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The Pearson Guide to

Physical Chemistry

for the IIT JEE

- Short-cut methods and problem-solving tricks
- As per the latest IIT JEE format
- Original questions from competitive exams
- Numerous examples and fully solved problems

Atul Singhal

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The Pearson Guide to

Physical Chemistry for the IIT JEE

ATUL SINGHAL

PEARSON
Chandigarh • Delhi • Chennai

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To my grandparents,
parents and teachers

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The Pearson Guide to Physical Chemistry for the IIT JEE is an invaluable book for all the students preparing for the prestigious engineering entrance examination. It provides class-tested course material and problems that will supplement any kind of coaching or resource the students might be using. Because of its comprehensive and in-depth approach, it will be especially helpful for those students who do not have enough time or money to take classroom courses.

- A careful scrutiny of previous years' IIT papers and various other competitive examinations during the last 10 to 12 years was made before writing this book. It is strictly based on the latest IIT syllabus (2009–10) recommended by the executive board. It covers the subject in a structured way and familiarizes students with the trends in these examinations. Not many books in the market can stand up to this material when it comes to the strict alignment with the prescribed syllabus.
- It is written in a lucid manner to assist students to understand the concepts without the help of any guide.
- The objective of this book is to provide this vast subject in a structured and useful manner so as to familiarize the candidates taking the current examinations with the current trends and types of multiple-choice questions asked.
- The multiple-choice questions have been arranged in following categories:

Straight Objective Type Questions (Single Choice), Brainteasers Objective Type Questions (Single Choice), Multiple Correct Answer Type Questions (More than one choice), Linked-Comprehension Type Questions, Assertion-Reason Type Question, Matrix-Match Type Questions and the IIT JEE Corner.

This book is written to pass on to another generation, my fascination with descriptive physical chemistry. Thus, the comments of the readers, both students and instructors, will be sincerely appreciated. Any suggestions for added or updated additional readings would also be welcome.

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The contentment and ecstasy that accompany the successful completion of any work would remain essentially incomplete if I fail to mention the people whose constant guidance and support has encouraged me.

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CHAPTER 1

Mole Concept and Stoichiometry

Chapter Contents

Concept of atoms and molecules, Dalton's atomic theory; Mole concept; Chemical formulae; Chemical equations; Calculations (based on mole concept) involving common oxidation, reduction, neutralization and displacement reactions; Concentration in terms of mole fraction, molarity, molality and normality, and Various levels of multiple-choice questions.

DALTON'S ATOMIC THEORY

An atom is the smallest particle of an element which is neutral in nature, retains all the properties of the element and takes part in a chemical reaction. The word atom was introduced by Dalton (*alamos* means undivided).

The Dalton's atomic theory was proposed by Dalton on the basis of laws of chemical combination.

Main Assumptions

- Matter (of any type) is composed of atoms.
- An atom is the smallest, fundamental, undivided particle.
- An atom can neither be created nor destroyed.
- Atoms of an element have similar size, energy and properties while atoms of different element differ in these aspects.
- Atoms combine in whole number ratios to form a molecule, therefore, a molecule is the smallest identity that exists individually.

Modern view about the atom

According to the modern view:

- An atom is divisible into other smaller particles which are known as subatomic particles. It can also combine in non-whole number ratio as in the case of non-stoichiometric compounds (Berthollide compounds) like $Fe_{0.93}O$.
- Atoms of same element also differ in mass and mass related properties as in the case of isotopes.

Molecule The term molecule was introduced by Avogadro. It is the smallest particle (identity) of matter that can exist independently and retains all the properties of the substance. Normally, the diameter of the molecules is in the range of 4–20 Å and the molecular mass is between 2–1000. In case of macromolecules, the diameter is in the range of 50–250 Å and the molecular weight may be in lakhs.

Berzelius Hypothesis According to the Berzelius hypothesis, "Equal volumes of all the gases contain same number of atoms under the similar conditions of temperature and pressure." This hypothesis on application to law of combining volume confirms that atoms are divisible which is in contrary to Dalton's theory.

AVOGADRO'S LAW

- Avogadro's law explains law of combining volumes.
- According to this law, "Under similar conditions of temperature and pressure, equal volume of gases contain equal number of molecules."

It means 10 ml of H_2, O_2, N or a mixture of gases have same number of molecules.

It is used in:

(i) Deriving molecular formula of a gas

(ii) Determining atomicity of a gas

(iii) Deriving a relation

molecular mass = 2 × vapour density

$\boxed{M = 2 \times V.D.}$

(iv) Deriving the gram molecular volume

- Avogadro number (N^0 or NA) = 6.023×10^{23}.
- Avogadro number of gas molecules occupy 22.4 litre or 22400 ml or cm^3 volume at STP.
- The number of molecules in 1 cm^3 of a gas at STP is equal to Loschmidt number, that is, 2.68×10^{19}
- Reciprocal of Avogadro number is known as Avogram.

MOLE

- Mole is a unit which represents 6.023 × 1023 particles, atoms, molecules or ions etc., irrespective of their nature.
- Mole is related to the mass of substance, the volume of gaseous substance and the number of particles

$$\text{Mole} = \frac{W}{M}$$

$$= \frac{\text{Wt. of substance in gm.}}{\text{Molar mass of substance (G.m.m)}}$$

Here G.m.m. = Gram molecular mass

$$\text{Mole} = \frac{\text{Volume of substance in litre}}{22.4 \text{ litre}}$$

Volume of one mole of any gas is equal to 22.4 litres of dm^3 at STP. It is known as molar volume.

$$\text{Mole} = \frac{\text{Number of identities}}{\text{Avogadro's number}}$$

$$\text{Mole} = \frac{PV}{RT}$$

Here P = Pressure in atmosphere

V = Volume in litre

T = Temperature in Kelvin

R = Universal gas constant

Relationship of Mole:

A mole of any substance (like N_2) stands for:

- 6.023×10^{23} molecules of N_2
- $2 \times 6.023 \times 10^{23}$ atoms of nitrogen
- 28 gm of nitrogen
- 22.4 litre of N_2 at STP.

To Find Total Number of Identities

- Total number of Molecule = mole(n) × N_A
- Total number of Atoms = mole (n) × N_A × No. of atoms present in one molecule
- Total number of Electrons = mole (n) × N_A × No. of electron present in one electron
- Total charge on any ion = mole (n) × N_A × charge on one ion × 1.6×10^{-19}C

Illustrations

1. If a piece of copper weights 0.635 g, how many atoms does it contain?

Solution Number of moles of Cu in 0.635 g

$$= \frac{0.635 \text{ g}}{63.5 \text{ g mol}^{-1}} = 10^{-2} \text{ mol}$$

As 1 mole Cu contains 6.023×10^{23} atoms of Cu

So 10^{-2} mole Cu contains $6.023 \times 10^{23} \times 10^{-2}$

$= 6.023 \times 10^{21}$ atoms of Cu

2. Oxygen is present in a one litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate the number oxygen molecules in the flask at 0°C.

Solution PV = nRT

$$\frac{7.6 \times 10^{-10}}{760} \text{ atm} \times 1 \text{ L}$$

$$= n \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}$$

$$n = \frac{7.6 \times 10^{-10} \text{ L atm}}{760 \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}.$$

$$= \frac{10^{-12}}{22.41} \text{ mol}$$

Number of molecules

$= (6.02 \times 10^{23} \text{ mol}^{-1}) (10^{-12}/22.41 \text{ mol})$

$= 2.68 \times 10^{10}$

3. Calculate the total number of electrons present in 1.6 gram of methane.

Solution Molecular mass of methane = 16 g mol^{-1}

As 16 g CH_4 contains 6.02×10^{23} molecules of CH_4

So 1.6 g CH_4 contains 6.02×10^{22} molecules of CH_4

As one molecule of CH_4 contains (6 + 4) = 10 electrons, so 6.02×10^{22} molecules of CH_4 contain $10 \times 6.02 \times 10^{22}$.

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

4. How many years would it take to spend Avogadro number of rupees at the rate of 10 lac rupees per second?

Solution As Avogadro number = 6.023×10^{23}

So total rupees = 6.023×10^{23} Rs

Rate of spending = 10 lac rupees/s = 10^6 Rs/s

Number of years to spend all the rupees

$$= \frac{6.023 \times 10^{23} \text{ Rs}}{10^6 \times 60 \times 60 \times 24 \times 365 \text{ Rs/year}}.$$

$= 1.90988 \times 10^{10}$ years

5. Calculate the number of atoms of oxygen present in 88 g of CO_2. What would be the mass of CO having the same number of oxygen atoms?

Solution Number of moles of $CO_2 = \frac{88 \text{ g}}{44 \text{ g mol}^{-1}}$.

= 2 moles

As one mole of CO_2 contains two moles of oxygen atoms, so two moles of CO_2 contain 4 moles of oxygen atoms.

Number of oxygen atoms = $4 \times 6.023 \times 10^{23}$

$= 2.5092 \times 10^{24}$

As 1 mole oxygen atom is present in 1 mole of CO so 4 moles oxygen atoms are present in 4 moles of CO. Its mass is 4 (12 + 16) = 112 g

6. How many atoms of carbon has a young man given to his bride-to-be if the engagement ring contains 0.5 carat diamond? (1 carat = 200 mg)

Solution Mass of diamond (C) = 0.5 × 200 mg

= 100 mg = 100×10^{-3} g = 0.1 g

$$\text{Number of mole of C} = \frac{0.1 \text{ g}}{12 \text{ g mol}^{-1}}.$$

= 1/120 mole

$$\text{Number of C atoms} = \frac{1}{120} \times 6.023 \times 10^{23}$$

$= 5.02 \times 10^{21}$

7. If the Faraday were to be 60230 coulombs instead of 96500 coulombs, what will be the charge on an electron?

Solution One mole electron carries 1 Faraday charge.

As 6.023×10^{23} electrons carry = 60230 C

$$\text{So 1 electron carries} = \frac{60230}{6.023 \times 10^{23}} \text{ C}$$

$= 1 \times 10^{-19}$ C.

MASS

Mass can be expressed in terms of atoms or molecules as follows:

Atomic Mass

It is the relative mass of an atom which shows how many times an atom is heavier than 1/12 mass of C-12.

- The atomic mass of any element expressed in grams is called G.A.M. (gram atomic mass).

  Atomic mass = E × V

  Here E = Equivalent weight

  V = Valency

- Atomic mass = $\frac{6.4}{\text{Specific Heat in cal.}}$.

  It is known as Dulong Petit's law.

REMEMBER

Gram atomic weight is atomic weight expressed in grams but it has a special significance with reference to a mole.

Molecular Mass

Molecular mass represents the total mass of a molecule, that is, number of times a molecule is heavier than that of 1/12 weight of C-12.

- It is non-variable.
- It is now called relative molecular mass.

Determination of Molar Mass

It is possible by these methods

Vapour Density Method

Vapour density of a gas is defined as the ratio of the weight of a certain volume of the gas to the weight of the same volume of hydrogen at the same temperature and pressure.

Vapour density of a gas

$$= \frac{\text{Weight of 'V' litres of the gas}}{\text{Weight of 'V' litres of } H_2 \text{ at the same temperature and pressure}}.$$

Suppose 'V' litres of the gas contains 'n' molecules.

Vapour density of gas

$$= \frac{\text{Weight of 'n' molecules of the gas}}{\text{Weight of 'n' molecules of } H_2}.$$

$$= \frac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 1 molecule of } H_2}.$$

$$= \frac{1}{2} \times \frac{\text{Weight of 1 molecule of the gas}}{\text{Weight of 1 atom of } H_2}.$$

$$\text{V.D.} = \frac{W \times 22400}{\text{Volume at STP (in ml)}}.$$

Here W = Weight of substance in gm.

Molecular mass = 2 × Vapour density

Graham Diffusion Method

$r_1/r_2 = \sqrt{(M_2/M_1)}$

Here r_1, r_2 are rates of diffusion for two species while M_1, M_2 are their molecular masses respectively.

(iii) By Colligative Properties Methods:

$$\pi V = \frac{W}{m} RT$$

Here π = Osmotic pressure in atm.

V = Volume in litre

W = Weight in grams

R = Universal gas constant

T = Given temperature

m = Molar mass

Illustrations

8. The weight of one litre sample of ozonized oxygen at NTP was found to be 1.5 g. When 100 ml of this mixture at NTP were treated with terpentine oil, the volume was reduced to 90 ml. Hence calculate the molecular weight of ozone.

Solution Volume absorbed by terpentine oil = 10 ml

As volume of ozone = 10 ml (as terpentine oil absorbed O_3)

So Volume of O_2 = 100 – 10 = 90

Mol. wt. of ozonized oxygen

$$= \frac{WRT}{PV} = \frac{1.5 \times 0.0821 \times 273}{1 \times 1}$$

= 33.62

As volume or mole ratio of O_2 and O_3 is 900 : 100

So mol. wt. of ozoniz ed oxygen

$$= \frac{900 \times 32 + 100 \times X}{1000}$$

$$33.62 = \frac{900 \times 32 + 100 \times X}{1000}$$

X = 48.2

Hence mol. wt. of ozone = 48.2

Equivalent Weight

- Equivalent weight is the weight of an element or a compound which combines with or displaces 1.008 part by weight of H_2 or 8 part by weight of O_2 or 35.5 part by weight of Cl_2.
- Equivalent weight is a number and when it is denoted in grams, it is called gram equivalent.
- It depends upon the nature of chemical reaction in which substance takes part.

Methods to Find Equivalent Weight

(i) **For Acids**

$$E = \frac{\text{Molecular weight}}{\text{Protocity or Basicity of Acid}}.$$

For example, for H_3PO_4, E = M/3

For H_2SO_4, E = M/2

(ii) **For Bases**

$$E = \frac{\text{Molecular weight}}{\text{Acidity or number of } OH^- \text{ ions}}.$$

For example, for $Ca(OH)_2$, E = M/2

For $Al(OH)_3$, E = M/3

(iii) **For Ions**

$$E = \frac{\text{Molecular weight}}{\text{Charge on ion}}$$

For example, for SO_4^{2-}, E = M/2

For PO_4^{3-}, E = M/3

(iv) **For Compounds**

$$E = \frac{\text{Molecular weight}}{\text{Valency of cation or anion}}.$$

For example, for $CaCO_3$, E = M/2

$AlCl_3$, E = M/3

(v) **For Redox Reactions**

$$E = \frac{\text{Molecular weight}}{\text{Change in oxidation number}}$$

For example, for $KMnO_4$

(a) In acidic medium: E = M/5

$$K\overset{+7}{M}nO_4 + 3H_2SO_4 \rightarrow$$

$$K_2SO_4 + 2\overset{+2}{M}nSO_4 + 3H_2O + 5\,[O]$$

5 unit change in oxidation number.

(b) In basic medium: E = M/1

$$2K\overset{+7}{M}nO_4 + 2KOH \rightarrow$$

$$2K_2\overset{+6}{M}nO_4 + H_2O + [O]$$

one unit change in oxidation number

(c) In neutral medium: E = M/3

$$2K\overset{+7}{M}nO_4 + H_2O \rightarrow$$

$$2KOH + 2\overset{+4}{M}nO_2 + 3[O]$$

3 unit change in oxidation number

(vi) **For Acidic Salt**

$$E = \frac{\text{Molecular weight}}{\text{Number of replaceable H-atoms}}.$$

For example, for H_3PO_4

$$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O$$

E = M/2

(vii) **Some other methods**

(a) *Hydrogen displacement method*

$$E = \frac{w \times 11200}{\text{Volume of } H_2 \text{ at NTP}}$$

(b) *Oxide formation method*

$$E = \frac{\text{Wt. of metal}}{\text{Wt. of oxygen}} \times 8$$

Weight of oxygen = weight of metal oxide – weight of metal

(c) *Chloride formation method*:

$$E = \frac{\text{Wt of metal}}{\text{Wt. of chloride}} \times 35.5$$

Weight of chloride = weight of metal chloride – weight of metal

(d) *Double decomposition methods*

$$\frac{\text{Eq. wt. of salt taken}}{\text{Eq. wt. of salt ppt.}} = \frac{\text{Wt. of salt taken}}{\text{Wt. of salt ppt.}}$$

(e) *Metal displacement methods*

$$\frac{E_1}{E_2} = \frac{W_1}{W_2}$$

Illustrations

9. Find the equivalent mass of H_3PO_4 in the reaction:

$$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O$$

Solution As in this reaction only two hydrogen atoms are replaced so its equivalent mass will be given by the following expression:

Equivalent mass of H_3PO_4

$$= \frac{\text{Molecular mass of } H_3PO_4}{2}$$

$$= \frac{98}{2} = 49$$

10. On heating 0.199 g of a metallic oxide in a current of hydrogen 0.045 g of water is formed. Find the equivalent weight of the metal.

Solution Weight of Metallic oxide = 0.199 g

As 16 g oxygen is present in = 18 g H_2O

So O_2 present in 0.045g $H_2O = \frac{16 \times 0.045}{18}$

$= 0.04$ g

Weight of metal = 0.199 – 0.04

= 0.159

Equivalent weight of metal $= \frac{0.159 \times 8}{0.04}$

= 31.8

11. 4.215 g of a metallic carbonate was heated in a hard glass tube and the CO_2 evolved was found to measure 1336 ml at 27°C and 700 mm pressure. What is the equivalent weight of the metal?

Solution Metallic carbonate → metallic oxide + CO_2

$$\text{Wt. of } CO_2 = \frac{44 \times 1120}{22400}$$

$= 2.2$ g

Wt. of metallic oxide = 4.125 – 2.2 = 2.015 g

By law of equivalent : $\frac{E + CO3"}{E + O"}$

$$= \frac{4.125}{2.015}$$

Hence, E (eq. wt. of metal) = 12.58

Chemical Formula

A chemical formula represents the combination of atoms of all the elements which makes up a compound. It represents the relative ratio of atoms of its constituent elements. In case of a compound, it represents one molecule, one mole, one gram molecular weight of the compound Example, S_8 represents one molecule of phosphorous and one mole of phosphorous.

Example, $CuSO_4.5H_2O$ represents one molecule, one mole and one gram molecular weight of hydrated copper sulphate.

Empirical and Molecular Formulas

Empirical Formula

It gives the simplest ratio of the number of atoms of different elements present in one molecule of a compound. It does not represent the actual number of atoms of different elements present in one molecule of the compound.

Calculation of the Empirical Formula: It involves the following steps, one by one:

(i) First determine the percentage composition by weight of each element present in the compound.

$$C\ \% = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of organic comp.}} \times 100$$

$$H\ \% = \frac{2}{18} \times \frac{\text{wt of } H_2O}{18 \text{ wt. of org. comp.}} \times 100$$

Duma's method

$$N\ \% = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at S.T.P}}{\text{wt. of Org. comp}} \times 100$$

OR

$$N\ \% = \frac{\text{Vol of } N_2 \text{ at S.T.P.}}{8 \times \text{Wt of Org comp.}}$$

Kjeldahl's Method

$$N\ \% = \frac{1.4 \times N \times V}{\text{Wt. of org. compound}}$$

Here N = normality of acid the used to neutralize ammonia

V = volume of acid the used to neutralize ammonia

(ii) Now the percentage of each element is divided by its atomic weight to get the relative number of atoms of each element.

(iii) These relative numbers obtained are divided by smallest number to get the simplest ratio numbers.

(iv) If the simplest ratio number is not a whole number it should be multiplied by a suitable integer to get a whole number.

(v) The ratio of these simple whole numbers gives the empirical formula of the compound.

Molecular Formula

It shows the actual number of atoms of different elements present in one molecule of the compound.

- $n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$.
- Molecular formula = empirical formula × n.
- Molecular weight of a substance can be determined by methods like Vapour density method, Elevation in boiling point method, Depression in freezing point methods etc.
- The molecular weight of volatile compounds is determined by Victor Mayer's method.
- Molecular Weight = 2 × Vapour density
- Molecular weight = empirical formula wt. × 'n'.
- For some compounds the molecular formula and empirical formula may be same also.

Illustrations

12. A certain organic compound was found to contain 33.6 % C, 5.6 % H and 49.6 % chlorine. Find the empirical formula of the organic compound.

Solution

Element	%	Atomic ratio	Simplest Ratio
C	33.8	33.8/12 = 2.8	2.8/0.7 = 4
H	5.6	5.6/1 = 5.6	5.6/0.7= 8
Cl	49.6	49.6/35.5 =1.4	1.4/0.7 =2
O	11.0	11/16 = 0.7	0.7/0.7=1

Thus $C_4H_8Cl_2O$ is the empirical formula of the compound.

13. A well-known antibiotic penicillin, contains C 57.49 %, H 5.39 %, N 8.39 5, S 9.58 %; the remainder being oxygen. Given that penicillin contains one atom of sulphur per molecule, calculate the molecular formula of the antibiotic.

Solution % C = 57.49

% H = 5.39

% N = 8.39

% S = 9.58

% O = 100 – (57.49 + 5.39 + 8.39 + 9.58)

= 19.15

Empirical formula

Element	%	Relative no. of atoms	Simplest Ratio
C	57.49	57.49/12 = 4.79	16
H	5.39	5.39/1 = 5.39	18
N	8.39	8.39/14 = 0.599	2
S	9.58	9.58/32 = 0.299	1
O	19.15	19.15/16 = 1.196	4

Empirical formula is $C_{16}H_{18}N_2SO_4$

As the given antibiotic contains only one atom of sulphur per molecule. The calculated empirical formula $C_{16}H_{18}N_2SO_4$, contains only one atom of sulphur. Hence the same is the molecular formula of the antibiotic.

14. A compound has molar mass of 147 g. It contains 49 % C and 2.72 % H. On Carius estimation, 2.561 mg of the compound gave 5 mg of AgCl. Find the empirical and molecular formula.

Solution

Element	%	Atomic ratio	Simplest Ratio
C	49	49/12 = 4.1	3
H	2.72	2.72/1 = 2.72	2
Cl	$\frac{(35.5/143.5) \times 5 \times 100}{2.581}$		
	= 47.9	47.9/35.5 = 1.34	1

C_3H_2Cl is the empirical formula.

n = 147/73.5 = 2

The molecular formula is $C_6H_4Cl_2$.

15. Methyl orange, an acid-base indicator, is the sodium salt of an acid that contains C, H, N, S and O. Quantitative analysis gave 51.4 % C, 4.3 % H, 12.8 % N, 9.8 % S and 7.0 % Na. What is the empirical formula of methyl orange?

Solution % C = 51.4

% H = 4.3

% N = 12.8

% S = 9.8

% Na = 7.0

% O = 14.7

Element	%	Relative no. of atoms	Simplest Ratio
C	51.4	51.4/12 = 4.28	14
H	4.3	4.3/1 = 4.3	14
N	12.8	12.8/14 = 0.914	3
S	9.8	9.8/32 = 0.306	1
Na	7.0	7/23 = 0.304	1
O	14.7	14.7/16 = 0.918	3

So empirical formula is $C_{14}H_{14}N_3SO_3Na$

Expression of Concentration of Solution

The solution whose concentration is exactly known is referred as standard solution and such solutions are prepared in volumetric or standard flask.

Concentration

It is the amount of solute present in one litre of solution. It is denoted by C or S.

$$C \text{ or } S = \frac{\text{Weight of solute in gram}}{\text{Volume in litre}}$$

$$C = N \times E$$

Here N = normality

E = Eq. wt.

Molarity

It is the number of moles or gram moles of solute dissolved per litre of the solution. Molarity is denoted by 'M'.

$$M = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{volume in litre}}$$

- When molarity of a solution is one, it is called a molar solution. and when it is 0.1, solution is called decimolar solution.

- Molarity depends upon temperature and its unit is mol/litre.

$$M_1V_1 = M_2V_2$$

- On dilution water added = $V_2 - V_1$
- When the solution of two different substances react together then

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Here M, V, n are molarity, volume and number of molecules taking part in a reaction respectively.

- When a mixture of different solutions having different concentrations are taken the molarity of the mixture is calculated as follows:

$$M = \frac{M_1V_1 + M_2V_2 \ldots\ldots}{V_1 + V_2 \ldots\ldots}$$

- When density and % by weight of a substance in a solution are given molarity is find as follows:

$$M = \frac{\%\text{ by weight} \times d \times 10}{\text{Molecular weight}}$$

Here d = density

Molality

It is the number of moles or gram moles of solute dissolved per kilogram of the solvent. It is denoted by 'm'.

$$m = \frac{\text{Weight of solute in gram}}{\text{Molar mass} \times \text{wt. of solvent in Kg}}$$

- If molality is one solution, it is called molal solution.
- One molal solution is less than one molar solution.
- Molality is preferred over molarity during experiments as molality is temperature independent while molarity is temperature dependent.

Normality

It is the number of gram equivalents of solute present in one litre of the solution and it is denoted by 'N'.

$$N = \frac{\text{Weight of solute in gram}}{\text{Equivalent mass} \times \text{volume in litre}}$$

- When normality of a solution is one, the solution is called normal solution and when it is 0.1, the solution is called deci-normal solution.

Normality Equation

$$N_1V_1 = N_2V_2$$

- Volume of water added = $V_2 - V_1$

Here V_2 = volume after dilution

V_1 = volume before dilution

- When density and % by weight of a substance in a solution are given normality is find as follows:

$$N = \frac{\%\text{ by weight} \times d \times 10}{\text{Equivalent weight}}$$

Here d = density of solution

- When a mixture of different solutions having different concentrations are taken the normality of the mixture is calculated as follows:

$$N = \frac{N_1V_1 + N_2V_2 \ldots\ldots}{V_1 + V_2 \ldots\ldots}$$

- In case of acid base neutralization the normality of the resulting solution

$$N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

- To find weight of substance

$$W = \frac{NEV}{1000}$$

Relation between Normality and Molarity

$N \times \text{Eq wt.} = \text{molarity} \times \text{molar mass}$

$N = \text{molarity} \times \text{valency}$

$N = \text{molarity} \times \text{number of } H^+ \text{ or } OH^- \text{ ion.}$

Mole fraction

It is the ratio of moles of one component to the total number of moles present in the solution. It is expressed by X for example, for a binary solution two component A and B.

$$X_A = \frac{n_A}{n_A + n_B}$$

$$X_B = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

Mole fraction of solute $(X_A) = \frac{n_2}{n_1 + n_2}$.

or

X_2

Here n_1, n_2 represent moles of solvent and solute respectively.

Mole fraction does not depend upon temperature as both solute and solvent are expressed by weight.

Illustrations

16. Calculate the volume of water to be added to a 100 ml of 5N solution to make it 0.01 N.

Solution According to normality equation,

$N_1 V_1 = N_2 V_2$

$0.01 \times V_1 = 5 \times 100$

$V1 = \frac{5 \times 100}{0.01} = 50000$ ml

So volume of water to be added

$= 50000 - 100$

$= 49900$ ml

$= 49.9$ l

17. 10 ml of 0.02 M $KMnO_4$ is required to oxidize 20 ml of oxalic acid of certain strength. 25 ml of the same oxalic acid is required to neutralize 20 ml of NaOH of unknown strength. Find the amount of NaOH in a litre of the solution.

(Molecular weight of NaOH = 40)

Solution In acidic medium

1 M $KMnO_4$ = 5 N $KMnO_4$

0.02 M $KMnO_4$ = 0.1 N $KMnO_4$

According to normality equation,

$N_1 V_1$ ($KMnO_4$) = $N_2 V_2$ (Oxalic acid)

$0.1 \times 10 = N_2 \times 20$

$N_2 = \frac{10 \times 0.1}{20} = 0.05$ N

Again

$N_1 V_1$ (Oxalic acid) = $N_2 V_2$ (NaOH)

$0.05 \times 25 = N_2 \times 20$

$N_2 = \frac{0.05 \times 25}{20} = 0.0625$ N

As $S = N \times E$

So $S = 0.0625 \times 40 = 2.5$ g L^{-1}

18. 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 neutralized by 95.0 cm^3 of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid?

Solution Normality of acid $= \frac{39}{82/n \times 1}$

Normality of NaOH $= \frac{40}{40} \times \frac{1000}{1000} = 1$

Now, Mew. of acid = Meq. of NaOH

$\frac{39\,n}{82} \times 100$

$= 1 \times 95$

So n = 2; Hence here acid is dibasic.

19. What volume at NTP of ammonia gas will be required to be passed into 30 ml of H_2SO_4 solution bring down the acid normality to 0.2 N?

Solution Meq. of original $H_2SO_4 = 30 \times 1 = 30$

Meq. of H_2SO_4 after passing $NH_3 = 30 \times 0.20 = 6$

Meq. of H_2SO_4 lost $= 30 - 6 = 24$

Meq. of NH_3 passed = Meq. of H_2SO_4 lost

$\frac{w}{17} \times 1000 = 24$

$w_{NH_3} = 0.408$ g

Volume of NH_3 at STP $= \frac{22.4 \times 0.408}{17}$

$= 0.5376$ litre

$= 537.6$ ml

20. What volume of a solution of hydrochloric acid containing 73 g of acid litre would suffice for

the exact neutralization of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water?

Solution $Na + H_2O \rightarrow NaOH + \frac{1}{2} H_2$

$NaOH + HCl \rightarrow NaCl + H_2O$

Thus, meq. of Na = Meq. of NaOH formed = Meq. of HCl used

$$\frac{0.46}{23} \times 1000 = \frac{73}{36.5} \times V$$

(Meq. of HCl = N × V)

= 10 ml

Limiting Reagent

When two reagents or reactants react to give various product then the number of moles of product form according to the reagent or reactant which is completely consumed during the reaction. The reagent or reactant which is completely consumed during the reaction is called limiting reagent that is, the reagent which gives the least number of moles of the product is called limiting reagent.

Illustrations

21. 2 g H_2 reacts with 10 g O_2 to form water. How much water is formed?

Solution Hydrogen reacts with oxygen as follows:

$2H_2 + O_2 \rightarrow 2H_2O$

Number of moles of $H_2 = \frac{2}{2} = 1$ moles

Number of moles of $O_2 = \frac{10}{32} = 0.3125$ moles

As 2 moles of H_2 reacts with 1 mole of O_2 to form 2 moles of H_2O so, for 1 mole of H_2 only 0.3125 moles of O_2 is present. Thus O_2 is the limiting reagent here.

As 1 mole of O_2 gives 2 moles of H_2O.

So 0.3125 mole of O_2 gives $\frac{2}{1} \times 0.3125$

= 0.625 moles of H_2O

Weight of H_2O formed = Moles × Mol. weight

= 0.625 × 18

= 11.25 g H_2O

Chemical Equations and Numerical Calculations

- A balanced chemical reaction represents a stoichiometric equation.
- In a stoichiometric equation, the coefficient of reactants and products represents their stoichiometric amounts.
- The reactant which is completely used during an irreversible reaction is called limiting reagent while the reactant left is called excess reagent.

  For example, if 20 g of calcium is burnt in 32 g of O_2 then Ca is limiting reagent while O_2 is excess reagent.
- Stoichiometric calculations help in finding whether the production of a particular substance is economically cheap or not.
- These stoichiometric calculations are of following four types:
  (a) Calculations based on weight: weight relationship
  (b) Calculations based on weight: volume relationships.
  (c) Calculations based on volume: volume relationships
  (d) Calculations based on weight: volume – energy relationships
- If the amount of the reactant in a particular reaction is known, then the amount of the other substance needed in the reaction or the amount of the product formed in the reaction can be found out.
- For stoichiometric calculations, the following steps must be considered:
  (a) A balanced chemical equation using chemical formulas of reactants and products must be written.
  (b) Here the coefficients of balanced chemical equation provide the mole ratio of the reactants and products.
  (c) This mole ratio is convertible into weight – weight ratio (w/W), weight –volume (w/V) ratio or volume –volume (v/V) ratio. These are called percentage by weight, percentage by volume and percentage by strength respectively.

Gravimetric Analysis

It is an analytical technique based on the measurements of mass of solid substances or the volume of the gaseous species. It is also divided into three categories:

(i) Mass-Mass (weight-weight) relation

(ii) Mass-Volume relation

(iii) Volume-Volume relation

(i) Problems Involving Mass–Mass or Weight–Weight Relationship

This relationship relates the mass of a reactant or product with the mass of another reactant or product.

For solving such problems, one should proceed according to the following instructions given below:

- First, write down the balanced equation to represent the chemical change.
- Now write the number of moles below the formula of the reactants and product. We must also write the relative weights of the reactants and products (which are calculated from the respective molecular formula) below the respective formula.
- Finally, apply the unitary method to calculate the unknown factor(n or s).

Illustrations

22. Find weight of iron which will be converted into its oxide by the action of 18 g of steam on it.

Solution $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$

$3 \times 56 \quad 4 \times 18$

As by 72 g steam the weight of Fe oxidized = 168 g

So by 18 g " " " " "

$= \frac{168 \times 18}{72} = 72$ g

23. 0.9031 g of NaCl and KCl on reaction with H_2SO_4 gave 1.0784 g of a mixture of Na_2SO_4 and K_2SO_4. Find the percentage composition of the compound.

Solution For X g NaCl = $\frac{142\,X}{117}$

For (0.9031 – X) g KCl = $\frac{174}{149}(0.9031 - X)$

that is, $\frac{142}{117}X + \frac{174}{149}(0.9031 - X) = 1.0784$ g

On solving, we get X = 0.518

Percentage of NaCl = 57.36 %

Percentage of KCl = 42.64 %

24. The mineral haematite is Fe_2O_3. Haematite ore contain unwanted material called gangue in addition of Fe_2O_3. If 5.0 kg of ore contains 2.78 kg of Fe, what per cent of ore is Fe_2O_3?

Solution $2Fe \equiv Fe_2O_3$

2×55.85 g $\quad$ 159.7 g

As 2×55.85 g Fe is present in 159.7 g Fe_2O_3

So 2.78 kg Fe is present in

$= \frac{159.7 \text{ g} \times 2.78 \text{ kg}}{2 \times 55.85 \text{ g}}$

$= 3.97$ kg Fe_2O_3

As 5 kg ore contains = 3.97 kg Fe_2O_3

So 100 kg ore contains = $\frac{3.97 \times 100}{5}$

$= 79.4$ kg Fe_2O_3

Thus % of Fe_2O_3 in ore = 79.4 %

25. 0.256 g sample of iron alloy (a mixture of iron with other elements) was dissolved in hydrochloric acid to give a solution of Fe^{2+} ion. This solution titrated to the end point with 35.6 ml of 0.1 N $KMnO_4$, which oxidized Fe^{2+} to Fe^{3+}. What is the mass percentage of iron in the mixture?

Solution Reaction of MnO_4^- and Fe^{2+} in acidic medium is as follows:

$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

So $MnO_4^- \equiv 5Fe^{2+}$

or 5000 mL N $KMnO_4 = 5 \times 55.8$ g of Fe

35.6 mL of 0.1 N $KMnO_4$

$= \frac{5 \times 55.8 \times 35.6 \times 0.1}{5000}$

$= 0.2$ g Fe

As 0.256 g alloy contains = 0.2 g Fe

So 100 g iron alloy contains = $\frac{0.2 \times 100}{0.256}$

= 78.125 %

(ii) Problems Involving Mass–Volume or Weight–Volume Relationship

This relationship relates the mass of a reactant or product with the volume of another gaseous reactant or product involved in a chemical reaction.

For example,

Weight of a solid substance can be compared with the volume of gases with the help of the fact that 1 mole or 1 gram molecule of a gas occupies 22.4 litres or 22400 c.c. at N.T.P. So in brief, the weight-volume relationship can be represented as follows:

$$Ca + 2HCl \rightarrow CaCl_2 + H_2$$

By mole	1	2	1	1
By amu	40	73	113	2
By gm.wt.	40 g	73 g	113 g	2g
By wt.	40 g	73 g	113 g	22.4
or vol.				lit at NTP.

For solving such problems one should proceed according to the following instructions given below:

- First, write down the relevant balanced chemical equation (s).
- Now write the weights of various solid reactants and products.
- Gases are normally expressed in terms of volumes. In case the volume of the gas is measured at the room temperature and pressure (that is, any condition other than NTP), convert it into N.T.P. by applying gas laws.
- The volume of a gas at any temperature and pressure can be converted into its weight an vice versa by using this relation,

  PV = (g/M) × RT

  Here g is weight of gas, M is molecular weight of gas and R is gas constant.
- Finally, calculate the unknown factor (n or s) by unitary method.

REMEMBER

One should not forget that if other conditions are not mentioned, the chemical reaction that is assumed to occur at N.T.P. that is, at 0°C (273 K) temperature and 760 mm (1 atmospheric) pressure.

Illustrations

26. A mixture of aluminium and zinc weighing 1.67 grams was completely dissolved in acid and the evolved 1.69 litres of hydrogen gas measured at 273 K and one atmosphere pressure. What was the mass of aluminium in the original mixture?

Solution Let the mass of aluminium in the sample be 'A' g. The mass of Zn = (1.67 – A) g

The volume of H_2 at N.T.P. given by Al

$= \frac{3 \times 22.4 \times A}{2 \times 27}$ L

The volume of H_2 at NTP given by Zn

$= \frac{(1.67 - A)\ 22.4}{65.4}$ L

$$\frac{3 \times 22.4 \times A}{54} + \frac{(1.67 - A)\ 22.4}{65.4} = 1.69$$

$$142.2 \times A = 176.26$$

$$A = 1.248 \text{ g}$$

27. In a titration experiment, 23.05 ml of 0.100 N NaOH was required to neutralize 10.00 ml of a solution of H_2SO_4 of unknown strength. What was the normality of the acid solution?

Solution In a titration using NaOH and H_2SO_4

Meq of NaOH = Meq of H_2SO_4

The meq. of NaOH used in the titration

$$23.05 \text{ ml NaOH} \times 0.100 \frac{\text{meq of NaOH}}{\text{ml NaOH}}$$

$$= 2.31 \text{ meq. NaOH}$$

The normality of the H_2SO_4 solution

$$\frac{2.32 \text{ meq } H_2SO_4}{10.00 \text{ ml } H_2SO_4} = 0.231 \frac{\text{meq. } H_2SO_4}{\text{ml } H_2SO_4}$$

$$= 0.231 \text{ N } H_2SO_4$$

28. A 0.311 g sample of crude NaOH when dissolved in water required 46.1 ml of 0.122 N H_2SO_4 to neutralize the NaOH in the sample. Calculate the per cent of NaOH in the sample.

Solution In a titration using NaOH and H_2SO_4

Meq of NaOH = meq. of H_2SO_4

The meq of H_2SO_4

$$0.122 \frac{\text{meq } H_2SO_4}{\text{ml solution}} \times 46.1 \text{ ml solution}$$

$$= 5.62 \text{ meq } H_2SO_4$$

The 5.62 meq. of NaOH

$$5.62 \text{ meq NaOH} \times 0.040 \frac{\text{g NaOH}}{\text{meq. NaOH}} .$$

$$= 0.225 \text{ g NaOH}$$

The per cent of NaOH in the sample is as follows:

$$\frac{0.225 \text{ g NaOH}}{0.311 \text{ g sample}} \times 100 = 72.3 \text{ \% NaOH.}$$

29. A volume of 22.5 ml of 2.50 N NaOH was required to neutralize 10.5 ml of a solution of H_2SO_4 of unknown strength. The density of the H_2SO_4 solution was 1.16 g per ml. Calculate the per cent by weight of H_2SO_4 in the solution.

Solution In a titration using NaOH and H_2SO_4

Meq. of NaOH = meq. of H_2SO_4

The meq. of NaOH:

$$2.50 \frac{\text{meq NaOH}}{\text{ml solution}} \times 22.5 \text{ ml solution}$$

$$= 56.3 \text{ meq NaOH}$$

The 56.3 meq. of H_2SO_4:

$$56.3 \text{ meq. } H_2SO_4 \times 0.0491 \frac{\text{g } H_2SO_4}{\text{meq. } H_2SO_4}$$

$$= 2.76 \text{ g } H_2SO_4$$

The weight of the 10.5 ml of H_2SO_4:

$$10.5 \text{ ml} \times 1.16 \frac{\text{g}}{\text{ml}} = 12.2 \text{ g}$$

The per cent H_2SO_4 is

$$\frac{2.76 \text{ g } H_2SO_4}{12.2 \text{ g solution}} \times 100$$

$$= 22.6 \text{ \% } H_2SO_4 \text{ by weight}$$

30. If required 33.6 ml of a 0.100 N $K_2Cr_2O_7$ solution to oxidize the Fe^{2+} to Fe^{3+} in 21.6 ml of a solution of $FeSO_4$ of unknown strength.

Solution The equation is as follows:

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ Fe^{2+} \rightarrow$$

1.00 mole 6.00 moles

6.00 g-eq wt 6.00 g-eq wt

$$2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

According to this equation, 1.00 g-eq wt of Fe^{2+} ion will originate from 1.00 g-eq wt of $FeSO_4$, we get meq. of $Cr_2O_7^{2-}$ = meq. of Fe^{2+} = meq. of $FeSO_4$

meq. of $Cr_2O_7^{2-}$ is:

$$0.100 \frac{\text{meq } Cr_2O_7^{2-}}{\text{ml solution}} \times 33.6 \text{ ml solution}$$

$$= 3.36 \text{ meq. } Cr_2O_7^{2-}$$

The normality of the $FeSO_4$ solution is:

$$\frac{3.36 \text{ meq. } FeSO_4}{21.6 \text{ ml solution}} = 0.156 \text{ N } FeSO_4$$

As $FeSO_4$ solution is 0.156 N with respect to Fe^{2+} ion, and the number of mg Fe^{2+} per ml is as follows:

$$0.156 \frac{\text{meq } Fe^{2+}}{\text{ml solution}} \times 55.85 \frac{\text{mg } Fe^{2+}}{\text{meq. } Fe^{2+}} .$$

$$= 8.71 \frac{\text{mg } Fe^{2+}}{\text{ml solution}} .$$

31. What should be the weight of $NaNO_3$ to make 50 ml of an aqueous solution so that it contains 70 mg Na^+ ml^{-1}?

Solution Molecular mass of $NaNO_3 = 23 + 14 + 3 \times 16$

$$= 85 \text{ g mol}^{-1}$$

As 23 mg Na is present in 85 mg of $NaNO_3$

So 70 mg Na is present in $\frac{85 \times 70}{23}$

$$= 258.7 \text{ mg } NaNO_3$$

As 1 ml solution contains 258.7 mg $NaNO_3$

So 50 ml solution contains

$$= \frac{258.7 \text{ mg} \times 50 \text{ ml}}{1 \text{ ml}}$$

= 13935 mg

= 13.935 g

(iii) Problems Based on Volume–Volume Relationship

This relationship relates the volume of gaseous reactant or product with the volume of another gaseous reactant or product involved in a chemical reaction. For solving such problems, one should proceed according to the following instructions given below:

- First write down the relevant balanced chemical equation.
- Now write down the volume of reactants and products below the formula to each reactant and product using the fact that one gram molecule of every gaseous substance occupies 22.4 litres at N.T.P.
- If volume of the gas is measured under particular or room temperature, convert it to N.T.P. with the help of ideal gas equation.
- Now use Avogadro's hypothesis "gases under similar conditions of temperature and pressure contain the same number of molecules". Thus under similar conditions of temperature and pressure, the volume of reacting gases are proportional to the number of moles of the gases in the balanced equation.

Example,

N_2 (g)	+	$3H_2$ (g)	→	$2NH_3$ (g)
1 mole		3 moles		2 moles
22.4 lit		3 × 22.4 lit		2 × 22.4 lit
1 volume		3 volumes		2 volumes
1x volume		3 × volume		2 × volumes

From the above equation, it is clear that 22.4 litres of N_2 will react with 3×22.4 litres of H_2 to form 2×22.4 litres of NH_3.

Illustrations

32. A mixture of HCOOH and $(COOH)_2$ is heated with concentrated H_2SO_4. The gas produced is collected and on its treatment with KOH solution the volume of the gas decreases by 1/6th. Calculate the molar ratio of two acids in the original mixture.

Solution

Reactions

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO\uparrow$$
a mole — a mole

$$H_2C_2O_4 \xrightarrow{H_2SO_4} H_2O + CO + CO_2$$
b mole — b mole — b mole

Total number of moles of CO and CO_2

= a + b + b = a + 2b

Total number of moles of CO_2 = b

So Mole fraction of CO_2 absorbed in KOH

$$= \frac{b}{a+2b}$$

$$\frac{b}{a+2b} = \frac{1}{6}$$

a = 4b

Thus ratio of HCOOH and $H_2C_2O_4$ is 4 : 1.

33. A gas mixture of 3 litre of produce (C_3H_8) and butane (C_4H_{10}) on complete combustion at 25°C produced 10 litre CO_2. Find out the composition of gas mixture

Solution $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$ (l)

$C_4H_{10} + 13/2\ O_2 \rightarrow 4CO_2 + 5H_2O$ (l)

Suppose×litre of C_3H_8 and y litre of C_4H_{10} are present in the mixture.

So $x + y = 3$ ----------(1)

As volume of CO_2 formed = 10 = CO_2 formed by C_3H_8 + CO_2 formed by C_4H_{10}

$10 = 3x + 4b$ ----------(2)

Solving Eqs. 1. and 2.

y = 1litre

x = 2litre

n-Factor or Valence Factor

It is very important for both redox reactions and non-redox reactions by which we can obtain following informations:

(i) It calculates the molar ratio of the species taking part in reactions that is, reactants. The reciprocal of n-factor's ratio of the reactants represents the molar ratio of the reactants.

Example, If A (having n-factor = a) reacts with B (having n-factor = b) then its n-factor's ratio is a : b, so molar ratio of A to B is b : a.

It can be represented as follows:

$$bA + aB \rightarrow \text{Product}$$

(n-factor = a) (n-factor = b)

(ii) $$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{n-factor}}$$

or

$$\frac{\text{Atomic weight}}{\text{n-factor}}$$

Calculation of n–Factor

Before calculating the n-factor of any of the reactant in a given chemical reaction we must have a clear idea about the type of reaction. The reaction may be any of these types:

(i) Acid base or neutralization reaction

(ii) Redox reaction

(iii) Precipitation or double decomposition reaction

(i) Acid–Base or Neutralization Reactions: As we know that according to the Arrhenius concept, "An acid provides H^+ ion(s) while a base provides OH^- ion(s) in neutralization these H^+ and OH^- ion/ions combines together".

The number of H^+ ion(s) and OH^- ion(s) represent n-factor for acid and base respectively, that is, basicity and acidity respectively.

Example,

$HX \rightarrow H^+ + Cl^-$

(n = 1) that is, monobasic acid

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

(n = 2) that is, dibasic acid

$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$

(n = 3) that is, tribasic acid

$KOH \rightarrow K^+ + OH^-$

(n = 1) that is, monoacidic base

$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$

(n = 2) that is, diacidic base

$Al(OH)_3 \rightarrow Al^{3+} + 3OH^-$

(n = 3) that is, triacidic base

(ii) Redox Reactions: These reactions involve oxidation and reduction simultaneously. Here exchange of electrons occurs. To find n-factor for oxidizing or reducing agent we must find out the change in oxidation state of these species.

Example (1) When only one atom undergoes oxidation or reduction

$$\overset{+3\times2}{C_2O_4^{2-}} \rightarrow \overset{+4\times2}{2CO_2}$$

n = 2

n-factor = | (+4) × 2 – (+3) × 2 | = 2

$$\overset{+6\times2}{Cr_2O_7^{2-}} \rightarrow \overset{+3\times2}{2Cr^{3+}}$$

n = 6

n-factor = | (+3) × 2 – (+6) × 2 | = 6

Example (2) For the salt which react in such a way that one atom undergoes change in oxidation state but appear in two product having same oxidation state.

$$\overset{+6\times2}{Cr_2O_7^{2-}} \rightarrow \overset{+3}{Cr^{3+}} + \overset{+3}{Cr^{3+}}$$

n-factor = | (+6) × 2 – (+3) × 2 | = 6

Example (3) For the salts which react in such a way that one atom undergoes change in oxidation state but appear in two product having different oxidation state.

$$\overset{+7}{3MnO_4^-} \rightarrow \overset{+2}{2Mn^{2+}} + \overset{+6}{Mn^{6+}}$$

= | 2 × (+2) – 2 × (+7) | + | 1 × (+6) – 1 (+7) |= | 4 – 14 | + | 6 – 7 | = 11

Hence n-factor = 11/3.

Example (4) For the salts which react in such a way that one atom undergoes change in oxidation state in

two products one with changed oxidation state from that of reactant and another having same oxidation state as that of reactant.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

Here, out of 14 moles of Cl^- (in HCl) only 6 moles of Cl^- are changing the oxidation state from –1 to 0 in the product Cl_2 while the oxidation state of remaining 8 Cl^- ions remains the same in HCl and $CrCl_3$. Hence the total number of moles of electrons lost by 14 moles of HCl is 6 here. So each mole of HCl takes up 6/14 that is, 3/7 moles of electrons and hence n-factor of HCl is 3/7.

Example (5) For the salt which react in such a way that two or more atoms undergoes change in oxidation states.

$$FeC_2O_4 \rightarrow Fe^{3+} + 2CO_2$$

Here, the oxidation state of Fe in this form +2 to +3 while that of C change from +3 to +4. Here n-factor can be find out by calculating the total change in oxidation state per mole of the salt. Here 1 mole of FeC_2O_4 have one of Fe^{2+} and one mole of $C_2O_4^{2-}$ so the total change in oxidation state is given as

$$= |1 \times (+2) - 1 \times (+3)| + |2 \times (+3) - 2 \times (+4)|$$

$$= 1 + 2 = 3$$

Hence n-factor of FeC_2O_4 is 3.

Example (6) Salts or compounds which undergo intramolecular redox reaction that is, in which an atom undergoes oxidation while another atom undergoes reduction. Here n-factor can be find out by knowing the balanced chemical reaction and considering only one process.

$$\overset{+5}{2}K\overset{(-2)}{Cl}O_3 \rightarrow 2K\overset{(-1)}{Cl} + 3\overset{(0)}{O_2}$$

In this reaction, oxidation atom is getting oxidized while chlorine atom is getting reduced so

n-factor of $KClO_3$ considering oxidation

$$= |3 \times (-2) - 3 \times (0)| = 6$$

n-factor of $KClO_3$ considering reduction

$$= |1 \times 5 - 1 \times (-1)| = 6$$

Example (7) Salts or compounds which undergo disproportion reaction that is, in which a single species undergoes oxidation as well as reduction. Here, n-factor can be found out by knowing the balanced chemical reaction and considering only one process.

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

Here out of these two H_2O_2 molecules shown by the reaction one mole of H_2O_2 is oxidized and one mole is reduced.

For oxidation reaction

$$\overset{(-1)\times 2}{H_2O_2} \rightarrow \overset{2\times 0}{O_2}$$

n-factor = $|2 \times 0 - (-1) \times 2| = 2$

For reduction reaction

$$\overset{(-1)\times 2}{H_2O_2} \rightarrow \overset{(-2)\times 2}{2H_2O}$$

n-factor = $|(-2) \times 2 - (-1) \times 2| = 2$

Hence n-factor of H_2O_2 in both oxidation and reduction reaction is same that is, 2.

In the disproportion reactions in which moles of compounds undergoing oxidation and reduction are not same like.

$$6X_2 + 12OH^- \rightarrow 10X^- + 2XO_3^- + 6H_2O$$

Here out of 6 moles of X_2, 5 moles of X_2 undergo reduction and accept 10 moles of electrons (oxidizing agent) while 1 mole of X_2 undergoes oxidation by loosing 10 moles of electrons (reducing agents)

$$X_2 \rightarrow 2X^{5+} + 10\ e^-$$

$$5X_2 + 10\ e^- \rightarrow 10\ X^-$$

$$\underset{(n=10)}{X_2} + \underset{(n=2)}{5X_2} \rightarrow \underset{(n=1)}{10X^-} + \underset{(n=5)}{2X^{5+}}$$

Reducing agent Oxidizing agent

Hence n-factor of X_2 acting as oxidizing agent is 2 and that X_2 acting as reducing agent has n-factor 10.

(iii) Precipitation or Double decomposition Reaction: It is the reaction in which there is no change in oxidation state for any atom. Here n-factor of the salt used in the reaction can be found out by multiplying the oxidation state of the cation or anion by the total number of atoms per molecule of the salt.

$BaCl_2 + K_2SO_4 \rightarrow BaSO_4 + 2KCl$

(n = 2) (n = 2)

For $BaCl_2$

n-factor = Oxidation state of Ba atom in $BaCl_2$×number of Ba atoms in one molecule of $BaCl_2$

= (+2) × 1 = 2

For K_2SO_4

n-factor = Oxidation state of K×number of K-atoms in one molecule of K_2SO_4

= (+1) × 2 = 2

Laws of Equivalence

According to law of equivalence, for each and every reactant and product,

Equivalents of each reactant reacted = Equivalents of each product formed.

Example,

Suppose the reaction is taking place as follows:

$P + Q \rightarrow R + S$

According to law of equivalence,

Equivalents of P reacted

= Equivalents of Q reacted

= Equivalents of R produced

= Equivalents of S produced

Equivalents of any substance

$$= \frac{\text{Weight of substance (in g)}}{\text{Equivalent weight}}$$

= Normality (N) × Volume (V) (In litre)

Normality (N) = n-Factor × Molarity (M)

Normality and molarity are temperature dependent. As on changing the temperature, the volume of solution changes, so normality and molarity change.

POAC (Principle of Atom Conservation) Method

For any chemical reaction, mole atom of any element remain conserved during the chemical reaction.

Illustrations

34. 2.68×10^{-3} moles of a solution containing an ion A^{n+} required 1.61×10^{-3} moles of MnO_4^- for the oxidation of A^{n+} to AO_3^- in an acidic medium. What is the value of n?

Solution As 1.61×10^{-3} M $KMnO_4$

$\equiv 2.68 \times 10^{-3}$ M solution of A^{n+}

$$\text{So M/5 } KMnO_4 = \frac{2.68 \times 10^{-3}\text{ M}}{1.61 \times 10^{-3}} \times \frac{\text{M}}{5}$$

= 0.33 M solution of A^{n+}

$$0.33\text{ M} = \frac{\text{M}}{5-\text{n}}.$$

$$5 - \text{n} = \frac{1}{0.33} = 3$$

n = 2

35. One g of impure Na_2CO_3 is dissolved in water and the solution is made upto 250 ml. To 50 ml of this made up solution, 50 ml of 0.1 N HCl is added and the mixture after shaking well required 10 ml of 0.16 N sodium hydroxide solution for complete neutralization. Calculate the per cent purity of the sample of Na_2CO_3.

Solution Strength of the Na_2CO_3 solution = 4 g L^{-1}

Suppose the normality of Na_2CO_3 solution = Nx

As after mixing Na_2CO_3 and HCl solution, NaOH solution is added so according to normality equation

$50 \times Nx + 0.16 \times 10 = 50 \times 0.1$

Nx = 0.068 N

Strength (g L^{-1}) = Normality × Equivalent mass

= $0.068 \times 53 = 3.6$ g L^{-1}

$$\text{So purity of } Na_2CO_3 = \frac{3.6 \times 100}{4}$$

= 90 %.

36. 0.257 g of a nitrogeneous compound was digested with sulphuric acid and then distilled with excess of strong alkali. The gas evolved was absorbed in 50 ml N/10 H_2SO_4. At the end of the experiment, the acid required 20.2 ml of

N/10 NaOH for neutralization. Determine the percentage of nitrogen in the substance.

Solution 23.2 ml of N/10 NaOH ≡ 23.2 ml of N/10 H_2SO_4

Volume of N/10 H_2SO_4 neutralized by NH_3

= 50 – 23.2 = 26.8 ml

26.8 ml of N/10 H_2SO_4 ≡ 26.8 ml of N/10 NH_3

≡ 26.8 ml of N/10 nitrogen

26.8 ml of N/10 nitrogen will contain

$\frac{14}{1000} \times \frac{26.8}{1000}$ g nitrogen

The mass of nitrogen was originally present in 0.257 g of the organic substance.

So % of nitrogen

$= \frac{14}{10} \times \frac{26.8}{1000} \times \frac{100}{0.257} = 14.6\ \%$

Volumetric Analysis (Titration)

Volumetric analysis is an analytical method used to find the concentration of a substance in a solution by adding exactly same number equivalents of some another substance present in a solution of known concentration (standard solution).

Volumetric analysis is also called titrimetric analysis. Here the substance whose solution is used to find the concentration of unknown solution is known as titrant and the substance whose concentration is to be calculated is known as titrate.

Types of Titration

Titration or volumetric analysis is of following types:

1. Simple titration
2. Double titration
3. Back titration
4. Iodimetric and iodometric titration

Simple Titration

The purpose of this titration is to find the concentration of an unknown solution by using the known concentration of another solution. Here a known volume the solution of unknown concentration is taken in a flask and the essential reagents are ended in it. Now the solution of known concentration is added from the burette in this solution till complete reaction occurs between them and the end point or equivalence point of the two reacting species are equal.

For example,

If we take two solution X and Y then at the end point

$N_X V_X = N_Y V_Y$

Here N_X = Normality of solution X

VX = Volume of solution X

N_Y = Normality of solution Y

V_Y = Volume of solution Y

Double Titration

This titration is used for specific compounds using various indicators. When the solution having NaOH and Na_2CO_3 is titrated using phenolphthalein indicator, at phenolphthalein end point following reactions take place:

$NaOH + HCl \rightarrow NaCl + H_2O$

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

Here Equivalents of NaOH + ½ equivalents of Na_2CO_3 = Equivalents of HCl ..... (i)

When methyl orange is used, Na_2CO_3 is converted into $NaCl + CO_2 + H_2O$

Equivalents of NaOH + Equivalents of Na_2CO_3 = Equivalents of HCl ..... (ii)

These titrations are carried out by using phenolphthalein and methyl orange in continuation as well as separately also.

We apply law of equivalents to find the percentage composition of the mixture with the help of equation (i) and (ii) if the HCl consumption in two different steps is given.

■ Phenolphthalein indicates end point when Na_2CO_3 is converted into $NaHCO_3$.

Back Titration

Suppose we have an impure solid substance 'O' weighing 'w' gm and we have to find the percentage purity of 'O' in the given sample. We have also

been given two solutions 'M', 'N' here the concentration of 'N' is known 'N_1' and that of 'M' is unknown. For a back titration to be carried out; the following conditions must be satisfied.

(i) Compounds 'M', 'N' and 'O' must be such that 'M' and 'N' can react with each other.

(ii) 'M' and pure 'O' can also react with each other however the impurities present in 'O' must not react with 'M'.

(iii) The product of 'M' and 'O' should not react with 'N'.

Now we will take a certain volume of 'M' in a flask but remember the equivalents of 'M' taken must be greater or equal to equivalents of pure 'O' in the sample and perform a simple titration using 'N'. Here we assume that the volume of 'N' use is 'V_1' litre.

Equivalents of 'N' reacted with 'M' = N_1V_1

Hence initial equivalents of 'M' = $N_1 V_1$

Now we will take same volume of 'M' in another flask however now 'O' is added in the flask. Here pure part of 'O' reacts with 'M' and excess of 'M' is back titrated with 'N'. Suppose the volume of 'N' consumed is V_2 litre here.

Equivalents of 'N' reacted with excess of 'M'

$= N_1 V_2$

Hence equivalent of 'M' in excess = $N_1 V_2$

that is, equivalent of 'M' reacted pure 'O'

$= (N_1 V_1 - N_1 V_2)$

Equivalents of pure 'O' = $(N_1 V_1 - N_1 V_2)$

Suppose the n-factor of 'O' in its reaction with 'M' is 'a' then the moles of pure 'O'

$$= \frac{(N_1 V_1 - N_1 V_2)}{a}$$

Hence mass of pure 'O'

$$= \frac{(N_1 V_1 - N_1 V_2)}{a} \times \text{Molar mass of 'O'}$$

Percentage purity of 'O'

$$= \frac{(N_1 V_1 - N_1 V_2)}{a} \times \frac{\text{Molar mass of 'O'}}{w} \times 100$$

Iodimetric and Iodometric Titrations

When in redox titrations iodine is used as an oxidizing agent these titration are called iodine titration. These are of two types:

Iodimeric Titration

In such titrations iodine solution is used as an oxidant and iodine is directly titrated against a reducing agent. This type of titrations are used for the determination of strength of reducing agents like sulphides, arsenides, thiosulphates etc., by titrating them against a standard solution of iodine.

This type of titration involves free iodine. Here iodine solution is treated with known sodium thiosulphate solution having a normality, N and volume V litre.

$$I_2 + \underset{(n=2)}{2Na_2S_2O_3} \rightarrow \underset{(n=1)}{2NaI} + Na_2S_4O_6$$

Equivalents of I_2 = Equivalents of $Na_2S_2O_3$ used

$= N \times V$

$$\text{Moles of } I_2 = \frac{N \times V}{2}$$

$$\text{Mass of free } I_2 \text{ in the solution} = \left(\frac{N \times V}{2} \times 254\right) \text{ g}$$

Iodometric Titration

It is an indirect method of estimation of iodine. In this titration an oxidizing agent is used to liberate from iodine solution and the librated iodine is treated with a standard solution of a reducing agent added from a burette. Here a neutral or an acidic solution of an oxidizing agent is used and the amount of liberated I_2 is equal to the quantity of this oxidizing agent.

These titrations are used to determine the concentration of $K_2Cr_2O_7$, $KMnO_4$, $CuSO_4$, Ferric ions, H_2O_2 etc.

Oxidizing agent (X) + KI $\rightarrow$ I_2 + reduced state of oxidant

$\downarrow$ $2Na_2S_2O_3$

$2NaI + Na_2S_4O_6$

Equivalents of (X) = Equivalents of I_2 = Equivalents of $Na_2S_2O_3$ used = N × V

Equivalents of I_2 liberated from KI = N × V

Equivalents of (X) = N × V

Let the n-factor of (X) in its reaction with KI be x, then

Mass of (X) consumed = $\frac{N \times V}{x} \times MX$

(Here M_X is the molar mass of (X)).

REMEMBER

$I_2 + KI \rightarrow KI_3$

(complex soluble in water and provide K^+ and I_3^-)

Illustrations

37. How many mL of a 0.05 M $KMnO_4$ solution are required to oxide 2.0 g of $FeSO_4$ in a dilute solution (acidic)?

Solution $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow$

$10 \times 151.8 \quad 2 \times 158$

$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

10×151.8 g of $FeSO_4$ require $KMnO_4 = 2 \times 158$ g

2 g of $FeSO_4$ will require $KMnO_4 = \frac{2 \times 158 \times 2}{10 \times 151.8}$

Suppose V ml of $KMnO_4$ solution (0.05 M) is required .

Amount of $KMnO_4$ in this solution

$= \frac{158 \times 0.05}{1000} \times V$

Thus, $\frac{158 \times 0.05 \times V}{1000} = \frac{2 \times 158 \times 2}{10 \times 151.8}$

$V = 52.7$ ml

38. 0.1 M $KMnO_4$ is used for the following titration. What volume of the solution in mL will be required to react with 0.158 g of $Na_2S_2O_3$?

$S_2O_3^{2-} + MnO_4^- + H_2O \rightarrow$

MnO_2 (s) + SO_4^{2-} + OH^- (not balanced)

Solution $S_2O_3^{2-} \rightarrow 2SO_4^{2-}$

Change in oxidation number of sulphur per molecule of $S_2O_3^{2-}$

$= 2 \times (6 - 2) = 8$

Change in oxidation number of Mn per molecule of MnO_4^-

$= 7 - 4 = 3$

No. of moles in 0.158 g of $Na_2S_2O_3$

$= \frac{0.158}{158} = 1 \times 10^{-3}$

No. of equivalents $= 8 \times 10^{-3}$

Normality of 0.1 M $KMnO_4$ solution

$= 0.1 \times 3 = 0.3$

Suppose V ml of $KMnO_4$ is required then

$\frac{V}{1000} \times 0.3 = 8 \times 10^{-3}$

So $V = \frac{8}{0.3} \times 10^{-3} \times 10^3$

$= 26.7$ ml

39. (a) Give a half-equation for the oxidation of the ethanedioate ion, $C_2O_4^{2-}$ (aq), to carbon dioxide CO_2 (g).

(b) Give a half equation for the reduction of the manganate (VII) ion, MnO_4^- (aq), to manganese (II) ions, Mn^{2+} (aq), in acidic conditions.

(c) Calculate the volume of an acidified solution of 0.02 M potassium manganate (VII), $KMnO_4$, which would be needed to oxidize 100 cm^3 of a saturated solution of magnesium ethanedioate, MgC_2O_4.

Solubility of magnesium ethanedioate at 20°C is 9.3×10^{-3} mol dm^{-3}.

Solution (a) $C_2O_4^{2-}$ (aq) $\rightarrow 2CO_2$ (g) + $2e^-$

(b) MnO_4^- (aq) + $8H^+$ (aq) + $5e^- \rightarrow$

Mn^{2+} (aq) + $4H_2O$ (l)

(c) $5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 10CO_2(g) + 8H_2(l) + 2Mn^{2+}(aq)$

100 cm³ of saturated MgC_2O_4 solution at 20°C contains 9.3×10^{-4} mol.

According to the equation,

As 5 mol of $C_2O_4^{2-}$ react with 2 mol MnO_4^-.

So 9.3×10^{-4} mol of $C_2O_4^{2-}$ react with

$$\frac{2 \times 9.3 \times 10^{-4}}{5} \text{ mol}$$

As 1000 cm³ of 0.02 M MnO_4^- contains 0.02 mol MnO_4^-.

So $\frac{1000 \times 2 \times 9.3 \times 10^{-4}}{0.02 \times 5}$ cm³

of 0.02 M MnO_4^-

contains $\frac{2 \times 9.3 \times 10^{-4}}{5}$ mol

= 18.6 cm³

40. A solution of arsenic (III) oxide containing 0.248 g required 50 cm³ of acidified potassium manganate (VII) solution (0.02 mol dm^{-3}) for complete oxidation. What is the oxidation state of arsenic in the product? [A_r (O) = 16, A_r (As) = 75]

Solution $As^{3+}(aq) \rightarrow As^{n+}(aq) + (n-3)e^-$

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

$5As^{3+}(aq) + (n-3)\,MnO_4^-(aq) + 8(n-3)H^+(aq) \rightarrow (n-3)\,Mn^{2+}(aq) + 4(n-3)H_2O(l) + 5As^{n+}(aq)$

Number of moles $As_2O_3 = \frac{0.248}{150 + 48}$.

= 0.00125 moles

Number of moles As^{3+} = 0.0025 moles

50 cm³ of potassium permanganate (VII) (0.02 mol dm^{-3}) contains

$\frac{50 \times 0.02}{1000}$ moles

= 0.001 moles potassium permanganate (VII)

As 0.0025 moles As^{3+} reacts with 0.001 mole MnO_4^-

So 2.5 mole As^{3+} reacts with 1 mole MnO_4^-

In this equation,

Ratio $\frac{2.5}{1} = \frac{5}{n-3}$.

Oxidation state of arsenic in the product = +5.

Volume Strength of H_2O_2 Solution

The concentration of H_2O_2 is usually represented in terms of volume, If a sample of H_2O_2 is labelled as 'X' volume, it means that 1 volume of H_2O_2 solution gives 'X' volumes of O_2 gas at STP on complete decomposition.

Consider the decomposition of H_2O_2 as

$$2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$$

2×34 g 22.4 L at STP

As 22400 ml of O_2 gas is liberated by 68 g of H_2O_2 solution

So X ml of O_2 gas will be liberated by

$$= \frac{68\,X}{22400} = \frac{17\,X}{5600} \text{ g of } H_2O_2$$

It means that 17X/5600 g of H_2O_2 will be present in 1 ml of solution.

1000 ml of solution contains H_2O_2

$$= \frac{17X}{5600} \times 1000 = \frac{17\,X}{5.6}$$

Strength (g L^{-1}) = Normality × Equivalent wt.

$\frac{17X}{5.6} = N \times \frac{34}{2}$ (n-factor of H_2O_2 = 2)

$X = 5.6 \times N$

that is, **Volume strength of H_2O_2 = 5.6 × Normality**

Illustrations

41. The label on a H_2O_2 bottle reads as 10 Vol. Find the concentration of the H_2O_2%.

Solution $2H_2O_2 \rightarrow 2H_2O + O_2$

10 vol. means 1 vol H_2O_2 = 10 ml O_2

1 g $H_2O_2 = \frac{22400}{68}$ = 329 ml

1 litre of 10 vol. means = 10000 ml of O_2

Weight of H_2O_2 to give 10000 ml

$= \frac{1}{329} \times 10000 = 30.4$ g

Conc. = 30.4 g/lit

Conc. % = $30.4 \times \frac{100}{1000} = 3.04$ %

Percentage Labelling of Oleum

Oleum or fuming sulphuric acid contains SO_3 gas dissolved in sulphuric acid. When water is added to oleum, SO_3 reacts with H_2O to form H_2SO_4 as a result mass of the solution increases.

$SO_3 + H_2O \rightarrow H_2SO_4$

The total mass of H_2SO_4 obtained by diluting 100 g of sample of oleum with desired amount of water, is equal to the percentage labelling of oleum.

% labelling of oleum = Total mass of H_2SO_4 present in oleum after dilution.

= mass of H_2SO_4 initially present + mass of H_2SO_4 produced on dilution.

Suppose the mass of oleum sample be 100 g, which on dilution becomes 109 g. This implies that 9 g of H_2O was added.

$SO_3 + H_2O \rightarrow H_2SO_4$

Moles of H_2O added = 9/18 = Moles of SO_3 present in oleum sample.

Mass of SO_3 in oleum = $\frac{9}{18} \times 80 = 40$ g

Thus, oleum sample contained 40 % SO_3 and 60 % H_2SO_4.

Illustrations

42. Find the percentage of free SO_3 in an Oleum sample which is labelled 112 % H_2SO_4.

Solution Oleum = $H_2SO_4 + SO_3 = H_2S_7O_7$

If initial weight of labelled $H_2S_2O_7$ = 100 gm

Weight of H_2SO_4, after dilution = 112

Wt. of H_2O = 12 gm

Moles of H_2O = moles of $SO_3 = \frac{12}{18} = 0.66$

Wt. of SO_3 $= 0.66 \times 80 = 52.8$

$$\% \text{ of } SO_3 = \frac{\text{Wt. of } SO_3 \times 100}{100}$$

$= 52.8$ %

Hardness of Water

The hardness of water is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium. Bicarbonates causes temporary hardness while chlorides and sulphates causes permanent hardness. The extent of hardness is called degree of hardness. It is defined as the number of parts by weight of calcium carbonate present in one million parts by weight of water that is, in ppm (milligram per litre) of $CaCO_3$.

$$\text{Hardness of water} = \frac{\text{gm of calcium carbonate}}{10^6 \text{ gm of water}}$$

Illustrations

43. 50 litres of water containing $Ca(HCO_3)_2$ when converted into soft water required 22.2 g $Ca(OH)_2$. Calculate the amount of $Ca(HCO_3)_2$ per litre of hard water.

Solution Reaction

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$

162 g 74 g

As 74 g $Ca(OH)_2$ reacts with 162 g $Ca(HCO_3)_2$

So 22.2 g $Ca(OH)_2$ will react with

$= \frac{162 \times 22.2}{74}$

$= 48.6$ g $Ca(HCO_3)_2$

As 50 L water contains = 48.6 g $Ca(HCO_3)_2$

So 1 L water contains = $\frac{48.6}{50}$

$= 0.972$ g L^{-1}

44. One litre of a sample of hard water contains 0.9 mg of $CaCl_2$ and 0.9 mg of $MgCl_2$. Find the total hardness in terms of parts of $CaCO_3$ per 10^6 parts of water by mass.

Solution Mol. mass of $CaCl_2$ = 111

Mol. mass of $MgCl_2$ = 95

111 g of $CaCl_2$ ≡ 100 g of $CaCO_3$

0.9 mg of $CaCl_2 \equiv \frac{100}{111} \times 0.9$ mg of $CaCO_3$

= 0.81 mg of $CaCO_3$

95 g of $MgCl_2$ ≡ 100 g of $CaCO_3$

0.9 g of $MgCl_2 \equiv \frac{100}{95} \times 0.9$ of $CaCO_3$

= 0.94 mg of $CaCO_3$

Thus, one litre of hard water contains (0.81 + 0.94) = 1.75 mg of $CaCO_3$

One litre of water 10^3 g = 10^6 mg

Degree of hardness = 1.75 ppm

Enhance Your Knowledge

- 1 mole of $H_2O \neq 22400$ ml or cc. of H_2O (since it is liquid)

  1 mol of H_2O = 18 cc. of H_2O (as density of H_2O = 1gm/cc)

- Mass of one mole of e^- = mass of one $e^- \times N_A$

  $= 9.1 \times 10^{-31} \times 6.02 \times 10^{23}$

  = 0.55 mg.

- Some substances like $CuSO_4.5H_2O$, $Na_2CO_3.10H_2O$ have a tendency to lose water in air. These are called efflorescent and this tendency is called efflorescence.

- Some solid substances like NaOH, KOH, which have a tendency to absorb moisture greatly from air and to get wet are called 'Deliquescent' and this tendency is called Deliquescence.

- Hygroscopic substances like quicklime (CaO) anhydrous P_2O_5 etc., absorb moisture from air.

- To find equivalent weight of an acid:

  It is possible by Silver Salt Formation Method.

$$\frac{\text{Eq. wt. of R–COOAg}}{108} = \frac{\text{Wt. of R–COOAg}}{\text{wt. of Ag}}$$

- Eq. wt. of R–COOH = Eq. wt. of R–COOAg – 107

In Redox Titration

V (oxidizing agent) × M (oxidizing agent) =

V (reducing agent) × M (reducing agent)

$$\times \frac{\text{No. of moles of oxidizing agent}}{\text{No. of moles of reducing agent}}$$

In Acid Base Titration

V (acid) × M (acid) =

$$\text{V (base)} \times \text{(M base)} \times \frac{\text{No. of moles of acid}}{\text{No. of moles of base}}$$

$$Z_1 M_1 V_1 = Z_2 M_2 V_2$$

Here Z_1 = acidity or basicity of substance – 1

and Z_2 = acidity or basicity of substance – 2

For a mixture of solution of non reacting substances.

$$N_1 V_1 + N_2 V_2 + N_3 V_3 = N_{mix.} V_{mix.}$$

If all the three acids are monobasic or bases are monoacidic,

$$M_1 V_1 + M_2 V_2 + M_3 V_3 = M_{mix.} V_{mix.}$$

If we mix HCl and H_2SO_4 then, 'M' of H_2SO_4 will be multiplied by 2 because H_2SO_4 is dibasic acid.

Law of equivalence is used only in following conditions

If either a substance or solution reacts completely with a known volume of a standard solution, then

Number of equivalents of substance = Number of equivalents of standard solution.

$$\frac{W_{Sub}}{\text{Eq. wt.}_{Sub}} = \frac{NV}{1000}$$

$$N_1V_1 = N_2V_2$$

Number of eq. of metal = Number of eq. of solution

$$\frac{W}{\text{Eq. wt.}} = \frac{NV}{1000} \text{ solution.}$$

Solved Problems from the IITs

1. A mixture of $H_2C_2O_4$ and $NaHC_2O_4$ weighing 2.02 g was dissolved in water and the solution made up to one litre. 10 ml of this solution required 3.0 ml of 0.1 N NaOH solution for complete neutralization. In another experiment 10 ml of same solution in hot dilute H_2SO_4 medium required 4 ml of 0.1 N $KMnO_4$ for complete neutralization. Calculate the amount of $H_2C_2O_4$ and $NaHC_2O_4$ in the mixture.

[IIT 1990]

Solution Suppose mass of $H_2C_2O_4$ present in the mixture is 'X' g in 1 litre and mass of $NaHC_2O_4$ present in the mixture is 'Y' g in 1 litre.

For acid–base reaction

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

$$\text{Equivalent mass of } H_2C_2O_4 = \frac{\text{Mol. mass}}{2}$$

$$= \frac{90}{2} = 45$$

$$NaHC_2O_4 + NaOH \rightarrow Na_2C_2O_4 + H_2O$$

$$\text{Equivalent mass of } NaHC_2O_4 = \frac{\text{Mol. mass}}{1}$$

$$= 112$$

Equivalent of $H_2C_2O_4$ in 10 ml solution + Equivalents of $NaHC_2O_4$ in 10 ml solution

$$= \frac{3 \times 0.1}{1000}$$

$$\frac{X \times 10}{45 \times 1000} + \frac{Y \times 10}{112 \times 1000} = \frac{3 \times 0.1}{1000}$$

$$112\,X + 45\,Y = \frac{3 \times 0.1 \times 45 \times 112}{10} = 151.2 \quad \ldots\ldots (i)$$

For redox reaction

$$\text{Equivalent mass of } H_2C_2O_4 = \frac{90}{2} = 45.$$

$$\text{Equivalent mass of } NaHC_2O_4 = \frac{112}{2} = 56$$

(Change in oxidation number of carbon per molecule = 2; $C_2^{3+} \rightarrow 2C^{4+}$)

Now,

Equivalents of $H_2C_2O_4$ in 10 ml solution + Equivalents of $NaHC_2O_4$ in 10 ml solution

$$= \frac{4 \times 0.1}{1000}.$$

$$\frac{X \times 10}{45 \times 1000} + \frac{Y \times 10}{56 \times 1000} = \frac{4 \times 0.1}{1000}$$

$$56\,X + 45\,Y = 100.8 \quad \ldots\ldots (ii)$$

On solving equations (i) and (ii), we get

$X = 0.9$ g

$Y = 1.12$ g

2. A solid mixture (5.0 g) consisting of lead nitrate and sodium nitrate was heated below 600°C until the mass of the residue was constant. If the loss in mass is 28.0 %. Find the amount of lead nitrate and sodium nitrate in the mixture.

[IIT 1990]

Solution Let the amount of $NaNO_3$ in the mixture be 'X' g.

The amount of $Pb(NO_3)_2$ in the mixture

$= (5.0 - X)$ g.

$$\underset{(2 \times 85)\text{g}}{2NaNO_3} \xrightarrow{\text{Heat}} 2NaNO_2 + \underset{32\text{ g}}{O_2}$$

$$\underset{(2 \times 331)\text{ g} = 662\text{ g}}{2Pb(NO_3)_2} \xrightarrow{\text{Heat}} 2PbO + \underset{(4 \times 46)\text{ g} = 216\text{ g}}{4NO_2 + O_2}$$

170 g of $NaNO_3$ evolve oxygen = 32 g

X g of $NaNO_3$ evolve oxygen = $\frac{32}{170} \times X$ g

662 g of $Pb(NO_3)_2$ evolve gas = 216 g

$(50 - X)$ g of $Pb(NO_3)_2$ evolve gas

$$= \frac{216}{662} \times (5.0 - X) \text{ g}$$

Total loss = $\frac{32}{170}$ X + $\frac{216}{662}$ × (5.0 – X)

Loss given in the problem = $\frac{28}{100}$ × 5 = 1.4 g

$\frac{32}{170}$ X + $\frac{216}{662}$ (5.0 – X) = 1.4

On solving, we get

X = 1.676 g

So mass of $NaNO_3$ = 1.676 g

Mass of $Pb(NO_3)_2$ = (5.0 – 1.676) g

= 3.324 g.

3. Calculate the molality of one litre solution of 93% H_2SO_4 (weight/volume). The density of the solution is 1.84 g/ml.

[IIT 1990]

Solution Given,

93 % H_2SO_4 solution (weight/volume)

It means 93 g of H_2SO_4 present in 100 ml of solution, therefore

Weight of H_2SO_4 = 93 g

Volume of solution = 100 ml

So weight of solution = 100 × 1.84 = 184 g

Weight of water = 184 – 93 = 91 g

$$\text{Molality} = \frac{\text{moles of } H_2SO_4}{\text{Weight of water in (g)}} \times 1000$$

$$\text{Moles of } H_2SO_4 = \frac{93}{98} = 0.948$$

$$\text{So Molality} = \frac{0.948}{91} \times 1000 = 10.42$$

4. A 1.0 g sample of Fe_2O_3 solid of 55.2 % purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 ml. An aliquot of 25.0 ml of this solution requires for titration. Calculate the number of electrons taken up by the oxidant in the reaction of the above titration.

[IIT 1991]

Solution The redox changes are:

For reduction of Fe_2O_3 by zinc dust

$Fe_2^{3+} + 2e^- \rightarrow 2Fe^{2+}$

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

Oxidant + n e^- → Reductant

Meq. of Fe_2O_3 in 25 ml

= Meq. of Fe^{3+} in Fe_2O_3

= Meq. of Fe^{2+} formed

= Meq. of oxidant used to oxidize Fe^{2+}

So Meq. of Fe_2O_3 in 25 ml = Meq. of oxidant

= 17 × 0.0167 × n

Here 'n' is the number of electrons gained by 1 molecule of oxidant

So Meq. of Fe_2O_3 in 100 ml

= 17 × 0.0167 × n × $\frac{100}{25}$

$$\frac{1 \times 55.2 \times 1000}{100 \times M/2} = 17 \times 0.0167 \times n \times 4$$

As molecular weight of Fe_2O_3 = 160

$$\text{So } n = \frac{1 \times 55.2 \times 2 \times 1000}{100 \times 160 \times 17 \times 0.0167 \times 4} = 6$$

Thus, number of electrons gained by one molecule of oxidant = 6.

5. A solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions on titration with 0.02 M $KMnO_4$ in presence of H_2SO_4 consumes 22.6 ml oxidant. The resulting solution is neutralized by Na_2CO_3, acidified with dilute acetic acid and titrated with excess of KI. The liberated iodine required 11.3 ml of 0.05 M $Na_2S_2O_3$ for complete reduction. Find out the mole ratio of Cu^{2+} and $C_2O_4^{2-}$ in the compound.

[IIT 1991]

Solution

Ist Case

Only $C_2O_4^{2-}$ ions are oxidized by $KMnO_4$ solution.

Normality of $KMnO_4$ solution = 0.02 × 5 = 0.1N

22.6 ml of 0.1 N $KMnO_4$ =

22.6 ml of 0.1 N $C_2O_4^{2-}$ solution

Mass of $C_2O_4^{2-}$ ions in the solution

$$= \frac{N \times E \times V}{1000} = \frac{N \times M \times V}{1000 \times 2}$$

Number of moles of $C_2O_4^{2-}$ ions in the solution

$$= \frac{N \times M \times V}{1000 \times 2 \times M}$$

$$= \frac{N \times V}{2000} = \frac{0.1 \times 22.6}{2000}$$

$$= 11.3 \times 10^{-4}$$

IInd Case

Only Cu^{2+} ions are reduced by KI and iodine liberated is neutralized by $Na_2S_2O_3$ solution.

11.3 ml of 0.05 M $Na_2S_2O_3$

≡ 11.3 ml of 0.05 N $Na_2S_2O_3$

= 11.3 ml of 0.05 N I_2

= 11.3 ml of 0.05 N Cu^{2+}

Mass of Cu^{2+} ions in the solution

$$= \frac{N \times E \times V}{100} = \frac{N \times M \times V}{1000}$$

Number of moles of Cu^{2+} ions in the solution

$$= \frac{N \times M \times V}{1000 \times M}$$

$$= \frac{N \times V}{1000} = \frac{0.05 \times 11.3}{1000}$$

$$= 5.65 \times 10^{-4}$$

Molar ratio of $\frac{Cu^{2+}}{C_2O_4^{2-}} = \frac{5.65 \times 10^{-4}}{11.3 \times 10^{-4}} = \frac{1}{2}$.

6. A 2.0 g sample of a mixture containing sodium carbonate, sodium bicarbonate and sodium sulphate is gently heated till the evolution of CO_2 ceases. The volume of CO_2 at 750 mm Hg pressure and at 298 K is measured to be 123.9 ml. A 1.5 g of the same sample requires 150 ml of (M/10) HCl for complete neutralization. Calculate the per cent composition of the components of the mixture.

[IIT 1992]

Solution According to ideal gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_1}$$

Volume of CO_2 at NTP

$$(V_2) = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}.$$

$$= \frac{750 \times 123.9}{298} \times \frac{273}{760}$$

$$= \frac{25368525}{226480} = 112 \text{ ml}$$

As weight of 22400 ml of CO_2 at NTP = 44 g

So weight of 112 ml of CO_2 at NTP

$$= \frac{44}{22400} \times 112 \text{ g}$$

$$= 0.22 \text{ g}$$

On heating a mixture of $NaHCO_3$, Na_2CO_3 and Na_2SO_4, only $NaHCO_3$ is decomposed according to following equation.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

$$2(23+1+12+48) = 168$$

As 44 g CO_2 is required = 168 g of $NaHCO_3$

So 0.22 g CO_2 is required

$$= \frac{168}{44} \times 0.22 \text{ g of NaHCO3}$$

$$= 0.84 \text{ g of } NaHCO_3$$

As the weight of $NaHCO_3$ in the mixture = 0.84

So the percentage of $NaHCO_3$ in the mixture

$$= \frac{0.84}{2.0} \times 100 = 42.0\ \%$$

When 1.5 g of mixture is treated with HCl. Therefore Na_2SO_4 is not reacted while Na_2CO_3 is reacted with HCl as follows:

$$Na_2CO_3 + 2HCl \longrightarrow$$

$$2 \times 23 + 12 + 48 \quad 2(1 + 35.5)$$

$$= 106 \quad = 73$$

$$2NaCl + H_2O + CO_2$$

Let the amount of Na_2CO_3 in 1.5 g of mixture be 'Y' g.

So the amount of HCl used with Na_2CO_3

$$= \frac{73}{106} \times Y \text{ g}$$

$NaHCO_3$ reacts with HCl as follows:

$NaHCO_3$ + HCl

23 + 1 + 12 + 48 (1 + 35.5)

= 84 g = 36.5

$NaCl + H_2O + CO_2$

Amount of HCl used with $NaHCO_3$

$\frac{36.5}{84} \times 0.63 = 0.2737$ g

Number of millimoles of HCl used with mixture

= Molarity × Volume in ml

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

Weight of HCl used with mixture

= millimole × mol. wt. × 10^{-3}

= $15 \times 10^{-3} \times 36.5 = 0.5475$ g

Total HCl = Used HCl with Na_2CO_3

+ Used HCl with $NaHCO_3$

$0.5475 = \frac{75}{106} \times Y + 0.2737$

On solving, we get

Y = 0.3975

So % of Na_2CO_3 in the mixture

$= \frac{0.3975}{1.5} \times 100 = 26.5$ %

% of Na_2SO_4 in the mixture

= 100 – % of $NaHCO_3$ – % of Na_2CO_3

= 100 – 42 – 26.5

= 31.5 %

7. One gram of commercial $AgNO_3$ is dissolved in 50 ml of water. It is treated with 50 ml of a KI solution. The silver iodide thus precipitated is filtered off. Excess of KI in the filtrate is titrated with (M/10) KIO_3 solution in presence of 6 M HCl till all I^- ions are converted into ICl. It requires 50 ml of (M/10) KIO_3 solution. 20 ml of the same stock solution of KI requires 30 ml of (M/10) KIO_3 under similar conditions. Calculate the percentage of $AgNO_3$ in the sample.

Reaction:

$KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$

[IIT 1992]

Solution Number of millimoles of KIO_3 in 30 ml of solution

= Molarity × Volume in ml

$= \frac{1}{10} \times 30 = 3$

Equation:

$KIO_3 + 2KI + 6HCl \rightarrow 3ICl + 3KCl + 3H_2O$

According to the equation

1 mole of KIO_3 is equivalent to 2 moles of KI

As Number of millimoles of KI in 20 ml of stok solution

$= 2 \times 3 = 6$

So, number of millimoles of KI in 50 ml of the same solution = $6 \times \frac{50}{20} = 15$

Number of millimoles of KIO_3 in 50 ml of solution

$= \frac{1}{10} \times 50 = 5$

So number of millimoles of KI used with 50 ml of KIO_3 solution = 2 × 5 = 10

Number of millimoles of KI used with $AgNO_3$ = 15 – 10 = 5

$AgNO_3 + KI \rightarrow AgI + KNO_3$

1 mole of $AgNO_3$ reacts with 1 mole of KI. So number of millimoles of $AgNO_3$ is equal to 5.

Weight of $AgNO_3 = 5 \times 10^{-3} \times 170$ g

$= 0.85$ g

% of $AgNO_3 = \frac{0.85 \times 100}{1.0} = 85.0$ %.

8. Upon mixing 45.0 ml of 0.25 M lead nitrate solution with 25 ml of 0.1 M chromic sulphate solution, precipitation of lead sulphate takes place. How many moles of lead sulphate are formed? Also calculate the molar concentrations of the species left behind in the final solution. Assume that lead sulphate is completely insoluble.

[IIT 1993]

Solution The reaction is

$3Pb(NO_3)_2 + Cr_2(SO_4)_3 \rightarrow 3PbSO_4 + 2Cr(NO_3)_3$

3 mole 1 mole 3 mole 2 mole

Number of moles of $Pb(NO_3)_3$

$= 45 \times 10^{-3} \times 0.25$

$= 11.25 \times 10^{-3}$ mole

Number of moles of $Cr_2(SO_4)_3$

$= 25 \times 10^{-3} \times 0.1$

$= 2.5 \times 10^{-3}$ mole

So $Cr_2(SO_4)_3$ has limiting concentration. It will be consumed fully and the number of moles of lead sulphate produced will be

$= 3 \times 2.5 \times 10^{-3} = 7.5 \times 10^{-3}$ mole

Number of moles of lead nitrate left

$= 11.25 \times 10^{-3} - 7.5 \times 10^{-3}$

$= 3.75 \times 10^{-3}$ mole

Total volume = 45.0 + 25.0 = 70 ml

$= 70 \times 10^{-3}$ litre

$$\text{Molarity} = \frac{3.75 \times 10^{-3}}{70 \times 10^{-3}} = 0.0536 \text{ M}$$

Number of moles of $Cr(NO_3)_3$ formed

$= 2 \times 2.5 \times 10^{-3} = 5 \times 10^{-3}$ mole

$$\text{Molarity} = \frac{5 \times 10^{-3}}{70 \times 10^{-3}} \quad 0.0714 \text{ M}$$

$Pb(NO_3)_2$ and $Cr(NO_3)_3$ will be present in solution in ionic form,

So,

$[Pb^{2+}] = 0.0536$ M

$[Cr^{3+}] = 0.0714$ M

$[NO_3^-] = (2 \times 0.0536) + (3 \times 0.0714)$

$= 0.3214$ M.

9. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molarity, molality and mole-fraction of Na_2SO_4 in the solution.

[IIT 1994]

Solution In 1 dm^3 solution, weight of Glauber's salt

$(Na_2SO_4.10H_2O) = 8.0575 \times 10^{-2}$ kg

Mass of solution = Volume × density

$= 1\ dm^3 \times 1077.2 \times 10^{-3}$ kg dm^{-3}

$= 1.0772$ kg

So in solution weight of solvent

= Weight of solution – Wt. of Glauber's salt

$= 1.0772 - 0.080575$

$= 0.996625$ kg

Molarity of solution

$$= \frac{\text{Weight of } Na_2SO_4.10H_2O \text{ in g}}{dm^3/\text{mol. wt. of } Na_2SO_4.10H_2O}$$

$$= \frac{80.575 \text{ g/dm}^3}{322} = 0.250 \text{ M}$$

Molality of solution

$$= \frac{\text{Molarity of solution}}{\text{Weight of solvent in kg/dm}^3}$$

$$= \frac{0.250}{1.0772} = 0.232 \text{ m}$$

$$\text{Moles of solvent (water)} = \frac{996.625}{18} = 55.34$$

$$\text{Moles of } Na_2SO_4.10H_2O = \frac{80.575}{322} = 0.250$$

Mole fraction of $Na_2SO_4.10H_2O$

$$= \frac{\text{Moles of } Na_2SO_4.10H_2O}{\text{Total moles}}$$

$$= \frac{55.34}{55.34 + 0.25} = 0.995$$

10. 'A' is a binary compound of a univalent metal. 1.422 g of (A) reacts 1.743 g of a white crystalline solid (B), that forms a hydrated double salt (C) with $Al_2(SO_4)_3$. Identify (A), (B) and (C).

[IIT 1994]

Solution Compound (B) form hydrated crystals with $Al_2(SO_4)_3$. As (B) is formed with univalent metal on heating with sulphur. So compound (B) should be M_2SO_4, so compound (A) must be oxide of M which reacts with sulphur to give M_2SO_4.

So (A) + S $\rightarrow M_2SO_4$

As 1.422 g of (A) reacts with 0.321 g of sulphur completely and gives 1.743 g of M_2SO_4.

So 32.1 g of S will give = $\frac{1.743 \times 32.1}{0.321}$

= 174.3 g

As molecular wt. of M_2SO_4 = 173.4

So 2 × (A) + 32.1 + 64 = 1723.4

So (A) (atomic weight of M) = 39

Monovalent metal is K (as at. wt. of K is 39)

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow$
Compound (B)

$K_2SO_4.Al_2(SO_4)_3.24H_2O$
Compound (C)

As 0.321 g of sulphur react with 1.422 g of (A)

So 32.1 g of sulphur react with

$\frac{1.422 \times 32.1}{0.321}$ g of (A) = 142.2 g

$2MO_X + S \xrightarrow{Heat} M_2SO_4$

142.2 g wt. is related to two moles of MO_X or KO_X.

2 [39 + 16X] = 142.2

78 + 32X = 142.2

X = 2

So compound (A) is KO_2 (Potassium superoxide) which is a binary compound.

Compound (A) = KO_2

Compound (B) = K_2SO_4

Compound (C) = $K_2SO_4.Al_2(SO_4)_3.24H_2O$

11. The composition of a sample of wustite is $Fe_{0.93}O_{100}$. What percentage of the iron is present in the form of Fe(III)?

[IIT 1994]

Solution Let the percentage of Fe(III) be X and Fe(II) would be (100 – X).

Number of oxygen molecules in Fe_2O_3 = (3/2)X

Total iron atoms = 100 – X + X = 100

Total oxygen atoms = (3/2)X + 100 – X

= 100 + (X/2)

Ratio = $\frac{0.93}{1.00} = \frac{100}{100 + (X/2)}$

93 × 0.465 X = 100

X = 15.05

X = 15.05 %

12. A mixture of ethane and ethene occupies 40 litre at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, find the mole fractions of C_2H_6 and C_2H_4 in the mixture.

[IIT 1995]

Solution Volume of the mixture at NTP

= $\frac{40 \times 1}{400} \times \frac{273}{1}$ = 27.3 litre

Suppose the volume of ethane is X litre.

Volume of ethene = (273 – X) litre

Equations:

$C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3H_2O$
1 vol. 7/2 vol.

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
1 vol. 3 vol.

Total volume of oxygen required for complete combustion of the mixture is:

$[\frac{7}{2} X + (27.3 - X) \times 3]$ litre

or $\frac{[7X + (27.3 - X) \times 6]}{2}$ litre

Mass of oxygen = $\frac{[7X + (27.3 - X) \times 6]}{2} \times \frac{32}{22.4}$.

$130 = (X + 163.8) \times \frac{16}{22.4}$.

X = 18.2

So, mole fraction of ethane = $\frac{18.2}{27.3} \times 100$

= 66.66

Mole fraction of ethene = 33.34

13. A 20.0 cm^3 mixture of CO, CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm^3. A further contraction of 14.0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage.

[IIT 1995]

Solution $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Suppose 'X' is the volume of CO 'Y' is the volume of CH_4

$\frac{1}{2} X + Y = 13$ ..... 1.

$X + Y = 14$

$X = 10$ cc and $Y = 4$ cc

So % $CH_4 = 20$, % CO = 50, % He = 30

14. A 3.0 g sample containing Fe_3O_4, Fe_2O_3 and an inert impure substance is treated with excess of KI solution in presence of dilute H_2SO_4. The entire iron is converted to Fe^{2+} along with the liberation of iodine. The resulting solution is diluted to 100 ml. A 20 ml of the dilute solution requires 11.0 ml of 0.5 M $Na_2S_2O_3$ solution to reduce the iodine present. A 50 ml of the diluted solution after complete extraction of iodine requires 12.8 ml of 0.25 M $KMnO_4$ solution in dilute H_2SO_4 medium for oxidation of Fe^{2+}. Calculate the percentage of Fe_2O_3 and Fe_3O_4 in the original sample.

[IIT 1996]

Solution Fe_3O_4 is an equimolar mixture of Fe_2O_3 and FeO. Thus, the sample contains Fe_2O_3, FeO and impurities. The amount of iodine liberated depends on the amount of Fe_2O_3 and the entire iron is converted into Fe^{2+}.

$Fe_3O_4 + 2KI + H_2SO_4 \rightarrow 3FeO + H_2O + K_2SO_4 + I_2$

$Fe_2O_3 + KI + H_2SO_4 \rightarrow 2FeO + H_2O + K_2SO_4 + I_2$

5×11.0 ml of 0.5 M $Na_2S_2O_3$

$\equiv$ 55.0 ml of 0.5 N $Na_2S_2O_3$ solution

$\equiv$ 55.0 ml of 0.5 N I_2 solution

$\equiv$ 55.0 ml of 0.5 N Fe_2O_3 solution

$= 27.5 \times 10^{-3}$ eq. Fe_2O_3 solution

$= 13.75 \times 10^{-3}$ moles Fe_2O_3

2×12.8 ml of 0.25 M $KMnO_4$ solution

$\equiv$ 25.6 ml of 1.25 N $KMnO_4$ solution

$\equiv$ 25.6 ml of 1.25 N FeO solution

$= 32.0 \times 10^{-3}$ equivalent FeO

$= 32.0 \times 10^{-3}$ moles FeO

Moles of FeO in $Fe_3O_4 = 0.032 - 0.0275$

$= 0.0045$

Mass of $Fe_3O_4 = 0.0045 \times 232 = 1.044$ g

Moles of Fe_2O_3 existing separately

$= 0.01375 - 0.0045 = 0.00925$

Mass of $Fe_2O_3 = 0.00925 \times 160 = 1.48$ g

$$\% Fe_3O_4 = \frac{1.044}{3} \times 100 = 34.8$$

$$\% Fe_2O_3 = \frac{1.48}{3} \times 100 = 49.33$$

15. To a 25 ml H_2O_2 solution, excess of acidified solution of potassium iodide was added. The iodine liberated required 20 ml of 0.3 N sodium thiosulphate solution. Calculate the volume strength of H_2O_2 solution.

[IIT 1997]

Solution $2KI + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + 2H_2O + I_2$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2\,NaI$

Meq. of $Na_2S_2O_3 = 20 \times 0.3 = 6$

(Normality $\times$ volume)

Meq. of $Na_2S_2O_3$ = Meq. of $I_2 = 6$

Meq. of I_2 = Meq. of $H_2O_2 = 67$

Weight of H_2O_2 = Meq. × E × 10^{-3}

= 6 × 17 × 10^{-3} = 0.102 g

(As eq. wt. of H_2O_2 = 34/2 = 17)

Strength of H_2O_2 = $0.102 \times \frac{1000}{25}$

= 0.408 g/L

Molarity of H_2O_2 = $\frac{0.408 \text{ g . L}}{\text{Mol. wt. (34)}}$

= 0.012 M

$2H_2O_2 \rightarrow 2H_2O + O_2$

2 moles 1 mole

0.012 moles 0.06 moles

So volume of O_2 at STP = 0.06 × 22.4 L

= 1.344 L

So the volume strength of H_2O_2 = 1.344 L

16. An aqueous solution containing 0.10 g KIO_3 (formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated iodine consumed 45.0 ml of thiosulphate solution to decolorize the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.

[IIT 1998]

Solution $2KIO_3 + 10\ KI + 12HCl \rightarrow 12\ KCl + 6I_2 + 6H_2O$

$[2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6] \times 6$

$2KIO_3 + 10\ KI + 12\ Na_2S_2O_3 + 12HCl \rightarrow$

2 moles 12 moles

$12KCl + 12NaI + 6Na_2S_4O_6 + 6H_2O$

Number of moles of KIO_3 = $\frac{0.10}{214}$

Number of moles of $Na_2S_2O_3$ required for 0.10/214 moles of KIO_3

= $\frac{12}{2} \times \frac{0.10}{214} = \frac{0.60}{214}$

Molarity of $Na_2S_2O_3$ = $\frac{0.6}{214} \times \frac{1000}{45}$.

= 0.0623 M

17. How many milliliteres of 0.5 M H_2SO_4 are needed to dissolve 0.5 g of copper (II) carbonate?

[IIT 1999]

Solution $N_1 V_1 = N_2 V_2$

N_1 = Normality of H_2SO_4 = 0.5 × 2 = 1 N

V_1 = Volume of H_2SO_4

N_2 = Normality of copper (II) carbonate

= $\frac{0.5 \times 2}{123.5}$ N

V_2 = Volume of copper (II) carbonate

= 1000 ml

So $1.0 \times V_1 = \frac{0.5 \times 2}{123.5} \times 1000$

V_1 = 8.09 ml

18. A plant virus is found to consist of uniform cylindrical particles of 150 Å in diameter and 5000 Å long. The specific volume of the virus is 0.75 cm^3 /g. If the virus is considered to be a single particle, calculate its molecular mass.

[IIT 1999]

Solution Volume of cylindrical virus = $\pi r^2 l$

= $3.14 \times (\frac{150}{2} \times 10^{-8})^2 \times 5000 \times 10^{-8}$

= 0.884×10^{-16} cm^3

Mass of virus = $\frac{\text{Volume}}{\text{Specific volume}}$.

= $\frac{0.884 \times 10^{-16}}{0.75} = 1.178 \times 10^{-16}$ g

Molar mass of virus

= Mass of single virus × 6.023 × 10^{23}

= $1.178 \times 10^{-16} \times 6.023 \times 10^{23}$

= 7.095×10^7.

19. Hydrogen peroxide solution (20 ml) reacts quantitatively with a solution of $KMnO_4$ (20 ml) acidified with dilute H_2SO_4. The same volume of the $KMnO_4$ solution is just decolorized by 10 ml of $MnSO_4$ in neutral medium simultaneously forming a dark brown precipitate of hydrated MnO_2. The brown precipitate is dissolved in 10 ml of 0.2 M sodium oxalate under boiling condition in the presence of dilute H_2SO_4. Write the balanced equations involved in the reactions and calculate the molarity of H_2O_2.

[IIT 2001]

Solution

(i)

$$MnO_2\downarrow + Na_2C_2O_4 + 2H_2SO_4 \rightarrow$$

1 mole 1 mole

$$MnSO_4 + Na_2SO_4 + 2CO_2 + 2H_2O$$

mM of MnO_2 = mM of $Na_2C_2O_4$

$= 10 \times 0.2 = 2$

(ii)

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 2 \text{ mole}$$

$$5MnO_2\downarrow + K_2SO_4 + 2H_2O$$

5 mole

mM of $KMnO_4$ = mM of $MnO_2 \times \frac{2}{5}$.

$= 2 \times \frac{2}{5} = \frac{4}{5}$.

(iii)

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow$$

mole 5 mole

$$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

mM of H_2O_2 = mM of $KMnO_4 \times \frac{5}{2}$

$= \frac{4}{5} \times \frac{5}{2} = 2$

$M \times 20 = 2$

$M(H_2O_2) = \frac{2}{20} = 0.1$ M

20. How many grams of CaO are required to neutralize 852 g of P_4O_{10}?

[IIT 2005]

Solution The reaction is as follows:

$$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$$

852 g $P_4O_{10} \equiv 3$ mol P_4O_{10}

As 1 mole of P_4O_{10} neutralizes 6 moles of CaO.

So 3 moles of P_4O_{10} will neutralize 18 moles of CaO.

Mass of CaO = $18 \times 56 = 1008$ g.

21. 20 % surface sites have adsorbed N_2. On heating N_2 gas evolved from sites and were collected at 0.001 atm and 298 K in a container of volume is 2.46 cm^3. Density of surface sites is $6.023 \times 10^{14}/cm^2$ and surface area is 1000 cm^2, find out the number of surface sites occupied per molecule of N_2.

[IIT 2005]

Solution Density of surface site = 6.023×10^{14} cm^{-2}

Total surface area = 1000 cm^2

Total number of surface sites

= Density × Total surface area

$= 6.023 \times 10^{14} \times 1000$

$= 6.023 \times 10^{17}$

Sites occupied by nitrogen molecule (20%)

$= \frac{20}{100} \times 6.023 \times 10^{17} = 1.2046 \times 10^{17}$

Number of nitrogen molecule = $\frac{PV}{RT} \times NA$

T = 298 K, PP = 0.001 atm

V = 2.46 $cm^3 = 2.46 \times 10^{-3}$ L

R = 0.0821 L-atm/K/mol

Number of nitrogen molecule

$= \frac{0.001 \times 2.46 \times 10^{-3}}{0.0821 \times 298} \times 6.023 \times 10^{23}$

$= 6.02 \times 10^{16}$

Thus number of sites occupied by each nitrogen molecule

$= \frac{\text{Sites occupied by } N_2 \text{ molecules}}{\text{Number of } N_2 \text{ molecules}}$

$= \frac{1.2046 \times 10^{17}}{6.02 \times 10^{16}} = 2$

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. If 0.50 mole of $BaCl_2$ is mixed with 0.20 mol of Na_3PO_4, the maximum number of moles of $Ba_3(PO_4)_2$ that can be formed is

a. 0.10 **b.** 0.20
c. 0.30 **d.** 0.40

2. One mole of N_2H_4 loses ten moles 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. +2 **b.** –2
c. +3 **d.** +4

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

a. MnO **b.** MnO_4^{2-}
c. MnO_2 **d.** MnO_4^-

4. In which mode of expression, the concentration of a solution remains independent of temperature?

a. Formality **b.** Molality
c. Molarity **d.** Normality

5. One litre hard water contains 12.00 mg Mg^{2+}. Milliequivalents of washing soda required to remove its hardness is

a. 1 **b.** 12.16
c. 1×10^{-3} **d.** 12.16×10^{-3}

6. At STP the density of CCl_4 vapour in g/l will be nearest to

a. 8.67 **b.** 6.87
c. 5.67 **d.** 4.26

7. 1 c.c. N_2O at NTP contains

a. $\frac{1.8}{224} \times 10^{22}$ atoms

b. $\frac{6.02}{22400} \times 10^{23}$ molecules

c. $\frac{1.32}{224} \times 10^{23}$ electrons

d. all of above

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

a. 3.0 **b.** 4.8
c. 8.0 **d.** 8.4

9. The number of gram-molecule of oxygen which contain 6.02×10^{24} CO molecules is

a. 10 g molecule **b.** 5 g molecule
c. 1 g molecule **d.** 0.5 g molecule

10. The mass of 1×10^{22} molecules of $CuSO_4.5H_2O$ is

a. 41.59 g **b.** 415.9 g
c. 4.159 g **d.** none of these

11. The weight of one molecule of a compound $C_{60}H_{122}$ is

a. 1.2×10^{-20} gm
b. 1.4×10^{-21} gm
c. 5.025×10^{23} gm
d. 6.023×10^{23} gm

12. The percentage weight of Zn in white vitriol [$ZnSO_4.7H_2O$] is approximately equal to (Zn = 65, S = 32, O = 16 and H = 1)

a. 33.65 % **b.** 32.56 %
c. 23.65% **d.** 22.65%

13. The volume of carbon dioxide gas evolved at STP by heating 7.3 gm of $Mg(HCO_3)_2$ will be

a. 1100 ml **b.** 1120 ml
c. 2230 ml **d.** 3240 ml

14. The amount of Zinc (atomic weight = 65) necessary to produce 224 ml of H_2 by the reaction with an acid will be

a. 0.65 gm **b.** 7.6 gm
c. 6.5 gm **d.** 8.5 gm

15. Number of atoms in 4.25 gm of NH_3 is approximately

a. 6×10^{23} **b.** 15×10^{23}
c. 1.5×10^{23} **d.** 2.5×10^{23}

16. The number of molecules in 4.25 g of ammonia is

a. 1.5×10^{23} **b.** 2.5×10^{23}
c. 3.5×10^{23} **d.** 15×10^{23}

17. The weight of a single atom of oxygen is

a. 5.057×10^{23} g **b.** 1.556×10^{23} g
c. 2.656×10^{-23} g **d.** 4.538×10^{-23} g

18. In the reaction

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$,

when 1 mole of ammonia and 1 mole of O_2 are made to react to completion

a. 1.0 mole of H_2O is produced

b. 1.0 mole of NO will be produced

c. all the oxygen will be consumed

d. all the ammonia will be consumed

19. The equivalent weight of phosphoric acid (H_3PO_4) in the reaction:

$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$ is

a. 89 **b.** 98

c. 59 **d.** 29

20. Assuming fully decomposed, the volume of CO_2 released at STP on heating 9.85 g of $BaCO_3$ (atomic mass, Ba = 137) will be

a. 2.24 l **b.** 4.96 l

c. 1.12 l **d.** 0.84 l

21. What is the volume (in litres) of CO_2 liberated at STP, when 2.12 gram of sodium carbonate (mol. wt. = 106) is treated with excess dilute HCl?

a. 11.2 **b.** 2.12

c. 0.448 **d.** 4.26

22. Percentage of Se in peroxidase anhydrase enzyme is 0.5 % by weight (at. wt. = 78.4) then minimum molecular weight of peroxidase anhydrase enzyme is

a. 1.568×10^3 **b.** 15.68

c. 2.136×10^4 **d.** 1.568×10^4

23. What is the volume (in litres) of oxygen at STP required for complete combustion of 32 g of CH_4 (mol. wt. of CH_4 = 16)

a. 89.6 **b.** 189.6

c. 98. 4 **d.** 169.5

24. How many water molecules are there in one drop of water (volume 0.0018 ml) at room temperature?

a. 4.86×10^{17} **b.** 6.023×10^{24}

c. 2.584×10^{19} **d.** 6.023×10^{19}

25. The weight of one molecule of a compound $C_{60}H_{122}$ is

a. 1.3×10^{-20} g **b.** 5.01×10^{-21} g

c. 3.72×10^{23} g **d.** 1.4×10^{-21} g

26. 3 g of an oxide of a metal is converted to chloride completely and it yielded 5 g of chloride. The equivalent weight of the metal is

a. 3.325 **b.** 13.25

c. 23.52 **d.** 33.25

27. In Haber process, 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end?

a. 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen

b. 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen

c. 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen

d. 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen

28. 25 ml of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a titre value of 35 ml. The molarity of barium hydroxide solution was

a. 0.07 **b.** 0.14

c. 0.28 **d.** 0.35

29. What volume of hydrogen gas, at 273 K and 1 atm pressure will be consumed in obtaining 21.6 g of elemental boron (atomic mass = 10.8) from the reduction of boron trichloride by hydrogen?

a. 89.6 L **b.** 67.2 L

c. 44.8 L **d.** 22.4 L

30. A compound has haemoglobin like structure. It has one Fe. It contain 4.6 % of Fe. The approximate molecular mass is

a. 1400 g mol^{-1} **b.** 1000 g mol^{-1}

c. 1100 g mol^{-1} **d.** 1200 g mol^{-1}

31. The maximum number of molecules is present in

a. 15 L of H_2 gas at STP

b. 5 L of N_2 gas at STP

c. 0.5 g of H_2 gas

d. 10 g of O_2 gas

32. To neutralize completely 20 ml of 0.1 M aqueous solution of phosphorus acid, the volume of 0.1 M aqueous KOH solution required is

a. 10 ml **b.** 40 ml

c. 60 ml **d.** 80 ml

33. 6.02×10^{20} molecules of urea are present in 100 mlof its solution. The concentration of urea solution is

a. 0.02 M **b.** 0.001 M
c. 0.01 M **d.** 0.1 M

34. g of $CaCO_3$ is completely decomposed to X and CaO. X is passed into an aqueous solution containing one mole of sodium carbonate. What is the number of moles of sodium bicarbonate formed?

(mol. wt. of $CaCO_3$ = 100, Na_2CO_3 = 106, $NaHCO_3$ = 84)

a. 0.010 **b.** 0.2
c. 0.4 **d.** 10

35. An organic compound containing C and H has 92.3% of carbon. Its empirical formula is

a. CH_4 **b.** CH_3
c. CH_2 **d.** CH

36. 4 g of copper was dissolved in concentrated nitric acid. The copper nitrate on strong heating gave 5 g of its oxide. The equivalent weight of copper is

a. 12 **b.** 16
c. 32 **d.** 34

37. A gas mixture contains 50 % helium and 50 % methane by volume. What is the per cent by weight of methane in the mixture?

a. 83 % **b.** 73.0 %
c. 18.01 % **d.** 80.0 %
e. 90.1 %

38. Number of water molecules in the drop of water, if 1 ml of water has 20 drops and 'A' is Avogadro's number, is

a. 0.5 A **b.** 0.5 A/18
c. 0.05 A/18 **d.** 0.05 A

39. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is (at. mass of Al = 27)

a. 270 kg **b.** 540 kg
c. 90 kg **d.** 180 kg

40. 100 g $CaCO_3$ is treated with 1 litre of N HCl. What would be the weight of CO_2 liberated after the completion of the reaction?

a. 11 g **b.** 22 g
c. 33 g **d.** 44 g
e. 5.5 g

41. An alkaloid contains 17.28 % of nitrogen and its molecular mass is 162. The number of nitrogen atoms present in one molecule of the alkaloid is

a. One **b.** Two
c. Three **d.** Four
e. Five

42. If 30 ml of H_2 and 20 ml of O_2 react to form water, what is left at the end of the reaction?

a. 5 ml of O_2 **b.** 5 ml of H_2
c. 10 ml of O_2 **d.** 10 ml of H_2

43. Density of a 2.05 M solution of acetic acid in water is 1.02 g/ml. The molality of the solution is

a. 1.14 mol kg^{-1} **b.** 3.28 mol kg^{-1}
c. 2.28 mol kg^{-1} **d.** 0.44 mol kg^{-1}

44. The decomposition of a certain mass of $CaCO_3$ gave 11.2 dm^3 of CO_2 gas at STP. The mass of KOH required to completely neutralize the gas is

a. 56 g **b.** 28 g
c. 42 g **d.** 20 g

45. One mole of acidified $K_2Cr_2O_7$ on reaction with excess KI will liberate …… moles (s) of I_2

a. 2 **b.** 3
c. 6 **d.** 7

46. $KMnO_4$ (mol. wt. = 158) oxidizes oxalic acid in acidic medium to CO_2 and water as follows.

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

What is the equivalent weight of $KMnO_4$?

a. 158 **b.** 31.6
c. 39.5 **d.** 79

47. 500 ml of NH_3 contains 6.0×10^{23} molecules at STP. How many molecules are present in 100 ml of CO_2 at STP?

a. 6×10^{23} **b.** 1.5×10^{23}
c. 1.2×10^{23} **d.** none of these

48. In the reaction, $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$, when one mole of ammonia and one mole of oxygen are made to react to completion, then

a. 1.0 mole of H_2O is produced
b. all the oxygen is consumed
c. 1.5 mole of NO is formed
d. all the ammonia is consumed

49. 4 moles each of SO_2 and O_2 gases are allowed to react to form SO_3 in a closed vessel. At equilibrium, 25 % of O_2 is used up. The total number of moles of all the gases at equilibrium is

a. 2.0 **b.** 6.0
c. 7.0 **d.** 8.0

50. 1.520 g of hydroxide of a metal on ignition gave 0.995 g of oxide. The equivalent weight of the metal is

a. 0.995 **b.** 190
c. 1.90 **d.** 9

51. The molarity of the solution obtained by dissolving 2.5 g of NaCl in 100 ml of water is

a. 0.427 moles **b.** 427 moles
c. 0.0472 moles **d.** 0.00427 moles

52. 0.532 gram of chloroplatinate of an organic base (mol. wt. 244) gave 0.195 gram of platinum on ignition. The number of nitrogen atoms per molecule of base is

a. 4 **b.** 3
c. 2 **d.** 1

53. One litre solution containing 490 g of sulphuric acid is diluted to 10 litres with water. What is the normality of the resulting solution?

a. 1.0 N **b.** 10.0 N
c. 0.5 N **d.** 5.0 N

54. An element, X has the following isotopic composition;

^{200}X : 90 %

^{199}X : 8.0 %

^{202}X : 2.0 %

The weighted average atomic mass of the naturally occurring element X is closest to

a. 200 amu **b.** 201 amu
c. 202 amu **d.** 199 amu

55. The crystalline salt $Na_2SO_4.xH_2O$ on heating loses 55.9 % of its weight. The formula of the crystalline salt is

a. $Na_2SO_4.10H_2O$
b. $Na_2SO_4.6H_2O$
c. $Na_2SO_4.7H_2O$
d. $Na_2SO_4.5H_2O$
e. $Na_2SO_4.2H_2O$

56. 10 litres of O_2 gas is reacted with 30 litres of CO at STP. The volume of each gas present at the end of the reaction are

a. O_2 = 10 litres, CO = 30 litres
b. O_2 = 10 litres, CO_2 = 20 litres
c. CO = 10 litres, CO_2 = 20 litres
d. CO = 20 litres, CO_2 = 10 litres
e. O_2 = 10 litres, CO = 10 litres

57. 0.3 g of an acid is neutralized by 40 cm^3 of 0.125 N NaOH. Equivalent mass of the acid is

a. 20 **b.** 60
c. 30 **d.** 46

58. 5 g of $CaCO_3$ completely reacts with

a. 3.65 g of HCl
b. 7.35 g of HCl
c. 36.5 g of HCl
d. 0.365 g of HCl

59. Sodium nitrates on reduction with Zn in presence of NaOH solution produces NH_3. Mass of sodium nitrate absorbing 1 mole of electron will be

a. 5.550 **b.** 10.625
c. 9.000 **d.** 9.876

60. In transforming 0.01 mole of PbS to $PbSO_4$ the volume of '10 volume' H_2O_2 required will be

a. 10.3 **b.** 22.7
c. 23.0 **d.** 44.8

61. An unknown element forms an oxide. What will be the equivalent weight of the element if the oxygen content is 20% by weight?

a. 14 **b.** 32
c. 2 **d.** 54

62. 2 N HCl solution will have same molar conc. as a

a. 4.0 N H_2SO_4 **b.** 1 N H_2SO_4
c. 0.5 N H_2SO_4 **d.** 2 N H_2SO_4

63. Number of moles of MnO_4^- required to oxidize one mole of ferrous oxalate completely in acidic medium will be

a. 7.5 moles **b.** 0.2 moles
c. 0.6 moles **d.** 0.4 moles

64. How many grams of carbon dioxide can form when a mixture of 4.95 g ethylene (C_2H_4) and 3.25 g of oxygen is ignited, assuming complete combustion to form carbon dioxide and water?

a. 5.96 g **b.** 1.49 g
c. 1.98 g **d.** 2.98 g

65. Hardness of water sample is 300 ppm $CaCO_3$. Hence its molarity is

a. 0.30 M **b.** 0.003 M
c. 0.030 M **d.** 0.0013 M

Brainteasers Objective Type Questions (Single choice only)

66. Specific volume of cylindrical virus particle is 6.02×10^{-2} cc/gm. Whose radius and length 7 Å and 10 Å respectively. If $N_A = 6.02 \times 10^{23}$, find the molecular weight of virus.

a. 3.08×10^3 kg/mol
b. 3.08×10^4 kg/mol
c. 1.54×10^4 kg/mol
d. 15.4 kg/mol

67. A 6.977 g sample of a mixture was analysed for barium ion by adding a small excess of sulphuric acid to an aqueous solution of the sample. The resultant reaction produced a precipitate of barium sulphate, which was collected by filtration, washed, dried and weighed. If 0.4123 g of barium sulphate was obtained, what was the mass percentage of barium in the sample?

a. 6.952 %
b. 3.476 %
c. 4.376 %
d. 1.738 %

68. Volume occupied by one molecule of water (density = 1 g cm^{-3}) is

a. 3.0×10^{-23} cm^3
b. 5.5×10^{-23} cm^3
c. 9.0×10^{-23} cm^3
d. 6.023×10^{-23} cm^3

69. In the reaction,

$$Al\ (s) + 6HCl\ (aq) \rightarrow 2Al^{3+}\ (aq) + 6Cl^-\ (aq) + 3H_2\ (g)$$

a. 33.6 L H_2 (g) is produced regardless of temperature and pressure for every mole Al that reacts
b. 67.2 L H_2 (g) at STP is produced for every mole Al that reacts
c. 11.2 L H_2 (g) at STP is produced for every mole HCl (aq) consumed.
d. 6 L HCl (aq) is consumed for every 3L H_2 (g) produced.

70. How many grams of calcium hydroxide, $Ca(OH)_2$, must be dissolved in water to give 250.0 millilitres of 0.0200 M $Ca(OH)_2$ solution?

a. 0.37 gm
b. 3.76 gm
c. 0.185 gm
d. 0.74 gm

71. For the formation of 3.65 g of hydrogen chloride gas, what volumes of hydrogen gas and chlorine gas are required at NTP conditions?

a. 1 lit, 1 lit
b. 1.12 lit, 2.24 lit
c. 3.65 lit, 1.83 lit
d. 1.12 lit, 1.12 lit

72. A metal oxide has the formula Z_2O_3. It can be reduced by hydrogen to give free metal and water 0.1596 g of the metal oxide requires 6 mg of hydrogen for complete reduction. The atomic weight of the metal is

a. 27.9
b. 159.6
c. 79.8
d. 55.8

73. 61.5 gm of a saturated solution (at 25°C) of a dilvalent metal sulphate is made upto 250 ml. 25 ml of this made up solution produces 1.375 gm of dry $BaSO_4$ with excess $BaCl_2$. The solubility of the metal sulphate at 25°C in gm per 100 g of water is (Ba = 137; S = 32; O = 16 ; MSO_4 = 148)

a. 14.6
b. 17.6
c. 16.6
d. 19.6

74. Liquid benzene (C_6H_6) burns in oxygen according to

$$2C_6H_6\ (l) + 15O_2\ (g) \rightarrow 12CO_2\ (g) + 6H_2O(g)$$

How many litres of O_2 at STP are needed to complete the combustion of 39 g of liquid benzene? (Mol. wt. of O_2 = 32, C_6H_6 = 78)

a. 74 L
b. 11.2 L
c. 22.4 L
d. 84 L

75. 3.92 g of ferrous ammonium sulphate are dissolved in 100 ml of water. 20 ml of this solution requires 18 ml of potassium permanganate during titration for complete oxidation. The weight of $KMnO_4$ present in one litre of the solution is

a. 13.47 g
b. 3.476 g
c. 14.76 g
d. 34.78 g

76. The number of oxalic acid molecules in 100 ml of 0.02 N oxalic acid solution is

a. 6.023×10^{22}
b. 10^{-3}
c. 6.022×10^{20}
d. none

77. The advantage of using KO_2 as gas masks in spaceships is that it absorbs CO_2, at the same time releasing oxygen. If 0.001 mole of KO_2 is present in an atmosphere containing 22.4 cm^3 of CO_2 at STP

free from moisture, what will be the volume of O_2 released at STP?

a. 16.8 cm^3 **b.** 18.6 cm^3
c. 18.8 cm^3 **d.** 17.8 cm^3

78. Rearrange the following (I to IV) in the order of increasing masses and choose the correct answer from (a), (b), (c) and (d) (At. mass : N = 14, O = 16, Cu = 63)

I. 1 molecule of O

II. 1 atom of nitrogen

III. 1×10^{-10} g molecular mass of oxygen

IV. 1×10^{-7} g atomic mass of copper

a. II < I < III < IV
b. IV < III < II < I
c. II < III < I < IV
d. III < IV < I < II

79. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl?

a. 0.011 **b.** 0.029
c. 0.044 **d.** 0.333

80. In the photographic developing process, silver bromine is dissolved by adding sodium thiosulphate:

$$AgBr\ (s) + 2Na_2S_2O_3\ (aq) \rightarrow Na_3Ag\ (S_2O_3)_2\ (aq) + NaBr\ (aq)$$

If you want to dissolve 0.250 g of AgBr, what volume of 0.0138 M $Na_2S_2O_3$, in milliliters, should be used?

a. 143 ml **b.** 139 ml
c. 96.5 ml **d.** 193 ml

81. A mixture of 0.002 mole of $KBrO_3$ and 0.01 mole of KBr was treated with excess of KI and acidified. The volume of 0.1 M $Na_2S_2O_3$ solution required to consume the liberated iodine will be

a. 150 ml **b.** 90 ml
c. 120 ml **d.** 100 ml

82. A sample was analysed and reported to contain 20 % NaOH. Later it was found that the basic material is KOH rather than NaOH. The percentage KOH in the sample is

a. 42.9 **b.** 19.4
c. 21 **d.** 29.4

83. The percentage of an element M is 53 in its oxide of molecular formula M_2O_3. Its atomic mass is about

a. 54 **b.** 32
c. 27 **d.** 41

84. 0.2g of a sample of an oxalate salt is dissolved in 100 cc of water. It required 90 cc of N/20 $KMnO_4$ solution for complete oxidation. The percentage of oxalate ($C_2O_4^{2-}$) in the given sample is

a. 33 **b.** 66
c. 26 **d.** 96

85. For the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$, the volume of carbon monoxide required to reduce one mole of ferric oxide is

a. 67.2 dm^{-1} **b.** 44.8 dm^3
c. 21.5 dm^2 **d.** 89.7 dm^1

86. The mass percentage of chloride ion in a 25.00 ml sample of sea water was determined by titrating the sample with silver nitrate, causing precipitation of silver chloride. If required 42.58 ml of 0.2997 M silver nitrate solution to reach the equivalence point in the titration. What is the mass percentage of chloride ion in the sea water if its density is 1.025 g/ml?

a. 2.676 % **b.** 0.883 %
c. 1.766 % **d.** 3.766 %

87. Like many metals, aluminium also reacts with a halogen to give a metal halide

$$2Al\ (s) + 3Br_2\ (l) \rightarrow Al_2Br_6\ (s)$$

What quantity of Br_2 (in grams) is required for complete reaction with 2.56 g of Al?

What mass of white, solid Al_2Br_6 is expected respectively?

a. Br_2 = 11.2 gm, Al_2Br_6 = 25.3 gm
b. Br_2 = 22.7 gm, Al_2Br_6 = 15.3 gm
c. Br_2 = 22.7 gm, Al_2Br_6 = 25.3 gm
d. Br_2 = 11.2 gm, Al_2Br_6 = 50.6 gm

88. Study the following table:

Compound (mol. wt.)	Wt. of compound (in gm) taken
I. CO_2 (44)	4.4
II. NO_2 (46)	2.3
III. H_2O_2 (34)	6.8
IV. SO_2 (64)	1.6

Which two compounds have least weight of oxygen

a. I and II **b.** I and III
c. II and IV **d.** III and IV

89. MnO_4^- ions are reduced in acidic condition to Mn^{2+} ions whereas they are reduced in neutral condition to MnO_2. The oxidation of 25 ml of a solution X containing Fe^{2+} ions required in acidic condition 20 ml of a solution Y containing MnO_4^- ions. What volume of solution Y would be required to oxidize 25 ml of solution X containing Fe^{2+} ions in neutral condition?

a. 10.4 ml **b.** 12.89 ml
c. 33.3 ml **d.** 23.9 ml

90. Cobalt (III) ion forms many compounds with ammonia. To find the formula of one of these compounds, you t itrate the NH_3 in the compound with standardized acid.

$$Co(NH_3)_xCl_3\ (aq) + {}_xHCl\ (aq) \rightarrow$$

$${}_xNH_4^+\ (aq) + Co^{3+}\ (aq) + (x + 3)\ Cl^-\ (aq)$$

Assume that 23.63 m l of 1.500 M HCl is used to titrate 1.580 g of $Co(NH_3)_x\ Cl_3$. What is the value of X?

a. $[Co(NH_3)_6]Cl_3$ **b.** $[Co(NH_3)_5Cl]cl_3$
c. $[Co(NH)_3Cl_3$ **d.** $[Co(NH_3)_4Cl_2]Cl$

91. A mixture of 0.5 g of ethanol and acetaldehyde when heated with Fehling's solution gave 1.2 g of red precipitate of Cu_2O.
What is the percentage of acetaldehyde in the mixture?

a. 54 % **b.** 47 %
c. 74 % **d.** 36 %

92. If 70.0 g of Fe_3O_4 and 12.0 g of O_2 are present in a reaction mixture, determine how many grams of each reactant will be left unreacted upon completion of the following reaction.

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$$

a. Zero g Fe_3O_4 and 6.9 g O_2
b. Zero g Fe_3O_4 and 9.6 g O_2
c. 6.9 g Fe_3O_4 and 9.6 g O_2
d. 9.6 g Fe_3O_4 and zero g O_2

93. $CaCO_3$ is decomposed by HCl (density 1.825 g/cc)

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

Volume of HCl required to decompose 10 g of 50% pure $CaCO_3$ is:

a. 1.22 ml **b.** 2.0 ml
c. 0.242 ml **d.** 3.2 ml

94. The reaction between 113.4 g of I_2O_5 and 132.2 g of BrF_3 was found to produce 97.0 g of IF_5. The equation for the reaction is

$$6\ I_2O_5 + 20\ BrF_3 \rightarrow 12\ IF_5 + 15\ O_2 + 10\ Br_2$$

What is the per cent yield of IF_5?

a. 37.7 % **b.** 75.4 %
c. 150.8 % **d.** 57.4 %

95. What volume of 0.955 M HCl, in milliliters, is needed to titrate 2.152 g of Na_2CO_3 to the equivalence point?

$$Na_2CO_3\ (aq) + 2HCl\ (aq) \rightarrow$$

$$2NaCl\ (aq) + CO_2\ (g) + H_2O\ (l)$$

a. 4.25 ml **b.** 21.5 ml
c. 84.0 ml **d.** 42.5 ml

96. Ammonia gas can be prepared by the following reaction:

$$CaO\ (s) + 2NH_4Cl\ (s) \rightarrow$$

$$2NH_3\ (g) + H_2O\ (g) + CaCl_2\ (s)$$

If 103 g of ammonia is obtained, but the theoretical yield is 136 g, what is the per cent yield of this gas?

a. 75.7 % **b.** 25.1 %
c. 57.5 % **d.** 15.7 %

97. The allowable concentration level of vinyl chloride, C_2H_3Cl, in the atmosphere in a chemical plant is 2.0×10^{-6} g/L. How many molecules are present per litre?

a. 1.47×10^{16} m/L
b. 1.97×10^{16} m/L
c. 2.97×10^{16} m/L
d. 1.07×10^{16} m/L

98. 0.7 g of a sample of $Na_2CO_3.xH_2O$ were dissolved in water and the volume was made to 100 ml. 20 ml of this solution required 19.8 ml of N/10 HCl for complete neutralization. The value of 'x' is:

a. 3 **b.** 2
c. 4 **d.** 6

99. A mixture (15 ml) of CO and CO_2 is mixed with V ml (excess) of oxygen and electrically sparked.

The volume after explosion was (V + 12)ml, what would be the residual volume if 25ml of the original mixture is exposed to alkali

a. 10 ml **b.** 9 ml
c. 8 ml **d.** 12 ml

100. An element A is converted to its bromide and the bromine precipitated as AgBr. Atomic weight of A = 91.2. 0.722 g of the bromide gives 1.32 g of AgBr. Valency of the element A is (Ag = 108; Br = 80)

a. 2 **b.** 3
c. 4 **d.** 5

Multiple Correct Answer Type Questions

101. 1 mole of $Mg(OH)_2$ can exactly neutralize

a. 1 mole HNO_3
b. 2 mole of H_3PO_2
c. 1 mole of H_2SO_4
d. 1 mole of H_3PO_3

102. A solution of $Na_2S_2O_3$ is iodometrically titrated against 0.25050 g of $KBrO_3$. This process requires 90 ml of $Na_2S_2O_3$ solution the strength of the $Na_2S_2O_3$ is

a. 0.2 M **b.** 0.1 M
c. 0.05 M **d.** 0.1 N

103. The iodide content of a solution was determined by titration with cerium (IV) sulphate in the presence of HCl, in which I^- is converted to ICl. A 250 ml sample of the solution required 20 ml of 0.05 N Ce^{4+} solution. What is the iodide concentration in the original solution?

a. 2×10^{-3} moles
b. 0.254 g/litre
c. 2.54×10^{-2} moles
d. 0.508 g/lit

104. 3.16 g of $KMnO_4$ is dissolved in water and the solution is made upto 1 litre. An unknown salt containing 6.88 g Fe^{2+} ion was dissolved in water and solution was made upto 100 ml. It was found that 20 ml of salt solution decolourised 27.25 ml of the above permanganate solution. Which of the following statements are correct?

a. normality of ferrous ion = 0.15 N
b. actual strength of ferrous ion 68.8 g lit^{-1}
c. percentage of ferrous ion is 10.58
d. normality of ferrous ion is 0.13 N

105. H_3BO_3, Boric acid is

a. Aprotic acid
b. dibasic acid
c. tribasic acid
d. monobasic acid

106. An aqueous solution containing 288 g of a non-electrolyte compound having the stoichiometric composition $C_nH_{2n}O_n$ in 90g water boils at 101.24°C and 1 atm pressure. K_b = 0.512 K mol^{-1} kg. Which of the following statements are correct?

(i) molecular mass of $C_nH_{2n}O_n$ = 1321.2 g
(ii) molecular formula of $C_nH_{2n}O_n = C_{44}H_{88}O_{44}$
(iii) molecular mass of $C_nH_{2n}O_n$ = 104.2 g
(iv) empirical formula of $C_nH_{2n}O_n$ is CH_2O

a. (i) & (iv) **b.** (ii) & (iv)
c. (i) & (ii) **d.** (iv) & (ii)

107. 1.66 g KI reacts with excess of KIO_3 to produce I_2, which converts $Na_2S_2O_3$ into SO_4^{2-}. If the hypo solution was decimolar, then the volume required to reach equivalent point will be

a. 0.015 litre **b.** 15 ml
c. 0.02 litre **d.** 20 ml

108. Which of the following is/are incorrect for 17 g /l of H_2O_2 solution?

a. The normality of solution is 3 M
b. Volume strengths is 5.6 at 273 K and 1 atm
c. 1 mL of this solution gives 1.4 mL O_2 at 273 K and 2 atm
d. Molarity of solution is 0.1 M

109. Mole fraction of ethanol (C_2H_5OH) in ethanol-water system is 0.25. Thus it has:

a. 46 % ethanol by weight of solution
b. 54 % water by weight of solution
c. 25 % ethanol by weight of solution
d. 75 % water by weight of solution

110. In diammonium hydrogen phosphate, $(NH_4)_2HPO_4$, percentage as:

a. P is maximum
b. N is maximum
c. P_2O_5 is 53.78 %
d. NH_3 is 25.76 %

111. A certain compound has the molecular formula X_4O_6 having 57.2 % X. Thus:

a. X can be a non-metal

b. X is an electropositive metal

c. Atomic mass of X is 32.

d. X may contain five valence electrons.

112. Which one of the following statements is/are correct?

a. One mole of CH_4 and 17 g NH_3 at NTP occupies same volume

b. One gram mole of silver equals $108/6.023 \times 10^{23}$ g

c. One gram mole of CO_2 is 6.023×10^{23} times heavier than one molecule of CO_2

d. One mole Ag weighs more than that of two moles of Ca

113. 1 g atom of oxygen can have

a. 22.4 litre of O_2 at N.T.P.

b. 6.02×10^{23} O_2 molecules

c. 16 g of O_2

d. 11.2 litre of O_2 at N.T.P.

114. For the reaction

$$H_3PO_4 + Mg(OH)_2 \rightarrow CaHPO_4 + 2H_2O$$
1 mole 1 mole

Then which of the following statement are correct?

a. 1 mole of H_3PO_4 is completely neutralized by 1 mole of $Mg(OH)_2$

b. 1 mole of H_3PO_4 is completely neutralized by 1.5 mole of $Mg(OH)_2$

c. the equivalent weight of H_3PO_4 is 49.

d. the resulting solution is neutralized by 1 mole of NaOH

115. Which of the following have same number of atoms?

a. 22.4 L of O_2 at STP

b. 5.0 g of He

c. 1.7 gm of NH_3

d. 6.4g of O_2

116. Consider the given reaction and select the correct statements.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

a. the mass of ammonia formed when 2 kg. N_2 react with 1 kg H_2 is 2.428 gm.

b. the mass of ammonia formed when 2 kg. N_2 react with 1 kg H_2 is 4.856 gm.

c. H_2 remain unreacted also and the mass left unreacted is 0.571 kg.

d. H_2 remain unreacted also and the mass left unreacted is 0.4286 kg.

Linked-Comprehension Type Questions

Comprehension 1

Chemical reactions involve interaction of atoms and molecules. A large number of atoms/ molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolyzed. This leads to the evolution of chlorine gas at one of the electrodes (atomic masses: Na = 23, Hg = 200, 1 Faraday = 96500 coulombs).

117. The total number of moles of chlorine gas evolved is

a. 0.5 **b.** 1.0

c. 2.0 **d.** 3.0

[IIT 2007]

118. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is

a. 200 **b.** 225

c. 400 **d.** 446

[IIT 2007]

119. The total charge (coulombs) required for complete electrolysis is

a. 24125 **b.** 48250

c. 96500 **d.** 193000

[IIT 2007]

Comprehension 2

Oleum is considered as a solution of SO_3 in H_2SO_4, which can be obtained by passing SO_3 in solution of H_2SO_4. When 100 g sample of oleum is diluted with desired weight of H_2O then the total mass of H_2SO_4 obtained after dilution is called as % labeling in oleum.

For example, an oleum bottle labeled as '118 % H_2SO_4' means the 118 g total mass of pure H_2SO_4 will be formed when 100g of oleum is diluted by 18 g of H_2O which combines with all the free SO_3 present in oleum to form H_2SO_4 as $SO_3 + H_2O \rightarrow H_2SO_4$.

120. What is the % of free SO_3 is an oleum that is labelled as '109 % H_2SO_4?

a. 10 **b.** 40

c. 20 **d.** 9

121. 4.5 g water is added into oleum sample labeled as "106% H_2SO_4" then the amount of free SO_3 remaining in the solution is :

a. 1.493 L at STP

b. 1.792 L at STP

c. 3.73 L at STP

d. 1.12 L at STP

122. If excess water is added into a bottle sample labeled as "112 % H_2SO_4" and is reacted with1.06 g Na_2CO_3, then find the volume of CO_2 evolved at 1 atm pressure and 300 K temperature after completion of the reaction :

a. 2.4615 L **b.** 24.6 L

c. 0.24615 L **d.** 12.3 L

123. 1 g of volume sample is diluted with water. The solution required 27 mL of 0.8 N NaOH for complete neutralization. The %v of free SO_3 in the sample is :

a. 74 **b.** 26

c. 20 **d.** 80

Comprehension 3

The strength of H_2O_2 is expressed in many ways like molarity, normality, % (w /V), volume strength, etc. The strength of "15 V" means 1 volume of H_2O_2 on decomposition gives 15 volumes of oxygen at STP or 1 litre of H_2O_2 gives 15 litre of O_2 at STP. The decomposition of H_2O_2 can be shown as follows:

$H_2O_2(aq) \rightarrow H_2O(l) + \frac{1}{2} O_2(g)$

H_2O_2 can act as oxidizing as well as a reducing agent, as an oxidizing agent H_2O_2 converts into H_2O and as a reducing agent H_2O_2 converts into O_2, in both these cases it's n- factor is 2.

Hence normality of H_2O_2 solution = 2 × Molarity of H_2O_2 solution

124. What is the molarity of "16.8 V" of H_2O_2 ?

a. 1.5 M **b.** 1 M

c. 5.6 M **d.** 0.5 M

125. 25 ml of H_2O_2 solution were added to excess of acidified solution of KI. The iodine so liberated required 20 ml of 0.1 N $Na_2S_2O_3$ for titration. Calculate the strength of H_2O_2 in terms of normality.

a. 0.04 **b.** 0.08

c. 0.06 **d.** 0.12

126. 10 ml. of H_2O_2 solution is reacted with 40 ml of $KMnO_4$ in acidic medium then what is the volume strength of H_2O_2 ?

a. 2.8 **b.** 5.6

c. 11.2 **d.** 8.4

127. What is the percentage strength (% w/ V) of "16.8 V" H_2O_2 ?

a. 1.7 **b.** 5.1

c. 34 **d.** 1.68

Comprehension 4

A redox reaction involves oxidation and reduction simultaneously by exchange of electrons. The species undergoing oxidation and reduction are reductant and oxidant respectively. In order to get n -factor or any oxidant or reductant change of oxidation number is first find out.

128. The ion X^{+n} is oxidized to XO_3^- by MnO_4^- giving Mn^{2+} in acid solution. Given that 2.68×10^{-3} mole of X^{+n} requires 1.61×10^{-3} mole of MnO_4^-, what is the value of n? What is the wt. of one g. equivalent of XCl_n for the above reaction if the atomic mass of X is 97.0?

a. 80 **b.** 84

c. 168 **d.** 72

129. How many gram HCl can be oxidized into free chlorine by 40 g. of $K_2Cr_2O_7$ in an acidic solution, the latter being reduced to Cr^{+3} ions?

(Cr = 52, K = 39, O = 16)

a. 29.579 **b.** 29.785

c. 29.795 gm. **d.** 29. 859

130. Which of the following is not correct here

a. For the reaction

$Cu_2S \rightarrow CuO + SO_2$

$E_{Cu2S} = M/8$

b. a $Cu_2O + bNO_3^- + 14H^+ \rightarrow Cu^{2+} + NO + 7H_2O$

Here a : b is 3 : 2

c. $FeS_2 \rightarrow Fe_2O_3 + SO_2$

Here $E = \frac{M}{11}$

d. The value of n- factor of $Fe(SCN)_2$ when it oxidizes into Fe^{+3}, SO_4^{-2} and $(CN)_2$ is 12

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given Mark.

a. if A and R both are correct and R is the correct explanation of A;
b. if A and R both are correct but R is not the correct explanation of A;
c. A is true but R is false;
d. A is false but R is true,
e. A and R both are false.

131. **(A)**: One mole of NaCl contains 6.023×10^{23} molecules of sodium chloride.

(R): 58.5 g of NaCl also contains 6.023×10^{23} molecules of NaCl.

132. **(A)**: 22.4 L of N_2 at NTP and 5.6 L O_2 at NTP contain equal number of molecules.

(R): Under similar conditions of temperature and pressure all gases contain equal number of molecules.

133. **(A)**: Number of gm-molecules of SO_2Cl_2 in 13.5 g of sulphuryl chloride is 0.2.

(R): Gram molecules is equal to those molecules which are expressed in gram.

134. **(A)**: In CO molecule 12 parts by mass of carbon combine with 16 parts by mass of oxygen and in CO_2, 12 parts by mass of carbon combine with 32 parts by mass of oxygen.

(R): When two elements combine separately with a fixed mass or a third element, then the ratio of their masses in which they do so is either the same or whole number multiple of the ratio in which they combine with each other.

135. **(A)**: The molality of the solution does not change with change in temperature.

(R): The molality is expressed in units of moles per 1000 gm of solvent.

136. **(A)**: Molarity of a solution and molality of a solution both change with density

(R): Density of the solution changes when percentage by mass of solution changes.

137. **(A)**: The percentage of nitrogen in urea is 46.6 %.

(R): Urea is ionic compound.

138. **(A)**: 0.28 g of N_2 has equal volume as 0.44 g of another gas at same conditions of temperature and pressure.

(R): molecular mass of another gas is 44 g mol^{-1}.

139. **(A)**: In $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$, MnO_4^- acts as oxidizing agent and Fe^{2+} acts as reducing agent.

(R): The reactions nvolving simultaneous loss or gain of electron among the reacting species are called oxidation reduction reactions.

140. **(A)**: Equivalent mass of a base which contains one mole of replaceable OH^- ion in a molecule.

(R): It is the mass of a base which completely reacts with one gram equivalent mass of an acid.

141. **(A)**: Decomposition of H_2O_2 is a disproportionation reaction.

(R): H_2O_2 molecule simultaneously undergoes both oxidation and reduction.

142. **(A)**: Molarity of a solution and molality of a solution both change with density.

(R): Density of the solution changes when percentage by mass of solution changes.

143. **(A)**: The molality of the solution does not change with change in temperature.

(R): The molality is expressed in units of moles per 1000g of solvent.

144. **(A)**: In the balanced redox reaction $x\ Cu_2O + y\ NO_3^- + 14\ H^+ \rightarrow 6Cu^{2+} + NO + 7H_2O$, the n-factor of Cu_2O and NO_3^- is 2 and 3 respectively.

(R): Since reciprocal of n-factor's ratio is molar ratio and so, x : y = 3 : 2

145. **(A)**: For the reaction

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$ The equivalent weight of Na_2CO_3 is 106.

(R): Because the n-factor Na_2CO_3 is 1 and equivalent weight =

$$\frac{\text{molecular weight}}{\text{n-factor}}$$

146. **(A)**: A bottle is labeled as "10 V" of H_2O_2. So its percentage strength is 5%.

(R): % strength of H_2O_2 is nothing but it is the number of grams of H_2O_2 in 100 mL solution of H_2O_2 and it is related with volume strength as under 1 "vol" of H_2O_2 = 0.303 %.

Matrix-Match Type Questions

147. Match the following:

Column I	Column II
A. 1.12 L CO_2	(p) 0.5 N_A molecules
B. 0.8 gm CH_4	(q) 0.05 N_A molecules
C. 11.2 L SO_2	(r) 0.15 N_A atoms
D. 16 gm O_2	(s) N_A no. of oxygen atoms

148. Match the following:

List I (Reaction)	List II (Maximum yield of the product)
A. $2H_2$ (1g) + O_2 (1g) $\rightarrow 2H_2O$	(p) 1.125 g
B. $3H_2$ (1g) + N (1g) $\rightarrow 2NH_3$	(q) 1.028 g
C. H_2 (1g) + Cl_2 (1g) $\rightarrow$ 2HCl	(r) 1.214 g
D. $2H_2$ (1g) + C (1g) $\rightarrow CH_4$	(s) 1.333 g

149. Match the following:

List I	List II
A. $NH_3 \rightarrow NO_3^-$	(p) M/5
B. $Fe_2S_3 \rightarrow 2FeSO_4 + SO_2$	(q) M
C. $KMnO_4$ H^+ $MnSO_4$	(r) M/20
D. $CuS \rightarrow CuSO_4$	(s) M/8

150. Match the stoichiometric coefficients in List I with the species in List II and involved in the balanced equation of the following reaction:

$$FeC_2O_4 + MnO_4^- \rightarrow CO_2 + Mn^{2+}$$

List I	List II
A. FeC_2O_4	(p) 3
B. MnO_4^-	(q) 5
C. H^+	(r) 10
D. CO_2	(s) 24

151. Match the following:

List I	List II
A. A 0.5 g sample of dichromate ore required 20 ml of 0.22 M ferrous ammonium sulphate for complete reduction. What is the percentage of chromium in the sample?	(p) 29.4
B. A sample was analysed and reported to contain 21 % NaOH. Later it was found that the basic material is KOH rather than NaOH. What is the percentage of KOH in the sample.	(q) 20.6
C. 25 ml of H_2O_2 solution when added to excess acidified KI solution, evolves iodine, which require 20 ml of 0.3125 N sodium thiosulphate solution. What is the volume strength of H_2O_2?	(r) 1.4
D. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. This solution is completed neutralized by 26.7 ml of 0.4 N NaOH. What is the percentage of free SO_3 in the sample?	(s) 15.25

152. Match the following:

List I	List II
A. Change of NO to NO_3^-	(p) Oxidation number changes from +7 to+2
B. Change of P_4 to $H_2PO_2^-$	(q) Oxidation number changes +6 to +3
C. $KMnO_4$ in acidic medium	(r) Oxidation number changes from 0 to +1
D. $K_2Cr_2O_7$ in acidic medium	(s) Oxidation number changes from +2 to+5.

153. Match of the following:

Column I	Column II
A. 5.55 mole	(p) 4.48 L of SO_2 at N.T.P
B. 0.1 mole	(q) 100 mL H_2O

C. 0.2 mole (r) 22 gm CO_2
D. 0.5 mole (s) 2.24 L NH_3
(t) 0.1 gm atom of Fe

154. Match the following:

List I (1D = 10^{-18} esu cm, 1D = 3.33×10^{-30} cm)	**List II (Electronic charge = 4.8×10^{-10} esu)**
A. A diatomic molecule has a dipole moment equal to 1.2 D. If bond length is 1.0 Å. What fraction (%) of electronic charge exists on each atom.	(p) 40 %
B. The dipole moment of LiH is 1.94×10^{-29} cm and intermolecular distance between Li and H in this molecule is 1.596 Å. What is percent ionic character in molecule.	(q) 60 %
C. One litre of mixture of CO and CO_2 is passed through red hot charcoal in tube. The new volume becomes 1.4 litre. Find out % composition of CO at same P and T.	(r) 76 %
D. Given sample of oleum is labeled as 109 %. Calculate the % of free SO_3 in it.	(s) 25 %

155. Match the following:

List I	**List II**
A. 10 'vol' H_2O_2	(p) 0.032 g of O_2
B. 11.2 'vol' H_2O_2	(q) 0.5 M
C. 5.6 'vol' H_2O_2	(r) 3.03 %
D. 20 'vol' H_2O_2	(s) 2N

The IIT-JEE Corner

156. The number of moles of $KMnO_4$ that will be needed to react completely with one mole of ferrous oxalate in acidic solution is

a. 1 **b.** 2/5
c. 3/5 **d.** 4/5

[IIT 1997]

157. The normality of 0.3 M phosphorous acid (H_3PO_3) is

a. 0.1 **b.** 0.3
c. 0.6 **d.** 0.9

[IIT 1999]

158. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralizes 10 mL of this solution is

a. 40 mL **b.** 20 mL
c. 10 mL **d.** 4 mL

[IIT 2001]

159. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is

a. same as molecular weight
b. molecular weight/2
c. molecular weight/4
d. molecular weight/6

[IIT 2001]

160. How many moles of electrons weigh one kilogram?

(mass of electron = 9.108×10^{-31} kg, Avogadro number = 6.023×10^{23})

a. 6.023×10^{23}

b. $1/9.108 \times 10^{31}$

c. $\frac{6.023}{9.08} \times 10^{54}$

d. $\frac{1}{9.108 \times 6.023} \times 10^{8}$

[IIT 2002]

161. Which has maximum number of atoms?

a. 24 g of C (12)
b. 56 g of Fe (56)
c. 27 g of Al (27)
d. 108 g of Ag (108)

[IIT 2003]

162. Mixture X = 0.02 mol of $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5\ Br]SO_4$ was prepared in 2 litre of solution.

1 litre of mixture X + excess $AgNO_3$ → Y.

I litre of mixture X + excess $BaCl_2$ → Z.

Number of moles of Y and Z are

a. 0.02, 0.01 **b.** 0.01, 0.01

c. 0.01, 0.02 **d.** 0.02, 0.02

[IIT 2003]

163. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenyl amine as indicator. The number of moles of Mohr's salt required per mole of dichromate is

a. 3 **b.** 4

c. 5 **d.** 6

[IIT 2007]

164. Given that the abundances of isotopes ^{54}Fe, ^{56}Fe and ^{57}Fe are 5%, 90% and 5% respectively, the atomic mass of Fe is

a. 55.85 **b.** 55.95

c. 55.75 **d.** 56.05

[IIT 2009]

ANSWERS

Straight Objective Type Questions

1. a	**2.** c	**3.** c	**4.** b	**5.** a	**6.** b	**7.** d	**8.** d	**9.** b	**10.** c	**11.** b	**12.** d
13. b	**14.** a	**15.** c	**16.** a	**17.** c	**18.** c	**19.** b	**20.** c	**21.** c	**22.** d	**23.** a	**24.** d
25. d	**26.** d	**27.** c	**28.** a	**29.** b	**30.** d	**31.** a	**32.** b	**33.** c	**34.** b	**35.** d	**36.** c
37. d	**38.** c	**39.** c	**40.** b	**41.** b	**42.** a	**43.** c	**44.** b	**45.** b	**46.** b	**47.** c	**48.** b
49. c	**50.** d	**51.** a	**52.** a	**53.** a	**54.** a	**55.** a	**56.** c	**57.** b	**58.** a	**59.** b	**60.** d
61. b	**62.** a	**63.** c	**64.** d	**65.** b							

Brainteasers Objective Type Questions

66. d	**67.** b	**68.** a	**69.** c	**70.** a	**71.** d	**72.** d	**73.** c	**74.** d	**75.** b	**76.** c	**77.** a
78. a	**79.** b	**80.** d	**81.** c	**82.** d	**83.** c	**84.** b	**85.** a	**86.** c	**87.** c	**88.** c	**89.** c
90. a	**91.** c	**92.** b	**93.** b	**94.** b	**95.** d	**96.** a	**97.** b	**98.** b	**99.** a	**100.** c	

Multiple Correct Answer Type Questions

101. b,c,d	**102.** b, d	**103.** a, b	**104.** b,c,d	**105.** a, d	**106.** a ,c	**107.** a, b	**108.** a,c,d
109. a, b	**110.** c, d	**111.** a,c,d	**112.** a,c,d	**113.** c, d	**114.** b,c,d	**115.** c, d	**116.** a, c

Linked-Comprehension Type Questions

Comprehension 1

117. b **118.** d **119.** d

Comprehension 2

120. b **121.** c **122.** c **123.** b

Comprehension 3

124. a **125.** b **126.** b **127.** b

Comprehension 4

128. b **129.** c **130.** d

Assertion Reason Type Questions

131. b	**132.** e	**133.** e	**134.** b
135. a	**136.** a	**137.** c	**138.** b
139. a	**140.** a	**141.** a	**142.** a
143. a	**144.** a	**145.** a	**146.** d

Matrix-Match Type Questions

147. A - (q, r), B - (q), C - (p, s), D - (p, s)

148. A-(p), B-(r), C-(q), D-(s)

149. A-(s), B-(r), C-(p), D-(s)

150. A-(q), B-(p), C-(s), D-(r)

151. A-(s), B-(p), C-(r), D-(q)

152. A-(s), B-(r), C-(p), D-(q)

153. A - (q), B - (s, t), C - (p), D - (r)

154. A-(s), B-(r), C-(p), D-(q)

155. A-(r), B-(s), C-(q), D-(p)

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156. c **157.** c **158.** a **159.** d **160.** d **161.** a **162.** b **163.** d **164.** b

Hints and Explanations

Straight Objective Type Questions

1. $3BaCl_2 + 2Na_3PO_4 \rightarrow Ba_3(PO_4)_2 + 6NaCl$
0.5 0.2

Limiting reagent is Na_2PO_4 (0.2 mol), which gives 0.1 mol of $Ba_3(PO_4)_2$.

2. $N_2H_4 \rightarrow Y + 10\ e^-$

Oxidation state of N in N_2H_4 :

$2X + 4 = 0$

$X = -2$

The two, nitrogen atoms will balance the charge of 10 e^{-1}.

So oxidation state of N will increase by +5, that is, from –2 to +3.

3. $\text{Eq. mass} = \dfrac{\text{molecular weight}}{\text{Change in oxidation no. of Mn}}$

$= \dfrac{\text{mol. wt.}}{4-2} = \dfrac{\text{mol. wt.}}{2}$

(oxidation number of Mn in $MnSO_4$ = +2 and Mn in MnO_2 = +4)

4. Molality of a solution remains independent of temperature.

5. $Mg^{++} + Na_2CO_3 \rightarrow MgCO_3 + 2Na^+$

1 g eq. 1 g eq.

1 g eq. of Mg^{2+} = 12 g of Mg^{2+} = 12000 mg = 1000 milli eq. of Na_2CO_3

Hence 12 mg Mg^{2+} = 1 milli eq. Na_2CO_3

6. As 1 mol CCl_4 vapour = $12 + 4 \times 35.5$

= 154 g ≡ 22.4 L at STP

So density = $\dfrac{W}{V} = \dfrac{154}{22.4}\ gL^{-1}$

= 6.875 g L^{-1}

7. 22400 cc = 6.02×10^{23} molecules

1 cc $N_2O = \dfrac{6.02 \times 10^{23}}{22400}$ molecules

$= \dfrac{3 \times 6.02 \times 10^{23}}{22400}$ atoms

$= \dfrac{1.8}{224} \times 10^{22}$ atoms

number of electrons in a molecule of N_2O = 7 + 7 + 8 = 22

hence number of electrons

$= \dfrac{6.02 \times 10^{23}}{22400} \times 22$ electrons

8. As normality of 10 volume of H_2O_2 = 1.78 N

So volume strength of 1.78 N solution = 10

Volume strength of 1.5 N H_2O_2

$= 1.5 \times \dfrac{10}{1.78} = 8.4.$

9. Number of oxygen atoms = number of CO molecules = 6.022×10^{24}

Number of oxygen molecule

= ½ × number of oxygen atoms

$= ½ \times 6.022 \times 10^{24} = 3.011 \times 10^{24}$

number of g molecule of O_2 molecules

$= \frac{3.011 \times 10^{24}}{6.022 \times 10^{23}} = 5$ g molecule

10. Mol. Mass of $CuSO_4.5H_2O$

$= 63 + 32 + 16 \times 4 + 5 \times 18 = 249$

6.02×10^{23} molecules of $CuSO_4.5H_2O$ has a mass = 249 g

1×10^{22} molecules of $CuSO_4.5H_2O$ has a

mass $= \frac{(249\text{ g}) \times 1 \times 10^{22}}{6.02 \times 10^{23}} = 4.159$ g

11. Molecular wt of $C_{60}H_{122} = (12 \times 60) + 122 = 842$

therefore weight of one molecule

$= \frac{\text{molecular weight of } C_{60}H_{122}}{\text{Avogadro's number}}$

$= \frac{842}{6.023 \times 10^{23}} = 1.4 \times 10^{-21}$ g

12. Mol. wt. of $ZnSO_4.7H_2O$

$= 65 + 32 + (4 \times 16) + 7(2 \times 1 + 16) = 287$

percentage mass of Zn

$= \frac{65}{287} \times 100 = 22.65\ \%$

13. Wt. of $Mg(HCO_3)_2 = 7.3$ gm.

$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2$

Mol. wt. of $Mg(HCO_3)_2$

$= 24 + (1 + 12 + 48) \times 2 = 146$ gm

As 146 gm of $Mg(HCO_3)_2$ evolves 22.4 L of CO_2 at STP.

So 7.3 gm of $Mg(HCO_3)_2$ evolves

$\frac{7.3 \times 22.4}{146} = 1.12\ l = 1120$ ml

14. Atomic weight of Zn = 95 and volume of $H_2 = 224$ ml

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

$\frac{\text{Volume of } H_2}{22400} = \frac{\text{Weight of Zn}}{\text{Atomic weight of Zn.}}$

Wt. of Zn $= \frac{224 \times 65}{22400} = 0.65$ gm

15. Number of moles of $NH_3 = \frac{\text{mass in gm}}{\text{Mol. mass}}$

$= \frac{4.25}{17} = 0.25$ mole

Number of atoms $= 0.25 \times 6 \times 10^{23}$

$= 1.50 \times 10^{23}$ atoms

16. Mol. wt. of ammonia $= 14 + (3 \times 1) = 17$.

As wt. of ammonia = 4.25 gm

So 17 gm of ammonia contains 6.02×10^{23} atoms

4.25 gm of ammonia contain

$= \frac{6.02 \times 10^{23} \times 4.25}{17} = 1.5 \times 10^{23}$.

17. Atomic wt. of oxygen = 16 gm

Wt. of 6.02×10^{23} atoms of oxygen is 16 gm

So weight of 1 atom $= \frac{16}{6.02 \times 10^{23}}$.

$= 2.656 \times 10^{-23}$ gm

18. According to stoichiometry they should react as follows:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$

4 moles	5 moles	4 moles	6 moles
0.8 moles	1 mole	0.8 mole	1.2 moles

Thus for 1 mole O_2 only 0.8 mole of NH_3 is consumed. So O_2 is consumed completely.

19. Mol. wt. of H_3PO_4 is 98 and change in its valence = 1.

Eq. wt. of $H_3PO_4 = \frac{\text{mol. wt.}}{\text{Change in valency}}$.

$= 98/1 = 98$.

20. $BaCO_3 \rightarrow BaO + CO_2$

197 gm

197 gm of $BaCO_3$ released $CO_2 = 22.4$ litre

1 gm of $BaCO_3$ released $CO_2 = \frac{22.4}{197}$ litre

9.85 gm of $BaCO_3$ released CO_2

$= \frac{22.4}{197} \times 9.85 = 1.12$ litre

21. $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

106 gm gives 22.4 lit

2.12 gm gives $\frac{2.12 \times 22.4}{106} = \frac{22.4}{50}$

= 0.448 litre.

22. Suppose the mol. wt. of enzyme = x

So in 100 g of enzyme wt. of Se = 0.5 gm

In x g of enzyme wt. of Se = $\frac{0.5}{100} \cdot x$

hence $78.4 = \frac{0.5 \cdot x}{100}$

$x = 15680 = 1.568 \times 10^4$

23. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

16 g $\quad 2 \times 22.4$

32 g $\quad \frac{2 \times 22.4 \times 32}{16} = 4 \times 22.4$

= 89.6 litre of O_2.

24. Volume of one drop of water = 0.0018 ml.

As the density of water is 18 g/cc,

So 18 ml of water = 1 mole of water = 6.02×10^{23} molecules of water.

Thus 0.0018 ml of water = 18×10^{-4} gm of water molecules of water

$= (6.023 \times 10^{23}) \times 10^{-4}$

$= 6.023 \times 10^{19}$ molecules.

25. As molecular weight of $C_{60}H_{122}$

$= (12 \times 60) + 122 = 842$.

So weight of one molecule

$= \frac{\text{mol. wt. of } C_{60}H_{12}}{\text{Avogadro's number}} = \frac{842}{6.023 \times 10^{23}}$.

$= 1.4 \times 10^{-21}$ g

26. $\frac{\text{Mass of metal oxide}}{\text{Mass of metal chloride}}$

$= \frac{\text{Eq. mass of metal + Eq. mass of oxide}}{\text{Eq. mass of metal + Eq. mass of chloride}}$

$= \frac{3}{5} = \frac{E + 8}{E + 35.5}$.

On solving, we get

E = 33.25

27. $N_2 + 3H_2 \rightarrow 2NH_3$

1 vol 3 vol 2 vol

10 lit 30 lit 20 lit

now 10 litre of NH_3 is formed

N_2 used = 5 liters, left = 30 – 5 = 25 lit

H_2 used = 15 liters, left = 30 – 15 = 15 lit

28. Let molarity of $Ba(OH)_2 = M_1$

Normality = $2M_1$

Molarity of HCl = 0.1 M = 0.1 N

$N_1V_1 = N_2V_2$

$2M_1 \times 25 = 0.1 \times 35$

$M_1 = 0.07$ M

29. $2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$

2 mol 3 mol 2 mol

21.6 g = 2 mol

21.6 g B = 2 mol B ≅ 3 mol H_2

As PV = nRT

So $V = \frac{nRT}{P} = \frac{3 \times 0.0821 \times 273}{1} = 67.2$ L

30. 1 g atom of Fe (56 g Fe) is present in 1 mole of the compound

As 4.6 g Fe are present in 100 g of the compound

So 56 g Fe will be present in

$= \frac{100}{4.6} \times 56$ g

= 1217 g of the compound.

So approximate molecular mass = 1200.

31. Number of molecules in different cases

a. $\frac{15}{22.4} \times 6.023 \times 10^{23}$

b. $\frac{5}{22.4} \times 6.023 \times 10^{23}$

c. $\frac{0.5}{2} \times 6.023 \times 10^{23}$

d. $\frac{10}{32} \times 6.023 \times 10^{23}$

Thus 15 L of H_2 gas at STP will have maximum number of molecules.

32. H_3PO_3 is a dibasic acid (containing two ionizable protons attached to O directly)

$H_3PO_3 \leftrightarrow 2H^+ + HPO_4^{2-}$

0.1 M H_3PO_3 = 0.2 N H_3PO_3

0.1 M KOH = 0.1 N KOH

$N_1V_1 = N_2V_2$

(KOH) (H_3PO_3)

$1.1\ V_1 = 0.2 \times 20$

V_1 = 40 mL

33. $N_A = 6.02 \times 10^{23}$ = 1 mol

6.02×10^{20} molecules = 0.001 mol in 100 ml (0.1 L) solution

so molar concentration = $\frac{\text{vol}}{\text{volume in L}}$.

$= \frac{0.001}{0.1} = 0.01$ M

34. 10 g that is, 0.1 mole $CaCO_3$ is decomposed to 0.1 mole CO_2 and 0.1 mole CaO.

$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$
1 mole 0.1 mole 0.2

Because here limiting reagent is CO_2. $NaHCO_3$ is always twice the number of moles of CO_2.

35.

Element	Carbon	Hydrogen
% Composition	92.3	7.7
Atomic ratio	92.3/12	7.7/1
	= 7.69	= 7.7
Simple ratio	7.69/7.69	7.7/7.69
	= 1	= 1

So empirical formula is 'CH'

36. Given:

As Cu = 4 g, CuO = 5 g

So oxygen = 1 g

As 1 g of oxygen combines with Cu = 4 g

So 8 g of oxygen combine with Cu = 4 × 8 = 32 g

Thus, equivalent weight of Cu = 32.

37. As equal volumes contains equal number of moles

So molar ratio of He : CH_4 = 1 : 1

Ratio by weight = 4 : 16 = 1 : 4

Thus, CH_4 present by weight

= 4/5 × 100 = 80 %

38. 1 drop of water = $\frac{1}{20}$ ml = $\frac{1}{20}$ g

(as dH_2O = 1 g ml^{-1})

18 g of water = 'A' molecules

$\frac{1}{20}$ g water = $\frac{A}{18} \times \frac{1}{20}$

= 0.05 A/18 molecules

39. Eq. wt. of Al = 27/3 = 9

Eq. of wt. of C = 12/4 = 3

$(\overset{0}{C} \rightarrow \overset{+4}{CO})$

no. of gm eq. of Al = $\frac{270 \times 10^3}{9} = 30 \times 10^3$

hence no. of gm eq. of C = 30×10^3

again,

number of gm eq. of C = $\frac{\text{mass in gram}}{\text{gram equivalent wt}}$.

$30 \times 10^3 = \frac{\text{mass}}{3\ \text{gm}}$

mass = 90×10^3 g = 90 kg

40. $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
100 g 2(36.5) = 73 g 44 g

1 L of 1 N HCl contains 1 g eq. of HCl, as HCl is the limiting agent.

As 73 g HCl liberate CO_2 = 44 g

So 36.5 g HCl will liberate CO_2 = 22 g.

41. Assume one molecule of the alkaloid contains 'X' N-atoms.

Then % of N = $\frac{14\ X}{162} \times 100 = 17.28$

Thus, X = 2.

42. $2H_2 + O_2 \rightarrow 2H_2O$

2 ml 1 ml

As 2 ml of H_2 react with 1 ml of O_2.

So 30 ml of H_2 will react with 15 ml of O_2

Thus, O_2 left = 20 – 15 = 5 ml.

43. $m = \frac{\text{moles of } CH_3COOH}{\text{wt. of solvent in kg}} = \frac{2.05 \times 1000}{897}$

$= 2.285$

wt. of solvent = wt. of solution – wt. of solute

$= [1000 \times 1.02 - 20.5 \times 60] = 897$ g

44. Weight of 11.2 dm^3 of CO_2 gas at STP is 44/2 = 22 g

$KOH + CO_2 \rightarrow KHCO_3$

56 g 44g

KOH required for complete neutralization of 22 g

$CO_2 = \frac{56}{44} \times 22 = 28$ g

45. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$6I^- \rightarrow 3I_2 + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

One mole of acidified $K_2Cr_2O_7$ on reaction with excess KI will liberate 3 moles of I_2.

46. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Equivalent weight of $KMnO_4$ in acidic medium

$= \frac{\text{molecular weight}}{5}$

$= \frac{158}{5} = 31.6$

47. $\frac{PV_1}{n_1 RT} = \frac{PV_2}{n_2 RT}$

$V_1/n_1 = V_2/n_2$

$\frac{500}{1} = \frac{100}{n_2}$

$n_2 = 1/5$

As 1 mole of CO_2 contains 6.0×10^{23} molecules.

So 1/5 mole of CO_2 contains 1.2×10^{23} molecules.

48. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

$1NH_3 + 1.25\ O_2 \rightarrow 1\ NO + 1.5\ H_2O$

Hence 1 mole of NH_3 reacts with 1.25 moles of O_2 to produce 1 mole of NO and 1.5 moles of H_2O.

When one mole of ammonia and one mole of oxygen are made to react to completion, then all the oxygen is consumed.

49. $2SO_2 + O_2 \rightarrow 2SO_3$

Initial moles	4	4	0
At eq.	$4 - 2$	$4 - \frac{25}{100} \times 4$	2
	= 2	= 3	= 2 moles

Total number of moles at all gases at equilibrium

$= 2 + 3 + 2 = 7$.

50. $\frac{\text{Weight of metal hydroxide}}{\text{Weight of metal oxide}}$

$= \frac{\text{Equivalent weight of metal hydroxide}}{\text{Equivalent weight of metal oxide}}$

$\frac{1.520}{0.995} = \frac{E_m + 17}{E_m + 8}$

(here E_m = Equivalent weight of metal)

$1.528 = \frac{E_m + 17}{E_m + 8}$

$0.528\ E_m = 4.78$

On solving, we get $E_m = 9$.

51. Molarity $= \frac{\text{Mole of solute}}{\text{Volume of solution in litre}}$.

$= \frac{\text{Weight of solute}}{\text{Mol. wt. of solute} \times \text{V in litre}}$.

$= \frac{\text{Weight of solute} \times 1000}{\text{Mol. wt. of solute} \times \text{V in ml}}$.

$= \frac{2.5 \times 1000}{58.5 \times 100} = 0.427$

52. $\frac{2E + 410}{195} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$

$= \frac{0.532}{0.195}$

$E = 61$

Number of nitrogen atoms per molecule of base

$= \frac{244}{61} = 4$

53. As $N_1V_1 = N_2V_2$

$\frac{490}{49} \times 1 = N_2 \times 10$

$N_2 = \frac{490}{49 \times 10} = 1$ N

54. $\bar{A} = \Sigma f_i A_i$

(Here f_i = Fractional abundance, A_i = Atomic mass)

$= 0.90 \times 200 + 0.08 \times 199 + 0.02 \times 202$

$= 180 + 15.92 + 4.04$

≈ 200 amu

55. 44.1 g of anhydrous Na_2SO_4 are associated with H_2O = 55.9 g

Molar mass of anhydrous Na_2SO_4

$= 2 \times 23 + 32 + 4 \times 16 = 142$ g

So 142 g of anhydrous Na_2SO_4 will be associated with H_2O

$= \frac{55.9}{44.1} \times 142 \text{ g} = 180 \text{ g}$

= 10 moles of H_2O

56. $CO + \frac{1}{2} O_2 \rightarrow CO_2$

As 1 L of CO reacts with ½ L of O_2 to produce 1 L of CO_2. So 10 L O_2 will react with 20 L of CO to produce 20 L of CO_2

Thus, CO left = 10 L and CO_2 produced = 20 L, O_2 left = 0 L

57. As 40 cm^3 of 0.125 N NaOH neutralize acid = 0.3 g

So 1000 cm^3 of 1 N NaOH will neutralize acid

$= \frac{0.3}{40} \times \frac{1000}{0.125} \text{ g} = 60 \text{ g}$

1000 cm^3 of 1 N NaOH contain one gram equivalent of NaOH. It will neutralize one gram equivalent of the acid.

Thus, equivalent weight of acid = 60

58. $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$

100 g 2(36.5)
= 73 g

So 5 g $CaCO_3$ will completely react with HCl

$= \frac{73}{100} \times 5 = 3.65$ g

59. Ammonia is formed by reduction of nitrates and nitrites with Zn and NaOH. Zn and caustic soda produce nascent hydrogen which reacts with nitrates to form ammonia.

$$NaNO_3 + 8H^+ + 8e \xrightarrow{Zn/NaOH} NaOH + NH_3 + 2H_2O$$

From the equation –

Mass of 8 moles of electron absorbs 85 g $NaNO_3$

As Mass of 1 mole of electron absorbs

$\frac{85}{8}$ = 10.65 g of $NaNO_3$.

60. When blackened statues are treated with H_2O_2, the PbS is oxidized to $PbSO_4$. which is colourless (White)

$PbS + 4H_2O_2 \rightarrow \underset{\text{White}}{PbSO_4} + 4H_2O$

$4H_2O_2 \rightarrow 4H_2O + 2O_2$

4 (2 + 32) 2×22.4 litre
= 136 g at N.T.P.

From the above equation, we can derive that –

In transferring 1 mole of PbS to $PbSO_4$ the volume of ' 10 volume' of H_2O_2 required is 44.8 time at NTP.

61. Let the oxide of unknown element be *M*O.

Given that oxygen content is 20% by weight.

Then

Eq. weight of unknown element (M) = $\frac{80}{20 \times 8 \text{ g}}$

Equivalent weight of unknown element (M) = 32 g.

62. From the reaction

$$\frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = n$$

For 2 N HCl

$$\text{Molarity} = \frac{\text{Normality} \times \text{Equivalent weight}}{\text{Molecular weight}}$$

$$\text{Molarity} = \frac{2 \times 36.5}{36.5} = 2$$

For 4 N H_2SO_4

$$\text{Molarity} = \frac{\text{Normality} \times \text{Equivalent weight}}{\text{Molecular weight}}$$

$$\text{Molarity} = \frac{4 \times 49}{98} = 2$$

Hence 4 N H_2SO_4 and 2 N HCl solution will have same alcohol and nitrogen is evolved.

63. $[5e + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ ..(i)$] \times 2$

$[C_2O_4^{2-} \rightarrow 2e + 2CO_2$ ….(ii)$] \times 5$

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2$

As 2 moles of MnO_4^- required to oxidize 5 moles of oxalate

So number of moles of MnO_4^- required to oxidize 1 mole of oxalate = 2/5 = 0.4

65. Molarity (M) $= \frac{300/100}{10^6/10^3} = \frac{3}{10^3} = 0.003$ M

Brainteasers Objective Type Questions

66. Specific volume (vol of 1 gm) cylindrical virus particle = 6.02×10^{-2} cc/gm

Radius of virus (r) = 7 Å = 7×10^{-8} cm

Length of virus = 10×10^{-8} cm

Volume of virus $\pi r^2_1 = \frac{22}{7} \times (7 \times 10^{-8})^2 \times 10 \times 10^{-8}$

$= 154 \times 10^{-23}$ cc

wt. of one virus particle $= \frac{\text{volume}}{\text{specific volume}}$.

mol. wt. of virus = wt. of N_A particle

$= \frac{154 \times 10^{-23}}{6.02} \times 10^{-2} \times 6.02 \times 10^{23}$

= 15400 g/ mol = 15.4 kg/mole

67. Ba^{2+} (aq) + SO_4^{2-} (aq) → $BaSO_4$ (s)

0.4123 g $BaSO_4 \times \frac{137.3 \text{ g Ba}}{233.4 \text{ g } BaSO_4}$.

= 0.2425 g Ba

Mass % $= \frac{\text{g Ba}}{\text{g sample}} \times 100$

$= \frac{0.2425 \text{ g Ba}}{6.977 \text{ g sample}} \times 100$

= 3.476 % Ba

68. Weight of 6.023×10^{23} molecule of water = 18 g

As volume occupied by 6.023×10^{23} molecule of water (density = 1g cm^{-3}) will be

$= \frac{18 \text{ g}}{1 \text{ g cm}^{-3}} = 18 \text{ cm}^3$ or ml

So volume occupied by one molecule of water

$= \frac{18}{6.023 \times 10^{23}} = 2.988 \times 10^{-23}$

$= 3.0 \times 10^{-23}$ cm^3

69. 2Al (s) + 6HCl (aq) →

$2Al^{3+}$ (aq) + $6Cl^-$ (aq) + $3H_2$ (g)

As 6 moles of HCl evolved H_2 at STP

$= 3 \times 22.4$ L

So 1 mole of HCl will evolve H_2 at STP

$= \frac{3 \times 22.4}{6} = 11.2$ L

70. Suppose X g of $Ca(OH)_2$ will be dissolved X g $Ca(OH)_2$

= 250.0 ml sol. × (1 L sol./1000 ml sol.) × (0.0200 mol $Ca(OH)_2$/1 L sol.) × [74.10 g $Ca(OH)_2$/1 L sol.]

On solving we get, = 0.370 g $Ca(OH)_2$

71. H_2 (g) + Cl_2 (g) → 2HCl (g)

1 mole	1 mole	2 mole
22.4 L	22.4 L	2 × 36.5 g

For the formation of 3.65 g HCl, H_2 or Cl_2 required

$= \frac{22.4}{2 \times 36.5} \times 3.65$ L = 1.12 L

72. Valency of metal in Z_2O_3 = 3

$Z_2O_3 + 3H_2 \rightarrow 2Z + 3H_2O$

0.1596 g of Z_2O_3 react with H_2 = 6 mg = 0.006 g

1 g of H_2 react with

$= \frac{0.1596}{0.006} = 26.6$ g of Z_2O_3

Eq. Wt. of Z_2O_3 = 26.6

Eq. wt. of Z + Eq. wt of O = E + 8 = 26.6

Eq. wt. of Z = 26.6 – 8 = 18.6

Atomic wt. of Z = 18.6 × 3 = 55.8

73. Wt. of $MSO_4 = 1.375 \times \frac{148}{233} = 0.8734$ g

Wt. of MSO_4 in the original solution (61.5 g) $= 0.8734 \times 10 = 8.734$ g

Wt. of solvent $= 61.5 - 8.734 = 52.766$ g

Wt. of MSO_4 per 100 g of solvent

$= 8.734 \times \frac{100}{52.766} = 16.55$ g

Solubility of MSO_4 is 16.55 g per 100 g of solvent.

74. $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$
$2(78) \qquad 15(32)$

156 gm of benzene required oxygen $= 15 \times 22.4$ litre

1 gm of benzene required oxygen

$= \frac{15 \times 22.4}{156}$ litre

39 gm of benzene required oxygen

$= \frac{15 \times 22.4 \times 39}{156} = 84.0$ litre

75. Eq. mass of ferrous ammonium sulphate = 392

Normality of the salt solution

$= \frac{3.92}{392} \times \frac{1}{100} \times 1000 = 0.1$ N

20 ml of 0.1 N salt solution = 18 ml of $KMNO_4$ solution

Normality of $KMnO_4$ solution

$= \frac{20 \times 0.1}{18} = \frac{1}{9}$ N

Eq. mass of $KMnO_4 = 31.6$

So strength of $KMnO_4$ solution $= 1/9 \times 31.6 = 3.511$ g L^{-1} approx

76. 1000 ml of 0.02 N oxalic acid has = 0.02 g eq.

So 100 ml of 0.02 N oxalic acid has = 0.002 g eq = 0.001 mole

(M = N × basicity)

Thus number of molecules

$= 10^{-3} \times 6.022 \times 10^{23}$

$= 6.022 \times 10^{20}$

77. In the absence of H_2O,

$2KO_2 + CO_2 \rightarrow K_2CO_3 + 3/2\ O_2$
$10^{-3} \qquad 10^{-3}$ mole

The limiting reagent is KO_2 in the sense that it limits the amount of CO_2 consumed.

CO_2 consumed $= 10^{-3}/2$ mole

O_2 produced $= \frac{10^{-3}}{2} \times \frac{3}{2}$ mole

$\equiv 22.4\ cm^3 \times ¾$ at STP $= 16.8\ cm^3$ at STP

78. (I) mass of one O atom $= \frac{16}{6.02 \times 10^{23}}$ g

$= 2.66 \times 10^{-23}$ g

(II) mass of one N atom $= \frac{14}{6.02 \times 10^{23}}$ g

$= 2.33 \times 10^{-23}$ g

(III) 1 g molecule of oxygen = 32 g 1×10^{-10} g molecule of oxygen

$= 32 \times 10^{-10} = 3.2 \times 10^{-9}$ g

(IV) 1 g atom of copper = 63 g 1×10^{-7} g atom of copper

$= 63 \times 10^{-7} = 6.3 \times 10^{-6}$ g

so the correct order is

II < I < III < IV

79. $PbO + 2HCl \rightarrow PbCl_2 + H_2O$
X mol $\qquad$ 2X mol $\qquad$ X mol

$\frac{6.5}{224}$ mol $\qquad \frac{3.2}{36.5}$ mol

$= 0.029 \qquad = 0.087$ mol

Thus, 0.029 moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl.

81. $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$
$0.002 \qquad 0.01 \qquad\qquad 0.006$

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

$Br_2 \equiv I_2 \equiv 2Na_2S_2O_3$

Amount of $Na_2S_2O_3$ reacting $= 0.006 \times 2$

$= 0.012$ mole

$= 0.1 \times v \times 10^{-3}$ mole,

Here 'v' is the volume of $Na_2S_2O_3$ in ml.

$$v = \frac{0.012 \text{ ml}}{0.1 \times 10^{-3}} = \frac{0.012 \text{ ml}}{10^{-4}} = 120 \text{ ml}$$

82. Suppose the weight of the sample = 100 g

So the number of equivalent of NaOH = 21/40

If the sample, contains KOH instead of NaOH same number of equivalent of KOH should be present in the sample.

So weight of KOH $= \frac{21}{40} \times 56 = 29.4$

83. 100 gm of metal oxide contains 53 g of metal

As Equivalent mass of element

$$= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8 = \frac{53}{47} \times 8 = 9$$

So, Atomic mass = Equivalent mass of an element × valency

$= 9 \times 3 = 27$ gm

84. Equivalents of oxalate present = Equivalents of $KMnO_4$ used

$$= 90 \times \frac{1}{20} \times 10^{-3}$$

Mass of oxalate present

$$= \frac{90 \times 1}{20 \times 10^{-3}/2} \times 88 = 0.198 \text{ g}$$

% of oxalate in the given sample

$$= \frac{0.198}{0.3} \times 100 = 66$$

85. $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

1 vol.	3 vol.	2 vol.	3 vol.
1 mol.	3 mol.	2 mol.	3mol.

(As vol% = mol%).

One gram mol of any occupies 22.4 litre at NTP.

1 mol of Fe_2O_3 requires 3 mol of CO for its reduction that is, 1 mol of Fe_2O_3 requires 3×22.4 litre or 67.2 dm^3 CO to get itself reduced.

91. Ethanol does not react with Fehling's reagent, only acetaldehyde reacts as follows:

$$2CuO + CH_3CHO \rightarrow Cu_2O \downarrow + CH_3COOH$$

Red ppt.

Moles of $Cu_2O = \frac{1.2}{143}$.

Moles of $CH_3CHO = \frac{1.2}{143}$.

So % of acetaldehyde $= \frac{44 \times 1.2}{143 \times 0.5} \times 100$

$= 74$ %

93. Weight of $CaCO_3 = 5$ gm

$$\text{Mole} = \frac{5}{100} = 0.05$$

Mole of HCl $= 0.05 \times 2 = 0.1$

Weight $= 0.1 \times 36.5 = 3.65$

$$\text{Volume of HCl} = \frac{3.65}{1.825} = 2 \text{ ml}$$

98. $2 \times \frac{0.7}{106 + 18x} = 5 \times 19.8 \times \frac{1}{10} \times \frac{1}{1000}$.

On solving, we get

$x = 2$

100. Weight of bromine in the bromide

$$= 1.32 \times \frac{80}{188} = 0.562 \text{ g}$$

Weight of A = 0.722 – 0.562 = 0.16 g

$$\text{Eq. weight of A} = 0.16 \times \frac{80}{0.562} = 22.8$$

$$\text{Valency of A} = \frac{\text{atomic weight}}{\text{Equivalent weight}}.$$

$$= \frac{91.2}{22.8} = 4$$

Multiple Correct Answer Type Questions

109. Suppose the mole of C_2H_5OH is n_1 and mole of H_2O is n_2.

$$\frac{n_1}{n_1 + n_2} = \frac{1}{4}.$$

$$\frac{n_1}{n_2} = \frac{1}{3}.$$

$$\frac{W_1}{W_2} = \frac{n_1 \times M_1}{n_2 \times M_2} = \frac{1}{3} \times \frac{46}{18} = \frac{46}{54}$$

% by weight of C_2H_5OH

$$= \frac{46 \times 100}{46 + 54} = 0.46$$

% by weight of H_2O

$= \frac{54}{54+46} \times 100 = 0.54$

111. $\frac{4 \times A_x}{4A_x + 96} = 0.572$

$\frac{A_x}{A_x + 24} = 0.572$

$A_x = \frac{0.572 \times 24}{(1 - 0.572)}$

$A_x = 32$

116. As 1 mol or 28 gm N_2 reacts with 3 mol or 6 gm H_2

So 2000 g of N_2 will react with $H_2 = \frac{6}{28} \times 2000g$

= 428.6 g

Here N_2 is the limiting reagent while H_2 is the excess reagent

As 1 mol of N_2 produces NH_3 = 2 mol = 34 g

So 2000 g of N_2 will produce $NH_3 = \frac{34}{28} \times 2000g$

= 2.428 kg

Mass left unreacted (for H_2) = 1000 – 428.6

= 0.571 kg H_2

Hence statements a., c. are correct.

Linked-Comprehension Type Questions

117. $NaCl \rightarrow Na^+ + Cl^-$

At anode:

$2Cl^- \rightarrow Cl_2$

Moles of Cl^- = 2 in 500 ml.

Therefore 1 mole of Cl_2 evolves.

118. Na – Hg (amalgam) formed = 2 moles at cathode

119. Moles of electrons (2 Faraday) are required.

1F = 96500

2F = 193000

120. $H_2O + SO_3 \rightarrow H_2SO_4$;

As 18 g water combines with 80g SO_3

So 9 g of H_2O combines with 40 g of SO_3.

100g of oleum contains 40 g of SO_3

or 40 % free SO_3

121. Intial moles of free SO_3 present in oleum

$= \frac{6}{18} = \frac{1}{3}$ moles

= moles of water that can combines with SO_3 moles of free SO_3 combined with water

$= \frac{4.5}{18} = \frac{1}{4}$ mole

moles of free SO_3 remains $= \frac{1}{3} - \frac{1}{4} = \frac{1}{12}$ mole

volume of free SO_3 at STP $= \frac{1}{12} \times 22.4$

= 1.792 L

122. $Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$

Moles of CO_2 formed = Moles of Na_2CO_3

reacted $= \frac{1.06}{106} = 0.01$

volume of CO_2 formed at 1 atm pressure and 300 K can be given as

$= \frac{0.01 \times 300 \times 22.4}{273}$

$= 0.01 \times 24.615 = 0.24615$ L

123. eq of H_2SO_4 + eq of SO_3 = eq. of NaOH

$\frac{x}{98} \times 2 + \frac{(1-x) \times 2}{80} = 27 \times 0.8 \times 10^{-3}$

On solving x = 0.74

% of free $SO_3 = \frac{1 - 0.74}{1} \times 100 = 26$ %

124. Here 1 L H_2O_2 gives 16.8 L O_2 at STP

Moles of $O_2 = \frac{16.8}{22.4}$

= 0.75

Moles of H_2O_2 = 0.75 ×2

= 1.5

Hence $M = \frac{1.5}{1}$

= 1.5 M

125. The redox change are

$2e + O_2^{1-} \rightarrow 2O^{2-}$

$2I^- \rightarrow I_2 + 2e$

$2S_2^{2+} \rightarrow S_4^{5/2+} + 2e$

$I_2 + 2e \rightarrow 2I^-$

Meq. of H_2O_2 = Meq. of I_2 = Meq. of $Na_2S_2O_3$

$N \times 25 = 0.1 \times 20$

$N_{H_2O_2} = 0.08$

126. m –eq. of H_2O_2 = m –eq. of $KMnO_4$

$10 \times N = 0.05 \times 5 \times 40$

So N = 1

N = volume strength of H_2O_2

5.6

volume strength of $H_2O_2 = 5.6 \times 1$

$= 5.6$

127. % (w/V) means how many gm of H_2O_2 is present in 100 mL

As here molarity is 1.5 which means 51 gm H_2O_2 is present in 1 L so 100 mL contents 5.1 gm H_2O_2

128. (+n) (+7) (+5)

$X + MnO_4^- \rightarrow XO_3^- + Mn^{+2}$

Changing in ox. no. of MnO_4^- = 5 (reduction)

Eq. wt. of MnO_4^- = ionic wt./5

Change in ox. no. of X in X^{+n} = (5–n) (oxidation)

Eq. wt. of X^{+n} = (ionic wt/5– n)

No. of equivalents of MnO_4^- in 1.61×10^{-3} moles

$= 1.61 \times 10^{-3} \times 5$

No. o equivalents X^n in 2.86×10^{-3} moles

$= 2.68 \times 10^{-3} \times (5–n)$

$1.61 \times 10^{-3} \times 5 = 2.68 \times 10^{-3} \times (5 –n)$

or $5 – n = \frac{8.05}{2.68}$

≈ 3

hence n = 5 –3 =2 and formula of XCl_n in XCl_2 Eq. wt. of XCl_2 = mole. wt./2

$= \frac{97+ 71}{2}$

$= \frac{168}{2}$

$= 84$

129. The redox equation can be given as

$Cr_2O_7^{-2} + 14H^+ + 6Cl^- \rightarrow Cr^{+3} + 7H_2O + 3Cl_2 \uparrow$

1 mol. of $Cr_2O_7^{-2}$ ion or $K_2Cr_2O_7$ oxidises $6Cl^-$ ion or 6 equivalents of HCl to 3 Cl_2 molecules.

So 40 g $K_2Cr_2O_7$ will oxides HCl

$= \frac{219.0 \times 40}{294}$

= 29.795 gm.

130. Since for this process n – factor is 15 and not 12

Assertion-Reason Type Questions

131. Both A and R are true but R is not the correct explanation of A.

According to mole concept, 1 mole of molecules = Gram molecular mass = 6.023×10^{23} molecules

So 58.5 g of NaCl also contains 6.023×10^{23} Molecules of NaCl.

132. Both A and R are false. Molar volume (at NTP) = 22.4 L

22.4 L of N_2 = volume occupied by 1 mole of N_2 = 28 g = 6.023×10^{23} molecules

similarly

$O_2 = 2 \times 16 = 32$ g, 32g = 6.023×10^{23} molecules = 22.4 L

22.4 L = 6.023×10^{23}

$5.6 \text{ L} = \frac{6.023 \times 10^{23} \times 5.6}{22.4} \times 1 \times 6.023 \times 10^{23}$

According to Avogadro's hypothesis, equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure.

133. Both A and R are false.

Number of g molecules or mole molecules

= wt. of Sub./GMM

SO_2Cl_2 = 135 g (GMM)

So number of gm molecules = $\frac{13.5}{135} = 0.1$

The IIT-JEE Corner

156. $FeC_2O_4 \rightarrow Fe^{2+} + C_2O_4^{2-}$

MnO_4^- oxidizes Fe^{2+} and $C_2O_4^{2-}$ both

$F^{2+} + C_2O_4^{2-} \rightarrow Fe^{3+} + 2CO_2 + 3e^-$

$MnO_4^- + 5e^- \rightarrow Mn^{2+}$

$5\ FeC_2O_4 \equiv 3MnO_4^-$

$1\ FeC_2O_4 \equiv 3/5\ MnO_4^-$

157. As H_3PO_3 is a dibasic acid

So its molecular weight = 2×equivalent wt.

1 M = 2N

0.3 M = 2 × 0.3 = 0.6 N

158. Eq. mass of $COOH \cdot 2H_2O$

$|$

$COOH$

$= \frac{\text{Mol mass}}{\text{basicity}} = \frac{126}{2} = 63$

so normality of oxalic acid solution

$= \frac{6.3 \times 1000}{63 \times 250} = 0.4$ N

$N_1V_1 = N_2V_2$

NaOH oxalic acid

1.1 × V1 = 0.4 × 10 mL

on solving

V_1 = 40 mL

159. In iodometry, $K_2Cr_2O_7$ liberates I_2 from iodides (NaI or KI) which is titrated with $Na_2S_2O_3$ solution.

$K_2Cr_2O_7 + I^- + H^+ \rightarrow Cr^{3+} + I_2$

Here, one mole of $K_2Cr_2O_7$ accepts 6 mole of electrons.

Equivalent weight = $\frac{\text{Molecular weight}}{6}$

160. As Mass of one electron = 9.108×10^{-31} kg So 1 kg of electrons = $1/9.108 \times 10^{-31}$

$= \frac{10^{31}}{9.108 \times 6.022 \times 10^{23}}$ mol

$= \frac{10^{31-23}}{9.108 \times 6.022}$ mole

$= \frac{10^8}{9.108 \times 6.022}$ mol

161. Here

24 g of C–12 contain = $2 \times 6.022 \times 10^{23}$ atoms

56 of Fe–56 contain = 6.022×10^{23} atoms

27 g of Al–27 contain = 6.022×10^{23} atoms

108 g of Ag–108 contain = 6.022×10^{23} atoms here 24 g of C–12 contains maximum number of atoms as it has maximum moles (2).

162. $Ag^+ + Br^- \rightarrow AgBr$

Excess 0.01 mole 0.01 mole

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$

Excess 0.01 mole 0.01 mole

163. $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Fe^{3+} + Cr^{3+}$

n factor of $Cr_2O_7^{2-} = 6$

n factor of $Fe^{2+} = 1$

So to reduce one mole of dichromate 6 moles of Fe^{2+} are required.

164. $\bar{A} = \frac{\sum A_i x_i}{\sum x_i}$

$\bar{A} = 54 \times 0.05 + 56 \times 0.90 + 57 \times 0.5$ (where $\bar{A}$ is atomic mass of Fe)

$\bar{A} = 55.95$

Numericals for Practice

1. In photosynthesis CO_2 (g) and H_2O (l) are converted into glucose, $C_6H_{12}O_6$ (a sugar), and O_2. If 0.256 mol of $C_6H_{12}O_6$ is formed by the reaction of CO_2 with water, how many grams of CO_2 would be needed?

   a. 0.256 g **b.** 67.6 g
   c. 33.8 g **d.** 76.6 g

2. What is the percentage yield of C_2H_2 when 50.0 g of CaC_2 (s) (molar mass = 64.01 g) reacts with an excess of water to yield 13.5 g of C_2H_2 (molar mass = 26.04 g) according to the following reaction:

   $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

   a. 33.3 % **b.** 86.5 %
   c. 66.5 % **d.** 56.6 %

3. How many moles of $KClO_3$ are required to produce 2.51 g of O_2? (Mass of one mole: K = 39.1 g, Cl = 35.5 g, O = 16.0 g)

   $2KClO_3 \rightarrow 2KCl + 3O_2$

   a. 5.23×10^{-2} mol
   b. 2.53×10^{-1} mol
   c. 1.53×10^{-2} mol
   d. 1.84×10^{-1} mol

4. What is the per cent yield if 25.0 g of I_2 is formed when 130.0 g of HNO_3 reacts with 285.0 g of HI as follows:

   $2HNO_3 + 6HI \rightarrow 2NO + 3I_2 + 4H_2O$

   a. 16.68 % **b.** 4.42 %
   c. 4.42 % **d.** 8.84 %

5. A 3.000 g sample of a soluble chloride is titrated with 52.60 mL of 0.2000 M $AgNO_3$. What is the percentage of chloride in the sample?

   a. 24.86 % **b.** 12.43 %
   c. 32.43 % **d.** 6.23 %

6. The allowable concentration level of vinyl chloride, C_2H_3Cl, in the atmosphere in a chemical plant is 2.0×10^{-6} g/L. How many molecules are present per litre?

   a. 1.47×10^{16} m/L
   b. 1.97×10^{16} m/L
   c. 2.97×10^{16} m/L
   d. 1.07×10^{16} m/L

7. An oxybromate compound, $KBrO_x$, where x is unknown, is analysed and found to contain 52.92 % Br. What is the value of x?

   a. 1 **b.** 2
   c. 3 **d.** 3.5

8. Consider a sample of calcium carbonate in the form of a cube measuring 1.25 in. on each edge. If the sample has a density of 2.71 g/cm^3, how many oxygen atoms does it contain?

   a. 1.07×10^{24} **b.** 3.14×10^{24}
   c. 1.57×10^{24} **d.** 0.785×10^{23}

9. How many kilograms of CO_2 are obtained when a sample of 0.15 m^3 of C_8H_{18} (l), whose density is 0.69 g/mL, is combusted in air?

   a. 3.2×10^2 kg **b.** 1.6×10^2 kg
   c. 6.4×10^2 kg **d.** 2.2×10^2 kg

10. A solution is made by mixing 50.0 mL of 6.00 M HCl, 100.0 mL of 1.00 M HCl, and enough water to make 250.0 mL of solution. What is the molarity of HCl in the final solution?

    a. 0.8 M **b.** 3.2 M
    c. 2.5 M **d.** 1.6 M

11. Aluminium reacts with oxygen to give aluminium oxide

    $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

    If you have 6.0 mol of Al, how many moles of O_2 are needed for complete reaction?

    a. 204 mole **b.** 305 mole
    c. 504 mole **d.** 405 mole

12. 100 ml of $NaHC_2O_4$ required 50 ml of 0.1 M $KMnO_4$ solution in acidic medium. Volume of 0.1 M NaOH required by 100 ml of $NaHC_2O_4$ is.

    a. 25 ml **b.** 75 ml
    c. 125 ml **d.** 135 ml

13. Menthol, from oil of mint, has a characteristic cool taste. The compound contains only C, H and O. If 95.6 mg of menthol burns completely in O_2, and gives 269 mg of CO_2 and 110 mg of H_2O, what is the empirical formula of menthol?

    a. **b.**
    c. $C_{10}H_{20}O$ **d.**

14. In an experiment, 1.056 g of a metal carbonate containing an unknown metal M, is heated to give the metal oxide and 0.376 g CO_2.

MCO_3 (s) + heat → MO (s) + CO_2 (g)

What is the identity of the metal M?

a. Zn **b.** Ni
c. Ba **d.** Cu

15. Titanium (IV) oxide (TiO_2) is heated in hydrogen gas to give water and a new titanium oxide, Ti_XO_Y. If 1.598 g of TiO_2 produces 1.438 g of Ti_XO_Y, what is the formula of the new oxide?

a. TiO_3 **b.** Ti_2O_3
c. TiO_2 **d.** Ti_3O_2

16. What volume of 0.125 M HNO_3 in milliliters, is required to react completely with 1.30 g of $Ba(OH)_2$?

$2HNO_3$ (aq) + $Ba(OH)_2$ (s) →

$Ba(NO_3)_2$ (aq) + $2H_2O$ (l)

a. 121 ml **b.** 221 ml
c. 242 ml **d.** 60.5 ml

17. What volume of 0.750 M $Pb(NO_3)_2$, in milliliters, is required to react completely with 1.00 L of 2.25 M NaCl solution? The balanced equation is

$Pb(NO_3)_2$ (aq) + 2NaCl (aq) →

$PbCl_2$ (s) + $2NaNO_3$ (aq)

a. 1.0×10^3 ml **b.** 3.0×10^{-3} ml
c. 1.5×10^3 ml **d.** 1.5×10^{-3} ml

18. What volume of 0.812 M HCl, in milliliters, is required to titrate 1.33 g of NaOH to the equivalence point?

NaOH (aq) + HCl (aq) → NaCl (aq) + H_2O (l)

a. 20.4 ml **b.** 40.9 ml
c. 80.9 ml **d.** 409 ml

19. When one gram mole of $KMnO_4$ reacts with HCl, the volume of chlorine liberated at NTP will be:

a. 16.5 lit **b.** 22.4 lit
c. 52.0 lit **d.** 56 lit

20. What is the molarity of KNO_3 in a solution prepared by dissolving 3.765 grams of KNO_3 in enough water to make 375 millilitres of solution?

a. 0.2482 **b.** 0.1241
c. 0.062 **d.** 1.12

21. What is the molarity of a 20.00 % solution of sodium nitrate ($NaNO_3$)? The solution density is 1.143 g/mL.

a. 2.40 **b.** 4.68
c. 0.468 **d.** 2.68

22. How many grams of $AgNO_3$, are required to react with 75.00 millilitres of 0.420 M K_2CrO_4?

$2AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4 + 2KNO_3$

a. 5.355 g **b.** 1.071 g
c. 10.71 g **d.** 21.42 g

23. What is the molarity of a barium hydroxide solution if 15.48 millilitres of it are required to react with 25.00 millilitres of 0.3026 M HCl solution?

$2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O$

a. 0.2443 M **b.** 0.1225 M
c. 2.443 M **d.** 0.36 M

24. The poisonous gas hydrogen cyanide can be produced by treating cyanide compounds with acid. How many grams of HCN could be produced from the reaction of 28.0 grams of $Ca(CN)_2$ and 28.0 grams of HCl?

$Ca(CN)_2 + 2HCl \rightarrow CaCl_2 + 2HCN$

a. 8.2 g **b.** 32.6 g
c. 16.4 g **d.** 64.8 g

25. If 2.82 grams of CCl_4 are produced from the reaction of 2.25 grams of CS_2 with 14.60 grams of Cl_2, what per cent yield of CCl_4 is obtained?

a. 31 % **b.** 62 %
c. 46 % **d.** 88 %

26. Which has highest molarity of the solute in the solution that results when the following mixtures are prepared?

a. 200.0 ml of water is added to 30.0 ml of 6.00 M NaOH

b. 600.0 ml of water is added to 20.0 ml of 0.480 M NaOH solution

c. 300.0 ml of 12.0 M HNO_3 is added to 100.0 ml of 3.00 M HNO_3

d. 30.0 ml of 0.800 M KBr is added to 80.0 ml of 0.350 M KBr

27. What volume of 0.407 M KOH solution is just sufficient to react completely with 3.16 grams of $CuSO_4 \cdot 5H_2O$ according to the equation below?

The $CuSO_4.5H_2O$ dissolves as the KOH is added to form aqueous $CuSO_4$.

$CuSO_4 + 2KOH \rightarrow Cu(OH)_2 + K_2SO_4$

a. 31.1 ml **b.** 62.2 ml
c. 93.6 ml **d.** 6.22 ml

28. What is the per cent by mass of HNO_3 in an aqueous 7.911 M HNO_3 solution if the solution has a specific gravity of 1.249?

a. 40 % **b.** 56 %
c. 32 % **d.** 88 %

29. How many grams of NaCl are needed to make 675 grams of 2.55 % by mass NaCl solution?

a. 8.6 g **b.** 1.72 g
c. 17.2 g **d.** 3.4 g

30. Calculate the volume of CO_2 produced by the combustion of 40 ml of acetone vapours in presence of excess of oxygen.

a. 120 ml **b.** 1.20 ml
c. 12 ml **d.** 20 ml

31. If 74.30 g of HCl were produced from 2.130 g of H_2 and an excess of Cl_2 according to the reaction

$H_2 + Cl_2 \rightarrow 2HCl$

What was the per cent yield of HCl?

a. 48.22 % **b.** 192.88
c. 96.44 % **d.** 66.44 %

32. A mixture of composition 70.0 % methane and 30.0 % ethane (C_2H_6) by mass is burned in oxygen to produce CO_2 and H_2O. The reactions that occur are

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

How many grams of O_2 are needed to react completely with 75.0 g of mixture?

a. 294 g **b.** 147 g
c. 588 g **d.** 197 g

33. Hydrogen sulphide burns in oxygen to form sulphur dioxide and water

$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$

How many grams of hydrogen sulphide must react in order to produce a total of 100.0 of products?

a. 14.53 g **b.** 20.76 g
c. 83.06 g **d.** 41.53 g

34. The following process has been used for obtaining iodine from oilfield brines

$NaI + AgNO_3 \rightarrow AgI + NaNO_3$

$2AgI + Fe \rightarrow FeI_2 + 2Ag$

$2FeI_2 + 3Cl_2 \rightarrow 2FeCl_3 + 2I_2$

How much $AgNO_3$, in grams is required in the first step for every 5.00 g of I_2 produced in the third step?

a. 6.69 g **b.** 3.34 g
c. 13.28 g **d.** 16.69 g

35. 20 ml of 'X' M HCl neutralizes 5 ml of 0.2 M Na_2CO_3 solution to phenolphthalein end point. The value of 'X' is.

a. 0.05 M **b.** 0.126 M
c. 0.184 M **d.** 0.150 M

ANSWER KYES

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	b	2.	c	3.	a	4.	d	5.	b
6.	b	7.	b	8.	c	9.	a	10.	d
11.	d	12.	c	13.	c	14.	d	15.	b
16.	a	17.	c	18.	b	19.	d	20.	b
21.	d	22.	c	23.	a	24.	c	25.	b
26.	c	27.	b	28.	a	29	c	30.	a
31.	c	32.	a	33.	d	34.	a	35.	a

Hints and Explanations

1. Chemical reaction is as follows:

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

Grams CO_2 = (0.256 mol $C_6H_{12}O_6$)

$$\text{x } \frac{(6 \text{ mol } CO_2)}{(1 \text{ mol } C_6H_{12}O_6)} \text{ x } \frac{(44.01 \text{ g } CO_2)}{(1 \text{ mol } CO_2)}$$

= 67.6 g CO_2.

5. The reaction is as follows:

Cl^- (aq) + $AgNO_3$ (aq) → AgCl (s) + NO_3^- (aq)

Grams Cl^- = (52.60 mL $AgNO_3$) (1L/1000 ml) × (0.2000 mol $AgNO_3$/1 L $AgNO_3$) × (1 mol Cl^-/1 mol $AgNO_3$) × (35.45 g Cl^-/1 mol Cl^-)

= 0.3729 g Cl^-

% Cl^- in sample

$$= \frac{\text{Mass of } Cl^- \text{ in sample}}{\text{Sample mass}} \times 100$$

= 12.43 %

12. $NaHC_2O_4 + KMnO_4 \rightarrow Mn^{2+} + CO_2$

Eq. of $NaHC_2O_4$ = Eq. of $KMnO_4$

$0.1 \times M \times 2 = 0.05 \times 0.1 \times 5$

$$M = \frac{0.25}{2} = 0.125$$

Mole of $NaHC_2O_4$ = Mole of NaOH

$$\frac{0.25}{2} \times 0.1 = 0.1 \times V$$

V = 0.125 litre = 125 ml.

19. $5 \times 1 = 2 \times n\ (Cl_2)$

$n\ (Cl_2) = 5/2$

$$VCl_2 = \frac{5}{2} \times 22.4 \text{ lit} = 56 \text{ lit}$$

30. $CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O$

$VCO_2 = 3 \times 40 = 120$ ml

35. $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

$X \times 20 \times 10^3 = 0.2 \times 5 \times 10^{-3}$

On solving, we get

X = 0.05

CHAPTER 2

Gaseous and Liquid States

Chapter Contents

Absolute scale of temperature, ideal gas equation; Deviation from ideality, van der Waal's equation; Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature; Law of partial pressures; Vapour pressure; Diffusion of gases and Various levels of multiple-choice questions.

Matter is a substance having mass and volume. Matter has three states, solid, liquid and gas. Plasma is considered to be its fourth state.

$$\text{Solid} \rightleftharpoons \text{Liquid} \rightleftharpoons \text{Gas}$$

Molecular interaction energy, thermal energy increases

CHARACTERISTICS OF GAS

Some of the important characteristics of a gas are as follows:

(i) Composition of gases is always from non-metals. Example, O_2, N_2, He, Cl_2 etc.

(ii) Gases always form a homogenous mixture regardless of the identities and proportions.

(iii) Gases have high diffusibility, thermal expansion and high compressibility as there are large empty spaces between molecules so on applying pressure molecules get closer.

(iv) Volume: Volume of the gas is equal to volume of the container in which gas is taken as a gas tries to occupy the entire available space. It is expressed in litres or m^3 or ml or cm^3 etc.

(v) Pressure: A gas can exert pressure on all the interior boundaries of the vessel due to molecular motion of its molecules which leads to collisions between these molecules and walls of the vessel. Gaseous pressure is measured by manometer while atmospheric pressure is measured by Barometer.

Gaseous pressure is measured in Newton per m^2 or nm Hg or atmosphere or torr.

1 atm = 760 mm Hg or torr

$= 1.013 \times 10^5$ N/m^2 or Pascal (Pa)

$= 1.013 \times 10^6$ Dyne/cm^2

$= 1.013$ bar

(vi) Mass: Mass of a gas can be determined by usual weight determination methods using weighing difference methods. It is related to number of moles of the gas.

$$n \text{ (mole)} = \frac{W}{M}.$$

Here W = Weight in gm.

M = Molar mass of the gas

(vii) Temperature: Temperature of a gas tells the energetic level of the gaseous molecules.

Kinetic energy α Temperature.

The energy and velocity of gas molecules increase with the increase of temperature and their motion becomes random. At standard condition temperature is 298 K and pressure of gas is 1 atm and this is called Standard temperature and pressure state (STP or NTP).

(viii) The molecules of gases have maximum energy and minimum force of attraction so they do not have a definite volume or shape.

(ix) Gases have low densities and the density of gases with respect to hydrogen is called relative density.

Vapour: It is gaseous form of a solid or liquid at room temperature. Vapour state can be liquefied by increasing pressure while gaseous state can be liquefied by increasing pressure and decreasing temperature. A gas below its critical temperature is a vapour.

Triple Point: Solid, liquid and gas, all phases can exist together at a particular temperature and pressure, it is known as triple point. Example, at 4.58 mm pressure and 0.0098°C, water has all the three phases (Ice, vapour, water).

GAS LAWS

As gases show their dependency on pressure , volume and temperature so the relationship of these factors can be explained through gas laws as follows:

Boyle's Law: According to it, "At constant temperature, the volume of a given mass of a gas is inversely proportional to its pressure. " that is,

$V \alpha 1/P$

Or $V = K/P$

Here K = constant

PV = constant (K) at constant temp.

Or $\log_{10} P + \log_{10} V$ = Constant (K)

$P_1V_1 = P_2V_2$ (at constant temp.)

Initial Conditions — final conditions

The differential form of Boyle's law can be written as

$$P.\delta_V + V.\delta_P = 0$$

So,

$$(dP/dV)_T = -P/V = -K/V^2.$$

Relation between Density and Pressure

According to Boyle's law at constant temperature and constant mass

$V \alpha 1/P$ (As T and mass are constant)

$V \alpha 1/d$ (Here d is the density)

As V = Mass/density

So $1/d \alpha 1/P$

that is, $d \alpha P$ or $d = K/P$

or $\log_{10} P = \log_{10} 1/V + \log_{10} K$

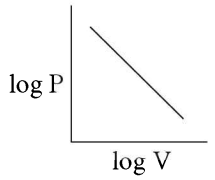
$$d_1/P_1 = d_2/P_2$$

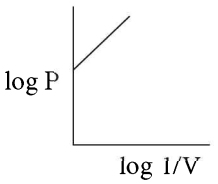
REMEMBER

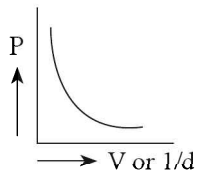
- Air at the sea level is dense as it is compressed by the mass of air present above it but the density and pressure decreases with the increase in altitude.
- The size of weather balloons becomes larger and larger as it rises or goes to higher altitude as the external pressures becomes lower and lower.

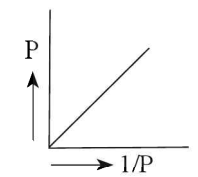
Various Plots between Pressure vs Volume

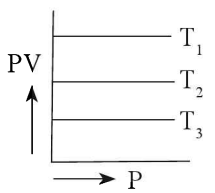
These plots are called Isotherms.



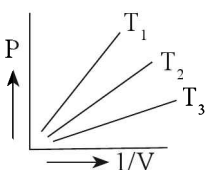








Here $T_1 > T_2 > T_3$



Here $T_1 > T_2 > T_3$

Illustrations

1. A 1.103 L flash containing nitrogen at a pressure of 710.6 torr is connected to an evacuated flash of unknown volume. The nitrogen which acts ideally is allowed to expand into the combined system of both flasks isothermally. If the final pressure of nitrogen is 583.1 torr, determine the volume of the evacuated flask.

Solution As the flasks are isothermally combined so temperature is constant. According to Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$(710.6 \text{ torr})\ (1.103 \text{ L}) = (583.1 \text{ torr}) \times V_2$$

$$V_2 = \frac{710.6 \times 1.103}{583.1} \text{ L} = 1.344 \text{ L}$$

As V_2 is final volume so the volume of evacuated flask is 1.344 – 1.103 = 0.241 L.

2. Oxygen gas is commonly sold in 49.0 litre steel containers at a pressure of 150 atm. What volume (in litre) would the gas occupy at a pressure of 1.02 atm if its temperature remained unchanged? If its temperature was raised from 20.0°C to 35.0°C at constant P = 150 atm?

Solution As n and T are constant,

Therefore $nRT = P_i V_i = P_f V_f$

$$V_f = \frac{P_i V_i}{P_f} = \frac{150 \times 49.0}{1.02}$$

= 7210 litre

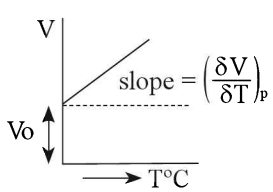
As n and P are constant

Therefore $\frac{nR}{P} = \frac{V_i}{T_i} = \frac{V_f}{T_f}$

$$V_f = \frac{V_i T_f}{T_i} = \frac{49.0 \times 308}{293} = 51.5 \text{ litre}$$

Charle's Law

In order to explain it, let us consider the following plot between volume and temperature.



It shows that the volume of a definite amount of a gas varies linearly with temperature on Celsius scale.

It can be given as $V_t = a + bt$

Here a and b are constant

$a = V_0$ at 0°C

b = slope $(\partial V/\partial T)_P$

So according to Charle's law, "At constant pressure, the volume of a given mass of a gas increases or decreases by 1/273 of its volume of 0°C for every one degree centigrade rise or fall in temperature" that is,

$$V_t = V_0 + \frac{V_0}{273} \times t°C \text{ (at const. temp.)}$$

$$= V_0 (1 + t°C/273) = V_0 (273 + t°C/273)$$

$$= V_0 \frac{T}{273}.$$

Therefore

$V_t \propto T$ or $V \propto T$ at constant pressure i.e.,

Or $\boxed{V/T = \text{constant}}$

Hence "At constant pressure, the volume of a given mass of a gas is directly proportional to its temperature in Kelvin."

$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$ At constant pressure

Relation between Density and Temperature

As $V \propto 1/d$ (d = density), So

$V \propto T$

So $d\,T$ = constant

that is, $\boxed{d_1 T_1 = d_2 T_2}$

REMEMBER

Charle's Law is not applicable to liquids.

Volume Coefficient (α_V)

It represents the ratio of increase in volume of a gas at constant pressure per degree rise of temperature to its volume at 0°C. Its value is 1/273 for all gases.

$$\alpha_V = \frac{Vt - V0}{V_0 \times t°c}$$

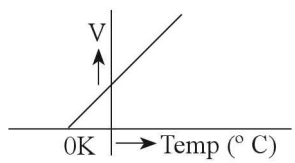
Absolute Scale of Temperature or Absolute Zero

As according to Charle's law $V_0 (1 + t°C/273)$

If the temperature of a gas is lowered upto –273°C the volume of the gas becomes zero. This temperature is known as absolute zero and this zero point on the scale is called as Kelvin scale.

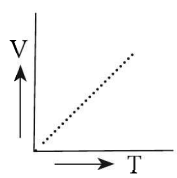
The absolute value of this temperature is –273.15°C. At this temperature, pressure, kinetic energy and heat content of the gas is also zero. Absolute zero does not indicate thus volume of the gas is zero. There is no significance of gas laws at this temperature as gas phase is not observed here as a gas liquefied or solidified before this temperature.

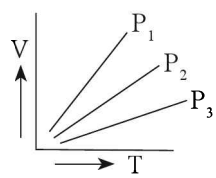
When a graph is plotted between the volume of the gas against this temperature at constant pressure, it is called isobar and it is always a straight line.



Plots between V vs T

These are called Isobars.





Here $P_1 < P_2 < P_3$

As $P \propto T$

Illustrations

3. A flask is of a capacity of one litre. What volume of air will escape from the flask if it is heated from 27°C and 37°C? Assume pressure to be constant.

Solution T = 27°C = 300 K

T_1 = 37°C = 310 K

V = 1 litre,

V_1 = ?

$\frac{V}{T} = \frac{V_1}{T_1}$ (At constant pressure)

$\frac{1}{300} = \frac{V_1}{310}$

$V_1 = \frac{310}{300} = 1.0333$ litre

As capacity of flask is 1 litre.

So volume of air escaped out = 1.033 – 1

= 33.3 ml.

4. To what temperature must an ideal gas be heated under isobaric conditions to increase the volume from 100 cm^3 at 25°C to 1.00 dm^3?

Solution According to the Charle's law,

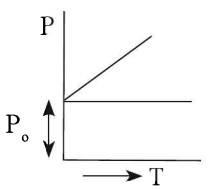
$\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$\frac{100\ cm^3}{300K} = \frac{1.00 \times 10^3\ cm^3}{T_2}$

$T_2 = \frac{1000 \times 298}{100} = 2980$ K

Temperature = 2980 – 273 = 2707°C

Pressure–Temperature Law (Gay-Lussac's Law) In order to explain it, let us consider



It shows that the pressure of a definite amount of a gas at constant volume varies linearly with temperature on Celsius scale.

It can be given as $P_t = a + bt$

Here a and b are constant

$a = P_0$ at 0°C

b = slope $(\partial P/\partial T)_V$

According to pressure- temperature law "At constant volume, the pressure of a given mass of a gas increases or decreases by 1/273 of its pressure at 0°C for every 1°C rise or fall in temperature," that is,

$P_t = P_0 + \frac{P_0}{273} \times t°C$

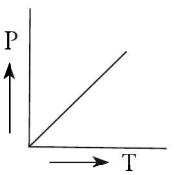
$= P_0 \frac{(273 + t°C)}{273} = P_0 \frac{T}{273}$.

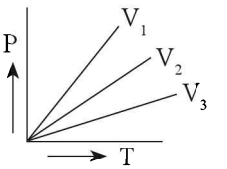
$P \propto T$ that is, $\frac{P}{T}$ = constant

At constant volume

$$\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$$

Plots between P vs T





Here $V_3 > V_2 > V_1$

As $V \propto T$ (i.e. $T_1 < T_2 < T_3$)

Here curves are called Isochors and the slope will be greater for lower volumes.

Pressure Coefficient (α_p)

It represents the ratio of increase in pressure of the gas at constant volume per degree rise of temperature to its pressure at 0°C. Its value is 1/273 for all gases.

$\alpha_P = \frac{P_t - P_0}{P_0 \times t°C}$

Avogadro's Law

According to Avogadro's law, "At constant temperature and pressure, equal volume of gases will have same number of molecules or moles."

$V \propto N$ or n

V/n = constant

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2}}$$

$$\boxed{\frac{V_1}{N_1} = \frac{V_2}{N_2}}$$

Here n = Number of moles of gas used

N = Number of molecules of gas used

Molar Volume or Gram Molecular Volume

1 mole of a gaseous substance has 22.4 litre volume at NTP which is known as it's molar volume.

Avogadro Number

1 mole of a substance contains 6.02×10^{23} number of molecules.

- 1 gram atom of any element contains 6.02×10^{23} atoms.

  Hence $N_A = 6.02 \times 10^{23}$

REMEMBER

Avogadro law is applicable under the conditions of high temperature and low pressure that is, for an ideal gas.

Combined Gas Laws and Ideal Gas Equation

On combining Boyle's, Charle's and other gas laws we get

As $V \propto \frac{1}{P}$ [Boyle's law]

$V \propto T$ [Charle's law]

$V \propto n$ [Avogadro law]

So $V \propto \frac{nT}{P}$

Or $PV \propto nT$

Or $PV = nRT = nST$

$PV = \frac{w}{M} RT$

$P = \frac{w}{MV} RT$

$P = CRT$ [As $C = \frac{w}{MV}$]

$P = \frac{d}{M} RT$ [As d = w/V]

- R or S : Molar gas constant or universal gas constant

  Values of R = 0.0821 lit, atm, K^{-1}, mol^{-1}

  $= 8.314$ joule K^{-1} mol^{-1}

  $= 8.314 \times 10^7$ erg K^{-1} mol^{-1}

  $= 2$ cal K^{-1} mol^{-1}

- For a single molecule, gas constant is known as Boltzmann constant (k).

  $k = R/N_0$

  $= 1.38 \times 10^{-23}$ J/deg-abs/molecule

  $= 1.38 \times 10^{-16}$ erg/deg-abs/molecule

As $\frac{PV}{T}$ = constant

So Ideal gas equation can be written as

$$\frac{P_1V_1}{T_1} = \frac{P_2U_2}{T_2}$$

Illustrations

5. How large a balloon could you fill with 4.0 g of He gas at 22°C and 720 mm of Hg?

Solution P = 720/760 atm

T = 295 K

w = 4 g

m = 4 (He)

$PV = \frac{w}{m} RT$

$V = \frac{w\,RT}{m \times P} = \frac{4 \times 0.0821 \times 295 \times 760}{4 \times 720}$

= 25.565 litre

6. Calculate the density of CO_2 at 100°C and 800 mm Hg pressure.

Solution P = 800/760 atm

T = 373 K

$PV = \frac{w}{m} RT$

$P = \frac{d}{m} RT$ (As w/v = density)

$\frac{800}{760} = \frac{d}{44} \times 0.0821 \times 300$

d = 1.5124 g $litre^{-1}$.

7. When 2 g of a gusions substance P is introduced into an initially evacuated flask kept at 25°C the pressure is found to be 202.65 kPa. The flask is evacuated and 3 g of $Q_{(g)}$ is introduced as a result the pressure become 101.325 kPa at 298 k. How much time Q is heavier than P here?

Solution As $PV = \frac{W}{M} RT$

For Gas 'P' → $202.65 \times V = \frac{2 \times 10^{-3}}{M_p} \times R \times T$ —— 1

For Gas Q → $101.325 \times V = \frac{3\times10^{-3}}{M_Q} \times R \times T$ —— 2

From Eq 1 and 2

$$2 = \frac{2}{3} \times \frac{M_Q}{M_p}$$

$$\boxed{M_Q = 3\ M_p}$$

8. In Victor Mayer's experiment 0.23 g of a volatile solute displaced air which measures 112 ml at NTP. Find the vapour density and mol. wt. of substance.

Solution Volume occupied by solution at NTP

= volume of air displaced at NTP = 112 ml

$PV = \frac{w}{m} RT$

At NTP, P = 1 atm, T = 273 K

$$1 \times \frac{112}{1000} = \frac{0.23}{m} \times 0.0821 \times 273$$

Molecular weight = 46.02

$$\text{Vapour density} = \frac{\text{mol. wt}}{2} = 46.02/2 = 23.01.$$

9. A certain amount of an ideal gas occupies a volume of 10 m^3 at a given temperature and pressure. What would be its volume after reducing its pressure to half the initial value and raising the temperature twice the initial value?

Solution $P_2 = 0.5\ P_1$

$T_2 = 2\ T_1$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P_1 V_1}{T_1} = \frac{0.5\ P_1 V_2}{2T_1}$$

$V_2 = 4\ V_1$

$V_1 = 1\ m^3$

$V_2 = 4.0\ m^3$

10. A 5.00 litre vessel contains 25.0 g of PCl_3 and 3.00 g of O_2 at 15°C. The vessel is heated to 200°C and the contents react to give $POCl_3$. What is the final pressure in the vessel, assuming that the reaction goes to completion and that all reactants and products are in the gas phase?

Solution Mol. weight of PCl_3 = 137.3

Mol. weight of O_2 = 32.00

Mol. weight of $POCl_3$ = 153.3

$2PCl_3\ (g) + O_2\ (g) \rightarrow 2POCl_3\ (g)$

$$\text{mol } PCl_5 = 25.0 \times \frac{1 \text{ mol } PCl_3}{137.3 \text{ g } PCl_3}.$$

= 0.182 mol PCl_3

$$\text{mol } O_2 = 3.00 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.0937 \text{ mol } O_2$$

For limiting reactant

$$\text{Mol } O_2 \text{ required} = \frac{0.182 \text{ mol } PCl_3 \times 1 \text{ mol } O_2}{2 \text{ mol } PCl_3}.$$

= 0.0910 mol O_2 required

There is a slight excess of O_2

So PCl_3 is the limiting reactant here.

$$\text{Mol } POCl_3 = \frac{0.182 \text{ mol } PCl_3 \times 2 \text{ mol } POCl_3}{2 \text{ mol } PCl_3}$$

= 0.182 mol $POCl_3$

Mol O_2 left over = 0.0937 – 0.0910

= 0.0027 mol O_2

T = 200°C = 200.0 + 273.15 = 473.1 K

As $PV = nRT$

$$P = \frac{nRT}{V}$$

$$= \frac{(0.182 + 0.0027) \times (0.08206) \times (473.1)}{5.00 \text{ litre}}$$

= 1.43 atm.

11. When 2 g of a gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be one atmosphere. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molecular masses $M_A : M_B$.

Solution $PV = nRT$

$PV = (m/M)\ RT$

$$M = \frac{mRT}{PV}$$

The molecules masses of gases A and B are M_A and M_B respectively.

$$M_A = \frac{2RT}{(1\text{ atm})\,V}.$$

$$M_B = \frac{3RT}{(0.5\text{ atm})\,V}.$$

$$\frac{M_A}{M_B} = \frac{2RT}{1\text{ atm} \times V} \times \frac{0.5\text{ atm} \times V}{3RT} = \frac{1}{3}$$

$$M_A : M_B = 1 : 3.$$

Dalton's Law of Partial Pressure

According to Dalton's law, "Total pressure of a mixture of non-reacting gases is equal to the sum of partial pressure of these gases at constant temperature and constant volume."

$$P_{mix} = P_1 + P_2 + P_3 \ldots\ldots$$

Here P_{mix} = pressure of the gaseous mixture

P_1, P_2, P_3 = partial pressure of gases

$$\text{Partial pressure of any gas} = \frac{\%\text{ of that gas}}{100} \times P_{mix.}$$

% of a gas in a mixture

$$= \frac{\text{Partial pressure of the gas}}{\text{Total pressure of gaseous mixture}} \times 100$$

- Partial pressure of any component A is given as

$$P_A = \frac{\text{moles of A}}{\text{Total moles}} \times P_{Total}$$

- Total pressure of a mixture having different components is given as

$$P_{mix} = (n_1 + n_2 + n_3 \ldots..) \frac{RT}{V}$$

$$P_{mix} = \left(\frac{w_1}{m_1} + \frac{w_2}{m_2} + \frac{w_3}{m_3}\right)\ldots.. \frac{RT}{V}$$

Here w_1, w_2, w_3 = weight of components or non-reacting gases and m_1, m_2, m_3 are their molar masses.

T = Temperature in Kelvin.

V = Volume in litre.

- When a gas is collected over water it mixes with water vapours so the correct pressure of moist gas is given as

P(moist gas) = P(dry gas) + P (V.P. of water)

P(dry gas) = P(moist gas) – P (V. P. of water)

Aqueous tension = Partial pressure of water vapour in moist gas.

- Vapour pressure of water varies with temperature. Example, At 0°C it is 4.6 torr while at 25°C it is 23.8 torr.

REMEMBER

Dalton's law is not applicable for a mixture of reacting gases like N_2 and O_2, SO_2 and O_2.

Illustrations

12. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases. Given R = 0.082 litre atm K^{-1} mol^{-1}.

Solution Given V = 10 litre

Mole of He = 0.4/4 = 0.1

Mole of O_2 = 1.6/32 = 0.05

Mole of N_2 = 1.4/28 = 0.05

Total mole = 0.1 + 0.05 + 0.05 = 0.2

As PV = nRT

$$P_{total} = \frac{n\,RT}{V} = \frac{0.2 \times 0.082 \times 300}{10}$$

= 0.492 atm

P_{He} = Mole fraction of He × Total pressure

$$= \frac{0.1}{0.2} \times 0.492 = 0.246 \text{ atm}$$

13. A special gas mixture used in bacterial growth chambers contains 1.00 % by weight CO_2 and 99.0 % O_2. What is the partial pressure (in atmospheres) of each gas at a total pressure of 0.977 atm?

Solution Let the sample be 100 g.

CO_2 = 1.00 g

$O_2 = 99.0$ g

$$\text{mol } CO_2 = 1.00 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g } CO_2}.$$

$= 0.0227$ mol CO_2

$$\text{mol } O_2 = 99.0 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2}.$$

$= 3.094$ mol O_2

$n_{total} = 3.094 + 0.0227 = 3.117$ mol

$$X_{O2} = \frac{3.094 \text{ mol}}{3.117 \text{ mol}} = 0.993$$

$$X_{CO2} = \frac{0.0227 \text{ mol}}{3.117 \text{ mol}} = 0.00728$$

$P_{O2} = X_{O2} \cdot P_{total}$

$= 0.993 \times 0.977 = 0.970$ atm

$P_{CO2} = X_{CO2} \cdot P_{total}$

$= 0.00728 \times 0.977 = 0.00711$ atm

14. 20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture.

Solution

N_2O_4	↔	$2NO_2$
1 mol	0	At t = 0
(1 – 0.2) mol	0.4	At equilibrium

Total moles = 0.8 + 0.4 = 1.2

PV = nRT

$1 \times V = 1.2 \times 0.0821 \times 300$

V = 29.556 litre

$$d\ N_2O_4 = \frac{m}{V} = \frac{0.8 \times 92}{V\ 29.556} = 2.490$$

$dNO_2 = m = 0.4 \times 46 = 0.6225$ V 29.556

$d_{mix} = 2.490 + 0.6225 = 3.113$ g/litre.

Graham's Law of Diffusion

According to it "At constant pressure and temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density or molecular weight" It is applicable only at low pressure.

$$r \propto \frac{1}{\sqrt{M}} \text{ or } \frac{1}{\sqrt{d}}$$

Here r = rate of diffusion or effusion of a gas or liquid.

M and d are molecular weight and density respectively.

■ For any two gases the ratio of rate of diffusion at constant pressure and temperature can be shown as

$r_1/r_2 = \sqrt{M_2/M_1}$ or $\sqrt{d_2/d_1}$

If pressure are different and we take two gases then

$r_1/r_2 = P_1/P_2 .(\sqrt{M_2/M_1}$ or $\sqrt{d_2/d_1})$

Hence diffusion or effusion of a gas or gaseous mixture is directly proportional to the pressure difference of the two sides and is inversely proportional to the square root of the gas or mixture effusing or diffusing out.

Some other relations based on Graham's law

As r = V/t

= volume/time

So

$$\boxed{\frac{V_1\ t_2}{V_2\ t_1} = \sqrt{M_2/M_1}}$$

$$\text{As } r = \frac{n}{t} = \frac{d}{t} = \frac{w}{t}.$$

So

$$\boxed{\frac{n_1\ t_2}{n_2\ t_1} = \sqrt{M_2/M_1}}$$

$$\boxed{\frac{w_1\ t_2}{w_2\ t_1} = \sqrt{M_2/M_1}}$$

$$\boxed{\frac{d_1\ t_2}{d_2\ t_1} = \sqrt{M_2/M_1}}$$

Here n represents number of moles, w represents weight in gram and d represents distance traveled by a particular gas or liquid.

Differentiation between Diffusion and Effusion

Diffusion

It is the movement of gaseous or liquid molecules without any porous bars that is, spreading of molecules in all directions.

Effusion

It is movement of gases molecules or liquid molecules through porous bar that is, a small hole or orifice.

Uses of Graham's law

(i) Detecting the presence of Marsh gas in mines.

(ii) Separation of isotopes by different diffusion rates. Example, U-235 and U-238

(iii) Detection of molecular weight and vapour density of gases using this relation.

$$\frac{r_1}{r_2} = \left(\frac{m_2}{m_1}\right)^{1/2} \text{ or } \left(\frac{d_2}{d_1}\right)^{1/2}$$

Illustrations

15. What is the molecular mass of a gas that diffuses through a porous membrane 1.86 times faster than Xe? What might the gas be?

Solution $r_{Xe}/r_Z = \sqrt{(M_Z/M_{Xe})}$

$1/1.86 = \sqrt{(M_Z/131.29)}$

$\sqrt{M_Z} = \frac{\sqrt{131.29}}{1.86}$

$M_Z = \frac{131.29}{(1.86)^2} = 37.9$ g/mol

Molecular mass = 37.9 amu

So the gas may be F_2.

16. 20 dm^3 of SO_2 diffuse through a porous partition in 60 sec. What volume of O_2 will diffuse under similar conditions in 30 seconds?

Solution $r_{SO2} = \frac{V_{SO2}}{t_{SO2}} = \frac{20}{60} = 0.333$ dm^3/sec

$r_{O2} = \frac{V_{O2}}{t_{O2}} = \frac{V}{30}$ dm^3/sec

$r_{SO2}/r_{O2} = \sqrt{(M_{O2}/M_{SO2})}$

$0.333/V/30 = \sqrt{(32/64)}$

$V = 14.14$ dm^3

17. The rate of effusion of an unknown gas (X) through a pin hole is found to be 0.279 times the rate of effusion of hydrogen (H_2) gas through the same pin hole. If both gases are at STP. What is the molecular mass of the unknown gas?

Solution $r_1/r_2 = \sqrt{(m_2/m_1)}$

Assume 1 and 2 stands for hydrogen gas and unknown gas respectively.

$1/0.279 = \sqrt{(m_2/2)}$

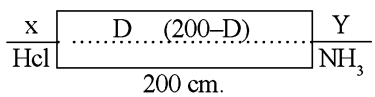
$m_2 = \frac{2}{0.279 \times 0.279} = 25.7$ g mol^{-1}

18. A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. White fumes first appear at a point P inside the tube. Find the distance of P from X.

Solution Molecular mass of HCl = 36.5

Molecular mass of NH_3 = 17.0

$r_1/r_2 = \sqrt{(M_2/M_1)}$



Assume the distance between P and X be D cm.

$\frac{D}{(200 - D)} = \sqrt{(17/36.5)} = 0.6824$

$D = 0.6824 \times (200 - D)$

$D + 0.6824\ D = 0.6824 \times 200$

$D = \frac{0.6824 \times 200}{1.6824} = 81.12$ cm

19. If an unknown homonuclear diatomic gaseous molecule effuses at a rate of 0.355 times to that of oxygen under similar conditions of temperature and pressure. Find the identity of this gas.

Solution $r_g/r_{O2} = \sqrt{(M_{O2}/M_X)}$

$0.355 = \sqrt{(32/M_X)}$

$M_X = \frac{32}{(0.355)^2} = 254$

The molecular weight suggest that this homonuclear diatomic gaseous molecules I_2.

20. Ammonia and the hydrogen chloride gases are introduced simultaneously at the ends of a 90 cm tube. At what distance ammonium chloride is formed from the end at which HCl is introduced?

Solution According to Graham's law of diffusion

$r_1/r_2 = \sqrt{(d_2/d_1)} = \sqrt{(M_2/M_1)}$

$r_{HCl}/r_{NH3} = \sqrt{(M_{NH3}/M_{HCl})}$

$= \sqrt{(17/36.5)} = 4.123/6.040$

$r_{HCl} = 4.123$ if $r_{NH3} = 6.040$

If the total length of the tube is 10.163 cm, HCl will travel 4.123 cm. If the total length of the tube is 90 cm, HCl will travel

$$= \frac{4.123}{10.163} \times 90 = 36.51 \text{ cm.}$$

So NH_4Cl is formed at a distance of 36.51 cm from the end where HCl is introduced.

Kinetic Theory of Gases

Kinetic theory of gases was put forward by Bernoulli and was developed by Clausius and Kelvin.

- It was explained by Maxwell and Boltzmann.
- It is also known by other names, such as dynamic particle model and microscopic model.

Main Assumptions

(i) Each gas is composed of a large number of tiny particles called molecules and these molecules are identical in mass, size and shape.

(ii) The volume of gaseous molecules is negligible to the volume of the gas.

(iii) Molecules show random motion in straight lines in all possible directions but at a constant speed.

(iv) Molecules undergo collisions which are perfectly elastic that is, no change in energy.

(v) The force of attraction between molecules is negligible thus gas molecules can move freely and independent of each other.

(vi) The effect of gravity on molecular motion is negligible.

(vii) Pressure of the gas is due to collisions of molecules with the walls of the container.

(viii) At any particular instance molecules have different speeds so have different kinetic energies, however, the average kinetic energy of these molecules is directly proportional to absolute temperature

Kinetic energy α absolute temperature

Kinetic Gas Equation

On the basis of above assumptions it can be given as

$PV = (1/3)\ mnu^2_{r.m.s}$

Here P = pressure of gas

V = volume of gas

n = number of molecules of gas

$u_{r.m.s}$ = root mean square velocity (R.M.S)

Kinetic Energy Calculation

As for one mole PV = RT

$PV = 1/3\ Mnu^2_{r.m.s}$

so $\frac{1}{3} Mu^2_{r.m.s} = RT$

$u^2_{r.m.s} = \frac{3RT}{M}$

$u_{r.m.s} = \sqrt{(3PV/M)} = \sqrt{(3RT/M)} = \sqrt{(3P/d)}$

$u^2_{r.m.s} \alpha T$

$u_{r.m.s} \alpha \sqrt{T}$

As from kinetic gas equation

$$\frac{1}{3} \frac{Mu^2_{r.m.s}}{N} = \frac{RT}{N}$$

As $R/N = k$

Here k = Boltzman constant

$\frac{1}{3} mu^2_{r.m.s} = kT$

$\frac{1}{2} mu^2_{r.m.s} = \frac{3}{2} kT$

$K.E. = \frac{3}{2} kT$

or

$$\boxed{K.E = \frac{3}{2} \frac{RT}{N}}$$

Here k is known as Boltzmann constant and its value is 1.38×10^{-16} erg.

Illustrations

21. Find out the kinetic energy of 10 mol of gas at 200°C.

Solution K.E. $= \frac{3}{2}$ RT

R = 8314×10^7 erg/K/mol

T = 200 + 273 = 473 K

n = 10 moles of gas

K.E. $= \frac{3}{2} \times 10 \times 8314 \times 10^7 \times 473$

$= 58987.83 \times 10^7$ erg.

22. Calculate the average kinetic energy in joules of the molecules in 8.0 g of methane at 27°C.

Solution As kinetic energy of the molecule

K.E. $= \frac{3}{2}$ RT

So average K.E. = n (3/2 RT)

Here n = Number of moles of the gas

Molecular mass of $CH_4 = 12 + 4 = 16$

Number of moles of CH_4 in 8.0 g

$= \frac{8.0 \text{ g}}{16 \text{ g mol}^{-1}} = 0.5$ mole

K.E. = (0.5 mol) (3/2) (8.314 JK^{-1} mol^{-1}) (300K)

= 1870.65 J.

23. Find the pressure exerted by 10^{23} gas molecules, each of mass 10^{-25} kg, in a container of volume 0.001 m^3 and having root mean square velocity of 1000 ms^{-1}. Also calculate total kinetic energy and temperature of gas.

Solution As $P = \frac{1}{3} \frac{m N u^2}{V}$

$= \frac{1 \times 10^{-25} \times 10^{23} \times (10^3)^2}{3 \times 10^{-3}}$

$= 3.33 \times 10^6$ Nm^{-2}

K.E. = (½ m u^2) × N

$= \frac{1}{2} \times 10^{-25} \times (10^3)^2 \times 10^{23} = \frac{1}{2} \times 10^4$

$= 0.5 \times 10^4$ J

K.E $= \frac{3}{2}$ n RT

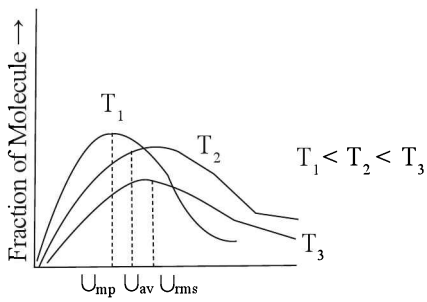
Here n (mole) $= \frac{10^{23}}{N_0}$

$= \frac{10^{23}}{6.023 \times 10^{23}}$.

$0.5 \times 10^4 = \frac{3}{2} \times \frac{10^{23}}{6.023 \times 10^{23}} \times 8.314 \times T$

$T = \frac{0.5 \times 10^4 \times 2 \times 6.023}{3 \times 8.314} = 2415$ K

Molecular Speed Graph or Maxwell Distribution of Velocities



According to it

- Molecules have different speeds due to frequent molecular collisions with the walls and among themselves.
- Rare molecules have either very high or very low speed
- Maximum number of molecules of the gas have maximum velocity which is called most probable velocity and after Vmp velocity decreases
- Zero velocity is not possible.
- All these velocities increase with the increase in temperature but fraction of molecules having these velocities decreases.

Different Velocity Terms

The Maxwell relation gives the fraction of molecules in one mole (d_N/N_A) having a velocity in the Z-direction between U_Z and $U_Z + d\,U_Z$ as

$$\frac{d_N/N_A}{d\,U_Z} = A\, e^{-m\,U_z^2/2\,k\,T}$$

Here A = constant

N_A = Avogadro number

The above relation in three dimensions can be written as

$$\frac{d_N/N_A}{d_U} = 4\,\pi\,U^2\,[M/2\,\pi\,k\,T]^{3/2}\,e^{-m\,U^2/2\,K\,T}$$

The velocity of gases can be expressed as follows:

(i) Average Speed ($\bar{u}$): It is the average of different velocities possessed by the molecules.

$$Ua.v. = \frac{U_1 + U_2 + U_3}{n}$$

$$Ua.v. = \frac{n_1U_1 + n_2U_2 + n_3U_3}{n_1 + n_2 + n_3}$$

Here n_1, n_2 ,n_3 are the number of molecules having U_1, U_2, U_3 velocities respectively.

■ Relation between Ua.v., temperature and molar mass is given as

$$Uav. = \sqrt{(8RT/\pi M)}$$
$$= \sqrt{(8PV/\pi M)}$$

It is also denoted by $\bar{u}$.

(ii) Root Mean Square Velocity ($u_{r.m.s}$): It is square root of the mean of the square of the velocities of different molecules.

$$Urms = \frac{\sqrt{(U_1^2 + U_2^2 \ldots)}}{n}$$

$$= \frac{\sqrt{(n_1\,U_1^2 + n_2\,U_2^2 + n_3\,U_3^2)}}{n_1 + n_2 + n_3}$$

$$\boxed{Urms = \sqrt{(3RT/M)}}$$

$$\boxed{\begin{aligned} Urms &= \sqrt{(3PV/M)} \\ &= \sqrt{(3P/d)} \end{aligned}}$$

(iii) Most Probable Velocity (α): It is velocity possessed by maximum number of molecules.

$$\boxed{\begin{aligned} Um.p. &= \sqrt{(2RT/M)} \\ &= \sqrt{(2PV/M)} \end{aligned}}$$

■ These velocities increase with increase in temperature but the fraction of molecules having these velocities decreases.

Relation between α, $\bar{u}$ and $u_{r.m.s.}$

$\alpha : \bar{u} : u_{r.m.s.} =$

$\sqrt{(2RT/M)} : \sqrt{(8RT/\pi M)} : \sqrt{(3RT/M)}$

$= \sqrt{2} : \sqrt{(8/\pi)} : \sqrt{3}$

$= 1.414 : 1.595 : 1.732$

$= 1 : 1.128 : 1.224$

$= 0.8164 : 0.9213 : 1$

that is, $u_{r.m.s} > \bar{u} > \alpha$.

$$\boxed{\begin{aligned} Ua.v. &= Urms \times 0.9213 \\ \alpha\ (Um.p.) &= 0.8164 \times Urms \end{aligned}}$$

Illustrations

24. Find out the RMS velocity of O_2 molecules at NTP (density of O_2 = 0.001429 g/cc at NTP, density of Hg = 13.6 g /cc, g = 981 cm/sec^2).

Solution h = 76 cm

$u_{r.m.s} = \sqrt{(3P/d)} = \sqrt{(3 \times h \times d \times g/d)}$

$$= \frac{\sqrt{(3 \times 76 \times 13.6 \times 981)}}{\sqrt{0.001429}}$$

$= 46137.6$ cm sec^{-1}

25. Two flasks A and B have equal volumes. Flask A contains H_2 at 27°C while B contains equal mass of C_2H_6 at 627°C. In which flask and by how many times are molecules moving faster? Assume ideal gas nature for both.

Solution For H_2 , Average velocity

$= \sqrt{(8RT/\pi M)} = \sqrt{(8R \times 300/\pi \times 2)}$

For C_2H_6 Average velocity

$= \sqrt{(8RT/\pi M)} = \sqrt{(8R \times 900/\pi \times 30)}$

$$\frac{\text{Average velocity } H_2}{\text{Average velocity } C_6H_6} = \frac{\sqrt{(300 \times 30)}}{\sqrt{(900 \times 2)}}$$

$= 2.236 : 1$

26. Calculate the temperature at which the root mean square velocity of SO_2 molecules is the same as that of O_2 at 27°C.

Solution $u = \sqrt{(3\,RT_{SO2}/M_{SO2})} = \sqrt{(3\,RT_{O2}/M_{O2})}$

$\sqrt{(3\,RT_{SO2}/64)} = \sqrt{(3R \times 300/32)}$

$T_{SO2} = 600\ K$

27. Find the V_{rms} of a missed particle having a mass of 10^{-12} g at 27°C if value of Boltzmann constant k is 1.31×10^{-16} ergs per degree per molecule.

Solution $V_{rms} = \sqrt{(3kT/M)}$

$$= \frac{\sqrt{(3 \times 1.31 \times 10^{-16} \times 300)}}{\sqrt{10^{-12}}}$$

$= 0.342\ cm\ sec^{-1}$

28. Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure.

Solution As given volumes are

$V_1 = 22400\ cm^3$, $V_2 = ?$

$P_1 = 76$ cm, $P_2 = 82$ cm

$T_1 = 273\ K$, $T_2 = 273 + 20 = 293\ K$

As

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

So

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$= \frac{76 \times 22400 \times 293}{273 \times 82} = 22282\ cm^3$$

Molecular mass of $O_3 = 3 \times 16 = 48\ g\ mol^{-1}$

$P = 82\ cm \times 13.6\ g\ cm^{-3} \times 981\ cm\ sec^{-2}$

So $$u = \frac{\sqrt{(3PV)}}{\sqrt{M}}$$

$$= \frac{\sqrt{(3 \times 82 \times 13.6 \times 981 \times 22282)}}{\sqrt{(48)}}$$

$= 3.90 \times 10^4\ cm\ sec^{-1}$

Ideal Gas

These gases obey gas laws under all the conditions of temperature and pressure.

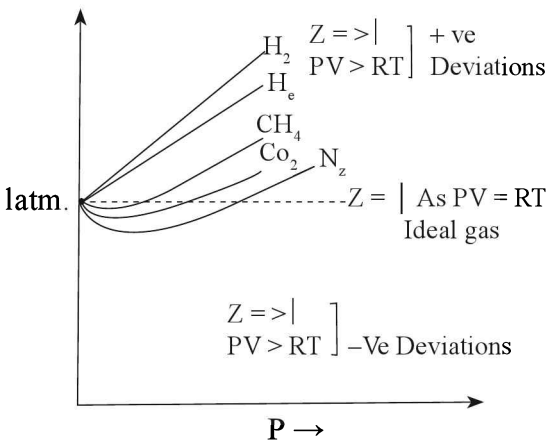
- No gas is ideal in reality (hypothetical).
- No force of attraction is present between molecules in them.
- Volume of molecules is negligible to the total volume of the gas (container).

Real Gas

These gases obey gas laws only at high temperature and low pressure.

- All the gases are real.
- Here force of attraction between molecules cannot be neglected at high pressure and low temperature
- Here volume occupied by gas molecule is not negligible specially at high pressure and low temperature.

Deviation of Real Gases from Ideal++ Gas Behaviour



- The extent of deviation of a real gas from ideal gas behaviour is expressed in terms of compressibility factor Z. It is an empirical correction for the non-ideal behaviour of real gases which allows the simple form of the combined gas law to be retained. It is given as

$$Z = \frac{PV}{nRT}$$

When Z = 1 (ideal gas behaviour)

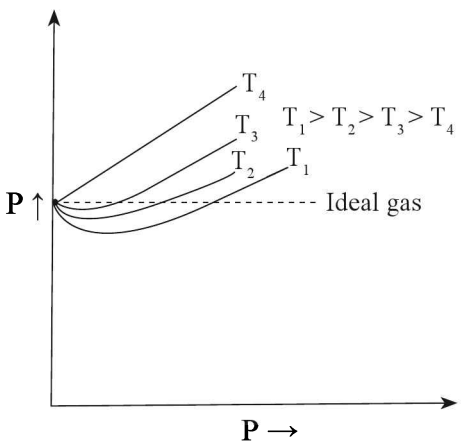
When Z < 1 (negative deviations)

When Z > 1 (positive deviations)

When Z < 1 gas is more compressible

When Z > 1 gas is less compressible

- For He and H_2 Z > 1 as PV > RT [as $a/V^2 = 0$] that is, positive deviations.
- At Very Low Pressure : PV ≈ RT (as a/V^2 and b are neglected) that is, Z ≈ 1 so nearly ideal gas behaviour.
- At Low Pressure : PV < RT
  that is, Z < 1 so negative deviation
- At Moderate Pressure : PV = RT
  i.e, Z = 1 so ideal gas behaviour.
- At High Pressure : PV > RT
  (as b can not be neglected). that is, Z > 1 so positive deviation.
- An increase in temperature shows a decrease in deviation from ideal gas behaviour.



It shows that curve for a real gas has a lendency to Coincide with that of an ideal gas at high temperatures. It means, at high temperatures, gases show ideal gas behaviour.

Van der Waal's Equation

Van der waal's equation is a modification of the ideal gas equation that takes into account the non-ideal behaviour of real gases.

Van der Waal's equation modified kinetic theory of gases by considering these two points of kinetic theory of gases not to be fully correct or are not followed by real gases.

- The force of attraction between gaseous molecules is negligible.
- The volume of gaseous molecules is negligible to the total volume of the gas.

He made following two corrections:

A. Volume Correction: According to him, at high pressure the volume of the gas becomes lower so volume of molecules can not be ignored. Hence the actual space available inside the vessel for the movement of gas molecules is not the real volume of the gas, actually it is given as

$$V_{real\ gas} = V - b$$

Here V is the volume of the container while b is volume occupied by gas molecules and it is called co-volume or excluded volume.

The excluded volume for 'n' molecules of a gas $= 4nV_m$ or $(4 \times 4/3\ \pi r^3)$

Here V_m = Volume of one molecule $(4/3\ \pi r^3)$

Now ideal gas equation can be written as -

$P.(V - b) = RT$

$P(V - nb) = nRT$ ..... (1)

B. Pressure Correction: According to him, at high pressure the gaseous molecules are closer so attraction forces cannot be ignored hence, pressure of the real gas is given as:

Pressure of the Real gas = pressure developed due to collisions (P) + pressure loss due to attraction (p')

$$P_{real\ gas} = P + p'$$

Here p' is pressure loss due to force of attraction between molecules or inward pull.

As : $p' \propto n^2$ [n^2 is number of molecules attracting or attracted]

$$p' \propto n^2 \propto d^2 \propto \frac{1}{V^2}$$

So

$$p' = \frac{a}{V^2} = \frac{a\,n^2}{V^2}$$

Here 'a' is van der waal's force of attraction constant, d is density and V is volume.

Hence

$$P_{real\ gas} = P + a/V^2$$

$P + an^2/V^2$ .....(2)

Now ideal gas equation can be written after correction of pressure and volume as

For one mole

$$\left(P + \frac{a}{V^2}\right).(V - b) = RT$$

For n number of moles

$$\left(P + \frac{n^2 a}{V^2}\right).(V - nb) = nRT$$

Units of a and b

a = $lit^2\ mol^{-2}$ atm
or cm^4, mol^{-2} dyne
or $m^4\ mol^{-2}$ Newton

b = lit/mol
or cm^3 /mol
or m^3 /mol

■ The values of 'a' and 'b' are 0.1 to 0.01 and 0.01 to 0.001 respectively.

Significance of a and b

a. It gives the magnitude of attraction forces present between gas molecules.

Liquefication of gases $\propto$ a

Hence more the value of 'a' or force of attraction between the molecules of a gas more will be its liquefaction: Example,

Values of 'a'

$He < H_2 < O_2 < N_2 < CO_2 < HCl < NH_3 < SO_2$

a→(0.034) (0.244) (1.36) (1.39) (3.59) (3.8) (4.17) (6.71)

Increasing order of liquefication of some gases

b. Its constancy in value shows that gas molecules are incompressible.

$b = 4N\ (4/3\ \pi r^3)$

■ At low pressure 'a' dominates but at high pressure 'b' dominates.

Limitations of Van der Waal's Equation

As the value of Van der Waal's constants 'a' and 'b' do not remain constant over the entire ranges of temperature and pressure so this equation is also valid over some specific ranges of temperature and pressure only.

Van der waal's equation in terms of Compressibility Factor

$$[P + \frac{n^2 a}{V^2}]\ [V - nb] = n\ RT$$

$$P = \frac{nRT}{(V - nb)} - \frac{a\ n^2}{V^2}$$

$$\text{As } Z = \frac{V_m}{V_m\ (\text{ideal gas})} = \frac{V_m}{n\ RT/P}$$

$$Z = \frac{PV_m}{nRT}.$$

$$= [\frac{nRT}{V_m - nb} - \frac{a\ n^2}{V_m^2}] \times \frac{V_m}{nRT}$$

$$Z = \frac{V_m}{V_m - nb} - \frac{an}{RTV_m}$$

Explanations for Real Gas Behaviour

(i) At very low pressure for one mole of a gas, the value of 'p' and 'b' can be ignored so Van der Waal's equation becomes equal to ideal gas.

$PV = RT$

(ii) At moderate pressure the value of 'nb' or 'b' can be ignored so Van der Waal's equation becomes

$[P + a/V^2]\ [V] = RT$

$PV + \frac{a}{V} = RT$

$PV = RT - \frac{a}{V}.$

Hence $PV < RT$

So $Z = \frac{PV}{RT}.$

$Z < 1$

(iii) At high pressure, the value of 'p' can be ignored so Van der Waal's equation can be written as

$P\ (V - b) = RT$

$PV - Pb = RT$

$PV = RT + Pb$

$PV > RT$

$Z = \frac{PV}{RT}.$

So $Z > 1$

■ In case of H_2, He, p' is always ignored so for them Van der Waal's equation becomes

$P\ (V - b) = RT$

$PV = RT + Pb$

i.e., $Z > 1$

Illustrations

29. 2 moles of ammonia occupied a volume of 5 litres at 27°C. Calculate the pressure if the gas obeyed Van der Waal's equation. (a = 4.17 atm lit^2 mol^{-2}, b = 0.0371 lit mol^{-1})

Solution n = 2 , V = 5 litres ,

T = 273 + 27 = 300 K

R = 0.082 lit atm deg^{-1} mole^{-1}

$\left(P + \frac{n^2 a}{V^2}\right) . (V - nb) = nRT$

$[P + (4.17 \times 2^2/5^2)]\ [5 - 2 \times 0.037]$

$= 2 \times 0.082 \times 300$

P = 9.33 atm

30. Using Van der Waal's equation find the pressure (in atm) of 45 g of ammonia in a one liter vessel at 0°C, if for ammonia 'a' = 4.17 litre^2 atm mol^{-2} and 'b' = 0.0371 litre mol^{-1}.

Solution Moles of ammonia $= \frac{45}{17} = 2.64$

Using Van der Waal's equation

$\left(P + \frac{n^2 a}{V^2}\right) . (V - nb) = nRT$

$\frac{P + (2.64)^2 \times 4.17}{1^2} \times (1 - 2.64 \times 0.0371)$

$= 2.64 \times 0.082 \times 273$

On solving,

P = 36.5 atm

31. If for nitric oxide (NO) the value of Van der Waal's constant b is 0.02788 litre mol^{-1}. Find the diameter of NO.

Solution b = 4N (4/3 π r^3)

Here b = 0.02788 litre/mol = 27.88 cc/mole

$27.88 = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times 3.14 \times r^3$

$r^3 = \frac{27.88 \times 3 \times 10^{-23}}{4 \times 6.023 \times 4 \times 3.14}$.

$= 2.8 \times 10^{-8}$ cm

32. Calculate the pressure exerted by 2 dm^3 mol^{-1} of ethane at 27°C if it follows van der Waal's equation a = 5.489 dm^6 atm mol^{-2}, b = 0.0638 dm^3 mol^{-1}. Compare the value if the gas is ideal.

Solution As

$\left(P + \frac{n^2 a}{V^2}\right) . (V - nb) = nRT$

$P = \frac{RT}{V - b} - \frac{a}{V^2}$.

$= \frac{0.0821 \times 300}{(2.0 - 0.0638)} - \frac{5.489}{(2)^2}$

$= 12.72 - 2.7445 = 9.976$ atm

From ideal gas equation

PV = RT

$P = \frac{RT}{V} = \frac{0.0821 \times 300}{2}$

= 12.315 atm

33. The Van der Waal's constant 'b' for helium gas is 0.0237 litre mole^{-1}. Calculate the approximately diameter of the helium molecule assuming the molecule to be spherical.

Solution As $b = 4\ N \frac{4}{3} \pi\ r^3$

Here b = 0.0237 litre mole^{-1} = 23.7 ml mol^{-1}

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

$23.7 = 4 \times 6.02 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$

$r^3 = \frac{23.7 \times 21}{16 \times 6.02 \times 10^{23} \times 22}$.

On solving

$r = 1.33 \times 10^{-8}$ cm.

So the diameter of helium molecule is 2.66×10^{-8} cm.

Gas Analysis or Eudiometry

It is the process of gas analysis used to determine molecular formula percentage composition of gaseous mixture.

Gas eudiometry is based on Avogadro's law which states that "equal volume of all gases under similar conditions of temperature contain equal number of molecules or equal number of moles". It means volume ratio among gases is same as mole ratio at constant temperature and constant pressure.

During gas analysis, the eudiometer tube filled with mercury is inverted over a trough having mercury. A calculated volume of the gas or gaseous mixture is introduced, which displaces an equivalent

amount of mercury. Now a known excess of oxygen is introduced and is electrically sparked, where by the combustible material gets oxidized. the volume of CO_2, H_2O or other gaseous products of combustion are next determined by absorbing them in a suitable reagent. After each electric spark the reaction mixture is brought to the room conditions.

Example,

O_2 : Alkaline pyrogallol

N_2 : Heated Mg

Acidic gases CO_2, SO_2, NO_2, X_2 : NaOH or KOH solution

Water vapour produced during the reaction can be determined by noting contraction in volume caused due to cooling.

From this data we got some useful conclusions regarding gaseous reactions as follows:

(i) Composition of the gaseous mixture

(ii) Molecular formula of gases

(iii) Volume-volume relationship between gases

Illustrations

34. When 100 ml sample of methane and ethane along with excess of O_2 is subjected to electric spark, the contraction in volume was observed to be 212 ml. When the resulting gases were passed through KOH solution, further contraction in volume was?

Solution $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

X 2X X

$C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2O_2(g) + 3H_2O(l)$

(100-X) 7/2(100-X) 2(100-X)

Total contraction in volume

$2X + 2.5(100 - X) = 212$

$2X - 2.5X = 212 - 250$

On solving, we get

$X = 76$

So contraction in volume when passed through KOH solution

= volume of CO_2 evolved

$= X + 2(100 - X) = 124$ ml

LIQUID STATE

Liquids are characterized by the following properties.

1. They have no definite shape but have definite volume.
2. They have more density than gases but lower than solids.
3. They have more compressibility than solids but less than gases as small voids are present between liquid molecules.
4. They have slower diffusion rate than gases but more than solids due to small voids and slow molecular motion by liquids.
5. The distance of separation between the molecules of a liquid is in the range 10^{-7} to 10^{-9} meter.
6. The attraction and repulsion present between molecules of liquids can be explained by Lennard-Jones 6-12 potential model.
7. H. Eyring and T. Ree introduced Hole theory or Vacancy theory of liquids.
8. Liquids diffuse slowly as the molecules of liquids undergo large number of collisions with the neighbouring molecules.
9. A liquid resembles a gas near critical temperature of the gas and with a solid near the m.p. of solid.

Guldberg's Rule

According to it, normal boiling point (T_b) of a liquid is nearly two third of its critical temperature (T_c) when both the quantities are expressed on the absolute scale as follows:

$$T_b = \frac{2}{3} T_c$$

Here T_b = Boiling point

T_c = Critical temperature

Trouton's Law

According to it, in case of liquids having non-associated nature and not having very high boiling points, the ratio of the heat of vapourization to the normal boiling point of the liquid on the absolute scale is nearly equal to 21 cal K^{-1} mol^{-1} or 88 J K^{-1} mol^{-1}.

$$\frac{\Delta H_{vap}}{T_b} = 21 \text{ cal } K^{-1} mol^{-1}. \text{ (When } \Delta H_v \text{ is in cal)}$$

or

$$\frac{\Delta H_{vap}}{T_b} = 88 \text{ J } K^{-1} mol^{-1}. \text{ (When } \Delta H_v \text{ is in J)}$$

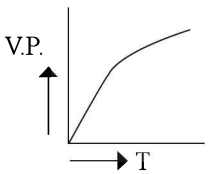
Here ΔH_{vap} = Heat of vapourisation

T_b = Boiling point of a liquid

Vapour Pressure

At a particular temperature, it is the pressure exerted by vapours over liquid surface when vapours are in equilibrium with liquid.

- Vapour pressure increases with increase of temperature.



- The variation of vapour pressure of liquid with temperature is given as

$$\log P = -\frac{A}{T} + 1$$

Here A = Constant

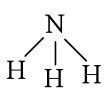
P = Vapour pressure of liquid

T = Temperature

- The plot of log P vs 1/T will be in a straight line.
- The vapour pressure of H_2O at 373 K is 76 cm.
- At critical temperature the meniscus between liquid and vapour disappears.
- Vapour pressure $\propto$ Extent of H-bonding

or

Strength

example., H – F > H – O – H > 

- Heat of vaporization $\propto$ H-bonding
example, HF > H_2O > NH_3
- The amount of heat needed to convert one gram of a liquid into its vapours at its B.P. is known as heat or enthalpy or latent heat of vaporization.
- **Clausius – Clapeyron Equation:** It explains the effect of temperature on vapour pressure of a liquid and also the effect of pressure on the boiling point of a liquid.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap.}}{2.303} \frac{(T_2 - T_1)}{(T_1 . T_2)}$$

REMEMBER

- Formation of bubbles in a liquid in due to vapour pressure.
- Rate of evaporation does not change with time at a particular temperature however rate of condensation increases with time.
- At equilibrium rate of condensation and rate of evaporation are equal

Difference Between Evaporation and Boiling Processes

- During evaporation cooling occurs as the average kinetic energy of the liquid decreases since molecules with higher kinetic energy leave the surface.
- Boiling occurs only at a specific temperature while evaporation can take place at any temperature.
- Boiling occurs below the surface while evaporation occurs only at surface.

Surface Tension

It is the force at right angles to the surface of a liquid along one cm or one metre length of the surface.

- Units: Newton metre^{-1} or [Nm^{-1}], dyne cm^{-1}.
- Due to surface tension the surface area of the liquid decreases upto minimum. example., Falling drops are spherical that is, minimum surface area for a given volume.
- Due to surface tension a liquid rises in capillary tube, water move upward in soil and walking of insects over water surface.
- Surface tension $\propto$ 1/Temperature.
- At critical temperature surface tension is zero.
- The effect of temperature is given by Eotvos equation.

$\gamma = K (T_C - T) (d/M)^{2/3}$

Here K = Constant

d = Density

M = Molar mass

Measurement of Surface Tension: To measure surface tension, Stalgmometer is used. It is based upon the fact that surface tension is directly proportional to the amount or weight of the spherical drop falling from the vertically kep capillary tube.

$\gamma \propto M$ so $\gamma_1/\gamma_2 = M_1/M_2$.

Surface Energy: It is work in ergs needed to increase the surface area by 1 square centimetre. Its units are erg/cm^2 or Joule/metre^2.

REMEMBER

- Soap, detergent, alcohol, cholesterol are some surface active substances or surfactants which decrease surface tension.
- Due to force of adhesion water drops stick to a glass surface.

Viscosity: It is the internal resistance of a liquid to flow which exists due to the relative motion between two layers. It decreases with increase of temperature. It is calculated as the force per unit area needed to maintain a velocity difference of unity between two parallel layers of liquid unit distance apart.

Viscosity Coefficient (η): It is the force of friction needed to maintain a velocity difference of 1 cm sec^{-1} between any two parallel layers of 1 cm^2 area and which are 1 cm apart.

$$\eta = \frac{f \,.\, x}{A \,.\, v} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm sec}^{-1}} = \text{dyne cm}^{-2}\ \text{sec}$$

= 1 poise

Here f = Force

a = Area

v = Velocity difference

x = Distance between two layers

1 Poise = 1 gm cm^{-1} sec^{-1}

Since dyne = gm × cm × sec^{-2}

1 Poise = 1/10 Newton metre^2 sec^{-1}

or Pas or Kg m^{-1} s^{-1}

Effect of Temperature on Viscosity: On increasing temperature, viscosity decreases as average thermal energy of molecules increases hence the effect of intermolecular attraction forces decreases.

It can be shown by Arrhenius equation as follows:

$\eta = Ae^{Ea/RT}$

Here T = Temperature

R = Universal gas constant

Ea = Activation energy

Measurement of Viscosity:

- To measure viscosity Ostwald viscometer is used which is based on Poiseville's equation.

$$\eta = \frac{\pi P r^4 t}{\delta V l}$$

Here 'V' volume of liquid needs time 't' to flow through a capillary tube of radius (r) and length 'l' under a pressure (P).

- When the same volume of two liquids say X and Y are flowing from the same height and through the same capillary then

$$\eta_X = \frac{\pi P_X r^4 t_X}{8 V l}$$

$$\eta_Y = \frac{\pi P_Y r^4 t_Y}{8 V l}$$

On dividing them

$$\frac{\eta_X}{\eta_Y} = \frac{P_X t_X}{P_Y t_Y}$$

As $P = \eta d g$

So

$$\frac{\eta_x}{\eta_y} = \frac{d_x t_x}{d_y t_y}$$

or $\eta_X = (d_X t_X / d_X t_Y)\, \eta_Y$

Here d_x = Density of liquid x

d_y = Density of liquid y

t_x = Time for flow of liquid x

t_y = Time for flow of liquid y.

Fluidity: It is the reciprocal of viscosity coefficient of a liquid denoted by ϕ.

$$\phi = \frac{1}{\eta}\,.$$

REMEMBER

- In case of super fluid liquids, the resistance to flow becomes almost zero. It is called super fluidity.
- He at 2.18 K becomes super fluid liquid.
- Viscosity α H-bonding

  α Molecular weight

  Example, Glycerol > Glycol > Ethanol > CH_3OH

Enhance Your Knowledge

Critical Phenomenon and Liquefication of Gases

Critical Temperature (Tc):

It is the temperature above which the gas can not be liquified with the help of high pressure also. It is denoted by T_c.

$$Tc = \frac{8a}{27Rb}$$

- Each gas has a definite critical temperature. E.g.2 T_c for CO_2, O_2 and H_2 are 31.1°C, 118.8°C and –240°C respectively.

Critical Volume (V_c): It is the volume occupied by one mole of the gas at critical temperature and critical pressure. It is denoted by V_c.

$$V_c = 3b$$

Critical Pressure: It is the minimum pressure required to liquefy any gas at critical temperature. It is denoted by P_c.

$$P_c = \frac{a}{27\ b^2}$$

Relation Between Tc, Vc and Pc

PcVc = 3/8 RTc

Liquefication of Gases: A gas can be liquefied by decrease in temperature or increase in pressure. When a gas is compressed at any temperature the intermolecular distance decreases as a result intermolecular forces become effective and decreases kinetic energy this cause liquefaction.

liquefication α 'a' (Intermolecular force)

Methods of Liquefication of Gases

(1) Linde's process, By adiabatic expansion of compressed gas that is, Joule – Thomson effect.

(2) Claude's process, By adiabatic expansion of compressed gas involving mechanical work.

(3) Through adiabatic demagnetization.

(4) Cooling by freezing mixtures. Example, NaCl and ice (251 K), $CaCl_2$ and ice (218 K)

Boyle's Temperature: It is the temperature at which real gases obey gas laws or The temperature above which the gases behave like an ideal gas. It is denoted by T_b.

$$T_b = \frac{a}{R_b}$$

Easily liquefiable gases have high value of T_b. example., T_b of O_2 is 40 K.

Inversion Temperature (Ti): It is the temperature at which a gas shows neither cooling nor heating effect in Joule-Thomson adiabatic expansion. ($\mu_{J.T} = 0$)

- Below inversion temperature cooling effect occurs. ($\mu_{J.T}$ = –ve)
- Above inversion temperature heating effect occurs ($\mu_{J.T}$ = +ve)

$$Ti = \frac{2a}{Rb}$$

- **Relative Humidity (R_H):** It represents the ratio of the mass of water vapours (m) actually present in a definite volume of air at room temperature to the maximum mass of water vapours (M) needed to saturated the same volume at the same temperature.

$$R_H = m/M$$

$$= \frac{\text{Vapour pressure of water or gas}}{\text{Saturated vapour pressure}}$$

(As vapour pressure α mass)

REMEMBER

As at dew point a gas becomes saturated so vapour pressure of H_2O at room temperature is equal to saturated vapour pressure of water at dew point.

$$R_H = \frac{\text{Saturated vapour pressure at dew point}}{\text{Saturated vapour pressure at room temperature}}$$

REMEMBER

- The order of kinetic energy is solid < liquid < gas.
- Kinetic energy at absolute zero temperature is zero.
- Boyle's Law according to kinetic theory:

  $PV = \frac{1}{2} MV^2$ r.m.s
- Charle's.Law according to kinetic theory:

  $V = (M/3P)\, V^2$ r.m.s
- **Gay Lussac Law**

  $P = (M/3V)\, V^2$ r.m.s
- **Loschmidt Number:** It is the number of molecules present in 1 cm^3 of a gas or vapour at S.T.P (value = 2.7678×10^{19} per c.c)
- At constant P, V/T = constant, hence plot of V versus T is linear passing through the origin
- Gas constant is work done per degree per moles.
- Saturated vapours do not obey gas laws except Dalton's law as their pressure is independent of volume.
- Saturated vapours do not obey gas laws except Dalton's law as their pressure is independent of volume. Aqueous tension depends only on temperature.
- With increase in temperature most probable velocity increases but the fraction possessing it decreases.
- Hydrogen and helium show heating effect on adiabatic expansion (Joule–Thomson effect) because their inversion temperatures are low.
- Cp – Cv = R for 1 mole of an ideal gas.
- A thermometer used only for the measurement of small differences in temperature like depression in freezing point etc. is Beckmann thermometer.
- **Escape Velocity (V_e):** It is the minimum velocity needed by an object to escape from the gravitational field of the body.

  $V_e = \sqrt{2gr}$

Solved Problems from the IITs

1. At 27°C, hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure as that of H_2 is leaked through the same hole for 20 minutes. After the effusion of the gases, the mixture exerts a pressure of 6 atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular weight of the unknown gas?

[IIT/JEE 1992]

Solution Let P_{H_2} and p be the partial pressures of hydrogen and unknown gas respectively and w be the number of moles of unknown gas.

$$P_{H_2} = \frac{0.7}{3} \times 0.0821 \times 300 \quad \ldots (i)$$

$$p \text{ (unknown)} = \frac{w}{3} \times 0.0821 \times 300 \quad \ldots . (ii)$$

By adding equation (i) and (ii), we get

$$P_{H_2} + p = 6 = \frac{1}{3} \times 0.0821 \times 300\,(0.7 + w)$$

On solving, we get

$w = 0.0308$ mole

According to law of diffusion,

$$\frac{0.7/20}{0.0308/20} = \sqrt{(M/2)}$$

$M = 1033$

2. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 N m^{-2}. Calculate the root mean square (r.m.s) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root mean square speed is 0.82, calculate the most probable speed for these molecules at this temperature.

[IIT 1993]

Solution Amount of gas $= \frac{2.0 \times 1021}{6.023 \times 1023}$ mole

As Pv = nRT

$T = \frac{PV}{nR}$

$T = \frac{10^{-3} \times 7.57 \times 10^{3}}{2.0 \times 10^{21} \times 8.314} = 274.2$ K

6.023×10^{-23}

RMS speed = $\sqrt{(3RT/M)}$

$= \frac{\sqrt{(3 \times 8.314 \times 274.2)}}{\sqrt{(28 \times 10^{-3})}}$

$= 494.22\ ms^{-1}$

Most probable speed = 0.8 × RMS

$= 0.8 \times 494.22\ ms^{-1}$

= 395.376 ms-1

3. A 4 : 1 molar mixture of He and CH^4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially?

[IIT 1994]

Rate of effusion = $K \cdot \frac{P}{\sqrt{M}}$.

Here P is partial pressure of the gas

M = Molar mass, M of He = 4,

M of CH^4 = 16

$\frac{\text{Rate of effusion of He}}{\text{Rate of effusion of } CH_4} = \frac{KPHe,\sqrt{MHe}}{KPCH_4,\sqrt{MCH_4}}$

$= \frac{PHe}{PCH_4} \times \sqrt{(MCH_4/MHe)}$

$= \frac{4}{1}\sqrt{(16/4)} = 8$

4. The composition of the equilibrium mixture ($Cl^2 \leftrightarrow 2Cl$), which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as Krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Atomic wt. of Kr = 84)

[IIT 1995]

Solution According to Graham's law of diffusion

$\frac{rmi_x}{r_K r} = \sqrt{(M_K r/Mix)}$

that is, $1.16 = \sqrt{(84/M)}$ (As P1 = P2)

On solving

M = 62.425

$Cl_2 \rightarrow 2Cl$

1	0	Initially
(1 – α)	2α	at equilibrium

$\frac{\text{Normal molecular weight}}{\text{Exp. Molecular weight}} = 1 + \alpha$

$\frac{71}{62.425} = 1 + \alpha$

So $\alpha = 0.1374 = 13.7\ \%$

5. One way of writing the equation of state for real gases is

PV = RT [1 + B/V + …..]

where B is a constant. Derive an approximate expression for B is terms of van der Waal's constants a and b.

[IIT 1997]

Solution $[P + \frac{a}{V^2}]\ [V - b] = RT$

$P = \frac{RT}{(v - b)} - \frac{a}{V^2}$.

If we multiply it by V then

$PV = \frac{RTV}{(V - b)} - \frac{a}{V}$.

$= RT\ [\frac{V}{V - b} - \frac{a}{VRT}]$

$= RT\ [(\frac{1 - b}{V})\text{-}1 - \frac{a}{VRT}]$

As

$[1 - \frac{b}{V}]^{-1} = 1 + \frac{b}{V} + (\frac{b}{V})^2 + \ldots.$

$PV = RT\ [1 + \frac{b}{V} + \ldots\ldots - \frac{a}{VRT}]$

$PV = RT\ [1 + (b - \frac{a}{RT}).\frac{1}{V} + \ldots.]$

$B = b - \frac{a}{RT}$.

6. 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 atm

spheres at a temperature of 300 K. The value of 'b' is 0.05 lit.mol-1.

[IIT 1998]

Solution For n moles of a gas

$$\left(P + n^2 \frac{a}{V^2}\right).(V - nb) = nRT$$

$$[1 + (2^2a/4^2)]\,[4 - 2 \times 0.05] = 2 \times 0.082 \times 300$$

$$a = 6.46 \text{ atm litre}^2 \text{ mol}^{-2}$$

7. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300K. Determine the molecular weight of the gas.

[IIT 1998]

Solution Van der Waal's equation for n mole of gas is given as:

$$\left[P + \frac{n^2 a}{V^2}\right][V - nb] = nRT$$

Here V = 4 litre, P = 11.0 atm, T = 300 K,

b = 0.05 litre mol-1, n = 2

$$\left[11 + \frac{(2)^2 a}{(4)^2}\right][4 - 2 \times 0.05] = 2 \text{ x } 0.082 \text{ x } 300$$

$$a = 6.46 \text{ atm litre}^2 \text{ mol}^{-2}$$

8. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

[IIT 1999]

$$\frac{r1}{r2} = \sqrt{(M2/M1)} \times \frac{P1}{P2}$$

$$\frac{n1}{t1} \times \frac{t2}{n2} = \sqrt{(M2/M1)} \times \frac{P1}{P2}$$

$$\frac{1}{38} \times \frac{57}{1} = \sqrt{(Mg/28)} \times \frac{0.8}{1.6}$$

$$Mg = (57/38 \times 1.6/0.8)2 \times 28$$

On solving

$$Mg = 252$$

Thus, compound is XeF6 because it can have only one xenon atom.

9. One mole of nitrogen gas at 0.8 atm takes 38 s to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 s to diffuse through the same hole. Calculate the molecular formula of the compound.

[IIT 1999]

Solution Apply Grahams law of diffusion

$$\frac{r_1}{r_2} = \sqrt{(M_2/M_1)} \times \frac{P_1}{P_2}$$

As $r = n/t$

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{(M_2/M_1)} \times \frac{P_1}{P_2}$$

$$\frac{1}{38} \times \frac{57}{1} = \sqrt{(Mg/28)} \times \frac{0.8}{1.6}$$

On squaring both sides

$$Mg = \left[\frac{57}{38} \times \frac{1.6}{0.8}\right]^2 \times 28$$

$$Mg = 252$$

So compound may be XeF_6 because it can have only one xenon atom (since for two xenon atoms, 2 × atomic weight of Xe = 2 × 131 = 262) i.e., greater than 252

$$XeF_6 = 131 + 6 \times 19$$
$$= 131 + 114$$
$$= 245$$

10. The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10 %. Calculate the temperature t and volume V (mol. weight of the gas = 120).

[IIT 1999]

At constant volume, pressure law is used

$$\frac{P1}{P2} = \frac{T1}{T2}$$

$$\frac{1}{1.1} = \frac{t + 273}{t + 283}$$

$$t = -173°C = 100 \text{ K}$$

Now according to gas equation

$$PV = nRT$$

$$V = \frac{n}{P} RT$$

$= \frac{12 \times 0.082 \times 100}{120 \times 1}$

= 0.82 litre

11. (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.

[IIT 2000]

Solution According to van der Waal's equation for n mole

$$[P + \frac{n^2 a}{V^2}] [V - nb] = nRT$$

$$[P + \frac{25 \times 3.592}{1}] [1 - 5 \times 0.0427]$$

$$= 5 \times 0.0821 \times 320$$

On solving

P = 77.218 atm

Also it gas behaves ideally, then PV = nRT

$$P \times 1 = 5 \times 0.0821 \times 320$$

$$= 131.36 \text{ atm}$$

For 1 mole

$$[P + \frac{a}{V^2}] [V - b] = RT$$

If b is negligible we can use

$$P = \frac{RT}{V} - \frac{a}{V^2}.$$

that is, $PV^2 - RTV + a = 0$

or $$V = \frac{+RT \pm \sqrt{[(-RT)^2 - 4Pa]}}{2P}$$

At given P and T, V has only one value and thus discriminant = 0

So $(RT)^2 - 4Pa = 0$

or $$P = \frac{R^2 T^2}{4a}$$

$$= \frac{(0.082)^2 \times (273)^2}{4 \times 3.592}$$

= 34.88 atm

12. The compression factor (compressibility factor) for 1 mole of a van der Waal's gas at 0°C and 100 atmospheric pressure is found to be 0.5. Assuming that the volume of gas molecule is negligible calculate the van der Waal's constant 'a'.

[IIT 2001]

Solution As $Z = \frac{PV}{RT} = 0.5$

So $$\frac{100 \times V}{0.082 \times 273} = 0.5$$

On solving

V = 0.112 litre

Now applying van der Waal's equation

$$[P + \frac{a}{V^2}] [V] = bT$$

As b is negligible)

$$[P + \frac{a}{V^2}] = \frac{RT}{V}$$

$$[100 + \frac{a}{(0.112)^2}] = \frac{0.082 \text{ x } 273}{0.112}$$

= 199.88

$$\frac{a}{(0.112)^2} = 99.88$$

a = 1.253 litre^2 mol^2 atm.

13. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same conditions?

(a) Determine (i) molecular weight, (ii) molar volume (iii) compression factor (Z) of the vapours and (iv) which forces among gas molecules are dominating, the attractive or the repulsive?

(b) If the vapours behave ideally at 1000 K, determine the average translational kinetic energy of a molecule.

[IIT 2002]

Solution According to Graham's law of diffusion

(a)

(i) $r_v/r_{O_2} = \sqrt{(M_{O_2}/M_v)}$

$1.33 = \sqrt{(32/Mv)}$

On solving

Mv = 18.1

(ii) Molar volume at 500 K

$$= \frac{\text{Molecular weight}}{\text{Density of one mole}}$$

$$= \frac{18.1 \times 10^{-3}}{0.36}$$

$$= 50.25 \times 10^{-3}\ m^{-3}$$

(iii) Compression factor (Z) $= \frac{PV}{RT}$

$$= \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500}$$

$$= 1.225$$

(iv) Repulsive forces operates among molecules as $Z > 1$.

(b) Average K.E. $= \frac{3}{2}\ \frac{RT}{N} = \frac{3}{2}\ KT$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000$$

$$= 2.07 \times 10^{-20}\ J$$

14. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature.

[IIT 2003]

Solution Average velocity are given as

$$V_{AV} = \sqrt{(8RT/\pi M)} \quad \ldots\ldots \text{(i)}$$

$$V_{rms} = \sqrt{(3RT/M)} \quad \ldots\ldots \text{(ii)}$$

Now divide equation (ii) by (i)

$$V_{rms}/V_{AV} = \sqrt{(3\pi/8)}$$

As $V_{AV} = 400$ m/sec.

$$V_{rms} = \sqrt{(3 \times 31.4/8)} \times V_{AV}$$

$$= \sqrt{(3 \times 3.14/8)} \times 400$$

$$= 434 \text{ m/sec}$$

15. C_v value of He is always 3R/2 but C_v value of H_2 is 3R/2 at low temperature and 5R/2 at moderate temperature and more than 5R/2 at higher temperature. Explain.

[IIT 2003]

Solution As we know that heat absorbed is used in increasing kinetic energy, rotational energy and vibrational energy of molecules.

(i) As helium is monoatomic so heat given is used to increase its kinetic energy (= 3RT/2) only and hence

$$C_v = \frac{3R}{2}.$$

(ii) As H_2 is diatomic and at low temperature heat given is used in increasing its kinetic energy

that is, $C_V = \frac{3R}{2}$.

(iii) At moderate temperature, heat given is used to increase both kinetic and rotational energies

$$(= \frac{3RT}{2} + RT) \text{ and } C_v = \frac{5R}{2}.$$

(iv) At high temperature, heat given is used to increase all the kinetic, rotational and vibrational energies and hence

$$C_V > \frac{5R}{2}.$$

16. For a real gas obeying van der Waal's equation, a graph is plotted between PV_m (y-axis) and P(x-axis) where V_m is molar volume. Find y-intercept of the graph.

[IIT Mains 2004]

Solution At very low pressure the Van der Waal's equation reduces to ideal gas equation.

that is, $PV = nRT$

$PV_m = RT$ (for 1 mole of the gas)

Hence y-intercept of the graph = RT.

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. The correct equation for Boyle's law is

a. $\frac{d^2P}{P} = -\frac{dV}{dT}$ **b.** $\frac{d^2P}{P} = +\frac{d^2V}{dT}$

c. $\frac{dP}{P} = -\frac{dV}{V}$ **d.** $\frac{dP}{P} = +\frac{dV}{V}$

2. Under which of the following conditions, Van der Waal's gas approaches ideal behaviour?

a. Extremely low pressure
b. High pressure
c. Low product of PV
d. Low temperature

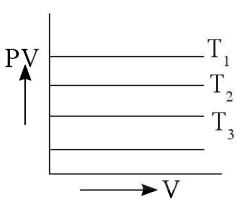
3. Slope of the plot between PV and P at constant temperature is

a. ½ **b.** 1
c. Zero **d.** $1/\sqrt{2}$

4. Molar volume of CO_2 is maximum at

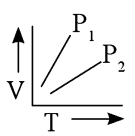
a. 0°C and 2.0 atm
b. N.T.P.
c. 273°C and 2 atm
d. 127°C and 1 atm

5. Consider the graph given below and select the correct choice:



a. $T_1 > T_2 > T_3$ **b.** $T_1 < T_2 < T_3$
c. $T_1 = T_2 = T_3$ **d.** $T_1 = T_2 > T_3$

6. V vs T curves at constant pressure P_1 and P_2 for an ideal gas are shown below.



Which of these is correct?

a. $P_1 > P_2$ **b.** $P_1 < P_2$
c. $P_1 = P_2$ **d.** All of above

7. In an open end manometer, one end of a U-tube filled with mercury is attached to a gas-filled container and the other end is open to the atmosphere. If the gas pressure in the container is less than atmospheric pressure

a. The Hg level will be higher in the arm open to the atmosphere
b. Hg will be forced out of the open end of the U-tube.
c. The difference between the Hg levels in the two arms will be greater than 76 cm.
d. The Hg level will be higher in the arm connected to the container.

8. A gas behaves like an ideal gas under conditions of

a. high pressure and low temperature
b. high temperature and high pressure
c. low pressure and high temperature
d. low pressure and low temperature.

9. Suppose one needs to closely monitor small changes in pressure inside a container using an open end manometer. For the best accuracy, the substance in the manometer should

a. be mercury
b. have a low density
c. have a high density
d. be a solid

10. When the temperature is raised, the viscosity of the liquid decreases. This is because

a. Attraction between the molecules increases
b. Covalent and hydrogen bond forces decrease
c. Volume of the solution decreases
d. Increase in temperature increases the average kinetic energy of the molecules which overcomes the attractive force between them

11. At constant volume and temperature conditions the rates of diffusion D_A and D_B of gases A and B having densities ρ_A and ρ_B are related by the expression

a. $D_A = [D_B \rho_A/\rho_B]^{1/2}$

b. $D_A = [D_B \rho_B/\rho_A]^{1/2}$

c. $D_A = D_B [\rho_A/\rho_B]^{1/2}$

d. $D_A = D_B [\rho_B/\rho_A]^{1/2}$

12. Which of the following gases has the lowest average speed at 25°C?

a. NH_3 b. O_2
c. CH_4 d. H_2S

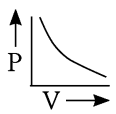
13. If the four tubes of a car are filled to the same pressure with N_2, O_2, H_2 and Ne separately, then which one will be filled first?

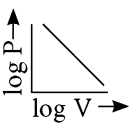
a. O_2 b. H_2
c. Ne d. N_2

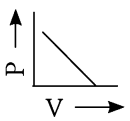
14. At constant volume for a fixed number of a moles of a gas, the pressure of the gas increases with the rise in temperature due to

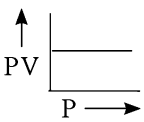
a. increase in average molecular speed
b. increase in rate of collisions
c. increase in molecular attraction
d. increase in mean free path.

15. Which curve does not represent Boyle's law?

a. 

b. 

c. 

d. 

16. An ideal gas expands according to PV = constant. On expansion, the temperature of gas

a. will rise
b. will drop
c. will remain constant
d. cannot be determined because the external pressure is not known

17. For which of the following parameters, the structural isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same vaules? (assume ideal behaviour)

a. Gaseous densities at the same temperature and pressure
b. Heat of vapourization
c. Boiling points
d. Vapour pressure at the same temperature

18. Which of the following has maximum root mean square velocity at the same temperature?

a. H_2 b. O_2
c. SO_2 d. CO_2

19. The density of neon will be highest at

a. STP b. 0°C, 2 atm
c. 273°C, 1 atm d. 273°C, 2atm

20. When the temperature of an ideal gas in increased from 27°C to 927°C, the kinetic energy will be

a. same b. eight times
c. four times d. twice

21. The values of van der Waal's constant 'α' for the gases O_2, N_2, NH_3 and CH_4 are1.360, 1.390, 4.170 and 2.253 L atm. mol^{-2} respectively. The gas which can most easily be liquefied is

a. O_2 b. N_2
c. NH_3 d. CH_4

22. Some assumptions from the kinetic molecular theory are listed below. Which one is most frequently cited to explain Charles's law?

a. Collisions of gas particles are elastic and total kinetic energy of the gas is constant
b. A gas consists of tiny particles moving in random straight line motion.
c. The volume of the particles is negligible compared to the volume of the gas.
d. The average kinetic energy of gas articles is proportional to the Kelvin temperature.

23. Universal gas constant (R) is divided by Avogadro's number (N_0) then the value is equivalent to

a. van der Waal's constant
b. Rydberg's constant
c. Planck's constant
d. Boltzmann's constant

24. The term that accounts for intermolecular force in van der Waal's equation for non ideal gas is

a. RT b. V – b
c. $(P + \alpha/V^2)$ d. $(RT)^{-1}$

25. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecules travels

a. in a circular path
b. in a wavy path

c. in a straight line path
d. with an accelerated velocity

26. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is

a. same as that of a hydrogen molecule
b. half that of a hydrogen molecule
c. two times that of a hydrogen molecule
d. four times that of a hydrogen molecule

27. a/V^2 given in van der Waal's equation is for

a. internal pressure
b. intermolecular attraction
c. Both (a) and (b)
d. temperature correction

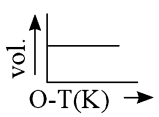
28. Kinetic theory of gases presumes that collision between the molecules to be perfectly elastic because

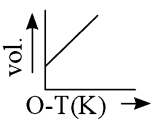
a. the molecules are rigid
b. the molecules are tiny
c. the temperature remains constant irrespective of collision
d. collision will not split the molecules

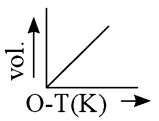
29. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called

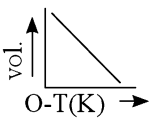
a. Critical temperature
b. Boyle temperature
c. Inversion temperature
d. reduced temperature

30. The correct representation of Charle's law is given in

a. 

b. 

c. 

d. 

31. 0.1 mole of gas absorbs 41.75 J of heat, the rise in temperature occurs 20°C, the gas must be

a. triatomic
b. diatomic
c. monoatomic
d. Both b. and c.

32. Which pair of the gases diffuses with the same rate at same temperature and pressure?

a. CO and NO
b. NO_2 and CO_2
c. NH_3 and PH_3
d. NO and C_2H_6

33. A real gas at a very high pressure occupies

a. Less volume than that of an ideal gas under identical conditions
b. More volume than that of an ideal gas under identical conditions
c. Same volume than that of an ideal gas under identical conditions
d. Cannot be predicted

34. Which one of the following, is van der Waal's equation, describing the behaviour of one mole of a real gas over wide ranges of temperature and pressure

a. $(P + a/V^2)(V + b) = RT$
b. $(P + a/V^2)(V - b) = RT$
c. $(P - a/V^2)(V - b) = RT$
d. $(P + a/V^2)(V - b) = R/T$

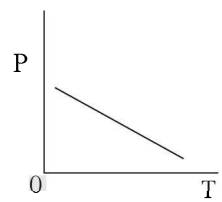
35. You are given two flasks of equal volume. One contains H_2 at 0°C and 1 atm while the other contains CO_2 at 0°C and 2 atm. which of the following quantities will be the same for both flasks?

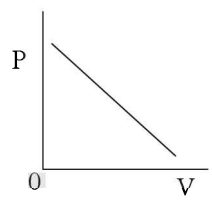
a. Density
b. Number of molecules present
c. Average molecular speed
d. Average molecular kinetic energy

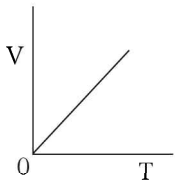
36. Temperature according to kinetic theory, is a measure of

a. Average translational kinetic energy of gas molecules
b. Intermolecular attraction
c. Intermolecular distances
d. Volume of gas

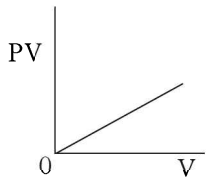
37. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas? (T is measured in K).

a. Constant V 

b. Constant T 



c. Constant P

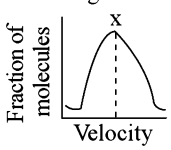


d. Constant T

38. Which of the following gases has the highest average speed at 400 K?

a. SF_6 **b.** UF_6
c. CO_2 **d.** N_2O_4

39. Distribution of fraction of molecules with velocity is represented in the figure



Velocity corresponding to poing X is

a. $\sqrt{2RT/M}$ **b.** $\sqrt{3RT/M}$
c. $\sqrt{8RT/\pi M}$ **d.** none

40. Which of the following represents total kinetic energy of one mole of gas?

a. 2/3 RT **b.** 3/2 RT
c. 1/2 RT **d.** $(C_p - C_v)$ RT

41. An unknown gas effuses 2.3 times faster than N_2O_4 at the same temperature. What is the identity of the unknown gas?

a. O_3 **b.** N_2O
c. NH_3 **d.** CN_2

42. If V is the volume of one molecule of gas under given conditions, the van der Waal's constant 'b' is

a. 4V **b.** $4 V N_0$
c. $\frac{N_0}{4V}$ **d.** $\frac{4V}{N_0}$

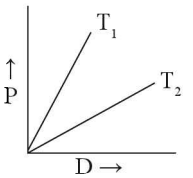
43. A gas deviates from ideal behaviour at a high pressure because its molecules

a. Show the Tyndall effect
b. Have kinetic energy
c. Attract one another
d. Are bound by covalent bonds

44. In van der Waal's equation of state of the gas law, the constant 'b' is a measure of

a. intermolecular attraction
b. intermolecular repulsions
c. intermolecular collision per unit volume
d. volume occupied by the molecules

45. Pressure vs density curve for an ideal gas at two different temperatures T_1 and T_2 is shown below. Which is correct relation here?



Which of these is correct?

a. $T_1 > T_2$ **b.** $T_1 < T_2$
c. $T_1 = T_2$ **d.** can not be said

46. Which statement about real gases is true?

a. Forces of attraction and repulsion exist between gas particles at close range.
b. The behaviour of real gases can be exactly predicted using the ideal gas law.
c. The volume of the gas particles is zero.
d. The mass of the gas particles is zero.

47. If α is the volume coefficient of expansion and β, the compressibility coefficient of an ideal gas, α/β is

a. T/P **b.** VR
c. RT **d.** P/T

48. The ratio a/b (a and b being the van der Waal's constant of real gases) has the dimensions of

a. L mol^{-1} **b.** atm mol^{-1}
c. atm L mol^{-2} **d.** atm L mol^{-1}

49. A perfect gas of a given mass is heated first in a small vessel and then in a large vessel, such that their volume remains unchanged. The P – T curves are:

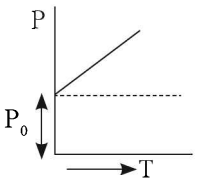
a. Linear with same slope
b. Linear with different slope
c. Parabolic with same curvature
d. Parabolic with different curvature

50. It is easier to liquefy oxygen than hydrogen because

a. Oxygen has a higher critical temperature and a higher inversion temperature than hydrogen
b. The critical temperature and inversion temperature of oxygen is very low
c. Oxygen has a higher critical temperature and lower inversion temperature than hydrogen
d. Oxygen has a lower critical temperature and higher inversion temperature than hydrogen

Brainteaser Objective Type Questions (Single choice only)

51. Consider the figure given below and find the value of slope.



a. Slope = $(\partial T/\partial P)_V$

b. Slope = $(\partial P/\partial T)_V$

c. Slope = $(\partial V/\partial T)_P$

d. Slope = $(\partial P/\partial T)_P$

52. X ml of H_2 has effuse through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is

a. 10 seconds : He

b. 20 seconds : O_2

c. 25 seconds : CO

d. 55 seconds : CO_2

53. 0.5 mole of each of H_2, SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be

a. $\rho(CH_4) > \rho(SO_2) > \rho(H_2)$

b. $\rho(H_2) > \rho(CH_4) > \rho(SO_2)$

c. $\rho(SO_2) > \rho(CH_4) > \rho(H_2)$

d. $\rho(H_2) > \rho(SO_2) > \rho(CH_4)$

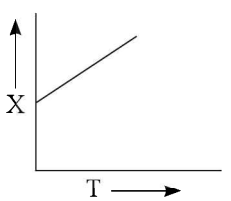
54. Van der Waal's equation for a real gas is

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

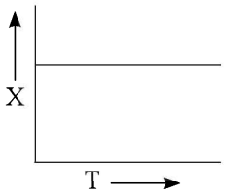
Plot of quantity $X = \frac{ab}{a+b}$

with temperature is

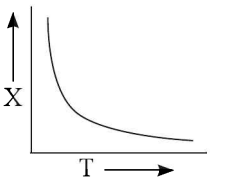
a.



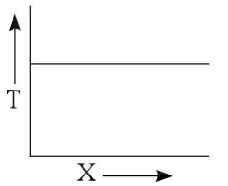
b.



c.



d.



55. Which of the following statement (s) is (are) correct

1. A plot of log Kp versus 1/T is linear
2. A plot of log (X) versus time is linear for a first order reaction X → P
3. A plot of log P versus 1/T is linear at constant volume
4. A plot of P versus 1/V is linear at constant temperature.

a. 1, 2 **b.** 2, 4

c. 2, 3 **d.** 1, 4

56. The ratio between the root mean square velocity of H_2 a 50 K and that of O_2 at 800 K is.

a. 4 **b.** 2

c. 1 **d.** ¼

57. Consider the following statement(s) for viscosity (η) variation with T and P for an ideal gas and select the incorrect statement

1. η of a gas increases with increase in both T and P
2. η of a gas in independent of temperature and pressure
3. η of a gas decreases with increase in T and increase with increase in P
4. η of a gas increases with increase in temperature (T), but it is independent of pressure.

a. 1 and 3 **b.** 2 and 3

c. 1, 2 and 3 **d.** 2, 3 and 4

58. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction to total pressure exerted by hydrogen is

a. 1:2 **b.** 1:1

c. 1:16 **d.** 15:16

59. A closed vessel contains equal number of molecules of O_2 and H_2. Consider the following statements:

1. The average speed of hydrogen molecules will be greater.
2. Weight of hydrogen is $1/8^{th}$ of the weight of oxygen.
3. Hydrogen molecules strike the walls more often.
4. The two gases have different average energies.

The statements are wrong in

a. 2 and 4 **b.** 2 and 3

c. 1 and 4 **d.** 1 and 3

60. The rate of diffusion of methane at a given temperature is twice that of a gas X. The molecular weight of X is

a. 64.0 **b.** 32.0

c. 4.0 **d.** 8.0.

61. At STP which of the following real gases is likely to have the smallest molar volume (in m^3)?

a. oxygen **b.** nitrogen

c. hydrogen **d.** ammonia

62. The average velocity of an ideal gas molecules at 27°C is 0.3 m/sec. The average velocity at 927°C will be

a. 0.6 m/sec **b.** 0.3 m/sec

c. 0.9 m/sec **d.** 3.0 m/sec

63. The ratio between the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is

a. 1/4 **b.** 1

c. 2 **d.** 4

64. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be

a. at the centre of the tube

b. near the hydrogen chloride bottle

c. near the ammonia bottle

d. throughout the length of the tube.

65. Three identical flasks contain three different gases at standard temperature and pressure. Flask (P) contains CH_4, flask (Q) contains CO_2, flask (R) contains N_2. Which flask contains the largest number of molecules?

a. Flask (Q)

b. Flask (R)

c. Flask (P)

d. All three flasks have the same number of molecules

66. Equal masses of methane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is

a. 1/2 **b.** 8/9

c. 1/9 **d.** 16/17

67. A flask filled with CCl_4 vapour was weighed at a temperature and pressure. The flask was then filled with oxygen at the same temperature and pressure. The mass of CCl_4 vapours would be about

a. Five times as heavy as oxygen

b. Twice as heavy as oxygen

c. The same as that of the oxygen

d. One-fifth as heavy as oxygen

68. The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is

a. 1 : 1.086 **b.** 2 : 1.086

c. 1.086 : 1 **d.** 1.086 : 2

69. Equal weights of methane and oxygen are mixed in an empty container at 25°C. the fraction of the total pressure exerted by oxygen is

a. 1/2 **b.** 2/3

c. $1/3 \times 273/298$ **d.** 1/3

70. A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20°C are 400 mm Hg for pentane and 120 mm Hg for hexane. The mole fraction of pentane in the vapour phase would be

a. 0.200 **b.** 0.549

c. 0.786 **d.** 0.478

71. A general form of equation of state for gases is $PV = RT[A + B/V + C/V^2 + \ldots.]$, where V is the molar volume of the gas and A, B, C .... are constants for the gas. The values of A and B, if the gas obeys van der Waal's equation, are respectively

a. $1, \frac{a}{27\,b}$ **b.** $1, b - \frac{a}{RT}$

c. $\frac{a}{RT}, b$ **d.** $\frac{2a}{RT}, b$

72. Equation for Boyle's law is

a. $\frac{d^2P}{P} = -\frac{dV}{dT}$ **b.** $\frac{d^2P}{P} = \frac{+d^2V}{dT}$

c. $\frac{dP}{P} = -\frac{dV}{V}$ **d.** $\frac{dP}{P} = \frac{+dV}{V}$

73. If v_{rms} is 30 $R^{1/2}$ at 27°C, then the molar mass of the gas in kilogram is

a. 0.001 **b.** 0.1

c. 1.0 **d.** 2

74. The density of a gas is 1.964 g dm^{-3} at 273 K and 76 cm Hg. The gas is

a. CH_4 **b.** C_2H_6

c. CO_2 **d.** Xe

75. The rate of effusion of two gases 'a' and 'b' under identical conditions of temperature and pressure are in the ratio of 2 : 1. What is the ratio of rms velocity of their molecules if T_a and T_b are in the ratio of 2 : 1?

a. $\sqrt{2}$: 1 **b.** 2 : 1

c. 1 : $\sqrt{2}$ **d.** $2\sqrt{2}$: 1

76. Two gas bulbs A and B are connected by a tube having a stopcock. Bulb A has a volume of 100 ml and contains hydrogen. After opening the gas from A to the evacuated bulb B the pressure falls down by 40 %. The volume (ml) of B must be

a. 75 **b.** 150

c. 125 **d.** 200

77. A gas has double the average velocity of SO_2 gas at any temperature. The gas may be

a. CO_2 **b.** C_2H_4

c. CH_4 **d.** O_2

78. If increases in temperature and volume of an ideal gas is two times, then the initial pressure P changes to

a. 4P **b.** 2P

c. P **d.** 3P

79. Which of the following statement(s) regarding critical constants of van der Waal's gases is/are incorrect?

I. Critical temperature of a gas is

II. The larger the T_C/P_C value of a gas, the larger would be the excluded volume.

III. At the critical point, (dp/dv) = 0

a. I and II **b.** II and III

c. I and III **d.** I only

80. 6.4 g SO_2 at 0°C and 0.99 atm pressure occupies a volume of 2.241 L. Predict which of the following is correct?

a. the gas is ideal

b. the gas is real with intermolecular attraction

c. the gas is real without intermolecular repulsion

d. the gas is real with intermolecular repulsion greater than intermolecular attraction.

81. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct?

a. $(T_f)irrev > (T_F)rev$

b. $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

c. $(T_f)irrev = (T_F)rev$

d. $T_f = T_i$ for both reversible and irreversible processes

82. A gaseous mixture of NH_3 gas and H_2S gas contains 20 mol% of NH_3. The vapour density of the mixture of

a. 11.32 **b.** 25.2

c. 15.3 **d.** 18.6

83. Dominance of strong repulsive forces among the molecules of the gas (Z = compressibility factor)

a. depends on Z and indicated by Z = 1

b. depends on Z and indicated by Z > 1

c. depends on Z and indicated by Z > 1

d. is independent of Z.

84. X ml of H_2 effuse out through a hole in a container in 5 seconds. The time taken for the effusion of the same volume for the gas specified below under identical conditions is

a. 25 sec; CO **b.** 55 sec; CO_2

c. 10 sec; H_2 **d.** 20 sec; O_2

85. A monoatomic gas 'X' and a diatomic gas 'Y', both initially at the same temperature and pressure are compressed adiabatically from a volume V to V/2. The gas which has higher temperature is

a. Y

b. X

c. Both have same temperature

d. Can not be said

86. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is

a. 1/3 x 273/298 **b.** 1/3
c. 1/2 **d.** 2/3

87. A 4 : 1 mixture of helium and methane is contained in a vessel at 10 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. The composition of mixture effusing out initially is

a. 1 : 1 **b.** 2 : 1
c. 4 : 1 **d.** 8 : 1

88. A large cylinder of helium filled at 2000 mm of Hg had a small orifice through which helium escaped into evacuated space at the rate of 6.4 moles/hour. How long would it take for 10 mole of CO to leak through a similar orifice if the CO were confined at the same pressure?

a. 6.5 hour **b.** 8.4 hour
c. 4.2 hour **d.** 12.4 hour

89. If the ratio of masses of SO_3 and O_2 gases confined in a vessel is 1 : 1, then the ratio of their partial pressures would be

a. 1 : 1 **b.** 1 : 2
c. 2 : 1 **d.** 2 : 5

90. What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely one litre of propane gas (C_3H_8) measured under the same conditions?

a. 5 L **b.** 10 L
c. 7 L **d.** 6 L

91. If the critical temperature of the gas be

$T_C = \frac{8a}{27\,Rb}$.

and T_B is the Boyle's temperature, then which of the following is the correct relation between T_C and T_B ?

a. $T_C = \frac{4}{27}\,T_B$ **b.** $T_C = \frac{27}{6}\,T_B$

c. $T_C = \frac{8}{27}\,T_B$ **d.** $T_C = \frac{27}{8}\,T_B$

92. If a gas expands at constant temperature, it indicates that:

a. Kinetic energy of molecules remains the same
b. Number of the molecules of gas increases
c. Kinetic energy of molecules decreases
d. Pressure of the gas increases

93. In order to increase the volume of a gas by 10% , the pressure of the gas should be

a. Decreased by 10%
b. Decreased by 1%
c. Increased by 10%
d. Increased by 11%

94. Critical temperature and critical pressure value of four gases are given

Gas	Critical temp (K)	Critical press. (atm)
A	5.1	2.2
B	33	13
C	126	34
D	135	40

Which of the following gas/gases cannot be liquefied at a temperature 100 K and pressure 50 atm?

a. A and B **b.** C and D
c. A and D **d.** A, B and D

95. Which of the following is the correct increasing order of compressibility of the gases CO_2, CO, O_2, NH_3?

a. $O_2 < NH_3 < CO < CO_2$
b. $NH_3 < O_2 < CO < CO_2$
c. $CO_2 < CO < NH_3 < O_2$
d. $NH_3 < O_2 < CO_2 < CO$

96. Let 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 (2t + 273)°C then the new r.m.s. velocity is

a. $2\sqrt{3}\,V_0$ **b.** $\sqrt{6}\,V_0$
c. $\sqrt{(2/3)}\,V_0$ **d.** $\sqrt{[3(2 + 273/t)]}\,V_0$

Multiple Correct Answer Type Questions

97. The factor which measure the deviation from ideal behaviour of a gas are

a. collision frequency
b. collision diameter
c. compressibility factor
d. Van der Waal's constant 'a'

98. The correct statement(s) amongst the following is/are

a. A gas above its critical temperature can be liquefied by applying the minimum pressure
b. Deviation of real gases from ideal behaviour becomes more pronounced as pressure is increased and temperature is decreased.

c. At 0°C, H_2 and He show positive deviation throughout with increasing pressure indicating thereby that the Boyle's temperatures for these two gas are below 0°C

d. N_2 (g) shows ideal behaviour for some range of pressure (0 – 100atm) at 51.1°C indicating that 51.1°C is the Boyle's temperature for N_2 (g).

99. Which is/are not correct according to the kinetic theory of gases?

a. the pressure exerted by a gas is proportional to mean square velocity of the molecules

b. the pressure exerted by the gas is proportional to the root mean square velocity of the molecules

c. the root mean square velocity is inversely proportional to the temperature

d. the mean translational K.E. of the molecule is directly proportional to the absolute temperature.

100. Which of the following statement(s) is/are true about the effect of an increase in temperature on the distribution molecular speeds in a gas?

a. the most probable speed increases

b. the fraction of the molecules with the most probable speed increases

c. the distribution becomes broader

d. the area under the distribution curve remains the same as the under the lower temperature

101. If a gas expands at constant temperature

a. the pressure decreases

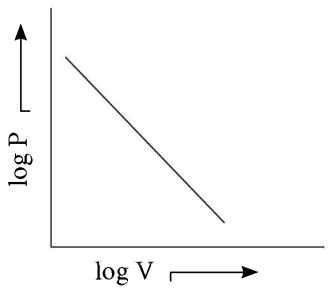
b. the kinetic energy of the molecules remains the same

c. the kinetic energy of the molecules decreases

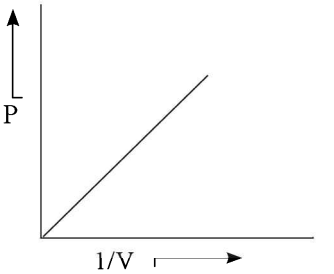
d. the number of molecules of the gas increase.

102. Which of the following graphs represents Boyle's law?

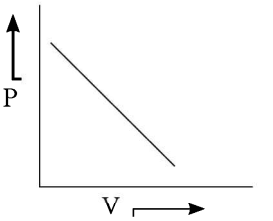
a.



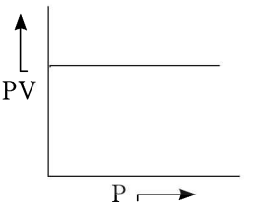
b.



c.



d.



103. Which of the following gases fairly deviates from ideal behaviour?

a. H_2 **b.** NH_3

c. He **d.** SO_2

104. Which of the following statement is/are correct on the basis of Charle's law here?

a. The pressure of an ideal gas can be zero.

b. The volume of an ideal gas can never be zero.

c. It is not possible to achieve absolute zero temperature.

d. At zero pressure, all molecular motion ceases in a gas, and it does not exert any pressure on the walls of the container.

105. Which of the following is/are the characteristics of a real gas?

a. It obeys the gas law at low temperature and high pressure

b. The gas molecules attract each other

c. It shows deviation from the ideal gas law

d. The mass of gas molecule is negligible

106. Which of the following statement is/are correct here?

a. Gases cannot be directly condensed into solids without passing through liquid state

b. Gases and liquids have viscosity as common property

c. Gases and liquids have pressure as common property

d. Particles in all the three states have random translational motion.

107. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to

a. Increased rate of collisions amongst molecules

b. Decrease in mean free path

c. Increase in average molecular speed

d. Increase in molecular attraction

108. Which of the following masses of gas would occupy about 3 dm^3 at 25°C and one atmosphere?

a. 2.25 g of Neon

b. 8.0 g of SO_2

c. 5.5 g of CO_2 10

d. 4.0 g of O_2

109. Which of the following equation(s) is/are incorrect on the basis of ideal gas equation?

a. $PV = \frac{d}{m}RT$ **b.** $PV = dRT$

c. $PV = \frac{N}{N_0}RT$ **d.** $PV = Nk_B T$

(Here N = number of molecules, N_0 = Avogadro's number, k_B = Boltzmann constant)

110. A two litre flask containing 4 g of oxygen is heated from 27°C to 327°C. Which of the following statements are correct?

a. The number of mole of the gas increases

b. The energy of the gaseous molecules increases

c. The pressure of the gas increases

d. The rate of collision increases

111. Which of the following is correct for critical temperature?

a. At this temperature, the surface tension of the system is very high.

b. At this temperature, the gas and the liquid phases have different critical densities.

c. It is the highest temperature at which liquid and vapour can exist together.

d. Beyond this temperature, there is no distinction between the two phases and a gas cannot be liquefied by compression.

112. Which of the following statements is/are correct regarding marsh gas indicator

a. It can be used at marshy places only

b. It measures the rate of radioactive disintegration of ^{14}C in methane

c. It is used to detect the presence of excess of methane in coal mines

d. Its working is based upon Graham's law of diffusion

113. Four gas balloons P, R, Q and S of equal volumes containing, H_2, N_2O, CO, CO_2 respectively were pricked with needle and immersed in a tank concentration CO_2. Which of them will shrink after some time?

a. P **b.** Q

c. R **d.** S

114. At low pressures, the van der Waal's gas equation for 1 mole of a gas may be written as

a. $PV = RT - \frac{a.}{V}$

b. $PV = RT$

c. $PV = RT + Pb$

d. $P + \frac{a}{V^2} = \frac{RT}{V}$

115. A gas can be easily liquefied:

a. Under reversible adiabatic expansion

b. At low pressure and above critical temperature

c. When its inversion temperature equals the Boyle's temperature

d. Under pressure when it is cooled below the critical temperature

116. Which statement is/are correct regarding van der Waal's constant 'a' and 'b'?

a. 'b' is excluded or co-volume of the gas

b. 'a' is the measure of force of attraction in between the particles

c. Lower is the value of 'b', easier is the liquefaction of the gas

d. Higher is the value of 'a', easier is the liquefaction of the gas

117. If the volume of two gases X and Y are the same under identical conditions of temperature and pressure. Then they would differ in

a. Rate of diffusion

b. Kinetic energy

c. Boiling point

d. Number of molecules

118. The correct relation is

a. $V_c = 3b$ **b.** $\frac{P_c V_c}{RT_c} = \frac{3}{8}$

c. $T_c = \frac{8a}{27\,Rb}$ **d.** $P_c = \frac{a}{27\,b^2}$

119. According to Maxwell-Boltzman distribution of speeds among gas molecules, what is true?

a. The value of r.m.s. increases with rise in temperature

b. Area under the curve gives the total number of molecules.

c. The maxima in plot of $\Delta N/N$ vs speeds pertains to average speed

d. The plot of $\Delta N/N$ vs speeds is straight line with slope > 0

120. Which of the following statement about molecules of gaseous hydrogen and oxygen is/are correct here?

a. At the same temperature, the hydrogen molecules will have the greater speed

b. At the same temperature, the mean kinetic energies will be equal

c. The mean molecular velocity increases with temperature in each case.

d. The mean speed is directly proportional to the temperature in each case

121. Which of the following statement is/are correct?

a. Helium escapes at a rate 2 times as fast as O_2 does.

b. Helium escapes at a rate 4 times as fast as SO_2 does.

c. Helium escapes at a rate 2.65 times as fast as CO does.

d. Helium diffuses at a rate 8.65 times as much as CO does.

122. Van der Waal's constants for three different gases are given:

Gas	a	b
A	3.0	0.025
B	10.0	0.030
C	6.0	0.035

Which of these is correct?

a. Most easily liquefiable gas is A

b. Maximum critical temperature – B

c. Maximum molecular volume – C

d. Most ideal behaviour – A

123. The incorrect statement/s is/are

a. Gases tend to become ideal at inversion temperature

b. Gases tend to become ideal at Boyle's temperature over a wide range of pressure

c. Gases deviate maximum from ideal behaviour when the temperature is very high and pressure is very low.

d. Gases deviate minimum from the ideal behaviour when the temperature is very low and pressure is very high.

124. Consider the following equation:

$$PV_m = RT\left(1 + \frac{B}{V_m} + \frac{B}{V_m^2} + \ldots..\right)$$

Here which statement is/are correct about V_m?

a. It is independent of temperature

b. It is equal to RT/P at Boyle's temperature

c. It has the dimension of molar volume

d. It is equal to P/RT at critical temperature

125. Which of the following matching is/are incorrect?

a. a/Rb ... T_c

b. $(8\,kT/\pi m)^{1/2}$ ... u_{rms}

c. 8aRT/27 ... Boyle's temperature

d. $(3PV/M)^{1/2}$ ..... α

126. Indicate the correct statement for equal volumes of N_2 (g) and CO_2 (g) at 25°C and 1 atm.

a. The rms speed remains constant for both N_2 and CO_2

b. The average translational KE per, molecule is the same for N_2 and CO_2

c. The total translational KE of both N_2 and CO_2 is the same

d. The density of N_2 is more that that of CO_2

127. Which of the following statement is/are correct?

a. At a temperature below T_C, the molecules are close enough for the attractive forces to act, the condensation occurs.

b. The kinetic energy of the gas molecules is higher above T_C, and the attraction between temperature decreases.

c. No condensation takes place above T_C.

d. It is not possible to compress a gas at a temperature below T_C.

128. When an ideal gas is allowed to expand into another evacuated vessel through a tiny hole, then

a. The temperature of the gas remains constant

b. The temperature of the gas is decreased

c. There is no intermolecular force of attraction between an ideal gas

d. Energy is absorbed from the surroundings

129. Which of these quantities are same for all ideal gases at any particular temperature?

a. The number of molecules in 1 gm

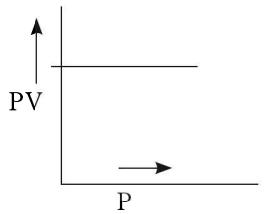
b. The kinetic energy of 1 mole

c. The kinetic energy of 1 gm

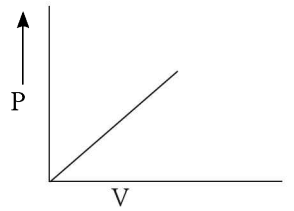
d. The number of molecules in 1 mole

130. Which of the following graphs does not represent Boyle's law

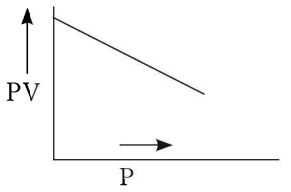
a.



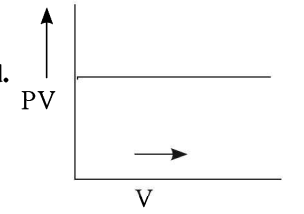
b.



c.



d.



131. If two vessels of equal volumes have H_2 and He at 1 and 2 atm pressure respectively at the same temperature. Then which relation is/are correct?

a. $u_{rms}\ H_2 = u_{rms}\ He$

b. $r_{H_2} = r_{He}/\sqrt{2}$

c. $u_{rms}\ H_2 = \sqrt{2}\ u_{rms}\ He$

d. $r_{H_2} = \sqrt{8} \times r_{He}$

132. The correct statement about van der Waal's constant 'b' is/are

a. It depends on intermolecular force

b. Its value depends on molecular size

c. It is exclude volume

d. Its unit is mole per litre.

133. Which of the following statement is/are correct here?

a. Larger is the excluded volume of gas, less will be its critical volume

b. Larger is the value of T_C/P_C for a gas larger would be its excluded volume

c. The excluded volume for He is more than H_2.

d. The slope for an isochore obtained for a gas showing $P(V - b) = RT$ is $[R/(V - b)]$

134. 4.4 g CO_2 gas and 2.24 *l* of H_2 gas are taken in a one litre container at 300 K. The total pressure of the gas in container will be

a. 14.856 atm

b. 4378.15 mm of Hg

c. 4.926 atm

d. 3743.76 mm of Hg

135. Which is/are correct for molecular speed of gases?

a. $u_{rms} > u_{av}$

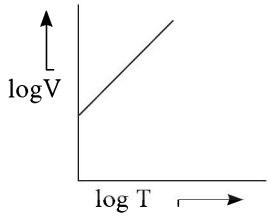
b. $u_{mp} = \sqrt{(8RT/\pi M)}$

c. $u_{rms} = \sqrt{(3PV/M)}$

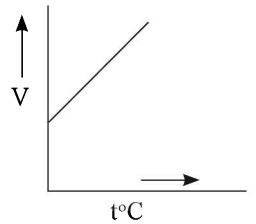
d. $u_{mp} > u_{av}$

136. Which of the following graph correctly represents Charle's law?

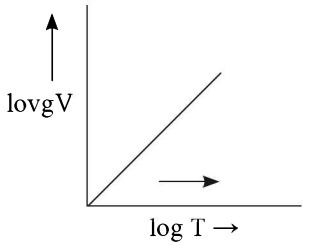
a.



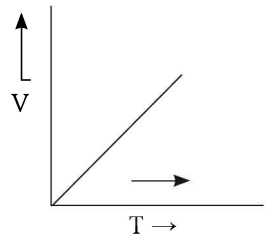
b.



c.



d.



137. Regarding H_2 gas, the correct statement(s) is/are

a. The critical temperature of H_2 gas is very high

b. The value of van der Waal's constant 'a' is very low for H_2

c. For H_2 gas, $Z > 1$ at 0°C

d. When H_2 gas expands at above inversion temperature, then it shows heating effect

138. Which of the following statements are correct?

a. He escapes at a rate of 2.65 times as fast as CO does

b. He diffuses at a rate of 4.65 times as much as CO does

c. He escapes at a rate of 4 times as fast as SO_2 does

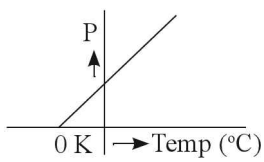
d. He escapes at a rate of 8 times as CO_2 does

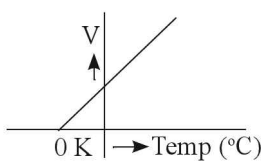
139. A 50 ml sample of a hydrogen-oxygen mixture was placed in a gas burette at 18°C and confined at 1 atm. A spark was passed through the sample so that the formation of water could go to completion. The resulting pure gas had a volume of 10 ml at atmospheric pressure. The initial mole fraction of hydrogen in the mixture would be

a. 0.534 **b.** 0.734

c. 0.634 **d.** 1.534

140. What conclusion would you draw from the following graphs?





a. As the temperature is lowered, the volume as well as the pressure increases

b. As the temperature is lowered, the volume as well as the pressure decreases

c. A point is reached where, theoretically, the volume as well as the pressure become zero.

d. As the temperature is lowered, the volume becomes zero and the pressure becomes infinity.

Linked-Comprehension Type Questions

Comprehension 1

Graham's Law of Diffusion: The phenomenon of spontaneous intermixing of gases against the law of gravitation is known as diffusion. If diffusion occurs through small orifice of the container then it is known as effusion.

The rate of diffusion is expressed as

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time}}$$

$$= \frac{\text{Moles of gas diffused}}{\text{Time}}$$

$$= \frac{\text{Distance travelled by gas}}{\text{Time}} = \frac{1}{\sqrt{M}}.$$

Here M = molar mass of gas.

141. 100 ml of O_2 gas diffuses in 10 seconds. 100 ml of gas 'X' diffuses in 't' seconds. Gas 'X' and time 't' can be respectively

a. He, 4 seconds
b. H_2, 2.5 seconds
c. SO_2, 14 seconds
d. CO, 12 seconds

142. 1 mole of gas H_2 and 4 moles of gas O_2 is taken inside the vessel, which effuse through the small orifice of the vessel having same area of cross section and at the same temperature, then which of the correct percentage of effused volume of gas H_2 and O_2 initially respectively? (Assume that the gas H_2 does not react with O_2 gas)

a. 25% and 75%
b. 20% and 80%
c. 50% and 50%
d. 65% and 34%

143. He and Ar are monoatomic gases and their atomic weights are 4 and 40 respectively. Under similar conditions He will diffuse through semi permeable membrane

a. 13 times as fast as Ar
b. 3.16 times as fast as Ar
c. 16 times as fast as Ar
d. 5.62 times as fast as Ar

Comprehension 2

The van der Waal's equation of state for one of a mole real gas is written as

$$\left[P + \frac{a}{V^2}\right](V - b) = RT$$

The virial equation for one mole of a real gas is given as follows:

$$PV = RT\left[1 + \frac{X}{V} + \frac{Y}{V^2} + \frac{Z}{V^3} + \right.$$

$\left. \ldots \text{ to higher power of 'n'} \right]$

Here X, Y and Z are constants which are known as second, third and fourth virial coefficient respectively.

The temperature at which real gas obeys ideal gas equation i.e., (PV = nRT) is known as Boyle's temperature.

144. The third virial coefficient of a He gas is 4×10^{-2} (litre/mole)^2 then what will be volume of 2 mole He gas at NTP?

a. 45.2 lit
b. 11.3 lit
c. 22.6 lit
d. 4.52 lit

145. If the critical temperature of the gas be

$$T_C = \frac{8a}{27\,Rb}$$

and T_B is the Boyle's temperature, then the correct relation between T_C and T_B is

a. $T_C = \frac{4}{27} T_B$
b. $T_C = \frac{27}{6} T_B$
c. $T_C = \frac{8}{27} T_B$
d. $T_C = \frac{27}{8} T_B$

146. Which of the following is the incorrect statement about the Boyle's temperature (T_B)?

a. The value of T_B is equal to a/Rb
b. Temperature at which second virial coefficient becomes zero
c. Temperature at which first virial coefficient becomes zero
d. Both **a.** and **b.**

Comprehension 3

The density of the vapour of a substance at one atmospheric pressure and 500 K temperature is 0.36 kg m–3. The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under same conditions of temperature and Pressure.

147. The molecular weight of the vapour is?

a. 36
b. 18
c. 27
d. 9

148. The value of compressibility factor (Z) for this vapour is?

a. 1.11
b. 2.44
c. 1.22
d. 2.22

149. If the vapour shows ideal gas behaviour at 1000 K than its average transitional kinetic energy will be?

a. 1.035×10^{-10} J
b. 2.07×10^{-30} J
c. 4.41×10^{-20} J
d. 2.07×10^{-20} J

Comprehension 4

As in reality no gas shows behaviour of ideal gas and such gases are known as real gases. In order to modify ideal gas equation for such gases van der Waal introduced an equation as follows:

$$(P + a\frac{n^2}{V^2})(V - nb) = nRT$$

Here constant 'a' is an indirect measurement of magnitude of attractive force present between the molecules of the gas. Its higher value shows ease of liquefication.

The constant 'b' is known as covolume or excluded volume. It is four times of the actual volume occupied by a molecule.

150. Gases X, Y, Z and P have the Van der Waal's constants 'a' and 'b' (in CGS) as follows:

	X	Y	Z	P
a	6	620	0.05	
b	0.025	0.15	0.1	0.02

The gas with the highest critical temperature is:

a. P **b.** X
c. Y **d.** Z

151. At high pressure, Van der Waal's equation becomes:

a. PV = RT + a/V

b. PV = RT

c. PV = RT + Pb

d. PV = RT – a/V.

152. Which of the following statement is incorrect here?

a. More the value of excluded volume of a gas more will be its critical volume

b. The excluded volume of hydrogen is less than that of helium

c. Higher the value of T_C/P_C for a gas more is the value of its excluded volume

d. Ammonia is more easily liquefied than hydrogen

153. Find Boyle's temperature range in case of CO_2 if for it the values of 'a' and 'b' are 3.592 atm lit^2/mol^2 and 0.0427 lit/mole respectively

a. 752°C **b.** 650°C
c. 562°C **d.** 572°V

154. The gas equation for a real gas is:

P (V – b) = RT

Here, the parameter 'b' is Van der Waal's constant. The graph of pressure against temperature (isochore) will give straight line of slope:

a. Negative **b.** Zero
c. R/(V – b) **d.** R/P

Comprehension 5

The van der Waals equation is one of the equation many equation of state suggested in order to account for the behaviour of real gases. There are two other simple equations of state which involve just two arbitrary constants. The first of these, equation given as follow

$$(P + a\frac{n^2}{TV^2})(V - nb) = nRT$$

Here a and b are known as Berthelot's constants and are characteristics of the gas.

The second equation, Dieterici, is given as

{pexp (na/VRT} (V– nb) = nRT

All these three equation of state can be expressed approximately in one common from, known as the virial equation of state it can be given as

$$Z = \frac{pVm}{RT} = 1 + B\frac{1}{Vm} + C\frac{1}{V^2m} + D\frac{1}{V^3m} + \ldots\ldots$$

here B,C, ….are temperature dependent constants known as second, third, etc., virial coefficients.

155. The van der Waals and the Dieterici equation can give the same value of P at

a. High Density **b.** Low Density
c. At no temperature **d.** At Entity

156. When a graph is plotted between Vm {pVm/RT – 1} versus 1/Vm is extra plotted to 1/Vm = 0 we get the value of

a. A **b.** B
c. C **d.** Any of these

157. The numerical value of virial coefficients …….very sharply with higher powers of volume

a. Decrease

b. Increase

c. Increase or Decrease

d. First increase than decrease

Assertion-Reason Type Questions

In the following question, two statements (Assertion) A and Reason (R) are given. Mark

a. if A and R both are correct and R is the correct explanation of A;

b. if A and R both are correct but R is not the correct explanation of A;

c. A is true but R is false;

d. A is false but R is true,

e. A and R both are false.

158. **(A):** The viscosity of an ideal gas is independent of pressure at constant temperature.

(R): As the pressure is increased, the effect of the increase in number density of molecules in compensated by a proportionate decrease in the mean free path.

159. **(A):** Considering van der Waal's equation of state for a real gas $(P + n^2a/V^2)$

$(V - nb) = nRT$; The constant 'a' for O_2 is less than that for H_2O (g).

(R): The molar mass of O_2 is almost twice that of H_2O

160. **(A):** In the Joule-Thomson expansion of hydrogen and helium, the temperature of the gases increases.

(R): These gases have very high inversion temperature.

161. **(A):** The heat capacities of all the diatomic molecules attain a limiting value at higher temperatures.

(R): At room temperature, the translational and rotational degrees of freedom contribute to the heat capacities of gases, while the vibrational degree of freedom becomes active only at higher temperatures.

162. **(A):** All molecules of an ideal gas move with the same speed.

(R): There is no attraction between the molecules in an ideal gas.

163. **(A):** Considering the van der Waal's equation of state

$(P + a/V^2) + (V - b) = RT$

for ammonia (NH_3) and nitrogen (N_2), the value of a for NH_3 is larger than that of N_2.

(R): Ammonia has a lower molecular weight than nitrogen.

164. **(A):** The hydrogen gas warms up during the Joule-Thomson expansion.

(R): The temperature at which the Joule Thomson coefficient becomes negative is called Joule-Thomson inversion temperature

165. **(A):** The gases He and CO_2 are very different in their behaviour at any temperature and pressure, but their compressilibility factors are nearly the same.

(R): The 'Law of corresponding states' states that the compressibility factor of any gas can be written as a universal function of the reduced variables.

166. **(A):** In Van der Waal's equation $(P + a/V^2)(V - b) = RT$ pressure correction (a/V^2), is due to force of attraction between molecules.

(R): Due to force of attraction, volume of molecules cannot be neglected.

167. **(A):** A lighter gas diffuses more rapidly than a heavier gas.

(R): At a given temperature , the rate of diffusion of a gas is inversely proportional to the square root of its density.

168. **(A):** When temperature of an ideal gas increases from 27°C to 127°C at constant P, volume increases by 100 L.

(R): $V \propto T$ at constant P.

169. **(A):** Van der Waal's constant 'a' is a measure of force of attraction between molecules.

(R): This constant is the volume correction.

170. **(A):** $Cp - Cv = R$ for an ideal gas

(R): R is the work done when temperature of one mol of an ideal gas is increased by 1°.

171. **(A):** Van der Waal's 'b' is expressed in the unit of atm L_2 mol^{-2}.

(R): 'b' is pressure correction due to force of attraction.

172. **(A):** $Cp - Cv = R$ for an ideal gas

(R): $(\partial E/\partial V)_T = 0$ for an ideal gas

173. **(A):** The Joule-Thomson coefficient for an ideal gas is zero.

(R): There are no intermolecular attractive forces in an ideal gas.

174. **(A):** H_2 and He show some ideal gas behaviour.

(R): All real gases deviate from ideal gas behaviour at low temperature and high pressure

175. **(A):** An ideal gas cannot be liquefied even by attaining 0.003 K with the help of adiabatic demagnetization.

(R): The Van der Waal's constant 'a' is negligible for an ideal gas and molecules are assumed as point mass.

176. **(A):** 8 grams of methane occupies 11.207 litres of volume at 273 K and 1 atm pressure.

(R): one mole of any gas at STP occupies 22.414 litres of volume.

177. **(A):** The heat capacities of all the diatomic molecules attain a limiting value at higher temperature.

(R): At room temperature, the translational and rotational degrees of freedom become active only at higher temperature.

178. **(A):** The triple point of a pure substance having three phases in equilibrium has zero degree of freedom.

(R): None of the variables like temperature and pressure can be changed without change in the number of phases.

179. **(A):** Whatever be the temperature , liquid CO_2 does not exist at normal atmospheric pressure.

(R): The triple point of CO_2 lies above 1.0 atm.

180. **(A):** A value of Van der Waal's constant 'a' is larger for NH_3 than PH_3.

(R): Hydrogen bonding is present in NH_3

181. **(A):** Absolute zero is the lowest possible temperature.

(R): A lower temperature would correspond to negative value of volume of gas which is physically meaningless.

182. **(A):** H_2 when allowed to expand at room temperature, it causes heating effect.

(R): H_2 has inversion temperature much below room temperature.

Matrix-Match Type Questions

	p	q	r	s
(A)	O	O	O	O
(B)	O	O	O	O
(C)	O	O	O	O
(D)	O	O	O	O

183. Match the following:

Column I	**Column II**
A. Rate of effusion/diffusion	(p) Absolute temperature
B. Kinetic energy	(q) Mole fraction
C. Partial pressure of a gas	(r) Density
D. Liquification of a gas	(s) Critical temperature
	(t) Value of 'a'

184. Match the following

Column I	**Column II**
A. Critical temperature	(p) Litre mol^{-1}
B. Co-volume (b)	(q) 8a/27 Rb
C. Molar volume of a gas at NTP (22.4)	(r) Lit^2 atm mol^{-2}
D. Van der Waal's constant (a)	(s) M^4 newton mol^{-2}

185. Match the following:

Column I	**Column II**
A. Boyle's law	(p) $\frac{d_1 t_2}{d_2 t_1} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$
B. Graham diffusion law	(q) $P_1 V_1 = P_2 V_2$
C. Avogadro law	(r) $V_1/n_1 = V_2/n_2$
D. Kinetic equation	(s) $(\delta P/\delta V)_T = -K/V^2$
	(t) $PV = 1/3\ mn\ u^2_{rms}$

186. Match the following:

Column I (Gases)	**Column II (Van der Waal's constant 'a')**
A. He	(p) 2.25
B. CH_4	(q) 3.59
C. SO_2	(r) 6.71
D. CO_2	(s) 0.034

187. Match the following

Column I	**Column II**
A. $P \propto 1/V$ at constant T	(p) Graham's law
B. $P \propto T$ at constant V	(q) Gay Lussac's law
C. $V \propto T$ at constant P	(r) Charle's law
D. $V \propto n$ at constant T and P	(s) Boyle's law

188. Match the following:

Column I	Column II
A. Critical temperature	(p) a/R_b
B. Boyle temperature	(q) $2a/R_b$
C. Inversion temperature	(r) T/Tc
D. Reduced temperature	(s) $8a/27\ R_b$

189. Match the following:

Column I	Column II
A. RMS speed	(p) 3/2 RT
B. Average speed	(q) $\sqrt{(8\ KT/nm)}$
C. Mole fraction	(r) $\sqrt{(3KT/m)}$
D. Kinetic energy of more atoms of gas	(s) $n/\sum n$

190. Match the following:

Column I	Column II
A. Dalton's law	(p) $v_1/v_2 = \sqrt{(M_2/M_1)}$ (at constant temp. & pressure)
B. Dulong and Petit's Law	(q) At. wt x Specific heat ≈ 6.4
C. Graham's Law	(r) Pgas = x gas x K_H
D. Henry's law	(s) P_A = mole fraction x Total pressure

191. Match the following:

Column I	Column II
A. Gas constant (R)	(p) mol dm^{-3}
B. Ionic product of water (Kw)	(q) $mol^2\ dm^{-6}$
C. Van der Waal's constant (A)	(r) $dm^3\ atm\ K^{-1}\ mol^{-1}$
D. Equilibrium constant of HA_c (k)	(s) $dm^6\ atm\ mol^{-2}$

192. Match the following:

Column I	Column II
A. $(2RT/M)^{1/2}$	(p) torr
B. work done $degree^{-1}$ mol^{-1}	(q) gram molar volume
C.–22.4 litre at S.T.P	(r) universal gas constant
D. unit of low pressure	(s) most probable velocity

193. Match the following:

Column I	Column II
A. density of ideal gas	(p) effusion
B. escape of gas from punctured tube	(q) $\sqrt{(8RT/\pi M)}$
C. average speed	(r) $\sqrt{3RT/M}$
D. R.M.S velocity	(s) $ML^2T^{-1}\ \theta$
	(t) PM/RT

194. Match the following:

Column I (Gases under specified condition)	Column II (Properties)
A. Hydrogen gas (P = 200 atm, T = 273 K)	(p) Compressibility factor ≠ 1
B. Hydrogen gas (P ~ 0, T = 273 K)	(q) Attractive forces are dominant
C. CO_2 (P = 1 atm, T = 273 K)	(r) PV = nRT
D. Real gas with very large molar volume	(s) P (V – nb) = nRT

[IIT 2007]

The IIT-JEE Corner

195. The compressibility factor for an ideal gas is

a. 1.5 **b.** 1.0

c. 2.0 **d.** ∞

[IIT 1997]

196. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

a. fewer electrons than O_2

b. two covalent bonds

c. V-shape

d. dipole moment

[IIT 1997]

197. The following statement (s) is (are) correct

(1) A plot of log Kp versus 1/T is linear

(2) A plot of log (X) versus time is linear for a first order reaction X → P

(3) A plot of log P versus 1/T is linear at constant volume

(4) A plot of P versus 1/V is linear at constant temperature.

a. 1, 2 **b.** 2, 4

c. 2, 3 **d.** 1, 4

[IIT 1999]

198. At 100°C and 1 atm. if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3}, then the volume occupied by water molecules in 1 litre of steam at that temperature

a. 6 cm^3 **b.** 60 cm^3

c. 0.6 cm^3 **d.** 0.06 cm^3

[IIT 2000]

199. The compressibility factor of a gas is less than unity at STP. Therefore

a. Vm > 22.4 litres

b. Vm < 22.4 litres

c. Vm = 22.4 litres

d. Vm = 44.8 litres

[IIT 2000]

200. The r.m.s. velocity of hydrogen is $\sqrt{7}$ times the r.m.s. velocity of nitrogen. If T is the temperature of the gas

a. $T(H_2) = T(N_2)$

b. $T(H_2) > T(N_2)$

c. $T(H_2) < T(N_2)$

d. $T(H_2) = \sqrt{7}\, T(N_2)$

[IIT 2000]

201. The root mean square velocity of a ideal gas at constant pressure varies with density d as

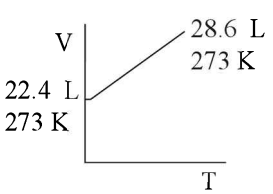
a. d^2 **b.** d

c. $\sqrt{d}$ **d.** $1/\sqrt{d}$

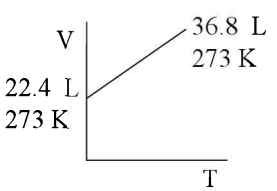
[IIT 2001]

202. Which of the following volume (V)-temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?

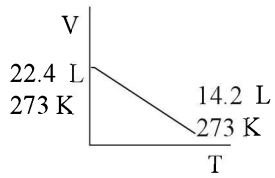
a.



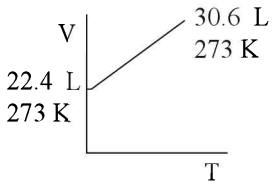
b.



c.



d.



203. Positive deviation from ideal behaviour takes place because of

a. molecular interaction between atoms and $\frac{PV}{nRT} > 1$

b. molecular interaction between atoms and $\frac{PV}{nRT} < 1$

c. finite size of atoms and $\frac{PV}{nRT} > 1$

d. finite size of atoms and $\frac{PV}{nRT} < 1$

[IIT 2003]

204. The root mean square velocity of one mole of a monoatomic gas having molar mass M is Urms. The relation between the average kinetic energy (E) of the gas and Urms is

a. Urms = $\sqrt{(3E/2M)}$

b. Urms = $\sqrt{(2E/3M)}$

c. Urms = $\sqrt{(2E/M)}$

d. Urms = $\sqrt{(E/3M)}$

[IIT 2004]

205. The ratio of rate of diffusion of helium with respect to methane under similar conditions of constant temperature and pressure

a. 2 **b.** 0.5

c. 16 **d.** 4

[IIT 2005]

206. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas?

a. 4R/2 **b.** 3R/2

c. 5R/2 **d.** 0

[IIT 2006]

207. A gas described by van der Waal's equation

a. Behaves similar to an ideal gas in the limit of large molar volumes

b. Behaves similar to an ideal gas in the limit of large pressures

c. Is characterized by van der Waal's coefficients that are dependent on the identity of the gas but are independent of the temperature

d. Has the pressure that is lower than the pressure exerted by the same gas behaving ideally

[IIT 2008]

208. The terms that corrects for the attractive forces present in a real gas in the van der Waals equations

a. nb **b.** $\frac{an^2}{V^2}$

c. $\frac{an^2}{V^2}$ **d.** nb

[IIT 2009]

ANSWERS

Straight Objective Type Questions

1. c	**2.** a	**3.** c	**4.** d	**5.** a	**6.** b	**7.** d	**8.** c	**9.** b	**10.** d
11. d	**12.** d	**13.** b	**14.** a	**15.** c	**16.** c	**17.** d	**18.** a	**19.** b	**20.** c
21. c	**22.** d	**23.** d	**24.** c	**25.** c	**26.** a	**27.** b	**28.** c	**29.** b	**30.** c
31. d	**32.** d	**33.** b	**34.** b	**35.** d	**36.** a	**37.** c	**38.** c	**39.** a	**40.** b
41. c	**42.** b	**43.** c	**44.** d	**45.** a	**46.** a	**47.** d	**48.** d	**49.** b	**50.** a

Brainteasers Objective Type Questions

51. b	**52.** b	**53.** c	**54.** b	**55.** b	**56.** c	**57.** c	**58.** d	**59.** a	**60.** a
61. d	**62.** a	**63.** b	**64.** B	**65.** d	**66.** b	**67.** a	**68.** c	**69.** d	**70.** c
71. b	**72.** c	**73.** a	**74.** c	**75.** d	**76.** b	**77.** c	**78.** c	**79.** d	**80.** a
81. a	**82.** c	**83.** b	**84.** d	**85.** b	**86.** b	**87.** d	**88.** c	**89.** d	**90.** a
91. c	**92.** a	**93.** a	**94.** b	**95.** c	**96.** b				

Multiple Correct Answer Type Questions

97. c, d	**98.** b, c, d	**99.** a, b, c	**100.** a, c, d	**101.** a, b	**102.** a, b, d
103. b, d	**104.** b, c, d	**105.** b, c	**106.** b, c	**107.** a, c	**108.** b, c, d
109. a, b	**110.** b, c, d	**111.** c, d	**112.** c, d	**113.** a, c	**114.** a, d
115. a, d	**116.** a, b, d	**117.** a, c	**118.** a, b, c, d	**119.** a, b	**120.** a, b, c
121. a, b, c	**122.** b, c, d	**123.** a, c, d	**124.** b, c	**125.** a, c	**126.** b, c
127. a, b, c	**128.** a, c	**126.** b, d	**130.** b, c	**131.** a, b, c	**132.** b, c, d
133. b, d	**134.** c, d	**135.** a, c	**136.** a, b, d	**137.** b, c, d	**138.** a, c
139. a, b	**140.** b, c				

Linked-Comprehension Type Questions

Comprehension 1

141. b **142.** c **143.** b

Comprehension 2

144. a **145.** c **146.** c

Comprehension 3

147. b **148.** c **149.** d

Comprehension 4

150. b **151.** c **152.** b **153.** a **154.** c

Comprehension 5

155. b **156.** b **157.** a

Assertion Reason Type Questions

158. a **159.** b **160.** c **161.** a **162.** d

163. b **164.** c **165.** e **166.** c **167.** a

168. d **169.** c **170.** a **171.** e **172.** a

173. a **174.** b **175.** a **176.** a **177.** d

178. a **179.** a **180.** a **181.** a **182.** a

Matrix-Match Type Questions

183. A-(r), B-(p), C-(p, q), D-(s, t)

184. A-(q), B-(p, r), C-(p), D-(r, s)

185. A-(q, s), B-(p), C-(r), D-(t)

186. A-(s), B-(p), C-(r), D-(q)

187. A-(s), B-(q), C-(r), D-(p)

188. A-(s), B-(p), C-(q), D-(r)

189. A-(r), B-(q), C-(s), D-(p)

190. A-(s), B-(q), C-(p), D-(r)

191. A-(r), B-(q), C-(s), D-(p)

192. A-(s), B-(r), C-(q), D-(p)

193. A-(t), B-(p), C-(q), D-(r)

194. A-(p, s), B-(r), C-(p, q), D-(p, s)

The IIT-JEE Corner

195. b **196.** d **197.** b **198.** c **199.** b **200.** c **201.** d **202.** d

203. b **204.** c **205.** a **206.** a **207.** b, c, d **208.** b

Hints and Explanations

Straight Objective Type Questions

1. According to Boyle's law

$PV = Cosntant.$

By differentiating this equation, we have

$PdV = VdP = 0$

$VdP = -PDV$

$$\frac{dP}{P} = -\frac{dV}{V}$$

2. At very low pressure, the real gas approaches ideal behaviour.

3. Plot is a horizontal line. Hence slope = 0.

4. $PV = RT$ or $V = RT/P$.

Greater the value of T/P, greater is the volume.

12. As its molecular weight is maximum so it will have minimum average speed.

13. Lower the density of the gas, faster it will be filled As H_2 has lowest density, it will be filled first.

17. Density = $\frac{\text{mass}}{\text{Volume}}$

Due to ideal behaviour at a given temperature and pressure volume and molar mass are same so they have same vapour density.

18. $u = \sqrt{(3RT/M)}$.

At constant temperature, $u \propto \sqrt{(1/M)}$.

As H_2 has least molecular mass, u will be maximum for H_2.

19. As d $\propto$ pressure

$\propto$ 1/temperature

20. As kinetic energy is $\propto$ temperature

So it will become four times as temperature is increased from 300 K to 1200 K.

21. As liquification of gas $\propto$ 'a'

i.e., $NH_3 > CH_4 > N_2 > O_2$

26. Average kinetic energy depends only on temperature and does not depend upon the nature of the gas.

28. The collision between the molecules to be perfectly elastic because the temperature remains constant irrespective of collision.

29. The temperature at which a real gas behaves like an ideal gas is called Boyle's temperature or Boyle's point.

31. As the condition of constant pressure or constant volume is not mentioned so the gas may be monoatomic or diatomic.

36. Average translational kinetic energy of gas molecules = 3/2 kT.

37. According to Charles' law,

At constant pressure, V/T = constant

i.e., V = kT.

So plot of V vs T is a straight line passing through the origin.

38. As CO_2 has lowest molecular mass here so it will have highest average speed.

39. It represents most probable velocity given by $\sqrt{2RT/M}$.

40. K.E. = $\frac{3}{2}$ nRT

K.E. = $\frac{3}{2}$ RT

When $n = 1$

42. Van der Waal's constant 'b' is four times the actual volume of 1 mole molecules i.e., $4VN_0$

44. Van der Waal's equation for one mol of a gas is given as

$[P + a/V^2] (V - b) = RT$

where b is volume correction. It arises due to finite size of gaseous molecules.

48. $a = \frac{PV^2}{n^2}$ (atm L^2 mol^{-2})

$b = L\ mol^{-1}$

So $\frac{a}{b} = (\frac{\text{atm } L^2 \text{ mol}^{-2}}{L \text{ mol}^{-1}})$ = atm L mol^{-1}

Brainteasers Objective Type Questions

52. Using Graham's law, TO_2 is 20 seconds.

53. Initially, partial pressures were equal.

As $r \propto \sqrt{(1/d)}$ or $\sqrt{(1/M)}$, therefore amounts diffused out in the same time will be $H_2 > CH_4 > SO_2$. So amounts left will be $H_2 < CH_4 < SO_2$ or $SO_2 > CH_4 > H_2$.

Thus, $\rho(SO_2) > \rho(CH_4) > \rho(H_2)$.

55. At constant temperature

V = K/P (Boyle's law)

So P = K/V

As such, a graph plotted between P and 1/V is linear at a constant temperature.

56. $\mu_1/\mu_2 = \sqrt{(T_1M_2/M_1T_2)}$

$= \sqrt{(50 \times 32/800 \times 2)}$

$= 1$

58. Applying Dalton's law

$PH_2 = \frac{W/2}{W/2 + W/30} \times P\text{total}$

On solving

PH_2 = 15/16 Ptotal

59. At the same temperature, oxygen and hydrogen molecules will have the same average energy; weight of H_2 molecules is 1/16 of O_2 molecules.

60. $r_{CH_4}/rx = \sqrt{(Mx/MCH_4)}$

$2 = \sqrt{(Mx/16)}$

$Mx = 64$

61. Molar volume (M^3) at STP are

NH_3 : 0.022094

O_2 : 0.022392

N_2 : 0.022403

H_2 : 0.022432

NH_3 has a dipole moment. Dipole-dipole interaction, most likely plays its role in reducing the volume.

62. $V_1/V_2 = \sqrt{(T_1/T_2)}$

$0.3/V_2 = \sqrt{(300/1200)}$

$V_2 = 0.6$ m/sec

63. $U_{rms} = \sqrt{(3RT/M)}$

$$\frac{U_{rms}(H_2)_{50\,K}}{U_{rms}(O_2)_{800\,K}}$$

$= \sqrt{[(TH_2/TO_2) \times (MO_2/MH_2)]}$

$= \sqrt{[(50/800) \times (32/2)]}$

$= 1$

64. As ammonia will have more diffusion rate than NH_3 due to less molecular weight.

66. Applying Dalton's law

$$PH_2 = \frac{W/2}{W/2 + W/16} \times P\text{total}$$

On solving

$PH_2 = 8/9$ Ptotal

67. At constant pressure, temperature, and volume, the number of moles of CCl_4 and O_2 will be same. But the molar mass of CCl_4 is approximately 5 times than that of O_2.

68. Urms : Uav

$\sqrt{(3RT/M)} : \sqrt{(8RT/\pi M)}$

$\sqrt{3} : \sqrt{(8/\pi)} = 1.086 : 1$

69. Pressure exerted by oxygen will proportional to mole fraction of O_2.

$$\text{Mole fraction of } O_2 = \frac{W/32}{W/16 + W/32} = 1/3$$

70. Given P (pentane) = 440 m

P (hexane) = 120 mm

From Dalton's law of partial pressure

P (total) = P (pentane) + P (hexane)

= (440 + 120) mm = 560 mm

mole fraction,

X (pentane) = 440/560 = 0.786

72. According to Boyle's law

PV = Cosntant.

By differentiating this equation, we have

$PdV = VdP = 0$

$VdP = -PDV$

$$\frac{dP}{P} = -\frac{dV}{V}$$

73. $v_{rms.} = \sqrt{(3RT/M)}$

$$(30\ R^{1/2})^2 = \frac{3RT}{M}$$

$$900\ R = \frac{3R \times 300}{M}$$

On solving, we get

$M = 1\ g\ mol^{-1} = 0.001\ kg\ mol^{-1}$

74. $$M = \frac{w}{V} \cdot \frac{RT}{P} = d\,\frac{RT}{P}$$

$$\text{i.e, } M = \frac{1.964 \times 10^{-3} \times 82.1 \times 273}{1}$$

= 44 i.e., the gas is CO_2

75. $r_a/r_b = 2/1 = \sqrt{(M_b/M_a)}$

$V_{rms} \propto \sqrt{(T/M)}$

(As $V_{rms} = \sqrt{(3RT/M)}$

$V_{rms\,(a)}/V_{rms\,(b)} = \sqrt{[(T_a/T_b) \times (M_b/M_a)]}$

$$= \frac{2}{1} \times \frac{\sqrt{2}}{1} = \frac{2\sqrt{2}}{1}$$

$2\sqrt{2} : 1$

76. According to Boyle's law

$P_A \times V_A = 0.4P_A \times V_B$

$100 \times P_A = 0.4\ P_A \times V_B$

$V_B = 250$ cc

Before opening the stopcock, volume of gas in bulb B must be (250 – 100) = 150 ml.

77. As Vav. $\propto \sqrt{(1/M)}$

$$\text{So } \frac{V(SO_2)}{V(\text{gas})} = \sqrt{[M(\text{gas})/M(SO_2)]}$$

On solving

M (gas) = 16 i.e., CH_4

78. $\frac{PV}{T} = \frac{P'V'}{T'}$.

Here V' = 2V, T' = 2T

$\frac{PV}{T} = \frac{P' \times 2V}{2T}$ or P = P'

i.e., pressure remains same.

80. 6.4 g of SO_2 at N.T.P. (i.e., at 0°C temperature and 1 atm pressure) occupies a volume of 2.24 lit.

64 g of SO_2 i.e., 1 mole SO_2 at N.T.P. occupies a volume of 22.41 lit.

now 1 mole of an ideal gas occupies 22.4 litre at N.T.P. condition.

Therefore SO_2 acts as an ideal gas.

81. Work done is reversible process is maximum. Thus $T_2 << T_1$ in reversible process or $T_{2rev} << T_2$ irr.

82. $M_{mix} = M_1 X_1 + M_2 X_2$

$= 17 \times \frac{20}{100} + 34 \times \frac{80}{100} = 30.6$

Vapour density of mixture = $\frac{30.6}{2} = 15.6$

83. When the value of Z < 1, it is due to attractive forces between molecules, At high pressure, when Z > 1, it is due to repulsive forces between electron clouds of the molecules of gases

84. **(c)** is not possible as gas is same (H_2).

(d) is possible

$\frac{t_1}{t_2} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$

$\frac{5}{t_2} = \frac{\sqrt{2}}{\sqrt{32}}$.

t_2 = 20 sec.

86. Let the mass of methane and oxygen is w

Mole fraction of oxygen = $\frac{w/32}{w/32 + w/16}$.

$= \frac{1/32}{1/32 + 1/16} = \frac{1/32}{3/32} = 1/3$

Let the total pressure be P.

The pressure exerted by oxygen (partial pressure) = $X_{O_2} \times P_{total} = P \times 1/3$

87. Pressure of helium = 8 bar

Pressure of methane = 2 bar

$\frac{r(He)}{r(CH_4)} = \frac{P_1}{P_2} \frac{\sqrt{MCH_4}}{\sqrt{MHe}} \rightarrow \frac{\sqrt{MCH_4}}{\sqrt{MH_e}}$

$= 8/2 \quad \frac{\sqrt{16}}{\sqrt{4}}$

= 8 : 1

88. $\frac{r_{He}}{r_{CO}} = \frac{\sqrt{M_{CO}}}{\sqrt{M_{He}}} = \sqrt{(28/4)} = 2.65$

$r_{CO} = \frac{r_{He}}{2.65} = \frac{6.4}{2.65} = 2.4$ mole/hour

$t = \frac{10}{2.4} \approx 4.2$ hours

89. $SO_3 = O_2$ = w g

n (SO_3) = w/80

n (O_2) = w/32

The partial pressures will be in the ratio of their moles.

So, $p(SO_3) : p(O_2) = \frac{w}{80} : \frac{w}{32}$.

$\frac{1}{80} : \frac{1}{32} = \frac{1}{5} : \frac{1}{2} = 2 : 5$

90. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

1 5 3 4 volume

So 1 volume or 1 litre of propane requires to 5 volume or 5 litre of O_2 to burn completely.

92. The average translational K.E. of one molecule of an ideal gas is as follows:

$K_t = \frac{K.E.}{N_A} = \frac{3\ 2\ RT}{N_A} = \frac{3}{2} KT$

When R/N_A = Boltzmann constant

i.e., $E_t \propto T$

Thus, at constant temperature K.E. of molecules remains same.

93. According to Boyle's law, Pressure is inversely proportional to volume.

i.e., $P = \propto \frac{1}{V}$

or PV = constant

As, $P_1V_1 = P_2V_2$

$P_2 = P \times \frac{V}{1.1\ V}$

$P_2 = 0.9 \times P$ (i.e., 10% decrease in pressure).

Multiple Correct Answer Type Questions

100. As most probable velocity increases and fraction of molecule possessing most probable velocity decreases.

101. As temperature is constant pressure decreases during expansion while kinetic energy remains same.

115. Reversible adiabatic expansion lowers the temperature hence facilitates the liquefication of gas. A gas can be liquefied below the critical temperature by increasing the pressure.

129. As one mole of a gas has always N_0 number of molecules and kinetic energy depends only on temperature.

139. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$(50 - X) \quad X \quad 0$

Case 1

Suppose H_2 is the limiting reagent

So after the reaction volume of O_2 remains

$$= X - \frac{(50 - X)}{2} = \frac{3X - 50}{2}$$

$$\frac{3X - 50}{2} = 10$$

$X = 70/3 = 23.33$

So mole fraction of $H_2 = \frac{(50 - 23.33)}{50}$

$= 0.534$

Case 2

Suppose O_2 is the limiting reagent

After the reaction volume of H_2 remains

$= (50 - X - 2X) = (50 - 3X)$

So $(50 - 3X) = 10$

$X = 40/3 = 13.33$

Mole fraction of H_2 in the original mixture

$$= \frac{(50 - 13.33)}{50} = 0.733$$

Linked-Comprehension Type Questions

Comprehension 3

147. $\frac{r_{vapour}}{r_{O_2}} = \sqrt{(MO_2/Mvapour)}$

$1.33 = \sqrt{(32/Mvapour)}$

$Mvapour = 18$

148. As volume of vapour (Vreal) = 1 m^3

= 1000 litre.

Mass of the vapour = 0.36 kg = 360 gm.

So moles of the vapour (n)

$$= \frac{360}{18} = 20$$

As PVideal = nRT

$$Videal = \frac{nRT}{P}$$

$$= \frac{20 \times 0.082 \times 500}{1} = 820 \text{ litre}$$

Hence compressibility factor (Z)

$$= \frac{V_{real}}{V_{ideal}} = \frac{1000}{820} = 1.22$$

149. As $(K.E.)_{Av} = \frac{3}{2} \frac{nRT}{N_0}$

$$= \frac{3}{2} \times \frac{1 \times 8.314 \times 1000}{6.02 \times 10^{23}}$$

$= 2.07 \times 10^{-20}$ J.

Comprehension 4

150. As critical temperature, $T_c = \frac{8a}{27\,Rb}$.

So greater is the value of (a/b), more is the critical temperature of gas

For gas X, T_c will be maximum,

$T_c = \frac{8a}{27\,Rb}$.

a/b for X = 6/0.025 = 240; for all other gases (a/b) is lesser.

151. $(P + a\frac{n^2}{V^2})(V - nb) = nRT$

For one mole gas

$(P + \frac{a}{V^2})(V - b) = RT$

At high pressure,

$(P + \frac{a}{V^2}) \approx P$

So $P(V - b) = RT$

$PV = RT + Pb$

152. As value of 'b' for hydrogen is 0.021 $dm^3\ mol^{-1}$ while 'b' for He is 0.019 $dm^3\ mol^{-1}$.

153. $T_b = \frac{a}{R_b} = \frac{3.592}{0.0821 \times 0.0427}$.

$= 1024.7\ K = 752^oC$

So CO_2 behaves ideal in nature in the temperature range $752 \pm t^oC$.

Assertion-Reason Type Questions

160. These gases have very low inversion temperature.

162. All molecules of the ideal gas does not move with same speed their average speed is same.

164. The temperature of which the Joule-Thomson coefficient becomes zero is called Joule-Thomson inversion temperature.

Matrix-Match Type Questins

194. (A) $Z = \frac{PV_m}{RT}$ at high pressure and low temp.

Equation $(P + an^2/V^2)(V - nb) = nRT$ reduces to $P(V - nb) = nRT$.

(B) For hydrogen gas value of $Z = 1$ at $P = 0$ and it increase continuously on increasing pressure.

(C) CO_2 molecules have larger attractive forces, under normal conditions.

(D) $Z = \frac{PV_m}{RT}$,

at very large molar volume $Z \neq 1$.

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196. More the dipole moment more is the critical temperature.

197. At constant temperature

$V = K/P$ (Boyle's law)

So $P = K/V$

As such, a graph plotted between P and 1/V is linear at a constant temperature.

198. $1L = 1000\ mL = 1000\ cm^3$

mass = density × volume

$= (0.0006\ g\ cm^{-3}) \times (1000\ cm^3)$

$= 0.6\ g$

as 18 g of water = $18\ cm^3$

so 0.6 g of water = $0.6\ cm^3$

hence actual volume occupied by molecules

$= 0.6\ cm^3$

199. $Z = PV/nRT$

Given $Z < 1$

$PV/nRT < 1$ or $PV < nRT$

$(1\ atm) \times V < 1\ mol \times (0.0821\ L\ atm\ K^{-1}\ mol^{-1}) \times (273\ K)$

$Vm < 0.0821 \times 273\ L$

$Vm < 22.4\ L$

200. $\mu H_2/\mu N_2 = \sqrt{[(T_{H_2}/M_{H_2}) \times (M_{N_2}/T_{N_2})]}$

$\sqrt{7} = \sqrt{(T_{H_2} \times 28/T_{N_2} \times 2)} = T_{H_2} \times 14/N_2$

$TN_2 = 2\ T_{H_2}$

so $TN_2 > T_{H_2}$

201. As $u = \sqrt{(3PV/m \times N_0)} = \sqrt{(3P/N_0)}.\ (1/d)$

So $u \propto 1/\sqrt{d}$

202. Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22.4 L. Volume at 373 K and 1 atm pressure will be

$V = \frac{RT}{P} = \frac{0.082 \times 373}{1}$

$= 30.58\ L = 30.6\ L.$

203. For positive deviation

$PV/nRT > 1$

$PV = nRT + nPb$

$PV/nRT = 1 + Pb/RT$

$PV/nRT > 1.$

204. RMS of one mole of monoatomic gas is

$Urms = \sqrt{(3RT/M)}$

Average K.E. is $E = \frac{3}{2}RT$ or $2E = 3RT$

$Urms = \sqrt{(2E/M)}$

205. According to Graham's diffusion law,

$$\frac{r(He)}{r(CH_4)} = \frac{\sqrt{M(CH_4)}}{\sqrt{M(He)}}$$

$M(CH_4) = 12 + 4 = 16$

$M(He) = 4$

$$\frac{r(He)}{r(CH_4)} = \frac{\sqrt{16}}{4} = 2.$$

207. See Text part.

208. See Text part.

Numericals For Practice

1. Find volume of O_2 that can be prepared at 333 K and 1 atm pressure due to decomposition of 20 gm of H_2O_2.

a. 4.01 lit **b.** 8.04 lit
c. 2.01 lit **d.** 6.03 lit

2. 50 gm H_2O on electrolysis give H_2, O_2 which are enclosed in a vessel of 60 litre at 290 K. Find partial pressure of each gases.

a. 1.102 and 0.551 atm
b. 0.551 and 1.102 atm
c. 1.421 and 1.612 atm
d. 0.331 and 0.872 atm

3. One litre flask having vapours of CH_3OH at a pressure of 1 atm and 298 K was evacuated till the pressure was 0.0001 mm. Now how many moles of CH_3OH will be left in flask?

a. 6.02×10^{21} **b.** 3.24×10^{15}
c. 3.24×10^{18} **d.** 6.02×10^{15}

4. In the study of pressure volume relationship, the following data were collected at room temperature

	(I)	(II)	(III)	(IV)
V (L)	10.5	5.25	3.5	3.3
P (atm)	1	2	3.0	3.5

In which observation the volume was not recorded correctly?

a. I only **b.** II and III
c. IV only **d.** III and IV

5. An iron cylinder contains He at a pressure of 250 kPa at 300 K. This cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict which is correct statements about cylinder (melting point of cylinder 1800 K)?

a. Will melt and burst
b. Neither melt nor burst
c. Will melt but not burst
d. Can not be predicted

6. A gas cylinder containing cooling gas can withstand pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicate 12 atm at 27°C due to a sudden fire in the building, its temperature starts rising. At what temperature will the cylinder explode?

a. 362.5 K **b.** 390 K
c. 372.5 K **d.** 426 K

7. When 18 g of H_2O is heated at 400 K and 2 atm pressure H_2 gas is evolved. Find the volume it will occupy. If the ratio of H : O by weight in H_2O is 1 : 8. One g of H_2 occupy 11.2 litre at N.T.P?

a. 22.4 lit **b.** 11.2 lit
c. 15.4 lit **d.** 16.4 lit

8. A vessel of volume 0.02 m^3 contain a mixture of H_2 and He at 320 K and 41.5×10^4 N m^{-2}. The mass of the mixture is 10^{-2} kg. Find the mass of H_2 and He in mixture respectively.

a. 2.48 g, 7.52 g respectively
b. 7.52 g, 2.48 g respectively
c. 3.26 g, 6.74 g respectively
d. 4.48 g, 5.52 g respectively

9. If at a distance of 100 miles above earth the temperature is –160°C and pressure of atmosphere is 2×10^{-6} mm. What will be the number of moles at this altitude for 2 ml of a gas?

a. 4.36×10^{-11}
b. 11.72×10^{-9}
c. 5.66×10^{-13} moles
d. 8.42×10^5 moles

10. If at a certain temperature, a student wants to decrease the volume of a gas by 5 %. How much pressure should he must increase for it?

a. 15% **b.** 8.34%
c. 5.26% **d.** 56%

11. The volume of average adult lung was found to be 6 litre nearly at 98.4°F during expansion. If the pressure of O_2 in inhaled air is found to be 168 mm of Hg. What will be the mass of O_2 needed to occupy the lung at this temperature?

a. 1.67 g **b.** 2.07 g
c. 8.34 g **d.** 0.923 g

12. An LPG cylinder at 300 K has 15 kg of butane at 10 atmosphere pressure. After a leakage it was found that its pressure fell down to 8 atmosphere in one day. The gas leaked in 3 days will be

a. 5 kg **b.** 6 kg
c. 3 kg **d.** 9 kg

13. A student has a flask containing air. He heated it from 300 K to 500 K. What % of air escaped to the atmosphere will be?

a. 40% **b.** 50%
c. 30% **d.** 100%

14. A manometer is connected to a gas containing bulb. If the open arm read 43.6 cm, while the arm joined to bulb reads 15.5 cm. If the barometer reads a pressure of 742 mm of Hg. What will be pressure of gas in bar?

a. 1.06 bar **b.** 4.32 bar
c. 1.36 bar **d.** 9.82 bar

15. Pressure of 1 g of an ideal gas 'X' at 300 K is 2 bar. When 2 g of another ideal gas 'Y' is added in same flask at same temperature, the pressure is found to be 3 bar. What will be the relationship between M_X and M_Y (masses of X and Y)?

a. $M_Y = 4\ M_X$ **b.** $M_Y = ½\ M_X$
c. $M_X = 3\ M_Y$ **d.** $M_X = 4\ M_Y$

16. At 273 K, it is found that density of N_2 at 5 bar is equal to a gaseous oxide at 2 bar. What will be the molecular weight of gaseous oxide?

a. 60 **b.** 68.5
c. 82 **d.** 70

17. A student found at the top of mountain and bottom of it, the values of temperature and pressure respectively are

	Bottom	Top
Temp.	30°C	0°C
Pr.	760 mm	710 mm

The ratio of density at top and bottom is

a. 1 : 1.04 **b.** 1.04 : 1
c. 2 : 1 **d.** 1 : 3

18. Find volume occupied by 5 g C_2H_2 at 50°C and 740 mm pressure?

a. 5.23 lit **b.** 3.23 lit
c. 6.26 lit **d.** 8.23 lit

19. 0.55 lit of a gas is collected over water at 298 K and 755 mm pressure. Now gas is saturated with water vapours. Find volume of gas at NTP in dry condition. Vapour pressure of H_2O at 298 K is 23.8 mm.

a. 0.625 lit **b.** 0.485 lit
c. 0.373 lit **d.** 0.175 lit

20. 100 cc of methane at 600 mm if Hg pressure and 2000 cc of oxygen at 400 mm of Hg pressure were enclosed in a three litre flask. Calculate the total pressure when the temperature is constant.

a. 268.4 mm **b.** 286.7 mm
c. 362.1mm **d.** 270.5 mm

21. A mixture of gas in a cylinder has 20% CO_2, 15% O_2 and 65% N_2 at 760 mm and 300 K. The partial pressure of each gas will be respectively?

a. 152, 114 and 494 mm
b. 494, 114 and 152 mm
c. 114, 494 and 152 mm
d. 210, 214 and 336 mm

22. Ammonia and the hydrogen chloride gases are introduced simultaneously at the ends of a 90 cm tube. At what distance ammonium chloride is formed from the end at which HCL is introduced?

a. 55.53 **b.** 182.5cm
c. 36.51 cm **d.** 18.25 cm

23. Find the relative rates of diffusion of $^{235}UF_6$ and $^{238}UF_6$ respectively?

a. 1 : 1.526 **b.** 1.526 : 1
c. 1 : 1.0023 **d.** 1.0043 : 1

24. Three similar balloons were filled respectively with O_2, CO_2 and Cl_2 under similar conditions. In ten hours one-half the CO_2 had escaped. How much of each of the other gases escaped during the same period of time?

a. $O_2 = 0.6$; $Cl_2 = 0.4$
b. $O_2 = 0.4$; $Cl_2 = .6$
c. $O_2 = 0.8$; $Cl_2 = 0.2$
d. $O_2 = 0.0.2$; $Cl_2 = 0.6$

25. A porous container was filled with equal amounts of oxygen and a gas of unknown molecular weight.

The oxygen escaped 1.77 times faster than the unknown gas. Calculate the molecular weight of the unknown gas.

a. 44 **b.** 99
c. 66 **d.** 189

26. If the temperature of 1 mole of a gas is increased by 50 °C, calculate the change in kinetic energy of the system.

a. 62.32 J **b.** 6.235 J
c. 623.5 J **d.** 6235.0 J

27. Find the temperature at which H_2 at one atm pressure has the same root mean square velocity similar to O_2 at N.T.P.

a. –255 K **b.** 325 K
c. 17.06 K **d.** –17.06 K

28. If the temperature of 1 mole of a gas is increased by 50°C, calculate the ratio of average velocity of SO_2 to CH_4:

a. 1 : 2 **b.** 3 : 4
c. 2 : 3 **d.** 1 : 6

29. The van der Waals constant b for helium gas is 0.02337 litre $mole^{-1}$. Calculate the approximate diameter of the helium molecule assuming the molecule to be spherical.

a. 6.22×10^{-8} cm.

b. 5.66×10^{-8} cm.

c. 26.6×10^{-8} cm.

d. 2.66×10^{-8} cm.

30. The average velocity of an ideal gas molecule at 27°C is 0.3 m/s. The average velocity at 927°C will be

a. 0.6 m/s **b.** 0.3 m/s
c. 0.9 m/s **d.** 3.0 m/s

31. The ratio of $V_{r.m.s.}$ and $V_{av.}$ at a particular temperature is

a. 1.086 : 2 **b.** 1.086 : 1
c. 1 : 1.086 **d.** 2 : 1.086

32. Using van der waal's equation find the pressure of 15 mol of Neon at 303 K in 1200 ml vessel. (Given: $a = 0.2107\ L^2\ atm/mol^2$, $b = 0.0171$ L/mol)

a. 13.23 atm **b.** 31.4 atm
c. 21.34 atm **d.** 7.12 atm

33. If 'X' is the volume of one molecule of a gas under given conditions then van der waal's constant 'b' is

a. 4X **b.** $4X/N_0$
c. $4X\ N_0$ **d.** None of these

34. Find the temperature at which the average speed of Hydrogen = that of oxygen at 320 K.

a. 200 k **b.** 300 K
c. 100 K **d.** 20 K

35. Find the pressure exerted by 22 gm of CO_2 in 0.5 dm^3 at 298 .15 K using van dar Waal's equation if

$a = 363.76$ kPa $dm^6\ mol^{-2}$ and $b = 42.67 cm^3\ mol^{-1}$

a. 2.2255 kPa **b.** 222.55 kPa
c. 2225.5 kPa **d.** 0.22255 kPa

ANSWER KEYS

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	b	2.	a	3.	b	4.	c	5.	b
6.	c	7.	d	8.	a	9.	c	10.	c
11.	a	12.	d	13.	a	14.	c	15.	a
16.	d	17.	b	18.	a	19.	b	20.	b
21.	a	22.	c	23.	d	24.	a	25.	b
26.	c	27.	c	28.	a	29	d	30.	a
31.	b	32.	b	33.	c	34.	d	35.	b

Hints and Explanations

1. $2H_2O_2 \rightarrow 2H_2O + O_2$

As $V = \frac{n\,RT}{P}$

On solving n = 8.04 litre

2. $2H_2O \rightarrow 2H_2 + O_2$

50 gm

3. First find moles

$(n) = \frac{PV}{RT}$.

$= \frac{10^{-4}}{760} \times \frac{1 \times 1}{0.082 \times 298}$.

Number of molecules = $n \times N_0$

On solving we get

$= 3.24 \times 10^{15}$ molecules

4. Only in case of IV as correct volume must be 10.5/3.5 = 3 litre.

5. As $P \propto T$

So $\frac{P_1}{T_1} = \frac{P_2}{T_2}$.

On solving, we get

$T_2 = 1200$ K

As T_2 is less than melting point of the cylinder so it will neither melt nor burst..

6. As $P \propto T$

So $\frac{P_1}{T_1} = \frac{P_2}{T_2}$.

$\frac{12}{300} = \frac{14.9}{T_2}$.

On solving, we get

$T_2 = 372.5$ K

7. (i) First find weight of H_2

As ratio of H : O in H_2O is 1 : 8 so weight of H_2 in 2 g water

$= \frac{2 \times 18}{18} = 2$ g

(ii) Volume of 2 gm H_2 at NTP

$= 2 \times 11.2 = 22.4$ lit

(iii) Now apply

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$\frac{2 \times 760 \times V_1}{400} = \frac{760 \times 22.4}{273}$

On solving, we get

$V_1 = 16.4$ lit

8. Weight of mixture = 10 g

Suppose weight of H_2 = X g

So weight of He = (10 – X) g

n (H_2) = (X/2)

n (He) = (10 – X)/4

PV = n RT

$n = \frac{PV}{RT}$.

$\left(\frac{X}{2}\right) + \left(\frac{10-X}{4}\right) = \frac{41.5 \times 10^4 \times 0.02}{8.314 \times 320}$

After solving, X = 2.48 g [mass of H_2]

So weight of He = 10 – 2.48 = 7.52 g

9. As $n = \frac{PV}{RT}$.

P = 2 x 10^{-6}/760 atm

T = –160 + 273 = 113 K

R = 0.082

V = 2/1000 L or 2×10^{-3} L.

On solving, we get

n = 5.66×10^{-13} moles

10. If initial volume is V

Then final volume is 0.95 V.

$P_1 V_1 = P_2 V_2$

$P_2 = \frac{P_1 \times V}{0.95\,V} = 1.0526\,P_1$

i.e. 0.0526 is the increase in pressure

so % = 0.0526 × 100

= 5.26 % of initial pressure

11. First apply

$C = \frac{5}{9}(F - 32)$

= 36.88°C or 309.88 K

Now $w = \frac{PV.M}{RT}$

$= \frac{168 \times 6 \times 32}{760 \times 0.081 \times 309.88} = 1.67$ g.

(12) As $PV = nRT$

Since V, T are constant so $P \propto n$

$\frac{P_1}{P_2} = \frac{w_1}{w_2}$.

On solving, we get

$w_2 = 12$ kg

So 3 kg gas leaked in one day.

After 3 days total gas leaked will be

= 3 × 3 = 9 kg

13. Here P, V, R are same

So $n_1 T_1 = n_2 T_2$

i.e. $n_1 \times 300 = n_2 \times 500$

$n_2 = 3/5\ n_1$

Number of moles escaped

$= n_1 - \frac{3}{5} n_1 = \frac{2}{5} n_1$

$= 0.4\ n_1 = 40$ %

14. Height developed due to pressure of gas

= 43.7 – 15.6 = 28.1 cm

Now $P = n \times d \times g$

$= \frac{28.1 \times 13.6 \times 980}{76 \times 13.6 \times 980} = 0.37$ atm

P (gas) = P (atm) + 0.37

$= \frac{743}{760} + 0.37$

= 1.347 atm

= 1.347/0.987 bar

= 1.36 bar

15. As $PV = \frac{w}{M} RT$

So $P_X V = \frac{w_X}{M_X} RT$ [V, T, R are same]

$P_Y V = \frac{w_Y}{M_Y} RT$

$\frac{P_X}{P_Y} = \frac{w_X}{w_Y} \times \frac{M_Y}{M_X}$

On solving, we get

$M_Y = 4\ M_X$

16. As $d = \frac{PM}{RT}$

So $\frac{P_{N_2} \times 28}{RT} = \frac{P_{oxide} \times M_{oxide}}{RT}$

$M_{oxide} = \frac{5 \times 28}{2} = 70$

17. As $d \propto 1/V$

So $\frac{d_T}{d_B} = \frac{V_b}{V_t} = \frac{T_b P_t}{T_t P_b}$

$= \frac{303 \times 710}{273 \times 760} = \frac{1.04}{1}$

= 1.04 : 1

18. As $PV = \frac{w}{M} RT$

$V = \frac{w}{M \times P} \times RT$

$= \frac{5}{26} \times \frac{0.082 \times 323}{740} \times 760$

= 5.23 litre

19. Apply $V_2 = \frac{(P_1 - f)\, V_1\, T_2}{P_2\, T_1}$

$= \frac{(755 - 23.8) \times 0.55 \times 273}{760 \times 298}$

$V_2 = 0.485$ litre.

21. Apply $P_A = \frac{\%\ \text{of A} \times P_{mix}}{100}$

On solving

$P_{CO_2} = 152$ mm

$P_{O_2} = 114$ mm

$P_{N_2} = 494$ mm

23. Mol. wt. of $^{235}UF_6 = 235 + 19 \times 6$

= 349

Mol. wt. of $^{238}UF_6 = 238 + 19 \times 6$

= 352

So

$r_1/r_2 = \sqrt{[\text{M. wt. of } {}^{238}UF_6/\text{M. wt. of } {}^{235}UF_6]}$

$= \sqrt{(352/349)}$

$= 1.0043/1$

so $r_1 : r_2 = 1.0043 : 1$

26. $E = \frac{3}{2} RT$ (Kinetic energy of 1 mole gas)

$\Delta = \frac{3}{2} R(T + 50) - \frac{3}{2} RT$

$= \frac{3}{2} R \times 50 = \frac{3}{2} \times 8.314 \times 50$

$= 623.55$ j

27. $V_{r.m.s} = \frac{\sqrt{3RT}}{\sqrt{M}}$.

So $\sqrt{(3RT/2)} = \sqrt{[(3R \times 273)/32]}$

On solving, we get

$T = 17.06$ K

28. $v_{av} = \frac{\sqrt{8RT}}{\sqrt{\pi m}}$

$v_{SO2} = \frac{\sqrt{m_{CH_4}}}{\sqrt{m_{SO_2}}}$

$= \frac{\sqrt{16}}{\sqrt{64}}$

$= \frac{1}{2}$

29. $b = 4 N \frac{4}{3} \pi r^3$

$b = 0.0237$ litre $mole^{-1} = 23.7$ ml $mole^{-1}$;

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

30 $7 = 4 \times 6.02 \times 10^{23} \times (4/3) \times (22/7) \times r^3$

$r^3 = 23.7 \times 21$

$16 \times 6.02 \times 10^{23} \times 22$

$r = \frac{(237 \times 21 \times 10^{-24})^1}{^3/(16 \times 6.02 \times 22)}$

$(16 \times 6.02 \times 22)^{1/3}$

$= 1.33 \times 10^{-8}$ cm

$= 2.66 \times 10^{-8}$ cm

31. As $\frac{V_1}{V_2} = \frac{\sqrt{T_1}}{\sqrt{T_2}}$

On solving,

$V_2 = 0.6$ m/s.

32. $V_{r.m.s} = \frac{1}{Va._v}$.

0.9213

$= 1.086 : 1$

33. Apply $P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$

$= \frac{15 \times 0.082 \times 303}{(12 - 15 \times 0.0171)} - \frac{(15)^2 \times 0.2107}{12}$

$= 31.4$ atom.

34. As volume of one molecule = X

Volume of N_0 molecule = $X N_0$

So $b = 4 N_0 X$

As 'b' is equal to 4 times of volume of N_0 molecules present in one mole of a gas.

CHAPTER 3

Atomic Structure

Chapter Contents

Bohr model, spectrum of hydrogen atom, quantum numbers, Wave-particle duality, de Broglie hypothesis; Uncertainty principle; Qualitative quantum mechanical picture of hydrogen atom, shapes of s, p and d orbitals; Electronic configurations of elements (up to atomic number 36); Aufbau principle; Pauli's exclusion principle and Hund's rule and Various levels of multiple-choice questions.

ATOMIC THEORY

The word atom and atomic theory was introduced by John Dalton in 1808 in terms of an atomic model.

Main Postulates of Atomic Theory

- Atom is the smallest, undivided fundamental particle. which can neither be created nor destroyed. However, it is interconvertible.
- Atoms undergo chemical combination to form molecules but in whole number ratio, that is, molecule is the smallest identity that exists individually.
- Atoms of same element have same mass, size, property etc., but atoms of different element differ in these properties.

Modern View of Atomic Theory

According to J. J. Thomson, an atom is divisible into subatomic particles. Atoms can also combine in non-whole number ratio in non-stoichiometric compounds example. $Fe_{0.93}O$.

Atoms of same element also differ in properties related to mass even in case of isotopes also.

Sub-Atomic Particles or Constituents of Atoms

Electrons ($_{-1}e^0$ or e–)

Electron was discovered by J. J. Thomson during the study of cathode rays (stream of electrons) and named by J. L. Stoney

Location of electron: It is present in extra nuclear region in atom outside the nucleus.

Mass: Mass of electron = $\frac{1}{1837}$ of H-atom

= 0.00055 a.m.u

= 9.1×10^{-31} kg

Charge: It is confirmed by Milikan's oil drop experiment and its values are 1.6×10^{-19} Q or -4.8×10^{-10} e.s.u.

Thomson gave e/m ratio or specific charge ratio for electron and the value is 1.76×10^8 c/gm.

Cathode rays are beam or stream of electrons and e/m ratio for cathode rays is constant and independent of nature of gas in discharge tube and nature of cathode or electrodes of tube that is, electron is an universal fundamental particle.

- Mass of one mole of electron is 0.55 mg.
- Mass of moving $e^- = \frac{m_{rest}}{\sqrt{1-(V/C)^2}}$.

  Here V = Velocity of electron

  C = Velocity of light
- Electron can leave its orbit for maximum 10^{-8} sec.
- Particle nature of electron is confimed by scintillation effect on ZnS screen.
- Photoelectric effect, emission of β-particle, thermal emission or heating of metal filament confirm fundamental particle nature of electron.
- Density of electron is 2.17×10^{17} gm/c.c.

REMEMBER

e/m ratio or specific charge ratio or Thomson ratio order:

$_{-1}e^{o} > {}_{1}p^{1} > {}_{2}\alpha^{4} > {}_{0}n^{1}$

zero as it is charge less particle

Proton ($_1^1H$ or p)

Proton was discovered by Goldstein during the study of anode rays or canal rays or +ve rays which originate in the region between cathode and anode in discharge tube. Proton was named by Rutherford.

For anode rays, e/m ratio depends upon nature of gas taken in a discharge tube. It is maximum for hydrogen gas.

Charge on proton is $+ 1.6 \times 10^{-19}$ or $+ 4.8 \times 10^{-10}$ e.s.u

Mass of proton is that of H-atom that is, 1.673×10^{-27} kg or 1.0072 a.m.u.

e/m ratio is 9.5×10^4 c/gm

1 a.m.u. = 1/12 mass of C-atom

1 a.m.u = 1.66×10^{-27} kg= 931.5 MeV

Neutron ($_0^1n$)

Neutron was discovered by Chedwick as follows

$_4Be^9 + {}_2He^4 \rightarrow {}_6C^{12} + {}_0n^1$

Neutron was discovered late because it is chargeless.

- It is heavier than electron and proton.
- Isolated neutron is unstable and disintegrates as follows:

  $_0n^1 \rightarrow {}_{-1}e^0 + {}_1p^1 + \upsilon$
- It is stable inside the nucleus but unstable out side the nucleus.
- It is the best projectile as it is chargeless.
- H-atom has no neutron.

  Mass of neutron is 1.674×10^{-27} kg or 1.0086 a.m.u

  Density of neutron is 1.5×10^{14} g/c.c.

Atomic Number (Z) Moseley postulated the frequency of the X-rays was related to the charge present on the nucleus of the atom of the element used as anticathode and found that

$\sqrt{\upsilon} = a(Z - b)$

Here υ is the frequency, Z is the nuclear charge and a and b are constants.

a = probability constant

b = a constant having same values for all lines of X-ray spectrum.

The number of unit positive charges carried by the nucleus of an atom is called the atomic number of the element that is,

Z = p = e (from atoms)

Z = p (for ions)

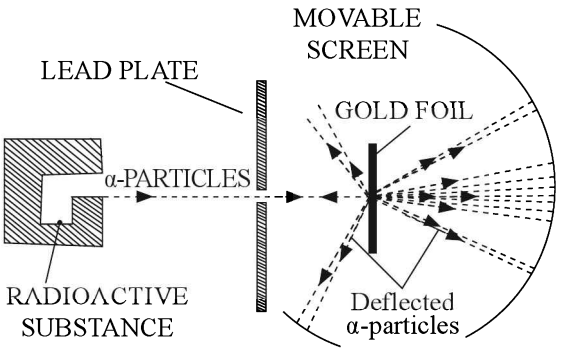
Facts about Atomic number

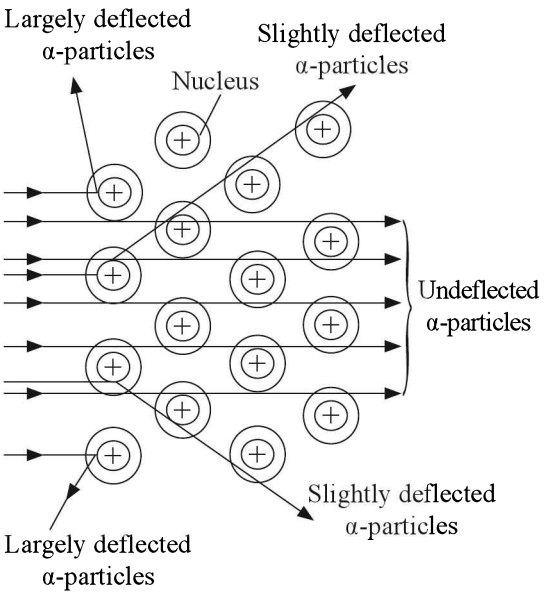
- It is always a whole number, and a permanent value for each element.
- It is serial number of elements in periodic table that is, determines their exact position.
- Periodic properties are related to the atomic number of elements.

Mass number (A): Mass number is nearly equals to atomic weight and mathmetically, it is the sum of proton + neutron.

$A = p + n = Z + n$

RUTHERFORD'S ATOMIC MODEL





During α-particle or helium nuclei bombardment experiment on 10^{-4} mm thick gold foil, Rutherford observed that:

(i) Most part of the atom is empty as most of the α-particles passed straight through the foil without any deflection.

(ii) Electrons occupy position in this empty space (extra nuclear region).

(iii) Centrally located solid compact small part having all positive charge and nearly the whole mass is called nucleus. (as few one out of 20,000 α-particles get defected >up to 90° and maximum 180°

(iv) The size or radius of nucleus can be calculated by this relation and Radius of atom is 10^{-10} m. or 10^{-8} cm.

$r = 1.3 \times 10^{-13} \times A^{1/3}$ cm

Here A=Mass number

r = radius of nucleus

The density of nucleus (Assumed as spherical) can be find out as

$$d = \frac{M}{V} = \frac{A}{N_A} \times \frac{1}{4/3\ \pi r^3} = 1.8 \times 10^4 \text{ g /cm}$$

Radius of nucleus = 10^{-15} m. or 10^{-13} cm.

Atomic radius > nucleus radius by 10^5 times.

Density of nucleus is 10^{17} kg/m^3 or 10^{14} gm/cm^3 and volume of nucleus is 10^{-39} cm^3.

REMEMBER

■ Scattering of α-particles $\propto \frac{1}{\text{Sin}^4(\theta/2)}$

(v) Centrifugal force develops between electrons and nucleus so electron revolve around the nucleus as stars move around the sun. (that is, planetary or solar model).

Merits

(i) Explains discovery of nucleus.

(ii) Explains Circulatory rotation of electron around the nucleus.

Demerits

(i) It cannot explain stability of atom.

(ii) It cannot explain the number and velocity of electrons.

(iii) According to him, atomic spectrum is continuous and non-linear but infact it may be linear and discontinuous.

Quantum Theory

It was introduced by Max Planck and then extended by Einstein.

Quantum Theory states that hot vibrating body does not emit or absorb energy continuously but emits or absorbs discontinuously in the form of small energy packets or bundles known as quanta and photon in case of light energy.

The energy of radiation (E) is directly proportional to frequency of radiation (υ).

$E \propto \upsilon$

$E = h\upsilon = h\frac{c}{\lambda} = hc\bar{v}$

Here h is Planck's constant and its values is 6.6253×10^{-34} Js or Kg m^2 s^{-1}.

λ = Wavelength , $\bar{v}$ = wave number

Absorption or emission in the form of multiples of quantum is known as quantization of energy that is,

$$\boxed{E = n h \upsilon}$$

A hollow sphere coated inside with platinum black and having a small hole in its wall acts as a black body. It is a perfect absorber and perfect emitter of radiant energy.

At a given temperature the intensity of radiation increases with wavelength, approaching towards maximum and then starts decreasing.

As Planck's quantum theory can explain only the black body radiations so Einstein extended quantum theory to all types of electromagnetic radiations.

Illustrations

1. Calculate the frequency of the light ray emitted when an electron drops from a higher to a lower energy level of an atom, the difference between the energies of which is 35.64×10^{-13} erg.

(Plancks's constant; $h = 6.624 \times 10^{-27}$ erg s)

Solution $E = h\upsilon$

$$\upsilon = \frac{E}{h} = \frac{35.64 \times 10^{-13}}{6.624 \times 10^{-27}}$$

$$= 5.38 \times 10^{14}\ s^{-1}$$

2. 3×10^{18} photons of a certain light radiation produce 1.5 J of energy. Find out the wave length of this radiation ($h = 6.626 \times 10^{-34}$ JS).

Solution $E = h\upsilon$ (for one photon)

$E = Nh\upsilon$ (for N photons)

$$E = \frac{N hc}{\lambda}$$

$$\lambda = \frac{N hc}{E} = \frac{3 \times 10^{18} \times 6.62 \times 10^{-34} \times 3 \times 10^{8}}{1.5}$$

$$= 39.75 \times 10^{-8}\ m = 3975\ Å.$$

3. How many mole of photons would contain sufficient energy to raise the temperature of 220 g of water from 25°C to 100°C? Specific heat of water is 4.184J g^{-1} K^{-1} and frequency of light radiation used is 2.40×10^9 Hz.

Solution The energy need to change the temperature from 25°C to 100°C is given as follows:

$E = m\ s\ \Theta$

Here m = Mass

s = Specific heat

Θ = Temperature change

$E = 220 \times 4.184 \times 75$ Joule

$E = 69036$ Joule

For a radiation of 2.4×10^9 Hz

The energy is given as follows:

$E = n\ hv$

$= 2 \times 6.626 \times 10^{-34} \times 2.4 \times 10^{9}$

So,

$n \times 15.9024 \times 10^{-25} = 69036$

$$n = \frac{69036}{15.9024} \times 10^{25}$$

$n = 4.34123 \times 10^{28}$

Hence moles of photons $= \frac{n}{N_0}$.

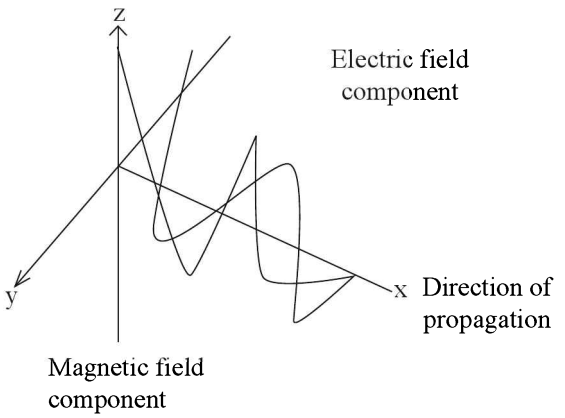
$$= \frac{4.34123 \times 10^{28}}{6.02 \times 10^{23}} = 7.211 \times 10^{4}\ \text{moles}$$

Electronic Structure of Atoms

Wave Theory

It is described in brief as follows:

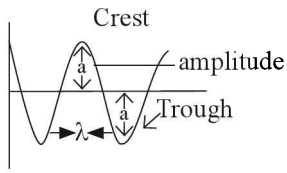
- All radiant energy propagates in terms of waves.
- Radiant energy is in the form of electromagnetic waves
- The radiations are associated with electric and magnetic field perpendicular to one another.
- In the propagation of an electromagnetic radiation there is only propagation of wave but not that of the medium.



The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength. frequency. speed and amplitude. but they vibrate in two mutuaily perpendicular planes.

Wavelength

It is the distance between any two successive crests or two successive troughs of waves. It is denoted by λ and it is measured in Å (Angstroms) or nm (nanometers) etc.



Frequency

It is the number of waves per second passing at a given point. It is denoted by υ or f. The units of frequency are Hertz or cycles sec^{-1}.

Velocity of Light

It is the distance traveled by one wave in one second.

Velocity of light = frequency × wave length

$C = \upsilon\lambda$.

$\lambda \propto 1/\upsilon$

Light or all electromagnetic radiations travels in vacuum or air with same velocity.

Wave Number

It is the number of waves spread in one cm and it is denoted by $\bar{\upsilon}$.

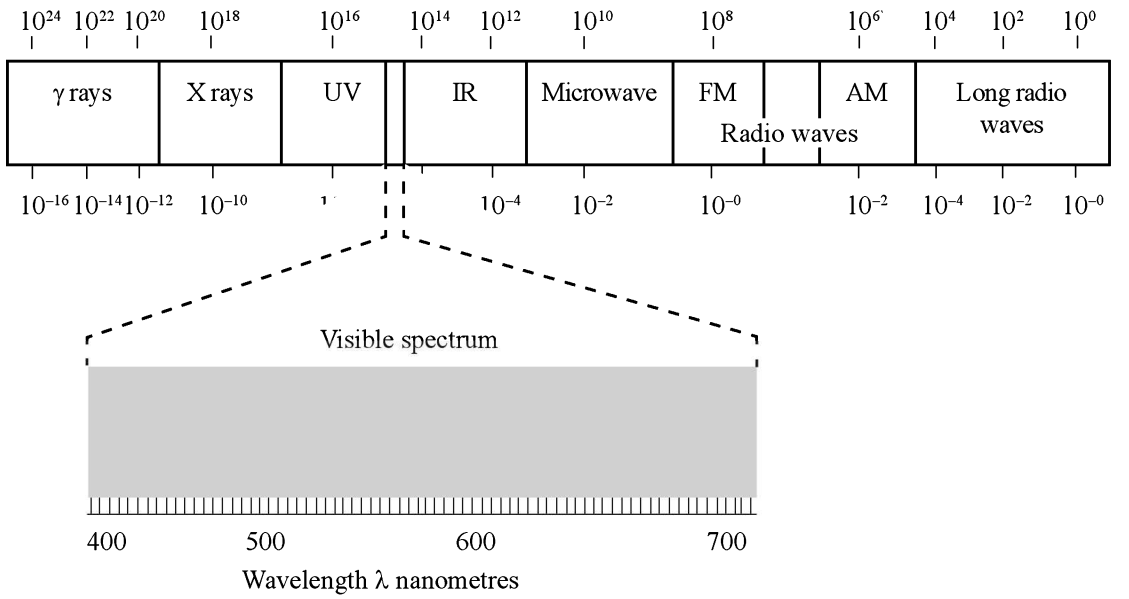
It is the reciprocal of wavelength.

$$\bar{\upsilon} = \frac{1}{\lambda}, \text{ as } \quad \bar{\upsilon} = \frac{C}{\lambda}$$

So $\bar{\upsilon} = C\,\upsilon$

Its units are cm^{-1} or m^{-1}.

Electromagnetic Spectrum



The spectrwn of electromagnetic radiation. The visible region is only a small part of the entire spectrwm (a) Overall spectrwm (b) Visible region.

Corpuscular Theory of Light

It was first introduced by Newton. According to this theory, light is propagated in the form of small invisible particles.

Photoelectric Effect

It was introduced by P. Lenard and explained by Einstein. It is the emission of electrons from a metal surface on exposing it to radiation of suitable frequency or wavelength. It is readily shown by alkali metals like K and Cs having very low ionization energy.

When a photon strikes the metal, its energy is absorbed by the electrons and emission of electrons takes place.

A part of the energy of photon is used to escape the electron from the attractive forces and the remaining energy is used in increasing the kinetic energy of electron.

$$\text{K.E. } (\tfrac{1}{2} mv^2) = E - \Phi$$

Here E = energy of radiation.

Φ = work function (minimum energy needed for electron emission).

$$\text{K.E} = h\upsilon - h\upsilon_0$$

υ_0 = threshold frequency (minimum frequency of light radiation needed for electron emission).

If $\upsilon > \upsilon_0$

K.E. is +ve electron is emitted

If $\upsilon = \upsilon_0$

K.E = 0 electron is not emitted (remains on surface)

If $\upsilon < \upsilon_0$

K.E is –ve no emission of electrons.

Photoelectric effect α Frequency of light radiation

Kinetic energy of electrons does not depend upon intensity of light, however, number of ejected electrons depend upon intensity of light.

Stopping Potential

The minimum potential applied by which velocity of ejected photoelectron becomes zero. This potential is called stopping potential.

$$\frac{1}{2} mv^2 = eVs$$

$$V_s = \frac{mv^2}{2e}$$

Here

V_s = Stopping potential

m = Mass of electron

v = Velocity of ejected electron

e = charge of electron

Einstein's Photoelectric Equation

$$E = W + \text{K.E.}$$

$$h\nu = h\nu_0 + \frac{1}{2} mv^2$$

$$h\nu = h\nu_0 + eV_s$$

Here v = Frequency of incident radiation.

Work Function

The minimum energy required for the photoelectric effect is called work function.

$$W = h\nu_0$$

$$W = \frac{hc}{\lambda_0}.$$

Here

c = Velocity of light

λ_0 = Threshold wavelength

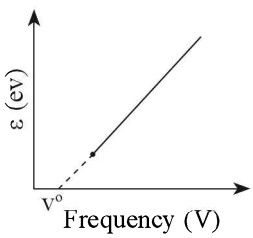


Fig. 3A

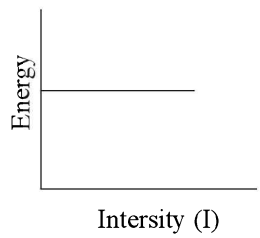


Fig. 3B

Illustrations

4. Determine the wave length of a photon of electromagnetic radiation having energy 2.99×10^{12} erg mol^{-1} ($h = 6.625 \times 10^{-34}$).

Solution $\lambda = \dfrac{N\,hc}{E}$

$$= \frac{6.023 \times 10^{23} \times 6.625 \times 10^{-34} \times 3 \times 10^{8}}{2.99 \times 10^{12}}$$

$$= 4000 \text{ Å}.$$

5. When a certain metal was irradiated with a light of frequency 1.5×10^{16} Hz, the photoelectrons

emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 1.0×10^{16} Hz. Find v_0 (threshold frequency) for the metal.

Solution $E_1 = h(v_1 - v_0)$ .... (i)

$E_2 = h(v_2 - v_0) = E_{1/2}$ .....(ii)

On diving equation (ii) by (i), we get

$$\frac{v_2 - v_0}{v_1 - v_0} = \frac{1}{2}$$

$$\frac{1.0 \times 10^{16} - v_0}{1.5 \times 10^{16} - v_0} = \frac{1}{2}$$

$$2.0 \times 10^{16} - 2v_0 = 1.5 \times 10^{6} - v_0$$

On solving, we get

$v_0 = 5 \times 10^{15}$ Hz

6. Calculate the kinetic energy of the electron emitted by an atom by 400 nm light when its threshold wavelength is 600 nm ($n = 6.63 \times 10^{-34}$ Js and $c = 3 \times 10^8$ ms^{-1}).

Solution As $K.E. = h(v - v_0) = hc(1/\lambda - 1/\lambda_0)$

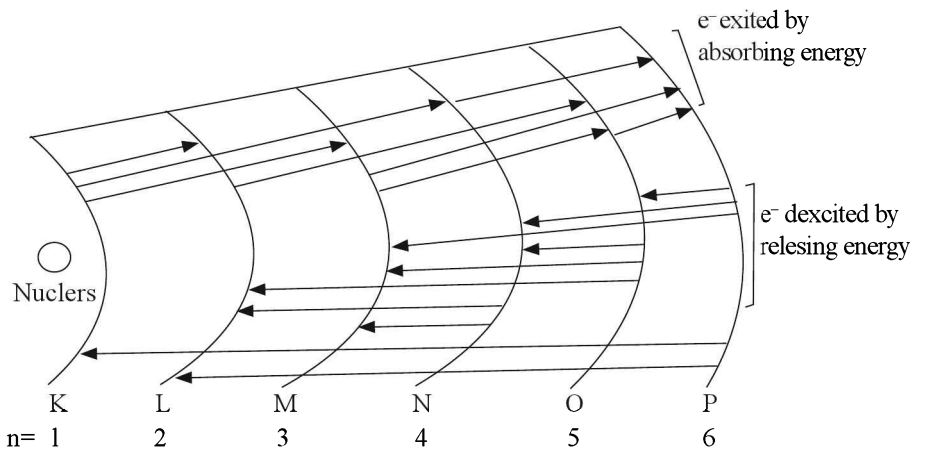
$$K.E. = 6.626 \times 10^{-34} \times 3 \times 10^8 \times \left(\frac{1}{400} - \frac{1}{600}\right) \times 10^9$$

$$K.E. = \frac{6.626 \times 3 \times 10^{-17}}{1200} = \frac{6.626 \times 10^{-19}\ J}{4}$$

$K.E. = 1.656 \times 10^{-19}$ J

BOHR'S ATOMIC MODEL

Bohr introduced Circular orbit concept based on (Linear hybrid combination of classical and early quantum physics) and Planck's quantum theory and it's main postulates are as follows:



■ Around the nucleus there are circular regions or spherical surfaces which are called orbits or shells. Each orbit has a fix amount of energy so it is called energy level.

	K	L	M	N	O .....
n =	1	2	3	4	5 .....

Energy and distance from nucleus increase

■ Angular momentum (mvr) of an electron moving in any orbit is quantized and given as

$$Mvr = n\frac{h}{2\pi} \quad = n\hbar$$

here h is plank's constant.

Here n is an integer with whole number values 1,2,3,..... and known as Principal Quantum number

n	→	1	2	3	4	5	
mvr	→	$\frac{h}{2\pi}$	$\frac{h}{\pi}$	$\frac{3h}{2\pi}$	$\frac{2h}{\pi}$	$\frac{5h}{2\pi}$	.....

■ An electron revolves round the nucleus in a particular orbit having definite energy without any

change of energy or any radiation of energy that is why these orbits are called stationary states ar stable or non-radiating orbits. The force of attraction between the nucleus and the electron is equal to centrifugal force of the revoul electron. When electron changes its orbit energy change occurs in quanta which is given as follows

$$\Delta E = E_2 - E_1 = h\upsilon \text{ or } = \frac{hc}{\lambda} \text{ quanta}$$

Quanta is a small bundle of any type of energy, while Photon is a small mass less bundle of light energy and not a material body.

- In excited state: electron jumps from lower to higher orbit or energy level by absorbing energy in quanta. While in de-excited, electron jumps from higher to lower energy level by releasing energy in quanta.

Advantages

- It can explain linear nature of spectrum of hydrogenic species (that is, with one e^-)

  Example, H, He^+, Li^{+2} etc.

Bohr's Theory for Hydrogen Atomd

Let the electron of mass be 'm' is moving around the nucleus with velocity 'v' and radius of circular path 'r'. When electron moves around the nucleus, it experiences coulomb force and centrifugal force. Both these force balance to each other.

Coulomb force (F_1) = Centrifugal force (F_2)

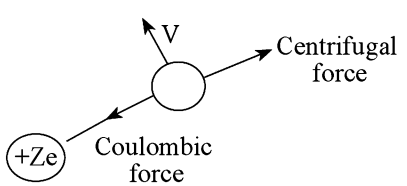
$$\frac{K(Ze)e}{r^2} = \frac{mv^2}{r}$$

$$\frac{KZe^2}{r} = mv^2 \qquad \text{.....(1)}$$

$$v^2 = \frac{KZe^2}{rm}$$

Here

$$K = \frac{1}{4\pi\epsilon o}$$



- **In the calculation of radius of nth orbit (rn):**

$$\text{As } mvr = \frac{nh}{2\pi} \qquad \text{.....(2)}$$

$$\text{So } v = \frac{nh}{2\pi rm}$$

On putting the value of v in equation number 1 we get the value of radius (r) as follows

$$r_n = \frac{n^2h^2}{K4\pi^2Ze^2m}$$

On putting the values of h, e, m, n and Z for H-atom in Ist orbit radius is given as

$r_1 = 0.53A^o$

(The value of $\frac{h^2}{K4\pi^2e^2m}$ is found to be 0.53 Å)

so for nth orbit radiun (r_n)

$$\boxed{r_n = 0.53 \times \frac{n^2}{Z} \text{ Å}}$$

As $r \propto 1/n \propto Z$ so radius ratio in two different orbits for two different species is given as

$$\frac{r_{n1}}{r_{n2}} = \frac{n_1^2}{n_2^2} \times \frac{Z_2}{Z_1}$$

- **In the calculation of velocity of electron in nth orbit (Vn)**:

Similarly from eq (1) and (2) we get

$$Vn = \frac{2\pi^2 K Z e^2}{nh}$$

As for an electron in first orbit of Hydrogen atom velocity is given as

$V_1 = 2.18 \times 10^6$ m/s (The value of $\frac{2\pi^2 K e^2}{h}$ is found to be 2.18×10^6 m/s)

so $Vn = 2.18 \times 10^6 \times \frac{Z}{n}$ m/sec

As

$$V \propto Z \propto \frac{1}{n}$$

So the ratio of velocity in two different orbit for two different species can be given as

$$\frac{Vn_1}{Vn_2} = \frac{Z_1}{Z_2} \times \frac{n_2}{n_1}$$

REMEMBER

V_1 for H-Atom = V_2 of He^+ = V_3 for Li^{+2} = 2.18 x 10^6 m/s(Bohr's velocity)

■ **In the calculation of energy of electron in nth orbit (E_n):**

The total Energy (Et) for an electron in any orbit is given as:

as $E_T = E_{K.E.} + E_{P.E.}$

$= \frac{1}{2} MV^2 + E_{P.E}$ [as $MV^2 = \frac{KZe^2}{r}$]

$E_T = \frac{1}{2} \frac{KZe^2}{r} + \frac{(-KZe^2)}{r}$ [as $P_{.E.} = \frac{-KZe^2}{r}$]

$E_T = \frac{-1}{2} \frac{KZe^2}{r}$

It means

$E_{K.E} = -E_T$

$2E_{KE} + P.E = Zero$

$E_n = \frac{-KZe^2}{2r_n}$

On putting the value of r_n here we got

$En = \frac{-2K^2 \pi^2 Z^2 me^4}{n^2 h^2}$

If the value of $\frac{2K^2 \pi^2 Me^4}{h^2}$

$= 2.18 \times 10^{-18}$ j/atom

$= 13.6$ e.v /atom

$En = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$ j /atom

$= -13.6 \times \frac{Z^2}{n^2}$ e.v/atom

$= -313.6 \times \frac{Z^2}{n^2}$ K.cal./mole

As $En \propto Z^2 \propto \frac{1}{n^2}$

So $\frac{En_1}{En_2} = \frac{Z_1^2}{Z_2^2} \times \frac{n_2^2}{n_1^2}$

REMEMBER

Bohr energy = –13.6 eV/atom (It is also E_1 for H-Atom, E_2 for He^+ and E_3 for Li^{+2}

■ Number of revolutions per sec. $= \frac{Vn}{2 \pi r_n}$

$= \frac{Z^2}{n^3} \times 6.666 \times 10^{15}$.

■ Time Period of revolution in nth orbit (Tn)

$= \frac{2 \pi r_n}{Vn} = \frac{n^3}{Z^2} \times 1.5 \times 10^{-16}$ sec

Illustrations

7. Calculate the velocity (cm s^{-1}) of an electron placed in the third orbit of the hydrogen atom. Also calculate the number of revolutions per second that this electrons makes around the nucleus.

Solution Velocity of an electron in the nth orbit

$V_n = \frac{2 \pi e^2}{nh}$

$= \frac{2 \times 3.14 \times (4.8 \times 10^{-10} \text{ esu})^2}{3 \times 6.626 \times 10^{-27} \text{ erg s}}$

$= 7.27 \times 10^7$ cm s^{-1}

Revolution per second

$= \frac{V_n}{2 \pi r_n} = \frac{2 \pi e^2}{nh} \times \frac{1}{2\pi} \times \frac{4 \pi^2 Z m e^2}{n^2 h^2}$

$= \frac{4 \pi^2 Z m e^4}{n^3 h^3}$

$= \frac{4 \times (3.14)^2 \times 1 \times 9.10 \times 10^{-28} \times (4.8 \times 10^{-10})^4}{(3)^3 \times (6.626 \times 10^{-27})^3}$

$= 2.42 \times 10^{14}$

8. An electron is in one of the excited state in H-atom, whose radius is 2.115 Å. Find the wavelength of a photon which will remove this electron H-atom. $R_H = 1.097 \times 10^7$ m^{-1}.

Solution $r_n = 0.529 \times \frac{n^2}{Z}$ Å

$2.116 = 0.529 \times \frac{n^2}{1}$ Å

On solving $n = 2$

To find λ, use this relation

$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$.

$\frac{1}{\lambda} = 109678 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right)$.

On solving

$\lambda = 3.646 \times 10^{-5}$ cm

$= 3.646 \times 10^{-7}$ m

$= 3646$ Å

Ionization Energy and Excitation Energy

Excitation potential for $n_1 \rightarrow n_2$

$$= \frac{En_2 - En_1}{\text{Electronic charge}}$$

Ionization potential for $n_1 \rightarrow \infty$

$$= \frac{En_1}{\text{Electronic charge}}$$

The energy required to remove an electron from the ground state to form cation, that is. to take the electron to infinity, is known as ionisation energy (I.E. or I).

$$\text{I.E.} = E_\infty - E_{\text{Ground}}$$

$$\text{I.E.} = 0 - E_1\,(H) = 13.6 \text{ eV atom}^{-1}$$

$$= 2.17 \times 10^{-18} \text{ J atom}^{-1}$$

$$\text{I.E.} = \frac{Z^2}{n^2} \times 13.6 \text{ eV}$$

$$\frac{I_1}{I_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}$$

$$(\text{I.E.})_Z = \frac{(\text{I.E.})_H \times Z^2}{n^2}$$

If an electron is already present in the excited state, the energy required to remove that electron is called separation energy.

$$E_{\text{Separation}} = E_\infty - E_{\text{Excited}}$$

$$= 13.6 \times \frac{Z^2}{n^2} \quad \text{e.v}$$

Illustrations

9. The ionization energy of hydrogen atom is 13.6 eV. What will be the ionization energy of He^+ and Li^{2+} ions.

Solution Ionization energy of hydrogen ($H \rightarrow H^+ + e^-$) is 13.6 eV.

As the ionization energy of hydrogen like ion may be given as Z^2 (I.E.), so ionization energy of He^+ is $2^2 \times 13.6 = 54.4$ eV and
Li^{2+} is $3^2 \times 13.6 = 122.4$ eV.

10. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.

Solution $E_3 - E_2 = h\upsilon$

$$\upsilon = \frac{E_3 - E_2}{h}$$

$$= \frac{(-2.41 \times 10^{-12}) - (-5.42 \times 10^{-12})}{6.626 \times 10^{-27}}$$

$$= 0.4543 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\upsilon} = \frac{3 \times 10^8}{0.4543 \times 10^{15}} = 6.6036 \times 10^{-7}$$

m = 6603.6 Å

11. The ionization energy of He^+ is 19.6×10^{-18} J $atom^{-1}$. Calculate the energy of the first stationary state of Li^{2+}.

Solution Energy of the first orbit of Li^{2+}

$$(E_{He^+})_1 = -Z^2_{He} \text{ (constant)}$$

$$(E_{Li^{2+}})_1 = -Z^2_{Li} \text{ (constant)}$$

$$(E_{Li^+})_1 = \frac{Z^2_{Li}}{Z^2_{He}} (E_{He^+})_1$$

$$= \frac{3^2}{2^2} \times 19.6 \times 10^{-18} \text{ J atom}^{-1}$$

$$= 44.1 \times 10^{-18} \text{ J atom}^{-1}$$

Drawbacks of Bohr's Theory

- It is not applicable for species having more than one electron like Li, He etc.
- It cannot explain fine spectrum of H, Li^{++} also.
- It gives no explanation of Zeeman and Stark effects.

Zeeman Effect

It is the splitting of main spectrum line in to several lines in a strong magnetic field.

Stark Effect

It is the splitting of main spectrum line in to several lines in a strong electric field

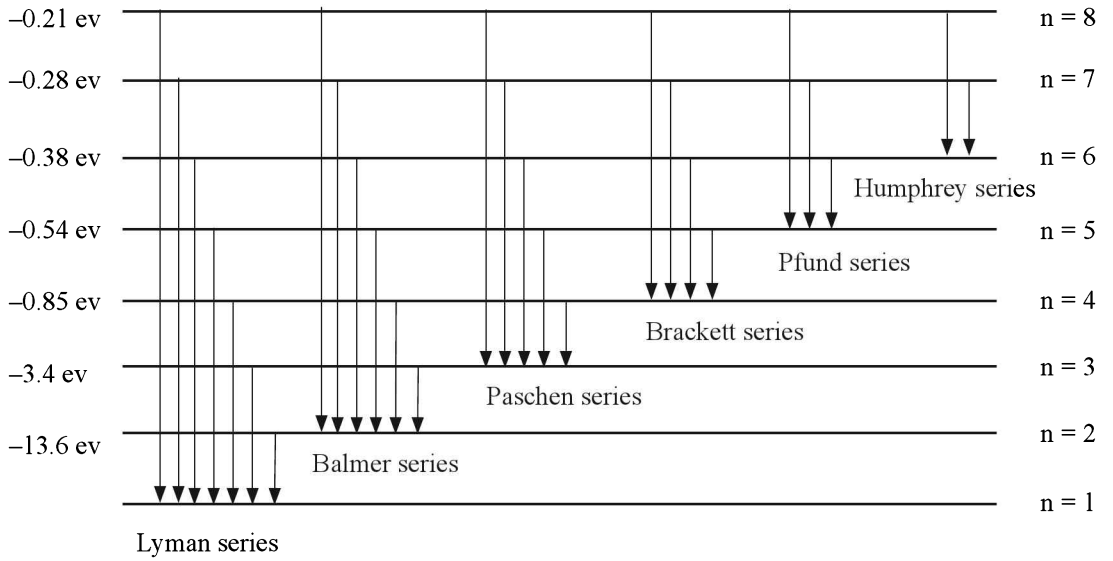
- It can not explain chemical bonding or why atoms combined together to form molecules.
- It can explain only particle nature that is, no explanation of wave nature. (that is, against de Broglie, Heisenberg's, Plank's theory etc.)

SPECTRUM OF HYDROGEN ATOM

The atoms of hydrogen in gas discharge tube emit radiations whose spectrum shows line characteristics (line spectra) and lies in the infra red, visible and ultraviolet region of the electromagnetic spectrum.

The most striking feature in hydrogen spectrum is that only some sharply defined discrete wavelength are observed in the emitted radiations.

Example, when a light of wavelength 6563 Å is observed and then light of wavelength 4861 Å is observed. Hydrogen atom do not emit any radiation between 6563 and 4861 Å.

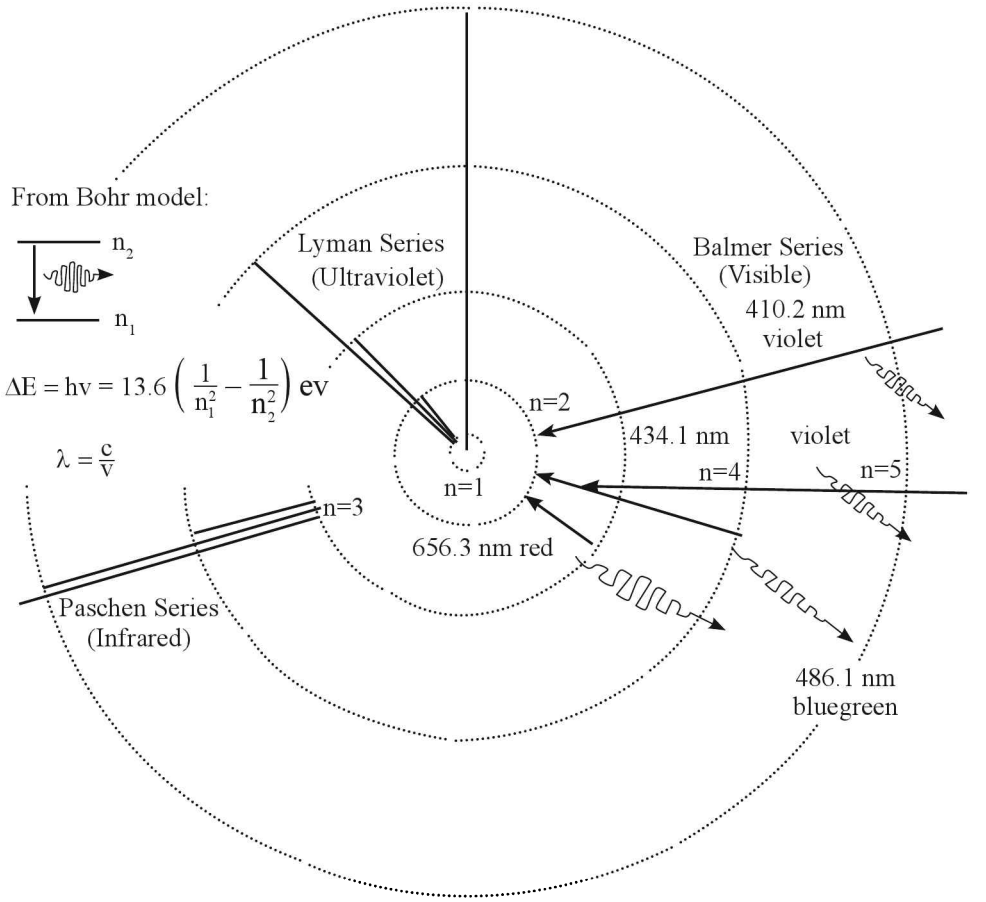


(ENERGY LEVEL DIAGRAM OF HYDROGEN SPECTRUM)

Hydrogen spectrum has following type of lines:-

	n_1	n_2	spectrum region	
Lyman	1	2,3,.∞	U.V	912–1216
Balmer	2	3,4,.∞	Visible	3646–6561
Paschen	3	4,5,.∞	Near Infra Red	8201–18746 A°
Bracket	4	5,6,.∞	FAR I.R	14580–40501 A°
Pfund	5	6,7,.∞	FAR I.R	22782–74588 A°
Humphries	6	7,8,.∞	FAR I.R	32822–123751 A°

Electronic transition	Name of line	Wave number	Wavelength	Colour
$n_2 = 3 \rightarrow n_1 = 2$ (M) (L)	H_α (First line)	$\bar{v} = 5R/36$	$\lambda = 6563$ Å	Red
$n_2 = 4 \rightarrow n_1 = 2$ (N) (L)	H_β (Second line)	$\bar{v} = 3R/16$	$\lambda = 4861$ Å	Blue
$n_2 = 5 \rightarrow n_1 = 2$ (O) (L)	H_γ (Third line)	$\bar{v} = 21R/100$	$\lambda = 4340$ Å	Indigo
$n_2 = 6 \rightarrow n_1 = 2$ (P) (L)	H_δ (Fourth line)	$\bar{v} = 8R/36$	$\lambda = 4102$ Å	Violet



Balmer Series in the Hydrogen Spectrum

Red	Blue-green	Indigo	Violet
6563	4861	4340	4102

Balmer series contains four important lines whose wavelengths are 6563Å, 4862 Å, 4341 Å and 4102 Å. These are called H_α, H_β, H_γ and H_δ lines.

To find Spectrum lines

Maximum number of lines obtained when an electron jumps from nth level to ground level is given as

$$\text{Number of spectrum lines} = \frac{n(n-1)}{2}$$

Example. When n is 5, number. of lines $= \frac{5\,(5-1)}{2}$

= 10 lines

Maximum number of lines obtained when an electron returns from n_2 to n_1 is given as

$$\text{No. of lines} = \frac{(n_2 - n_1)\ (n_2 - n_1 + 1)}{2}$$

E.g., when $n_2 = 5$ $n_1 = 2$

$$\text{lines} = \frac{(5-2)\ (5-2+1)}{2}$$

$$= \frac{3(4)}{2} = 6$$

Derivation of Rydberg Equation

$$\Delta E = \frac{hc}{\lambda} = \frac{2\pi^2 Me^4 Z^2}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

$$\bar{v} = \frac{1}{\lambda} = \frac{2\pi^2 Me^4 Z^2}{h^3 C}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

$$\text{If } R_H = \frac{2\pi^2 Me^4 Z^2}{h^3 C}.$$

$$\bar{v} = \frac{1}{\lambda} = R_H Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right).$$

$\bar{v}$ = wave number, λ = wavelength

n_1 = lower orbit, n_2 = higher orbit

R_H = Rydberg constant and its values are 109678 cm^{-1} or 1.1×10^7 m.

REMEMBER

- For longest wavelength or shortest energy or first line of a series, n_2 must be nearest (next value) to n_1. While for shortest wavelength or highest energy, n_2 must be infinite.
- The intensities of spectral line in a series decrease with the increase in the value of n_2.

Illustrations

12. Find out the wavelength of radiations emitted produced in a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom. ($R_H = 1.1 \times 10^7\ m^{-1}$)

Solution $\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

For Lyman series $n_1 = 1$, $n_2 = 4$

$\frac{1}{\lambda} = 1.1 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{4^2}\right)$.

$= 0.9696 \times 10^{-7}$ m.

13. Find out the wavelength of H_α line of hydrogen spectxrum in the Balmer series. ($R_H = 109676\ cm^{-1}$)

Solution $\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

For Balmer series $n_1 = 2$ and for H,

$n_2 = 3$ (first line of Balmer series)

$\frac{1}{\lambda} = 109676 \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$.

$= 109676\ (1/4 - 1/9)$

$= 109676 \times \frac{5}{36}\ cm^{-1}$

$= \frac{36}{5 \times 109676}$ cm

$= 65.65 \times 10^{-6}$ cm

$= 6564$ Å.

14. Calculate the wavelength and energy of the radiation emitted for the electronic transition from infinity (∞) to stationary state first of the hydrogen atom. ($R_H = 1.09678 \times 10^7\ m^{-1}$, $h = 6.6256 \times 10^{-34}$ J-s)

Solution $n_1 = 1, n_2 = \infty$

$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

$\frac{1}{\lambda} = 1.09678 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$.

$\lambda = 9.11 \times 10^{-8}$ m

$E = hv = h \times c/\lambda$

$(C = 3 \times 10^8\ m\ sec^{-1})$

$= \frac{6.6256 \times 10^{-34} \times 3 \times 10^8}{9.11 \times 10^{-8}}$

$= 2.18 \times 10^{-21}$ kJ.

15. Calculate (in kJ mol^{-1}) the energy necessary to remove an electron from the first shell of a hydrogen atom. Given: $R = 1.097 \times 10^{-2}\ nm^{-1}$.

Solution $n_1 = 1, n_2 = \infty$, $R = 1.097 \times 10^{-2}\ nm^{-1}$

$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

$= R \frac{(1}{1^2} - \frac{1^2)}{\infty^2}$

$= R\ (1/1)$

$= 1.097 \times 10^7$ m

so $\lambda = \frac{1}{1.097 \times 10^7} = 0.912 \times 10^{-7}$ m

$= 912$ Å

$E = \frac{hc}{\lambda} \times N_0$

$= \frac{6.626 \times 10^{-34} \times 10^8 \times 6.023 \times 10^{23}}{912 \times 10^{-10}}$

$= 1.31 \times 10^6\ J\ mol^{-1} = 1310$ kJ

16. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra. Given: $R_H = 1.1 \times 10^7\ m^{-1}$, $c = 3 \times 10^8\ m\ sec^{-1}$, $h = 6.62 \times 10^{-34}$ sec.

Solution Visible line spectrum nearly Balmer series that is,

$n_1 = 2$ and for minimum energy transition $n_2 = 3$.

As $\frac{1}{\lambda} = R_H Z \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

[as Z = 1]

So $\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$.

$= 1.1 \times 10^7 \frac{(1}{4} - \frac{1)}{9}$

$= 1.1 \times 10^7 \times \frac{5}{36} = 6.55 \times 10^{-7}$ metre

$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{6.55 \times 10}$

$= 3.034 \times 10^{-19}$ J

Suppose N_0 electrons show this transition in 1 g atom of H then

Energy released = $E \times N_0$

$= 3.034 \times 10^{-19} \times 6.023 \times 10^{23}$

$= 18.29 \times 10^4$ J

= 182.9 kJ.

17. Calculate the ionization energy in kJ per mole for the removal of the valence electron from a hydrogen atom. Compare your answer with the experimentally accepted value of 1312 kJ mol^{-1}.

Solution

Here $n_1 = 1, n_2 = \infty$

$R_H = 2.18 \times 10^{-21}$ kJ.

$\Delta E = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

$\Delta E = 2.18 \times 10^{-21} \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$.

$\Delta E = 2.18 \times 10^{-21}$ kJ per electron

As in one mole number of electrons = 6.02×10^{23}

So for 1 mole $\Delta E = 2.18 \times 10^{-21} \times 6.023 \times 10^{23}$

$= 1.31 \times 10^3$ kJ

= 1310 kJ

This value is nearly equal to accepted value 1312 kJ.

De Broglie Equation and Dual Nature Theory

■ De Broglie introduced dual nature theory for matter that is, for sub atomic particle (e^-, p, n). According to it, matter has both particle as well as wave nature. Wave nature of electron was confirmed by Devisson and Germer on diffraction pattern experiment on nickel surface like X-rays.

de Broglie used Einstein theory and Plank theory to give the following equation:

$E = mc^2$ for particle

$E = hv$ for wave

$E = \frac{hc}{\lambda}$

$\frac{hc}{\lambda} = mc^2$

$\frac{1}{\lambda} = \frac{mc^2}{hc}$

$\lambda = \frac{h}{mc}$.

If c = v.

$\lambda = \frac{h}{mv}$.

$\lambda = \frac{h}{p}$ (As p = mv)

$\lambda \propto \frac{1}{p}$ at constant temperature

■ If a particle has more mass or momentum, it has less wavenature. Heavy objects have less wave length due to more mass.

E.g., e > p > > n > > > … Cricket ball

Derivation of Bohr's postulate

According to de Broglie's equation

$\lambda = \frac{h}{mv}$.

As an electron in a circular path must have its path length (circumference = $2\pi r$) equal to an integral multiple of wavelength so

$2\pi r = n \cdot \lambda$

$2\pi r = n \cdot \frac{h}{mv}$.

$mvr = n \cdot \frac{h}{2\pi}$.

So angular momentum of an electron is simple multiple of $h/2\pi$.

Relation between Wave Length and Kinetic Energy

$$\lambda = \frac{h}{\sqrt{2\, m\, K.E}}$$

As K.E = ½ mv^2 = e.V potential difference

½ mv^2 = e.V

$v^2 = 2\frac{e.V}{m}$

$v = \sqrt{2e.V/m}$

So $\lambda = \frac{h}{\sqrt{2\, m\ e.V}}$

For electron:

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ Å}$$

For proton:

$$\lambda = \frac{0.286}{\sqrt{V}} \text{ Å}$$

For α - particles:

$$\lambda = \frac{0.101}{\sqrt{V}} \text{ Å}$$

Illustrations

18. Find the wavelength of a 150 g rubber ball moving with a velocity 50 m sec^{-1}. ($h = 6.62 \times 10^{-34}$ Js).

Solution $\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34}}{0.150 \times 50} = 8.82 \times 10^{-35}$ m

$= 8.82 \times 10^{-33}$ cm

19. Calculate the momentum of a moving particle which has a de Broglie wave length of 2 Å.

Solution According to de Broglie equation

$$\lambda = \frac{h}{p}$$

$$p = \frac{h}{\lambda}$$

$$= \frac{6.62 \times 10^{-34}}{2 \times 10^{-10}} = 3.31 \times 10^{-24} \text{ Kg ms}^{-1}$$

Heisenberg Uncertainty Principle

It is applicable only for sub atomic microscopic particles.

According to it, it is impossible to measure simultaneously and correctly both change in position and change in momentum that is, if one thing is certain another is uncertain. It is also called principle of indeterminancy.

$$\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \,.\, m.\Delta v \geq \frac{h}{4\pi}$$

Here Δx = uncertainty in position

Δv = uncertainty in velocity

$$\Delta x \,.\, \Delta v \geq \frac{h}{4\pi m}$$

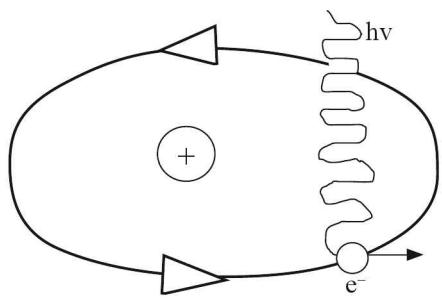
$$\Delta E \,.\, \Delta t \geq \frac{h}{4\pi}$$

here ΔE = change in energy

Δt = change in time

- If change in position is zero change in momentum will be infinite and vice versa.
- It applies when both Δx and ΔP are along with the same axis.
- In case of larger objects, the value of uncertainty principle is negligible if the position is known quite accurately (Δx is very small) there will be great uncertainty in the velocity (ΔV is very large)

An e^- cannot exist within the nucleus as using this principle ΔV is 5.8×10^{10} m/sec that is 200 time of velocity of light which is not possible.



Illustrations

20. Calculate the uncertainty in position of an electron whose velocity is 3.0×10^4 cm s^{-1} accurate upto 0.001 %. Mass of an electron = 9.1×10^{-28} g.

Solution $\Delta v = \frac{0.001}{100} \times 3.0 \times 10^4$ cm s^{-1}

$= 0.3$ cm s^{-1}

As $\Delta x = \frac{h}{4\pi (m\Delta v)}$.

$$= \frac{6.626 \times 10^{-27} \text{ erg s}}{4 \times 3.14 \times 9.1 \times 10^{-28} \text{ g} \times 0.3 \text{ cm s}^{-1}} .$$

$= 1.92$ cm (As erg = g cm^2 s^{-2})

21. A cricket ball weighing 100 g is to be located with 0.1 Å. What is the uncertainty in its velocity?

Solution $\Delta x \cdot m \Delta v = \frac{h}{4\pi}$

Δx = Location of ball= $0.1 Å = 0.1 \times 10^{-10}$ m

m = Mass of ball = 100 g = 0.1 kg

Δv = Uncertainty in velocity

$h = 6.626 \times 10^{-34}$ Js

$$0.1 \times 10^{-10} \times 0.1 \times \Delta v = \frac{6.626 \times 10^{-34}}{4 \times 3.14}$$

$\Delta v = 0.527 \times 10^{-22}$ ms^{-1}

Concept of Probability

As the position and momentum of an electron can not be found accurately at a particular time so the idea of definite orbits (sharply defined path) as suggested by Bohr has no meaning now for a moving electron in an atom. Hence the concept of probability was developed.

According to it, it is possible to predict or state the probability on locating an electron of a particular energy in a given region of space around the nucleus at a given time. This leads the concept of orbital.

Schrodinger Wave Equation

Schrodinger set up a mathematical model for hydrogen atom. This theory was based upon these two evidences:

(i) The probability or statistical character

(ii) The wave nature of an electron

The schrodinger's wave equation plains three dimensional wave nature of electron as follows

$$\frac{\delta^2\psi}{\delta X^2} + \frac{\delta^2\psi}{\delta Y^2} + \frac{\delta^2\psi}{\delta Z^2} + \frac{8\pi^2 m}{h^2}[E - V]\psi = 0$$

$$\bar{v}^2\psi + \frac{8\pi^2 m}{h^2}[E - V]\psi = 0$$

Here X, Y, Z are three co-ordinate axis, E is total energy, V is potential energy ($V = -Ze^2/r$),m is mass of electron wave and $v^2\psi$ is laplation operature.

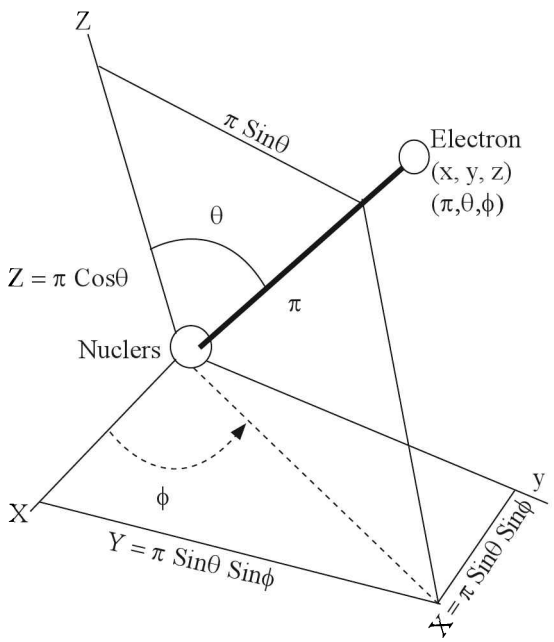
This equation possesses a number of solutions each corresponding to a discrete energy state and specified by the values of three quantum numbers n, l, m. The solutions have significance for certain definite values of total energy 'E'. These values are known as Eigon values and for an atom these values correspond to discrete sets of energy values postulated by the Bohr's theory.

Significance of ψ and ψ²

ψ: It has no physical significance. It represent amplitude of electron wave or boundary surface of an orbital.

ψ²: It is probable electron density or It is probability of finding electron in any region (3 dimensional around the nucleus). If ψ^2 is positive electron are present and if ψ^2 is zero electrons are absent.

- An orbital is represented by ψ ψ^* or ψ^2 for showing electron density.
- The probability of finding electron at a distance r from the nucleus in the region dr is given by $4\pi r^2 dr \psi^*$.



- Schrodinger gave another equation when energy of an atom or molecule does not change which is written as

$$\hat{H}\psi = E\psi$$

$$\hat{H} = \left[\frac{-h^2}{8\pi^2 m}\bar{v}^2 + \hat{v}\right]$$

$$\text{As} \quad \hat{H} = \hat{T} + \hat{V}$$

$$\text{So} \quad (\hat{T} + \hat{V})_{\psi} = E\,\psi$$

Here H = Hamiltonion factor

V = Potential energy

T = Kinetic energy

E = Total energy

Orbital

It is the three dimensional region of high electron density that is high probable electron density region having different shapes around the nucleus.

- The probability of finding an electron in any orbital is more than 90 per cent.
- An orbital is a mathematical function of the three co-ordinate r, θ and ϕ. which can be factorized into 3-separate parts each of which is a function of only one co-ordinate as follows

$$\psi(r, \theta, \phi) = R(r) \ominus(\theta)\ \phi\ \varphi$$

Here:

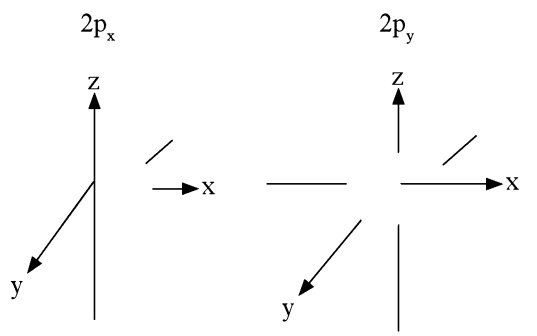
R (r): Radial function which depends upon n, l value and it shows dependence of an orbital upon distance r of electron from nucleus.

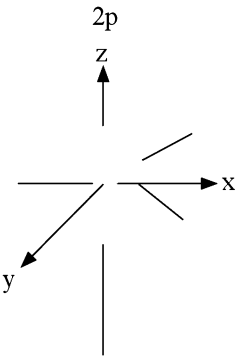
$\ominus(\theta)$ and ϕ (φ): It is angular function depending upon l, m values. It shows angular dependence of orbital on θ and ϕ respectively.

that is.

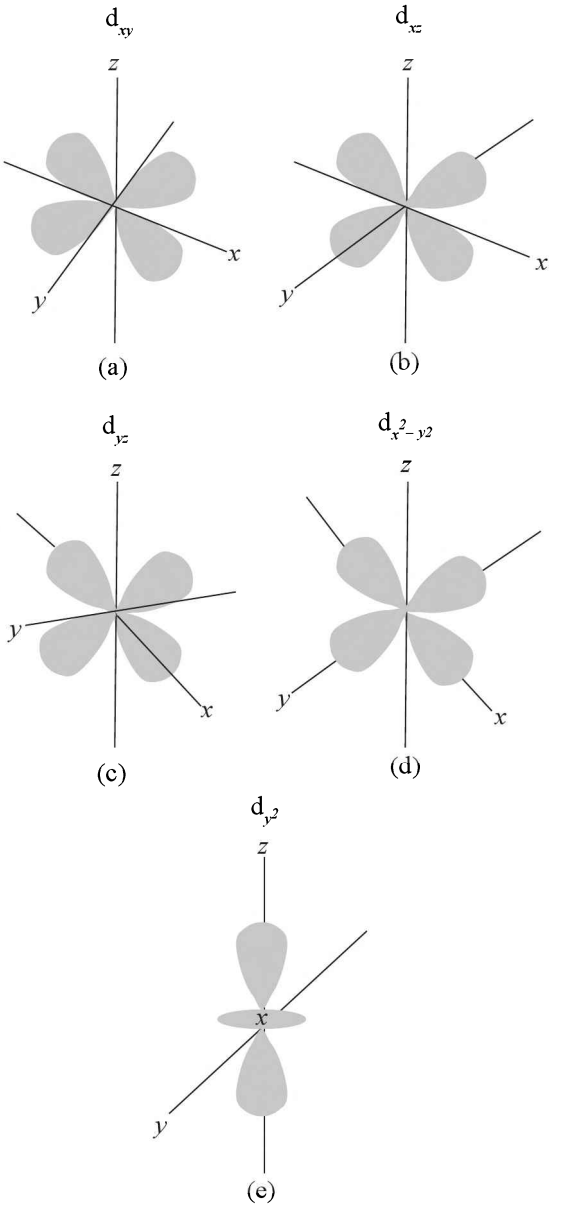
$$\psi_{n,l,m}(r, \theta, \phi) = \underset{\text{radial part}}{r_{n,l}} \cdot \underset{\text{angular part}}{\theta_{lm}\,\phi_m}\ \varphi$$

Shape of Orbitals





Boundry surface diagrams of the three 2p orbitals.



Some Facts about Orbitals

- Orbital represents both particle and wave nature of electron.
- It is directional in nature (except s-orbital).
- Any orbital can have maximum two electrons and these electrons are with opposite or antiparallel spin.
- dz^2 orbital has only two lobes lying along with z axis and a drought on x and y axis. It's shape is baby schooter type.
- In dx^2y^2 all the four lobes are lying along with molecular axis that is, x and y.

Degenerate Orbital

Orbitals with same value of n and of same sub shell are degenerate orbitals.

Example.,– 2px, 2py, 2pz

3dxy, 3dyz, 3dxz.

Radial Probability Distribution Function

- It is the probability of finding electrons in the region between r and dr δr. It is given by $4\pi r^2 \psi^2$ δr. It is directional independent.

Here r = radius or distance from nucleus

δr = thickness

Node

It is zero electron density region.

$\psi^2 = 0$

Radial Node

It is region between two successive 's' orbitals.

Nodal Point

It is a point where two lobes are joint and electron density is zero here.

Nodal Planes

It is plane by which two lobes are separated and electron density is zero here.

- Any s-orbital has no nodal plane or point.
- px, py, pz, dz^2 orbitals have one nodal plane or point.
- Rest of d-orbitals (dxy, dyz, dxz, $dx^2 - y^2$) have two nodal plane or points.

Calculation of Nodes

Node = n – 1

Radial nodes or spherical nodes = $n - l - 1$

Angular or non-spherical = l

Example, **1s**: Node = 1 –1 = 0

Example, **2s**: Node = 2 –1 = 1

Angular node = 0

Radial node = 2 – 0 – 1 = 1

Example, **3s**: Node = 3 –1 = 2

Angular node = 0

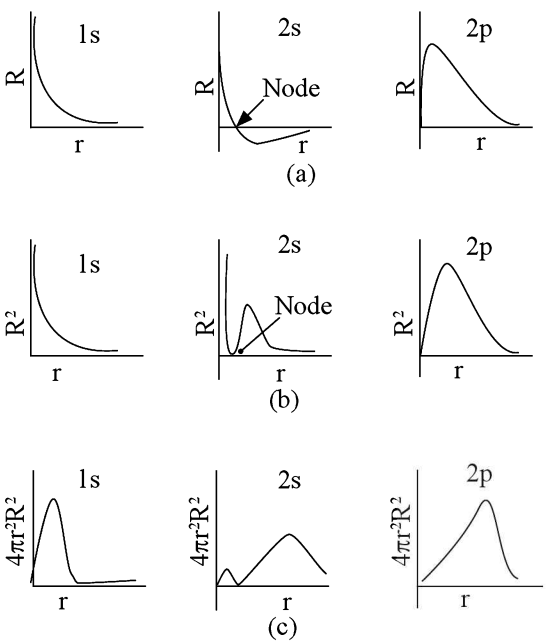
Radial node = 3 – 0 – 1 = 2

Example, **4d**: Node = 4 –1 = 3

Angular node = 0

Radial node = 4 – 0 – 1 = 3

Various Probability Curves



The plots of (a) the radial wave function R; (b) the radial probability density R^2 and (c) the radial density function $4\pi r^2R^2$ as a function of distance r of the electron from the nucleus for 1s, 2s and 2p orbitals. The plots are not drawn to scale.

QUANTUM NUMBERS

These are set of four numbers use to address electron as follows:

(i) To determine size, distance from nucleus and energy of electron in orbit.

(ii) To decide shape, energy of electron in sub orbit.

(iii) To find number of orbitals and their directional position or orientation in space.

(iv) To find number of electrons and their spin.

Principle Quantum Number

It was introduced by Bohr and It is denoted by 'n' It determines:

- Size of orbit (shell)
- Distance of orbit from nucleus
- Energy of electron in an orbit.
- Maximum number of electron in any orbit
- Angular momentum of electron in an orbit

$mvr = \frac{nh}{2} = n\hbar$

mvr = angular momentum in orbit.

h = plank's constant

Values of n = 1, 2 ,3, 4 …… ∞

n ≠ 0, –ve, fractional

Azimuthal or Secondary or Angular Momentum Quantum Number

It was introduced by Sommerfield and denoted by 'l'.

It determines shape of sub orbit, energy in sub shell and angular momentum of an electron in any orbital

Angular momentum of an electron in any orbital is given as:

$mvr = \sqrt{l(l+1)}\ \frac{h}{2\pi}$ or $\hbar$

Example, For any s orbital e^- (mvr) = 0 (as l = 0)

For any p orbital e^- (mvr) = $\sqrt{1(1+1)}\ \hbar$

= $\sqrt{2}\hbar$

For any d orbital e^- (mvr) = $\sqrt{2\ (2+1)}\ \hbar$

= $\sqrt{6}\hbar$

For any f orbital e^- (mvr) = $\sqrt{3\ (3+1)}\ \hbar$

= $\sqrt{12}\hbar$

It explains the existence so many closely packed spectrum lines in hydrogen spectrum.

- **Values of l** = 0 to n – 1

Example,

n :	1	2	3	4
l :	0	0, 1	0,1,2	0,1,2,3

l-value:	0	1	2	3	4
suborbit	s	p	d	f	g

Magnetic Quantum Number

It was introduced by Land and Zeeman and is denoted by m.

It determines:

1. Number of orbitals = total m values = n^2 (when n is given)

   = 2l +1 when 'l' is given.

   Example,– when n = 2

   m (total) = $2^2 = 4$

   when l = 2

   m (total) = 2 × 2 + 1 = 5

2. Directional position of orbitals or orientation in shape and Zeemann effect.

3. Angular magnetic momentum

   $mvr = m\frac{h}{2} = m\hbar$

   Values of m = –l to +1 including zero.

   Example, l=0, m=0

   l=1, m=–1, 0, +1

   l=2, m=–2, –1, 0, +1, +2

Spin Quantum Number

It was introduced by Uhlen back and Goud Smith. It is the intrinsic angular momentum measurement which is used to differentiate between two electrons in an orbital that is, it explains the fine structure of the spectral lines within atomic levels.

Spin angular momentum is given as:

$mvr = \sqrt{s\ (s+1)}\ \frac{h}{2\pi}$ or $\hbar$

The electron in an atom rotates not only around the nucleus but also rotates around its on axis and this rotation is called spin of the electron.

- For each value of m, s has two different values + ½ and – ½.

+ ½	– ½
α – spin	β – spin

- + ½ and – ½ are just to mechanical spin states with no classical importance now as other spin states are also possible. (Bosons and fermions)

Values of s

Total values of 's' or total number of electrons = 2m = $2n^2 = 2(l + 1)$

- Schrodinger cannot explain spin of electron and spin quantum number.

REMEMBER

Orbital	Orbital function
1s	$\frac{1}{\sqrt{\pi}} a_o^{-3/2} e^{-P}$
2s	$\frac{1}{4\sqrt{\pi}} a_o^{-3/2} (2-P) e^{-P/2}$
$2p_z$	$\frac{1}{4\sqrt{\pi}} a_o^{-3/2} Pe^{-P/2} \cos\phi$
$2p_x$	$\frac{1}{4\sqrt{\pi}} a_o^{-3/2} Pe^{-P/2} \sin\theta \cos\phi$
$2p_y$	$\frac{1}{4\sqrt{\pi}} a_o^{-3/2} e^{-P/2} \sin\theta \sin\theta$

Illustration

22. Write the suitable combinations of quantum numbers for each of the following electrons:

(a) A 4s electron

(b) A 3p electron

(c) A 5f electron

(d) A 5d electron

Solution (a) 4s, n = 4; l = 0; $m_l = 0$; $m_s = \pm ½$

(b) 3p, n = 3; l = 1; $m_l = -1, 0, +1$; $m_s = \pm ½$

(c) 5f, n = 5; l = 3; $m_l = -3, -2, -1, 0, +1, +2, +3$; $m_s = \pm ½$

(d) 5d, n = 5; l = 2; $m_l = -2, -1, 0, +1, +2$; $m_s = \pm ½$

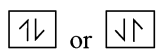
Electronic Configuration

It represents the distribution of electrons in various orbits, sub-orbits and orbitals in order to understand electronic behaviour. For the filling of electrons in various orbitals following three rules are considered.

Pauli Exclusion Principle

It has following two statements:

1. Any orbital can have maximum two electrons and these electrons must have opposite or anti-parallel spin.

 or

2. No two electrons of an atom can have a same set of all the four quantum numbers. If n, l, m are same 's' is definitely different.

E.g.,

$_{12}Mg \rightarrow 1s^2, 2s^2, 2p^6, 3s^2$

	n	l	m	s
for 11^{th} $e^- \rightarrow$	3	0	0	+ ½
for 12^{th} $e^- \rightarrow$	3	0	0	– ½

Uses of Pauli's Law

To find maximum number of electrons in any orbit, sub orbit and orbital as follows

(i) Orbit: Maximum number of electrons = $2n^2$

n = 1 for K $e^- = 2 \times 1^2 = 2e^-$

n = 2 for L $e^- = 2 \times 2^2 = 8e^-$

n = 3 for M $e^- = 2 \times 3^2 = 18\ e^-$

(ii) In Sub orbit :

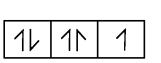
s	p	d	f	g
2	6	10	14	18

(iii) Orbital : Maximum two electrons are possible in any orbital.

E.g., p_x, p_y, p_z, d_z^2

Violation of Paulis Law

When electronic spin is same in any degenerate orbital the law is violated.



Example,

It is also violated when electrons are filled even after a maximum limit example. $1s^7$ configuration for nitrogen cannot be written because in 1st orbit only Max $2e^-$ can exit and any s-subshell can have two electrons.

Aufbau's Principle: It is a German word which means to build so it is also called building up rule. It states that as protons are added one by one to the nucleus to build by elements, electrons are similarly added to (n+ *l*) rule.

(n + l) Rule

According to it electrons are filled in different orbitals from lower (n +*l*) value orbital to higher (n + *l*) value orbital as follows:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s ,< 4f< 5d< 6p<7s<5f<6d

Increasing order of n + l value or energy.

In case (n + l) value is same Electron is filled first in orbital with lower value of n.

Example, 3p, 4s
n = 3 n = 4

In case of Hydrogenic species energy depends only upon 'n'-value

So Is <2s = 2p < 3s = 3p = 3d <

To Write Electronic Configuration

- First fill electrons in orbital according to (n + l) rule (initial configuration).
- If atomic number is > 20 arrange the orbitals/sub-orbits in the increasing order of n-value (for final configuration).

Example, $_{26}Fe$

$1s^2, 2s^2\ 2p^6\ 3s^2\ 3p^6, 4s^2, 3d^6$

$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^6, 4s^2$

(final configuration)

S.No.	Elements	Symbol	Atomic number	Electronic configuration
1	Hydrogen	H	1	$1s^1$
2	Helium	He	2	$1s^2$
3	Lithium	Li	3	$1s^2, 2s^1$
4	Beryllium	Be	4	$1s^2, 2s^2$
5	Boron	B	5	$1s^2, 2s^2\ 2p^1$
6	Carbon	C	6	$1s^2, 2s^2\ 2p^2$
7	Nitrogen	N	7	$1s^2, 2s^2\ 2p^3$
8	Oxygen	O	8	$1s^2, 2s^2\ 2p^4$
9	Fluorine	F	9	$1s^2, 2s^2\ 2p^5$
10	Neon	Ne	10	$1s^2, 2s^2\ 2p^6$
11	Sodium	Na	11	$1s^2, 2s^2\ 2p^6, 3s^1$
12	Magnesium	Mg	12	$1s^2, 2s^2\ 2p^6, 3s^2$
13	Aluminium	Al	13	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^1$
14.	Silicon	Si	14	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^2$
15.	Phosphorous	P	15	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^3$

S.No.	Elements	Symbol	Atomic number	Electronic configuration
16	Sulphur	S	16	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^4$
17	Chlorine	Cl	17	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^5$
18	Argon	Ar	18	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6$
19	Potassium	K	19	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6, 4s^1$
20	Calcium	Ca	20	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6, 4s^2$
21	Scandium	Sc	21	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^1, 4s^2$
22	Titanium	Ti	22	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^2, 4s^2$
23	Vanadium	V	23	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^3, 4s^2$
24	Chromium	Cr	24	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^1$
25	Manganese	Mn	25	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^5, 4s^2$
26	Iron	Fe	26	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^6, 4s^2$
27	Cobalt	Co	27	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^7, 4s^2$
28	Nickel	Ni	28	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^8, 4s^2$
29	Copper	Cu	29	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$
30	Zinc	Zn	30	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2$
31	Gallium	Ga	31	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^1$
32	Germanium	Ge	32	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^2$
33	Arsenic	As	33	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^3$
34	Selenium	Se	34	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^4$
35	Bromine	Br	35	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^5$
36	Krypton	Kr	36	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^2\ 4p^6$

Some Exceptional Configurations

In case of fully filled and half filled orbitals, stability is more due to more exchanges, exchange energy and symmetry. ($d^5 > d^4$ and $d^{10} > d^9$)

Exchange Energy

It is defined as the amount of energy needed to exchange the positions of electrons having same spin. Hence every exchange decreases the energy of the system and provides the stability to the system. Let each exchange associates with energy A so total decrease in energy of the system = $\Delta E = N \times A$. Here N = Total number of exchanges.

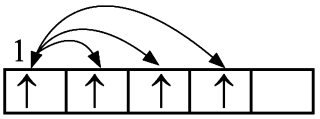
$$N = \frac{r!}{2(r-2)!} + \frac{s!}{2(s-2)} .$$

Here

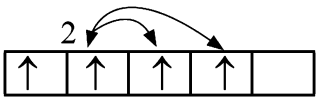
r = Number of electrons having clockwise direction

s = Number of electrons anticlockwise direction

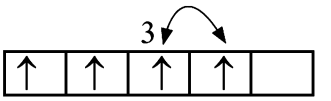
The number of exchanges that can take place in d^4 configuration are as follows:



3 EXCHANGES BY ELECTRON 1



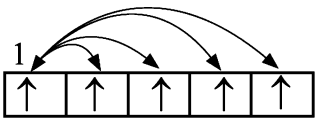
2 EXCHANGES BY ELECTRON 2



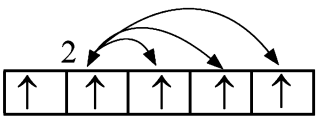
1 EXCHANGES BY ELECTRON 1

Total number of exchanges = 3 + 2 + 1 = 6

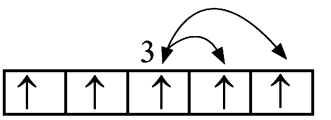
The number of exchanges that can take plece in d^5 configuration are as follows:



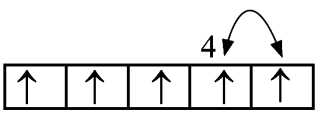
4 EXCHANGES BY ELECTRON 1



3 EXCHANGES BY ELECTRON 2



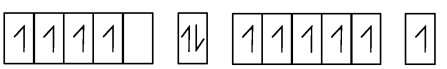
2 EXCHANGES BY ELECTRON 3



1 EXCHANGES BY ELECTRON 4

Total number of exchanges = 4 + 3 + 2 + 1 = 10

Case I:



$(n-1)d^4, ns^2$: $(n-1)d^5, ns^1$

incomplete d-orbital so Less stable

both orbitals are half filled so more stable.

Example–

$_{24}Cr$: $[_{18}Ar]\ 3d^4\ 4s^2$ [X]

$[_{18}Ar]\ 3d^5\ 4s^1$ [√]

Case II:

$(n-1)\ d^9\ ns^2$: $(n-1)\ d^{10}\ ns^1$

incomplete d-orbital so less stable

full filled more stable half filled

Example–

$_{29}Cu$: $[_{18}Ar]\ 3d^9, 4s^2$ [X]

$_{29}Cu$: $[_{18}Ar]\ 3d^{10}, 4s^1$ [√]

Some Other Exceptional onfigurations

$_{41}Nb$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^4\ 5s^1$

$_{42}Mo$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^5\ 5s^1$

$_{44}Ru$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

$4p^6\ 4d^7\ 5s^1$

or

$[Kr]\ 4d^7\ 5s^1$

$_{45}Rh$: $[Kr]\ 4d^8\ 5s^1$

$_{46}Pd$: $[Kr]\ 4d^{10}\ 5s^0$

$_{47}Ag$: $[Kr]\ 4d^{10}\ 5s^1$

$_{57}La$: $[Xe]\ 4f^0\ 5d^1\ 6s^2$

$_{58}Ce$: $[Xe]\ 4f^2\ 5d^0\ 6s^2$

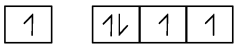
$_{61}Pm$: $[Xe]\ 4f^5\ 5d^0\ 6s^2$

$_{78}Pt$: $[Xe]\ 4f^{14}\ 5d^9\ 6s^1$

$_{79}Au$: $[Xe]\ 4f^{14}\ 5d^{10}\ 6s^1$

These exceptions are mainly because of interaction between nucleus and valence electron.

Violation of Aufbau Rule

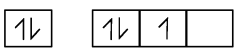


As in p-subshell electrons can be filled after completing the maximum limit of electrons in s-subshell.

Hund's Rule of Maximum Multiplicity

According to it, "In degenerate orbitals, electron are filled in such a way so that maximum stability and multiplicity can be obtained for it first each degenerate orbital is singly occupied than pairing of electron takes place", or, The most stable arrangement of electrons in sub-orbits is the one with the greatest number of parallel spins.

Hund's Violation



pairing empty degenerateorbital

Uses:

- To write the correct and stable electronic configuration

  Example,

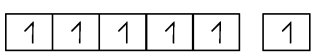
  $_{24}Cr$: [Ar] $3d^4\ 4s^2$ [X]

  [Ar] $3d^5\ 4s^1$

- To find number of unpaired electrons (n)

  Example,

  $_{24}Cr$: [Ar] $3d^5\ 4s^1$

  $3d^5$ $4s^1$

  n = 6

- To find multiplicity (m) :

  $m = (n + 1) = (2s + 1), \quad (s = \frac{n}{2})$

  Example–

  $_{24}Cr$: [$_{18}Ar$] $3d^5\ 4s^1$

  m = 6 + 1 = 7

- Number of spins = n/2 = 6 /2 = 3.
- To find magnetic nature and magnetic moment:

  n = 0 diamagnetic

  n = 1, 2 ,3 paramagnetic

  n = 4, 5, 6 ferromagnetic or highly paramagnetic

  magnetic moment (μ) = $\sqrt{n(n+2)}$ B. M

  B.M. = Bohr magneton

To Find Colour

- If n = 0 ion is colourless

  Example.,– Cu^+, Zn^{+2}, Cd^{+2}

- If n = 1, 2, 3 ion is coloured

  Example, Cu^{+2} , Fe^{+2}, Fe^{+3}

Configuration	n	μ in B.M	spin	examples
d^1 or d^9	1	$\sqrt{3}$	1/2	Cu^{2+}, Sc^{+2}
d^2 or d^8	2	$\sqrt{8}$	1	Ti, Ti^{+2}, Ni, Ni^{2+}
d^3 or d^7	3	$\sqrt{15}$	3/2	V, V^{+2}, Co, Co^{+2}, Cr^{+3}
d^4	4	$\sqrt{24}$	2	fe, fe^{+2}, Cr^{2+}
d^5	5	$\sqrt{35}$	5/2	mn, fe^{3+},mn^{2+}

Illustration

23. A compound of Nickel has a magnetic moment of 2.79 BM. Write the electronic configuration of the chromium ion in this compound.

Solution As $\mu = \sqrt{n(n+2)}$

$2.79 = \sqrt{n(n+2)}$

On solving,

n = 2

As there are two unpaired electrons so Ni is in Ni^{2+} state. Hence its configuration is written as

$_{28}Ni^{2+}$: [Ar] $3d^8$

Enhance Your Knowledge

- The radius, r of the nucleus of an atom is related to its mass number(A) according to the equation

  $r = R_0 A^{1/3}$

  where R_0 is a constant having value

  $= 1.4 \times 10^{-15}$ m.

- The shapes of the seven f-orbtials are complicated but their designations are as follows.

  $f x^3$, $f y^3$, $f z^3$, $fx(z^2 - y^2)$, $fy(z^2 - x^2)$,

  $fz(y^2 - x^2)$, $fxyz$.

- These are not possible $n \neq l$, $n \not< l$, $m \not> l$. If any of these is not obeyed arrangement of quantum numbers set is not permissible.
- Since l can not be equal to n so orbitals

  1p, 2d, 3f, 4g do not exist.

Solved Problems from the IITs

1. Calculate the wavelength in Angstroms of the photon that is emitted when an electron in Bohr orbit n = 2 returns to the orbit n = 1 in the hydrogen atom. The ionization potential of the ground state of hydrogen atom is 2.17×10^{-11} erg per atom.

[*IIT 1982*]

Solution Ionization potential of the ground state of hydrogen atom is 2.17×10^{-11} erg.

$$E_1 = -2.17 \times 10^{-11} \text{ erg}$$

$$E_2 = \frac{-2.17 \times 10^{-11} \text{ erg}}{2^2}$$

$$E_2 = -0.5425 \times 10^{-11} \text{ erg}$$

$$E_2 - E_1 = 1.6275 \times 10^{-11} \text{ erg}$$

$$E_2 - E_1 = h\nu = hc/\lambda$$

$$\lambda = \frac{hc}{E_2 - E_1}$$

$$= \frac{6.626 \times 10^{-27} \times 3 \times 10^8}{1.6275 \times 10^{-11}}$$

$$= 1221 \times 10^{-10} \text{ m} = 1221 \text{ Å}$$

2. According to Bohr's theory, the electronic energy of the hydrogen atom in the nth Bohr's orbit is given by

$$E_n = -\frac{21.76 \times 10^{-19} \text{ J}}{n^2}$$

Calculate the longest wavelength of light that will be needed to remove an electron from the third orbit of the He^+ ion.

[*IIT 1990*]

Solution The electronic energy of He^+ ion in the nth Bohr orbit

$$= -\frac{21.76 \times 10^{-19} \times Z^2 \text{ J}}{n^2}$$

Here Z = 2

So energy of He^+ in the third Bohr orbit

$$= -\frac{21.76 \times 10^{-19} \times 4 \text{ J}}{9}$$

$$\Delta E = E_\infty - E_3$$

$$= 0 - \frac{[-21.76 \times 10^{-19} \times 4]}{9}$$

$$= \frac{21.76 \times 10^{-19} \times 4}{9}$$

As $\lambda = \frac{hc}{\Delta E}$

$$= \frac{6.625 \times 10^{-34} \times 3 \times 10^8 \times 9}{21.76 \times 10^{-19} \times 4}$$

$$= 2.055 \times 10^{-7} \text{ m}$$

3. Estimate the difference in energy between the first and second Bohr orbit for hydrogen atom. At what minimum atomic number would a transition from n = 2 to n = 1 energy level result in the emission of X-rays with $\lambda = 3.0 \times 10^{-8}$ m? Which hydrogen like species does this atomic number correspond to?

[*IIT 1993*]

Solution $\Delta E = h\nu = \frac{h \cdot c}{\lambda}$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = R.h.c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$\Delta E = h \cdot c \cdot \frac{3}{4} R$

$= \frac{6.625 \times 10^{-34} \times 3 \times 10^{8} \times 1.09678 \times 10^{7} \times 3}{4}$

$= 1.635 \times 10^{-18}$ J

For hydrogen like species

$\Delta E = Z^2 R.h.c \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$\frac{1}{3.0 \times 10^{-8}} = Z^2 \times 1.09678 \times 10^{7} \times \frac{[1}{1^2} - \frac{1]}{2^2}$

$Z^2 = \frac{4}{3 \times 10^{-8} \times 1.09678 \times 10^{7} \times 3} = 4$

$Z = 2$

Hence the species is He^+.

4. The dipole moment of KCl is 3.336×10^{-29} coulomb meter which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

[*IIT 1993*]

Solution Dipole moment

$\mu = e \times d$ coulombs meter

For KCl $d = 2.6 \times 10^{-10}$ m

For complete separation of unit charge (electronic charge),

$e = 1.602 \times 10^{-19}$ C

Hence

$\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

$= 4.1652 \times 10^{-29}$ cm

μ (KCl) $= 3.336 \times 10^{-29}$ cm

Percent ionic character of KCl

$= \frac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100$

$= 80.09\ \%$

5. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He^+ spectrum?

[*IIT 1993*]

Solution For He^+,

$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{2^2} - \frac{1}{4^2}\right)$.

For H,

$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

Since λ is same

$Z^2 [1/2^2 - 1/4^2] = [1/n_1^2 - 1/n_2^2]$

$Z = 2$

$[1/1^2 - 1/2^2] = [1/n_1^2 - 1/n_2^2]$

n = 1 and n = 2.

6. Find the number of waves made by a Bohr electron in one complete revolution in the 3rd orbit.

[*IIT 1994*]

Solution Velocity of the electron in 3rd orbit $= \frac{3h}{2\pi mr}$

Here m = mass of electron

r = radius of 3rd orbit

According to de Broglie equation

$\lambda = \frac{h}{mv} = \frac{h}{m} \times \frac{2\pi mr}{3h} = \frac{2\pi r}{3}$

Number of waves $= \frac{2\pi r}{\lambda}$

$= \frac{2\pi r}{2\pi r} \times 3 = 3$

7. A bulb emits light of λ 4500 Å. The bulb is rated as 150 watt and 8 per cent of the energy is emitted as light. How many photons are emitted by the bulb per second?

[*IIT 1995*]

Solution Energy of one photon $= \frac{hc}{\lambda}$

$= \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}\ J}{4500 \times 10^{-10}}$

$= 4.42 \times 10^{-19}$ J

Energy emitted by the bulb $= 150 \times \frac{8}{100}$ J

$n \times 4.42 \times 10^{-19} = 150 \times \frac{8}{100}$

$n = 27.2 \times 10^{18}$

8. Iodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. (bond energy of I_2 = 240 kJ mol^{-1}).

[*IIT 1995*]

Solution Energy used for breaking up I_2 molecule

= bond energy of I_2 = 240 kJ mol^{-1}

$= 240 \times 10^3$ J mol^{-1}

$= \frac{240 \times 10^3}{6.023 \times 10^{23}}$ J $molecule^{-1}$

$= 3.984 \times 10^{-19}$ J $molecule^{-1}$

Energy absorbed by I_2 molecule $= \frac{hc}{\lambda}$

$= \frac{6.626 \times 10^{-34}\ Js \times 3 \times 10^8\ ms^{-1}}{4500 \times 10^{10}\ m}$

$= 4.417 \times 10^{-19}$ J

Energy used in imparting kinetic energy to one I_2 molecule

1. $= 4.417 \times 10^{-19} - 3.984 \times 10^{-19}$ J $= 4.33 \times 10^{-20}$ J

Energy used in imparting kinetic energy to each iodine atom

$= \frac{4.33 \times 10^{-20}}{2} = 2.165 \times 10^{-20}$ J

9. Consider the hydrogen atom to be a proton embedded in a cavity of radius a_0 (Bohr's radius), whose charge is neutralized by the addition of an electron to the cavity in vacuum, infinitely slowly.

(a) Estimate the average of total energy of an electron in its ground state in a hydrogen atom as the work done in the above neutralization process. Also if the magnitude of the average kinetic energy is half the magnitude of the average potential energy, find the average potential energy.

(b) Also derive the wavelength of the electron when it is a_0 from the proton. How does this compare with the wavelength of an electron in the ground state Bohr's orbit?

[*IIT 1996*]

Solution (a) Work done in bringing the electron from a to a_0 is given by

$$W = -\frac{e^2}{4\pi\varepsilon_0 a_0^2}$$

It is equal to total energy. As in the problem the kinetic energy at this condition is assumed to be zero so it will be equal to potential energy.

that is, Total energy = P.E. + K.E.

$$= \text{P.E.} = -\frac{e^2}{4\pi\varepsilon_0 a_0}$$

Now as the electron is to be captured by the proton to form ground state H-atom. There must be kinetic energy also which is half of the potential energy assume in this problem

that is, $(e^2/8\pi\varepsilon_0 a_0)$

Hence total energy = P.E. + K. E

$$= -\frac{e^2}{4\pi\varepsilon_0 a_0} + \frac{e^2}{8\pi\varepsilon_0 a_0}$$

$$= -\frac{e^2}{8\pi\varepsilon_0 a_0}$$

(b) Wavelength $(\lambda) = \frac{h}{p} = \frac{h}{mv}$ ... (i)

As K.E. $= \frac{1}{2}mv^2$ ....(ii)

$v = \frac{m}{p}$ ... (iii)

From these equation (i), (ii) and (iii)

$$\lambda = \frac{h}{\sqrt{(2\ m.\ K.E.)}}$$

As K.E. = 0 at this situation, so $\lambda = \infty$

When electron is at a distance a_0 in Bohr's orbit of H atom wave length is as follows:

$$\lambda = \frac{h}{\sqrt{(2\ m.\ K.E.)}}$$

$$= \frac{h}{\sqrt{(2me^2/8\pi\varepsilon_0 a_0)}}$$

$$\lambda = \frac{h}{\sqrt{(e^2\ m/4\pi\varepsilon_0 a_0)}}$$

10. Calculate the wavelength for the shortest wave length transition in the Balmer series of atomic hydrogen.

[*IIT 1996*]

Solution $\bar{V} = \frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$.

$= 109677\ (1/4 - 0) = \frac{109677}{4}$

$= 27419.25\ cm^{-1}$

11. A compound of vanadium has a magnetic moment of 1.73 B.M. Work out the electronic configuration of the vanadium ion in the compound.

[*IIT 1997*]

Solution Magnetic moment = 1.73 B.M = $\sqrt{N(N+2)}$

Here N = number of unpaired electrons

N =1

It means that in the compound vanadium ion must have one unpaired electrons.

$_{23}V = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 4s^2\ 3d^3$

$V^{+4} = 1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^1$

12. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å.

[*IIT 1997*]

Solution $\frac{1}{2} m u^2 = e V$

$$\lambda = \frac{h}{mu}$$

$$u = \frac{h}{m\lambda} \text{ or } u^2 = \frac{h^2}{m^2\lambda^2}$$

$$\frac{1}{2} m \times \frac{h^2}{m^2\lambda^2} = eV$$

$$V = \frac{1}{2} m \times \frac{h^2}{m^2\lambda^2 \times e}$$

$$V = \frac{1}{2} \times \frac{h^2}{m\lambda^2 e}$$

$$= \frac{1}{2} \times \frac{(6.62 \times 10^{-34})^2}{9.108 \times 10^{-31} .(1.54\ 10^{-10})^2 \times 1.602 \times 10^{-19}}$$

= 63.3 volt

13. State the number of protons, neutrons and electrons in C^{12} and C^{14}.

[*IIT 1997*]

Solution The atomic number of C^{12} is 6. So in it number of electrons = 6.

Number of protons = 6

Number of neutrons = 12 – 6 = 6

In $_6C^{14}$

Number of electrons = 6

Number of protons = 6

Number of neutrons = 14 – 6

14. Calculate the energy required to excite one litre of hydrogen gas at 1 atm and 298 K to the first excited state of atomic hydrogen. The energy for the dissociation of H – H bond is 436 kJ mol^{-1}. Also calculate the minimum frequency of photon to break this bond.

[*IIT 2000*]

Solution As $n = \frac{PV}{RT}$

So mole of H_2 present in one litre (n) = PV/RT

$$= \frac{1 \times 1}{0.0821 \times 298} = 0.0409$$

Hence energy needed to break H – H bonds in 0.0409 mole of H_2

= 0.0409x 436 = 17.83 kJ

Now energy needed to excite one H atom from first to second energy level

$$= 13.6 \left(1 - \frac{1}{4}\right) eV$$

= 10.2 eV

$= 10.2 \times 1.6 \times 10^{-19}$ J

So energy needed to excite $0.0409 \times 2 \times 6.02 \times 10^{23}$ atoms of H

$= 10.2 \times 1.6 \times 10^{-19} \times 0.0409 \times 2 \times 6.02 \times 10^3$ J

= 80.36 kJ

that is, total energy needed = 17.83 + 80.36

= 98.19 kJ

Now energy required to break (H – H) bond

$$= \frac{436 \times 10^3}{6.023 \times 10^{23}} \text{ Joule}$$

Using $E = hv$

that is, $\frac{436 \times 10^3}{6.023 \times 10^{23}} = 6.626 \times 10^{-34} \times v.$

On solving

$v = 10.93 \times 10^{14}$ sec^{-1} or Hz

15. Wavelength of high energy transition of H-atoms is 91.2 nm. Calculate the corresponding wavelength of He^+.

[*IIT 2003*]

Solution For H-atom

$$\frac{1}{\lambda_1} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \ldots\ldots (1)$$

For He^+ ion :

$$\frac{1}{\lambda_2} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad \ldots\ldots (2)$$

By (1) and (2),

$$\frac{\lambda_2}{\lambda_1} = \frac{1}{Z^2}$$

or $\lambda_{He^+} = \lambda_H \times \frac{1}{Z^2} = 91.2 \times \frac{1}{2^2} = 22.8$ nm

16. The wave function of 2s electron is given by

$$\psi^{2s} = \frac{1}{4\sqrt{(2\pi)}} (1/a_0)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/a\,0}$$

It has a node at $r = r_0$, find relation between r_0 and a_0.

[IIT 2004]

Solution The probability of finding of 2s electron at a point is given as follows:

$$\psi^2_{2S} = \frac{1}{32\pi} (1/a_0)^3 \left(2 - \frac{r}{a_0}\right)^2 e^{-2r/a}$$

As node is the point at which probability of finding an electron is zero

that is, ψ^2_{2S} = zero

It is possible when $r = r_0$

that is, $\frac{1}{32\pi} (1/a_0)^3 \left(2 \frac{r_0}{a_0}\right)^2 e^{-2r/a} = 0$

On solving $2 - \frac{r_0}{a_0} = 0$

$r_0 = 2\,a_0$

17. Find the wavelength for 100 g particle moving with velocity 100 ms^{-1}.

[IIT 2004]

Solution According to de Broglie equation:

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34}\ J.s}{(100 \times 10^{-3}\ kg) \times 100\ ms^{-1}}$$

$$= 6.626 \times 10^{-35}\ m$$

18. Find the velocity (ms^{-1}) of electron in first Bohr's orbit of radius a_0. Also find the de Broglie's wavelength (in m). Calculate the orbital angular momentum of 2p orbital of hydrogen atom in units of $h/2\pi$.

[IIT 2005]

Solution For hydrogen atom, Z = 1, n = 1

$$v = 2.18 \times 10^6 \times \frac{Z}{n}\ ms^{-1} = 2.18 \times 10^6\ ms^{-1}$$

de Broglie wavelength

$$\lambda = \frac{h}{mv} = \frac{6.26 \times 10^{-34}}{9.1 \times 10^{-31} \times 2.18 \times 10^6}$$

$$= 3.34 \times 10^{-10}\ m = 3.3\ Å$$

For 2p, l = 1

Orbital angular momentum (mvr)

$$= \sqrt{l\,(l+1)}\,\frac{h}{2\pi} = \sqrt{2}\,\frac{h}{2\pi}$$

19. What is the angular momentum of an electron in Bohr's hydrogen atom whose energy is –3.4 eV?

Solution As $E = -\frac{13.6}{n^2}$

$$-3.4 = -\frac{13.6}{n^2}$$

n = 2

The angular momentum quantization gives

$$L = mvr = \frac{nh}{2\pi}$$

On substituting n = 2, we have

$$L = \frac{2h}{2\pi} = \frac{h}{\pi}$$

20. Consider a hydrogen like atom whose energy in nth excited state is given by

$$E_n = -\frac{13.6\,Z^2}{n^2}$$

When this excited atom makes a transition from excited state to ground state, most energetic photons have energy E_{max} = 52.554 eV and least energetic photons have energy E_{min} =1.224 eV. Find the atomic number of atom and the state of excitation.

Solution Maximum energy is liberated for transition

$E_n \rightarrow 1$ and minimum energy for $E_n \rightarrow E_{n-1}$

$$\frac{E_1}{n^2} - E_1 = 52.224\ eV \quad \ldots\ldots (i)$$

$$\frac{E_1}{n^2} - \frac{E_1}{(n-1)^2} = 1.224 \text{ eV} \quad \ldots.(ii)$$

On solving the equations, we get

$E_1 = -54.4$ eV

$n = 5$

$$E_1 = -\frac{13.6\, Z^2}{1^2} = -54.4 \text{ eV}$$

$Z = 2$

Therefore the gas is helium, originally excited to n = 5 energy state.

21. An α-particle and a proton are fired through the same magnetic fields which is perpendicular to their velocity vectors. The α-particle and the proton move such that radius of curvature of their path is same. Calculate the ratio of their de Broglie wavelengths.

Solution Magnetic force experienced by a charged particle in magnetic field is given by,

$$F_B = q\vec{v} \times \vec{B} = qvB \sin\theta$$

As $\theta = 0$

So $F_B = q\, v\, B$

$$B\, qv = \frac{mv^2}{r}$$

or $mv = qBr$

The de Broglie wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{qBr}$$

$$\frac{\lambda\ (\alpha\text{–particle})}{\lambda\ (\text{proton})} = \frac{q_P\, r_P}{q_\alpha\, r_\alpha}$$

As $\frac{r_\alpha}{r_P} = 1$ and $\frac{q_\alpha}{q_P} = 2$

So $\frac{\lambda_\alpha}{\lambda_P} = \frac{1}{2}$

22. Calculate the ratio of de Broglie wavelength of a proton and an α-particle which have been accelerated through same potential difference.

Solution Kinetic energy gained by a charge 'q' after being accelerated through a potential difference V volt.

$$qV = \frac{1}{2} mv^2$$

$$v = \sqrt{(2qV/m)}$$

$$mv = \sqrt{(2mqV)}$$

According to de Broglie wavelength

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{(2mqV)}}$$

$$\frac{\lambda_P}{\lambda_\alpha} = \frac{\sqrt{(m_\alpha\, q_\alpha\, V_\alpha)}}{\sqrt{m_P\, q_P\, V_P}}$$

On Putting $V_\alpha = V_P$ we get

$$\frac{\lambda_P}{\lambda_\alpha} = \frac{\sqrt{(4 \times 2)}}{\sqrt{(1 \times 1)}} = 2\sqrt{2}$$

23. Calculate the wavelength for an n = 2 to n = 1 transition in molybdenum (Z = 42). What is the energy of such a photon?

Solution According to Bohr formula Z^2 is replaced by $(Z-1)^2 = (41)^2$. For n = 2 to n = 1 transition in hydrogen (Z = 1)

$$\lambda \ \alpha \ \frac{1}{(Z-1)^2}$$

$$\lambda = \frac{(1.22 \times 10^{-7})}{(41)^2} = 0.073 \text{ nm}$$

It is close to the measured value of 0.071 nm. Each of these photons would have energy (in eV) of:

$$E = hf = \frac{hc}{\lambda}$$

$$= \frac{6.63 \times 10^{-34} \times 3.00 \times 10^8}{7.3 \times 10^{-11} \times 1.60 \times 10^{-19}} = 17 \text{ KeV}$$

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. The quantum number 'm' of a free gaseous atom is associated with
   - **a.** the effective volume of the orbital
   - **b.** the shape of the orbital
   - **c.** the spatial orientation of the orbital
   - **d.** the energy of the orbital in the absence of a magnetic field

2. The angular momentum (L) of an electron in a Bohr orbit is given as
   - **a.** $L = nh/2\pi$
   - **b.** $\sqrt{[l(l+1)\, h/2\, \pi]}$
   - **c.** $L = mg/2\pi$
   - **d.** $L = h/4\, \pi$

3. When the azimuthal quantum number has the value of 2, the number of orbitals possible are
   - **a.** 0
   - **b.** 4
   - **c.** 1
   - **d.** 5

4. For a d-electron, the orbital angular momentum is
   - **a.** $\sqrt{6}\hbar$
   - **b.** $\sqrt{2}\hbar$
   - **c.** $\hbar$
   - **d.** $2\hbar$

5. The ratio of kinetic energy and potential energy of an electron in a Bohr orbit of a hydrogen like species is
   - **a.** –1
   - **b.** +1
   - **c.** $-\frac{1}{2}$
   - **d.** $+\frac{1}{2}$

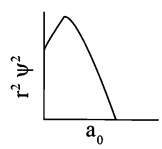
6. In which of the following sets do all species have the same number of electrons?
   - **a.** O, O^{2-}, O^{2+}
   - **b.** $Mg^{2+}, Sr^{2+}, Ba^{2+}$
   - **c.** Br^{-}, Kr, Sr^{2+}
   - **d.** C, N^{3-}, O^{2-}

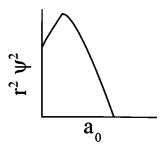
7. Of the following, which has the shortest de Broglie wavelength?
   - **a.** A nitrogen molecule moving at a velocity of 4000 mph.
   - **b.** A nitrogen molecule moving at a velocity of 1100 mph
   - **c.** A helium nucleus moving at a velocity of 1200 mph
   - **d.** An airplane moving at a velocity of 200 mph

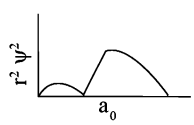
8. Gaseous metal ion M^{2+} has 5 unpaired electrons. What is its atomic number?
   - **a.** 25
   - **b.** 26
   - **c.** 27
   - **d.** 28

9. The electronic configuration $1s^2, 2s^2, 2p^6, 3s^1, 3p^1$ is correctly described by
   - **a.** the excited state of Mg^+
   - **b.** the excited state of Na^+
   - **c.** the excited state of Mg
   - **d.** the excited state of Al.

10. The orbital angular momentum of an electron in 2s orbital is
    - **a.** $+\frac{1}{2}\ \frac{h}{2\pi}$
    - **b.** zero
    - **c.** $\frac{h}{2\pi}$
    - **d.** $\sqrt{2}\ \frac{h}{2\pi}$

11. Which of the following radial distribution graphs correspond to l = 2 for Hydrogen atom:
    - **a.** 

    - **b.** 

    - **c.** 

    - **d.** Both (a) and (b)

12. In which of the following pairs are both the ions coloured in aqueous solution?
    - **a.** Sc^{3+}, Co^{2+}
    - **b.** Ni^{2+}, Cu^{+}
    - **c.** Ni^{2+}, Ti^{3+}
    - **d.** Sc^{3+}, Ti^{3+}

    (At. no. Sc = 21, Ti = 22, Ni = 28, Cu = 29, Co = 27)

13. Rutherford's α-particles scattering experiment led to the conclusion that:
    - **a.** Atoms are electrically neutral
    - **b.** Mass and energy are related
    - **c.** Mass and positive charge of an atom are concentrated in the nucleus
    - **d.** Neutrons are present in the nucleus

14. Each p-orbital and each d-orbital has lobes respectively as
    - **a.** 2, 4
    - **b.** 1, 2
    - **c.** 2, 2
    - **d.** 1, 1

15. The mass of an electron is m. Its charge is e and it is accelerated from rest through a potential difference V. The velocity acquired by the electron will be

a. $\sqrt{V/m}$ **b.** $\sqrt{eV/m}$
c. $\sqrt{2eV/m}$ **d.** none

16. For an orbital, a node is
a. A surface inside which there is a 90% chance of finding the electron.
b. The mid point of the orbital
c. A surface where there is no change of finding the electron
d. A surface where there is a maximum probability of finding the electron.

17. In the photoelectric effect, in order for an electron to be released from the surface of a clean metal, which one of the following conditions must exist?
a. The kinetic energy of photons striking the metal's surface must be less than that of the emitted electrons
b. The kinetic energy of photons striking the metal's surface must be greater than or equal to that of the emitted electrons plus the binding energy holding the electron in the metal
c. The metal must have a low temperature
d. The kinetic energy of photons striking the metal's surface must equal that of the emitted electron

18. Which of the following transitions will have minimum wavelength?
a. $n_4 \rightarrow n_2$ **b.** $n_4 \rightarrow n_1$
c. $n_2 \rightarrow n_1$ **d.** $n_3 \rightarrow n_1$

19. Which of the following relates to photons both as wave motion and as a stream of particles?
a. interference **b.** $E = mc^2$
c. diffraction **d.** $E = hv$

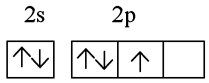
20. A metal surface is exposed to solar radiations
a. The emitted electrons have zero energy
b. The emitted electrons have energy equal to energy of photons of incident light
c. The emitted electrons have energy less than the maximum value of energy depending upon intensity of incident radiations.
d. The emitted electrons have energy less than a maximum value of energy depending upon the frequency of the incident radiation.

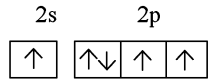
21. The ionization energy of hydrogen atom is 13.6 eV. What will be the ionization energy of He^+?
a. 13.6 eV **b.** 54.4 eV
c. 122.4 eV **d.** zero

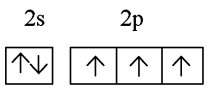
22. The H-spectrum shows
a. Polarization
b. Presence of quantized energy levels
c. Heisenberg's uncertainty principle
d. Diffraction

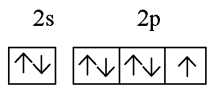
23. Which of the following represents the correct set up of the four quantum number of 4s electron
a. 4, 1, 0,+ ½ **b.** 4, 1, –1, – ½
c. 4, 2, 1, + ½ **d.** 4, 0, 0, ½

24. The orbital diagram in which the Aufbau principle is violated is

a.


b.


c.


d.


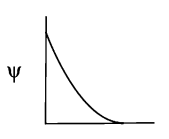
25. From the α-particle scattering experiment, Rutherford concluded that:
a. The radius of the nucleus is less than 10^{-12} m
b. α-particles can approach within a distance of the order of 10^{-14} m of the nucleus
c. The positively charged parts of the atom move with extremely high velocities
d. Scattering does not follow Coulomb's law.

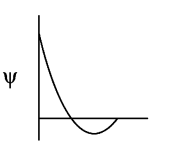
26. Electromagnetic radiation with maximum wavelength is
a. radiowave **b.** X-ray
c. infrared **d.** ultraviolet

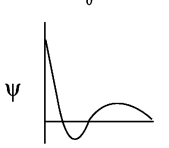
27. Which order of energies of orbitals is correct in a many electron atom?
a. 3d < 2s **b.** 2s = 2p
c. 4s > 5s **d.** 3s < 3p

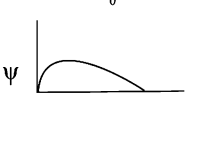
28. The subshell designations follows the alphabet after 'f '. What is the first shell in which an 'h' orbital would be allowed?
a. Fourth **b.** Fifth
c. Sixth **d.** Seventh

29. The graph representing two nodes is

a.


b.


c.


d.


30. When potassium metal is exposed to violet light
a. there is no effect
b. ejection of electron takes place

c. the absorption of electrons takes place
d. ejection of some potassium atoms occurs

31. Which of the following orbitals can have more than one nodal plane?

a. 1s b. 2s
c. 2p d. 3d

32. The radius of an atomic nucleus is of the order of

a. 10^{-8} cm b. 10^{-13} cm
c. 10^{-10} cm d. 10^{-15} cm

33. Find the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

a. 6.9 BM b. 5.9 BM
c. 4.9 BM d. 3.0 BM

34. Bohr model can explain

a. the solar spectrum
b. the spectrum of hydrogen molecule
c. the spectrum of hydrogen atom only
d. spectrum of an atom or ion containing one electron only

35. An electron is moving in Bohr's fourth orbit. Its deBroglie wavelength is λ. What is the circumference of the fourth orbit?

a. 2 λ b. 2/λ
c. 3/λ d. 4 λ

36. Which one of the following grouping represents a collection of isoelectronic species? (At numbers Cs-55, Br –35)

a. Na^+, Ca^{2+}, Mg^{2+}
b. N^{3-}, F^-, Na^+
c. Be, Al^{3+}, Cl^-
d. Ca^{2+}, Cs^+, Br

37. Which of the following represent electron configuration that violate the Pauli exclusion principle?

(I) [Ne] $3s^1 3p^5$

(II) [Kr] $4d^{12} 5s^2 5p^3$

(III) [Ar] $3d^{10} 4s^2 4p^2$

a. Only (II)
b. Only (I)
c. Both (I) and (III)
d. Both (II) and (III)

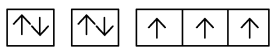
38. Which best describes the emission spectra of atomic hydrogen?

a. A discrete series of lines of equal intensity and equally spaced with respect to wavelength
b. A series of only four lines
c. A continuous emission of radiation of all frequencies
d. Several discrete series of lines with both intensity and spacing between lines decreasing as the wave number increases within each series

39. Which electronic level would allow the hydrogen atom to absorb a photon but not to emit a photon?

a. 1s b. 2s
c. 2p d. 3s

40. In the electronic configuration given below which rule is violated?

N: 

a. Aufbau rule
b. Pauli's exclusion principle
c. Hund's rule
d. No violation of any of these rules

41. The number of d-electrons in Ni (atomic number = 28) is equal to that of the

a. d-electrons in Ni^{2+}
b. Total electrons in N (atomic number = 7)
c. s and p-electrons in F^-
d. p-electrons in Ar (atomic number = 18)

42. In a multi-electron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic field and electric fields?

a. n = 1, l = 0, m = 0
b. n = 2, l = 0, m = 0
c. n = 3, l = 1, m = 1
d. n = 3, l = 2, m = 1
e. n = 3, l = 2, m = 0

a. b and c b. d and e
c. c and d d. a and b

Ans **b.**

43. Correct set of four quantum numbers for the valence (outermost) electron of rubidium (Z = 37) is

a. 5, 0, 0 , ± ½ b. 6, 0, 0 , + ½
c. 5, 1,1, ± ½ d. 5, 1, 0, ± ½

44. If n = 3, l = 0, m = 0, then atomic number is

a. 12, 14 b. 11, 13
c. 11, 12 d. 13, 14

45. How many lines in the spectrum will be observed when electrons return from 7th shell to 2nd shell?

a. 10 b. 15
c. 21 d. 30

46. The increasing order (lowest first) for the values of e/m (charge/mass) for electron (e), proton (p), neutron (n) and alpha particle (a) is:

a. n, p, a , e **b.** n, p, e, a
c. n, a, p, e **d.** e, p, n, a

47. For a hydrogen atom, which electronic transition would result in the emission of a photon with the highest energy?

a. 5f → 3d **b.** 4p → 2s
c. 3p → 6d **d.** 2s → 3p

48. The specific charge for positive rays is much less than the specific charge for cathode rays. This is because

a. Charge on positive rays is less
b. Positive rays are positive charged
c. Experimental method for determination is wrong
d. Positive rays comprise ionized atoms whose mass is much higher

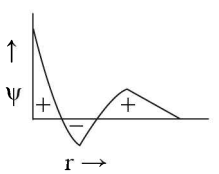
49. In iron, which of the following electrons, characterized by the four quantum numbers, has the lowest energy?

a. $n = 3, l = 2, m_l = 1, m_s = -\frac{1}{2}$
b. $n = 3, l = 2, m_l = 0, m_s = +\frac{1}{2}$
c. $n = 3, l = 1, m_l = 0, m_s = +\frac{1}{2}$
d. $n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}$

50. Rutherford's scattering experiment is related to the size of the

a. atom **b.** nucleus
c. neutron **d.** electron

51. Wave function of an orbital is given below in the variation or w.r.t. distance from nucleus.



It may be the graphical representation of

a. 1s **b.** 2s
c. 2p **d.** 3s

52. If the electron of a hydrogen atom is present in the first orbit, the total energy of the electron is .....

a. $-e^2/2r$ **b.** $-e^2/r$
c. $-e^2/r^2$ **d.** $-e^2/2r^2$

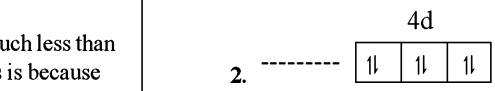
53. The principal quantum number of an atom is related to the

a. orientation of the orbital in space
b. spin angular momentum
c. orbital angular momentum
d. size of the orbital

54. Name the ions indicated by the following electronic configurations:

1.

2.



a. Ni^{2+}, Br^- **b.** Zn^{2+}, Rb^{2+}
c. Cu^{2+}, Se^{2-} **d.** Co^{3+}, Rb^+

55. Which of the following sets of quantum numbers represents the electron of the lowest energy?

a. $n = 2, l = 0, m = 0, s = -\frac{1}{2}$
b. $n = 2, l = 1, m = 0, s = +\frac{1}{2}$
c. $n = 4, l = 2, m = 0, s = +\frac{1}{2}$
d. $n = 4, l = 0, m = 0, s = -\frac{1}{2}$

56. The orbital angular momentum for an electron revolving in an orbit is given by $\sqrt{l(l+1)}\, h/2\pi$. This momentum for an s-electron will be given by:

a. $+\frac{1}{2}.h/2\pi$ **b.** zero
c. $h/2\pi$ **d.** $\sqrt{2}.h/2\pi$

57. Any p-orbital can accommodate upto

a. six electrons
b. four electrons
c. two electrons with opposite spins
d. two electrons with parallel spins

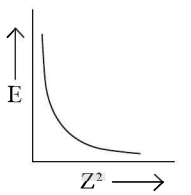
58. The energy of an electron moving in nth Bohr's orbit of an element is given by

$$E_n = \frac{13.6}{n^2} Z^2 \text{ eV /atom}$$

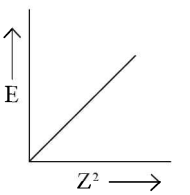
Here Z = atomic number

The graph of E vs Z^2 will be:

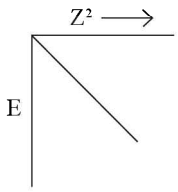
a.



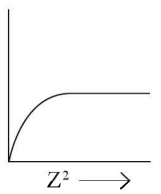
b.



c.



d.



59. The fourth electron of Be atom will have quantum numbers as

a. 1, 0, 0, ½ **b.** 2, 0, 0, - ½
c. 2, 1, 0, + ½ **d.** 1, 1, 1, + ½

60. Which of the following electronic configuration does not follow the Pauli's exclusion principle?

a. $1s^2\ 2s^2\ 2p^4$ **b.** $1s^2\ 2s^2\ 2p^6\ 3s^2$
c. $1s^2\ 2s^2$ **d.** $1s^2\ 2s^2\ 2p^6\ 3s^3$

61. In which of the following, pair both the ions have magnetic moment 2.83 B.M. respectively?

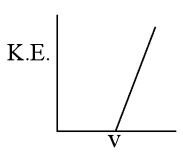
a. Fe^{2+}, Mn^{2+} **b.** Fe^{3+}, Mn^{2+}
c. Mn^{2+}, Cr^{3+} **d.** Mn^{2+}, V^{4+}

62. Uncertainty in position of a particle of 25 g in space is 10^{-5} m. Hence uncertainty in velocity (ms^{-1}) is (Planck's constant h = 6.6 x 10^{-34} Js)

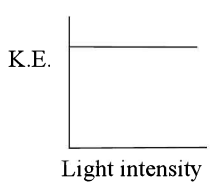
a. 2.1×10^{-28} **b.** 2.1×10^{-34}
c. 0.5×10^{-34} **d.** 5.0×10^{-24}

63. Which of the following options represent the correct graph for photoelectrons?

a.



b.



c. Both of the above
d. None of the above

64. Which of the following ions has the maximum magnetic moment?

a. Mn^{2+} **b.** Fe^{2+}
c. Ti^{2+} **d.** Cr^{2+}

65. The de Broglie wavelength of a tennins ball of mass 60 g moving with a velocity of 10 meters per second is approximately:
(Planck's constant h = 6.63 × 10^{-31} Js)

a. 10^{-33} m **b.** 10^{-31} meter
c. 10^{-16} m **d.** 10^{-25} m

66. The number of d-electrons retained in Fe^{2+} (At. number of Fe = 26) ions is

a. 3 **b.** 4
c. 5 **d.** 6

67. Which one of the following sets of ions represents the collection of isoelectronic species?

a. K^+, Ca^{2+}, Sc^{3+}, Cl^-
b. Na^+, Ca^{2+}, Sc^{3+}, F^-
c. K^+, Cl^-, Mg^{2+}, Sc^{3+}
d. Na^+, Mg^{2+}, Al^{3+}, Cl^-

68. Transition of an electron from n = 3 level to n = 1 level results in:

a. Band spectrum
b. IR spectrum
c. Emission spectrum
d. X-ray spectrum

69. For a particular orbital, as one goes away from the nucleus along the Z-axis, the probability density decreases to zero, then increases, and finally decreases without increasing a second time. This is consistent with a

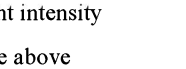
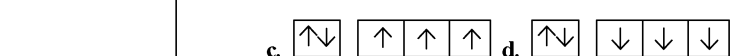
a. 2s or a 2pz orbital
b. 2s orbital
c. 3s-orbital
d. 2pz orbital

70. Of the following sets which one does not contain isoelectronic species?

a. PO_4^{3-}, SO_4^{2-}, ClO_4^-
b. CN^-, N_2, C_2^{2-}
c. SO_3^{2-}, CO_3^{2-}, NO_3^-
d. BO_3^{3-}, CO_3^{2-}, NO_3^-

71. The orbital diagram in which the Pauli's exclusion principle is violated is

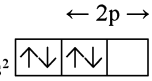
a. **b.**

c.  **d.** 

72. According to Bohr's theory, the angular momentum of an electron in 5th orbit is

a. 25 h/ π **b.** 1.0 h/ π
c. 10 h/π **d.** 2.5 h/π

73. If the electronic structure of oxygen atom is

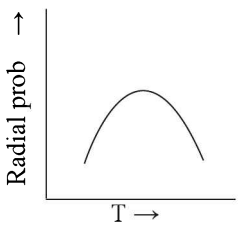
written as $1s^2, 2s^2$ ← 2p →  it would violate:

a. Hund's rule
b. Pauli's exclusion principle
c. Both Hund's and Pauli's principles
d. None of these

74. Passing an electrical charge through argon gas contained in a partially evacuated vessel yields which of the following?

a. A line spectrum
b. A continuous spectrum
c. No visible change
d. White light

75. Here radial probability distribution curve is shown for s-orbital. This curve is for



a. 3s
b. 1s
c. 2s
d. All of these

Brainteasers Objective Type Questions (Single choice only)

76. The number of waves made by a Bohr electron in an orbit of maximum magnetic quantum number –3 is

a. 4
b. 3
c. 2
d. 1

77. The correct order of number of unpaired electrons in the ion Cu^{2+}, Ni^{2+}, Fe^{3+} and Cr^{3+} is

a. $Cu^{2+} > Ni^{2+} > Cr^{3+} > Fe^{3+}$
b. $Ni^{2+} > Cu^{2+} > Fe^{3+} > Cr^{3+}$
c. $Fe^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$
d. $Fe^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+}$

78. In which of the following case would the probability of finding an electron residing in a dxy orbital be zero?

a. xz and yz-planes
b. xy and yz-planes
c. z-direction, yz and xz-planes
d. xy and xz-planes

79. A monoenergetic electron beam with a de Broglie wavelength of 'P' Å is accelerated till its wavelength is halved. By what factor will it kinetic energy change?

a. 2
b. ½
c. 4
d. Remains same

80. The first emission line in the atomic spectrum of hydrogen in the Balmer series appears at:

a. $\frac{3R}{4}$ cm^{-1}
b. $\frac{5R}{36}$ cm^{-1}
c. $\frac{36}{5R}$ cm^{-1}
d. $\frac{7R}{36}$ cm^{-1}

81. The isoelectronic pair is:

a. ClO_2^-, ClF_2^+
b. IF_2^+, I_3^-
c. Cl_2O_3, ICl_2^-
d. ICl_2^-, ClO_2

82. If Aufbau rule is not followed then percent change in total $(n + l)$ value for unpaired electrons in $_{25}Mn$ is:

a. 60
b. 50
c. 40
d. 30

83. A photon of wavelength 300 nm is absorbed by a gas and then re-emitted as two photon. One photon is red with wavelength of 760 nm. The wave number of the second photon will be

a. 2.20×10^7 m^{-1}
b. 2.02×10^6 m^{-1}
c. 4.04×10^7 m^{-1}
d. 1.01×10^6 m^{-1}

84. The de Broglie wavelength associated with a ball of mass 1 kg having a kinetic energy 0.5 J is

a. 6.626×10^{-34} m
b. 13.2×10^{-34} m
c. 10.38×10^{-21} m
d. 6.626 Å

85. If uncertainty in position and momentum are equal, then uncertainty in velocity is:

a. $1/m \sqrt{(h/\pi)}$
b. $\sqrt{(h/\pi)}$
c. $1/2m \sqrt{(h/\pi)}$
d. $\sqrt{(h/2\pi)}$

86. What is the wavelength of the radiation emitted producing in a line in the Lyman series when an electron falls from fourth stationary state in hydrogen atom? ($R_H = 1.1 \times 10^7$ m^{-1})

a. 96.97 nm
b. 969.7 nm
c. 9.697 nm
d. none

87. If the shortest wavelength of hydrogen atom in Lyman series is X, then longest wavelength in Paschen series of He^+ is

a. $\frac{36\times}{5}$ **b.** $\frac{36\times}{7}$

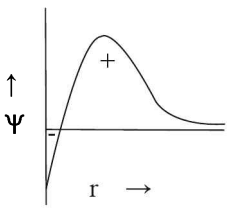
c. $\frac{7\times}{36}$ **d.** $\frac{6\times}{5}$

88. In the consideration of the Bohr theory for the hydrogenic species, which electron orbit of the Be^{3+} ion can have the same radius as the ground state electron orbit of the hydrogen atom?

a. 1 **b.** 2

c. 3 **d.** 4

89. Wave function vs distance from nucleus graph of an orbital is given below



The number of nodal (sphere) of this orbital is

a. Zero **b.** 1

c. 2 **d.** Can't be said

90. The electronic configuration of four elements P, Q, R and S given below. Choose the element that would most readily form a diatomic molecule.

$P = 1s^2 2s^2 2p^1$, $Q = 1s^2 2s^2 2p^5$

$R = 1s^2 2s^2 2p^6 3s^1$, $S = 1s^2 2s^2 2p^2$

a. Q **b.** S

c. P **d.** R

91. Consider the following sets of quantum numbers:

	n	l	m	s
(1)	3	0	0	- ½
(2)	2	2	2	- ½
(3)	4	3	-2	- ½
(4)	1	0	-1	- ½
(5)	3	2	3	+ ½

Which of the following sets of quantum number is not possible?

a. 2, 3 and 4 **b.** 1, 2, 3 and 4

c. 2, 4 and 5 **d.** 1 and 3

92. An atom A has the electronic configuration of $1s^2 2s^2 2p^1$. Atom B has the electronic configuration of $1s^2 2s^2 2p^3$. The empirical formula of the compound obtained from the reaction of A and B is

a. AB **b.** AB_3

c. A_3B_3 **d.** A_2B_6

93. The atomic numbers of elements X, Y, Z are 19, 21 and 25 respectively. The number of electrons present in the 'M' shells of these elements follow the order

a. Z > Y > X **b.** X > Y > Z

c. Z > X > Y **d.** Y > Z > X

94. Hydrogen atoms are excited on n = 4 state. In the spectrum of emitted radiation, number of lines in the ultraviolet and visible regions are respectively

a. 3 : 2 **b.** 3: 1

c. 1 : 3 **d.** 2 : 3

95. Photoelectric emission is observed from a surface for frequencies v_1 and v_2 of the incident radiation ($v_1 > v_2$). If the maximum kinetic energies of the photoelectrons in the two cases are in the ratio 1 : k then the threshold frequency v_0 is given by

a. $\frac{kv_2 - v_1}{k-1}$ **b.** $\frac{v_2 - v_1}{k}$

c. $\frac{v_2 - v_1}{k-1}$ **d.** $\frac{kv_1 - v_2}{k-1}$

96. A light source of wavelength (λ) illuminates a metal and ejects photoelectrons with $(K.E.)_{max} = 1$ eV

Another light source of wavelength $\lambda/3$, ejects photoelectrons from same metal with $(K.E.)_{max} = 4$ eV

Find the value of work function?

a. 1 eV **b.** 0.5 eV

c. 1.5 eV **d.** 2.5 eV

97. The ionization energy of He^+ is 19.6×10^{-18} J $atom^{-1}$. Calculate the energy of the first stationary state of Li^{2+}

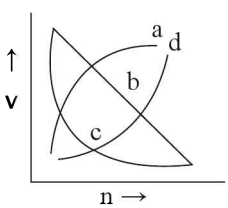
a. 19.6×10^{-18} J $atom^{-1}$

b. 4.41×10^{-18} J $atom^{-1}$

c. 19.6×10^{-19} J $atom^{-1}$

d. 4.41×10^{-17} J $atom^{-1}$

98. Which of the following curves may represent the speed of the electron in a hydrogen atom as a function of the principal quantum number n?



a. d **b.** c

c. b **d.** a

99. Energy of H-atom in the ground state is -13.6 eV, hence energy in the second excited state is

a. –6.8 eV **b.** –3.4 eV
c. –1.51 eV **d.** –4.53 eV

100. Among the following series of transition metal ions, the one where all metal ion have $3d^2$ electronic configuration is

a. Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}

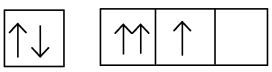
b. Ti^{+}, V^{4+}, Cr^{6+}, Mn^{7+}

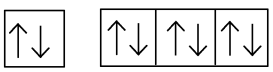
c. Ti^{4+}, V^{3+}, Cr^{2+}, Mn^{3+}

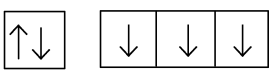
d. Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}

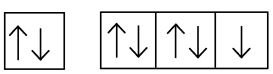
(At. wt. Ti = 22; V = 23; Cr = 24; Mn = 25)

101. The orbital diagram in which both the pauli's exclusion principle and Hund's rule are violated is

a. 

b. 

c. 

d. 

102. In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one of the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen?

a. $3 \rightarrow 2$ **b.** $5 \rightarrow 2$
c. $4 \rightarrow 1$ **d.** $2 \rightarrow 5$

103. The first orbital of H is represented by:

$$\psi = \frac{1}{\sqrt{\pi}}(1/a_0)^{3/2}\ e^{-r/a_0}$$

Here, a_0 is Bohr's radius. The probability of finding the electron at a distance r, from the nucleus in the region dV is:

a. $\psi^2\, 4\pi r^2\, dr$ **b.** $\int \psi\, dV$
c. $\psi^2\, dr$ **d.** $\int \psi^2\, 4\pi r^2\, dV$

104. Which orbital has only positive value of wave function at all distances from the nucleus?

a. 3d **b.** 2p
c. 2s **d.** 1s

105. Which of the following sets of quantum numbers is correct for an electron in 4f orbital?

a. n = 4, l = 3, m = +4, s = + ½
b. n = 4, l = 4, m = –4, s = - ½
c. n = 4, l = 3, m = +1, s = + ½
d. n = 3, l = 2, m = –2, s = + ½

106. Consider the ground state of Cr atom (Z = 24). The numbers of electrons with the azimuthal quantum numbers, l =1 and 2 are, respectively:

a. 12 and 4 **b.** 12 and 5
c. 16 and 4 **d.** 16 and 5

107. In the Bohr's orbit, what is the ratio of total kinetic energy and the total energy of the electron?

a. +1 **b.** +2
c. –2 **d.** –1

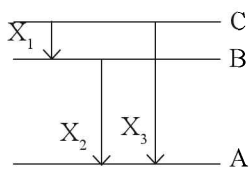
108. The angular momenta of 2s and 2p electrons, in units of $h/2\pi$, are respectively

a. 1, 2 **b.** 2, 2
c. 0, $\sqrt{2}$ **d.** 0, 1

109. The wavelength of the radiation emitted, when in a hydrogen atom electron falls from infinity to stationary state 1, would be (Rydberg constant = $1.097 \times 10^7\ m^{-1}$):

a. 91 nm **b.** 192 nm
c. 406 nm **d.** 9.1×10^{-8} nm

110. Energy levels A, B, C of a certain atom corresponds to increasing values of energy, i.e., $E_A < E_B < E_C$. If X_1, X_2 and X_3 are the wavelengths of radiations corresponding to the transitions C to B, B to A and C to A respectively, which of the following statement is correct?



a. $X_1 + X_2 + X_3 = 0$

b. $X_3 = X_1 + X_2$

c. $X_3^2 = X_1^2 + X_2^2$

d. $X_3 = \dfrac{X_1 X_2}{X_1 + X_2}$.

111. The Balmer-Rydberg equation can be extended to ions with only one electron, such as He^+. In that case it has the form:

$1/\lambda = Z^2 R (1/m^2 - 1/n^2)$, here Z is the atomic number. What is the energy of the photon required to promote an electron in He^+ from a 1s-orbital to a 2p-orbital?

a. 12 hcR **b.** 6 hcR
c. 3 hcR **d.** (3/4) hcR

112. A beam of protons is accelerated through a potential drop of 200 volts. The same experiment is done with a beam of deuterons. After acceleration each beam is bent by the same magnetic field in a directions perpendicular to that of the beam. Which beam will exhibit the greater curvature?

a. The same curvature for both
b. The beam with the larger velocity will exhibits the smaller curvature
c. The proton beam
d. The deuteron beam

113. The numerical value $\psi_{4,2,0}$ denotes

a. $4dx^2y^2$ **b.** $4dz^2$
c. $4p_z$ **d.** $4f_{xyz}$

114. In the Bohr's model of the hydrogen atom, which of the following statements is correct?

a. The transition n = 1 →n = 3 represents absorption of energy
b. The transition n = 2 → n = 4 represents emission of energy
c. When n = ∞, the electron is in its ground state
d. When n = 1, the electron is in an excited state

115. The number of photons of light having wave number 'a' in 3 J of energy source is

a. hc/3a **b.** 3hca
c. 3a/hc **d.** 3/hca

116. The wavelength of the de Broglie wave of the electron revolving in the sixth orbit of the hydrogen atom is

a. πr_0 **b.** $12 \pi r_0$
c. $6 \pi r_0$ **d.** $24 \pi r_0$
(r_0 is the Bohr's radius = 0.529 Å)

117. For an electron in a hydrogen atom, the wave function, ψ is proportional to $\exp-(r/a_0)$, where a_0 is the Bohr's radius. What is the ratio of probability of finding electron at the nucleus to the probability of finding it at 90?

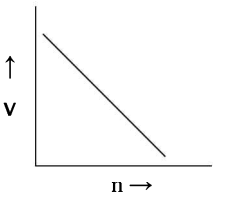
a. Zero **b.** e
c. e^2 **d.** $1/e^2$

118. The masses of photons corresponding to the first lines of the Lyman and the Balmer series of the atomic spectrum of hydrogen are in the ratio of

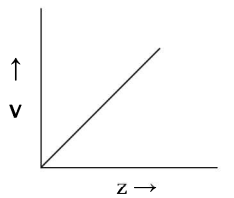
a. 4 : 9 **b.** 27 : 5
c. 9 : 4 **d.** 1 : 1

119. Select the correct graph for velocity of e^- in an orbit vs Z, 1/n and n:

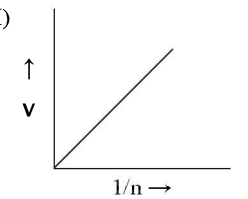
(I)



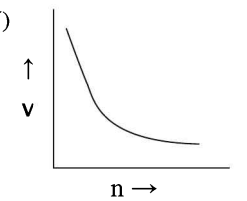
(II)



(III)



(IV)



a. I and II **b.** II and IV
c. I, II and IV **d.** II, III and IV

120. A mono electronic species in energy level with energy 'X' was provided with excess of energy so that it jumps to higher energy level with energy 'Y'. If it can emit 6 wavelengths originated from all possible transition between these group levels, then which of the following relation is correct?

a. $X/Y = (n-1)^2$
b. $X/Y = 1 + 3/n$
c. $\sqrt{(X/Y)} = 1 + 3/n$
d. $X/Y = n/6$

(Here n is the principal quantum number of energy level X)

Multiple Correct Answer Type Questions

121. Bohr's model of atom cannot explain

a. Zeeman effect

b. Stark effect

c. Linear spectrum of hydrogenic species

d. Fine spectrum of hydrogenic species

122. Select the correct statement(s) about Uncertainty principle.

a. The product of uncertainty in momentum in position is always constant

b. This principle can explain why electron cannot exist in nucleus

c. This principle is applicable to microscopic as well as macroscopic particle

d. Heisenberg uncertainty principle is ruled out the concept of definite trajectories around the nucleus.

123. Which of the following is/are true in Rutherford's nuclear model of atom?

a. The number of protons and neutrons are always equal

b. The number of electrons and protons are always equal

c. Protons and neutrons are present inside the nucleus

d. Volume of nucleus is very small as compared to the volume of atom

124. Which of the following statement is/are correct?

a. In silver atom, 23 electrons have a spin of one type and 24 of the opposite (atomic number of Ag = 47)

b. The number of unpaired electrons in both Fe^{2+} and Mn^{2+} are five

c. The electronic configuration of Cr is [Ar] $3d^4\ 4s^1$ (atomic number of Cr = 24)

d. The azimuthal quantum number may have a negative value.

125. Which of the following statement(s) is/are correct?

An atomic orbital

a. Describes trajectory of electron in an atom

b. Is a single electron wave function

c. Can be represented by boundary surface diagrams

d. Defines distribution of electron density in space

126. The kinetic energy of photoelectron emitted on irradiating a metal surface with frequency v is related by KE = hv – IE. The plots of KE vs. incidented frequency v shows:

a. A straight line with slope equal to Planck's constant.

b. A straight line with intercept on x-axis equal to the product of threshold frequency and Planck's constant.

c. A straight line with extrapolated intercept on y-axis equal to ionization energy

d. A straight line with intercept on x-axis equal to threshold frequency

127. Which of the following statements is/are correct?

a. Energy of the electron in hydrogen like atom/ion at infinite distance is zero and yet it is maximum

b. The position and momentum of a rolling ball can be measured accurately

c. Some spectral lines of an element may have the same wave number

d. Probabilities are found by solving Schrodinger wave equation

128. Which of these represent possible arrangement(s)?

	n	l	m	s
a.	2	1	-1	½
b.	3	0	0	-½
c.	3	2	-3	½
d.	5	3	-2	-½

129. Which of the following statement(s) is/are correct for orbital angular momentum of 2p and 3p-electron?

a. Orbital angular momentum of 3p-electron is more than that of 2p-electron

b. Orbital angular momentum of 2p-electron is more than that of 3p-electron

c. Orbital angular momentum of 2p electron is equal to 2s electron and 3p electron is equal to 3s electron

d. Orbital angular momentum of 2p-electron is same as that of 3p-electron

130. Which set of quantum number is consistant with theory?

a. n = 2, l = 1, m = 0, s = - ½

b. n = 4, l = 3, m = 2, s = - ½

c. n = 3, l = 2, m = 3, s = + ½

d. n = 4, l = 3, m = 3, s = + ½

131. Which among the following are impossible arrangements of quantum numbers?

	n	l	m	s
a.	3	1	-2	+ ½
b.	3	3	-1	- ½
c.	4	0	0	+ ½
d.	3	2	-3	- ½

132. Which of the following statements may be regarded as indicating a defect of the Bohr theory of the hydrogen spectrum?

a. The theory could not be extended to polyelectronic atoms.

b. The theory bypassed classical electromagnetism which states that orbiting electrons should spiral around the nucleus and fall in.

c. The theory had nothing to say about the intensities of spectral lines.

d. The theory ignored the wave nature of the electrons.

133. The ratio of the de-Broglie wavelengths of an α-particle and a proton can be 2 : 1 when

a. Their velocities are in 4 : 1 ratio

b. Their velocities are in 8 : 1 ratio

c. Their kinetic energies are in 128 : 1 ratio

d. Their kinetic energies are in 256 : 1 ratio.

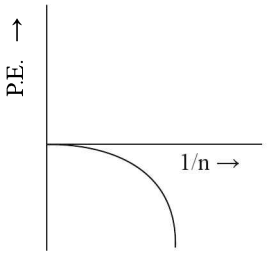
134. Select the correct curve(s):

If v = Velocity of electron in Bohr's orbitr = Radius of electron in Bohr's orbiP.E.

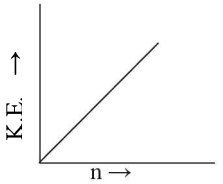
= Potential energy of electron in Bohr's orbit

K.E. = Kinetic energy of electron in Bohr's orbit

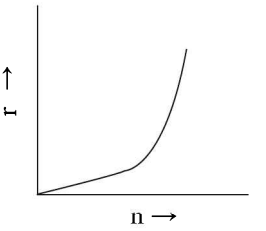
a.



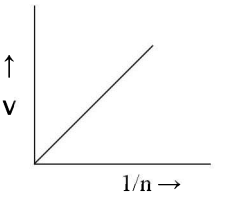
b.



c.



d.



135. Which of the following is/are correct?

a. the energy of an electron depends only on the principal quantum numbers not on the other quantum numbers

b. the energy of an electron depends only on the principal quantum number in case of hydrogen and hydrogen like atoms.

c. the difference in potential energies of any two energy level is always more than the difference in kinetic energies of these two levels.

d. an electron in an excited state can always emit a photon or two but can not absorb a photon

136. The angular momentum of any electron can have the value(s)

a. 3 (h/π) **b.** 2.5 (h/2π)

c. 0.5 (h/π) **d.** (h/π)

137. Which of the following statements in relation to the hydrogen atom is incorrect?

a. 3s and 3p orbitals are of lower energy than 3d orbital

b. 3p orbital is lower in energy than 3d orbital

c. 3s orbital is lower in energy than 3p orbital

d. 3s, 3p and 3d orbitals all have the same energy

138. Which of the following statements are false?

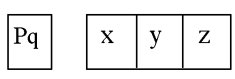
a. the uncertainty in position and momentum in Heisenberg's principle due to electron wave

b. the energy level order 4s < 3d < 4p < 5s may not hold good for all elements

c. the quantum number of light radiation is manifested in photoemission of electrons

d. according to Bohr's theory the energy decreases as an increases.

139. Five valence electrons of $_{15}P$ are labelled as



If the spin quantum number of q and z is + ½

The group of electrons with three of the quantum number same are

a. Pq

b. (xyz), (Pq)

c. (Pq), (xyz), (Pz)

d. (Pq), (xyz), (qy)

140. Which of the following statement(s) about spectral series is/are correct?

a. Paschen series appears in the infrared region

b. The lines in the Balmer series corresponds to electron transitions from energy levels higher than n = 2 energy level.

c. Transitions from higher energy levels to 5th energy level produce Pfund series which falls in the infrared region

d. The lines of Lyman series appear in the visible region

141. Which of the following are the limitations of Bohr's model?

a. It can not be applied to hydrogenic species

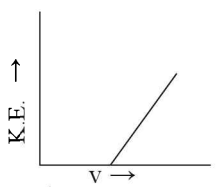
b. It can not explain the intensities or the fine spectrum

c. It can not explain the principle of quantization of angular momentum.

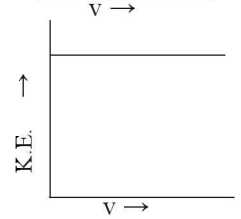
d. It can not explain circular orbit concept

142. Which do not represent correct graph(s) here?

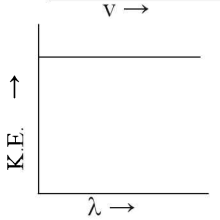
a.



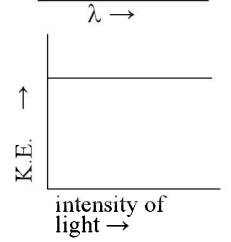
b.



c.



d.



143. Which of the following statement is/are correct regarding angular nodes?

a. They are independent from the radial wave function (R)

b. They are directional in nature

c. They are dependent on the radial wave function

d. They are dependent on angle θ and ϕ.

144. The correct matching is shown by

a. Wave mechanical model: The electron finding probability for 2s orbital in H-atom is zero at $r = a_0$ where $a_0 = 0.53$ Å.

b. Bohr's model: The angular momentum of electron in first excited state of H-atom is 5h/11

c. Rutherford's model : Very few α-particles get deflected by large angles because nucleus has much smaller volume than that of atom

d. Thomson's model: The electrons on disturbing by collision vibrate around their mean position and emit electromagnetic radiation.

145. Which of the following statement(s) is/are correct?

a. Planck's study of black-body radiation led to the hypothesis that radiation is emitted in quantas of energy

b. Photons of lower frequency radiation have lower energies.

c. Bohr's model of the hydrogen atom showed emission of energy by atoms occurs when an electron moves to a higher orbit.

d. The lowest energy state of an electron in an atom is known as the ground state

146. Which of the following match is/are correct?

a. 4f orbital (maximum 2 electrons)

b. 4s orbital (2 radial nodes)

c. 3dxy orbital (2 nodal planes)

d. 5px orbital (2 radial nodes)

147. Which of the following is/are not correctly matched?

a. e/m ratio of anode rays : Independent of gas in the discharge tube

b. Radius of nucleus : $(\text{Mass number})^{1/2}$

c. Momentum of H-atom when electrons returns from n = 2 to n = 1 : 3Rh/4

d. Momentum of photon : Independent of wave length of light

148. Select the correct statement(s):

a. Gravitation has a rest mass zero but spin 2 and it is exchanged during gravitational interaction between bodies

b. Rest mass of photon is zero and increases with its velocity

c. Photons are carrier of energy, momentum and angular momentum between interacting particles

d. Mass of a p-meson is about 276 times of an electron and it keeps nucleons together

149. Which statement is/are true for many electron atoms?

a. The 2Px and 2Py orbitals have the same energy in the absence of an applied magnetic field

b. The 2s and 2p orbitals are of differing energies, whereas in a hydrogen atom they are same.

c. Outer electrons penetrate the electron clouds of inner electrons

d. Outer electrons experience the full nuclear charge

150. Regarding the atomic orbital ψ_{1s} of the hydrogen atom, which of the following statements is/are true?

a. ψ_{1s} has no nodal plane.

b. ψ_{1s} has a non-zero value at the nucleus

c. $[\psi_{1s}]^2$ is a measure of the probability per unit volume of locating the electron.

d. The magnitude of ψ_{1s} is experimentally measurable.

Linked-Comprehension Type Questions

Comprehension 1

Elements are composed of tiny particles known as atoms. Atoms are made of fundamental particles (e, p, n). According to Rutherford's Atomic Model p, n are located in Nucleus. Bohr's model explained the existence of circular orbits (energy levels) around the nucleus. Bohr's model can explain the spectrum of hydrogenic species and helps in find e, v, r (energy, velocity and radius) in nth orbit.

151. The ratio of r_4 and r_3 for hydrogen atom and that of Li^{+2} ion

a. 1 :3 **b.** 3 : 1

c. 1 : 9 **d.** 1 :1

152. The value of electro static potential energy =

a. mv^2 **b.** $\frac{ze^2}{r}$

c. $\frac{1}{4\pi\epsilon} \times \frac{q_1 q_2}{r}$ **d.** $\frac{1}{4\pi\epsilon} \frac{ze^2}{r}$

153. Suppose Rutherford had used electron in place of alpha - particles. Than what conclusion is achieved

a. Wave nature of electron

b. Specific charge on electron

c. Position on electron

d. Charge on electron.

154. In an orbit the velocity of an electron in excited state of H-atom is 1.093×10^8 cm /s . What is the circumference in this orbit.

a. 6.65 Å **b.** 13.3 Å

c. 3.33 Å **d.** 26.65 Å

Comprehension 2

An electromagnetic radiation is emitted when an electric discharge is passed through H_2 gas. When passed through a prism of diffraction grating, this radiation is found to have a series of components in U.V, visible, and Infrared ragions. Rydberg used the relation $\frac{1}{\lambda} =$

$R_H \left(\frac{1 - 1}{n_1^2 \; n_2^2}\right)$ to find wavelength.

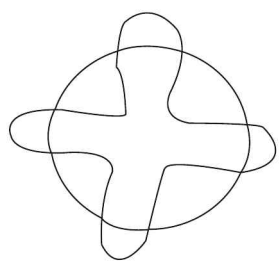
Here R_H = Rydberg's constant ($1.1 \times 10^7 \; m^{-1}$)

155. Same wavelength is observed with respect to Li^{2+} from a transition of $n_2 = 6$ to $n_1 = 3$

a. $4 \rightarrow 2$ of Be^{+3} **b.** $3 \rightarrow 1$ of H-atom

c. $4 \rightarrow 2$ of He^+ **d.** $4 \rightarrow 2$ of He-atom

156. The wave motion of an electron in a Bohrs Orbic of Hydrogen atom can be shown by the figure given below find potentisn energy



a. +1.7 eb **b.** -1.7 eb

c. -3.4 eb **d.** -13.1 eb.

157. The Balmer-Rydberg equation can be extended to ions with only one electron, such as He^+. In that case it has the form:

$1/\lambda = Z^2 R (1/m^2 - 1/n^2)$, here Z is the atomic number. What is the energy of the photon required to promote an electron in He^+ from a 1s-orbital to a 2p-orbital?

a. 12 hcR **b.** 6 hcR

c. 3 hcR **d.** (3/4) hcR

158. For hydrogen, what is the wavelength of the photon emitted when an electron drops from a 4d-orbital to a 2p-orbital in a hydrogen atom? The Rydberg constant is $1.097 \times 10^{-2} \; nm^{-1}$.

a. 2.86 .4 nm
b. 584.6 nm
c. 486.2 nm
d. 648.2 nm

Comprehension 3

The ground state electronic Configuration of a multielectron atom is possible by using these rules.

i. The lowest energy orbital is filled first (Aufbau).
ii. Any orbital can have max. $2e^-$ having opposite spin (Pauli).
iii. In case of degenerate orbitals each is half filled before any of these is completely filled (Hund's Rule).

159. Which of the following represent electron configuration that violate the Pauli exclusion principle?

I. [Ne] $3s^1\,3p^5$
II. [Kr] $4d^{12}\,5s^2\,5p^3$
III. [Ar] $3d^{10}\,4s^2\,4p^2$

a. Only (II)
b. Only (I)
c. Both (I) and (III)
d. Both (II) and (III)

160. List all the elements that have a ground state configuration with five unpaired electrons in the 3d-subshell.

a. Mn **b.** Cr
c. Cr and Mn **d.** Mn, Fe, Co,

161. Which have the largest number of unpaired electrons in p-orbitals in their ground state electronic configurations?

a. Te, I, Xe **b.** F, Cl, Br
c. Ne, Ar, Kr **d.** N, P, As

162. Which of the following represent electronic configurations that are allowed but do not represent ground-state configurations?

I. [Ne] $3s^1\,3p^5$
II. [Kr] $4d^{12}\,5s^2\,5p^3$
III. [Ar] $3d^{10}\,4s^2\,4p^2$

a. I and II **b.** II and III
c. only II **d.** only I

Comprehension 4

Schrodinger proposed Quantum Mechanical model in 1926. He described an atom by an equation similar to that used to explain wave motion. The behaviour of each electron in an atom is characterized by a wave function (ψ). ψ^2 defines the brobability of finding the electron in a given volume of space. Each wave function has a set of three variable known as Quantum Numbers (n, l, m).

163. Select the correct statements.

i. At a node the wavefunction ψ has zero amplitude.
ii. the number of peaks (maxima) in radial distribution.
iii. ψ is (n-l) represents probability of finding electrons and it is direction independent.
iv. ψ 4, 2, 0 stands for $4dz^2$

a. i, ii, iii **b.** i, ii , iv
c. ii, iii, iv **d.** i, ii, iii, iv

164. For a particular orbital, as one goes awayfrom the nucleus along the Z-axis, the probability density decreases to zero, then increases, and finally decreases without increasing a second time. This is consistent with a

a. $2p_z$ orbital
b. 2s orbital
c. 3s-orbital
d. 2s or 2Pz orbital

165. Which orbitals have two nodal planes passing through the nucleus?

a. d **b.** p
c. s **d.** All in the third shell

Assertion-Reason Type Questions

In the following questions, two statements (Assertion) A and Reason (R) are given. Mark

a. If A and R both are correct and R is the correct explanation of A
b. If A and R both are correct but R is not the correct explanation of A
c. A is true but R is false
d. A is false but R is true
e. A and R both are false

166. **(A):** The shortest wavelength of transition of Lyman series is observed when electron jumps from orbit number, $n = \infty$ to $n = 1$.
(R): Since the wavelength of transition is given by $hc/\lambda = \Delta E$

167. **(A):** The kinetic energy of the photo-electron ejected increases with increase in intensity of incident light.
(R): Increase in intensity of incident light increases the rate of emission.

168. **(A):** Limiting line in the Balmer series of H-spectrum has a wavelength of 364.4 nm.

(R): Limiting line is obtained for a jump of electron from n = ∞ to n = 2.

169. **(A):** $3dZ^2$ orbital is spherically symmetrical.

(R): $3dZ^2$ orbital is the only d-orbital which is spherical in shape.

170. **(A):** Shapes of the orbitals are represented by boundary surface diagrams of contrast probability density.

(R): Boundary surface diagram helps in interpreting and visualizing an atomic orbital.

171. **(A):** Half-filled and fully-filled degenerate orbitals are more stable.

(R): Extra stability is due to the symmetry of degenerate orbitals.

172. **(A):** A spectral line will be observed for a 2px – 2py transition.

(R): The energy is released in the form of wave of light when electron drops from 2px to 2py orbital.

173. **(A):** The angular momentum of d-orbital is $\sqrt{6}\ h/2\pi$

(R): d-orbitals have double dumb-bell shaped except dz^2.

174. **(A):** Electron can have wavelength equal to that of proton of Ve = 1836 Vp.

(R): Electron has mass 1/1836 of the mass of proton.

175. **(A):** The kinetic energy of photoelectrons increases with increase in frequency of incident light.

(R): The number of photoelectron ejected increases with increase in intensity of light.

176. **(A):** Fluorescence is the emission of light which has been absorbed by the molecule

(R): It may continue for appreciable time after the exciting light is switched off.

177. **(A):** Fe^{2+} has 24 electrons hence, its electronic configuration, is similar to that of Cr(24) [Ar] $3d^5\ 4s^1$.

(R): All the five unpaired electrons in 3d gives stability to the ion.

178. **(A):** On heating a solid for a longer time, radiations become white and then blue as the temperature becomes very high.

(R): Radiations emitted go from a lower frequency to higher frequency as the temperature increases.

179. **(A):** Cu^{2+} is a coloured ion.

(R): Every ion with unpaired electron is coloured.

180. **(A):** The paramagnetism of Cu^+ ion is zero.

(R): Paramagnetism is given by the relation $\mu = \sqrt{S(S+1)}$ magnetons where S is the total spin.

181. **(A):** Electrons are negatively charged.

(R): The application of electric and magnetic field deflected the rays in the discharge tube towards the cathode.

182. **(A):** Electronic configuration of K (19) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$.

(R): Energy of 4s < 3d hence, 4s is filled before 3d as decided by Aufbau rule.

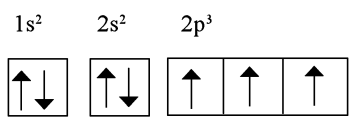
183. **(A):** Atoms can neither be created not destroyed.

(R): Under similar conditions of temperature and pressure, equal volumes of gases do not contain equal number of atoms.

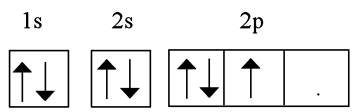
184. **(A):** For n = 3, l may be 0, 1 and 2 and m may be 0; 0±l; 0, ±1 and ±2

(R): For each value of n, there are 0 to (n – 1) possible values of l; and for each value of l, there are 0 to ±l values of m.

185. **(A):** The electronic configuration of nitrogen atom is represented as:



and not as



(R): The electronic configuration of the group state of an atom is the one which has the greatest multiplicity.

Matrix-Match Type Questions

	p	q	r	s
A.	O	O	O	O
B.	O	O	O	O
C.	O	O	O	O
D.	O	O	O	O

186. Match list I with list II and select the correct answer using the codes given below the lists.

Column I (Metal ions)	Column II (Magnetic moment)
A. Cr^{3+}	(p) $\sqrt{35}$
B. Fe^{3+}	(q) $\sqrt{8}$
C. Ni^{2+}	(r) $\sqrt{24}$
D. Mn^{2+}	(s) $\sqrt{15}$

187. Match the following:

Column I (Principle)	Column II (Discoverer)
A. Exclusion principle	(p) Hund
B. Multiplicity rule	(q) Heisenberg
C. Uncertainty principle	(r) Einstein
D. Quantum theory	(s) Planck
	(t) Pauli

188. Match the following:

Column I	Column II
A. Number of values of 'l' for an energy level …… (n – 1)	(p) 0, 1, 2
B. Actual values of 'l' for a particular type of orbital	(q) +l …… +2, +1, 0, -1
C. Number of 'm' values	(r) -2, …. -1
D Actual values of 'n' for a particular type of orbital	(s) n

189. Match the following:

Column I	Column II
A Energy per molecule	(p) E = hv
B. Wave number	(q) C/λ
C. Frequency	(r) 1/λ
D. Energy of one quantum	(s) N hυ

190. Match the following:

Column I	Column II
A. Energy of e^- in nth orbit	(p) α n^2
B. Wavelength of e^- in nth orbit	(q) α _ $1/n^2$
C. Velocity of e^- in nth orbit	(r) α n
D. Radius of e^- in nth orbit	(s) α 1/n

191. Match the following:

Column I	Column II
A. Principal quantum number	(p) Shape of orbital
B. Magnetic quantum number	(q) Orientation of orbital
C. Azimuthal quantum number	(r) Spinning of electron
D. Spin quantum number	(s) Size of orbital

192. Match the following:

Column I	Column II
A. 2s	(p) Sum of (n+1) is 3
B. 2p	(q) total number nodes are two
C. 3s	(r) only one node
D. 3p	(s) no radial node

193. Match the following:

Column I	Column II
A. Na	(p) Last valence e^- in 3^{rd} orbit
B. Cl	(q) Last valence e^- in 2^{nd} orbit
C. Li	(r) m-value is zero for last e^-
D. Mg	(s) one un-paired e

194. Match the following:

Column I	Column II
A. He^+	(p) 1s1 configuration
B. Li^{+2}	(q) μ is 1.732 B.M
C. H-atom	(r) 0.529 Å value of radius in 1^{st} or 2^{nd} orbit
D. Be^{+3}	(s) -13.6 e.v/atom energy in 1^{st} orbit

195. Match the following:

Column I	Column II
A. Cr	(p) $4s^1$ state Configuration state.
B. Cu	(q) Unpaired e^- in 4s- orbit .
C. K	(r) Un-paired electron in 3d-orbital
D. Fe	(s) Ferro magnetic

The IIT-JEE Corner

196. Among KO_2, AlO_2^-, BaO_2 and NO_2^+, unpaired electron is present in

a. NO_2^+ and BaO_2
b. KO_2 and AlO_2^-
c. KO_2 only
d. BaO_2 only

[IIT 1997]

197. The first use of quantum theory of explain the structure of atom was made by

a. Heisenberg **b.** Bohr
c. Planck **d.** Einstein

[IIT 1997]

198. Which of the following statement(s) are correct?

1. the electronic configuration of Cr is [Ar] $3d^5$ $4s^1$ (atomic number of Cr = 24)
2. the magnetic quantum number may have a negative value
3. in silver atom, 23 electrons have a spin of one type and 24 of the opposite type (atomic number of Ag = 47)
4. the oxiation state of nitrogen in HN_3 is –3.

a. 1, 2, 3 **b.** 2, 3, 4
c. 3, 4 **d.** 1, 2, 4

[IIT 1998]

199. One mole of calcium phosphide on reaction with excess of water gives

a. one mole of phosphine
b. two moles of phosphoric acid
c. two moles of phosphine
d. one mole of phosphorus pentoxide

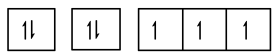
[IIT 1999]

200. The electrons, identified by quantum numbers n and l (i) n = 4, l = 1 (ii) n = 4, l = 0 (iii) n = 3, l = 2 (iv) n = 3, l = 1 can be placed in order of increasing energy from the lowest to highest as

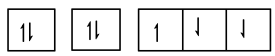
a. (iv) < (ii) < (iii) < (i)
b. (ii) < (iv) < (i) < (iii)
c. (i) < (iii) < (ii) < (iv)
d. (iii) < (i) < (iv) < (ii)

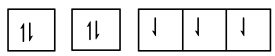
[IIT 1999]

201. Ground state electronic configuration of nitrogen atom can be represented by


(1)

(2)


(3)


(4)

a. 1 only **b.** 1, 2
c. 1, 4 **d.** 2, 3

[IIT 1999]

202. The quantum number + ½ and – ½ for the electron spin represent

a. rotation of the electron in clockwise and anti-clockwise direction respectively.
b. rotation of the electron in anti-clockwise and clockwise direction respectively.
c. magnetic moment of the electron pointing up and down respectively.
d. two quantum mechanical spin states which have no classical analogues.

[IIT 2000]

203. The electronic configuration of an element is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^5$ $4s^1$. This represents

a. excited state **b.** ground state
c. cationic form **d.** anionic form

[IIT 2000]

204. The number of nodal planes is a px orbital is

a. 1 **b.** 2
c. 3 **d.** 0

[IIT 2000]

205. The wavelength associated with a golf ball weighing 200 g and moving at a speed of 5 m/h is of the order

a. 10^{-10} m **b.** 10^{-20} m

c. 10^{-30} m **d.** 10^{-40} m

[IIT 2001]

206. How many moles of electrons weigh one kilogram?

(mass of electron = 9.108×10^{-31} kg, Avogadro number = 6.023×10^{23})

a. 6.023×10^{23}

b. $1/9.108 \times 10^{31}$

c. $\frac{6.023}{9.108} \times 10^{54}$

d. $\frac{1}{9.108 \times 6.023} \times 10^{8}$

[IIT 2002]

207. If the nitrogen atom has electronic configuration $1s^7$, it would have energy lower than that of the normal ground state configuration $1s^2\,2s^2\,2p^3$, because the electrons would be closer to the nucleus. Yet $1s^7$ is not observed because it violates.

a. Heisenberg uncertainty principle

b. Hund's rule

c. Pauli's exclusion principle

d. Bohr postulates of stationary orbits.

[IIT 2002]

208. Rutherford's experiment, which established the nuclear model of the atom, used a beam of

a. β–particles, which impinged on a metal foil and got absorbed

b. γ–rays, which impinged on a metal foil and ejected electrons

c. Helium atoms, which impinged on a metal foil and got scattered

d. Helium nuclei, which impinged on a metal foil and got scatterd.

[IIT 2002]

209. An aqueous solution of 6.3 g of oxalic acid dihydrate is made upto 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this sol is

a. 40 ml **b.** 20 ml

c. 10 ml **d.** 4 ml

[IIT 2002]

210. Which has maximum number of atoms?

a. 24 g of C (12)

b. 56 g of Fe (56)

c. 27 g of Al (27)

d. 108 g of Ag (108)

[IIT 2003]

211. The radius of which of the following orbits is same as that of the first Bohr's orbit of hydrogen atom?

a. He^+ (n = 2) **b.** Li^{2+} (n = 2)

c. Li^{2+} (n = 3) **d.** Be^{3+} (n = 2)

[IIT 2004]

212. Radial nodes present in 3s and 2p-orbitals are respectively

a. 0, 2 **b.** 2, 0

c. 2, 1 **d.** 1, 2

[IIT 2005]

213. Match the entries in **Column I** with the correctly related quantum number (s) in **Column II**.

Column I	Column II
(a) Orbital angular momentum of the electron in a hydrogen-like atomic orbital	(p) Principal quantum number
(b) A hydrogen –like one-electron wave function obeying Pauli principle	(q) Azimuthal quantum number
(c) Shape, size and orientation of hydrogen-like atomic orbitals	(r) Magnetic quantum number
(d) Probability density of electron at the nucleus in hydrogen like atom	(s) Electron spin quantum number

[IIT 2005]

ANSWERS

Straight Objective Type Questions

1. c	**2.** a	**3.** d	**4.** a	**5.** c	**6.** c	**7.** d	**8.** a	**9.** c
10. b	**11.** b	**12.** c	**13.** c	**14.** a	**15.** c	**16.** c	**17.** b	**18.** b
19. d	**20.** d	**21.** b	**22.** b	**23.** D	**24.** b	**25.** b	**26.** a	**27.** d
28. c	**29.** c	**30.** b	**31.** d	**32.** b	**33.** b	**34.** d	**35.** d	**36.** b
37. a	**38.** d	**39.** a	**40.** d	**41.** a	**42.** b	**43.** a	**44.** c	**45.** b
46. c	**47.** b	**48.** d	**49.** c	**50.** b	**51.** d	**52.** a	**53.** d	**54.** a
55. a	**56.** b	**57.** c	**58.** c	**59.** b	**60.** d	**61.** b	**62.** a	**63.** c
64. a	**65.** a	**66.** d	**67.** a	**68.** c	**69.** b	**70.** c	**71.** b	**72.** d
73. a	**74.** a	**75.** b						

Brainteasers Objective Type Questions

76. a	**77.** c	**78.** a	**79.** c	**80.** b	**81.** a	**82.** c	**83.** b
84. a	**85.** c	**86.** a	**87.** b	**88.** b	**89.** b	**90.** a	**91.** c
92. a	**93.** a	**94.** a	**95.** d	**96.** b	**97.** d	**98.** b	**99.** c
100. d	**101.** a	**102.** b	**103.** a	**104.** d	**105.** c	**106.** b	**107.** d
108. c	**109.** a	**110.** d	**111.** c	**112.** c	**113.** b	**114.** a	**115.** d
116. b	**117.** a	**118.** b	**119.** d	**120.** c			

Multiple Correct Answer Type Questions

121. a,b,d	**122.** a,b,d	**123.** b,c,d	**124.** a,c,d	**125.** b,c,d	**126.** a,c,d
127. a,b,d	**128.** a,b,d	**129.** a,b,c	**130.** a,b,d	**131.** a,d	**132.** a,c,d
133. b,d	**134.** a,c,d	**135.** b,d	**136.** a,c,d	**137.** a,b,c	**138.** b,d
139. a,b	**140.** a,b,c	**141.** b,c	**142.** b,c	**143.** a,b,d	**144.** b,c,d
145. a,b,d	**146.** a,b,c	**147.** a,b,d	**148.** a,b,c,d	**149.** a,b,c	**150.** a,b,c

Linked-Comprehension Type Questions

Comprehension 1

151. b	**152.** c	**153.** a	**154.** b

Comprehension 2

155. c	**156.** b	**157.** c	**158.** c

Comprehension 3

159. a	**160.** c	**161.** d	**162.** d

Comprehension 4

163. b	**164.** b	**165.** a

Assertion Reason Type Questions

166. a	**167.** d	**168.** a	**169.** e
170. a	**171.** b	**172.** e	**173.** b
174. a	**175.** b	**176.** c	**177.** d
178. a	**179.** c	**180.** c	**181.** a
182. a	**183.** c	**184.** a	**185.** a

Matrix-Match Type Questions

186. A-(s), B-(r), C-(t), D-(p)

187. A-(t), B-(p), C-(q), D-(s)

188. A-(s), B-(p), C-(r), D-(q)

189. A-(s), B-(r), C-(q), D-(p)

190. A-(q), B-(r), C-(s), D-(p)

191. A-(s), B-(q), C-(p), D-(r)

192. A-(r, s), B-(p, r, s), C-(p, q, s), D-(q)

193. A-(p, r, s), B-(p, r, s), C-(q, r, s), D-(p, r)

194. A-(p, q), B-(p, q, r), C-(p, q), D-(p, q, r, s)

195. A-(p, q, r, s), B-(p, q), C-(p, q), D-(r, s)

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196. c **197.** b **198.** a **199.** c **200.** a **201.** c **202.** d **203.** b

204. a **205.** c **206.** d **207.** c **208.** d **209.** a **210.** a **211.** d

212. b **213.** A–q, B–s, C–p, q, r, D–p

Hints and Explanations

Straight Objective Type Questions

3. Total values of m = ($2l + 1$) = no. of orbitals in subshell.

As $l = 2$ represents 'd' subshell and d subshell has five orbitals . (d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}).

8. M^{2+} has 5 unpaired electrons.

Atomic number is 25.

$M \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$

$M^{2+} \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

12. As Ni^{2+}, Ti^{3+} has 2, 1 unpaired electrons respectively so both are coloured.

18. $\Delta E = h\nu = h\ \frac{c}{\lambda}$.

$\lambda = \frac{hc}{\Delta E}$

i.e., $\lambda \propto 1/\Delta E$

$\Delta E = E_4 - E_1$ will be maximum and hence λ will be minimum.

21. I.E. of $He^+ = 13.6\ eV \times Z^2$

$= 13.6\ eV \times 4 = 54.4\ eV$

32. The radius of nucleus is of the order of 1.5×10^{-13} to 6.5×10^{-13} cm or 1.5 to 6.5 Fermi (1 Fermi = 10^{-13} cm)

33. It is Mn^{2+} having five unpaired electrons so its magnetic moment is

$\mu = \sqrt{5\ (5+2)}$

$= 5.9$ BM.

34. Bohr model can explain spectrum of atoms/ions containing one electron only.

35. As circumference = $n\lambda$

$= 4\lambda$

36. As N^{3-}, F^- and Na^+ have 10 electrons.

39. It is the 1s level, the ground state, where the H-atom can only absorb a photon and go to higher excited states.

41. $_{28}Ni = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

$Ni^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

Hence d-electrons in Ni and Ni^{2+} are same.

42. Orbitals having same ($n + l$) value in the absence of electric and magnetic field will have same energy.

43. Rb has the configuration, $1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^1$; so n = 5, l = 0, m = 0 and s = ½

44. $n = 3$, $l = 0$ indicates last shell is 3s.

So electronic configuration will be $1s^2\ 2s^2\ 2p^6\ 3s^{1\text{-}2}$

Atomic number is 11 or 12.

45. No. of lines $= \dfrac{(n_2 - n_1)\,(n_2 - n_1 + 1)}{2}$

$= \dfrac{(7-2)\,(7-2+1)}{2} = 15$

50. The central part consisting whole of the positive charge and most of the mass, called nucleus, is extremely small in size compared to the size of the atom.

53. The principal quantum number (n) is related to the size of the orbital (n = 1, 2, 3….)

56. As for s-orbital l = 0

57. One p-orbital can accommodate up to two electrons with opposite spin while p-subshell can accommodate upto six electrons.

61. Rutherford's scattering experiment led to the discovery of nucleus.

62. Apply

$\Delta x \,.\, \Delta v \geq \dfrac{h}{4\pi m}$.

64. Here Mn^{2+} has 5 unpaired electrons so it has maximum magnetic moment.

65. $\lambda = h/mv$

$\lambda = \dfrac{6.626 \times 10^{-34}}{60 \times 10^{-3} \times 10} = 10^{-33}$ m (nearly)

67. As these have 18 electrons.

70. Number of electron in SO_3^{2-} =

$16 + 8 \times 3 + 2 = 42$

No. of e^- in $CO_3^{2-} = 6 + 8 \times 3 + 2 = 32$

No. of e^- in $NO_3^- = 7 + 8 \times 3 + 1 = 32$

These are not isoelectronic species as number of electrons are not same.

72. As $mvr = nh/2\pi$

$= 5h/2\,\pi = 2.5h/\,\pi$

Brainteasers Objective Type Questions

77. As they have 5, 3, 2, 1 number of unpaired electrons respectively.

79. $\lambda = \dfrac{h}{\sqrt{2mE}}$.

$\lambda E^{1/2}$ = constant.

So $\lambda_1 \sqrt{E_1} = \lambda_2 \sqrt{E_2}$

$\lambda_1/\lambda_2 = \sqrt{(E_2/E_1)} = 2$

Therefore $E_2/E_1 = 4$

80. $\dfrac{1}{\lambda} = R \times 1^2 \left[\dfrac{1}{2^2} - \dfrac{1}{3^2}\right]$

On solving, we get

$\dfrac{1}{\lambda} = \dfrac{5R}{36}\ cm^{-1}$

81. Number of electrons in ClO_2^-

$= 17 + 2 \times 8 + 1 = 34$

Number of electrons in ClF_2^+

$= 17 + 2 \times 9 - 1 = 34$

83. $E = hc/\lambda$ …….(1)

$E_1 = hc/\lambda_1$ …….(2)

$E_2 = hc/\lambda_2$ ……..(3)

$E = E_1 + E_2 = hc\,(1/\lambda_1 + 1/\lambda_2)$

$\dfrac{1}{\lambda} = \dfrac{1}{\lambda_1} + \dfrac{1}{\lambda_2}$.

$\dfrac{1}{(300 \times 10^{-9})} = \dfrac{1}{(760 \times 10^{-9})} + \dfrac{1}{\lambda_2}$.

$1/\lambda_2 = \left(\dfrac{1}{300} - \dfrac{1}{760}\right) \times 10^9$

$= (0.00333 - 0.00131) \times 10^9$

$= 2.02 \times 10^6\ m^{-1}$

84. $\lambda = h/\sqrt{2m\ E}$

$= \dfrac{6.626 \times 10^{-34}}{\sqrt{2 \times 1 \times 0.5}}$ m

$= 6.626 \times 10^{-34}$ m

85. According to Heisenberg Uncertainty Principle

$\Delta p \,.\, \Delta x \geq \dfrac{h}{4\pi}$.

$m\Delta v \,.\, \Delta x \geq \dfrac{h}{4\pi}$.

$(m.\Delta v)^2 \geq \dfrac{h}{4\pi}$.

$\Delta v \geq \dfrac{1}{2m}\ \sqrt{(h/\pi)}$

86. $n_1 = 1$, $n_2 = 4$

now use $1/\lambda = R_H\,[1/n_1^2 - 1/n_2^2]$

$= 1.1 \times 10^7\,[1/1^2 - 1/4^2]$

after solving

$\lambda = 96.9$ nm.

87. For the shortest wave length transition, here $n_1 = 1$, $n_2 = \infty$

$$\frac{1}{X} = R_H \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] \quad \ldots..(1)$$

and for longest wavelength transition in Paschen series $n_1 = 3$, $n_2 = 4$

$$\frac{1}{\lambda} = R_H \times 2^2 \left[\frac{1}{3^2} - \frac{1}{4^2}\right] \quad \ldots.(2)$$

On considering eq. (1) and (2), we get

$\lambda = 36X/7$

88. As we know that $r_n \propto n^2/Z$.

For hydrogen r = 1, z = 1.

For Be^{3+}, Z = 4, n =2 for the same radius.

90. As Q is fluorine and it exists as F_2.

92. Both A and B have the valencies 3

So the formula is AB.

93. As Z has 13 electrons, Y has 9 electrons and X has 8 electrons in M shell.

95. $hv_1 = hv_0 + \frac{1}{2} m u_1^2 \quad \ldots\ldots(1)$

$hv_2 = hv_0 + \frac{1}{2} m u_2^2 \quad \ldots\ldots(2)$

$$\frac{1}{2} m u_1^2 = \frac{1}{k} \left(\frac{1}{2} m u_2^2\right.$$

From equation (1)

$$hv_1 = hv_0 + \frac{1}{2k} m u_2^2 \quad \ldots..(3)$$

$$\frac{1}{2} m u_2^2 = k hv_1 - khv_0 \quad \ldots.(4)$$

Bu equation (2) and (4), we get

$hv_2 = hv_0 - k hv_0 + k hv_1$

$v_0 (1 - k) = v_2 - kv_1$

So $v_0 = \frac{kv_1 - v_2}{(k-1)}$

96. $\frac{hc}{\lambda} = 1 + \Phi \quad \ldots.(1)$

$3 \times \frac{hc}{\lambda} = 4 + \Phi \quad \ldots.(2)$

From equation (1) and (2), we get

$\Phi = 0.5$ eV

97. I.E. of $He^+ = E \times 2^2$ (as Z for He = 2)

I.E. of $Li^{2+} = E \times 3^2$ (as Z for Li = 3)

Hence

$$\frac{\text{I.E. } (He^+)}{\text{I.E. } (Li^{2+})} = \frac{4}{9}$$

i.e., I.E. $(Li^{2+}) = \frac{9}{4} \times$ I.E. (He^+)

$= \frac{9}{4} \times 19.6 \times 10^{-18}$

$= 4.41 \times 10^{-17}$ J atom^{-1}

99. $En = \frac{13.6}{n^2}$ eV

For second excited state n = 3,

$$E_3 = -\frac{13.6}{9} = -1.51 \text{ eV}$$

102. The lines at the red end suggest Balmer series. These are obtained for the jumps n = 2 from n = 3 and second line from n = 4 and third line from n = 5 i.e., $5 \rightarrow 2$.

103. According to Schrodinger wave equation Probability = $\psi^2 dV$

Ist orbital is spherically symmetrical

$V = \frac{4}{3} \pi r^3$

$\frac{dV}{dr} = 4 \pi r^2$

So probability = $\psi^2 4\pi r^2 dr$

105. Any sub-orbit is represented as nl such that n is the principle quantum number (in the form of values) and *l* is the azimuthal quantum number (its name).

Value of $l <$ n,	l	0	1	2	3	4
		s	p	d	f	g

value of m: $-l, -l + 1 \ldots.0, +l$

value of s: $+\frac{1}{2}$ or $-\frac{1}{2}$

thus for 4f : n = 4, l = 3, m = any value between –3 to +3.

106. E.C of Cr (Z = 24) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

so electrons with l = 1 (p), are 12

with l = 2 **d.** , are 5

107. K.E. = $\frac{1}{2} mv^2$

P.E. = $-Ze^2/r$

But electrostatic force,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r}$$

(centrifugal force)

P.E. = $-mv^2$

Total energy = $\frac{1}{2} mv^2 - mv^2 = -\frac{1}{2} mv^2$

So K.E./Total energy = –1.

108. Angular momentum = $\sqrt{\ell(\ell+1)} \cdot \frac{h}{2\pi}$

For 2s electron : $\ell = 0$;

Angular momentum = $\sqrt{0} \times 1 \cdot \frac{h}{2\pi} = 0$

For 2p electron : $\ell = 1$;

Angular momentum = $\sqrt{1} \times 2 \frac{h}{2\pi} = \sqrt{2} \cdot \frac{h}{2\pi}$

109. $\frac{1}{\lambda} = v_H = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$.

$= 1.097 \times 10^7 \left(\frac{1}{1^2} - \frac{1}{\infty^2} \cdot \right)$

$\lambda = \frac{1}{1.097 \times 10^7}$ m $= 9.11 \times 10^{-8}$ m

$= 91.1 \times 10^{-9}$ m

= 91.1 nm (1 nm = 10^{-9} m)

115. $E = nhv = \frac{n\,hc}{\lambda} = n\,hc\ddot{v}$

(as $\ddot{v} = 1/\lambda$)

As E = 3J

$3 = nhc\ddot{v}$

$n = \frac{3}{hc\,\ddot{v}} = \frac{3}{hca}$.

116. Radius of the 6th orbit = $6^2 r_0 = 36\ r_0$ Circumference $= 2\pi(36\ r_0) = 72\ \pi r_0$

As $n\lambda = 2\pi r_n$.

$6\lambda = 72\ \pi r_0$

So $\lambda = 12\ \pi\ r_0$.

118. $\Delta E = mc^2$.

For Lymann series, $m_1c^2 \propto (1/1^2 - 1/2^2)$

For Balmer series, $m_2c^2 \propto (1/2^2 - 1/3^2)$

$m_1/m_2 = 3 \times 36/4 \times 5$

$m_1 : m_2 = 27 : 5$

120. Let 'n' is the principal quantum number of energy level corresponding to energy (X), the principal quantum number of energy level (Y) is (n + 3) as it emit 6 wavelengths.

So

$-\frac{13.6\ Z^2}{n^2} = X$ .....(1)

$-\frac{13.6\ Z^2}{(n+3)^2} = Y$ .....(2)

On diving equation (1) by (2), we get

$\frac{X}{Y} = \frac{(n+3)^2}{n^2}$

On solving, we get

$\sqrt{(X/Y)} = 1 + 3/n$

Multiple Correct Answer Type Questions

125. As an atomic orbital does not describe the trajectory of the electron but represents the probability of the electron in space around the nucleus.

137. They don't have same energy as they have different n + l values and for hydrogen the energy order of orbital is 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f.

Linked-Comprehension Type Questions

Comprehension 1

154. As $V_n = 2.186 \times 108 \times \frac{Z}{n}$ c.m/s

$1.093 \times 10^8 = 2.186 \times 10^8 \times \frac{1}{n}$

n=2

Circumferance = $2\pi r_n$ [as $r_n = 0.529 \times \frac{n_2}{Z}$

$= 2 \times \frac{22}{7} \times 0.529 \times 10^{-10} \times \frac{22}{1}$

$= 13.3 \times 10^{-10}$ m

= 13.3 Å

156. Here the number of waves are four so n = 4

Hence $Ep = -27 \times \frac{Z_2}{n_2}$ ev

= -27.2 = -1.7 ev

The IIT-JEE Corner

202. These represent two quantum mechanical spin states which have no classical analogues.

205. $\lambda = h/mv = \frac{6.626 \times 10^{-34}}{200 \times 10^{-3} \times 5}$

$= 6.626 \times 10^{-32}$

206. As Mass of one electron = 9.108×10^{-31} kgSo 1 kg of electrons = $1/9.108 \times 10^{-31}$

$$= \frac{10^{31}}{9.108 \times 6.022 \times 10^{23}} \text{ mol}$$

$$= \frac{10^{31-23} \text{ mole}}{9.108 \times 6.022} = \frac{10^{8}}{9.108 \times 6.022} \text{ mol}$$

207. As maximum number of electrons in any orbit, sub orbit or orbital is decided by Pauli's law.

209. Normality of oxalic acid solution (N)

W x 1000/E . V

= 6.3/63 x 1000/250 = 0.4 N

(Acid) (Base)

as $N_1 V_1 = N_2 V_2$

so $0.4 \times 10 = 0.1 \times V_2$

$$V_2 = \frac{0.4 \times 10}{0.1} = 40 \text{ ml}$$

210. As 24 g of C has maximum moles i.e., two rest have only one mole so it has maximum number of molecules.

Numericals For Practice

1. The ratio of the speeds of an electron in the first orbit of hydrogen atom to that in the 4th orbit of He^+ will be

a. 1 : 3 **b.** 2 : 1
c. 1 : 2 **d.** 1 : 4

2. The ionization potential for the electron in the ground state of the hydrogen atom is 13.6 eV $atom^{-1}$. What would be the ionization potential for the electron in the first excited state of Li^{2+}?

a. 34 eV **b.** 30.6 eV
c. 10.26 eV **d.** 16.80 eV

3. The ratio of first orbits of H, He^+ and Li^{2+} is:

a. 1 : 2 : 3 **b.** 6: 3 : 2
c. 1 : 1 : 1 **d.** 1 : 4 :9

4. The ratio of the difference between 2nd and 3rd Bohr's orbit energy to that between 3rd and 4th orbit energy is

a. 20/7 **b.** 7/20
c. 27/9 **d.** 6/28

5. The distance between 3rd and 2nd orbits in the hydrogen atom is nearly

a. 2.126×10^{-9} cm
b. 2.64×10^{-8} cm
c. 10.529×10^{-4} cm
d. 11.058×10^{-9} cm

6. The ratio of velocity of an electron in second orbit of He^+ with the velocity of light is

a. 1:9 **b.** 1:237
c. 1 : 137 **d.** 2: 237

7. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition, n = 4 to n = 2 in the He^+ spectrum?

a. n = 4 to n = 1 **b.** n = 3 to n = 2
c. n = 3 to n = 1 **d.** n = 2 to n = 1

8. Assuming Rydberg constant (R_H) to be 109670 cm^{-1}, the longest wavelength line in the Lyman series of the hydrogen spectrum is

a. 1215 Å **b.** 1125 Å
c. 970 Å **d.** 940 Å

9. In which transition of He^+ the wave number will be similar to that first line in the Balmer series of hydrogen atom

a. $3 \rightarrow 2$ **b.** $6 \rightarrow 4$
c. $5 \rightarrow 4$ **d.** $7 \rightarrow 6$

10. The wave number of the first line in the Balmer series of hydrogen atom is 15200 cm^{-1} then wave number of first line in Balmer series of Be^{3+} is nearly

a. 2.43×10^5 cm^{-1}
b. 10.86×10^4 cm^{-1}
c. 2.43×10^6 cm^{-1}
d. 11.87×10^5 m^{-1}

11. Using the Bohr model, calculate the wavelength of radiant energy associated with the transition of an electron in the hydrogen atom from the n = 4 orbit to the n = 2?

a. 5860Å **b.** 2430Å
c. 4860 Å **d.** 9720 Å

12. A 1.0 g projectile is shot from a gun with a velocity of 100 ms^{-1}, de Broglie wavelength is

a. 3.63×10^{-35} m
b. 6.63×10^{-30} m
c. 6.63×10^{-33} m
d. 3.63×10^{-32} m

13. For silver metal, the threshold frequency v_0 is 1.12×10^{17} Hx. What is the maximum kinetic energy of photoelectrons produced by shining U.V. light of 15.0 Å wavelength on the metal?

a. 3.00×10^{17} J **b.** 5.8×10^{-17} J
c. 3.9×10^{-17} J **d.** 2×10^{15} J

14. An electron has wavelength 1 Å. The potential by which the electron is accelerated will be

a. 0.0726 V **b.** 0.0505 V
c. 0.0826 V **d.** 50.25 V.

15. Suppose 10^{-14} of light energy is needed by the interior of human eye to see an object. The photons of green light ($\lambda = 550$ nm) needed to see the object are

a. 26 **b.** 280
c. 28 **d.** 300

16. The work function for a metal is 4 eV. To emit a photo electron of zero velocity from the surface of the metal, the wavelength of incident light should be

a. 2500 Å **b.** 3100 Å
c. 5600 Å **d.** 1600 Å

17. If the total energy of an electron in a hydrogen like atom in an excited state is –3.4 eV, then the de Broglie wavelength of the electron will be

a. 6.6×10^{-10} **b.** 3.5×10^{-19}
c. 5×10^{-8} **d.** 9.33×10^{-11}

18. An electron is moving with a kinetic energy of 4.55×10^{-25} J. What will be the de Broglie wavelength for this electron?

a. 7.26×10^{-8} m
b. 3×10^{-6} m
c. 3×10^{-10} m
d. 7.28×10^{-7} m

19. Calculate the number of quanta of radiations of frequency 4.66×10^{12} s^{-1} that must be absorbed in order to melt 5 g of ice (the energy required to melt 1 g of ice is 333 J)

a. 3.33×10^{18} **b.** 1900
c. 5.38×10^{23} **d.** 30.96×10^{-20}

20. The uncertainty in the momentum of an electron is 1.0×10^{-5} kg ms^{-1}. The uncertainty in its position will be ($h = 6.62 \times 10^{-34}$ kg m^2 s^{-1})

a. 11.05×10^{-29} m
b. 61.06×10^{-26} m
c. 5.27×10^{-30} m
d. 5.526×10^{-26} m

21. Energy equivalent to rest mass of electron is nearly

a. 8.19×10^{-14} J
b. 3.6×10^{9} J
c. 6.11×10^{-31} J
d. 61.96×10^{-13} J

22. The uncertainty in the position of an electron (mass = 9.1×10^{-28} g) moving with a velocity of 3.0×10^{4} cm s^{-1} accurate upto 0.011 % will be

a. 1.92 cm **b.** 7.68 cm
c. 0.175 cm **d.** 3.84 cm

23. Magnetic moment of any ion m^{3+} of 3d series is $\sqrt{35}$ BM. The atomic number of this metal ion is

a. 25 **b.** 26
c. 27 **d.** 24

24. The radius of hydrogen atom is 0.529 Å and that of proton is 1.5×10^{-15} m. If we assume that both of these pieces are spherical. What fraction of space in atom of hydrogen will be occupied by the nucleus?

a. 2.6×10^{-15} m
b. 3.2×10^{-14} m
c. 2.3×10^{-14} m
d. 9.2×10^{-14} m

25. The energy of an α- particle is 6.8×10^{-18} j. What will be the wavelength associated with it?

a. 4.4×10^{-12} **b.** 1.1×10^{-12}M
c. 2.2×10^{-8}M **d.** 2.2×10^{-12}M

ANSWER KYES

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	b	2.	b	3.	b	4.	a	5.	b
6.	c	7.	d	8.	a	9.	b	10.	a
11.	c	12.	c	13.	b	14.	c	15.	b
16.	b	17.	a	18.	d	19.	c	20.	c
21.	a	22	c	23	b	24	c	25	d

Hints and Explanations

1. Speed of electron in nth orbit,

$V = 2.19 \times 10^6 \, z/n \, ms^{-1}$

Hence $\frac{V_H}{VHe^+} = \frac{Z \, H^n \, He^+}{ZHe^+ \, n \, H}$

$= \frac{1 \times 4}{2 \times 1} = \frac{2}{1}$

i.e., $VH : VHe^+ = 2 : 1$

2. As

$\Delta E = 13.6 \, Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) eV \, atom^{-1}$

For the ionization of Li^{2+} (Z = 3) from first excited state, $n_1 = 2$ and $n_2 = \infty$

Hence,

$I.E. = \Delta E = 13.6 \times 3^2 \left(\frac{1}{2^2} - \frac{1}{\infty^2} \right)$

$= 30.6$ eV.

3. $r = \frac{n^2}{Z} \times 0.529$ Å

$r_H : r_{He} : r_{Li}^{2+}$

$1 : \frac{1}{2} : \frac{1}{3}$

$6 : 3 : 2j$

4. As $E_n = -1312/n^2$ kJ/mole

$\Delta E_{3-2} = -\frac{1312}{9} - \frac{(-1312)}{4}$

$= -1312 \left(\frac{1}{9} - \frac{1}{4} \right)$

$= \frac{-1312 \times -5}{36}$

Similarly

$\Delta E_{4-3} = -1312 \left(\frac{1}{16} - \frac{1}{9} \right)$

$= \frac{-1312 \times -7}{16 \times 9}$

$\frac{\Delta E_{3-2}}{\Delta E_{4-3}} = \frac{20}{7}$.

5. As $r_n = 0.529$ Å $\times \frac{n^2}{Z}$.

So $r_3 = 0.529 \times 3^2 = 4.761$ Å

$r_2 = 0.529 \times 2^2 = 2.116$ Å

Hence $r_3 - r_2 = 4.761 - 2.116$ Å

$= 2.6$ Å

7. For H-like particles

$\bar{v} = R \, Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

As for He^+ spectrum, for Balmer transaction

$n = 4$ to $n = 2$

So

$\bar{v} = \frac{1}{\lambda} = R \, Z^2 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = \frac{3R}{4}$

Similarly for H-spectrum

$\bar{v} = \frac{1}{\lambda} = R \left(\frac{1}{n_2^2} - \frac{1}{n_2^2} \right) = \frac{3R}{4}$

i.e., $\frac{1}{n_1^2} - \frac{1}{n_2^2} = \frac{3}{4}$ [as $n_1 = 1$]

On solving, we get

$n_2 = 2$

8. Here longest wavelength means smallest wave number. In Lyman series, it is for jump from $n_2 = 2$ to $n_1 = 1$.

$v = 109670 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$

$= 109670 \times \frac{3}{4} = 82252.5 \, cm^{-1}$

$\lambda = \frac{1}{\bar{v}} = \frac{1}{82252.5 \, cm^{-1}}$.

$= 1215 \times 10^{-8}$ cm = 1215 Å

9. As $E_n = \frac{-E_{1H}}{n^2}$

So $E_3 - E_2$ for $H = \frac{-E_{1H}}{9} + \frac{E_{1H}}{4} = \frac{5 \, E_{1H}}{36}$

Similarly

$E_6 - E_4$ for $He^+ = \frac{-E_{1H} \times 2^2}{6^2} + \frac{E_{1H} \times 2^2}{4^2}$

Hence En $He^+ = \frac{-E_{1H} \times Z^2}{n^2} = \frac{+5E_{1H}}{36}$

13. As $v = \frac{c}{\lambda} = \frac{3 \times 10^8 \, ms^{-1}}{15 \times 10^{-10} \, m}$

$= 2 \times 10^{17} \, s^{-1}$ (or Hz)

$K.E = hv - hv_0 = h(v - v_0)$

$= 6.626 \times 10^{-34} \times (2 \times 10^{17} - 1.12 \times 10^{17})$

$= 5.8 \times 10^{-17}$ J

14. As $\lambda = \frac{h}{\sqrt{(2MeV)}}$.

$1 \times 10^{-16} = \frac{6.626 \times 10^{-34}}{\sqrt{(2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V)}}$.

On solving, we get

$V = 0.0826$ V

17. As total energy $= \frac{-e^2}{2r_n} = -3.4$ eV $= \frac{E_1}{n^2}$

So $n^2 = \frac{-13.6}{-3.4} = 4$

Here $n = 2$

The velocity in second orbit

$= \frac{V_1}{2} = \frac{2.18 \times 10^8}{2}$ cm sec^{-1}

So $\lambda = \frac{h}{mu}$.

$= \frac{6.6 \times 10^{-27} \times 2}{9.108 \times 10^{-28} \times 2.18 \times 10^8}$.

$= 6.6 \times 10^{-10}$

18. As $\lambda = \frac{h}{\sqrt{(2m \text{ K.E.})}}$.

$= \frac{6.626 \times 10^{-34}}{\sqrt{(2 \times 9.1 \times 10^{-31} \times 4.55 \times 10^{-25})}}$.

$= 7.28 \times 10^{-7}$ m

19. As energy required to melt 5g of ice

$= 5 \times 333 = 1665$ J

As energy of one quantum = hv

$= 6.626 \times 10^{-34} \times 4.66 \times 10^{12}$

$= 30.19 \times 10^{-12}$

20. As $\Delta x \cdot \Delta p = \frac{h}{4\pi}$.

So $\Delta x = \frac{h}{4\pi \Delta p}$.

$= \frac{6.63 \times 10^{-34}}{4 \times 3.143 \times 10^{-5}}$.

$= 0.527 \times 10^{-29}$

$= 5.27 \times 10^{-30}$ m

21. As rest mass of electron (m_e)

$= 9.11 \times 10^{-31}$ kg

As energy (E) = mc^2

$= 9.11 \times 10^{-31} \times (3 \times 10^8)^2$ J

$= 81.99 \times 10^{15}$ J

$= 8.19 \times 10^{-14}$ J

22. As $\Delta x \cdot \Delta v = (h/4\pi)$.

Here $\Delta v = \frac{0.011}{100} \times 3 \times 10^4$ ms^{-1}

$= 3.3$ cm s^{-1}

So $\Delta x = \frac{h}{4\pi m \Delta v}$.

$= \frac{6.6 \times 10^{-27}}{4 \times 3.143 \times 9.1 \times 10^{-28} \times 3.3}$.

On solving, we get

$\Delta x = 0.175$ cm.

24. As $v = \frac{4}{3} \pi r^3$

So nucleus $= \frac{4}{3} \pi (r_n)^3$

Similarly,

v (hydrogen) $= \frac{4}{3} \pi (r_H)^3$

$0.529 \text{ n} = 0.0529 \times 10^{-9}$ m

So $\frac{\text{v (nucleus)}}{\text{v (hydrogen)}} = \frac{r^3_N}{r^3_H}$

$= (1.5 \times 10^{-15})^3 = 2.3 \times 10^{-14}$

$(0.0529 \times 10^{-9})^3$

25. $\lambda = \frac{h}{\sqrt{2mE}}$

$= \frac{6.626 \times 10^{-34}}{\sqrt{6.8 \times 10^{-18} \times 4 \times 1.66 \times 10^{-27}}}$

$= 2.2 \times 10^{-12}$ m

CHAPTER 4

Energetics

Chapter Contents

First law of thermodynamics; Internal energy, work and heat, pressure–volume work; enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity and Various levels of multiple-choice questions.

THERMODYNAMICS

Thermodynamics is the branch of science which deals with the quantitative relationships between different forms of energy. Or, It deals with the energy changes accompanying physical and chemical transformations.

Main objectives of Thermodynamics

Its main objectives are as follows:

- To decide the feasibility of a given transformation.
- To derive various energy changes and their inter relations.
- To derive laws like—Phase rule, Law of mass action etc.
- Presentation of experimental data in a correct manner.

Limitations

Its limitations are as follows:

- It is not applicable when substance is present in less amount.
- It gives no explanation of rate of reaction.
- It gives no explanation of system far from equation.
- It does not deal with internal structure of atoms and molecules.

Terms Related to Thermodynamics

System

It is the region or space to be investigated or the origin at which study of pressure, temperature etc., are to be made and which is isolated from rest of the universe with a bounding surface.

Surroundings

It is region apart from the system which might be in a position to exchange energy and mass with the system.

Homogeneous and Heterogeneous Systems

Homogeneous Systems

It is all over uniform that is made of one phase only.

Example, pure liquid or pure solid or pure gas present alone.

Heterogeneous Systems

It is non uniform as it consist of two or more phases. Example, ice and water, solid in contact with a liquid.

Type of Systems

Systems are divided into three parts:

(i) ***Open System:*** In such a system, both matter and energy can be exchanged with the surrounding.

Example, Boiling of water in a beaker,

Lime kiln or ice in an open beaker

Zinc granules reacting with dilute HCl to give hydrogen gas is also an example of open system as hydrogen gas escapes and the heat of reaction is transferred to the surroundings.

(ii) ***Closed System:*** In such a system, exchange of energy takes place only with the surroundings.

Example, Heating of liquid in a sealed tube or ice in a closed beaker.

(iii) ***Isolated System:*** In such a system, there is no exchange of matter or energy with the surroundings. Example, Liquid in a sealed thermous flask or ice in thermous flask.

Macroscopic system and Macroscopic Properties

A system is said to be macroscopic system when it has a large number of molecules, atoms or ions and the properties associated with it are called macroscopic properties.

Example, pressure, volume, temperature, position, density, colour, refractive index, viscosity and surface tension etc.

State Variables or Functions

The state of a system is fixed by its macroscopic properties if any of the macroscopic property is changed the state of a system also changes so these properties are called state variables.

These determine the state of a system. These are fundamental properties or thermodynamic parameters which depend only upon initial and final states.

Example, Pressure, temperature, volume, mass and composition are the most important state variables. Some other examples are enthalpy, free energy, internal energy, entropy, pressure, volume and number of moles.

REMEMBER

In case of a single gas composition is not one of the variables as it always remains 100%.

In a closed system having one or more components, mass is not a state variable.

Properties of System

All macroscopic properties of a system irrespective of the fact whether they are state variable or not are divided into two types:

1. ***Intensive Properties***

   Such properties remains same on any division in system that is, do not depend upon amount of substance present in the system.

   Example, Temperature, pressure, concentration, density, viscosity, surface tension, specific heat, refractive index, pH, EMF of dry cell, vapour pressure dipole moment etc.

2. ***Extensive Properties***

   Such properties depend upon amount of substance that is, their values are different in the divided system than in the entire system

   Example, Mass, volume, energy, work, internal energy, entropy, enthalpy, heat capacity, length.

- An extensive property can be made intensive by specifying it in unit amount of matter.

Example, Density $\approx \left(\frac{\text{Mass}}{\text{Volume}}\right)$

Thermodynamic Process

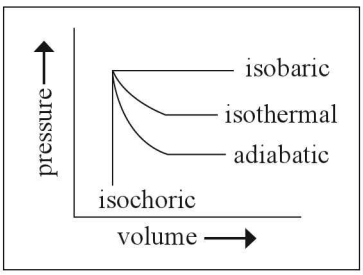
It is the path along which a change of state occurs.

or

It is a path of change of a system from one equilibrium state or another which is usually accompanied by a change in energy or mass.

Types of Process

Processes are of the following types



1. Isothermal Process

Here temperature is kept constant during each step of the process. Example,

$\Delta T = 0, \Delta E = 0$

- It is achieved by using a thermostatic control.
- Heat can be absorbed or evolved here that is, can be exchange with the surroundings.

  Example, Freezing, melting, evaporation, condensation.

2. Isobaric Process

Here pressure is kept constant ($\Delta P = 0$) during each step of the process.

Example, Expansion of gas in an open system.

- Vaporization and heating of water up to its boiling point occurs at the same atmospheric pressure.

3. Isochoric Process

Here volume is kept constant. [$\Delta V = 0$] during each step of the process.

Example, Heating of substance in a closed vessel (system) or non-expanding chamber.

4. Adiabatic Process

Here no exchange of heat takes place between the system and the surroundings that is, $\Delta Q = 0$

- It is achieved by insulating the system or in closed insulated containers (thermos)

5. Cyclic Process

- Here the System undergoes a series of changes but finally comes back to initial state.
- $\Delta E = 0, \Delta H = 0$

Reversible or Quasi-Static Process

It is carried out in such a way that the system remains in a state of equilibrium. All changes occurring at any part of the process will be exactly reversed when change in carried out in the opposite direction.

- It involves slow changes during operation.
- This process may occur in any direction.
- It gives rise to maximum work.
- Here driving force and opposing force differ with each other by a small value.

Irreversible Process

Here direction of change can not be reversed by small changes in variables. All processes occurring naturally are reversible.

- It involves fast changes during operation.
- It is uni-directional process.
- It gives rise to net work that is W rev. > W irr.
- Here, driving and opposing forces differs by a large amount.

Polytropic Process

PV^m = constant is known as general or polytropic process.

If m = 0, the process is at constant pressure.

If m = 1, the process is at isothermal.

If m = ∞, the process is constant volume.

If m = γ, the process is at adiabatic.

The value of molar specific heat is given as

$$C_m = C_v \frac{(\gamma - m)}{1 - m}$$

Thermodynamic Equilibrium

A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

If a system is heterogeneous and it is in equilibrium the macroscopic properties in the various phases remain unchanged with time.

Types: It is of three types.

(i) Mechanical Equilibrium

Here no mechanical work is done by one of the system on another part of the system and it is possible if the pressure remains the same through out the system that is, there is no flow of matter from one part to another.

(ii) Thermal Equilibrium

There is no flow of heat from one part to another that is, temperature is constant.

(iii) Chemical Equilibrium

There is no change in composition of any part of the system with time.

HEAT AND WORK

Heat

Heat is the energy transfer due to difference in temperature. Heat is a form of energy which the system can exchange with the surroundings if they are at different temperatures. The heat flows from higher temperature to lower temperature.

Heat is expressed as 'q'.

Heat absorbed by the system = +q

Heat evolved by the system = –q

Heat is expressed in calorie and the amount of heat required to raise the temperature of one gram of water by 1°C is equal to one calorie.

Now it is also expressed in joule as joule proved that there is a relation between mechanical work done (W) and heat produced (H) as

$W \propto H$

$W = J H$

Here J = mechanical equivalent of heat

J = 4.185 Joule

Work

It is the energy transfer due to difference in pressure that is, mode of energy transfer.

W = Intensity factor × Capacity factor

Here intensity factor is a measure of force responsible for work while capacity factor is a measure of extent for which work is done.

Types of work

(i) Mechanical Work (Pressure volume work)
= Force × Displacement

(ii) Electrical Work = Potential difference × charge flow
V × Q = EnF

(iii) Expansion Work = P × ΔV
= –Pext . $[V_2 - V_1]$
P = external pressure
ΔV = increase or decrease in volume.

(iv) Gravitational Work = mgh
Here m = mass of body,
g = acceleration due to gravity
h = height moved.

Units: dyne cm or erg (C.G.S.)
Newton meter (joule)

(i) If the gas expands, $[V_2 > V_1]$ and work is done by the system and W is negative.

(ii) If the gas contracts, $[V_2 < V_1]$ and work is done on the system and W is positive.

Different Types of Works and the Formulas

(i) Work done in reversible isothermal process

$$W = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$$

$$W = -2.303\ nRT \log_{10} \frac{P_1}{P_2}$$

(ii) Work done in irreversible isothermal process

$W = -P_{ext.}(V_2 - V_1)$

that is, $W = -P\,\Delta V$

Illustrations

1. Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 20 to 60 litres.

Solution $W = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

$= -2.303 \times 2 \times 2 \times 298 \times \log_{10} \frac{60}{20}$

$= -1309.7$ Calories

2. Calculate the minimum work necessary to compress 64 g of O_2 from 10 to 5 litres at 300 K. How much heat is evolved in this process?

Solution $W = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

$W = -2.303 \times \frac{64}{32} \times 2 \times 300 \log \frac{5}{10}$

$= -831.8$ calories

$Q = W = 831.8$ calories

3. Calculate the work done by 10 g of an ideal gas of molecular weight 44 in expanding reversibly and isothermally from a volume of 5 to 10 litre at 300 K.

Solution $W = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

Number of moles of ideal gas $n = \frac{10\ g}{44\ g\ mole^{-1}}$

$= \frac{10}{44}$ mole

$R = 1.987$ cal deg^{-1} $mole^{-1}$

$T = 300$ K

$V_2/V_1 = 10/5 = 2$

On substituting the values, we get

$W = -2.303 \times \frac{10}{44} \times 1.987 \times 300 \times \log_{10} 2$

On solving

$W = -93.93$ cal

Internal Energy or Intrinsic Energy

The energy stored within a substance is called its internal energy. The absolute value of internal energy cannot be determined.

Or

It is the total energy of a substance depending upon its chemical nature, temperature, pressure, and volume, amount of substrate. It does not depend upon path in which the final state is achieved.

$E = E_t + E_r + E_v + E_e + E_n + E_{P.E} + E_B$

E_t = Transitional energy

E_r = Rotational energy

E_v = Vibrational energy

E_e = Electrical energy

E_n = Nuclear energy

E_{PE} = Potential energy

E_b = Bond energy

The exact measurement of it is not possible so it is determined as ΔE as follows:

$\Delta E = \sum E_P - \sum E_R$

$\Delta E = E_f - E_i$

Here E_f = final internal energy

Ei = Initial internal energy

Ep = Internal energy of products

Er = Internal energy of reactants

Facts about Internal Energy

- It is an extensive property.
- Internal energy is a state property.
- The change in the internal energy does not depend on the path by which the final state is reached.
- Internal energy for an ideal gas a function of temperature only so when temperature is kept constant ΔE is zero for an ideal gas.
- For a cyclic process ΔE is zero (E = state function) $E \alpha T$
- For an ideal gas it is totally kinetic energy as there is no molecular interaction.

- Internal energy for an ideal gas is a function of temperature only hence, when temperature is kept constant it is zero.
- At constant volume (Isochoric) $Q_V = \Delta E$
- In adiabatic expansion, gas cooled as ΔE decreases.
- For exothermic process, ΔE is negative as $E_R > E_P$ but For endothermic process ΔE is positive as $E_R < E_P$.
- It is determined by using a Bomb calorimeter.

$$\Delta E = \frac{Z \times \Delta T \times m}{w}$$

Z = Heat capacity of Bomb calorimeter

ΔT = Rise in temperature

w = Weight of substrate (amount)

m = Molar mass of substrate

Illustrations

4. Calculate the standard internal energy change for the following reaction at 25°C:

$2H_2O_2$ (l) → $2H_2O$ (l) + O (g).

ΔH°_f at 25°C for H_2O_2 (l) = –188 kJ mol^{-1}

H_2O (l) = –286 kJ $mole^{-1}$

Solution $\Delta H^\circ = \sum \Delta H^\circ$ (Products) – ΔS° (Reactants)

= 2 (–286) + 0 – 2 (–188)

= –572 + 376 = –196 kJ

Δn (g) = 1 – 0 = 1

$\Delta H^\circ = \Delta E^\circ + \Delta n$ (g) RT

= $-196 - 1 \times 8.314 \times 10^{-3} \times 298$

= 198.4775 kJ

5. Calculate standard internal energy change (E°) for the reaction

C (graphite) + H_2O (g) → CO (g) + H_2 (g)

ΔH°_f of H_2O (g) = –241.8 kJ mol^{-1}

ΔH°_f of CO (g) = –110.5 kJ mol^{-1}

Solution C (s) + H_2O (g) → CO (g) + H_2 (g)

ΔH°reaction = $\sum \Delta H^\circ_f$ (Products) – $\sum \Delta H^\circ_f$ (Reactants)

= ΔH°_f (CO) + ΔH°_f (H_2) – [ΔH°_f (H_2O) + ΔH°_f (C)]

= 1 × (–110.5) + (0) – [1 × (–241.8) + 0]

= –110.5 + 241.8

= +131.3 kJ

Δn = Moles of gaseous products–Moles of gaseous reactants

= (1 + 1) – 1

= 1 mol

$\Delta nRT = 1 \times 8.314 \times 298 = 2477.6$ J = 2.48 kJ

$\Delta H = \Delta E + \Delta nRT$

$\Delta E = \Delta H - \Delta nRT$

= +131.3 – 2.48 = +128.82 kJ

First Law or Law of Conservation of Energy

It was introduced by Helmholtz and according to it "Energy can neither be created nor destroyed but can be converted from one form to another or the total energy of universe is constant".

It can also be written as:

- Energy of an isolated system must remain constant, although it may be transformed from one form to another.
- Energy in one form, if it disappears will make its appearance in an exactly equivalent in another form.
- When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.
- It is never possible to construct a perpetual motion machine that could produce work without consuming any energy.

Thus if heat is supplied to a system it is never lost but it is partly converted into internal energy and partly in doing work in the system that is,

Heat supplied = Work done by the system

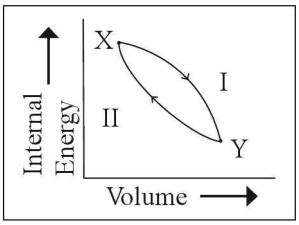
+

Increase in internal energy

So increase in internal energy

= Heat supplied – work done by the system

Mathematical Formulation of the First Law



If a system absorbs 'q' amount of heat and its state changes from X to Y and this heat is used up.

(i) On increasing the internal energy of the system

$\Delta E = E_Y - E_x$

(ii) In order to do some external work (W) on the surrounding by the system.

From first law we get the relation

$\Delta E = Q - W$ (that is, work done by the system)

$\delta E = \delta Q - \delta W$

(Work done by the system or in expansion)

or

$\Delta E = Q + W$ (that is, work done on the system)

$\delta E = \delta Q + \delta W$ or $\delta E = \delta Q + P\delta V$

(Work done on the system or in compression).

REMEMBER

+q = Heat absorbed by system

–q = Heat evolved by system

+W = Work done on the system

–W = Work done by the system

Some Useful Relations Based Upon First Law of Thermodynamics

For a Reversible Cycle: ΔE or $\delta E = 0$,

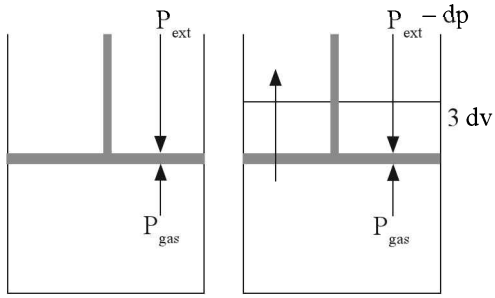
So $\delta W = \delta q$

$Q = -W_{max} = P\Delta V = 2.303nRT \log_{10} \frac{V_2}{V_1}$ or $\frac{P_1}{P_2}$

For Isochoric Process: $\Delta E = Q$ ($\Delta V = 0$)

For Adiabatic Process: $\Delta E = W$ (as $q = 0$)

PRESSURE–VOLUME WORK



Pressure Volume and Work

Let us consider a cylinder fitted with a frictionless and weightless piston having an area of cross section as 'A'. If the external pressure (P) is applied on this piston and the value of P is slightly less than that of the internal pressure of the gas.

When the gas undergoes a little expansion and the piston is pushed out by a small distance dx the work done by the gas on the piston is given by as

dw = force × distance = pressure × area × distance

dw = P.A.dx

As A.dx = dV

$\boxed{dw = P.dV}$

dw = P.dV

When the volume of the gas changes from V_1–V_2, the total work done (W) can be given as

$W = P.\int .dV$

If we consider the external pressure (P) to be constant than

$W = P\int dV = P(V_2 - V_1) = P.\Delta V$

$\boxed{W = P.\Delta V}$

Isothermal irreversible expansion of an ideal gas

When a gas expands against a constant external pressure (P_{ext} = constant). There is considerable difference between the gas pressure (inside the cylinder) and the external pressure. The temperature does not change during the process.

$$W = -\int_{V_1}^{V_2} P_{ext}\, dV$$

$$= -P_{ext} \int_{V_1}^{V_2} dV$$

$$= -P_{ext} (V_2 - V_1)$$

$$W = -P_{ext} . \Delta V$$

Work done in Isothermal reversible expansion of an ideal gas

As a small amount of work done δW on reversible expansion of a gas through a small volume dV against an external pressure 'P' can be given as

$$\delta W = -PdV$$

So the total work done when the gas expands from initial volume V_1 to final volume V_2 is given as

$$\int dW = \int_{v_1}^{v_2} PdV$$

As according to ideal gas equation PV = nRT

$$P = \frac{nRT}{V}$$

So $W_{rev.} = \int_{v_1} nRT\, dV$ (as temp. is constant)

So $W_{rev} = -nRT \ln \frac{V_2}{V_1} = -2.303\, nRT \log_{10} \frac{(V_2)}{(V_1)}$

$$W_{rev} = -2.303\, nRT \log_{10} \frac{(P_1)}{(P_2)}$$

Here negative sign indicates work of expansion and it is maximum and greater than work in the irreversible process.

As in such a case, temperature is kept constant and internal energy depends only on temperature so it internal energy is constant.

So $\Delta E = 0$

$$\Delta E = q + W$$

$$q = -W$$

Hence, during isothermal expansion, work is done by the system at the expanse of heat absorbed.

Here ΔH can be found out as follows:

$$\Delta H = \Delta E + \Delta n_g RT$$

As, for isothermal process, $\Delta E = 0$, $\Delta T = 0$

So $\Delta H = 0$

Adiabatic Reversible Expansion of An Ideal Gas

As in an adiabatic change there is no transfer of heat that is, q = 0 or dq = 0

So $\Delta E = -W$

$$dE = -dW$$

Suppose only mechanical work of expansion or contraction is made here so dW = PdV

As $dE = C_V dT = nC_v dt$

So $C_V dT = -PdV$

In a system of 1 mole of an ideal gas, for an adiabatic and reversible expansion from temperature T_1 to T_2 and volume V_1 to V_2, we get

$$C_V dT = \frac{-RT}{V} dV$$

or $$\frac{dV}{V} = \frac{-C_V}{R} . \frac{dT}{T}$$

or $$\int \frac{dV}{V} = \frac{-C_V}{R} \int \frac{dT}{T}$$

$$\ln \frac{V_2}{V_1} = \frac{-C_V}{R} \ln \frac{T_2}{T_1} = \frac{C_V}{R} \ln \frac{T_1}{T_2}$$

or $$\ln \frac{V_2}{V_1} = \ln (T_1/T_2)^{Cv/R}$$

or $$(V_1T_1)^{Cv/R} = (V_2T_2)^{Cv/R} = K$$

$$C_P - C_V = R$$

$$\ln \frac{V_2}{V_1} = \frac{C_V}{C_P - C_V} \ln \frac{T_1}{T_2}$$

or $$\frac{C_P - C_V}{C_V} \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$$

or $$(\gamma - 1) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$$ (as $\gamma = C_P/C_V$)

$$\ln (V_2/V_1)^{\gamma - 1} = \ln T_1/T_2$$

or $$(V_2/V_1)^{\gamma - 1} = (T_1/T_2)$$

or $$V_2^{\gamma - 1} T_2 = V_1^{\gamma - 1} T_1 = K$$

On substituting T by $\frac{PV}{R}$ we get

$$\frac{PV}{R} V^{\gamma - 1} = \text{Constant}$$

$$PV^{\gamma} = R \times \text{Constant} = \text{Constant}$$

Similarly

$$TV^{\gamma-1} = T(RT/P)^{\gamma-1} = \text{Constant}$$

$$T^{\gamma} P^{1-\gamma} = \text{Constant}$$

Irreversible Adiabatic Expansion

As In a free expansion the value of external pressure is zero so work done is zero.

that is, $\Delta E = W = 0$

$\Delta T = 0, \Delta H = 0$

During intermediate expansion the volume changes from V_1 to V_2 against external pressure (P_{ext})

$$W = -P_{ext}(V_2 - V_1) = -P_{ext}\frac{(RT_2 - RT_1)}{P_2 P_1}$$

$$= -P_{ext}\frac{(T_2P_1 - T_1P_2)}{P_1 P_2} \times R$$

$$W = C_V(T_2 - T_1) = -RP_{ext}\frac{(T_2P_1 - T_1P_2)}{P_1 P_2}$$

Adiabatic Compression Work

$$W = -C_V T = -C_V(T_2 - T_1) = C_V(T_1 - T_2)$$

As T_1, T_2 are initial and final temperatures respectively

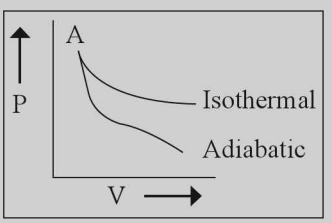
For 1 mole of gas $T = \frac{PV}{R}$

Hence adiabatic work is given as

$$W = C_V\frac{(P_1V_1 - P_2V_2)}{R\ R} = \frac{C_V}{R}(P_1V_1 - P_2V_2)$$

$$W = \frac{(P_1V_1 - P_2V_2)}{(\gamma - 1)}$$

REMEMBER



Illustrations

6. Calculate Q, W, ΔE and ΔH for the isothermal reversible expansion of 1 mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.

Solution As in isothermal process as temperature remains constant so both ΔE and ΔH are zero.

$\Delta E = 0$

$\Delta H = 0$

According to first law of thermodynamics,

$\Delta E = W + Q$

$0 = W + Q$

$$Q = -W = -2.303\ nRT \log_{10}\frac{P_1}{P_2}$$

$$= -2.303 \times 1 \times 8.314 \times 273 \log_{10}\frac{1}{0.1}$$

$= 5227.169$ J

$= 5.227$ kJ

7. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 litre to 5 litre. Calculate q, w, ΔE and ΔH for this process.

(R = 2 cal K^{-1} mol^{-1}, log 2 = 0.30, atomic weight of Ar = 40)

Solution $W = -2.303\ nRT \log_{10}\frac{V_2}{V_1}$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log_{10}\frac{5}{10}.$$

$= 103.635$ cal

$\Delta E = 0$

$q = \Delta E - W$

$q = -W = -103.635$ cal

8. A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10.0 mole of water of temperature 290.0 K. Calculate the final temperature of water (Specific heat of water = 4.184 JK^{-1} g^{-1}).

Solution

Work done = P × dV

= 3.0 × (5.0 – 3.0)

= 6.0 litre-atm = 6.0 × 101.3 J

= 607.8 J

Let ΔT be the change in temperature

Heat absorbed = m × s × ΔT

= 10.0 × 18 × 4.184 × ΔT

P × dC = m × s × ΔT

or $\Delta T = \frac{P \times dV}{m \times s}$

$= \frac{607.8}{10.0 \times 18.0 \times 4.184}$

= 0.807

Final temperature = 290 + 0.807 = 290.807 K

9. Two moles of an ideal gas initially at 300 K and one atm are compressed reversibly to half the initial volume. Find q, W, ΔE and ΔH when the process is carried on isothermally.

Solution

$W = 2.303\ nRT \log_{10} \frac{V_2}{V_1}$

T = 300 K

n = 1

R = 1.98 cal deg^{-1} $mole^{-1}$

As $V_2 = ½\ V_1$

$W = 2 \times 2.303 \times 1.98 \times 300 \log_{10} ½$

= –1914.0 cal

As the process is being carried on isothermally that is, no change of temperature.

ΔH = 0 and ΔE = 0

According to first law of thermodynamics,

q = ΔE + PΔV

q = ΔE + W

q = 0 + W

q = –1914 cal

W = –1914 cal ΔE = 0, ΔH = 0

q = –1914 cal.

10. Find the value of Q, W and ΔE for the reversible adiabatic expansion of 1 mole of an ideal gas (C_V = 3/2 R) from 5.00 to 25.00 litres at 27°C.

Solution

For adiabatic process Q = 0.

$\Delta E = W = C_V (T_2 - T_1)$ (for adiabatic)

$T_1 (V_1)^{R/Cv} = T_2 (V_2)^{R/Cv}$

$T_2 = T_1 (V_1/V_2)^{R/Cv}$

$= 300.0\ (5/25)^{2R/3R}$

$= 300.0\ (5/25)^{2/3}$

$T_2 = 102.6$ K

$\Delta E = W = 3/2\ R\ (T_2 - T_1)$

$= 1.500 \times 1.98\ (102.6 - 300)$

ΔE = –588.4 cal/mol.

11. One mole of an ideal gas which C_V = 3/2 R is heated at a constant pressure of 1 atm from 298 K to 373 K. Find ΔH and ΔU.

Solution

$C_V = \frac{3}{2} R$

$C_P = C_V + R = \frac{3}{2} R + R = \frac{5}{2} R$

Heat given at constant pressure = m. C_P ΔT

H or $q_P = 1 \times \frac{5}{2} R \times (373 - 298)$

$\Delta H = 1 \times \frac{5}{2} \times 1.987 \times 75 = 372.56$ cal

Now work done in the process = –PΔV

W = –P ($V_2 - V_1$)

$= -P \frac{(nRT_2}{P} - \frac{nRT_1)}{P}$

(As PV = nRT)

$= -nR\ (T_2 - T_1)$

$= -1 \times 1.987 \times (373 - 298)$

$= -1 \times 1.987 \times 75$

= –149.025 cal

According to first law of thermodynamics

$\Delta U = q + W$

$= 372.56 - 149.05$

$= 223.51$ cal.

12. 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.

Solution

For isothermal reversible expansion:

$$W = -2.303\ nRT \log_{10} \frac{P_1}{P_2}.$$

$$= -2.303 \times 1 \times 8.314 \times 2.73 \log_{10} \frac{1.0}{0.1}$$

At constant temperature , for expansion $\Delta T = 0$, therefore $\Delta U = 0$

$\Delta U = 1 \times C_V \times \Delta T = 0$ (for 1 mole)

$\Delta U = q + w$

So $q = -W = 5227.2$ J

At constant temperature, $P_1V_1 = P_2V_3$ or PV is constant.

So $\Delta H = \Delta U + \Delta(PV)$

$\Delta H = 0$

Limitations of the First Law of Thermodynamics

- It fails to explain why heat cannot be completely converted into work.
  that is, W = J H
- If fails to tell the spontaneity of the process.
- It can establish the relation between +q and –W but it puts no restriction regarding the direction of flow of heat.
- This law fails to tell us under what conditions and to what extent it is possible to bring about conversion of one form of energy into the other.
- The first law fails to contradict the non-existence of a 100 per cent efficient heat engine or a refrigerator.
- It fails to explain the expansion of gases in vacum when $\Delta E = 0$, $\Delta H = 0$, $W = 0$.
- It fails to explain the expansion of gases invacum when $\Delta E = 0$, $\Delta h = 0$ $w = 0$.

Heat Content or Enthalpy Change or Heat content (H)

If we deal a process in open vessel (at constant pressure), it becomes essential to use a new thermodynamic function heat enthalpy in place of internal energy. It is defined as "The amount of heat absorbed or evolved by a system at constant pressure". Mathematically, it is the sum of internal energy pressure volume energy.

- It is not a state function.
- It is denoted by H at constant pressure.
- It is denoted by E at constant volume.
- Enthalpy of the elements in gaseous, liquid or solid or combined state is taken as zero.
  Example, C, O_2 , H_2 etc.

Relation Between ΔH and ΔE: Mathematically, enthalpy change is equal to the sum of internal energy(E)

And pressure volume energy which is given as,

$H = E + PV$

The change in enthalpy of a given system is given as:

$\Delta H = H_2 - H_1$

or $\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$

$\Delta H = (E_2 - E_1) + (P_2V_2 - P_1V_1)$

or $\Delta H = \Delta E + \Delta (PV)$

If 'P' is constant

$\Delta H = \Delta E + P\Delta V$

or $\Delta H = Q$

Hence the change in enthalpy of the system ΔH may be defined as the amount of heat absorbed at constant pressure.

As $P\Delta V = \Delta n_g RT$

So $\Delta H = \Delta E + \Delta n_g RT$

Here ΔH = change in enthalpy in constant pressure

ΔE = change in enthalpy in constant volume.

Δn_g = difference in the moles of gaseous reactants and product

Illustrations

13. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured of constant volume and at 27°C. Calculate heat of combustion of benzene at constant pressure at 27°C. (R = 8.314 J/mol/K).

Solution $C_6H_6(l) + 7½\ O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta n = 6 - 7½ = -3/2$

$\Delta H = \Delta E - \Delta nRT$

(ΔE per mole for benzene = $(327 \times 78)/7.8$

$= -327$ kJ)

$= -3270 \times 10^3 + (-3/2) \times 8.314 \times 300$

$= -32737413 = -3273.74$ kJ

14. Calculate the standard internal energy change for the following reaction at 25°C.

$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$.

ΔH°_f at 25°C

$H_2O_2(l) = -188.0$ kJ mole^{-1}

$H_2O(l) = -286.0$ kJ mole^{-1}

($R = 8.314$ JK^{-1} mol^{-1})

Solution $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

$\Delta H^\circ = \Delta H^\circ_f$ (products) $- \Delta H^\circ_f$ (reactants)

$= (2 \times 286 + 0.0) - (2 \times -188)$

$= -196$ kJ

$\Delta n = 3 - 2 = 1$

$\Delta E^\circ = \Delta H^\circ - \Delta nRT$

$= -196 \times 10^3 - 1 \times 8.314 \times 298$

$= -193.58$ kJ

Heat Capacity

The heat capacity of a system is defined as "The quantity of heat required for increasing the temperature of one mole of a system through 1°C". It is given as follows:

$$C = \frac{\delta q}{dT} \qquad \ldots\ldots (1)$$

(i) Heat capacity at constant volume

According to first law of thermodynamics,

$\delta q = dE + PdV$ .....(2)

On substituting the value of δq in equation (2)

$$C = \frac{dE + PdV}{dT} \qquad \ldots\ldots (3)$$

If volume is constant then

$C_V = (dE/dT)_V$ ..... (4)

Hence the heat capacity at constant volume of a given system may be defined as the rate of change of internal energy with temperature.

(ii) Heat capacity at constant pressure

If pressure is constant, equation (3) becomes as follows:

$$C_P = \frac{dE + PdV}{dT}$$

or $C_P = (\delta q/dT)_V$

Hence the heat capacity at constant pressure of a system may be defined as the rate of change of enthalpy with temperature.

■ For one mole of a gas C_P and C_V are known as molar heat capacities and the difference between them is equal to the work done by one mole of gas in expansion on heating it through 1°C.

At constant pressure work done by the gas

$= P\Delta V$

For one mole of gas $PV = RT$

On increasing temperature by 1°C, the volume becomes $V + \Delta V$

Hence $P(V + \Delta V) = R(T + 1)$

or $P\Delta V = R$

that is, $\boxed{C_P - C_V = P\Delta V = R}$

Thermochemistry

It deals with the heat changes during chemical reactions. It is called chemical energetics and based on first law of thermodynamics. It is called as chemical energetics and based on first law of thermodynamics.

Exothermic Reaction

- Heat is evolved here.
- ΔH is –ve as $H_R > H_P$
- $\Delta H = H_P - H_R$ = –ve (at constant pressure)

At constant volume,

$\Delta E = (E_P - E_R)$ = –ve

that is. $E_R > E_P$

Endothermic Reaction

- Here heat is absorbed.
- ΔH or ΔE = +ve for endothermic
- $\Delta H = H_P - H_R$ = +ve (at constant pressure as)
- As $H_P > H_R$ or $E_P > E_R$
- At constant volume

$\Delta E = (E_P - E_R)$ = +ve

Heat or Enthalpy of Reaction

It is the change in enthalpy (amount of heat evolved or absorbed) when the number of gm-moles of the substance indicated by a chemical reaction have undergone complete reaction.

- It is determined by water and Bomb calorimeters. Mathematically, it is given as

$= \sum H_P - \sum H_R$

- It can be express by $[\Delta H]_P$ or $[\Delta E]_V$ at constant pressure and volume respectively.

Example,

$C_2H_4\,(g) + 3O_2\,(g) \rightarrow$

$2CO_2\,(g) + 2H_2O\,(l) + 335.8$ kcal

Here 335.8 kcal heat is evolved or 335.8 kcal of internal energy of the system is decreased.

Factors Effecting Heat of Reaction

1. Nature or Physical State of Reactant and Products

Heat of reaction changes with the change of physical state of the reactants or the products.

Example,

$H_2\,(g) + \frac{1}{2}O_2\,(g) \leftrightarrow H_2O\,(g)$ ΔH = –57.8 K.cal

$H_2\,(g) + \frac{1}{2}O_2\,(g) \leftrightarrow H_2O\,(l)$ ΔH = –68.32 K.cal

that is, when steam condenses heat is evolved.

2. Allotropic Forms of the Element

$C_{diamond} + O_2\,(g) \rightarrow CO_2\,(g)$

ΔH = –94.3 Kcal

$C\,(amorphous) + O_2\,(g) \rightarrow CO_2\,(g)$ ΔH = –97.6 Kcal

that is, $C\,(d) \rightarrow C\,(amp.)$ ΔH = 3.3 Kcal

This Heat is called **Heat of Transition**.

3. Enthalpies of Solution

Heat of reaction changes when in one case dry substance react and in another case the solution state of the substance react.

Example,

$H_2S\,(g) + I_2\,(g) \rightarrow 2HI + S$; ΔH = –17.3 Kcal

$H_2S\,(sol) + I_2\,(sol) \rightarrow 2HI + S$; ΔH = –21.93 Kcal

4. Temperature

The effect of temperature on heat of reaction is given by Kirchoff equation as follows:

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_P\,dT = \Delta C_P \int_{T_1}^{T_2} dT = \Delta C_P \Delta T$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_P$$

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_V\,dT = \Delta C_V \int_{T_1}^{T_2} dT = \Delta Cv\,\Delta T$$

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_V$$

For a Reaction at Constant Pressure or Constant Volume:

$\Delta H = \Delta E + \Delta nRT$

$\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + \Delta(PV)$

* Δn = number of gaseous product – number of reactant molecules.

Illustrations

15. A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and R = 8.314 J K^{-1} mol^{-1}.

Solution Heat of combustion at constant volume,

ΔE = Heat capacity of calorimeter system × rise in temperature × $\frac{\text{Mol. mass of compound}}{\text{Mass of compound}}$

$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$

that is, $\Delta E = -885$ kJ mol^{-1}

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta n = 1 - 3 = -2$

$T = 27 + 273 = 300$ K

$R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

$\Delta H = \Delta E + \Delta nRT$

$= -885 + (-2) \times 8.314 \times 10^{-3} \times 300$

$= -885 - 4.988$

$= -889.988$ kJ mol^{-1}

16. The molar heat of formation of NH_4NO_3 (s) is –367.54 kJ and those of N_2O (g), H_2O (l) are 81.46 and –285.8 kJ respectively at 298 K and 1 atm pressure. Find ΔH and ΔU of the reaction.

$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$

Solution

$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$; $\Delta H = ?$

$\Delta H_{Reaction} = \Delta H_{Products} - \Delta H_{Reactants}$

$= \Delta HN_2O + \Delta HH_2O \times 2 - \Delta HNH_4NO_3$

$\Delta HN_2O = +81.46$ kJ

$\Delta HH_2O = -285.8$ kJ

$\Delta HNH_4NO_3 = -367.54$ kJ

ΔHReaction = +81.46 + 2(–285.8) – (–367.54)

$\Delta H = -122.6$ kJ

$\Delta H = \Delta U + \Delta nRT$

Here $\Delta n = 1 - 0 = 1$

R = 8.314 J

T = 298 K

$-122.6 \times 10^3 = \Delta U + 1 \times 8.314 \times 298$

$\Delta U = -125077$ Joule

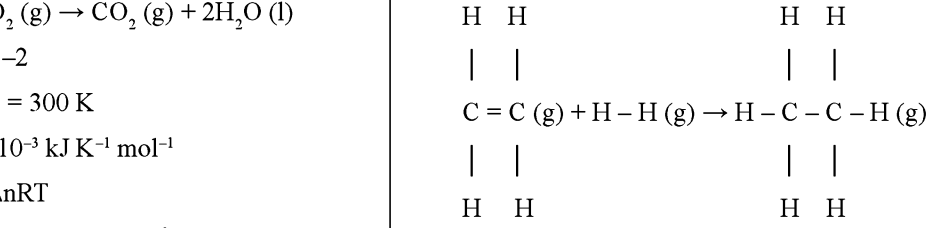
$= -125.077$ kJ

17. Calculate the enthalpy of the following reaction:

$H_2C = CH_2(g) + H_2(g) \rightarrow CH_3 - CH_3(g)$

The bond energies of C – H, C – C, C = C and H –H are 99, 83, 147 and 104 kcal respectively.

Solution



$\Delta H = ?$

ΔH = Sum of bond energies of reactants – Sum of the bond energies of products

$= [\Delta H_{C=C} + 4 \times \Delta H_{C-H} + \Delta H_{H-H}] - [\Delta H_{C-C} + 6 \times \Delta H_{C-H}]$

$= (147 + 4 \times 99 + 104) - (83 + 6 \times 99)$

$= -30$ kcal.

Heat of Formation

The amount of heat evolved or absorbed or change in enthalpy when 1 mole of a substance is obtained from its constituents or free elements.

Example,

$N_2 + 3H_2 \leftrightarrow 2NH_3$; $\Delta H = -22$ Kcal

$N_2 + O_2 \leftrightarrow 2NO$; $\Delta H = +42$ Kcal

$H_2 + Cl_2 \leftrightarrow 2HCl$; $\Delta H = -44$ Kcal

- Heat of formation of NH_3 is –11 Kcal

  Heat of formation of NO is +21 Kcal.

  Heat of formation of HCl is –22 Kcal.

- Heat of formation at 25°C and 1 atm pressure is called standard heat of formation (ΔH°).

State	Standard State
Solid	Stable crystalline form at a given temperature and 1at pressure.
Liquid	Pure liquid at a given temperature and 1at pressure
Gas	Idea gas at a given temperature and 1at pressure

$\Delta H^\circ = \sum H^\circ p - \sum H^\circ r$

Once the value of H° at 25° C for any species has been assigned the value of H° at other temperature

Can be find out by using kirchoff's equation as follows.

$$\int_{298}^{T} dH^\circ = \int_{298}^{T} C_p \, dT$$

$$Ht^\circ - H^\circ_{298} = \int_{298}^{T} Cp^\circ dT$$

$$Ht^\circ = H^\circ_{298} + \int_{298}^{T} Cp^\circ dT$$

- Standard heat of formation of free element is taken as zero.

  Example, In carbon—graphite form is taken as standard state and in sulphur, monoclinic form is standard state.

- Heat of formation may be +ve or –ve.

  If ΔH is –ve compound is exothermic.

  If ΔH is +ve compound is endothermic.

- Stability of exothermic compound is more than that of endothermic compound hence,greater the liberated energy greater is the stability of compound.

  Example, HF > HCl > HBr > HI

Illustrations

18. The molar heat of formation of NH_4NO_3 (s) is –367.5 kJ and those of N_2O (g) and H_2O (l) are +81.46 kJ and –285.78 kJ respectively at 25°C and 1 atmospheric pressure. Calculate ΔH and ΔE for the reaction.

NH_4NO_3 (s) → N_2O (g) + $2H_2O$ (l)

Solution $\Delta H^\circ = \Delta H^\circ_f$ (products) – ΔH°_f (reactants)

$= [\Delta H^\circ_f (N_2O) + 2 \times \Delta H^\circ_f (H_2O)] - [\Delta H^\circ_f (NH_4NO_3)]$

$= 81.46 + 2 \times (-285.78) - (-367.5)$

$= 81.46 - 571.56 + 367.5$

$= -122.56$ KJ

$\Delta H = \Delta E + \Delta nRT$

$\Delta E = \Delta H - \Delta nRT$

$\Delta n = 1$

$R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}

$T = 298$ K

$\Delta E = -122.56 - (1) \times (8.314 \times 10^{-3}) \times 298$

$= -122.56 - 2.477$

$= -125.037$ kJ

19. The standard heats of formation at 298 K for CCl_4 (g), H_2O (g), CO_2 (g) and HCl (g) are — 25.5, –57.8, –94.1 and –22.1 kcal mol^{-1} respectively, Calculate $\Delta H^\circ_{298\,K}$ for the reaction

CCl_4 (g) + $2H_2O$ (g) → CO_2 (g) + 4HCl (g)

Solution $\Delta H_{(reaction)} = \sum$ Heat of formation of products

$- \sum$ Heat of formation of reactants

$= [\Delta H_f (CO_2) + 4 \Delta H_f (HCl)] - [\Delta H_f (CCl_4) + 2\Delta H_f (H_2O)]$

$= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2 \times (-57.8)]$

$= -41.4$ kcal.

20. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of HCl (g).

Solution Reaction

$$\tfrac{1}{2}\,H_2\,(g) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow HCl\,(g) \qquad \Delta H = ?$$

$$\Delta H = [\tfrac{1}{2}\,\Delta H_{H-H} + \tfrac{1}{2}\,\Delta H_{Cl-Cl}] - [\Delta H_{H-Cl}]$$

$$= \tfrac{1}{2} \times 104 + \tfrac{1}{2} \times 58 - 103$$

$$= -22 \text{ kcal mol}^{-1}$$

Heat of Combustion

- It is change in enthalpy when one mole of a substance is completely oxidized or combusted or burnt.
- ΔH is –ve here as heat in always evolved here that is, exothermic process.
- Heat of combustion is useful in calculating calorific value of food and fuels.
- It is also useful in confirming structure of organic molecules having C,H,O,N etc.
- Enthalpy change by combustion of 1 gm solid or 1 gm liquid or 1 cc gas is called calorific value.

$$C.V = \frac{\text{Heat of combustion}}{\text{Molecular wt.}}$$

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -94 \text{ Kcal}$$

$$C.V = -\frac{94}{12} = -7.83 \text{ Kcal}$$

$$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$$

$$\Delta H = -1349 \text{ Kcal}$$

$$C.V = -\frac{1349}{342} = 3.94$$

$$\Delta H(\text{heat of reaction}) = -\sum \Delta H^\circ_P - \sum H^\circ_R$$

Illustrations

21. The standard molar heats of formation of ethane, carbon dioxide and liquid water are –21.1, –94.1 and –68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane.

Solution Reaction for combustion of ethane is as follows.

$$2C_2H_6\,(g) + 7O_2\,(g) \rightarrow 4CO_2\,(g) + 6H_2O\,(l)$$

$$\Delta H^\circ = ?$$

This reaction involves 2 moles of C_2H_6;

$$\text{Heat of combustion of ethane} = \frac{\Delta H^\circ}{2}$$

$$\Delta H^\circ = \Delta H^\circ_f\,(\text{products}) - \Delta H^\circ_f\,(\text{reactants})$$

$$= [4\ \Delta H^\circ_f\,(CO_2) + 6\ \Delta H^\circ_f\,(H_2O)] - [2\ \Delta H^\circ_f\,(C_2H_6) + 7\ \Delta H^\circ_f\,(O_2)]$$

$$= [4 \times (-94.1) + 6 \times (-68.3)] - [2 \times (-21.1) + 7 \times 0]$$

$$= -376.4 - 409.8 + 42.2$$

$$= -744.0 \text{ kcal}$$

$\Delta H^\circ/2$ = Heat of combustion of ethane

$$= -\frac{744.0}{2}$$

$$= -372.0 \text{ kcal}$$

22. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Find the fuel value per cm^3 of the mixture. Heat of formation and densities are as follows:

$H_f\,(Al_2O_3) = -399 \text{ kcal mol}^{-1}$

$H_f\,(Fe_2O_3) = -199 \text{ kcal mol}^{-1}$

Density of Al = 2.7 g/cm^3

Density of Fe_2O_3 = 5.2 g/cm^3

Solution Reaction

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe, \quad \Delta H = ?$$

$$\Delta H = \Delta H_f\,(\text{products}) - \Delta H_f\,(\text{reactants})$$

$$= [\Delta H_f\,(Al_2O_3) + 2\ \Delta H_f\,(Fe)] - [2\ \Delta H_f\,(Al) + \Delta H_f\,(Fe_2O_3)]$$

$$= [-399 + 2 \times 0] - [2 \times 0 + (-199)]$$

$$= -399 + 199 = -200 \text{ kcal}$$

Atomic mass of Al = 27

Molecular mass of Fe_2O_3 = 160

$$\text{Volume of reactants} = \frac{160}{5.2} + 2 \times \frac{27}{2.7}$$

$$= 50.77 \text{ cm3}$$

$$\text{Fuel value per cm}^3 = \frac{200}{50.77} = 3.92 \text{ kcal}$$

23. Given the heats of formation of benzene (liquid), water and carbon dioxide gas at 298 K as 11.718, –68.32 and –94.052 Kcal. Calculate the heat of combustion of liquid benzene at 298 K.

Solution The reaction is as follows:

C_6H_6 (l) + 7 ½ O_2 (g) → 6CO_2 (g) + 3H_2O (l)

The given data:

6C (s) + 3H_2 (s) → C_6H_6 (l), ΔH = 11.718 Kcal ..... (i)

H_2 (s) + ½ O_2 (g) → H_2O (l), ΔH = –68.32 Kcal ..... (ii)

C (s) + O_2 (g) → CO_2 (g), ΔH = –94.052 Kcal ..... (iii)

Multiply reaction (ii) by 3 and reaction (iii) by 6, and then add reaction (ii) and (iii)

3H_2 (s) + 3/2 O_2 (g) → 3H_2O (l), ΔH = –204.96 kcal

6C (s) + 6O_2 (g) → 6CO_2 (g), ΔH = –564.312 kcal

3H_2(g) + 6C(s) + 7 ½ O_2 (g) → 6CO_2 (g) + 3H_2O(l)

ΔH = –769.272 kcal ... (iv)

Subtract reaction (i) from reaction (iv)

7½ O_2 (g) → C_6H_6 (l) + 6CO_2 (g) + 3H_2O (l)

ΔH = –780.99 kcal

or C_6H_6 (l) + 7½ O_2 (g) → 6CO_2 (g) + 3H_2O (l)

ΔH = –780.990 kcal

Therefore heat of combustion of benzene is—780.99 kcal.

Heat of Neutralization

It is enthalpy change during neutralization of 1 gm mole of an acid and base. It is also heat of formation of water.

Example,

$H^+ Cl^- + Na^+ OH^- \rightarrow NaCl + H_2O +$

13.7 Kcal/mole or 57.3 kJ/mole

$H^+ + OH^- \rightarrow H_2O$ + 13.7 Kcal

or 57.3 kJ/mole

ΔH = –13.7 Kcal or –57.3 kJ/mole

- It is always exothermic ΔH = –ve
- Heat of neutralization of strong acid and strong base is always 13.7 Kcal/mole or 57.3 kJ/mole
- It is independent of nature of strong acid or strong base.
- If one electrolyte is weak than ΔH will be less than –13.7 Kcal as some amount of heat will be absorbed in ionization of weak electrolyte.

Example,

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

+ 55.2 kJ/mole or 13.4 Kcal/mole

Example,

$HCl + NH_4OH \leftrightarrow NH_4Cl + H_2O$

ΔH = –12.3 K.cal

i.e., heat of ionization of CH_3COOH is 0.3 Kcal or 1.9 kJ/mole

- If both electrolytes are weak then

$CH_3COOH + NH_3 \rightarrow CH_3COONH_4 + H_2O$

+ 50.4 kJ/mole

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

ΔH = –11.9 K.cal

- In case of HF, ΔH is more due to more hydration of F^- ions.

Measurement

In laboratory it is measured by using polythene on polystyrene bottles as follows.

Here 10 ml of each of acid and alkali having same normality are taken in separate bottles and temperature is noted at regular intervals. When constant temperature is achieved, the alkali solution is added to the acid solution. The mixture is stirred and the highest temperature is noted.

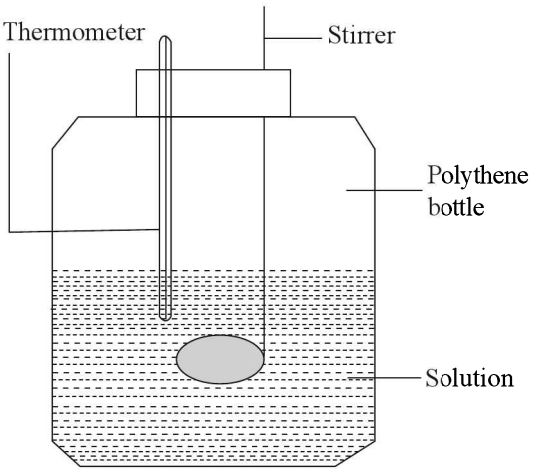
Suppose T_1 and T_2 are initial and final temperatures here then

Rise in temperature = $(T_2 - T_1)$ K

Here specific heat capacity of the solution is assumed to be the same as that of water while heat capacity can be ignored as it is quite less than that of solution.

$Q = ms (T_2 - T_1)$

Hence, $\Delta H = \frac{Q}{100} \times 1000 \times \frac{1}{N}$



Neu.

Here, Q = Heat change during the process

S = Specific heat of solution

M = Mass of solution

N = Normality of acid/base.

Illustrations

24. The heat of neutralization is due to the following reaction:

$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l) + 57.1$ kJ

Calculate the amount of heat evolved when

(i) 0.25 mole of H_2SO_4 is neutralized by 0.5 mole of NaOH and

(ii) 0.25 mole of CH_3COOH is mixed with 0.25 mole of NaOH, assuming 0.25 J of heat is utilized in the ionization of CH_3COOH.

Solution

(i) As 1 mole of H_2SO_4 = 2 mole H^+

So 0.25 mole of H_2SO_4 = 0.25 × 2 mole H^+

= 0.50 mole H^+

As 1 mole of H^+ + 1 mole OH^- = 57.1 kJ

So 0.50 mole H^+ + 0.50 mole OH^-

= 57.1 × 0.5 kJ = 28.55 kJ

(ii) 1 mole CH_3COOH = 1 mole H^+

0.25 mole CH_3COOH = 0.25 mole H^+

(If it is completely ionized)

Assuming the complete ionization of CH_3COOH, we get

0.25 mole of CH_3COOH + 0.25 mole NaOH gives 0.25 × 57.1 kJ

Heat expected = 16.27

But the actual heat obtained

= 16.27 – heat used in the ionization

= 16.27 – 0.25

= 16.02 kJ

25. Calculate the heat of neutralization from the following data, 200 ml of 1 M HCl is mixed with 400 ml of 0.5 M NaOH. The temperature rise in calorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is cal/ml/degree for solution.

Solution The heat produced (ΔH_1) during neutralization of 200 Meq. of NaOH and HCl each (Meq. = N × V) is taken up by calorimeter and solution in it.

ΔH_1 = Heat taken up calorimeter and solution in it.

$\Delta H_1 = m_1 S_1 \Delta T + m_2 S_2 \Delta T = 12$

Total solution = (200 + 400) ml = 2692.8 cal

As neutralization of 200 Meq. gives heat

= –2692.8 cal

So neutralization of 1000 Meq. gives heat

= –2692 × 5 = –13464 cal

= –13.464 kcal

Heat of Hydration

The enthalpy change during hydration of one gm mole substance is called heat of hydration.

$CuSO_4 + 5H_2O \rightarrow CuSO_4.5H_2O$

+ 78.21 kJ/mole

or 18.7 Kcal/mole

ΔH = –18.7 K.cal/mole

- It is exothermic mostly

$H_{sol} = \Delta H_{hy}$: Lattice energy

- If ΔH_H > L.E.: solute dissolve in H_2O

- ΔH_H < L.E.: solute does not dissolve in H_2O
- $\Delta H \simeq$ L.E.: solute is in equilibrium with solvent in H_2O

Bond Energy

It may be defined as, "The quantity of heat evolved when a bond is formed between two free atoms in a gaseous state to form a molecular product in a gaseous state". It is also known as enthalpy of formation of the bond.

Or

It may also be define as, "The average quantity of heat required to break (dissociate) bonds of that type present in one mole of the compound".

Example,

$C(g) + 4H(g) \rightarrow CH_4(g) \quad \Delta H = -398$ Kcal

The average bond energy per mole of C – H bond =

$$\frac{-398}{4} = -99.5 \text{ Kcal}$$

$H - OH \rightarrow H + O - H$

$\Delta H = 497.8$ Kj/m

$$(B.E.)_{AV} = \frac{497.8 + 428.5}{2} = 463.15 \text{ Kj/m}$$

When a reaction is carried out in the gas phase at constant pressure, then enthalpy of the reaction can be given as

$$\Delta H = \sum B.E_R - \sum B.E_P$$

ΔH = (Energy needed to break the bonds in the molecules of the reactants) – (Energy released when bonds in the molecules of the products are formed).

Example, In the case of formation of HCl (g) from H_2 (g) and Cl_2 (g), $\Delta H = -185$ kJ/mol

$E_{H-H} = 437$ kJ

$E_{C-Cl} = 244$ kJ

$E_{H-Cl} = 433$ kJ

So $\Delta H = E_{H-H} + E_{C-Cl} - (2E_{H-Cl})$

$= 437 + 244 - (2 \times 433)$

$= -185$ kJ

Illustrations

26. Calculate the enthalpy of combustion (enthalpy change) of the given reaction:

$CH_4(g) + 2O = O(g) \rightarrow$
$O = C = O(g) + 2H - O - H(g)$

From the following B.E. data.

BE of C – H = 414 kJ/mol

BE of C = O = 741 kJ/mol

BE of O = O = 395 kJ/mol

BE of O – H = 464 kJ/mol

Solution $\sum$(B.E.) reactants

$= 4 \times$ B.E. of C – H $+ 2 \times$ B.E. of O = O

$= 4 \times 414 + 2 \times 395$

$= 1656 + 790 = 2446$ kJ

(B.E.) products

$= 2 \times$ B.E. of C = O $+ 2 \times (2 \times$ B.E. of O – H)

$= 2 \times 741 + 4 \times 1856$

$= 3338$ kJ

$\Delta H = (\sum \text{B.R.})_R - (\sum \text{B.E})_P$

$= 2446 - 3338$

$= -892$ kJ

27. Calculate the resonance energy of N_2O from the following data:

ΔH°_f of $N_2O = 82$ kJ mol^{-1}

Bond energy of N ≡ N, N = N, O = O and N = O bonds is 946, 418, 498 and 607 kJ mol^{-1} respectively.

Solution $N \equiv N(g) + \frac{1}{2}(O = O) \rightarrow N = N = O(g)$

$\Delta H_f(N_2O) = [\Delta H(N \equiv N) + \frac{1}{2}\Delta H(O = O)]$

$- [\Delta H(N = O) + \Delta H(N = N)]$

$= (946 + \frac{1}{2} \times 498) - (607 + 418)$

$= 946 + 249 - 607 - 418$

$= 1195 - 1025$

$= 170$ kJ mol^{-1}

Resonance energy = Observed heat of formation

~ Calculated heat of formation

= 82 ~ 170

= 88 kJ mol^{-1}

Heat of Dilution

It is change in enthalpy when solution containing one mol of solute is diluted from one concentration to another concentration. Its value depends upon the concentration of solution and on the amount of the solvent added.

$KCl \rightarrow KCl$

$(x\ H_2O) \quad (Y\ H_2O)$

$HCl + 10\ H_2O \rightarrow HCl.10\ H_2O$

$\Delta H = -69$ KJ /M.

Heat of Solution

It is change in enthalpy when one mole of a solute is dissolved in excess of solvent.

- ΔH = +ve for (hydrated salts)
- ΔH = –ve for (anhydrous salts)

Example,

$KCl + H_2O \rightarrow KCl\ (aq)$

$\Delta H = -18.6$ KJ/Mole

$H_2SO_4 + H_2O \rightarrow H_2SO_4$

$\Delta H = -20.2$ K.Cal.

Heat of Fusion

It is change in enthalpy in converting one mole of solid into the liquid state at its melting point. It is equal to latent heat of fusion per gram multiplied by the molar mass. It is always positive as heat is needed to overcome the intermolecular forces between constituents particles of solid.

Example, Heat of fusion of H_2O

$H_2O \rightarrow H_2O$; ΔH = + 0.6 kJ/mole

(s) (l) = 1.44 K.Cal.

Heat of Vaporization

It is the change in enthalpy in converting 1 mole of liquid into the gaseous state at its boiling point

Example,

$H_2O \rightarrow H_2O$; ΔH = 42 kJ/mole

(l) (g) = 10.5 K.cal.

Heat of Sublimation

It is the change in enthalpy in converting one mole of a solid directly into vapour at a temperature below its melting point.

$I_2 \rightarrow I_2$; ΔH = 62.4 kJ/mole

(s) (g) = 14.9 K.cal /mole

- $\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus}$

Heat of Atomization

It is the enthalpy change (heat required) when bonds of one mole of a substance are broken down completely to obtain atoms in the gaseous phase (isolated) or it is the enthalpy change when one mole of atoms in the gas phase is formed from the corresponding element in its standard state.

In case of diatomic molecules it is also called bond dissociation enthalpy.

It is denoted by ΔH_a or $\Delta H^{\cdot}$.

Example,

$H_2\ (g) \rightarrow 2H\ (g) - 435$ kJ

$\Delta H = +435$ kJ/mol

$CH_4\ (g) \rightarrow C\ (g) + 4H\ (g) + 1665$ kJ

$\Delta H = +1665$ kJ/mol

Enthalpy of Dissociation or Ionization

It is defined as, "The quantity of heat absorbed when one mole of a substance is completely dissociated into its ions". Example,

$H_2O\ (l) \rightarrow H^+ + OH^- \quad \Delta H = 13.7$ Kcal

Phase Transition and Transition Energy

- The change of matter from one state (solid, liquid or gas) to another state is called Phase Transition.
- Such changes occur at definite temperatures such as melting point (solid to liquid), boiling point (liquid to vapours) etc., and are accompanied by absorption or evolution of heat. The enthalpy change during such phase transitions is called heat of transition or transition energy.

Example,

C (diamond) → C (amorphous)

$\Delta H = 3.3$Kcal

Illustrations

28. Calculate the amount of heat needed to convert 20 g of ice at 0°C to steam at 100°C. If specific heat of water is 1 cal/g, heat of fusion is 80 cal /g and heat of vapourisation is 540 cal/g.

Solution

$\Delta H_{total} = \Delta H_{fus} + \Delta H_{heat} + \Delta H_{vap}$

$= (20 \times 80) + (20 \times 1 \times 100) + (20 \times 540)$

$= 1600 + 2000 + 10800$

$= 14400$ cal. $= 14.4$ kcal

Law's of Thermochemistry

Lavosier and Laplace Law

The heat which is required to break a compound into its element is equal to the heat evolved during its formation.

$\Delta H_D = -\Delta H_f$

Example,

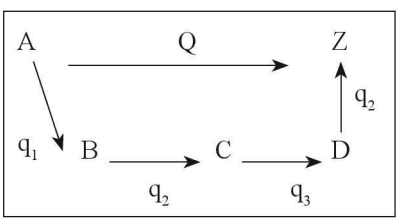
$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -94.3$ kcal

$CO_2(g) \rightarrow C(g) + O_2(g)$; $\Delta H = +94.3$ kcal

Hess's Law

This rule is a consequence of first Law of Thermodynamics and according to it,

"The enthalpy change for a process is independent of path or way of a process. The enthalpy change (ΔH or ΔE). for any physical or chemical process remains same whether process is carried out in one step or in many steps."



$Q = q_1 + q_2 + q_3 + q_4 \ldots\ldots$

Example,

$C + O_2 \rightarrow CO_2$; $\Delta H = -94.3$ K.cal

$C + \frac{1}{2} O_2 \rightarrow CO$; $\Delta H = -68.3$ K.cal

$CO + \frac{1}{2} O_2 \rightarrow CO_2$; $\Delta H = -26$ K.cal

that is, $Q = Q_1 + Q_2 = -194.3$

Hence it proves that

- ΔH or ΔE is not proportional to path or way of reaction
- ΔH or ΔE is a state function which depends only on initial and final state (first law of thermodynamics)

Applications Hess Law

It has the following applications:

1. It helps in finding enthalpy changes for those reactions also which are experimentally not possible.

   Example, C_2H_6, C_2H_4
2. It also helps in finding $\Delta H_{formation}$, $\Delta H_{combustion}$ etc.
3. For the determination of resonance energy and lattice energy.
4. For the determination of enthalpies of reactions occurring very slowly.

Second Law of Thermodynamics

It is not possible to convert heat into work without compensation.

- Work can always be converted into heat but the conversion of heat into work does not take place under all conditions.
- It is impossible to construct a machine that is able to convey heat by a cyclic process from a colder to a hotter body unless work is done on the machine by some outside agency (Clausius statement).
- The heat of the coldest body among those participating in a cyclic process cannot serve as a source of work (Thomson statement).
- It is impossible by means of inanimate material agency to derive mechanical work or effort from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects (Kelvin-Planck statement).
- Nature tends to pass from a less probable to more probable state (Ludwig Boltzmann statement).

- Whenever a spontaneous process takes place it is accompanied by an increase in the total entropy of the universe.

Spontaneous Process

It is defined as one that proceeds on it's own without any outside influence. It's reverse is always non spontaneous which occurs in presence of some continues external influence. Or

The chemical or physical process which occurs in a particular set of conditions either of its own or after proper initiation is known as spontaneous process.

Example,

(i) All natural processes

(ii) $2H_2 + O_2 \rightarrow 2H_2O$
g g I

Formation of water is spontaneous however it's decomposition is not spontaneous as it's possible by applying electrical energy for electrolysis.

- Spontaneous Process always occur with the decrease in energy and, increase in disorder (Entropy) and decrease of free energy.

Spontaneous changes which take place by themselves	**Spontaneous changes which take place in intiation**
Dissolution of KNO_3 in water	Lighting of a candle
Evaporation of water	Decomposition of calcium corbonate .
Flow of heat energy from higher temperature to lower temperature.	Combination of H_2 and O_2 to form water.
Flow of water from higher level to lower level.	Combustion of methane gas.

ENTROPY

It is a thermodynamic state quantity which is used to measure disorder or randomness of the molecules in a system The disorder or randomness in a system is measured in terms of entropy (S). The absolute value of 'S' is not determined so mostly change in entropy ΔS is measured.

Randomness α Entropy

It is a state function which depends only on the initial and final state of the system that is, it is independent of the path used in going from the initial to final state.

$$\Delta S = S_{Final} - S_{Initial}$$

For a general chemical reaction at 298K and 1 atm:

$$m_1P + m_2Q \rightarrow n_1R + n_2S$$

$$\Delta S^o = [(n_1S^o_R + n_2S^o_S) - (m_1S^o_P + m_2S^o_Q)]$$

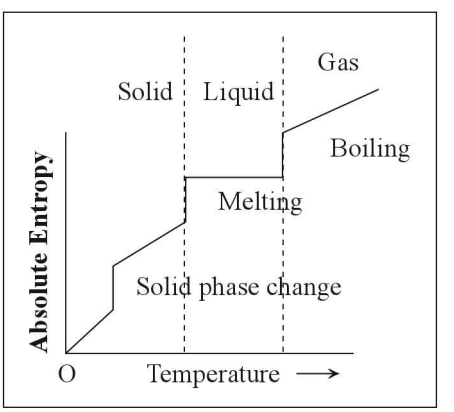
$$\Delta S^o = \sum S^o_P - \sum S^o_R$$

- It is an extensive property and a state function which depends on state variables like T, P, V and n which govern the state of a system.

Entrophy and Temprature

Entropy increases with the increase of temperature as it is associated with the molecular motion which increases with the increase of temperature due to increase in the average kinetic energy of the molecules.

The entropy of a perfectly ordered Crystalline substance is taken as zero at Zero Kelvin (0K) . It is third law of Thermodynamics. However in case of N_2O, NO, LO, Solid Cl_2 etc. the value of entropy is not found to be zero at O Kelvin also.



Mathematical Definition of Entropy

For a reversible isothermal process, Clausius defined it as the integral of all the terms involving heat exchange (q) divided by the absolute temperature T.

$$ds = \int \frac{q_{rev}}{T}$$

OR

$$\Delta S = \frac{q_{rev}}{T}$$

Unit: $J\ K^{-1}\ mol^{-1}$

Here mol^{-1} is also used as entropy being an extensive property depends upon the mass of substance.

Entropy Changes in Processes

1. During isothermal reversible expansion of an ideal gas

   As for a reversible path $\Delta E = 0$

   So $q_{rev} = -W_{rev.} = -2.303 \frac{nR}{T} \log_{10} \frac{V_2}{V_1}$

   Hence, $\Delta S = 2.303\ nR \log_{10} \frac{V_2}{V_1}$

   $$\Delta S = 2.303\ nR\ \log_{10} \frac{(P_1)}{(P_2)}$$

2. During adiabatic reversible expansion

   As $q = 0$, so $\Delta S = 0$

3. **Isobaric process:**

   $$\Delta S = 2.303\ n\ C_P \log_{10} \frac{(T_2)}{(T_1)} \text{ or } \frac{(V_2)}{(V_1)}$$

4. **Isochoric process:**

   $$\Delta S = 2.303\ n\ C_V \log_{10} \frac{(T_2)}{(T_1)} \text{ or } \frac{(P_2)}{(P_1)}$$

5. **Entropy change in irreversible processes:**

   Suppose in a system at higher temperature T_1 and its surroundings at lower temperature T_2. 'q' amount of heat goes irreversibly from the system to the surroundings.

   $$\Delta S_{system} = -\frac{q}{T_1}.$$

   $$\Delta S_{surroundings} = +\frac{q}{T_2}.$$

   $$\Delta S_{process} = \Delta S_{system} + \Delta S_{surroundings}$$

   $$= -\frac{q}{T_1} + \frac{q}{T_2} = q\frac{[T_1 - T_2]}{T_1 T_2}$$

   But $T_1 > T_2$

   So $T_1 - T_2 = +ve$

   $$\Delta S_{process} > 0$$

   So entropy increases in an irreversible process like conduction radiation etc.

6. **Entropy changes during phase transition:**

   $$\Delta S = S_2 - S_1 = \frac{q_{rev.}}{T} = \frac{\Delta H}{T}$$

   For fusion

   Solid ⇌ Liquid

   ΔH = Heat of fusion [Heat required to convert one mole of a solid at constant temperature (melting point) and constant pressure into liquid keeping solid and liquid]

   $$\Delta S_{fusion} = S_{liquid} - S_{solid}$$

   $$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{fusion\ or\ M.P}}$$

   ΔH_{fusion} = Latent heat of fusion

   For Vapourization

   Liquid ⇌ Vapour

   $$\Delta S_{vap.} = S_{vapour} - S_{liquid}$$

   $$\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_{vap\ or\ B.P.}}$$

   $\Delta H_{vap.}$ = Latent heat of vapourization

   For Sublimation

   Solid ⇌ Vapour

   $$\Delta S_{sub} = S_{vapour} - S_{solid}$$

   $$\Delta S_{sub} = \frac{\Delta H_{sub}}{T}$$

   ΔH_{sub} = Heat of sublimation

7. **Entropy change when liquid is heated:**

   When a definite amount of liquid of mass 'm' and specific heat 's' is heated

   $$\partial q = m\ s\ T$$

   $$\partial S = \frac{m\ s\ dT}{T}$$

   or $\Delta S = m\ s \log_e \frac{T_2}{T_1}$

8. **Entropy Change in Mixing of Ideal Gases**:

   Suppose n_1 mole of gas 'P' and n_2 mole of gas 'Q' are mixed; then total entropy change can be calculate as:

   $$\Delta S = -2.303\ R\ [n_1 \log_{10} X_1 + n_2 \log_{10} X_2]$$

Here X_1 and X_2 are mole fractions of gases P and Q respectively.

$$X_1 = \frac{n_1}{n_1 + n_2}.$$

$$X_2 = \frac{n_2}{n_1 + n_1}.$$

$$\Delta S/\text{mol} = -2.303R \frac{[n_1 \log_{10} X_1}{n_1 + n_2} + \frac{n_2 \log_{10} X_2]}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303\ R\ [X_1 \log_{10} X_1 + X_2 \log_{10} X_2]$$

Some Facts About Entropy

- In nature all process are irreversible followed by an increase in entropy. Entropy of universe tends towards a maximum.

  $S_{\text{Universe}} > 0$

- $\Delta S_{sys} + \Delta S_{surr.} = 0$ for reversible process

  $S_{sys} + \Delta S_{surr.} > 0$ for irreversible process

- ΔS for a cyclic process and at the equilibrium state is zero.

- For a reversible process

  S_{Total} or $\Delta S_{\text{Universe}} = 0$

  So $\Delta S_{\text{system}} = \Delta S_{\text{surrounding}}$

- For adiabatic reversible process entropy change is zero.

  $\Delta S_{\text{Total}} = 0$ so

  Hence $\Delta S_{\text{system}} = \Delta S_{\text{surrounding}}$

- Entropy change associated which change in temperature from T_2 to T_1 at constant pressure P is given as

  $$\Delta S = 2.303 \times C_P \log \frac{T_2}{T_1}$$

- C_P = Molar heat capacity at constant pressure.

Some Examples of Entropy Change

- When a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence arranged in a more ordered manner that is randomness decreases.

- When an egg is boiled, the entropy increases because denaturation occurs resulting into a change of proteins from helical form into random coiled form.

- Molecule kept in large volume container will have high entropy.

- Cases of increase in entropy—(1) dissolution of solute in water (2) decomposition of compound (3) vaporization and fusion (4) expansion of ideal gas from one container to an evacuated chamber.

- Decrease of entropy cases are crystallization, combination.

- Entropy is directly proportional to atomic weight for example—$I_2 > Br_2 > Cl_2$

- Entropy is directly proportional to number of bonds example—Ethane > ethylene > ethylene

Physical Significance of Entropy

1. Randomness in a system α Entropy.

2. As according to the 2nd law of thermodynamics, the lost energy is directly proportional to absolute temperature during the process. Hence Entropy is unavailable energy of a system that is,

   Unavailable energy α Temperature

   Unavailable energy = Entropy × temperature

   $$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{T in Kelvin}}$$

3. Entropy and Probability: It may be defined as a function of probability of a thermodynamic state as both entropy and thermodynamic probability increase simultaneously in a process so the state of equilibrium is the state of maximum probability.

   Boltzman told that the entropy of a particular state is related to the number of ways that the state can be achieved as follows

   $S = K \ln W$

   Here W is the natural logarithm of the number of ways that the state can be achieved.

   K is the Boltzman constant

   $$K = \frac{R}{N_A} = 1.38 \times 10^{-23}\ \text{J/K}.$$

Illustrations

29. Calculate the entropy change involved in the conversion of one mole of water at 373 K to vapour at the same temperature. (Latent heat of vapourization of water = 2.257 kJ g^{-1}).

Solution $\Delta S_V = \dfrac{\Delta H_V}{T_b}$

$\Delta H_V = 2.257 \times 18 \times 10^3$ J mol^{-1}

$T_b = 373$ K

$\Delta S_V = \dfrac{2.257 \times 18 \times 10^3}{373} = 108.9$ J K^{-1} mol^{-1}

30. Calculate the standard entropy change associated with the following reaction at 298K.

$P_4 (s) + SO_2 (g) \rightarrow P_4O_{10} (s)$

At 298 K S° for $P_4 = 41.1$ JK^{-1} mol^{-1}

$O_2 = 205.0$ JK^{-1} mol^{-1} and

$P_4O_{10} = 231.0$ JK^{-1} mol^{-1}

Solution $\Delta S^\circ = \sum \Delta S^\circ_P - \sum \Delta S^\circ_R$

$\Delta S^\circ = [\Delta S^\circ P_4O_{10} - (\Delta S^\circ P_4 + 5\Delta S^\circ O_2)]$

$= 231 - (41.1 + 5 \times 205.0)$

$= 231 - 1066.1 = -835.1$ JK^{-1} mol^{-1}.

31. 5 moles of an ideal gas expand reversibly from a volume of 8 dm^3 to 80 dm^3 at a temperature of 27°C. Calculate the change in entropy.

Solution $\Delta S = 2.303\ nR \log_{10} \dfrac{V_2}{V_1}$

$\Delta S = 2.303 \times 5 \times 8.314 \times \log_{10} \dfrac{80}{8}$

$= 95.736 \times 1$

$= 95.736$ JK^{-1}

32. Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{total} at 25°C for the reaction

$N_2 (g) + 2O_2 (g) \rightarrow N_2O_4 (g)$

Is this reaction spontaneous under standard state conditions at 25°C?

Here $\Delta H^\circ_f (N_2O_4) = 9.16$ kJ,

$S^\circ (N_2) = 191.5$ J K^{-1} mol^{-1},

$S^\circ (O_2) = 205.0$ J K^{-1} mol^{-1},

$S^\circ (N_2O_4) = 304.2$ J K^{-1} mol^{-1}

Solution $N_2 (g) + 2O_2 (g) \rightarrow N_2O_4 (g)$

$\Delta H^\circ = \Delta H^\circ_f (N_2O_4) = 9.16$ kJ

$\Delta S_{sys} = \Delta S^\circ = S^\circ(N_2O_4) - [S^\circ(N_2) + 2S^\circ(O_2)]$

$\Delta S_{sys} = (1)\ (304.2) - [(1)\ (191.5) - (2)\ (205.0)]$

$= -297.3$ J/K

$\Delta S_{surr} = \dfrac{-\Delta H^\circ}{T} = -\dfrac{9.16\ kJ}{298} = -0.0307$ kJ/K

$= -30.7$ J/K

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

$= -297.3$ J/K + (–30.7 J/K)

$= -328.0$ J/K

Because $\Delta S_{total} < 0$, the reaction is non-spontaneous.

33. Consider a two fold expansion of an ideal gas at 25°C in the isolated system.

(a) What are the values of ΔH, ΔS and ΔG for the process?

(b) How does this process illustrate the second law of thermodynamics?

Solution (a) $\Delta H = 0$

$\Delta S = R\ In\ \dfrac{V_{final}}{V_{initial}}$.

$= (8.314$ J/K) In 2 $= 5.76$ J/K

$\Delta G = \Delta H - T\Delta S$

As $\Delta H = 0$, $\Delta G = -T\Delta S$

$= -(298$ K) (5.76 J/K)

$= -1717$ J $= -1.72$ kJ

(b) For a process in an isolated system, $\Delta S_{surr} = 0$. Therefore, $\Delta S_{total} = \Delta S_{sys} > 0$, and the process is spontaneous.

Gibbs's Free Energy

It was introduced in order to relate H, S and to explain spontaneity. According to J. Willard Gibb's Free energy of a system is defined as the maximum

amount of energy available to a system during a process that can be converted into useful work.

or

It is the thermodynamic quantity specially characterizing the system, the decrease in whose value during a process is equal to the useful work done by the system.

It is denoted by G and it is given mathematically as follows:

As enthalpy (H) is a function of S and P which is given as follows:

$H = f(S, P)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P ds + \left(\frac{\partial H}{\partial P}\right)_s dP \quad \text{---------(i)}$$

As $dH = TdS + VdP$ --------(ii)

On comparing these two equation

$$\left(\frac{\partial H}{\partial S}\right)_P = T$$

On integrating equation (ii) wet get,

$\int dH = \int TdS$ + Intiegration Constant

$= \int TdS + G$

$H = TS + G$

$G = H - TS$

H = Enthalpy

T = Absolute temperature

S = Entropy

As $H = E + PV$

So $G = E + PV - TS$

Free energy change at constant temperature and pressure is given as:

$\Delta G = \Delta E + P\Delta V - T\Delta S$

As $\Delta H = \Delta E + P\Delta V$

So $\Delta G = \Delta H - T\Delta S$

At standard conditions that is, 298 K and 1 atm pressure

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

It is called Gibbs Helmholtz's equation and it is used to explain criterion of spontaneity, driving force etc.

■ It is a state function and an extensive property. So it is determined as ΔG or ΔG°.

For a general reaction, it can be given as follows:

$$p\,A + q\,bB \rightarrow r\,C + s\,D$$

$$\Delta G^\circ = \sum \Delta G^\circ_P - \sum \Delta G^\circ_R$$

$$= [(r \sum \Delta G^\circ_C + s \sum \Delta G^\circ_P) - (p. \sum \Delta G^\circ_A + q \sum \Delta G^\circ_S)]$$

ΔG and Criteria of Spontaneity

Suppose we consider a system which is not isolated from its surroundings then for such a system ΔS is given as:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \quad \ldots\ldots \text{(i)}$$

If we consider that q_p amount of heat is given by the system to the surroundings at constant temperature and constant pressure then

$$(q_p)_{surroundings} = -(q_p)_{system} = -\Delta H_{system}$$

$$\Delta S_{surroundings} = \frac{(q_p)_{surroundings}}{T} = \frac{-\Delta H_{system}}{T} \quad \ldots. \text{(ii)}$$

So from equation (i) and (ii)

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

or $T\,\Delta S_{total} = T\Delta S_{system} - \Delta H_{system}$

$$-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system} \quad \ldots\ldots \text{(iii)}$$

As according to Gibb-Helmholtz equation,

$\Delta G = \Delta H - T\Delta S$

So $\Delta G_{system} = \Delta H_{system} - T\Delta S_{system}$

$\Delta G_{system} = -T\Delta S_{total}$

As for spontaneous process

$\Delta S_{total} > 0$

Hence $\Delta G = -ve$

Thus for a spontaneous process $T\Delta S_{total}$ must be positive or ΔG must be negative.

Case I: Suppose both energy and entropy factors oppose a process that is,

$\Delta H = +ve$ and $T\Delta S = -\Delta e$

$\Delta G = \Delta H - T\Delta S$

$= (+ve) - (-ve) = +ve$

Thus, ΔG is positive for a non-spontaneous process.

Case II: Suppose both tendencies be equal in magnitude but opposite, that is,

ΔH = +ve and $T\Delta S$ = +ve

$\Delta H = T\Delta S$

$\Delta G = \Delta H - T\Delta S$

= 0

Thus, the process is said to be at equilibrium.

Case III: Suppose entropy and energy, both factors are favourable for a process, that is,

ΔH = –ve and $T\Delta S$ = +ve

$\Delta G = \Delta H - T\Delta S$

= (–ve) – (+ve) = –ve

Thus, ΔG is negative for a spontaneous process.

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Remark
–	+	Always –ve	Spontaneous
+	–	Always +ve	Non-spon.
+	+	+ve at low temp –ve at high temp	Non spon. Spontaneous.
–	–	–ve at low temp +ve at high temp	Spontaneous Non-spon.

- ΔG = –ve (spontaneous process)
- ΔG = +ve (non spontaneous process)
- ΔG = 0 (process in equilibrium)
- In exoergonic reaction ΔG = –ve
- In endoergonic reaction ΔG = +ve
- Temperature also plays an important role to decide the spontaneity of a process. A process which is not spontaneous at low temperature can become spontaneous at high temperature and vice-versa.

Relationship between ΔG or ΔG° with E or E°:–

Free energy change (ΔG) in an electrochemical cell can be related to electrical work done (E) in cell as follows

$\Delta G = -nFE$

when we use standard conditions than

$\Delta G^\circ = -nFE^\circ$

Here E° = standard E.M.F of the cell

n = No. of moles of e^- transferred

F = Faraday's constant

Relationship between ΔG° and Equlibrium constant (K_{eq}.)

for a reversible reaction

$P + Q \rightleftharpoons R + S$

ΔG , ΔG° and Reaction Quotient (Q) are related as follows

$\Delta G = \Delta G^\circ + RT \log_e Q$

as at equilibrium $\Delta G = 0$

$Q = K_{eq}$

$0 = \Delta G^\circ + RT \log_e K_{eq}$

$\Delta G^\circ = -RT \log_e K_{eq}$

$\Delta G^\circ = -2.303\ RT \log_{10} K_{eq}$

Illustrations

34. $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

$\Delta H = -270.6\ kJ\ mol^{-1}\ K^{-1}$

$\Delta S = -139\ J$

(i) Is the reaction favoured by entropy, enthalpy both or none?

(ii) Find ΔG it T = 300 K

Solution

(i) As ΔH = negative, exothermic process and is favoured, so it will be spontaneous.

(ii) $\Delta G = \Delta H - T\Delta S$

$= -270.6 \times 1000 - 300 \times (-139)$

$= -228900\ J$

$= -228.9\ kJ$

35. Urea (NH_2CONH_2), an important nitrogen fertilizers is produced industrially by the reaction

$2NH_3\ (g) + CO_2\ (g) \rightarrow NH_2CONH_2\ (aq) + H_2O\ (l)$

Given that ΔG° = –13.6 kJ, Calculate ΔG at 25°C for the following set of conditions

(a) 10 atm NH_3, 10 atm CO_2, 1.0 M NH_2CONH_2

(b) 0.10 atm NH_3, 0.10 atm CO_2, 1.0 M NH_2CONH_2

Is the reaction spontaneous for the conditions in part (a) or part (b)?

Solution $\Delta G = \Delta G^\circ + RT \ln \frac{[NH_2CONH_2]}{(PNH_3)^2 (PCO_2)}$

(a) $\Delta G = -13.6 + [8.314 \times 10^{-3}] (298\ K) \ln [1.0/(10)^2 (10)]$

$= -30.7$ kJ/mol

As ΔG is negative, the reaction is spontaneous.

(b) $\Delta G = -13.6 + [8.314 \times 10^{-3}] (298\ K) \ln [1.0/(0.10)^2 (0.10)]$

$= +3.5$ kJ/mol

As ΔG is positive, the reaction is non-spontaneous.

36. Calculate K_P at 25°C for this reaction

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

What is ΔG for this reaction at 25°C when each reactant and product is present at a partial pressure of 20 atm?

Here $\Delta G^\circ_f (CH_3OH) = -161.9$ kJ/mol

$\Delta G^\circ_f (CO) = -137.2$ kJ/mol

Solution $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

$\Delta G^\circ = \Delta G^\circ_f (CH_3OH) - \Delta G^\circ_f (CO)$

$\Delta G^\circ = 1 \times (-161.9) - (1)(-137.2) = -24.7$ kJ

$\Delta G^\circ = -RT \ln K_P$

$\ln K_P = \frac{-\Delta G^\circ}{RT} = \frac{-(-24.7)}{(8.314 \times 10^{-3})(298)} = 9.97$

$K_P = e^{9.97} = 2.1 \times 10^4$

$\Delta G = \Delta G^\circ + RT \ln Q$

$= (-24.7) + (8.314 \times 10^{-3}) + (298\ K)$

$\ln \frac{[20]}{(20)(20)^2}$

$= -39.5$ kJ/mol

37. For a reaction $M_2O(s) \rightarrow 2M(s) + \frac{1}{2} O_2(g)$; $\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at atm. Calculate upto which temperature, the reaction would not be spontaneous.

Solution

$\Delta H = 30 \times 10^3$ J mol^{-1}

$\Delta S = 70$ JK^{-1} mol^{-1}

For a spontaneous reaction

$\Delta G = +ve$

As $\Delta G = \Delta H - T\Delta S$

So $\Delta H - T\Delta S$ should be positive

$\Delta H > T\Delta S$

$T < \frac{\Delta H}{\Delta S}$

$T < \frac{30 \times 10^3}{70}$

$T < 428.57$ K

Enhance Your Knowledge

Calorimeter

It is used to find enthalpy of reaction

$$\Delta H = \frac{Z \times \Delta T \times M}{W}$$

- It fails when (i) reaction is slow (ii) ΔH is low (iii) reaction does not complete
- ΔH does not change with temperature appreciably

Resonance Energy

Resonance energy = Expected heat of hydrogenation – calculate heat of hydrogenation

Example,

Resonance energy of CO_2 is 32 calorie per mole.

- For adults, 2500–3000 Kcal energy per day is needed.

Trauton's Law

$$\frac{\Delta H_{vap}}{T_b} = 88 \text{ Joule/K mol}$$

Solved Problems from the IITs

1. A gas mixture of 3.67 litre of ethylene and methane on complete combustion at 25°C produces 6.11 litre of CO_2. Calculate the heat evolved on burning 1 litre of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-1} at 25°C.

[IIT 1991]

Solution $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

a litre 2a litre

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

(3.67 – a) lit (3.67 – a) lit

$2a + 3.67 - a = 6.11$

$a = 2.44$ litre

Volume of ethylene in mixture = 2.44 litre

Volume of methane in mixture = 1.23 litre

Volume of ethylene in 1 lit mixture = $\frac{2.44}{3.67}$.

= 0.6649 lit

Volume of methane 1 lit mixture = $\frac{1.23}{3.67}$.

= 0.3351 lit

24.45 litre of a gas at 25°C correspond to 1 mole.

So heat evolved by burning 0.6649 litre of ethylene

$= -\frac{1423}{24.5} \times 0.6649 = -38.69$ kJ

Heat evolved by burning 0.3351 litre of methane

$= -\frac{891}{24.45} \times 0.3351 = -12.21$ kJ

So total heat evolved by burning 1 litre of mixture

= –38.69 – 12.21

= –50.90 kJ

2. The polymerization of ethylene to linear polyethylene is represented by the reaction

$nCH_2 = CH_2 \rightarrow [—CH_2 - CH_2—]n$

Where n has a large integral value. Given that the average enthalpies of bond dissociation for C = C and C – C at 298 K are +590 and +331 kJ mol^{-1} respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K.

[IIT 1995]

Solution During the polymerization of ethylene, one mole of ethylene breaks that is, one double bond breaks and the two CH_2– groups are linked with single bonds so forming three single bonds. But in the whole unit of polymer, number of single bonds formed/mole of ethylene is 2.

Energy released = Energy due to formation of 2 single bonds

= 2 × 331 = 662 kJ mol^{-1} of ethylene

Energy absorbed = Energy due to dissociation of 1 double bond

= 590 kJ mol^{-1} of ethylene

Enthalpy of polymerization/mol of ethylene or ΔH (Polymerization) = 590 – 662 kJ mol^{-1}

= –72 kJ mol^{-1}

3. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are –156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is –119 kJ mol^{-1}. Use these data of estimate to magnitude of the resonance energy of benzene.

[IIT 1996]

Solution Cyclohexene (l) + H_2 (g) → Cyclohexane (l)

ΔH = –119 kJ

Enthalpy of formation of cyclohexane (l)

= –156 kJ mol^{-1}

So enthalpy of formation of cyclohexane

= –156 – (–119) kJ

= –37 kJ mol^{-1}

As $\Delta H_{Cyclohexane}$ is –156 kJ mol^{-1}, for every double bond the energy decreases by an amount +119 kJ mol^{-1} and therefore for the introduction of three double bonds (present in benzene ring) the energy required.

$= 3 \times 119 \text{ kJ mol}^{-1} = 357 \text{ kJ mol}^{-1}$

So, theoretical ΔH_f for benzene

$= (357 - 156) \text{ kJ mol}^{-1}$

$= 201 \text{ kJ mol}^{-1}$

Resonance energy

= Theoretical ΔH_f – Observed ΔH_f

$= (201 - 49) \text{ kJ mol}^{-1}$

$= 152 \text{ kJ mol}^{-1}$

4. Compute the heat of formation of liquid methyl alcohol in kJ per mole using the following data. Heat of vapourization of liquid methyl alcohol = 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states are H = 218 kJ mol^{-1}, C = 715 kJ mol^{-1} and O = 249 kJ mol^{-1}.

Average bond energies are:

C – H = 415 kJ mol^{-1}

C – O = 356 kJ mol^{-1}

O – H = 463 kJ mol^{-1}

[IIT 1997]

Solution The thermochemical reaction is as follows:

$$C(g) + 4H(g) + O(g) \rightarrow H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-O-H$$

$\Delta H_f = ?$

$\Delta H_f = [\Delta H_{C(S) \rightarrow C(g)} + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_O = 0]$

$- [3\Delta H_{C-H} + \Delta H_{C-O} + \Delta H_{O-H} + \Delta H_{\text{vap. CH3 OH (l)}}]$

$= [715 + 2 \times 436 + 249] - [3 \times 415 + 356 + 463 + 38]$

$= 1836 - 2102 \text{ kJ mol}^{-1}$

$= -266 \text{ kJ mol}^{-1}$

5. The enthalpy change involved in the oxidation of glucose is –2880 kJ mol^{-1}. 25% 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 120 g of glucose?

[IIT 1997]

Solution As energy available for muscular work by 1 mole of glucose

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

So 180 g glucose (mol. wt. of glucose) supplies 720 kJ.

120 g of glucose will supply = $\frac{720}{180} \times 120$

= 480 kJ

100 kJ is needed to walk 1 km.

480 kJ is needed to walk $\frac{1}{100} \times 480 = 4.8$ km.

6. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO_2 (g), H_2O (l) and propene (g) are –393.5, –285.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomeriyation of cyclopropane to propene is –33.0 kJ mol^{-1}.

[IIT 1998]

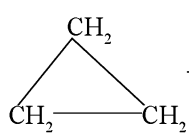
Solution $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ ..... (i)

$H_2(g) + \frac{1}{2} O_2(l) \rightarrow H_2O(l)$; $\Delta H = -285.8$ kJ ..... (ii)

$3C(s) + 3H_2(g) \rightarrow C_3H_6(g)$; $\Delta H = 20.42$ ..... (iii)

Cyclopropane $\rightarrow$ Propene(C_3H_6); $\Delta H = -33.0$ kJ ..... (iv)

The required thermochemical reaction is



$+ 9/2\ O_2 \rightarrow 3CO_2 + 3H_2O$

$\Delta H = ?$ .... (v)

This equation (v) can be obtained by multiplying equation (i) and (ii) by 3, reversing equation (iii), keeping equation (iv) as such and adding, so formed new equation as follows:

ΔH =[(i) × 3]+[(ii) × 3]+[Reverse of (iii) + (iv)]

$= [-393.5 \times 3] + [-285.8 \times 3] + [-20.42] + [-33.0]$

$= -1180.5 - 857.4 - 20.42 - 33.0$

$= -2091.32$ kJ.

7. Estimate the average S – F bond energy in SF_6. The standard heat of formation values of SF_6 (g), S (g) and F (g) are –1100, 275 and 80 kJ mol^{-1} respectively.

[IIT 1999]

Solution Given

$S(s) \rightarrow S(g); \Delta H = 275 \text{ kJ mol}^{-1}$ ... (i)

$[\frac{1}{2} F_2(g) \rightarrow F(g); \Delta H = 80 \text{ kJ mol}^{-1}] \times 6$ ..... (ii)

$S(s) + 3F_2(g) \rightarrow SF_6(g); \Delta H = -1100 \text{ kJ mol}^{-1}$ ..... (iii)

The required reaction

$S(g) + 6F(g) \rightarrow SF_6(g); \Delta H = ?$

is obtained by adding the reverse of equations (i) and (ii) with the direct reaction (iii)

$S(g) + 3F_2(g) + S(s) + 6F(g) \rightarrow$

$SF_6(g) + S(s) + 3F_2(g);$

$\Delta H = -1100 - 275 - 80 \times 6$

$S(g) + 6F(g) \rightarrow SF_6(g);$

$\Delta H = -1855 \text{ kJ mol}^{-1}$

Total bond energy in $SF_6 = 1855$ kJ

Average S – F bond energy is SF_6

$= \frac{1855}{6} = 309.16 \text{ kJ mol}^{-1}$

8. A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm^3 to 2.50 dm^3. Calculate the enthalpy change in this process. $C_{v.m.}$ for argon is 12.48 J K^{-1} mol^{-1}.

[IIT 2000]

Solution Number of moles of argon present in the sample

$$= \frac{PV}{RT} = \frac{1.25 \times 1}{0.0821 \times 300} = 0.05075$$

For adiabatic expansion,

$T_1/T_2 = (V_2/V_1)^{\gamma - 1}$

$300/T_2 = (2.50/1.25)^{1.66 - 1}$

$T_2 = 188.55$ K

$C_P = C_V + R$

$= 12.48 + 8.314$

$= 20.794 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta H = n \times C_P \times \Delta T$

$= 0.05075 \times 20.794 \times (300 - 188.55)$

$= 117.6$ J

9. Show that the reaction,

$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$

at 300 K is spontaneous and exothermic, when the standard entropy change is –0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1} respectively.

[IIT 2000]

Solution $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO(g)$

$\Delta G^\circ = G^\circ(CO_2) - G^\circ(CO) - \frac{1}{2} G^\circ(O_2)$

$= -394.4 - (-137.2) - 0$

$= -257.2 \text{ kJ mol}^{-1}$

$\Delta G^\circ = \Delta H^\circ - T\Delta S$

$-257.2 = \Delta H^\circ - 298 \times (0.094)$

$\Delta H^\circ = -288.2$ kJ

As ΔG° is negative so the process is spontaneous and ΔH° is also negative so the process is also exothermic.

10. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$

From the following data, calculate the enthalpy change for the combustion of diborane:

$2B(s) + 3/2\ O_2(g) \rightarrow B_2O_3(s);$

$\Delta H = -1273$ kJ

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l); \Delta H = -286$ kJ

$H_2O(l) \rightarrow H_2O(g); \Delta H = 44$ kJ

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g); \Delta H = 36$ kJ

[IIT 2000]

Solution $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$

This reaction can be obtained as follows:

Eq, (i) + 3 × Eq (ii) + 3 × Eq. (iii) – Eq. (iv)

$= -1273 - 858 + 132 - 36$

$= -2035 \text{ kJ mol}^{-1}$

11. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is slowly converted into an equilibrium mixture of 1.3 % of 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria:

$B \rightleftharpoons A \qquad \Delta G^\circ_1 = ?$

$B \rightleftharpoons C \qquad \Delta G^\circ_2 = ?$

From the calculated value of ΔG°_1 and ΔG°_2 indicate the order of stability of (A), (B) and (C). Write a reasonable reaction mechanism showing all intermediates leading to (A), (B) and (C).

[IIT 2001]

Solution Pentyne-1 $\rightleftharpoons$ Pentyne-2 + 1,2-pentadiene

	(A)	(B)	(C)
t_{eq}	1.3	95.2	3.5

$$K_{eq} = \frac{[B][C]}{[A]} = \frac{95.2 \times 3.5}{1.3} = 256.31$$

$B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]} = \frac{[C]}{K_{eq}} = \frac{3.5}{256.31} = 0.013$$

$\Delta G^\circ_1 = -2.303 \text{ RT} \log_{10} K_1$

$= -2.303 \times 8.314 \times 448 \log_{10} 0.013$

$= 16178 \text{ J}$

$= 16.178 \text{ kJ}$

$B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_{eq}[A]}{[B]^2} = \frac{256.31 \times 1.3}{(95.2)^2} = 0.037$$

$\Delta G^\circ_2 = -2.303 \text{ RT} \log_{10} K_2$

$= -2.303 \times 8.314 \times 448 \log_{10} 0.037$

$= 12282 \text{ J} = 12.282 \text{ kJ}$

The stability order is as follows:

B > C > A.

12. An insulated container contains 1 mole of a liquid, molar volume 100 ml at 1 bar. When liquid is steeply passed to 100 bar, volume decreases to 99 ml. Find the ΔH and ΔU for the process.

[IIT 2004]

Solution According to first law of thermodynamics

$\Delta U = q + W$

$\Delta U = q + P\Delta U$

$= 0 + [-100 (99 - 100)]$

$= 100 \text{ bar ml}$

$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$

$= 100 + (100 \times 99 - 1 \times 100)$

$= 9900 \text{ bar ml}$

13. For the reaction, $2CO + O_2 \rightarrow 2CO_2$, $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.

(1 L atm = 0.1 kJ)

[IIT 2006]

$\Delta H = \Delta U + \Delta(PV)$

$\Delta H = \Delta U + V\Delta P$

$\Delta U = \Delta H - V\Delta P = -560 + 1 \times 30 \times 0.1$

$= -557$

Absolute value = 557 kJ

Calorimetry

Heat exchange

= Heat capacity × temp change

(heat exchange – when no chemical change or state change occurs)

MULTIPLE-CHOICE QUESTIONS

Straight Objective Type Questions (Single Choice only)

1. Under the same conditions how many ml of 1 M KOH and 0.5 MH_2SO_4 solutions, respectively, when mixed to form total volume of 100 ml, produces the highest rise in temperature?

   a. 67, 33 **b.** 33, 67
   c. 40, 60 **d.** 50, 50

2. Identify the state function among the following:

   a. q **b.** q – w
   c. q/w **d.** q + w

3. For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be

   a. less than ΔH
   b. zero
   c. more than ΔH
   d. equal to ΔH.

4. Which of the following equations represent standard heat of formation of C_2H_4?

   a. $2C\ (diamond) + 2H_2\ (g) \rightarrow C_2H_4\ (g)$
   b. $2C\ (graphite) + 2H_2\ (g) \rightarrow C_2H_4\ (g)$
   c. $2C\ (diamond) + 4H\ (g) \rightarrow C_2H_4\ (g)$
   d. $2C\ (graphite) + 4H\ (g) \rightarrow C_2H_4\ (g)$

5. A glucose solution in 100 gm of water boils at 100.26°C. If this solution is heated to 101°C. What will be the mass of water left at equilibrium?

   a. 76 gm **b.** 120 gm
   c. 100 gm **d.** 26 gm

6. The enthalpy of hydrogenation of cyclohexene is –119.5 kJ mol^{-1}. If resonance energy of benzene is –150.4 kJ mol^{-1}, its enthalpy of hydrogenation would be

   a. –269.9 kJ mol^{-1}
   b. –358.5 kJ mol^{-1}
   c. –508.9 kJ mol^{-1}
   d. –208.1 kJ mol^{-1}

7. A reaction is non-spontaneous at the freezing point of water but is spontaneous at the boiling point of water then

	Δ	Δ
a.	+ve	+ve
b.	–ve	–ve
c.	–ve	+ve
d.	+ve	–ve

8. The enthalpy change (ΔH) for the reaction,

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

   is –92.38 kJ at 298 K. The internal energy change ΔU at 298 K is

   a. –92.38 kJ **b.** –87.42 kJ
   c. –97.34 kJ **d.** –89.9 kJ

9. For a phase change

   $H_2O\ (l) \xleftrightarrow{0°C,\ 1\ bar} H_2O\ (s)$

   a. ΔG = 0 **b.** ΔS = 0
   c. ΔH = 0 **d.** ΔU = 0

10. The enthalpy and entropy change for the reaction

    $Br_2\ (l) + Cl_2\ (g) \rightarrow 2BrCl\ (g)$

    are 30 kJ mol^{-1} and 105 J K^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is

    a. 450 K **b.** 300 K
    c. 285.7 K **d.** 273 K

11. For a spontaneous process, the correct statement is

    a. entropy of the system always increases
    b. free energy of the system always increases
    c. total entropy change is always negative
    d. total entropy change is always positive

12. A heat engine absorbs heat q_1 from a source at temperature T_1 and heat q_2 from a source at temperature T_2. Work done is found to be J $(q_1 + q_2)$. This is in accordance with:

    a. first law of thermodynamics
    b. second law of thermodynamics
    c. joules equivalent law
    d. none of these

13. Identify the correct statement for change of Gibb's energy for a system (ΔG_{system}) at constant temperature and pressure:

    a. if $\Delta G_{system} = 0$, the system is still moving in a particular direction

b. if ΔG_{system} = –ve, the process is not spontaneous

c. if ΔG_{system} = +ve, the process is spontaneous

d. if $\Delta G_{system} = 0$, the system has attained equilibrium

14. For the reaction of one mole of Zn –dust with one mole of H_2SO_4 in a bomb calorimeter, ΔU an W corresponds to:

a. $\Delta U < 0, W = 0$

b. $\Delta U < 0, W < 0$

c. $\Delta U > 0, W = 0$

d. $\Delta U > 0, W > 0$

15. ΔH°_f (298) of methanol is given by chemical equation

a. $CH_4(g) + \frac{1}{2} O_2(g) \rightarrow CH_3OH(g)$

b. $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$

c. $C(\text{graphite}) + \frac{1}{2} O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$

d. $C(\text{diamond}) + \frac{1}{2} O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$

16. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta U$?

a. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

b. $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

c. $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

d. $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$

17. The absolute enthalpy of neutralization of the reaction

$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$

will be

a. –57.33 kJ/mole

b. > – 57.33 kJ/ mole

c. < – 57.33 kJ/mole

d. 57.33 kJ /mole.

18. A reaction occurs spontaneously if

a. $T\Delta S < \Delta H$ and both ΔH, ΔS are +ve

b. $T\Delta S > \Delta H$ and ΔH = +ve, ΔS = –ve

c. $T\Delta S > \Delta H$ and both ΔH, ΔS are +ve

d. $T\Delta S = \Delta H$ and both ΔH, ΔS are +ve

19. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}, the value of enthalpy change for the reaction

$H_2C = CH_2(g) + H_2(g) \rightarrow H_3C - CH_3(g)$

at 298 K will be

a. +250 kJ **b.** –250 kJ

c. +125 kJ **d.** –125 kJ

20. A gas expands into a vacuum (external pressure = 0) while in thermal isolation from the surroundings. For this expansion

a. ΔE does not change

b. ΔE increases

c. $\Delta E = T^1S$

d. ΔE decreases

21. For a process at constant volume,

a. w = 0 and $\Delta E = \Delta H$

b. w = 0 and ΔH = q

c. q = 0, w = 0 and $\Delta E = 0$

d. w = 0 and ΔE = q

22. In an irreversible process taking place at constant T and P and in which only pressure –volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria:

a. $(dS)_{V,E} < 0, (dG)_{T,P} < 0$

b. $(dS)_{V,E} > 0, (dG)_{T,P} < 0$

c. $(dS)_{V,E} = 0, (dG)_{T,P} = 0$

d. $(dS)_{V,E} = 0, (dG)_{T,P} > 0$

23. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?

a. exothermic and increasing disorder

b. exothermic and decreasing disorder

c. endothermic and increasing disorder

d. endothermic and decreasing disorder

24. The internal energy change when a system goes from state A to B is 40 kJ/mol. if the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy?

a. 40 kJ **b.** > 40 kJ

c. < 40 kJ **d.** zero

25. Standard state Gibbs free energy change for isomerization reaction,

Cis-2-pentene ↔ trans-2-pentene

is –3.67 kJ/mol at 400 K. if more trans-2-pentene is added to the reaction vessel, then:

a. more cis-2-pentene is formed

b. additional trans-2-pentene is formed

c. equilibrium remains unaffected

d. equilibrium is shifted in the forward direction

26. An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is

a. –900 kJ **b.** –900 J
c. 270 kJ **d.** 940 kJ

27. For a reaction to occur spontaneously

a. ($\Delta H - T\Delta S$) must be negative
b. ($\Delta H + T\Delta S$) must be negative
c. ΔH must be negative
d. ΔS must be negative

28. Which one of the following has ΔS° greater than zero?

a. $CaO(s) + CO_2(g) \leftrightarrow CaCO_3(g)$
b. $NaCl(aq) \leftrightarrow NaCl(s)$
c. $NaNO_3(s) \leftrightarrow Na^+(aq) + NO_3^-(aq)$
d. $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

29. For an explosion in an open vessel, one would expect

a. ΔH to be negative and ΔE to be greater than ΔH
b. ΔH to be negative and ΔE to be less than ΔH
c. ΔH to be positive and ΔE to be less than ΔH
d. ΔH to be positive and ΔE to be greater than ΔH

30. Which of the following is correct equation?

a. $\Delta U = \Delta Q - W$
b. $\Delta W = \Delta U + \Delta Q$
c. $\Delta U = \Delta W + \Delta Q$
d. none of these

31. Consider the reaction $N_2 + 3H_2 \leftrightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction. Which of the following expressions is true?

a. $\Delta H = 0$ **b.** $\Delta H = \Delta U$
c. $\Delta H < \Delta U$ **d.** $\Delta H > \Delta U$

32. 1 mol of an ideal gas at 300 K is expanded isothermally and reversible from an initial volume of 1 litre to 10 litre. The work in this process is (R = 2 cal mol^{-1} K^{-1})

a. 163.7 cal **b.** zero
c. –1381.8 cal **d.** 9 litre atm

33. Identify the correct statement regarding entropy.

a. At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero
b. At absolute zero of temperature the entropy of a perfectly crystalline substance is +ve
c. At absolute zero of temperature the entropy of all crystalline substance is to be zero
d. At 0°C, the entropy of a perfectly crystalline substance is taken to be zero

34. A gas expands against a non-zero external pressure while in thermal isolation from the surroundings. For this expansion

a. $\Delta E = q$
b. ΔE increases
c. ΔE does not change
d. ΔE decreases

35. The standard enthalpy of formation ($\Delta_f H^\circ$) at 298 K for methane, $CH_4(g)$ is –74.8 kJ mol^{-1}. the additional information required to determine the average energy for C – H bond formation would be

a. the dissociation energy of H_2 and enthalpy of sublimation of carbon
b. latent heat of vapourization of methane
c. the first four ionization energies of carbon and electron gain enthalpy of hydrogen
d. the dissociation energy of hydrogen molecule, H_2

36. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as

$S_2(s) + 2O_2(g) \rightarrow 2SO_2(g)$; $\Delta G = -544$ kJ

$2Zn(s) + S_2(s) \rightarrow 2ZnS(s)$; $\Delta G = -293$ kJ

$2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$; $\Delta G = -480$ kJ

the ΔG for the reaction,

$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$

will be

a. –357 kJ **b.** –731 kJ
c. –773 kJ **d.** –229 kJ

37. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If Ti is the initial temperature and T_f is the final temperature, which of the following statements is correct?

a. $(T_f)_{irrev} > (T_F)_{rev}$
b. $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
c. $(T_f)irrev = (T_F)rev$
d. $T_f = T_i$ for both reversible and irreversible processes

38. The entropy change in the fusion of 1 mol of a solid melting at 27°C (Latent heat of fusion, 2930 J mol^{-1}) is

a. 9.77 JK^{-1} mol^{-1}
b. 10.73 JK^{-1} mol^{-1}

c. 2930 JK^{-1} mol^{-1}

d. 108.5 JK^{-1} mol^{-1}

39. As a given temperature and pressure, which of the following would be expected to have the greatest molar entropy?

a. Br_2 (g)

b. Br_2 (s)

c. Br_2 (l)

d. All of these would be expected to have the same molar entropy.

40. The standard enthalpy of formation ($\Delta_f H^\circ$) at 298 K for methane, CH_4(g) is –74.8 kJ mol^{-1}. the additional information required to determine the average energy for C – H bond formation would be

a. the dissociation energy of H_2 and enthalpy of sublimation of carbon

b. latent heat of vapourization of methane

c. the first four ionization energies of carbon and electron gain enthalpy of hydrogen

d. the dissociation energy of hydrogen molecule, H_2

41. When 1 mol gas is heated at constant volume temperature is raised from 298 to 308 K. Heat supplied to the gas is 500 J. Then which statement is correct?

a. $q = W = 500$ J, $\Delta U = 0$

b. $q = \Delta U = 500$ J, $W = 0$

c. $q = W = 500$ J, $\Delta U = 0$

d. $\Delta U = 0$, q =

42. For the reaction:

$S_8 (s) + 8O_2 (g) \rightarrow 8SO_2 (g)$

a. $\Delta H < \Delta E$

b. $\Delta H = \Delta E$

c. $\Delta H > \Delta E$

d. ΔH is independent of the physical state of reactants.

43. 2 mol of an ideal gas at 27°C temperature is expanded reversibly from 2 L to 20 L. Find entropy change in cal. (R = 2 cal/mol K)

a. 92.1 **b.** 0

c. 4 **d.** 9.2

44. ($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is

a. –1238.78 J mol^{-1}

b. 1238.78 J mol^{-1}

c. –2477.57 J mol^{-1}

d. 2477.57 J mol^{-1}

45. For the reaction,

$C_3H_8 (g) + 5O_2 (g) \rightarrow 3CO_2 (g) + 4H_2O (l)$

at constant temperature, $\Delta H - \Delta E$ is

a. + 3RT **b.** –RT

c. +RT **d.** –3RT

46. What is the entropy change (in JK^{-1} mol^{-1}) when 1 mol of ice is converted into water at 0°C? (The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C)

a. 2.198 **b.** 21.98

c. 20.13 **d.** 2.013

47. An ideal gas expand against a constant external pressure of 5.0 atmosphere from 40 to 60 litre and absorb 40 kJ of energy from surrounding. The change in internal energy of the system will be

a. 20.52 kJ **b.** 52.75 kJ

c. 32.75 kJ **d.** 35.95 kJ

48. The molar heat capacity of water at constant pressure, C, is 75 JK^{-1} mol^{-1}. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is

a. 4.8 K **b.** 6.6 K

c. 1.2 K **d.** 2.4 K

49. The incorrect statement amongst the following is

a. at equilibrium $\Delta H_{S,P} = 0$

b. the condition of equilibrium at constant P and T is that G must be minimum

c. at equilibrium $\Delta G_{P,T} = 0$

d. ΔG° calculated using the equation; $\Delta G^\circ = -RT$ In Kp, is the free energy change of the reaction when each of the species (reactants and products) is in the standard state of unit activity that is, roughly unit concentration.

50. The heat liberated on complete combustion of 7.8 gm of benzene is 327 kJ. This heat was measured at constant volume and at 27°C. Calculate the heat of combustion of benzene at constant pressure (R = 8.3 J/mole/K)

a. –1637 kJ/mole **b.** –3274 kJ/mole

c. –3270 kJ/mole **d.** none of these

51. AB, A_2 and B_2 are diatomic molecule if the bond enthalpies of A_2, AB and B_2 are in the ratio 1:1 : 0.5 and the enthalpy of formation of AB from A and B_2 is 100 kJ/mole. What is the bond enthalpy of A_2?

a. 400 kJ/mole **b.** 300 kJ/mole
c. 200 kJ/mole **d.** 100 kJ/mole

52. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

a. $\Delta S_{system} + \Delta S_{surroundings} > 0$
b. $\Delta S_{system} - \Delta S_{surroundings} > 0$
c. $\Delta S_{system} > 0$ only
d. $\Delta S_{surroundings} > 0$ only

53. The gas in a refrigerator causes cooling on expansion because

a. work done by the gas is converted into heat
b. heat of the gas is lost as work is done by the gas
c. the heat is spread over a larger space
d. None

54. The standard heats of formation of NO_2 (g) and N_2O_4 (g) are 8.0 and 2.0 kcal mol^{-1} respectively. The heat of dimerization of NO_2 in kcal is

a. 10.0 **b.** –6.0
c. –12.0 **d.** –14.0

55. Calculate the work done during isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 300K.

a. –1382 cal **b.** –1382 joule
c. –13.82 cal **d.** –1.382 cal

56. The heats of neutralization of four acids a, b, c and d when neutralized against a common base and 13.7, 9.4, 11.2 and 12.4 kcal respectively. the weakest among these acids is

a. a **b.** b
c. c **d.** d

57. Which of the following salts shall cause maximum cooling when one mole of the salt is dissolved in the same amount of water? (integral heat of solution at 298 K is given for each solute)

a. KNO_3, ΔH = 35.4 kJ mol^-
b. NaCl, ΔH = –5.35 kJ mol^-
c. KOH, ΔH = –55.6 kJ mol^-
d. KBr, ΔH = – 83.3 kJ mol^-

58. The melting point of a solid is 27°C and it's latent heat of fusion is 600 calories per mole. The entropy change for the fusion of one mole of the solid (in cal K^{-1}) is

a. 180 **b.** 22.2
c. 2 **d.** 0.5

59. Devitrification of glass is a process for which change in entropy (ΔS)

a. –ve
b. +ve
c. 0
d. ΔS value depend on the nature of glass

60. In a flask, colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium, the brown colour deepens on heating the flask to 100°C and on cooling it become less coloured. ΔH for the system is

a. positive **b.** negative
c. zero **d.** undefined

61. Which of the following modes of energy constitute both kinetic and potential energy?

a. nuclear energy
b. transitional energy
c. rotational energy
d. vibrational energy

62. Which of the following is not expected to be correct?

a. $\Delta H^\circ_f (CO_2)$ = negative
b. ΔH_{comb} (NO) = positive
c. $\Delta H_{hyd} (BaCl_2)$ = negative
d. ΔH_{neut} = negative

63. The standard heat of formation of diamond is

a. same as that of graphite
b. greater than that of graphite
c. less than that of graphite
d. taken as zero

64. How many calories are required to heat 40 gram of argon from 40 to 100°C at constant volume? (R = 2 cal/mol.K)

a. 120 **b.** 180
c. 1800 **d.** 2400

65. Which of the following does not express criterion of spontaneity?

a. $(dS)_{P.T.} > 0$ **b.** $(dA)_{V.T.} \geq 0$
c. $(dG)_{P.T.} < 0$ **d.** All of these

66. Which one of the following set of units represents the smallest and the largest amount of energy respectively?

a. eV and lit atm
b. Cal and eV
c. J and erg
d. erg and cal

67. If $K < 1.0$, what will be the value of ΔG° of the following?

a. Zero **b.** Negative
c. Positive **d.** 1.0

68. Which of the following are not state functions?

(I) q + w (II) q
(III) w (IV) H –TS

a. (I), (II) and (III)

b. (II) and (III)

c. (I) and (IV)

d. (II), (III) and (IV)

69. Oxidizing power of chlorine in aqueous solution can be determined by the parameters indicated below:

$$\tfrac{1}{2}Cl_2(g) \xrightarrow{\tfrac{1}{2}\Delta_{diss}H^-} Cl(g) \xrightarrow{\Delta_{eg}H^-}$$

$$Cl^-(g) \xrightarrow{\Delta_{hyd.}H^-} Cl^-(aq)$$

The energy involved in the conversion of $\tfrac{1}{2}Cl_2$ (g) to Cl^- (g)

(Using the data, Δ_{diss} H-Cl_2 = 240 kJ mol^{-1}, Δ_{eg} H-Cl = –349 kJ mol^{-1}, Δ_{hyd} H-Cl = –381 kJ mol^{-1})

will be

a. +152 kJ mol^{-1} **b.** –610 kJ mol^{-1}
c. –850 kJ mol^{-1} **d.** +120 kJ mol^{-1}

70. For the gas phase reaction,

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Which of the following conditions are correct?

a. $\Delta H < 0$ and $\Delta S < 0$
b. $\Delta H > 0$ and $\Delta S < 0$
c. $\Delta H = 0$ and $\Delta S < 0$
d. $\Delta H > 0$ and $\Delta S > 0$

71. Using the following thermochemical equations

(i) $S_{(rh)} + 3/2\ O_{2(g)} \rightarrow SO_{3(g)}$; $\Delta H = -2x$ kJ mol^{-1}

(ii) $SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow SO_{3(g)}$; $\Delta H = -y$ kj mol^{-1}

Find out the heat of formation of $SO_{2(g)}$ in kJ mol^{-1}.

a. (× + y) **b.** (2x + y)
c. (2x/y) **d.** (y – 2x)
e. (2x – y)

72. When compared to ΔG° for the formation of Al_2O_3, the ΔG° for the formation of Cr_2O_3 is

a. Lower **b.** Unpredicted
c. Higher **d.** Same

73. For one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then

a. $\Delta H = \Delta U$

b. $\Delta H < \Delta U$

c. There is no relationship

d. $\Delta H > \Delta U$An s = (A)

74. At a given pressure and volume, in the P – V plot, of an ideal gas,

$$\frac{\text{Slope of an adiabatic curve}}{\text{Slope of an isothermal curve}} \text{ is}$$

a. C_P/R **b.** C_V/C_P
c. C_P/C_V **d.** R

75. Enthalpy is equal to

a. $-T^2\,[\partial(G/T)/\partial T]_V$

b. $T^2\,[\partial(G/T)/\partial T]_V$

c. $-T^2\,[\partial(G/T)/\partial T]_p$

d. $T^2\,[\partial(G/T)/\partial T]_p$

Brainteasers Objective Type Questions (Single choice only)

76. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are—156 and +49 kJ mol^{-1} respectively. The standard enthalpy of hydrogenation of Cyclohexene (l) at 25°C is –119 kJ/mol. Find resonance energy of benzene.

a. –152 kJ mol^{-1} **b.** –159 kJ mol^{-1}
c. + 152 kJ mol^{-1} **d.** + 159 kJ mol^{-1}

77. 0.50mol of ammonium nitrate is added to 50.0 mL or water in a thermally insulated reaction vessel. Both are initially at 20.0°C. After stirring the temperature of the solution is found to be less than 10°C. Which statement best explains the temperature change?

a. Heat is evolved from the system to the surroundings.

b. Heat is absorbed from the surroundings by the system.

c. Heat is absorbed by ammonium nitrate when it dissolves and becomes hydrated.

d. Heat is evolved by ammonium nitrate when it dissolves and becomes hydrated.

e. The heat energy of the hydrated ions is less than the ions in solid ammonium nitrate.

78. Determine the sign of ΔS° for each of the following processes:

(I) $C_6H_6(s) \rightarrow C_6H_6(l)$

(II) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

a. ΔS° should be positive for I and positive for II.

b. ΔS° should be positive for I and negative for II

c. ΔS° should be negative for I and negative for II.

d. ΔS° should be negative for I and positive for II.

79. The difference between heats of reaction at constant pressure and constant volume for the reaction

$2\,C_6H_6(l) + 15\,O_2(g) \rightarrow 12\,CO_2(g) + 6H_2O(l)$

at 25°C in kJ is

a. –7.43 **b.** +3.72

c. –3.72 **d.** + 7.43

80. 100 ml of 0.3 M HCl solution is mixed with 100 ml of 0.33 M KOH solution. The amount of heat liberated is

a. 1.713 kJ **b.** 17.42 kJ

c. 1.31 kJ **d.** 17.13 kJ

81. An athlete is given 100 g of glucose of energy equivalent to 1560 kJ. He utilizes 50 % of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. Enthalpy of H_2O for evaporation is 44 kJ mol^{-1}.

a. 346 g **b.** 316 g

c. 323 g **d.** 319 g

82. The enthalpies of formation of CO_2 (g) and CO (g) at 298 K are in the ratio 2.56: 1. For the reaction,

$CO_2(g) + C(s) \rightarrow$

CO (g), $\Delta H = 177.5$ kJ, ΔH_f of CO (g) is

a. –113.78 kJ mol^{-1}

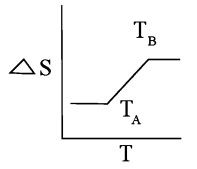
b. 113.78 kJ mol^{-1}

c. –141.6 kJ mol^{-1}

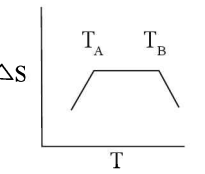
d. –180.6 kJ mol^{-1}

83. If for a given substance, T_B is the m.p. and T_A is the freezing point, then correct variation of entropy by graph between entropy change (ΔS) and temperature is

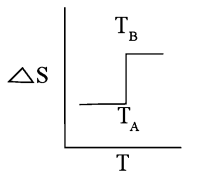
a.



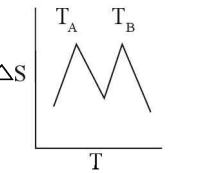
b.



c.



d.



84. The standard enthalpy of combustion at 25°C of H_2, C_6H_{10} and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ mol^{-1} respectively. Calculate heat of hydrogenation of cyclohexane (C_6H_{10})

a. –161 kJ mol^{-1} **b.** –131 kJ mol^{-1}

c. –121 kJ mol^{-1} **d.** None

85. Classify each of the following processes as spontaneous or non spontaneous.

I. $H_2O(l) \rightarrow H_2O(g)$ T = 25°C vessel open to atmosphere with 50 % relative humidity.

II. $H_2O(s) \rightarrow H_2O(l)$ T = 25°C, P = 1 atm

a. I and II are both non spontaneous

b. I and II are both spontaneous

c. I is non spontaneous and II is spontaneous

d. I is spontaneous and II is non spontaneous.

86. The standard heats of formation of CH_4 (g), CO_2 (g) and H_2O (g) are –76.2, –394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1m^3 methane measured under normal conditions.

a. 162897.3 kJ **b.** 64078.2 kJ

c. 35182 kJ **d.** none

87. For an explosion in an open vessel, one would expect

a. ΔH to be negative and ΔE to be greater than ΔH

b. ΔH to be negative and ΔE to be less than ΔH

c. ΔH to be positive and ΔE to be less than ΔH

d. ΔH to be positive and ΔE to be greater than ΔH

88. Calculate the resonance energy of N_2O from the following data: ΔH_f of N_2O = 82 kJ mol^{-1}. Bond energies of N ≡ N, N = N, O = O and N = O bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively.

a. –88 kJ mol^{-1} **b.** –170 kJ mol^{-1}
c. –82 kJ mol^{-1} **d.** –258 kJ mol^{-1}

89. The enthalpy changes for the following processes are listed below

$Cl_2(g) = 2Cl(g)$; 242.3 kJ mol^{-1}

$I_2(g) = 2I(g)$; 151.0 kJ mol^{-1}

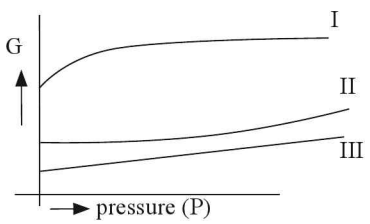
$ICl(g) = I(g) + Cl(g)$; 211.3 kJ mol^{-1}

$I_2(s) = I_2(g)$; 62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are I_2 (s) and Cl_2 (g), the standard enthalpy of formation for ICl (g) is

a. –14.6 kJ mol^{-1} **b.** –16.8 kJ mol^{-1}
c. +16.8 kJ mol^{-1} **d.** +244.8 kJ mol^{-1}

90. The following curve represents the variation of Gibbs function 'G' with pressure at constant temperature.



Correct match of given plots with the physical state of a substance is

a. I – solid, III– gas, II – liquid
b. I – gas, II – liquid, III – solid
c. I – liquid, II – solid, III – gas
d. III – gas, II – solid, I - liquid

91. Which of the following is in accord with the three laws of thermodynamics?

(I) The entropy of the universe never decreases.

(II) A non-spontaneous process can occur if it is coupled to a process that is sufficiently spontaneous.

a. I is true and II is false.
b. I is false and II is true.
c. Both I and II are true.
d. Both I and II are false.

92. Which of CH_4 (g), C_2H_2 (g) and CH_3OH (l) provides the most energy per gram upon combustion and which provides the least?

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H^\circ = -890$ kJ

$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$

$\Delta H^\circ = -2599$ kJ

$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

$\Delta H^\circ = -1453$ kJ

a. C_2H_2 provides the most energy per gram and CH_3OH the least.
b. C_2H_2 provides the most energy per gram and CH_4 the least.
c. CH_4 provides the most energy per gram and C_2H_2 the least.
d. CH_4 provides the most energy per gram and CH_3OH the least.

93. Calculate ΔH°_f for chloride ion from the following data:

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$

$\Delta H^\circ_f = -92.4$ kJ

$HCl(g) + nH_2O(l) \rightarrow H^+(aq) + Cl^-(aq)$

$\Delta H_{298} = -74.8$ kJ

$\Delta H^\circ_f[H^+] = 0.0$ kJ

a. –189 kJ **b.** –167 kJ
c. + 167 kJ **d.** –191 kJ

94. The signs of ΔG, ΔH and ΔS at 25°C are shown below for three reactions.

Reaction	ΔG	ΔH	ΔS
I.	–	+	+
II.	–	–	+
III.	–	–	–

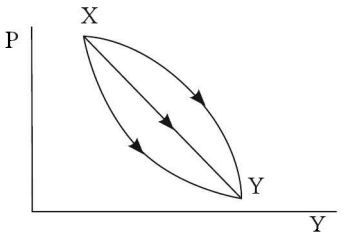
Which reaction could go in the reverse direction at high temperature?

a. II only **b.** III only
c. I and II **d.** II and III

95. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat was measured at constant volume and at 27°C. Calculate the heat of combustion of benzene at constant pressure (R = 8.3 J mol^{-1} K^{-1})

a. –3274 kJ mol^{-1} **b.** –1637 kJ mol^{-1}
c. –3270 kJ mol^{-1} **d.** –3637 kJ mol^{-1}

96. A given masss of gas expands from the state × to the staste Y by three paths 1, 2 and 3 as shown I in the figure. If w1 and w_2 and w_3 respectively be the work done by the gas along three paths then:



a. $w_1 > w_2 > w_3$

b. $w_2 < w_1 < w_2$

c. $w_1 = w_2 = w_3$

d. $w_1 < w_2 < w_3$

97. Calculate ΔG° for the reaction below and tell whether it is spontaneous or non-spontaneous under standard conditions at 25°C.

$2S\ (s) + 3O_2\ (g) + 2H_2O\ (l) \rightarrow 2H_2SO_4\ (l)$

$\Delta H^\circ = -1056$ kJ/mol

$\Delta S^\circ = -505$ J/mol

a. $\Delta G^\circ = -906$ kJ and the process is spontaneous

b. $\Delta G^\circ = -1206$ and the process is spontaneous

c. $\Delta G^\circ = -906$ kJ and the process is non-spontaneous

d. $\Delta G^\circ = -1206$ kJ and the process is non-spontaneous

98. Generally, alkali metals form their oxides by an average increment of 6 kJ mol^{-1} K^{-1} in their entropies. If at 25°C, ΔG°_f of Al_2O_3 (s) = –1582 kJ mol^{-1} ; ΔH°_f of Li_2O (s) = 1244 kJ and ΔH°_f of Na_2O (s) = 1411 kJ. The aluminium oxide can be reduced to Al metal by

a. Lithium **b.** Sodium

c. Both (a) and (b) **d.** None of these

99. For the reaction,

$A\ (g) + 2B\ (g) \rightarrow 2C\ (g) + 3D\ (g)$

The value of ΔH at 27°C is 19.0 kcal. The value of ΔE for the reaction would be

(given R = 2.0 cal K^{-1} mol^{-1})

a. 20.8 kcal **b.** 19.8 kcal

c. 18.8 kcal **d.** 17.8 kcal

100. Determine ΔH and ΔE for reversible isothermal evaporation of 90 g of water at 100°C. Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540 cal g^{-1} (R = 2.0 cal mol^{-1} K^{-1})

a. 48600 cal, 44870 cal

b. 43670 cal, 47700 cal

c. 47700 cal, 43670 cal

d. 44870 cal, 48670 cal

101. If work done by a gas is 144.5 J when heat given to the gas in isobaric process is 506 J. then the gas is

a. SO_2 **b.** NH_3

c. He **d.** O_2

102. A process is carried out at constant pressure. Given that ΔH is negative and ΔE is less than ΔH,

a. The system loses heat and contracts during the process

b. The system loses heat and expands during the process

c. The system absorbs heat and expands during the process

d. The system absorbs heat and contracts during the process

103. ΔG° for the reaction, $x + y \leftrightarrow z$ is –4.606 kcal. The value of equilibrium constant of the reaction at 227°C is.

a. 0.01 **b.** 100

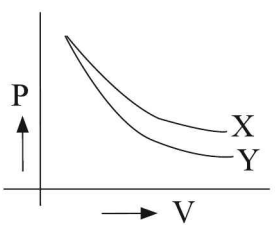
c. 2 **d.** 10

104. Assume a heteronuclear diatomic molecule, AB, forms a one dimensional crystal by lining up along the X-axis. Also assume that each molecule can only have one of six possible orientations, corresponding to atom A facing in either the positive or negative direction along the X-, Y-, or Z-axis. If the molecules are arranged randomly in the six directions, the molar entropy at absolute zero should be

a. zero **b.** R In 60

c. R In 6 **d.** R In 6^6

105. P–V plot for two gases (assuming ideal) during adiabatic process are given in the fig. Plot X and plot Y should correspond respectively to:



a. He and H_2 **b.** H_2 and He

c. Cl_2 and H_2 **d.** H_2 and Cl_2

106. The solubility of manganese (II) fluoride in water is 6.6 g/ml at 40°C and 4.8 g/litre at 100°C. Based on this data, what is the sign of ΔH° and ΔS° for the following process?

$MnF_2(s) \rightleftharpoons Mn^{2+}(aq) + 2F^-(aq)$

a. ΔH° is negative and ΔS° is positive

b. ΔH° is negative and ΔS° is negative

c. ΔH° is positive and ΔS° is positive

d. ΔH° is positive and ΔS° is negative

107. For the system represented by the equation

$CaCO_3(s) + 42.5\ Kcal \rightarrow CaO(s) + CO_2(g)$

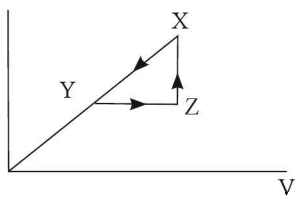
a. the reaction is exoenergic

b. the size of ΔE is negative

c. the net energy flow is from the system to the environment

d. the internal chemical energy of one mole $CaCO_3$ (s) is less than that of [one mole CaO (s) + one mole CO_2 (g)]

108. P



(I) $Q_X \rightarrow Y = (-)$ ve

(II) $\Delta U_Y \rightarrow Z = (+)$ ve

(III) $\Delta U_Z \rightarrow \times = (-)$ ve

(IV) $W_{ZXY} = (-)$ ve.

a. I, II, III **b.** I, II, IV

c. I, III, IV **d.** II, III, IV

109. Consider these two statements.

(i) The reversible work done by 2 moles of an ideal gas, isothermally at 300 k, as it expands from 10 atm to 1 atm. pressure is roughly 2.764 k. cal.

(ii) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 ml. The work done by the gas is roughly 3 cal.

a. (i) and (ii) are correct

b. (i) and (ii) are incorrect

c. (i) is incorrect, (ii) is correct

d. (i) is correct, (ii) is incorrect

110. The reversible adiabatic expansion of an ideal monatomic gas, the final volume is 10 times to the initial volume. The ratio

$$\frac{\text{Final temperature}}{\text{Initial temperature}} \text{ is}$$

a. $(1/10)^{0.666}$ **b.** $10^{1.666}$

c. $10^{0.666}$ **d.** $(1/10)^{1.666}$

111. 4.8 g of C (diamond) on complete combustion evolves 1584 kJ of heat. The standard heat of formation of gaseous carbon is 725 kJ/mol. The energy required for the process

(i) C (graphite) → C (gas)

(ii) C (diamond) → C (gas) are

a. 725, 723 **b.** 725, 727

c. 727, 725 **d.** None of these

112. Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is

a. –93 kJ mol^{-1}

b. 245 kJ mol^{-1}

c. 93 kJ mol^{-1}

d. –245 kJ mol^{-1}

113. Consider the reaction:

$N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$

$\Delta H^\circ = -249$ kJ and $\Delta S^\circ = -278\ JK^{-1}$ at 25°C

Calculate ΔG° and state whether the equilibrium composition should favour reactants or products at standard conditions.

a. $\Delta G^\circ = -166$ kJ; the equilibrium composition should favour reactants.

b. $\Delta G^\circ = -166$ kJ; the equilibrium composition should favour products.

c. $\Delta G^\circ = -322$ kJ; the equilibrium composition should favour products.

d. $\Delta G^\circ = -166$ kJ; the equilibrium composition should favour reactants.

114. Which provides the greatest increase in entropy?

a. H_2O (l, 0°C) → H_2O (l, 25°C)

b. H_2O (s, 0°C) → H_2O (l, 0°C)

c. H_2O (l, 100°C) → H_2O (g, 100°C)

d. H_2O (g, 0.1°C) → H_2O (s, 0.1°C)

115. Consider these two statements.

(I) The reversible work done by 2 moles of an ideal gas, isothermally at 300 k, as it expands from 10 atm to 1 atm. pressure is roughly 2.764 k. cal.

(II) 2 moles of a gas expand against a constant pressure of 1 atm, the change in the volume being 82.12 ml. The work done by the gas is roughly 3 cal.

a. (i) and (ii) are correct

b. (i) and (ii) are incorrect

c. (i) is incorrect, (ii) is correct

d. (i) is correct, (ii) is incorrect

116. (Standard free energies of formation (in kJ /mol) at 298 K are –237.2, –394.4 and –8.2 for H_2O (l), CO_2 (g) are pentane (g) respectively. The value of E°_{cell} for the pentane-oxygen fuel cell is:

a. 1.0968 V **b.** 0.0698 V

c. 1.968 V **d.** 2.0968 V

Given that

$3C\ (s) + 2Fe_2O_3\ (s) \rightarrow 4Fe\ (s) + 3CO_2\ (g)$

$\Delta H^\circ = -93657$ kcal at 25°C

$C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$

$\Delta H^\circ = -94050$ kcal at 25°C

The value of $\Delta H^\circ\ (Fe_2O_3)$ is

a. –19.650 kcal **b.** –196.5 kcal

c. 93.657 kcal **d.** –286.4 kcal

117. The enthalpy of solution of $BaCl_2$ (s) and $BaCl_2.2H_2O$ (s) are –20.6 and 8.8 kJ mol^{-1} respectively. The enthalpy change for the hydration of $BaCl_2$ (s) is

a. 29.8 kJ **b.** –11.8 kJ

c. –20.6 kJ **d.** –29.4 kJ.

118. The heat of formation of CO_2 is –409 kJ/mol. The energy required for the process

$3CO_2\ (g) \rightarrow 3C\ (g) + 2O_3\ (g)$ is

a. Is equal to 1227 kJ

b. Less than 1227 kJ

c. More than 1227 kJ

d. Cannot be predicted

119. Calculate Q and W 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.

a. 5.22 kJ, –5.22 kJ

b. –27.3 kJ, 27.3 kJ

c. 27.3 kJ, –27.3 kJ

d. –5.22 kJ, 5.22 kJ

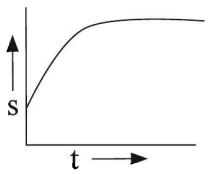
120. Calculate the heat of combustion of methane at constant volume. The thermal capacity of the calorimeter system is 177 kJ K^{-1} (R = 8.314 J K^{-1} mol^{-1})

a. –695 kJ mol^{-1} **b.** –1703 kJ mol^{-1}

c. –890 kJ mol^{-1} **d.** –885 kJ mol^{-1}

121. If a copper block of mass m at temperature 'T1' is kept in the open atmosphere at temperature 'T2' and T2 > T1. The variation of entropy of the copper block with time can be best illustrated by which of these graph.

a.



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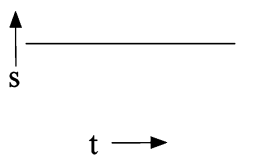
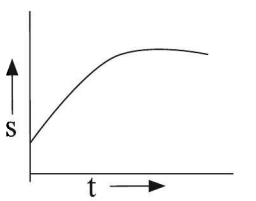


c.



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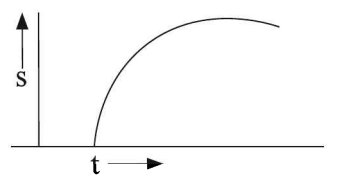


122. The lattice energy of NaCl is 780 kJ mol^{-1} The enthalpies of hydration of Na^+ (g) and Cl^- (g) ions are –406 kJ mol^{-1} and –364 kJ mol^{-1}. The enthalpy of solution of NaCl (s) is

a. 10 kJ mol^{-1} **b.** –10 kJ mol^{-1}

c. 736 kJ mol^{-1} **d.** 100 kJ mol^{-1}

124. The enthalpy (heat) of formation of water is 286 kJ $mole^{-1}$. From this it can be concluded that

a. the enthalpy change when 1 g of hydrogen is burnt in oxygen is –286 kJ

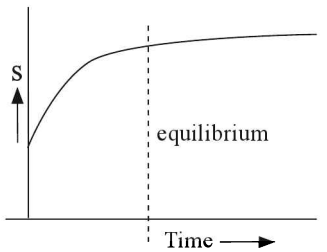
b. there is a decrease in the enthalpy of the system when water is formed

c. the mean bond dissociation energy of O–H is 143 kJ mol^{-1}.

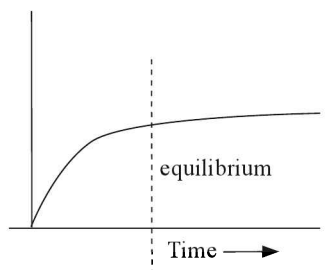
d. the enthalpy change for the reaction $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ is –286 kJ mol^{-1}

125. Which of these correctly represents the entropy (s) of an isolated system during a process?

a.



b.



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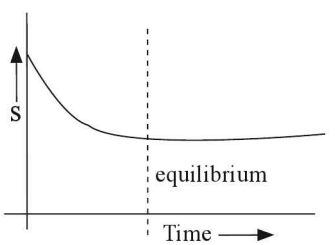
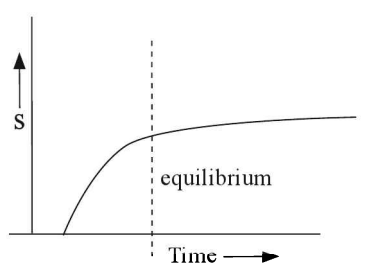


d.



Multiple Correct Answer Type Questions

126. Which of the following statement is/are correct?

a. From the following reaction

$CO(g) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = q_1$

Heat of formation of CO_2 (g) is q_1

b. From the following reaction

C (graphite) $+ \frac{1}{2} O_2(g) \rightarrow CO(g)$, $\Delta H = q_2$

Heat of combustion of carbon is q_2.

c. From the above reaction, heat of combustion of CO (g) is q_1 and that of carbon is $q_1 + q_2$.

d. From the above reaction, heat of formation of CO_2 is $q_1 + q_2$.

127. Which of the following statements is/are true?

a. A highly spontaneous process need not occur rapidly

b. A non spontaneous process cannot be caused to occur.

c. The reverse of a spontaneous reaction is always non spontaneous.

d. A spontaneous process always moves towards equilibrium.

128. $C_P - C_V = R$. This R is not equal to:

a. Change in rotational energy

b. Change in KE

c. Change in PE

d. Work done which system can do on expanding the gas per mol per degree increase in temperature.

129. For which of the following reaction is the standard entropy of reaction ΔS° positive?

a. $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

b. $2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$

c. $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$

d. $C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

130. The enthalpy change for a reaction depend upon the

a. physical state of reactants and products

b. use of different reactants for the same product

c. nature of intermediate reaction steps

d. difference in initial or final temperatures of involved substances

131. Which of the following always increase with increase in temperature?

a. pressure of the gas at constant volume

b. solubility of gas

c. entropy

d. rate of reaction

132. Which of the following is/are spontaneous process?

a. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ if $p_{NH_3} = 1$ atm, $p_{H_2} = P_{N_2} = 0$ and $Kp = 2 \times 10^{-6}$

b. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ if $pH_2 = PN_2 = 1$ atm, $pNH_3 = 0$ and $Kp = 4 \times 10^5$

c. the expansion of gas into a vacuum

d. dissolving more solute in a saturated solution

133. Internal energy and entropy are state functions

a. internal energy (U) is a state function and ΔU is independent of path.

b. In a cyclic process: $\Delta S = 0$ but $\Delta U \neq 0$

c. Cv values of H_2 and He are equal at all temperatures

d. q and w are path dependent

134. For which of the following processes will the entropy decrease?

a. Reaction of magnesium with oxygen to form magnesium oxide.

b. Reaction of nitrogen and hydrogen to form ammonia.

c. Sublimation of dry ice.

d. Condensation of steam.

135. Which of the following statements must be true for the entropy of a pure solid to be zero?

a. Temperature must be 0 K.

b. The solid must be perfectly ordered

c. The solid must be an element.

d. The solid must be crystalline, not amorphous

136. For an ideal gas undergoing isothermal and reversible process

a. ΔU and ΔH both are zero

b. $\Delta U = 0$ but $\Delta H \neq 0$

c. ΔS is +ve during expansion and –ve during compression

d. $\Delta S = 0$ and $\Delta U = 0$

137. In certain chemical process both ΔH and ΔS have values greater than zero. Under what conditions, the reaction would not be spontaneous?

a. $\Delta H > T\Delta S$ **b.** $\Delta H < T\Delta S$

c. $\Delta G > 0$ **d.** $\Delta G < 0$

138. Which statement is/are not true about the standard states of $F_2(g)$ and $C_6H_{12}O_6(aq)$?

a. The standard state for $F_2(g)$ is the pure gas at 1 atm and for $C_6H_{12}O_6(aq)$ is the solution at a concentration of 1 mol/L.

b. The standard state for $F_2(g)$ is the pure gas at 1 mol/L and for $C_6H_{12}O_6(aq)$ is the solution at a concentration of 1 mol/L.

c. The standard state for $F_2(g)$ is the pure gas at 1 atm and for $C_6H_{12}O_6(aq)$ is the pure solid at 1 atm.

d. The standard state for $F_2(g)$ is the pure gas at 1 mol/L and for $C_6H_{12}O_6(aq)$ is the pure solid at atm.

139. The heat evolved during the combustion of 46 gm of ethanol in a bomb calorimeter wad determined to be 670.5 kcal/mol at 25°C. The value of ΔU of the reaction at the same temperature is

a. –335.25 Kcal **b.** –660.3 Kcal

c. –670.5 Kcal **d.** –2802.6 kJ

140. Which of the following process/es proceed towards more disordered state?

a. sublimation of dry ice

b. crystallization of salt from solution

c. dissolution of sugar in water

d. stretching of the rubber

141. Identify the incorrect statement/s regarding entropy.

a. at absolute zero temperature , entropy of perfectly crystalline substance is taken to zero

b. at absolute zero temperature , the entropy of perfectly crystalline substance is positive

c. at 0°C the entropy of perfectly crystalline substance is positive

d. at absolute zero temperature, the entropy of all crystalline substances is taken to be zero

142. xy, x_2 and y_2 are diatomic molecules if ΔH_{x-x}, ΔH_{y-y} and ΔHxy are in the ratio of 2 : 1 : 2 and enthalpy of formation of x – y form x_2 and y_2 is –100 kJ/mol. The value of $\Delta Hx - x$ is

a. 47.85 Kcal/mol

b. 23.92 Kcal/mol

c. 100 kJ/mol

d. 200 Kcal/mol

143. Which of the following statement is/are true?

a. work is a state function

b. temperature is a state function

c. change in the state is completely defined when the initial and final state are specified

d. all of them

144. Which of the following is/are true?

a. A spontaneous process is one that can proceed on its own.

b. The reverse of a non-spontaneous process is always spontaneous.

c. A spontaneous process need not occur immediately.

d. A spontaneous process must be exothermic and must have an increase in entropy.

145. Which of the following expression is correct for an adiabatic process?

a. $(T_2/T_1) = (V_1/V_2)^{\gamma - 1}$

b. $P_2/P_1 = (T_1/T_2)^{\gamma - 1/r}$

c. $P_2V_2^{\gamma} = P_1V_1^{\gamma}$

d. $P_1V_1^{\gamma - 1} = P_2\ V_2^{\gamma - 1}$

146. For which change $\Delta H = \Delta E$

a. $H_2 + I_2 \leftrightarrow 2HI$

b. $HCl + NaOH \rightarrow NaCl + H_2O$

c. $C(s) + O_2\ (g) \leftrightarrow CO_2\ (g)$

d. $N_2 + 3H_2 \rightarrow 2NH_3$

147. Which statement is/ are not true about the formation of $CaCO_3$ (s) from CaO (s) and CO_2 (g) at 1.00 atm?

$CaO\ (s) + CO_2\ (g) \rightarrow CaCO_3\ (s)$

$\Delta H^\circ = -178.7$ kJ and $\Delta S^\circ = -150.4\ JK^{-1}$

a. The reaction is spontaneous at low temperature.

b. The reaction is spontaneous at all temperatures.

c. The reaction is not spontaneous at any temperature

d. The reaction is spontaneous at high temperatures.

148. The correct statement/s among the following is/are

a. mass plus energy of the universe remains always constant while entropy of the universe remains increasing continuously

b. an exothermic reaction with ΔS being positive, will be spontaneous only at high temperature

c. in a reversible process, the system always in equilibrium with surroundings

d. in any cyclic process $\Delta X = 0$ where X is a state fuction.

149. Which of the following reaction is exothermic?

a. C (diamond) → C (graphite)

b. $C_2H_6 \rightarrow C_2H_4 + H_2$

c. $C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3H_2O\ (l)$

d. $2NaOH\ (aq) + H_2SO_4\ (aq) \rightarrow$

$Na_2SO_4\ (aq) + 2H_2O\ (l)$

150. For which reaction change of entropy will be negative?

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

b. $MgO_{(s)} + H_{2(g)} \rightleftharpoons Mg_{(g)} + H_2O_{(l)}$

c. $NH_4NO_{3(s)} \rightleftharpoons N_2O_{(g)} + 2H_2O_{(g)}$

d. $HCl_{(g)} + NH_{3(g)} \rightleftharpoons NH_4Cl_{(s)}$

151. The correct statement amongst the following is/are

a. at equilibrium $\Delta H_{S,P} = 0$

b. the condition of equilibrium at constant P and T is that G must be minimum

c. at equilibrium $\Delta G_{P,T} = 0$

d. ΔG° calculated using the equation; $\Delta G^\circ = -RT$ In Kp, is the free energy change of the reaction when each of the species (reactants and products) is in the standard state of unit activity that is, roughly unit concentration.

152. Correct statement among the following is/are

a. mass plus energy of the universe remains always constant while entropy of the universe remains increasing continuously

b. an exothermic reaction with ΔS being positive, will be spontaneous only at high temperature

c. in a reversible process the system always in equilibrium with surroundings

d. in any cyclic process $\Delta X = 0$ where Xs a state fuction.

153. The enthalpy change for a reaction depends upon:

a. The differences in initial or final temperatures of involved substances

b. The nature of intermediate reaction steps

c. Use of different reactants for the same product

d. The physical states of reactants and products

154. Which of the following is/are correct?

a. Numerical value of ΔH is less than that of ΔE for the reaction $C\ (s) + \frac{1}{2}\ O_2\ (g) \rightleftharpoons CO\ (g)$

b. In an exothermic reaction, the enthalpy of products is less than that of the reactants

c. ΔH (fusion) = ΔH (sub) – ΔH (vap)

d. A reaction for which $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$ is possible at all temperatures.

155. Among the following, the state function(s) is/are

a. Internal energy

b. Irreversible expansion work

c. Reversible expansion work

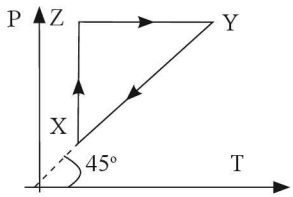
d. Molar enthalpy

[IIT 2009]

Linked-Comprehension Type Questions

Comprehension 1

A cyclic process XYZX is shown in figure. The process is for 2 mole of monatomic gas. As the gas behaves ideally. So one can apply PV = nRT for the gas. The work done by the gas in a process is given as $W = \int PdV$ P

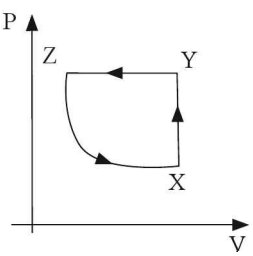


156. The process X→Y is isochoric. The volume of the gas numerically in this process is

a. 3R **b.** 3R

c. 5/2 R **d.** 2R

157. The same cyclic process in the PV – diagram is

a.


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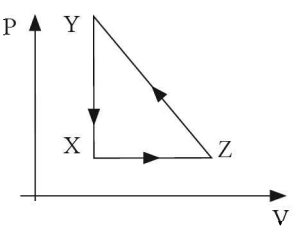

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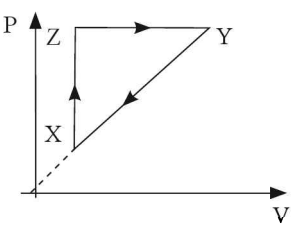
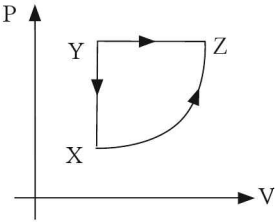


d.


158. During the process X→ Y, The internal energy of the gas

a. Depends on volume

b. Decreases

c. Increases

d. Does not change

Comprehension 2

The values of ΔH and ΔS generally do not vary much with temperature. As a consequence, the dependence of ΔG with temperature is governed mainly by the value of T in then expression ΔG = ΔH – TΔS. The entropy term – TΔS has the greater effect on the spontaneity of the process.

Under non-standard conditions, ΔG is related to ΔG° and the value of the reaction quotient, Q : Δ = ΔG° – RT ln Q. At equilibrium (ΔG = 0, Q = K), ΔG° = –RT ln

159. If the value of equilibrium constant for the reaction given below is 4.4×10^{-4} at 298 K.

$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

Find ΔG° for this reaction.

a. –38.28 kJ **b.** –19.14 kJ

c. –9.57 kJ **d.** Zero

160. Find the value of ΔG when $[H^+] = 3.0 \times 10^{-10}$ M, $[CH_3NH_3^+] = 8.0 \times 10^{-3}$ M, and $[CH_3NH_2]$ =0.070M.

a. +11.8 **b.** –5.9

c. –10.8 **d.** – 11.8

161. A particular reaction given below can be spontaneous if

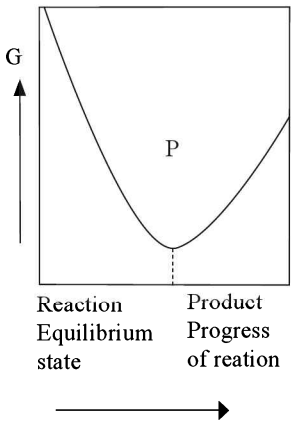
$2POCl_3(g) \rightarrow 2PCL_3(g) + O_2(g)$

$\Delta H° = 572$ kJ; $\Delta S° = 179$ J/K

a. T > 1200 K **b.** T > 1600 K
c. T > 2400 K **d.** T >3200 K

Comprehension 3

For a reversible reaction at constant temperature and at constant pressure the equilibrium composition of reaction mixture corresponds to the lowest point on Gibbs energy Vs progress of reaction diagrams as shown. At equilibrium, Gibbs energy of reaction (ΔG) is equal to zero.



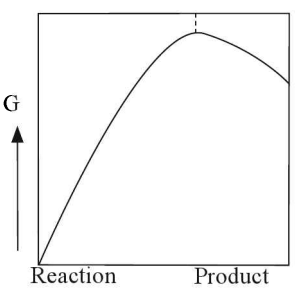
162. The value of $\log_{10} k_{eq}$ (equilibrium constant) can be given as

a. $\frac{\Delta G^\circ}{RT}$ **b.** $\frac{T\Delta S^\circ - \Delta H^\circ}{2.303RT}$

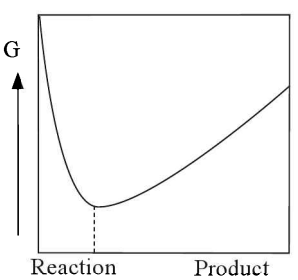
c. $\frac{\Delta H^\circ - T\Delta S^\circ}{2.303\ RT}$ **d.** $\frac{2.303\ RT}{T\Delta\ S^\circ - \Delta\ H^\circ}$

163. Which diagram represents the large value of equilibrium constant for the reversible reaction?

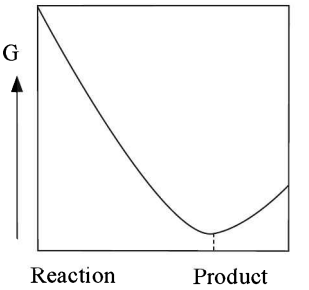
a.



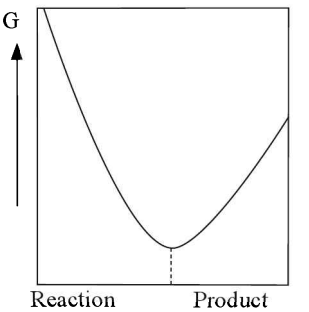
b.



c.



d.



164. The temperature dependence of the equilibrium constant can be given by the equation

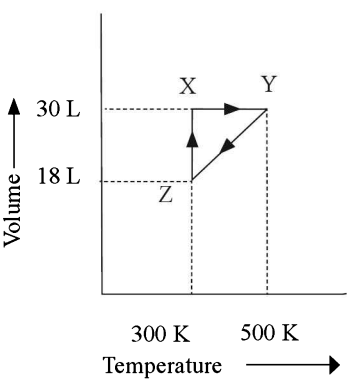
a. $\ln K = \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$

b. $\ln K = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$

c. $\ln K = \frac{\Delta G^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$

d. $\ln K = -\frac{\Delta G^\circ}{R}(T) + \frac{\Delta S^\circ}{R}$

Comprehension 4



Answer the following questions based on the given diagram:

165. Process , X → Y represents

a. Isobaric **b.** isochoric

c. isothermal **d.** adiabatic

166. The pressure at Z is

a. 3.518 atm **b.** 1.368 atm

c. 0.0821 atm **d.** 0.821 atm

167. The process which occurs in going from, Y → Z is

a. isothermal **b.** adiabatic

c. isochoric **d.** isobaric

Comprehension 5

Entropy is a measurement of randomness or disorder of any system. When a liquid is converted to the vapour state entropy of the system increases. Entropy in any of the phase transformation can be calculated by using this relation $\Delta S = \Delta H/T$.

In a reversible adiabatic process ΔS is zero. The rise in temperature in isobaric or isochoric process increases the randomness of system and it can be given by

$$\Delta S = 2.303n\ C \log_{10} \frac{T_2}{T_1}$$

Here $C = C_P$ or C_V

168. The element gallium, Ga, freezes at 2.8°C, and its enthalpy of fusion is $\Delta H_{fus} = 5.59$ kJ /mol. Calculate the value of ΔS for the freezing of 90.0 g of Ga(*l*) at 29.8°C.

a. 47.6 J/K **b.** 23.8 J/K

c. 4.76 J/K **d.** 32.86 J/ K

169. Write the correct sequence of entropy change when a solid melt, a gas liquefies, liquid vapourizes and a solid dissolves in water.

a. Increases, increases, increases, increases respectively

b. Increases , decreases, increases, decreases respectively

c. Increases , decreases, increases, increases respectively

d. Decreases, increases, decreases, increases respectively

170. Find the entropy change when 0.5 M of an ideal gas expands at a constant temperature from an initial volume of 10 L to a final volume of 75 L.

a. 8.376 J /K **b.** 4.188 J/K

c. 16.752 J /K **d.** 7.367 J/ K

Assertion-Reason Type Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark

a. if A and R both are correct and R is the correct explanation of A;

b. if A and R both are correct but R is not the correct explanation of A;

c. A is true but R is false;

d. A is false but R is true,

e. both A and R are false.

171. **(A):** The enthalpy of formation of H_2O (*l*) is greater than that of H_2O (g).

(R): Enthalpy change is –ve for the condensation reaction,

$$H_2O\ (g) \rightarrow H_2O\ (l)$$

172. **(A):** Cp – Cv = R for ideal gas

(R): $(dU/dV)_T = 0$ for ideal gas

173. **(A):** All combustion reactions are exothermic.

(R): Products are more stable than reactants in exothermic process.

174. **(A):** Chlorine when tried to be solidified does not have zero entropy when at absolute zero.

(R): Chlorine contains a mixture of isotopes and is difficult to solidify.

175. **(A):** Heat of neutralization of HF is more than that of HCl by NaOH.

(R): HCl is stronger acid than HF.

176. **(A):** The thermodynamic function which determines the spontaneity of a process is the free energy, for a process to be spontaneous, the change in free energy must be negative.

(R): The change in free energy is related to the change in enthalpy and change in entropy. The change in entropy for a process must be always positive if it is spontaneous.

177. **(A):** All exothermic reactions are spontaneous at room temperature.

(R): In ($\Delta G = \Delta H - T\Delta S$), ΔG becomes negative and negative sign of ΔG indicates spontaneous reaction.

178. **(A):** Endothermic reaction is spontaneous at all temperatures.

(R): ΔG is negative when $T\Delta S > \Delta H$

179. **(A):** As temperature increases, heat of reaction also increases for exothermic as well for endothermic reactions.

(R): ΔH varies with temperatures as given by

$$\Delta H_2 \text{ (at } T_2) = \Delta H_1 \text{ (at } T_1) + \Delta C_P (T_2 - T_1)$$

180. (A): Efficiency of a reversible engine is maximum (100%) when temperature of the sink is –273°C (T_1)

(R): η (efficiency) $= \dfrac{T_2 - T_1}{T_2}$

181. (A): As solid changes to liquid and then to vapour state, entropy increases.

(R): As going from solid to liquid and then to vapour state, disorder increases.

182. (A): In the case of an ideal gas, the changes in Gibbs and Helmholtz free energies are equal to each other ($\Delta G = \Delta A$) for isothermal reversible processes.

(R): There is no change in internal energies and enthalpies for ideal gases at constant temperature.

183. (A): When H_2O is added to CaO, heat is liberated.

(R): Reaction between CaO and H_2O is exothermic.

184. (A): In the following reaction

$$C(s) + O_2(g) \rightarrow CO(g),$$

$$\Delta H = \Delta E - RT$$

(R): ΔH is related to ΔE by equation

$$\Delta H = \Delta E + \Delta n_g RT$$

185. (A): In the following reaction

$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2, \Delta H = -68 \text{ kcal}$$

and thus

$$\Delta H_f(CO_2) = -68 \text{ kcal mol}^{-1}$$

(R): 1 mol of CO_2 is formed and enthalpy change is the heat of formation of CO_2.

186. (A): Heat of neutralization of HF (aq), a weak acid, with NaOH (aq) is less than 13.7 kcal, in an exothermic reaction.

(R): Some heat is lost in the ionization of a weak acid.

187. (A): The standard enthalpy of formation of graphic is taken as zero but of diamond is not zero but it is equal to 1.816 kJ/mol.

(R): Among carbon allotropes, diamond is taken as standard state.

188. (A): In case of some glassy solids having mixture of isotopes, crystals of CO, N_2O, NO etc. entropy is not zero even at absolute zero temperature

(R): These kind of solids do not have perfect order even at absolute zero temperature.

189. (A): Enthalpy changes are positive when $Na_2SO_4.10H_2O$, $CuSO_4.5H_2O$ and salts like NaCl, KCl etc. which do not form hydrates are dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.

(R): The difference in the behaviour is due to large differences in the molecular weights of hydrated and anhydrous salts. The substances with larger molecular weights usually show positive enthalpy change on dissolution.

190. (A): ΔE is state function of the system.

(R): As it depends upon the final and initial state of the system.

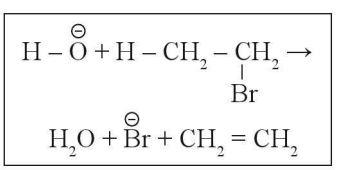
191. (A): In any reversible cycle process, the net increase in entropy of the system is zero.

(R): As $\Delta S_{universe} = \Delta S_{system} + \Delta S$surr as in case of reversible cyclic process ΔSsystem is positive, but of surrounding is negative in same amount. That is why $\Delta S_{universe} = 0$

192. (A): The enthalpy of neutralization of equivalent of HF and 1 equivalent NaOH is 14 kcal/mol. which is higher than HCl and NaOH?

(R): It is because the enthalpy of hydration of F^- is higher that of is heat enthalpy of dissociation.

193. (A): The entropy change in the reaction.



is positive

(R): Entropy increase when no. of particles or (i.e. molecules or ions) of the product or, in the product directions increases.

(194) (A) The amount of work done in the isothermal expansion is greater than work done in the adiabatic system for same final volume.

(R) In the adiabatic expansion of a gas temperature and pressure both decrease due to decrease in internal energy of the system.

195. (A): There is a natural asymmetry between converting work to heat and converting heat to work.

(R): No process is possible in which the sole result in the absorption of heat from a reservation and its complete conversion into work

Matrix-Match Type Questions

196. Match the following:

List I	List II
A. Cyclic process	(p) ΔH is positive
B. Spontaneous	(q) $\Delta E = 0, \Delta H = 0$
C. Endothermic	(r) ΔG is negative
D. A process in equilibrium	(s) $\Delta G = 0$

197. Match the following:

List I	List II
A. Reversible adiabatic compression	(p) $\Delta_{Surrounding} < 0$
B. Reversible vaporization of liquid	(q) $\Delta_{Surrounding} = 0$
C. $2N(g) \rightarrow N_2(g)$	(r) $\Delta S_{system} > 0$
D. $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$	(s) $\Delta S_{system} < 0$

198. Match the following:

List I	List II
A. Reversible isothermal expansion	(p) $w = -RPext \dfrac{[T_2P_1 - T_1P_2]}{P_1P_2}$
B. Irreversible isothermal expansion	(q) $w = \dfrac{R}{\gamma - 1}[T_2 - T_1]$
C. Reversible adiabatic expansion	(r) $w = -Pext\,(V_2 - V_1)$
D. Irreversible adiabatic expansion	(s) $w = -2.303\ RT \log_{10} V_2/V_1$

199. Match the following.

List I	List II
A. Ice $\rightleftharpoons$ H_2O (l) at room temperature 25°C	(p) ΔH = –ve, ΔS = +ve
B. $NH_2COONH_4(s) \rightarrow 2NH_3(g) + CO_2(g)$	(q) ΔG = +ve
C. $2O_3(g) \rightarrow 3O_2(g)$	(r) ΔH = +ve, ΔS = –ve
D. $3O_2(g) \rightarrow 2O_3(g)$	(s) ΔG = –ve

200. Match the following:

List I	List II
A. Internal energy of O_2 gas at 0 K (–273°C)	(i) exothermic reaction
B. heat of combustion of N_2	(ii) < 13.7 Kcal
C. heat of neutralization of HCl and CH_3COOH	(iii) 0
D. $2CO + O_2 \rightarrow CO_2$	(iv) +ve

201. Match the following:

List I	List II
A. Formation of ammonia	(p) Endothermic
B. Formation of nitric oxide	(q) Exothermic
C. Heat of neutralization of HF	(r) > 13.7 kcal
D. Heat of combustion	(s) may be exothermic or endothermic

202. Match the following:

List I	List II
A. ΔS gas for isothermal of an ideal gas	(p) $nR \ln\left(\dfrac{P_1}{P_2}\right)$
B. Work done in reversible isothermal ideal gas expansion	(q) –nFE
C. ΔG for reversible isothermal expansion of an ideal gas	(r) $nRT \ln\left(\dfrac{P_2}{P_1}\right)$
D. $(\Delta G_{system})T, P$	(s) $nR \ln\left(\dfrac{V_2}{V_1}\right)$

203. Match the following:

List I	List II (Heat of neutralization)
A. H_2SO_4 + NaOH	(p) 13.7 Kcal
B. $H_2SO_4 + NH_4OH$	(q) > 13.7 kcal
C. $CH_3COOH + NH_4OH$	(r) < 13.7 kcal
D. NaOH + HF	(s) cannot be said

204. Match the following:

List I	List II
1. Exothermic substance	(i) Less stable
2. Endothermic substance	(ii) More stable
3. Heat of formation	(iii) Exothermic
4. Heat of combustion	(iv) May be exothermic or endothermic
	(v) Endothermic

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205. Molar heat capacity of water in equilibrium with ice at constant pressure is

a. zero
b. infinity
c. 40.45 J K^{-1} mol^{-1}
d. 75.48 J K^{-1} mol^{-1}

[IIT 1997]

206. Standard molar enthalpy of formation of CO_2 is equal to

a. zero
b. the standard molar enthalpy of combustion of gaseous carbon.
c. the sum of standard molar enthalpies of formation of CO and CO_2
d. the standard molar enthalpy of combustion of carbon (graphite)

[IIT 1997]

207. 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 eating 120 g of glucose?

a. 7.9 km **b.** 9.7 km
c. 4.8 km **d.** 8.4 km

[IIT 1997]

208. Anhydrous $AlCl_3$ is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (ionization energy of Al = 5137 kJ mol^{-1}, $\Delta H_{hydration}$ for Al^{+3} = – 4665 kJ mol^{-1}, $\Delta H_{hydration}$ for Cl^- = –381 kJ mol^{-1})

a. ionic **b.** covalent
c. both **d.** none

[IIT 1997]

209. Calculate the enthalpy change for the combustion of cyclopropane at 298 K, if the enthalpy of formation CO_2 (g), $H_2O(l)$ and propene (g) are –393.5, –385.8 and 20.42 kJ mol^{-1} respectively. The enthalpy of isomerization of cyclopropane to propene is –33.0 kJ mol^{-1}.

a. 1802 kJ mol^{-1} **b.** 2091 kJ mol^{-1}
c. 2196 kJ mol^{-1} **d.** none

[IIT 1998]

210. Which of the following is not an endothermic reactions?

a. combustion of methane
b. decomposition of water
c. dehydrogenation of ethane or ethylene
d. conversion of graphite to diamond

[IIT 1999]

211. The ΔH°_f for CO_2(g), CO(g) and H_2O(g) are –393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is

a. 524.1 **b.** 41.2
c. –262.5 **d.** –41.2

[IIT 2000]

212. Which of the following statement is false?

a. work is a state function
b. temperature is a state function
c. change of state is completely defined when initial and final states are specified.
d. work appears at the boundary of the solution.

[IIT 2001]

213. In thermodynamics, a process is called reversible when

a. surroundings and system change into each other
b. there is no boundary between system and surroundings
c. the surroundings are always in equilibrium with the system
d. the system changes into the surroundings spontaneously

[IIT 2001]

214. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) → (4.0 atm, 5.0 L, 245 K) with a change in internal energy, ΔU = 30.0 L atm. The change in enthalpy (ΔH) of the process in L atm is

a. 40.0
b. 42.3
c. 44.0
d. not defined, because pressure is not constant

[IIT 2002]

215. Which of the following reaction defines ΔH°_f?

a. C (diamond) + O_2 (g) → CO_2 (g)

b. ½ H_2 (g) + ½ F_2 (g) → HF (g)

c. N_2(g) + 3H_2 (g) → 2NH_3 (g)

d. CO (g) + ½ O_2 (g) → CO_2 (g)

[IIT 2003]

216. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre of 10 litre at 300 K. The enthalpy change (in kJ) for the process is

a. 11.4 kJ **b.** –11.4 kJ

c. 0 kJ **d.** 4.8 kJ.

[IIT 2004]

217. The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is 5 J mol^{-1} K. The boiling point of the liquid at 1 atm is

a. 250 K **b.** 400 K

c. 450 K **d.** 600 K

[IIT 2004]

218. One mole of monatomic ideal gas at T (K) is expanded from 1_l to 2_l adiabatically under a constant external pressure of 1 atm the final temperature of the gas in Kelvin is

a. T

b. $T/2^{5/3-1}$

c. $T - \frac{2}{3 \times 0.0821}$

d. $T + \frac{3}{2 \times 0.0821}$

[IIT 2005]

219. For the reaction, 2CO + O_2 → 2CO_2, $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2, the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of ΔU at 500 K.

(1 L atm = 0.1 kJ)

a. 557 KJ **b.** 55.7 KJ

c. 278 KJ **d.** 27.8 KJ

[IIT 2006]

220. The direct conversion of A to B is difficult, hence it is carried out by the following shown path:

C → D
↑ ↓
A B

Given

$\Delta S_{(A \to C)} = 50$ e.u.

$\Delta S_{(C \to D)} = 30$ e.u.

$\Delta S_{(B \to D)} = 20$ e.u.

where e.u. is entropy unit then ΔS (A → B) is

a. +100 e.u. **b.** +60 e.u.

c. –100 e.u. **d.** –60 e.u.

221. For the process

H_2O (l) (1 bar, 373 K) → H_2O (g) (1 bar, 373 K), the correct set of thermodynamic parameters is

a. $\Delta G = 0$, $\Delta S = +ve$

b. $\Delta G = 0$, $\Delta S = -ve$

c. $\Delta G = +ve$, $\Delta S = 0$

d. $\Delta G = -ve$, $\Delta S = +ve$

[IIT 2007]

222. The value of $\log_{10} K$ for a reaction A ⇌ B is (Given: $\Delta_r H^\circ_{298\,K} = -54.07$ kJ mol^{-1}, $\Delta_r S^\circ_{298\,K} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$)

a. 10 **b.** 100

c. 5 **d.** 95

[IIT 2007]

223. In a constant volume calorimeter, 3.5 of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

a. 10 **b.** 100

c. 5 **d.** 95

[IIT 2009]

ANSWERS

Straight Objective Type Questions

1. d	**2.** d	**3.** d	**4.** b	**5.** d	**6.** d	**7.** a	**8.** b	**9.** a
10. c	**11.** d	**12.** c	**13.** d	**14.** a	**15.** c	**16.** c	**17.** c	**18.** c
19. d	**20.** a	**21.** d	**22.** d	**23.** a	**24.** d	**25.** a	**26.** b	**27.** a
28. c	**29.** b	**30.** a	**31.** c	**32.** c	**33.** a	**34.** d	**35.** a	**36.** b

37. a	**38.** a	**39.** a	**40.** a	**41.** b	**42.** b	**43.** d	**44.** b	**45.** d
46. b	**47.** d	**48.** d	**49.** c	**50.** b	**51.** a	**52.** a	**53.** b	**54.** d
55. a	**56.** b	**57.** a	**58.** c	**59.** a	**60.** a	**61.** d	**62.** b	**63.** b
64. b	**65.** d	**66.** a	**67.** c	**68.** b	**69.** b	**70.** d	**71.** d	**72.** c
73. a	**74.** c	**75.** c						

Brainteasers Objective Type Questions

76. a	**77.** c	**78.** b	**79.** a	**80.** a	**81.** d	**82.** a	**83.** a
84. c	**85.** b	**86.** c	**87.** b	**88.** a	**89.** c	**90.** b	**91.** c
92. d	**93.** b	**94.** b	**95.** a	**96.** d	**97.** a	**98.** a	**99.** d
100. a	**101.** d	**102.** b	**103.** b	**104.** c	**105.** b	**106.** b	**107.** d
108. b	**109.** d	**110.** a	**111.** a	**112.** a	**113.** b	**114.** c	**115.** d
116. a	**117.** b	**118.** d	**119.** c	**120.** a	**121.** d	**122.** a	**123.** a
124. b	**125.** a						

Multiple Correct Answer Type Questions

126. c, d	**127.** a, c, d	**128.** a, b, c	**129.** a, d	**130.** a, b, d	**131.** a, c, d
132. a, b, c	**133.** a, d	**134.** b, c, d	**135.** a, b, d	**136.** a, c	**137.** a, c
138. b,c,d	**139.** c, d	**140.** c, d	**141.** b, c, d	**142.** a, d	**143.** b, c
144. a, b, c	**145.** a, c	**146.** a,b,d	**147.** b,c,d	**148.** a,c.d	**149.** a,c,d
150. a, b, d	**151.** a, b, d	**152.** a, c, d	**153.** a, c, d	**154.** b, c, d	**155.** a, c, d

Linked-Comprehension Type Questions

Comprehension 1

156. d **157.** a **158.** c

Comprehension 2

159. b **160.** d **161.** d

Comprehension 3

162. b **163.** c **164.** b

Comprehension 4

165. b **166.** b **167.** d

Comprehension 5

168. b **169.** c **170.** a

Assertion-Reason Type Questions

171. a	**172.** b	**173.** a	**174.** a
175. b	**176.** a	**177.** a	**178.** a
179. d	**180.** a	**181.** a	**182.** a
183. b	**184.** d	**185.** e	**186.** e
187. c	**188.** a	**189.** a	**190.** a
191. c	**192.** a	**193.** a	**194.** a
195. a			

Matrix-Match Type Questions

196. A-(q), B-(r), C-(p), D-(s)

197. A – (q), B – (p, r), C – (s), D – (p, r)

198. A-(s), B-(r), C-(q), D-(p)

199. A - (s), B – (q), C- (p, s), D – (q, r)

200. A – (r), B- (s), C – (q), D - (p)

201. A -(q), B – (p), C – (r), D – (q)

202. A – (q), B – (r), C – (r), D – (p, s)

203. A – (p), B – (r), C – (r), D – (q)

204. A – (q), B – (p), C- (s), D – (r)

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205. b	**206.** d	**207.** c	**208.** a	**209.** b	**210.** a	**211.** b	**212.** a
213. c	**214.** c	**215.** b	**216.** c	**217.** b	**218.** c	**219.** a	**220.** b
221. a	**222.** a	**223.** c					

Hints and Explanations

1. It gives the neutralization of 1 mole H^+ and 1 mole of OH^- ions.

2. $q = \Delta E - w$ (first law of thermodynamics)

$q + w = \Delta E$

Now q + w is a state function as it is equal to ΔE (state function).

3. Equal to ΔH.

4. Standard heat of formation of C_2H_4 is the heat change when 1 mole of C_2H_4 is formed from its elements in the standard state [carbon as graphite and hydrogen as H_2]

6. $\Delta H_{obs} = \Delta H$ + Energy needed to disturb resonance

$= 3 \times -119.5 + 150.4 = -208.1$ kJ mol^{-1}

8. $\Delta H = \Delta U + \Delta nRT$

(here Δn = number of molecules of products – no. of molecules of reactants)

$-92.38 \times 1000 = \Delta U - 2 \times 8.314 \times 298$

$\Delta U = -87424$ J $= -87.424$ kJ.

9. $\Delta G^\circ = -RT \ln K$

[ΔG° = standard free energy change,

K = equilibrium constant

If a substance is in equilibrium between two phases at constant temperature and pressure , its chemical potential must have the same value in both the phases.

So $\Delta G^\circ = 0$

10. At equilibrium $\Delta G = 0$. So $\Delta H = T\Delta S$

So $T = \Delta H/\Delta S = 30 \times 10^{-3}/105$

$= 285.7$ K

11. $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

For a spontaneous process ΔS_{total} must be positive that is, $\Delta S_{total} > 0$

13. At equilibrium $\Delta G = 0$

14. Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed,

so w = 0 and $\Delta U = q$.

$\Delta U < 0$, w = 0.

15. Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gases under pressure in the presence of a catalyst.

$C\ (graphite) + \frac{1}{2}\ O_2 \rightarrow CO\ (g)$ ...(i)

$CO\ (g) + 2H_2\ (g) \rightarrow CH_3OH\ (l)$ ...(ii)

$C(graphite) + \frac{1}{2}\ O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$

16. As $\Delta n = 0$ so $\Delta H = \Delta U$

17. MgO is the oxide of weak base and we know that heat of neutralization of 1 eq. of strong acid with strong base is –57.33 kJ/mol.

$\Rightarrow$ With weak base some heat is absorbed in dissociation of weak base.

$\Rightarrow$ Heat of neutralization of weak base with strong acid will be –57.33 kJ/mol.

18. $\Delta G = \Delta H - T\Delta S$

ΔG = –ve for spontaneous reaction

when ΔS = +ve, ΔH = +ve

and $T\Delta S > \Delta H \Rightarrow \Delta G$ = –ve

When randomness favours and energy factor do nor favour then spontaneity depends upon the temperature dependent means at high temperature.

$T\Delta S > \Delta H$, ΔG = –ve and reaction is feasible.

19. $CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

ΔH = (BE)reactants – (BE)products

$= 4\ (BE)_{C-H} + (BE)_{C=C}^{+} + (BE)_{H-H}$

$- [6(BE)_{C-H} + (BE)_{C-C}]$

= –125 kJ

23. For a spontaneous reaction ΔH = –ve,

ΔS = +ve spontaneity depends upon both critical minimum energy and maximum randomness/disorder.

24. $\Delta E = 0$, in a cyclic process.

26. Work done due to change in volume against constant pressure is

$W = -P(V_2 - V_1) = -1 \times 10^5\ Nm^{-2}$

$(1 \times 10^{-2} - 1 \times 10^{-3})\ m^3$

= –900 Nm = –900 J.

28. From solid state to liquid state entropy increases.

31. $N_2 + 3H_2 \rightarrow 2NH_3$

$\Delta n = 2 - 4 = -2$

$\Delta H = \Delta U + \Delta nRT = \Delta U - 2RT$

$\Delta H < \Delta U$.

32. $W = -2.303\ nRT \log \frac{V_2}{V_1}$

$= -2.303 \times 1 \times 2 \times 300 \times \log \frac{10}{1}$

= –1381.8 cal.

37. Work done is reversible process is maximum. Thus $T_2 << T_1$ in reversible process or $T_{2rev} << T_2 irr$.

42. $\Delta H = \Delta E + \Delta ng\ RT$

as $\Delta ng = np - nr = 8 - 8 = 0$,

thus $\Delta H = \Delta E$.

44. $C(s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$; $(\Delta n = 1 - \frac{1}{2}) = \frac{1}{2}$

$\Delta H - \Delta U = \Delta nRT = +\frac{1}{2} \times 8.314 \times 298$

$= +1238.78\ J\ mol^{-1}$

45. For the reaction

$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 3CO_2\ (g) + 4H_2O\ (l)$

$\Delta n = n_P - n_R$

$= 3 - 6 = -3$

$\Delta H = \Delta E + \Delta nRT$

$\Delta H - \Delta E = \Delta nRT = -3RT$

46. $\Delta S = \frac{\Delta H_f}{T} = \frac{6.0}{273} = 0.02198\ kJ\ K^{-1}\ mol^{-1}$

$= 0.02198 \times 1000\ JK^{-1}\ mol^{-1}$

$= 21.98\ JK^{-1}\ mol^{-1}$

48. $C = \frac{q}{m(T_2 - T_1)}$.

$75 = \frac{1000}{5.55(\Delta T)}$ (m = 100/8 = 5.55)

$\Delta T = \frac{1000}{5.55 \times 75} = 2.4\ K$

50. In irreversible process

$\Delta S_{system} + \Delta S_{surroundings} > 0$

so in the spontaneous process ΔS is positive

54. (i) $\frac{1}{2} N_2 + O_2 \rightarrow NO_2$; $\Delta H = 8.0$ kcal

(ii) $N_2 + 2O_2 \rightarrow N_2O_4$; $\Delta H = 2.0$ kcal

$2NO_2 \rightarrow N_2O_4$; $\Delta H = ?$

multiply (i) by 2 subtract from (ii), we get

$2NO_2 \rightarrow N_2O_4$; $\Delta H = -14$ kcal

55. $W = -2.303\ nRT \log \frac{P_1}{P_2}$

$= -2.303 \times 1 \times 2 \times 300 \log \frac{10}{1}$

$= -1381.8 \approx -.1382$ cal

56. Weakest acid has the lowest heat of neutralization because more heat is absorbed in the ionization of weak acid

57. A salt which absorbs more heat for dissolution in water give maximum cooling.

58. T (m.p) = 27 + 273 = 300 K

$\Delta H_{fus.} = 600$ cal/mole

$\Delta S = \frac{\Delta H}{T} = \frac{600}{300} = 2$

59. On set of crystallization in a super cooled liquid is called Devitrification. The process of crystallization leads to decrease in entropy.

60. $N_2O_4 \leftrightarrow 2NO_2$

On heating, since the colour depends that is more of NO_2 is formed and the forward reaction is favoured. Thus, the forward reaction is endothermic that is, ΔH = +ve

62. Heat of combustion is always negative.

63. ΔH°_f of graphite is taken as zero. For diamond, its value is 1.9 kJ mol^{-1} that is, greater than graphite.

64. The molar heat capacity is the heat required to raise the temperature of one mole of the gas by 1°C.

$C_V = \frac{3}{2} R$

40 gram of argon means 1 mole.

Here $C_V = 3$ cal

Thus the heat required to raise the temperature by 60°C is $60 \times 3 = 180$ cal.

66. Smallest = eV and largest = lit atm

1 eV = 1.6×10^{-19} J,

1 cal = 4.186 J,

1 erg = 10^{-7} J

1 lit atm = 101.3 J

67. As $\Delta G^\circ = -RT \ln K$.

When $K < 1.0$, ΔG° = +ve

68. State functions or state variables depend only on the state of the system. Here 'w' represents work done and 'q' represents amount of heat so both of these are not state functions.

69. For this process $\frac{1}{2} Cl_2 (g) \rightarrow Cl^- (aq)$

$\Delta H = \frac{1}{2} \Delta H_{diss}$ of $Cl_2 + \Delta_{eq}$ Cl + Δ_{hyd} Cl^-

$= +\frac{240}{2} - 349 - 381$

70. $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$

$\Delta H = \Delta E + \Delta nRT$

Here, Δn = Change in number of moles of product and reactant

As Δn + ve, so ΔH = +ve

$\Delta S = S_{Product} - S_{Reactant}$

ΔS = +ve

71. $S(rh) + 3/2O_{2(g)} \rightarrow SO_{3(g)}$, $\Delta H_1 = 2x$kJ mol^{-1} (i)

$SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow SO_{3(g)}$, $\Delta H_2 = -y$ J mol^{-1} (ii)

From equation (i) – (ii) we have

$S_{(rh)} + O_{2(g)} \rightarrow SO_{2(g)}$; $\Delta H_f = \Delta H_1 = \Delta H_2 = -2x + y$

Here of formation of SO_2 (ΔH_f) = y – 2x

72. Al acts as a good reducing agent and reduces oxides of metals like Cr, Fe, Mn, etc.

$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$ + heat

Therefore ΔG° for the formation of Al_2O_3 is lower in comparison to ΔG° for the formation of Cr_2O_3.

73. $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(g)}$

Δn = no. of moles of product – no. of moles of reactant

= 1 – 2

$\Delta n = -1$

Now, $\Delta H = \Delta E + \Delta nRT$

$\Delta H = \Delta E - RT$ or $\Delta E = \Delta H + RT$

As, $\Delta E > \Delta H$ ($\Delta E - \Delta U$) = change in internal energy.

75. It can be derived as

$[\partial (\Delta G/T)/\partial T]_P = -\Delta H/T^2$

$\Delta H = -T^2 [\partial(G/T)/\partial T]_P$

It is a form of Gibbs-Helmholtz equation.

Brainteasers Objective Type Questions

76. Given

(i) $C_6H_{10} + H_2 \rightarrow C_6H_{12}$; $\Delta H = -119$ kJ mol^{-1}

This reaction involves breaking up of one double bond and addition of one H_2 molecule.

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$;

$\Delta H = 3 \times -119 = -357$ kJ

(because, this reaction involves breaking up of one double bond and addition of three H_2 molecules).

Also given

$6C + 6H_2 \rightarrow C_6H_{12}$; $\Delta H = -156$ kJ

$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$; $\Delta H = -357$ kJ

$6C + 3H_2 \rightarrow C_6H_6$; $\Delta H = +201$ kJ

Thus, resonance energy = difference between ΔH_f (obs) – ΔH_f (calc) = 49 – 201 = – 152 kJ

77. (c) For the temperature of the solution decrease the solvent water must lose energy. The process of ammonium and nitrate ions in solid ammonium nitrate dissolving and becoming hydrated must therefore absorb energy from water.

79. $\Delta H - \Delta E = \Delta ng\ RT$

$= (12 - 15) \times \dfrac{8.314}{1000} \times 298$

$= -7.433$ kJ mol^{-1}

80. Amount of HCl added $= \dfrac{100 \times 0.3}{1000}$

$= 0.03$ mol

Amount of NaOH added $= \dfrac{100 \times 0.33}{1000}$

$= 0.033$ mol

limiting reagent = 0.03 mol of HCl

So amount of heat evolved = 57.1×0.03

$= 1.713$ kJ

81. Amount of energy left unused

$= \dfrac{1560}{2} = 780$ kJ

Amount of water perspired

$= \dfrac{\text{Energy left unused}}{\text{Enthalpy of evaporation of water}}$

$= \dfrac{780 \text{ kJ}}{44 \text{ kJ mol}^{-1}} = \dfrac{780}{44}$ mole

$= \dfrac{780 \times 18}{44} = 319.14$ g

82. $\Delta H_{CO_2}/\Delta H_{CO} = 2.56$

$\Delta H_{CO2} = 2.56\ \Delta H_{CO}$

$177.5 = \Delta H_{CO} - \Delta H_{CO2}$

$= \Delta H_{CO} - 2.56\ \Delta H_{CO}$

$\Delta H_{CO} = -\dfrac{177.5}{1.56} = -113.78$ kJ mol^{-1}

83. For dissolution of gases in water, ΔS = –ve (non-favorable factor). Since this process is spontaneous (ΔG = –ve) so ΔH has to be –ve (favorable factor) and the process is exothermic.

84. Given that

(i) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$;

$\Delta H = -241$ kJ

(ii) $C_6H_{10} + 17/2\ O_2 \rightarrow 6CO_2(g) + 5H_2O$;

$\Delta H = -3800$ kJ

(iii) $C_6H_{12} + 9O_2 \rightarrow 6CO_2(g) + 6H_2O(l)$;

$\Delta H = -3920$ kJ

Our aim is to get

$C_6H_{10} + H_2 \rightarrow C_6H_{12}$; $\Delta H = ?$

So Add (i) and (ii) and then subtract (iii), to get

$\Delta H = -121$ kJ mol^{-1}

86. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$= [\Delta H_f(CO_2) + 2\ \Delta H_f(H_2O)] - [\Delta H_f(CH_4) + 2\ \Delta H_f(CO_2)]$

$= [-394.8 + 2 \times -241.6] - [-76.2 + 0]$

$= -878.0 + 76.2 = 802.2 \text{ kJ mol}^{-1}$

now 22.4 L (or 22.4×10^{-3} m^3) of CH_4 on combustion give heat = 802.2 kJ mol^{-1}

$$1 \text{ m}^3 = \frac{802.2}{22.4 \times 10^{-3}}.$$

$= 35812 \text{ kJ mol}^{-1}$

88. $N \equiv N + \frac{1}{2} O = O \rightarrow N = N = O$

$\Delta H^\circ_f = \sum BE \text{ of reactants} - \sum BE \text{ of products}$

$= [BE (N \equiv N) + \frac{1}{2} BE(O=O)] - [BE(N=N) + BE(N=O)]$

$= (946 + \frac{1}{2} \times 498) - (418 + 607) = 170 \text{ kJ}$

resonance energy

$= \Delta H^\circ_f \text{ (observed)} - \Delta H^\circ_f \text{ (calculated)}$

$= 82 - 170 = -88 \text{ kJ mol}^{-1}$

89. $I_2 (s) + Cl_2 (g) \rightarrow 2ICl (g); \Delta H$

$\Delta H = [\varepsilon Cl_2 + \varepsilon 2(s) \rightarrow (g) + \varepsilon I_2(g)] - 2 \times [\varepsilon ICl]$

$= [242.3 + 62.76 + 151.0] - 2 \times [211.3]$

$= 33.46$

$$\Delta H_f = \frac{33.46}{2} = 16.83 \text{ kJ mol}^{-1}$$

93. Our aim is $\frac{1}{2} Cl_2 (g) + (aq) \rightarrow Cl^- (aq)$;

$\Delta H = ?$

Given is

(i) $\frac{1}{2} H_2 (g) + \frac{1}{2} Cl_2 (g) \rightarrow HCl (g)$

$\Delta H = -92.4 \text{ kJ}$

(ii) $HCl (g) + (aq) \rightarrow H^+ (aq) + Cl^- (aq)$

$\Delta H = -74.8 \text{ kJ}$

(iii) $\frac{1}{2} H_2 (g) + (aq) \rightarrow H^+ (aq);$

$\Delta H = 0.0 \text{ kJ}$

Operate (i) + (ii) – (iii), we obtain

$\Delta H^\circ_f \text{ of } Cl^- (aq) = -167.2 \text{ kJ}$

0.16 g of methane is subjected to combustion at 27°C in a bomb calorimeter system. The temperature of the calorimeter system (including water) was found to rise by 0.5°C.

95. $\Delta E \text{ per mole} = \frac{327}{7.8} \times 78 = -3270 \text{ kJ}$

$T = 27 + 273 = 300 \text{ K},$

$R = 8.3/1000 \text{ kJ mol}^{-1} \text{ K}^{-1}$

$C_6H_6 (l) + 15/2 O_2 (g) \rightarrow 6CO_2 (g) + 3H_2O(l)$

$\Delta n_g = n_p - n_r = 6 - 15/2 = -3/2$

$\Delta H = \Delta E + \Delta n_g RT$

$\Delta H = -3270 + [(-3/2) \times (8.3/1000) \times 300]$

$\Delta H = -3274 \text{ kJ}]$

98. For Li_2O,

$2Li (s) + \frac{1}{2} O_2 (g) \rightarrow Li_2O (s)$

$\Delta G^\circ_f (Li_2O) = \Delta H^\circ_f - T\Delta S^\circ$

$= 1244 - (298 \times 6) = -544 \text{ kJ mol}^{-1}$

For Na_2O,

$2Na (s) + \frac{1}{2} O_2 (g) \rightarrow Na_2O (s)$

$\Delta G^\circ_f (Na_2O) = \Delta H^\circ_f - T\Delta S^\circ$

$= 1411 - (298 \times 6) = -377 \text{ kJ mol}^{-1}$

For reaction,

$Al_2O_3 (s) + 6Na (s) \rightarrow 3Na_2O (s) + 2Al (s)$

$\Delta G^\circ = 3 \times \Delta G^\circ_f (Na_2O) - \Delta G^\circ_f (Al_2O_3)$

$= 3 \times (-377) - (-1582) = +451 \text{ kJ mol}^{-1}$

Similarly when Li is used, then

$\Delta G^\circ = 3 \times \Delta G^\circ_f (Li_2O) - \Delta G^\circ_f (Al_2O_3)$

$= 3 \times (-544) - (-1582)$

$= -1632 + 1582 = -50 \text{ kJ mol}^{-1}$

As ΔG° is negative when Li is used for the reduction, so the reaction is feasible.

99. $\Delta n_g = n_p - n_r = 5 - 3 = 2$

$\Delta H = \Delta E + \Delta n_g RT$

$\Delta E = \Delta H - \Delta n_g RT$

$= 19 - (2 \times 2 \times 10^{-3} \times 300)$

$= 19 - 1.2 = 17.8 \text{ kcal}$

100. $\Delta H = m \times T_b$

$= 90 \times 540 = 48600$ cal

$\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + P(V_g - V_t)$

since the volume of liquid is negligible as compared to volume of its vapour, so

$V_g >>> V_l$

$\Delta H = \Delta E + P.V_g$

$\Delta H = \Delta E + nRT$ (PV = nRT)

$\Delta E = \Delta H - nRT$

$= 48600 - (90/18 \times 2 \times 373)$

$= 44870$ cal.

101. $W = P(V_2 - V_1)$

$= nRT_2 - nRT_1$

$T_2 - T_1 = \frac{W}{nR}.$

$Q = n C_P (T_2 - T_1)$

$506 = n C_P \frac{W}{nR}.$

$506 = \frac{C_P W}{R}$

$C_P = \frac{506\ R}{144.5} = 7/2\ R$

So gas is diatomic O_2.

103. $\Delta G^\circ = -2.303\ RT \log K$

$-4.606 = -2.303 \times \frac{2}{100} \times 500 \log K$

$\log K = \frac{-4.606}{-2.303 \times 2/100 \times 500} = 2$

$K = \text{antilog}\ (2) = 100$

107. $CaCO_3\ (s) + 42.5\ Kcal \rightarrow CaO\ (s) + CO_2\ (g)$

Energy is supply to the system for complete the reaction that is, energy of the reactant side is less than the product side.

108. Here, option c is not correct as

$Z \rightarrow x$ is isochoric process

$V \rightarrow$ constant

i.e., $P \alpha T$

$P_X > P_Z$

$T_X > T_Z$ or ΔUZ. × is positive and not negative.

109. (i)

W_{rev}, isothermal $= n \times 2.303\ RT \log \frac{P_1}{P_2}$

$= 2\ mol \times 2.303 \times 2\ cal\ K^{-1}\ mol^{-1} \times 300\ K x 1$

$= 2764$ cal

(ii) Work of expansion = P. ΔV

$= 1\ atm \times 0.08212$ lit

$= 0.08212$ lit-atm $= 2$ cal

110. For reversible adiabatic change,

$T.V^{\gamma - 1} =$ constant

$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} = (1/10)^{\gamma-1} = (1/10)^{0.666}$

Since γ for a monobasic gas $= 5/3 = 1.666$.

111. As C (graphite) → C (gas)

$\Delta H = 725$ kJ/mol

As graphite is thermodynamically more stable than diamond therefore the heat required to convert graphite to gaseous carbon should be more.

112. $H_2 + Cl_2 \rightarrow 2HCl$

ΔHreaction = Σ(B.E)reactant – Σ(B.E) product

$= [(B.E)H - H + (B.E)Cl - Cl] - [2(B.E)H - Cl]$

$= 434 + 242 - (431) \times 2$

$= -186$ kJ

As $\Delta_{Hreaction} = -186$ kJ

So, enthalpy of formation of HCl

$= \frac{-186}{2}$ kJ $= -93$ kJ mol^{-1}

115. (i)

W_{rev}, isothermal $= n \times 2.303\ RT \log \frac{P_1}{P_2}$

= 2 mol × 2.303 × 2 cal K^{-1} mol^{-1} × 300 Kx1

= 2764 cal

(ii) Work of expansion = P. ΔV

= 1 atm × 0.08212 lit

= 0.08212 lit-atm = 2 cal

116. C_5H_{12} (g) + $8O_2$ (g) → $5CO_2$ (g) + $6H_2O$ (*l*)

ΔG° = [(–394.4 × 5) + (–237.2 × 6)] – [(–8.2) + (8 × 0)]

= –3387.5 kJ.

The standard free energy change of elementary substances is taken as zero.

For the fuel cell, the complete cell reaction is:

C_5H_{12} (g) + $8O_2$ (g) → $5CO_2$ (g) + $6H_2O$ (*l*)

This reaction is the combination of the following two half reactions:

$C_5H_{12}(g) + 10H_2O(l) \rightarrow 5CO_2(g) + 32H^+ + 32e$

$8O_2$ (g) + 32 H^+ + 32e → $16H_2O$ (*l*)

As the number of electrons exchanged is 32 here, so n = 32

$\Delta G^\circ = -nFE^\circ$

-3387.5×10^3 J = –32 × 96500 J/Volt × E°

On solving, we get

E° = 1.09698 V.

117. 2Fe (s) + 3/2 O_2 (g) → Fe_2O_3 (s)

ΔH° = ?

Given

3C (s) + $2Fe_2O_3$ (s) → 4Fe (s) + $3CO_2$ (g)

ΔH° = –93657 kcal …(1)

C (s) + O_2 (g) → CO_2 (g)

ΔH° = –94050 kcal ….(2)

On subtracting equation (1) from (2), we get

4Fe + $3O_2$ → $2Fe_2O_3$ (s),

ΔH° = –393 kcal

So

2Fe + 3/2 O_2 → Fe_2O_3 (s)

ΔH° = –196.5 kcal at 25°C

118. Given

(i) $BaCl_2$ (s) → $BaCl_2$ (aq) ; ΔH_1 = –20.6 kJ

(ii) $BaCl_2.2H_2O$ (s) → $BaCl_2$ (aq);

ΔH_2 = 8.8 kJ

now subtract (ii) from (i), we obtain

$BaCl_2$ (s) → $BaCl_2.2H_2O$ (s);

$\Delta H = \Delta H_1 - \Delta H_2$ = –29.4 kJ

119. $3CO_2$ (g) → 3C (g) + $2O_3$ (g)

$\Delta H = 3\Delta H_{atomisation}$ [C(s) → C(g)] + $2\Delta H^\circ_f$ [O_3 (g)] – $3\Delta H^\circ_f$ [CO_2 (g)]

$\Delta H = 3\Delta_{Hatomisation}$ [C(s) → C(g)] + $2\Delta H^\circ_f$ [O_3 (g)] – 3 × 409

As energy will be required for the processes

C (s) → C (g) and

$3O_2$ (g) → $2O_3$ (g)

So ΔH will be more than 1227 kJ.

120. n = 1, P_1 = 1 bar,

P_2 = 0.1 bar, T = 273 K

$W = -2.303\ nRT \log P_1/P_2$

= –2.303 × 1 × 8.314 × 273 log 1/0.1

= –2.303 × 1 × 8.314 × 273 × 1

= –5227 J

= –5.227 kJ

now, q = ΔE – w

since temperature is constant, ΔE = 0

q = –w = + 5.227 kJ

121. Heat produced by the combustion of 0.16 g of CH_4 = 17.7 × 0.5 = 8.85 kJ

Heat produced by the combustino of 1.0 mole of

CH_4 (16 g) = $\frac{8.85 \times 16}{0.16}$ = 885 kJ

As combustion has been carried in bomb, calorimeter (closed vessel), the heat produced is qv that is,

qv = –885 kJ

123. $NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \Delta H = +780$ kJ

$Na^+(g) + aq \rightarrow Na^+(aq)\ \Delta H = -406$ kJ

$Cl^-(g) + aq \rightarrow Cl^-(aq)\ \Delta H = -364$ kJ

The net reaction is dissolution of NaCl (s). $\Delta H_{solution} = 780 - (406 + 364) = 10$ kJ mol^{-1}

Multiple Correct Answer Type Questions

150. Entropy of gas is greater than that of liquid and solid. In option (c) solid is converted in to gaseous phase.

Entropy of gas > liquid > solid.

Linked-Comprehension Type Questions

161. To be spontaneous, ΔG must be negative ($\Delta G < 0$)

Thus, $\Delta H^\circ - T\Delta S^\circ < 0$;

$\Delta H < T\Delta S^\circ$;

$T > \Delta H^\circ / \Delta S^\circ$

$$T > \frac{572\ kJ}{0.179 kJ / K}$$

= 3200 K

The IIT-JEE Corner

206. $C(graphite) + O_2(g) \rightarrow CO_2(g)$

The standard molar enthalpy of formation of CO_2 is equal to the standard molar enthalpy of combustion of carbon (graphite).

207. As energy available for muscular work

$$= \frac{2880 \times 25}{100} = 720 \text{ kJ mol}^{-1}$$

so energy available for muscular work for 120 g of

$$\text{glucose} = 720 \times \frac{120}{180} = 480 \text{ kJ}$$

as 100 kJ is used for walking = 1 km

so 480 kJ is used for walking

$$= 1 \times \frac{480}{100} = 4.8 \text{ km}$$

208. If $AlCl_3$ is present in ionic state in aqueous solution (Al^{+3} and three Cl^- ions), then standard heat of hydration of Al^{3+} and three Cl^- ions.

ΔH° (hydration) = – 4665 + (3 × –381)

= – 5808 kJ mol^{-1}.

As hydration energy is greater than ionization energy of Al, so $AlCl_3$ would be ionic in solution.

210. Combustion is always exothermic.

ΔH = –ve

211. $\Delta H = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$

$= [\Delta H^\circ_f(CO) + \Delta H^\circ_f(H_2O)] - [\Delta H^\circ_f(CO_2) + \Delta H^\circ_f(H_2)]$

= [–110.5 – 241.8] – [–393.5 + 0]

= – 352.3 + 393.5 = + 41.2 kJ

212. Statement A is false, as work is a path function213 The driving force and the opposing force differ by infinitesimal small amount. So, the system and surroundings always remain in equilibrium state with one another

214. $\Delta H = \Delta U + \Delta(PV)$

$= \Delta U + (P_2V_2 - P_1V_1)$

$= 30 + (4 \times 5 - 2 \times 3)$

$= 30 + 14 = 44$ atm

216. As $\Delta H = nC_P \Delta T$

As for isothermal process, $\Delta T = 0$,

hence $\Delta H = 0$

217. As $\Delta S = \frac{\Delta Q\ rev}{T}$

So $T = \frac{\Delta Q}{\Delta S} = 30 \times \frac{1000}{75} = 400$ K

218. During adiabatic irreversible process, W surr. = $\Delta E = -P\Delta V$, $nC_v\Delta T = -P\Delta V$

$$1 \times \frac{R}{\gamma - 1} \times (T_f - T) = -P(V_2 - V_1)$$

$$T_f = T - \frac{(\gamma - 1)}{R} P(V_2 - V_1)$$

$$T_f = \frac{T\ (5/3 - 1) \times 1 \times (2 - 1)}{0.0821}$$

$$T_f = T - \frac{2}{3 \times 0.0821}.$$

219. $\Delta H = \Delta U + \Delta(PV)$

$\Delta H = \Delta U + V\Delta P$

$\Delta U = \Delta H - V\Delta P = -560 + 1 \times 30 \times 0.1$

$= -557$

absolute value = 557 kJ

220. $\Delta S(A \rightarrow B) = \Delta S(A \rightarrow C) + \Delta S(C \rightarrow D) - \Delta S(B \rightarrow D)$

$= 50 + 30 - 20 = 60$ e.u.

221. H_2O (l) $\rightleftharpoons$ H_2O (g)
(1 bar, 373 K) (1 bar, 373 K)

At 100°C, H_2O (*l*) has equilibrium with H_2O (g) therefore $\Delta G = 0$.

As liquid molecules are converting into gases molecules therefore ΔS = positive.

222. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$= -54.07 \times 1000 - 298 \times 10$

$= -57050$ J mol^{-1}

$-57050 = -5705 \log_{10} K$

$\log_{10} K = 10$

Numericals For Practice

1. Calculate the heat evolved when 0.500 g of Cl_2(g) reacts with an excess of HBr(g) to form HCl(g) and Br_2 (*l*), given the following standard enthalpies of formation (kJ/ mol): HCl(g), – 92.30; HBr (, –36.20)

a. 0.791 **b.** 7.91
b. 79.1 **d.** 791.0

2. For the reaction,

$2N_2$ (g) + O_2 (g) → $2N_2O$ (g), at 298 K, ΔH is 164 kJ mol^{-1}. The ΔE of the reaction is

a. 269 kJ mol^{-1}
b. 166.5 kJ mol^{-1}
c. 144.05 kJ mol^{-1}
d. 151.8 kJ mol^{-1}

3. The temperature above which a reaction would become spontaneous, if ΔH and ΔS of the reaction, at this temperature, are respectively 90 kJ and 90 J K^{-1} is

a. 0°C **b.** 1000°C
c. 2000 K **d.** 1000 K

4. The enthalpies of combustion of carbon and carbon monoxide are –393.5 and –283 kJ mol^{-1} respectively. The enthalpy of formation of carbon monoxide per mole is

a. –676.5 kJ **b.** –110.5 kJ
c. 110.5 kJ **d.** 676.5 kJ

5. Given that $\Delta H^\circ = -311$ kJ for the hydrogenation of acetylene, C_2H_2

$H - C \equiv C - H(g) + 2H_2(g) \rightarrow CH_3 - CH_3(g)$

and the following bond dissociation energies, estimate a value for the C – to –C triple bond dissociation energy.

Bond	D, kJ/mol
C – C	350
C – H	410
H – H	436

a. 1807 kJ/mol
b. 807 kJ/mol
c. 8017 kJ/mol
d. 708 kJ/mol

6. The enthalpy of combustion of methane is –880 kJ. The volume of the methane at STP to be burnt to produce 2640 kJ of heat is

a. 67.2 L **b.** 89.8 L
c. 22.4 L **d.** 11.2 L

7. Calculate the standard free energy change at 25°C for the reaction

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Species	ΔH_f kJ/mol	S°, J K^{-1} mol^{-1}
NO (g)	90.25	210.8
O_2 (g)	0.00	205.1
NO_2 (g)	33.18	240.1

a. –140.46 kJ **b.** –40.86 kJ
c. –70.46 kJ **d.** –270.56 kJ

8. The molar entropy of vapourization of acetic acid is 14.5 cal K^{-1} mol^{-1} at its boiling point 117°C. The latent heat of vapourization of acetic acid is

a. 84 cal g^{-1} **b.** 94.25 cal g^{-1}
c. 64 cal g^{-1} **d.** 47.25 cal g^{-1}

9. A gas absorbs 120 J of heat and expands against the external pressure of 1.5 atm from a volume of 0.5 L to 1 L. The change in internal energy is

a. 54.02 J **b.** 4.42 J
c. 44.02 J **d.** –44.02 J

10. Find ΔH for:

C_3H_8 (g) + $6H_2O$ (g) → $3CO_2$ (g) + $10H_2$

Given:

C_3H_8 (g) + $3H_2O$ (g) → 3CO (g) + $7H_2$ (g)

ΔH = 499 kJ

CO (g) + H_2O (g) → CO_2 (g) + H_2 (g)

ΔH = –41 kJ

a. 316 kJ **b.** 476 kJ
c. 296 kJ **d.** 376 kJ

11. Given the following data:

$2SO_2$ (g) + O_2(g) → $2SO_3$ (g)

ΔH = –196.7 k/mol

SO_3(g) + H_2O (*l*) → H_2SO_4 (*l*)

ΔH = –130.1 kJ/mol

What is the enthalpy of reaction for

$2SO_2 + O_2 + 2H_2O \rightarrow 2H2_sO_4$
g g l l

a. –456.9 kJ **b.** 326.7 kJ
c. 456.9 kJ **d.** –326.7 kJ

12. Given the following:

$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
l g g l

ΔH = –1366.9kJ

$CH_3CO_2H + 2O_2 \rightarrow 2CO_2 + 2H_2O$

ΔH = –869.9kJ

What is the enthalpy of reaction for

$C_2H_5OH + 2O_2 \rightarrow CH_3CO_2H + H_2O$
l g l l

a. 497.0kJ **b.** 2237kJ
c. –497.0 kJ **d.** –2237kJ

13. The $\Delta_f H^\circ$ for CO_2 (g), CO (g) and H_2O (g) are—393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

CO_2 (g) + H_2 (g) →CO (g) + H_2O (g) is:

a. –41.4 **b.** –14.2
c. –241.4 **d.** + 41.2

14. At 300 K, the standard enthalpies of formation of C_6H_5COOH (s), CO_2 (g) and H_2O (s) are –408, –393 and –286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at constant volume.

a. –3296 kJ mol^{-1} **b.** –3200 kJ mol^{-1}
c. –3201 kJ mol^{-1} **d.** –3603 kJ mol^{-1}

15. Calculate the standard free energy for the reaction given

$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l)$

Species	ΔG°_f kJ mol^{-1}
CH_3OH (l)	–166.3
O_2 (g)	0.00
CO_2 (g)	–394.4
H_2O (l)	–237.1

a. –1404.6 kJ **b.** –404.6 kJ
c. –2404.6 kJ **d.** 1804.8 kJ

16. Heats of solution of $BaCl_2$ (s) and $BaCl_2.2H_2O$ (s) are –22.8 kJ mol^{-1} and 10.8 kJ mol^{-1} respectively. ΔH hydration of $BaCl_2$ to $BaCl_2.2H_2O$ is

a. 33.6 kJ **b.** –33.6 kJ
c. 12.0 kJ **d.** –12.0 kJ

17. The molal freezing point constant of naphthalene is 6.9 K mol^{-1}. The enthalpy of fusion of solid naphthalene is 4.635 k cal mol^{-1}. The melting point of solid naphthalene is

a. 40.6°C **b.** 75.7°C
c. 80.45°C **d.** 82.0°C

18. The bond energies of C = C and C – C at 298 K are 592 and 333 kJ mol^{-1} respectively. The enthalpy of polymerization per mole of ethylene is

a. –66 kJ **b.** 76 kJ
c. –76 kJ **d.** –75 kJ

19. If the bond dissociation energies of XY, X_2 and Y_2 are in the ratio of 1 : 1 : 0.5 and ΔH_f for the formation of XY is –200 kJ/mole. The bond dissociation energy of X_2 will be ?

a. 100 kJ/mole **b.** 400 kJ/mole
c. 600 kJ/mole **d.** 800 kJ/mole

20. The maximum work done in expanding 16 g oxygen at 300 K and occupying a volume of 7 dm^3 isothermally until the volume becomes 35 dm^3 is:

a. $+2.02 \times 10^3$ J **b.** -1.30×10^3 J
c. -2.01×10^3 J **d.** -12.11×10^3 J

21. Use the given standard enthalpies of formation to calculate ΔH° for the following reaction:

$3Fe_2O_3(s) + CO(g) \rightarrow 2Fe_3O_4(s) + CO_2(g)$

Species	ΔH°_f, kJ/mol
Fe_2O_3 (s)	–824.2
Fe_3O_4 (s)	–1118.4
CO (g)	–110.5
CO_2 (g)	–393.5

a. +47.2 kJ **b.** –477.2 kJ
c. –417.2 kJ **d.** –47.2 kJ

22. Standard enthalpy and standard entropy changes for the oxidation of ammonia at 298 K are –382.64 kJ mol^{-1} and –145.6 JK^{-1} mol^{-1}, respectively. Standard Gibbs energy change for the same reaction at 268 K is

a. –221.1 kJ mol^{-1}
b. –339.3 kJ mol^{-1}
c. –439.3 kJ mol^{-1}
d. –523.2 kJ mol^{-1}

23. The enthalpies of formation of N_2O and NO are 30 and 90 kJ mol^{-1} respectively. The enthalpy of the reaction,

$2N_2O(g) + O_2(g) \rightarrow 4NO(g)$ is equal to

a. 300 kJ **b.** –360 kJ
c. 360 kJ **d.** –300 kJ

24. Calculate the work done when 50 g of iron reacts with HCl in an open beaker at 25°C.

a. –221.32 J **b.** –2212.2 J
c. –22.122 J **d.** none

25. Using bond energy data, calculate heat of formation of isoprene. Given B.E. of C – H = 98.8 kcal, H – H = 104 kcal, C – C = 83 kcal, C = C = 147 kcal and C(s) → C(g) = 171 kcal.

a. 28.3 kcal **b.** 20.3 kcal
c. 283 kcal **d.** 206 kcal.

26. For the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$, ΔH = –85.4 kJ and ΔS = –188.3 JK^{-1}. The temperature at which ΔG will be zero is

a. 0 K **b.** 548 K
c. 253 K **d.** 453.53 K

27. Calculate ΔS°_f at 25°C for PCl_5 (g). Given ΔH°_f = –374.9 kJ/mole and ΔG°_f = –305 kJ/mol

a. –235 J/mole K
b. –23.5 J/mole K
c. –2.35 J/mole K
d. None

28. Given enthalpy of combustion of glucose is 2870 kJ/mol. What will be the amount of glucose a man has to eat in order to climb a height of 100 m assuming 100% efficiency of the body system (weight of man = 60 kg)

a. 37 g **b.** 3.7 g
c. 370 g **d.** 180 g

29. The enthalpy change accompanying the formation of 1 mole NH_3 (g) from its elements at 298 K is –56.1 kJ. The internal energy is

a. 44.6 kJ **b.** –53.6 kJ
c. –34.6 kJ **d.** 53.6 kJ

30. ΔG° for a reaction is 46.06 Kcal/mole. K_P for the reaction at 300 K is

a. $10^{-33.33}$ **b.** 10^{-8}
c. $10^{-22.22}$ **d.** None of these

31. Heat of combustion of carbon monoxide at constant volume and at 17°C is –67, 710 calories. The heat of combustion at constant pressure is

a. +68,900 calories
b. –68,000 calories
c. –67,800 calories
d. –67,060 calories

32. Standard heat of formation for CCl_4, H_2O, CO_2 and HCl at 298 K are –25.5, –57.8, –94.1 and –22.1 kJ/mole respectively. For the reaction

$CCl_4 + 2H_2O \rightarrow CO_2 + 4HCl$

What will be ΔH?

a. – 41.4 kJ **b.** 45.5 kJ
c. –31.4 kJ **d.** 21.7 kJ

33. The bond dissociation energies for Cl_2, I_2 and ICl are 242.3, 151.0 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mole. What is the standard enthalpy of formation for ICl (g) nearly equal to?

a. 11.6 kJ/mole **b.** –15.8 kJ/mole
c. 19.8 kJ/mole **d.** 16.8 kJ/mole

34. Consider the following reactions:

(1) $H^+ (aq) + OH^- (aq) = H_2O (l)$

$\Delta H = -X_1$ kJ mol^{-1}

(2) $H_2 (g) + ½ O_2 (g) = H_2O (l)$

$\Delta H = -X_2$ kJ mol^{-1}

(3) $CO_2 (g) + H_2 (g) = CO (g) + H_2O (l)$

$\Delta H = -X_3$ kJ mol^{-1}

(4) $C_2H_2 (g) + 5/2 O_2 (g) = 2CO_2(g)+H_2O(l)$

$\Delta H = +X_4$ kJ mol^{-1}

Enthalpy of formation of $H_2O(l)$ is

a. $-X_2$ kJ mol^{-1} **b.** $+X_3$ kJ mol^{-1}
c. $-X_4$ kJ mol^{-1} **d.** $+ X_1$ kJ mol^{-1}

35. Given that bond energies of H–H and Cl–Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is –90 kJ mol^{-1}, bond enthalpy of HCl is

a. 290 kJ mol^{-1} **b.** 380 kJ mol^{-1}
c. 425 kJ mol^{-1} **d.** 245 kJ mol^{-1}

36. If 150 kJ of energy is needed for muscular work to walk a distance of one km. Then how much amount of glucose one has to consume to walk a distance of 5 km, provided only 30% of energy is available for muscular work. The enthalpy of combustion of glucose is 3000 kJ mol^{-1}.

a. 35 g **b.** 45 g
c. 150 g **d.** 175 g

37. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction,

$1/2\ X_2 + 3/2\ Y_2 \rightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be

a. 1250 K **b.** 500 K
c. 750 K **d.** 1000 K

38. A reversible isothermal evaporation of 90 g of water is carried out at 100°C. Heat of evaporation of water is 9.73 kcal mol^{-1}. Assuming water vapour to behave like an ideal gas, what is the change in internal energy of the system?

a. 22.41kcal **b.** 44.82 kcal
c. 54.18 kcal **d.** –44.48 kcal

39. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per cm^3 of the mixture. Heats of formation and densities are as follow:

$Hf_{(Al2O3)} = -399$ kcal mol^{-1};

$Hf_{(Fe2O3)} = -199$ kcal mol^{-1}

Density of $Fe_2O_3 = 5.2$ g/cm^3;

Density of Al = 2.7 g/ cm^3

a. 39.4 kcal **b.** 3.94 kcal
c. 2.42 kcal **d.** 0.394

40. Calculate the enthalpy change for the process: $CCl_4(g) \rightarrow C(g) + 4Cl(g)$

Calculate bond enthalpy by C – Cl in CCl_4 (g)

C Given:

$\Delta H°$ vap $CCl_4 = 305$ kjmol^{-1}

$\Delta_f H°\ CCl_4 = -135.5$ kj mol^{-1}

$\Delta_a H°$ (C) = 715 kj mol^{-1} (Enthalpy of atomization)

$\Delta_a H°$ (Cl_2) = 242 kj mol^{-1} (Enthalpy of atomization)

a. 326 kjmol^{-1} **b.** 163 kjmol^{-1}
c. –326 kj mol^{-1} **d.** –163 kj mol^{-1}

ANSWER KEYS

Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.	Q.	Ans.
1.	a	2.	b	3.	b	4.	b	5.	b
6.	a	7.		8.	b	9.	c	10.	d
11.	a	12.	c	13.	d	14.	b	15.	a
16.	b	17.	c	18.	c	19.	d	20.	c
21.	d	22.	b	23.	b	24.	a	25.	b
26.	b	27.	d	28.	a	29	b	30.	b
31.	a	32.	b	33.	a	34.	d	35.	a
36.	c	37.	c	38.	c	39.	b	40.	a

Hints and Explanations

1. As $\Delta H = \Delta E + \Delta n\, RT$

$\Delta n = -1$

$164 \times 10^3 = \Delta E - 1 \times 8.314 \times 298$

$= \Delta E - 2.478 \times 10^3$

$\Delta E = 164 \times 10^3 + 2.478 \times 10^3$

$= 166.5 \text{ kJ mol}^{-1}$

2. At equilibrium, $\Delta G_{T.P.} = 0 = \Delta H - T\Delta S$

$= (90000 - T \times 90)$ J.

$$T = \frac{90000}{90} = 1000 \text{ K}$$

If T is > 1000 K, ΔG will be negative and the reaction is spontaneous

4. (i) $C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta H = -393.5$ kJ

(ii) $CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$

$\Delta H = -283.0$ kJ

eq. (i) and (ii) gives

(iii) $C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$,

$\Delta H = -110.5$ kJ

This equation (iii) also represents formation of one mole of CO and thus enthalpy change is the heat of formation of CO (g).

5. $$\Delta S = \frac{\Delta H}{T(K)}.$$

$$14.4 = \frac{\Delta H}{390}.$$

$\Delta H = 390 \times 14.5 = 5655 \text{cal.mol}^{-1}$

$$= \frac{5655}{60} = 94.25 \text{ cal g}^{-1}$$

6. ΔH combustion for 1 mole of methane

= 880 kJ

2640 kJ of heat will be evolved by 3 moles of methane

3 moles can occupy at STP = 3×22.4

= 67.2 L

9. $W = -P\Delta V = -1.5(1 - 0.5)$

$= -0.75$ L atm

$= -0.75 \times 101.3$ J $= -75.98$ J

(as 1 L atm = 101.3 J)

$\Delta E = q + W$

$= 120 + (-75.98) = 44.02$ J

11. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$\Delta H = -196.7$ k/ mol

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

$\Delta H = -130.1$ kJ /mol

$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$

$\Delta H = -456.9$kJ

12. $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

$\Delta H = -1366.9$ kJ

$2CO_2 + 2H_2O \rightarrow CH_3CO_2H + 2O_2$

$\Delta H = 869.9$kJ

$C_2H_5OH + O_2 \rightarrow CH_3CO_2H + H_2O$

$\Delta H = -497.0$ kJ

13. $C + O_2 \rightarrow CO_2$, $\Delta H^\circ = -393.5$ kJ ……(i)

$C + \frac{1}{2} O_2 \rightarrow CO$, $\Delta H^\circ = -110.5$ kJ …..(ii)

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, $\Delta H^\circ = -241.8$ kJ …(iii)

By equations (ii) + (iii) – (i), we get

$CO_2 + H_2 \rightarrow CO + H_2O$, $\Delta H^\circ = +41.2$ kJ

14. The reaction is

$C_6H_5COOH(s) + 15/2\ O_2(g) \rightarrow$

$7\ CO_2(g) + 3H_2O(l)$

$\Delta H = \sum \Delta H^\circ_f$ (products) $- \sum \Delta H^\circ_f$ (reactants)

$= [7 \times \Delta H_f(CO_2) + 3 \times \Delta H_f(H_2O)]$

$- [\Delta H_f(C_6H_5COOH) + 15/2\ \Delta H_f(CO_2)]$

$= [7 \times (-393) + 3 \times (-286)] - [-408 + 0]$ kJ

$= -3201$ kJ

Now $\Delta E = \Delta H - \Delta n_g RT$

$\Delta n_g = 7 - 15/2 = -1/2$;

$R = 8.314/1000$ kJ mol^{-1}

Putting the values, we get

$\Delta E = -3199.9$ kJ $= -3200$ kJ

16. $BaCl_2(s) + aq \rightarrow BaCl_2(aq)$

$\Delta H_1 = -22.8$ kJ

$BaCl_2.2H_2O(s) + aq \rightarrow BaCl_2(aq)$

$\Delta H_2 = +10.8$ kJ

$\Delta H_3 = \Delta H_1 - \Delta H_2 = -22.8 - 10.8 = -33.6$ kJ

$BaCl_2(s) + 2H_2O \rightarrow BaCl_2.2H_2O$

17. $K_f = \dfrac{0.002\ T^2 \times 128}{1}$

$6.9 = \dfrac{0.002\ T^2 \times 128}{4635}$

$T^2 = \dfrac{6.9 \times 4635}{0.002 \times 128}$

$T = 353.45$ K $= 80.45^\circ$C

18. Polymerization reaction

$n\ CH_2 = CH_2 \rightarrow (-CH_2 - CH_2 -)_n$

One mole of C = C bond is broken and two moles of C – C bonds are formed per mole of ethylene.

$\Delta H = 592 - 2 \times 333$

$= 590 - 666 = -76$ kJ per mole of ethylene

19. Let the bond dissociation energy of XY, $X_2$and Y_2 be as x kJ mol^{-1}, x kJ mol^{-1} and 0.5 × kJ mol^{-1} respectively.

$\frac{1}{2} X_2 + \frac{1}{2} Y_2 \rightarrow XY$; $\Delta H_f = -200$ kJ mol^{-1}

ΔH reaction = [(sum of bond dissociation energy of all reactants) – (sum of bond dissociation energy of product)]

$= [\frac{1}{2} \Delta H_{X_2} + \frac{1}{2} \Delta H_{Y_2} - \Delta H\ X_Y]$

$= \dfrac{x}{2} + \dfrac{0.5x}{2} - x = -200$

$x = \dfrac{200}{0.25} = 800$ kJ mol^{-1}

22. $w = -2.303 \times \dfrac{1}{2} \times 8.314 \times 300 \log_{10} \dfrac{35}{7}$

$= -2.01 \times 10^3$ Joule.

23. Given that

$\Delta H = -382.64$ kJ mol^{-1}

$\Delta S = -145.6$ J K^{-1} mol^{-1} $= -145.6 \times 10^{-3}$ kJ K^{-1}

$\Delta G = \Delta H - T\Delta S$

so $\Delta G = -382.64 - (298 \times -145.6 \times 10^{-3})$

$= -339.3 \text{ kJ mol}^{-1}$

23. $N_2 + \frac{1}{2} O_2 \rightarrow N_2O$, $\Delta H = 30$ kJ ….(i)

$\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow NO$, $\Delta H = 90$ kJ ….(ii)

By equation [4 × eq. (ii)] – [2 × eq. (i)], we get

$2N_2O + O_2 \rightarrow 4NO$, $\Delta H = 300$ kJ

24. $W = -P_{ext.} \Delta V$

$\Delta V = V_{final} - V_{initial} = V_{final} = \frac{nRT}{P_{ext}}$

$W = -P_{ext.} \frac{nRT}{P_{ext}} = -nRT.$

$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$

1 mole 1 mole

No. of moles of Fe = No. of moles of H_2

$= \frac{50}{56}$

$W = -\frac{50}{56} \times 8.314 \times 296$

$= -2212.11$ J.

25. $5C(s) + 4H_2(g) \rightarrow H_2C = \underset{|}{\overset{CH_3}{C}} - \underset{|}{\overset{H}{C}}$; $\Delta H = ?$

$\Delta H = \sum$B.E.(reactants) – $\sum$B.E. (products)

$= [5Cs \rightarrow g + 4BE_{H-H}] - [2BE_{C-C} + 2BE_{C-C} + 8BE_{C-H}]$

$= [5 \times 171 + 4 \times 104] - [2 \times 83 + 2 \times 147 + 8 \times 98.8]$

$= 20.6$ kcal.

26. $\Delta G = \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S$

$T = \frac{\Delta H}{\Delta S} = \frac{-85.4 \times 1000}{-188.3} = 453.53$ K.

27. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$T\Delta S^\circ = \Delta H^\circ + \Delta S^\circ$

$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$

$= \frac{-374.9 - (-305)}{298}$

$= \frac{-374.9 + 305}{298} = \frac{-69.9}{298}$

$= -0.2346$ kJ/mole K

$= -234.56$ J/mole K

28. $W = mgh$

$= 60 \text{ kg} \times 9.8 \text{ ms}^{-1} \times 100 \text{ m}$

$= 58800 \text{ J} = 58.8 \text{ kJ}$

2870 kJ of heat or work is obtained = 180 g glucose

58.8 kJ of heat or work is obtained from

$= \frac{180 \times 58.8}{2870} = 3.7$ g glucose

29. $3/2 H_2(g) + \frac{1}{2} N_2(g) \rightarrow NH_3(g)$

$\Delta n = 1 \text{ mole} - 1.5 \text{ mole} - 0.5 \text{ mole}$

$= -1.00$ mole

$RT = \frac{8.314 \times 298}{1000} = 2.48$ kJ

$\Delta E = \Delta H - nRT$

$= -56.1 - (-1) \times 2.48$

$= -56.1 + 2.48 = -53.6$ kJ.

30. $\Delta G^\circ = -RT \ln K_P$

1 cal = 4.182 joule

R = 8.314 J/mol

$46.06 \times 1000 \times 4.182$

$= -2.303 \times 8.314 \times 300 \log K_P$

$192622.92 = -5744.142 \log K_P$

$\log K_P = -33.53$

i. $K_P = 10^{-33.33}$

31. $\Delta E = -67710$ cal.

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$\Delta n = 2 - 3 = -1$

$t = (273 + 17) = 290$ K

Heat of combustion at constant pressure,

$\Delta H = \Delta E + \Delta nRT$

$= -67710 + (-1) \times 2 \times 290$

$= -67710 - 580$

$= -68290$ cal.

32. $C(s) + 2Cl_2(g) \rightarrow CCl_4(l)$

$\Delta H_1 = -25.5$ kJ/mol

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$\Delta H_2 = -57.8$ kJ/mol

$C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta H_3 = -94.1$ kJ/mol

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$

$\Delta H_4 = -22.1$ kJ/mol

$CCl_4(l) + 2H_2O(l) \rightarrow CO_2(g) + 4HCl(g)$

$\Delta H = (25.5 + 2 \times 57.8 - 94.1 - 4 \times 22.1)$

$= -41.4$ kJ

33. $Cl - Cl(g) \rightarrow 2Cl(g)\ \Delta H_1 = 242.3$ kJ/mol

$I - I(g) \rightarrow 2I(g)\ \Delta H_2 = 151.0$ kJ/mol

$I - Cl(g) \rightarrow I(g) + Cl(g)$

$\Delta H_3 = 211.3$ kJ/mol

$I_2(s) \rightarrow I_2(g)\ \Delta H_4 = 62.8$ kJ/mol

$\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \rightarrow ICl(g)\ \Delta H = ?$

$$\Delta H = \left[\frac{62.8 + 151.0 + 242.3}{2} - \frac{211.3}{1}\right]$$

$= 228.05 - 211.3 = 16.75$ kJ/mol

34. $H_2(g) + \frac{1}{2} O_2(g) = H_2O(l)$

$\Delta H = -X_2$ kJ mol^{-1}

This reaction represents the enthalpy of formation of $H_2O(l)$.

35. $\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g)$,

$\Delta_f H = -90$ kJ mol^{-1}

$\Delta_r H = \frac{1}{2}$ BE $(H_2) + \frac{1}{2}$ BE (Cl_2) – BE (HCl)

$-90 = \frac{1}{2}(430) + \frac{1}{2}(240)$ – BE (HCl)

BE (HCl) = 215 + 120 + 90 = 425 kJ mol^{-1}

36. Energy consumed for walking a distance of 5 km = 150 × 5 = 750 kJ

1 mole of glucose, $C_6H_{12}O_6$ (180 g) gives theoretically energy = 3000 kJ

Actual energy available $= \frac{30}{100} \times 3000$

= 900 kJ

As, For 900 kJ of energy, glucose required = 180 g

So, for 750 kJ of energy, glucose required

$= \frac{180}{900} \times 750$ g = 150 g

37. $1/2\ X_2 + 3/2\ Y_2 \rightarrow XY_3$

$\Delta S_{reaction} = 50 - (3/2 \times 40 + \frac{1}{2} \times 60)$

$= -40$ J mol^{-1}

$\Delta G = \Delta H - T\Delta S$

As at equilibrium $\Delta G = 0$.

So $\Delta H = T\Delta S$

$30 \times 10^3 = T \times 40$

On solving, we get

T = 750 K.

38. Change in enthalpy (ΔH)

= Heat of evaporation × Number of moles

$= 9.73 \times 5 = 48.65$kcal

As $\Delta H = \Delta E + \Delta nRT$

So $\Delta E = 48.65 - (5 \times 2 \times 10^{-3} \times 373)$

= 44.82 kcal.

39. The required equation is:

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe\ ,\ \Delta H = ?$

$\Delta H = \Delta H_{f(products)} - \Delta H_{f\ (reactants)}$

$= [\Delta Hf_{(Al_2O_3)} + 2\Delta H_{f(Fe)}] - [2\Delta H_{f(Al)} + H_{f(Fe_2O_3)}]$

$= [-399 + 2 \times 0] - [2 \times 0 + (-199)]$

$= -399 + 199 = -200$ kcal

At. mass of aluminium = 27,

Mol. mass of $Fe_2O_3 = 160$

$$\text{Volume of reactants} = \frac{160}{5.2} + \frac{2 \times 27}{2.7}$$

= 50.77 cm

Fuel value per $cm^3 = \frac{200}{5077}$

= 3.94 kcal

40. (i) $CCl_4 \rightarrow CCl_4$ (g) $\Delta H^\circ = +30.5$ kj mol^{-1}

(ii) C (s) + $2Cl_2$(g) $\rightarrow CCl_4$ (g)

$\Delta H^\circ = -135.5$ kj mol^{-1}

(iii) C(s) $\rightarrow$ C(g) $\Delta H^\circ = +715$ kj mol^{-1}

(iv) Cl_2(g) $\rightarrow$ 2Cl(g) $\Delta H^\circ = +242$ kj mol^{-1}

Required equation

CCl_4(g) $\rightarrow$ C(g) + 4Cl(g) $\Delta H = ?$

Equation (iii) + 2 × Equation (iv) – Equation (ii) – Equation (i) gives the required equation

$\Delta H = 715 + 2(242) - 30.5 - (-135.5)$

= 1304 kj mol^{-1}

Bond enthalpy of (C-Cl) bond $= \frac{1304}{4}$

= 326 kj mol^{-1}