT, 1985]**

2. The reaction $2C + O_2 \rightarrow 2\,CO$ 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 mole of CO are formed?
(d) How many 'g' of other reactant should be taken so that nothing is left at the end of the reaction.? **[Roorkee, 1986]**

3. What is the strength in gm per litre of a solution of H_2SO_4, 12 ml of which neutralised 15 ml of $\frac{N}{10}$ NaOH solution? **[IIT, 1987]**

4. *n*-butane is produced by the monobromination of ethane followed by wurtz reaction. Calculate the volume of ethane at NTP to produce 55 gm *n*-butane if the bromination takes place with 90 % yield and the wurtz reaction with 85 % yield.? **[IIT, 1989]**

5. A solid mixture 5 gm consists of lead nitrate and sodium nitrate was heated below 600° C until weight of residuce was constant. If the loss in weight is 28 %. Find the amount of Pb $(NO_3)_2$ and $NaNO_3$ in the mixture.? **[IIT, 1990]**

6. Calculate Molality of 1 litre solution of 93 % H_2SO_4 by volume. The density of solution is $1.84\ g\ ml^{-1}$.? **[IIT, 1990]**

7. Upon mixing 45 ml of 0.25 M lead nitrate solution with 25 ml 0.10 M chromic sulphate precipitate of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentration of species left behind in final solution. Assume that lead sulphate is completely insoluble.? **[IIT, 1993]**

8. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtained. 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate molarity, molality and mole fraction of Na_2SO_4 in solution.? **[IIT, 1994]**

9. A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 gm of O_2 to produce CO_2 and H_2O. Assuming ideal behavior. Calculate the mole fraction of C_2H_4 and C_2H_6 in the mixture.? **[IIT, 1995]**

10. 1.20 gm sample of Na_2CO_3 and K_2CO_3 was dissolved in water to form 100 ml of solution. 20 ml of this solution required 40 ml of 0.1 N HCl for complete neutralisation. Calculate the weight of Na_2CO_3 in mixture. If another 20 ml of thin solution is treated with excess of $BaCl_2$. What will be the weight of precipitate? **[Roorkee, 1997]**

11. For the reaction $N_2O_5(g) = 2\,NO_2(g) + 0.5\,O_2(g)$ Calculate the mole fraction of $N_2O_5(g)$ decomposed at constant volume and temperature., if the initial pressure is 600 mm Hg and pressure at any time is 960 mm of Hg. (Assume ideal gas behaviour)? **[IIT, 1998]**

12. A plant virus is found to consists of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3/g. If the virus is considered to be single particle. Find its molecular weight.? **[IIT, 1999]**

13. How many millilitre of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper II carbonate? **[IIT, 1999]**

14. A mixture in which the mole H_2 and O_2 is 2 : 1 is used to prepare water by the reaction.

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

The total pressure in this container is 0.8 atm at 20° C before the reaction. Determine the final pressure at 120° C after reaction assuming 80 % yield of H_2O.? **[Roorkee, 1999]**

15. The formula weight of an acid is 82.0. 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 aq. NaOH containing 40 g of NaOH per litre. What is the basicity of the acid? **[Roorkee, 2000]**

16. 1 gm charcoal is placed in 100 ml of 0.5 M CH_3 COOH to form an adsorbed monolayer of acetic acid molecules and thereby the molarity of CH_3COOH reduces to 0.49. Calculate

17. Density of water = 1000 kg/m^3

∴ Molarity = $\frac{1000\times10^3\times1000}{18\times1000\times10^3}$ = 55.5 **Ans.**

18. $6\,CaO + P_4O_{10} = 2\,Ca_3(PO_4)_2$

$P_4O_{10} = 31\times4 + 16\times10$

Since 284 gm $P_4O_{10} \equiv 6\times56$ gm CaO

∴ 852 gm $P_4O_{10} \equiv \frac{6\times56\times852}{284}$ gm CaO

$\equiv$ 1008 gm CaO

19. According to question

$P_{N_2} = 10^{-3}$ atm, $T = 298$ K, $V_{N_2} = 2.46$ cm^3

∴ $10^{-3}\times2.46\times10^{-3} = \eta_{N_2}\times0.082\times298$

$\Rightarrow \eta_{N_2} = 1.0\times10^{-7}$

∴ No. of molecules of N_2 in the sites = $6.02\times10^{23}\times10^{-7} = 6.02\times10^{16}$

Total surface area = density × area

$= 6.02\times10^{14}\times10^3$ cm^2

$= 6.02\times10^{17}$

Since only 20 % of this site is occupied by N_2

∴ Total area occupied by

$N_2 = 0.2\times6.02\times10^{17}$

$= 12.04\times10^{16}$

∴ No. of surface site occupied per molecule of $N_2 = \frac{12.04\times10^{16}}{6.02\times10^{16}} = 2$

IIT WINDOW–VI

Matching Type

Match the *Set A* with *Set B*

1.

Set A	*Set B*
(a) $E_{H_3PO_3}$ is	(p) Mol. Mass/1
(b) $E_{H_3BO_3}$ is	(q) Mol.Mass/11
(c) E_{FeS_2} in the reaction ($FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$) is	(r) Mol. Mass/2
(d) $E_{MnO_4^-}$ in the reaction ($3\,MnO_4^- = 2\,MnO_2 + MnO_4^{2-}$) is	(s) 3 × Mol. Mass/13
(e) $E_{MnO_4^-}$ in the reaction ($3\,MnO_4^- = 2\,Mn^{2+} + MnO_2$) is	(t) 3 × Mol. Mass/7

2.

Set A	*Set B*
(a) 20 ml (N) HCl reacts with 50 ml $\frac{N}{5}$ NaOH.	(p) No. of molecules of HCl left = 0
(b) 10 ml $\frac{N}{2}$ HCl reacts with 50 ml $\frac{N}{10}$ NaOH.	(q) No. of molecules of HCl left = 6.02×10^{21}
(c) 50 ml $\frac{N}{10}$ HCl reacts with 100 ml $\frac{N}{50}$ NaOH.	(r) No. of molecules of HCl left = 2.71×10^{22}
(d) 100 ml $\frac{N}{2}$ HCl reacts with 50 ml $\frac{N}{10}$ NaOH.	(s) No. of molecules of HCl left = 1.8×10^{21}

3.

Set A	*Set B*
(a) 4 gm Ca & 2 gm H_2 reacts together to form CaH_2.	(p) 5.783 gm H_2 left unreacted
(b) 2 gm Mg and 2 gm H_2 reacts together to form Mg H_2	(q) 1.8 gm H_2 left unreacted.
(c) 5 gm Na and 6 gm H_2 reacts to form NaH.	(r) 0.7 gm H_2 Left unreacted.
(d) 2.7 gm Al and 1 gm H_2 reacts to from AlH_3.	(s) 1.83 gm H_2 left unreacted.

4.

Set A	*Set B*
(a) No. of mole/litre of solution is	(p) Normality
(b) No. of mole/kg of solution is	(q) Formality
(c) No. of formula unit/ litre of solution is	(r) Molarity
(d) No. of equivalent/ litre of solution is	(s) Molality

5.

Set A	*Set B*
(a) Minimum molecular mass of Heamoglobin if it contain 0.056 % iron is [Fe = 56]	(p) 96000
(b) Minimum molecular mass of chlorophyl if it contain 0.025 % Mg is (Mg = 24)	(q) 2,08,000
(c) Minimum mol. mass of a nickel dimethyl glyoxime if it contain 0.025 % is [Ni = 58]	(r) 1,00,000
(d) Minimum mol. Mass of chromianotrin if it contain 0.025 % Cr is [Cr = 52]	(s) 2,32,000

6.

Set A	*Set B*
(a) Titration of NH_4OH with HCl solution	(p) Phenolphthalein
(b) Titration of $K_2Cr_2O_7$ with $Na_2S_2O_3$ solution.	(q) Methyl orange
(c) Titration of H_2SO_4 with NaOH solution	(r) No need of indicator
(d) Titration of $K_2Cr_2O_7$ with I_2 solution in acid medium.	(s) Alizarin

➤ Matrix-Matching Type

Matrix – 1

(a) 1 mole SO_2 at STP	(p) 24.7 litre
(b) 1-mole O_2 gas at SATP.	(q) 22.4 litre
(c) 32 gm O_2 gas.	(r) 1.204×10^{24} atoms
(d) 64 gm SO_2 gas	(s) 1.809×10^{24} atoms

Matrix – 2

(a) $E_{H_3PO_3} = \dfrac{\text{Molar Mass}}{2}$	(p) 42
(b) $E_{HCOOH} = \dfrac{\text{Molar Mass}}{1}$	(q) One H-atom directly attached with central atom.
(c) $E_{CH_3COOH} = \dfrac{\text{Molar Mass}}{1}$	(r) 46
(d) $E_{KMnO_4} = \dfrac{\text{Molar Mass}}{5}$	(s) H-attached with central atom have shorter bond length.
	(t) 31.6

Matrix – 3

(a) $V_1N_1 = V_2N_2$	(p) Applicable for acid & base
(b) $V_1M_1 = V_2M_2$	(q) Application for base.
(c) $V_mN_m = V_1N_1 + V_2N_2 + V_3N_3$	(r) Law of equivalence
(d) Milli equivalent of the two reacting substance must be the same.	(s) Applicable for dilution.

Matrix – 4

(a) Alkaline solution	(p) CO
(b) Alkaline Pyragallol	(q) CO_2
(c) Ammonical Cu_2Cl_2	(r) C_2H_2
(d) Charcoal	(s) SO_2
	(t) O_2

Matrix – 5

(a) '5V' H_2O_2 sample	(p) H_2O_2 has open book structure
(b) 109 % oleum	(q) 40 % SO_3

3. 8 gm methane is burnt with 4.48 litre of O_2 at STP. Find out the volume of CO_2 gas produced at STP and also the weight of CO_2 formed.
(a) 22.4 litre, 4.4 gm (b) 2.24 litre, 44 gm
(c) 2.24 litre, 4.4 gm (d) 224 litre, 44 gm

[D] All such titration which involves the direct titration of iodine with a reducing agent are grouped under iodimetry. Iodimetry is employed to determine the strength of reducing agent such as sodium thiosulphate

$$I_2 + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$$

If liberated Iodine involves oxidation of an iodide ion by a strong oxidising agent in neutral or acidic medium the liberated iodine is then litrated with reducing agent. Iodometry is used to estimate the strength of oxidising angent e.q.

$$Cu^{2+} + F^- \rightarrow Cu_2F_2 + F_2$$

$$I_2 + S_2O_3^{2-} \rightarrow S_4O_6^{2-} + I^-$$

Starch used as indicator near the end point which form blue colour complex with I_3^-. The blue colour disappears when there is no more or free I_2.

➤ Questions

1. 100 ml of 0.1 N $Na_2S_2O_3$ decolourises iodine by the addition of '*X*' gm of crystalline blue vitriol to excess of KI. The volue of *X* is:
(a) 5 gm (b) 2.5 gm
(c) 10 gm (d) 1.25 gm

2. In the reaction $2\ CuSO_4 + 4\ KI \rightarrow Cu_2I_2 + K_2SO_4 + I_2$, the ratio of equivalent weight of $CuSO_4$ to its molar weight is:
(a) 1/8 (b) 1/4
(c) 1/2 (d) 1

3. In iodine titration, Iodine remains in solution in the form of
(a) I_3^- (b) I_2
(c) I_3^+ (d) I^-

[E] Methyl orange and phenolphthalein are generally used as an indicators in acid range base titrations. Methyl orange acts in acid range having P^H range 3.1 – 7.0 while phenolphthalein acts in the P^H range of 7.1 to 10. Phenolphthalein changes its colour as soon as CO_2 and SO_2 starts forming in a reaction, although reaction is not complete; Methyl orange changes its colour after completion of the overall neutralisation.

➤ Questions

1. 25 ml of Na_2CO_3 solution requires 100 ml of 0.1 N HCl to reach end point with phenolphthalein as indicator. Molarity of resulting solution with respect to HCO_3^- ion is:
(a) 0.008 M (b) 0.004 M
(c) 0.16 M (d) 0.08 M

2. 0.01 Mole of H_3PO_4 and 0.01 mole of H_3PO_2 reacts with '*V*' ml of standard NaOH in presence of phenolphthalein indicator, volume '*V*' is:
(a) 500 ml (b) 400 ml
(c) 300 ml (d) 200 ml

3. 20 ml of '*X*' M HCl neutralises completely, 10 ml of 0.1 M $NaHCO_3$ solution and a further 5 ml of 0.2 M Na_2CO_3 solution to methyl orange end point. The value of *X* is
(a) 0.167 M (b) 0.133 M
(c) 0.15 M (d) 0.2 M

ANSWER KEYS: IIT WINDOW-II (A)

1. (b) 2. (a) 3. (a) 4. (c) 5. (b)
6. (c) 7. (d) 8. (d) 9. (d) 10. (c)
11. (d) 12. (b) 13. (b) 14. (d) 15. (c)
16. (b) 17. (a) 18. (c) 19. (b) 20. (b)

ANSWER KEYS: IIT WINDOW-II (B)

1. (d) 2. (a) 3. (d) 4. (c) 5. (a)
6. (c) 7. (b) 8. (b) 9. (a) 10. (b)
11. (b) 12. (a) 13. (d) 14. (b) 15. (b)

ANSWER KEYS: IIT WINDOW-II (C)

1. (b) 2. (b) 3. (c) 4. (b) 5. (a)
6. (c) 7. (b) 8. (d) 9. (d) 10. (b)
11. (b) 12. (b) 13. (a) 14. (d) 15. (a)

ANSWER KEYS: IIT WINDOW-II (D)

1. (a) 2. (c) 3. (c) 4. (a) 5. (c)
6. (d) 7. (b) 8. (a) 9. (a) 10. (a)
11. (c) 12. (a) 13. (d) 14. (c) 15. (c)
16. (c) 17. (b) 18. (c) 19. (a) 20. (a)

ANSWER KEYS: IIT WINDOW-II (E)

1. (d) 2. (b) 3. (d) 4. (a) 5. (c)
6. (b) 7. (b) 8. (a) 9. (b) 10. (d)
11. (a) 12. (d) 13. (b)

ANSWER KEYS: IIT WINDOW-II (F)

1. (b) 2. (b) 3. (a) 4. (b) 5. (b)
6. (b) 7. (b) 8. (c) 9. (a) 10. (b)

ANSWER KEYS: IIT WINDOW-III

1. (b), (c), (d) 2. (a), (b), (c)
3. (b), (c) 4. (a), (d)
5. (a), (b), (c) 6. (a), (b), (c), (d)
7. (a), (b), (c) (d) 8. (c), (d)
9. (b), (c) 10. (a), (b) (d)
11. (a), (d) 12. (a), (c), (d)
13. (a), (c) 14. (a), (c)
15. (a), (b), (c)

ANSWER KEYS: IIT WINDOW-IV

1. 40. 75 2. 24
3. 28 4. 107. 76
5. 26, 18 6. 32
7. 232 gm 8. 90. 65
9. 595.4 10. 86. 113
11. 32 12. 20. 06
13. Al; 0. 55 gm Mg: 0. 45 gm 14. 8
15. (a) M/11 (b) M/3 16. 6. 125
17. 46. 72 mp 18. 2
19. 12. 01 20. 45. 99% Na_2CO_3 54. 01% NaCl
21. 100. 04 22. 47. 9%
23. 16 ml 24. 0. 4
25. 2/10 26. 10
27. $(y - x)$ ml 28. 0. 1356
29. 5. 8 gm/l, 2. 69 gm l 30. 11. 68 (NaOH)

ANSWER KEYS: IIT WINDOW-V

1. 6. 528 gm 2. 6. 125 gm/litr
4. 55. 55 litr 5. 3. 32 & 1. 68 gm
6. 10. 42 8. 4.3×10^{-3}
9. 0. 66, 0. 34 10. 0.394
11. 0. 4 12. $> .095 \times 10^{7}$
13. 8. 09 ml 14. 0. 787 atm
15. 2 16. $5 \times 10^{-19}\,m^2$
17. 55. 5 18. 1008
19. 2

ANSWER KEYS: IIT WINDOW-VI

1. $a - r, b - p, c - q, d - T, e - s$
2. $a - q, b - p, c - s, d - r$
3. $a - q, b - s, c - p, d - r$
4. $a - r, b - s, c - q, d - p$
5. $a - r, b - p, c - s, d - q$
6. $a - q, b - r\ c - p\ \&\ q\ d - r$

Neutron

1. Discoverer : Chadwick .
   Symbol : $_0n^1$ or n
   Experiment: Bombardment of α–particles on Lithium or Beryllium foil
   $$_3Li^7 + {_2He^4} \rightarrow {_5B^{10}} + {_0n^1}$$
   $$_4Be^9 + {_2He^4} \rightarrow {_6C^{12}} + {_0n^1}.$$
2. Mass on neutron is found to be 1.675×10^{-27} kg.
3. Charge on neutron is zero.

Important Concepts

1. The Path of an electron in an electric field is parabolic.
2. 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
3. Mass of moving electron = $\frac{\text{rest mass electron}}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$
4. Rutherford concluded that the number of particles (N) scattered at an angle θ is such that
   $$N\alpha \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$
5. The graph between angle of scattering and the number of α particles scattered in corresponding directions is shown as

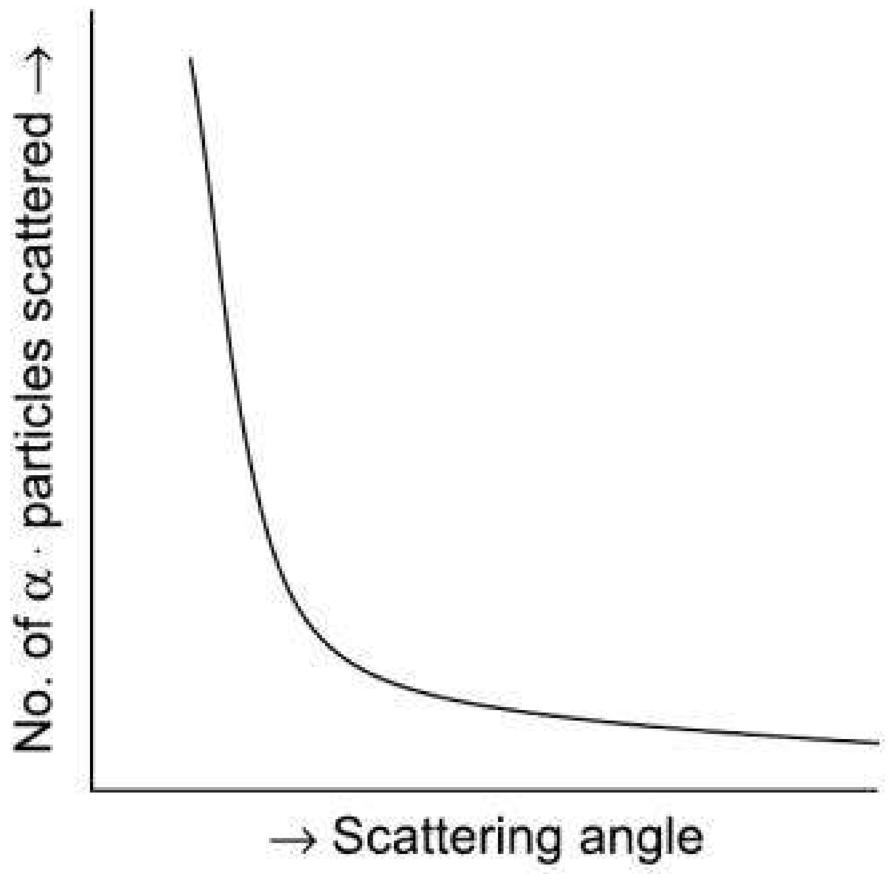


Fig 2.1

6. The volume of the nucleus is very small and is only a minute fraction of the 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}
   $$\frac{\text{Diameter of the atom}}{\text{Diameter of the nucleus}} = \frac{10^{-8}}{10^{-13}} = 10^5$$
7. Density of the hydrogen nucleus containing only one proton.
   $$= \frac{\text{Mass}}{\text{Volume}} = \frac{\left[A \times 1.66 \times 10^{-24}\text{g}\right]}{4/3 \times \pi r^3 \text{cm}^3}$$
   $$\Rightarrow d = 1.685 \times 10^{14} \text{ g/cm}^3$$
8. The Relation between Volume of the atom and nucleus is shown as
   $$\frac{\text{Volume of the atom}}{\text{Volume of the nucleus}} = \frac{\left(10^{-8}\right)^3}{\left(10^{-13}\right)^3} = \frac{10^{-24}}{10^{-39}} = 10^{15}$$
9. Number of revolution per second made by an electron in a shell
   $$\frac{\text{Velocity}}{\text{Circumference}} = \frac{v}{2\pi r} = \frac{-E_1}{h}\left(\frac{2}{n^3}\right)$$
   Where E_1 = Energy of first shell
10. Maximum number of lines produced when an electron jumps from nth level to ground level
    $$= \frac{n(n-1)}{2}$$
11. When an electron returns from n_2 to n_1 state, the number of lines in the spectrum
    $$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$$
12. Line of longest wavelength or line of shortest energy in any series of hydrogen spectrum
    $$\bar{v}_{\text{first}} = \frac{1}{\lambda_{\text{first}}} = R\left[\frac{1}{n_1^2} - \frac{1}{(n_1+1)^2}\right]$$
    $n_2 = (n_1+1)$
13. Line of shortest wavelength or line of highest energy (series limit) in any series of hydrogen spectrum

$$\bar{v}_{\text{last}} = \frac{1}{\lambda_{\text{last}}} = \frac{R}{n_1^2}$$

$$n_2 = \infty$$

14. Excitation potential for $n_1 \rightarrow n_2$

$$= \frac{E_{n_2} - E_{n_1}}{\text{Electronic charge}}$$

Ionisation potential $n_1 \rightarrow \infty$

$$= \frac{E_{n_1}}{\text{Electronic charge}}$$

15. ***Separation Energy:*** If an electron is already present in the excited state, then the energy required to remove that electron is called separation energy. It is shown as

$$E_{\text{separation}} = E_{\infty} - E_{\text{excited}}$$

16. λ of an electron $= \dfrac{h}{p} = \dfrac{h}{\sqrt{2Em}}$ or,

$$\lambda = \frac{h}{\sqrt{2eVm}}$$

17. $\Delta p \, \Delta x = \Delta E \, \Delta t$

$$\Delta E \, \Delta t \geq \frac{h}{4\pi} \text{ (for energy and time)}$$

18. $\Delta\phi \, \Delta\theta \geq \dfrac{h}{4\pi}$ (for energy and motion)

19. The number of waves made by a Bohr electron in one complete revolution $= \dfrac{2\pi r}{\lambda}$

$$= \frac{2\pi r}{2\pi r} \times n$$

20. 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 nodes planes = l

21. Orbital angular momentum of an electron is calculated using the following expression

$$\mu_1 = \sqrt{l(l+1)}\frac{h}{2\pi} = \sqrt{l(l+1)}\hbar$$

$$\hbar = \frac{h}{2\pi}$$

22. The region of maximum electron density is called **antinode**

23. There are seven f – orbitals designated as

$$f_{x(x^2-y^2)}, f_{y(x^2-y^2)}, f_{z_{(x^2-y^2)}}, f_{xyz}, f_{z^3}, f_{yz^2}, f_{xz^2}$$

24. Spin angular momentum $= \sqrt{s(s+1)}\dfrac{h}{2\pi}$
Where $s = \frac{1}{2}$

Total spin of an atom $= n \times \dfrac{1}{2}$ Where n = no. of unpaired electrons

25. Spin magnetic moment $= \sqrt{s(s+1)}\dfrac{eh}{2\pi mc}$

26. ***Planck's Quantum Theory:*** Energy is emitted or absorbed only in discrete units or packets of energy called photon (quantum). The energy associated with a quantum is given by

$$E = h\nu = \frac{hc}{\lambda} = h\,c\,\bar{v} \quad \left(\because \frac{1}{\lambda} = \bar{v}\right)$$

where $h = 6.625 \times 10^{-34}$ J. sec $= 6.625 \times 10^{-27}$ erg – sec.
$c = 3 \times 10^8\ m/\text{sec} = 3 \times 10^{10}$ cm / sec

27. ***Bohr's Model***

- Energy released or absorbed (ΔE) in given by $\Delta E = En_2 - En_1 = h\mu$.
  if $n_2 > n_1$, emission spectrum
  $n_1 > n_2$, absorption spectrum
- Angular momentum is an integral multiple of $h/2\pi$
  $\therefore \text{mur} = \dfrac{nh}{2\pi}$
  where $n = 1,2,3 \ldots\ldots \infty$.

28. ***Bohr's Radius***

Radius of nth orbit ($r_{n\text{th}}$) is given by

$$r_{n\text{th}} = \frac{n^2h^2}{4\pi^2 mze^2 k}$$

- The solution of Schrodinger's equation is

$$\lambda = \frac{h}{[2m(E-v)]^{1/2}}$$

i.e. greater in the value of $(E - V)$, shorter is the wavelength of wave function. Cartersion and polor coordinates

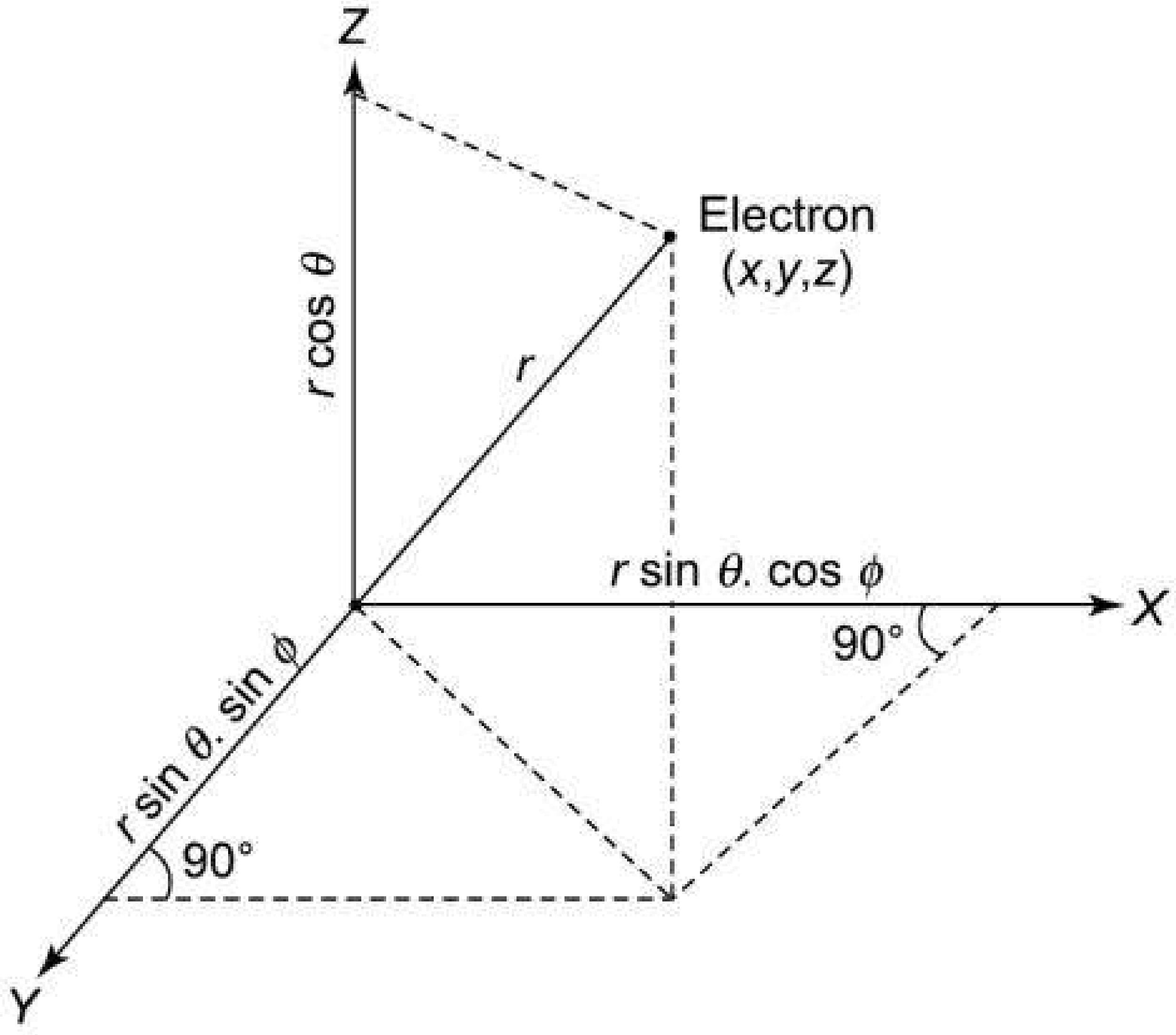


Fig 2.4

$X = r\sin.\theta.\cos\phi$
$Y = r\sin\theta.\sin\phi$
$Z = r\cos\phi$
$x^2 + y^2 + z^2 = r^2.$

- The energy of an orbit is given by

$$E_n = -\frac{me^4}{8\varepsilon_0^2 h^2} \times \frac{1}{n^2}$$

IIT WINDOW–I

Solved Numerical Problems

Example 2.1

Calculate the force of attraction between an electron and a body having two protonic charge when they are 0.529×10^{-8} cm apart.?
$[\,e = -1.6 \times 10^{-19}$ c, $P^+ = +1.6 \times 10^{-19}$ c.]

Solution

Force of attraction $(F) = \dfrac{kq_1q_2}{d^2}$

$\Rightarrow K = 9 \times 10^9\ Nm^2\ C^{-2}$
$F = 1.65 \times 10^{-7}\ N.$ **Ans.**

Example 2.2

Calculate the velocity of an electron in the Ist Bohr's orbit of hydrogen.?

Solution

For H-atom, Z = 1, n = 1 (ground state)

$$u_1 = \frac{2\pi ze^2}{nh} = \frac{2\times 3.14\times\left(4.8\times 10^{-10}\right)^2}{1\times 6.6^{25}\times 10^{-27}}$$

$$= 2.19 \times 10^6 \text{ m/sec}$$ **Ans.**

Example 2.3

AIR Services on FM is transmitted 97.2 m band. What is its frequency in Hertz ?

Solution

$$v = c/\lambda = \frac{3\times 10^8}{97.2} = 3.086 \times 10^6 \text{ Hertz}$$

Example 2.4

The dissociation energy of H_2 is 430.53 kJ mole^{-1}. If H_2 is exposed to radiation energy of $\lambda = 253.7$ nm. What % of radiant energy will be converted into K.E.

Solution

$$E_{\text{H-H}} = \frac{430.53\times 10^3}{6.02\times 10^{23}} \text{ joule/molecule}$$

$$= 7.15 \times 10^{-19} \text{ J/molecule}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.625\times 10^{-34}\times 3\times 10^8}{253.7\times 10^{-9}}$$

$$= 7.83\times 10^{-19} \text{ J.}$$

Energy converted to K.E = $(7.83 - 7.15) \times 10^{-19}$ joule
$= 0.68 \times 10^{-19}$ J.

% of energy converted into K.E.

$$= \frac{0.68\times 10^{-19}}{7.83\times 10^{-19}}\times 100$$

$$= 8.68\%$$ **Ans.**

Example 2.5

I_2 molecule dissociates into atoms after absorbing light of 4500 A°. If one quantum of radiation is ab-

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(c) orbital angular momentum of an orbital is given by

$= \sqrt{l(l+1)}\ h/2\pi$

Thus for 2p orbital

orbital momentum

$= \sqrt{1(1+1)}\ h/2\pi$

$= \sqrt{2}\ h/2\pi$

$= \sqrt{2}\hbar$ **Ans.**

➤ Example 2.20

Calculate the momentum of electron moving with 1/3rd velocity of light.

➤ Solution

$$\text{mass of } e^- \text{ in motion} = \frac{\text{Rest mass}}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$$

Since $v = c/3$

momentum = 9.69×10^{-18} g cm sec^{-1} **Ans.**

➤ Example 2.21

An electron beam can undergo diffraction by crystals. Through what potential should a beam of e^- be accelerated so that its wavelength became equal to 1.54 A° **[IIT, 1997]**

➤ Solution

As we Know,

$$\frac{1}{2}mv^2 = \text{ev and } \lambda = \frac{h}{mv}$$

$$\Rightarrow \frac{1}{2}\,\text{m}\,\frac{h^2}{m^2\lambda^2} = \text{e.v.} \Rightarrow v = \frac{1}{2}\frac{h^2}{m\lambda^2 e}$$

$$v = \frac{\left(6.625\times10^{-34}\right)^2}{2\times9.108\times10^{-31}\times\left(1.54\times10^{-10}\right)^2\times1.602\times10^{-19}}$$

= 63.3 volt. **Ans.**

➤ Example 2.22

The dust particle having mass equal to 10^{-11} g diameter = 10^{-4} cm and velocity 10^{-4} cm sec^{-1}. The error in measurement of velocity is 0.1%. Calculate uncertainty in its position. Comment on the result.

➤ Solution

$$\Delta u = 10^{-4}\times\frac{1}{100} = 1\times10^{-7}\text{ cm sec}^{-1}$$

$$\therefore\ \Delta u\,\Delta x = \frac{h}{4\pi m}$$

$$\therefore\ \Delta x = \frac{6.625\times10^{-27}}{4\times3.14\times10^{-11}\times1\times10^{-7}} = 5.27\times10^{-10}\text{cm.}$$

The uncertainty in its position

$$= \frac{\Delta x}{\text{diameter}} = \frac{5.27\times10^{-10}}{10^{-4}} = 5.27\times10^{-6}\text{ cm.}$$

The factor being small and almost being negligible for microscopic particles.

➤ Example 2.23

What is the maximum precision with which the momentum of the electron can be known if the uncertainty in the position of electron in ±0.001 A°. Will there be any problem in decreasing the momentum if it has a value of $h/2\pi$ 90. Where r_o = Bohr's radius.

➤ Solution

$$\Delta x = 0.001\text{Å} = 0.001\times10^{-10}\,m = 10^{-17}\,m.$$

$$\Delta\text{P} = \frac{6.625\times10^{-34}}{4\times3.14\times10^{-13}} = 5.27\times10^{-22}\text{ Ns.}$$

$$\text{if momentum} = \frac{h}{2\pi r_o} = \frac{6.625\times10^{-34}}{2\times3.14\times0.529\times10^{-10}}$$

$$= 2\times10^{-24}\text{ Ns.}$$

uncentainty in momentum is about

$$\frac{5.27\times10^{-22}}{2\times10^{24}}\ \text{i.e } 263.5$$

times as large as the momentum itself is.

IIT WINDOW–II

➤ Multiple Choice Questions (Having only one Correct option)

1. The maximum number of electrons with clockwise spin that can be accommodate in a *f* subshell are

(a) 14 (b) 7

(c) 5 (d) 10

(a) 3 (b) 5
(c) 7 (d) 9

22 If r is the radius of first orbit, the radius of nth orbit of the hydrogen atom will be
(a) rn^2 (b) rn
(c) r/n (d) r^2n^2

23. The ratio of radius of 2nd, 4th and 6th orbit of hydrogen atom is:
(a) 2:4:6 (b) 1:4:9
(c) 1:4:6 (d) 1:2:3

24. The distance between 3rd and 2nd orbits in the hydrogen atom is
(a) 2.646×10^{-8} cm
(b) $2.\ 116 \times 10^{-8}$ cm
(c) 1.058×10^{-8} cm
(d) 0.529×10^{-8} cm

25. $E_n = -313\ 6/n^2$ kcal/mole. If the value of $E = -34.84$ kcal/mole, to which value does 'n' correspond?
(a) 4 (b) 3
(c) 2 (d) 1

26. The ratio of the difference between 1st and 2nd Bohr's orbits energy to that between 2nd and 3rd orbits energy is:
(a) 1/2 (b) 1/3
(c) 27/5 (d) 5/27

27. The ionization energy of the electron in the 1s orbital of the hydrogen atom is – 13.6 eV. The energy of the electron after promotion to 2s orbital is:
(a) – 3.4 eV (b) – 13.6 eV
(c) – 27.2 eV (d) 0.0 eV

28. 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) $\frac{c}{137}$

29. The wave number of the line of Balmer series of hydrogen is 15200 cm^{-1}. The wave number of the first Balmer line of Li^{2+} ion is:
(a) 15,200 cm^{-1} (b) 60,800 cm^{-1}
(c) 76,000 cm^{-1} (d) 1,36,800 cm^{-1}

30. Which one of the following orbitals has the shape of baby-soother type?
(a) d_{xy} (b) $d_{x^2-y^2}$
(c) d_{z^2} (d) p_y

31. An ion which has 18 electrons in the outermost shell is
(a) K^+ (b) Cu^+
(c) Cs^+ (d) Th^{4+}

32. In Millikan's oil drop experiment, we make use of:
(a) Ohm's Law (b) Ampere's Law
(c) Stoke's Law (d) Faraday's Law

33. 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

34. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number +2:
(a) 3 (b) 4
(c) 2 (d) 1

35. An electron of mass m and charge e, is accelerated from rest through a potential difference V in vacuum. Its final speed will be:
(a) $\sqrt{(\text{eV}/\text{m})}$ (b) $2e\ \text{V}/\text{m}$
(c) $\sqrt{(\text{eV}/2\text{m})}$ (d) $\sqrt{(2\text{eV}/\text{m})}$

36. 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) $(n-1)h/2\pi$

37. X–ray;
(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

38. 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):
(a) –3.4eV (b) –4.2eV
(b) –6.8eV (d) +6.8eV

39. 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:

(a) -871×10^{-20} J (b) -435×10^{-20} J
(c) -217.9×10^{-20} J (d) -108.9×10^{-20} J

40. The wavelength associated with a golf ball weighing 200 *g* and moving with a speed of 5 *m*/*h* is of the order of
(a) 10^{-10} m (b) 10^{-20} m
(c) 10^{-30} m (d) 10^{-40} m

41. The Bohr orbit radius for the hydrogen atom ($n = 1$) is approximately 0.530 $\overset{o}{A}$. The radius for the first excited state ($n = 2$) orbits is
(a) 0.13 A^{o} (b) 10.6 A^{o}
(c) 4.77 A^{o} (d) 2.12 A^{o}

42. The angular momentum (L) of an electron in a Bohr's orbital is given as:
(a) $L = \dfrac{nh}{2\pi}$
(b) $L = \sqrt{l(l+1)}\,\dfrac{h}{2\pi}$
(c) $L = \dfrac{mg}{2\pi}$
(d) $h - \dfrac{h}{4\pi}$

43. The quantum numbers $+\dfrac{1}{2}$ and $-\dfrac{1}{2}$ for the electron spin represents:
(a) rotation of the electron in clockwise and anticlockwise direction respectively
(b) rotation of the electron in anticlockwise and clockwise direction respectively
(c) magnetic moment of electron pointing up and down respectively
(d) two quantum mechanical spin states which have no classical analogues

44. How many moles of electrons weigh one kilogram?
(a) 6.023×10^{23}
(b) $\dfrac{1}{9.108} \times 10^{31}$
(c) $\dfrac{6.023}{9.108} \times 10^{23}$
(d) $\dfrac{1}{9.108 \times 6.023} \times 10^{8}$

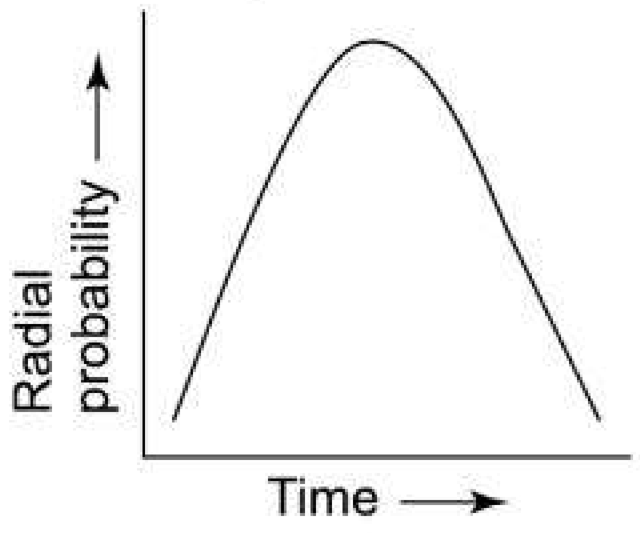
45. If the electronic configuration of nitrogen has $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2 2s^2 2p^3$ because the electrons would be close to the nucleus. Yet $1s^7$ is not observed because it violates:
(a) Heisenburg uncertinity principle
(b) Hund's rule
(c) Pauli's exclusion principle
(d) Bohr postulates of stationary orbits

46. No. of visible lines when an electron returns from 5th orbit to ground state in H spectrum :
(a) 5 (b) 4
(c) 3 (d) 10

47. 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 $3d_{z2}$ orbital is zero
(C) 2*s* 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), (D)

48. The first emission line in the H-atom spectrum in the Balmer series appears at:
(a) $\dfrac{5R}{36}$ cm^{-1} (b) $\dfrac{3R}{4}$ cm^{-1}
(c) $\dfrac{7R}{144}$ cm^{-1} (d) $\dfrac{9R}{400}$ cm^{-1}

49. Radial probability distribution curve is shown for *s* orbital in figure below. The curve is:



(a) 1*s* (b) 2*s*
(c) 3*s* (d) 4*s*

50. 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 a ring along *Z*-axis

51. Which of the following statement is wrong 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 = + ½

52. Which of the following statement is/are wrong
(a) If the value of I = 0, electron distribution is spherical
(b) The shape of the orbital is given by magnetic quantum no.
(c) Angular moment of 1*s*, 2*s*, 3*s* electrons are equal
(d) In an atom, all electrons travel with the same velocity

53. In Hydrogen atom the energy of an electrons determined by quantum number/s
(a) *n* (b) *n* and *l*
(c) *n*, *l* and *m* (d) *n*, *l*, *m* and *s*

54. The first line in the Balmer series in the hydrogen spectrum will have the frequency
(a) $4.57 \times 10^{14}\ s^{-1}$ (b) $3.29 \times 10^{15}\ s^{-1}$
(c) $8.22 \times 10^{15}\ s^{-1}$ (d) $8.05 \times 10^{13}\ s^{-1}$

55. The maximum value of *l* for an electron in fifth energy level is
(a) 5 (b) 4
(c) 3 (d) 2

56. The minimum value of *n* for which *g* – subshell is possible is
(a) 6 (b) 5
(c) 4 (d) 3

57. If the value of principal quantum number is 3, the total possible values for magnetic quantum number will be
(a) 1 (b) 4
(c) 9 (d) 12

58. The uncertainty in the position of an electron (mass $9.1 \times 10^{-28} g$) moving with a velocity of 3.0×10^{4} cm s^{-1} accurate up to 0.011% will be
(a) 1.92 cm (b) 7.68 cm
(c) 0.175 cm (d) 3.84 cm

59. The momentum of a photon having frequency 1.0×10^{15} ms^{-1}is about
(a) 2.21×11^{-11} kg ms^{-1}
(b) 2.21×10^{-27} kg ms^{-1}
(c) 2.21×10^{-19} kg ms^{-1}
(d) 6.63×10^{-19} kg ms^{-1}

60. The work function of a metal is 4.0 *eV*. If the metal is irradiated with radiation of wavelength 200 nm, then the maximum kinetic energy of the photo electrons would be about
(a) 6.4×10^{-19} J (b) 3.5×10^{-19} J
(c) 1.0×10^{-18} J (d) 2.0×10^{-19} J

61. The maximum kinetic energy of the photoelectrons is found to be 6.6×10^{-19} J when the metal is irradiated with a radiation of frequency 3×10^{15} Hz. The threshold frequency of the metal is
(a) 1×10^{15} Hz (b) 3×10^{15} Hz
(c) 2×10^{16} Hz (d) 2×10^{15} Hz

62. If threshold wavelength (λ_o) for ejection of electron from metal is 300 nm, then work function for the photo electric emission is
(a) 6×10^{-10} J (b) $1 .2 \times 10^{-18}$ J
(c) 3×10^{-19} J (d) 6×10^{-12} J

63. Radial part of the wave function depends on quantum numbers
(a) *n* and *s* (b) *l* and *m*
(c) *l* and *s* (d) *n* and *l*

64. If *E* is the kinetic energy of the particle then which of the following expressions is correct for the de-Broglie wavelength of the particles?
(a) $\lambda = \dfrac{h}{2mE}$ (b) $\lambda = \sqrt{\dfrac{h}{2mE}}$
(c) $\lambda = \dfrac{h}{\sqrt{2mE}}$ (d) $\lambda = \dfrac{\sqrt{2mE}}{h}$

65. At 200°C hydrogen molecules have velocity 10^{5} cm sec^{-1}. The de-Broglie wave length in this case is approximately
(a) 2 Å (b) 1000 Å
(c) 100 Å (d) 10 Å

66. 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, as
(a) (iv) < (ii) < (iii) < (i)
(b) (ii) < (iv) < (i) < (iii)
(c) (i) < (iii) < (ii) < (iv)
(d) (iii) < (i) < (iv) < (ii)

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➤ Solution

At radioactive equilibrium A $\longrightarrow$ B

$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{(t_{1/2})_A}{(t_{1/2})_B}$$

$$\therefore \qquad \frac{3.1 \times 10^9}{1} = \frac{2 \times 10^{10}}{(t_{1/2})_B}$$

$$\therefore \qquad (t_{1/2})_B = 6.45 \text{ year}$$

Nuclear Transformation or Nuclear Transmutation

The conversion of one element into another by artificial means, i.e. by means of bombarding with some fundamental particles, is known as **artificial transmutation**. The phenomenon was first applied by Rutherford on nitrogen whose nucleus was bombarded with α-particles to produce oxygen.

$$\underset{\text{Nitrogen isotope}}{{}_7\mathrm{H}^{14}} + \underset{\alpha\text{-Particle}}{{}_2\mathrm{He}^4} \rightarrow \underset{\text{Oxygen isotope}}{{}_8\mathrm{O}^{17}} + \underset{\text{Proton}}{{}_1\mathrm{H}^1}$$

In case, the element so produced shows radioactivity, the phenomenon is known as induced radioactivity. Following important fundamental particles have been used in the bombardment of different elements.

(i) **α-Particle:** Helium nucleus represented as $(\mathrm{He})^{2+}$

(ii) **Proton:** Hydrogen nucleus represented as ${}_1\mathrm{H}^1$

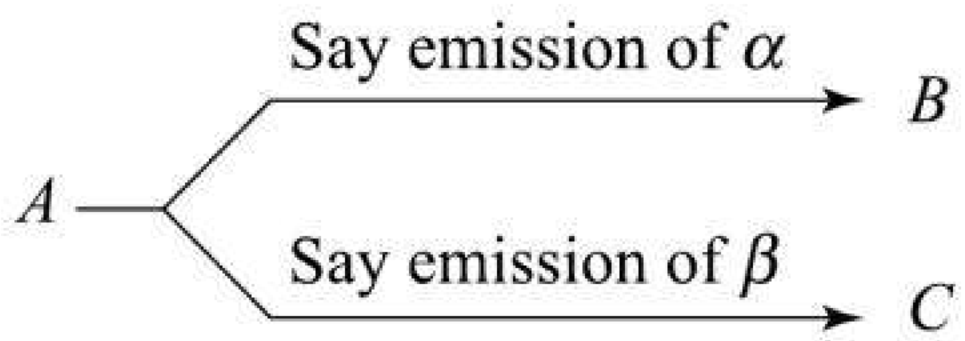
(iii) **Deutron:** Deuterium nucleus represented as ${}_1\mathrm{H}^2$ or ${}_1\mathrm{D}^2$

(iv) **Neutron:** A particle of mass number 1 but no charge represented as ${}_0\mathrm{n}^1$.

- Since α-particles, protons and deutrons carry positive charge, they are repelled by the positively charged nucleus and hence are not good projectiles.
- Neutrons, which carry no charge at all, are the best particles.
- Further among α-particles, protons and deuterons; the latter two carrying single positive charge are better projectiles than the α-particles.
- However, the positively charged α-particles, protons and deuterons can be made much more effective if they are imparted with high velocity.
- **Cyclotron** is the most commonly used instrument for accelerating these particles, the particles leave the instrument with a velocity of about 25,000 miles per second.
- A more recent accelerating instrument, called the **synchotron** or **bevatron** makes use of the induced current or force exerted on the electron in a changing magnetic field.
- Neutrons, being neutral, cannot be accelerated by particle accelerators.

Parallel Path Decay

A radioactive element A decay to B and C in two parallel paths as:



The average decay constant for the element A can be expressed as

$$\boxed{\lambda_{\text{average}} = \lambda_{\alpha \text{ path}} + \lambda_{\beta \text{ path}}}$$

$$\lambda_{\alpha \text{ path}} = [\text{Fractional yield of B}] \times \lambda_{\text{av}}$$

$$\lambda_{\beta \text{ path}} = [\text{Fractional yield of C}] \times \lambda_{\text{av}}$$

Maximum yield of Daughter Element

A radioactive element A decays to give a daughter element B which further decays to another daughter element C and so on till a stable element is formed (A $\rightarrow$ B $\rightarrow$ C). Also if number of daughter atoms at $t = 0$ is zero and parent atom is much more lived than daughter (i.e. $\lambda_A < \lambda_B$) where, λ_A and λ_B are decay constant of A and B respectively, then number of atoms of daughter element B after time t is

$$N_B = \frac{N_0 \lambda_A}{\lambda_B - \lambda_A}\left[e^{-\lambda_A t} - e^{\lambda_B t}\right]$$

Maximum activity of daughter element can be expressed at $t_{\max}$.

$$t_{\max} = \frac{2.303}{\lambda_B - \lambda_A} \log_{10}\left[\frac{\lambda_B}{\lambda_A}\right]$$

involved in many reactions of industrial importance such as alkylation, polymerisation, catalytic synthesis etc.

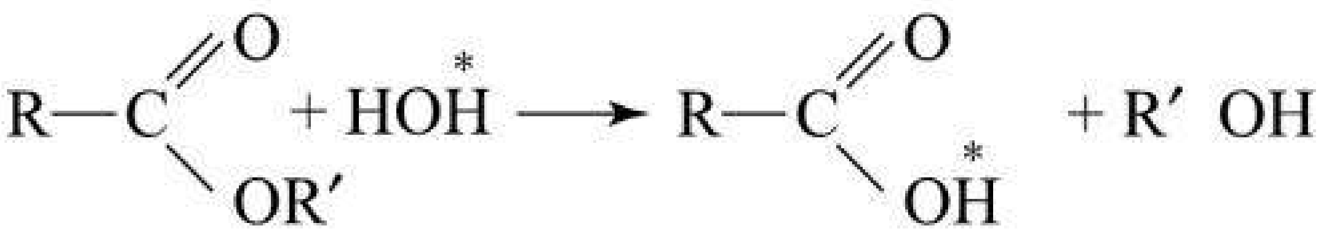
(iv) Analytical studies Several analytical procedures can be used employing radioisotopes as tracers.

(a) Adsorption and occlusion studies A small amount of radioactive isotope is mixed with the inactive substance and the activity is studied before and after adsorption. Fall in activity gives the amount of substance adsorbed.

(b) 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.

(c) Ion-exchange technique Ion exchange process of separation is readily followed by measuring activity of successive fractions eluted from the column.

(d) Reaction mechanism By labelling oxygen of the water, mechanism of ester hydrolysis has been studied.



$$R-C(=O)OR' + HO\overset{*}{H} \longrightarrow R-C(=O)\overset{*}{O}H + R'OH$$

(e) 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.

IIT WINDOW—II

Multiple Choice Questions (Having only one Correct option)

1. A certain nuclide has a half life of 30 minutes. If one starts with 48 g of it, amount left at the end of 30 minutes will be

(a) 24 g (b) 16 g
(c) 8 g (d) 6 g

2. The sample of radioactive isotope with a half life of 20 days weighs 1.0 g. After 40 days, the weight of the remaining element is

(a) 0.5 (b) Zero
(c) 0.25 g (d) 1/6 g

3. If 5.0 g of a radioactive substance has $t_{1/2} = 14$ hours, 20 g of the same sample will have a $t_{1/2}$ of?

(a) 56 hr (b) 3.5 hr
(c) 14 hr (d) 28 hr

4. The half life of a radioactive substance is 100 days. After 400 days, one gm of element will be reduced to

(a) 0.5 g (b) 0.25 g
(c) 0.0625 g (d) 0.125 g

5. 8.0 g of a radioactive substance is reduced to 0.5 g. after one hour. The half life period of the radioactive substance is?

(a) 15 min (b) 30 min
(c) 45 min (d) 10 min

6. Mass number of a nuclide is 216. Its approximate radius in Fermi units is

(a) 6.0 (b) 7.0
(c) 8.0 (d) 7.8

7. A sample of radioactive element with $t_{1/2}$ of 11.2 years weighs 2.0 g. After 33.6 years how much amount of that element is left?

(a) 0.25 g (b) 0.5 g
(c) 0.75 g (d) 1.0 g

8. The radioactivity due to C–14 isotope (half life = 6000 years) of a sample of wood from an ancient tomb was found to be nearly half that of fresh wood. The tomb is there for about?

(a) 3000 yr old (b) 6000 yr old
(c) 9000 yr old (d) 12000 yr old

9. A substance is kept for 2 hours an three fourth disintegrates during this period. The half life of the substance?

(a) 2 hours (b) 1 hours
(c) 30 minutes (d) 4 hours

10. After three half lives, the percentage of fraction of amount left is?

(a) 6.35 (b) 12.5
(c) 50 (d) 75

11. The reactor moderated by heavy water is called

15. Fertile nuclides are **[CPMT, 2000]**

(a) Isotopes (b) Fissionable

(c) Not fissionable (d) None of these

16. If 1/16th of a substance is left after 40 days then the half–life is **[CPMT, 2000]**

(a) 40 days (b) 30 days

(c) 20 days (d) 10 days

17. The nuclei which can undergo fission reactions are called **[PMT (DELHI), 2000]**

(a) Fertile nuclide (b) Infertile nuclides

(c) Fissile nuclides (d) Infissile nuclides

18. Initially 300 g of a substance has half–life of 30 minutes. The amount left after 3 hr is **[CBSE, 2000]**

(a) 3.69 g (b) 4.69 g

(c) 6.66 g (d) 5.69 g

19. The carbon dating is based on **[PMT (MP), 2001]]**

(a) ${}_6C^{15}$ (b) ${}_6C^{14}$

(c) ${}_6C^{13}$ (d) ${}_6C^{11}$

20. If the binding energy of an atom is 128 MeV and binding energy per nucleon is 8 MeV. Then the number of nucleons in the atom (nucleus) is **[CMPT, 2001]**

(a) 8 (b) 16

(c) 18 (d) 28

21. The half life of ${}_6C^{14}$, if decay constant is 6.31×10^{-4} is **[CBSE, 2001]**

(a) 1098 years (b) 109.8 years

(c) 10.98 years (d) 1.098 years

22. The first artificial disintegration of an atomic nucleus was achieved by **[Kerala (E), 2002]**

(a) Geiger (b) Wilson

(c) Madam Curie (d) Rutherford

23. To differentiate between C–12, C–13 and C–14, the instrument that you would use is **[Kerala (E), 2002]**

(a) Infrared spectrometer

(b) Atomic absorption spectrometer

(c) Mass spectrometer

(d) Ultraviolet spectrometer

24. Which one of the following statements is correct **[EAMCET (E), 2002]**

(a) The radius (R) of a nuclide of mass number A is given by $R = R_0 A^{1/2}$ (R_0 is constant)

(b) ${}_7N^{15}$ and ${}_8O^{16}$ are isobars

(c) The end nuclide formed in thorium series (4n) is ${}_{83}Bi^{209}$

(d) ${}_{20}Ca^{40}$ has magic number of protons and magic number of neutrons

25. In a radioisotope, the value of $t_{1/2}$ and λ are identical in magnitude. The value of λ is **[Karnataka (M), 2002]**

(a) $(0.693)^2$ (b) 0.693

(c) $(0.693)^{1/2}$ (d) 1/0.693

26. The elements ${}_{19}K^{40}$ and ${}_{20}Ca^{40}$ are **[CMPT, 2002]**

(a) Isobaric (b) Isotopic

(c) Isotonic (d) Isoelectronic

27. According to the nuclear reaction ${}_4Be^M + {}_2He^4 \to {}_6C^{12} + {}_0n^1$ the mass number M of Be is **[AFMC, 2002]**

(a) 4 (b) 6

(c) 7 (d) 9

28. Half life period of ${}_{53}I^{125}$ is 60 days. Percentage of radioactivity present after 180 days is **[CBSE (AIEEE), 2002]**

(a) 50% (b) 75%

(c) 36% (d) 12.5%

29. If ${}_{92}U^{235}$ nucleus absorbs a neutron and disintegrates in ${}_{54}Xe^{139}$, ${}_{38}Sr^{95}$ and X. Then what will be the product X. **[CBSE, 2002]**

(a) α-particle (b) β-particle

(c) 2-neutrons (d) 3-neutrons

IIT WINDOW–IV

Subjective Problems

1. Complete the following reactions:

(i) $${}^{234}_{90}\text{Th} \longrightarrow \ldots. + 7\ {}^{4}_{2}\text{He} + 6\ {}_{-1}\beta^{o}$$ **[IIT, 2004]**

(ii) $${}^{235}_{92}\text{U} + {}_0n^1 \longrightarrow \ldots. + {}^{137}_{52}\text{Te} + {}^{92}_{40}\text{Zn}$$ **[IIT, 2005]**

(iii) $${}^{84}_{34}\text{Se} \longrightarrow Z\ {}_{-1}e^0 + \ldots..$$ **[IIT, 2005]**

2. ^{64}Cu (T_{50} = 12.8 year) decays β^- emission (38%), β^+ decay products and calculate partial half–lives for each of the decay processes. **[IIT, 2002]**

$$\log\frac{a}{a-143430}=\frac{6.909\times0.693}{2.303\times66.6}=0.0312$$

$$\text{or}\ \log\frac{a}{a-2.3814\times10^{-19}}=0.0312$$

Taking antilogarithm

$$\frac{a}{a-2.3814\times10^{-19}}=1.07$$

$a = 1.07\ (a - 2.3814\times10^{-19})$

$0.07a = 2.518\times10^{-19}$ mole

$a = 3.597\times10^{-18}$ mole

At. wt. of Mo = 99

Amount of Mo $= 3.597\times10^{-18}\times99$

$= 3.56\times10^{-16}$ g

9. ${}_{90}Th^{234} \longrightarrow {}_{82}Pb^{206}$

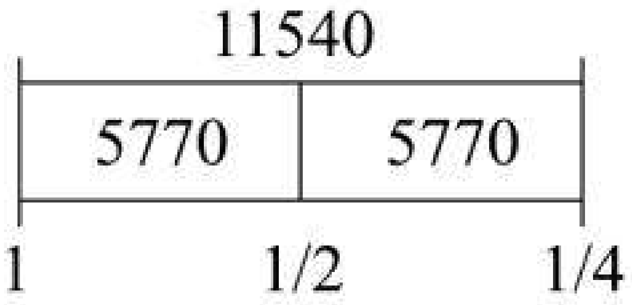
$$\text{No. of }\alpha\text{-particles} = \frac{\text{change in Mass No}}{4}$$

$$=\frac{28}{4}=7$$

No. of β-particle = (Atomic No. of Product) – (Atomic No. of reactant – Z × No of α)

$= 82 - 90 + 2\times7 = 6.$

10. $t_{1/2}$ of carbon = 5770 years.



It means ¼ remain.

11. $W_{c^{14}} = 7\text{ mg} = 7\times10^{-3}$ gm.

$$\text{Mole of carbon} - 14 = \frac{7\times10^{-3}}{14}=0.5\times10^{-3}$$

Atoms of $C^{14} = 0.05\times10^{-3}\times6.02\times10^{23}$

$= 3.01\times10^{20}$

$\underset{n=8}{\boxed{{}_6C^{14}}}$ $\therefore$ No. of 'n' in $C^{14} = 3.01\times10^{20}\times8$

$= 2.40\times10^{21}.$

Total Mass of Neutron

$$=\frac{3.01\times10^{20}\times8\times1.00}{6.02\times10^{23}}$$

$= 4\times10^{-3}$ gm.

IIT WINDOW–V

➤ Match the column I with column II

Matrix Matching

1.

Column I	Column II
A. Nuclear Fission	P. U^{235}
B. Nuclear Fusion	Q. U^{239} or Pu^{241}
C. Bleeder Reactor	R. Steller Energy
D. Atomic Reactor	S. Atom bomb.

2.

Column I	Column II
A. 4n Series	P. Thorium series
B. (4n + 1) Series	Q. Actinium Series
C. (4n + 2) Series	R. Uranium Series
D. (4n + 3) Series	S. Naptunium Series

3.

Column I	Column II
A. Half life	P. Dependent of Initial conc.
B. Average life	Q. Infinity
C. Complete life	R. 0.693/av. Life.
D. Decay life.	S. $1.044\times t_{1/2}$.

4.

Column I	Column II
A. Isosters	P. ${}_1H^2$ and ${}_2He^3$
B. Isotopes	Q. CO_2 and N_2O
C. Isobars	R. ${}_1H^2$ and ${}_1H^1$
D. Isotones	S. ${}_{20}Ca^{40}$ and ${}_{19}K^{40}$

5.

Column I	Column II
A. Isoelectronic	P. ${}_2He^3$ and ${}_2He^4$.
B. Isodiaphers	Q. CO_2 and N_2O.
C. Isotones	R. ${}_AX^Z$ and ${}_{A-2}X^{Z-4}$
D. Isosters	S. Na^+, F^-, O^{2-}
	T. ${}_1H^2$ and ${}_2He^3$.

$$P_1 = n_1\,\frac{RT}{v} \text{ and } P_2 = n_2\,\frac{RT}{v}$$

$$P_{\text{Total}} = P_1 + P_2 \text{ [for two components only]}$$

$$P_T = \frac{RT}{v}\,(n_1 + n_2)$$

$$\Rightarrow \boxed{P_1 = \frac{n_1}{n_1 + n_2}P_T} \text{ and } \boxed{P_2 = \frac{n_2}{n_1 + n_2}P_T}$$

⇒ Partial pressure = Mole fraction × Total pressure.

⇒ Partial pressure = Volume fraction × Total pressure

(vii) Graham's law of diffusion

Diffusion The process of intermixing or intermingling of two or more gases against the law of gravity due to movement of molecule of gases by random motion is called diffusion.

Effusion The process by which a gas comes out from a higher pressure region to lower pressure region through a small orifice or hole is called effusion.

Graham's law Under similar condition of temperature and pressure. The rates of diffusion of different gases are inversely proportional to the square roots of their molecular mass or density.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Rate of diffusion is always taken as moles of a gas diffused per unit time or volume of a gas diffused per unit time or distance travelled per unit time.

In totality, the rate of diffusion is also proportional to the pressure of the gas at a given temperature. Thus,

$$r \propto \frac{p}{\sqrt{d}} \Rightarrow \frac{r_1}{r_2} = \frac{p_1}{p_2}\sqrt{\frac{d_2}{d_1}} = \frac{p_1}{p_2}\sqrt{\frac{M_2}{M_1}}$$

In case of effusion.

$$r = \frac{PA}{\sqrt{2\pi RTM}}.$$

Where P = Partial pressure of gas
R = Gas constant
A = Area of orifice.

Other terms have their usual meaning.

Kinetic Theory of Gases

Basic Assumptions: of kinetic theory

(i) A gas consists of extremely small discrete particles called molecules.
(ii) The molecules of a gas are similar in shape and size but different from other gases.
(iii) The gas molecules more randomly in to and fro direction, colliding with one another and with the walls of container.
(iv) The collision between molecules are supposed to be perfectly elastic
(v) The force of attraction between the gas molecules are supposed to be negligible.
(vi) The average kinetic Energy per molecule of gas is proportional to the absolute temperature.
(vii) The pressure exerted by a gas is due to collision of the gas.
(viii) The volume of a molecule is so small that it may be neglected in comparison to total volume of the gas.

On this basis,

$$PV = \frac{1}{3}mn\,v_{\text{rms}}^2 \Rightarrow V_{\text{rms}} = \sqrt{\frac{3p}{d}} = = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3Pv}{M}}$$ [where m = mass of gas molecules
n = no of gas molecule

$$\Rightarrow PV = \frac{2}{3} \times \frac{1}{2}Mv_{\text{rms}}^2$$

$$= \frac{2}{3} \times \text{Kinetic Energy. } (\text{E}_{\text{kinetic}})$$

$$\Rightarrow \boxed{RT = \frac{2}{3}\cdot E_{\text{kinetic}}}$$

$$\Rightarrow E_{\text{kinetic}} = \frac{3}{2}RT \text{ (for one mole)}$$

$$\Rightarrow \boxed{E_{\text{kinetic}} = \frac{3}{2}nRT} \text{ [for n-mole of gas]}$$

Velocities of Gas Molecules

Gas molecules have tremendous velocities in to and fro direction. Due to which molecules colloid with each other and their velocities changes.

(a) Root Mean Square Velocity The square root of average of the square velocity is called root mean square velocity (V_{rms})

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gases we assume planes at a distance of mean free path. Coefficient of viscosity (η) is given by

$$\eta = \frac{5}{16\sigma^2}\left(\frac{mKT}{\pi}\right)^{\frac{1}{2}}$$

where K is the Boltzmann constant equal to R/N

σ = diameter of molecule

m = Mass of molecule.

Molar Heat Capacity

The amount of heat energy required to raise the temperature of 1 gm of substance through 1°C is called specific heat capacity. (Its unit is cal.)

If the heat energy required to raise the temperature of 1 mole of substance by 1°C, it is called molar heat capacity.

Molar heat capacity = sp. Heat × Molecular mass of gas.

Molar heat at constant volume (Cv) and molar heat capacity at constant pressure (Cp)

$\Rightarrow \quad C_P - C_V = \text{R} = 2$ cal.

For Monoatomic gas, $C_P = 5$ cal $C_V = 3$ cal

$$: \gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67.$$

For Diatomic gas, $C_P = 7$ cal. $C_V = 5$ cal.

$$\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.40$$

For Triatomic gas $C_p = 8$ cal. and $C_V = 6$ cal. (Non polar).

$$\gamma = \frac{8}{6} = 1.33.$$

IIT WINDOW–I

➤ Solved Numerical Problems

➤ Example 4.1

A gas occupying a volume of 725 ml at a pressure of 0.970 atm is allowed to expand at constant temperature until its pressure becomes 0.541 atm. What is its final volume?

➤ Solution

Given $P_1 = 0.970$ atm. $V_1 = 725$ ml

$P_2 = 0.541$ atm. $V_2 = ?$

Since Temperature remain constant,

$\therefore P_1V_1 = P_2V_2$

$\Rightarrow \quad 0.970 \times 725 = 0.541 \times V_2$

$\Rightarrow \quad V_2 = 1299.9$ ml **Ans.**

➤ Example 4.2

Cyanogen is a compound of carbon and nitrogen. On combustion in excess oxygen 500 ml of cyanogen give 500 ml of N_2 and 1000 ml. of CO_2 measured at same temperature and pressure. What is the formula of Cyanogen?

➤ Solution

Let the formula of cyanogen be C_xN_y.

$$C_xN_y + xO_2 \longrightarrow x\,CO_2 + \frac{y}{2}N_2$$

1 mole $\qquad x$ mole $\qquad \frac{y}{2}$ mole.

According to question 500 ml cyanogen give 1000 ml CO_2 it means $x = 2$.

and 500 ml cyanogen give 500 ml N_2 it means $y = 2$.

$\therefore$ the formula of cyanogen = $(CN)_2$. **Ans.**

➤ Example 4.3

A gas filled balloon having a volume of 2.5 L at 1.2 atm and 25°C is allowed to rise to the stratosphere (about 30 km above the surface of the earth) where the temperature and pressure are – 23°C and 3.00×10^{-3} atm. respectively. Calculate the final volume of the balloon.?

➤ Solution

Given $P_1 = 1.2$ atm. $\qquad P_2 = 3.00 \times 10^{-3}$ atm.

$T_1 = 25°C \qquad T_2 = -23°C$

$= 298$ K $\qquad = 250$ K

$V_1 = 2.5$L $\qquad V_2 = ?$

using $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2} \qquad V_2 = 8.389 \times 10^2$ L. **Ans**

➤ Example 4.4

Dry ice is solid CO_2. A 0.050 gm sample of dry ice is placed in an evacuated vessel of volume 4.6 L at 30°C. Calculate the pressure inside the vessel after all the dry ice has been converted into CO_2 (gas).?

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Mass of air displaced by balloon

$$= \frac{1.2 \times 4190 \times 10^6}{10^3} = 5028 \times 10^4 \text{ gm.}$$

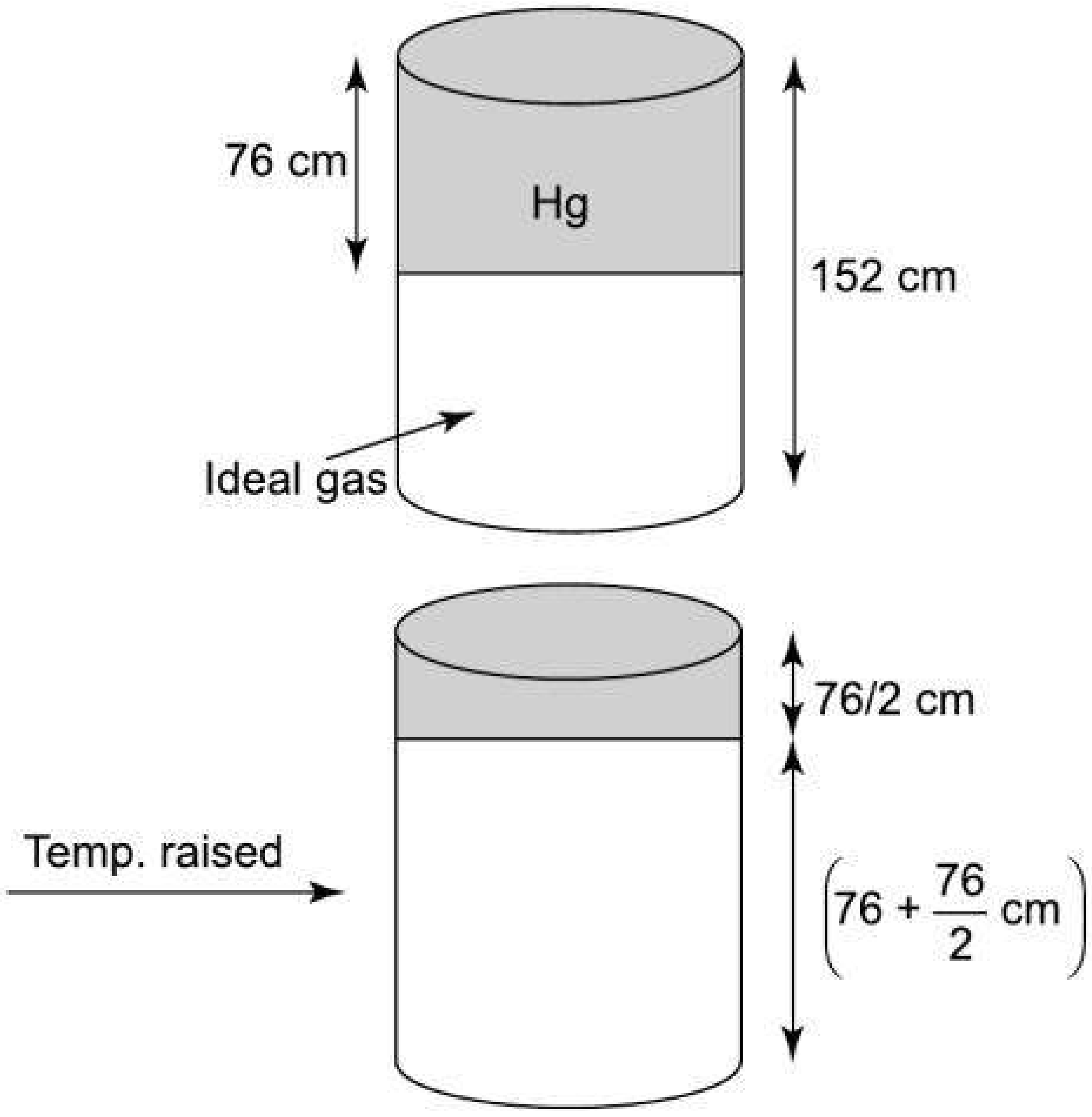
Pay load = Mass of air displaced – Total mass of balloon.

$$= 502.8 \times 10^4 - 78.13 \times 10^4$$
$$= 424.68 \times 10^4 \text{ gm.} \qquad \textbf{Ans.}$$

➤ Example 4.15

A vertical hallow cylinder of hight 152 cm is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and upper half is filled with Hg. The cylinder is initially as shown in figure. If temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.? **[Roorkee, 1993]**

➤ Solution



Before heating

$P_1 = (76 + 76) = 152$ cm of Hg.

$T_1 = 300$ K

$V_1 = $ (of air) $= V/2$.

After heating.

$P_2 = (76 + 38) = 114$ cm of Hg.

$V_2 = ¾\, V$

$T_2 = ?$

using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\Rightarrow \quad \frac{152 \times \frac{V}{2}}{300} = \frac{114 \times \frac{3}{4}V}{T_2}$$

$$\Rightarrow \quad T_2 = 337.5 \text{ K.} \qquad \textbf{Ans.}$$

➤ Example 4.16

20% N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of equilibrium mixture? **[Roorkee , 1996]**

➤ Solution

	N_2O_4 (g)	$\rightleftharpoons 2NO_2$ (g)
Initially (mole)	1	0
At eqlm	$1-\alpha$	2α

Here $\alpha = 0.2$

∴ Mole of $N_2O_4 = 0.8$

Mole of $NO_2 = 0.4$.

$$\text{Molecular Mass of Mixture} = \frac{0.8 \times 92 + 0.4 \times 46}{1.2}$$
$$= 76.66$$

$$\therefore \quad \text{Density} = \frac{W}{V} = \frac{Pm}{RT} = \frac{76.66 \times 1}{0.0821 \times 300}$$
$$= 3.117 \text{ gm L}^{-1}.$$

➤ Example 4.17

One way of writing the equation of state for real gases is

$$P\bar{V} = RT\left[1 + \frac{B}{V} + ...\right]$$

Where B is constant. Derive an approximate expression for B in terms of the Vander Waal constants '*a*' and '*b*'.? **[IIT, 1997]**

➤ Solution

Vander-Waal equation is written as

$$\left(P + \frac{a}{\bar{v}^2}\right)(\bar{v} - b) = RT \text{ (For 1 mole)}$$

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17. A mixture of methane and ethene in the mole ratio X : Y has a mean molecular weight = 20. What would be the mean molecular weight if the same gases are mixed in the ratio Y : X

(a) 22 (b) 24
(c) 20.8 (d) 19

18. If the most probable velocity of hydrogen molecules at a temperature *t*°C is V_0. Suppose all the molecules dissociate into atoms when temperature is raised to (2*t* + 273)°C then the new rms velocity is?

(a) $\sqrt{\frac{2}{3}}V_0$ (b) $\sqrt{3(2+273/t)}V_0$
(c) $2/\sqrt{3}V_0$ (d) $\sqrt{6}V_0$

19. An open vessel at 27°C is heated until 3/8th of the air in it has been expelled. Assuming that the volume remains constant, The temperature at which the vessel was heated. is?

(a) 307°C (b) 107°C
(c) 480°C (d) 207°C

20. The vapour pressure of water at 80°C is 355 mm of Hg. A 100 mL vessel contains water saturated with O_2 at 80°C, the total pressure being 760 mm of Hg. The contents of the vessel were pumped into a 50 mL vessel at the same temperature. What is the partial pressure of O_2?

(a) 1115 mm (b) 810 mm
(c) 405 mm (d) 355 mm

21. At STP, 0.48 g of O_2 diffused through a porous partition in 1200 seconds. The volume of CO_2 diffused under same condition is?

(a) 286.5 ml (b) 346.7 ml
(c) 112.2 ml (d) 224.8 ml

22. A bubble of gas released at the bottom of a lake increases to eight times its original volume when it reaches the surface. Assuming that atmospheric pressure is equivalent to the pressure exerted by a column of water 10 m high, what is the depth of the lake?

(a) 90m (b) 10m
(c) 70m (d) 80m

23. A gas can be easily liquefied.

(a) when its inversion temperature equals the Boyle temperature
(b) under reversible adiabatic expansion
(c) under pressure when it is cooled to below the critical temperature
(d) at low pressure and above the critical temperature

24. Which of the following is correct for critical temperature?

(a) It is the highest temperature at which liquid and vapour can coexist.
(b) Beyond this temperature, there is no distinction between the two phases and a gas cannot be liquefied by compression.
(c) At this temperature, the surface tension of the system is zero.
(d) At this temperature, the gas and the liquid phases have difficult critical densities.

25. 40.0 mL of a gaseous mixture of CO and C_2H_2 is mixed with 100 mL of O_2 and burnt. The volume of the gas after the combustion is 55 mL. Calculate the composition of the original mixture

(a) 25 mL of CO and 15 mL of C_2H_2
(b) 15 mL of CO and 25 mL of C_2H_2
(c) 10 mL of CO and 30 mL of C_2H_2
(d) 20 mL of CO and 20 mL of C_2H_2

26. 80 mL of oxygen is added to 50 mL of a mixture of H_2, C_2H_2 and CO, after which the total mixture is burnt. The volume of the cooled mixture after combustion measures 65 mL. This is reduced to 15 mL by treatment with a KOH solution. Calculate the volume of each gas in the original mixture.

(a) 20 mL of H_2, 20 mL of C_2H_2, 10 mL of CO
(b) 10 mL of H_2, 20 mL of C_2H_2, 20 mL of CO
(c) 15 mL of H_2, 15 mL of C_2H_2, 20 mL of CO
(d) 20 mL of H_2, 25 mL mL of C_2H_2, 5 mL of CO

27. 50 mL of a mixture of C_2H_4, and C_2H_2 was mixed with 150 mL of O_2 and burnt. The volume of the cooled mixture of gases after the combustion is 112.5 mL. The percentage of C_2H_4 in the original mixture is

Calculate, (a) what volume of gas would remain and (b) what weight of iodine would be liberated assuming the volume to have been measured at NTP?

23. A certain container has 5×10^{23} molecules of a gas A at a pressure of 900 torr. By a photochemical combination allowing light to fall on the molecules, the pressure drops to 500 due to dimerisation. If the temperature and volume remain the same, how many monomer, dimmer and total molecules are present after exposure to light?

24. 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 tyre increases to 47°C.

(a) What would be the pressure at this temperature?

(b) How many litre of air measured at 47°C and pressure of 1 atm should be let out restore the tyre to 3 atm at 47°C?

25. A mixture of N_2 and water vapours is admitted to a flask which contains a solid drying agent. Immediately after admission, the pressure of the flaks is 760 mm. After standing some hours, the pressure reached a steady value of 745 mm.

(a) Calculate the composition in mole % of original mixture.

(b) If the experiment is done at 20°C and the drying agent increases in weight by 0.15 what is the volume of flask?

26. In a space shuttle, the CO_2 output per astronaut has been estimated as 44g per hour. catalytic converter reduces CO_2 into H_2O at a rate of 600 mL (at STP) per min. What fraction of the time would such a converter be operated in order to keep up the CO_2 out of one astronaut.?

27. A container holds 3 litre of $N_{2(g)}$ and $H_2O_{(l)}$ at 29°C. The pressure is found to be 1 atm. The water in container is instantaneously electrolysed to give H_2 and O_2 following the reaction, $H_2O_{(l)} \longrightarrow H_{2(g)} + \frac{1}{2}\ O_{2(g)}$. At the end of electrolysis the pressure was found to be 1.86 atm. Calculate the amount of water present in the container if the aqueous tension of water at 29°C is 0.04 atm.?

28. A closed bulb contains 0.01 mole of inert helium gas and a sample of solid white NH_4Cl. The pressure of the He is measured at 27°C and is found to be 114 mm Hg. The bulb then heated to 327°C. All the NH_4Cl decomposes according to the equation.

$NH_4Cl_{(s)} \longrightarrow NH_{3(g)} + HCl_{(g)}$

The final total pressure in the bulb after complete decomposition of solid is 908 mm Hg. Assume all the gases are ideal.

(a) What is the partial pressure of $HCl_{(g)}$in the bulb at 327°C when reaction is complete?

(b) How many grams of $NH_4Cl_{(s)}$ were in the bulb at 27°C?

29. An under water bubble with a radius of 0.5 cm at the bottom of tank, where temperature is 5°C and pressure is 3 atm rises to the surface where temperature is 25°C and pressure is 1 atm. What will be the radius of bubble when it reaches to surface.?

30. An open vessel at 27°C is heated until three-fifths 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.?

31. A spherical balloon of 21 cm diameter is to be filled with hydrogen at N.T.P. from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up.

32. Calculate the relative rates of diffusion for $^{235}UF_6$ and $^{238}UF_6$ in gaseous form. Also if naturally occurring uranium ore having U^{235} and U^{238} as 0.72 and 99.28 percent by moles and if it is desired to enrich the U^{235} to 10% of the sample making use of relative rates of diffusion of UF_6 having U^{235} and U^{238} isotopes, how many diffusion stages are required.?

33. 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 horizontally. The middle 5 cm containing Hg

10. 20 dm^3 of SO_2 diffuses through a porous patition in 60 second. What volume be O_2 will diffuse under similar condition in 30 second? **[Roorkee, 1996]**

11. One mole of nitrogen gas at 0.8 atm takes 38 seconds to diffuse through a pinhole whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 5 seconds to diffuse through the same hole. Calculate the molecular formula of the compound. **[IIT, 1999]**

12. The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$), which is attained at 1200°C is determined by measuring the rate of effusion through a pinhole. It is observed that a 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast a krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (Atomic wt. of Kr = 84). **[IIT, 1995]**

13. A mixture containing 1.12 litre D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D_2. Determine the % by weight of the gases in second bulb. **[Roorkee, 1998]**

14. At 27°C, H_2 is leaked through a tiny hole into a vessel for 20 minute. Another unknown gas at the same T and P as of the H_2 is leaked through the same hole for 20 minute. After the effusion of the gases, the mixture exerts a pressure of 6 atm. The H_2 content of the mixture is 0.7 mole. If volume of container is 3 litre, what is mol. wt. of unknown gas? **[IIT, 1992]**

15. The average speed at T_1 *K* and the most probable speed at T_2 *K* of CO_2 gas is 9×10^4 cm sec^{-1}. Calculate the value of T_1 and T_2. **[IIT, 1990]**

16. The average speed of an ideal gas molecule at 27°C is 0.3 m sec^{-1}. Calculate average speed at 927°C **[IIT, 1986]**

17. A glass bulb of 1 litre capacity contains 2×10^{21} molecules of nitrogen exerting pressure of 7.57×10^3 Nm^{-2}. Calculate the root mean square speed and the temperature of gas molecules. If the ratio of $Cl_{m.p.}$ to u_{rms} is 0.82, calculate $Cl_{m.p.}$ for these molecules at this temperature. **[IIT, 1993]**

18. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. **[IIT, 2003]**

19. (a) Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der Waal's equation. Also report the pressure of gas if it behaves ideally in nature.

Given that $a = 3.592$ atm litre^2 mol^{-2}, $b = 0.0427$ litre mol^{-1}.

(b) If volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K. $a = 3.592$ dm^6 atm mol^{-2} **[IIT, 2000]**

20. Using van der Waal's equation, calculate the constant, '*a*' when two mole of a gas confined in a four litre flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K. The value of '*b*' is 0.05 lit. mol^{-1}. **[IIT, 1998]**

21. One way of writing the equation of state for real gases is $PV = RT\left[1+\frac{B}{V}+...\right]$, where B is constant. Derive an approximate expression for B in terms of van der Waal's constants *a* and *b*. **[IIT, May 1997]**

IIT WINDOW–V

➤ MCQ (Having one or more than one Answer)

1. The value of the molar gas constant is

(a) 8.3145×10^3 J (Kg mol)$^{-1}$ K^{-1}

(b) 1.987 cal mol K^{-1}

(c) 0.083145×10^3 dm^3 bar mol^{-1} K^{-1}

(d) 0.083145 dm^3 bar mol^{-1} K^{-1}

V. Match the compression factor under different condition (in list I) with its value (in list II)

	List I		List II
A.	Compression factor (z) for ideal gas	1.	3/8
B.	Z for real gas at low P	2.	$(1 + pb/RT)$
C.	Z for real gas at high P	3.	1
D.	Z for critical state	4.	$(1 - a/RTv)$

VI. Match the different temperatures (in list I) with its value (in list II)

	List I		List II
A.	Critical temperature	1.	a/Rb
B.	Boyle temperature	2.	$2a/Rb$
C.	Inversion temperature	3.	T/Tc
D.	Reduced temperature	4.	$8a/27\,Rb$

VII. Match the factors in column I with column II.

	Column I	Column II
A.	Diffusion of gas	1. Temperature
B.	Density	2. Pressure
C.	Critical temperature	3. Attractive forces
D.	Kinetic Energy	4. Molecular Mass.

VIII. Match the column I & column II.

	Column I	Column II
A.	Hydrogen gas ($P = 200$ atm. $T = 273$ k)	1. Compressibility factor $\neq 1$
B.	Hydrogen gas ($P \approx O$, $T = 273$ k)	2. Attractive forces are dominant
C.	CO_2 (P = 1atm T = 273 K)	3. $PV = nRT$
D.	Real gases with very large molar Mass	4. $P(V - n) = nRT$.

IX.

	Column I	Column II
A.	Boyle's temperature. (T_B)	1. a/Rb
B.	Inversion temperature. (Ti)	2. $3a/Rb$
C.	Critical temperature. (Tc)	3. $2a/Rb$
D.	Kraft temperature.	4. $\frac{8a}{27Rb}$
		T. Minimum temperature for micell formation.

IIT WINDOW–VII

➤ Assertion and Reason

1. Statement-I: The ideal gas could be easily liquefied.

Statement-II: The ideal gas has no attractive or repulsive forces.

2. Statement-I: The experimently determined value with critical parameters of 'R' is much different from 8.314 J K^{-1} mole^{-1}.

Statement-II: The simple Vander Waal's attraction doesn't exist at the critical state.

3. Statement-I : Compressibility factor (z) for a non-ideal gas could be greater than 1.

Statement-II: Non-ideal gas molecule may have significant intermolecular attraction.

4. Statement-I : In the plot of PV Vs P. the deviation dip from ideal state for N_2,CH_4 and CO_2 gradually increases

Statement-II: The deviation from ideality depends on the nature of gas.

5. Statement-I: The rate of diffusion or effusion can be assumed to be directly proportional to the root mean square speed or any other average speed.

where n is number of moles of gases 'a' and 'b' are Vander Waals constants both being characteristic of a gas.

(1) If the observed molar volume of a gas at 25°C is 20 litre. The gas
  (a) do not deviate from its ideal behaviour.
  (b) deviates from its ideal behaviour and become more compressible
  (c) deviates from its ideal behaviour and become less compressible
  (d) none of these.

(2) The dip of the curve shown above, shows that
  (a) Repulsive force between gaseous particles dominates
  (b) Attractive force between gaseous particles dominates
  (c) The magnitude of repulsive force decrease with increase in pressure
  (d) The magnitude of attractive force increases with increase in pressure.

(3) The unit of Vander Waal constant 'a' is
  (a) atm litre mole^{-1}
  (b) atm litre^2 mole^{-2}
  (c) atm mole^2 litre^{-2}
  (d) atm mole litre^{-1}

5. When the pressure is considerably high, V_m will be quite small. The pressure correction $\frac{an^2}{v^2 m}$ may become negligible and Van der Waal's equation reduces to

$$P\,(V_m - nb) = nRT$$

This explains why the PV_m after reacting a minimum value, increases with increase in pressure. For a real gas, PV versus P plot is not linear. Hence P/p or m/PV is not independent of P for calculation of p and molecular mass M we must obtain P/p at $P = 0$.

$$\text{As } P \to 0,\ P\,(V - nb) = nRT$$

$$\Rightarrow PV = n\,(RT + pb) = \frac{m}{M}\ (RT + Pb)$$

$$p = \frac{m}{V}\left(\frac{RT}{M} + \frac{Pb}{M}\right) = p\left(\frac{RT + Pb}{M}\right)$$

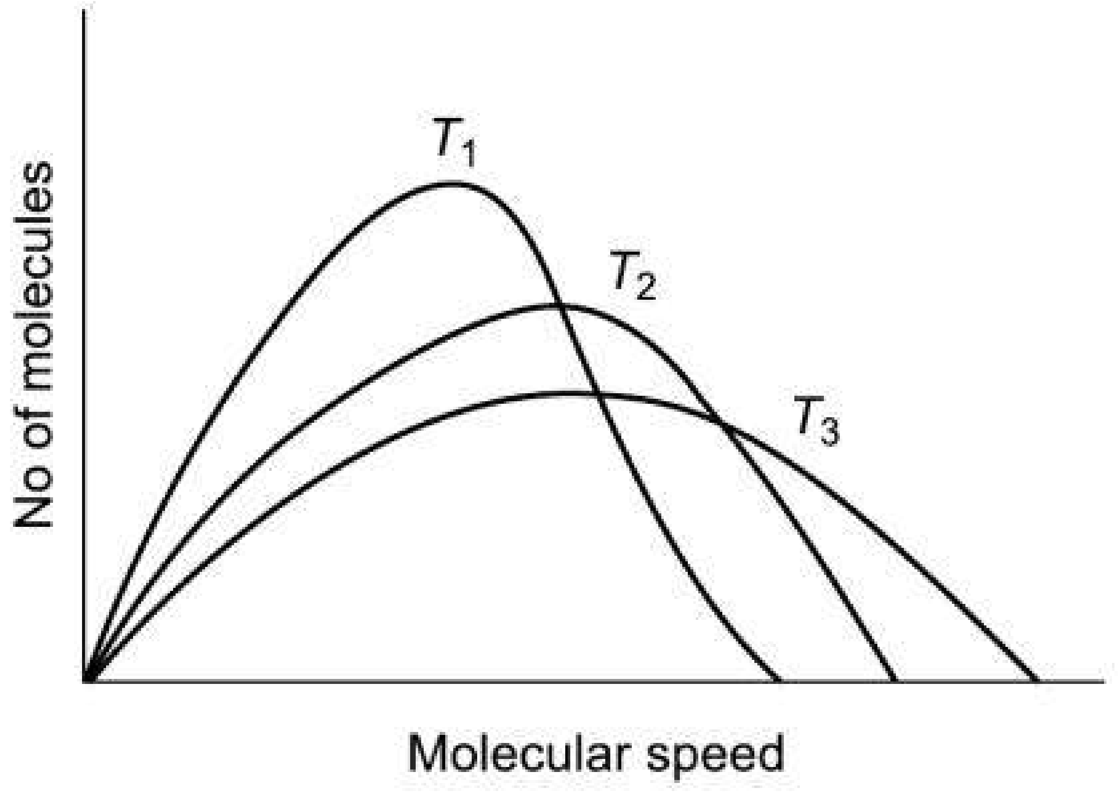
$$\therefore\ \frac{P}{p} = \frac{M}{RT} - \frac{Mb}{(RT)^2}P$$

(1) The nature of graph plotted for P on x-axis versus bp. on y-axis will be:
  (a) Hyperbola
  (b) Straight line
  (c) Parallel to x-axis
  (d) None of these

(2) Calculate the density of N_2 gas at room temperature of 25°C and atmospheric pressure, given that $b = 0.0694\ \text{dm}^3\ \text{mol}^{-1}$
  (a) 1.36 g/L (b) 0.568 g/L
  (c) 2.27 g/L (d) 13.6 g/L

(3) The slope of the graph is
  (a) $\frac{M}{RT}$ (b) $\frac{P}{p}$
  (c) $\frac{M}{(RT)^2}$ (d) None of these

6.



Graph shows typical Maxwell speed distribution curves for N_2 gas at three different temperatures T_1, T_2 and T_3. The peak of each curve represents the most probable speed. On increasing temperature, curve begins to flatten out and shift towards right. But at constant temperature T, same nature of graph is obtained for three gases. A, B and C corresponding to T_1 T_2 and T_3. In an apparatus a beam of atoms (or molecules) exits from an oven at a known temperature and passes through a pinhole. Two circular plates mounted on the same shaft is rotated by a motor. The first plate is called chopper which allows small bursts of atoms and second plate is detector. Eventually

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13. (b), (c), (d)
14. (a), (b), (c)
15. (a), (c)
16. (a), (d)
17. (b), (c), (d)
18. (a), (b), (c)

ANSWER KEYS: IIT WINDOW-VI

I A – 3
B – 4
C – 5
D – 2
E – 1

II A – 4
B – 3
C – 1
D – 2

III A – 4
B – 3
C – 1
D – 2

IV A – 3
B – 4
C – 1
D – 5
E – 2

V A – 3
B – 4
C – 2
D – 1

VI A – 4
B – 1
C – 2
D – 3

VII A – 1, 2
B – 2, 3, 4
C – 1
D – 1, 4

VIII A – P, S
B – R
C – P, Q
D – R

IX A – 1
B – 3
C – 4
D – 5

ANSWER KEYS: IIT WINDOW-VII

1. 4 or ‘d’
2. 1 or ‘a’
3. 2 or ‘b’
4. 3 or ‘c’
5. 1 or ‘a’
6. 1 or ‘a’
7. 1 or ‘a’
8. 1 or ‘a’
9. 1 or ‘a’
10. 3 or ‘c’

ANSWER KEYS: IIT WINDOW-VIII

[1] 1. (a)
2. (b)
3. (a)
4. (b)

[2] 1. (a)
2. (d)
3. (a)
4. (b)

[3] 1. (a)
2. (d)
3. (a)
4. (b)

[4] 1. (c)
2. (b)
3. (b)

[5] 1. (b)
2. (a)
3. (c)

[6] 1. (b)
2. (a)
3. (c)

[7] 1. (a)
2. (b)
3. (d)

Non-polar solvents like benzene and carbon tetrachloride do not solvate the ions as their dielectric constants are low. Ionic compounds are, therefore insoluble in non-polar solvents.

Ionic compounds like sulphates and phosphates of barium and strontium are insoluble in water (because lattice energy is greater than hydration energy). This can be attributed to the high lattice energies of these compounds due to polyvalent nature of both the cation and the anion. In these cases, hydration of ions fails to liberate sufficient energy to offset the lattice energy.

Covalent Bond (By Mutual Sharing of Electrons)

The covalent bond is formed when two atoms achieve stability by the *sharing of an electron pair*, each contributing one electron to the electron pair.

The arrangement of electrons in a covalent molecule is often shown by a Lewis structure in which only *valency shells* (outer shells) are depicted. For sake of clarity, the electrons on different atoms are denoted dots and crosses.

Polarity of Bonds

A covalent bond is set up by sharing of electrons between two atoms. It is further classified as polar or non-polar depending upon the fact whether the electron pair is shared unequally between the atoms or shared equally. For example, the covalent bonds in H_2 and Cl_2 are called non-polar as the electron pair is equally shared between the two atoms.

In the case of hydrogen fluoride the bond is polar as the electron pair is unequally shared. Fluorine has a greater attraction for electrons or *has higher electronegativity* than hydrogen and the shared pair of electrons is nearer to the fluorine atom than hydrogen atom. The hydrogen end of the molecule, therefore, appears positive with respect to fluorine.

Bond polarities affect both physical and chemical properties of compounds containing polar bond. The polarity of a bond determines the kind of reaction that can take place at that bond and even affects the reactivity at nearby bonds. The polarity of bonds can lead to polarity of molecules and affect melting point, boiling point and solubility.

Dipole Moment

It is vector quantity and is defined as the product of the magnitude of charge on any of the atom and the distance between the atoms. It is represented by μ.

Magnitude of dipole moment $|\mu|$ =

$$\underset{(\text{charge in esu})}{q} \times \underset{(\text{Distance in A})}{r}$$

The unit = 10^{-18} (esu) cm (D) is used in practice. In SI units charge q is measured in coulombs (C) and the distance, r in metre, m

$$1\text{ C} = 2.998 \times 10^{9}\text{ esu and }1\text{ m} = 10^{2}\text{ Cm}$$

$$\therefore \quad 1\text{ Cm} = 2.998 \times 10^{9} \times 10^{2} = 2.998 \times 10^{11}\text{ (esu) cm}$$

Therefore in SI system, the unit of dipole moment is coulomb metre

$$\therefore \quad 1\text{ Cm} = \frac{2.998 \times 10^{11}}{10^{-18}} = 2.998 \times 10^{29}\,D$$

$$\text{or} \quad 1\text{D} = \frac{1}{2.998 \times 10^{29}} = 3.336 \times 10^{-30}\text{ Cm}$$

Dipole moment is a vector quantity and is often indicated an arrow parallel to the line joining the point of charge and pointing towards the negative end e.g., $\overrightarrow{\text{H}-\text{F}}$.

% Ionic character of a covalent bond

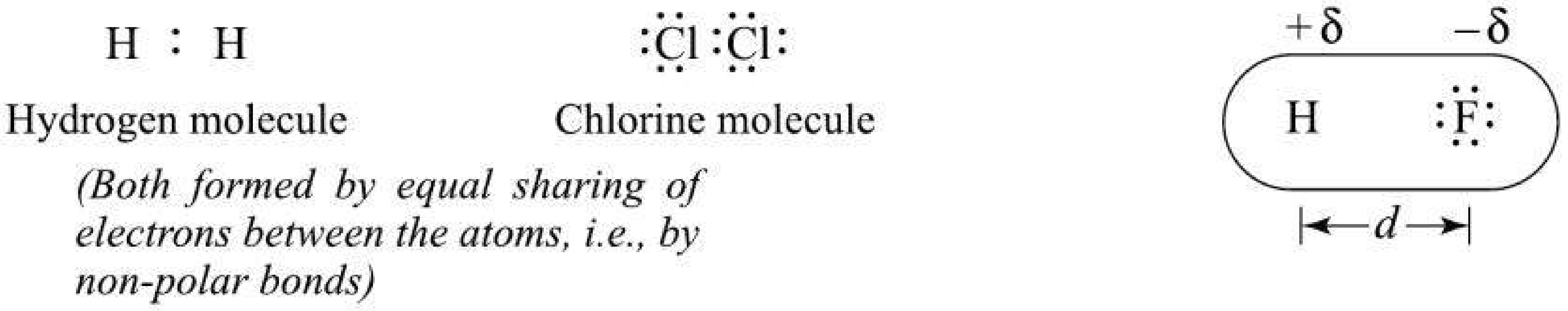
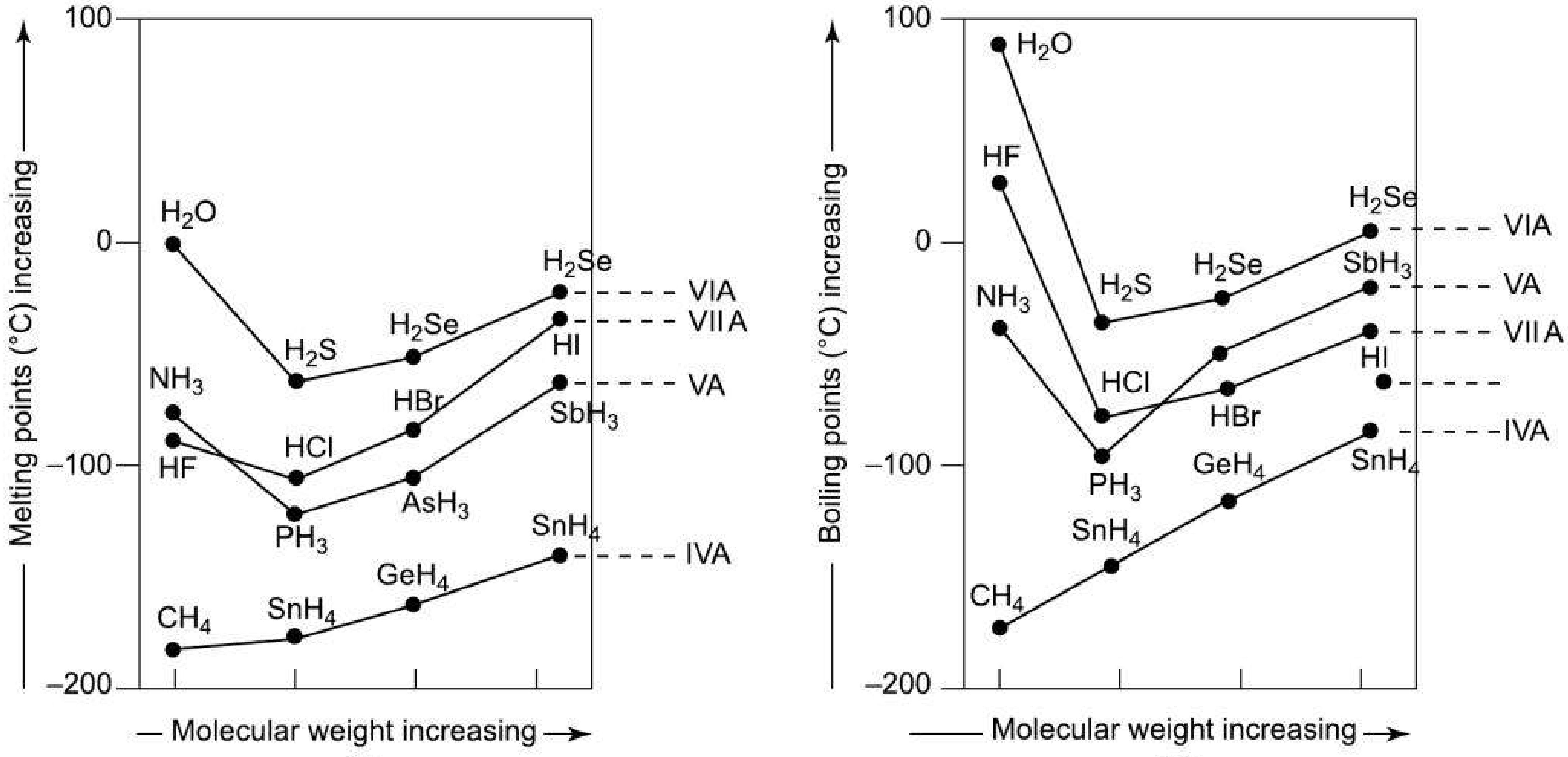


Fig. 5.1

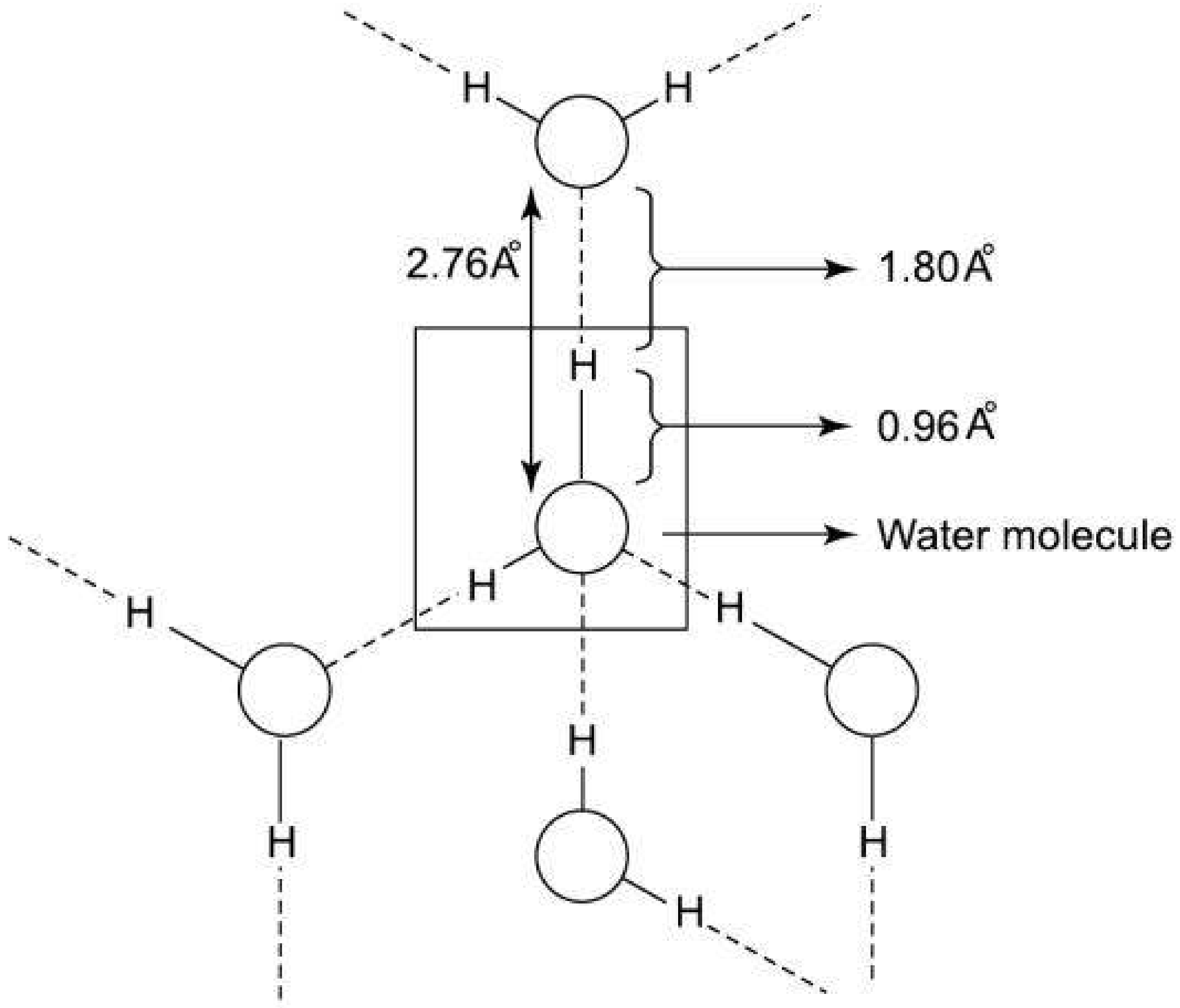


(a) (b)

Fig. 5.3

Having no power to form H-bonds, the simple carbon family hydrides (SnH_4, GeH_4, SiH_4 and CH_4) show a decrease in their bp's and mp's with the decrease in their molecular weights.

(ii) Ice has less density than water. The explanation of this fact is as follows: In the crystal structure of ice, the O-atom is surrounded by four H-atoms. Two H-atoms are linked to O-atom by covalent bonds as shown (by normal covalent bond) and the remaining two H-atoms are linked to O-atom by two H-bonds shown by dotted lines. Thus in ice every water molecule is associated with four other water molecules by H-bonding in a tetrahedral fashion. Ice has an open cage like structure with a large empty space due to the existence of H-bonds. As ice melts at 0°C, a number of H-bonds are



Open cage-like tetrahedral crystal structure of ice. Circles indicate oxygen atoms Bonds represented by solid line are normal covalent bonds while those represented by dotted lines are hydrogen bonds.

Fig. 5.4

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pair repulsions are weakest. Groups at 90° repel each other strongly, while groups 120° apart repel each other much less.

Structure I is the most symmetrical, but has six 90° repulsions between lone pairs and atoms.

Structure II has one 90° repulsion between two lone pairs, plus three 90° repulsions between lone pairs and atoms. These factors indicate that structure III is the most probable. The observed bond angles are 80°40′, which is close to the theoretical 90°. This confirms that the correct structure is III, and the slight distortion from 90° is caused by the presence of the two lone pairs.

As a general rule, if lone pairs occur in a trigonal bipyramid they will be located in the equatorial position (round the middle) rather than the axial positions (top and bottom), since this arrangement minimizes repulsive forces.

Sulphur hexafluoride (SF_6): The electronic structure of S is $ls^2 2s^2 2p^6 3s^2 3p^6$. All six of the outer electrons are used to from bonds with the *F* atom. Thus in SF_6, the *S* has six electron pairs in the outer shell: hence the structure is octahedral. There are no lone pairs, so the structure is completely regular with bond angles of 90°.

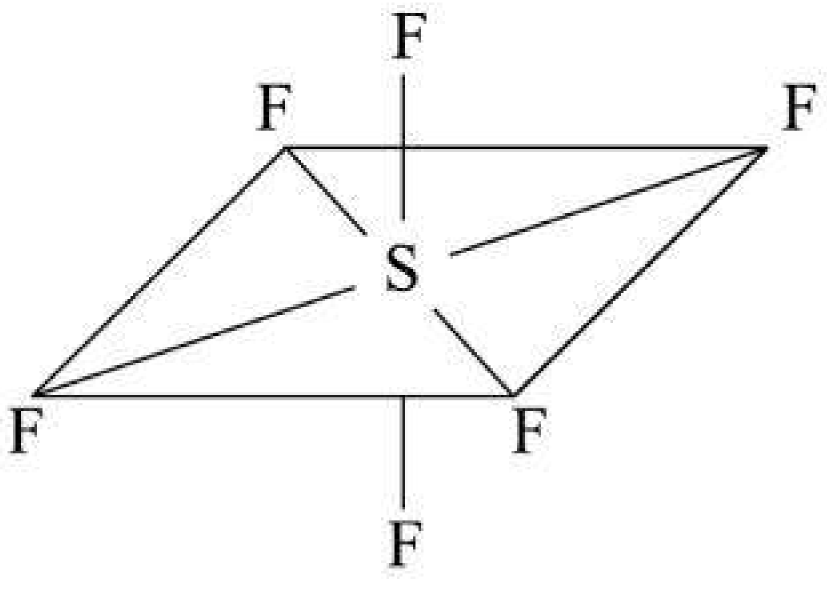


Fig 5.7

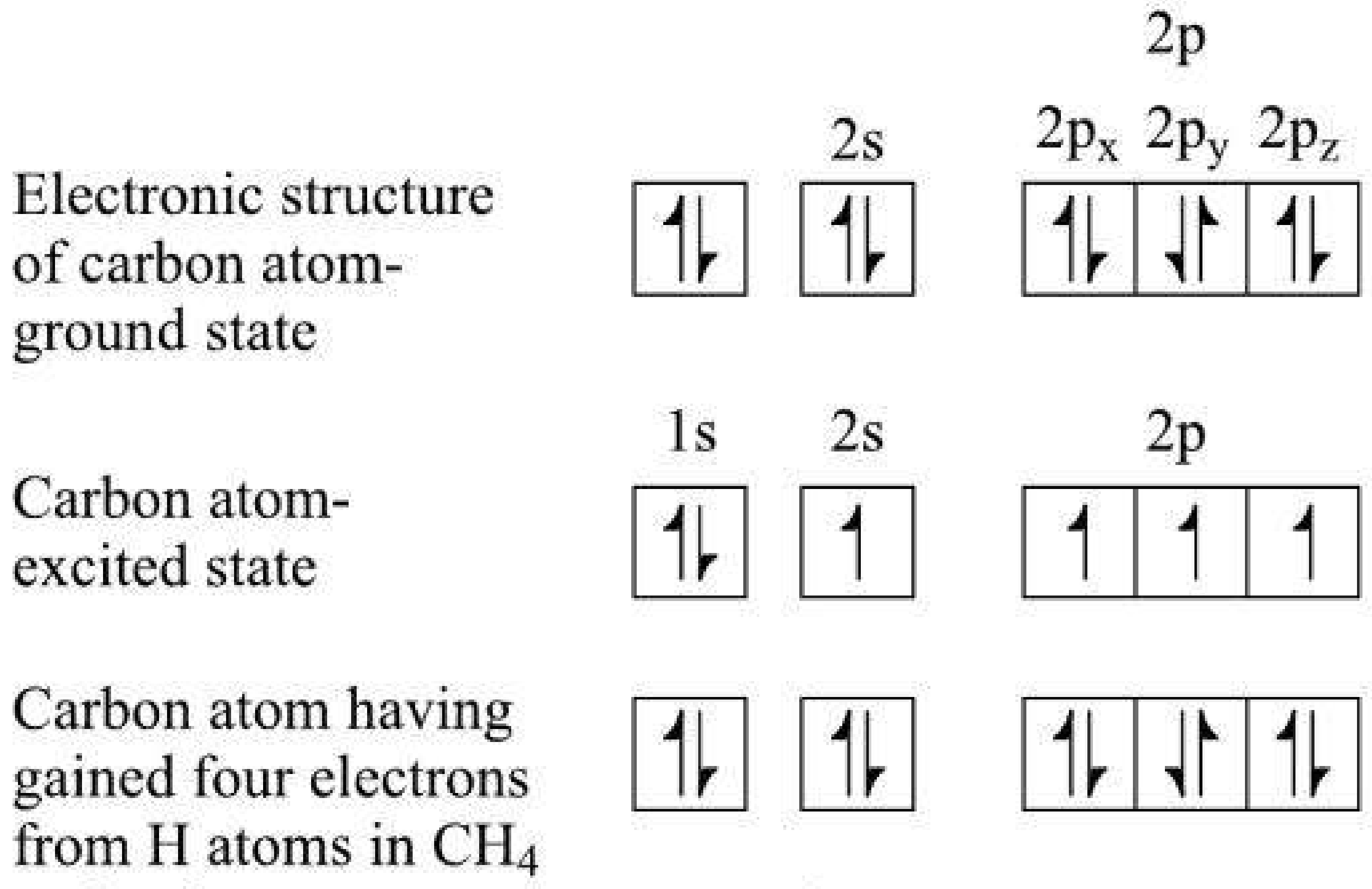
Valence Bond Theory

This theory was produced by Linus Pauling, who was awarded the Noble Prize for Chemistry 1954.

Atoms with unpaired electrons tend to combine with other atoms which also have unpaired electrons. In this way the unpaired electron are paired up, and the atoms involved, & all attain a stable electronic arrangement. This is usually a full shell of electrons (i.e. a noble gas configuration). Two electrons shared between two atoms constitute a bond. The number of bonds formed by an atom is usually the same as the number of unpaired electrons in the ground state, i.e. the lowest energy state. However, in some cases the atom may form more bonds than this. This occurs by excitation of the atom (i.e. providing it with energy) when electrons which were paired in the ground state are unpaired and promoted into suitable empty orbitals. This increases the number of unpaired electrons, and hence it increases number of bond which can be formed.

A covalent bond results from the pairing of electrons (one from each atom). The spins of the two electrons must be opposite (antiparallel) because of the Pauli exclusion principle that no two electrons in one atom can have all four quantum numbers the same.

1. In HF, H has a singly occupied s-orbital that overlaps with a singly filled 2p orbital on F.
2. In H_2O, the O atom has two singly filled 2p orbitals, each of which overlaps with a single occupied s-orbital from two H atoms.
3. In NH_3, there are three singly occupied p orbitals on N which overlap with s orbitals from three H atoms.
4. In CH_4, the C atom in its ground state has the electronic configuration ls^2, $2s^2$, $2p_x^1$, $2p_y^1$ and only has two unpaired electrons, and so can form only two bonds. If the C atom is excited, then the 2s electrons may be unpaired, giving ls^2, $2s^2$, $2p_x^1$, $2p_{y,}^1$ $2p_x^1$. There are now four unpaired electrons which overlap with singly occupied s orbitals on four H atoms.



sp^3 hybridisation

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PF_5	$COCl_2$	NH_4^+	ClO_4^-
$X = \frac{1}{2}[5 + 5]$ $= 5$ Hybrid state of P is sp^3d	$X = \frac{1}{2}[2 + 4]$ $= 3$ Hybrid state of C is sp^2	$X = \frac{1}{2}[4 + 5 - 1]$ $= 4$ Hybrid state of N is sp^3	$X = \frac{1}{2}[0 + 7 + 1]$ $= 4$ Hybrid state of Cl is sp^3
NO_3^-	IF_5	CO_2	XeF_4
$X = \frac{1}{2}[0 + 5 + 1]$ $= 3$ sp^2	$X = \frac{1}{2}[5 + 7]$ $= 6$ sp^3d^2	$X = \frac{1}{2}[0 + 4]$ $= 2$ sp	$X = \frac{1}{2}[4 + 8]$ $= 6$ sp^3d^2
PCl_6^-	PH_3	SF_3^+	SF_4
$X = \frac{1}{2}[6 + 5 + 1]$ $= 6$ Hybrid state sp^3d^2	$X = \frac{1}{2}[3 + 5]$ $= 4$ Hybrid state sp^3	$X = \frac{1}{2}[3 + 6 - 1]$ $= 4$ Hybrid state sp^3	$X = \frac{1}{2}[4 + 6]$ $= 5$ Hybrid state sp^3d

Molecular Orbital Theory

Why He_2 molecule does not exist and why O_2 is paramagnetic? These questions cannot be explained by valence bond theory. In 1932 F. Hund and R.S. Mulliken put forward a theory known as Molecular Orbital Theory to explain above questions and many others. According to this theory, as the electrons of an atom are present in various atomic orbitals, electrons of a molecule are present in various molecular orbitals. Molecular orbitals are formed by the combination of atomic orbitals of comparable energy and proportional symmetry. While an electron in atomic orbital is influenced by one nucleus, in a molecular orbital, it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric. The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed . One is known as bonding molecular orbital (BMO) whereas other is anti-bonding molecular orbital (ABMO). BMO has lower energy and hence greater stability than the corresponding ABMO. First BMO are filled, then ABMO starts filling because BMO has lower energy than that of ABMO.

Molecular orbitals like the atomic orbitals are filled in accordance with the Aufbau Principle obeying the Pauli's Principle and the Hund's rule.

Order of energy of various molecular orbitals is as follows:

For O_2 and higher molecules

σ ls, σ^*ls, $\sigma 2s$, σ^*2s, $\sigma\ 2p_x$,$[\pi 2p_y = \pi 2p_z]$, $[\pi^*2py = \pi^*2pz]$, σ^*2px

For N_2 and Lower molecules

σls, σ^*ls, $\sigma 2s$, σ^*2s, $[\pi 2p_y = \pi 2p_z]$, $\sigma 2p_x$, $[\pi^*2p_y = \pi^*2p_z]$, σ^*2p_x

Bond order

It may be defined as the half the difference between the number of electrons present in the boding orbitals and the anti-bonding orbitals i.e.

Bond order (B.O)

$$= \frac{\text{No. of } e^- \text{in BMO} - \text{No. of } e^- \text{in ABMO}}{2}$$

A positive bond order suggest stable molecule while zero or –ve B.O suggest unstability of the species.

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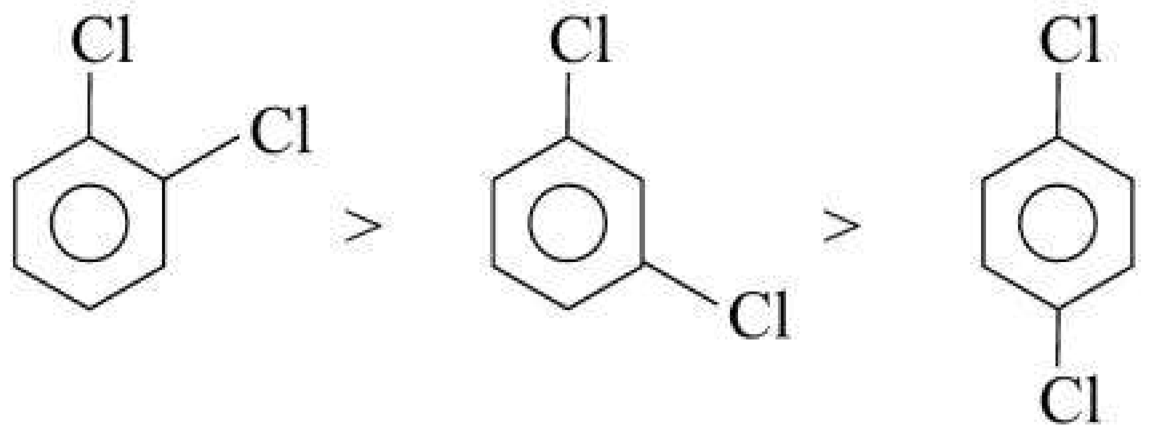
➤ Solution

Since both the groups attached on benzene ring are the same, their dipole moment is decided by the formula

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1\,\mu_2\cos\theta$$

High the value of θ, lesser is the value of μ. Thus



IIT WINDOW–II

➤ MCQ (Single Choice Questions)

1. Which of the following is required for the formation of an ionic bond?
- (a) An electron from the more electronegative element should be transferred to the less electronegative element.
- (b) The total energy of the resulting molecule should be less than the total energy of the reactants.
- (c) The lattice energy of the resultant molecule should be as low as possible.
- (d) The ionic potentials of the reactants should be identical.

2. Which of the following statements is incorrect?
- (a) NH_3 is more basic than PH_3
- (b) NH_3 has a higher boiling point than that of HF
- (c) N_2 is less reactive than P_4
- (d) The dipole moment of NH_3 is less than that of SO_2.

3. $AlCl_3$ is covalent while AlF_3 is ionic. This can be justified on the basis of
- (a) the valence-bond theory
- (b) Fajans' rules
- (c) the molecular-orbital theory
- (d) hydration energy

4. Which of the following pairs have nearly identical values of bond energy ?
- (a) O_2 and H_2 (b) N_2 and CO
- (c) F_2 and I_2 (d) O_2 and Cl_2

5. Which of the following is the most ionic ?
- (a) P_4O_{10} (b) MnO
- (c) CrO_3 (d) Mn_2O_7

6. Among LiCl, $BeCl_2$, BCl_3 and CCl_4, the covalent bond character varies as
- (a) $LiCl < BeCl_2 > BCl_3 > CCl_4$
- (b) $LiCl > BeCl_2 < BCl_3 < CCl_4$
- (c) $LiCl < BeCl_2 < BCl_3 < CCl_4$
- (d) $LiCl > BeCl_2 > BCl_3 > CCl_4$

7. In a metallic crystal the
- (a) valence electrons remain within the fields of influence of their own kernels
- (b) valence electrons constitute a sea of mobile electrons
- (c) valence electrons are localized between the two kernels
- (d) Kernels as well as the electrons move rapidly

8. Polarization involves the distortion of the shape of an anion by an adjacently placed cation. In this context, which of the following statements is correct ?
- (a) Maximum polarization is brought about by a cation of high charge.
- (b) Maximum polarization is brought about by a cation of low radius
- (c) A large cation is likely to bring about a high degree of polarization
- (d) The polarizing power of a cation is less than that of an anion.

9. Which of the following oxyacids of phosphorus are monoprotic (monobasic) ?
- (a) H_3PO_4 (b) H_3PO_3
- (c) H_3PO_2 (d) $H_4P_2O_7$

10. Which of the following has greater bond length ?
- (a) P—O (b) S—O
- (c) Cl—O (d) O=O

11. Which of the following has been arranged in order of increasing covalent character?
- (a) $KCl < CaCl_2 < AlCl_3 < SnCl_4$
- (b) $SnCl_4 < AlCl_3 < CaCl_2 < KCl$
- (c) $AlCl_3 < CaCl_2 < KCl < SnCl_4$
- (d) $CaCl_2 < SnCl_4 < KCl < AlCl_3$

12. Orthonitrophenol is steam volatile but paranitrophenol is not because

(a) Na_2O_2 (b) O_3
(c) N_2O (d) KO_2

6. The species having bond order different from that of CO is **[IIT, 2007].**
(a) NO^- (b) NO^+
(c) CN^- (d) N_2

7. Which species has the maximum number of lone pair of electron on the central atom? **[IIT, 2005]**
(a) $[ClO_3]^-$ (b) XeF_4
(c) SF_4 (d) $[I_3^-]$

8. According to M.O. theory, **[IIT, 2004]**
(a) O_2^+ is paramagnetic and bond order is greater than O_2
(b) O_2^+ is paramagnetic and bond order is less than O_2
(c) O_2^+ is diamagnetic and bond order is less than O_2
(d) O_2^+ is diamagnetic and bond order is more than O_2

9. Number of lone pair (s) in $XeOF_4$ is/are **[IIT, 2004]**
(a) 0 (b) 1
(c) 2 (d) 3

10. Which of the following has – O – O – linkage ? **[IIT, 2004]**
(a) $H_2S_2O_6$ (b) $H_2S_2O_8$
(c) $H_2S_2O_3$ (d) $H_2S_4O_6$

11. Which of the following are iso electronic and iso structural ? **[IIT, 2003]**
$NO_3^-, CO_3^{2-}, ClO_4^-, SO_3$
(a) NO_3^-, CO_3^{2-} (b) SO_3, NO_3^-
(c) ClO_3^-, CO_3^{2-} (d) CO_3^{2-}, SO_3

12. Which of the following molecular species has unpaired electrons ? **[IIT, 2002]**
(a) N_2 (b) F_2
(c) O_2^- (d) O_2^{2-}

13. Identify the least stable ion amongst the following **[IIT, 2002]**
(a) Li^- (b) Be^-
(c) B^- (d) C^-

14. Specify the coordination geometry around hybridisation of N and B atom in a 1:1 complex of B F_3 and NH_3. **[IIT, 2002]**
(a) N : Tetrahedral – sp^3, O tetrahedral –sp^3
(b) N : pyramidal – sp^3, B : pyramidal –sp^3
(c) N : pyramidal sp^3, B : planar – sp^2
(d) N : pyramidal – sp^3; B : Tetrahedral – sp^3

15. The common features among the species CN^-, CO and NO^+ are. **[IIT, 2001]**
(a) Bond order three and isoelectronic
(b) Bond order three and weak field legands
(c) Bond order two and π - acceptors
(d) isoelectronic and weak field legands.

16. The correct order of hybridisation of the central atom in the following species **[IIT, 2001]**
NH_3, $[PCl_4]^{2-}$, PCl_5 and BCl_3 is
(a) dsp^2,dsp^3, sp^2, and sp^3
(b) sp^3, dsp^2, dsp^3 and sp^2
(c) dsp^2, sp^2, sp^3 and dsp^3
(d) dsp^2, sp^3, sp^2 and dsp^3.

17. Molecular shapes of SF_4, CF_4 and Xe F_4 are **[IIT, 2000]**
(a) the same, with 2,0, and 1 ; lone pairs of e^- respectively.
(b) the same, with 1,1 and 1 lone pair of e^- respectively.
(c) different with 0,1 and 2 lone pair of e^- respectively.
(d) different with 1,0 and 2 lone pair of e^- respectively.

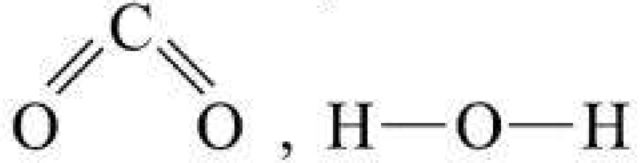
18. The hybridisation of atomic orbitals of Nitrogen in NO_2^+, NO_3^- and NH_4^+ are **[IIT, 2000]**
(a) sp, sp^3 and sp^2 respectively
(b) sp, sp^2 and sp^3 respectively
(c) sp^2, sp and sp^3 respectively
(d) sp^2, sp^3 and sp respectively

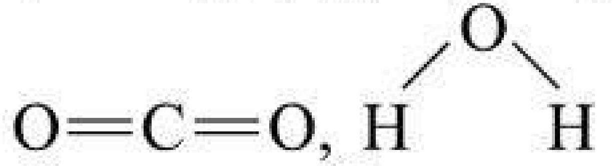
19. The geometry of H_2S and its dipole moment are **[IIT, 1999]**
(a) Angular and non-zero
(b) Angular and zero
(c) Linear and non-zero
(d) Linear and zero

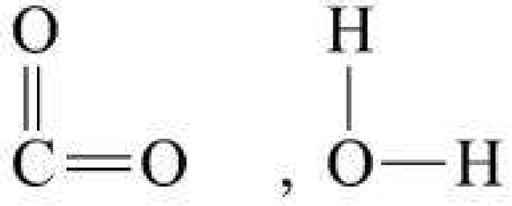
20. The correct order of the increasing C – O bond length of CO, CO_3^{2-} and CO_2 is **[IIT, 1999]**
(a) $CO_3^{2-} < CO_2 < CO$
(b) $CO_2 < CO_3^{2-} < CO$

1. Experiment shows that H_2O has a dipole moment whereas CO_2 has not. Point out the structure which best illustrate these factor

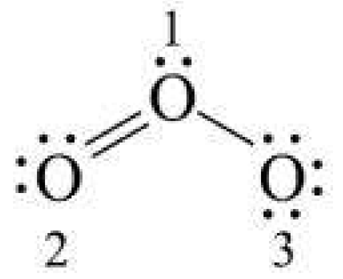
(a) O=C=O, H—O—H

(b)


(c)


(d)


2. It has been seen that in O_3, the central O atom is bonded to two other oxygen atoms as



Arrange oxygen atoms marked as 1,2 and 3 in order of their decreasing formal charge

(a) $1 < 2 < 3$ (b) $1 > 3 > 2$

(c) $1 > 2 > 3$ (d) $2 > 1 > 3$

3. Considering a diatomic molecule HCl, its dipole moment and bond length determined experimentally are μHCl = 1.03 Debye, and 1.275 Å respectively. What is the charge contained by each dipole

(a) 8.07×10^{-11} esu (b) 4.03×10^{-11} esu

(c) 16.15×10^{-11} esu (d) 2.01×10^{-11} esu

4. Among LiCl, $BeCl_2$, BCl_3, CCl_4, covalent bond character follows the order:

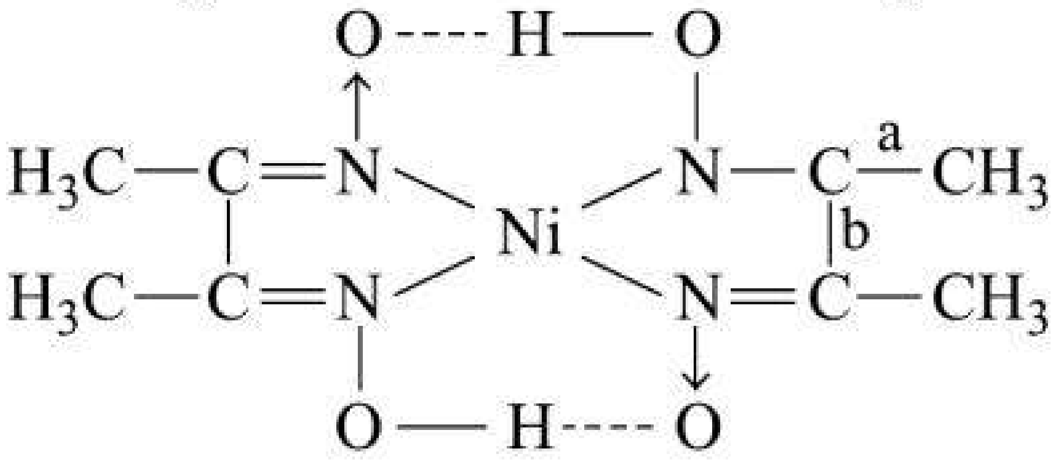
(a) $LiCl > BeCl_2 > BCl_3 > CCl_4$

(b) $LiCl < BeCl_2 < BCl_3 < CCl_4$

(c) $LiCl > BeCl_2 > CCl_4 > BCl_3$

(d) $LiCl < BeCl_2 < BCl_3 > CCl_4$

(II) Dimethyl glyoxime is an important reagent, which is used in the detection of Ni^{2+} ion in fourth group of qualitative analysis and also in its gravimetric estimation. The compound formed by Ni^{2+} ions with dimethyl glyoxime is diamagnetic with the structure as given below



'*a*' and '*b*' are C – C bond length'

1. Which of the following is correct regarding the bond length '*a*' and '*b*'

(a) a = b

(b) a > b

(c) b > a

(d) none of the above

2. How many sigma bond are associated with carbon atom in the given structure are:

(a) 5 (b) 10

(c) 11 (d) 22

3. The atomic orbitals which the central atom is using in hybridisation are:

(a) 4s, $4p_x$, 4_y, p_z and $4p_z$

(b) $3dz^2$, 4s, p_x and $4p_y$

(c) $3d_{x^2-y^2}$, 4s, $4p_x$ and $4p_y$

(d) $3d_{x^2-y^2}$, 4s, $4p_y$ and $4p_z$

4. The necessary conditions for the formation of intramolecular hydrogen bonding is

(a) The ring formed as a result of hydrogen bond should be planner

(b) A five or six membered ring should be formed

(c) Interacting atoms should be placed in such a way that there is minimum strain during the ring formation

(d) All of these

(III) The degree of polarity of a covalent bond is measured by the dipole moment (μ bond) of the bond defined as μ bond = charge on one of the poles × bond length μ bond is a vector quantity. The dipole moment of a molecule is the vector addition of all the bond moment present in it. For a triatomic molecule containing two bonds like H_2O, μ molecule is given by
μ^2 molecule = $\mu^2_{\text{bond}} + \mu^2_{\text{bond}}$
$^{+}2\mu_{\text{bond}}\,\mu$ bond cos θ
θ = bond angle
μ molecule is an experimental property so is also the bond length is measured by microwave spectroscopy which is based on the principle that absorption of microwave radiation by a molecule causes rotational transition of molecules. However, a molecule with permanent dipole moment equal to zero is microwave inactive.

ANSWER KEYS: IIT WINDOW-V

(I)	1. (c)	(II)	1. (b)	(III)	1. (c)
	2. (c)		2. (d)		2. (d)
	3. (a)		3. (c)		3. (a)
	4. (b)		4. (d)		4. (b)
(IV)	1. (b)	(V)	1. (a)	(VI)	1. (b)
	2. (b)		2. (b)		2. (d)
	3. (c)		3. (a)		3. (d)
	4. (c)				4. (c)
	5. (b)				

ANSWER KEYS: IIT WINDOW-VI

1. A — S
B — S
C — S
D — T

2. A — P, Q, R
B — P, Q
C — Q, S
D — P, Q, R, T

3. A — T
B — Q
C — S
D — S

4. A — P, R
B — P, R
C — Q
D — S

5. A — P
B — S
C — Q
D — R

6. A — P
B — R, S
C — P
D — P, Q

7. A — Q, R
B — Q
C — Q, S
D — Q, S

8. A — Q, S
B — P, R, S
C — P, R
D — R, S

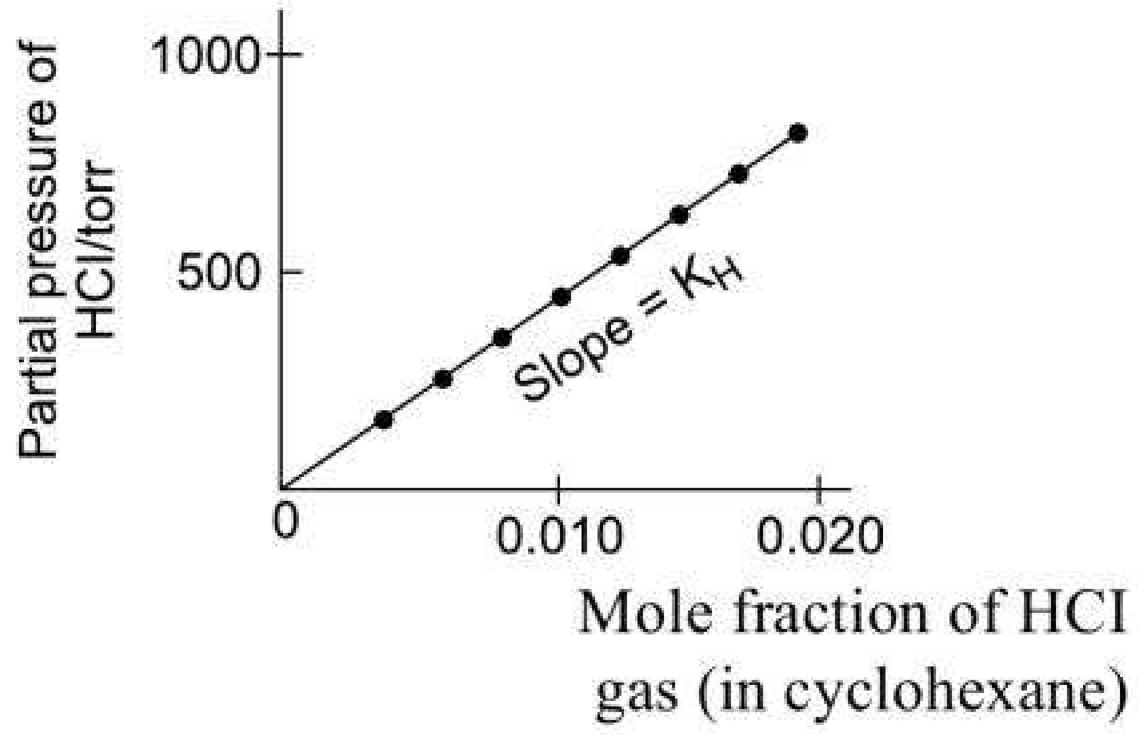


Fig 6.1

solution. Or Mole fraction of the gas in solution is proportional to the partial pressure of the gas.

Mathematically, Henry's Law can be expressed as

$$m \propto P \text{ or } p \propto X - X$$
$$m = K_H P \text{ or } p = K_H X$$

where X is the mole fraction of gas.
m is the mass of gas dissolved per unit volume.
P is the pressure of the gas in equilibrium with the solution.

K_H is proportionality constant.

Value of K_H depends upon nature of gas and temperature. Higher the value of K_H at a given pressure, lower is the solubility of the gas in the liquid. K_H value for O_2 and N_2 increases with increase in temperature indicating that solubility of gases decreases with increase of temperature.

Note:

Aquatic species are more comfortable in cold water rather than warm water because solubility of gases decreases with increase of temperature.

Henry's Law is applicable only if

1. The pressure is not too high.
2. The temperature is not too low.
3. The gas is not highly soluble i.e. the gas does not react with solvent.

When a mixture of gases is brought in contact with a given solvent then the solubility of the gas is proportional to its partial pressure.

Nature of Solute

Easily liquefiable gases are more soluble in water and the gases that can form ions in aqueous solutions are more soluble.

Methods of Expressing the Concentration of a Solution

(i) Mass percentage It is defined as the amount of solute in grams present in 100 grams of the solution

$$\boxed{\text{Mass percentage of solute} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100}$$

$$= \frac{\text{Mass of solute}}{\text{Mass of solute} + \text{Mass of solvent}} \times 100$$

$$= \frac{\text{Mass of solute}}{\text{Volume of solution} \times \text{Density of solution}} \times 100$$

The ratio $\frac{\text{Mass of solute}}{\text{Mass of solution}}$ is termed as **mass fraction.**

Thus, $\boxed{\begin{array}{l}\text{Mass percentage of solute} = \\ \text{Mass fraction of solute} \times 100\end{array}}$

(ii) Percent by Volume Percent of solute by volume

$$= \frac{\text{Volume of solute}}{\text{Volume of soution}} \times 100$$

(iii) Percent mass by Volume Percent of solute

$$\text{mass by volume} = \frac{\text{Mass of solute}}{\text{Volume of solution}} \times 100$$

(iv) Strength (Grams per litre) Concentration of

$$\text{solution} = \frac{\text{Mass of solute in grams}}{\text{Volume of the solution in litres}}$$

$$= \frac{\text{Mass of solute in grams}}{\text{Volume of the solution in mL}} \times 1000$$

(v) Parts per Million (ppm)

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

(vi) Mole fraction It is defined as the ratio number of moles of one component to the total number of moles of the solution (i.e., all the components).

Let n moles of solute (A) and N moles of solvent (B) be present in a solution.

$$\text{Mole fraction of solute} = \frac{n}{N+n} = X_A$$

Lowering in vapour pressure = $p_0 - p_s$

Relative lowering in vapour pressure = $\frac{p^0 - p_s}{p_0}$

According to Raoult's Law: "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,

$$\boxed{\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}} \quad \text{or} \quad \frac{p_o - p_s}{p_o} = \frac{W_B / M_B}{\frac{W_B}{M_B} + \frac{W_A}{M_A}}$$

$$\Rightarrow \boxed{\frac{p_o - p_s}{p_o} = \frac{W_B.M_A}{M_B.W_A}} \qquad .....(1)$$

Since 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, $\frac{p_0}{p_0 - p_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$

$$\text{or} \qquad \frac{p_0}{p_0 - p_s} - 1 = \frac{N}{n} \quad \text{or} \quad \frac{p_s}{p_0 - p_s} = \frac{N}{n}$$

$$\text{or} \qquad \boxed{\frac{p_0 - p_s}{p_s} = \frac{n}{N} = \frac{w_A}{M_A} \times \frac{M_B}{w_B}} \qquad ... (2)$$

Note:

Equation (2) provides more accurate result during mathematical calculation.

Determination of Lowering of vapour pressure

Lowering vapour pressure is determined by Ostwaid and Walker dynamic method. It is based on the principle when air is allowed to pass through a solvent or solution, it takes up solvent vapour with it to get itself saturated with vapours at that temperature.

Set A and B are weighed separately before and after passing dry air. Loss in weight of each set, gives the lowering of vapour pressure. The temperature of air, the solution and the solvent is kept constant.

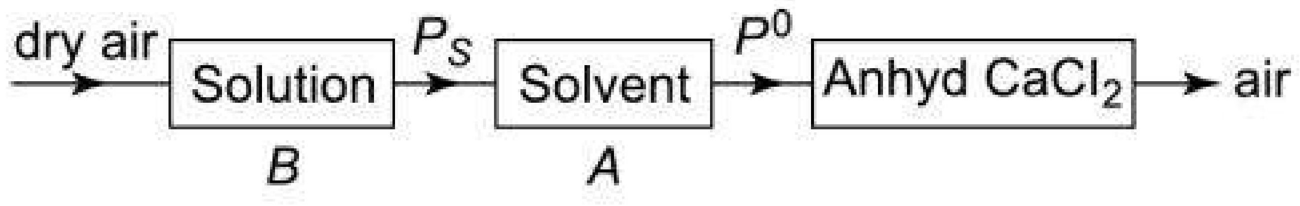


Fig 6.3

Loss in weight of solution (w_1) ∝ P_s

Loss in weight of solvent (w_2) ∝ $P^o - P_s$

Gain in weight of anhydrous $CaCl_2$ ∝ P^o

$$\boxed{\frac{P^o - P_s}{P^o} = \frac{w_2}{w_1 + w_2}}$$

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 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. The difference in the boiling point of the solution and the boiling point of the pure solvent is termed **elevation of boiling point.** 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.

From ΔBAD & ΔCAE, we have $\frac{AC}{AB} = \frac{AE}{AD}$

$$\text{or} \qquad \frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

$$\text{or} \qquad \frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\text{or} \qquad \Delta T \propto \Delta P$$

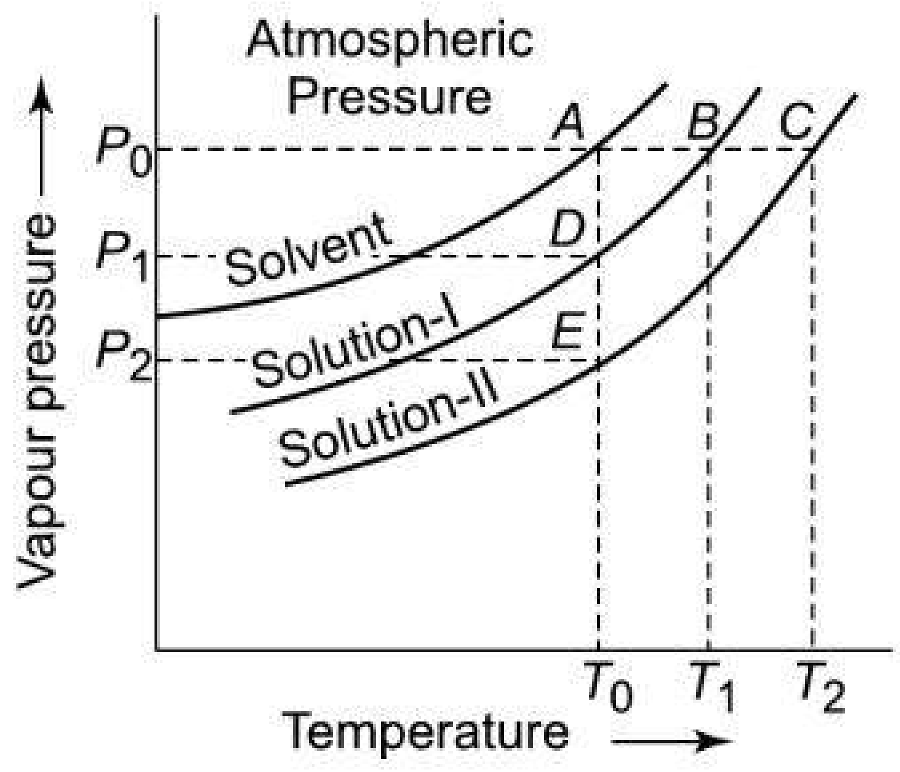


Fig 6.4

$$\Rightarrow \quad X_{\text{solute}} = 0.120$$

$$\Rightarrow \quad X_{\text{solute}} = \frac{\text{molality} \times 60}{1000}$$

$$\Rightarrow \quad \text{Molality} = \frac{1000 \times 0.120}{60} = 2 \text{ molal}$$

Ans.

➤ Example 6.2

At a certain temperature vapour pressure of pure ether is 646 mm and that of pure acetone is 283 mm. Calculate the mole fraction of each component in the vapour state if the mole fraction of ether in the solution is 0.50.?

➤ Solution

From Raoult's law.

$$P_{\text{Total}} = P_{\text{Acetone}} + P_{\text{ether}}$$

$$= P^{o}_{\text{Acetone}} X_{\text{Acetone}} + P_{\text{ether}} X_{\text{ether}}$$

$$\Rightarrow \quad P_{T} = 646 \times 0.5 + 283 \times 0.5$$

$$= 464.5 \text{ mm of Hg.}$$

$$\therefore \quad X_{\text{ether}} = \frac{P_{A}}{P_{\text{Total}}} = \frac{P^{0}_{A} X_{A}}{P_{\text{Total}}} = \frac{646 \times 0.5}{464.5}$$

$$= 0.695.$$

$$X_{\text{acetone}} = \frac{P_{B}}{P_{\text{Total}}} = \frac{P^{0}_{B} X_{B}}{P_{\text{Total}}} = \frac{283 \times 0.5}{464.5}$$

$$= 0.305.$$

➤ Example 6.3

A Decimolar solution of potassium ferrocyanide $K_4[Fe(CN)_6]$ is 80% dissociated at 27°C in a particular medium. Calculate the osmotic pressure of the solution?

➤ Solution

$$\text{Molar Concentration of solution} = \frac{M}{10} = 0.1 \text{ M},$$

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^{+} + [Fe(CN)_6]^{4-}$$

Initially	1	0	0
After dissociation	1 – 0.8	4 × 0.8	0.8

∴ Total mole after dissociation = $0.2 + 3.2 + 0.8 = 4.2$

$$\therefore \quad \text{i (Vant's Hoff factor)} = \frac{4.2}{1}$$

$$\Rightarrow \quad i = 4.2$$

cese, $\pi = \text{i C R T.}$

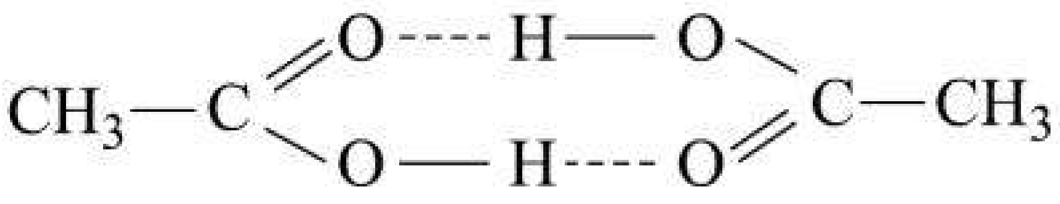
$$= 4.2 \times 10^{-1} \times 0.0821 \times 300$$

$$= 10.3446 \text{ atm.}$$

➤ Example 6.4

A millimolar solution of acetic acid demerises to the extent of 60% in benzene at 27°C. Calculate the osmotic pressure of acetic acid in benzene ?

➤ Solution



Dimer of acetic acid.

$$(2CH_3COOH \rightarrow (CH_3COOH)_2$$

Initially	1	0
After association	1 – 0.6	0.3

Total mole after association = 0.4 + 0.3 = 0.7

i (van't Hoff factor

$$= \frac{0.7}{1} = 0.7$$

use $\pi = \text{i CRT}$

$$= 0.7 \times 10^{-3} \times 0.0821 \times 300$$

$$= 17.241 \times 10^{-3} \text{ atm.}$$ **Ans.**

➤ Example 6.5

Calculate the molecular mass of Cellulose acetate if its 0.5% (wt/mole) solution in acetone having sp. gravity 0.9 gm/ml shows an osmotic rise of 23 mm against pure acetone at 27°C.?

➤ Solution

$\pi = 23$ mm against acetone

$$\Rightarrow \pi = \frac{23 \times 0.9}{10 \times 13.6} \text{ cm of Hg}$$

(since dHg = 13.6

$$= 0.1522 \text{ cm of Hg.}$$

$$= \frac{0.1522}{76} = 0.002 \text{ atm.}$$

$$= 2 \times 10^{-3} \text{ atm.}$$

$$\text{Molality (m)} = \frac{W_{\text{sucrose}} \times 1000}{M_{\text{sucrose}} \times W_{H_2O}}$$

$$= \frac{34.2 \times 1000}{342 \times 180}$$

$$= 0.555 \text{ m}$$ **Ans.**

$$\text{Molarity (M)} = \frac{W_{\text{sucrose}} \times 1000}{M_{\text{sucrose}} \times V_{\text{solution}}}$$

$$= \frac{34.2 \times 1000 \times 0.9}{342 \times 214.2}$$

$$= 0.42$$ **Ans.**

➤ Example 6.18

The density of 3 *M* solution of $Na_2S_2O_3$ is 1.25 gm ml^{-1}. Calculate

(a) mole fraction of $Na_2S_2O_3$

(b) 1 Molalities of Na^+ and $S_2O_3^{2-}$ ions in solution.

➤ Solution

Mol. wt of $Na_2S_2O_3$ = 158

Wt of solution = 1000 × 1.25 = 1250 gm.

Wt of $Na_2S_2O_3$ = 158 × 3 = 474 gm.

Weight of water = 1250 – 474 = 776 gm.

(a) ∴ Mole fraction of $Na_2S_2O_3$

$$= \frac{\text{mole of } Na_2S_2O_3}{\text{Mole of solution}}$$

$$= \frac{3}{3 + 776/18} = 0.065$$

(b) $$\text{Molality of } Na^+ = \frac{\text{Mole of } Na^+}{\text{Mass of water}} \times 1000$$

$$= \frac{6 \times 1000}{776} = 7.732$$ **Ans.**

[Since $Na_2S_2O_3 \rightleftharpoons 2Na^+ + S_2O_3^{2-}$]

$$\text{Molality of } S_2O_3^{2-} = \frac{\text{Mole of } S_2O_3^{2-}}{\text{Mole of solution}}$$

$$= \frac{3 \times 1000}{776} = 3.865$$ **Ans.**

➤ Example 6.19

A complex is represented by $COCl_3.x\ NH_3$ Its 0.1 molal solution in water shows $\Delta T_f = 0.558°$ K_f for H_2O is 1.86 K molality^{-1}. Assuming 100% Ionisation of complex having coordination No. = 6. Calculate its formula.

➤ Solution

According to question $C_m = 0$

$\Delta T_f = 0.558.$ $K_f = 1.86 \text{ mole}^{-1}\text{K}^{-1}$.

using the formula, $\Delta T_f = i\, K_f\, m$.

Where i = Vant's Hoff factor

$$\Rightarrow \quad 0.558 = 1.86 \times 0.1 \times i$$

$$\Rightarrow \quad i = \frac{0.558}{0.186} = 3$$

i = 3 it means the complex ionises to form three ions i.e. total primary & secondary ligands are

3+5 = 8 ie *x* = 5.

$$COCl_3.5NH_3 \rightarrow [CO(NH_3)_5\,Cl]^{2+} + 2Cl^-$$

Initially	1	0	0
After ionisation	$1 - \alpha$	α	2α

$$\Rightarrow \quad i = \frac{1 - \alpha + \alpha + 2\alpha}{1} = \frac{1 + 2\alpha}{1}$$

If ∝ = 100% it means *i* = 3

Hence the complex is $[CO(NH_3)_5Cl]Cl_2$.

➤ Example 6.20

Cellobiose is sugar obtained by degration of cellulose. If 200 ml of aq solution containing 1.5 gm cellobiose at 25°C gives rise to an osmotic pressure of 407.2 mm Hg. What is the molecular mass of cellobiose.?

➤ Solution

$$\text{Given } \pi = \frac{407.2}{760} \text{ atm}$$

$V_{\text{solution}} = 200$ ml. $W_{\text{Solute}} = 1.5$ gm.

$T = 298$ k.

$$\text{The molarity of solution} = \frac{1.5 \times 1000}{M \times 200} = \frac{7.5}{M}$$

using the formula

π = C R T = M R T.

Where *M* = Molarity.

$$\Rightarrow \frac{407.2}{760} = \frac{7.5}{M} \times 0.082 \times 298$$

$$\Rightarrow M = \frac{760 \times 7.5 \times 0.082 \times 298}{407.2}$$

$$= 342.47$$ **Ans.**

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(b) The lattice energy of barium sulphate is less than the hydration energy
(c) The lattice energy has no role to play in solubility
(d) The hydration energy of beryllium sulphate is less than its lattice energy

42. The solubility of a solid in a liquid depends on :
(a) Nature of solute
(b) Nature of solvent
(c) Temperature
(d) All of these

43. Solubility of deliquescent substances in water is generally :
(a) High (b) Low
(c) Moderate (d) Cannot be said

44. If ΔT_b is the elevation in boiling point for the electrolyte and ΔT_b^0 of non-electrolyte of the same concentration, then Van't Hoff's factor i is equal to
(a) $\Delta T_b \times \Delta T_b^0$ (b) $\Delta T_b^0 / \Delta T_b$
(c) $\frac{\Delta T_b - \Delta T_b^0}{2}$ (d) $\Delta T_b / \Delta T_b^0$

45. A 1 molal solution of NaCl solution in water freezes at a temperature of –3.72°C. The best explanation for this is (K_f for water = 1.86)
(a) incomplete dissociation of NaCl
(b) Hydrogen bonding
(c) increased pressure of the solvent
(d) NaCl molecules are completely dissociated

46. Which solvent would show the largest depression in freezing point when one mole of non-volatile solid is dissolved in it.
(a) $H_2O, K_f = 1.86$
(b) comphor, $K_f = 40.0$
(c) Naphthalene, $K_f = 6.8$
(d) $C_6H_6, K_f = 5.2$

47. Sea water is converted into fresh water based upon the phenomenon of
(a) plasmolysis (b) sedimentation
(c) reverse osmosis (d) diffusion

48. Solute A is a ternary electrolyte and solute *B* is non electrolyte. If 0.1 *M* solution of solute *B* produces an osmotic pressure of 2 *P*, then 0.05 *M* solution of *A* at the same temperature will produced an osmotic pressure equal to
(a) *P* (b) 1.5 *P*
(c) 2*P* (d) 3*P*

49. The molecular weight of NaCl determined by studying freezing point depression of its 0.5% aqueous solution is 30. The apparent degree of dissociation of NaCl is
(a) 0.95 (b) 0.5
(c) 0 6 (d) 0.3

50. Pure Benzene freezes at 5.4°C. A solute 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 this observation, one can conclude that
(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

IIT WINDOW–III

Level II

1. Two liquids *A* and *B* form an ideal solution. At 300 *K* the vapour pressure of a solution of 1 mole of *A* and *x* moles of *B* is 550 mm. If the vapour pressures of pure *A* and *B* are 400 mm and 600 mm respectively, then *x* is
(a) 1 (b) 2
(d) 3 (d) 4

2. A sample of tooth paste weighing 500 g, on analysis, was found to contain 0.2 g of fluorine. The concentration of fluorine in ppm is
(a) 4×10^3 (b) 4×10^2
(c) 4×10^1 (d) 2×10^2

3. 10% aqueous solution of certain substance is isotonic with 5% aqueous solution of fructose ($C_6H_{12}O_6$).The molecular mass of the substance is
(a) 90 (b) 360
(c) 180 (d) 540

4. Osmotic pressure of 30% solution of glucose is 1.20 bar and that of 3.42% of solution of cane sugar is 2.5 bar. The osmotic pressure of

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(c) Solvent molecules to the total number of molecules in solution

(d) Solvent molecules to the total number of ions in solution **[CBSE, 1991]**

7. 500g tooth paste sample has 0.2 g fluoride ion concentration. What is the concentration of fluoride in terms of ppm level? **[AIIMS, 1991]**

(a) 250 (b) 200

(c) 400 (d) 1000

8. Molal depression constant depends upon **[Pb CET, 1991]**

(a) Nature of the solute

(b) Nature of the solvent

(c) Vapour pressure of solution

(d) Heat of solution

9. Mole fraction of glycerine $C_3H_5(OH)_3$ in solution containing 36 gm of water and 46 gm of glycerine is

(a) 0.46 (b) 0.40

(c) 0.20 (d) 0.36

[CPMT], 1991]

10. The molecular mass of sodium chloride as determined by osmotic pressure method is : **[Haryana CET Sample Paper, 1992]**

(a) Equal to 58.5

(b) Greater than 58.5

(c) Less than 58.5

(d) None of the information is correct

11. The molarity of pure water is **[KCET, 1993]**

(a) 55.5 (b) 50

(c) 100 (d) 18

12. Which of the following liquid pairs will show positive deviation from Raoult's Law ? **[MPCEE, 1993]**

(a) Water-hydrochloric acid

(b) Water-nitric acid

(c) Acetone-chloroform

(d) Benzene-methanol

13. The law which states that the mass of a gas dissolved in given mass of the solvent at any temperature is directly proportional to the pressure of the gas above the solution is : **[PMT, 1998]**

(a) Joule's law (b) Boyle's law

(c) Henry's law (d) Charle's law

14. Increasing the temperature of an aqueous solution will cause **[IIT, 1993]**

(a) Decrease in molarity

(b) Decrease in molality

(c) Decrease in mole fraction

(d) Decrease in % (w/w)

15. The vapour pressure of a solution 5g of non electrolyte in 100g of water at a particular temperature is 2985 Nm^{-2}. The vapour pressure of pure water at this temperature is 3000 Nm^{-2}. The molecular mass of solute is **[IIT, 1993]**

(a) 180 (b) 90

(c) 270 (d) 200

16. The molal freezing point for water is 1.86° C/m. 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

17. Van't Hoff factor for 0.1 M ideal solution is **[MLNR, 1994]**

(a) 0.1 (b) 1

(c) 0.01 (d) None of these

18. At 25°C the highest osmotic pressure is expected by 0.1 M solution is **[CBSE, 1994]**

(a) $CaCl_2$ (b) KCI

(c) Glucose (d) Urea

19. Which of the following salts will have the same value of Van't Hoff factor (i) as that of $K_4[Fe(CN)_6]$ **[CBSE, 1994]**

(a) $Al_2(SO_4)_3$ (b) NaCl

(c) $Al(NO_3)_3$ (d) Na_2SO_4

20. 12 g of urea is dissolved in 1 litre of water and 68.4g of sucrose is also dissolved in 1 litre of water. The lowering in the vapour pressure of first case is **[EAMCET, 1995]**

(a) equal to second

(b) greater than second

(c) less than second

(d) double the second

21. Isotonic solutions have same **[AFMC, 1995]**

(a) Molar concentration

(b) Molality

(c) Normality

(d) None of these

22. When mango is placed in a aqueous solution of hydrochloric acid, it **[CPMT, 1995]**

7. Mark out the incorrect combination of intermolecular forces.
 (a) KCl in H_2O .... ion-dipole
 (b) C_6H_6 in CCl_4 .... dispersion force
 (c) HCl in CH_3CN .... ion-dipole
 (d) HCl in H_2O .... hydrogen bonding

8. Camphor $C_{10}H_{16}$ which has a freezing point of 174°C has a freezing point depression constant at 40°C/m. Choose the correct statement regarding camphor.
 (a) Camphor has law freezing point depression constant and could be used as a solvent for determination of molecular weight.
 (b) Camphor has high freezing point depression constant and could be used as solvent for determination of molecular weight.
 (c) High molecular weight solute is preferred with Camphor for precise determination.
 (d) Low molecular weight solute is preferred with Camphor for precise determination.

9. The total vapour pressure of a binary solvent is given by $R = (110X_A + 125X_B)$ mm Hg Where x_A and x_B are the mole fractions of components A and B respectively. It suggests that
 (a) the vapour pressure of solution $(n_A = n_B)$ is less than the pure B component
 (b) the vapour pressure of solution $(n_A = n_B)$ is more than that of pure component A.
 (c) Vapour pressure of pure A component is 110 mm Hg and that of pure B is 125 mm Hg
 (d) The vapour pressure of pure A and B are 125 mm Hg and 110 mm Hg respectively.

10. Consider 0.1 M solutions of two solutes X and Y. The solute X behaves as univalent electrolyte while the solute Y dimerises in solution. Which of the following statement (s) is / are correct regarding these solutions ?
 (a) The boiling point of the solution of X will be higher than that of Y.
 (b) The osmotic pressure of solution of Y will be lower than that of X.
 (c) The freezing point of the solution of X will be lower than that of Y.
 (d) The relative lowering of vapour pressure of both the solution will be the same.

11. In the depression of freezing point experiment, it is found that
 (a) The vapour pressure of the solution is less than that of pure solvent.
 (b) The vapour pressure of the 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.

12. If P^0 and P_s are the vapour pressures of the solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and solute respectively, then
 (a) $P_s = P^0 N_2$
 (b) $P^0 - P_s = p^0 N_2$
 (c) $P_s = P^0 N_1$
 (d) $(P^0 - P_s / P_s = N_1 / (N_1 + N_2)$

13. 1 Mole benzene (P^0_{benzene} = 42 mm) and 2 mole toulene (P^0_{toulene} = 36 mm) will have :
 (a) total vapour pressure 38 mm
 (b) mole fraction of vapour of benzene above liquid mixture is 7/19
 (c) positive deviation from Raoult's law
 (d) negative deviation from Raoult's law.

14. Which is / are correct statement (s) ?
 (a) When mixture is less volatile, there is positive deviation from Raoult's law
 (b) When mixture is more volatile, there is negative deviation from Raoult's law
 (c) When mixture is less volatile, there is negative deviation from Raoult's law
 (d) When mixture is more volatile, there is positive deviation from Raoult's law

15. 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 solutions
 (d) behave like a single component and boil at constant temperature

16. Ideal solution is formed when its components
 (a) have zero heat of mixing
 (b) have zero volume change
 (c) obey Raoult's law
 (d) can be converted into gases

B.	Vapour pressure	2.	Inversely proportional to van't Hoff factor (i) (in the same solvent)
C.	Freezing point	3.	Directly proportional to molecular mass or the solute (in the same solvent)
D.	Boiling point	4.	Directly proportional to molecular mass of the solvent (for the same solute)

IIT WINDOW–IX

➤ Paragraph

1. A solution of sucrose (molar mass = 342) has been prepared by dissolving 68.4g of sucrose in one Kg of water. K_f for water is 1.86 K kg mol^{-1} and vapour pressure of water at 298 K is 0.024 atm.

1. The vapour pressure of the solution at 298K will be

(a) 0. 230 atm (b) 0.233 atm
(c) 0.236 atm (d) 0. 0239 atm

2. The osmotic pressure of the solution at 298 K will be

(a) 4. 29 atm (b) 4.49 atm
(c) 4.69 atm (d) 4.89 atm

3. The freezing point of the solution will be

(i) – 0. 684°C
(ii) – 0. 342 °C
(iii) – 0. 372° C
(iv) – 0.186°C

2. According to Raoult's law (which is applicable for a mixture of volatile liquids) the partial vapour pressure of a liquid is directly proportional to mol fraction of that component. Further assuming ideal behaviour for vapours and applying Dalton's law we can write different equation as follows:

$$P_A = P^o_A X_A , P_B = P^o_B X_B$$
$$P_{\text{Total}} = P_A + P_B$$
$$= P^o_A x\, A + P^o_B + (P^o_A - P^o_B) \times A$$

Further mol fraction of a component in vapour phase is equal to the ratio of partial vapour pressure to total vapour pressure of mixture.

The vapour pressure of two pure liquids A and B which form an ideal solution are 300 to 500 torr respectively at temperature T. A mixture of the vapour of A and B for which the mol fraction of A is 0.25 is slowly compressed at temperature T.

4. The total pressure when first drop of condensate is formed will be.

(a) 428 torr (b) 400 torr
(c) 388 torr (d) 358 torr

5. The pressure when only the last bubble of vapour remains will be

(a) 350 torr (b) 375 torr
(c) 525 torr (d) 450 torr

6. The mol fraction of B in the last bubble of vapour will be

(a) 0.16 (b) 0. 84
(c) 0. 20 (d) 0.80

3. Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogenous solution. These are called colligative properties. Application of colligative properties are very useful in day to day life. One of its example is the use of ethylene glycol and water mixtures 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 water = 1. 86 K kg mol^{-1}
Freezing point depression constant of ethanol
(K_f ethanol) = 2. 0 K kg mol $^{-1}$
Boiling point elevation constant of water
(K_b $^{\text{water}}$) = O. 52 K kg mol^{-1}
Boiling point elevation constant of ethanol
(K_B ethanol) = 1. 2 K kg mol^{-1}
Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155. 7K
Standard boiling point of water = 373 K
Standard boiling point of ethanol =351.5 K

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CHAPTER 7

Chemical Kinetics

Rate of Reaction

The rate of reaction means the speed with which the reaction takes place. This is expressed either in terms of decrease in the concentration of a reactant per unit time or increase in the concentration of a product per unit time. Or the rate of reaction is the change in the concentration of any one of the reactant or products per unit time. It is expressed by the graph for the reaction A → B.

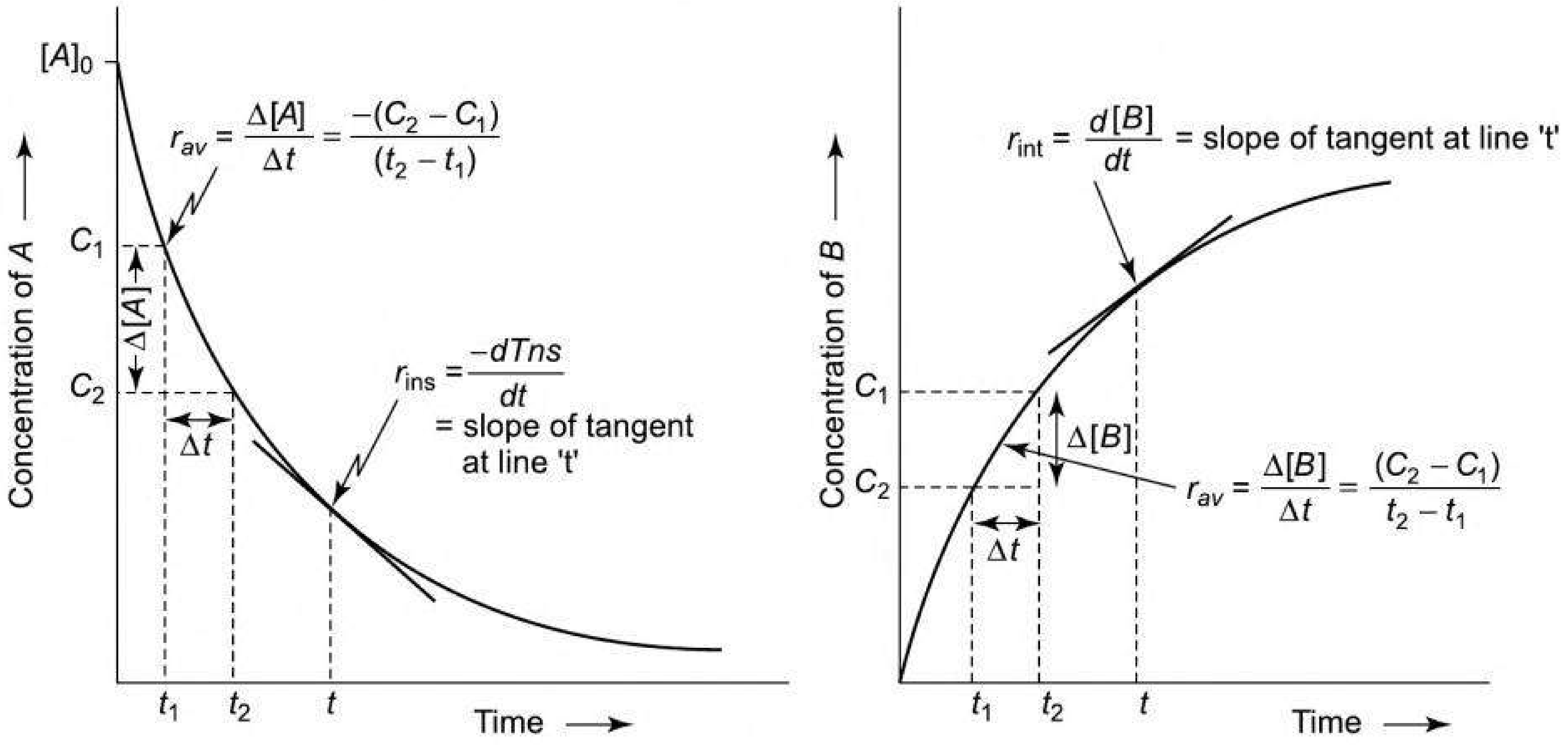


Fig. 7.1

It is clear from the graph that the concentration of reactant 'A' decreases and concentration of product 'B' increases with the lapses of time. The rate of reaction is expressed in two ways:

1. Average rate of reaction

The rate when determined during a certain time interval, it is called average rate of reaction.

Pseudo First Order Reaction

Consider the following acid-catalysed reactions:
(i) Hydrolysis of ethylacetate.

$$CH_3\,COO\,C_2H_5 + H_2O \xrightarrow{H^{(+)}} CH_3\,COOH + C_2H_5OH$$

(ii) Inversion of cane-sugar

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^{(+)}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose.}}{C_6H_{12}O_6}$$

The above reactions are bimolecular but experimently it is found that order is one.

Thus.

Rate of (I) reaction $\alpha\,[CH_3\,COO\,C_2\,H_5]$.

and Rate of (II) reaction $\alpha\,[C_{12}\,H_{22}\,O_{11}]$.

Thus the reactions in which molecularity is two but order is one because the other component of the reactants are used as medium and large excess, called as Pseudo Unimolecular Reaction.

Examples of 1st order Reaction

1. Hydrolysis of esters

$$CH_3\,COOC_2\,H_5 + H_2O \xrightarrow{H^{(+)}} CH_3\,COOH + C_2\,H_5\,OH.$$

In this reaction acetic acid is one of the products and the amount of which can be found by titrating against standard NaOH solution.

Since catalyst acid also neutralise NaOH.

Let the data observed for this titration is as follows.

Time	Vol. of NaOH used.
$t = o$	$V = V_0$
$t = t_1$	$V = V_1$
$t = t_2$	$V = V_2$
$t = t_\infty$	$V = V_\infty$

So V_o α Volume of acid catalyst (No CH_3 COOH yet to formed)

V_t α Volume of acid catalyst + Volume of CH_3 COOH formed.

$\therefore$ Amount of acetic acid formed $\alpha\, V_t - V_o$.

Thus $x \propto V_t - V_o$

Again

$V_\infty \propto$ Amount of acid catalyst + Maximum amount of CH_3 COOH formed.

$\therefore$ Maximum amount acetic acid produced $\alpha\, V_\infty - V_o$

$\therefore a\;\alpha\;V_\infty - V_o$

$$\therefore \quad K_t = 2.303 \log_{10} \frac{V_\infty - V_o}{V_\infty - V_t}.$$

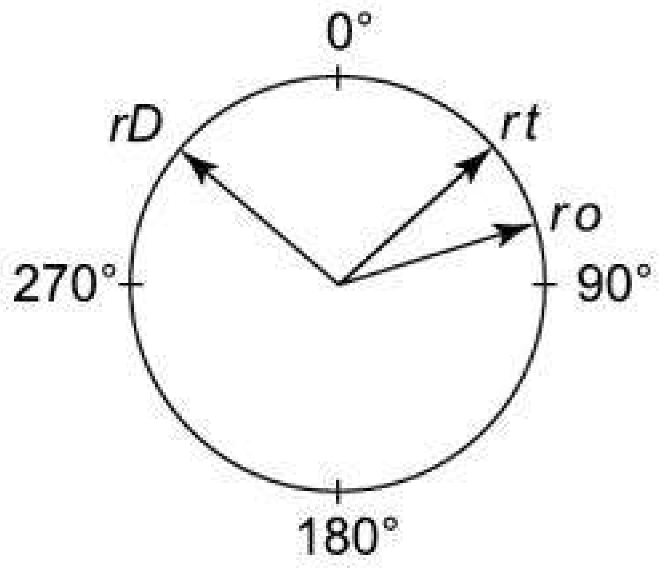
$$\Rightarrow \quad \boxed{t = \frac{2.303}{K}\log_{10}\frac{V_\infty - V_o}{V_\infty - V_t}.}$$

2. Inversion of Cane Sugar

$$\underset{\text{Sucrose}}{C_{12}\,H_{22}\,O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6\,H_{12}\,O_6} + \underset{\text{Fructose.}}{C_6\,H_{12}\,O_6}$$

The hydrolysis of dextro–rotatory sucrose produce a mixture of glucose (dextrorotatory) and fructose (Laevorotatory). The rate is measured by measuring the change in the angle of rotation by a polarimeter. The change produced in rotatory power in time '*t*' gives a measure of *x* i.e. the quantity of sucrose decomposed in that time. The total change in the rotatory power produced at the end of the reaction gives the measure of CO. the initial concentration of sucrose

If r_0, r_1 and r_∞ represent rotations at the start of reaction after time '*t*' and at the end of reaction respectively, then



$C_o\;\alpha\;r_o - r_\infty$ and $x = r_o - r_t$

$\Rightarrow \quad C_o - x\;\alpha\;r_t - r_\infty.$

$$\Rightarrow \quad K_t = 2.303 \log_{10} \frac{r_o - r_\infty}{r_t - r_\infty}$$

3. Gaseous Reaction involving First order

The gaseous reaction rate is measured in terms of change in pressure

and $$\frac{d[C]}{dt} = K_1[B] \qquad ....(3)$$

From equation (2) by integrating we have $[A] = [A]_o\, e^{-kt}$ ....(4)

Substituting the value of $[A]$ into (2)

$$\frac{d[B]}{dt} = K_1[A]_o\, e^{-kt} - K_2[B].$$

$$\Rightarrow \quad \frac{d[B]}{dt} = K_2[B] = K_1[A]_o\, e^{-kt}.$$

The left side expression is equal to $d[B]e^{K_2t}/dt$ Thus

$$d[B]e^{K_2t} = K_1[A]_0\, e^{-(K_1-K_2)t}dt.$$

Now on integrating the above equation with $B = 0$ and $t = 0$, we get,

$$[B] = [A]_0 \frac{K_1}{K_2-K_1}\left(e^{-K_1t} - e^{-K_2t}\right) \qquad ....(5)$$

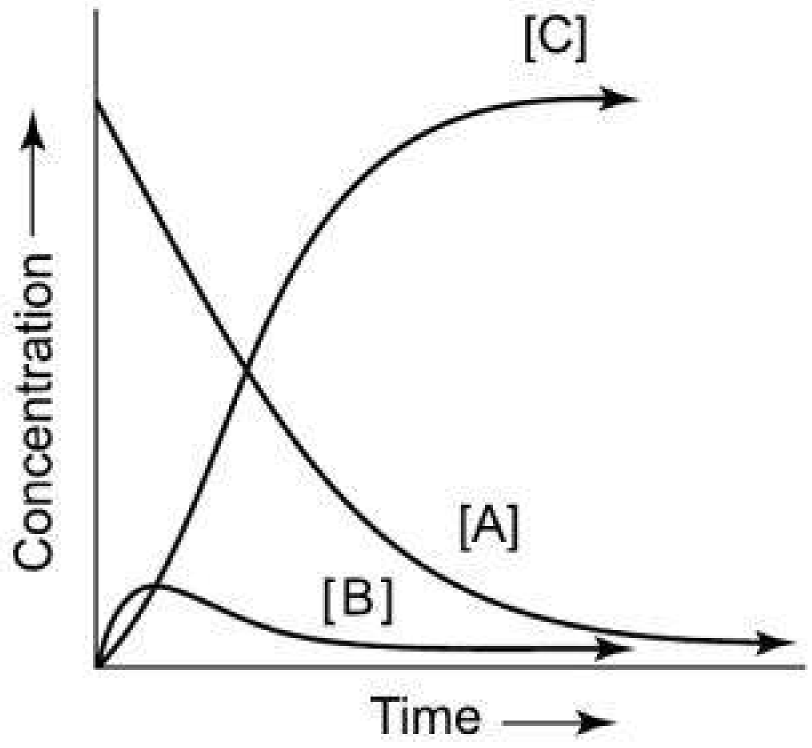
Similarly

$$[C] = [A]_0\left[1 + \frac{K_1e^{-K_2t} - K_2e^{-K_1t}}{K_2-K_1}\right] \qquad ....(6)$$

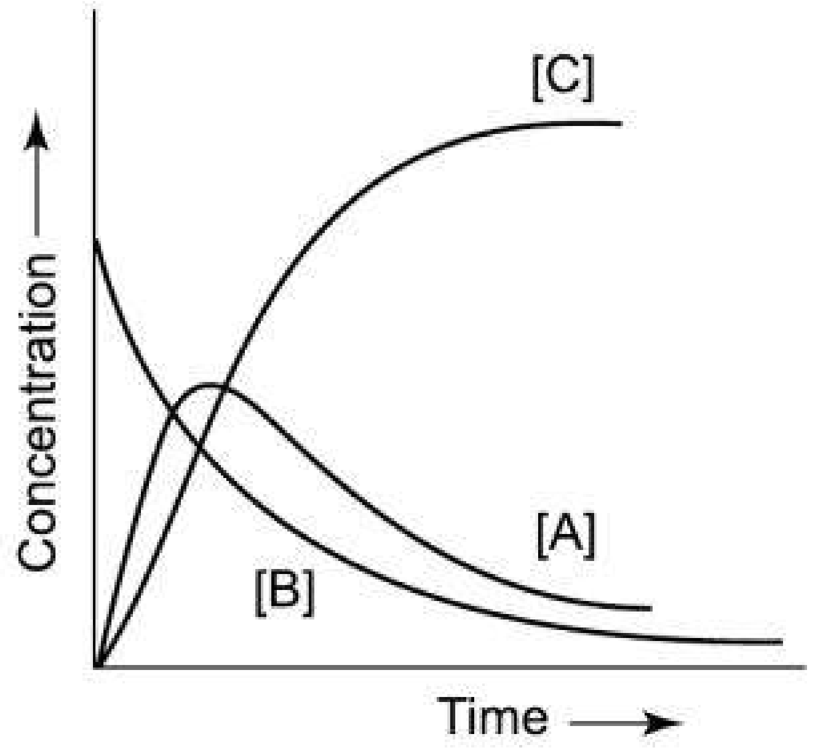
Since for the consecutive reaction.

$[A]_0 = [A] + [B] + [C]$

assuming $[B]_0 = [C]_0 = 0$



$K_2/K_1 = 10$



$K_2/K_1 = 0.5$

Fig. 7.8

$[B]$ is maximum if $\frac{d[B]}{dt} = 0$

$$\Rightarrow \quad K_1[A] = K_2[B]_{\max}$$

$$\therefore \quad \frac{d[B]}{dt} = -K_1e^{-K_1t} + K_2e^{-K_2t} = 0$$

$$\Rightarrow K_1e^{-K_1t} = K_2e^{-K_2t}$$

$$\Rightarrow \quad \boxed{t = \frac{1}{K_2-K_1}\,\text{In}\,\frac{K_2}{K_1}}$$

$$[B]_{\max} = [A]_0\left(\frac{K_2}{K_1}\right)^{K_2/K_1-K_2}$$

(B) Reversible Reaction

Let us suppose a reaction

$$A \rightleftharpoons B.$$

Both forward and backward reaction are 1st order. Let x mole/L of A changes into B then concentration B increases.

	A $\underset{K_2}{\overset{K_1}{\rightleftharpoons}}$	B
Initially	a	b
After time 't'	$a-x$	$b+x$.

Rate $= K_1(a-x) - K_2(b+x)$ [$\because$ Both occur simultaneously]

At equilibrium, net rate is zero.

Thus,

$K_1(a-x_e) = K_2(b+x_e)$ where e represent equilibrium.

$$\Rightarrow \quad b = \frac{K_1}{K_2}(a-x_e) - x_e$$

Rate of reaction $\frac{dx}{dt}$

$$= K_1(a-x) - K_2\left[\frac{K_1}{K_2}(a-Xe) - Xe + X\right]$$

on solving we get

Rate $= (K_1+K_2)(X_e - X)$

Again $$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}} = \frac{K_1}{K_2}$$

(C) Parallel Reactions or side Reactions

A reaction which do not follow only one path but follow different path to give different products and

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After 30 min from start of the decomposition in a closed vessel the total pressure developed is found to be 250 mm of Hg and on complete decomposition the total pressure is 500 mm. Calculate rate constant of the reaction.?

➤ Solution

The given reaction

	$2N_2O_5(g)$	$\rightarrow$ $4NO_2(g)$	$+ O_2(g)$
Initially	P_o	0	0
After time 't'	$P_o - 2x$	$4x$	x
At $t = \infty$	0	$2P_o$	$P_o/2$

Total pressure (P_t) after time 't' $= P_o - 2x + 4x + x$
$= P_o + 3x$

$$\Rightarrow x = \frac{1}{3}(P_t - P_o)$$

And $P_\infty = 2P_o + \frac{1}{2}P_o = 5/2\, P_o$

$$\Rightarrow \quad P_o = \frac{2}{B}P_\infty = 2/5 \times 500 = 200 \text{ mm of Hg.}$$

$$\Rightarrow \quad x = \frac{1}{3}(P_t - P_o) = \frac{1}{3}(250 - 200) = 50/3.$$

Now apply first order kinetics

$$K = \frac{2.303}{t}\log\frac{P_o}{P_o - 2x}.$$

[since concentration α partial pressure]

$$\Rightarrow \quad K = \frac{2.303}{30}\log\frac{200}{200 - \frac{100}{3}}$$

$$\Rightarrow \quad K = 6.08 \times 10^{-3}\text{ min}^{-1}.$$

➤ Example 7.12

The activation energy of the reaction A + B → Products is 105.73 KJ/mole. At 40°C the products are formed at the rate of 1.33 mole L^{-1} min^{-1}. What will be rate of formation of product at 80°C?

➤ Solution

For A + B → Product

The rate law expression at different temp. are given as

At 40°C, $r_{40} = K_1[A]^x[B]^y$

At 80°C, $r_{80} = K_2[A]^x[B]^y$

$$\Rightarrow \quad r_{80} = r_{40}\left(\frac{K_2}{K_1}\right) \quad \text{.........(1)}$$

From Arrhenius equation

$$\log\frac{K_2}{K_1} = \frac{Ea}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rightarrow \quad \log\frac{K_2}{K_1} = \frac{105.73 \times 10^3}{2.303 \times 8.314}\left(\frac{1}{313} - \frac{1}{353}\right)$$

$$\Rightarrow \quad \log\frac{K_2}{K_1} = 2 \quad \Rightarrow \quad \frac{K_2}{K_1} = \text{antilog } 2.$$

$$\Rightarrow \quad \frac{K_2}{K_1} = 10^2 = 100.$$

$$\therefore \quad r_{80} = r_{40}(100)$$

$$\Rightarrow \quad \boxed{r_{80} = 100\, r_{40}}$$

$$\Rightarrow \quad r_{80} = 100 \times 0.133 \text{ mole L}^{-1}\text{ min}^{-1}$$
$$= 13.3 \text{ mole L}^{-1}\text{ min}^{-1}.$$

➤ Example 7.13

The rate constant at 25°C for the reaction of NH_4^+ and OH^- to form NH_4OH (aq. NH_3) is 4.0×10^{10} M^{1-} S^{-1}. Calculate the rate constant for proton transfer to NH_3. Ionisation constant for eq. NH_3 is 1.8×10^{-5}.?

➤ Solution

The reaction,

$$NH_4^+ + OH^- \xrightarrow{K_1} NH_4OH$$

$$\frac{d[NH_4OH]}{dt} = K_1[NH_4^+][OH^-] \quad (1)$$

Again, $NH_3 + H_2O \xrightarrow{K_2} NH_4\,OH.$

$$\Rightarrow \quad \frac{d\, NH_4OH}{dt} = K_2[NH_3][H_2O] \quad (2)$$

From equation (1) and (2) we get

$$K_2[NH_3] = K_1[NH_4^+][OH^-].$$

$$\Rightarrow \quad K_2 = K_1\frac{[NH_4^+][OH^-]}{[NH_3]} = K_1K_b$$
$$= 4 \times 10^{10} \times 1.8 \times 10^{-5}$$
$$= 7.2 \times 10^5 \text{ sec}^{-1}.$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^5$$

where Kb = (Ionisation constant. of aq. NH_3).

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$$(CH_3)_2\,O \rightarrow CH_4 + H_2 + CO$$

Time (sec)	0	400	x	∞
Total pressure (mm)	312	468	585	y

The values of (x, y) missing above are:

(a) $x = 800, y = 936$ (b) $x = 620, y = 624$
(c) $x = 620, y = 936$ (d) $x = 800, y = 624$

3. For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate $-\frac{d[NH_3]}{dt} = 2 \times 10^4\ Ms^{-1}$. Therefore the rate $-\frac{d[N_2]}{dt}$ is given as:

(a) 10^{-4} M sec^{-1} (b) 10^4 M sec^{-1}
(c) 10^{-2} M sec^{-1} (d) 10^{-4} sec^{-1} M^{-1}

4. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ under certain conditions of temperature and partial pressure of the reactants, the rate of formation of NH_3 is 0.001 kg h^{-1}. The rate of conversion of H_2 under same conditions is:

(a) 0.0015 kg h^{-1} (b) 1.76×10^{-4} kg h^{-1}
(c) 0.002 kg h^{-1} (d) 0.003 kg h^{-1}

5. The rate constant for a zero order reaction is 2×10^{-2} mol L^{-1} sec^{-1}. If the concentration of the reactant after 25 sec is 0.5 M, the initial concentration must have been:

(a) 0.5 M (b) 1.25 M
(c) 12.5 M (d) 1.0 M

6. Given that for a reaction of nth order, the integrated rate equation is:

$$K = \frac{1}{t(n-1)}\left[\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}}\right],$$ where C and C_o are the concentration of reactant at time t and initially respectively. The $t_{3/4}$ ad $t_{1/2}$ are related as ($t_{3/4}$ is time required for C to become $C_1/4$):

(a) $t_{3/4} = t_{1/2}[2^{n-1} + 1]$
(b) $t_{3/4} = t_{1/2}[2^{n-1} - 1]$
(c) $t_{3/4} = t_{1/2}[2^{n+1} + 1]$
(d) $t_{3/4} = t_{1/2}[2^{n+1} - 1]$

7. For a chemical reaction A $\rightarrow$ Products, the rate of disappearance of A is given by:

$$-\frac{dC_A}{dt} = \frac{K_1 C_A}{1 + K_2 C_A}$$ At low C_A, the reaction is of the ….. order with rate constant ….. (Assume K_1, K_2 are lesser than 1)

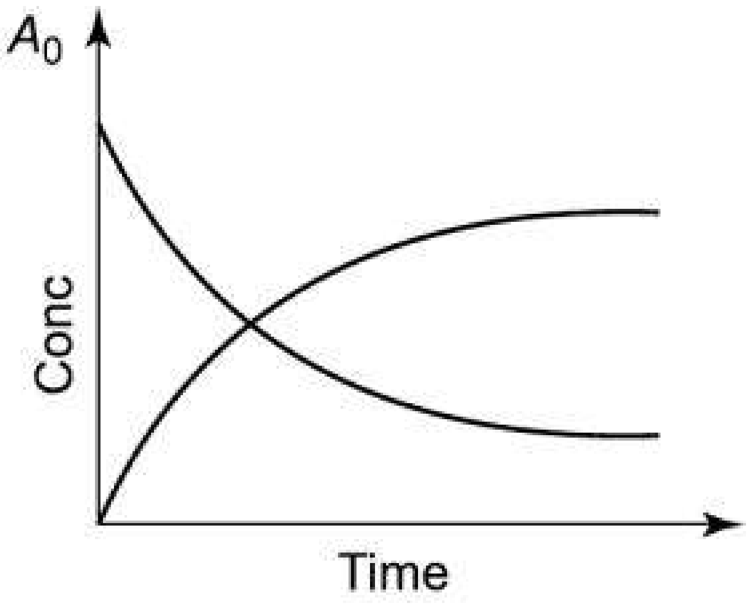
(a) I, K_1/K_2 (b) I, K_1
(c) II, K_1/K_2 (d) II, $K_1/K_2 + K_2$

8. The rate equation for an autocatalytic reaction;
$A + R \xrightarrow{K} R + R$ is $\frac{-dC_A}{dt} = KC_A.C_R$

The rate of disappearance of reactant A is maximum when:

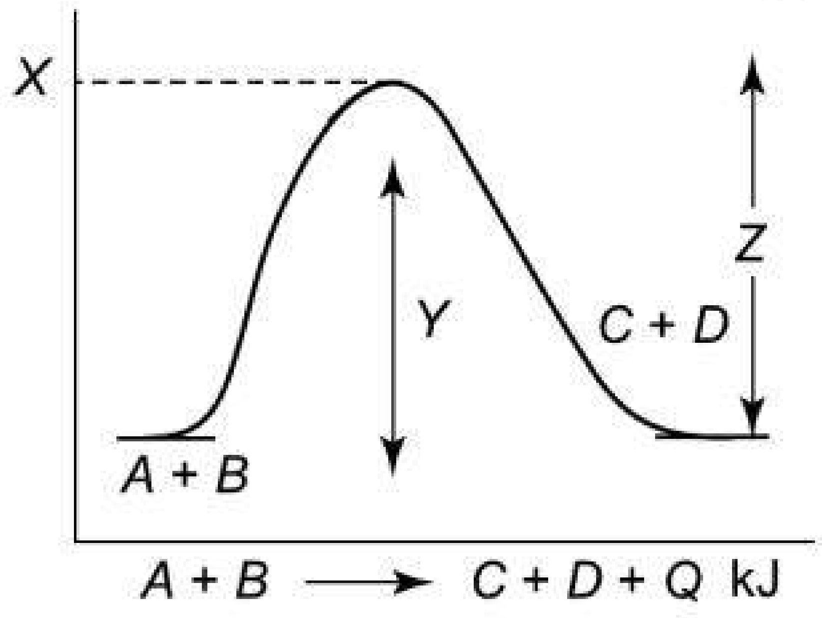
(a) $C_A = 2C_R$ (b) $C_A = C_R$
(c) $2C_A = C_R$ (d) $C_A = (C_R)^{1/2}$

9. At the point of intersection of the two curves shown, the conc. of B is given by …… for, $A \rightarrow nB$:



(a) $\frac{nA_0}{2}$ (b) $\frac{A_0}{n-1}$
(c) $\frac{nA_0}{n+1}$ (d) $\left(\frac{n-1}{n+1}\right)A_0$

10. Mark the correct statement about given graph:



(a) X is threshold energy level
(b) Y and Z are energy of activation for forward and backward reaction respectively
(c) Q is heat of reaction and reaction is exothermic
(d) All of these

11. Consider the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$.
The equally relationship between $-\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is:

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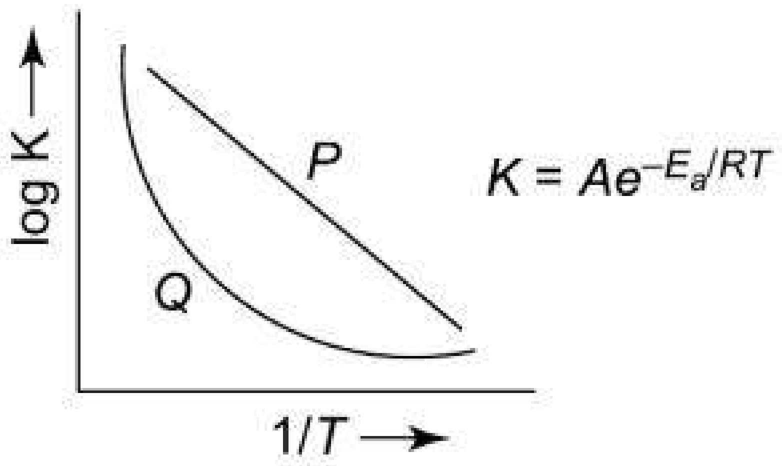
37. If for two reaction $E_{a_1} > E_{a_2}$ and TC_1 and TC_2 are temperature coefficient respectively, then which alternative is correct:

(a) $TC_1 > TC_2$ (b) $TC_1 < TC_2$
(c) $TC_1 = TC_2$ (d) None of these

38. Which of the following statement are ture regarding the log *K* Vs 1/*T* plot shown in the given diagram:

(i) Plot *P* shows that the energy of activation is independent of temperature

(ii) Plot *Q* describes the behaviour of temperature dependence of energy of activation



(iii) Arrhenius behaviour is described by *P*. Select the correct answer using the codes given below:

(a) (i) and (ii) (b) (ii) and (iii)
(c) (i) and (iii) (d) (i), (ii) & (iii)

39. The rate law of a reaction, $A + B \rightarrow$ Product is 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 reaction will be:

(a) $n - m$ (b) 2^{n-m}
(c) $\frac{1}{2^{m+n}}$ (d) $m + n$

40. In a first order reaction, the concentration of the reactant decreases form 0.8 M to 0.4 M in 15 minute. The time taken for the concentration to change from 0.1 M to 0.025 M is

(a) 60 minute (b) 15 minute
(c) 7.5 minute (d) 30 minute

41. The rate equation for the reaction;
$2A + B \rightarrow C$ is rate $= K[A][B]$. The correct statement about this is:

(a) *K* is independent of [*A*] and [*B*]
(b) $t_{1/2}$ is constant
(c) Unit of *K* is sec^{-1}
(d) Rate of formation of *C* is twice the rate of disappearance of *A*

42. The energy of activation for forward and backward change for an endothermic reaction; $X \rightarrow Y$ are E_f and E_b respectively. Which is correct:

(a) $E_b < E_f$
(b) $E_b > E_f$
(c) $E_b = E_f$
(d) No relation between them

43. A reaction involving two different reactants can never be:

(a) Unimolecular reaction
(b) I order reaction
(c) II order reaction
(d) Bi-molecular reaction

44. $t_{1/4}$ can be taken as the time taken for concentration of reactant to drop to 3/4 of its initial value. If the rate constant for a first order reaction is K, then $t_{1/4}$ can be written as:

(a) 0.10/K (b) 0.29/K
(c) 0.69/K (d) 0.75/K

45. The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr;

$$NO_{(g)} + Br_{2(g)} \xrightleftharpoons{\text{fast}} NOBr_{2(g)}$$

$$NOBr_{2(g)} + NO_{(g)} \xrightleftharpoons{\text{slow}} 2NOBr_{(g)}$$

If the second step is the rate determining step, the order of the reaction with respect to $NO_{(g)}$ is:

(a) 1 (b) 0
(c) 3 (d) 2

46. Rate of reaction can be expressed by Arrhenius equation as:

$K = Ae^{-Ea/RT}$

In this equation E_a represents:

(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 reactant molecules at a temperature *T*
(d) The fraction of molecules with energy greater than the activation energy of the reaction

47. The rate constant, the energy of activation and the Arrhenius parameter of a chemical reac-

47. (b) $K = A.e^{-Ea/RT}$ if $T \to \infty$, $e^{-Ea/RT} = 1$

or $K = A$

48. (d) $r = K\,[N_2O_5]$ I order as unit of $K = \text{sec}^{-1}$

$2.40 \times 10^{-5} = 3.0 \times 10^{-5}\,[N_2O_5]$

$$\therefore\quad [N_2O_5] = \frac{2.40}{3.0} = 0.8\,M$$

49. (c) $$K = \frac{2.303}{t}\log\frac{C_0}{C} = \frac{2.303}{2\times10^4}\log\frac{800}{50} = 1.38\times10^{-4}\ \text{sec}^{-1}$$

50. (c) $$K = \frac{2.303}{40}\log\frac{0.1}{0.025} = 0.0347$$

$$\text{rate} = K\times[X] = 0.0347\times0.01 = 3.47\times10^{-4}\,M\,\text{min}^{-1}$$

IIT WINDOW–IV

➤ One or more correct Answer

1. Which of the following is/are incorrect regarding activation energy?

(a) Large the activation energy, smaller is the value of rate constant.

(b) The higher the $E_{a,}$ higher the value of temperature co-efficient, $\frac{K_T + 10}{K_T}$

(c) At lower temperature, increase in temperature causes more change in the value of K than at higher temperature.

(d) A plot made between K and $1/T$ gives a straight line of slope $-\frac{E_a}{R}$

2. $A + B \rightleftharpoons C + D$; $\Delta H = -217$ KJ / mole

Mark out the incorrect statements, regarding the reaction:

(a) The rate of disappearance of B increases on increase of the concentration of A.

(b) The rate of formation of D increases on increasing temperature.

(c) The rate of formation of C increases on increasing temperature.

(d) The use of catalyst doesn't affect the rate of formation of B or C

3. A general reaction

$$A(g) + B(g) \rightarrow C(g) + D(l)$$

proceeds in a container of volume V at temperature T, which of the following is/are correct?

(a) $\frac{-d[A]}{dt} = \frac{1}{V}\frac{dnc}{dt}$

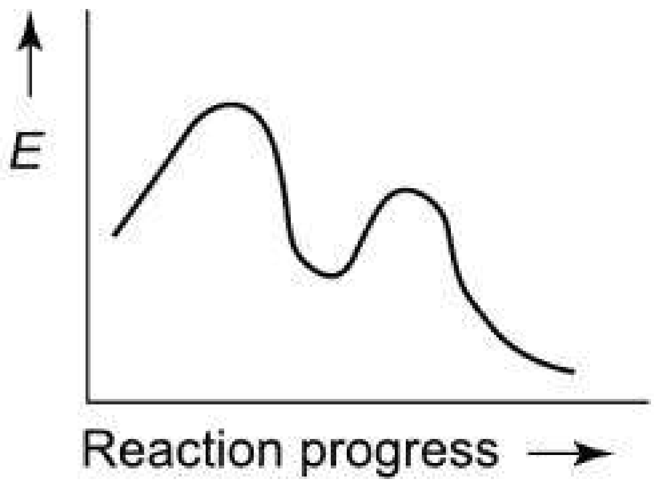
(b) $-\frac{1}{V}\frac{dnB}{dt} = V\frac{dnc}{dt}$

(c) $-\frac{1}{V}\frac{dnB}{dt} = -\frac{1}{RT}\frac{dp_A}{dt}$

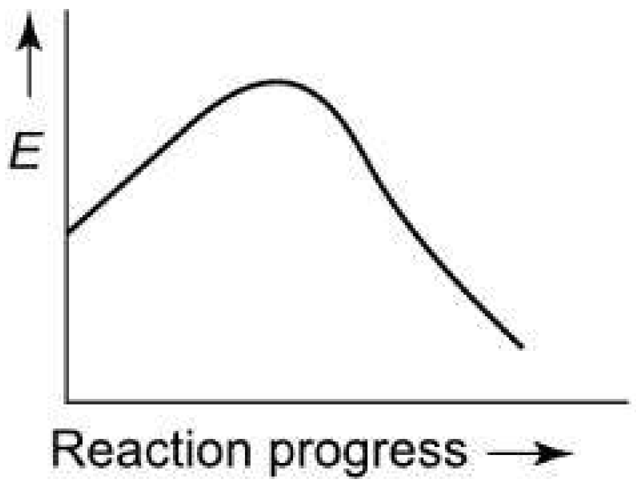
(d) $\frac{d[C]}{dt} = \frac{1}{RT}\frac{dp_B}{dt}$

4. $AB + m \rightarrow Am + B$

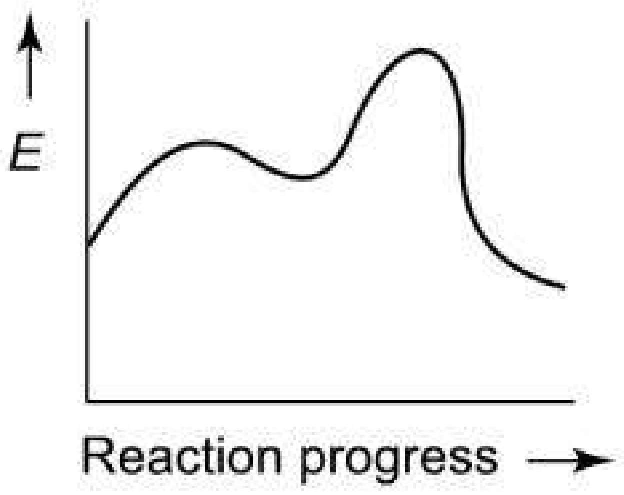
For the reaction the time required to complete a definite fraction is inversely proportional to the initial concentration. Which of the following graphs express the reaction progress clearly?



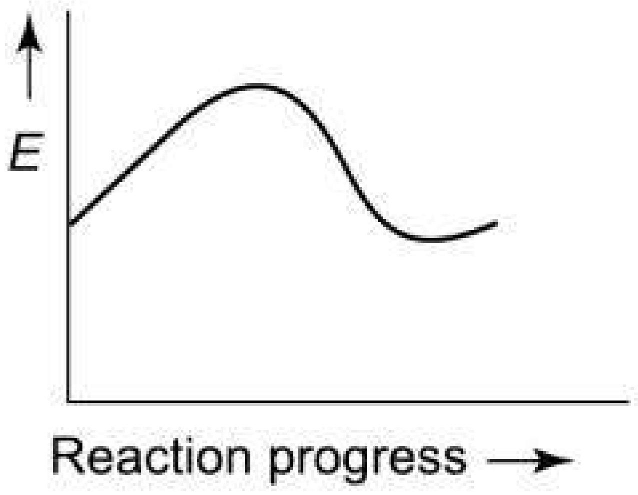
(a)



(b)



(c)



(d)

5. The acid-catalysed iodination of propanone may be investigated by reacting dilute aqueous iodide with solutions containing known concentration of propanone and acid.

Large excess of propanone is used deliberately sometimes.

(a) to buffer the acid concentration

(b) to observe the effect of change in concentration of I_2 and H^+

ment. The 10 mL of this mixture at STP possess the rate of 10^4 disintegration per minute. How many milli-curie of radioactive carbon is needed to prepare 60 litre of such a mixture?

19. A solution contains 1 milli-curie of L-phenyl alanine C^{14} (uniformly labeled) in 2.0 mL solution. The activity of labeled sample is given as 150 milli-curie/milli-mole. Calculate:

(a) The concentration of sample in the solution in mole/litre.

(b) The activity of the solution in terms of counting per minute/mL at a counting efficiently of 80%.

20. For the following sequential reaction, $A \xrightarrow{K_1} B \xrightarrow{K_2} C$, find out the concentration of C at time $t = 1$ day, given the $K_1 = 1.8 \times 10^{-5}\ s^{-1}$ and $K_2 = 1.1 \times 10^{-2}\ s^{-1}$ and initial molar concentration of A is 1.8.

21. A solution contains a mixture of isotopes of X^{A_1} ($t_{1/2} = 14$ days) and X^{A_2} ($t_{1/2} = 25$ days). Total activity is curie at $t = 0$. The activity reduces by 50% in 20 days. Find:

(a) The initial activities of X^{A_1} and X^{A_2}.

(b) The ratio of their initial no. of nuclei.

22. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 KJ mol^{-1} and 157.7 KJ mol^{-1} as well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

23. A given sample of milk turns sour at room temperature (20°C) in 64 hours. In a refrigerator at 3°C, milk can be stored three times as long before it sours. Estimate

(a) The activation energy for souring of milk,

(b) How long it take milk to sour at 40°C?

24. A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate:

(i) the concentration of oxygen atoms needed so that the reaction $O + O_3 \rightarrow 2O_2$ having rate constant equal to 1.5×10^7 litre mol^{-1} sec^{-1} can proceed with a rate of 0.15 mol $litre^{-1}$ sec^{-1}.?

(ii) the rate of formation of oxygen under this condition.

25. Two Ist order reactions having same reactant concentration proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reactions is 3. Find the ratio of the rates of these reactions at 75°.C?

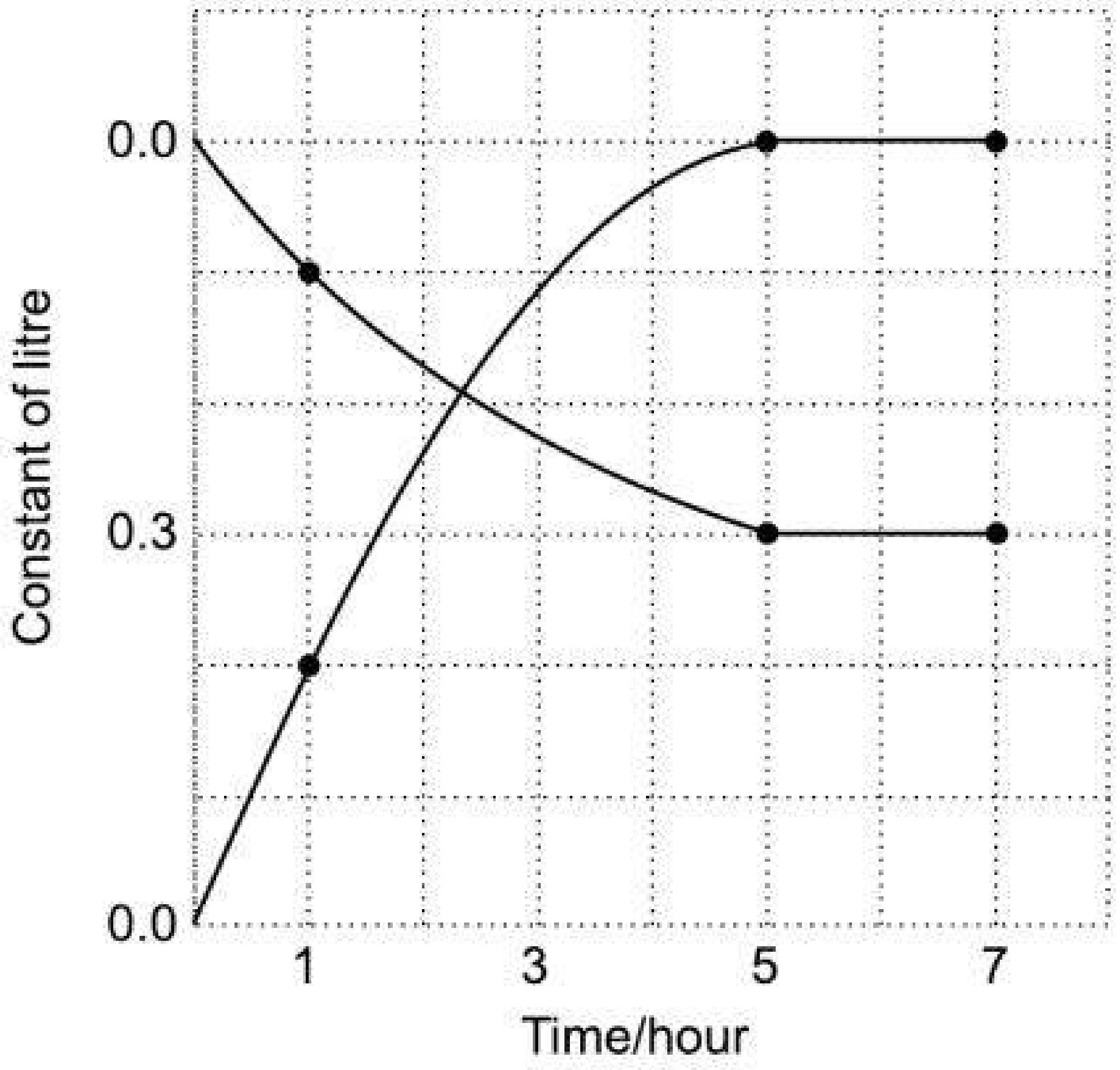
26. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open due to this some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100 mL 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ acidified solution. Calculate the rate constant for decomposition of H_2O_2.?

27. The progress of the reaction $A \rightleftharpoons nB$ with time is presented in the figure. Determine:

(i) the value of n

(ii) the equilibrium constant, K and

(iii) the initial rate of conversion of A



28. $_{92}U^{238}$ is radioactive and it emits α and β particles to form $_{82}Pb^{206}$. Calculate the number of α and β particles emitted in this conversion. An ore of $_{92}U^{238}$ is found to contain $_{92}U^{238}$ and $_{82}Pb^{206}$ in the weight ratio of 1:0.1. The half-life period of $_{92}U^{238}$ is 4.5×10^9 years. Calculate the age of the ore.?

(c) Three natural life time
(d) Four natural life time

5. Number of natural life times (τ) required for a first – order reaction to achieve 99.9% level of completion is
(a) 2.3 (b) 6.9
(c) 9.2 (d) 0.105

Passage V

The rate law for the decomposition of gaseous

N_2O_5 is $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$, A reaction mechanism which has been suggested

$$N_2O_5 \xrightleftharpoons{\text{Keg.}} NO_2 + NO_3 \text{ (fast equilibrium)}$$

$$NO_2 + NO_3 \xrightarrow{k_1} NO_2 + NO + O_2 \text{ (slow)}$$

$$NO + NO_3 \xrightarrow{k_2} 2NO_2 \text{ (fast)}$$

1. In 20 minutes of 80% of N_2O_5 is decomposed find rate constant
(a) 0.08 (b) 0.05
(c) 0.12 (d) 0.2

2. When graph is plotted between $t_{1/2}$ *V*s initial concentration then slop is
(a) O (b) ∞
(c) > O (d) < O

3. At the equilibrium state N_2O_5, NO_2 and NO_3 concentration are 0.2, 0.4 and 0.4 *M* respectively. Find K_1?
(a) 0.1 (b) 0.2
(c) 1 (d) 2

4. If the concentration of N_2O_5 is doubled then rate becomes
(a) 2 times
(b) 4 times
(c) 8 times
(d) constant remain same

Passage VI

Chemical reaction occurs only as a result of collisions between the reaction molecules. During this process atoms are rearranged by breaking up old bonds and new bonds are formed.

1. Rate of the reaction (r) B given by the expression
(a) $r = f \times z$ (b) $r = \frac{f}{z}$
(c) $r = \frac{z}{f}$ (d) $r = f \times z^2$

2. Fraction of the molecules (f) in a gas possessing energy greater than Ea(B) given by
(a) $f = e^{Ea/RT}$ (b) $f = e^{-Ea/RT}$
(c) $f = EaRT$ (d) $f = Ea - RT$

3. Rate constant K for the reaction is given by the expression
(a) $K = Ze^{-Ea/RT}$
(b) $K = Ea - RT$
(c) $K = Z \times RT$
(d) $K = f \times RT$

4. The temperature coefficient for most of the reaction is
(a) 1 (b) 1.5
(c) 2 (d) 2.5

Passage VII

The rate of reaction is defined as the change of concentration of any one of its reactants or products per unit time. In general, for a reaction

$$aA + bB \rightarrow cC + dD$$

The instantaneous rate may be expressed as

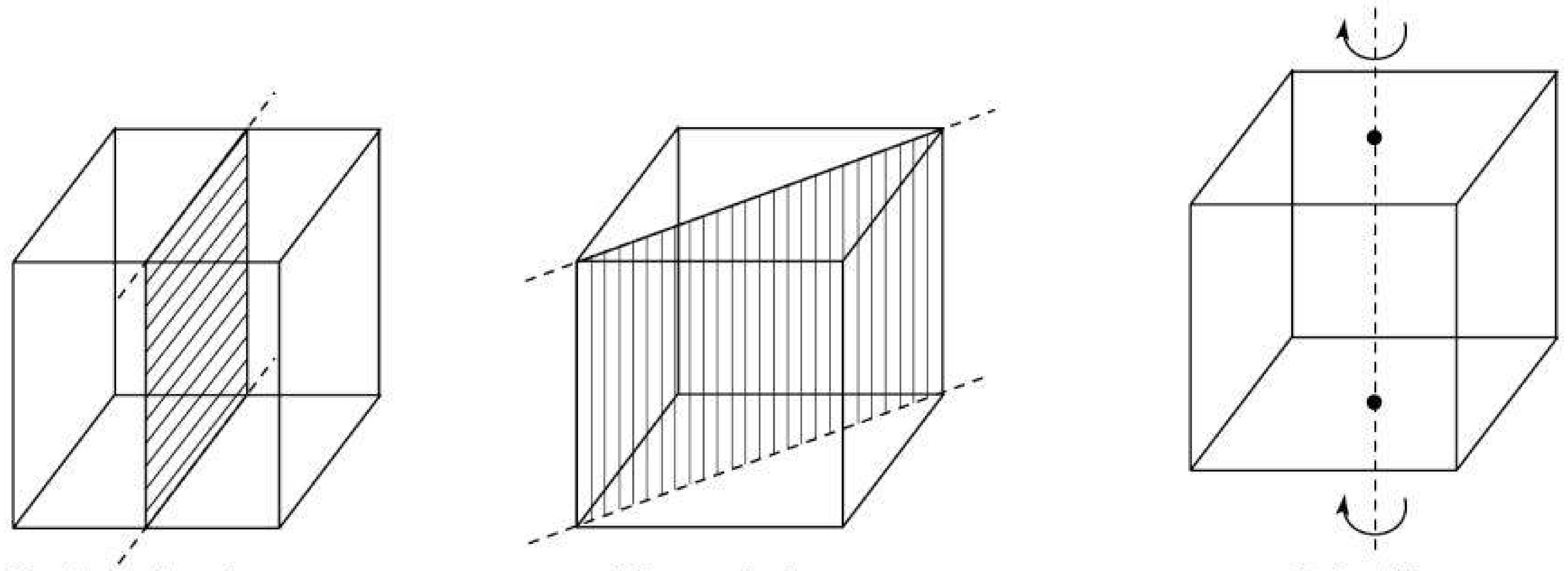
$$r = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

1. $xA + yB \rightarrow zC$

If $\frac{-d[A]}{dt} = -\frac{d(B)}{dt} = 1.5\frac{d(c)}{dt}$ then x, y and z are
(a) 1, 1, 1 (b) 3, 2, 3
(c) 3, 3, 2 (d) 2, 2, 3

2. The rate reaction that does not involve gases, is not dependent on:
(a) Pressure (b) temperature
(c) Concentration (d) Catalyst

3. For a hypothetical reaction $2A \rightarrow 3C$, the reaction rate 'r' is given by
(a) $r = -d[A]/dt$ (b) $r = \frac{-1}{2}\frac{d[A]}{dt}$



Rectangular plane of symmetry

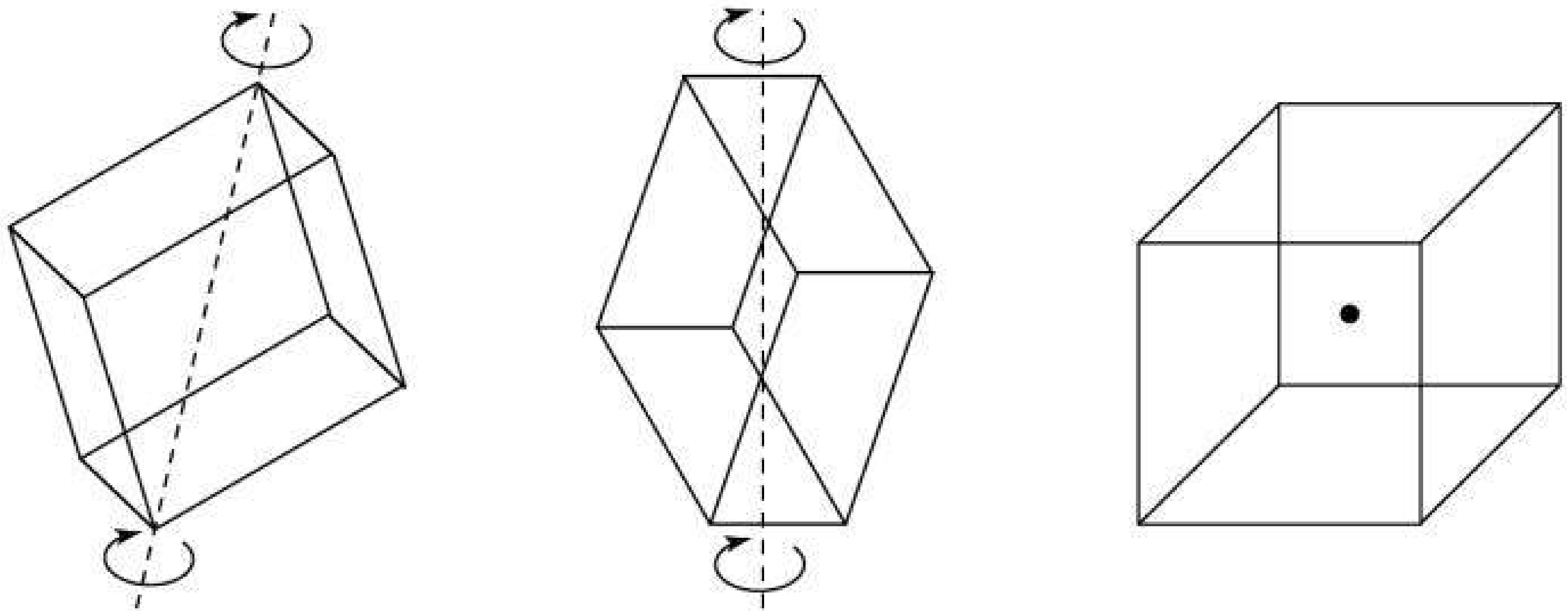
(a)

Diagonal plane of symmetry

(b)

Axis of four fold symmetry

(c)



Axis of there fold symmetry (four)

(d)

Axis of two fold symmetry (six)

(e)

Centre of symmetry

(f)

Fig. 8.1

4. 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 possess a total of 23 elements of symmetry.

Plane of Symmetry = (3 + 6) = 9 [Fig 8.1 (a) and (b)]

Axes of Symmetry = (3 + 4 + 6) = 13 [Fig 8.1 (c), (d), and (e)]

Centre of Symmetry = 1 [Fig 8.1 (f)]

The total number of symmetry element = 23

Crystal Lattice

The regular three dimensional arrangement of the points in a crystal is called space lattice. The space lattice is also called crystal lattice. The location of the points in the space lattice are called lattice point or lattice site.

Unit Cell

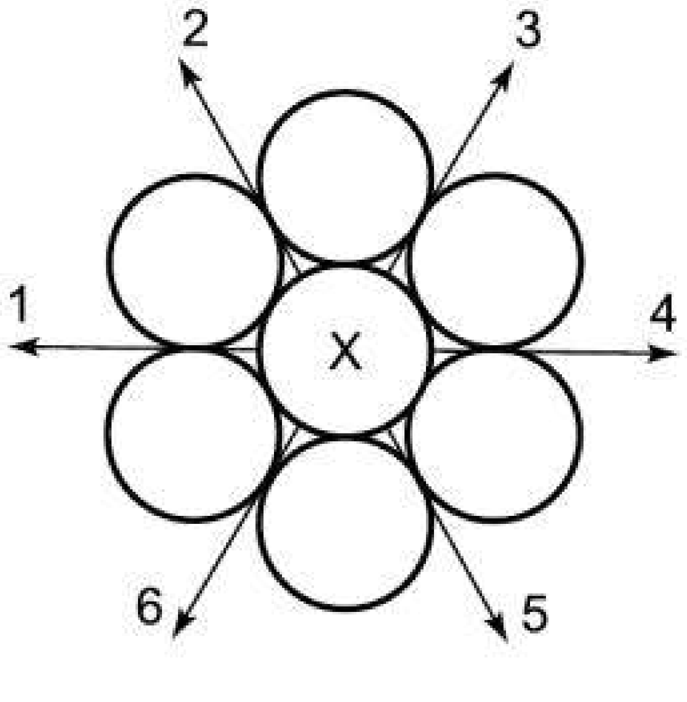
The smallest but complete unit in the space lattice which when repeated over and over again in the three dimensions generates the crystal of the given substance.

Types of Unit Cells

Unit cell are basically of two types: These are primitive and non-primitive.

Primitive Unit Cells

A unit cell is called primitive unit cell if it has particles (or points) only at the corners. It is also called simple unit cell.



(a)

Fig. 8.21 Closed packed structure
(a) Hexagonal closed packing
(b) Cubical closed packing

5 then the sites marked 2, 4 and 6 are left unoccupied. Let us denote the second layers of spheres by B.

The second layer again has two types of vacant sites. Around any atom in the second layer, one set of vacant sites lies just above the vacant sites 2, 4 and 6 of the first layer and the other set lies above the centres of the spheres of the first layer. Thus after the second layer is complete, there are two different ways of placing the spheres in the third layer. If the spheres in the third layer are placed in the vacant sites which are above the centres of the spheres of the first layer, then the third layer repeats the arrangement of the first layer and we have only two types of layers, viz, AB AB……. etc. This is called a hexagonal closets packing. hcp (fig 8.20 (a)). On the other hand if the spheres are placed in the vacant sites above 2, 4 and 6, a new arrangement (c) of the spheres in produced, (fig 8.20 (b)). The entire arrangement is now of the type ABC ABC …… etc, and is reffered to as a cubical closest packing ccp or face centered cubical closest packing, fcc.

The number of nearest neighbours (Known as the co-ordination number) in each arrangement is twelve; six in the same layer three in the layer above and three in the layer below it.

In the fcc structure, there are two types of vacant sites or holes: tetrahedral and octahedral. A tetrahedral hole is surrounded by four spheres while an octahedral hole is the empty space surrounded by six spheres. These vacant sites can accommodate other smaller atoms or molecules giving rise to a variety of different structures.

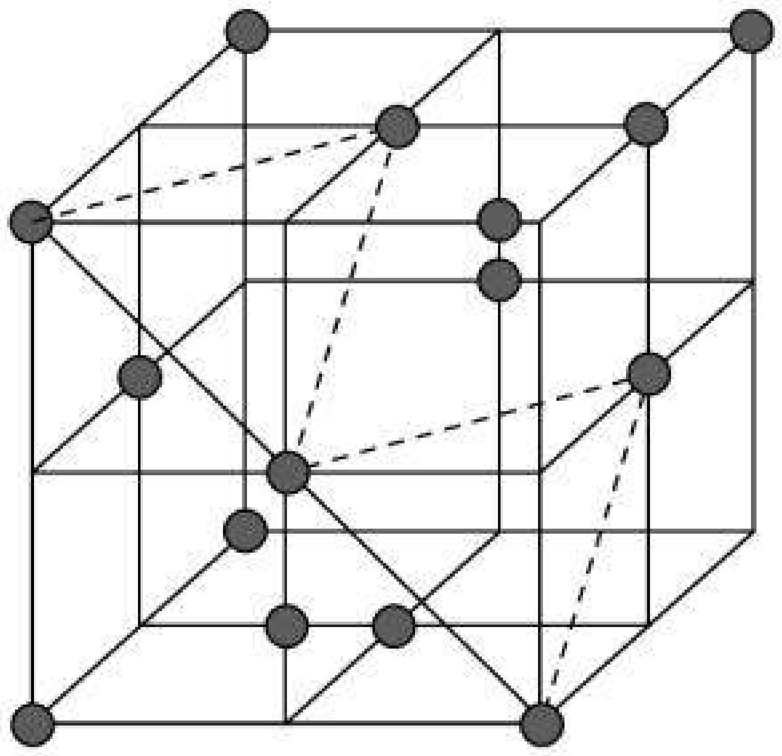


Fig. 8.22 (a) Tetrahedral holes in an fcc structure

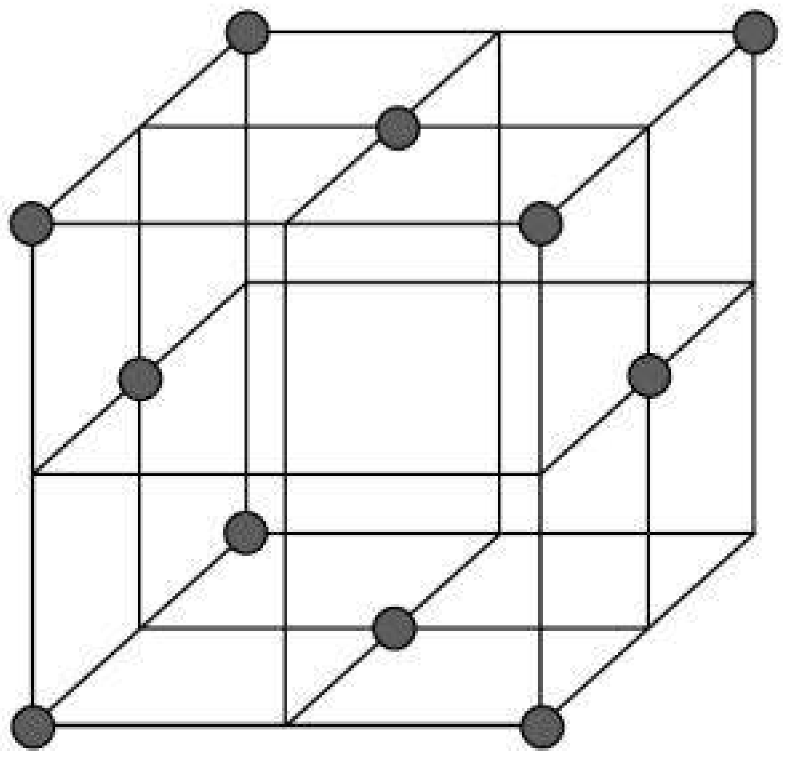


Fig. 8.23 (b) Octahedral holes in an fcc structure

In an Fcc Structure, there are eight tetrahedral holes per unit cell as shown in fig (a). The number of octahedral holes in the unit cell of the fcc structure is four as can be deduced from the following consideration. In fig (b) each (x) mark represent a vacant site and there are tewelve such vacant sites at the edges of unit cubic lattice. The vacancy at an edge is common to four unit cells and hence the number of such vacant sites per unit cell is $\frac{12}{4}=3$. In addition to these vacancies there is one octahedral hole at the centre of the unit cell. Thus the total number of octahedral holes per unit cell is four.

In fig. 8.24 Body centered cubical closed-packed structure. Another less packed arrangement of sphere is the body centered cubic arrangement as shown fig. above in which each sphere has eight nearest neighbours; four in the same plane, two above and two

Hence No. of atom γ in a unit cell

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

and No. of atoms γ in the unit cell

$$= 8 \times \frac{2}{3} = \frac{16}{3}$$

Thus formula of compound

$$= x_{16/3}\, y_4 \text{ or } x_4\, y_3$$

➤ Example 8.6

Copper Crystallises in face centred cubic close packed arrangement having unit cell length of 361 pm. What is the radius of copper atom?

[AIEEE, 2009]

➤ Solution

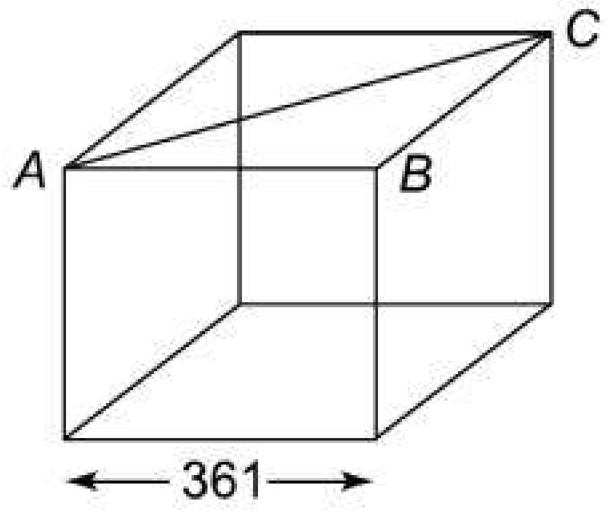


Fig. 8.29

$$AC = a\sqrt{2} \text{ (in f.c.c.)}$$

In face diagonal,

$$4r_{cu} = a\sqrt{2}$$

$$\therefore \quad r_{cu} = \frac{a\sqrt{2}}{4} = \frac{361\sqrt{2}}{4} = 127 \text{ pm.}$$

➤ Example 8.7

The edge length of a face centred cubic cell of an ionic substance is 508 pm. If the radius of cation is 110 pm, calculate the radius of anion?

[AIEEE, 2010]

➤ Solution

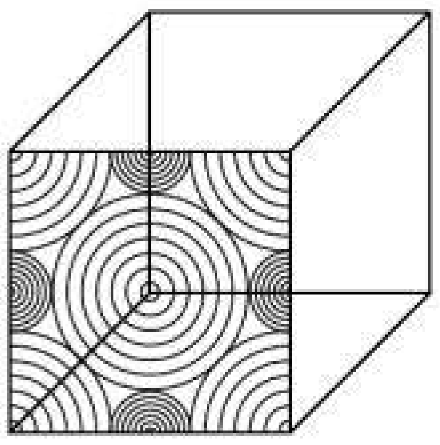


Fig. 8.30

Its structure like NaCl

Thus 2 r_{cation} + 2 r_{anion} = edge length

$$\Rightarrow \quad r_{cation} + r_{anion} = \frac{\text{Edge Length}}{2}$$

$$110 + r_{anion} = \frac{508}{2}$$

$$\Rightarrow \quad r_{anion} = 254 - 110 = 144 \text{ pm.}$$

➤ Example 8.8

A metal crystallises into two cubic phases face centred cubic and body centred cubic whose unit lengths are 3.5 and 3.0 A^0 respectively. Calculate the ratio of densities of fce. and b.c.c.?

[IIT, 1999]

➤ Solution

$$\text{Density } (d) = \frac{Z \times M}{a^3 \times N_A}$$

$$\therefore \quad \frac{d_{fcc}}{d_{bcc}} = \frac{Z_{fcc} \times a^3{}_{bcc}}{Z_{bcc} \times a^3{}_{fcc}}$$

$$= \frac{4 \times (3.0 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259$$

➤ Example 8.9

In face centred crystal lattice edge length of the unit cell is 400 pm. Find the diameter of the greatest sphere which can be fitted into the interstial site without distertion of lattice **[IIT, 2005]**

➤ Solution

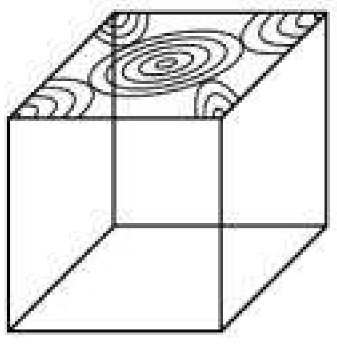


Fig. 8.31

In f.c.c. structure

$$a\sqrt{2} = 4r$$

$$\Rightarrow \quad r = \frac{a\sqrt{2}}{4} = \frac{400\sqrt{2}}{4}$$

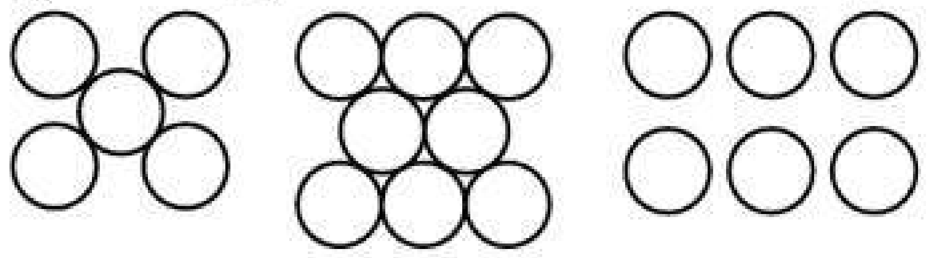
$$= 141.4 \text{ pm}$$

Answer the following questions

1. The number of atoms in the HCP unit cell is
   (a) 4 (b) 6
   (c) 12 (d) 17
2. The volume of this HCP unit cell is
   (a) $24\sqrt{2}\,r^3$ (b) $16\sqrt{2}\,r^3$
   (c) $12\sqrt{2}\,r^3$ (d) $64/3\,\sqrt{3}\,r^3$
3. The empty space in this HCP unit cell is
   (a) 74% (b) 47.6%
   (c) 32% (d) 26%

(D) Subjective Numerical Integer Type

1. The density of mercury is 13.6 gm/ml. Calculate approximately the diameter of an atom of mercury assuming that each atom is occupying a cube of edge length equal to the diameter of the mercury atom. **[IIT, 1983]**
2. Sodium metal crystallises in body centred cubic lattice with cell edge '*a*' = 4.29 Å. What is the radius of sodium atom? **[IIT, 1994]**
3. A metallic element crystallises into a lattice containing a sequence of layer of ABABAB … any packing of sphere leaves out void in the lattice. What percentage by volume of this lattice in emply space? **[IIT, 1996]**
4. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of NaCl? **[IIT, 1997]**
5. 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 gm/cm^3. **[IIT, 1997]**
6. A metal crystallizes into two cubic phases face centred cubic (FCC) and BCC. Whose unit cell length are 3.5 and 3.0 and 3.0 Å respectively. Calculate the ratio of densities of F.C.C. and B.C.C. **[IIT, 1999]**
7. The figure given below show the location of atoms in three crystallographic planes in F.C.C. lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram. **[IIT, 2000]**



8. You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangement of marble in a plane so that maximum no. of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area? **[IIT, 2003]**
9. A compound AB has rock salt type structure. The formula wt. of AB is 6.023 γ amu. And the closed A – B distance is $\gamma^{1/3}$ nm. Where γ is an arbitrary number
   (a) Find the density of lattice
   (b) If density of lattice is found to be 20 kg m^{-3} then predict the type of defect? **[IIT, 2004]**
10. In f.c.c. crystal lattice, edge length is 400 pm. Find the diameter of greatest sphere which can be fit into interstitial void without distortion of lattice **[IIT, 2005]**
11. The edge length of unit cell of a metal having molecular weight 75 gm/mole is 5 Å, which crystallizes in cubic lattice. If the density is 2 gm cc then find the radius of metal atom (NA = 6×10^{23}) Give the answer in pm. **[IIT, 2006]**
12. Silver (at. Mass- 108 gm mole^{-1}) has a density of 10.5 gm/ cm^3. The number of Ag atoms on a surface of area 10^{-12} m^2 can be expressed in Scientific notation as $y \times 10^x$. The value of x is. **[IIT, 2010]**

ANSWER KEY - IIT WINDOW II

1. (a)	2. (b)	3. (c)	4. (c)	5. (d)
6. (a)	7. (b)	8. (d)	9. (c)	10. (b)
11. (b)	12. (b)	13. (d)	14. (b)	15. (d)
16. (b)	17. (a)	18. (c)	19. (a)	20. (d)
21. (b)	22. (a)	23. (d)	24. (c)	25. (c)
26. (d)	27. (b)	28. (a)	29. (d)	30. (c)
31. (b)	32. (b)	33. (b)	34. (c)	35. (a)
36. (a)	37. (a)	38. (d)	39. (a)	40. (c)
41. (a)	42. (c)	43. (c)	44. (d)	45. (d)
46. (a)	47. (b)	48. (b)	49. (b)	50. (c)

CHAPTER 9

Surface Chemistry

Introduction

The branch of chemistry which deals with the nature of surface and changes occuring on the surface is called Surface Chemistry.

Adsorption

The phenomenon of higher concentration of molecular species (gases or liquids) on the surface of a solid than in the bulk is called adsorption eg.

(i) If silica gel is placed in a vessel containing water vapour, the latter are adsorbed on the former. On the other hand, if anhydrous $CaCl_2$ is kept in place of silica gel, absorption take place as the water vapours are uniformly distributed in $CaCl_2$ to form hydrated calcium chloride ($CaCl_2.2H_2O$)

(ii) Ammonia gas placed in contact with charcoal gets adsorbed on the charcoal whereas ammonia gas placed in contact with water gets absorbed into water, giving NH_4OH solution of uniform concentration.

Adsorbent and adsorbate

The solid substance on the surface of which adsorption occur is known as adsorbent. The substances that get adsorbed on the solid surface due to intermolecular attraction are called **adsorbate**.

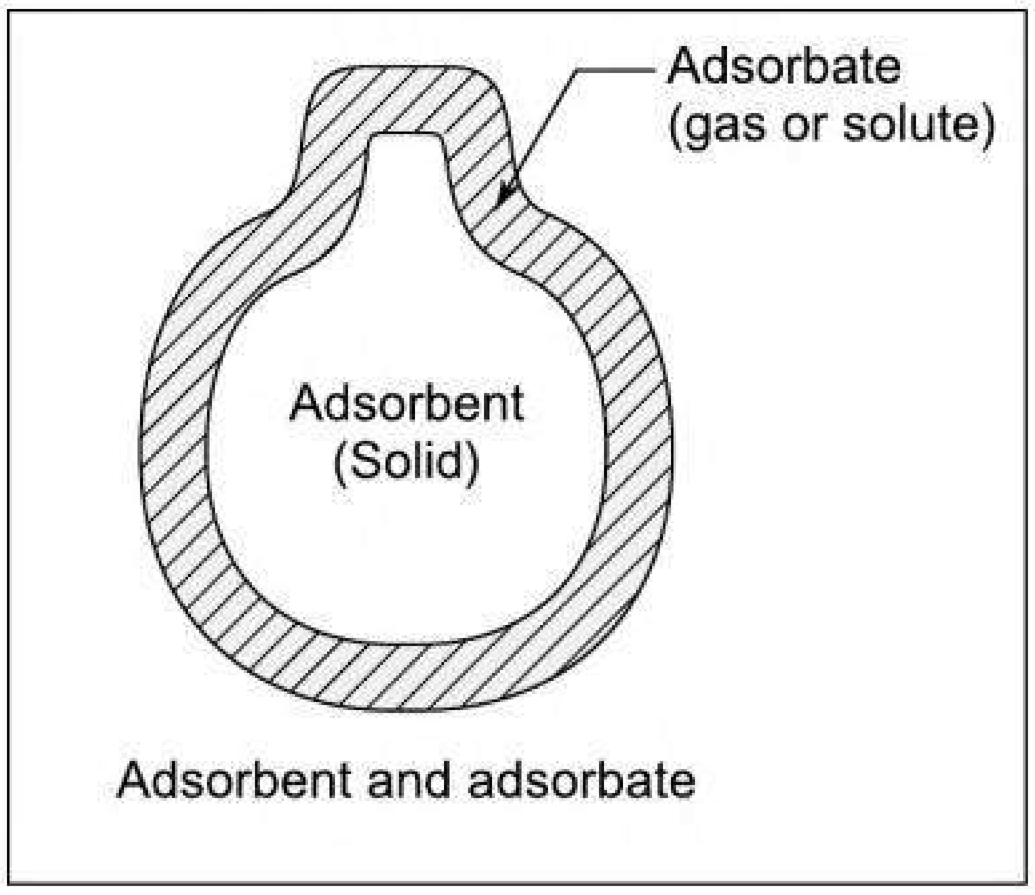


Fig 9.1

Desorption

The process of removal of an adsorbent from the surface on which it is adsorbed is called desorption. It is the reverse of adsorption and can be brought by heating or by reducing the pressure. The adsorbent may be a solid or a liquid and the adsorbate may be a gas or a solute in some solution.

Difference between Adsorption and Absorption

	Absorption	Adsorption
1.	It is the phenomenon in which the particles of gas or liquid get uniformly distributed throughout the body of the solid	It is the phenomenon of higher concentration of particles of gas or liquid on the surface than in the bulk of the solid.
2.	The concentration is the same throughout the material. Therefore, it is a bulk phenomenon.	The concentration on the surface of the adsorbent is different from than in the bulk. Therefore, it is a surface phenomenon.
3.	Absorption occurs at uniform rate.	Adsorption is rapid in the begining and its rate slowly decreases.

Sorption

When both absorption and adsorption occur together and are not distinguishable, the substance gets uniformly distributed into the bulk of the solid but at the same time its concentration is higher at the surface than in the bulk, the phenomenon is called sorption eg. Dyes get adsorbed as well as absorbed in the cotton fibers.

Positive and Negative Adsorption

Positive adsorption When the concentration of adsorbate is more on the surface of adsorbent relative to its concentration in the bulk, it is called positive adsorption.

Negative adsorption When the concentration of the adsorbate is less on the surface relative to its concentration in the bulk, it is called negative adsorption.

Factors affective adsorption of gases by solids

Almost all solids adsorb gases to some extent. The extent of adsorption of a gas on a solid surface depends on the following factors.

1. Nature of the gas (or adsorbate) The adsorption depends upon the nature of the gas adsorbed. The physical adsorption is non-specific in nature and therefore, every gas gets adsorbed on th surface of any solid to a lesser or a greater extent. However, under given condition of temperature and pressure, the easily liquifiable gases such as CO_2, HCl, NH_3, Cl_2 ete are adsorbed more than the permanent gases such as H_2, N_2 and O_2

The higher the critical temperature, the more easily a gas is liquified and hence more readily it will be adsorbed

Gas	SO_2	NH_3	CO_2	CH_4	CO	N_2	H_2
Critical temperature	430	406	304	190	134	126	33
Amt. adsorbed (in ml)	380	180	48	16.2	9.3	8.0	4.5

Ease of liquification decrease from SO_2 to H_2. However, the chemical adsorption is highly specific in nature and a gas gets adsorbed on the solid only if it forms chemical bonds.

2. Nature of adsorbent The extent of adsorption of a gas depends upon the nature of adsorbent.

3. Specific area of the absorbent The specific area of the adsorbent is the surface area available adsorption per gram of the adsorbent. The large the surface area of the solid, the greater would be its adsorbing capacity. Therefore, the porous and finely divided forms of adsorbents adsorb large quantities of adsorbate. However the pores of the adsorbent should be large enough to allow the gas molecules to enter them.

4. Effect of pressure The extent adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas.

5. Effect of temperature : Adsorption isobar Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic and therefore, extent of adsorption decreases with increasing temperature at constant pressure. However as expected for endothermic adsorption processes, adsorption increase with increase in temperature.

6. Activation of adsorbent Activation of adsorbent means the increasing of the adsorbing power of the adsorbent. This can be done by the following methods

(i) Metallic adsorbents are activated by mechanical rubbing or by subjecting it to some chemical reactions.

(ii) To increase the adsorbing power of adsorbent, they are sub-divided into smaller pieces. As a

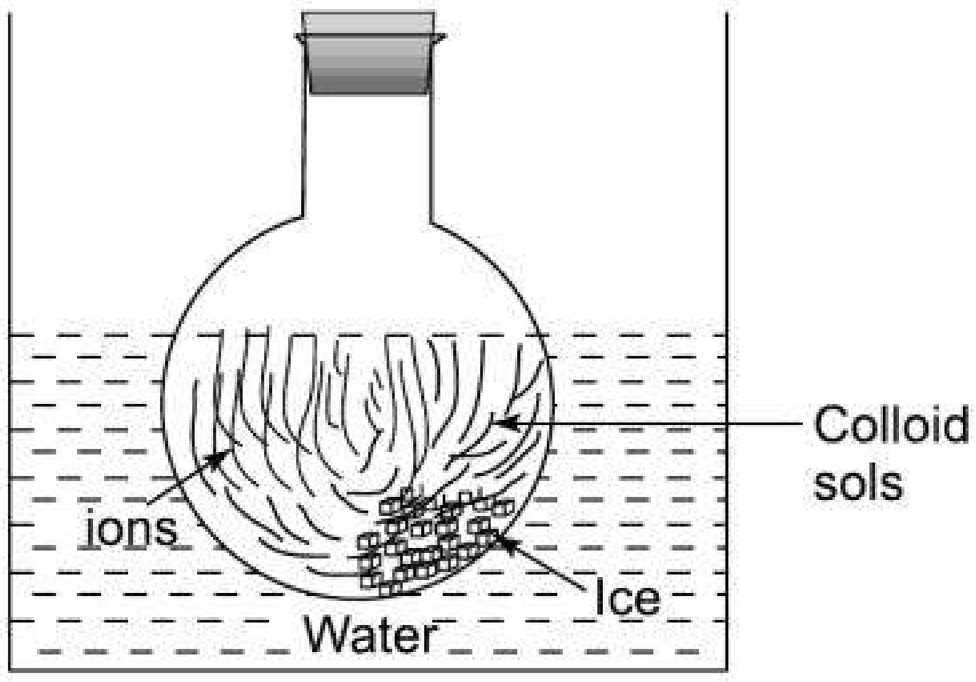


Fig 9.8 (a)

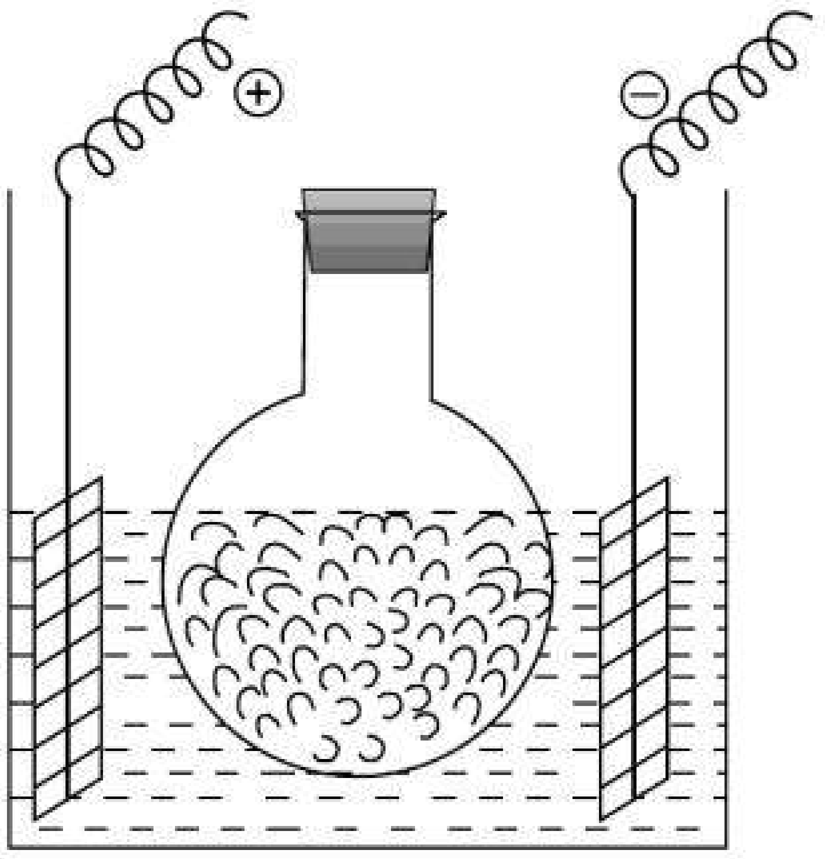


Fig 9.8 (b)

(ii) Electrodialysis

When the rate of dialysis can be increased by using electrodes immersed in water in called electrodialysis fig 9.8 (b)

(iii) Ultra filtration

The process of removing impurities by passing through graded filter paper (such as whatmann no-41, 42) is called ultrafilteration

(iv) Ultra centrifiguration

The process in which colloid or solutions settled down on centrifugation while impurities remains down and separated out.

Properties of colloidal solution

(A) Physical Properties

(i) Nature— Colloids or solutions are heterogeneous in nature.

(ii) Filterability — Passed through ordinary filter paper but filtered through whatmann no – 41,42 filter paper.

(iii) Settlement — Colloid do not settle under gravity.

(iv) Particle size — The particle size in between 10A° to 2000A°.

(v) Diffusibility — They have comparatively low diffusibility.

(vi) Viscosity — Colloids have almost same viscosity to that of pure solvent.

(vii) Surface tension — Colloids or solutions have almost same surface tension.

(B) Electrical properties

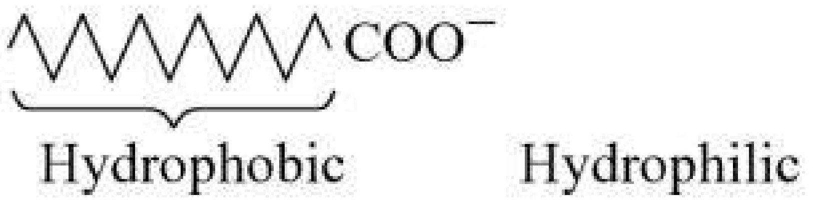
(i) Solutions particles are generally charged and their stability depend on magnitude of charge. They have either + ve or – ve charges.

+ vely charged colloids – $Fe(OH)_3$

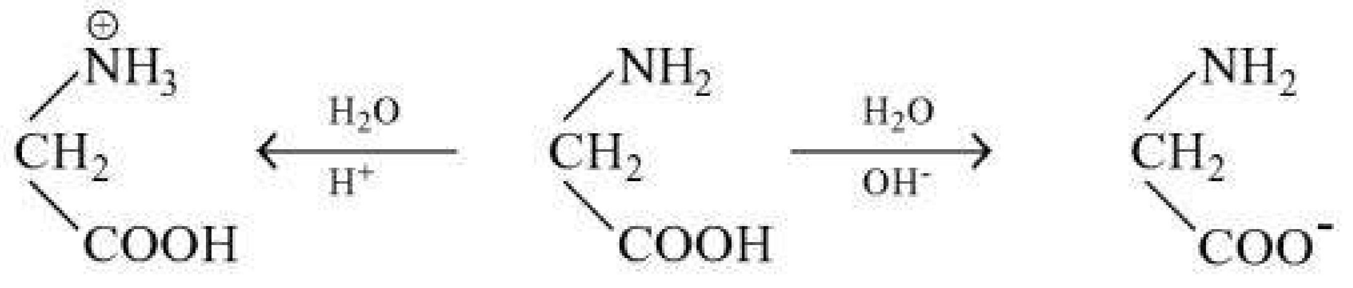
– vely charged colloids smoke, blood, metals.

The charge on sols or colloids arises due to friction between phase & medium, due to electron capture on cavity of electrons.

$$R\,COONa \longrightarrow R\,COO^- + Na^+$$



Proteins are made up of condensation of α amino acid in which +ve and –ve charge developed on respective ions.



(ii) Preferential ion adsorption theory According to this theory solution particles possess the tendency for adsorption of common ion present in solution and there by acquiring charges.

Addition of KF drop-by-drop to dilute cold solution of $AgNO_3$ given rise to +ve sol of AgI. Since AgI particles adsorb Ag^+ ions present in excess in solution.

$$KI + AgNO_3 \rightarrow AgI + KNO_3$$

$$AgI + Ag^+ \ldots\ldots \underset{\text{medium}}{AgI} \vdots \underset{\text{positive solution}}{Ag^+}$$

(b) Concentration at which micelle formation starts
(c) Concentration of electrolyte added to destroy the micelles
(d) Concentration of micelles at room temperature

44. In Brownian movement or motion the paths of the particles are:
(a) Linear (b) Zig-Zag
(c) Uncertain (d) Curved

45. Blood may be purified by:
(a) Dialysis (b) Electro osmosis
(c) Coagulation (d) Filtration

46. Gold number was given by:
(a) Ostwald (b) Zsigmondy
(c) William and Chang (d) Langmuir

47. The blue colour of water in the sea is due to
(a) absorption of other colours except blue by water molecules
(b) scattering of blue light by water molecules
(c) refraction of blue light by impurities in sea water
(d) reflection of blue sky by sea water

48. Which is a natural colloid?
(a) Sodium chloride (b) Urea
(c) Cane sugar (d) Blood

49. An aerosol is a colloidal system of
(a) a liquid dispersed in a solid
(b) a liquid dispersed in a gas
(c) a gas dispersed in a liquid
(d) a solid dispersed in a gas

50. Which of the following statements is not true for a lyophobic solution ?
(a) It can be easily solvated
(b) It carries charges
(c) The coagulation of this solution is irreversible in nature
(d) It is less stable in a solvent

51. Which of the following statements is not true for a lyophilic solution?
(a) It can be easily solvated
(b) It carries no charge
(c) The coagulation of this solution is reversible in nature
(d) It is not very stable in a solvent

52. Which of the following colloidal system represents a gel?
(a) Solid in liquid (b) Solid in gas
(c) Liquid in solid (d) Liquid in gas

53. Which of the following colloidal system represents a solution?
(a) Solid in liquid (b) Solid in gas
(c) Liquid in solid (d) Liquid in gas

54. Which of the following represents a multimolecular colloidal particles?
(a) Sol of sulphur (b) Starch
(c) Soap (d) Proteins

55. Which of the following represents a maromolecular colloidal particles?
(a) Sol of gold
(b) Cellulose
(c) Soap
(d) Synthetic detergent

56. Which of the following represents an associated colloids?
(a) Sol of gold (b) Starch
(c) Proteins (d) Soaps

57. Which of the following ions is most effective in the coagulation of a ferric hydroxide sol?
(a) Cl^- (b) Br^-
(c) NO_3^- (d) SO_4^{2-}

58. A colloidal solution can be purified following the method of
(a) dialysis
(b) peptization
(c) mechanical dispersion
(d) oxidation

59. Which of the following sols is negatively charged?
(a) Arsenius sulphide
(b) Aluminium hydroxide
(c) Ferric hydroxide
(d) Silver iodide in $AgNO_3$ solution

60. Which of the following sols is positively charged?
(a) Silver iodide in potassium iodide solution
(b) Ferric hydroxide
(c) Gold
(d) Silver

61. Which of the following cations will have maximum flocculation value for the arsenious sulphide sol?
(a) Na^+ (b) Mg^{2+}
(c) Ca^{2+} (d) Al^{3+}

IIT WINDOW–IV

Matching Type

1.

	Column I		**Column II**
A.	Emulsifier	P.	Colloidal solution of graphite
B.	Colloidal Electrolyte	Q.	Detergent
C.	Oil dag	R.	Cellophane
D.	Xerogel	S.	Dextrix

2.

	Column I		**Column II**
A.	Tyndal effect	P.	Scattering of light
B.	Dialysis	Q.	Purification of colloidal sol.
C.	Peptisation	R.	Addition of electrolyte
D.	Coagulation	S.	Precipitation of colloidal sol

3.

	Column I		**Column II**
A.	Physiosorption	P.	High heat of activation
B.	Chemisorption	Q.	Multimolecular
C.	Activated adsorption	R.	High temp is required
D.	Desorption	S.	Low temp is required

4.

	Column I		**Column II**
A.	Tyndal effect	P.	Avogadro's number
B.	Brownian movement	Q.	Sky is blue
C.	Electrophoresis	R.	Coagulation of colloidal
D.	Hardy Sulze Rules	S.	Charge on colloidal solution

5.

	Column I		**Column II**
A.	Gold sol	P.	Bredig arc method
B.	Purification of colloidal solution	Q.	– vely charged
C.	As_2S_3 Sol	R.	ultracentrifiguration
D.	Zeta potential	S.	Electro kinetic potential
		T.	Double decomposits react

6.

	Column I		**Column II**
A.	Suspension	P.	Setted under gravity
B.	Colloid	Q.	Show Tyndal effect
C.	True solution	R.	ultra filtration possible
D.	Saturated solution	S.	Show Brownian movements
		T.	Diffuse rapidly

7.

	Column I		**Column II**
A.	Aerosol	P.	Chease
B.	Foam	Q.	Milk
C.	Emulsion	R.	Whipped cream
D.	Gel	S.	Smoke
		T.	Cloud

8.

	Column I		**Column II**
A.	Surface tension decreases	P.	Lyophilic sol
B.	Viscosity increases	Q.	Lyophilic sol
C.	Viscosity decreases	R.	Associated colloid
D.	Surface tension decreases	S.	Macromolecular colloid

CHAPTER 10

Chemical Equilibrium

Chemical reactions are of different types, some reactions occur very fast, some occur comparatively slow, some reactions are reversible, some are irreversible and so on. In this chapter we are going to study mainly about reversible reactions. i,e, the reactions which proceed from both the directions.

Some Irreversible Reactions

(i) Reactions of Metal with Acid to Liberate H_2 gas

$Ca + HCl \rightarrow CaCl_2 + H_2\uparrow$

$Zn + HNO_3 \rightarrow Zn(NO_3)_2 + H_2\uparrow$

(ii) Reaction of amphotexic metal with alkali

$Al + NaOH \rightarrow NaAlO_2 + H_2\uparrow$

$Zn + NaOH \rightarrow Na_2ZnO_2 + H_2\uparrow$

$Pb + NaOH \rightarrow Na_2PbO_2 + H_2\uparrow$

(iii) Neutralisation reactions of strong acid and strong base

$NaOH + HCl \rightarrow NaCl + H_2O$

$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$

(iv) Precipitation Reactions

$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl\downarrow + NaNO_3(aq)$

$Pb(NO_3)_2(aq) + KI(aq) \rightarrow PbI_2\downarrow + KNO_3(aq)$

(v) Combustion Reactions

$$CH_4 + 2O_2 \xrightarrow{\Delta} CO_2 + 2H_2O$$

$$CH \equiv CH + \frac{5}{2}O_2 \rightarrow 2CO_2 + H_2O$$

(vi) Redox Reactions

$SnCl_2 + FeCl_3 \rightarrow SnCl_4 + FeCl_2$

$KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + H_2O$

(vii) Decomposition reaction in which all the components are solid.

$$\underset{(s)}{Fe_3O_4(s)} \xrightarrow{\Delta} \underset{(s)}{Fe_2O_3} + \underset{(s)}{FeO}$$

Some Reversible Reactions

Chemical reaction which takes place in both the directions under similar conditions are called reversible reaction. These reactions never go on completion. If the reaction is gaseous it may be reversible if occurs in a close container.

(i) Dissociation Reaction

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$$

(ii) Reaction of acid and base in which at least one component is weak

$NaOH + CH_3COOH \rightleftharpoons CH_3COONa + H_2O$

$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$

$NH_4OH + CH_3COOH \rightleftharpoons CH_3COONH_4 + H_2O$

(iii) Gaseous Reaction occurring in a closed container

$$= \frac{\left(\frac{2x \cdot P_{\text{Total}}}{a+b-2x}\right)^2}{\left(\frac{a-x}{a+b-2x}.P_{\text{Total}}\right)\left(\frac{b-3x}{a+b-2x}.P_{\text{Total}}\right)^3}$$

$$= \frac{2x\cdot(a+b-2x)^2}{(a-x)(b-3x)^3\cdot P_{\text{Total}}{}^2}$$

Le-Chatelier's Principle

According to this principle, if any external factor such as temperature, pressure or concentration is imposed on a reversible chemical reaction which is at equilibrium, then the equilibrium shift in the direction in which the effect of the imposed factors in nullified or reduced to zero.

e.g. formation of NH_3 is represented as,

$$N_2(g) + 3H_2(g) \overset{\text{Fe}}{\rightleftharpoons} 2NH_3(g),\ \Delta H = -22.4\ \text{K}$$

(a) Effect of temperature

The formation of NH_3 is exothermic in nature, thus if temperature is increased backward reaction starts more rapidly and hence more and more ammonia dissociates into N_2 and H_2 Hence low temperature is favourable for the formation of NH_3.

(b) Effect of pressure

If all the components are gaseous, by increasing pressure, volume is reduced, it means the reaction proceed in the direction so that no of gaseous mole is less. It is possible when more and more ammonia is formed. Thus for the formation of NH_3, favourable condition is high pressure.

(c) Effect of concentration

By increasing concentration of N_2 and H_2, more and more ammonia is formed, and if the concentration of NH_3 is increased backward reaction starts.

Favourable condition for formation of NH_3

Temperature ⇒ 450°C (optimum temperature for Haber's process)
Pressure → 20 – 100 atm.
Catalyst → Iron
Promoter → Mo.

Degree of dissociation from density measurements

Degree of dissociation is defined as the fraction of one molecules dissociated, let us consider a reaction

	$(A)n \rightleftharpoons$	nA
Initially	c	0
At equilibrium	$c(1-\alpha)$	$nc\alpha$

Total mole at equilibrium = $c(1-\alpha) + nc\alpha$

let 'd' be the observed vapour density at a particular temperature and 'D' be the vapour density initially.

Thus $\quad D\ \alpha\ \frac{1}{\text{c.n.}}$ ……(I)

and $d\ \alpha\ \frac{1}{[C(1-\alpha)+nc\alpha]\cdot v}$ ……(II)

From (I) and II

$$\frac{D}{d} = 1 + \alpha(n-1)$$

$$\Rightarrow \quad \alpha = \frac{D-d}{d(n-1)}$$

or $\quad \alpha = \frac{M-m}{m(n-1)}$

where $\quad$ M = Mol. Mass initially
m = observed mol. mass.

Le-chatelier's principle and physical equilibrium

Consider the physical equilibrium

Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

Effect of pressure on melting

when ice melts its volume decreases and hence in this type of system increasing pressure will reduce the melting point of the system. So high pressure will favour the melting of ice.

Effect of pressure on boiling point

By increasing pressure on the equilibrium liquid change into vapour, vapour condense and hence lower the vapour pressure. Thus boiling point of the solution (or liquid) increases on increasing pressure.

➤ Solution

$$N_2 + O_2 \rightleftharpoons 2NO$$

Initially	a	$(100 - a)$	0
At equilibrium	$a-x$	$(100 - a - x)$	$2x$

Mole % of NO. at equilibrium

$$= \frac{2x}{a-x+100-a-x+2x} = 1.8$$

$\Rightarrow x = 0.9$

$\Rightarrow$ Mole of $N_2 = a - 0.9$

Mole of $O_2 = 100 - a - 0.9 = 99.1 - 9$

Mole of NO. = 1.8

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = \frac{(1.8/V)^2}{\left(\frac{a-0.9}{V}\right)\left(\frac{99.1-a}{V}\right)}$$

$$2.1 \times 10^{-3} = \frac{(1.8)^2}{(a-0.9)(99.1-a)} \Rightarrow a = 79.47\ \%$$

$\therefore X_{N_2} = 0.7946$ and $X_{O_2} = 0.2054$ **Ans.**

➤ Example 10.15

A vessel at 100K contains CO_2 with a pressure of 0.5 atm, some of the CO_2 is converted into CO an addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.8 atm. **[Roorkee, 1993]**

➤ Solution

The reaction given is

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Initially	0.5	0	0
At equilibrium	0.5 – p	0	2p

According to question $0.5 - p + 2p = 0.8$

$\Rightarrow P = 0.3$ atm,

$P^1_{CO_2}$ at eqlm. $= 0.5 - 0.3 = 0.2$ atm

$P^1_{CO_2}$ at eqlm $= 2p = 2 \times 0.3 = 0.6$ atm

$$\therefore Kp = \frac{P_{CO^2}}{P_{CO_2}} = \frac{(0.6)^2}{0.2} = 1.8 \text{ atm}$$

➤ Example 10.16

Solid ammonium carbamate dissociate as

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

The total pressure at equilibrium is found to be 0.225 atm. Calculate Kp ?

➤ Solution

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

Initially	1	0	0
At Equilibrium	$1-x$	$2x$	x

Given $2x + x = 0.225$

$$\Rightarrow \quad x = \frac{0.225}{3} = 0.075$$

$$\therefore P_{NH_3} = \frac{0.150}{0.225} \cdot P_T$$

$$P_{CO_2} = \frac{0.075}{0.225} \cdot P_T$$

$$\therefore Kp = P_{NH_3}^{\ 2} \cdot P_{Cl_2}$$

$$= \left(\frac{0.150}{0.225} \times 0.225\right)^2 \times \frac{0.075}{0.225} \times 0.225$$

$= 1.6875 \times 10^{-3}$ atm^3. **Ans.**

➤ Example 10.17

7 gm. sample of IBr in 0.2 litre flask is heated to 227°C to decompose as $2IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$. If partial pressure of $Br_2(g)$ is 3 atm. Calculate Kc and K_P.

➤ Solution

$$2IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$$

Initially	$\frac{7}{207}$	0	0
At equilibrium	$(0.0338 - x)$	$x/2$	$x/2$

Total mole at equilibrium $= 0.0338 - x + 0.5x + 0.5x$
$= 0.0338$

$$P_{Br_2} = \frac{0.5x}{0.0338} \times P_T$$

According to question, $\frac{0.5x}{0.0338} P_T = 3$ atm (1)

From Gas law, PV, = nRT

$P \times 0.2 = 0.338 \times 0.082 \times 500$

$\Rightarrow \quad P = 6.929$ atm

From (1)

of 2:1 initially. The total P at equilibrium is found to be 1 atm. If the moles of NOCl are $\frac{1}{4}$ of Cl_2 at equilibrium, Kp for the reaction is

(a) $\frac{26}{512}$ (b) $\frac{13}{256}$
(c) $\frac{13}{256}$ (d) $\frac{9}{512}$

48. The equilibrium constant is 3.8×10^{-7} and $P^H = 6$ for the reaction $CO_2 + 2H_2O \rightleftharpoons HCO^-_3 + H_3O^+$. The ratio of $[HCO_3^-]/[CO_2]$ is

(a) 0.38 (b) 3.8
(c) 3.8×10^{-18} (d) 13.4

49. XY_2 dissociates as $XY_2(g) \rightleftharpoons XY(g) + Y(g)$. Intial 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 Kp is

(a) 500 mm Hg (b) 100 mm Hg
(c) 200 mm Hg (d) 400 mm Hg

50. Consider the reaction $CaCO_3(s) \rightleftharpoons CaO(S) + CO_2(g)$ in a closed container at equilibrium. What would be the effect of addition of $CaCO_3$ on the equilibrium pressure of CO_2

(a) Increase
(b) Decrease
(c) Remains unaffected
(d) Data is not sufficient to predict

IIT WINDOW–III

➤ M.C.Q. (More than one answer correct)

1. Chemical equilibrium can be seen

(a) By the constancy of concentration temperature and pressure.
(b) By constancy of colour for specific reaction.
(c) By constancy of molarity of each component.
(d) By constancy of Normality of all the components.

2. If α is degree of dissociation of N_2O_4 at equilibrium. Which is/are correct?

(a) No of mole of N_2O_4 remain at equilibrium is $C(1 - \alpha)$. Where C is initial concentration.
(b) α can be given as

$$\alpha = \frac{D - d}{D(n-1)} \text{ where}$$

D=46
d = expt. density

(c) α can be given as

$$\alpha = \frac{d - D}{D(n-1)}$$

(d) No of mole of NO_2 formed at equilibrium is equal to $2C\alpha$

3. What will be the effect of adding catalyst at constant temperature ?

(a) The value of Keq remain constant
(b) ΔH remain constant
(c) K_b and K_f increases to some extent
(d) Keq will change

4. For the phase change reaction in $H_2O(l) \rightleftharpoons H_2O(g)$ the increases in pressure causes.

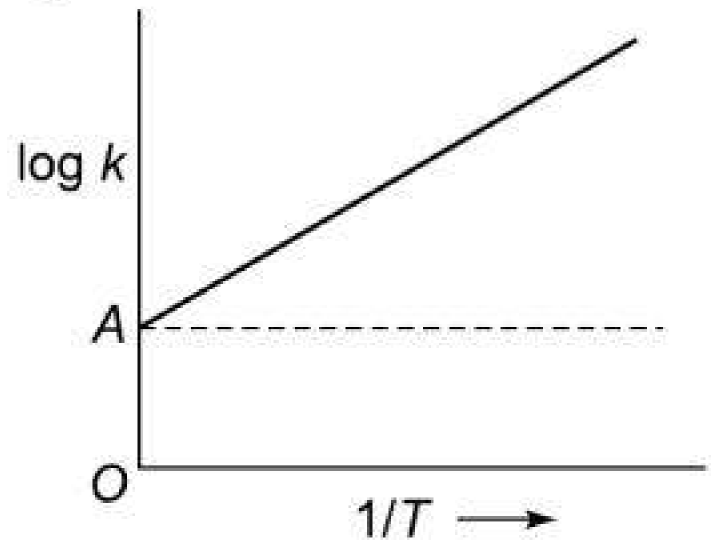
(a) Formation of $H_2O\ (l)$
(b) Formation of $H_2O\ (g)$
(c) Increasing boiling point of $H_2O(l)$
(d) Decreasing boiling point of $H_2O(l)$

5. When any component of a chemical reaction is added at equilibrium.

(a) Keq. remain same.
(b) Keq. changes
(c) Partial pressure of components changes
(d) Partial pressure of components remain same.

6. Plot of graph between log K and $\frac{1}{T}$ is a straight line as shown.

(a) Slope is –Ea/2.303 R
(b) OA is log A.
(c) Frequency facter = antilog OA
(d) Slop is Ea.



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volume 1L and 2L respectively. If Kc for the container A is x. The Kc in the container B is (suppose other factors are the same)

(a) x (b) $x/2$

(c) $2x$ (d) $4x$

Passage -III

For the reaction $aA + bB \rightleftharpoons lL + mM$. The equilibrium constant has the following characteristics

(i) Kc changes by changing stoichiometric coefficient

(ii) Kc is inversed when reaction is reversed.

(iii) Kc remain unchanged if any component is added at equilibrium.

7. If Kc for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 4. The equilibrium constant for the reaction

$$HI \rightleftharpoons \frac{1}{2} H_2 + \frac{1}{2} I_2 \text{ is}$$

(a) 4 (b) $\frac{1}{4}$

(c) $\frac{1}{2}$ (d) 16

8 If NH_3 is added at equilibrium in the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

The equilibrium constant is given by

(a) P^2 (b) 2P

(c) $4P^3$ (d) $2P^3$

Where P is partial pressure of CO_2 at equilibrium.

9. By addition NH_3 at equilibrium in the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

Then Partial pressure

1 NH_2COONH_4 changes

2 NH_3 changes

3 CO_2 changes

4 NH_3 and CO_2 both changes

Passage -IV

Equilibrium is the state of a chemical reaction which is seen by the constancy of concentration temperature, pressure and sometimes colour. It is dynamic in nature and attain from either end of a chemical reaction. At equilibrium the concentration of each and energy component is fixed and non zero.

10 5 mole H_2 and 3 mole I_2 reacts to form HI by $H_2 + I_2 \rightleftharpoons 2HI$, the component which react completely is

(a) H_2 (b) I_2

(b) HI (d) neither H_2 nor I_2

11 For the reation $2NO(g) + O_2 \rightleftharpoons 2NO_2(g)$ the equilibrium is reached at which

(a) Brown colour is completely changes to colourless

(b) Brown colour intensity increases and reached a maximum point.

(c) Brown colour intensity remain constant but not maximum.

(d) Can't say.

12 If equal mole of N_2 and H_2 reacts in a closed container to form NH_3 by a reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$. At equilibrium

(a) Concentration of N_2 and H_2 are equal

(b) Concentration of N_2 and $NH_3$are equal

(c) Concentration of H_2 and $NH_3$are equal

(d) Concentration of any two components may not same.

Passage -V

For the reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ $\Delta H = -180$ KJ mol^{-1}.

13. Which of the following facts does not hold good.

(a) The Pressure changes at constant temperature do not effect the equilibrium constant.

(b) The volume changes at constant temperature don't effect the equilibrium constant.

(c) Dissociation of NO is favoured more at high temperature.

(d) Dissociation of NO is favoured less at high temperature.

14 Kc of the reaction when 2 mole NO. dissociated to the extent of 50% at equilibrium is given by

1 $\frac{1}{4}$ 2. $\frac{1}{8}$

3 4 4. 16

➤ Ranker's Choice

1. For the equilibrium, $SnO_2(s) + 2H_2(g) \rightleftharpoons 2H_2O_{(g)} + Sn(s)$ at 600K, the equilibrium steam-hydrogen mixture was 45% H_2 by volume and at 700 K, the equilibrium steam-hydrogen mixture was 24% H_2 by volume. Calculate the bond enthalpy of O – H bond. Given $\Delta H_f[SnO_2 s] = -65.8$ kcal/mol, $E_{H-H} =$ 104.2 kcal/mol and $E_{0=0}$ 190.2 kcal/mol.

2. An equilibrium mixture of 2 moles each of PCl_5, PCl_3 and Cl_2 is maintained in a vessel of volume 'V' litre at temperature 'T' K and a total pressure of 3 atm. Cl_2 is now added maintaining the same pressure and temperature till the volume is doubled. Determine the number of moles of Cl_2 added.

3. 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 $CaCO_3$ was put into a 10.0L container and heated to 800°C, what percent of the $CaCO_3$ would remain unreacted at equilibrium ?

4. 73.8 g of $SrCO_3$ was placed in a 10 litre container at 127°C. After some time, excess of graphite was added in the container, when equilibrium, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ is then established. The K_p for $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$ is 2 atm at 127°C and the total pressure of gases in the container is 3 atm at 127°C, calculate K_p for the equilibrium,
$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$.

5. NO and Br_2 at initial partial pressures of 98.4 and 41.3 torr respectively, were allowed to react at 300 K. At equilibrium, the total pressure was 110.5 torr. Calculate the value of equilibrium constant (K_p) and the standard free energy change at 300 K for the reaction,

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g).$$

6. Ammonium hydrogen Sulphide dissociates as follows,

$$NH_4HS(s) \rightleftharpoons H_2S(g) + NH_3(g)$$

If solid NH_4HS is placed in an evacuated flask at a certain temperature, it will dissociate unit the total gas pressure is 500 torr. (a) Calculate the value of the equilibrium constant for the dissociation reaction. (b) Additional NH_3 is introduced into the equilibrium mixture without change in temperature until the partial pressure of ammonia is 700 torr. What is the partial pressure of H_2S under these conditions ? What is the total pressure in the flask ?

7. Solid ammonium hydrogen Sulphide dissociates as follows,

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

If solid NH_4HS is placed in an evacuated 5 litre vessel at 27°C, it will dissociate until the total gas pressure is 500 torr.

(a) Calculate the value of the equilibrium constant for the dissociation reaction at 27°C.

(b) Calculate the minimum weight of solid NH_4HS required to establish the equilibrium.

(c) Additional NH_3 is introduced into the equilibrium mixture without change in temperature until the partial pressure of NH_3 at new equilibrium becomes 700 torr. What is the total pressure in the flask ? Also calculate the minimum weight of NH_4HS required to establish equilibrium under this condition ?

8. When gaseous NO and NO_2 are mixed in a vessel of 'V' litre capacity, following equilibria are readily attained at temperature T.K.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)\ ;\ K_{p_1} = 6.8\ \text{atm}^{-1}$$

$$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$$

In an experiment when NO and NO_2 are mixed in the ratio of 1 : 2, the final total pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate

(a) The equilibrium partial pressure of NO; and

(b) K_p for the second equilibrium.

9. A saturated solution of iodine in water contains 0.330g I_2/L. More than this can dissolve in a KI solution because of the following equilibrium,

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

A 0.1 M KI solution actually dissolves 12.5g of iodine/L, most of which is coverted to I_3^-. Assuming that the concentration of I_2 in all saturated solution is the same, calculate the

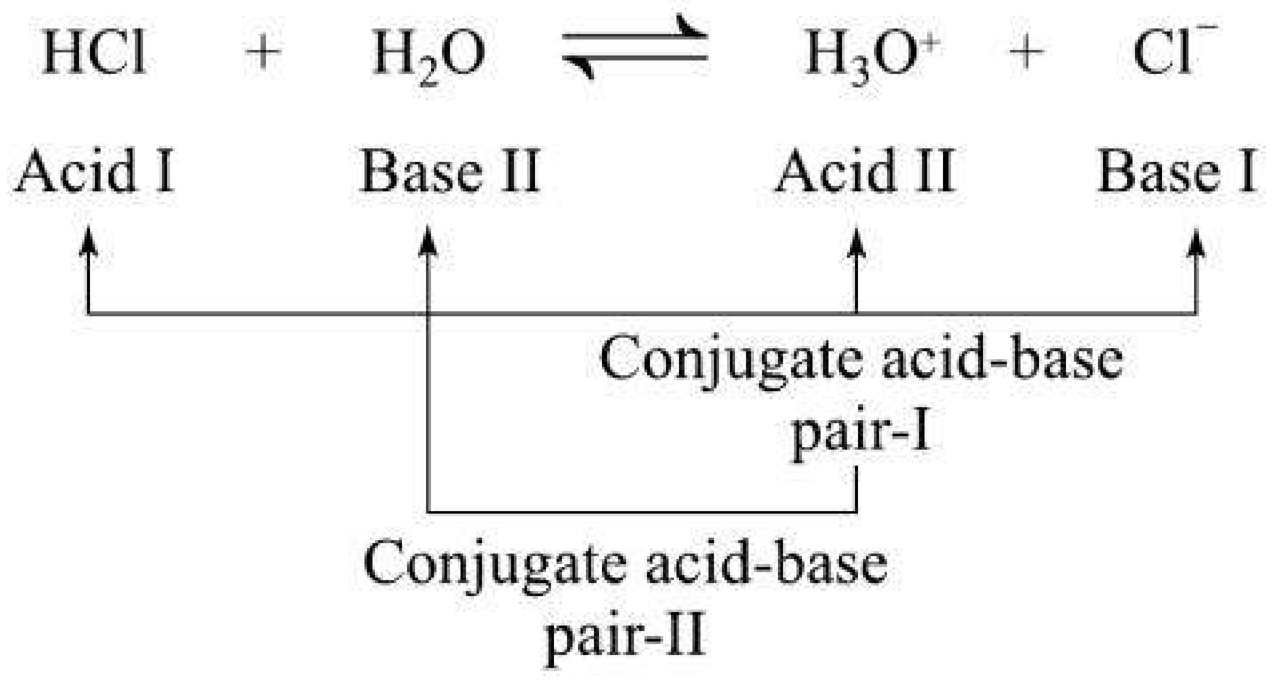
$$\text{bases}\begin{cases} NH_3 + H^+ & \rightleftharpoons NH_4^+ \\ HCO_3^- + H^+ & \rightleftharpoons H_2CO_3 \\ [Fe(H_2O)_5OH^-]^+ + H^+ & \rightleftharpoons [Fe(H_2O)_6]^{2+} \end{cases}$$

This concept generates a word conjugate i.e. the acid when looses a proton, the species formed is called conjugate base and if a base accept a proton the species formed is called conjugate acid. The strength of conjugate species is just opposite to that of either base or acid.

$$\text{Acids} \xrightarrow{-H^+} \text{Conjugate Base}$$
$$HCl \longrightarrow Cl^- + H^+$$
$$NH_4^+ \longrightarrow NH_3 + H^+$$
$$HCO_3^- \longrightarrow CO_3^{2-} + H^+$$
$$BH_3 \longrightarrow BH_2^- + H^+$$
$$C_2H_5OH \longrightarrow C_2H_5O^- + H^+$$

Similarly

$$\text{Base} \xrightarrow{+H^+} \text{Conjugate Acid}$$
$$NH_3 \xrightarrow{+H^+} NH_4^+$$
$$HCO_3^- \xrightarrow{+H^+} H_2CO_3$$
$$CO_3^{2-} \xrightarrow{+H^+} HCO_3^-$$
$$CH_4 \xrightarrow{+H^+} CH_5^+$$



- If acid or bases are strong its corresponding conjugate base or acids respectively are weak and vice-versa.

Lewis Concept (Electron Pair Donor and Acceptor System)

This concept is said to be modern concept to distinguish acid and base. According to this concept the species which are electron deficient called as Lewis acid and the species which are electron rich are called as Lewis base.

Lewis Acid

(a) Neutral species: $BF_3, AlCl_3, BCl_3, ZnCl_2, FeCl_3$ etc.

(b) Ions: $Na^+, Mg^{2+}, Al^{3+}, K^+$, etc.

Lewis Base

(a) Neutral species: $\ddot{N}H_3$, $\ddot{P}H_3$, $H_2\ddot{O}$: H_2S: H_2Se, $\ddot{P}Cl_3$, $\ddot{P}Br_3$ etc.

(b) Ions: $Cl^-, F^-, Br^-, F^-, O^{2-}, N^{3-}$ etc.

Strength of Acids

An acid is said to be stronger if it release H^+ ion easily. Hence stronger the bond strength, weaker is the acid and bigger the bond length, stronger is the acid.

Levelling Effect and Levelling Solvent

The apparent strength of an acid is dependent on the solvent in which the particular acid is dissolved. Thus all the acids such as H_2SO_4, HCl, $HClO_4$ when dissolved in H_2O producing H_3O^+ ion and thus appears to be equally stronger. Thus water behave here as a levelling solvent. The solvent in which an acid is 100% ionised is called levelling solvent. But in most cases glacial acetic acid solution behave as levelling solvent. Solvent are generally different types such as,

(a) Protic solvent → H_2O, CH_3COOH.
(b) Aprotic solvent → C_6H_6, Toluene, Xylene, NH_3.
(c) Amphiprotic → H_2O.

Hydracids

$CH_4 < NH_3 < H_2O < HF$.

This trend is supported by the stability of their conjugate bases.

$CH_3^- < NH_2^- < OH^- < F^-$.

- $H_2O < H_2S < H_2Se < H_2Te$.
- $HF < HCl < HBr < HI$.

In these cases the bond energy decreases down the group due to increase of bond length.

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Applying law of mass action,

$$Ka = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha} \quad \text{[where Ka = dissociation constant of acid].}$$

For weak electrolyte if $1 - \alpha \simeq 1$.

$$Ka = C\alpha^2 \Rightarrow \alpha = \sqrt{Ka/C}$$

$$\text{Again } [H^+] = C\alpha = C \cdot \sqrt{\frac{Ka}{C}} = \sqrt{C \cdot Ka}$$

Now,

$$P^H = -\log[H^+] = -\log(C \cdot Ka)^{½}$$

$$\Rightarrow P^H = \frac{1}{2}[\log C + \log Ka].$$

$$\Rightarrow P^H = -\frac{1}{2}\log Ka - \frac{1}{2}\log C.$$

$$\boxed{P^H = \frac{1}{2}Pka - \frac{1}{2}\log C} \text{(where log Ka = PKa)}$$

For Weak Base

Let weak base is represented by 'BOH' and its concentration be 'C'. If α is degree of dissociation, then,

	BOH ⇌	B^+ +	OH^-
Initially	'C'	O	O
At eqlm.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

Applying law of mass action,

$$Kb = \frac{[B^+][OH^-]}{[BOH]} = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha}$$

For weak electrolyte, $1 - \alpha \simeq 1$, then,

$$Kb = C\alpha^2 \Rightarrow \alpha = \sqrt{Kb/C}$$

Again,

$$[OH^-] = C\alpha = C\sqrt{\frac{Kb}{C}} = \sqrt{CKb}$$

And,

$$P^{OH} = -\log_{10}[OH^-] = -\log_{10}(C \cdot Kb)^{½}$$

$$\Rightarrow P^{OH} = -\frac{1}{2}\log Kb - \frac{1}{2}\log C$$

$$\boxed{P^{OH} = \frac{1}{2}pKb - \frac{1}{2}\log C}$$

Hydrolysis of Salt

The soluble salt ionises to produce cation and anion and they intract with H^+ and OH^- ions furnished by H_2O and hence P^H of solution changes and this phenomenon is called "hydrolysis of water".

Different types of hydrolysis are as follow:

Hydrolysis of Salt of Strong Acid and Weak Base

Salt such as $ZnCl_2$, $FeCl_3$, $SnCl_2$, $PbCl_2$, $ZnSO_4$, $Fe_2(SO_4)_3$, $FeSO_4$, $Zn(NO_3)_2$, etc. behave as salt of strong acid and weak base and hence when dissolved in water, its P^H is less than 7 i.e. acidic in nature.

Let 'BA' is a salt of this category and its hydrolysis is represented as,

$$B^+ + A^- + H_2O \rightleftharpoons \underset{\text{(weak)}}{BOH} + \underset{\text{(strong)}}{HA}$$

or, $B^+ + H_2O \rightleftharpoons BOH + H^+(aq.)$

(Cationic Hydrolysis)

	B^+	BOH	H^+
Initially	C	O	O
At eqlm.	C(1 – h)	Ch	Ch

(where h is degree of hydrolysis)

According to law of Mass action,

$$Kh = \frac{[BOH][H^+]}{[B^+]} = \frac{Ch \cdot Ch}{C(1-h)} = \frac{Ch^2}{1-h}$$

$$\text{If } 1 - h \simeq 1, Kh = Ch^2 \Rightarrow h = \sqrt{Kh/C}$$

BOH is a weak base here and hence,

$$Kb = \frac{[B^+][OH^-]}{[BOH]}$$

$$\text{and } Kw = \frac{[H^+][OH^-]}{[H_2O]}$$

Thus we get a conclusion on the basis of above expressions, ie

$$Kh = \frac{Kw}{Kb} \Rightarrow h = \sqrt{\frac{Kw}{C \cdot Kb}}$$

Again,

$$[H^+] = Ch = C\sqrt{\frac{Kw}{CKb}} = \sqrt{\frac{CKw}{Kb}}$$

And,

$$P^H = -\log_{10}[H^+] = -\log_{10}\left(\frac{CKw}{Kb}\right)^{½}$$

	Indicators	pH-range	Colour		
			Acidic	Neutral	Basic
1.	Methyl orange	3.1– 4.4	Pink	Pink	Yellow
2.	Methyl red	4.2 – 6.2	Pink	Yellow	Yellow
3.	Phenol phthalein	8.2–10.0	Colourless	Colourless	Pink
4.	Thymol phthalein	9.2–10.2	Colourless	–	Pink

Acidic Indicator

Let us consider an acidic indicator (HIn) which attain equilibrium as

$HIn \rightleftharpoons H^+ + In^-$

(Colourles) (Pink)

$$\Rightarrow KIn = \frac{[H^+][In^-]}{[HIn]}$$

If the solution is acidic, the H^+ ion concentration increases and since Kin is constant, it means equilibrium shift towards left ie solution remain colourless when some alkali is added, OH^- combine with H^+ and form H_2O, i.e equilibrium shift towards right ie pink colour start depeening. That is why HIn appers colourless in acid medium and pink in basic.

$$\boxed{P^H = PKIn + \log\frac{[In^-]}{[HIn]}}$$

Basic Indicators

When Methyl Orange (MeOH) is dissolved in H_2O, it attain equilibrium as follows:

$MeOH \rightleftharpoons Me^+ + OH^-$

Yellow red colourless

If solution is acidic, H^+ interact with OH^- and hence equilibrium shift towards right and red colour appears. But in alkaline medium OH^- ion which is common ion shift the equilibrium to the left and hence yellow colour appears.

In general P^H range of indicator lies between $PKin^{-1}$ to $PKin^{+1}$.

Case I, If $P^H = PKin^{-1}$

ie $\frac{[In^-]}{[HIn]} = 10^{-1} = 10\%$

∴ % Ionisation of indicator would be

$$\frac{[In^-]}{[In^-][HIn]} \times 100\% = \frac{0.10[HIn]}{0.10\,HIn + [HIn]} \times 100\%$$

$$= \frac{1}{11} \times 100 = 9.1\%.$$

In fact, $P^H = PKin^{-1}$ is the maximum P^H up to which the solution has a distinct colour characteristics of HIn.

Case II, If $P^H = PKin^{+1}$

ie $\frac{[In^-]}{[HIn]} = 10$

% Ionisation of indicator is

$$\frac{[In^-]}{[In^-]+[HIn]} \times 100\% = \frac{10[HIn]}{10[HIn]+(HIn)} \times 100\%$$

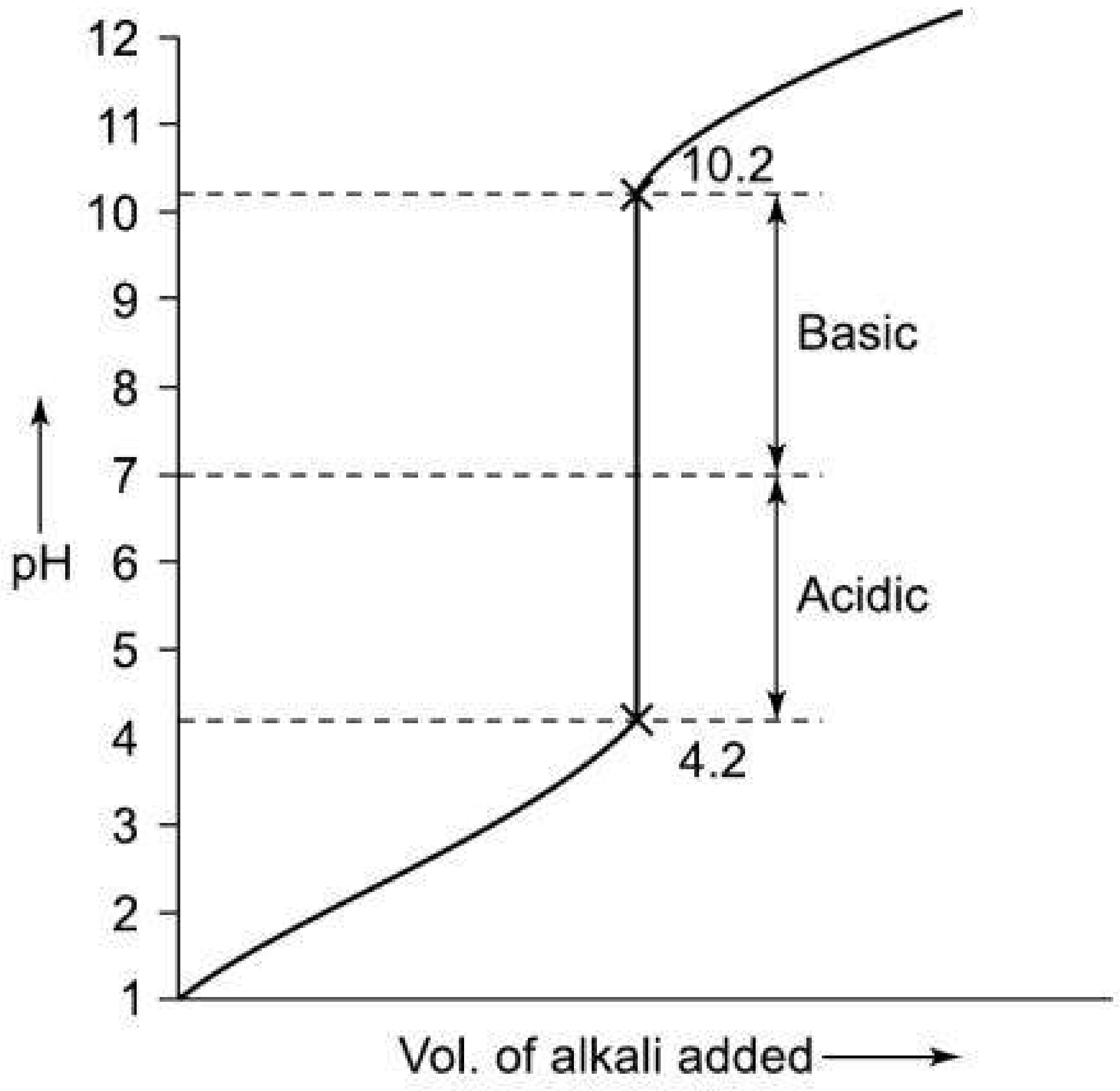
$$= \frac{1000}{11} = 91\%.$$

Acid Base Titration Curve

Acid-base titration are generally four types in which different strength of acid and bases are used, such as,

(a) Strong Acid Vs Strong Base Titration

When base i.e. OH^- ion is added to acid solution P^H goes on increasing. At the point of equivalence, H^+ ion rapidly reduced and hence P^H increases sharply. Thus all the indicators are used which P^H-range lies between 4.2 to 10.2.



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➤ Example 11.11

Calculate $[H^+]$ in a solution containing 0.1 M HCOOH and 0.1M HOCN Ka for HCOOH and HOCN are 1.8×10^{-4} and 3.3×10^{-4}.

➤ Solution

Both the acids contribute for $[H^+]$ due to appreciable dissociation.

$$HCOOH \rightleftharpoons H^+ + HCOO-$$
$$0.1 - x \qquad x + y \qquad x$$
$$HOCN \rightleftharpoons H^+ + OCN^-$$
$$0.1 - y \qquad x + y \qquad y$$

$$\Rightarrow \quad K_{HCOOH} = \frac{[H^+HCOO^-]}{[HCOOH]} = 1.8 \times 10^{-4}$$

$$\Rightarrow \quad K_{HCOOH} = \frac{(x+y)x}{0.1} = 1.8 \times 10^{-4} \qquad \ldots(1)$$

Similarly

$$K_{HOCN} = \frac{(H^+)(OCN^-)}{(HOCN)}$$

$$= \frac{(x+y)y}{0.1} = 3.3 \times 10^{-4} \qquad \ldots(2)$$

From (1) and (2) we get

$$\frac{x}{y} = \frac{1.8}{3.3} \text{ or } y = 1.83x$$

From (1) we get $(x + 1.83x)x = 1.8 \times 10^{-4}$

$\Rightarrow \quad x = 2.52 \times 10^{-3}$

Thus $\quad y = 4.61 \times 10^{-3}$

And $\quad (H^+) = x + 4 = 2.52 \times 10^{-3} + 4.61 \times 10^{-3}$
$= 7.13 \times 10^{-3}$M.

➤ Example 11.12

How much AgBr could dissolve in 1.0L of 0.4 M NH_3? Assume that $[Ag(NH_3)_2]^+$ is the only complex formed the dissociation constant for

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$$
$$K_{dissociation} = 6.0 \times 10^{-8}$$
$$K_{sp}\,(Ag\,Br) = 5.0 \times 10^{-13}$$

➤ Solution

Let us suppose solubility of AgBr be x M. Thus $[Br^-] = X$m but $[Ag^+] \neq X$m. This is because Ag^+ react with NH_3 to form $[Ag(NH_3)_2]^+$

So let $\quad [Ag^+] = $y M.

$$AgBr \rightleftharpoons Ag^+(ag) + Br^-(ag)$$

$\Rightarrow \quad K_{sp} = [Ag^+][Br^-] = y.x = 5.0 \times 10^{-13}$

Again $\quad Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$

$$x \qquad 0.4 \qquad 0$$
$$0.4 - 2x \qquad x$$
$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$
$$x \qquad\qquad 0.4 - 2x$$
$$x - 4 \qquad y \quad 0.4 - 2x + 2y$$
$$\simeq 0.4$$

Thus,

$$K_{diss} = \frac{[Ag+][NH_3]^2}{[Ag(NH_3)_2]^+} = \frac{y(0.4 - 2x + 2y)}{x - y}$$
$$= 6.0 \times 10^{-8}$$

If $\quad x - y \simeq x$, K_{diss} is low

$$\therefore \quad K_{dissociation} = \frac{y(0.4)^2}{x}$$

$\Rightarrow \quad x = 1.15 \times 10^{-3}$M

➤ Example 11.13

A sample of AgCl was treated with 5.0ml of 1.5M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026gm of Cl^- per litre Calculate the solubility product of AgCl $[K_{sp}\,(Ag_2CO_3) = 8.2 \times 10^{-12}]$ **[IIT, 1997]**

➤ Solution

$$[Na_2CO_3] = [CO_3^{2-}] = 1.5M$$

At equilibrium

$$[Cl] = [NaCl] = \frac{0.026}{35.5}$$
$$= 0.0000732M.$$

$$AgCl(s) + Na_2CO_3 \rightleftharpoons Ag_2CO_3(s) + 2NaCl$$
$$[1.5 - 0.0000366] \qquad 0.0000732$$
$$\simeq 1.5M \qquad\qquad M$$

$$[Ag+] = \sqrt{\frac{K_{sp}(Ag_2CO_3)}{(CO_3^{2-})}} = \sqrt{\frac{8.2 \times 10^{12}}{1.5}}$$
$$= 2.34 \times 10^{-6}M.$$

K_{sp} of AgCl

$= [Ag^+][Cl^-]$

$= 2.34 \times 10^{-6} \times 0.0000732$

$= 1.71 \times 10^{-10}$.

22. Which one of the following order of acid strength is correct?
(a) $RCOOH > ROH > HOH > HC \equiv CH$
(b) $RCOOH > HOH > ROH > HC \equiv CH$
(c) $RCOOH > HOH > HC \equiv CH > ROH$
(d) $RCOOH > HC \equiv CH > HOH > ROH$

23. At 90°C pure water has $H_3O^+ = 10^{-6}$ mol litre^{-1}. The value of K_w at 90°C is
(a) 10^{-6} (b) 10^{-12}
(3) 10^{-14} (d) 10^{-8}

24. A weak acid (HA) after treatment with 12ml of 0.1M strong base (BOH) has a P^H of 5. At the end point the volume of same base required is 26.6ml. Thus K_a of acid is
(a) 2.8×10^{-5} (b) 8.2×10^{-6}
(c) 2.8×10^{-4} (d) 8.2×10^{-5}

25. The ratio of dissociation constant of two weak acids HA and HB is 4. At what molar concentration ratio, the two acid will have same P^H?
(a) 2 (b) 0.5
(c) 4 (d) 0.25

26. The P^H of a 10^{-10} MHCl solution is approximately
(a) 10 (b) 7
(c) 1 (d) 14

27. The solubility product of A_2X_3 is. 1.08×10^{-23}. Its solubility in pure water will be
(a) 1.0×10^{-3}M (b) 1.0×10^{-4}M
(c) 1.0×10^{-5}M (d) 1.0×10^{-6}M

28. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp}. 's' is given in terms of K_{sp} by the relation
(a) $s = \left(\frac{K_{SP}}{128}\right)^{1/4}$ (2) $s = \left(\frac{K_{SP}}{256}\right)^{1/5}$
(c) $s(256\, K_{SP})^{1/5}$ (d) $s = (128\, K_{SP})^{1/4}$

29. The dissociation constants of two weak acids are K_1 and K_2. The relative strength of the two acids is given by
(a) K_1/K_2 (b) $(K_1K_2)^{1/2}$
(c) $(K_1/K_2)^{3/2}$ (d) $K_1–K_2$

30. An aqueous solution of Borax ($Na_2B_4O_7$) is
(a) Acidic
(b) Basic
(c) Neutral
(d) Cannot be predicted

31. pH of 0.01 $M(NH_4)_2SO_4$ and 0.02 M NH_4OH buffer (pKa of $NH_4^+ = 9.26$) is
(a) 4.74 + log 2 (b) 4.74 – log 2
(c) 4.74 + log 1 (d) 9.26 – log 1

32. 0.1 mole of CH_3NH_2($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution?
(a) 8×10^{-2} M (b) 8×10^{-11}M
(c) 1.6×10^{-11}M (d) 8×10^{-5}M

33. A buffer solution contains 1 mole of $(NH_4)_2SO_4$ and 1 mole of NH_4OH($K_b = 10^{-5}$). The P^H of solution will be:
(a) 5 (b) 9
(c) 5.3010 (d) 8.6990

34. The increasing order of basic strength of Cl^- ,CO_3^{2-}, CH_3COO^-, OH^-, F^- is :
(a) $Cl^- < F^- < CH_3COO^- < CO_3^{2-} < OH–$
(b) $Cl^- < F^- < CO_3^{2-} < CH_3COO^- < OH^-$
(c) $CH_3COO^- < Cl^- < F^- < CO_3^{2-} < OH^-$
(d) None of these

35. Which one is hard base :
(a) Ag^+ (b) Cr^{3+}
(c) F (d) F^-

36. Arrange NH_4^+, H_2O, H_3O^+, HF and OH^- in increasing order of acidic nature:
(a) $OH^- < H_2O < NH_4^+ < HF < H_3O^+$
(b) $H_3O^+ < HF > H_2O > NH_4^+ > OH^-$
(c) $NH_4^+ < HF < H_3O^+ < H_2O < OH^-$
(d) $H_3O^+ < NH_4^+ < HF < OH^- < H_2O$

37. Which of the following is most soluble in water:
(a) MnS ($K_{sp} = 8 \times 10^{-37}$)
(b) ZnS ($K_{sp} = 7 \times 10^{-16}$)
(c) Bi_2S_3 ($K_{sp} = 1 \times 10^{-70}$)
(d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)

38. pH for the solution of salt undergoing anionic hydrolysis (say CH_3COONa) is given by :
(a) $pH = \frac{1}{2}[pK_w + pK_a + \log C]$
(b) $pH = \frac{1}{2}[pK_w + pK_a - \log C]$
(c) $pH = \frac{1}{2}[pK_w + pK_b - \log C]$
(d) None of these

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C.	NH_4CN	R.	Both cationic & anionic hydrolysis
D.	CH_3COONH_4	S.	Does not undergo hydrolysis

10.

	Column I (Indicatos)		**Column II (Types of titration)**
A..	Phenolphthalein (8.3-10.0)	p.	NaOH + HCl
B .	Phenol red (6.8–8.4)	q.	$H_2SO_4 + NH_4OH$
C.	Bromo cresol green (3.8–5.4)	r.	CH_3COOH + NaOH
D.	Methyl orange (3.1–4.4)	s.	$KOH + H_2SO_4$

11.

	Column I		**Column II**
A..	20 ml of 0.1 M CH_3COOH +50 ml of 0.1 M NaOH	p.	PH>7
B .	20 ml of 0.1 M NH_4OH + 50 ml of 0.1 M CH_3COOH	q.	PH<7
C.	50 ml of 0.1M NaOH+50 ml of 0.1 M CH_3COOH	r.	Phenolphthalein is suitable indicator
D.	20 ml of 0.1 M NH_4OH+20 ml of 0.1 M H_2SO_4	s.	MeOH is suitable indicator

IIT WINDOW–V

Asserition and Reasoning

1. Assertion – HCl is not acidic in benzene.
Reason – Benzene does not accept proton

2. Assertion – H_3O^+ is the strongest acid in aqueous solution.
Reason – Water levels the strength of hydronium ion

3. Assertion – ClO_4^- is the weakest base
Reason – In ClO_4, chlorine atom is $–SP^3$ hybridised

4. Assertion – All Bronsted bases are Lewis bases
Reason – A species that accepts a proton necessarily should donate a lone pair of electrons

5. Assertion – HNO_3 is not a Bronsted acid in $CHCl_3$
Reason – $CHCl_3$ is an example aprotic solvent

6. Assertion – Ethoxide ion acts as a strong base
Reason – Ethyl alcohol is a weak acid

7. Assertion – $H_2P0_3^-$is a Lowry Bronsted acid & base
Reason – $H_2PO_3^-$ is a proton donor as well as proton acceptor

8. Assertion – P^H of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.
Reason – Dissociation of acetic acid is suppressed by the addition of sodium acetate due to common ion effect.

9. Assertion – At 90°C the P^H of pure water is less than 7.
Reason – Ionic product of water increases with increase in temperature.

10. Assertion – The aqueous solution of CH_3COONa is alkaline in nature
Reason – Acetate ion undergoes anionic hydrolysis.

11. Assertion – Aqueous solution of $ZnSO_4$ is neutral.
Reason – Salt of strong acid and strong base doesn't undergo hydrolysis.

IIT WINDOW–VI

Previous Year asked Questions

1. How many moles of Sodium propionate should be added to 1L of an aqueous solution containing 0.020 moles of propionic acid to obtain a buffer solution of P^H 4.75? What will be P^H of 0.010 moles of HCl are dissolved in the above buffer solution. Compare the last ph value with the P^H of 0.010 M HCl solution. Dissociation constant of propionic acid Ka at 25°C is 1.34×10^{-5}.

[IIT JEE,(1981)]

2. 20ML of 0.2M sodium hydroxide is added to 50ml of 0.2 M acetic acid to give 70 ml

NH_4OH. The solution contain C_3 mole/litre of NH_4^+ ions.

4. The dissociation constant of NH_4OH is given by.

(a) $K_b = \frac{C_3^2}{C_2 - C_3}$ (b) $K_b = \frac{C_3^2}{C_2}$

(c) $K_b = \frac{C_3}{C_2 - C_3}$ (d) $K_b = \frac{C_3}{C_1 - C_2}$

3. The total $[NH_3]$ which is determined by volumetric analysis is

(a) C_1 (b) $C_1 + C_2 + C_3$

(c) $C_1 + C_3$ (d) $C_2 + C_3$

6. The degree of dissociation of NH_4OH is given by

(a) C_1 (b) ${}^{C_3}/_{C_1}$

(b) ${}^{C_3}/_{C_2+C1}$ (d) ${}^{C_3}/_{C_2}$

Passage -III

Buffer solution resist the change in P^H against addition of small quantity of acid or base from outside. Acidic buffer is prepared by mixing weak acid and its corresponding salt with strong acid. A 0.2 M HCOOH solution having $[H^+ = 6.4 \times 10^{-3}$ mole/litre, and in it HCOONa solution is added to adjust the $[CH_3COONa]$ = 1M.

7. The buffer solution P^H is given by

(a) $P^H = PKa + \log \frac{(Salt)}{(Acid)}$

(b) $P^H = PKb + \log \frac{(Salt)}{(Acid)}$

(c) $P^{OH} = PKb + \log \frac{(Salt)}{(Base)}$

(d) $P^{OH} = PKb + \log \frac{(Base)}{(Salt)}$

8. The ionisation constant of HCOOH is equal to

(a) 1.2×10^{-5} (b) 1.2×10^{-4}

(c) 2.1×10^{-5} (d) 1.2×10^{-4}

9. The P^H of buffer is

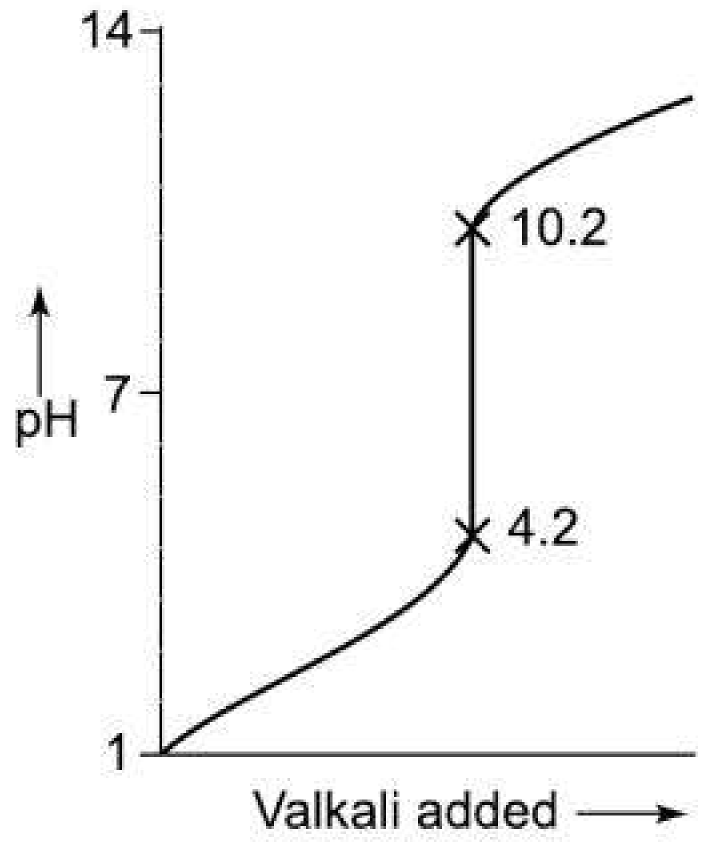
(a) 4.38 (b) 5.69

(c) 3.21 (d) 3.99

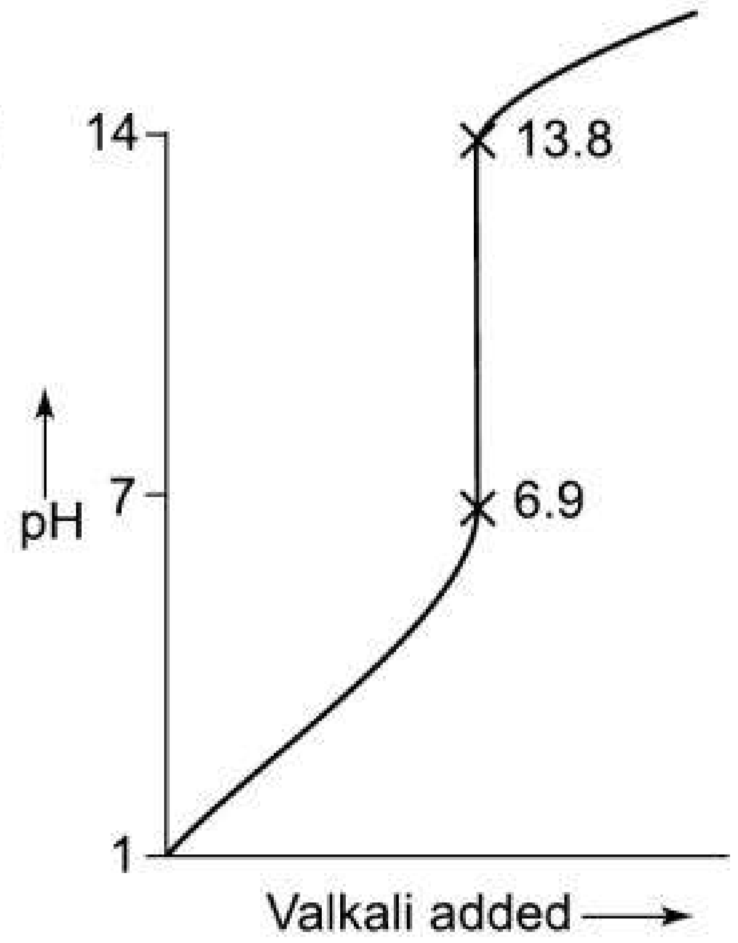
Passage -IV

The indicator theory explain that all the indicator can't be used in any type of acid-base titration Methyl orange in an acidic indication while phenol phthalein is a basic one. The graph of acid base are as follow:

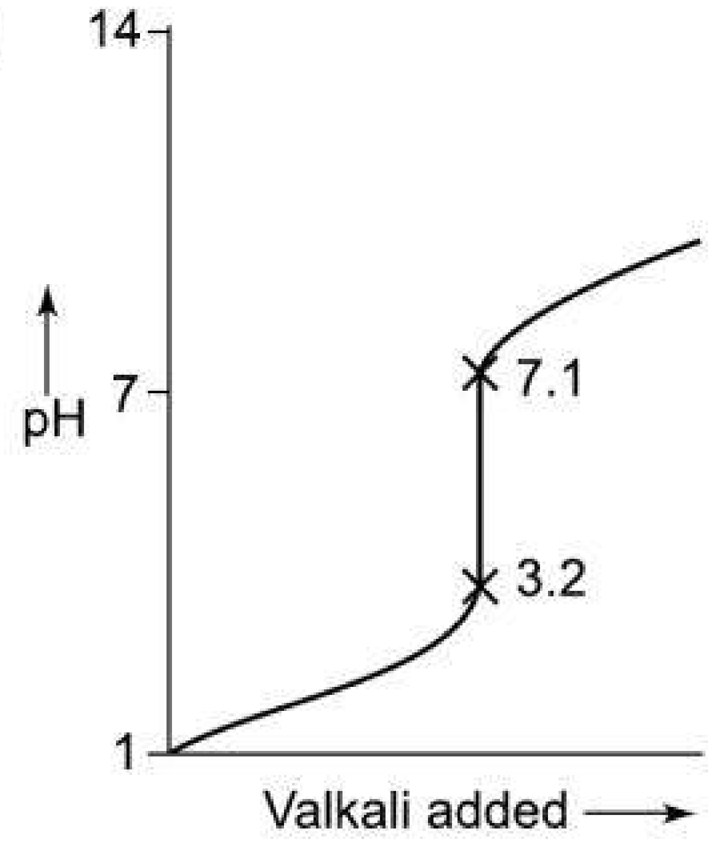
(a)



(b)

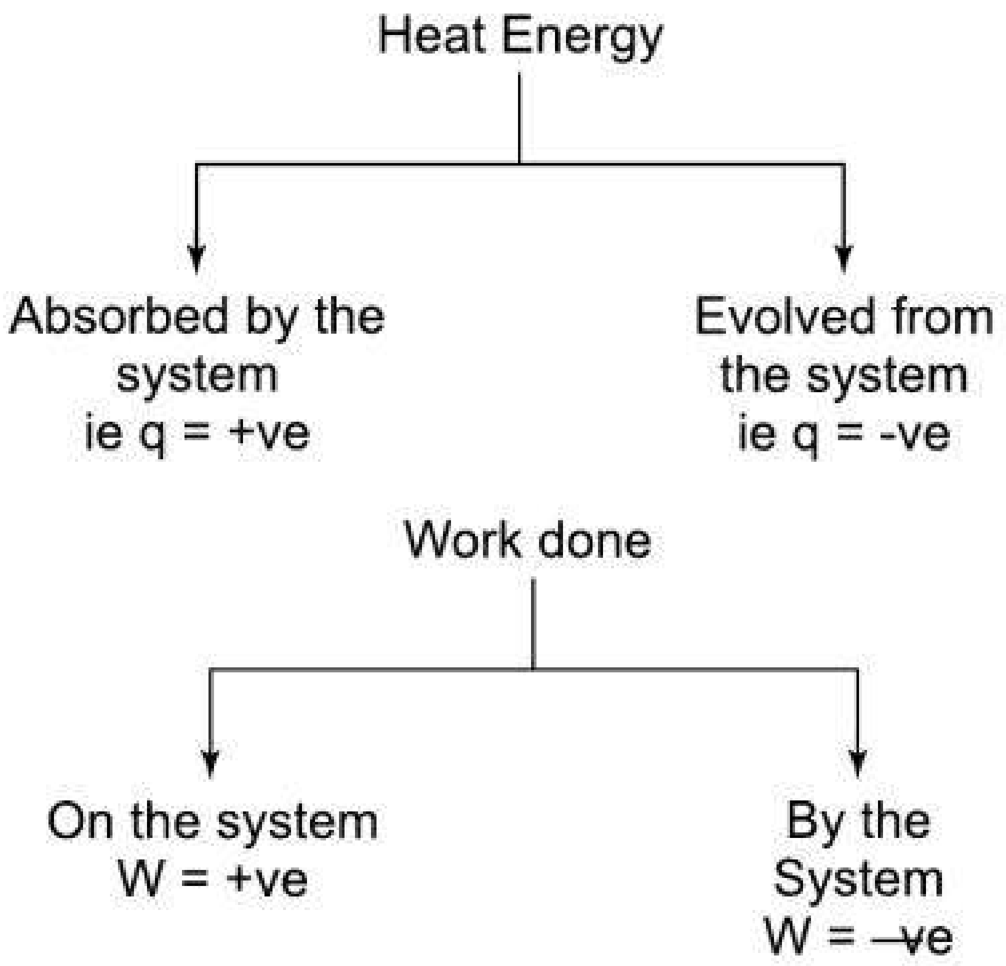


(c)



(k) Heat Energy, work done and its sign The energy exchanged between a system and surrounding, when their temperature are different is termed as heat energy. When a system transfer heat energy to the surrounding, the temperature of system decrease, while that of surrounding increases. This transfer of heat energy continue till the temperature of both system and surrounding are the same.

Sign Conversion

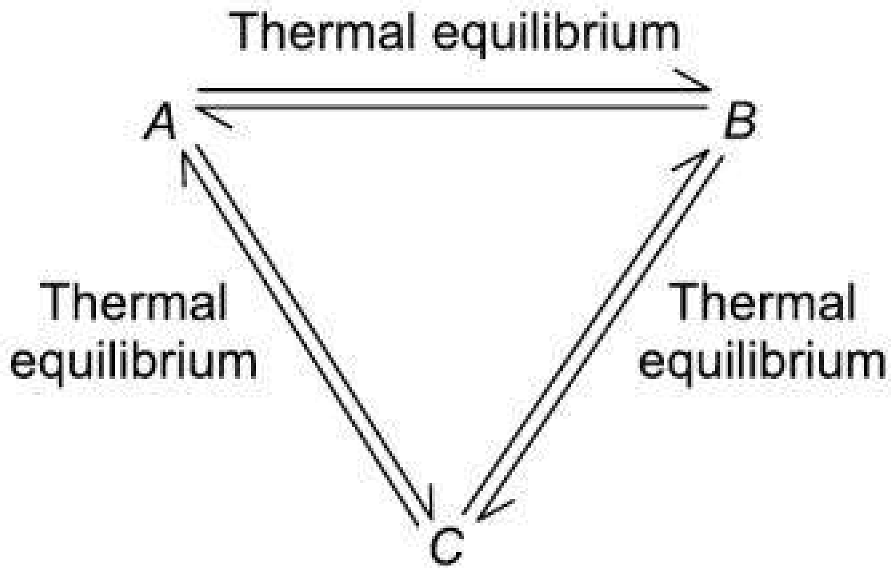


Work is the product of force and distance. Thus work is said to be done if the point of application of force moves through a certain distance.

If a system looses energy, then the work is said to have been done by the system. On the other hand if the system gains energy from the surrounding, then the work is said to have been done on the system.

Zeroth Law of Thermodynamics

It is also known as law of thermal equilibrium. This law states that the two systems '*A*' and '*B*' are in thermal equilibrium with a third system '*C*' separately, then '*C*' is also in thermal equilibrium with each other.



First Law of Thermodynamics

It is nothing but the law of conservation of energy to the thermodynamic system. This law states that 'the total energy of an isolated system remain constant'.

or

It is impossible to construct a perpetual motion machine that can produce work without taking energy from outside

or

Whenever a particular type of energy disappear, an equivalent amount of another type must be produced.

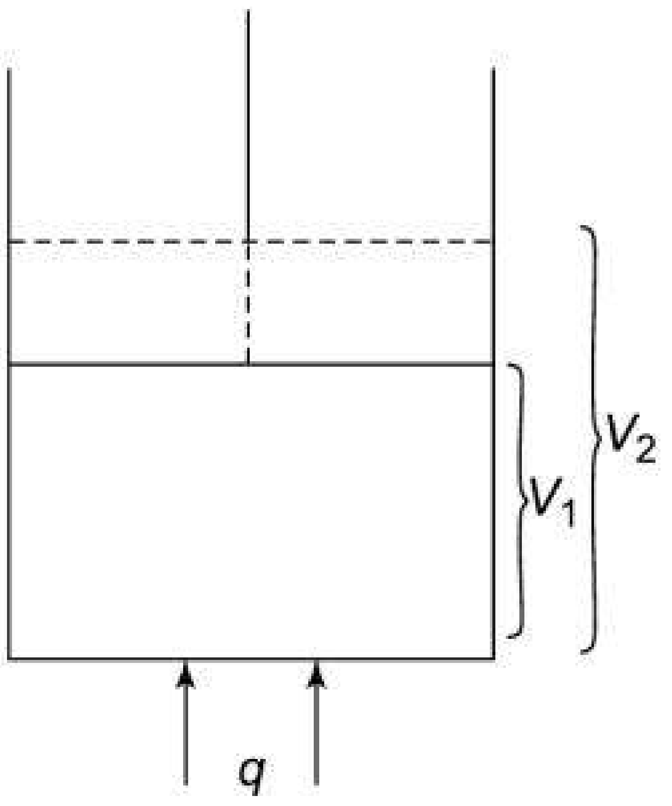
Mathematical Expression of 1st Law

Let a system take 'q' amount of heat energy from the surrounding and due to which the volume of gas enclosed in a cylindrical system changes from 'V_1' to 'V_2' whereas its internal energy change is ΔE.

$$\text{Thus} \qquad \Delta E = q - P(V_2 - V_1)$$

$$\Rightarrow \qquad \Delta E = q - w$$

Where 'w' is work done by the system.



Case I For a cyclic process involving isothermal process, then, $\Delta E = 0$.

$$\text{Then} \qquad q = w$$

i.e. total amount of heat energy taken is converted into work.

Case II For an adiabatic process $q = 0$, i.e. $\Delta E = -w$ i.e. the system without taking energy from outside doing some work.

➤ Solution

1st law: $\Delta U = q + w = 40 - 8 = 32$ Joule.

➤ Example 12.2

2.8 gm of N_2 gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate, ΔU, q and W for the gas.

➤ Solution

$$n = \frac{2.8}{28} = 0.1,$$

$$20 \times V_1 = 0.1 \times 0.0821 \times 300$$

$$\Rightarrow \quad V_1 = 0.123 \text{ litre.}$$

Finally, $1 \times V_2 = 0.1 \times 0.0821 \times 300$

$$\Rightarrow \quad V_2 = 2.463 \text{ litre.}$$

Since process is irreversible,

$$\begin{aligned} W &= -P_{ext}(V_2 - V_1) \\ &= -1(2.463 - 0.123) = -2.340 \text{ lit. atm,} \\ &= \frac{-2.340 \times 1.987 \times 4.184}{0.082} \text{ Joule.} \\ V &= -236.95 \text{ J} \end{aligned}$$

Since $\Delta U = q + w'$ & ΔU for isothermal process is zero

$$0 = q - 236.95$$

$$\Rightarrow \quad q = 236.95 \text{ Joule.}$$

➤ Example 12.3

Calculate the work done when a system raises a column of water of radius 5.0 mm through 10 cm.

➤ Solution

Since, $w = -\text{Mgh}$ & Mass $= v \times d$

$$\begin{aligned} &= \pi r^2 l \times d \\ &= 3.14 \times (0.5)^2 \times 10 \times 1 \end{aligned}$$

$$\begin{aligned} \Rightarrow \quad w &= -3.14 \times (0.5)^2 \times 10 \times 1 \times 980 \times 10/2 \\ &= -3.85 \times 10^3 \text{ erg} = -3.85 \times 10^3 \text{ Joule.} \end{aligned}$$

(The centre of mass of column lies half way along its length 'l').

➤ Example 12.4

Calculate the work done when 50 g of iron reacts with HCl in (i) a closed vessel of fixed volume (ii) an open beaker at 25°C.

➤ Solution

(i) Vessel is of fixed volume, $\Delta V = 0$, $w = 0$.

(ii) The gas drives back the atm. hence,

$$w = -P_{ext.}\,\Delta V, \quad \Delta V = nRT/P_{ext}$$

$$\therefore \quad w = -P_{ext}\frac{nRT}{P_{ext}} = -nRT$$

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

$$n = \frac{50}{56} = 0.8929 \text{ mole}$$

$$\begin{aligned} \therefore \quad w &= -0.8929 \times 8.314 \times 298 \text{ J} \\ &= -2212.22 \text{ J} \end{aligned}$$

➤ Example 12.5

Calculate q, w, ΔU and ΔH for the isothermal reversible expansion of one 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?

[Roorkee, 2000]

➤ Solution

For isothermal reversible expansion,

$$\begin{aligned} w &= -2.303\, nRT \log\frac{P_1}{P_2} \\ &= -2.303 \times 1 \times 8.314 \times 273 \log\frac{1.0}{0.1} \\ &= -5227.2 \text{ J.} \end{aligned}$$

At constant T, for expansion, $\Delta T = 0$, $\therefore\ \Delta U = 0$,

And $\Delta u = nC_V \Delta T \quad \Rightarrow \quad w = 0,$

& $q = -w = +5227.2$ J.

Also when temp is constant, $P_1V_1 = P_2V_2$ or

$$PV = \text{Constant.}$$

$$\Delta H = \Delta u + \Delta(PV)\ ;\ \Delta H = 0.$$

➤ Example 12.6

Calculate W and ΔE for the conversion of 1 mole of H_2O into 1 mole of steam at a temp. of 100°C and a pressure of 1 atm. Latent heat of vaporisation of H_2O is 9720 cal/mole.

➤ Solution

$$\begin{aligned} P &= 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dyne/cm}^2 \\ &= 1.013 \times 10^6 \text{ dyne/cm}^2. \end{aligned}$$

V_1 = vol. of 1 mole of H_2O at 100°C = 18 ml.

V_2 = vol. of 1 mole of steam at 100°C

➤ Example 12.24

The standard heat of formation of $CCl_4(g)$; $H_2O(g)$ $CO_2(g)$ and $HCl(g)$ are – 25.5, –57.8, – 94.1, and – 22.1 Kcal respectively. Calculate ΔH_{298} for the reaction.

$$CCl_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 4HCl(g).$$

➤ Solution

$$\begin{aligned}\Delta H^\circ_{\text{Reaction}} &= \Delta H^\circ_{\text{Products}} - \Delta H^\circ_{\text{Reactants}}\\ &= (\Delta H^\circ_{CO_2} + 4 \times \Delta H^\circ_{HCl})\\ &\qquad - (\Delta H^\circ_{CCl_4} + 2\Delta H^\circ_{H_2O})\\ &= -41.4 \text{ kcal.}\end{aligned}$$

➤ Example 12.25

Determine enthalpy change for
$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$ at 25°C using heat of combustion value under standard conditions.

H_2	CH_4	C_2H_6	$C_{(\text{Graphite})}$
– 285.8	– 890.0	– 1560	– 393.5 kJ/mole.

$\Delta H_f\, C_3H_{8(g)} = -103.8$ kJ/mole. **[IIT, 92]**

➤ Solution

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad ...(i)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad ...(ii)$$

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \qquad ...(iii)$$

$$C_{(G)} + O_2 \rightarrow CO_2 \qquad ...(iv)$$

$$3C_{(G)} + 4H_2 \rightarrow C_3H_8(g) \qquad ...(v)$$

Operation $\rightarrow -\text{v} - \text{iii} - \text{ii} + 3 \times \text{iv} + 5 \times \text{i}$

$\therefore \quad \Delta H = -55.7$ kJ.

IIT WINDOW–II

➤ Multiple Choice Questions (only one correct answer)

THERMO CHEMISTRY

1. Equal values of C_2H_2 and H_2 are combusted under identical condition. The ratio of heat evolved in i.e.

$$H_2(g) + 2O_2(g) = H_2O(g)\ \Delta H = -241.8 \text{ kJ}$$

$$C_2H_2(g) + 2\frac{1}{2}O_2(g) = 2CO_2(g) + H_2O(g)$$

$$\Delta H = -1300 \text{ kJ}$$

(a) 5.37/1 (b) 1/5.37
(c) 1/1 (d) None of these

2. Heat of neutralisation of a strong acid increased by 5° when 5 ml of a strong base is added to it. If 10 ml of each are mixed, temperature should increased by

(a) – 27.4 kcal/eq (b) 13.7 kcal/mol
(c) – 13.7 kcal/eq (d) – 13.7 kcal/mol

3. The temperature of a 5 ml of strong acid increased by 5° when 5 ml of a strong base is added to it. If 10 ml of each are mixed temperature should increased by

(a) 5°
(b) 10°
(c) 15°
(d) Can not be known

4. The heat of formation of HCl(g) from the reaction

$H_2(g) + Cl_2(g) = 2HCl(g) : \Delta H = -44$ kcal

(a) + 44 kcal (b) – 44 kcal
(c) + 22 kcal (d) – 22 kcal

5. Given $N_2(g) + 2H_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H^\circ = -22$ kcal. The standard enthalpy of formation of NH_3 gas is

(a) – 11 kcal/mol (b) 11 kcal/mol
(c) – 22 kcal/mol (d) 22 kcal/mol

6. If for $H_2(g) = 2H(g) : \Delta H = 104$ kcal, heat of atomization of hydrogen is

(a) 52 kcal (b) 104 kcal
(c) 208 kcal (d) None of these

7. Heat of combustion of CH_4, C_2H_4, C_2H_6 are – 890, –1411, and –1560 kJ/mol respectively. Which has the lowest fuel value in kJ/g

(a) CH_4 (b) C_2H_4
(c) C_2H_6 (d) All same

8. Heat of neutralisation of a strong acid and a strong base is equal to ΔH of

(a) $H^+ + OH^- = H_2O$
(b) $H_2O + H^+ = H_3O^+$
(c) $2H_2 + O_2 = 2H_2O$
(d) $CH_3COOH + NaOH = CH_3COONa + H_2O$

(c) $\Delta H = 0$ and $\Delta S < 0$
(d) $\Delta H < 0$ and $\Delta S < 0$

99. All the natural process in this universe produce
(a) a decrease in entropy of the universe
(b) an increase in entropy of the universe
(c) no change in entropy
(d) some times increase or sometimes decrease in entropy

100. 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

101. One mole of a perfect gas expands isothermally to ten times its original volume. The change in entropy is
(a) 0.1 R (b) 2.303 R
(c) 10.0 R (d) 100.0 R

102. In which of the following case ΔH and ΔE both are zero.
(a) Adiabatic (b) Isobaric
(c) Isocaloric (d) Cyclic

103. One applying pressure to the equilibrium,
ice $\rightleftharpoons$ water
Which phenomenon will happen
(a) More ice will be formed
(b) More water will be formed
(c) Equilibrium will not be disturbed
(d) Water will evaporate

IIT WINDOW–III

➤ Multiple Choice Questions (More than one correct answer)

1. In a process a system does 140 J of work on the surrounding and only 40 J of heat is added to the system, hence change in internal energy is
(a) 180 J (b) 46.92 cal
(c) – 23.92 cal (d) – 100 J

2. In an isothermal expansion of an ideal gas
(a) $\Delta U = 0$ (b) $\Delta T = 0$
(c) $q = 0$ (d) $w = -q$

3. 2 mole of an ideal gas (monoatomic) undergo a reversible process for which PV^{γ} = constant. The gas is expanded from initial volume of 1 L to final volume of 3 L starting from initial temperature of 300 K. Find ΔH for the process
(a) – 600 R (b) – 3000 R
(c) – 1000 R (d) – 2 kcal $\text{mole}^{-1}\text{k}^{-1}$

4. Which of the following reaction have same heat of reaction at constant temperature and at constant volume.
(a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl\,(g)$
(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(d) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

5. For the gaseous reaction; if ΔH is the change in enthalpy and ΔU is the internal energy then,
(a) ΔH is always greater than ΔU
(b) ΔH is always less than ΔU
(c) $\Delta H < \Delta U$ only if the no. of mole of the products is less than that of the reactant
(d) $\Delta U < \Delta H$ only if the no. of mole of the reactant is less than that of the product

6. If $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T\left[\dfrac{d(\Delta G)}{dT}\right]_P$ then variation of *emf* of a cell E, with temp. T is given by
(a) $\dfrac{\Delta H}{nF}$ (b) $\dfrac{\Delta G - \Delta H}{nFT}$
(c) $\dfrac{\Delta S}{nF}$ (d) $-\dfrac{\Delta S}{nF}$

7. If the inversion temperature of a gas is –80°C, then it will produce cooling under Joule-Thomson effect at
(a) 298 K (b 273 K
(c) 193 K (d) 173 K

8. Sign of ΔG for the melting of ice is negative at
(a) 265 K (b) 270 K
(c) 277 K (d) 274 K

9. If a gas absorbs 200 J of heat and expands by 500 cm^3 against a constant pressure of 2×10^5 Nm^{-2} then change in internal energy is
(a) 23.92 cal (b) – 100 J
(c) + 100 J (d) + 300 J

$C(s) \rightarrow C(g); \Delta H = 172$ kcal
$H_2 \rightarrow 2H; \Delta H = 104$ kcal
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (l); $\Delta H = -68.0$ kcal
$C(s) + O_2 \rightarrow CO_2; \Delta H = -94.0$ kcal
Heat of combustion of $C_2H_6 = -372.0$ kcal
Heat of combustion of $C_3H_8 = -530.0$ kcal.

17. Estimate the average S – F bond enthalpy in SF_6. The standard heats of formation of SF_6 (g), S(g) and F(g) are: – 1100, 275 and 80 kJ mol^{-1} respectively.

18. The enthalpy change for the following reactions at 25°C are given below

$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g);$

$\Delta H = -10.06$ kcal ...(i)
$H_2(g) \rightarrow 2H(g); \Delta H = 104.18$ kcal ...(ii)
$O_2(g) \rightarrow 2O(g); \Delta H = 118.32$ kcal ...(iii)

Calculate OH bond energy for hydroxyl radical.

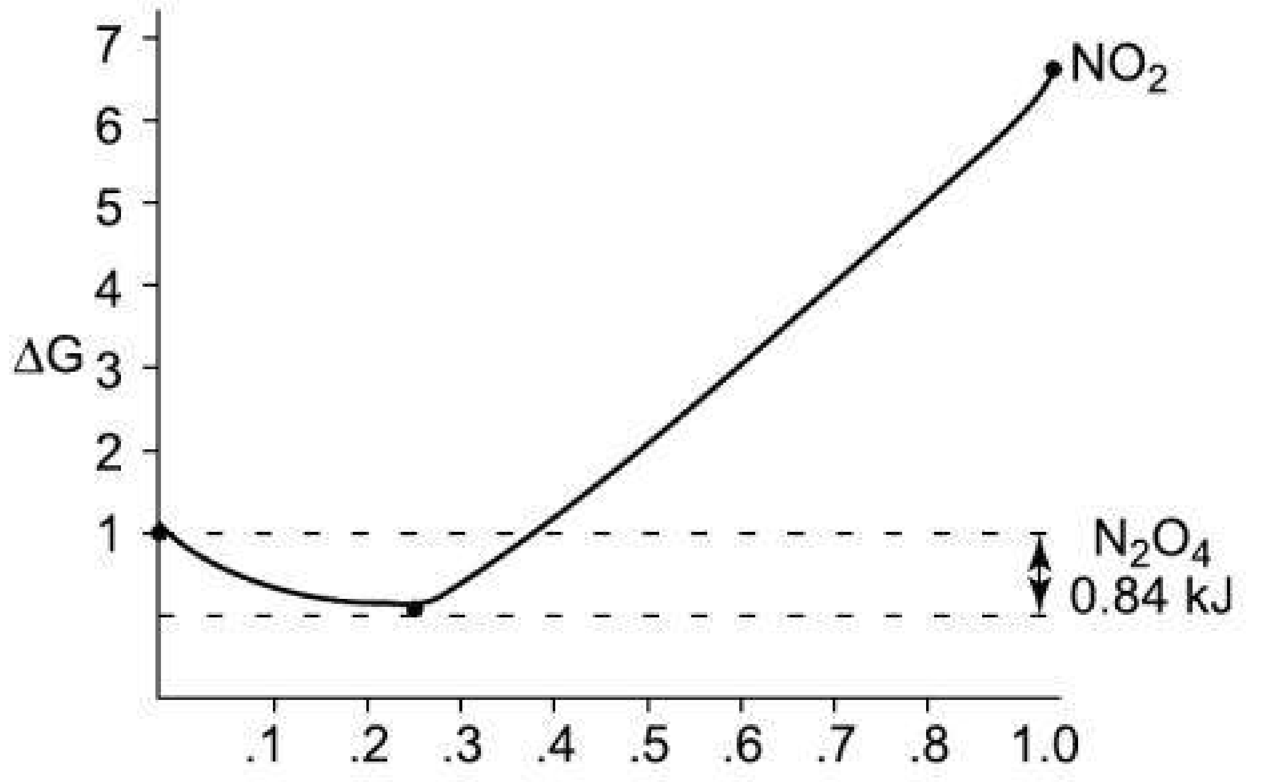
19. The enthalpy change involved in the oxidation of glucose is – 2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose?

20. 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 J mol^{-1} K^{-1})

IIT WINDOW–VIII

Passage - I

The dissociation reaction of N_2O_4 (dimmer) is given as follows.
$N_2O_4(g) \rightarrow 2NO_2(g)$
The Gibb's free energy at 298 K and 1 atmospheric pressure is plotted with fraction of N_2O_4 dissociation as follows.



1. Calculate ΔG° when one mole of N_2O_4 change into equilibrium mixture with N_2O_4?
(a) – 0.84 kJ (b) 0.84 kJ
(c) 6.24 kJ (d) – 5.4 kJ.

2. When two mole N_2O_4 is dissociated into NO_2 which is correct?
(a) ΔH = –ve, Δ*S* = +ve
(b) ΔH = +ve, Δ*S* = +ve
(c) ΔH = –ve, Δ*S* = –ve
(d) ΔH = +ve, Δ*S* = –ve.

3. As the N_2O_4 start dissociation, the graphs shows that first Δ*G* decreases, and then increases. This is due to
(a) The decrease is due to first association and then dissociation.
(b) The decrease shows that allotropic change first and then dissociated.
(c) The first decrease because the process undergo spontaneous and then non-spontaneous.
(d) None of these.

Passage - II

The enthalpy change when one gm-equivalent of an acid is neutralised with one gm-equivalent of a base, is called enthalpy of neutralisation.
NaOH(aq) + HCl(aq) → NaCl(aq) + H_2O.
Δ*H* = – 13.7 kcal
= – 57.1 kJ.

4. Calculate the enthalpy of neutralisation for
$H_2SO_4(aq) + Ca(OH)_2 \rightarrow CaSO_4(aq) + 2H_2O$.
ΔH = – *x* kJ.
(a) – *x* kJ (b) – 2 *x* kJ
(c) – *x*/2 kJ (d) 4*x* kJ

5. The enthalpy of neutralisation for the reaction

CHAPTER 13

Electrochemistry

Electrochemistry is the branch of chemistry which deals with the study of relationship between electrical energy and chemical energy or the inter conversion of one form into another.

Electrolytes

The substance which is either in fused state, or in aqueous state produce, different ions on passing electricity is called electrolytes. Electrolytes are two types:

Strong Electrolytes

The electrolytes which is completely ionised in fused or aqueous state is called strong electrolytes e.g. NaCl, NaOH, KOH, HCl, H_2SO_4, HNO_3 etc.

Weak Electrolytes

The electrolytes which ionises partially or freely in aqueous or fused state are called as weak electrolytes e.g. CH_3OOH, NH_4OH, $PbSO_4$, $BaSO_4$, ZnS etc.

Part-A

Electrolysis

It is the process in which different ions are discharged at the different electrodes (cathode and anode) by passage of electric current through the electrolytes. When electricity is passed though the electrolytic solution it ionises into cation and anions which accumulate at different electrodes either by loosing or gaining electrons.

Cathode

The electrode at which reduction occur is called cathode. It is –vely charged during electrolysis.

Anode

The electrode at which oxidation occurs is called anode. It is +vely charged during electrolysis. For example NaCl fused is electrolysed as follows:

$NaCl\ (fused) \rightarrow Na^+ + Cl^-$

At cathode (– ve)

Na^+ ion is discharged.

$Na^+ + e \rightarrow Na(s)$

At anode (+ve)

Cl^- ion is discharged

$Cl^- \rightarrow Cl + e^-$

$2Cl \rightarrow Cl_2\ (g).$

$$\Rightarrow \qquad \Lambda_m = \frac{K \times 1000}{C} \text{ or } \Lambda_m = \frac{K \times 1000}{M}$$

(where M = Molarity)

Unit of molar conductivity, is $\dfrac{ohm^{-1}cm^{-1}cm^3}{mole}$

In SI unit it is expressed in S cm^2 $mole^{-1}$.

Equivalent Conductivity

Equivalent conductivity of a solution at a dilution is defined as the conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in 1ml of a solution. Mathematically, it is denoted by Λ_{eq}.

Λ_{eq} = K.V.

where V is the Vol. of solution containing 1gm equivalent of the solute in cm^3

$$\Rightarrow \boxed{\Lambda_{eq} = \frac{K \times 1000}{Ceq.} = \frac{K \times 1000}{N.}}$$

where N = Normality of solution
unit of equivalent conductance
= ohm^{-1} cm^2 or mho cm^2 (g.eq)
= S cm^2 $(g.eq)^{-1}$.

Effect of Concentration on Conductivity

- Molar conductivity (Λ_m) of the strong electrolyte increases to a small extent with dilution due to decrease in interionic attractions with dilution.
- Molar conductivity of the weak electrolyte also increases with dilution as the degree of dissociation increases on dilution.
- Equivalent conductivity of the electrolyte (strong or weak) also increases with dilution and reaches to a maximum or limiting value which is termed Λ_∞.
- The conductivity of all electrolyte increases with temperature.
- The conductivity slighty varies with pressure due to change in viscosity of the medium.
- The viscosity of dilute solution decreases with increasing pressure.

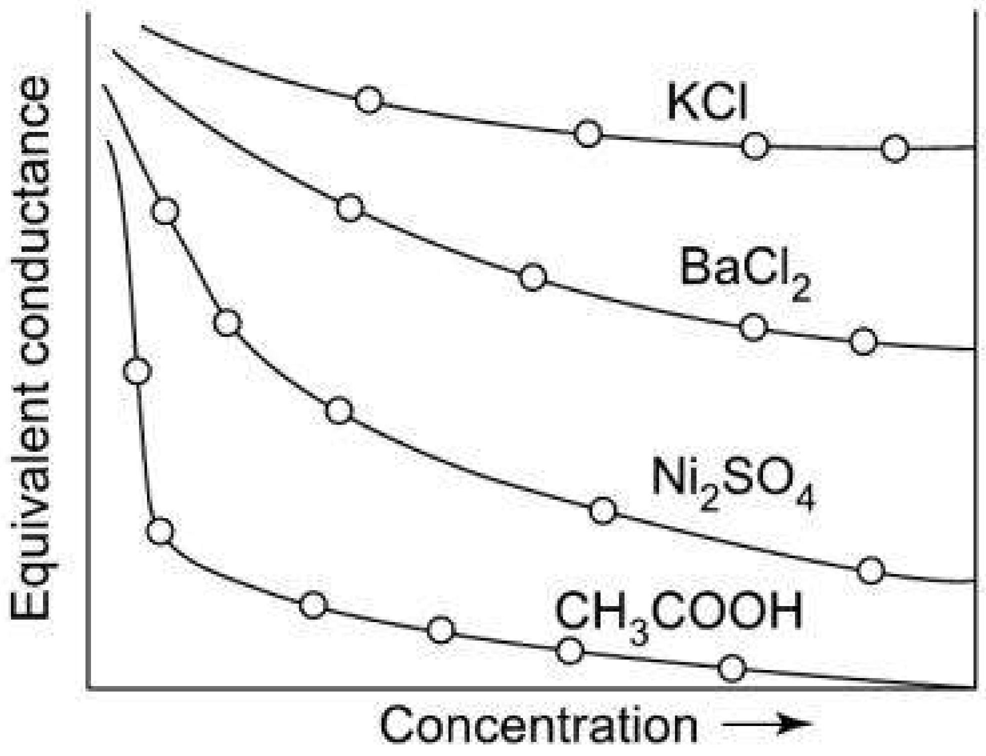


Fig 13.1

Kohlrausch's Law

This law states that "at infinite dilution, when the dissociation is complete, each ion makes a definite contribution towards molar conductivity of the electrolyte irrespective of the nature of the other ion present" i.e. the equivalent conductivity of the electrolyte at infinite dilution is the sum of the equivalent conductories of the cation and anions i.e.

$$\lambda_\infty = \lambda_a + \lambda_c$$

where λ_a and λ_c are the ionic conductance of cation and anion at infinite dilution respectively. Again ionic conduction can be mathematically expressed as

$$\lambda_c = k\,U_c \text{ and } \lambda_a = k\,U_a$$

where U_a and U_c are the ionic mobilities of anion and cation respectively at infinite dilution and k is a constant equal to 96,500 coulomb.

$$\text{i.e. Ionic Mobility} = \frac{\text{Ionic velocity}}{\text{Potential gradient}}$$

$$= \frac{\text{Ionic velocity}}{\text{Potential difference (volt)}}$$

Mathematical expressions

Equivalent conductance (Λ_{eq}) can be expressed as

$$\Lambda^\infty_{eq} = \frac{1}{Z^+}\lambda^\infty_c + \frac{1}{Z^-}\lambda^\infty_a$$

where Z^+ and Z^- are charges on cation and anion

e.g.

$$\Lambda^\infty_{BaCl_2} = \frac{1}{2}\lambda^\infty_{Ba^{2+}} + \frac{1}{1}\lambda^\infty_{Cl^-}$$

$$\Delta G = \Delta G^o + 2.303\ RT \log_{10}\frac{[\text{Products}]}{[\text{Reactants}]} \quad ...(1)$$

where ΔG^o represent free energy change for the reaction when various reactants and products are at standard state. The free energy change is given by

$$\Delta G = -\,nFE_{cell}.$$

and $$\Delta G^o = -\,nFE^o_{cell}.$$

Substituting the value of ΔG and ΔG^o in (1)

$$-\,nFE_{cell} = -\,nFE^o_{cell} + 2.303\ RT \log_{10}\frac{[\text{Products}]}{[\text{Reactants}]}$$

$$\Rightarrow \quad E_{cell} = E^o_{cell} - \frac{2.303\ RT}{nF}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]} \quad ...(2)$$

$$\Rightarrow \quad E_{cell} = E^o_{cell} - \frac{2.303\ RT}{nF}\log_{10} Q$$

where $Q = \dfrac{[\text{Products}]}{[\text{Reactants}]}$ called as reaction quotient

Equation (2) is called Nernst equation if R = 8.314 JK^{-1} $mole^{-1}$ and T = 298 K, F = 96,500 C. Equation (2) written as

$$E_{cell} = E^\circ_{cell}\ \frac{-2.303\times 8.314\times 298}{96500\ F}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

$$\Rightarrow \quad E_{cell} = E^o_{cell} - \frac{0.0591}{F}\log\frac{[\text{Products}]}{[\text{Reactants}]} \quad ...(3)$$

Electrode Potential for Half Cell

Let us consider Daniel cell i.e.

$$Zn(s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s).$$

Oxidation half reaction

The half reactions are written as

$$Zn \rightarrow Zn^{2+} + 2e^-$$

If we apply Nernst equation for this reaction as

$$E_{zn/zn^{2+}} = E^o_{zn/zn^{2+}} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Zn]}$$

Since [Zn] = unity

$$E_{zn/zn^{2+}} = E^\circ_{zn/zn^{2+}} - \frac{0.0591}{2}\log[Zn^{2+}] \quad ...(4)$$

Similarly Reduction half reaction

$$Cu^{2}+ + 2e^- \rightarrow Cu(s)$$

$$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{[Cu]}{[Cu^{2+}]}$$

Since [Cu] = unity

Then, $E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} + \dfrac{00591}{2}\log[Cu^{2+}]$ ...(5)

From equation (4) & (5)

$$E_{cell} = E_{Zn/Zn^{2+}} + E_{Cu^{2+}/Cu}$$

$$= (E^o_{Zn/Zn^{2+}} + E^o_{Cu^{2+}/Cu}) - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\Rightarrow \quad E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} \quad ...(6)$$

Standard Cell Potential and Equilibrium Constant

The standard free energy change for a reaction is related to the standard cell potential by the equation

$$\Delta G^\circ = -n\ FE^o_{cell},\ \Delta G^\circ = -RT\ \ln K$$

Thus $$-nF\ E^o_{cell} = -RT\ \ln K.$$

or $$E^o_{cell} = \frac{RT}{nF}\ln K = \frac{2.303\ RT}{nF}\log K$$

$$\Rightarrow \quad \frac{2.303\ RT}{F} = 0.0591\ V \text{ at } 25°C.$$

Thus $$E^o_{cell} = \frac{0.0591}{n}\log K \text{ at } 25°C$$

or $$\log K = \frac{nE^\circ_{cell}}{0.0591}$$

$$\Rightarrow \quad K = \text{antilog}\ \frac{nE^\circ_{cell}}{0.0591}$$

Heat Energy, Free Energy and Work done

The work done by the system or on the surrounding during the chemical change is given by

$$\Delta G = -\,nFE_{cell}$$

The work done (*W*) is the product of charge and potential. i.e.

$$W_{max} = \text{charge} \times \text{potential}$$

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book.

(a) 0.05 mole of Cu^{2+} ions passed into solution
(b) 0.112 litre of Cl_2 was liberated
(c) 0.56 litre O_2 was liberated
(d) 0.1 mole of Cu^{2+} ions passed into the solution

9. The cell reaction for the given cell is spontaneous if

$$\underset{P_1}{Pt(H_2)}|H^+(1M)||H^+(1M)|\underset{P_2}{(H_2)Pt}, (s)$$

(a) $P_1 > P_2$ (b) $P_1 < P_2$
(c) $P_1 = P_2$ (d) $P_1 = 1$ atm

10. 10^{-2} g atoms of Ag can be oxidised to Ag^+ during the electrolysis of AgO_3 solution using silver electrode by
(a) 965 coulomb (b) 96500 coulomb
(c) 9650 coulomb (d) 96.500 coulomb

11. For the cell, $TI|TI^+(0.001\ M)||Cu^{2+}(0.1\ M)|Cu$, E_{cell} at 25°C is 0.83 V. E_{cell} can be increased
(a) by increasing $[Cu^{2+}]$
(b) by increasing $[TI^+]$
(c) by decreasing $[Cu^{2+}]$
(d) none of these

12. 1 coulomb of charge passes through solution of $AgNO_3$ and $CuSO_4$ connected in series and the concentration of two solution being in the ratio 1 : 2. The ratio of amount of Ag and Cu deposited on Pt electrode is
(a) 107.9 : 63.54 (b) 54 : 31.77
(c) 107.9 : 31.77 (d) 54 : 63.54

13. A hydrogen electrode placed in a buffer solution of CH_3COONa and acetic acid in the ratio's $x : y$ and $y : x$ has electrode potential values E_1 volt and E_2 volt respectively at 25°C. The pKa values of acetic acid is (E_1 and E_2 are oxidation potential)
(a) $-\dfrac{E_1+E_2}{0.118}$ (b) $\dfrac{E_2-E_1}{0.118}$
(c) $\dfrac{E_1+E_2}{0.118}$ (d) $\dfrac{E_1-E_2}{0.118}$

14. Silver is removed electrolytically from 200 mL of a 0.1 N solution of $AgNO_3$ by a current of 0.1 ampere. How long will it take to remove half of the silver from the solution?
(a) 10 sec (b) 16 sec
(b) 100 sec (d) 9650 sec

15. Maximum number of mole of oxygen gas that can be obtained by the electrolytic decomposition of 90 g of water will be
(a) 1 (b) 2.5
(c) 5 (d) 9

16. Two electrolytic cells, one containing acidified ferrous chloride and another acidified ferric chloride are in the two cells when electricity is passed through the cells will be
(a) 3 : 1 (b) 2 : 1
(c) 1 : 1 (d) 3 : 2

17. The metal that cannot be on produced on reduction of its oxide by aluminium is
(a) K (b) Mn
(c) Cr (d) Fe

18. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 MY and 1 MZ at 25°C. If the reduction potential of Z > Y > X, then
(a) Y will oxidise X and not Z
(b) Y will oxidise Z and not X
(c) Y will oxidise both X and Z
(d) Y will reduce both X and Z

19. 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 power of the corresponding metals is
(a) Y > Z > X (b) X > Y > Z
(c) Z > Y > X (d) Z > X > Y

20. The correct order of chemical reactivity with water according to electrochemical series is
(a) K > Mg > Zn > Cu
(b) Mg > Zn > Cu > K
(c) K > Zn > Mg > Cu
(d) Cu > Zn > Mg > K

21. An electric current of c ampere was passed through a solution of an electrolyte for 't' second depositing P g of the metal M on the cathode. The equivalent weight E of the metal will be
(a) $E = \dfrac{c\times t}{P\times 96500}$
(b) $E = \dfrac{c\times P}{t\times 96500}$

$$\text{Efficiency} = \frac{\Delta G°}{\Delta H°} = \frac{-nE°F}{\Delta H°}$$

$$E° = \frac{\text{Efficiency} \times \Delta H°}{-nF}$$

$$= \frac{70 \times (-300 \times 10^{+3})}{100 \times (-10 \times 96500)} = 2.176 \text{ V}$$

75. Ans. (c)

$E°_{OP} = -E°_{RP}$

76. Ans. (c)

$$E_{RP} = E°_{RP} + \frac{0.059}{1} \log \frac{[H^+]}{P_{H_2}}$$

77. Ans. (b)

Follow text

78. Ans. (d)

IIT WINDOW–III

➤ MCQ (Having one or more answer correct)

1. A gas 'R at 1 atm is bubbled through a solution containing a mixture of 1 MQ$^-$ and 1MR$^-$ at 25°C (298 K). If the reduction potential is in the order R > Q > P then

(a) Q will oxidise P only

(b) Q will oxidise S only

(c) S will oxidise both P & Q

(d) S will reduce both P & Q

2. For the strong electrolyte λ increases slowly with dilution and can be represented by the equation

$\lambda = \lambda° - AC^{1/2}$

Which electrolytes (s) have the same value of the constant 'A'

(a) NaCl (b) $CaCl_2$

(c) $ZnCl_2$ (d) $AlCl_3$

3. Which of the following reactions is / are said to be spontaneous?

(a) Sn^{4+} (aq) + Ni(s) → Ni^{2+} (aq) + Sn^{2+}(aq)

(b) Ni^{2+} (aq) + Fe → Fe^{2+}(aq) + Ni(s)

(c) Ag^+ (aq) + Cu → Cu^{2+} (aq) + Ag

(d) Hg^{2+} (aq) + Cu → Cu^{2+} + Hg (s)

4. Which of the followings is are correct

(a) Li < Mg < Fe < Ni < Cu → oxidising power

(b) Li < Mg < Fe < Ni < Cu → reducing power

(c) Li < Mg < Fe < Ni < Cu → E° red

(d) Li < Mg < Fe < Ni < Cu → E° ox

5. When a voltmeter is connected between Ni and Pb electrodes it shows 0.12 V and after 0.1 mole of electrons have passed through the voltmeter, the mass of Ni electrode will be

(a) more than 6.0 gm

(b) more than 8 gm

(c) more than 4 gm

(d) more than 2.8 gm

6. During the electrolysis of aq NaOH solution

(a) Na is deposited at cathode

(b) H_2 is deposited at cathode

(c) O_2 is liberated at anode

(d) H_2 and O_2 both liberated at anode.

7. In the calomel electrode its E° red depend on the strength of KCl solution as

(a) E° red for SCE is 0.2415 V

(b) E° red for NCE is 0.2800 V

(c) E° red for DNCE is 0.3338 V

(d) E° red for DNCE is 0.2316 V

8. In the lead storage cell

(a) The pH on discharging increases

(b) The pH on discharging decreases

(c) The pH on charging increases

(d) The pH on charging or discharging remain the same.

9. A concentration cell is represented as Pt (s) Cl_2(g), 1 atm | HCl (aq) C_1 | HCl(C_2) (aq) | Cl_2 (g) | pt(s)1 atm

The incorrect statement is/are

(a) Cell is spontaneous if $C_1 > C_2$

(b) Cell is spontaneous if $C_1 < C_2$

(c) Cell diagram represent electrolyte concentration cell.

(d) Cell diagram represent the electrolyte Concentration. cell.

10. The changes that increase the emf of the cell is /are

CO(s) | $COCl_2$ (M_1) || HCl(M_2) | Pt (H_2) (g)

(a) Increase the volume of $COCl_2$ solution from 100 ml to 200 ml

(b) Increase M_2 from 0.01 M to 0.50

8 The E°cell for the electrolytic is
(a) 1.36 V (b) −1.36V
(c) 2.19 V (d) −2.19V

9. How long the electrolysis will take to produce 1kg of Cl_2
(a) 27.1 hr (b) 31.0 hr
(c) 39.6hr (d) 48.7 hr

Passage IV

The concentration of potassium ion inside the biological cell is at least 20 times higher than the outside. The resulting potential difference across the cell is important in several process 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) | M^+aq(0.05M)|| M^+(aq) M(s) For the above electrolytic cell the magnitude of the cell potential $|E_{cell}| = 70$ mV.

[IIT,2010]

10. For the above cell
(a) $E_{cell} < 0, \Delta G > 0$ (b) $E_{cell} > 0, \Delta G > 0$
(c) $E_{cell} < 0, \Delta G^o > 0$ (d) $E_{cell} > 0\ \Delta G^0 > 0$

11. If the 0.5 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution then the magnitude of cell potential would be
(a) 35 mV (b) 70 mV
(c) 140 mV (d) 200 mV

12. The above cell is a type of
(a) Concentration cell with transference
(b) Concentration cell without transference
(c) Concentration cell with electrolyte
(d) Concentration cell without electrolyte

Passage V

Redox reaction play a vitol role in chemistry and biology. The value of standard redox potential (E°red) of two half cell reactions decides which way the reaction is expected to proceed. A simple example is a Daniel cell in which Zinc goes into solution and copper gets, deposited. Given below are the set of half reaction (acidic medium) along with their E°(w.r. to NHE) values using this data the correct explanations to given questions

$I_2 + 2e^- \rightarrow 2I^-$ ---- E° = 0.54V
$Cl_2 + 2e^- \rightarrow 2Cl^-$ ---- E° = 1.36V
$Mn^{3+} + e^- \rightarrow Mn^{2+}$ – ---- E° = 1.50V
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ – ---- E° = 0.77V
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ---- E° = 1.23V

[IIT,2007]

13. Among the following identify the correct statements.
(a) Cl^- ion is oxidised by O_2
(b) Fe^{2+} ion is oxidised by iodine
(c) I^- is oxidised by Cl_2
(d) Mn^{2+} is oxidised by chlorine

14. While Fe^{3+} ion 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+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(c) Fe^{3+} oxidises H_2O into O_2
(d) Mn^{3+} oxidises H_2O into O_2.

15. Sodium fusion extract obtained from aniline, on treatment with Iron (II) sulphate and H_2SO_4 in presence of air gives prussian blue precipitate. The blue colour is due to the formation of
(a) $Fe_4[Fe(CN)_6]$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe_4[Fe(CN)_6]_2$ (d) $Fe_4[Fe(CN)_6]_3$

IIT WINDOW—VIII

Subjective Questions

1. Find the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 25°C and 1 atm.

2. A Zn rod weighing 25 g was kept in 100 mL of 1M $CuSO_4$ solution. After a certain time the molarity of Cu^{2+} in solution was 0.8. What was molarity of SO_4^{2-}? What was the weight of Zn rod after cleaning? At. Weight of Zn = 65.4.

3. 50 mL of 0.1 M $CuSO_4$ solution is electrolysed using Pt electrode with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate $[Cu^{2+}]$, $[H^+]$ and $[SO_4^{2-}]$ after electrolysis. What will be the concentration of each species if current is passed using Cu electrodes?
$[Cu^{2+}]=0.094M, [H^+]=0.12M [SO_4^{2-}]=0.1M.$

4. 19 g fused $SnCl_2$ was electroslysed using inert electrodes. 0.11g Sn was deposited at cathode.

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CHAPTER 14

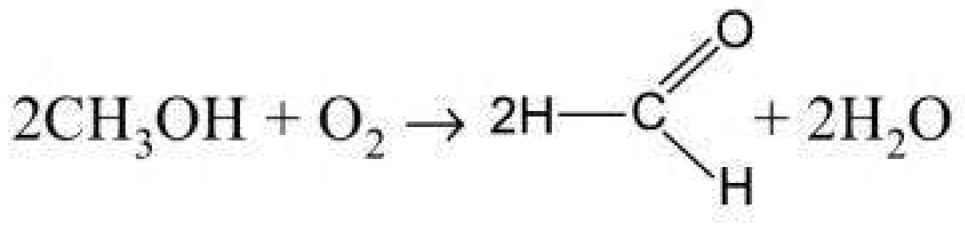
Redox

Oxidation and Reduction

Oxidation and reduction are explained on the basis of different manners are discussed as below:

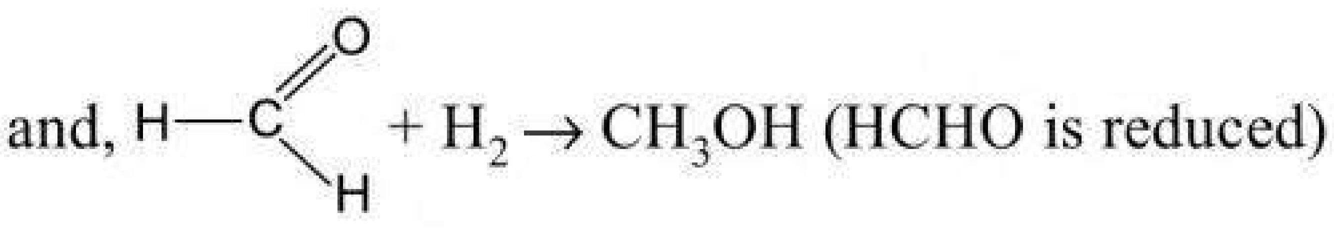
(A) On the basis of Hydrogen

The removal of hydrogen in any chemical reaction is called oxidation whereas addition of hydrogen is said to be reduction e.g.



$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$$

(oxidation in terms of CH_3OH)



and, $HCHO + H_2 \rightarrow CH_3OH$ (HCHO is reduced)

(B) On the basis of Oxygen

The addition of oxygen in any chemical reaction is said to be oxidation while its removal is called reduction e.g.

$HNO_2 + O_2 \rightarrow HNO_3$ (HNO_2 is oxidized)

$CuO + H_2 \rightarrow Cu + H_2O$ (CuO is reduced)

$Ag_2O \xrightarrow{\Delta} 2Ag + 1/2O_2$ (Ag_2O is reduced)

(C) On the basis of Electronegative Element

The addition of electronegative element in chemical reaction is called oxidation while removal of electronegative element is called reduction. e.g.

$SnCl_2 + Cl_2 \rightarrow SnCl_4$. [$SnCl_2$ is oxidized]

$FeCl_3 \rightarrow FeCl_2 + Cl_2$ [$FeCl_3$ is reduced]

(D) On the basis of Electron

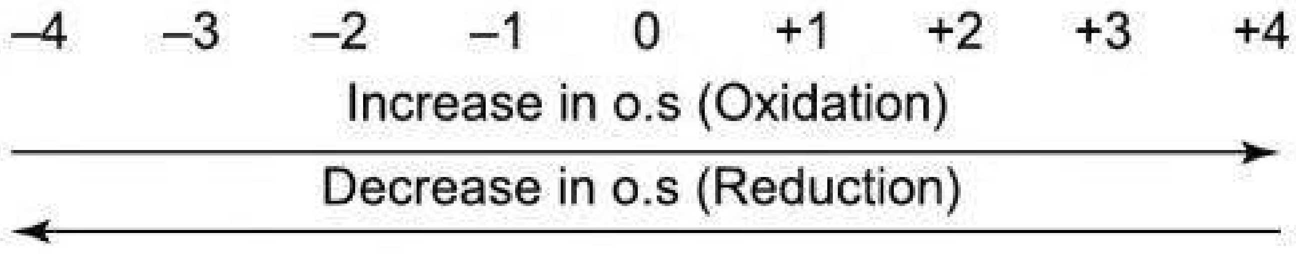
In any chemical reaction if loss of electron is observed, it is called oxidation and if there is gain of electron is observed is called reduction e.g.

$$\left.\begin{array}{r} Cu \rightarrow Cu^{2+} + 2e^- \\ Fe \rightarrow Fe^{3+} + 3e \end{array}\right\} \text{Oxidation}$$

$$\left.\begin{array}{r} Na^+ + e \rightarrow Na \\ Ca^{2+} + 2e^- \rightarrow Ca \end{array}\right\} \text{reduction}$$

(E) On the basis of Oxidation Number

Increase in oxidation number is called oxidation while its decrease is called reduction. e.g.



19. The highest oxidation state of s is found in
(a) H_2SO_4 (b) $H_2S_2O_3$
(c) $Na_2S_4O_6$

20. In order to balance the half reaection $Cr_2O_7^{2-} \rightarrow Cr^{3+}$, the no. of e, H^+ and H_2O are added is
(a) 5, 2, 9 (b) 7, 14, 6
(c) 6, 14, 7 (d) 14, 6, 7

21. The number of electrons required in the reduction of nitrate ion (NO_3^-) into Hydrazine (NH_2NH_2) is
(a) 8 (b) 7
(c) 5 (d) 3

22. 1 mole of MnO_4^{2-} in neutral aqueous solution disproportionate to
(a) 2/3 mole of Mn_2O_7 and $\frac{1}{3}$ mole of MnO_2
(b) $\frac{1}{3}$ mole of Mn_2O_7 and $\frac{1}{3}$ mole of MnO_2
(c) $\frac{1}{3}$ mole of MnO_4^- and $\frac{1}{3}$ mole of MnO_2
(d) $\frac{2}{3}$ mole of MnO_4^- and $\frac{1}{3}$ mole of MnO_2

23. A compound is made up of three elements A,B and C. If oxidation state of A, B and C are +2 + 5 and –2 respectively the correct formula of compound is
(a) ABC_2 (b) $A_3(B_4C)_2$
(c) $A_3(BC_4)_2$ (d) $A_2\,(BC_3)_2$

24. In the reaction
$M^{x+} + MnO_4^- \rightarrow MO_3^- + Mn^{2+}$
If one mole of MnO_4^- oxidise 1.67 mole of M^{x+} to MO_3^-. The value of x is
(a) 2 (b) 4
(c) 3 (d) 5

25. The no. of mole of Cl_2 required per mole of NaOH in order to form $NaClO_3$ and NaCl is
(a) 0.25 (b) 0.5
(c) 0.75 (d) 1

26. The no of O_2 mole required per mole of NH_3 in order to form NO is
(a) 2 (b) 3
(c) 4 (d) 5

27. One mole of N_2H_4 loses 10 mole of electrons to form a new compound Y. Assuming that all the nitrogen appears in the new compound. What is the oxidation state of nitrogen in Y. (There is no change in the oxidation state of hydrogen.
(a) –3 (b) +3
(c) + 5 (d) +1

28. The oxidation state of nitrogen in NH_4NO_3 are
(a) –3, –3 (b) +3, +3
(c) –3 + 5 (d) –3 –5

29. The oxidation state of carbon in CH_3CHO is
(a) –3 + 1 (b) +3, +1
(c) +1, +1 (d) +3, +3

30. The no. of mole of NHO_3 required to react per mole of Zn in order to form NH_4NO_3 along with other products is
(a) 3.5 (b) 1.5
(c) 1.0 (d) 2.5

IIT WINDOW–II

➤ MCQ (One or more than one correct An

1. The oxidation state of S in $Na_2S_4O_6$ is / are
(a) Zero (b) +6
(c) +5 (d) 4.

2. The correct statement is/are
(a) Oxidation state of Cr in CrO_5 is six.
(b) CrO_5 contain 4 oxygen atoms having oxidation state -1.
(c) CrO_5 has two peroxide bonds.
(d) CrO_5 has butterfly structure.

3. The oxidation state of S in thiosulphate ion is/are.
(a) +5 (b) +6
(c) –1 (d) –2

4. The oxidation state of M in the complex $[M(H_2O)_4\,(NO)/_2]^{\pm 6}$ is/are.
(a) +2 (b) +4
(c) –1 (d) +3

5. In the reaction
$KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$.
The correct statement is/are
(a) $KMnO_4$ is a reducing agent.
(b) $KMnO_4$ is redued.
(c) H_2O_2 is oxidised.
(d) H_2O_2 is a reducing agent

6. In the Marshall's acid ($H_2S_2O_8$) the incorrect statements is/are.

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Compound	**Formula**	**Uses**
Magnesite	$MgCO_3$	Basic flux.
Milk of Magnesia	$Mg(OH)_2$	Antacid.
Magnesia	MgO	Basic flux.
Magnesium Sulphate	$MgSO_4$	Purgative.
Magnecia Alba	$(MgCO_3)_x[Mg(OH)_2]_y.2H_2O$	Antacid.Laxative.
Mica	$K_2O.3Al_2O_v6SiO_2.2H_2O$	Insulator.
Mohr's Salt	$FeSO_4.(NH_4)_2SO_4.6H_2O$	Analytical ragent.
Norwegian Salt Paper	$CaO.Ca(NO_3)_2$	Fertlizer.
Nitrolim	$CaCN_2+C$	Nitrogeneous fertilizer.
Nitrochalk	$NH_4NO_3+(NH_4)_3CO_3$	Nitrogeneous fertilizer.
Nitre	KNO_3	Manufacturing gun powder & medicine.
Pink Salt	$(NH_4)_2SnCl_6$	Mordant in dyeing.
Philosopher's Wool	ZnO	Antiseptic, Semiconductor.
Pharaoh Serpent	$Hg(CNS)_2$,	Red paint.
Phosphorite	$Ca_3(PO_4)_2$	Super phosphate of lime.
Plaster of Paris	$(CaSO_4)_2.\ H_2O$	Plastering, Making statue, Moulds
Permutit	$Na_2Al_2Si_2O_8.XH_2O$	Softening water.
Quartz	SiO_2	In watches.
Quick Silver	Hg	Thermometer, For medicine.
Quick Lime	CaO	Preparing slacked lime, Bleaching powder, Dehydrating agent in Lab.
Red Lead	PbO	Flint glass, Paints, etc.
Realgar	As_2S_3	Aurvedic medicines, Paints
Rouge	Fe_2O_3	Red paint, Polishing powder.
Sodamide	$NaNH_2$	Eliminating agent for alkyl halides.
Salt Peter(Indian)	KNO_3	Gun powder, Fertilizer.
Sorel's Cement	$MgCl_2.5MgO.XH_2O$	Cement for tiles.
Spinel	$MgAl_2O_4$	Extraction of Aluminium.
Slacked Lime	$Ca(OH)_2$	Preparation of NH_3,CaC_2, $Ca\begin{matrix}OCl\\Cl\end{matrix}$
Sugar of Lead	$(CH3COO)_2Pb$	Lab.reagent.
Scheele's Green	$Cu(AsO_3)_2$	Paints.
Soda Lime	$NaOH/CaO$	Manufacturing of hydrocarbons.
Soda Ash	Na_2CO_3	Washing powder, Softering of water, Glass, Cement etc.
Tetra Ethyl Lead(TEL)	$(C_2H_s)_4.Pb$	Antiknocking agent.
Thermite	Fe_2O_3+Al	Rocket fuel, Extraction of Cr, Mn etc.
Thomas Slag	$CO_3(PO_4)_2+CaSiO_3$	Fertilizer
Tincal	$Na_2B_4O_7.10H_2O$	Glazes and enamels.

Contd

Gases	Distinguishing Reagent	Remarks
N_2O & O_2	Alkaline pyrogallol solution.	O_2→Is absorbed by alkaline pyrogallol solution
		N_2O→No reaction.
NH_3 & HCl	(a) Litmus Paper.	NH_3→Turns moist red litmus blue.
		HCl→Turns moist blue litmus red.
	(b) Nesseler's reagent	NH_3→Turns Nesseler's reagent.
		HCl→No reaction.
H_2 & O_2	Alkaline pyrogallol solution.	O_2→Absorbed in Sol^n.
		H_2→Does not absorb.
SO, & H_2S	Lead acetate Paper.	H_2S→Turns lead acetate paper black.
		SO_2→No reaction.
HCl & Cl_2	Starch Iodide Paper.	Cl_2→Turns moist starch iodide paper blue and thin bleached.
		HCl→No reaction.
HBr & HI	Cone. H_2SO_4.	HBr→Brown Br_2 vapour is produced.
		HI→Violet vapour OH_2 produced.
Cl_2 & Br,(g)	Moist Starch Iodide Paper.	Cl_2→Turns moist starch iodide paper blue and bleached.
		Br_2→Turns moist starch paper blue.
NH_3 & NO	Nesseler's reagent	NH_3→Turns Nesseler's reagent brown.
		NO→No reaction.

Table 8 Important Pigments in Inorganic Chemistry

Name of the Pigment	Chemical Formula
Chrome Yellow	$PbCrO_4$
Zinc Yellow	$Zn(OH)_2\ ZnCrO_4.H_2O$
Chrome Red	$PbCrO_4.PbO$
Red Lead	Pb_3O_4
Gulgret's Green	$Cr_2O_3\ 2H_2O$
Prussian Blue	$Fe_4[Fe(CN)_6]_3$
Sheela's Green	$CuH.AsO_3$
Thenard's Blue	$CoO.Al_2O_3$
Vedigris / Basic Copper Acetate	$(CH_3COO)_2\ Cu.Cu(OH)_2$
Rinnman's Green	Zn.CoO.
White Zinc Oxide	ZnO
Lithopone	$ZnS + BaSO_4$
White Lead	$2PbCO_3Pb(OH)_2$
14. White Basic Zinc chromate	$ZnCrO_4.Zn(OH)_2$