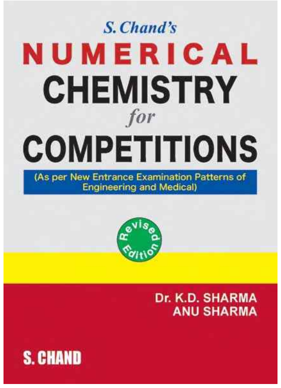

S. Chand's

NUMERICAL CHEMISTRY *for* COMPETITIONS

(As per New Entrance Examination Patterns of Engineering and Medical)

Revised Edition

Dr. K.D. SHARMA
ANU SHARMA

S. CHAND

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Numerical Chemistry
for
Competitions

(As per new entrance examinations pattern of Engineering & Medical)

An ideal book for the students of XI and XII (CBSE, ISC and the State Boards who are using Core Curriculum) and also useful for the students preparing for various Engineering & Medical Entrance Examinations.

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PREFACE TO THE SECOND REVISED EDITION

We feel immense pleasure in conveying to the students studying in Classes XI and XII throughout the country that all the numericals set in boards of different states and in various competition examinations pertaining to admission in engineering and medical colleges are from the types solved in this text, in one way or the other.

In order to keep this book up-to-date, we have incorporated almost all the numericals set up to 2013 examinations at the proper place in the concerned chapters. We are now completely satisfied that the purpose for which this attempt was made, has borne fruit for the concerned readers (students as well as teachers).

This edition will be useful for :

- JEE (Main + Advanced), previously known as IIT/JEE.
- JEE (Main), previously known as AIEEE.
- JEE– AIIMS (Advanced)
- NEET-UG called national eligibility - cum- entrance test, previously known as AIPMT, and
- For all the boards in different states of India, such as CBSE, ISC and the State Boards who are using Core Curriculum.
- Brain storming new numericals and numericals of different types set in the previous years of different state boards have been included. Some new formulae have been introduced in the chapter on Chemical Kinetics for easy understanding of the students.
- Since calculators are not allowed in +1 and + 2 examinations, the use of logarithm tables has been explained by taking suitable examples in Chapter 1.
- Though extra care has been taken to remove printing errors, yet these might have crept in. We will endeavour to correct those in the future edition.

Critical suggestions for the improvement of this book are welcome.

We are thankful to the management and the editorial team of S. Chand & Company Pvt. Ltd. for all help and support in the publication of this book.

Dr. K.D. SHARMA
ANU SHARMA

PREFACE TO THE FIRST EDITION

In order to understand the concept of general chemistry in a better way, one must solve many problems on each topic. The problem should be read carefully and solved, otherwise a small difference in the wording of the problem can lead to a large difference in its solution. A problem can be solved by more than one methods. So, one should attempt to solve the problem before looking at the solution given in this book. If you get the correct answer by a reasonable method but other than the one used in this book, you may use your method to solve other similar problems.

Some special features of this book are :

1. Attempts have been made to include all types of problems related to the topics along with their simple solution. Wherever necessary, related problems to the given solved example, are given side by side for practice.
2. The concepts of logarithm and antilogarithm have been explained to solve problems involving the uses of logarithm and antilogarithm.
3. The chapters on measurement-units, mole concept and significant figures have been explained so that the problems in other chapters are easily understood.
4. Problems have been solved in terms of different units including SI units.
5. Main formulae have been given in each chapter for help in solving different types of numericals.
6. Proper hints have been given wherever necessary to solve unsolved problems.
7. Numericals based on subjective and objective types (e.g., AIEEE examination) and set in various competitive examinations such as the following have been solved in sufficiently large number.

AIEEE, AFMC, AIIMS (New Delhi), Annamalai University, BCA, BHU, BIT (Mesra), B-Tech, CBSE-PMT, CET (Karnataka, J and K), CEE (Delhi) CMC (Ludhiana), Vellore, DCE, DPMT, EAM-CET, G.G.S.I.U (Delhi), IIT-JEE/PMT, IIT (Allahabad, Hyderabad, Kolkata,) IMS-BHU, I.P. University. JIPMER, I.S.C., Kerala PMT, MHCET, Orissa-JEE, PET (Rajasthan), SCRA, SRMC (Chennai), St. Johns Medical College, UPCPMT, UPSEAT, Wardha MGIMS, WB-JEE, Gujarat CET, Punjab PMT/CET, Punjab, Haryana and Himachal School Education Boards etc.

Though extra care has been taken to remove printing errors, yet some of these might have crept in. These are ours. We will endeavour to correct them in future edition.

We are grateful to Mr. Navin Joshi, Vice-President (Publishing) of S. Chand & Company Ltd. who took keen interest in making this project a success. We are also grateful to Dr. Rakesh Sharma and Dr. Babita Sharma for their day to day help in preparing the manuscript of this book. Critical suggestions for the improvement of the book are welcome.

Dr. K.D. SHARMA
ANU SHARMA

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1

CHAPTER

Measurements – Units

1.1 SOME BASIC CONCEPTS

1. **Physical Quantity.** It is a product of a numerical value and a unit. Thus:

Physical quantity = Numerical value × Unit.

For example, when a body weighs, 21 kg, we say that 21 is the numerical value while kg is the unit.

2. **Unit.** *A unit of a physical quantity is that standard which contains a definite, stable, durable and easily reproducible amount of the same kind of physical quantity and with which other similar quantities are compared.*

Metric system. In 1791, the French Academy of Science devised a simple system, called *metric system*. This system uses a decimal system. India adopted this system in 1957. The main advantage of this system is that the various units are either multiples or sub-multiples of 10. To convert one unit to other, we have to shift the decimal point to the left or right, to the required number of spaces.

S.I. Units. General conference on weights and measures adopted a modified version of metric system, called International System of Units, abbreviated **SI** (from the French name, **Le Syste'me international d'unites**)

1.2 BASIC S.I. UNITS

There are **seven basic units** in SI system and are given below :

Physical quantity with symbol	*SI unit with symbol*	*Physical quantity with symbol*	*SI unit with symbol*
Length ; l	metre ; ***m***	Thermodynamic temperature ; ***T***	Kelvin ; **K**
Mass ; ***m***	kilogram ; **kg**		
Time ; ***t***	Second ; ***s***	Electric current ; ***I***	Ampere ; **A**
Amount of substance ; ***n***	mole ; **mol**	Luminous intensity ; ***Iv***	Candela ; **Cd**

1.3 DERIVED UNITS

The derived unit of a physical quantity is also called *dimensional formula*. Some physical quantities like area, volume, density, pressure, etc. can be derived from seven basic SI units. For example, let us derive the SI unit of area.

Area = Length × length = (metre) × (metre) = (metre)^2 = m^2

So, SI unit of area is m^2. Some units derived from SI units are given below :

Quantity and its relation with other basic quantities	*SI units*
Area (A) = (Length)^2	m^2
Volume (V) = (Length)^3	m^3
d or ρ or Density = Mass/volume	kg m^{-3} or kg/m^3
U or Speed or velocity = Distance/time	ms^{-}
g or Acceleration = Speed/time	ms^{-2} *i.e.*, ms^{-}/s
F or Force = Mass × acceleration	kg ms^{-2} (= **Newton, N**)
P or Pressure = Force/area	kg m^{-} s^{-2} (= **Pascal, Pa**) or kg ms^{-2}/m^2
mol for amount	mol = weight/mol. wt.
Electric potential (V)	1 V = 1 W/A = 1 J/C
E = Energy = Force × distance	kg m^2 s^{-2} = J
Power = Energy/time	kg m^2 s^{-3} or J s^{-} (= **Watt, W**)
Q = Electrical charge = current × time	As (= Coulomb, C)
Potential difference = V	kg m^2 s^{-2} A^{-} or JA^{-} or JC^{-} (= **volt**, V)
R = Electrical resistance $= \dfrac{\text{Potential difference}}{\text{current}}$	VA^{-} (= **ohm**)
S = Electrical conductance = 1/Resistance	AV^{-} (ohm^{-} or Siemen, S)
v = Frequency = Cycles/sec.	s^{-} (= Hertz, Hz)
Concentration	kg m^{-3} (= gL^{-})

Notes. (*i*) **SI unit of force = Newton, N**
(*ii*) **SI unit of Pressure = Pascal, Pa**
(*iii*) **SI unit of Energy = Joule.**

1.4 UNITS CONTRARY TO SI UNITS

Some important familiar units contrary to SI units are atmosphere, litre, angstrom, erg. calorie, dyne and millimeter of mercury. *Millimeter of mercury is the practical unit of pressure and must be converted to* Nm^{-2} before any calculation is made. Some units together with their SI equivalents are given below.

Physical quantity, unit and its symbol	*SI equivalent unit*
1. **Length** (*i*) angstrom, **Å**	10^{-10} m = 10^{-1} nm = 100 pm = 10^{-8} cm
(*ii*) Inch, **in**	2.54×10^{-2} m
(*iii*) micron, **μm**	10^{-6} m
(*iv*) mile, **mile**	1.6×10^{3} m
(*v*) 1 meter, m	10^{2} cm = 10^{9} nm = 10^{10} Å = 10^{12} pm
2. **Volume.** Litre, **L**	10^{-3} m^{3} = dm^{3} = 1000 cm^{3}
3. **Force.** (*i*) dyne, **dyn**	10^{-5} N
(*ii*) Pound force, **lbf**	4.448 N
4. **Pressure** (*i*) **atmosphere, atm**	101325 $Nm^{-2} \approx 10^{5}$ Pa
(*ii*) torr, **Torr**	(101325/760) Nm^{-2}
(*iii*) Pascal, **Pa**	Nm^{-2}
(*iv*) millimeter of Hg, **mm Hg**	$103.5951 \times 980.665 \times 10^{-2}$ Nm^{-2}
(*v*) Pound force per square inch, **lbf (inch)$^{-2}$**	6.896 kPa
(*vi*) bar, **bar**	10^{5} Pa
5. Energy (*i*) erg, **erg**	10^{-7} J
(*ii*) calorie, **cal**	4.184 J
6. Mass; Pound, **lb**	0.453592 kg

1.5 SOME POINTS TO USE SI UNITS

1. Small letters are used as symbols of units. For example, symbol for kilogram is kg and not Kg.

2. If symbol of unit is derived from the name of **scientist,** then **capital** letter is used as a symbol but name of unit will be written with small letters. For example, the name of the unit of force is written as newton but its symbol will be written as Newton, N.

3. The symbol of unit does not end with a full stop. For example, symbol of mass is written as kg and not kg.

4. Symbol for gram is 'g' and not 'gm'. Symbol for kilogram is 'kg' and not 'kgm'.

5. Use index notation to write derived units in terms of base units. For example, write kg m^{2} s^{-2} and not kg m^{2}/s^{2}.

6. **Even if the unit is in the plural form,** 's' is not mentioned at the end of the unit. For example, write 5 kg, 20 kg etc. instead of 5 kgs, 20 kgs etc.

7. When units are divided, the quotients can be abbreviated as powers or as fractions. For example, meter per second is ms^{-} or m/s. Never write abbreviations with a sequence of two slant lines. For example JK^{-} mol^{-} can be written as J/K mol^{-} but not J/K/mol.

8. In case of temperature, do not write degree kelvin (K°) but write only kelvin (K). For example, write 273 K, 300 K etc. instead of 273° K, 300° K etc.

1.6 UNITS OF IMPORTANT PHYSICAL QUANTITIES

Conversion of a given type of unit into SI unit. For this purpose, choose and use the required relation from the following:

1. **Length or distance (SI unit is meter, m).**
   (*a*) 1 **mile** = 1760 **yards** = 6.336×10^{4} **in** = 1.609×10^{5} **cm** = 1.609×10^{6} **mm** = 1.609 **km** = 1.609×10^{3} **m** = 1.609×10^{13} **Å** = 1.609×10^{15} **pm** *i.e.*, picometer = 1.609×10^{9} **μm** (micrometer)

   (*b*) 1 **yard** = 3 **ft.** = 91.44 **cm** = 914.4 **mm** = 0.9144 **m.**

   (*c*) 1 **meter** = 10^{-3} **km** = 100 **cm** = 1000 **mm** = 39.37 **in** and

   1 m = 10^{2} cm = 10^{9} nm = 10^{10} Å = 10^{12} pm

   1 pm = 10^{-10} cm

   (*d*) 1 **inch** = 2.54 **cm** = 25.4 **mm** = 0.0254 **m** = 2.54×10^{7} **nm** (nanometer)

   (*e*) 1 **foot** = 12 **inch** = 12 × 2.54 **cm** or 30.48 **cm** = 304.8 **mm** = 0.3048 **m**

   (*f*) **Size of atoms and molecules is expressed in angstrom units (Å)**

   1 **Å** = 10^{-10} **m** = 10^{-8} **cm** = 10^{-7} **mm** = 10^{2} **pm** = 10^{-4} **micron** (μ) = 10^{-1} **nm**

   (*g*) **Size of nucleus is expressed in fermi (f)**

   1 fermi (f) = 10^{-15} m

   (*h*) 1 micrometer, μm = 10^{-6} m = 10^{-4} cm = 10^{-3} mm = 10^{3} mμ (millimicron)

   Note. μ is micron and 1μ = 10^{-6}

   (*i*) 1 km = 10^{3} m = 10^{5} cm = 10^{2} dam or dkm (dekameter) = 10^{4} dm (decimeter)

   (*j*) 1 Astronomical unit (A.U.) = 1.496×10^{11} meter

   (*k*) 1 Par sec = 3.08×10^{16} m

   (*l*) 1 light year = speed of light × time in seconds in one year = 9.46×10^{15} m = 9.46×10^{12} km

2. **Time (SI unit is second, s)**
   (*i*) 1 year (yr) = 365 days = 365 × 24 hours (hr) = 365 × 24 × 60 minutes (min) = 365 × 24 × 60 × 60 seconds(s) = 3.1×10^{7} s = 52 weeks.

   (*ii*) 1 hr = 60 min = 3600 s

3. **Temperature (SI unit is kelvin, K)**
   (*i*) $\frac{K-273}{5}=\frac{C}{5}=\frac{F-32}{9}=\frac{R}{4}$; K, C, F and R represent kelvin, centigrade (or celsius),

Fahrenheit and Reaumur scale temperature respectively.

(*ii*) t°C = (t + 273) K; More accurately, t°C = (t + 273.15) K

4. **Pressure (SI unit is Pascal, Pa or Nm^{-2})**

(*i*) 1 atmosphere (atm) = 1.01325 **bar** = 1.01325×10^5 **Pa** = 101.325 **kPa** = 1.01325×10^5 **Nm^{-2}** = 1.01325×10^5 **$kg\ m^{-}\ s^{-2}$** = 76 **cm of Hg** = $76 \times 981 \times 13.59$ **dyne cm^{-2}** = 760 **mm of Hg** = 760 **torr** = 14.693 lbf $(in.)^{-2}$ *i.e.*, pound force per square inch.

(*ii*) 1 bar = 10^6 dyne cm^{-2} = 10^5 Nm^{-2} = 10^5 Pa = 10^3 millibar

(*iii*) Pascal, Pa = Nm^{-2} = $kg\ m^{-1}\ s^{-2}$

(*iv*) Newton, N = $kg\ m\ s^{-2}$

(*v*) Pressure = hdg = $0.76\ m \times 13.6 \times 10^3\ kg\ m^{-3} \times 9.8\ m\ s^{-2} = 1.103 \times 10^5\ kg\ m^{-}\ s^{-2} = 1.103 \times 10^5$ Pa $\approx 10^5$ Pa

5. **Volume [SI unit is $(meter)^3$ *i.e.*, m^3]**

(*i*) 1 **Litre (L)** = 1 **dm^3** = 10^{-3} **m^3** = 10^3 **cm^3** = 10^3 cc = 10^3 mL = 1.06 quartz* (qt) = 10 dL *i.e.*, 10 decilitre

(*ii*) 1 mL = 1.000027 cc.

(*iii*) 1 L = volume of 1 kg H_2O at 4°C

Note. (*a*) Volume of cube = $(one\ edge)^3$ = $side^3$

(*b*) Volume of sphere

$$= \frac{4}{3}\pi\,(radius)^3 = \frac{4}{3}\pi r^3$$

(*c*) Volume of cylinder = $\pi r^2 \times$ height = $\pi r^2 h$

(*d*) Volume of cone

$$= \frac{1}{3}\pi r^2 \times \text{height} = \frac{\pi r^2 h}{3}$$

(*e*) Volume of cuboid = Length × breadth × height = *l*bh.

6. **Mass (SI unit is kilogram, kg)**

(*i*) 1 **kg** = 10^3 **g** = 10^6 **mg** = 2.2 **lb** = 10^{-3} **metric ton** = 35.2734 **ounce** (oz)

(*ii*) 1 **metric ton** (or tonne) = 1000 **kg** = 10^6 **g** = 10 **quintal**

(*iii*) 1 **mega ton** = 10^6 **tonne**

(*iv*) 1 **pound** (lb) = 0.4536 **kg** = 453.6 **g** = 4.536×10^5 **mg**

(*v*) 1 **ounce** (oz) = (1/16) **lb** = (1/16) × 453.6 **g** = 28.35 **g** = 0.02835 **kg**

(*vi*) 1 **a.m.u.** (or **U**) = 1.66×10^{-27} **kg** = 1.66×10^{-24} **g**

Note. Mass of 1L (= 1000 mL) of H_2O at 4°C = 1 kg

(*vii*) 1 microgram, μg = 10^{-6} g = 10^{-3} mg = 10^{-9} kg

7. **Energy (SI Unit is joule, J)**

(*i*) 1 Joule (J) = 10^7 erg = 0.239 cal. = $kg\ m^{-2}\ s^{-2}$ = 6.25×10^{18} eV = 1 NM

(*ii*) 1 cal = 4.184 J

(*iii*) 1 erg = 6.2419×10^{11} eV i.e., electron volt

(*iv*) 1 eV = 1.6×10^{-19} J

8. **Force (SI unit is Newton, N)**

1 Newton, N = 10^5 dyne (dyn) = 0.2248 lbf *i.e.*, pound force.

9. **Density (SI unit is kg m^{-3}) and C.G.S. unit is g cm^{-3}**

1 g cm^{-3} = 10^3 kg m^{-3}

10. **Work (SI unit is newton meter, Nm or joule, J)**

(*i*) 1 newton meter, Nm = 1 J = 1 $kg\ m^{-2}\ s^{-2}$ = 10^7 dyne cm = 10^7 erg = 0.239 cal

(*ii*) erg = dyne cm

(*iii*) 1 eV i.e., electron volt = 1.6×10^{-19} J (unit of atomic particles)

Note. (*a*) 1 kJ = 10^3 J

(*b*) 1 mega joule or 1 MJ = 10^6 J

(*iv*) Work 'W' done in moving a charge Q across the ends of a conductor is given as:

$$W = QV\ \text{Joule} = VI\ t\ \text{joule} = I^2Rt\ \text{joule} = \frac{V^2 t}{R}$$

joule where potential difference, V = IR and I is current in ampere and R is resistance in ohm and t is the time in second.

11. **Speed or velocity (SI unit is ms^{-})**

Speed or velocity = distance/time = m/s = ms^{-}

12. **Momentum (SI unit is kg ms^{-})**

$$\text{Momentum} = \text{Mass} \times \text{velocity} = kg \times \frac{\text{meter}}{\text{second}}$$

= kg ms^{-}

13. **1 L atm** = 100 J

14. **Radioactivity [SI unit is Becquerel (Bq)]**

1 Bq = 1 decay s^{-} = 1 disintegration per second = 1 dps

1 curie, ci = 3.7×10^{10} Bq = 3.7×10^{10} dps

1 Rutherford; 1 rd = 10^6 Bq = 10^6 dps

1 Microcurie (μc) = 3.7×10^4 dps = 1.0×10^{-6} curie

1 millicurie (mc) = 3.7×10^7 dps = 1.0×10^{-3} curie

15. **Electric Charge (SI Unit is coulomb, C)**

1 electrostatic unit, esu = 3.3356×10^{-10} C

Note. C.G.S. means in C.G.S. units; SI means in SI units; C = coulomb.

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* 1 quartz = 0.946 L (in U.S.) and 1 qt. = 1.136 L (in U.K.)

1.7 SOME PHYSICAL CONSTANTS AND CONVERSION FACTORS

Acceleration due to gravity (g)	980.665 cm s^{-2} (CGS) = 9.80665 m s^{-2} (SI)
1 a.m.u. (atomic mass unit)	1.660531×10^{-24} g (CGS) = 1.660531×10^{-27} kg (SI) = 931.2 MeV (million electron volt) = 1.49×10^{-10} J = 1.49×10^{-3} erg. = 9.31×10^{8} eV =3.56×10^{-11} cal
Atmospheric pressure (P)	1.013250×10^{6} dyne cm^{-2} (CGS) = 1.013250×10^{5} Nm^{-2} (SI)
Avogadro's no. (N)	6.022169×10^{23} mol^{-} (CGS) or 6.023×10^{23} mol^{-} = 6.022169×10^{23} mol^{-} (SI)
1 Barn	1.0×10^{-24} cm^{2}
1 Bohr's radius (for H)	= 0.529×10^{-8} cm (C.G.S.); 0.529×10^{-10} m (SI)
Boltzmann's constant (k)	1.380×10^{-16} erg K^{-} (C.G.S.) = 1.380×10^{-23} JK^{-} (SI)
1 cal	4.184×10^{7} erg (C.G.S.) = 4.184 J (SI)
Charge on electron (e)	4.80291×10^{-10} esu (C.G.S.) = 1.60210×10^{-19}C (SI) ($\because$ 1 C = 3×10^{9} e.s.u.)
Charge on neutron	Zero
Charge on proton	4.80291×10^{-10} esu (C.G.S.) = 1.602×10^{-19} C (SI)
1 cm^{-} (energy unit)	12 J mol^{-} = 1.99×10^{-23} J atom^{-}
1 Coulomb (C)	1 ampere × 1 second = 3.0×10^{9} esu
1 curie (ci)	3.7×10^{10} dps = 3.7×10^{10} Bq
density	g cm^{-3} (C.G.S.); kg m^{-3} (SI)
dyne	g cm s^{-2}
E$_{n}$ (H-atom)	$= -\dfrac{21.76 \times 10^{-19}\ Z^{2}\ \text{erg}}{n^{2}}$ (C.G.S.) $= -\dfrac{21.76 \times 10^{-12}\ Z^{2}\ \text{J}}{n^{2}}$ (SI)
1 eV (electron volt)	1.6018×10^{-12} erg (C.G.S.) = 1.602×10^{-19} J (SI) = 23.06 kcal mol^{-}
1 e.s.u. (electrostatic unit)	g$^{1/2}$ cm$^{3/2}$ s^{-} (C.G.S.) = 3.333×10^{-10} C (SI)
1 erg	6.2419×10^{11} eV; g cm^{2} s^{-2} (C.G.S.)
1 Faraday (F)	2.89461×10^{14} e.s.u. = 9.6487×10^{7} C kg^{-} (SI) = 96500 coulomb g. equiv^{-}
Gas constant or universal gas constant (R)	8.314×10^{7} erg K^{-} mol^{-} (C.G.S.) (P in dyne cm^{-2}, V in cm^{3}) = 8.314 JK^{-} mol^{-} = 0.0821 dm^{3} atm K^{-} mol^{-} (SI) = 0.0821 L atm K^{-} mol^{-} = 0.083 L bar K^{-} mol^{-} = 82.1 mL atm K^{-} mol^{-} = 62.3 L mm K^{-} mol^{-} = 8.314 Nm K^{-} mol^{-} or Pa m^{3} K^{-} mol^{-} (P in Pa or Nm^{-2}; V in m^{3}) = 1.987 or 2 cal K^{-} (or deg^{-}) mol^{-} (P in dynes cm^{-2}; V in cm^{3}) = 2×10^{-3} k cal K^{-} mol^{-} = 5.189×10^{19} eV K^{-} mol^{-}
Ice point (m.pt.)	0°C (C.G.S.) = 273.150 K (SI)
1 Joule (J)	= Coulomb (C) × Volt (V) = 1 Nm = 10^{7} ergs (C.G.S.) = 1 kg m^{2} s^{-2} (SI) = 6.2419×10^{18} eV = 1 Watt × 1 second = 0.239 cal mol^{-}
1 L	= 1 dm^{3} = 10^{-3} m^{3}
1 L atm	= 1 dm^{3} atm = 101. 3 J
Mass of electron in rest (m$_{e}$)	9.109558×10^{-28} g (C.G.S.) = 9.109558×10^{-31} kg (SI) = 0.000549 a.m.u.
Mass of hydrogen atom	1.0078 a.m.u.
Mass of neutron (m$_{n}$)	1.67492×10^{-24} g (C.G.S.) = 1.67492×10^{-27} kg (SI) = 1.008665 a.m.u.
Mass of proton (m$_{p}$)	1.67261×10^{-24} g (C.G.S.) = 1.67261×10^{-27} kg (SI) = 1.007276 a.m.u.
Microcurie (μc)	1×10^{-6} curie = 3.7×10^{4} dps
1 millicurie	= 1×10^{-3} curie = 3.7×10^{7} dps
1 million electron volt (MeV)	= 1.6018×10^{-6} erg = 10^{6} eV

Molal depression constant, k_f	°C kg mol^- = K kg mol^- (SI unit)
Molal elevation constant, k_b	°C kg mol^- = K kg mol^- (SI unit)
Molar Volume at NTP or STP	22414 cm^3 (C.G.S.) ≈ 22400 cm^3 = 0.0224 m^3 (SI)
Newton, N	kg m s^{-2} (SI unit)
Pressure (see atmosphere)	
Permittivity, ε°	8.85×10^{-12} C^2 J^- m^- $= 8.85 \times 10^{-12}$ C^2 N^- m^{-2}
Permittivity factor (4πε°)	1.11264×10^{-10} C^2 N^- m^{-2}
Planck's constant (h)	6.626×10^{-27} erg sec. (C.G.S.) $= 6.626 \times 10^{-34}$ J sec. (SI) $= 6.626 \times 10^{-34}$ kg m^2 s^- $= 9.52 \times 10^{-14}$ k cal. sec. mol^-
Specific charge of electron (e/m)	5.2764×10^{17} esu g^- $= 1.75880 \times 10^{11}$ C kg^-
Velocity of light (C)	3×10^{10} cm s^- (C.G.S.) $= 3 \times 10^8$ m s^- (SI)
Velocity of α-particles	2×10^9 cm s^- (C.G.S.) $= 2 \times 10^7$ m s^- (SI)
Velocity of β-particles	2.36×10^{10} cm s^- (C.G.S.) $= 2.36 \times 10^8$ ms^- (SI)
Velocity of γ-particles	3×10^{10} cm s^- (C.G.S.) $= 3 \times 10^8$ ms^- (SI)
Rydberg constant (R_H)	1.097373×10^5 cm^- (C.G.S.) $= 1.097373 \times 10^7$ m^- (SI)
Triple point of water	273.16 K (SI)
1 Volt (V)	1 ampere × 1 ohm $= \frac{J}{C}$
1 Watt	= 1 volt × 1 ampere per second = 10^7 erg s^-

EXAMPLE 1. *Give symbols of units of pressure and volume, their S.I. units and write their S.I. equivalents.*

SOLUTION. Pressure

(*i*) atmosphere (atm) = 101325 Nm^{-2}

(*ii*) torr (Torr) = (101325/760) Nm^{-2}

(*iii*) Pascal (Pa) = Nm^{-2}

(*iv*) millimeter of mercury (mm Hg) = $13.5951 \times 980.665 \times 10^{-2}$ Nm^{-2}

(*v*) Pound force per square inch [lbf $(in)^{2-}$] = 6.896 kPa

(*vi*) bar = 10^5 Pa

Volume : litre (L) = 10^{-3} m^3 = dm^3

1.8 EXPONENTS

Type. For *multiplication, exponents of like bases are added while for division, exponents of like bases are subtracted.* Solve non-exponential parts separately.

EXAMPLE 2. Simplify (*i*) $x^2 \times x^3$ (*ii*) 5×5 (*iii*) $(2 \times 10^2)(3 \times 10^3)$ (*iv*) $10^{-5} \times 10^3$

SOLUTION. (*i*) $x^2 \times x^3 = x^{2+3} = x^5$ (*ii*) $5^1 \times 5^1 = 5^{1+1} = 5^2$ (*iii*) $(2 \times 10^2)(3 \times 10^3) = 6 \times 10^{2+3} = 6 \times 10^5$ (*iv*) $10^{-5} \times 10^3 = 10^{-5+3} = 10^{-2}$

EXAMPLE 3. Simplify (*i*) x^4/x (*ii*) a^2/a^5 (*iii*) $(6 \times 10^4)/2 \times 10^{10}$ (*iv*) $(10 \times 10^{-7})/10^2 \times 10^{-4}$

SOLUTION. (*i*) $x^4/x^1 = x^{4-1} = x^3$ (*ii*) $a^2/a^5 = a^{2-5} = a^{-3}$ (*iii*) $6 \times 10^4/2 \times 10^{10} = 3 \times 10^{4-10} = 3 \times 10^{-6}$ (*iv*) $10^1 \times 10^{-7}/10^2 \times 10^{-4} = 10^{1-7-2+4} = 10^{-4}$

1.9 CONVERSION FACTOR AND TO GET REQUIRED INFORMATION

Method to convert a given unit into required unit (Dimensional analysis)

In science, the units of mass ranges from gram to kilogram; in medicine, it ranges from grains to drams and in engineering, it ranges from pounds to tons. So, it is necessary to know the method to convert one kind of unit into another one. For this purpose, conversion factor must be known

$$\textbf{Conversion factor} = \frac{\textbf{units required}}{\textbf{units given}} \quad \text{and}$$

$$\textbf{Required information} = \textbf{Conversion factor} \times \textbf{Given information}$$

Following steps are used to get required information

(a) *When the physical quantity involves one term e.g., inch to cm; kg to gram, etc.*

1. Write the name of the given unit equal to its 'required unit' along with its *conversion value.* Now, get the value of 1 (one) which is the *conversion factor.* For example, let us convert the length of 2.3 inches into centimeters. Here, name of given unit is **'inch'** and the name of required unit is **'cm'**. The conversion value is 2.54.

$$\text{Thus : } 1 \text{ inch} = 2.54 \text{ cm} \therefore\ 1 = \frac{2.54 \text{ cm}}{1 \text{ inch}}.$$

Here $\frac{2.54 \text{ cm}}{1 \text{ inch}}$ is the **conversion factor**

2. Use the relation:

Required information = Conversion factor × Given information, and substitute the values to get the required information. For example, for the above relation, required information is length (in cm) and given information is length (in inches) equal to 2.3 inches. Hence

$$\text{Length (cm)} = \text{Conversion factor} \times \text{Length (inches)}$$

$$= \frac{2.54 \text{ cm}}{1 \text{ inch}} \times 2.3 \text{ inch} = \textbf{5.84 cm} \quad \textbf{Ans.}$$

(b) *When the physical quantity involves more than one terms. e.g., conversion of speed m/s to mi/h; km/h to cm/s etc.*, calculate the *conversion factors* of both the units and multiply with the '*given information*'. Conversion factor of ***numerator*** is found by the same method as shown in step (*a*), 1 above. However, the conversion factor of **denominator** is calculated by reversing the equation to the one shown in step (*a*) 1, above. For example, for conversion of h to s in km/h to cm/s, we have :

$3600\text{ s} = 1\text{ h}$; $1 = \dfrac{1\text{h}}{3600\text{ s}}$. Here $\dfrac{1\text{h}}{3600\text{ s}}$ is a conversion factor.

EXAMPLE 4. *Convert 7.23 g cm^{-3} into μg μm^{-3}.*

SOLUTION. Given information = 7.23 g cm^{-3}; Required unit = μg μm^{-3}.

$$1\text{g} = 10^6\text{ μg} \quad \therefore\ 1 = \frac{10^6\text{ μg}}{\text{g}} \text{ (= conversion factor)}$$

$$1\text{ μm} = 10^{-4}\text{ cm} \ \therefore\ 1 = \frac{10^{-4}\text{ cm}}{\text{μm}} \text{ (= conversion factor)}$$

Required information = Conversion factor × Given information

$$= \frac{10^6\text{ μg}}{\text{g}} \times \frac{(10^{-4}\text{ cm})^3}{\text{μm}^3} \times \frac{7.23\text{ g}}{\text{cm}^3} = \frac{10^6\text{ μg}}{\text{g}} \times \frac{10^{-12}\text{ cm}^3}{\text{μm}^3} \times \frac{7.23\text{ g}}{\text{cm}^3}$$

$= \mathbf{7.23 \times 10^{-6}\ μg\ μm^{-3}}$ **Ans.**

EXAMPLE 5. *Convert 4.2 L h^{-2} into mL s^{-2}*

SOLUTION. Given information = 4.2 Lh^{-2}; Required unit = mL s^{-2}

$$10^{-3}\text{ L} = 1\text{ mL} \ \therefore\ 1 = \frac{1\text{ mL}}{10^{-3}\text{ L}} \text{ (= conversion factor)}$$

$$3600\text{ s} = 1\text{ hr} \ \therefore\ 1 = \frac{1\text{ h}}{3600\text{ s}} \text{ (= conversion factor)}$$

Required information = Conversion factor × Given information

$$= \frac{1\text{ mL}}{10^{-3}\text{ L}} \times \left(\frac{1\text{ h}}{3600\text{ s}}\right)^2 \times 4.2\text{ Lh}^{-2}$$

$$= \frac{1\text{ mL}}{10^{-3}\text{ L}} \times \frac{\text{h}^2}{(3600)^2\text{s}^2} \times 4.2\text{ Lh}^{-2}$$

$= 3.2 \times 10^{-4}$ mL s^{-2}

EXAMPLE 6. *Convert 111.23 torr to atm, if 1 atm = 760 torr.*

SOLUTION. Given information = 111.23 torr. We know:

$$760\text{ torr} = 1\text{ atm} \ \therefore\ 1 = \frac{1\text{ atm}}{760\text{ torr}} \text{ (= conversion factor)}$$

But, Required information = Conversion factor × Given information

$$= \frac{1\text{ atm}}{760\text{ torr}} \times 111.23\text{ torr} = \mathbf{0.14636\ atm}$$

Answer has five significant figures because 760 torr/atm is a definite or exact quantity.

EXAMPLE 7. *Convert the following in SI units.*

0.74 Å which is the bond length of H_2 molecule.

SOLUTION. Given information = 0.74 Å. SI unit = meter, m

$$1\text{ Å} = 10^{-10}\text{ m} \ \therefore\ 1 = \frac{10^{-10}\text{ m}}{\text{Å}} \text{ (= conversion factor)}$$

∴ Required information = Conversion factor × Given information

$$= \frac{10^{-10}\text{ m}}{\text{Å}} \times 0.74\text{ Å} = \mathbf{7.4 \times 10^{-11}\ m\ Ans.}$$

EXAMPLE 8. *Convert 12.34 km/h to cm/s.*

SOLUTION. First step is to get conversion factors of km to cm and h to s.

(*a*) km to cm; 1 km = 1000 m

$$\therefore \quad 1 = \frac{1000\text{ m}}{\text{km}} \text{ (conversion factor)}$$

$$1\text{ m} = 100\text{ cm} \ \therefore\ 1 = \frac{100\text{ cm}}{\text{m}} \text{ (conversion factor)}$$

(*b*) h to s. Since h is in the denominator, we have :

$$60\text{ min} = 1\text{ hour} \quad 1 = \frac{1\text{ hour}}{60\text{ min}} \text{ (conversion factor)}$$

$$60\text{ sec} = 1\text{ min} \quad 1 = \frac{1\text{ min}}{60\text{ sec}} \text{ (conversion factor)}$$

Second step. Required information = Conversion factor × Given information

12.34 km/h

$$= \left(\frac{1000\text{ m}}{\text{km}} \times \frac{100\text{ cm}}{\text{m}} \times \frac{1\text{ hour}}{60\text{ min}} \times \frac{1\text{ min}}{60\text{ sec}}\right) \times \frac{12.34\text{ km}}{\text{hour}}$$

= 342.8 cm/s Ans.

EXAMPLE 9. *Convert 2.14 mm s$^-$ to pm μ s$^-$.*

SOLUTION. Given information = 2.14 mm s$^-$

$$10^{-9}\text{ mm} = 1\text{ pm} \ \therefore\ 1 = \frac{1\text{ pm}}{10^{-9}\text{ mm}} \text{ (= conversion factor)}$$

$$\text{μs} = 10^{-6}\text{ s} \quad \therefore\ 1 = \frac{10^{-6}\text{ s}}{\text{μs}} \text{ (= conversion factor)}$$

Required information = Conversion factor × Given information

$$= \frac{1\text{ pm}}{10^{-9}\text{ mm}} \times \frac{10^{-6}\text{ s}}{\text{μs}} \times 2.14\text{ mm s}^- = \mathbf{2.14 \times 10^3\ pm\ μs^-}\ \textbf{Ans.}$$

EXAMPLE 10. *Find the capacity in litre of a tank 0.6 m long, 10 cm wide and 50 mm deep.*

SOLUTION. Volume of tank = Length × breadth × depth

$= 0.6\text{ m} \times 10^{-1}\text{ m} \times 5 \times 10^{-2}\text{ m}$

$= 3 \times 10^{-3}\text{ m}^3$

But $10^{-3}\text{ m}^3 = 1\text{L}$; $1 = \dfrac{1\text{ L}}{10^{-3}\text{ m}^3}$

$$\therefore \quad 3 \times 10^{-3}\text{ m}^3 = \frac{1\text{ L}}{10^{-3}\text{ m}^3} \times 3 \times 10^{-3}\text{ m}^3 = \mathbf{3\ L}\ \textbf{Ans.}$$

EXAMPLE 11. *A uniform aluminium bar is 16.0 inches long. Its mass is 6.25 lb. Determine the mass of the bar in gram per centimeter of length.*

Solution. 6.25 lb = 454 × 6.25 g = 2837.5 g ...(1)

$$1 \text{ inch} = \frac{2.54\times10^{-2}\text{ m}}{1\text{ inch}}\times\frac{100\text{ cm}}{1\text{ m}}$$

$$16.0 \text{ inches} = \frac{2.54\times10^{-2}\text{ m}}{1\text{ inch}}\times\frac{100\text{ cm}}{1\text{ m}}\times16.0\text{ inch}$$

$$= 40.64 \text{ cm} \quad ...(2)$$

Dividing relation (1) by (2), we get $\dfrac{2837.5\text{ g}}{40.64\text{ cm}}$

$$= \mathbf{69.8\ g\ cm^{-}} \quad \textbf{Ans.}$$

Example 12. *A tennis ball was observed to travel at a speed of 95 miles per hour. Calculate the speed of the ball in meters per second.*

Solution. $95 \text{ miles} = \dfrac{1.6\times10^{3}\text{ m}\times95\text{ miles}}{1\text{ mile}}$

$$= 152\times10^{3}\text{ m} \quad ...(1)$$

$$1\text{ hour} = \frac{60\times60\text{ s}}{1\text{ hour}}\times1\text{ hour} = 3600\text{ s} \quad ...(2)$$

Dividing (1) by (2), we get; $\dfrac{152\times10^{3}\text{ m}}{3600\text{ s}}$ = **42 ms¯. Ans.**

Example 13. *Ethyl alcohol boils at 78.5°C and freezes at –117°C, at one atmospheric pressure. What is the boiling point and freezing point of ethyl alcohol in degrees kelvin ?*

Solution. We know,

0°C = 273 K + 0 = 273 K

∴ 78.5°C = 273 + 78.5 = 351.5 K;

∴ B.p. = **351.5 K**

Similarly, – 117°C = 273 – 117 = **156 K**

∴ F.pt. = **156 K Ans.**

Example 14. *Calculate the mass in ounces of a 500 g package of breakfast cereal.*

Solution. $500\text{ g} = \dfrac{1\text{ oz}}{28.35\text{ g}}\times500\text{ g}$ = **17.64 oz Ans.**

Example 15. *A supplier packages hydrochloric acid in quarts (qt). However, you were instructed to buy a certain number of litres. What is the value in litres of 1.85 qt. of hydrochloric acid?*

Solution. $1.85\text{ qt} = \dfrac{0.946\text{ L}}{1\text{ qt}}\times1.85\text{ qt}$ = **1.75 L Ans.**

1.10 PREFIXES FOR FRACTIONS AND MULTIPLES OF SI UNITS

Type : Multiple Factors

Example. Write the symbol and multiple factor for the following prefixes. (*a*) yotta (*b*) zetta (*c*) exa (*d*) peta (*e*) tera (*f*) giga (*g*) mega (*h*) kilo (*i*) hecto (*j*) deka (*k*) deci (*l*) centi (*m*) milli (*n*) micro (*o*) nano (*p*) pico (*q*) femto (*r*) atto (*s*) zepto (*t*) yocto.

Solution. The symbol and multiple factors are :

(*a*) yotta, Y; 10^{24} (*b*) zetta, Z; 10^{21} (*c*) exa, E; 10^{18}
(*d*) peta, P; 10^{15} (*e*) tera, T; 10^{12} (*f*) giga, G; 10^{9}
(*g*) mega, M; 10^{6} (*h*) kilo, k; 10^{3} (*i*) hecto, h; 10^{2}
(*j*) deca or deka, da or dk; 10^{1} (*k*) deci, d; 10^{-1} (*l*) centi, c; 10^{-2}
(*m*) milli, m; 10^{-3} (*n*) micro, μ; 10^{-6} (*o*) nano, n; 10^{-9}
(*p*) pico, p; 10^{-12} (*q*) femto, f; 10^{-15} (*r*) atto, a; 10^{-18}
(*s*) zepto, z; 10^{-21} (*t*) yocto, y; 10^{-24}

Type : Numerical prefixes.

To know about numerical prefixes, use the following table.

Prefix	*Value*	*Prefix*	*Value*
Semi or hemi	$\frac{1}{2}$ or 0.5	Undeca	11
Mono	1	Dodeca	12
Bi or di	2	Tri deca	13
Sesqui	1.5	Tetra deca	14
Tri	3	Penta deca	15
Tetra	4	Hexa deca	16
Penta	5	Hepta deca or septa deca	17
Hexa	6		
Hepta or septa	7	Octa deca	18
Octa	8	Nona deca	19
Nona	9	Eicosa	20
Deca	10		

Example 16. *Write the symbol and multiple factor for the following prefixes. (a) tera (b) giga (c) mega (d) kilo (e) hecto (f) deca (g) deci (h) centi (i) milli (j) micro (k) nano and (l) pico.*

Solution. The symbol and multiple factors are (*a*) tera, T; 10^{12} (*b*) giga, G; 10^{9} (*c*) mega, M; 10^{6} (*d*) kilo, k; 10^{3} (*e*) hecto, h; 10^{2} (*f*) deca, da; 10 (*g*) deci, d; 10^{-1} (*h*) centi, c; 10^{-2} (*i*) milli, m; 10^{-3} (*j*) micro, μ; 10^{-6} (*k*) nano, n; 10^{-9} (*l*) pico, p; 10^{-12}.

Example 17. *Write the value of 5 nanometer in meters.*

Solution. 5 nanometer = 5×10^{-9} meter.

Example 18. *Write all the terms from 10^{-2} to 10^{+2} in powers of 10 together with their explicit meaning.*

Solution. $10^{-2} = \dfrac{1}{10^{2}} = \dfrac{1}{100} = 0.01$; $10^{1} = 10$

$10^{-1} = \dfrac{1}{10} = 0.1$; $10^{2} = 10\times10 = 100$

$10^{0} = 1$:

In the expression 10^{-2}, the base is 10 and the *exponent* is –2.

1.11 EXPONENTIAL NUMBERS

Type. To know how to write a number in *standard exponential form.* It can be done by expressing a number as an integral part of 10 or as the product of two numbers, one of which is an integral power of 10. The result is reported by placing a decimal point on the right of the first non-zero digit.

(*a*) *When the decimal point is moved to the right* by *n* places, the compensation is achieved by dividing at the same time by 10^{n}. For example, consider 0.00123. The non-zero digit 1 is at third place (n = 3) from the decimal point. So, $0.00123 = 1.23/10^{3} = 1.23\times10^{-3}$.

(*b*) *When the decimal point is moved to the left* by *n* places, the compensation is achieved by multiplying at the same time by 10^n. For example, consider 2345. There is no decimal point. Since, decimal point is placed on the right of first non-zero digit, we have 2.345. the decimal point is at three places to the left. So, the result is $\mathbf{2.345 \times 10^3}$. Similarly, 456 = 4.56×10^2.

EXAMPLE 19. *Write the numbers (a) 0.06 (b) 0.00009 (c) 56000 (d) 0.0378 and (e) 98725 in standard exponential form.*

SOLUTION. (*a*) $0.06 = 6 \times 10^{-2}$ (*b*) $0.00009 = 9 \times 10^{-5}$ (*c*) $56000 = 5.6 \times 10^4$ (*d*) $0.0378 = 3.78/10^2 = 3.78 \times 10^{-2}$ (*e*) $98725 = 9.8725 \times 10^4$.

Type : Any term raised to the power, zero is equal to 1 *i.e.*, one. Also, $a^{b/c} = \sqrt[c]{a^b}$ and $(a^b)^c = a^{b\times c} = a^{bc}$.

EXAMPLE 20. *Evaluate the expressions (i) x^0 (ii) $(5 \times 10)^0$ (iii) 2.5×10^0.*

SOLUTION. (*i*) $x^0 = 1$ (*ii*) $(5 \times 10)^0 = 1$ (*iii*) $2.5 \times 10^0 = 2.5 \times 1 = 2.5$.

EXAMPLE 21. *Express the following as radicals (a) $4^{3/2}$ (b) $10^{2/3}$ (iii) $10^{½}$ (iv) $10^{4/3}$.*

SOLUTION. (*i*) $4^{\frac{3}{2}} = \sqrt{4^3} = \sqrt{64} = 8$ (*ii*) $10^{\frac{2}{3}} = \sqrt[3]{10^2}$

(*iii*) $10^{\frac{1}{2}} = \sqrt{10}$ (*iv*) $10^{\frac{4}{3}} = \sqrt[3]{10^4}$.

EXAMPLE 22. *Simplify the following (a) $(x^2)^{-3}$ (b) $(10^3)^{-3}$ (c) $(5^2)^{-2}$.*

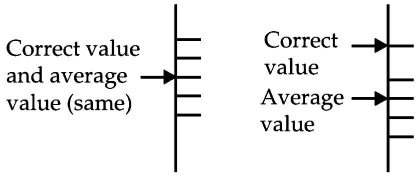
SOLUTION. (*a*) $(x^2)^{-3} = x^{2\times -3} = x^{-6}$ (*b*) $(10^3)^{-3} = 10^{3\times -3} = 10^{-9}$ (*c*) $(5^2)^{-2} = 5^{2\times -2} = 5^{-4}$.

1.12 DIFFERENCE BETWEEN ACCURACY AND PRECISION

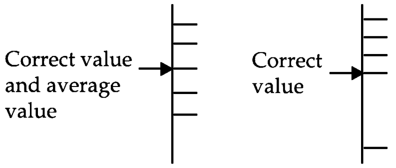
A measurement *is said to* ***be accurate*** *if the average value of different measurements is close to the correct value. A measurement is said to be* **precise** *if the values of different measurements are close to each other and hence close to their average value. For example*, suppose the actual length of a table is 2.1 metre. But the measurement reported by four different students is as given in the following table.

Measurement (metre)	1	2	3	4	5	Average
(*i*) Student, Ram	1.9	2.0	2.1	2.2	2.3	2.1
(*ii*) Student, Sham	1.6	1.7	1.8	1.9	2.0	1.8
(*iii*) Student, Kamla	1.7	1.9	2.1	2.3	2.5	2.1
(*iv*) Student, Kartar	1.6	2.3	2.5	2.7	2.9	2.4

The results are shown in the following figure.



(*i*) Both accurate and precise (*ii*) Poor accuracy but good precision



(*iii*) Good accuracy but poor precision (*iv*) Poor accuracy and poor precision.

It may be noted that good precision does not necessarily mean good accuracy. A measurement can have a good accuracy but poor precision.

EXAMPLE 23. *Which out of the two measurements, 5.0 metre and 5.00 metre, is more precise measurement?*

SOLUTION. (*i*) **For 5.0 m :** No. of significant figures (see chapter, 2) = 2

Precision = 0.1 part in 5

$\therefore$ Precision parts per thousand (p.p.t.) = $\frac{0.1}{5} \times 1000$

= 20 p.p.t.

(*ii*) **For 5.00 m :** No. of significant figures = 3

Precision = 0.01 in 5

$\therefore$ Precision parts per thousand (p.p.t.) = $\frac{0.01}{5} \times 1000$

= 2 p.p.t.

$\therefore$ 5.00 m is a more precision measurement than 5.0 m measurement.

EXAMPLE 24. *Verify the equation, $E = h\nu$ with the help of dimensional analysis.*

SOLUTION. $E = h\nu$ ...(1)

Dimensions of $E = \text{kg m}^2 \text{s}^{-2}$

Dimensions of $h = \text{kg m}^2 \text{s}^{-}$; Dimensions of frequency, $\nu = \text{s}^{-}$

Substituting the values in equation (1), we get :

$\text{kg m}^2 \text{s}^{-2} = \text{kg m}^2 \text{s}^{-} \times \text{s}^{-}$

Or $\text{kg m}^2 \text{s}^{-2} = \text{kg m}^2 \text{s}^{-2}$

Since, L.H.S. = R.H.S., equation (1) is true.

1.13 USE OF LOGARITHMS

Logarithm is a device that is used to calculate multiplication, division, extraction of roots and taking of powers to certain decimal points. Logarithm of a number to any base is the index of the power to which the base must be raised in order to be equal to the number. For example:

$100 = 10 \times 10 = 10^2$. Here, 2 is the logarithm of 100 to the base 10 *i.e.*, $\log_{10} 10^2 = 2$.

Also, 100 is called the antilogarithm of 2.

Logarithm of a number consists of two parts.

1. **Characteristic** and 2. **Mantissa**

Characteristic is the integral part while mantissa is the fractional decimal part. **Mantissa is always positive** *while characteristic can be positive and in some cases, it can be negative.*

Methods to know characteristic.

(*i*) **The characteristic of a number** = [Number of digits before the decimal point] – 1

For example, characteristic of (*a*) 2.456 = 1 – 1 = 0. (*b*) 24.56 = 2 – 1 = 1; (*c*) 245.6 = 3 – 1 = 2. Here number of digits before decimal point are (*a*) one *i.e.,* 2 (*b*) two *i.e,* 2 and 4 (*c*) three *i.e.,* 2, 4 and 5 respectively.

(*ii*) **If there is no decimal point :**

The characteristic of a number = [Total number of digits] – 1

For example, (*a*) Characteristic of (*a*) 2456 = 4 – 1 = 3 (*b*) 785 = 3 – 1 = 2 because total number of digits in (*a*) are four *i.e.,* 2, 4, 5 and 6 and in (*b*) are three *i.e.,* 7, 8 and 5 respectively.

(*iii*) **If there is no non-zero digit before decimal,** but *a non-zero digit after* the decimal point (*e.g.,* 0.236; 0.2036, etc);

Characteristic of a number = – 1.

For example, the characteristic of 0.2367, 0.2036, 0.4507 and 0.3450 is **– 1 in each case.**

(*iv*) **If there is no non-zero digit before** decimal (*e.g.,* 0.123, 0.378 etc) but there are one, two, three etc zeros, between decimal and first non-zero digit (*e.g.,* 0.0123, 0.0037, 0.0006, etc) then :

Characteristic of a number = – 1 – (number of zeros between decimal and first non-zero digit)

For example. Characteristic of 0.0123 = – 1 – (no. of zeros between decimal and first non-zero digit) = – 1 – 1 = **– 2.**

Characteristic of 0.0037 = – 1 – (no. of zeros between decimal and first non-zero digit) = – 1 – 2 = – 3.

Characteristic of 0.0006 = – 1 – (no. of zeros between decimal and first non-zero digit) = – 1 – 3 = **– 4.**

Methods to know mantissa: Mantissa is always taken as a positive quantity. The fractional (decimal) part of a logarithm of a number is called mantissa. **For example;** if the logarithm of a number is $\underbrace{2}_{\text{Characteristic}}\underbrace{.4679}_{\text{Mantissa}}$, then 2 is characteristic while .4679 is mantissa. In order to calculate the logarithm of a number, the mantissa of common logarithms of the numbers are calculated from available four or five figure logarithm tables. (See last pages of this book).

Method to use logarithm (or log) tables to calculate the log of a number. At the extreme left of the log tables, there is a vertical column containing numbers of two digits and the top row consisting of two parts. Ignore the 'decimal' in the number (whose log is taken) given *e.g.,* in the number 3.7219, take log of 7219 (and not .7219) from tables.

(*i*) The first part contains numbers from 0 to 9 while the second part contains numbers from 1 to 9 (mean difference)

(*ii*) If the mantissa of the logarithm of a one unit number (*e.g.,* 2) is required, it is found in the column headed by '0' against the required number. For example, the mantissa value of log 2 is 3010. If the mantissa of the logarithm of a two digit number only (*e.g.,* 46) is required, it is found in the column headed by **'0'** against the required number. **For example,** the mantissa value of log 46 = 6628 (see log table).

(*iii*) If the mantissa of the log of a **three digit number** only (*e.g.,* 468) is required, the first two digits (*i.e.,* 46 in this case) are located in the extreme left column and then by passing along the horizontal line, the mantissa is read under the column headed by the third digit (*i.e.,* 8 in this case) of the number. **For example,** The mantissa value of log 468 = 6702.

(*iv*) If the mantissa of the log of a **four digit number** only (*e.g.,* 4687) is required, the first two digits (*i.e.,* 46 in this case) are located in the extreme left column and then by passing along the horizontal line, the mantissa is read under the column headed by third digit (*i.e.,* 8 in this case) of the number. Lastly, by passing further along the same horizontal line, the mantissa is read under the column 'mean difference' headed by fourth digit (*e.g.,* 7 in this case). This number is now added to the mantissa of three digits already found. **For example,** the mantissa value of log 4687 = 6702 + 7 = **6709.**

1.14 ANTILOGARITHMS

If $x = \log y$, then y is called the antilogarithm (or antilog) of x. In this case, the log of a number is given and we are to find the antilog of this number from the antilog tables. Following procedure is adopted to find the antilog of a number whose log is given. An example is given side by side for better understanding. Let us take antilog of 2.7358.

(*i*) Ignore the characteristic (2 in this case) and consider the digits .7358 *i.e.,* mantissa.

(*ii*) Look for the first two digits (*i.e.,* .73 in this case) of the mantissa in the extreme left hand column and note the number written in the corresponding row under '0'. This value is 5370.

(*iii*) Now look for the third digit (*i.e.,* 5 in 7358) and note the number below column 5 along the horizontal line of 73. For 735, this value is 5433.

(*iv*) Now look for the fourth digit (*i.e.,* 8 in 7358) and note the number below column 8 along the horizontal line of 73 under 'mean difference columns'. Add this number to the value of first three digits. For 7358, this value is 5433 + 10 = 5443.

(*v*) If the **characteristic is positive,** place the decimal in the number (obtained in (*iv*) above) after the number of digits equal to (digit before decimal + 1).

For example, in the above case of 2.7358, the digit before decimal is 2. So, place the decimal in the number of antilog value (= 5443) after the number of digits equal to "digit before decimal + 1. *i.e.,* 2 + 1 = 3". Thus, we get the result, 544.3. In other words, antilog of 2.7358 = 544.3.

(*vi*) If the **characteristic is negative,** write the number of zeros numerically one less than the digits before decimal point (ignore negative sign) on the left hand side of the number found (from tables) and then fix decimal to the left of these zeros. For example, *consider the antilog of* $\bar{3}.2468$. Using antilog tables, the antilog of .2468 is 1765. Here characteristic is negative (–3). So, number of zeros to be placed before first non-zero digit (= 1) of 1765 = digit before decimal (3) – 1 = 2. So, the answer by placing decimal before two zeros will be 0.001765 or .001765.

(*vii*) **If the log value of a number is negative** (*e.g.*, – 2.3293), and its antilog is required, then change the mantissa to a positive value by subtracting 1 and adding 1 to the given number and solve. Thus: – 2.3293 = – 2 – 1 + 1 – 0.3293 = $\bar{3}.6707$. Now take antilog of $\bar{3}.6707$. Its value is 0.004685.

EXAMPLE 25. *Calculate the characteristic of the logarithm of (i) 3579 (ii) 357.9 (iii) 35.79 (vi) 3.579.*

SOLUTION. (*i*) **3579.** There is no decimal point in this number. So, characteristic of 3579 =(Total number of digits) – 1 = 4 (*i.e.*, 3, 5, 7 and 9) – 1 = 3 **Ans.**

(*ii*) **357.9.** There are three digits (*i.e.*, 3, 5 and 7) before the decimal point. So,

Characteristic of 357.9 = [Total no. of digits before decimal point] – 1

= 3 – 1 = **2 Ans.**

(*iii*) **35.79.** There are two digits (*i.e.*, 3 and 5) before the decimal point. So,

Characteristic of 35.79 = [Total no. of digits before decimal point] – 1

= 2 – 1 = **1 Ans.**

(*iv*) **3.579.** There is one digit (*i.e.*, 3) before the decimal point. So,

Characteristic of 3.579 = [Total no. of digits before decimal point] – 1

= 1 – 1 = **0 Ans.**

EXAMPLE 26. *Calculate the characteristic of the logarithm of (i) 0.2408 (ii) 0.02408 (iii) 0.002408.*

SOLUTION. (*i*) **0.2408.** There is no (*i.e.*, zero) non-zero digit before the decimal point but a non-zero digit just after decimal point. So,

Characteristic of 0.2408 = [Total no. of digits before decimal point] – 1

= 0 – 1 = – **1 Ans.**

(*ii*) **0.02408.** There is no non-zero digit before decimal point but there is **one zero** between decimal point and first non-zero digit. (*i.e.*, 2). So,

Characteristic of 0.02408 = – 1– [no. of zeros between decimal point and first non-zero digit]

= – 1 – 1 = – 2 = $\bar{2}$ (*i.e.*, 2 under the bar). **Ans.**

(*iii*) **0.002408.** There is no non-zero digit before decimal point but there are two zeros between decimal point and first non-zero digit (*i.e.*, 2). So,

Characteristic of 0.002408 = – 1 – [no. of zeros between decimal point and first non-zero digit]

= – 1 – 2 = – 3 = $\bar{3}$ (*i.e.*, 3 under the bar.) **Ans.**

EXAMPLE 27. *Find the logarithm of following numbers with the help of logarithm tables.*

(*i*) 2376 (*ii*) 237.6 (*iii*) 23.76 (*iv*) 2.376 (*v*) 0.2376 (*vi*) 0.02376 and (*vii*) 0.002376.

SOLUTION. Using rules given above, the characteristics of (*i*) = 3, (*ii*) 2 (*iii*) 1 (*iv*) 0 (*v*) – 1 (*vi*) – 2 and (*vii*) – 3. The mantissa of all these numbers is the same as the first four significant figures in each number are the same (*i.e.*, 2, 3, 7 and 6).

Mantissa of 2376. Using log tables we find that :

Value of 23 under column 7 = 3747

Value of 6 under column of mean difference = 11

Adding, we get log of 2376 = 3747 + 11 = 3758.

Hence mantissa of 2376 = 3758.

Using the value of characteristics of the numbers given in question, we have:

(*i*) log 2376 = 3.3758 (*ii*) log 237.6= 2.3758
(*iii*) log 23.76 = 1.3758 (*iv*) log 2.376 = 0.3758
(*v*) log 0.2376 = $\bar{1}.3758$ (*vi*) log 0.02376 = $\bar{2}.3758$
(*vii*) log 0.002376 = $\bar{3}.3758$

EXAMPLE 28. *Calculate the antilog of the following numbers (i) 2.4567 (ii) – 2.4567 (iii) 0.4567 (iv) 0.04567.*

SOLUTION. (*i*) 2.4567. Here the mantissa is positive. Using antilog tables for mantissa .4567, we find that :

Value of .456 under column 6 = 2858

Value of 7 under column of mean difference = 5

Adding, we get, 2858 + 5 = 2863.

The digit before decimal point in 2.4567 is 2. Adding 1 to 2, we get 3. Placing decimal point after three digits of 2863, we get 286.3 which is the answer.

(*ii*) – **2.4567.** Here mantissa is negative. To make it positive, we subtract 1 and add 1 to – 2.4567. So, we get – 2 – 1 + 1 – 0.4567 = $\bar{3}.5433$. Here, the mantissa .5433 is positive. Using antilog tables, we have:

Value of .543 under column, 3 = 3491.

Value of next 3 under column of mean difference = 2

Adding, we get, 3491 + 2 = 3493.

The digit before decimal point in $\bar{3}.5433$ is 3 (ignore – ive sign).

∴ no. of zeros to be placed before the first non-zero digit *i.e.*, 3 in 3493 is = 3 – 1 = 2. So, antilog of – 2.4567 = **0.003493. Ans.**

(*iii*) **0.4567.** Here mantissa is positive. The antilog of mantissa is 2863 (found in (*i*) above).

The digit before decimal point in 0.4567 is 0. Adding 1 to 0, we get 1. Placing decimal point after one digit of 2863, we get, 2.863 which is the answer.

(*iv*) **0.04567** or **0.0457.** Here mantissa, .0457 is positive.

Value of 0.045 under column 5 = 1109.

Value of 7 under the column mean difference = 2

Adding, we get, 1109 + 2 = 1111

The digit before decimal point in 0.0457 is 0. Adding 1 to 0, we get, 1. Placing decimal point after one digit of 1111, we get 1.111 which is the answer.

(*v*) 0.00457 = 0.0046. Here mantissa 0.0046 is positive.

Value of 0.004 under column 4 = 1009

Value of 6 under mean difference column = 1

Adding, we get, 1009 + 1 = 1010.

The digit before decimal point in 0.0046 is 0. Adding 1 to 0 we get 1. Placing decimal point after one digit of 1010, we get 1.010 which is the answer.

Type : Log a^b = b log a

EXAMPLE 29. *Solve log $(25)^7$.*

SOLUTION. log $(25)^7$ = 7 log 25 = 7 × 1.3979 = 9.7853

Note. To know log 25 (two digits number) from log table, read the number below '0' column along the horizontal line of 25.

Type. (*i*) Log abc = log a + log b + log c.

(*ii*) Log $\frac{a}{b}$ = log a – log b

(*iii*) Log $\frac{ab}{cd}$ = log a + log b – log c – log d

EXAMPLE 30. *Solve log 112 × 56 × 0.0417*

SOLUTION. Log 112 × 56 × 0.0417 = log 112 + log 56 + log 0.0417 = 2.0492 + 1.7482 + $(\bar{2}.6201)$

= 2.0492 + 1.7482 – 2 + 0.6201 = 2.4175 **Ans.**

EXAMPLE 31. *Solve log* $\frac{0.7231}{0.0023}$.

SOLUTION. log $\frac{0.7231}{0.0023}$ = log 0.7231 – log 0.0023

$= \bar{1}.8592 - (\bar{3}.3617) = -1 + 0.8592 - (-3 + 0.3617)$

$= -1 + 0.8592 + 3 - 0.3617 = 2.4975$ **Ans.**

EXAMPLE 32. *Solve* $\frac{1.4325 \times 0.6062}{72.14}$ *with the help of log tables.*

SOLUTION. Let $x = \frac{1.4325 \times 0.6062}{72.14}$. Taking logs of both sides, we get :

$$\begin{aligned} \log x &= \log 1.4325\ 1 + \log 0.6062 - \log 72.14 \\ &= 0.1559 + \bar{1}.7826 - 1.8581 \\ &= 0.1559 - 1 + 0.7826 - 1 - 0.8581 \\ &= -1.9196. \end{aligned}$$

Here mantissa is negative. To make it positive, we subtract 1 and add 1. So, we have :

$$\log x = -1 - 1 + 1 - 0.9196 = \bar{2}.0804\ .$$

Taking antilog of both sides, we get : x = antilog $\bar{2}.0804$ = **0.01203 Ans.**

Second method. By the use of calculator, we have

$$\begin{aligned} \log x &= \log 1.4325 + \log 0.6062 - \log 72.14 \\ &= 0.1559 - 0.2174 - 1.8582 = -1.9197. \end{aligned}$$

Here mantissa is negative. To make it positive, subtract 1 and add 1. So, we have,

$$\log x = -1 - 1 + 1 - 0.9197 = \bar{2}.0803$$

Taking antilog of both sides, we get,

x = antilog $\bar{2}.0803$ = 0.01203 **Ans.**

1.15 AIEEE–PATTERN EXAMPLES

EXAMPLE 33. *The prefix femto stands for :*

(*a*) 10^{-15} (*b*) 10^{-14}

(*c*) 10^{13} (*d*) 10^{12}

SOLUTION. 1 femto = 10^{-15}. So, the correct answer is (*a*)

EXAMPLE 34. *The S.I. unit of volume is :*

(*a*) *cm*^{2} (*b*) *cm*^{3}

(*c*) *m*^{3} (*d*) *Å*

SOLUTION. Volume = (length in m)^3 = m^3. So, the correct answer is (*c*)

EXAMPLE 35. *Candela is the S.I. unit of*

(*a*) *Luminous intensity* (*b*) *Electric current*

(*c*) *Energy* (*d*) *Pascal*

SOLUTION. Luminous intensity is measured in candela. So, the correct answer is (*a*).

EXAMPLE 36. *The S.I. unit of pressure is :*

(*a*) *Dyne m*$^{-2}$ (*b*) *Torr*

(*c*) *Pascal* (*d*) *Atmosphere*

SOLUTION. The S.I. unit of pressure is pascal. So, the correct answer is (*c*).

EXAMPLE 37. *1 dm*^{3} *equals.*

(*a*) *0.5 L* (*b*) 10^{-3} *m*^{3}

(*c*) 10^3 *m*^{3} (*d*) *10 L*

SOLUTION. We know that, 1L = 1 dm^3 and 1 dm^3 = $\frac{1}{10^3}$ m^3 or 1 dm^3 = 10^{-3} m^3. So, the correct answer is (*b*).

EXAMPLE 38. *One amu. stands for :*

(*a*) *One gram of all atoms*

(*b*) $\frac{1}{12}$*th of O-atom*

(*c*) $\frac{1}{12}$*th of a carbon atom,* ^{12}C

(*d*) *One atom of carbon.*

SOLUTION. a.m.u. (new symbol, U) is a mass unit which is exactly $\frac{1}{12}$th the mass of a carbon atom, ^{12}C. So, the correct answer is (*c*).

EXAMPLE 39. *1 Newton (N) is equal to*

(*a*) *kg m* (*b*) *kg m s*

(*c*) *kg m s*$^{-}$ (*d*) *kg m s*$^{-2}$

SOLUTION. $1\ \text{N} = \dfrac{\text{kg m}^{-}\ \text{s}^{-2}}{\text{m}^{-2}} = \text{kg m}^{-1+2}\ \text{s}^{-2} = \text{kg m s}^{-2}$.

So, the correct answer is (*d*).

EXAMPLE 40. *1 bar equals :*

(*a*) 10^2 millibar (*b*) 10^6 dynes cm^{-2}

(*c*) $10^4\ \text{N m}^{-2}$ (*d*) 10 Pa

SOLUTION. Since 1 bar = 10^6 dynes cm^{-2}, the correct answer is (*b*).

EXAMPLE 41. *The capacity in litres of a tank 0.5 m long, 12 cm wide and 60 mm deep is :*

(a) 4 L *(b) 2 L*

(c) 3 L *(d) 2.6 L*

SOLUTION.

$$\text{Length} = 0.5\ \text{m};\ \text{width} = 12\ \text{cm} \times \frac{1\ \text{m}}{100\ \text{cm}} = 0.12\ \text{m}$$

$$\text{Depth} = 60\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}} = 0.06\ \text{m.}$$

$$\begin{aligned} \therefore\ \text{Capacity} &= \text{Length} \times \text{width} \times \text{depth} \\ &= 0.5\ \text{m} \times 0.12\ \text{m} \times 0.06\ \text{m} \\ &= 3.6 \times 10^{-3}\ \text{m}^3 = 4 \times 10^{-3}\ \text{m}^3 = 4\ \text{L} \end{aligned}$$

$[\because 1\ \text{L} = 10^{-3}\ \text{m}^3]$

In case of multiplication, the result is given in minimum number of significant figures (see chapter, 2) (*i.e.*, 1 as in 0.5). So, 3.6 is taken as 4. So, the correct answer is (*a*).

EXAMPLE 42. *Conversion of 12 g* L^{-} *equals*

(a) $120\ mg\ (d\ L)^{-}$ *(b)* $1.2 \times 10^3\ mg\ (d\ L)^{-}$

(c) $1.02\ mg\ (d\ L)^{-}$ *(d)* $12\ mg\ (d\ L)^{-}$

SOLUTION. Hint.

$$12\ \text{g L}^{-} = \frac{12\ \text{g}}{\text{L}} \times \frac{10^3\ \text{mg}}{1\ \text{g}} \times \frac{10^{-1}\ \text{L}}{\text{d L}} = 1.2 \times 10^3\ \text{mg (dL)}^{-}$$

So, the correct answer is (*b*)

EXAMPLE 43. *In summer, the highest temperature in Delhi was 46°C. The value of this temperature in S.I. units is :*

(a) 227°C *(b) 227 K*

(c) 319°C *(d) 319.15 K*

SOLUTION. 0°C = 273.15 K. Hence 46°C = 46 + 273.15 = 319.15 K. So, the correct answer is (*d*).

EXAMPLE 44. *The mass of human DNA molecule is 1 fg. Its weight in kilogram will be :*

(a) 10^{-3} *kg* *(b)* 10^{3} *kg*

(c) 10^{-18} *kg* *(d)* 10^{18} *kg*

SOLUTION. 1 fg or 1 femto gram $= 10^{-15}$ g; 1 g $= 10^{-3}$ kg.

$$\therefore\ 1 = \frac{10^{-3}\ \text{kg}}{\text{g}}.$$

$$\text{So, } 10^{-15}\text{g} = 10^{-15}\ \text{g} \times \frac{10^{-3}\ \text{kg}}{\text{g}} = 10^{-18}\ \text{kg.}$$

So, the correct answer is (*c*)

EXAMPLE 45. *The value of 90 miles per hour in S.I units is:*

(a) 40 m s^{-} *(b) 40 cm* s^{-}

(c) 44 m s^{-} *(d) 20 m* s^{-}

SOLUTION. Hint.

$$\frac{90\ \text{miles}}{\text{hr}} = \frac{90\ \text{miles}}{\text{hr}} \times \frac{1.6 \times 10^3\ \text{m}}{1\ \text{mile}} \times \frac{1\ \text{hr}}{60 \times 60\ \text{s}} = 40\ \text{ms}^{-}$$

So, the correct answer is (*a*)

EXAMPLE 46. *The mass of loaded Jumbo jet is 450 Mg. Its mass in kilogram will be.*

(a) 4.5×10^4 *kg* *(b)* 4.5×10^3 *kg*

(c) 9.0×10^5 *kg* *(d)* 4.5×10^5 *kg*

SOLUTION. 1 Mg or 1 mega gram $= 10^6$ g

$$\begin{aligned} \therefore\quad 450\ \text{Mg} &= 450 \times 10^6\ \text{g} \\ &= 450 \times 10^6\text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} \\ \therefore\quad 450\ \text{Mg} &= 45 \times 10^4\ \text{kg} \\ &= 4.5 \times 10^5\ \text{kg.} \end{aligned}$$

So, the correct answer is (*d*)

EXAMPLE 47. *The distance of nearest star is 41 Pm. Its value in meter will be :*

(a) 41×10^5 *m* *(b)* 4.1×10^5 *m*

(c) 41×10^{16} *m* *(d)* 4.1×10^{16} *m*

SOLUTION. 1 Pm or 1 petameter $= 10^{15}$ meter.

So : 41 Pm = 41×10^{15} meter = 4.1×10^{16} m.

So, the correct answer is (*d*).

EXAMPLE 48. *The mass of a precious stone is specified in carat (1 carat = 3.168 grains; 1g = 15.4 grains). The total mass of a ring containing 6.0 g gold and 0.6 carat diamond is :*

(a) 3.05 kg *(b)* 6.1×10^{-3} *kg*

(c) 2.1×10^{-2} *kg* *(d) 3.05 g*

SOLUTION. Mass of gold = 6.0 g

Mass of diamond

$$= 0.6\ \text{carat} \times \frac{3.168\ \text{grain}}{1\ \text{carat}} \times \frac{1\ \text{g}}{15.4\ \text{grains}} = 0.1234\ \text{g}$$

$$\begin{aligned} \therefore\ \text{Total mass of ring} &= 6.0 + 0.1234\ \text{g} \\ &= 6.1234\ \text{g} \approx 6.1\ \text{g} = 6.1 \times 10^{-3}\ \text{kg.} \end{aligned}$$

So, the correct answer is (*b*).

PRACTICE PROBLEMS

1. Convert the following into SI units.

The typical speed of Rajdhani Express, 100 miles per hour

Hint. $$\left(\text{Speed} = \frac{1.60 \times 10^3 \text{ m}}{1 \text{ mile}} \times \frac{1 \text{ hr}}{3.6 \times 10^3 \text{ s}} \times \frac{100 \text{ miles}}{\text{hr}}\right)$$

(**Ans.** 44.4 ms^{-}.)

2. The distance of nearest star is 41 Pm. Convert it into meter. (**Ans.** 41×10^{15} m)

3. Write the value of 7 picometer in meters.

(**Ans.** 7×10^{-12} meter)

4. Write the numbers (*a*) 123 (*b*) 0.0050 in *standard exponential form.*

(**Ans.** (*a*) 1.23×10^2 (*b*) $0.0050 = 5.0 \times 10^{-3}$)

5. Verify the equation, $V = u + at$ with the help of dimensional analysis.

[**Hint,** dimensions of velocity; $V = \text{m s}^{-}$; $U = \text{m s}^{-}$; $a = \text{m s}^{-2}$; time, $t = \text{s}$. From dimensional point of view, L.H.S. dimensions, m s^{-} = R.H.S. dimensions, m s^{-}. So, the given equation is true.

6. Calculate the characteristic of the logarithm of (*i*) 2468 (*ii*) 24.68 (*iii*) 0.6789 (*iv*) 0.0732 (*v*) 0.0023 (*vi*) 0.0007.

Ans. (*i*) 3 (*ii*) 1 (*iii*) – 1 or $\bar{1}$ (*iv*) $\bar{2}$ or – 2 (*v*) $\bar{3}$ or – 3 (*vi*) $\bar{4}$ or – 4.

7. Convert 2×10^{-2} m^3 into litre. (**Ans.** 20 L)

8. Convert 0.50 Å into S.I. units. (**Ans.** 5.0×10^{-11} m)

9. What will be the value of –25°C on Kelvin scale?

(**Ans.** 248 K)

10. Write the value of 2 yotta in centimeter.

(**Ans.** 2×10^{24} cm)

2

CHAPTER

Significant Figures

2.1 SIGNIFICANT FIGURES

The total number of certain digits plus one doubtful digit (in a number used to express measurement) are called the significant figures.

2.2 RULES TO COUNT SIGNIFICANT FIGURES

These are given in following types.

Type : All non-zero digits are significant.

EXAMPLE 1. *Write the significant figures in (i) 235 (ii) 2.35 (iii) 45 (iv) 3.479*

SOLUTION. (*i*) $\overset{1}{2}\,\overset{2}{3}\,\overset{3}{5} \longleftarrow$ significant

The digits 1, 2 and 3 shown above 2, 3 and 5 digits indicate first, second and third significant figure respectively.

∴ Significant digits (or figures) = 3

(*ii*) $\overset{1}{2}.\overset{2}{3}\,\overset{3}{5} \longleftarrow$ significant as all are non-zero digits

Significant figures = 3

(*iii*) $\overset{1}{4}\,\overset{2}{5} \longleftarrow$ significant as all are non-zero digits

∴ Significant figures = 2

(*iv*) $\overset{1}{3}.\overset{2}{4}\,\overset{3}{7}\,\overset{4}{9} \longleftarrow$ significant as all are non-zero digits

∴ Significant figures = 4

Type : *Leading zeros* (*i.e.*, zeros which precede all the non-zero digits) *are* not significant.

EXAMPLE 2. *Count the significant figures in (i) 0.2 (ii) 0.03 (iii) 0.000456*

SOLUTION. (*i*) $0.\overset{1}{2} \longleftarrow$ significant because one zero that precedes non-zero digit 2, is leading zero.

∴ no. of significant figures = 1

(*ii*) $0.0\overset{1}{3} \longleftarrow$ significant because two zeros which precede non-zero digit 3, are leading zeros.

∴ no. of significant figures = 1

(*iii*) $0.000\overset{1}{4}\overset{2}{5}\overset{3}{6} \longleftarrow$ significant because four zeros which precede non-zero digits (456) are leading zeros. Hence, no. of significant figures = 3.

Type. *Captive zeros* (*i.e.*, zeros between non-zero digits) are significant.

EXAMPLE 3. *How many significant figures are there in (i) 4005 (ii) 3.04 (iii) 22.2007 ?*

SOLUTION. (*i*) $\overset{1}{4}\overset{2}{0}\overset{3}{0}\overset{4}{5} \longleftarrow$ significant because all the zeros are captive zeros.

So, the no. of significant figures = 4

(*ii*) $\overset{1}{2}\overset{2}{2}.\overset{3}{2}\overset{4}{0}\overset{5}{0}\overset{6}{7} \longleftarrow$ significant because all the zeros are captive zeros.

So, the number of significant figures = 6.

Type. Trailing zeros (*i.e.*, zeros at the right end of a number) are significant if the number contains a decimal point. Greater the number of zeros to the right of decimal point indicate greater accuracy in measurement.

EXAMPLE 4. *Write the number of significant figures in (i) 0.0300 (ii) 71.0.*

SOLUTION. (*i*) $0.0\overset{1}{3}\overset{2}{0}\overset{3}{0} \longleftarrow$ significant because the given number contains a decimal point and two zeros are to the right of decimal point.

So, the number of significant figures = 3 (*ii*) $\overset{1}{7}\overset{2}{1}.\overset{3}{0} \longleftarrow$ significant because the given number contains a decimal point and the zero is to the right of decimal point.

So, the number of significant figures = 3.

EXAMPLE 5. *Which out of the following represents most accurate measurement? (i) 3.0 g (ii) 3.00 g (iii) 3.000 g.*

SOLUTION. Out of the given data, 3.000 g represents the most accurate measurement because it has greater number of zeros to the right of decimal point.

Type. When a number ends in zeros that are not to the right of a decimal point, the zeros are not necessarily significant.

EXAMPLE 6. *How many significant figures are in (i) 470 (ii) 11200 ?*

SOLUTION. (*i*) (*a*) $\overset{1}{4}\overset{2}{7}0 \longleftarrow$ Significant

(*b*) $\overset{1}{4}\overset{2}{7}\overset{3}{0} \longleftarrow$ Significant

So, 470 can have two or three significant figures.

(*ii*) (*a*) $\overset{1}{1}\overset{2}{1}\overset{3}{2}00 \longleftarrow$ Significant (*b*) $\overset{1}{1}\overset{2}{1}\overset{3}{2}\overset{4}{0}0 \longleftarrow$ Significant

(*c*) $\overset{1}{1}\overset{2}{1}\overset{3}{2}\overset{4}{0}\overset{5}{0} \longleftarrow$ Significant

So, 11200 can have three, four or five significant figures.

Type. *Exact numbers.* These are such numbers which are usually determined by counting (*e.g.*, 4 bananas, 5 apples, 10 pens; 4 and 3 in 4/3 of $4/3\ \pi r^3$; 2 in $2\pi r$ etc.) or which result from definition. (*e.g.*, one foot = 12 inches). These have as many significant figures as we wish.

EXAMPLE 7. How many significant figures are there in (i) 10 pencils (ii) 12 inches ?

SOLUTION. (*i*) 10 in 10 pencils and (*ii*) 12 in 12 inches have as many significant figures as we wish.

2.3 SCIENTIFIC NOTATION

Very small and very large numbers are generally expressed in the *exponential form*, called the scientific notation. In this notation, *every number is written as* :

$N \times 10^n$ where **N** = a *number with a single non-zero digit to the left of the decimal point and* **'n'** is *an integer.* In exponential notation, the numerical portion 'N' represents the number of significant figures.

EXAMPLE 8. *Express the following in scientific notation. (A) 5000 (B) 2342000. Also, write their number of significant figures.*

SOLUTION. (A) 5000. Writing single non-zero digit before decimal point, we have (*i*) 5.0×10^3. So, no. of significant figures in $\overset{1}{5}.\overset{2}{0}$ = 2 when the value is determined upto two significant figures.

(*ii*) $\overset{1}{5}.\overset{2}{0}\overset{3}{0} \times 10^3$ which has three significant figures when the value is determined upto three significant figures.

(*iv*) $\overset{1}{5}.\overset{2}{0}\overset{3}{0}\overset{4}{0} \times 10^3$ which has four significant figures when the value is determined upto four significant figures.

(B) 2342000. Writing single non-zero digit before decimal point, we have, $\overset{1}{2}.\overset{2}{3}\overset{3}{4}\overset{4}{2} \times 10^6$. So, the number of significant figures = 4.

2.4 ROUNDING OFF FIGURES

In order to get the required number of significant figures, following rules for rounding off digits are used.

Type. If the digit, coming after the required number of significant figures, is less than 5, the preceding digit is not changed *i.e.,* the digit less than 5 is dropped.

EXAMPLE 9. *Round off 7.14262 to two significant figures.*

SOLUTION. 7.14262 rounds to **7.1** to get two significant figures. Here, the digit 4 (after 1) is less than 5 and hence dropped.

Type. If the digit, coming after the required number of significant figures, is more than 5, the preceding digit is increased by one.

EXAMPLE 10. *Round off 2.837 to three significant figures.*

SOLUTION. 2.837 rounds to 2.84 to get three significant figures. Here, the digit 7 (after 3) is more than 5. So, the preceding digit 3 is increased by one to get 4.

Type. If the digit coming after the required number of, significant figures, is 5, the preceding digit is increased by one if it is odd (*i.e.*, not divisible by 2) and the preceding digit is not changed if it is even (*i.e.*, divisible by 2).

EXAMPLE 11. *Round off (i) 4.5675 and (ii) 4.5685 to four significant figures.*

SOLUTION. (*i*) 4.5675 rounds to 4.568 because the preceding digit to 5 is odd *i.e.,* 7 (not divisible by 2). So, 1 is added to 7 to get 8. So, the correct answer is 4.568.

(*ii*) 4.5685 rounds to 4.568 because the preceding digit to 5 is even i.e., 8 (divisible by 2). So, the preceding digit (8) to 5 is not changed.

Type. While rounding off to get required number of significant figures, it is incorrect to round sequentially.

EXAMPLE 12. *Round off 8.5349 to three significant figures.*

SOLUTION. Given : $8.53\underset{\uparrow}{4}9$

Look only at the first number (*i.e.*, 4) to the right of the 3. Since, 4 is less than 5, it is dropped. So, the correct answer is **8.53**.

> **Note.** It is *not correct* to round 4 to 5 (because 9 > 5) to get 8.535 and then round it to get 8.54 (because the digit 3 before 5 is odd and hence increased by 1 to get 4).

2.5 ADDITION OR SUBTRACTION OF A NUMBER OF TERMS, INVOLVING SIGNIFICANT FIGURES

While carrying out *addition* or *subtraction* of a number of terms, the result should be reported to the same number of *decimal places* as that of the *term with least* number of decimal places.

EXAMPLE 13. *Add (i) 11.0 to 0.5512 (ii) 13.41 to 0.05512.*

SOLUTION.

1 ⟵ one decimal place
(*i*) 11.0
1234 ⟵ four decimal places
+ 0.5512
11.5512
1
= 11.6 **Ans.** (up to one decimal place being least out of 1 and 4 decimal places).

12 two decimal place
(*ii*) 13.41
12345 five decimal places
+ 0.05512
13.46512
12
= 13.46 **Ans.** (up to two decimal places, being least out of 2 and 5 decimal places).

EXAMPLE 14. *Perform the following calculation*

9.2306 – 0.046

making sure that the answer has proper number of significant figures.

SOLUTION.

1234 ⟵ four decimal places
9.2306
123 ⟵ three decimal places
– 0.046
9.1846
= 9.185 **Ans.** (up to three decimal places, being least out of 3 and 4 decimal places)

2.6 MULTIPLICATION OR DIVISION OF A NUMBER OF TERMS, INVOLVING SIGNIFICANT FIGURES

Type. While carrying out multiplication or division, the number of significant figures in the final answer should not be greater than the number of *significant figures* in the *least* precise factor.

EXAMPLE 15. *Perform the following calculations.*

4.3 m × 5.00 m

SOLUTION.

12 ⟵ Two significant figures
4.3 m
123 ⟵ Three significant figures
× 5.00 m
21.500 m^2

In this question, the number of significant figures in the least precise factor is two. So the correct answer is **21 m^2.**

EXAMPLE 16. *Perform the following calculations.*

0.3566 ÷ 6.1

SOLUTION.

1234 ⟵ four significant figures
0.3566
12 ⟵ two significant figures.
6.1

$$\therefore \quad \frac{0.3566}{6.1} = 0.058459016 = 0.058 \textbf{ Ans.}$$

In this question, out of four and 2 significant figures, 2 being least number, so the result will be given in two significant figures.

Type. If the mathematical calculations involve more than one *steps,* then the rounding off figures must be done only in the *final answer.*

EXAMPLE 17. *Using the concept of rounding off figures, perform the following calculations.*

(*i*) $\dfrac{3.120 \times 6.7}{273.15}$ (*ii*) $230 \times 0.0234 + 76$

SOLUTION. (*i*) $\dfrac{3.120 \times 6.7}{273.15} = \dfrac{20.904}{273.15} = 0.076529379$

$$= 0.076 = 7.6 \times 10^{-2}.$$

The final result must be rounded off to two significant figures because 6.7 (the least precise value) has two significant figures. So, the correct answer is 7.6×10^{-2}.

Now let us round off the intermediate results and get the result. $\dfrac{3.120 \times 6.7}{273.15} = \dfrac{20.904}{273.15} = \dfrac{21}{273.15}$ (rounded to two significant figures)

Now $\dfrac{21}{273.15} = 0.07688$. When this result is rounded off to two significant figures, the result will be 0.077 *i.e.,* 7.7×10^{-2}. This result is different to the result in which rounding off was done at the end. So, the result **7.7×10^{-2} is wrong.**

(*ii*) $230 \times 0.0234 + 76 = 5.382 + 76 = 81.382$. Since 76 contains only number up to decimal place, the correct answer is 81.

EXAMPLE 18. *State the number of significant figures in each of the following.*

(*i*) *23400 if the measurement is made up to nearest 1 cm.*

(*ii*) *23400 if the measurement is made up to nearest 10 cm.*

SOLUTION. (*i*)

12345 ⟵ Significant figures

$$\frac{23400}{1} = 23400$$

So, there are five significant figures.

(*ii*) $$\frac{23400}{10} = \overset{1234 \longleftarrow \text{ Significant figures}}{2340}$$

So, there are four significant figures.

Example 19. *According to 1981 census, population of Delhi is 1602000. Express it in scientific notation and calculate the number of significant figures.*

Solution. Population = 1602000. Writing single non-zero digit before decimal point, we have,

$$\overset{1234 \longleftarrow \text{Four significant figures}}{1.602} \times 10^{6}.$$

So, it has four significant figures.

Example 20. *The mass of H-atom is* 1.674×10^{-24} *g. Express it in decimal notation.*

Solution. $1.674 \times 10^{-24}\ \text{g} = \frac{1674}{1000} \times 10^{-24}\ g = \frac{1674}{10^{27}}$

$$= 1674 \times 10^{-27}.$$

Since the number of zeros after decimal point = 27 – 4 (∵ 1674 has four digits) = 23, the correct answer = 0.000, 000, 000, 000, 000, 000, 000, 001, 674

Example 21. *There are approximately 25,000,000,000,000 red cells in an average human being. Express the number of these red blood cells in scientific notation.*

Solution. Scientific notation = 2.5×10^{13} because decimal point is inserted on the right of first digit of a number.

Example 22. *A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL and 25.0 mL. The number of significant figures in the average titre value is what?* **(IIT-JEE, 2010)**

Solution. Average titre value = [(25.2 + 25.25 + 25.0)/3] = 25.15. Since in addition, result is reported in same number of decimal places as that of term with least number of decimal places, so 25.15 is rounded off to 25.2 to get three significant figures.

Example 23. *How many significant figures are there in each of the following measurements. (a) 10504 g (b) 0.000079 m (c) 800 L (d) 0.03080 mL?*

Solution. (*a*) 5 (*b*) 2 because of 79 only (*b*) ambiguous (*d*) 4 because of 3080 only.

Example 24. *Express the following in scientific notation. (a) 10504 g (b) 0.000079 cm (c) 802 L (d)* 105 g cm^{-3}.

Solution. (*a*) 1.0504×10^{4} g (*b*) 7.9×10^{-5} m (*c*) 8.02×10^{2} L (*d*) 1.05×10^{2} g cm^{-3}

Example 25. *Express the following numbers to four significant figures. (i) 5.607892 (ii) 32.392800 (iii)* 1.78986×10^{3} *(iv) 0.0078371.*

Solution. (*i*) 5.608 because the digit after 7 is more than 5 and one is added to 7. (*ii*) 32.39 because the digit after 9 is 2 which is less than five and hence rejected (*iii*) 1.790×10^{3} (*iv*) 0.007837.

Example 26. *A liquid weighing 100.1 g has a volume of 80.1 mL. Calculate the density of the liquid to the appropriate number of significant figures.*

Solution. Density = Mass/Volume = 100.1 g/80.1 mL = 1.24968789. In case of division, the answer is given in such a way that the final answer should not be greater than the number of significant figures in the least precise factor. Here least number of significant figures are three (in 80.1)

∴ Result is 1.25 g $(\text{mL})^{-}$

Example 27. *Which is the correct reading that has been recorded from a device calibrated to one tenth of a unit. (i) 5.452 or 5.45 or 5.4 (ii) 10.25 or 10.256 or 10.2 mL.*

Solution. Since the device is calibrated to one tenth of a unit (*i.e.*, 1/10 or 0.1), hence the correct answer will represent only one digit towards right side of decimal point. Hence answer for (*i*) is 5.4 and for (*ii*) is 10.2.

Example 28. *Perform the following calculations, making sure that each answer has the proper number of significant figures. Assume that each number is the result of a measurement. (i) 4.8 × 392 (ii) 7.255 ÷ 81.334 (iii) 14.5403 – 0.032.*

Solution. (*i*) 4.8 × 392 = 1881.6 = 1882. (*ii*) (7.255/81.334) = 0.08918 = 0.08920 because the least number of significant figures in given data are four *i.e.*, in 7.255 (*iii*) 14.5403 – 0.032 = 14.5083 = **14.508** because least number of digits after decimal are three *i.e.*, in 0.032.

Example 29. *What is the total volume on mixing 1.037 L of water with 5.44 mL of water ?*

Solution. 5.44 mL = (5.44/1000) L = 0.00544 L

∴ Total volume after mixing

= 1.037 L + 0.00544 L = 1.04244

= **1.042 L** **Ans.** (because least number of digits after decimal are three *i.e.*, in 1.037).

Example 30. *Express the following numbers to four significant figures*

(*i*) *5.607892* (*ii*) *32.392800*

(*iii*) *1.78986 ×* 10^{3} (*iv*) *0.007837.*

Solution. Four significant figures in (*i*) 5.607892 are **5.608** because the digit 8 to the right of 7 is more than 5 and hence '1' is to be added to 7 to get 8; in (*ii*) 32.392800 are **32.39** because the digit 2 to the right of 9 is less than 5 and hence 2 is to be rejected; in (*iii*) 1.78986×10^{3} are 1.790×10^{3} because of the reason shown in (*i*) above; in (*iv*) 0.007837 are 0.007837 because zeroes before first non-zero digit are not significant.

Example 31. *Which is the correct reading that has been recorded from a device calibrated to one hundredth of a unit ?*

(*i*) *5.452 or 5.45 or 5.4 g* (*ii*) *10.25 or 10.256 or 10.2 mL.*

Solution. Since 1/100 = 0.01, so, the correct answer will be in which there are two digits after decimal. So, the correct answer is (*i*) 5.45 g and (*ii*) 10.25 mL.

2.7 AIEEE PATTERN EXAMPLES

EXAMPLE 32. *The decimal equivalent of 3/5 may be written upto four significant figures are :*

(*a*) *0.6* (*b*) 6.0×10^{-1}

(*c*) *0.6000* (*d*) 0.06000

SOLUTION. 3/5 = 0.6. It can be written up to four significant figures as, 0.6000. So, the correct answer is (*c*).

EXAMPLE 33. *Two samples were weighed using different balances : (i) 3.529 g (ii) 0.40 g.*

How would the total weight of the sample be reported ?

(*a*) *3.929 g* (*b*) *3 g*

(*c*) *3.9 g* (*d*) *3.93 g*

[CET, Sample paper, 1994]

SOLUTION.

Add 3.529 g (number has three decimal places)
+ 0.40 g (number has two decimal places).
3.929 g

Since the answer is to be given for two decimal places (the least precise factor), so, the correct answer is **3.93 g.** So, the correct answer is (*d*).

EXAMPLE 34. *Calculate the correct result using the concept of significant figures. 4.26 – (15.635/5.0).*

(*a*) *1.1* (*b*) *1.13*

(*c*) *1.133* (*d*) *None of these.*

SOLUTION. $4.26 - \dfrac{15.635}{5.0} = 4.26 - 3.127 = 1.133$. This question involves multiple steps. So, the rounding off is done in the final result. So, the correct result = 1.13 because the least number of decimal places (least precise factor) is two (in 4.26). So, the correct answer is (*b*).

EXAMPLE 35. *The radius of a proton at the centre is* 1.5×10^{-5} *m while the radius of H-atom is* 5.32×10^{-11} *m. The ratio of radius of H-atom to the radius of proton is :*

(*a*) 3.5467×10^{-6} (*b*) 3.546×10^{-6}

(*c*) 3.54×10^{-6} (*d*) 3.5×10^{-6}.

SOLUTION. $\text{Ratio} = \dfrac{\text{Radius of H-atom}}{\text{Radius of Proton}} = \dfrac{5.32 \times 10^{-11}\ \text{m}}{1.5 \times 10^{-5}\ \text{m}}$ $= 3.5467 \times 10^{-6}$. In division, the number of significant figures in the final answer should not be greater than the number of significant figures in the least precise factor. The least number of significant figures = 2 (*i.e.*, in 1.5×10^{-5}). So, the correct answer is 3.5×10^{-6} *i.e.*, (*d*).

EXAMPLE 36. *The Rydberg constant is* $1.097373177 \times 10^{7}$ m^{-}. *It can be expressed to three significant figures as :*

(*a*) $1.0974 \times 10^{7}\ m^{-}$ (*b*) $1.10 \times 10^{7}\ m^{-}$

(*c*) $1.09 \times 10^{7}\ m^{-}$ (*d*) $1.10\ m^{-}$

SOLUTION. In 1.097373177, the digit to the right of 9 is 7 which is more than 5. So, one (1) is to be added to 9 to get 10. So, the three significant figures will be 1.10. Hence, the answer is $1.10 \times 10^{7}\ \text{m}^{-}$. So, correct answer is (*b*).

EXAMPLE 37. *1°C rise in temperature is equal to rise of :*

(*a*) *9/5° F* (*b*) *2° F*

(*c*) *17° F* (*d*) *5/9°F*

SOLUTION.

$$100°\,\text{C} = 180°\,\text{F}$$
$$1°\,\text{C} = \frac{180}{100} = \frac{9°}{5}F.$$

So, the correct answer is, (*a*).

EXAMPLE 38. *The number of significant figures in* $N_0 = 6.022 \times 10^{23}$ *i.e., Avogadro's number is :*

(*a*) *23* (*b*) *4*

(*c*) *3* (*d*) 19

SOLUTION. 6.022×10^{23} has four significant figures because in the exponential notation (*e.g.*, 10^{23}), the numerical portion (6.022) represents significant figures. So, the correct answer is (*b*).

EXAMPLE 39. *(4.50 ×* 10^{2} *mL) – (0.0245 L) can be written to correct significant figures:*

(*a*) 0.4255×10^{2} (*b*) 4.255×10^{2}

(*c*) 42.55×10^{2} (*d*) 4.26×10^{2}.

SOLUTION. Given :

(*i*) 4.50×10^{2} mL

(*ii*) $0.0245\ \text{L} = \dfrac{245}{10000} \times 1000\ mL$

$= 24.5\ \text{mL} = 0.245 \times 10^{2}\text{mL}.$

So, we have : 4.50×10^{2} mL (two decimal places)
$- 0.245 \times 10^{2}$ mL (three decimal places)
$= 4.255 \times 10^{2}$ mL

Since, the result pertains to least decimal places (= 2), $4.255 \times 10^{2}\ \text{mL} = 4.26 \times 10^{2}\ \text{mL}$. So, the correct answer is (*d*).

EXAMPLE 40. *Which one of the following numbers does not have four significant figures ?*

(*a*) *0.1234* (*b*) *0.0123*

(*c*) *1.111* (*d*) *13.12.*

SOLUTION. Out of the given data, (*b*) (= 0.0123) does not have four significant figures because leading zeros are not significant. So, the correct answer is (*b*).

EXAMPLE 41. *Forty thousand with three significant figures is written as :*

(*a*) 40.000×10^{2} (*b*) 4.00×10^{3}

(*c*) 4.00×10^{4} (*d*) 40.0×10^{4}

SOLUTION. 40,000 can be written in exponential form. In this form, the numerical portion N in $N \times 10^{n}$ (where N = a number with a single non-zero digit to the left of the decimal point) represents the number of significant figures. So, 4.00×10^{4} is the correct exponential form. It has three significant figures (= 4.00). So, the correct answer is (*c*).

EXAMPLE 42. *The value of* $(14.5)^2$ *up to correct number of significant figures is :*

(*a*) *210.25* (*b*) *210.2*

(*c*) *210.3* (*d*) *210*

SOLUTION. $(14.5)^2 = 14.5 \times 14.5 = 210.25$. In a multiplication process, the correct answer is written up to the least number of significant figures present in question. In the present case, there are three significant figures (in 14.5). So, correct answer is 210 *i.e.*, (*d*) which has three significant figures.

EXAMPLE 43. *The number of significant figures in* π *are :*

(*a*) *3* (*b*) *4*

(*c*) *8* (*d*) *infinite number*

SOLUTION. Since π (= 22/7) is an exct number *i.e.*, constant, it has infinite number of significant figures. So, the correct result is (*d*).

PRACTICE PROBLEMS

1. Round off 3.537 to two significant figures. (**Ans.** 3.5)
2. Express 3.01×10^{-6} in decimal notation. (**Ans.** 0.000,003,01)
3. Find the number of significant figures in the sum of 8.01, 10.11 and 9.123. (**Ans.** 4)
4. Multiply 2.1 m and 1.50 m. (**Ans.** 3.2 m^2)
5. Divide 0.1246 by 3.6 (**Ans.** 0.034)
6. Round off 2.2315 to four significant figures (**Ans.** 2.232)
7. Round off 1.12225 to five significant figures. (**Ans.** 1.1222)
8. Find the value and number of significant figures in the multiplication of 1.1 with 1.111. (**Ans.** 1.2,2)
9. Express 4000 in scientific notation (**Ans.** 4.0×10^3)
10. Solve $245 \times 0.0125 + 55 = ?$ (**Ans.** 58)

3

CHAPTER

Equivalent Weight

3.1 EQUIVALENT WEIGHT

Equivalent weight of an element or a compound is the number of parts by weight of that element or compound that combine with 1 part (or more exactly 1.008 parts) by weight of hydrogen, 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

Gram equivalent weight. When the weight of an element or a compound is expressed in gram, it is called its gram equivalent weight.

Elements having more than one valency values, have different equivalent weights and can be found by the relation.

$$\textbf{Equivalent weight of an element} = \frac{\textbf{Atomic weight of the element}}{\textbf{Valency of the element}}$$

For Example. At. wt. of Cu = 63.5 a.m.u. while valency of cuprous (Cu^+) is 1 and that of cupric (Cu^{2+}) is 2. So, eq. wts. of Cu^{+1} and Cu^{2+} are 63.5/1 and 63.5/2 *i.e.*, 63.5 a.m.u and 31.75 a.m.u respectively.

3.2 DIFFERENT METHODS TO DETERMINE EQUIVALENT WEIGHT OF ELEMENTS

I. **Hydrogen displacement method.** In this method, a known weight of the metal is treated with excess of dilute acid. H_2 gas so produced is collected over water and the volume so collected is converted to NTP or STP by the use of gas equation:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{or} \quad V_2 = \frac{P_1V_1T_2}{P_2T_1}.$$

P_1, V_1 and T_1 are given values of pressure, volume and temperature (in kelvin) while at NTP, P_2 = 760 mm, V_2 = ? and T_2 = 273 K. The equivalent weight of the metal is found by the relation :

$$\text{Eq. wt. of metal} = \frac{\text{wt. of metal}}{V_{NTP} \text{ of } H_2 \times 0.00009\ g} \times 1.008$$

$$\text{or; Eq. wt. of metal} = \frac{\text{Wt. of metal}}{V_{NTP} \text{ of } H_2 \text{ in mL}} \times 11200$$

Eq. wt. of a radical like NO_3^-, CO_3^{2-}, PO_4^{3-} etc.

$$= \frac{\text{Radical wt.}}{\text{valency}}$$

$$\textit{e.g.}, \text{ eq. wt. of } CO_3^{2-} = \frac{12+(3\times16)}{2} = 30.$$

EXAMPLE 1. *0.257 g of a metal when treated with excess dil. H_2SO_4, liberated 120 mL of H_2 at NTP. Calculate the equivalent weight of the metal.* **[AMU, 2010]**

SOLUTION. wt. of metal = 0.257 g;

V_{NTP} = 120 mL. We know that :

$$\text{Eq. wt. of a metal} = \frac{\text{wt. of metal}}{V_{NTP} \text{ of } H_2} \times 11200$$

$$= \frac{0.257\ g \times 11200\ mL}{120\ mL} = \textbf{23.99 g Ans.}$$

EXAMPLE 2. *A compound of hydrogen with another element was found to contain 1.25% hydrogen. Calculate the equivalent weight of the element.*

SOLUTION. Wt. of H_2 = 1.25 g; weight of element = 100 – 1.25 = 98.75 g. We know that :

$$\frac{\text{wt. of element}}{\text{wt. of } H_2} = \frac{\text{Eq. wt. of element}}{\text{Eq. wt. of } H_2\ (=1.008)};$$

$$\frac{98.75\ g}{1.25\ g} = \frac{\text{Eq. wt. of element}}{1.008}.$$

$$\therefore \text{ Eq. wt. of element} = \frac{98.75\times1.008}{1.25} = \textbf{79.63 Ans.}$$

EXAMPLE 3. *3.1 g of a metal was treated with excess of HCl. As a result, 1100.4 mL of H_2 was collected at 15°C and 750 mm pressure. Calculate the equivalent weight of the metal. Aqueous tension at 15°C = 12.5 mm; wt. of 1 mL of H_2 at NTP = 0.00009 g.*

Solution. Wt. of metal = 3.1 g;

P_1 = 750 mm – 12.5 mm = 737.5 mm;

V_1 = 1100.4 mL;

T_1 = 15 + 273 = 288 K;

At. *NTP*, P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

Using gas equation,

We have : $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\quad V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2};$$

$$V_2 = \frac{750\text{ mm}\times 1100.4\text{ mL}\times 273\text{ K}}{288\text{ K}\times 760\text{ mm}}$$

= 1029.4 mL.

wt. of 1 mL of H_2 = 0.00009 g

∴ wt. of 1029.4 mL of H_2 = 0.00009 × 1029.4 g

= 0.092646 g.

$$\text{We know: }\frac{\text{wt. of metal}}{\text{wt. of H}_2\text{ at NTP}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of H}_2\,(=1.008)}$$

$$\therefore\ \text{Eq. wt. of metal} = \frac{\text{wt. of metal}}{\text{wt. of H}_2\text{ at }NTP}\times 1.008$$

$$= \frac{3.1\times 1.008}{0.092646} = \mathbf{33.7\ Ans.}$$

Example 4. *5.47 g of magnesium metal reacted completely with 14.31 g of a non-metal. The compound of this non-metal with hydrogen contains 3.1% hydrogen. Calculate the equivalent weight of magnesium.*

Solution. Wt. of Mg = 5.47 g; wt. of non-metal that combined with Mg = 14.31 g; wt. of H_2 = 3.1 g; wt. of non-metal in hydrogen compound of non-metal = 100 – 3.1 = 96.9 g

96.9 g non-metal contain H_2 = 3.1 g

$$\therefore\ 14.31\text{ g non-metal contain H}_2 = \frac{3.1}{96.9}\times 14.31$$

= 0.46 g.

We know :

$$\text{Eq. wt. of metal} = \frac{\text{wt. of metal}}{\text{wt. of H}_2}\times 1.008$$

$$= \frac{5.47}{0.46\,g}\times 1.008 = \mathbf{11.98\ Ans.}$$

I. Oxide formation method

$$\text{Use: }\frac{\text{wt. of the metal}}{\text{wt. of oxygen at }NTP} = \frac{\text{Eq. wt. of the metal}}{\text{Eq. wt. of oxygen }(=8)} \quad ...(1)$$

II. Reduction of oxide method. Use above relation (1).

Example 5. *0.141 g of a metal when dissolved in dil. HCl evolved 31.1 mL of H_2 when collected over water at 13°C and 739.2 mm pressure. Calculate the weight of oxygen present in 102 g of the oxide of the metal (aqueous tension at 13°C = 11.2 mm),*

Solution. (*i*) Wt. of metal = 0.141 g.

According to gas equation :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\quad\text{or}\quad V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

where at *NTP*,

T_2 = 273 K, P_2 = 760 mm, V_2 = ?

P_1 = 739.2 – 11.2 = 728 mm, V_1 = 31.1 mL,

T_1 = 13 + 273 = 286 K.

$$\therefore\quad V_2 = \frac{728\ mm\times 31.1\ mL\times 273\ K}{286\ K\times 760\ mm} = 28.4\text{ mL.}$$

We know,

$$\frac{\text{wt. of metal}}{\text{wt. of H}_2\text{ at }NTP} = \frac{\text{Eq.wt. of metal}}{\text{Eq. wt. of hydrogen }(=1.008)}$$

$= V_2 \times 0.00009$

$$\therefore\ \text{Eq. wt. of metal} = \frac{\text{wt. of metal}\times 1.008}{28.4\times 0.00009\ g}$$

$$= \frac{0.141\ g\times 1.008}{28.4\times 0.00009\ g} = \mathbf{55.6}$$

(*ii*) Let wt. of metal = x g; wt. of oxygen = $(102 - x)$ g

$$\text{Eq. wt. of metal} = \frac{\text{wt. of metal}\times 8}{\text{wt. of O}_2};\ 55.6 = \frac{8x}{102-x}$$

∴(55.6 × 102) – 55.6 x = 8x; 63.6x = 5671.2

∴ x = 5671.2/63.6 = 89.17

∴ wt. of O_2 = 102 – 89.17 = **12.83 g Ans.**

Example 6. *0.426 g of a metallic oxide on heating in a current of hydrogen, liberated 0.12 g water. Calculate the equivalent weight of the metal.*

Solution. wt. of metal oxide = 0.426 g;

wt. of water = 0.12 g.

g. mol. wt. of water, H_2O = (2 × 1) + 16 = 18 g.

(*i*) 18g H_2O contain oxygen = 16 g

$$0.12\text{ g H}_2\text{O contain oxygen} = \frac{16\times 0.12}{18} = 0.107\text{ g}$$

∴ wt. of metal left behind = 0.426 – 0.107 g = 0.319 g,

$$\text{But }\frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of oxygen }(=8)}$$

$$\therefore\ \text{Eq. wt. of metal} = \frac{\text{wt. of metal}}{\text{wt. of oxygen}}\times 8$$

$$= \frac{0.319\,g\times 8}{0.107\,g} = \mathbf{23.8\ Ans.}$$

III. Chloride formation method

Use :

$$\frac{\text{wt. of metal}}{\text{wt. of chlorine at } NTP} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of chlorine } (= 35.5)}$$

EXAMPLE 7. *One gram of calcium combines with 4 g of bromine while 1 g of hydrogen combines with 80 g of bromine. Calculate the equivalent weight of calcium. (at.wt. of Br = 80).*

SOLUTION. (*i*) wt. of H_2 = 1 g; wt. of Br_2 = 80 g.

We know:

$$\frac{\text{wt. of bromine}}{\text{wt. of } H_2} = \frac{\text{Eq. wt. of bromine}}{\text{Eq. wt. of } H_2\ (=1.008)}$$

$$\therefore \text{ Eq. wt. of bromine} = \frac{\text{wt. of bromine} \times 1.008}{\text{wt. of } H_2}$$

$$= \frac{80 \times 1.008}{1} = \mathbf{80.64.}$$

(*ii*)
$$\frac{\text{wt. of Ca}}{\text{wt. of bromine}} = \frac{\text{Eq. wt. of Ca}}{\text{Eq. wt. of bromine } (= 80.64)}$$

$$\therefore \text{ Eq. wt. of Ca} = \frac{\text{wt. of Ca}}{\text{wt. of bromine}} \times 80.64$$

$$= \frac{1 \times 80.64}{4} = \mathbf{20.16\ Ans.}$$

EXAMPLE 8. *The oxide of a metal contains 47% oxygen. The bromide of the same metal contains 90% bromine. Calculate the equivalent weight of bromine.*

SOLUTION. Hint :

$$\text{Eq. wt. of metal} = \frac{\text{wt. of metal}}{\text{wt. of oxygen}} \times 8 = \frac{53 \times 8}{47} = \mathbf{9.02}$$

Eq. wt. of bromine

$$= \frac{\text{Eq. wt. of metal} \times \text{wt. of bromine}}{\text{wt. of metal}}$$

$$= \frac{9.02 \times 90}{10} = \mathbf{81.18\ \ Ans.}$$

IV. Metal displacement method

Use :

$$\frac{\text{weight of one metal}}{\text{weight of second metal}} = \frac{\text{Eq. wt. of one metal}}{\text{Eq. wt. of second metal}}$$

EXAMPLE 9. *1.212 g of zinc metal was heated with HNO_3 to dryness and as a result, 1.51 g of zinc oxide was formed. In another experiment, 0.56 g of zinc precipitated 0.551 g of copper from the copper salt solution. Calculate the equivalent weight of zinc as well as copper.*

SOLUTION. Hint. Wt. of Zn = 1.212 g;

wt. of ZnO = 1.51 g.

So, wt. of oxygen = 1.51 – 1.212 = 0.298 g.

$$\therefore \frac{\text{wt. of Zn}}{\text{wt. of oxygen}} = \frac{\text{Eq. wt. of Zn}}{\text{Eq. wt. of oxygen } (= 8)};$$

$$\text{Eq. wt. of Zn} = \frac{\text{wt. of Zn} \times 8}{\text{wt. of oxygen}} = \frac{1.212\ g \times 8}{0.298\ g}$$

$$= \mathbf{32.54\ \ Ans.}$$

$$\text{Eq. wt. of Cu} = \frac{\text{Eq. wt. of Zn} \times \text{wt. of Cu}}{\text{wt. of Zn}}$$

$$\therefore \quad = \frac{32.54 \times 0.551\ g}{0.56\ g} = \mathbf{32.02\ Ans.}$$

EXAMPLE 10. *When 1 g of zinc was treated with dil. H_2SO_4, 360 cm^3 of H_2 gas at 15°C and 758 torr. was liberated. When 1 g zinc was added to copper nitrate solution 0.965 g of copper was displaced. Calculate the equivalent weight of zinc and copper (1 L of H_2 gas weighs 0.09 g).*

SOLUTION.

(*i*) P_1 = 758 torr; $V_1 = 360\ cm^3$,
T_1 = 15 + 273 = 288 K;
P_2 = 760 torr; V_2 = ?, T_2 = 273 K.

Using gas equation, we have :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{758 \text{ torr.} \times 360\ cm^3 \times 273\ K}{288\ K \times 760 \text{ torr.}}$$

or $V_2 = 340.4\ cm^3$.

1000 cm^3 (= 1L) of H_2 weighs = 0.09 g

$$\therefore 340.4\ cm^3 \text{ of } H_2 \text{ weighs} = \frac{0.09 \times 340.4}{1000}\ g = 0.0306\ g.$$

$$\text{Eq. wt. of Zn} = \frac{\text{wt. of Zn} \times 1.008}{\text{wt. of } H_2 \text{ at } NTP} = \frac{1\ g \times 1.008}{0.0306\ g}$$

= **32.9 g Ans.**

(*ii*) wt. of Zn = 1.0 g; wt. of Cu = 0.965 g.

$$\text{Eq. wt. of Cu} = \frac{\text{Eq. wt. of Zn} \times \text{wt. of Cu}}{\text{wt. of Zn}}$$

$$= \frac{32.9 \times 0.965\ g}{1\ g} = \mathbf{31.75\ \ Ans.}$$

V. Double decomposition method.

Use :
$$\frac{\text{wt. of salt taken}}{\text{wt. of precipitated salt}} = \frac{\text{Eq. wt. of salt taken}}{\text{Eq. wt. of precipitated salt}}$$

Note. Eq. wt. of a radical like SO_4^{2-}

$$= \frac{\text{Formula wt. of Radical}}{\text{Valency of radical}}$$

EXAMPLE 11. *2.1 g of anhydrous barium chloride solution was treated with excess of dil. H_2SO_4. The weight of $BaSO_4$ ppt. after filtration, washing and drying was found to be 2.36 g. Calculate the equivalent weight of barium.*

SOLUTION. Wt. of $BaCl_2$ = 2.1 g; wt. of $BaSO_4$ = 2.36 g;

Eq. wt. of Ba = E;

$$\text{Eq. wt. of } Cl^- \text{ radical} = \frac{\text{Formula wt. of } Cl^- \text{ radical}}{\text{Valency of } Cl^-}$$

= 35.5/1 = 35.5;

$$\text{Eq. wt. of } SO_4^{2-} = \frac{\text{Formula wt. of } SO_4^{2-} \text{ radical}}{\text{Valency of } SO_4^{2-}}$$

$$= [32 + (4 \times 16)]/2 = 48.$$

$$\text{We know that}: \frac{\text{wt. of } BaCl_2}{\text{wt. of } BaSO_4} = \frac{\text{Eq. wt. of } BaCl_2}{\text{Eq. wt. of } BaSO_4};$$

$$\frac{2.1 \text{ g}}{2.36 \text{ g}} = \frac{E + \text{eq. wt. of } Cl^-}{E + \text{eq. wt. of } SO_4^{2-}} \text{ or } \frac{2.1\,g}{2.36\,g} = \frac{E + 35.5}{E + 48};$$

$$2.1\text{ E} + 48\,(2.1) = 2.36\text{ E} + 35.5\,(2.36);$$

$$2.1\text{ E} + 100.8 = 2.36\text{ E} + 83.78$$

$$0.26\text{ E} = 17.02;\ \text{E} = 17.02/0.26 = \mathbf{65.46\ Ans.}$$

EXAMPLE 12. *1.8 g of an acid when treated with excess of magnesium metal gave 2.34 g magnesium salt. Calculate the equivalent weight of the acid.*

SOLUTION.

$$\frac{\text{wt. of acid HX}}{\text{wt. of Mg} - \text{salt}} = \frac{\text{Eq. wt. of HX}}{\text{Eq. wt. of Mg} - \text{salt}}$$

$$\textit{i.e.,}\ \frac{\text{Eq. wt. of H} + \text{Eq. wt. of X}}{\text{Eq. wt. of Mg} + \text{Eq. wt. of X}};\ \frac{1.8\text{ g}}{2.34\text{ g}} = \frac{1 + \text{E}}{12 + \text{E}};$$

$$21.6\text{ g} + 1.8\text{ E} = 2.34\text{ g} + 2.34\text{ E};\ \ 0.54\text{ E} = 19.26\text{ g}$$

$$\therefore \quad \text{E} = \frac{19.26\text{ g}}{0.54} = \mathbf{35.67\ g}$$

$\therefore$ Eq. wt. of acid,

$$\text{HX} = \text{Eq. wt. of H} + \text{E} = 1 + 35.67$$

$$= \mathbf{36.67\ \ Ans.}$$

EXAMPLE 13. *Calculate the equivalent weight of sulphur dioxide in the following reactions.*

(*a*) $SO_2 + 2H_2S \longrightarrow 3\,S + 2H_2O$

(*b*) $5\,SO_2 + 2\,KMnO_4 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(*c*) *On heating in contact with tin, sulphuretted hydrogen (density 17) is converted into hydrogen without change of volume. Calculate the equivalent weight of sulphur from this data.* **(I.I.T. 1971)**

SOLUTION.

(*a*) Given reaction $SO_2 + 2H_2S \longrightarrow 3\,S + 2H_2O$ can be written as :

$$H_2S \longrightarrow H_2 + S] \times 2 \qquad ...(i)$$

$$SO_2 + 2H_2 \longrightarrow S + 2H_2O \qquad ...(ii)$$

$$\overline{2H_2S + SO_2 \longrightarrow 3\ S + 2\,H_2O.}$$

In reaction (*ii*)

$$SO_2 + 2H_2 \longrightarrow S + 2H_2O$$

$$32 + (2 \times 16) \qquad 2\,(2 \times 1)$$

$$= 64 \text{ parts } SO_2 \qquad = 4 \text{ parts H}$$

4 parts by weight of hydrogen react with SO_2 = 64 parts by wt.

$\therefore$ 1 part by weight of hydrogen react with $SO_2 = \frac{64}{4}$ = 16 parts by wt.

$\therefore$ Eq. wt. of SO_2 = **16 Ans.**

(*b*) The given reaction can be written as :

$$2\,KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3\,H_2O + 5O \qquad ...(i)$$

$$SO_2 + H_2O + O \longrightarrow H_2SO_4\ ] \times 5 \qquad ...(ii)$$

$32 + (2 \times 16)$ 16 parts

= 64 parts

$$\overline{2KMnO_4 + 5\,SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4.}$$

In partial equation (*ii*)

16 parts by wt. of oxygen react with SO_2 = 64 parts.

8 parts by wt. of oxygen react with $SO_2 = \frac{64}{16} \times 8$ = 32 parts.

$\therefore$ Eq. wt. of SO_2 = **32 Ans.**

(*c*) H_2S gives its own volume of H_2 because according to Avogadro's law, one molecule of H_2S contains one molecule of H_2. Hence

$$H_2\,S = 2H$$

$$(2 \times 1) + 32 \qquad 2 \times 1$$

$$= 34 \text{ parts} \qquad = 2 \text{ parts}$$

$\therefore$ wt. of S in $H_2S = 34 - 2 = 32$

2 parts by wt. of hydrogen reacts with sulphur = 32 parts

1 part by wt. of hydrogen reacts with sulphur $= \frac{32}{2}$ = 16 parts

$\therefore$ Eq. wt. of S = **16 Ans.**

EXAMPLE 14. *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?* **(I.I.T. 1979)**

SOLUTION.

Wt. of metal carbonate = 4.215 g;

$$P_1 = 700 \text{ mm},\ V_1 = 1336 \text{ mL},$$

$$T_1 = 27 + 273 = 300 \text{ K};\ \text{At } NTP,$$

$$P_2 = 760 \text{ mm},\ V_2 = ?,\ T_2 = 273 \text{ K}.$$

Using gas equation :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\qquad V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2};$$

$$V_2 = \frac{700\ mm \times 1336\ mL \times 273\ K}{300\ K \times 760\ mm}$$

$$\therefore \quad V_2 \text{ (at } NTP) = 1119.8 \text{ mL}$$

We know that :

$$\frac{\text{wt. of metal carbonate}}{V_{NTP} \text{ in mL}} \times 11200\ mL = \text{Eq. wt. of metal carbonate}$$

$$\therefore \quad \frac{4.215 \times 11200\ mL}{1119.8} = \text{Eq. wt. of metal carbonate}$$

$\therefore$ Eq. wt. of metal carbonate = 42.16

$\therefore$ Eq. wt. of metal = Eq. wt. of metal carbonate

$- \text{Eq. wt. of } CO_3^{2-}$

$= 42.16 - [12 + (3 \times 16)]/2$

$= 42.16 - 30 = \mathbf{12.16}$ **Ans.**

EXAMPLE 15. *What weight of a metal having equivalent weight 9 will give 1.14 g of its chloride?*

SOLUTION. Eq. wt. of metal chloride = Eq. wt. of metal + Eq. wt. of chlorine

$\therefore$ Eq. wt. of metal chloride = 9 + 35.5 = 44.5

For 44.5 g of metal chloride, wt. of metal needed = 9 g

For 1.14 g of metal chloride, wt. of metal needed $= \dfrac{9 \times 1.14}{44.5} = \mathbf{0.23\ g.}$ **Ans.**

EXAMPLE 16. *2.1 g of a metal carbonate left 1.01g of metal oxide on ignition. Calculate the equivalent weight of the metal.*

SOLUTION.

equivalent wt. of $CO_3^{2-} = [12 + (3 \times 16)]/2 = 30$

[$\because$ Valency of $CO_3^{2-} = 2$]

$$\frac{\text{wt. of metal carbonate}}{\text{wt. of metal oxide}} = \frac{\text{Eq. wt. of metal + eq. wt. of } CO_3^{2-}}{\text{Eq. wt. of metal + eq. wt. of oxygen}}$$

$$\frac{2.1\,g}{1.01\,g} = \frac{E + 30}{E + 8};\ 2.1\,E + 16.8 = 1.01\,E + 30.3$$

$2.1\,E - 1.01\,E = 30.3 - 16.8;\ 1.09\,E = 13.5; E = \mathbf{12.4}$ **Ans.**

3.3 EQUIVALENT WEIGHT OF OXIDANTS AND REDUCTANTS IN REDOX REACTIONS

An oxidant (or oxidising agent) is that whose oxidation number decreases in a redox reaction.

A reductant (or reducing agent) is that whose oxidation number increases in a redox reaction.

Oxidation number (O.N.) See chapter 16 on oxidation and reduction to calculate O.N.

Type. Equivalent weight of oxidant or reductant

$$= \frac{\text{Mol. wt. of oxidant or reductant}}{\text{No. of electrons gained or lost by the substrate}}$$

> **Note.** Only those ions are considered whose oxidation number undergoes a change on the reactant and product sides.

EXAMPLE 17. *Find the equivalent weights of each oxidant and reductant in the following reaction.*

$$FeSO_4 + KClO_3 \longrightarrow Fe_2(SO_4)_3 + KCl$$

SOLUTION. Writing the given equation in the ionic form and keeping those ions only whose oxidation number changes :

$$Fe^{2+} + Cl^{+5}O_3^{-} \longrightarrow Fe^{3+} + Cl^{-}$$

(*i*) $Fe^{2+} \longrightarrow Fe^{3+} + 1e^{-}$

$\therefore$ Eq. wt. of $FeSO_4$ (reductant)

$$= \frac{\text{Mol. wt. of } FeSO_4}{\text{no. of } e^{-}\text{s lost}} = \frac{56 + 32 + (4 \times 16)}{1} = \frac{152}{1} = \mathbf{152}\ \textbf{Ans.}$$

(*ii*) Cl^{+5} (of ClO_3^{-}) $+ 6e^{-} \longrightarrow Cl^{-}$

$\therefore$ Eq. wt. of $KClO_3$ (oxidant)

$$= \frac{\text{Mol. wt. of } KClO_3}{\text{no. of } e^{-}\text{s gained}} = \frac{39 + 35.5 + (3 \times 16)}{6} = \frac{122.5}{6} = \mathbf{20.42}\ \textbf{Ans.}$$

Type

Eq. wt. of an oxidant (or reductant)

$$= \frac{\text{Mol. wt. of oxidant (or reductant)}}{\text{no. of } \frac{1}{2}\text{O atoms that are formed from one molecule of oxidant (or no. of } \frac{1}{2}\text{O atoms that react with one molecule of reductant)}}$$

EXAMPLE 18. *Find the equivalent weight of potassium dichromate in the reaction*

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

(at wt., K = 39, Cr = 52, S= 32, O = 16)

SOLUTION. $K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

Here : $3O = 6 \times \left(\frac{1}{2}O\right)$

$\therefore$ Eq. wt. of $K_2Cr_2O_7$

$$= \frac{\text{Mol. wt. of } K_2Cr_2O_7}{\text{no. of ½O atoms that are formed from one molecule of } K_2Cr_2O_7}$$

$$= \frac{(2 \times 39) + (2 \times 52) + (7 \times 16)}{6} = \frac{78 + 104 + 112}{6} = \frac{294}{6} = \mathbf{49}\ \textbf{Ans.}$$

EXAMPLE 19. *Calculate the equivalent weight of potassium chlorate in the reaction :*

$$KClO_3 \longrightarrow KCl + 3O$$

(at. wt., K = 39, Cl = 35.5, O = 16)

SOLUTION.

$$KClO_3 \longrightarrow KCl + 3O$$

$$39 + 35.5 + (3 \times 16) \qquad 6 \times \left(\frac{1}{2}\,O\right)$$

$$= 122.5$$

$$\text{Eq. wt. of } KClO_3 = \frac{\text{Mol. wt. of } KClO_3}{\text{no. of } \frac{1}{2} \text{ O atoms formed in molecule of } KClO_3}$$

$$= \frac{39 + 35.5 + (3 \times 16)}{6} = \frac{122.5}{6}$$

$$= \mathbf{20.42 \ Ans.}$$

3.4 EQUIVALENT WEIGHT OF AN ELEMENT IN A REDOX REACTION

Type. Equivalent weight of an element in a redox reaction

$$= \frac{\text{At. wt. of element}}{\text{no. of electron (s) gained or lost during redox reaction by one atom of that element}}$$

EXAMPLE 20. *Calculate the equivalent weight of Mn^{4+} in, $Mn^{4+} \longrightarrow Mn^{2+}$ (at. wt., Mn = 55)*

SOLUTION. Reaction :

$$Mn^{4+} + 2e^- \longrightarrow Mn^{2+}$$

$$\therefore \text{ Eq. wt. of } Mn^{4+} = \frac{\text{At. wt. of Mn}}{\text{no. of electrons gained}}$$

$$= \frac{55}{2} = \mathbf{27.5 \ Ans.}$$

EXAMPLE 21. *If the molecular weight of $Na_2S_2O_3$ and I_2 are M_1 and M_2 respectively, then what will be the equivalent weight of $Na_2S_2O_3$ and I_2 in the following reaction*

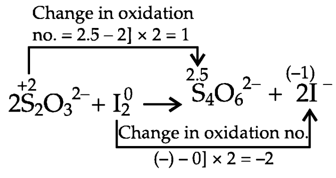
$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

(*a*) M_1, M_2 (*b*) $M_1, M_2/2$

(*c*) $2M_1, M_2$ (*d*) $M_1, 2M_2$

(*WB-JEE, 2011*)

SOLUTION.



$$\therefore \text{ Eq. wt. of } Na_2S_2O_3 = \frac{M_1}{\text{Change in O.N.}} = \frac{M_1}{1}$$

$$\text{Eq. wt. of } I_2 = \frac{M_2}{\text{Change in O.N.}} = \frac{M_2}{2}$$. So, the correct answer in (b).

3.5 EQUIVALENT WEIGHT OF A COMPOUND IN A REDOX REACTION

Type. Eq. wt. of a compound in a redox reaction

$$= \frac{\text{Mol. wt. of compound}}{\text{no. of electron(s) gained or lost during redox reaction by one molecule of that compound.}}$$

$$= \frac{\text{Mol. wt. of compound}}{\text{Change in oxidation number}}$$

EXAMPLE 22. *Calculate the equivalent weight of potassium permanganate ($KMnO_4$) in (i) neutral medium (ii) acidic medium (iii) alkaline medium, by oxidation number change method (at. wt., Mn = 55, K = 39, O = 16).* **(*MLNR, 1997*)**

SOLUTION. Mol. wt. of $KMnO_4 = 39 + 55 + (4 \times 16)$

$$= 158 \text{ g mol}^-$$

(*i*) In neutral medium : $Mn^{7+} + 3e^- \longrightarrow Mn^{4+}$

$\therefore$ Eq. wt. of $KMnO_4$

$$= \frac{\text{Mol. wt. of } KMnO_4}{\text{no. of electrons gained by one molecule of } KMnO_4}$$

$$= \frac{158}{3} = \mathbf{52.67 \ Ans.}$$

(*ii*) In acidic medium,

$$Mn^{7+} + 5\,e^- \longrightarrow Mn^{2+}$$

$$\therefore \text{ Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{\text{no. of electrons gained by one molecule of } KMnO_4}$$

$$= \frac{158}{5} = \mathbf{31.6 \ Ans.}$$

(*iii*) In alkaline medium, $Mn^{7+} + 1\,e^- \longrightarrow Mn^{6+}$

$$\therefore \text{ Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{\text{no. of electrons gained by one molecule of } KMnO_4}$$

$$= \frac{158}{1} = \mathbf{158 \ Ans.}$$

EXAMPLE 23. *Find the equivalent weight of $Na_2C_2O_4$ and $KMnO_4$ in the following redox reaction.*

$Na_2C_2O_4 + KMnO_4 \longrightarrow 2CO_2 + Mn^{2+}$ (acidic medium)

(at. wt., Na = 23, C = 12, O = 16, K = 39, Mn = 55).

SOLUTION. $Na_2C_2O_4 + KMnO_4 \longrightarrow 2CO_2 + Mn^{2+}$

(*i*) $C_2^{+3} \longrightarrow 2C^{+4} + 2e^-$

$$\therefore \text{ Eq. wt. of } Na_2C_2O_4 = \frac{\text{Mol. wt. of } Na_2C_2O_4}{\text{no. of electrons lost by one molecule of } Na_2C_2O_4}$$

$$= \frac{(2 \times 23) + (2 \times 12) + (4 \times 16)}{2}$$

$$= \frac{46+24+64}{2}$$

$$= \frac{134}{2} = \mathbf{67\ \ Ans.}$$

(*ii*) $Mn^{+7} + 5e^- \longrightarrow Mn^{+2}$

$$\therefore \quad \text{Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{\text{no. of electrons gained by one molecule of } KMnO_4}$$

$$= \frac{39 + 55 + (4 \times 16)}{5} = \frac{158}{5}$$

$$= \mathbf{31.6\ \ Ans.}$$

EXAMPLE 24. *Calculate the equivalent weight of* Fe_3O_4 *and* $KMnO_4$ *in the following reaction.*

$KMnO_4 + Fe_3O_4 \longrightarrow MnO_2 + Fe_2O_3$ *(neutral medium)*

(at. wt., K= 39, Mn = 55, O = 16, Fe = 56)

SOLUTION. Reaction : $KMnO_4 + Fe_3O_4 \longrightarrow MnO_2 + Fe_2O_3$

(*i*) $Mn^{+7} + 3e^- \longrightarrow Mn^{+4}$

[$\because$ O.N. of Mn in $KMnO_4$ = + 7]

$$\therefore \quad \text{Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt. of } KMnO_4}{\text{no. of electrons gained by one molecule of } KMnO_4}$$

$$= \frac{39+55+(4 \times 16)}{3}$$

$$= \frac{158}{3} = \mathbf{52.67\ \ Ans.}$$

(*ii*) $2Fe_3^{+\frac{8}{3}} \longrightarrow 3Fe_2^{+3} + 2e^-$

[$\because$ O.N. of Fe in $Fe_3O_4 = +\frac{8}{3}$; of Fe in Fe_2O_3

= + 3;

$\left(2 \times 3 \times \frac{8}{3}\right)$ *i.e.*, 16; (3 × 2 × 3) *i.e.*, 18 + $2e^-$ = 16]

$$2Fe_3^{+\frac{8}{3}} = 2e^-$$

$$\therefore \quad 1Fe_3^{+\frac{8}{3}} = 1e^-$$

$$\therefore \quad \text{Eq. wt. of } Fe_3O_4 = \frac{\text{Mol. wt. of } Fe_3O_4}{\text{no. of electrons lost by one molecule of } Fe_3O_4}$$

$$= \frac{(3 \times 56)+(4 \times 16)}{1}$$

$$= \frac{168+64}{1} = \frac{232}{1} = \mathbf{232\ \ Ans.}$$

EXAMPLE 25. *Find the value of equivalent weight of* $K_2Cr_2O_7$ *and* $H_2C_2O_4$ *in the following redox reaction.*

$K_2Cr_2O_7 + H_2C_2O_4 \longrightarrow 2Cr^{3+} + 2CO_2$

(at. wt., K = 39, Cr = 52, O = 16, C = 12, H = 1)

SOLUTION. Reaction :

$K_2Cr_2O_7 + H_2C_2O_4 \longrightarrow 2Cr^{3+} + 2CO_2$

(*i*) $Cr_2^{+6} + 6e^- \longrightarrow 2Cr^{3+}$

[$\because$ O.N. of Cr in $K_2Cr_2O_7$ = + 6]

$$\therefore \quad \text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt. of } K_2Cr_2O_7}{\text{no. of electrons gained by one molecule of } K_2Cr_2O_7}$$

$$= \frac{(2 \times 39)+(2 \times 52)+(7 \times 16)}{6}$$

$$= \frac{294}{6} = \mathbf{49\ \ Ans.}$$

(*ii*) $C_2^{+3} \longrightarrow 2C^{+4} + 2e^-$

[$\because$ O. N. of C in $H_2C_2O_4$ = + 3; of C in CO_2 = + 4]

$$\therefore \quad \text{Eq. wt. of } H_2C_2O_4 = \frac{\text{Mol. wt. of } H_2C_2O_4}{\text{no. of electrons lost by one molecule of } H_2C_2O_4}$$

$$= \frac{(2 \times 1)+(2 \times 12)+(4 \times 16)}{2}$$

$$= \frac{90}{2} = \mathbf{45\ \ Ans.}$$

EXAMPLE 26. *Calculate the equivalent weight of* NO_3^- *in the following redox reaction.*

$NO_3^- \longrightarrow N_2$

(at. wt., N = 14, O = 16)

SOLUTION. $NO_3^- \longrightarrow N_2$

$2N^{+5} \longrightarrow N_2^0 + 10e^-$

[$\because$ In NO_3^-, O. N. of N + 3 (O.N. of O) = – 1

$2N^{+5} = 10e^-$ $\quad\therefore$ O.N. of N + 3 (– 2) = – 1

$\therefore 1\,N^{+5} = \frac{10}{2} = 5e^-$ $\quad$ or O.N. of N = + 5]

$$\therefore \text{Eq. wt. of } NO_3^- = \frac{\text{Mol. wt. of } NO_3^-}{\text{no. of electrons lost by one molecule of } NO_3^-}$$

$$= \frac{14+(3 \times 16)}{5} = \frac{62}{5} = \mathbf{12.4\ \ Ans.}$$

3.6 EQUIVALENT WEIGHT OF A METAL IN ITS COMPOUND

Example 27. *An unknown metallic carbonate (mass 3.98 g) was heated and CO_2 gas evolved was found to occupy 1343 mL volume at 37°C and 720 mm pressure. Calculate the equivalent weight of the metal.*

Solution. Let metal carbonate = $M_2(CO_3)_n$; at. wt. of M = a; $T = 37 + 273 = 310$ K;

$P = \frac{720}{760}$ atm; $R = 0.0821$ L atm. K^{-} mol^{-}.

Reaction. $M_2(CO_3)_n \longrightarrow M_2O_n + nCO_2$...(A)

Mol. wt. $2a + [12 + (3 \times 16)] \times n$ $\quad n[12 + (2 \times 16)$

$= 2a + 60n$ $\quad = 44n$

To find weight of CO_2.

$$PV = nRT;$$

$$PV = \frac{\text{wt.}}{\text{Mol. wt.}} \times RT$$

$$\therefore \quad \text{wt. of } CO_2 = \frac{PV \times \text{mol. wt. of } CO_2}{RT}$$

$$= \frac{720}{760}\,\text{atm} \times \frac{1343}{1000}\,\text{L} \times \frac{44\ \text{g mol}^{-}}{0.0821\ \text{L atm K}^{-}\ \text{mol}^{-}} \times 310\ \text{K}$$

$$= 2.2\ \text{g}$$

wt. of $M_2(CO_3)_n$ = 3.98 g. From reaction (A), we have:

$2a + 60n$ $M_2(CO_3)_n$ form $CO_2 = 44n$

$$3.98\ \text{g}\ M_2(CO_3)_n \text{ form } CO_2 = \frac{44n}{2a + 60n} \times 3.98$$

$$\therefore \quad \frac{44n \times 3.98}{2a + 60n} = 2.2; \quad 175.12 = 4.4a + 132n$$

$$\therefore \quad 4.4a = 43.12n; \quad \frac{a}{n} = 9.8$$

$$\text{or Eq. wt. of metal} = \frac{\text{at. wt., a}}{\text{valency, n}} = \mathbf{9.8\ Ans.}$$

3.7 MILLIEQUIVALENTS OF A COMPOUND

Type. (*i*) Milliequivalent of a compound

$$= \frac{\text{Wt. of compound}}{\text{Eq. wt. of compound}} \times 1000$$

(*ii*) $$\text{Eq. wt.} = \frac{\text{Strength in gL}^{-}}{\text{normality}}$$

Example 28. *Calculate the milliequivalents of $Al(OH)_3$ in its 78 g. (At. wt., Al = 27, O = 16, H = 1).*

Solution. $Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^{-}$

1 mol $\quad$ 3 mol

$$\therefore \text{Eq. wt. of } Al(OH)_3 = \frac{\text{Mol. wt. of Al }(OH)_3}{3\,(\text{of } 3\,OH^{-})}$$

$$= \frac{27 + 3(16+1)}{3} = \frac{78}{3}$$

$$\therefore \text{M. eq. of } Al(OH)_3 = \frac{\text{Wt.}}{\text{Eq. wt}} \times 1000 = \frac{78\ \text{g}}{78\ \text{g}} \times 3 \times 1000$$

$$= \mathbf{3000\ Ans.}$$

Example 29. *Calculate the milliequivalents of H_2SO_4 in its 2.45 g. (at. wt., H = 1, S = 32, O = 16)*

Solution. $H_2SO_4 \rightleftharpoons 2H^{+} + SO_4^{2-}$

1 mol $\quad$ 2 mol

$$\text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt. of } H_2SO_4}{2\,(\text{of } 2\,H^{+})}$$

$$= \frac{(2 \times 1) + 32 + 4(16)}{2} = 49$$

$$\therefore \text{M.eq. of } H_2SO_4 = \frac{\text{wt.}}{\text{Eq. wt}} \times 1000 = \frac{2.45\ \text{g}}{49} \times 1000$$

$$= \mathbf{50\ Ans.}$$

Example 30. *Calculate the equivalent weight of Ca $(OH)_2$ if 1000 milliequivalents are present in 37 g of it. (at. wt., Ca = 40, O = 16, H = 1).*

Solution. We know that :

no. of milliequivalents of Ca $(OH)_2$

$$= \frac{\text{wt. of } Ca(OH)_2}{\text{Eq. wt. of } Ca(OH)_2} \times 1000\,.$$

Substituting the values, we get:

$$1000 = \frac{37}{\text{Eq. wt}} \times 1000\,;$$

$$\text{Eq. wt} = \frac{37 \times 1000}{1000} = \mathbf{37\ Ans.}$$

Example 31. *Calculate the milli-equivalents (Meq.) of the following solutions.*

(*i*) *20 mL of 0.1 M KOH* (*ii*) *25 mL of 0.1 N HCl*

(*iii*) *25 mL of 0.1 N H_2SO_4*

Solution. (*i*) $KOH \rightleftharpoons K^{+} + OH^{-}$

0.1 M $\quad$ 0.1 M (n = 1 because of one OH^{-})

$\therefore$ **Meq. of KOH = Vol in mL × molarity × n**

= 20 × 0.1 × 1 = **2 Ans.**

(*ii*) **Meq. of HCl = Vol in mL × normality**

= 25 × 0.1 = 2.5 Ans.

(*iii*) Meq. of H_2SO_4 = Vol in mL × normality

= 25 × 0.1 = **2.5 Ans.**

EXAMPLE 32. *500 mL of 0.1 N solution of iodine contains 6.35 g. Calculate the equivalent weight of iodine.*

SOLUTION. 500 mL = 0.5 L, 0.5 LI_2 = 6.35 g. So,

$$1 \text{L}I_2 = \frac{6.35}{0.5} = 12.7 \text{gL}^{-}. \text{ Thus, eq. wt.} = \frac{12.7}{0.1} = 127$$

3.8 EQUIVALENT WEIGHT OF AN ACID

Type. Eq. wt. of an acid $= \dfrac{\text{Mol. wt. of acid}}{\text{Basicity}}$

where basicity is the number of H-atoms replaced from one molecule of acid.

or Eq. wt. of an acid $= \dfrac{\text{Molecular wt. of acid}}{\text{n}}$

where, n = number of replaceable H-atoms in one molecule of an acid.

EXAMPLE 33. *Calculate the equivalent weight of phosphorous acid (H_3PO_3) in the following reaction.*

$$2\,NaOH + H_3PO_3 \longrightarrow Na_2HPO_3 + 2H_2O.$$

(at. wt., H = 1, P = 31, O = 16)

SOLUTION.

$$\underset{\substack{1 \text{ molecule} \\ = 3\text{H-atoms}}}{2NaOH + H_3PO_3} \longrightarrow \underset{\text{one H-atom}}{Na_2HPO_3} + 2H_2O$$

In the above reaction, number of replaceable H-atoms in one molecule of

H_3PO_3 = 3H-atoms – 1H-atom = 2H-atoms

$$\therefore \text{Eq. wt. of } H_3PO_3 = \frac{\text{Mol. wt. of } H_3PO_3}{\begin{array}{c}\text{no. of replaceable H-atoms} \\ \text{in one molecule of} \\ \text{acid (= basicity)}\end{array}}$$

$$= \frac{(3 \times 1) + 31 + (3 \times 16)}{2} = \frac{82}{2} = \mathbf{41}$$

EXAMPLE 34. *Calculate the equivalent weight of H_2SO_4 in the following reaction.*

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$$

(at. wt., H = 1, S = 32, O = 16)

SOLUTION. Mol. wt. of H_2SO_4

$= (2 \times 1) + 32 + (4 \times 16) = 98$ g mol¯

Reaction.

$$\underset{\substack{1 \text{ molecule} \\ = 2 \text{ H-atoms}}}{H_2SO_4} + 2NaOH \longrightarrow \underset{\text{no H-atom}}{Na_2SO_4} + 2H_2O$$

$$\text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt. of } H_2SO_4}{\begin{array}{c}\text{no. of H-atoms replaced in} \\ \text{one molecule of acid (= 2)}\end{array}}$$

$$= \frac{98}{2} = \mathbf{49 \text{ Ans.}}$$

EXAMPLE 35. *Calculate the equivalent weight of H_2SO_4 in the reaction,*

$$H_2SO_4 + KOH \longrightarrow KHSO_4 + H_2O$$

(at. wt., H = 1, S = 32, O = 16)

SOLUTION. Mol. wt. of H_2SO_4 = (2 × 1) + 32 + (4 × 16)

= 98 g mol¯

Reaction.

$$\underset{\substack{1 \text{ molecule} \\ = 2 \text{ H-atoms}}}{H_2SO_4} + KOH \longrightarrow \underset{\text{one H-atom}}{KHSO_4} + H_2O$$

∴ No. of replaceable H-atoms in one molecule of H_2SO_4 = 2 H-atoms – 1 H-atom = 1 H-atom

$$\therefore \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt. of } H_2SO_4}{\text{no. of replaceable H-atoms}}$$

$$= \frac{98}{1} = \mathbf{98 \text{ Ans.}}$$

3.9 EQUIVALENT WEIGHT OF A BASE

Type. Eq. wt. of a base

$$= \frac{\text{Mol. wt. of base}}{\text{acidity as shown by chemical equation}}$$

where *acidity* is the number of OH groups replaced from one molecule of a base.

or

$$\text{Eq. wt. of a base} = \frac{\text{Mol. wt. of base}}{\begin{array}{c}\text{no. of } H^+ \text{ ions that react with} \\ \text{one molecule of a base}\end{array}}$$

EXAMPLE 36. *Calculate the equivalent weight of KOH with the help of following reaction.*

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

(at. wt., K = 39 , O = 16, H = 1).

SOLUTION. Mol. wt. of KOH = 39 + 16 + 1 = 56 g mol¯

Reaction.

$$\underset{\substack{2 \text{ molecules} \\ \frac{2}{2} = 1 \text{ molecule}}}{2\,KOH} + \underset{\substack{2H^+ \text{ ions} \\ \frac{2}{2} = 1\,H^+ \text{ ion}}}{H_2SO_4} \longrightarrow \underset{\text{no } H^+\text{–ion}}{K_2SO_4} + 2H_2O$$

∴ no. of H^+ ions that react with one molecule of KOH = 1 – 0 = 1

$$\therefore \text{Eq. wt. of KOH} = \frac{\text{Mol. wt. of KOH}}{\begin{array}{c}\text{no. of } H^+ \text{ ions that react} \\ \text{with one molecule of KOH}\end{array}}$$

$$= \frac{56}{1} = \mathbf{56 \text{ Ans.}}$$

EXAMPLE 37. *Calculate the equivalent weight of $Ca(OH)_2$ in the following reaction.*

$$Ca\,(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$

(at. wt., Ca = 40, O = 16, H = 1)

SOLUTION. Mol. wt. of Ca $(OH)_2$ = 40 + 2 (16 + 1)

= 74 g mol¯

Reaction.

$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

1 molecule   no OH-group

= 2 OH-groups

∴No. of OH-groups replaced from one molecule of $Ca(OH)_2 = 2 - 0 = 2$

$$\therefore \text{Eq.wt.of}\,Ca(OH)_2 = \frac{\text{Mol. wt. of } Ca(OH)_2}{\begin{array}{c}\text{no. of OH- groups replaced}\\ \text{from one molecule of } Ca(OH)_2\end{array}}$$

$$= \frac{74}{2} = \textbf{37 Ans.}$$

Example 38. *Find the equivalent weight of* $Ca(OH)_2$ *in the following reaction.*

$Ca(OH)_2 + 2H_2SO_4 \longrightarrow Ca(HSO_4)_2 + 2H_2O$

(at. wt., Ca = 40, O = 16, H = 1)

Solution. First method.

Mol. wt. of $Ca(OH)_2 = 40 + 2(16 + 1) = 74 \text{ g mol}^{-}$

Reaction.

$Ca(OH)_2 + 2H_2SO_4 \longrightarrow Ca(HSO_4)_2 + 2H_2O$

1 molecule   no OH-group

= 2 OH-groups

∴No. of OH-groups replaced from one molecule of $Ca(OH)_2 = 2 - 0 = 2$

$$\therefore \quad \text{Eq. wt. of } Ca(OH)_2 = \frac{\text{Mol. wt. of } Ca(OH)_2}{\begin{array}{c}\text{no. of OH-groups replaced}\\ \text{from one molecule of } Ca(OH)_2\end{array}}$$

$$= \frac{74}{2} = \textbf{37 Ans.}$$

Second method.

$Ca(OH)_2 \; + \; 2H_2SO_4 \longrightarrow Ca(HSO_4)_2 + 2H_2O$

1 molecule $= 2 \times 2\,H^+$ ions $= 2 \times 1\,H^+$ions

$= 4\,H^+$ ion $= 2\,H^+$ ions

∴ No. of H^+ ions that react with one molecule of $Ca(OH)_2 = 4 - 2 = 2$

$$\therefore \quad \text{Eq. wt. of } Ca(OH)_2 = \frac{\text{Mol. wt. of } Ca(OH)_2}{\begin{array}{c}\text{No. of } H^+ \text{ ions that react}\\ \text{with one molecule of } Ca(OH)_2\end{array}}$$

$$= \frac{74}{2} = \textbf{37 Ans.}$$

Example 39. *Calculate the equivalent weight of NaOH in the following reaction.*

$2NaOH + H_3PO_3 \longrightarrow Na_2HPO_3 + 2H_2O$

(at. wt., Na = 23, H = 1, O = 16).

Solution. Mol. wt. of $NaOH = 23 + 16 + 1 = 40 \text{ g mol}^{-}$

Reaction.

$2NaOH + H_3PO_3 \longrightarrow Na_2HPO_3 + 2H_2O$

2 molecules   no OH-group

= 2 OH-groups

∴ 1 molecule of KOH

= 1 OH-group

∴ no. of OH-groups replaced from one molecule of $NaOH = 1 - 0 = 1$

$$\therefore \quad \text{Eq. wt. of NaOH} = \frac{\text{Mol. wt. of NaOH}}{\begin{array}{c}\text{no. of OH-groups replaced}\\ \text{from one molecule of NaOH}\end{array}}$$

$$= \frac{40}{1} = \textbf{40 Ans.}$$

3.10 EQUIVALENT WEIGHT OF AN ELEMENT AND A COMPOUND FROM ATOMIC WEIGHTS AND VALENCY

Type.

(*i*) $\text{Eq. wt. of an element} = \dfrac{\text{At. wt. of element}}{\text{Valency of element}}$

(*ii*) Eq. wt. of a compound

= Eq. wt. of one part of compound

+ Eq. wt. of second part of compound

$$= \frac{\text{Mol. wt. of compound}}{\begin{array}{c}\text{Total +ve charge on cation}\\ \text{or total } -\text{ve charge on anion}\end{array}}$$

> **Note.** (*a*) The above two relations (*i*) and (*ii*) are not valid for hydrated compounds.
>
> (*b*) The above two relations (*i*) and (*ii*) are valid for non-redox reactions.

Example 40. *Calculate the equivalent weight of aluminium element. (at. wt. of Al = 27 amu)*

Solution. At. wt. of Al = 27 amu; valency of Al = 3

$$\therefore \quad \text{Eq. wt. of Al} = \frac{\text{At. wt. of Al}}{3} = \frac{27}{3} = \textbf{9 Ans.}$$

Example 41. *Calculate the equivalent weight of* $CaCl_2$ *(at. wt., Ca = 40, Cl = 35.5)*

Solution. Mol. wt. of $CaCl_2 = 40 + (2 \times 35.5)$

$= 111 \text{ g mol}^{-}$

Total + ve charge on $Ca^{2+} = 2$

$$\therefore \quad \text{Eq. wt. of } CaCl_2 = \frac{\text{Mol. wt. of } CaCl_2}{2} = \frac{111}{2}$$

$$= \textbf{55.5 Ans.}$$

Example 42. *Find the equivalent weight of* $K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$

(at. wt., K = 39, S = 32, O = 16, Al = 27)

Solution. Mol. wt. of $K_2SO_4.\ Al_2\,(SO_4)_3.\ 24\ H_2O$

$= (2 \times 39) + 32 + (4 \times 16) + (2 \times 27) + 3\,[(32 + (4 \times 16)]$

$+ 24\,[(2 \times 1) + 16] = 948 \text{ g mol}^{-}$

Total +ve charge on $2K^+$ of $K_2SO_4 = 2 \times 1 = 2$

Total +ve charge on $2Al^{3+}$ of $Al_2\,(SO_4)_3 = 2 \times 3 = 6$

Total +ve charge on $K_2SO_4.\ Al_2\,(SO_4)_3.\ 24\ H_2O$

$= 2 + 6 = 8$

$$\therefore \quad \text{Eq. wt. of } K_2SO_4.\ Al_2(SO_4)_3.\ 24\ H_2O = \frac{948}{8}$$

$$= \mathbf{118.5\ Ans.}$$

$$\textbf{Type. } \text{Eq. wt. of an ion} = \frac{\text{Formula wt. of ion}}{\text{Charge on ion}}$$

EXAMPLE 43. *Calculate the equivalent weight of SO_4^{2-} ion. (at. wt., S = 32, O = 16).*

SOLUTION. Formula weight of $SO_4^{2-} = 32 + (4 \times 16) = 96$

Charge on $SO_4^{2-} = 2$

$$\therefore \quad \text{Eq. wt. of } SO_4^{2-} = \frac{96}{2} = 48 \ \textbf{Ans.}$$

EXAMPLE 44. *Find the equivalent weight of $[Fe(CN)_6]^{4-}$. (at. wt. of Fe = 56, C = 12, N = 14).*

SOLUTION. Formula weight of $[Fe(CN)_6]^{4-} = 56 + 6\ (12 + 14) = 56 + 156 = 212$

Charge on $[Fe(CN)_6]^{4-} = 4$

$$\therefore \quad \text{Eq. wt. of } [Fe(CN)_6]^{4-} = \frac{212}{4} = \mathbf{53\ Ans.}$$

3.11 EQUIVALENT WEIGHT OF AN ACID SALT

Type. Eq. wt. of an acid salt

$$= \frac{\text{Mol. wt. of acid salt}}{\text{no. of replaceable H-atoms in acid salt}}$$

Notes. (*i*) In oxy acids such as H_3PO_3, H_3PO_4 etc, only those H are replaceable which are attached to O-atom.

(*ii*) An acid salt is that which has replaceable H-atoms. For example, $NaHCO_3$, $NaHSO_4$, $Na_2\ HPO_4$ etc.

(*iii*) Sodium salt of H_3PO_3 is Na_2HPO_3. This salt is not an acid salt as it does not have replaceable H-atom because H-atom present in $NaHPO_3$ is not bonded to O-atom.

EXAMPLE 45. *Calculate the equivalent weight of $NaHCO_3$ in the following reaction*

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

(at. wt., Na = 23, H = 1, C = 12, O = 16)

SOLUTION.

Mol. wt. of $NaHCO_3 = 23 + 1 + 12 + (3 \times 16) = 84\ g\ mol^{-}$

Reaction.

$$\underset{\text{one H-atom}}{NaHCO_3} + HCl \longrightarrow \underset{\text{no H-atom}}{NaCl + CO_2 + H_2O}$$

$\therefore$ No. of replaceable H-atoms in $NaHCO_3 = 1 - 0 = 1$

$$\therefore \quad \text{Eq. wt. of } NaHCO_3 = \frac{\text{Mol. wt. of } NaHCO_3}{\begin{array}{c}\text{no. of replaceable}\\ \text{H-atoms in } NaHCO_3\end{array}} = \frac{84}{1}$$

$$= \mathbf{84\ Ans.}$$

EXAMPLE 46. *3.64 g of a metal needs 65 cm^3 of 1 N HNO_3 to dissolve. Calculate the equivalent weight of the metal.*

SOLUTION. Milliequivalent of HNO_3

= Normality of HNO_3 × Volume of HNO_3 in mL

= 1 × 65 = 65

$$\text{Milliequivalent of Metal} = \frac{\text{wt. of metal}}{\text{Eq. wt. of metal}} \times 1000$$

$$= \frac{3.64 \times 1000}{\text{Eq. wt. of metal}}$$

Since M. eq. of metal = M. eq. of HNO_3

$$\therefore \quad \frac{3.64 \times 1000}{\text{Eq. wt. of metal}} = 65$$

$$\therefore \text{Eq. wt. of metal} = \frac{3.64 \times 1000}{65} = \mathbf{56\ Ans.}$$

EXAMPLE 47. *2.8 g of a metal were dissolved in nitric acid and evaporated to get its nitrate. When this nitrate was strongly heated, 4.66 g of its oxide was formed. Calculate the equivalent weight of the metal.*

SOLUTION.

$$\text{Reactions : } M \xrightarrow{HNO_3} M(NO_3)_n \xrightarrow{\Delta} M_2O_n$$

where n = valency of the metal. we know that :

Equivalent of metal = equivalent of metal nitrate

= equivalent of metal oxide

= equivalent of oxygen.

Thus :

$$\frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of oxygen}};$$

wt. of oxygen = 4.66 – 2.8 = 1.86 g.

$$\therefore \quad \frac{2.8\ g}{1.86\ g} = \frac{\text{Eq. wt. of metal}}{8};$$

$$\text{Eq. wt. of metal} = \frac{2.8 \times 8}{1.86} = \mathbf{12\ Ans.}$$

EXAMPLE 48. *1.5 g of a metal nitrate yielded 1.28 g of metal sulphate. Find the equivalent weight of the metal.*

SOLUTION.

Hint. Let at. wt. of metal (M) = a;

valency of metal = *n*.

But

Equivalent of $M(NO_3)_n$ = equivalent of $M_2(SO_4)_n$

$$\therefore \quad \frac{\text{wt. of } M(NO_3)_n}{\text{wt. of } M_2\ (SO_4)_n} = \frac{\text{Eq. wt. of } M(NO_3)_n}{\text{Eq. wt. of } M_2(SO_4)_n};$$

$$\frac{1.5\ g}{1.28\ g} = \frac{\frac{a}{n} + 62}{\frac{a}{n} + 48}$$

$$\text{But} \qquad \frac{a}{n} = \text{Eq. wt.} = E$$

$$\therefore \quad \frac{1.5}{1.28} = \frac{E + 62}{E + 48};$$

$$1.5\ E + 72 = 1.28\ E + 79.36$$

or $0.22\text{ E} = 7.36$

Hence $\text{E} = \dfrac{7.36}{0.22} = \mathbf{33.4}$ **Ans.**

Example 49. *1.0 g of a metal sulphate gave 0.728 g of metal phosphate. Calculate the equivalent weight of the metal.*

Solution.

Hint. $M_2(SO_4)_n \longrightarrow M_3(PO_4)_n$;

n = valency of metal, M

$$\therefore \quad \frac{\text{wt. of } M_2(SO_4)_n}{\text{wt. of } M_3(PO_4)_n} = \frac{\text{Eq. wt. of } M_2(SO_4)_n}{\text{Eq. wt. of } M_3(PO_4)_n};$$

$$\frac{1.0\text{ g}}{0.728\text{ g}} = \frac{\text{E} + 48}{\text{E} + 31.67}$$

$$\text{E} + 31.67 = 0.728\text{ E} + 34.94\text{ g}$$

$$\text{E} - 0.728\text{ E} = 34.94 - 31.67$$

or $0.272\text{ E} = 3.27$

$\therefore$ $\text{E} = 12$

i.e., Eq.wt. of metal = **12 Ans.**

3.12 MISCELLANEOUS EXAMPLES

Example 50. *The volume of one atom of a metal M is 1.66×10^{-23} c.c. Find the atomic weight and Eq. wt. of M (valency, 3) (Given density of M = 2.7 g/c.c).* **(W.B.J.E.E. 1993)**

Solution. The volume of one atom of the metal M is 1.66×10^{-23} c.c.

Density = 2.7g/c.c.

Mass of one atom = Volume × density

$= 1.66 \times 10^{-23} \times 2.7$ g

$\therefore$ Mass of Avogadro's number of atoms

$= 1.66 \times 10^{-23} \times 2.7 \times 6.023 \times 10^{23}$g

= 27 g

Hence 1 gram atom of M = 27 g

$\therefore$ Atomic weight of M = 27;

$$\text{Eq. wt.} = \frac{\text{atomic wt.}}{\text{valency}} = \frac{27}{3} = 9 \textbf{ Ans.}$$

Example 51. *0.124 g of iron wire was dissolved in dilute H_2SO_4 in oxygen free atmosphere and the resultant solution was titrated against 0.09672N solution of $KMnO_4$. The titre value was 22.90 cm^3. Calculate the percentage purity of iron wire.*

(I.I.T. 1971)

Solution. $\underset{56\text{g}}{Fe} + H_2SO_4 \longrightarrow \underset{152\text{ g}}{FeSO_4} + H_2$

According to normality equation, $N_1V_1 = N_2V_2$

$\therefore$22.9 cm^3 of 0.09672N $KMnO_4$

= 22.9 cm^3 of 0.09672N $FeSO_4$

1000 cm^3 of 1 N $FeSO_4$ = 152 g $FeSO_4$

22.9 cm^3 of 0.09672 N $FeSO_4$ = $\dfrac{152}{1000} \times 22.9 \times 0.09672$

= 0.3366 g

152 g $FeSO_4$ = 56 g pure iron

0.3366 $FeSO_4$ = $\dfrac{56}{152} \times 0.3366 = 0.124$ g pure iron

$\therefore$ % age purity of iron = $\dfrac{0.124\text{ g}}{0.124\text{ g}} \times 100 = 100$

Hence the given iron wire is 100% pure.

3.13 AIEEE PATTERN EXAMPLES

Example 52. *The equivalent weight of a metal, 6 g of which evolve 5.6 L of H_2 at NTP from an acid is:*

(a) 6	*(b) 12*
(c) 24	*(d) 2.4*

Solution. Wt. of metal = 6.0 g;

volume at NTP = 5.6 L.

We know that :

$$\text{Eq. wt. of a metal} = \frac{\text{wt. of metal}}{V_{NTP} \text{ of } H_2 \text{ in L}} \times 11.2\text{ L}$$

$$\therefore \quad \text{Eq. wt. of metal} = \frac{6.0\text{ g}}{5.6\text{ L}} \times 11.2\text{ L} = \mathbf{12.0\text{ g}} \textbf{ Ans.}$$

So, the correct answer is (*b*)

Example 53. *The percentage of H_2 in the hydride of an element having equivalent weight 11.5 is:*

(a) 7.06	*(b) 8.06*
(c) 4.03	*(d) 12.09*

Solution. Eq. wt. of element

= 11.5; let wt. of metal = x g;

wt. of element = 100 – x g; Eq. wt. of H_2 = 1.008.

We know that :

$$\frac{\text{Wt. of element}}{\text{Wt. of hydrogen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } H_2 \ (= 1.008)}$$

or $\dfrac{100 - x}{x} = \dfrac{11.5}{1.008}$;

$11.5\,x = 100.8 - 1.008\,x$; $12.508\,x = 100.8$

$\therefore$ $x = 100.8/12.508 = 8.06$

$\therefore$Percentage of H_2 = **8.06%**

So, the correct answer is (*b*)

Example 54. *The equivalent weight of $SnCl_2$ in the following reaction, $SnCl_2 + Cl_2 \longrightarrow SnCl_4$ is*

(a) 190	*(b) 119*
(c) 95	*(d) 380*

(At. wt. of Sn = 119, Cl = 35.5)

Solution.

g. mol. wt. of $SnCl_2$ = 119 + (2 × 35.5) = 190 g;

g. mol. wt. of Cl_2 = 2 × 35.5 = 71 g.

Eq. wt. of $SnCl_2$ = ?

$$\underset{190\text{ g}}{Sn\,Cl_2} + \underset{71\text{ g}}{Cl_2} \longrightarrow SnCl_4$$

We know:

$$\frac{\text{Wt. of SnCl}_2}{\text{Wt. of Cl}_2} = \frac{\text{Eq. wt. of SnCl}_2}{\text{Eq. wt. of Cl}_2\,(= 35.5)}$$

$$\therefore \text{ Eq. wt. of SnCl}_2 = \frac{\text{Wt. of SnCl}_2}{\text{Wt. of Cl}_2} \times 35.5$$

$$= \frac{190\text{ g } \times 35.5\text{ g}}{71\text{ g}} = \mathbf{95\ g}$$

So, the corect answer is (*c*)

EXAMPLE 55. *Chloride of a metal M contains 47.23% of the metal. 1.0 g of this metal displaced 0.88 g of another metal N from a compound. The equivalent weight of M and N are respectively:*

(*a*) *39.77, 29.96*	(*b*) *63.54, 28*
(*c*) *31.77, 81.7*	(*d*) *31.77, 27.96*

(P.U. 1978)

SOLUTION.

Wt. of metal M = 47.23 g;

wt. of chlorine = 100 – 47.23 = 52.77 g.

$$\therefore \quad \text{Eq. wt. of metal M} = \frac{\text{Wt. of metal M} \times 35.5}{\text{Wt. of chlorine}}$$

$$= \frac{47.23 \times 35.5}{52.77} = 31.77$$

(*ii*) Wt. of metal M = 1.0 g; wt. of metal N = 0.88 g.

$$\text{We know : } \frac{\text{Wt. of metal M}}{\text{Wt. of metal N}} = \frac{\text{Eq. wt. of metal M}}{\text{Eq. wt. of metal N}}$$

$$\therefore \text{Eq. wt. of metal N} = \frac{\text{Eq. wt. of metal M} \times \text{wt. of metal N}}{\text{wt. of metal M}}$$

$$= \frac{31.77 \times 0.88}{1} = \mathbf{27.96\%.}$$

So, the correct answer is (*d*)

EXAMPLE 56. *On heating 0.398 g of a metal oxide in a current of dry hydrogen, 0.09 g of water were formed. The equivalent weight of the metal is :*

(*a*) *31.8*	(*b*) *63.6*
(*c*) *15.9*	(*d*) *2.0*

SOLUTION.

(*i*) Wt. of metal oxide = 0.398 g; wt. of H_2O = 0.09 g

$$H_2O = O$$

$$(2\times1) + 16 = 18\text{ g} \quad 16\text{ g}$$

18 g H_2O contain oxygen = 16 g

$$0.09\text{ g H}_2\text{O contains oxygen} = \frac{16\text{ g}}{18\text{ g}} \times 0.09\text{ g}$$

$$= 0.08\text{ g}$$

$\therefore$ Wt. of oxygen = 0.08 g;

wt. of metal = 0.398 – 0.08 = 0.318 g

$$(ii) \quad \frac{\text{Wt. of metal}}{\text{Wt. of oxygen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of oxygen}};$$

$$\frac{0.318\text{ g}}{0.08\text{ g}} = \frac{\text{Eq. wt. of metal}}{8}$$

$$\therefore \quad \text{Eq. wt. of metal} = \frac{0.318}{0.08} \times 8 = \mathbf{31.8}$$

So, the correct answer is (*a*).

EXAMPLE 57. *1.52 g of the hydroxide of a metal gave on ignition, 0.995 g of the oxide. The equivalent weight of the metal is :*

(*a*) *4.53*	(*b*) *9.06*
(*c*) *27.18*	(*d*) *36.24*

SOLUTION.

$$\frac{\text{Wt. of metal hydroxide}}{\text{Wt. of metal oxide}} = \frac{\text{Eq. wt. of metal} + \text{Eq. wt. of OH}^-}{\text{Eq. wt. of metal} + \text{Eq. wt. of O}^{-2}}$$

$$\frac{1.520\text{ g}}{0.995\text{ g}} = \frac{E + 17}{E + 8};\ \frac{1520}{995} = \frac{E + 17}{E + 8}$$

$$1520\,E + 1520 \times 8 = 995\,E + 995 \times 17;\ 1520\,E + 12160 = 995E + 16915$$

$$1520\,E - 995\,E = 16915 - 12160;\ \ 525\,E = 4755$$

$$\therefore \quad E = \frac{4755}{525} = \mathbf{9.06}$$

So, the correct answer is (*b*)

EXAMPLE 58. *The equivalent weight of $FeSO_4$ in the reaction,*

$$FeSO_4 + SnCl_4 \longrightarrow FeCl_3 + SnSO_4 \textit{ is :}$$

(*a*) *304* (*b*) *76* (*c*) *152* (*d*) *101.3*

(*at. wt. Fe = 56, S = 32, O = 16*)

SOLUTION.

$$FeSO_4 + SnCl_4 \longrightarrow FeCl_3 + SnSO_4$$

$$\text{or} \quad Fe^{2+} + Sn^{4+} \longrightarrow Fe^{3+} + Sn^{2+}$$

$$(i) \quad Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$$

$$\therefore \text{Eq. wt. of FeSO}_4 = \frac{\text{Mol. wt. of FeSO}_4}{\text{no. of electrons lost}}$$

$$= \frac{56 + 32 + (4 \times 16)}{1} = \mathbf{152}$$

So, the correct answer is (*c*)

EXAMPLE 59. *The equivalent weight of HNO_3 in the reaction $2HNO_3 \longrightarrow 2NO + H_2O + 3\,O$ is.*

(*a*) *21*	(*b*) *42*
(*c*) *63*	(*d*) *10.5*

SOLUTION. $2HNO_3 \longrightarrow 2NO + H_2O + 3\,O$

$2[1 + 14 + (3 \times 16)]$ $\quad$ $3 \times 16 = 48$ parts

= 216 parts

48 parts by weight of oxygen

= 126 parts by weight of HNO_3

∴ 8 parts by weight of oxygen

$$= \frac{126}{48} \times 8 = \mathbf{21.}$$

So, the correct answer is (*a*)

Example 60. *The equivalent weight of H_2SO_4 in the reaction*

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O \text{ is :}$$

(*a*) 98 (*b*) 49

(*c*) 32.6 (*d*) 16.3

Solution. Reaction :

$$\underset{\text{2 H-atoms}}{Na_2CO_3 + H_2SO_4} \longrightarrow \underset{\text{no. H atom = 0 H-atom}}{Na_2SO_4 + CO_2 + H_2O}$$

∴ No. of replaceable H-atoms = 2 – 0 = 2

$$\therefore \quad \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt. of } H_2SO_4}{\text{no. of replaceable H-atoms}}$$

$$= \frac{(2 \times 1) + 32 + (4 \times 16)}{2} = \mathbf{49.}$$

So, the correct answer is (*b*)

Example 61. *The equivalent weight of H_2SO_4 in the reaction*

$$Na_2CO_3 + H_2SO_4 \longrightarrow NaHSO_4 + CO_2 + H_2O \text{ is :}$$

(*a*) 49 (*b*) 4.9

(*c*) 98 (*d*) 196

Solution. Reaction :

$$\underset{\text{2 H-atoms}}{Na_2CO_3 + H_2SO_4} \longrightarrow \underset{\text{one H-atom}}{NaHSO_4} + CO_2 + H_2O$$

∴ No. of replaceable H-atoms = 2 – 1 = 1

$$\therefore \quad \text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt. of } H_2SO_4}{\text{no. of replaceable H-atoms}}$$

$$= \frac{(2 \times 1) + 32 + (4 \times 16)}{1} = \mathbf{98.}$$

So, the correct answer is (*c*)

Example 62. *The number of milliequivalents of Mg $(OH)_2$ in its 5.8 g are :*

(*a*) *100* (*b*) *200*

(*c*) *400* (*d*) *600*

Solution. $\underset{\text{1 mol}}{Mg\,(OH)_2} \rightleftharpoons Mg^{2+} + \underset{\text{2 mol}}{2OH^-}$

$$\text{Eq. wt. of Mg } (OH)_2 = \frac{\text{Mol. wt. of Mg } (OH)_2}{2}$$

$$= \frac{24 + 2(16+1)}{2} = \frac{58}{2} = 29$$

$$\therefore \quad \text{M. eq. of Mg } (OH)_2 = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000 = \frac{5.8}{29} \times 1000$$

$$= \mathbf{200}$$

So, the correct answer is (*b*)

Example 63. *The equivalent weight of $Ca(OH)_2$ whose 250 milliequivalent solution contains 18.5 g of it, is :*

(*a*) *37* (*b*) *18.5*

(*c*) *74* (*d*) *148*

Solution. wt. of $Ca(OH)_2$ = 18.5 g; no. of milliequivalents = 250.

We know that :

no. of milliequivalents of $Ca(OH)_2$

$$= \frac{\text{Wt. of } Ca(OH)_2}{\text{Eq. wt. of } Ca(OH)_2} \times 1000$$

$$250 = \frac{18.5}{\text{Eq. wt. of } Ca(OH)_2} \times 1000$$

$$\therefore \text{Eq. wt. of } Ca(OH)_2 = \frac{18.5 \times 1000}{250} = \mathbf{74.}$$

So, the correct answer is (*c*)

Example 64. *The number of milliequivalents present in 25 mL of 0.2 M $Mg(OH)_2$ are :*

(*a*) 5.0 (*b*) 10.0

(*c*) 15.0 (*d*) 20.0

Solution.

M. eq. of Mg $(OH)_2$ = Volume in mL × molarity × n ...(1)

where n = no. of replaceable OH groups

$$\underset{0.2\text{ M}}{Mg\,(OH)_2} \rightleftharpoons Mg^{2+} + \underset{2 \times 0.2\text{ M}}{2OH^-}$$

(n = 2 because of two OH^-)

∴ No. of M. eq. of $Mg(OH)_2$ = 25 × 0.2 × 2 = **10.0.**

So, the correct answer is (*b*)

Example 65. *The number of milliequivalents present in 25 mL of 0.2N $Mg(OH)_2$ are :*

(*a*) 0.5 (*b*) 0.25

(*c*) 5.0 (*d*) 10.0

Solution. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

M. eq. of $Mg(OH)_2$ = Volume in mL × normality

= 25 × 0.2 = **5.0**

So, the correct answer is (*c*)

Example 66. *The equivalent weight of NO_3^- in :*

$$NO_3^- \longrightarrow N_2O \quad \text{is:}$$

(*a*) 15.5 (*b*) 31.0 (*c*) 62 (*d*) 124

Solution.

(*i*) In NO_3^-, O.N. of N + 3 × O.N. of O = – 1

∴ O.N. of N + 3 (– 2) = – 1; O.N. of N = – 1 + 6 = + 5

(*ii*) In N_2O : 2 × O.N. of N + O.N. of O = 0;

2 × O.N. of N – 2 = 0

$$\therefore \quad \text{O.N. of N} = \frac{2}{2} = +1$$

$$\therefore \quad N^{+5}O_3^- + 4e^- \longrightarrow N_2^+\,O$$

$[\because \; +5 - 4 = +1]$

$$\therefore \quad \text{Eq. wt. of } NO_3^- = \frac{\text{Ionic weight of } NO_3^-}{\text{no. of electrons gained in one molecule of } NO_3^-}$$

$$= \frac{14+(3\times 16)}{4} = \frac{62}{4} = \mathbf{15.5}$$

So, the correct answer is (*a*)

EXAMPLE 67. *The equivalent weight of* SO_2 *in the reaction:*

$SO_2 + H_2O + O \longrightarrow H_2SO_4$ *is:*

(*a*) 8 (*b*) 16

(*c*) 32 (*d*) 64

(*at. wt., S = 32, O = 16*)

SOLUTION.

$$\underset{\substack{32+(2\times 16)\\ =64\text{ parts}}}{SO_2} + H_2O + \underset{2\times(\frac{1}{2}O)}{O} \longrightarrow H_2SO_4$$

$$\text{Eq. wt. of } SO_2 = \frac{\text{Mol. wt. of } SO_2}{\text{no. of } \frac{1}{2}\text{ O atoms reacted with one molecule of } SO_2}$$

$$= \frac{32+(2\times 16)}{2} = \frac{64}{2} = \mathbf{32}$$

So, the correct answer is (*c*).

EXAMPLE 68. *A 100% pure sample of a divalent metal carbonate weighing 2g on complete thermal decomposition releases 448 cc. of carbon dioxide at STP. The equivalent mass of the metal is :* **(Kerala PET, 2012)**

(*a*) 40 (*b*) 20 (*c*) 28

(*d*) 12 (*e*) 56

SOLUTION. Metal carbonate,

$$\underset{\substack{1\text{ mol}\\ 2\text{g}}}{MCO_3} \xrightarrow{\Delta} MO + \underset{\substack{22400\text{ cc}\\ 448\text{ cc}}}{CO_2(g)}$$

448 cc CO_2 is obtained from MCO_3 = 2g

22400 cc CO_2 is obtained from $MCO_3 = \frac{2}{448} \times 22400$

= 100 g

$\therefore$ Mol. wt. of MCO_3 = 100

$\therefore$ Mol. wt of M + 12 + (3 × 16) = 100

or Mol. wt. of M = 100 – 60 = 40 g mol^-.

$\therefore$ Eq. wt. of metal = Mol. wt/valency = 40/2 = 20

So, the correct answer is (*b*).

EXAMPLE 69. *Equivalent weight of* $KMnO_4$ *in alkaline solution is:* **(AMU (medical), 2012)**

(*a*) 1/5 of molar mass of $KMnO_4$

(*b*) 1/6 of molar mass of $KMnO_4$

(*c*) 1/3 of molar mass of $KMnO_4$

(*d*) 1/10 of molar mass of $KMnO_4$.

SOLUTION. Reaction in alkaline medium is:

$$Mn^{7+}O_4^- + 2H_2O + 3e^- \longrightarrow Mn^{4+}O_2 + 4OH^-$$

$\therefore$ Total change in oxidation number of Mn = 7 – 4 = 3 and total no. of electrons gained = 3.

$$\therefore \text{Eq. wt. of } KMnO_4 = \frac{\text{Molar mass of } KMnO_4}{3}.$$

So, the correct answer is (c).

Note: For more examples, see chapter, 22.

PROBLEMS FOR PRACTICE

1. Calculate the equivalent weight of $FeSO_4$ and $KClO_3$ in the following redox reaction.

   $KClO_3 + FeSO_4 \longrightarrow KCl + Fe_2(SO_4)_3$

   (at. wt., K = 39, Cl = 35.5, O = 16, Fe = 56, S = 32)

   (**Ans.** Eq. wt. of $FeSO_4$ =152; of $KClO_3$ = 20.42)

2. Calculate the equivalent weight of Na_2HPO_4 in the following reaction.

   $Na_2HPO_4 + NaOH \longrightarrow Na_3PO_4 + H_2O$

   (at. wt., Na = 23, H = 1, P = 31, O = 16). **(Ans. 142)**

3. If *x* g of a metal A displaces y g of another metal B from its salt solution and if the equivalent weights are E_1 and E_2 respectively, then the equivalent weight of A can be expressed as:

   (*a*) $E_1 = \frac{xE_2}{y}$ (*b*) $E_1 = \frac{xy}{E_2}$

   (*c*) $E_1 = xy$ (*d*) $\frac{x}{y}$ **[Ans. (*a*)]**

4. Calculate the equivalent weight of iodine in the reaction,

   $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$ **(Ans. 127)**

5. 2.5 g of a metal produces 0.21 g hydrogen at N.T.P. Calculate the equivalent weight of the metal. **(Ans. 12)**

6. The atomic weight of a metal is 40 amu. If its valency is two, find its equivalent weight. **(Ans. 20)**

7. 5.3 g of a metal carbonate, dissolved per litre of the given solution has 0.1 normality. Calculate the equivalent weight of the metal carbonate. **(Ans. 53)**

8. Calculate the equivalent weight of NaOH in the following reaction,

   $NaOH + HCl \longrightarrow NaCl + H_2O$ **(Ans. 40)**

9. Calculate the equivalent weight of $KHCO_3$ in the reaction,

   $KHCO_3 + HCl \longrightarrow KCl + CO_2 + H_2O$ **(Ans. 100)**

10. Calculate the milliequivalents of HCl in its 3.65 g (at. wt., H = 1, Cl = 35.5) **(Ans. 100)**

4 CHAPTER

Atomic Weight

4.1 ATOMIC WEIGHT (ATOMIC MASS)

The *atomic weight of an element is the average relative weight of its atoms as compared to the weight of carbon atom taken as 12 amu.* The *atomic weight of an element expressed* in gram is called its **gram atomic weight**.

4.2 DIFFERENT METHODS TO FIND ATOMIC WEIGHT OF ELEMENTS

These are given below :

I. **Average Method.** In this method, the average of atomic weight of all the isotopes of an element gives the atomic weight of the element.

EXAMPLE 1. (*a*) *Different naturally occurring isotopes of oxygen contain 0.204% ^{18}O with mass 17.9991 amu, 0.037% ^{17}O with mass 16.9991 amu and 99.759% ^{16}O with mass 15.9949 amu. Find the value of chemical atomic weight of natural oxygen.*

(*b*) *Which isotope of carbon is used to express relative atomic mass of an element ?* **(H.P. Board, 2007)**

SOLUTION.

(*a*) Since data is given in percentage, let total number of oxygen atoms be 100. So, the average atomic weight of oxygen will be:

$$\frac{(0.204 \times 17.9991) + (0.037 \times 16.9991) + (99.759 \times 15.9949)}{100}$$

$$= \frac{3.672 + 0.629 + 1595.635}{100}$$

$$= \mathbf{15.9994} \ \textbf{Ans.}$$

(*b*) The isotope of carbon, ^{12}C is used to express relative atomic mass of an element. The atomic mass of an element is the number of times one atom of the element is heavier than $\frac{1}{12}$ of a ^{12}C atom.

EXAMPLE 2. *Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron.* **(I.I.T. 1978)**

SOLUTION. Let

$$x = \text{\% age of isotope having at. wt. } 10.01$$

$$\therefore \quad 100 - x = \text{\% age of isotope having at. wt. } 11.01$$

$$\therefore \quad \text{Average at wt.} = \frac{x \times 10.01 + (100 - x) \times 11.01}{100}$$

$$\text{or} \quad 10.81 = \frac{10.01x + 1101 - 11.01x}{100};$$

$$11.01x - 10.01x = 1101 - 1081$$

$$x = \mathbf{20};\ 100 - x = 100 - 20 = \mathbf{80}$$

$\therefore$ Isotope with mass 10.01 = **20%**;

Isotope with mass 11.01 = **80% Ans.**

EXAMPLE 3. *Naturally occurring copper consists of isotopes of ^{63}Cu and ^{65}Cu in the ratio 8 : 3. What will be the mean atomic weight of copper?*

SOLUTION. Total number of atoms = 8 + 3 = 11. There are 8 atoms of ^{63}Cu and 3 atoms of ^{65}Cu.

$$\therefore \quad \text{Mean at. wt. of Cu} = \frac{8 \times 63 + 3 \times 65}{8 + 3 = 11}$$

$$= \frac{504 + 195}{11} = \frac{699}{11} = \mathbf{63.54} \quad \textbf{Ans.}$$

II. **Equivalent weight and valency method.** Equivalent weight, valency and atomic weight are related as:

At. wt. = Eq. wt. × valency.

Eq. wt. of an element can be determined by any one of the methods described in chapter 3.

Valency of an element is a **whole number**. **Valency** *of an element is equal to the number of H-atoms with which one atom of an element combines.* It is also equal to the number of electrons transferred or shared during combination by an atom of the element.

4.3 DETERMINATION OF VALENCY AND EXACT ATOMIC WEIGHT

1. **Dulong and Petit's law. (For metals only)** According to this law:

Approximate at wt. of an element

$$= \frac{6.4}{\text{Specific heat of element}}$$

$$\text{Valency} = \frac{\text{Approximate at. wt.}}{\text{Eq. wt.}}$$

The valency found above is changed to nearest whole number. For example, if valency comes out to be 2.99, it is changed to 3.

EXAMPLE 4. *A sample of a metal chloride weighing 0.22g required 0.51 g of silver nitrate to precipitate the chloride completely. The specific heat of the metal is 0.057. Find the molecular formula of the chloride if the symbol of the metal is M.* **(I.I.T. 1976)**

SOLUTION. Let eq. wt. of metal = E, wt. of metal chloride = 0.22 g; wt. of silver nitrate = 0.51 g. We know that:

$$\frac{\text{Wt. of metal chloride}}{\text{Wt. of } AgNO_3} = \frac{\text{Eq. wt. of metal chloride}}{\text{Eq. wt. of } AgNO_3}$$

$$\frac{0.22\text{ g}}{0.51\text{ g}} = \frac{E+35.5}{108+14+(3\times 16)}$$

$$= \frac{E+35.5}{170};$$

$$\frac{0.22\times 170}{0.51} - 35.5 = E = 37.83$$

$$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.057} = 112.28$$

$$\therefore \quad \text{Valency} = \frac{\text{approx. at. wt.}}{\text{Eq. wt.}} = \frac{112.28}{37.83}$$

$$= 2.96 \approx 3$$

$\therefore$ Molecular formula of metal chloride = $\mathbf{MCl_3}$ **Ans.**

EXAMPLE 5. (*a*) *A bivalent metal M has the equivalent weight of 12. Find the at. wt. of M; the formula of its chloride and the mol. wt. of its oxide.*

(*b*) *The chloride of a metal M having the formula MCl_3 contains 65.55% of chlorine. Find out its at. wt.*

(*c*) *What is the valency of the element of which the eq. wt. is 12 and specific heat is 0.25?* **(I.I.T. 1973)**

SOLUTION.

(*a*) At. wt. = Eq. wt. × valency = 12 × 2 = 24 **Ans.**

Formula of chloride of bivalent metal M = MCl_2 **Ans.**

Mol. wt. of bivalent metal oxide = MO = 24 + 16 = 40 **Ans.**

(*b*) Wt. of Cl_2 = 65.55 g; Wt. of metal 100 – 65.55 = 34.45 g.

$$\therefore \quad \frac{\text{Wt. of metal}}{\text{Wt. of } Cl_2} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } Cl_2 (= 35.5)};$$

$$\frac{34.45}{65.55} = \frac{E}{35.5}$$

$$\therefore \quad E = \frac{34.45\times 35.5}{65.55} = 18.66$$

From MCl_3, valency of metal, $M = 3$

$\therefore$ Exact at. wt. = Eq. wt. × Valency

= 18.66 × 3 = **55.98** **Ans.**

$$(c) \quad \text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.25} = 25.6$$

$$\therefore \quad \text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{25.6}{12} \approx 2 \quad \textbf{Ans.}$$

EXAMPLE 6. *2.0 g of a metal (specific heat = 0.057 cal g^{-}) on treatment with H_2SO_4 gives 4.51g of metal sulphate. Calculate the valency and atomic weight of the metal.* **(I.I.T. 1978)**

SOLUTION.

$$(i) \quad \text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.057} = 112.28$$

$$(ii) \quad \frac{\text{Wt. of metal}}{\text{Wt. of metal sulphate}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of metal sulphate}}$$

$$\frac{2.0\text{ g}}{4.51\text{ g}} = \frac{E}{E+48};$$

$$2E + 96 = 4.51\,E;$$

$$\therefore \quad E = \frac{96}{2.51} = 38.24$$

$$(iii) \quad \text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{112.28}{38.24} \approx 3.$$

$\therefore$ Exact at. wt. of metal = Eq. wt. × Valency

= 38.24 × 3 = **114.72** **Ans.**

EXAMPLE 7. *32.1 g of a metal were dissolved in HCl and the hydrogen evolved was burnt to form water which weighed 9.1 g. The specific heat of the metal is 0.094. Calculate its at. wt.*

SOLUTION. (*i*) Wt. of metal = 32.1 g; wt. of H_2O = 9.1 g.

18 g H_2O contains H_2 = 2g

[$\because H_2O \equiv 2H$; 18 = mol. wt. of H_2O]

$$\therefore 9.1 \text{ g } H_2O \text{ contain } H_2 = \frac{2}{18}\times 9.1 = 1.01\text{ g.}$$

We know:

$$\frac{\text{Wt. of metal}}{\text{Wt. of } H_2} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } H_2 (= 1)}; \frac{32.1}{1.01} = \frac{E}{1}$$

$$\therefore \quad E = \mathbf{31.78}$$

(*ii*) $$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.094} = 68.08$$

$$\therefore \quad \text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{68.08}{31.78}$$

$$= 2.1 \approx 2.$$

$$\therefore \quad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 31.78 \times 2 = 63.56 \quad \textbf{Ans.}$$

EXAMPLE 8. *A metal piece weighing 0.45 to 0.55 g when dissolved in dil. HCl produced 90 mL of H_2 at NTP. If exact at. wt. of metal is 65, calculate the exact weight of the metal.*

SOLUTION. Let wt. of metal = 0.5 g; wt. of H_2 at NTP. = 90 × 0.00009 g

Exact at. wt. of metal = 65; Eq. wt. of metal = *E*. We know:

$$\frac{\text{Wt. of metal}}{\text{Wt. of } H_2 \text{ at NTP}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } H_2 (= 1.008)} \qquad ...(1)$$

$$\frac{0.5}{90 \times 0.00009} = \frac{E}{1.008}$$

$$\therefore \quad E = \frac{0.5 \times 1.008}{90 \times 0.00009} = 62.2$$

$$\text{Valency} = \frac{\text{At. wt.}}{\text{Eq. wt.}} = \frac{65}{62.2} \simeq 1$$

$$\therefore \quad \text{Exact eq. wt.} = \frac{\text{Exact at. wt.}}{\text{Valency}} = \frac{65}{1} = 65.$$

Let x = exact wt. of metal

From relation (1), we have:

$$\frac{x}{90 \times 0.00009} = \frac{65}{1.008}$$

$$\therefore \quad x = \frac{65 \times 90 \times 0.00009}{1.008}$$

$$= 0.5223 \text{ g} \quad \textbf{Ans.}$$

EXAMPLE 9. *When 0.25 ampere current was passed through a metal salt solution for 10 minutes, 0.1677 g of the metal was deposited. If specific heat of the metal is 0.0556 cal g^{-} (degree)$^{-}$, find the at. wt. of metal. (1 faraday = 96500 coulomb)*

SOLUTION.

(*i*) Current passed, *C* = 0.25 ampere; time (*t*) in seconds = 10 × 60 = 600 s, Wt. of metal deposited = 0.1677 g.

∴ g. eq. wt. of metal

$$= \frac{\text{Wt. of metal deposited} \times 96500 \text{ coulomb}}{\text{Quantity of electricity passed } (= c\ t)}$$

$$= \frac{0.1677 \text{ g} \times 96500 \text{ coulomb}}{(0.25 \text{ ampere} \times 600\text{s}) \textit{ i.e., } 150 \text{ coulomb}} = 107.89 \text{ g.}$$

(*ii*) $$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.0556} = 115.1$$

$$\therefore \quad \text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}}$$

$$= \frac{115.1}{107.89} \simeq 1$$

$$\therefore \quad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 107.89 \times 1 = \mathbf{107.89} \quad \textbf{Ans.}$$

2. **Calculation of valency from the molecular weight of the volatile chloride.** Different steps to calculate valency by this method are:

(*i*) Find the **eq. wt.** of the element by usual methods. Let *E* = eq. wt. of the element.

(*ii*) Let x = valency of element. So, **at. wt.** = $E \times x$.

(*iii*) Let M be the one atom of the element having valency, x. So, formula of element chloride = $\mathbf{MCl_x}$.

(*iv*) Calculate vapour density (V.D.) of the chloride of the element. Then, mol. wt. of the chloride of element = 2 × V.D.

(*v*) Mol. wt. of $MCl_x = E\,x + 35.5\,x = x(E + 35.5)$

$$\therefore \quad x = \frac{\text{Mol. wt. of } MCl_x \textit{ i.e., } 2 \times \text{V.D.}}{E + 35.5}$$

EXAMPLE 10. *The chloride of a metal contains 79.8% chlorine. The vapour density of its chloride is 133.4. If sp. heat of the metal is 0.224, calculate the equivalent weight, valency, at. wt. and molecular formula of its chloride.*

SOLUTION.

(*i*) Wt. of chlorine = 79.8 g;

wt. of metal = 100 – 79.8 = 20.2 g;

sp-heat = 0.224;

V.D. of the metal chloride = 133.4. We know:

$$\frac{\text{Wt. of metal}}{\text{Wt. of chlorine}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of chlorine } (= 35.5)};$$

$$\frac{20.2 \text{ g}}{79.8 \text{ g}} = \frac{E}{35.5}$$

$$\therefore \quad E = \frac{20.2 \times 35.5}{79.8} = 9$$

(*ii*) $$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.224} = \mathbf{28.57}$$

$$\therefore \quad \text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{28.57}{9} \simeq 3$$

$$\therefore \quad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 9 \times 3 = 27 \quad \textbf{Ans.}$$

∴ Empirical formula of metal chloride = MCl_3.

But n × E.F. = Molecular formula, M.F.

$$\text{where} \quad n = \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= \frac{2 \times \text{V.D.}}{\text{E.F. wt.}} = \frac{2 \times 133.4}{133.5} \approx 2$$

$$\left[\begin{array}{l} \because \text{E.F. wt. of } MCl_3 \\ = \text{at. wt. of M} + (3 \times 35.5) \\ = 27 + 106.5 = 133.5 \end{array}\right.$$

$$\therefore \qquad \text{M.F.} = 2 \times MCl_3 = M_2Cl_6 \quad \textbf{Ans.}$$

EXAMPLE 11. *The oxide of a metal was found to contain 52.94% metal. If V.D. of the chloride of the metal is 66.75, what will be the at. wt. of the metal?*

SOLUTION. Hint.

We know:

$$\frac{\text{Wt. of metal}}{\text{Wt. of oxygen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of oxygen}};$$

$$\frac{52.94\text{ g}}{47.06\text{ g}} = \frac{E}{8};$$

$$E = 9$$

Mol. wt. or 2 × V.D. = Mol. wt. of MCl_x = M + 35.5 x

$$2 \times 66.75 = Ex + 35.5x = 9x + 35.5x = 44.5x$$

$$\therefore \qquad x = \frac{2 \times 66.75}{44.5} = 3$$

$$\therefore \qquad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 9 \times 3 = 27 \quad \textbf{Ans.}$$

EXAMPLE 12. *One gram of the chloride of an element was found to contain 0.835 g chlorine. Its vapour density is 85. Find its at. wt.* **(M.D.I.J. 1980)**

SOLUTION. Wt. of chlorine = 0.835 g; wt. of element = 1.0 – 0.835 = 0.165 g; V.D. = 85; Mol. wt. = 2 × V.D. = 2 × 85 = 170. We know:

$$\frac{\text{Wt. of metal}}{\text{Wt. of chlorine}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of chlorine}};$$

$$\frac{0.165\text{ g}}{0.835\text{ g}} = \frac{E}{35.5}$$

$$\therefore \qquad E = \frac{0.165}{0.835} \times 35.5 = \mathbf{7.02}$$

Also, Mol. wt. (given) = Mol. wt. of MCl_x where x = Valency of M.

$$170 = (E \times x) + (35.5 \times x)$$

$$= 7x + 35.5x = 42.5x$$

$$\therefore \qquad x = \frac{170}{42.5} = 4 = \text{Valency}$$

$$\therefore \qquad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 7.02 \times 4 = 28.08 \quad \textbf{Ans.}$$

EXAMPLE 13. *An experiment revealed that 100 g of silver reacted with all the chlorines in 55.993 g of arsenious chloride [V.D. 6.3, (air = 1)]. If sp. heat of arsenic is 0.082, calculate the formula of arsenious chloride and exact at. wt. of arsenic (1L of air at NTP weighs 1.293 g; at. wt., Ag = 108, Cl = 35.5).*

SOLUTION. Wt. of Ag = 100 g,

Wt. of arsenious chloride = 55.993 g.

1 L of air at NTP weighs = 1.293 g.

∴ 11.2 L of air at NTP weighs = 1.293 × 11.2 = 14.48

∴ V.D. of air = 14.48, V.D. of arsenious chloride

$$= 6.3 \times 14.48 = \mathbf{91.2}$$

$$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.082} = \mathbf{78}.$$

Mol. wt. of $AsCl_x$ = M + 35.5x (x = valency of As)

$$2 \times \text{V.D. of } AsCl_x = 78 + 35.5x$$

$$2 \times 91.2 = 78 + 35.5x;$$

$$\frac{182.4 - 78}{35.5} = x; \quad x = \frac{104.4}{35.5} \approx 3$$

∴ Molecular formula of arsenious chloride

$$= \mathbf{AsCl_3} \quad \textbf{Ans.}$$

Also,

Mol. wt. of $AsCl_x$ = Ex + 35.5x

(E = Eq. wt. = M, *i.e.*, at. wt.)

$$182.2 = 3E + 3 \times 35.5 = 3E + 106.5$$

or $$E = \frac{182.2 - 106.5}{3} = 25.23$$

$$\therefore \qquad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 25.3 \times 3 = 75.9 \quad \textbf{Ans.}$$

EXAMPLE 14. *In a victor Meyer apparatus 0.29 g of the chloride of a metal expelled 32 mL of moist air measured at 21°C and 758 mm pressure. In another experiment, 0.41 g of the same metal evolved 375mL moist air. Calculate the at. wt. of the metal (aq. tension at 21°C = 18.5 mm).*

SOLUTION. (*i*) P_1 = 758 – 18.5 = 739.5 mm, V_1 = 32 mL, T_1 = 21 + 273 = 294 K; at NTP, P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

But $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (gas equation);}$$

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} = \frac{739.5 \times 32 \times 294}{273 \times 760}$$

or V_2 = 33.5 mL. Thus:

Mol. wt. of chloride of metal

$$= \frac{W}{V_{\text{NTP}}} \times 22400 = \frac{0.29}{33.5} \times 22400$$

$$= \mathbf{193.9.}$$

(*ii*) Wt. of metal = 0.41 g; V_1 = 375 mL, P_1 = 739.5 mm, T_1 = 294 K; at NTP, P_2 = 760 mm, V_2 = ?, T_2 = 273 K. But

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}; \; V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2};$$

$$V_2 = \frac{739.5\text{ mm} \times 375\text{ mL} \times 273\text{ K}}{294\text{ K} \times 760\text{ mm}}$$

or V_2 = 338.8 mL.

We know: $$\frac{\text{Wt. of metal}}{\text{Wt. of } H_2 (= V_{\text{NTP}} \times 0.00009\text{ g})}$$

$$= \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } H_2 (= 1.008)}$$

$$\frac{0.41\text{ g}}{338.8 \times 0.00009\text{ g}} = \frac{E}{1.008};$$

$$E = \frac{0.41 \times 1.008}{338.8 \times 0.00009} = 13.5$$

Mol. wt. of chloride of metal MCl_x = M + 35.5x

$$193.9 = Ex + 35.5x = 13.5x + 35.5x = 49x$$

$$\therefore \quad x = \frac{193.9}{49} \approx 4 = \text{Valency}$$

So, at. wt. of metal = Eq. wt. × Valency

= 13.5 × 4 = **54.0 Ans.**

EXAMPLE 15. *A hydrated sulphate of a metal contained 8.1% metal and 43.2% of sulphate (SO_4^{2-}) by weight. Assuming the specific heat of the metal to be 0.242, determine the formula of the hydrated sulphate.* **(I.I.T. 1977)**

SOLUTION.

$$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.242} = 26.4$$

$$\text{Eq. wt. of } SO_4^{2-} = \frac{\text{Ionic weight}}{\text{Valency}} = \frac{32 + (4 \times 16)}{2}$$

$$= 48$$

43.2 g SO_4^{2-} combine with metal = 8.1 g

$$48\text{ g } SO_4^{2-} \text{ combine with metal} = \frac{8.1}{43.2} \times 48 = 9$$

$$\therefore \text{ Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{26.4}{9} \simeq 3;$$

Exact at. wt. = Eq. wt. × Valency = 9 × 3 = 27

∴ Formula of hydrated sulphate of metal,

M = $M_2(SO_4)_3 \cdot xH_2O$.

Calculation of ***x*****.**

Wt. of H_2O = 100 – (8.1 + 43.2)

= 100 – 51.3 = 48.7 g

8.1 g metal corresponds to H_2O = 48.7 g

2g at. wt. *i.e.,* 27 × 2 = 54 g metal correspond to

$$H_2O = \frac{48.7\text{ g}}{8.1\text{ g}} \times 54\text{ g} = 324.7\text{ g}.$$

$$[\because M_2(SO_4)_3\ xH_2O \equiv 2M]$$

∴ no. of H_2O molecules

$$= \frac{324.7\text{ g}}{\text{g. mol. wt. of } H_2O\ (= (2 \times 1) + 16 = 18\text{ g})} \simeq 18 = x$$

∴ Formula of hydrated sulphate = $M_2(SO_4)_3 \cdot 18H_2O$ **Ans.**

EXAMPLE 16. *The hydrated chloride of a metal M weighing 1.29 g was heated till constant weight of anhydrous chloride equal to 1.1 g was obtained. 1.57 g anhydrous chloride when heated with excess of H_2SO_4 gave 1.75 g of anhydrous sulphate. If specific heat of the metal is 0.043, calculate the exact at. wt. of the metal and write the formula of its hydrated chloride.*

SOLUTION. (*i*) Let E = eq. wt. of metal;

$$\text{eq. wt. of } SO_4^{2-} = \frac{\text{Ionic wt.}}{\text{Valency}}$$

$$\therefore \text{ Eq. wt. of } SO_4^{2-} = \frac{32+(4\times16)}{2} = 48.$$ We know

$$\frac{\text{Wt. of anhydrous chloride}}{\text{Wt. of anhydrous sulphate}}$$

$$= \frac{\text{Eq. wt. of anhydrous chloride}}{\text{Eq. wt. of anhydrous sulphate}}$$

$$\frac{1.57\text{ g}}{1.75\text{ g}} = \frac{E + 35.5}{E + 48};$$

1.57 E + 75.36 = 1.75 E + 62.12

$$\therefore \quad 0.18E = 13.24;\ E = \frac{13.24}{0.18} = 73.5$$

(*ii*) $$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.043} = 148.8$$

$$\therefore \text{ Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{148.8}{73.5} \simeq 2;$$

Exact at. wt. = 73.5 × 2 = 147.0

∴ Formula of anhydrous chloride = MCl_2.

(*iii*) *Calculation of formula of hydrated chloride.*

Wt. of anhydrous chloride = 1.1 g;

Wt. of hydrated chloride = 1.29 g

∴ Wt. of H_2O = 1.29 – 1.1 = 0.19 g.

Mol. wt. of anhydrous chloride,

MCl_2 = 147 + (2 × 35.5) = 218 g

1.1 g of anhydrous chloride is combined with H_2O = 0.19 g

∴ 218 g of anhydrous chloride is combined with

$$H_2O = \frac{0.19}{1.1\text{ g}} \times 218\text{ g} = 37.6\text{ g}$$

∴ No. of water molecules

$$= \frac{37.6}{\text{g. mol. wt. of } H_2O\ (=18)}$$

$$= \frac{37.6}{18} = 2$$

∴ Formula of hydrated chloride of metal = $MCl_2 \cdot 2H_2O$.

EXAMPLE 17. *Three oxides of an element A contain respectively 83.95%, 89.71% and 86.74% of element. 1.54 g of the chloride of an element on complete hydrolysis gave 1.27 g of the corresponding hydroxide. If specific heat of A is 0.03, calculate its exact at. wt. and the formula of its oxides, chloride and hydroxide.*

SOLUTION. (*i*) Let E = Eq. wt. of element A.

$$\text{Eq. wt. of } OH^- = \left(\frac{\text{ionic weight}}{\text{Valency}}\right) = \frac{(16+1)}{1} = 17.$$

We know

$$\frac{\text{Wt. of chloride of A}}{\text{Wt. of hydroxide of A}} = \frac{\text{Eq. wt. of chloride of A}}{\text{Eq. wt. of hydroxide of A}}$$

$$\frac{1.54\text{ g}}{1.27\text{ g}} = \frac{E+35.5}{E+17};\ 1.54\,E + 26.18$$

$$= 1.27\,E + 45.1$$

$$0.27\,E = 18.92;\quad E = \frac{18.92}{0.27} = 70.$$

$$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.03} = 213.3;$$

$$\text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{213.3}{70} \simeq \mathbf{3}$$

$$\therefore \quad \text{Exact at wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 70 \times 3 = 210 \quad \textbf{Ans.}$$

∴ Formula of oxide = A_2O_3, of chloride = ACl_3 and of hydroxide = $A(OH)_3$ because valency of A = 3 (found above).

(*ii*) Calculation of formula of oxides.

First oxide	*%age*	*At. wt.*	*Relative no. of atoms = % age/at. wt.*	*Simple ratio*	*Simple whole no. ratio*
Element	83.95	210	$\frac{83.95}{210} = 0.4$	$\frac{0.4}{0.4} = 1$	1 × 2 = 2
Oxygen	100 – 83.95 = 16.05	16	$\frac{16.05}{16} = 1.0$	$\frac{1.0}{0.4} = 2.5$	2 × 2.5 = 5

Hence formula of oxide = $\mathbf{A_2O_5}$ **Ans.**

Second oxide	*%age*	*At. wt.*	*Relative no. of atoms = % age/at. wt.*	*Simple ratio*	*Simple whole no. ratio*
Element	89.71	210	$\frac{89.71}{210} = 0.42$	$\frac{0.42}{0.42} = 1$	1 × 2 = 2
Oxygen	100 – 89.71 = 10.29	16	$\frac{10.29}{16} = 0.64$	$\frac{0.64}{0.42} = 1.5$	1.5 × 2 = 3

∴ Formula of oxide = $\mathbf{A_2O_3}$ **Ans.**

Third oxide	*%age*	*At. wt.*	*Relative no. of atoms = % age/at. wt.*	*Simple ratio*	*Simple whole no. ratio*
Element	86.74	210	$\frac{86.74}{210} = 0.41$	$\frac{0.41}{0.41} = 1$	1
Oxygen	100 – 86.74 = 13.26	16	$\frac{13.26}{16} = 0.82$	$\frac{0.82}{0.41} = 2$	2

∴ Formula of oxide = $\mathbf{AO_2}$ **Ans.**

4.4 CANNIZZARO'S METHOD

In this method, a large number of volatile compounds of the element (whose at. wt. is required) are analysed and percentage of the element present in them is determined. Also, vapour density (or mol. wt.) of all such compounds is determined and the weights of the element present in them is calculated. **The highest common factor (H.C.F.) *i.e.*, least weight of the element** gives the probable at. wt. of the concerned element. The other weights of the element present in the mol. wt. of such compounds may be simple multiples of that weight found.

EXAMPLE 18. *Phosphorus combines with hydrogen, oxygen, sulphur, fluorine and chlorine to form phosphine, phosphorus pentoxide, phosphorus pentasulphide, phosphorus penta fluoride and phosphorus trichloride. These compounds contain respectively the %age of P as 91.18, 43.66, 27.9, 24.6 and 22.5, while their vapour densities are respectively 17, 71, 111, 63 and 69. Calculate the exact at. wt. of phosphorus.*

SOLUTION. The probable at. wt. of phosphorus is found as follows.

Compound	*Mol. wt. = 2 × V.D.*	*% age of C*	*Wt. of P in the mol. wt.*	*H.C.F. or Least weight*
Phosphine	2 × 17 = 34	91.18	$\frac{34 \times 91.18}{100} = 31$	H.C.F. (or least weight) of 31, 62, 62, 31 and 31 is 31.
Phosphorus Pentoxide	2 × 71 = 142	43.66	$\frac{142 \times 43.66}{100} = 62$	
Phosphorus Pentasulphide	2 × 111 = 222	27.9	$\frac{222 \times 27.9}{100} = 62$	
Phosphorus Pentafluoride	2 × 63 = 126	24.6	$\frac{126 \times 24.6}{100} = 31$	
Phosphorus Trichloride	2× 69 = 138	22.5	$\frac{138 \times 22.5}{100} = 31$	

∴ Approximate at. wt. of phosphorus is 31.0

(*ii*) **Calculation of exact at. wt.** While calculating the exact at. wt. of P, we can take the help of any one of the given compounds. So, let us consider phosphine

$$\text{wt. of P} = 91.18\text{ g};$$

$$\text{wt. of H} = 100 - 91.18 = 8.82\text{ g}.$$

We know :

$$\frac{\text{wt. of P}}{\text{wt. of H}} = \frac{\text{Eq. wt. of P}}{\text{Eq. wt. of H}(= 1.008)};$$

$$\frac{91.18\text{ g}}{8.82\text{ g}} = \frac{\text{Eq. wt. of P}}{1.008}$$

$$\therefore \quad \text{Eq. wt. of P} = \frac{91.18 \times 1.008}{8.82} = 10.42$$

$$\text{Valency} = \frac{\text{Approx. at. wt}}{\text{Eq. wt}} = \frac{31.0}{10.42} = 3$$

$$\therefore \quad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 10.42 \times 3 = \mathbf{31.26} \ \textbf{Ans.}$$

EXAMPLE 19. *A metal (sp. heat, 0.055) forms three volatile chlorides containing 76.4%, 61.8% and 51.7% of metal respectively. The vapour densities of respective chlorides (H = 1) are 74.6, 92.9 and 110.6. Calculate the at. wt. of the metal and formula of its chlorides.*

SOLUTION.

Compound	*Mol. wt. = 2 × V.D.*	*% age of C*	*Wt. of metal in the mol. wt.*	*H.C.F. or Least weight*
First chloride	2 × 74.6 = 149.2	76.4	$\frac{76.4 \times 149.2}{100} = 114$	The H.C.F. or least wt. of 114, 114, 114 is 114.
Second chloride	2 × 92.9 = 185.8	61.8	$\frac{61.8 \times 185.8}{100} = 114.8 \simeq 114$	
Third chloride	2 × 110.6 = 221.2	51.7	$\frac{51.7 \times 221.2}{100} = 114.36 \simeq 114$	

∴ Approx. at. wt. of metal = 114.

(*ii*) Considering any one of the above chlorides, we can calculate the eq. wt. of the metal. Let us consider the third chloride.

$$\frac{\text{Wt. of metal}}{\text{Wt. of chlorine}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of chlorine } (= 35.5)}$$

$$\frac{51.7 \text{ g}}{100 - 51.7} = \frac{\text{Eq. wt. of metal}}{35.5} = 48.3 \text{ g}$$

$$\therefore \quad \text{Eq. wt. of metal} = \frac{51.7 \times 35.5}{48.3} = 38.$$

$$\text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{114}{38} \simeq 3.$$

$$\therefore \quad \text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency}$$

$$= 38 \times 3 = 114 \quad \textbf{Ans.}$$

(*iii*) *Calculation of formula of chlorides.* Let x, y and z atoms of chlorine combine with one atom of metal to form MCl_x, MCl_y and MCl_z compounds.

For first chloride, MCl_x, mol. wt. of $MCl_x = 149.2$

$$\therefore \quad 114 + 35.5x = 149.2; \quad x = \frac{149.2 - 114}{35.5} \simeq 1$$

$$\therefore \quad \text{Formula} = \text{MCl}.$$

For second chloride, MCl_y, mol. wt. of $MCl_y = 185.8$

$$\therefore \quad 114 + 35.5y = 185.8; \quad y = \frac{185.8 - 114}{35.5} \simeq 2$$

$$\therefore \quad \text{Formula} = MCl_2$$

For third chloride, MCl_z, mol. wt. of $MCl_z = 221.2$

$$\therefore \quad 114 + 35.5x = 221.2; \quad x = \frac{221.2 - 114}{35.5} \simeq 3$$

$$\therefore \quad \text{Formula} = MCl_3 \quad \textbf{Ans.}$$

4.5 LAW OF ISOMORPHISM

According to Mitscherlich, *isomorphous substances* are those which have the same number of atoms similarly arranged, *i.e.*, these have similar constitution. So, their chemical formula are similar. Thus, **according to law of isomorphism,** *isomorphous substances form crystals which can grow in the saturated solution of each other and have the same shape.* For example.

(*i*) $ZnSO_4{\cdot}7H_2O$ and $MgSO_4{\cdot}7H_2O$ are isomorphous substances.

(*ii*) $KMnO_4$ and $KClO_4$ are isomorphous substances.

Importance of above law

1. *To find valency of two elements.* The valency of two elements which form isomorphous salts are essentially the same. So, if valency of one element is known, that of the other will hence be the same. From this valency value, at. wt. of the element can be calculated.
2. Weights of two elements (A and B) forming isomorphous compounds are in the following ratio of their atomic weights.

$$\frac{\text{At. wt. of element A}}{\text{At. wt. of element B}} = \frac{\begin{array}{l}\text{Wt. of element A that combines with}\\ \text{a certain wt. of other elements}\end{array}}{\begin{array}{l}\text{Wt. of element B that combines with}\\ \text{the same wt. of other elements}\end{array}}$$

Hence if we know at. wt. of one of the elements and %age of two elements in their respective isomorphous compounds, the at. wt. of the other elements can be calculated from the above relation.

EXAMPLE 20. *A metal Y forms a sulphate which is isomorphous with $MgSO_4{\cdot}7H_2O$. Find the at. wt. of the metal if 0.8912 g of the metal displaces 2.97 g of silver (at. wt., Ag = 107.9).*

SOLUTION. Wt. of metal Y = 0.8912 g; wt. of Ag = 2.97g. We know:

$$\frac{\text{Wt. of metal Y}}{\text{Wt. of Ag}} = \frac{\text{Eq. wt. of Y}}{\text{Eq. wt. of Ag } (= 107.9)}$$

$$\left[\text{Eq. wt. of Ag} = \frac{\text{At. wt. of Ag}}{\text{Valency of Ag}} = \frac{107.9}{1}\right]$$

$$\frac{0.8912 \text{ g}}{2.97 \text{ g}} = \frac{E}{107.9};$$

$$E = \frac{0.8912 \times 107.9}{2.97} = 32.38$$

Since metal Y forms a sulphate which is isomorphous with $MgSO_4{\cdot}7H_2O$ and valency of Mg = 2, so valency of Y = 2.

$$\therefore \quad \text{At. wt. of Y} = \text{Eq. wt.} \times \text{Valency}$$

$$= 32.38 \times 2 = \mathbf{64.76} \ \textbf{Ans.}$$

Example 21. *The hydrated sulphate of a metal contains 22.64% of the metal. If this compound is isomorphous with* $MgSO_4$, $7H_2O$, *calculate the valency and atomic weight of the metal. (At. wt. H = 1, S = 32, Mg = 24, S = 32).*

Solution.

(*i*) Since the hydrated sulphate of the metal M is isomorphous with $MgSO_4 \cdot 7H_2O$, the valency of both metals will be the same. Since Mg has valency 2, **valency of M = 2.**

(*ii*) Let at. wt. of M = m. So, mol. wt. of $MSO_4 \cdot 7H_2O$ will be:

$$m + 32 + (4 \times 16) + 7[(2 \times 1) + 16] = 222 + m$$

$$\text{\%age of M in its mol. wt.} = \frac{m}{222 + m} \times 100$$

$$\therefore \quad \frac{100m}{222 + m} = 22.64 \text{ (given)};$$

$$100\,m = 22.64 \times 222 + 20.64\,m$$

$$77.36\,m = 5026; \quad m = \frac{5026}{77.36} = \mathbf{64.97}$$

∴ At. wt. of metal = **64.97** **Ans.**

Example 22. *Silver sulphide and cuprous sulphide are isomorphous with each other. The percentage of sulphur in former is 12.94 while that in second is 20.14. Calculate at. wt. of Ag if that of copper is 63.57.*

Solution. (*i*) **Silver sulphide.** Wt. of S = 12.94 g; Wt. of Ag = 100 – 12.94 = 87.06 g

(*ii*) **Cuprous sulphide.** Wt. of S = 20.14 g; Wt. of copper = 100 – 20.14 = 79.86 g.

(*iii*) To know wt. of copper that will combine with same wt. of sulphur as Ag combines.

20.14 g sulphur that combine with Cu = 79.86 g

12.94 g sulphur that combine with Cu =

$$\frac{79.86\text{ g}}{20.14\text{ g}} \times 12.94\text{ g} = \mathbf{51.31\text{ g}}.$$

According to law of isomorphism:

$$\frac{\text{Wt. of Ag}}{\text{Wt. of Cu}} = \frac{\text{At. wt. of Ag}}{\text{At. wt. of Cu}};$$

$$\frac{87.06\text{ g}}{51.31\text{ g}} = \frac{\text{At. wt. of Ag}}{63.57}$$

$$\therefore \quad \text{At. wt. of Ag} = \frac{87.06 \times 63.57}{51.31} = \mathbf{107.8} \quad \textbf{Ans.}$$

Example 23. *The oxides of two elements P and Q are isomorphous. The element P has at. wt. 52 and vapour density of its chloride is 79. Calculate the at. wt. of Q if its oxide contains 52.9% Q.*

Solution.

(*i*) Mol. wt. of PCl_x = 2 × V.D. = 2 × 79 = 158.

or At. wt. of $P + 35.5x = 158$

$$52 + 35.5x = 158;$$

$$35.5\,x = 106; \quad x = \left(\frac{106}{35.5}\right) \simeq 3$$

∴ Valency of $P = 3$

(*ii*) Wt. of Q = 52.9 g;

Wt. of oxygen = 100 – 52.9 = 47.1 g.

Thus:

$$\frac{\text{Wt. of } Q}{\text{Wt. of oxygen}} = \frac{\text{Eq. wt. of } Q}{\text{Eq. wt. of oxygen } (= 8)};$$

$$\frac{52.9\text{ g}}{47.1\text{ g}} = \frac{E}{8}$$

$$\therefore \quad E = \frac{52.9 \times 8}{47.1} = 8.98.$$

$$\therefore \quad \text{At. wt. of } Q = E \times \text{Valency}$$

$$= 8.98 \times 3 = \mathbf{26.94} \quad \textbf{Ans.}$$

Example 24. *Hydrated zinc sulphate contains 22.6% Zn and 33.5% sulphate. Hydrated magnesium sulphate contains 9.75% Mg and 39.02% sulphate. If above two salts are isomorphous, calculate the at. wt. of zinc if that of magnesium is 24.*

Solution.

(*i*) *Hydrated zinc sulphate:* Wt. of Zn = 22.6 g

∴ Wt. of other elements including water = 100 – 22.6 = 77.4 g.

(*ii*) *Hydrated magnesium sulphate:* Wt. of Mg = 9.75 g

∴ Wt. of other elements including water = 100 – 9.75 = 90.25 g

(*iii*) Calculation of wt. of Zn that will combine with same weight of other elements as Mg combines.

77.4 g of other elements that combine with Zn = 22.6 g

∴ 90.25 g of other elements that combine with

$$\text{Zn} = \frac{22.6\text{ g}}{77.4\text{ g}} \times 90.25\text{ g} = 26.35\text{ g}$$

$$= \text{Wt. of Zn}$$

According to law of isomorphism:

$$\frac{\text{Wt. of Zn}}{\text{Wt. of Mg}} = \frac{\text{At. wt. of Zn}}{\text{At. wt. of Mg}};$$

$$\frac{26.35\text{ g}}{9.75\text{ g}} = \frac{\text{At. wt of Zn}}{24}$$

$$\therefore \quad \text{At. wt. of Zn} = \frac{24 \times 26.35}{9.75} = 64.9 \quad \textbf{Ans.}$$

Example 25. *An element (eq. wt. = 13.16) forms an acidic oxide which reacts with KOH to form a salt, isomorphous with potassium sulphate. Find the atomic weight of the element.*

Solution. Let the element is *A*. Since *A* forms an acidic oxide, so *A* is a non-metal. It reacts with KOH to form a salt K_2AO_4 isomorphous with K_2SO_4.

Reaction. In K_2AO_4;

$2 \times$ O.N. of K + O.N. of A + $4 \times$ O.N. of O = 0

$2 \times (+1)$ + O.N. of A + $4(-2) = 0$; O.N. of A = +6

$$\therefore \quad A^{\circ} \longrightarrow A^{+6} + 6e^-$$

Eq. wt. of A = 13.16 (given)

$\therefore$ At. wt. of A = Eq. wt. of A $\times$ No. of electrons lost

$= 13.16 \times 6 = 78.96$ **Ans.**

Example 26. *Potassium selenate is isomorphous with potassium sulphate. Calculate the equivalent weight of potassium selenate and atomic mass of selenium if potassium selenate contains 45.42% selenium.*

Solution. Since potassium selenate is isomorphous with K_2SO_4, so its molecular formula is K_2SeO_4.

Let at. wt. of Se = a

Mol. wt. of $K_2SeO_4 = (2 \times 39) + a + (4 \times 16) = 142 + a$

$142 + a$ g K_2SeO_4 contain Se = a g

$$100 \text{ g of } K_2SeO_4 \text{ will contain Se} = \frac{a}{142+a} \times 100$$

$$\therefore \quad \frac{100\,a}{142+a} = 45.42;$$

$$100\,a = 45.42 \times 142 + 45.42\,a$$

$$\text{or} \quad 100\,a - 45.42\,a = 6449.64; \; 54.58a = 6449.64$$

$$\therefore \text{ At. wt. '}a\text{' of Se} = \frac{6449.64}{54.58} = 118.12$$

$$\therefore \text{Eq. wt. of } K_2SeO_4 = \frac{\text{Mol. wt. of } K_2SeO_4}{\text{Total +ve charge in } K_2SeO_4}$$

[$\because$ +ve charge of $2K^+$ in $K_2SeO_4 = 2 \times (+1) = +2$]

$$= \frac{(2 \times 39) + 118.12 + (4 \times 16)}{2}$$

= **130.06** **Ans.**

4.6 MOLE CONCEPT TO DETERMINE ATOMIC WEIGHT OF ELEMENTS

(*i*) g. at. wt. of an element = Avogadro's no. $\times$ Wt. of one atom of the element
$= 6.023 \times 10^{23} \times$ Wt. of one atom of the element

(*ii*) 22.4 L or 22400 mL of a gas of N.T.P. or S.T.P. weighs equal to its g. mol. wt.

Example 27. *An atom of magnesium weighs 3.98×10^{-23} g. Calculate the atomic weight of magnesium.*

Solution. Wt. of Mg-atom = 3.98×10^{-23} g. Hence:

g. at. wt. of Mg $= 6.023 \times 10^{23} \times 3.98 \times 10^{-23}$

= **23.97 g Ans.**

Example 28. *56 mL of N_2 gas at N.T.P. weighs 0.07 g. Calculate the atomic weight of nitrogen.*

Solution. We know 22400 mL of any gas at N.T.P. weighs equal to its g. mol. wt. So, we have:

56 mL of N_2 weighs = 0.07 g

$$\therefore \text{ 22400 mL of } N_2 \text{ weighs} = \frac{0.07}{56} \times 22400 = 28 \text{ g.}$$

Since 1 mole of N_2 consists of 2 mol atoms of nitrogen,

$$\text{g. at. wt. of nitrogen} = \frac{28}{2} = 14 \text{ g}$$

$\therefore$ at. wt. of nitrogen = **14.** **Ans.**

4.7 DETERMINATION OF at. wt. FROM eq. wt. AND VALENCY

Type. At. wt. = Eq. wt. $\times$ Valency

Example 29. *2.0 g of pure calcium was quantitatively converted to 2.8 g of its oxide. Calculate the atomic weight of calcium.*

Solution. Reaction.

$$Ca + \frac{1}{2}O_2 \longrightarrow CaO.$$

Equivalent of Ca = Equivalent of CaO.

$$\therefore \quad \frac{\text{Wt. of Ca}}{\text{Wt. of CaO}} = \frac{\text{Eq. wt. of Ca}}{\text{Eq. wt. of CaO}} \qquad \text{...(1)}$$

Let Eq. wt. of Ca = E;

Eq. wt. of CaO = Eq. wt. of Ca + Eq. wt. of oxygen

$$= E + \frac{\text{At. wt. of oxygen, 16}}{\text{Valency of oxygen; 2}}$$

$$= E + 8$$

Substituting the values in equation (1), we get,

$$\frac{2}{2.8} = \frac{E}{E+8}; \; 2E + 16 = 2.8E;$$

$$0.8E = 16. \text{ Hence } E = \frac{16}{0.8} = 20.$$

At. wt. of Ca = Eq. wt. of Ca $\times$ Valency of calcium

$= 20 \times 2 =$ **40** **Ans.**

4.8 DETERMINATION OF AT. WT. FROM WEIGHT OF ATOMS IN a.m.u.

Type. Atomic weight of an element in g
= Wt. of one atom of element in a.m.u.
$\times$ 1.66×10^{-24} g $\times$ Avogadro's no. (= 6.023×10^{23})

g. at. wt. is *the weight of Avogadro no.* (= 6.023×10^{23}) of atoms of an **element in gram.**

Example 30. *Calculate the gram atomic weight of oxygen if weight of its one atom is 16 a.m.u.*

Solution. 1 a.m.u. = 1.66×10^{-24} g

Wt. of one oxygen atom = 16 a.m.u. = $16 \times 1.66 \times 10^{-24}$g

($\because$ Wt. of 1 a.m.u. = 1.66×10^{-24} g)

$\therefore$ Wt. of Avogadro no. (= 6.023×10^{23}) of oxygen atoms

$= 16 \times 1.66 \times 10^{-24}$ g $\times 6.023 \times 10^{23}$

$\simeq 16$ g

$\therefore$ g. at. wt. of oxygen = **16 g.** **Ans.**

EXAMPLE 31. *Calculate the weight of one atom of nitrogen. (g. at. wt., N = 14 g).*

SOLUTION. g. at. wt. of N = 14 g;

Avogadro no. = 6.023×10^{23}.

We know that:

g. at. wt. of N = Wt. of one atom of N in amu × 1.66×10^{-24} g × Avogadro no. ($= 6.023 \times 10^{23}$)

14 g = Wt. of one atom of N in amu × 1.66×10^{-24} g × 6.023×10^{23}

$\therefore$ Wt. of one atom of N in amu

$$= \frac{14\text{ g}}{1.66 \times 10^{-24}\text{g} \times 6.023 \times 10^{23}}$$

$= \mathbf{14\ amu}$ **Ans.**

EXAMPLE 32. *g. at. wt. of carbon is 12 g. If one atom of carbon weighs 12 amu, what will be the value of Avogadro's number?*

SOLUTION. g. at. wt. of C = 12 g; Wt. of one atom of carbon = 12 amu.

We know that:

g. at. wt. of C = Wt. of one atom of C in amu. × 1.66×10^{-24} g × Avogadro's no.

12 g = 12 × 1.66×10^{-24} g × Avogadro no.

$$\therefore \text{ Avogadro no.} = \frac{12\text{ g}}{12 \times 1.66 \times 10^{-24}\text{g}}$$

$= \mathbf{6.024 \times 10^{23}}$ **Ans.**

4.9 ATOMIC WEIGHT FROM MOLECULAR WEIGHT AND ATOMICITY (DEDUCED FROM POISSON'S RATIO, $\gamma = C_p/C_V$)

Atomicity is the number of atoms present in a molecule of the element. The atomicity of most gases can be deduced from the measurement of γ (Poisson's ratio) where

$$\gamma = \frac{C_p}{C_v}.$$

C_p and C_v are the molar heat capacities of a gaseous element both at constant pressure and at constant volume respectively.

$\gamma = 1.667$ for monoatomic gases;

$\gamma = 1.4$ for diatomic gases and

$\gamma = 1.33$ for triatomic gases.

$$\text{Atomic weight} = \frac{\text{Mol. wt.}}{\text{Atomicity}}$$

$C_p - C_v = R$ where $R = 2$ cal.

C_p = Mol. wt. × specific heat capacity (or sp. heat);

C_v = mol. wt. × sp. heat.

EXAMPLE 33. *The ratio of molar heats of a gas (mol. wt. = 32) at constant pressure to constant volume is 1.41. Calculate the atomic weight of the gas.*

SOLUTION.

$$\gamma = \frac{C_p}{C_v} = 1.41$$

This value corresponds to diatomic gases. So, atomicity of gas = 2.

$$\therefore \quad \text{At. wt. of gas} = \frac{\text{Mol. wt.}}{\text{Atomicity}} = \frac{32}{2} = \mathbf{16}\ \textbf{Ans.}$$

EXAMPLE 34. *Molar mass of a gas is 48. If molar heat of the gas at constant volume is 28.9, find the atomic weight of the gas.* **(*R* = 8.3 J)**

SOLUTION. $C_v = 28.9$, $R = 8.3$ J, $C_p - C_v = R$; $C_p - 28.9 = 8.3$. $\therefore$ $C_p = 8.3 + 28.9 = 37.2$.

$$\text{Thus} \qquad \frac{C_p}{C_v} = \frac{37.2}{28.9} = 1.287 \simeq 1.3 = \gamma$$

Since the value of γ is 1.3, the gas is triatomic *i.e.*, atomicity = 3

$$\therefore \qquad \text{At. wt.} = \frac{\text{Mol. wt.}}{\text{Atomicity}} = \frac{48}{3} = \mathbf{16}\ \textbf{Ans.}$$

Note. For more examples, see Chapter 8.

4.10 AIEEE PATTERN EXAMPLES

EXAMPLE 35. *An element having three isotopes has mass numbers M, M + 1 and M + 2. Their mean atomic mass is M + 1.2. The ratio which corresponds to the given data is :*

(a) 1 : 1 : 1 *(b) 1 : 2 : 3*

(c) 2 : 3 : 4 *(d) 1 : 3 : 5*

SOLUTION.

$$(a) \quad \text{Mean atomic mass} = \frac{(1 \times M) + 1(M+1) + 1(M+2)}{1+1+1} = M + 1$$

$$(b) \quad \text{Mean atomic mass} = \frac{(1 \times M) + 2(M+1) + 3(M+2)}{1+2+3} = M + 1.3$$

$$(c) \quad \text{Mean atomic mass} = \frac{(2 \times M) + 3(M+1) + 4(M+2)}{2+3+4} = M + 1.2$$

$$(d) \quad \text{Mean atomic mass} = \frac{(1 \times M) + 3(M+1) + 5(M+2)}{1+3+5} = M + 1.4$$

So, the correct answer is (*c*).

EXAMPLE 36. *A certain metal is divalent. 2.65 g of its oxide when reduced in a current of hydrogen leaves 2.454 g of the metal. The atomic weight of the metal will be :*

(a) 100.16 *(b) 200.32* *(c) 50.08* *(d) 25.04.*

SOLUTION.

Wt. of oxygen = 2.65 – 2.454 = 0.196 g

$$\frac{\text{Wt. of metal}}{\text{Wt. of oxygen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of oxygen}};$$

$$\frac{2.454\text{ g}}{0.196} = \frac{\text{Eq. wt. of metal}}{8}$$

$\therefore$ Eq. wt. of metal = $\dfrac{2.454 \times 8}{0.196}$ = 100.16

$\therefore$ At. wt. = Eq. wt. × Valency

= 100.16 × 2 = **200.32 Ans.**

So, the correct answer is (*b*).

EXAMPLE 37. *0.45 g of a metal displaced 560 cm^3 of hydrogen at N.T.P. from an acid. If specific heat of metal is 0.214, the atomic weight of the metal is:*

(a) *27 amu* *(b)* *13.5 amu*

(c) *54 amu* *(d)* *None of these.*

SOLUTION. Wt. of 1 cm^3 H_2 at NTP = 0.00009 g

$\therefore$ Wt. of 560 cm^3 H_2 at NTP = 0.00009 × 560 = 0.0504 g

$$\text{Approximate at. wt. of metal} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.214}$$

$$= 29.9$$

$$\frac{\text{Wt. of metal}}{\text{Wt. of hydrogen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of hydrogen}};$$

$$560 \times 0.00009 = \frac{0.45\text{ g}}{0.0504\text{ g}} = \frac{\text{Eq. wt. of metal}}{1.008\text{ g}}$$

$$\therefore \text{Eq. wt. of metal} = \frac{0.45 \times 1.008}{0.0504} = 9.0$$

$$\text{Exact valency of metal} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{29.9}{9} \simeq 3$$

$\therefore$ At. wt. of metal = Eq. wt. × Valency

= 9 × 3 = **27 amu.**

So, the correct answer is (*a*).

EXAMPLE 38. *When a metal weighing 0.3g was treated with an acid, liberated 280 cm^3 of H_2 at STP. It forms an oxide MO where M stands for the metal. The atomic weight of the metal is:*

(a) *6 g* *(b)* *1.1 amu*

(c) *24 amu* *(d)* *12 amu.*

SOLUTION.

(*i*) $\dfrac{\text{Wt. of metal}}{\text{Wt. of } H_2} = \dfrac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } H_2}$;

$$0.00009 \times 280 = \frac{0.3}{0.0252} = \frac{\text{Eq. wt. of metal}}{1.008}$$

$$\therefore \quad \text{Eq. wt. of metal} = \frac{0.3 \times 1.008}{0.0252} = 12$$

(*ii*) To find valency of metal, M. Metal forms oxide, MO. Since valency of oxide is 2, so valency of metal in MO = 2.

$\therefore$ At. wt. of metal = Eq. wt. × Valency

= 12 × 2 = **24 amu**

So, the correct answer is (*c*).

EXAMPLE 39. *When a metal carbonate weighing 0.84 g was heated strongly, 0.40 g of metal oxide was left as the residue. The specific heat of the metal is 0.25. The atomic weight of the metal is:*

(a) *6 amu* *(b)* *12 amu*

(c) *18 amu* *(d)* *24 amu.*

SOLUTION.

(*i*) $\dfrac{\text{Wt. of metal carbonate}}{\text{Wt. of metal oxide}}$

$$= \frac{\text{Eq. wt. of metal carbonate}}{\text{Eq. wt. of metal oxide}}$$

$$\frac{0.84\text{ g}}{0.40\text{ g}} = \frac{E+30}{E+8}; \quad \frac{21}{10} = \frac{E+30}{E+8};$$

$$21E + 168 = 10E + 300$$

$$\therefore \quad 11E = 132; \quad E = \frac{132}{11} = 12$$

(*ii*) $\text{Approx. at. wt. of metal} = \dfrac{6.4}{\text{sp. heat}} = \dfrac{6.4}{0.25} = 25.6$

$$\therefore \quad \text{Exact valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}} = \frac{25.6}{12} \simeq 2$$

(*iii*) Exact at. wt. = Eq. wt. × Valency

= 12 × 2 = **24 amu.**

So, the correct answer is (*d*).

EXAMPLE 40. *The vapour densities of four compounds of a certain metal are 8.5, 22, 23 and 26 respectively. The percentages of same elements in these compounds are 82.4, 63.7, 89.4 and 58.8 respectively. The atomic weight of the metal is:*

(a) *14* *(b)* *41* *(c)* *28* *(d)* *30.5*

SOLUTION.

Compounds	*Mol. wt. = 2 × V.D.*	*% age of C*	*Wt. of element in mol. wt.*	*H.C.F. or Least weight*
First	2 × 8.5 = 17	82.4	$\dfrac{82.4 \times 17}{100} = 14$	14 ($\because$ H.C.F. of 14, 28, 42, 28 = 14)
Second	2 × 22 = 44	63.7	$\dfrac{63.7 \times 44}{100} = 28$	
Third	2 × 23 = 46	89.4	$\dfrac{89.4 \times 46}{100} = 41 \simeq 42$	
Fourth	2 × 26 = 52	58.8	$\dfrac{58.8 \times 52}{100} = 30.5 \simeq 28$	

Since the weights of elements in the mol. wt. found are nearly integral multiple of 14, so the atomic weight of element is 14. So, the correct answer is (*a*).

EXAMPLE 41. *Three atoms of a metal combine with two atoms of nitrogen to form metal nitride. If the metal nitride contains 81.08% metal and 18.92%, nitrogen, the atomic weight of the metal is:*

(a) *10* *(b)* *20* *(c)* *40* *(d)* *35.*

Solution. Let at. wt. of metal = *a*

Reaction.

$$\underset{3\times a=3a}{3M} \quad + \quad \underset{2\times 14=28\text{ g}}{2N} \longrightarrow \underset{\substack{(3\times a)+(2\times 14)\\ =3a+28\text{ g}}}{M_3N_2}$$

$$\therefore \quad (3a+28)\text{g } M_3N_2 \text{ contains metal} = 3a$$

$$100\text{ g } M_3N_2 \text{ contains metal} = \frac{3a}{3a+28}\times 100 = \frac{300a}{3a+28}$$

Hence, $\frac{300a}{3a+28} = 81.08;$

$$300a = 81.08(3a+28) = 243.24a + 2270.24$$

$$300a - 243.24a = 2270.24;\ 56.76a = 2270.4;\ a = \frac{2270.4}{56.76} \simeq 40.$$

So, the correct answer is (*c*).

Example 42. *1.5276 g of $CdCl_2$ was found to contain 0.9367 g of cadmium. The atomic weight of cadmium is:*

(a) 112.54 amu	*(b) 52.27 amu*
(c) 225.08 amu	*(d) None of these*

Solution.

$$\text{Eq. wt. of Cd} = \frac{0.9367}{0.5909}\times 35.5 = 56.27\text{ g}$$

$$[\because \text{wt. of chlorine} = 1.5276 - 0.9367 = 0.5909]$$

$$\text{Atomic weight} = \text{Eq. wt.} \times \text{Valency} = 56.27\times 2 = \mathbf{112.54\ amu}.$$

So, the correct answer is (*a*).

Example 43. *On dissolving 2.00 g of a metal in sulphuric acid, 4.51 g of the metal sulphate was formed. The specific heat of the metal is 0.057 cal(g^{-}). The valency of the metal and its exact atomic weight are:*

(a) 228 amu	*(b) 114.75 amu*
(c) 110 amu	*(d) 56 amu.*

Solution.

(*i*) *Calculation of equivalent weight*

$$\frac{\text{Weight of metal sulphate}}{\text{Weight of metal}} = \frac{\text{Eq. wt. of metal} + \text{Eq. wt. of } SO_4^{2-}}{\text{Eq. wt. of metal}}$$

Let the eq. wt. of metal be *E*. Then, $\frac{4.51}{2} = \frac{E+48}{E}$

$$(\because \text{Eq. wt. of } SO_4^{2-} = \frac{96}{2} = 48)$$

$$\therefore \quad (E+48)\times 2 = 4.51\,E$$

or $2.51\,E = 96;\ E = \frac{96}{2.51} = 38.25$

(*ii*) *Calculation of atomic weight*

$$\text{Approx. at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.057} = 112.3$$

$$\text{Approx valency} = \frac{112.3}{38.25} = 2.93;\ \text{Exact valency} = 3$$

$$\text{Exact atomic weight} = \text{Eq. wt.} \times \text{Valency} = 38.25 \times 3 = \mathbf{114.75.}$$

So, the correct answer is (*b*).

Example 44. *A compound contains 28 percent of nitrogen and 72 percent of a metal by weight. 3 atoms of the metal combine with 2 atoms of N. The atomic weight of the metal is:*

(a) 6 amu	*(b) 12 amu*
(c) 24 amu	*(d) 18 amu.*

Solution. As 3 atoms of metal (M) combine with 2 atoms of nitrogen, therefore, the molecular formula of the compound is M_3N_2. Let the atomic weight of M be *a*.

Then, 28 g of nitrogen is in combination with 3 atoms of the metal M.

Actually, 28 gm of nitrogen combines with 72 g of the metal $\therefore\ 3a = 72$ or $a = 24$

Thus, atomic weight of the metal is 24. So, the correct answer is (*c*).

Example 45. *In order to obtain 1 gm of hydrogen from dil. H_2SO_4, 32.5 g of zinc has to be dissolved. If the atomic weight of the zinc is 67, its valency is :*

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

Solution.

(*i*) *Calculation of equivalent weight*

$$\text{Eq. wt. of Zn} = \frac{\text{Wt. of Zn}}{\text{Wt. of } H_2}\times 1.008 = \frac{32.5}{1}\times 1.008 = 32.76$$

(*ii*) *Calculation of valency*

$$\text{Valency} = \frac{\text{Atomic weight}}{\text{Equivalent weight}} = \frac{67}{32.76} = 2.04 = 2.$$

So, the correct answer is (*b*).

Example 46. *A solid element has a specific heat of 1 J g^{-} K^{-}. The approximate atomic mass of the element is:*

(a) 17	*(b) 27*	*(c) 2.7*	*(d) 1.7.*

(I.S.C. 1987 Modified)

Solution. We know,

$$4.184\text{ J } g^{-} K^{-} = 1 \text{ calorie } g^{-}K^{-};$$

$$1\text{ J} = \frac{1}{4.184}\text{ cal.}$$

$$\text{Atomic mass} = \frac{6.4}{\text{sp. heat (in cal.)}}$$

$$= \mathbf{6.4 \times 4.184 = 26.7776 \approx 27.}$$

So, the correct answer is (*b*).

EXAMPLE 47. *The oxide of an element possesses the formula M_2O_3. If the equivalent weight of the metal is 9, then the atomic weight of the metal will be :*

(a) 18 *(b) 1.8* *(c) 2.7* *(d) 27.*

SOLUTION. In the compound M_2O_3, the valency of metal, M = 3. Eq. wt. of metal = 9 (given).

But : At. wt. = Eq. wt. × Valency. So, we have :

At. wt. = 9 × 3 = 27.

So, the correct answer is (*d*).

EXAMPLE 48. *The molecular formula of a compound is A_2O_3. If 5.0 g of this has 2.86 g of A, the atomic mass of A will be*

(a) 16.0 *(b) 24.0* *(c) 32.0* *(d) 40.0*

SOLUTION. Let at. mass of $A = a$.

So; $2a + (3 \times 16)$ g of A contain $A = 2a$ g.

$\therefore$ 5g of A contain $A = \frac{2a}{2a+48} \times 5.$ Hence, we have:

$$2.86 = \frac{10a}{2a+48};\ 5.72\,a + 137.28 = 10\,a;\ a = 32$$

So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. $KMnO_4$ is isomorphous with potassium perchlorate ($KClO_4$). If $KClO_4$ contains 28.16% of potassium, calculate the at. wt. of potassium (At. wt. Mn = 55, Cl = 35.5) (**Ans.** 39)
2. Calculate the g. at. wt. of Na-atom if weight of its one atom is 23 amu. (**Ans.** 23 g)
3. Naturally occurring chlorine consists of isotopes ^{35}Cl and ^{37}Cl in the ratio 3 : 1. Calculate the mean atomic weight of chlorine. (**Ans.** 35.5)
4. 1.0 g of a metal (sp. heat = 0.05 cal g^{-} deg^{-}) on treatment with HBr gave 3.0 g of metal bromide. Find the valency and atomic weight of metal. (**Ans.** 3;120)
5. An oxide of a metal contains 60% metal. If vapour density of chloride of metal is 47.5. Find the atomic weight of metal. (**Ans.** 24)
6. One atom of an element weighs 3.82×10^{-23} g. Calculate the atomic weight of the element. (**Ans.** 23)
7. 1120 mL of Cl_2 gas at N.T.P. weighs 3.55 g. Find the atomic weight of chlorine. (**Ans.** 35.5)
8. 1.2 g of magnesium was converted to 2.0 g of its oxide. Calculate the atomic weight of magnesium. (**Ans.** 24)
9. The ratio of molar heats of a gas (mol. wt. = 48) at constant pressure to constant volume is 1.33. Find the atomic weight of the gas. (**Ans.** 16)
10. Molar mass of a gas is 48. If molar heat of the gas at constant volume is 24.6, find the atomic weight of the gas. (R = 8.3 J) (**Ans.** 16)

5

CHAPTER

Density and Vapour Density

5.1 DENSITY (OR ABSOLUTE DENSITY)

The density of a substance is defined as *'its mass per unit volume' i.e.,*

$$\textbf{Density} = \frac{\textbf{Mass}}{\textbf{Volume}}.$$

Units (*i*) g $(\text{mL})^{-1}$ or g cm^{-3} (C.G.S. unit) (*ii*) kg m^{-3} (in S.I. unit); g $\text{cm}^{-3} = 10^3$ kg m^{-3}

5.2 RELATIVE DENSITY (OR SPECIFIC GRAVITY)

It is the **ratio** of absolute density of a substance to that of a standard substance.

or The weight in gram of 1 mL solution of a substance is called the specific gravity of that substance

or $$\text{Specific gravity} = \frac{\text{wt. of solution in g}}{\text{volume of solution in mL}}$$

(*i*) **For solids and liquids.**

$$\text{Sp. Gr. of a substance} = \frac{\text{Density of substance}}{\begin{array}{c}\text{Density of water at}\\ 4°\text{C } (= 1)\end{array}}$$

(*ii*) **For gases or vapours.** Sp. Gr. of a substance is called **vapour density** and the standard substance is hydrogen. Hence :

V.D. of a gas or vapour

$$= \frac{\text{Wt. of certain volume of a gas or vapour}}{\begin{array}{c}\text{Wt. of same volume of hydrogen}\\ \text{under similar conditions of}\\ \text{temperature and pressure}\\ (= V_{\text{NTP}} \text{ of } H_2 \text{ in mL } \times 0.00009\text{g})\end{array}}$$

Note. Wt. of 11.2 L or 11.2 dm^3 or 11200 mL of hydrogen at NTP or STP = 1 g.

Thus, **Vapour density** of a gas or vapour is defined as the ratio between weight of certain volume of a gas and weight of same volume of hydrogen under similar conditions of temperature and pressure.

or **V.D. of a gas or vapour**

$$= \frac{\text{Wt.}}{V_{\text{NTP}} \text{ of } H_2 \text{ in mL}} \times \frac{11200 \text{ mL}}{1 \text{ g}}$$

$$= \frac{\text{wt.}}{V_{\text{NTP}} \text{ of } H_2 \text{ in L}} \times \frac{11.2 \text{ L}}{1 \text{ g}}$$

Also, **density of a gas** = $\dfrac{\text{Mol. wt. in g mol}^{-}}{22400 \text{ cm}^3 \text{ mol}^{-}}$

Volume of a block = Length × Breadth × Height

Volume of a sphere of radius, $r = \dfrac{4}{3}\pi r^3$

Volume of a flat disk having a hole $= \pi h(r_1^2 - r_2^2)$

where h = thickness of disk; r_1 and r_2 are the radii of the disk and hole respectively.

Wt. of a substance in gL^{-1} = Molarity × mol. wt. of substance

Relative density (or Sp. Gr.) of a gas or vapour with respect to air = Relative density with respect to hydrogen × density of gas or vapour with respect to air.

5.3 DETERMINATION OF SPECIFIC GRAVITY AND DENSITY

Example 1. *Calculate the specific gravity of air if its vapour density is 14.48.*

Solution. Sp. gravity of a gas

$$= \frac{\text{V.D. of the gas} \times 1 \text{ g}}{11200 \text{ mL volume of } H_2 \text{ gas}}$$

$$= \frac{14.48 \text{ g}}{11200 \text{ mL}}$$

$$= \mathbf{0.001293\ g(mL^{-1})\ Ans.}$$

Note. For finding specific gravity (or relative density) of gases, a volume of 11200 mL of H_2 at N.T.P. (weighing unity *i.e.,* 1g) is considered as a convenient unit.

Example 2. *Calculate the density of ethanol if its 80 cm^3 weigh 63.3 g.*

Solution. $$\text{Density} = \frac{\text{Mass (in g)}}{\text{Volume (in cm}^3)} = \frac{63.3 \text{ g}}{80 \text{ cm}^3}$$

$$= \mathbf{0.791\ g\ cm^{-3}\ Ans.}$$

Example 3. *What volume will 200 g of mercury occupy if density of mercury is 13.6 g(mL)$^{-1}$?*

Solution. Volume $= \frac{\text{Mass}}{\text{Density}} = \frac{200\text{ g}}{13.6\text{ g(mL)}^{-}}$

$= \mathbf{14.7\ mL\ Ans.}$

Example 4. *The density of carbon tetrachloride is 1.6 g cm^{-3}. Calculate its density in kilogram per cubic metre.*

Solution. **Density** $= \frac{1.6\text{ g}}{\text{cm}^3} \times \frac{1\text{ kg}}{1000\text{ g}} \times \left(\frac{100\text{ cm}}{1\text{ m}}\right)^3$

$= \mathbf{1.6 \times 10^3\ kg\ m^{-3}}$ **Ans.**

[∵ 1 kg = 1000 g, 1 m = 100 cm]

Example 5. *Find the volume of 20 kg of CCl$_4$ having density 1.6 g/cm^3.*

Solution.

Volume $= \frac{\text{Mass}}{\text{Density}}$

$= 20\text{ kg} \times \left(\frac{1000\text{ g}}{1\text{ kg}}\right) \times \frac{1\text{ cm}^3}{1.6\text{ g}} \times \frac{1\text{ L}}{1000\text{ cm}^3}$

$= \mathbf{12.5\ L\ Ans.}$

[∵ 1 kg = 1000 g; 1 L = 1000 cm^3]

Since wt. is given in kg, the volume will be in litre. Also, since density is given in g/cm^3, the wt. in g should be converted into kg and volume to litre.

Example 6. *The density of platinum is 21.45 g cm^{-3}. Calculate the number of (i) cubic centimetres per gram and (ii) kilogram per cubic metre.*

Solution.

(*i*) For density of 21.45 g cm^{-3}; the no. of cubic centimetres per gram

$= \frac{1\text{ cm}^3}{21.45\text{ g}}$

$= \mathbf{0.047\ cm^3/g}$ **Ans.**

(*ii*) For density 21.45 g/cm^3, the no. of kg per cubic metre

$= \frac{21.45\text{ g}}{\text{cm}^3} \times \frac{1\text{ kg}}{1000\text{ g}} \times \left(\frac{100\text{ cm}}{\text{m}}\right)^3$

$= \mathbf{21.45 \times 10^3\ kg\ m^{-3}}$ **Ans.**

5.4 DENSITY OF BLOCKS

Example 7. *A metallic block 12.0 cm long, 2 cm thick and 3.5 cm wide has a mass of 1800 g. Calculate the density of the metal.*

Solution. Length = 12.0 cm, Breadth = 3.5 cm, Thickness = 2 cm

∴ Volume = Length × Breadth × Thickness

= 12 cm × 3.5 cm × 2 cm = 84.0 cm^3

Density $= \frac{\text{Mass}}{\text{Volume}} = \frac{1800\text{ g}}{84.0\text{ cm}^3}$

$= \mathbf{21.43\ g\ cm^{-3}}$ **Ans.**

5.5 DENSITY OF SPHERES

Example 8. *Calculate the density of a metallic ball having mass 1.75 g and diametre of 7.6 mm.*

Solution. Radius of ball,

r = Diameter/2 = 7.6 mm/2

= 3.8 mm.

∴ Volume $= \frac{4}{3} \times \pi \times r^3$

$= \frac{4}{3} \times \frac{22}{7} \times (3.8\text{ mm})^3$

= 230 mm^3

Density $= \frac{\text{Mass}}{\text{Volume}} = \frac{1.75\text{ g}}{230\text{ mm}^3}$

$= \frac{1.75 \times 10^{-3}\text{ kg}}{230 \times 10^{-9}\text{m}^3}$

[∵ 1 kg = 10^{3}g; 1 mm = 10^{-3}m]

Density $= \mathbf{7.61 \times 10^3\ kg\ m^{-3}}$ **Ans.**

5.6 DENSITY OF DISKS WITH HOLES

Example 9. *An alloyed flat disk weighs 19.9 g. The disk having diametre 31.2 mm has a hole of 7.6 mm diametre. If the thickness of diametre is 4.6 mm, calculate the density of the alloy.*

Solution. h = 4.6 mm, r_1 = 31.2/2 = 15.6 mm;

r_2 = 7.6/2 = 3.8 mm.

∴ $V = \pi h (r_1^2 - r_2^2)$

= 3.14 × 4.6 mm [(15.6 mm)^2 – (3.8 mm)^2]

= 3.14 × 4.6 mm [243.36 mm^2 – 14.44 mm^2)

= 3.14 × 4.6 mm × 228.92 mm^2

= 3306 mm^3 = 3.306 cm^3

[∵ 1 mm^3 = 10^{-3} cm^3]

Also, Density $= \frac{\text{Mass}}{\text{Volume}} = \frac{19.9\text{ g}}{3.306\text{ cm}^3}$

= 6.02 g cm^{-3}

= 6.02 × 10^3 kg m^{-3}

$= \mathbf{6020\ kg\ m^{-3}}$ **Ans.**

5.7 SOLUTIONS

Example 10. *A sample of 20 mL of conc. HCl (density 1.18 g (mL)$^{-}$ contains 7.8 g HCl (i) calculate the percent by weight of HCl in the concentrated acid and (ii) how many gram per millilitre of acid are present in acid solution ?*

Solution.

(*i*) Wt = Volume × Density

$= 20\text{ mL} \times \frac{1.18\text{ g}}{\text{mL}} = 20.36\text{ g}$

∴ % age by wt. of HCl $= \frac{7.8\text{ g}}{20.36\text{ g}} \times 100$

= **38.3% HCl Ans.**

(*ii*) g/mL of acid $= \frac{7.8\text{ g}}{20\text{ mL}}$

= **0.39 g/mL Ans.**

Example 11. *A sample of 96% H$_2$SO$_4$ has a density of 1.84 g (mL)$^{-}$. (i) How much pure H$_2$SO$_4$ is present in one litre of the acid and (ii) how many mL of this acid contains 100 g pure H$_2$SO$_4$.*

SOLUTION.

(*i*) $d = 1.84\ \text{g(mL}^{-}\text{)}$ or $1.84\ \text{kg L}^{-}$

$\therefore$ Amount of pure H_2SO_4

$$= 1\ \text{L acid} \times \frac{1.84\ \text{kg}}{1\ \text{L acid}} \times \frac{96\ \text{kg}\ H_2SO_4}{100\ \text{kg}\ H_2SO_4}$$

$$= 1.77\ \text{kg}$$

(*ii*) $d = 1.84\ \text{g (mL)}^{-}$; $H_2SO_4 = 96\%$.

$\therefore$ Volume in mL of 100 g pure H_2SO_4

$$= 100\ \text{g}\ H_2SO_4 \times \frac{100\ \text{g acid}}{96\ \text{g}\ H_2SO_4} \times \frac{1\ \text{mL acid}}{1.84\ \text{g acid}}$$

= 56.6 mL Ans.

5.8 DETERMINATION OF DENSITY AND VAPOUR DENSITY OF A GAS

$$\text{Density of a gas} = \frac{\text{Mass}}{\text{Volume}};$$

$$\text{V.D. of a gas} = \frac{\text{W}}{\text{V}_{\text{NTP}}\ \text{in mL}} \times 11200\ \text{mL}$$

EXAMPLE 12. *120 litre of a gas has a mass of 150 g. Calculate the density of the gas.*

SOLUTION. Mass = 150 g;

$$\text{Volume} = 120\ \text{L} = 120\ \text{L} \times \frac{1000\ \text{mL}}{1\text{L}}$$

$$= 120{,}000\ \text{mL}.$$

$$\therefore \quad \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{150\ \text{g}}{120000\ \text{mL}}$$

= 0.00125 g (mL)⁻ Ans.

EXAMPLE 13. *Calculate the vapour density of air having specific gravity equal to 0.001293 g (mL⁻)*

SOLUTION. Wt. of air = 0.001293 g;

Volume at NTP = 1 mL

$\therefore$ Vapour density of air

$$= \frac{\text{wt. of 1 mL air}}{\text{wt. of 1 mL}\ H_2\ (= 1 \times 0.00009\ \text{g})}$$

$$= \frac{0.001293\ \text{g}}{0.00009\ \text{g}}$$

= 14.37 Ans.

EXAMPLE 14. *1050 cm³ of air weighs equal to 1.3572 g. Calculate the specific gravity of air in terms of hydrogen if 1 g of H_2 gas occupies 11.2 L volume at NTP.*

SOLUTION. Mass of air = 1.3572 g;

Volume of air = 1050 cm^3

1050 cm^3 air weigh = 1.3572 g

$$11200\ \text{cm}^3\ \text{air weigh} = \frac{1.3572\ \text{g}}{1050\ \text{cm}^3} \times 11200\ \text{cm}^3$$

$$= 14.48\ \text{g}.$$

$[\because 11.2\ \text{L} = 11.2 \times 1000\ \text{cm}^3 = 11200\ \text{cm}^3]$

$\therefore$ Sp. gravity of air with respect to hydrogen

$$= \frac{\text{Mass}}{\text{Volume}} = \frac{14.48}{1}$$

= 14.48 Ans.

EXAMPLE 15. *Calculate the density of ammonia at 30°C and 5 atm pressure.* **(I.I.T. 1978)**

SOLUTION. Mol. wt. (1 mol) of $NH_3 = 14 + (3 \times 1) = 17$ g; density of NH_3 = ?

Given conditions

$P_1 = 5$ atm, $V_1 = ?$,

$T_1 = 30 + 273 = 303$ K

At *NTP* : $P_2 = 1$ atm, $V_2 = 22.4$ L, $T_2 = 273$ K.

We know that :

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

$$V_1 = \frac{P_2V_2}{T_2} \times \frac{T_1}{P_1}\ \text{(gas law)}$$

$$\therefore \quad V_1 = \frac{1\ \text{atm} \times 22.4\ \text{L} \times 303\ \text{K}}{273\ \text{K} \times 5\ \text{atm}} = 4.97\ \text{L}$$

$$\therefore \text{Density of}\ NH_3 = \frac{\text{Wt.}}{\text{Volume}} = \frac{17\ \text{g}}{4.97\ \text{L}}$$

= 3.42 gL⁻ Ans.

EXAMPLE 16. *An experiment on an unknown gas revealed that its density as compared to air is 2.247. If air is 14.48 times heavier than H_2, what would be the density of the gas as compared to hydrogen.*

SOLUTION. Given :

(*i*) Air is 14.48 times heavier than H_2

$\therefore$ Relative density of air = 14.48

(*ii*) Density of unknown gas with respect to air = 2.247. It means it is 2.247 times heavier than air

$\therefore$ Relative density of unknown gas = 14.48 × 2.247

= 32.54 Ans.

EXAMPLE 17. *A 6.9 M solution of KOH in water contains 30% by weight of KOH. Calculate the density of the solution. (at. wt., K = 39.1, O = 16, H = 1).* **(I.I.T. 1976)**

SOLUTION.

(*i*) Wt. of KOH in g L⁻ = Molarity of KOH × mol. wt. of KOH

$= 6.9 \times 56.1 = 387.09\ \text{gL}^{-}$

30% by wt. of KOH means that :

[Mol. wt. of KOH = 39.1 + 16 + 1 = 56.1 g mol⁻]

wt. of KOH = 30 g;

volume of solution = 100 mL.

(*ii*) 1000 mL solution contain KOH = 387.09 g

$$100\ \text{mL solution contain KOH} = \frac{387.09\ \text{g}}{1000\ \text{mL}} \times 100\ \text{mL}$$

$$= 38.709\ \text{g}$$

(*iii*) 30 g KOH is present in solution = 100 g

38.709 g KOH is present in solution

$$= \frac{100\ \text{g}}{30\ \text{g}} \times 38.709\ \text{g} = 129.03\ \text{g}$$

(*iv*) $$\text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{129.03 \text{ g}}{100 \text{ mL}}$$

$$= \mathbf{1.2903\ g\ (mL)^{-}\ Ans.}$$

Example 18. *The specific gravity of a sample of 30% pure ammonia is 0.90. Calculate the volume of it which is needed to get 75 g of pure ammonia.*

Solution.

(*i*) 30% pure ammonia means that :

30 g pure ammonia is present in solution = 100 g

∴ 75 g pure ammonia is present in solution

$$= \frac{100}{30} \times 75 = 250 \text{ g}$$

(*ii*) $$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{250 \text{ g}}{0.90 \text{ g(mL)}^{-}}$$

$$= \mathbf{277.8\ mL\ Ans.}$$

Example 19. *Solution A and solution B of ammonia in water have the specific gravities, 0.90 and 0.96 respectively. Which solution out of A and B will contain more ammonia and why ?*

Solution. Specific gravity (density as compared with water) may be considered as the total number of the molecules of the substance or substances (e.g., H_2O, NH_3) per unit volume. In solutions A and B, water molecules (H_2O = 18) per unit volume have been repalced by lighter ammonia molecules (NH_3 = 17) molecules. It means: *'Stronger the solution of ammonia, greater will be the number of ammonia molecules per unit volume', and hence lesser will be the density (mass per unit volume) of the solution. Hence:*

"Solution A having lesser sp. gravity will contain more ammonia and hence more concentrated than solution B".

Example 20. *The specific gravities of oxygen and nitrogen gases are 16.0 and 14.0 (H = 1) respectively. If the specific gravity of the mixture of these gases is 14.4 (H = 1), calculate the composition of the mixture by weight as well as by volume.*

Solution. Let total volume of $O_2 + N_2$ = 100 mL

Let Volume of $O_2 = x$ mL,

volume of $N_2 = (100 - x)$ mL.

(*i*) Mass of 100 mL mixture = Volume × Density

$= 100 \times 14.4 = 1440.$

(*ii*) Mass of O_2 = Volume × Density

$= x \times 16 = 16x$

Mass of N_2 = Volume × Density

$= (100 - x)\ 14$

∴ $16x + (100 - x)\ 14 = 1440;$

$16x + 1400 - 14x = 1440; 2x = 40; x = 20$

∴ Volume of O_2 = **20 mL;**

volume of N_2 = 100 – 20

= **80 mL Ans.**

To find composition of mixture by weight.

Let total wt. of $O_2 + N_2$ = 100 g

Let wt. of $O_2 = x$ g; wt. of $N_2 = (100 - x)$ g

(*i*) $$\text{Volume of 100 g mixture} = \frac{\text{Mass}}{\text{Density}} = \frac{100}{14.4}$$

(*ii*) $$\text{Volume of } x \text{ g } O_2 = \frac{x}{16};$$

$$\text{Volume of } (100 - x) \text{ g } N_2 = \frac{(100 - x)}{14}$$

$$\therefore \quad \frac{x}{16} + \frac{100 - x}{14} = \frac{100}{14.4};$$

$$\frac{14x + 1600 - 16x}{16 \times 14} = \frac{100}{14.4};$$

$$14x + 1600 - 16x = \frac{100 \times 16 \times 14}{14.4} = 1555.6;$$

$$-2x = -44.4; x = \frac{44.4}{2} = 22.2 \text{ g}$$

∴ Wt. of O_2 = 22.2 g;

Wt. of N_2 = 100 – 22.2

= **77.78 g Ans.**

Example 21. *The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 38.3 at 26.7°C. Calculate the number of moles of NO_2 in 100 g of the mixture.* **(I.I.T. 1979)**

Solution.

$$\text{V.D. of } NO_2 = \frac{\text{Mol. wt. of } NO_2}{2} = \frac{14 + (2 \times 16)}{2}$$

$$= \frac{46}{2} = 23.$$

$$\text{V.D. of } N_2O_4 = \frac{\text{Mol. wt. of } N_2O_4}{2}$$

$$= \frac{(2 \times 14) + (4 \times 16)}{2} = \frac{92}{2} = 46$$

(*i*) Difference of V.D. of mixture and NO_2

= 38.3 – 23 = 15.3

(*ii*) Difference of V.D. of mixture and N_2O_4

= 46 – 38.3 = 7.7

Ratio of difference of V.D. in (*i*) and (*ii*) above is

$15.3 : 7.7$; $\frac{15.3}{7.7} : \frac{7.7}{7.7}$ *i.e.*, **2 : 1**

$$\therefore \text{ Wt. of } NO_2 \text{ in 100 g mixture} = \frac{2}{1+2} \times 100 = \frac{200}{3}$$

$$\text{No. of mol of } NO_2 \text{ present} = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{200}{3} \times \frac{1}{46}$$

= **1.45 Ans.**

Example 22. *Calculate the density of air in kg m^{-3} at 25°C and 76 cm if it contains 20.78% O_2 and 79.22% N_2 by volume. Also calculate the composition of air by weight. (at. wt., O = 16 amu, N = 14 amu).*

Solution.

(*i*) 100 mL air contains O_2 = 20.78 mL

$$\therefore \text{ 1000 mL (= 1L) air contains } O_2 = \frac{20.78}{100} \times 1000$$

= **207.8 mL Ans.**

(*ii*) 100 mL air contains N_2 = 79.22 mL

$$\therefore \quad 1000 \text{ mL } (= 1\text{L}) \text{ air contain } N_2 = \frac{79.22}{100} \times 1000$$

$$= \mathbf{792.2\ mL\ Ans.}$$

(*iii*) 22400 mL O_2 weigh = g. mol. wt. of O_2

$$= 2 \times 16 = 32 \text{ g}$$

$$207.8 \text{ mL } O_2 \text{ weigh} = \frac{32}{22400} \times 207.8$$

$$= \mathbf{0.297\ g\ Ans.}$$

(*iv*) 22400 mL N_2 weigh = g. mol. wt. of N_2

$$= 2 \times 14 = 28 \text{ g.}$$

$$792.2 \text{ mL } N_2 \text{ weigh} = \frac{28}{22400} \times 792.2 = \mathbf{0.99\ g}$$

∴ Wt. of 1000 mL air at NTP = 0.297 + 0.99

$$= \mathbf{1.287\ g\ Ans.}$$

(*v*) $P_1 = 76 \text{ cm} = 76\ cm \times \dfrac{10 \text{ mm}}{1 \text{ cm}} = 760 \text{ mm},$

V_1 = 1000 mL, T_1 = 37 + 273 = 310 K

At *NTP* : P_2 = 760 mm, V_2 = ?, T_2 =273 K.

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

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} \text{ (gas law)}$$

$$\therefore \quad V_2 = \frac{760 \text{ mm} \times 1000 \text{ mL}}{310 \text{ K}} \times \frac{273 \text{ K}}{760 \text{ mm}}$$

$$= \mathbf{880.6\ mL\ Ans.}$$

(*vi*) 880.6 mL air at NTP weigh = 1.287 g

$$1000 \text{ mL air at NTP weigh} = \frac{1.287 \text{ g}}{880.6 \text{ mL}} \times 1000 \text{ mL}$$

$$= 1.4 \text{ g}$$

∴ Density of air at 37°C and 760 mm pressure

$$= 1.4 \text{ g L}^{-}$$

$$= \mathbf{1.4 \times 10^3\ kg\ m^{-3} Ans.}$$

$$[\because 1\text{g L}^{-} = 10^3 \text{ kg m}^{-3}]$$

(*vii*) **To find composition of air by weight.**

$$\% \text{ age of } O_2 = \frac{\text{wt. of } O_2}{\text{wt. of air}} \times 100$$

$$= \frac{0.297 \text{ g}}{1.287 \text{ g}} \times 100$$

$$= \mathbf{23.08\%\ Ans.}$$

$$\% \text{ age of } N_2 = \frac{\text{wt. of } N_2}{\text{wt. of air}} \times 100$$

$$= \frac{0.99 \text{ g}}{1.287 \text{ g}} \times 100$$

$$= \mathbf{76.92\%\ \ Ans.}$$

Note: For the same mass of two solutions, $V_1D_1 = V_2D_2$

EXAMPLE 23. *The specific gravity of a salt solution is 1.027. Calculate the volume of water in mL that should be added to 1L of this solution to make its density, 1.02.*

SOLUTION. Sp. Gr. of original salt solution, D_1 = 1.027; Volume, V_1 = 1L = 1000 mL

Required Sp. Gr. of salt solution, D_2 = 1.02; Volume, V_2 = ?

For the same mass of solutions, $V_1D_1 = V_2D_2$

$$1000 \text{ mL} \times 1.027 = V_2 \times 1.02$$

$$\therefore \quad V_2 = \frac{1000 \text{ mL} \times 1.027}{1.02} = 1006.9 \text{ mL}$$

∴ Volume of water to be added = 1006.9 – 1000

$$= \mathbf{6.9\ mL\ \ Ans.}$$

EXAMPLE 24. *Calculate the weight of 30% solution of sodium chloride having specific gravity 1.2 that would yield 0.9 g sodium chloride on evaporation of its solution.*

SOLUTION. 30% NaCl solution means that 30 g NaCl is present in 100 mL solution.

∴ 30 g NaCl is present in its solution = 100 mL

0.9 g NaCl is present in its solution

$$= \frac{100 \text{ mL}}{30 \text{ g}} \times 0.9 \text{ g} = 3 \text{ mL}$$

∴ wt. of 30% solution required = Volume × Density

$$= 3 \text{ mL} \times 1.2 \text{ g (mL}^{-})$$

$$= \mathbf{3.6\ g\ Ans.}$$

EXAMPLE 25. *How many grams of ammonia are there in 250 mL of a 30% solution, the specific gravity of which is 0.9 ?*

SOLUTION.

(*i*) Wt. of 250 mL solution = Volume × Sp. Gr.

$$= 250 \text{ mL} \times 0.9 \text{ g (mL)}^{-} = 225 \text{ g}$$

100 g ammonia solution contain ammonia = 30 g

225 g ammonia solution contain ammonia

$$= \frac{30 \text{ g}}{100 \text{ g}} \times 225 \text{ g}$$

$$= \mathbf{67.5\ g\ Ans.}$$

EXAMPLE 26. *How many grams of pure HNO_3 will be contained in 100 mL of acid solution containing 68.0% by weight of it and of specific gravity 1.45 ?*

SOLUTION. wt. of 100 mL HNO_3 = Volume × Sp. Gr.

$$= 100 \text{ mL} \times 1.45 \text{ g (mL}^{-}) = 145 \text{ g}$$

100 g solution contain HNO_3 = 68 g

$$145 \text{ g solution contain } HNO_3 = \frac{68}{100} \times 145$$

$$= \mathbf{98.6\ g\ \ Ans.}$$

5.9 VAPOUR DENSITY FROM VICTOR MEYER'S METHOD

(See chapter - 6)

5.10 AIEEE PATTERN EXAMPLES

EXAMPLE 27. *Density of ethanol is 0.791 g cm^{-3}. Its value in SI unit will be :*

(*a*) 7.91 g cm^{-3}	(*b*) 79.1 g cm^{-3}
(*c*) 791 g m^{-3}	(*d*) 791 kg m^{-3}

SOLUTION. $$\text{Density} = \frac{0.791 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \left(\frac{100 \text{ cm}}{1 \text{ m}}\right)^3$$

$$= 791 \text{ kg m}^{-3}.$$

So, the correct answer is (*d*)

EXAMPLE 28. *The mass of carbon tetrachloride having volume 6.25 L and density 1.6 g cm^{-3} will be :*

(a) 10 g *(b) 100 g*

(c) 10 kg *(d) 200 g*

SOLUTION. Mass = Volume × Density.

Since density is given in g cm^{-3}, the volume should be in cm^3 and mass should be in gram.

$$\therefore \quad \text{Mass} = 6.25\ \text{L} \times \frac{1000\ \text{cm}^3}{1\text{L}} \times \frac{1.6\ \text{g}}{\text{cm}^3} = 10^4\ \text{g}$$

$$= 10^4\text{g} \times \frac{1\ \text{kg}}{1000\ \text{g}} = 10\ \text{kg}$$

SO, THE CORRECT ANSWER IS (C)

EXAMPLE 29. *25 cm^3 of an unknown acid (density, 1.2 g cm^{-3}) contains 9.2 g of the acid. The percent by weight of the acid in the concentrated acid will be :*

(a) 69.33% *(b) 30.67%*

(c) 20% *(d) 80%*

SOLUTION. Wt. = Volume × Density

$$= 25\ \text{cm}^3 \times 1.2\ \text{g cm}^{-3} = 30\ \text{g}$$

$$\therefore \quad \text{Percentage by wt. of unknown acid} = \frac{9.2\ \text{g}}{30\ \text{g}} \times 100$$

$$= 30.67\%.$$

So, the correct answer is (*b*)

EXAMPLE 30. *At a particular place, 1000 mL of air weighs 1.248 g. The specific gravity of air in terms of hydrogen if 1g H_2 occupies 11200 mL volume will be :*

(a) 13.98 *(b) 10*

(c) 16 *(d) 2.47*

SOLUTION. Mass of air = 1.248 g;

Volume of air = 1000 mL.

Thus; 1000 mL air weigh = 1.248 g

$$11200\ \text{mL air weigh} = \frac{1.248}{1000} \times 11200$$

$$= 13.9776\ \text{g}$$

$$\therefore \quad \text{Sp. gravity of air with respect to } H_2 = \frac{\text{Mass}}{\text{Volume}} = \frac{13.9776}{1}$$

$$= 13.98.$$

So, the correct answer is (*a*)

EXAMPLE 31. *224 cm^3 of a gas at S.T.P. weighs 0.44 g. The vapour density of the gas will be :*

(a) 22 *(b) 11* *(c) 1.1* *(d) 3.3*

SOLUTION. Wt. of gas = 0.44 g;
Volume at S.T.P. = 224 cm^3.

$$\text{But, V.D. of a gas} = \frac{\text{Wt. of gas}}{\text{Volume at STP}} \times \frac{11200\ \text{cm}^3}{1\ \text{g}}$$

$$= \frac{0.44\ \text{g}}{224\,\text{cm}^3} \times \frac{11200\ \text{cm}^3}{1\ \text{g}} = 22$$

So, the correct answer is (*a*)

EXAMPLE 32. *The density of nitrogen gas at 35°C and 2 atmospheric pressure is :*

(a) 1.11 g cm^{-3} *(b) 2.22 g L$^-$*

(c) 3.1 g L$^-$ *(d) 4.5 kg m^{-3}*

SOLUTION.

Mol. wt. of N_2 = 2 × 14 = 28 g mol$^-$, density of N_2 = ?

Given conditions :

P_1 = 2 atm, V_1 = ?,

T_1 = 35 + 273 = 308 K;

At NTP: P_2 = 1 atm, V_2 = 22.4 L, T_2 = 273 K.

$$\text{So,} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \ \text{(gas law);}$$

$$V_1 = \frac{P_2V_2}{T_2} \times \frac{T_1}{P_1}$$

$$= \frac{1\ \text{atm} \times 22.4\ \text{L} \times 308\ \text{K}}{273\ \text{K} \times 2\ \text{atm}}$$

$$\therefore \quad V_1 = 12.6\ \text{L}.$$

$$\therefore \quad \text{Density of } N_2 = \frac{\text{Wt.}}{\text{Volume}} = \frac{28\ \text{g}}{12.6\ \text{L}} = 2.22\ \text{g L}^-.$$

So, the correct answer is (*b*)

EXAMPLE 33. *The specific gravity of a sample of 22% pure liquid is 1.1 g (mL$^-$). The volume of it required to get 56 g of it will be :*

(a) 10 mL *(b) 200 mL*

(c) 50 mL *(d) 231.4 mL*

SOLUTION. 22% liquid means that :

22 g liquid is present in solution = 100 g

$$56\ \text{g liquid is present in solution} = \frac{100}{22} \times 56 = \frac{5600}{22}\ \text{g}$$

$$\therefore \quad \text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{5600\ \text{g}}{22 \times 1.1\ \text{g(mL)}^-} = 231.4\ \text{mL}.$$

So, the correct answer is (*d*)

EXAMPLE 34. *A sample of 98% acid has a density of 1.9 g cm^{-3}. The amount of pure acid present in 2 L of the acid is :*

(a) 3.724 kg *(b) 372.4 g*

(c) 3.724 g *(d) 100 g*

SOLUTION. 1.9 g cm^{-3} means 1.9 kg L$^-$

∴ Amount of pure acid

$$= 2\text{L acid} \times \frac{1.9\text{kg}}{1\text{L acid}} \times \frac{98\ \text{kg acid}}{100\ \text{kg acid}}$$

$$= 3.724\ \text{kg}.$$

So, the correct answer is (*a*).

EXAMPLE 35. *The density of water at 4°C is 1.0×10^3 kg m^{-3}. The volume occupied by one molecule of water is approximately:*

(a) 3.0×10^{-23} *mL* *(b)* 6×10^{-22} *mL*

(c) 3×10^{-23} *mL* *(d)* 9×10^{-23} *mL*

SOLUTION. Per m^3 means, $1m^3 = 10^3$ kg $= 10^6$ g

[H.P. Board, 2012 modified]

$= \frac{10^6}{18}$ mole because 1 mol of $H_2O = (2 \times 1) + 16$

$= 18$ g mol^{-}.

$= \frac{10^6}{18} \times 6.02 \times 10^{23}$ molecules. Hence 1 molecule

$$= \frac{18 \text{ m}^3}{6.02 \times 10^{23} \times 10^6}$$

$$= \frac{18 \times 10^6}{6.02 \times 10^{23} \times 10^6} \text{cm}^3 \simeq 3 \times 10^{-23} \text{ mL}.$$ So; (*a*) is correct.

PROBLEMS FOR PRACTICE

1. Find the density of metal sphere having diameter 8.8 mm and mass 2.0 g. (**Ans.** 5.602×10^3 kg m^{-3})

2. Calculate the volume of 18 kg of an organic liquid having density 1.5 g cm^{-3} (**Ans.** 12 L)

3. If the specific gravity of a gas is 1.29×10^7 g cm^{-3}, what will be its density? (**Ans.** 14.48)

4. A metallic block is 10 cm long, 8 cm wide and 1.5 cm thick. Find the density of the metal if its mass is 1500 g. (**Ans.** 12.5 g cm^{-3})

5. A sample of 15 mL of HNO_3 (density, 1.1 g cm^{-3}) contains 5.2 g HNO_3. Calculate percent by weight of HNO_3. (**Ans.** 31.5%)

6. A sample of 38% HCl has density 1.18 g cm^{-3}. How much pure HCl is present in 500 mL of the acid? (**Ans.** 0.334 g)

7. Calculate the density of 100 L of a gas having mass 120 g. (**Ans.** 1.2×10^{-3} g $(mL)^{-}$

8. A 5.6 M solution of an alkali in water contains 25% by weight of alkali (mol. wt. 56) (**Ans.** 125.44 g)

9. The specific gravity of a 25% sample of pure liquid is 1.09 g cm^{-3}. The volume of it required to get 45 g of it will be:

(*a*) 150 mL (*b*) 160 mL

(*c*) 165.1 mL (*d*) 201.5 mL

[**Ans.** (c)]

10. The density of a liquid is 1.9 g cm^{-3}. Its value in SI unit will be:

(*a*) 1800 kg m^{-3} (*b*) 1900 kg m^{-3}

(*c*) 2000 kg m^{-3} (*d*) None of these

[**Ans.** (b)]

6

CHAPTER

Molecular Weight

6.1 MOLECULAR WEIGHT (RELATIVE MOLECULAR MASS)

Molecular mass of a substance is the average relative *mass of* one molecule of it as compared to the mass of an atom of carbon (^{12}C stable isotope) taken as 12 amu. **For example,** the molecular weight of nitrogen is 28. It means that one molecule of nitrogen is 28 times heavier than one-twelfth of an atom of carbon isotope, ${}^{12}_{6}C$.

It is also defined as the sum total of the relative atomic weights (masses) of all the component atoms in the molecule. For example, the relative molecular weight (mass) of sulphur dioxide (SO_2) is:

$$1 \times \text{at. wt. of sulphur} + 2 \times \text{at. wt. of oxygen}$$
$$= 32 + (2 \times 16) = 64 \text{ amu},$$

where amu represents atomic mass unit.

$$\mathbf{1\ amu = 1.66 \times 10^{-24}\ g.}$$

> **Note.** Mol. wt. = Atomicity × at. wt.; e.g.,
> Mol. wt. of $N_2 = 2 \times 14 = 28$ g mol^{-}

6.2 GRAM MOLECULAR WEIGHT (G.M.W) OR GRAM MOLECULAR MASS OR GRAM MOLAR MASS

The molecular weight of an element (e.g., noble gases, He, Ne, Ar etc) or a compound expressed in grams is called *gram molecular weight (G.M.W) or gram mole or mole.*

Gram molecular weight (G.M.W) of a substance

= *Sum total of g. at. wt. of all the component atoms in the molecule of the substance.*

Where g. at. wt. of an atom is the weight of Avogadro number (= 6.023×10^{23}) of atoms of the element in gram and

At. wt. of a element in gram

= wt. of one atom of an element in amu × 1.66×10^{-24}g × Avogadro number (= 6.023×10^{23}).

Also : 1 amu = 1.66×10^{-24} g.

6.3 ATOMIC MASS

$$= \frac{\text{Mass of an atom of an element}}{\frac{1}{12} \times \text{ mass of an atom of carbon } (= 12)}$$

6.4 NO. OF GRAM ATOMS

= Mass of the element in gram/g. atomic mass of element.

EXAMPLE 1. *Calculate the gram molecular weight of carbon dioxide if atomic weight of carbon and oxygen are 12 amu and 16 amu respectively.*

SOLUTION.

$$\text{g. atomic weight of C} = 12 \text{ amu} \times \frac{1.66 \times 10^{-24}\text{ g}}{1 \text{ amu}} \times 6.023 \times 10^{23} = 12 \text{ g}$$

g. at. wt. of oxygen

$$= 16 \text{ amu} \times \frac{1.66 \times 10^{-24}\text{ g}}{1 \text{ amu}} \times 6.023 \times 10^{23} = 16 \text{ g}$$

$$\therefore \quad \text{g. mol. wt. of } CO_2 = \text{g. at. wt. of C} + 2 \times \text{g. at. wt. of O}$$
$$= 12\text{ g} + (2 \times 16)\text{g} = \mathbf{44\ g\ mol^{-}\ Ans.}$$

6.5 MOLECULAR MASS OF ORGANIC ACIDS–SILVER SALT METHOD

Following method is used to determine the molecular mass (or mol. wt.) of organic acids.

Silver salt method for organic acids. In this method, aqueous solution of known weight of organic acid, RCOOH is treated with excess ammonia solution and excess ammonia is boiled off. Excess of $AgNO_3$ solution is then added to this neutral solution and purified white precipitate of silver salt of acid (RCOOAg) is dried and weighed. This salt is ignited to get pure silver.

$$\text{We know that : } \frac{\text{wt. of Ag-salt, RCOOAg}}{\text{wt. of Ag}}$$

$$= \frac{\text{Eq. wt. of Ag-salt, RCOOAg}}{\text{Eq. wt. of Ag } (= 108)}$$

$$\therefore \quad \text{Eq. wt. of Ag-salt, RCOOAg} = \frac{\text{wt. of Ag-salt}}{\text{wt. of Ag}} \times 108$$

But Eq. wt. of organic acid, RCOOH

$$= \begin{bmatrix} \text{Eq. wt. of Ag-salt, RCOOAg} \\ -\ \text{Eq. wt. of Ag + Eq. wt. of H} \end{bmatrix}$$

$$= \left(\frac{\text{wt. of Ag-salt}}{\text{wt. of Ag}} \times 108\right) - 108 + 1$$

$$= \left(\frac{\text{wt. of Ag-salt}}{\text{wt. of Ag}} \times 108\right) - 107$$

Hence,

Mol. wt. of organic acid, RCOOH

$$= \begin{matrix} [\text{Eq. wt. of organic acid, RCOOH}] \\ \times [\text{Basicity of acid}] \end{matrix}$$

Or Mol. wt. of organic acid, RCOOH

$$= \left[\left(\frac{\text{wt. of Ag} - \text{salt}}{\text{wt. of Ag}} \times 108\right) - 107\right] \times \text{Basicity}, n$$

where $n = 1$, $n = 2$, $n = 3$ etc. for monobasic, dibasic and tribasic etc organic acids respectively.

REACTIONS.

$$\text{RCOOH} \xrightarrow{\text{NH}_4\text{OH}} \text{RCOONH}_4 \xrightarrow{\text{AgNO}_3} \text{RCOOAg} \xrightarrow{\text{Ignite}} \text{Ag}\downarrow$$

EXAMPLE 2. *When heated cautiously in a crucible, 0.759 g of a silver salt of a dibasic acid gave 0.463 g of metallic silver. Calculate the molar mass of the acid.*

SOLUTION. Mass of Ag = 0.463 g ;

mass of silver salt = 0.759 g

Basicity of acid, $n = 2$. We know :

$$\text{Molar mass} = n\left(\frac{108 \times \text{mass of Ag - salt}}{\text{mass of Ag}} - 107\right)$$

$$= 2\left(\frac{108 \times 0.759}{0.463} - 107\right)$$

$$= 2\,(177 - 107) = \mathbf{140\ g\ mol^{-}\ Ans.}$$

EXAMPLE 3. *Silver salt of a dibasic acid contains 67.5% silver. Calculate the molar mass of the acid.*

SOLUTION. Mass of silver salt = 100 g ;

mass of Ag = 67.5 g ;

at. wt. of Ag = 108.

Basicity of acid, $n = 2$

67.5 g Ag is present in silver salt = 100 g

$$\text{108 g Ag is present in silver salt} = \frac{100}{67.5} \times 108 \text{ g}$$

$$\text{Molar mass of acid} = \text{Basicity}\left(\frac{108 \times 100}{67.5} - 107\right)$$

$$= 2\,(160 - 107) = \mathbf{106\ g\ mol^{-}\ Ans.}$$

6.6 CHLOROPLATINATE SALT METHOD FOR ORGANIC BASES

A known weight of organic base (amines) is dissolved in dil. HCl and treated with chloroplatinic acid (H_2PtCl_6) to get crystals of chloroplatinate ($B_2H_2PtCl_6$). A known weight of these dried crystals is ignited to get Pt metal. From the weight of Pt and that of $B_2H_2PtCl_6$, the molar mass of organic base is calculated.

Let wt. of $B_2H_2PtCl_6$ taken = m_1 g ; wt. of Pt = m_2 g

Molar mass of $H_2PtCl_6 = (2 \times 1) + 195 + (6 \times 35.5) = 410.$

m_2 g Pt is available from $B_2H_2PtCl_6 = m_1$ g

$\therefore$ 195 g Pt is available from $B_2H_2PtCl_6$

$$= \frac{m_1 \times 195}{m_2} \text{ g}$$

$$= \text{Molar mass of } B_2H_2PtCl_6 \text{ salt}$$

For polyacid base chloroplatinate salt $B_2(H_2PtCl_6)_n$;

(*i*) Molar mass of chloroplatinate = $\dfrac{n \times m_1 \times 195}{m_2}$

(*ii*) Molar mass of $(H_2PtCl_6)_n = n \times 410$

$\therefore$ Molar mass of base, B

$$= \frac{1}{2}\begin{bmatrix} \text{Molar mass of} & - & \text{Molar mass of} \\ \text{chloroplatinate} & & (H_2PtCl_6)_n \end{bmatrix}$$

$$= \frac{1}{2}\left[\frac{195\,n\,m_1}{m_2} - 410\,n\right] = \frac{n}{2}\left[\frac{195\,m_1}{m_2} - 410\right]$$

EXAMPLE 4. *When heated cautiously 0.49 g of the chloroplatinate of a diacid base gave 0.195 g of platinum on ignition. Calculate the molecular weight of the base.*

SOLUTION. Wt. of chloroplatinate, $B_2H_2PtCL_6$, $m_1 = 0.49$ g; wt. of platinum, $m_2 = 0.195$ g; Acidity of base = n= 2. We know that :

Mol. wt. of base, B

$$= \frac{1}{2}\begin{bmatrix} \text{Molar mass of} & - & \text{Molar mass of} \\ \text{chloroplatinate} & & (H_2PtCl_6)_n \end{bmatrix}$$

$$= \frac{n}{2}\left[\frac{195\,m_1}{m_2} - 410\right] \qquad [\because m_2 \text{ g Pt} \equiv m_1 \text{ g } B_2H_2PtCl_6$$

$$195 \text{ g Pt} \equiv \frac{m_1 \times 195}{m_2} \text{ g } B_2H_2PtCl_6]$$

$$= \frac{2}{2}\left[\frac{195 \times 0.49}{0.195} - 410\right]$$

$$= 490 - 410 = \mathbf{80\ g\ mol^{-}\ Ans.}$$

EXAMPLE 5. *Chloroplatinate of a monoacid organic base contains 39%platinum. Calculate the molar mass of the base.*

SOLUTION. Mass of chloroplatinate, m_1 = 100 g ; mass of platinum, m_2 = 39 g ; Acidity of base = n = 1.
We know that :

$$\text{Molar mass of base} = \frac{n}{2}\left[\frac{195\,m_1}{m_2} - 410\right]$$

$$= \frac{1}{2}\left[\frac{195\times100}{39} - 410\right]$$

$$= \frac{1}{2}(500-410) = \mathbf{45\ g\ mol^{-}\ Ans.}$$

6.7 VOLUMETRIC METHOD TO CALCULATE MOL. WT. OF ACIDS AS WELL AS BASES

1. **Mol. wt. of acids.** A known weight (W g) of the acid is dissolved in a suitable solvent (*e.g.*, water) and the solution is titrated against standard alkali using phenolphthalein as indicator.

Let V ml of N_1 alkali neutralize acid = W g.

$$1000 \text{ ml of 1 N alkali neutralize acid} = \frac{W}{VN_1} \times 1000 \text{ g}$$

$$= \text{g. eq. wt. of acid}$$

$$\therefore \text{ Eq. wt. of acid} = \frac{W}{VN_1} \times 1000 \text{ g}$$

$$\textbf{Mol. wt. of acid} = \textbf{Eq. wt.} \times \textbf{basicity}$$

$$= \left(\frac{W}{VN_1}\times1000\right) \times \text{basicity.}$$

Note. 1000 ml of 1 N alkali ≡ g. *eq*. wt. of alkali.

Example 6. *0.115 g of a dibasic acid required 25 ml of 0.1 N* NaOH *solution for complete neutralisation. Find the molar mass of the acid.*

Solution. 25 ml of 0.1 N NaOH neutralize acid = 0.115 g

$$\therefore \text{ 1000 ml of 1 N NaOH neutralise acid} = \frac{0.115\,g\times1000}{25\times0.1}$$

$$= 46 \text{ g} = \text{g. eq. wt. of acid.}$$

Basicity of acid = 2 (given)

$\therefore$ Mol. wt. of acid = Eq. wt. × basicity = 46 g × 2

$$= \mathbf{92\ g\ mol^{-}\ Ans.}$$

2. **Mol. wt. of bases.** A known weight (Wg) of the base is dissolved in a suitable solvent (usually water) and the solution is titrated with standard acid using phenolphthalein as indicator.

Let. V ml of N_1 acid neutralise base = W g

$$1000 \text{ ml of 1 N acid neutralise base} = \frac{W}{VN_1} \times 1000 \text{ g}$$

$$= \text{g. eq. wt. of base.}$$

$$\therefore \text{ Eq. wt. of base} = \frac{W}{VN_1} \times 1000 \text{ g}$$

$$\therefore \text{Mol. wt. of base} = \text{Eq. wt.} \times \text{acidity}$$

$$= \left(\frac{W}{VN_1}\times1000\right) \times \text{acidity.}$$

Note. 1000 ml of 1 N acid ≡ g. eq. wt. of the acid.

Example 7. *A diacid base weighing 0.2 g required 25 ml of decinormal* H_2SO_4 *for complete neutralisation. Find the molecular mass of the base.*

Solution. 25 ml of 0.1 N H_2SO_4 neutralise base = 0.2 g

1000 ml of 1 N H_2SO_4 neutralise base

$$= \frac{0.2}{25\times0.1}\times1000 \text{ g}$$

$$= \text{g. eq. wt. of base} = 80 \text{ g}$$

$\therefore$ Molecular mass of base = Eq. wt. of base × acidity

$$= 80 \text{ g} \times 2 = \mathbf{160\ g\ mol^{-}\ Ans.}$$

6.8 GRAM MOLECULAR WEIGHT OF A COMPOUND

Type. g. mol. wt. of a compound (= 1 g. molecule or 1 mole.) = wt. of one molecule of a compound in amu × 1.66 × 10^{-24} g × Avogadro no. (= 6.023 × 10^{23})

g. mol. wt. of a compound is the weight of Avogadro no. (= 6.023 × 10^{23}) of molecules of a compound in gram.

Example 8. *Calculate the gram molecular weight of* N_2 *molecule if weight of its one molecule is 28 amu.*

Solution. Wt of 1 amu = 1.66 × 10^{-24} g.

wt. of one nitrogen molecule = 28 amu

$$= 28 \times 1.66 \times 10^{-24} \text{ g}$$

$\therefore$ wt. of Avogadro no. (= 6.023 × 10^{23}) of N_2 molecules

$$= 28 \times 1.66 \times 10^{-24} \text{ g} \times 6.023 \times 10^{23} = 28 \text{ g.}$$

$\therefore$ g. mol. wt. of N_2 = **28 g. Ans.**

Example 9. *g. mol. wt. of* O_2 *is 32 g. If one molecule of* O_2 *weighs 32 amu, calculate the value of Avogadro's number.*

Solution. g. mol. wt. of O_2 = wt. of one molecule of O_2 in amu × 1.66 × 10^{-24} g × Avogadro's no.

$$32 \text{ g} = 32\times1.66\times10^{-24} \text{ g} \times \text{Avogadro's no.}$$

$$\therefore \text{ Avogadro's number} = \frac{32\,g}{32\times1.66\times10^{-24}\,g}$$

$$= \mathbf{6.024 \times 10^{23}\ Ans.}$$

Example 10. *A metal iodide M* I_x *(wt. = 2.1 g, sp. heat = 0.14 cal* g^{-}*) on heating with* HCl *(g) converted completely to 0.747 g* MCl_x*. Calculate the molecular weight of M* I_x*. (at. wt. I = 127, Cl = 35.5).*

Solution. Reaction : M I_x. + xHCl → MCl_x + xHI;

wt. of MI_x = 2.1 g ;

wt. of MCl_x = 0.747 g. We know that :

(*i*) Equivalent of MI_x = Equivalent of MCl_x

$$\therefore \quad \frac{\text{wt. of } MI_x}{\text{wt. of } MCl_x} = \frac{\text{Eq. wt. of } MI_x}{\text{Eq. wt. of } MCl_x} \quad \ldots (1)$$

$$\text{Eq. wt. of } MI_x = E + \frac{127}{1} = E + 127\,;$$

[Let eq. wt. of M = E]

$$\text{eq. wt. of } MCl_x = E + \frac{35.5}{1} = E + 35.5$$

$$\left(\because \text{ Eq. wt.} = \frac{\text{At.wt.}}{\text{Valency}}\right)$$

Where valency of I= valency of Cl = 1

Substituting the values in equation (1), we get :

$$\frac{2.1}{0.747} = \frac{E+127}{E+35.5}\,;$$

$$2.1\,\text{E} + (2.1 \times 35.5) = 0.747\,\text{E} + (127 \times 0.747)$$

Or $$2.1\,\text{E} + 74.55 = 0.747\,\text{E} + 94.869\,;$$

$$1.353\,\text{E} = 20.319$$

$$\therefore \quad \text{E} = \frac{20.319}{1.353} = 15.01$$

(*ii*) $$\text{Approx. At. wt.} = \frac{6.4}{\text{sp.heat}} = \frac{6.4}{0.14} = 45.7$$

(*iii*) $$\text{Exact Valency} = \frac{\text{Approx. at wt.}}{\text{Eq. wt.}} = \frac{45.7}{15.01} \approx 3.$$

(*iv*) $$\text{Exact at. wt.} = \text{Eq. wt.} \times \text{Valency} = 15.01 \times 3 = 45.03$$

(*v*) $$\text{Mol. wt. of } MI_x = \text{At. wt. of M} + x \times \text{at. wt. of I}$$
$$= 45.03 + (3 \times 127) = 45.03 + 381$$
$$= \mathbf{426.03\ g\ mol^{-}\ Ans.}$$

6.9 MOLAR VOLUME OR GRAM MOLECULAR VOLUME (G.M.V.)

The volume occupied by one gram mole or one mole of a gas at N.T.P. (or STP) is *called* molar volume or gram molecular volume (G.M.V.). At N.T.P., one gram mole of a gaseous substance occupies 22.4 L or 22.4 dm^3 or 22400 mL or 22400 cm^3 volume. For example : **2 g of H_2** (g. mol. wt. of H_2 = 2 g) , 32 g O_2 (g. mol. wt. of O_2 = 32 g) etc occupy 22.4 L (or dm^3) volume at N.T.P. Here, 2 g of H_2 and 32 g of O_2 represent 1 mole of H_2 and 1 mol of O_2 respectively.

6.10 DIFFERENT METHODS TO DETERMINE THE MOLECULAR WEIGHT OF SUBSTANCES

1. Gram Molecular volume (G.M.V.) method.

(*i*) *g. mol. wt.* of all gases at NTP or STP *occupy volume* = 22.4 L or 22.4 dm^3 or 22400 mL or 22400 cm^3.

(*ii*) 22400 mL of a gas weighs equal to its gram molecular weight.

EXAMPLE 11. *2 dm^3 of a gas weighs 4.12 g at S.T.P. Calculate the molecular weight of the gas.* **(J and K, 2010)**

SOLUTION. We know that g. mol. wt. of a gas occupies volume at

STP = 22.4 dm^3.

2 dm^3 of the gas weighs = 4.12 g

$$22.4\,\text{dm}^3 \text{ of the gas weighs} = \frac{4.12\,\text{g}}{2\,\text{dm}^3} \times 22.4\,\text{dm}^3 = 46.1\,\text{g}$$

∴ Mol wt. of gas = **46.1 g mol^{-} Ans.**

EXAMPLE 12. *1.96 g of the carbonate of a metal on ignition leave a residue of 1.40 g and 315 cm^3 of a gas at 27° C and 755 mm pressure. Calculate the molecular weight of the gas.*

SOLUTION. Given conditions. P_1 = 755 mm, V_1 = 315 cm^3, T_1 = 27 + 273 = 300 K.

At NTP : P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\,;\ V_2 = \frac{P_1V_1T_2}{P_2T_1} \qquad \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{755\,\text{mm} \times 315\,\text{cm}^3 \times 273\,\text{K}}{760\,\text{mm} \times 300\,\text{K}} = 284.8\,\text{cm}^3$$

wt. of gas = 1.96 – 1.40 = 0.56 g

284.8 cm^3 of gas weighs = 0.56 g

$$22400\,\text{cm}^3 \text{ of gas weighs} = \frac{0.56\,\text{g}}{284.8\,\text{cm}^3} \times 22400\,\text{cm}^3$$

= 44 g

∴ Mol. wt. of gas = **44 g mol^{-} Ans.**

EXAMPLE 13. *0.112 dm^3 of a gas weighs 0.146 g at 25 °C and 750 mm pressure. Calculate the molecular weight of the gas.*

SOLUTION. Given conditions : P_1 = 750 mm, V_1 = 0.112 dm^3, T_1 = 25 + 273 = 298 K

At NTP : P_2 = 760 mm, V_2 = ?, T_2 = 273 K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\,;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} \qquad \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{750\,\text{mm} \times 0.112\,\text{dm}^3 \times 273\,\text{K}}{298\,\text{K} \times 760\,\text{mm}}$$

= 0.101 dm^3

0.101 dm^3 of gas weighs = 0.146 g

$$22.4\,\text{dm}^3 \text{ of gas weighs} = \frac{0.146\,\text{g}}{0.101\,\text{dm}^3} \times 22.4\,\text{dm}^3$$

= 32.4 g

∴ Mol. wt. of gas = **32.4 g mol^{-} Ans.**

2. Regnault's method.

This method is used to determine the vapour density (V.D.) of a gas (or vapour) by direct weighing.

In this method, two glass globes of exactly same size and capacity are evacuated and suspended to the two sides of the balance. Firstly, one of the globes is filled with the gas whose V.D. is to be determined. The difference in the weights of empty globe and gas filled globe gives the weight of gas. Similarly, weight of H_2 gas under similar conditions of temperature and pressure is found. Then.

Vapour density (V.D.) of gas

$$= \frac{\text{wt. of known volume of the gas}}{\begin{array}{l}\text{wt. of same volume of } H_2 \text{ gas under similar} \\ \text{conditions of temperature and pressure} \\ (\text{e.g, NTP or STP}) = (V_{NTP} \text{ of } H_2 \text{ in mL} \times 0.00009\,\text{g})\end{array}}$$

∴ **Mol. wt. = 2 × V.D.**

wt. of 1 cm^3 or 1 mL H_2 gas at NTP or STP = 0.00009 g

wt. of 1 dm^3 or 1 L H_2 gas at NTP or STP = 1000 × 0.00009 = 0.09 g.

EXAMPLE 14. *The capacity of a glass bulb is 45.1 cm^3. 0.144 g of the gas is filled in the bulb at 27°C and 740 mm pressure. Calculate the vapour density and molecular weight of the gas.*

SOLUTION. *Given conditions:* P_1 = 740 mm, V_1 = 45.1 cm^3, T_1 = 27 + 273 = 300 *K*

At NTP: P_2 = 760 mm, V_2 = ?, T_2 = 273 *K*.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\,;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} \qquad \text{(Gas law)}$$

$$\therefore V_2 = \frac{740\ \text{mm} \times 45.1\ \text{cm}^3 \times 273\ \text{K}}{300\ \text{K} \times 760\ \text{mm.}} = 39.96\ \text{cm}^3 = 39.96\ \text{mL}$$

wt. of 1 ml H_2 at NTP = 0.00009 g

wt. of 39.96 ml H_2 at NTP = 0.00009 × 39.96 g

$$= 3.6 \times 10^{-3}\ \text{g}$$

$$\text{V.D.} = \frac{\text{wt. of 39.96 ml gas at NTP}}{\text{wt. of 39.96 ml } H_2 \text{ gas at NTP}}$$

$$\therefore \quad \text{V.D.} = \frac{0.144\ \text{g}}{3.6 \times 10^{-3}\ \text{g}} = \mathbf{40\ Ans.}$$

$$\therefore \quad \text{Mol. wt.} = 2 \times \text{V.D} = 2 \times 40 = \mathbf{80\ g\ mol^{-}\ Ans.}$$

EXAMPLE 15. *0.246 g of a gas is filled in a glass globe having a capacity of 72 mL at 117°C and 0.987 atm pressure. Calculate the vapour density and molecular weight of the gas. (1 dm^3 H_2 weighs 0.09 g).*

SOLUTION. Given conditions : $P_1 = 0.987$ atm, $V_1 = \frac{72}{1000}$ L, $T_1 = 117 + 273 = 390\ K$.

At NTP : $P_2 = 1$ atm, $V_2 = ?$, $T_2 = 273\ K$.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}\ \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{0.987\ \text{atm} \times 72\ \text{L} \times 273\ \text{K}}{390\ \text{K} \times 1\ \text{atm} \times 1000}$$

$$= 0.0497\ \text{L}$$

$$= 0.0497\ \text{dm}^3$$

Wt. of 1 dm^3 H_2 at NTP = 0.09 g

Wt. of 0.0497 dm^3 H_2 at NTP = 0.09 g × 0.0497

$$= 4.47 \times 10^{-3}\ \text{g}$$

$$\therefore \quad \text{V. D.} = \frac{\text{wt. of 0.0497 dm}^3 \text{ gas at NTP}}{\text{wt. of 0.0497 dm}^3\ H_2 \text{ at NTP}}$$

$$\text{V. D.} = \frac{0.246\ \text{g}}{4.47 \times 10^{-3}\ \text{g}} = \mathbf{55\ Ans.}$$

$\therefore$ Mol. wt. = 2 × V. D. = 2 × 55 = **110 g mol^{-} Ans.**

3. Ideal Gas law

According to this law :

$$PV = nRT = \frac{W}{M}\ RT\ ;\ \boldsymbol{M} = \frac{WRT}{PV}$$

Where P, V, n, W, M, R and T represent pressure, volume, no. of mol, wt., mol. wt, gas constant and absolute temperature respectively. $R = 0.821$ L atm K^{-} mol^{-}.

EXAMPLE 16. *72 cm^3 of a gas weighing 0.118 g has a pressure of 690 mm at 25°C. Calculate the molecular weight of the gas.*

SOLUTION.
$$P = 690\ \text{mm} \times \frac{1\ \text{atm}}{760\ \text{mm}} = \frac{69}{76}\ \text{atm}\ ;$$

$$V_1 = 72\ \text{cm}^3 \times \frac{1\,L}{1000\ \text{cm}^3} = 0.072\ \text{L}$$

$T = 25 + 273 = 298$ K; wt. of gas $= 0.118$ g

Let mol. wt. of gas= M.

We know that : $PV = nRT = \frac{W}{M}\ RT\ ;\ \text{M} = \frac{WRT}{PV}$

$$= \frac{0.118\,g \times 0.0821\,L\ \text{atm}\ K^{-}\ \text{mol}^{-} \times 298\ K \times 76}{69\ \text{atm} \times 0.072\ L} = 44.16$$

$\therefore$ Mol. wt. of gas = **44.16 g mol^{-} Ans.**

EXAMPLE 17. *Determine the formula weight of a gas if 20 g of the gas occupies a volume of 6 litre at a pressure of 2 atmosphere and a temperature of 27°C. Express your result in gram per mole. (R = 0.0821 litre atm deg^{-} mol^{-}).* **(ISC, 1982)**

SOLUTION. $P = 2$ atm, $V = 6\ L$, $R = 0.0821\ L$ atm K^{-} mol^{-},

$T = 27 + 273 = 300$ K, $n = \frac{\text{wt.}}{\text{mol.wt.,M}} = \frac{20\ \text{g}}{\text{M}}$.

We know that : $PV = nRT = \frac{\text{W}}{\text{M}}\ RT = \frac{20\ \text{g} \times RT}{\text{M}}$

$$\therefore \quad M = \frac{20\ \text{g} \times RT}{PV}$$

$$= \frac{20\ \text{g} \times 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-} \times 300\ \text{K}}{2\ \text{atm} \times 6\ \text{L}}$$

$$= \mathbf{41.05\ g\ mol^{-}\ Ans.}$$

EXAMPLE 18. *The weight of one litre sample of ozonised oxygen at NTP was found to be 1.5 g. When 100 mL of this mixture at NTP were treated with turpentine oil, the volume was reduced to 90 ml. Calculate the mol. wt. of ozone.* **(UPSEAT, 1996)**

SOLUTION. Wt. of 1 L (= 1000 ml) ozonised oxygen = 1.5 g ; R = 0.0821 L atm K^{-} mol^{-},

$T = 273$ K, $P = 1$ atm, $V = 1$ L.

Since turpentine oil absorbs ozone only, so.

Volume of ozone = 10 ml ; Volume of O_2 = 100 – 10 = 90 ml.

(*i*) $PV = \frac{\text{wt.}}{\text{Mol. wt.}} \times RT$; Mol. wt. of ozonised oxygen $= \frac{\text{wt.} \times RT}{PV}$

$\therefore$ Mol. wt. of ozonised oxygen

$$= \frac{1.5\ \text{g} \times 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-} \times 273\ \text{K}}{1\ \text{atm} \times 1\ \text{L}}$$

$$= 33.62\ \text{g mol}^{-}.$$

(*ii*) *To find mol. wt. of ozone.*

Volume or mole ratio of O_2 and ozone = 900 : 100.

At. wt. of oxygen = 16 ; mol. wt. of O_2 = 2 × 16 = 32 g mol^{-}.

Mol. wt. of ozone = m (say). Hence,

$$\text{Mol. wt. of ozonised oxygen} = \frac{(900 \times 32) + (100 \times m)}{900 + 100}$$

$$33.62 = \frac{28800 + 100\,m}{1000}\ ;\ (33.62 \times 1000) - 28800 = 100\ \text{m}$$

$\therefore$ 100 m = 4820 ; m = 48.2

$\therefore$ Mol. wt. of ozone = **48.2 g mol^{-} Ans.**

4. **Graham's law of diffusion** (See Chapter 8)

5. **Victor Meyer's method.** The molecular weight of the organic liquid is calculated with the help of following relation :

$$\text{Mol. wt.} = \frac{W}{V_{NTP}} \times 22400; \ \text{V. D.} = \frac{W}{V_{NTP}} \times 11200$$

where W = wt. of volatile liquid, V_{NTP} = volume of air displaced at NTP in mL or cm^3. 22400 mL or 22400 cm^3 is the volume occupied by gram molecular weight of the volatile liquid.

Note. For gases only: Mol. wt. = 2 × V.D.

Example 19. *An organic compound contains 54.54 percent of carbon, 9.10 percent of hydrogen and 36.36 percent of oxygen. 0.11 g of the same compound on vaporisation displaced 20 mL of air at STP. Find the molecular weight and molecular formula of the compound.* **(ISC, 1978)**

Solution. Volume of air displaced at STP = 20 mL

wt. of compound = 0.11 g

20 mL air weighs = 0.11 g

$$\therefore 22400 \text{ mL air weighs} = \frac{0.11\text{g} \times 22400\,\text{mL}}{20\,\text{mL}} = 123.2 \text{ g mol}^{-} = \text{Mol. wt.}$$

To find empirical formula

Element	*% age*	*At. wt.*	*Relative no. of atoms = % age/at. wt*	*Simple ratio*	*Whole no. ratio*
C	54.54	12	54.54/12 = 4.545	$\frac{4.545}{2.27} = 2$	2
H	9.10	1	$\frac{9.10}{1} = 9.10$	$\frac{9.1}{2.27} = 4$	4
O	36.36	16	$\frac{36.36}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

$\therefore$ E. F. = C_2H_4O ; E. F. wt. of C_2H_4O

= (2 × 12) + (4 × 1) + 16 = 44

Molecular formula = n × E. F.

$$n = \frac{\text{Mol. wt}}{\text{E. F. wt.}} = \frac{123.2}{44} = 2.8 \simeq 3$$

$\therefore$ M. F. = 3 × C_2H_4O = $C_6H_{12}O_3$ **Ans.**

Example 20. *In a Victor Meyer experiment, 0.062 g of a substance displaced 21.0 mL of moist air at 27°C and 736.7 mm pressure. Calculate the vapour density and molecular weight of the substance. (wt. of 1 ml H_2 at STP = 0.00009 g ; aqueous tension at 27°C = 26.7 mm).*

Solution. Given conditions. P_1 = 736.7 – 26.7 = 710 mm,

V_1 = 21.0 mL,

T_1 = 27 + 273 = 300 K ;

at NTP : P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

We know that :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \ ; V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} \quad \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{710\,\text{mm} \times 21\,\text{mL} \times 273\,\text{K}}{300\,\text{K} \times 760\,\text{mm}} = 17.8 \text{ mL}$$

$$\text{V.D.} = \frac{\text{wt. of 17.8 mL of substance}}{\text{wt. of 17.8 mL of } H_2}$$

$$= \frac{0.062\,\text{g}}{17.8 \times 0.00009} = \mathbf{38.7\ Ans.}$$

Mol. wt. = 2 × V.D. = 2 × 38.7 = **77.4 g mol¯ Ans.**

Second Method

$$\text{Mol. wt.} = \frac{\text{wt.}}{V_{NTP}} \times 22400 = \frac{0.062\,\text{g} \times 22400\,\text{mL}}{17.8\,\text{mL}}$$

= **78.02 g mol¯ Ans.**

$$\text{V.D.} = \frac{\text{Mol. wt.}}{2} = \frac{78.02}{2} = 39.01 \ \textbf{Ans.}$$

6.11 AIEEE PATTERN EXAMPLES

Example 21. *2 dm^3 of a gas at STP weighs 2.88 g. If 1 dm^3 of H_2 gas weighs 0.09 g at NTP, the mol. wt. of the gas would be :*

(a) 4 g mol¯ *(b) 8 g mol¯*
(c) 32 g mol¯ *(d) 64 g mol¯*

Solution. 1 dm^3 of H_2 at NTP or STP weighs = 0.09 g

2 dm^3 of H_2 at NTP weighs = 0.09 × 2 = 0.18 g

$$\therefore \text{ V. D. of gas} = \frac{\text{wt. of } 2\,dm^3 \text{ gas at NTP}}{\text{wt. of } 2\,dm^3\ H_2 \text{ gas at NTP}}$$

$$= \frac{2.88\,\text{g}}{0.18\,\text{g}} = 16$$

$\therefore$ Mol. wt. of gas = 2 × V.D. = 2 × 16 = 32 g mol¯.

So the correct answer is (*c*)

Example 22. *5 dm^3 of a gas at 14°C and 729 mm pressure weighs 8.96 g. The mol. wt. of the gas is :*

(a) 87 *(b) 44.0*
(c) 21.75 *(d) 17*

Solution. *Given conditions*: P_1 = 729 mm, V_1 = 5 dm^3, T_1 = 14 + 273 = 287 K

At NTP : P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \ ; V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} \quad \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{729\,\text{mm} \times 5\,dm^3 \times 273\,\text{K}}{287\,\text{K} \times 760\,\text{mm}} = 4.56\,dm^3$$

4.56 dm^3 of gas at NTP weighs = 8.96 g

$$22.4\,dm^3 \text{ of gas at NTP weighs} = \frac{8.96\,\text{g}}{4.56\,dm^3} \times 22.4\,dm^3$$

= 44.0 g

$\therefore$ Mol. wt. of gas = **44.0 g mol¯ Ans.**

So, the correct answer is (*b*).

Example 23. *If atomic weights of zinc and oxygen are 65 amu and 16 amu respectively, the molecular weight of zinc oxide in g mol¯ will be :*

(*a*) *8.1 g mol*$^{-}$ (*b*) *1.8 g mol*$^{-}$

(*c*) *81 g mol*$^{-}$ (*d*) *none of these*

Solution. In **ZnO:** At. wt. of Zn = 65 amu × $\dfrac{1.66 \times 10^{-24}\ \text{g}}{1\ \text{amu}}$ × 6.023×10^{23} = 65 g

($\because$ 1 amu = 1.66×10^{-24} g)

At. wt. of oxygen, O = 16 amu × $\dfrac{1.66 \times 10^{-24}\ \text{g}}{1\ \text{amu}}$ × 6.023 × 10^{23} = 16 g

$\therefore$ Mol. wt. of ZnO= At. wt. of Zn + at. wt. of O = 65 + 16 = 81 g mol^{-}

Thus the correct answer is (*c*).

Example 24. *The molecular weight of a gaseous substance is 80. The volume of the one gram of the gas at 0°C and 720 mm of mercury pressure will be :*

(*a*) *295.7 mL* (*b*) *0.2 L*

(*c*) *0.3 L* (*d*) *397 mL*

Solution. Volume, V = ?, $P = 720\ \text{mm} \times \dfrac{1\ \text{atm}}{760\ \text{mm}} = \dfrac{72}{76}\ \text{atm}$;

R = 0.0821 L atm K^{-} mol^{-}, T = 0 + 273 = 273 K.

We know that :

$$PV = nRT = \frac{W}{M}RT\ ;\ V = \frac{WRT}{MP}$$

$$= \frac{1\ \text{g}}{80\ \text{g mol}^{-}} \times \frac{0.0821\ \text{L atm K}^{-}\ \text{mol}^{-} \times 273\ \text{K} \times 76}{72\ \text{atm}}$$

or $V = 0.2957\ \text{L} = 0.2957\ \text{L} \times \dfrac{1000\ \text{mL}}{1\ \text{L}} = 295.7\ \text{mL}$.

So, the correct answer is (*a*)

Example 25. *The weight of sulphur dioxide contained in the same volume as that which contains 7.0 g nitrogen is :*

(*a*) *8 g* (*b*) *16 g*

(*c*) *32 g* (*d*) *64 g*

Solution. (*i*) Mol. wt. of N_2 = 2 × 14 = 28 g mol^{-}

28 g N_2 at NTP occupy volume = 22400 mL

7 g N_2 at NTP occupy volume = $\dfrac{22400\ \text{mL}}{28\ \text{g}} \times 7\ \text{g}$ = 5600 mL

(*ii*) Volume of SO_2 = 5600 mL; mol. wt. of SO_2 = 32 + (2 × 16) = 64 g mol^{-}

22400 mL SO_2 weigh = 64 g

5600 mL SO_2 weigh = $\dfrac{64\ \text{g}}{22400} \times 5600\ \text{mL} = 16\ \text{g}$.

So, the correct answer is (*b*)

Example 26. *1.25 g of the carbonate of a metal on ignition leave a residue of 0.7 g and a gas evolved occupying 312 cm*^{3} *at 27°C and 755 mm. The molecular weight of the gas would be :*

(*a*) *21.7 g* (*b*) *43.69 g*

(*c*) *87.28 g* (*d*) *0.55 g.*

Solution. *General condition*: P_1 = 755 mm, V_1 = 312 cm^3, T_1 = 27 + 273 = 300 K.

At NTP : P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{755\ \text{mm} \times 312\ \text{cm}^3 \times 273\ \text{K}}{300\ \text{K} \times 760\ \text{mm}} = 282\ \text{mL}$$

wt. of gas = wt. of carbonate of metal – wt. of residue = 1.25 g – 0.7 g = 0.55 g

282 mL of gas weigh = 0.55 g

22400 mL of gas weigh = $\dfrac{0.55}{282} \times 22400 = 43.69$ g.

So, the correct answer is (*b*).

Example 27. *2.24 cm*^{3} *of a gas is produced at NTP by the action of 8.24 mg of alcohol (ROH) on methyl magnesium bromide. The molar mass of alcohol is :*

(*a*) *92.29g* (*b*) *184.58 g*

(*c*) *369.16 g* (*d*) *22.4 g*

Solution. Reaction : $ROH + CH_3MgBr \rightarrow CH_4 \uparrow + Mg(OH)Br$.

Wt. of ROH (alcohol) = 8.24 mg = $\dfrac{8.24}{1000}$ g.

2.24 cm^3 of CH_4 is produced from alcohol = $\dfrac{8.24}{1000}$ g

$\therefore$ 22400 cm^3 CH_4 is produced from alcohol

$= \dfrac{8.24}{1000} \times 22400 = 184.58$ g

= Molar mass of alcohol

So, the correct answer is (*b*).

Example 28. *A compound on analysis was found to contain 8% sulphur by mass. The least molar mass of that compound will be.*

(*a*) *32 a.m.u* (*b*) *256 a.m.u*

(*c*) *400 a.m.u* (*d*) *92 a.m.u*

Solution. 8% sulphur in a compound means that :

8 g sulphur is present in a compound = 100 g

$\therefore$ 32 g sulphur is present in a compound = $\dfrac{100}{8} \times 32$

= 400 g ($\because$ at. wt. of S = 32)

Thus, the least molar mass, a compound containing only one sulphur atom will be 400 a.m.u. So, the correct answer is (*c*).

Example 29. *0.40 g of chloroplatinate of monoacid base on ignition gave 0.125 g of platinum. The molar mass of the base is :* **(UPCPMT, 2010)**

(*a*) *214 g mol*$^{-}$ (*b*) *107 g mol*$^{-}$

(*c*) *2.14 g mol*$^{-}$ (*d*) *12 g mol*$^{-}$. *(at. wt. Pt = 195).*

Solution. wt. of chloroplatinate = 0.40 g ; wt. of Pt = 0.125 g ;

Acidity (*n*) of base = 1

0.125 g Pt is obtained from chloroplatinate = 0.4 g

195 g Pt is obtained from chloroplatinate $= \frac{0.4\text{ g}}{0.125} \times 195\text{ g}$

$= 624$ g

$\therefore$ Molar mass of base $= \frac{n}{2}\,[624 - 410] = \frac{1}{2} \times 214$

$= 107\text{ g mol}^{-}$

So, the correct answer is (*b*).

EXAMPLE 30. *Silver salt of a dibasic acid weighing 1.8 g gave 1.08 g of silver. The molar mass of the acid is :*

(*a*) *166 g mol*$^{-}$ (*b*) *1.66 g mol*$^{-}$

(*c*) *146 g mol*$^{-}$ (*d*) *292 g mol*$^{-}$.

SOLUTION. Basicity (*n*) of acid = 2 ;

wt. of silver salt = 1.8 g ;

wt. of silver = 1.08 g ; at. wt. of Ag = 108 a.m.u.

1.08 g Ag is present in silver salt = 1.8 g

108 g Ag is present in silver salt $= \frac{1.8\text{ g}}{1.08\text{ g}} \times 108\text{ g}$

$\therefore$ Molar mass of acid = Basicity $\left[\frac{1.8}{1.08} \times 108\text{ g} - 107\right]$

$= 2\,(180 - 107) = 2 \times 73 = 146\text{ g mol}^{-}$

So, the correct answer is (*c*).

EXAMPLE 31. *0.45 g of a diacid base were dissolved in water and the solution was made up to 250 mL. 20 mL of this diluted acid required 15 ml of N/25* HCl *for complete neutralisation. The molecular weight of the base is :*

(*a*) *120 g mol*$^{-}$ (*b*) *60 g mol*$^{-}$

(*c*) *180 g mol*$^{-}$ (*d*) *none of these.*

SOLUTION. N_1V_1 (dilute base) $= N_2V_2$ (HCl)

$N_1 \times 20 = \frac{1}{25} \times 15\ ;\ N_1 = \frac{15}{20 \times 25} = \frac{15}{500}$ N

250 mL of $\frac{15}{500}$ N solution contains base = 0.45 g

1000 mL of 1N solution contains base

$= \frac{0.45}{250} \times \frac{500}{15} \times 1000 = 60$ g

= g. eq. wt. of base.

$\therefore$ Mol. wt. of base = Eq. wt. × acidity

$= 60 \times 2 = 120\text{ g mol}^{-}$.

So, the correct answer is (*a*).

EXAMPLE 32. *One molecule of a substance contains 6 carbon atoms, 12 hydrogen atoms and 1.5936 × 10*$^{-22}$ *g of the third component. The molecular weight of the substance is?*

(*a*) *84 g mol*$^{-}$ (*b*) *180 g mol*$^{-}$

(*c*) *8.4 g mol*$^{-}$ (*d*) *85.5936 × 10*$^{-22}$ *g mol*$^{-}$.

SOLUTION. The molecule of the substance contains *C*, *H* and the third component. Thus :

Wt. of 6 *C* - atoms = 6 × 12 = 72 a.m.u.

wt. of 12 *H* - atoms = 12 × 1 = 12 amu

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

So, 1.66×10^{-24} g of third component = 1 amu

1.5936×10^{-22} g of third component $= \frac{1}{1.66 \times 10^{-24}} \times$

$1.5936 \times 10^{-22} = 96$ amu

$\therefore$ Total wt. of one molecule of substance = 72 amu + 12 amu + 96 amu

$\therefore$Mol. wt. of substance $= 180\text{ g mol}^{-}$.

EXAMPLE 33. *A plant virus is found to consist of uniform cylindrical particles of 150 A° 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 simple particle, the molecular weight of the virus will be :*

(*a*) *108 g mol*$^{-}$ (*b*) *1.234 × 10*^{7} *g mol*$^{-}$

(*c*) *7.095 × 10*^{7} *g mol*$^{-}$ (*d*) *50,000 g mol*$^{-}$.

(Modified I.I.T. 1999)

SOLUTION. Volume of virus $= \pi r^2 \times l$; radius

$r = \frac{150\,A^\circ}{2} = \frac{150 \times 10^{-8}\text{ cm}}{2}$

$= 75 \times 10^{-8}$ cm ; length, $l = 5000$ A°

$= 5000 \times 10^{-8}$ cm ;

specific volume of virus $= 0.75\text{ cm}^3\text{ g}^{-}$. Thus :

Volume of virus $= \frac{22}{7} \times (75 \times 10^{-8}\text{ cm})^2 \times 5000 \times 10^{-8}\text{ cm}$

$= 8.839 \times 10^{-17}\text{ cm}^3$

$\therefore$ wt. of one virus $= \frac{8.839 \times 10^{-17}\text{ cm}^3}{0.75\text{ cm}^3\text{ g}^{-}} = 1.178 \times 10^{-16}\text{g}$

Since g. mol wt. of virus contains virus particles equal to Avogadro's number ($= 6.023 \times 10^{23}$), so we have :

Mol. wt. of virus $= 1.178 \times 10^{-16}\text{ g} \times 6.023 \times 10^{23}$

= 70950

$\simeq 7.095 \times 10^{7}\text{ g mol}^{-}$

So, the correct answer is (*c*).

EXAMPLE 34. *An organic compound made of C, H and N, contains 20% nitrogen. Its molecular weight is:*

(*a*) *70* (*b*) *140*

(*c*) *100* (*d*) *65*

(West Bengal JEE, 2009)

SOLUTION. Mol. wt. of $N_2 = 2 \times 14 = 28\text{ g mol}^{-}$. For organic compound containing 20% N_2:

Minimum mol. wt of compound $= \frac{100}{20} \times 28 = 140\text{g}$ mol^{-}. So, the correct answer is (*b*).

Example 35. *A bivalent metal has an equivalent mass of 32. The molecular mass of the metal nitrate is :*

(a) 168 *(b)* 192
(c) 188 *(d)* 182

(Karnataka CET, 2009)

Solution. Valency of metal = 2; Eq. mass = 32. Thus :

At. mass = Eq. mass × Valency; At. mass = 32 × 2 = 64

∴ Mol. mass of $M(NO_3)_2$ = At. mass of M + 2 (At. mass of N) + 2 (3 × At. mass of O) = 64 + (2 × 14) + 2 (3 × 16) = 188. So, the correct answer is (*c*).

Example 36. *The equivalent mass of a certain bivalent metal is 20. The molecular mass of its anhydrous chloride will be:*

(a) 91 *(b)* 111
(c) 55.5 *(d)* 75.5

(Karnataka, CET, 2012)

Solution. Let metal = M, Valency = 2.So, its anhydrous metal chloride = $M\ Cl_2$.

At. wt. of metal = Eq. wt. × Valency = 20 × 2 = 40.

∴ Molecular mass of $M\ Cl_2$ = 40 + (2 × 35.5) = 111 g mol^{-}. So, the correct answer is (*b*).

PROBLEMS FOR PRACTICE

1. Chloroplatinate of a monoacid organic base contains 33.4% of Pt. Calculate the mol. wt. of the base. (**Ans.** 86.9 g mol^{-})
2. 0.8 g of a silver salt of a dibasic acid gave 0.51 g of metallic silver. Find the molar mass of acid. (**Ans.** 124.8 g mol^{-})
3. 0.24 g of a dibasic acid required 30 mL of 0.1 N NaOH solution for complete neutralisation. Calculate the molar mass of the acid. (**Ans.** 160 g mol^{-})
4. A diacid base weighing 0.12 g required 10 mL of seminormal HCl for complete neutralisation. Find the molar mass of base. (**Ans.** 24 g mol^{-}).
5. If 300 mL of a gas weighs 0.368 g at NTP, what will be its mol. wt. ? (J and K-CET, 2010)
   (*a*) 27.5 g (*b*) 30.0g
   (*c*) 31.0 g (*d*) 17.5 g (**Ans.** (*a*))
6. 0.056 dm^3 of a gas weighs 0.073 g at 25°C and 750 mm pressure. Find the molar mass of the gas. (**Ans.** 32.7 g mol^{-})
7. The capacity of a glass bulb is 36 cm^3 at 107°C and 1.1 atmospheric pressure. If weight of gas filled is 0.123 g, calculate the vapour density and molecular weight of the gas. (1 dm^3 of H_2 weighs 0.09 g) (**Ans.** 36, 72 g mol^{-})
8. 36.0 mL of a gas weighing 0.059 g has a pressure of 350 mm at 25° C. Calculate the molecular weight of the gas. (**Ans.** 43.5 g mol^{-})
9. 0.4 L of a gas weighs 0.57 g at N.T.P. Calculate the mol. wt. of gas. (**Ans.** 31.92 g mol^{-})
10. In a Victor Meyer experiment, 0.054 g of a substance displaced 20.8 mL of moist air at 27°C and 755.7 mm pressure. Calculate the vapour density and molecular weight of the substance. (wt. of 1 mL H_2 at N.T.P. = 0.00009 g; aqueous tension at 27°C = 26.7 mm). (**Ans.** 66.0 g mol^{-})

7

CHAPTER

Laws of Chemical Combination

7.1 LAW OF CONSERVATION OF MASS

It states that matter can neither be created nor destroyed during any physical or chemical change **OR** *the sum total of mass of reactants before the reaction is equal to sum total of mass of products after the reaction.*

Example 1. *1.60 g of a hydrocarbon (containing carbon and hydrogen only) on complete combustion with oxygen yielded 4.4 g carbon dioxide and 3.6 g water. Show that these results obey the law of conservation of mass. (C = 12, O = 16, H = 1)*

Solution. Hydrocarbon contains carbon and hydrogen and weighs 1.60 g. From the weight of CO_2 and that of H_2O, the weight of carbon and hydrogen respectively can be calculated.

(*a*) gram molecular weight of $CO_2 = 12 + (2 \times 16)$
$= 44$ g.

$$44 \text{ g } CO_2 \equiv 12 \text{ g carbon } [\because CO_2 \equiv C]$$

$$4.4 \text{ g } CO_2 \equiv \frac{12 \times 4.4}{44} = \mathbf{1.2 \text{ g}} \text{ carbon}$$

(*b*) gram molecular weight of $H_2O = (1 \times 2) + 16 = 18$ g

$$18 \text{ g } H_2O \equiv 2 \text{ g H } (\because H_2O \equiv 2H)$$

$$3.6 \text{ g } H_2O \equiv \frac{2 \times 3.6}{18} = 0.4 \text{ g}$$

$\therefore$ Total weight of carbon and hydrogen $= 1.2 + 0.4$
$= \mathbf{1.6}$ **g.**

Since the weight of hydrocarbon (1.6 g) is equal to the total weight of carbon and hydrogen (= 1.6 g), the results obey the law of conservation of mass.

Example 2. *6 g of $MgCO_3$ yield 2.857 g of MgO and 1.585 L of carbon dioxide gas at standard temperature and pressure. Show that these figures support the law of conservation of mass within the limits of ± 0.5% error.*

Solution. wt. of $MgCO_3$ = 6.0 g; wt. of MgO = 2.857 g.

$$\text{Reaction } MgCO_3 \longrightarrow MgO + \underset{22.4 \text{ L}}{CO_2}$$

22.4 L CO_2 is produced from CO_2 = g. mol. wt. of CO_2
$= 12 + (2 \times 16) = 44$ g

$$1.585 \text{ L } CO_2 \text{ is produced from } CO_2 = \frac{44 \times 1.585}{22.4} = 3.1134 \text{ g}$$

$\therefore$ wt. of MgO + wt. of CO_2 = 2.857 g + 3.1134 g
= 5.9704 g

Error = 6.0 – 5.9704 = 0.0296 g

$$\therefore \quad \% \text{ age error} = \frac{0.0296 \times 100}{6} = 0.49\%$$

Hence the law of conservation of mass is valid within limits of ± 0.5% error.

Example 3. *If 6.3 g of $NaHCO_3$ are added to 15.0 g of CH_3COOH solution, the residue is found to weigh 18.0 g. What is the mass of CO_2 released in this reaction?*

Solution. Mass of CO_2 = *x*g (say); wt. of $NaHCO_3$ = 6.3g; wt. of CH_3COOH = 15.0 g; wt. of residue CH_3COONa and water = 18.0 g. The reaction is :

$$\underset{6.3 \text{ g}}{NaHCO_3} + \underset{15.0 \text{ g}}{CH_3COOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{18 \text{ g}} + \underset{x \text{ g.}}{CO_2}$$

According to law of conservation of mass, weight of reactants is equal to weight of products.

$\therefore$ $6.3 + 15 = 18 + x$ **or** $x = 6.3 + 15 - 18 = \mathbf{3.3 \text{ g}}$ **Ans.**

Example 4. *What weight of barium chloride will react with 2.36 g of sodium sulphate in solution so as to produce 3.88 g of barium sulphate and 1.94 g of sodium chloride in solution.*

Solution. wt. of $BaCl_2$ = *x*g(say); wt. of Na_2SO_4 = 2.36 g; wt. of $BaSO_4$ = 3.88 g; wt. of NaCl = 1.94 g.

The reaction is :

$$\underset{x}{BaCl_2} + \underset{2.36 \text{ g}}{Na_2SO_4} \longrightarrow \underset{3.88 \text{ g}}{BaSO_4} + \underset{1.94 \text{ g}}{2NaCl}$$

According to the law of conservation of mass, weight of reactants is equal to weight of products.

$\therefore$ $x + 2.36 = 3.88 + 1.94$. Thus $x = 3.88 + 1.94 - 2.36$
$= 3.46$ g

7.2 LAW OF DEFINITE OR CONSTANT COMPOSITION (OR PROPORTION)

It states that the *same compound regardless of its source, is made up of the same elements combined together in the fixed proportion by weight.* For example, water (H_2O) may be taken from any source, it always contains hydrogen and oxygen in the ratio 1 : 8 by weight.

EXAMPLE 5. *In one experiment, 1.59 g of cupric oxide on complete reduction with hydrogen yielded 1.27 g of pure copper. In another experiment, 3.18 g of cupric oxide yielded 2.54 g of pure copper on complete reduction with hydrogen. Show that the data obeys the law of definite composition.*

SOLUTION. In one experiment :

Weight of cupric oxide (CuO) = 1.59 g

Weight of copper (Cu) = 1.27 g

∴ wt. of oxygen = 1.59 – 1.27 = **0.32 g**

Ratio by weight of Cu : O = 1.27 : 0.32

$$= \frac{1.27}{0.32} : \frac{0.32}{0.32} = \mathbf{3.97 : 1}$$

In another experiment :

Weight of cupric oxide (CuO) = 3.18 g

Weight of copper (Cu) = 2.54 g

∴ Weight of oxygen = 3.18 – 2.54 = **0.64 g**

Ratio by weight of Cu : O = 2.54 : 0.64

$$= \frac{2.54}{0.64} : \frac{0.64}{0.64} = \mathbf{3.97 : 1}$$

Since the ratio by weight of Cu : O in both experiments is the same (= 3.97 : 1), the data obeys the law of definite composition.

EXAMPLE 6. *One sample of pure calcium carbonate ($CaCO_3$) contains 40% calcium, 12% carbon and 48% oxygen. Assuming the law of constant composition to be true, calculate the weight of calcium, carbon and oxygen in 10.0 g of pure $CaCO_3$ in another sample.*

SOLUTION. From the given data, it is clear that

(*a*) 100 g $CaCO_3$ contains calcium = 40 g

∴ 10 g $CaCO_3$ contains calcium $= \frac{40}{100} \times 10$

= **4.0 g** **Ans.**

(*b*) 100 g $CaCO_3$ contains carbon = 12 g

∴ 10 g $CaCO_3$ contains carbon $= \frac{12}{100} \times 10$

= **1.2 g** **Ans.**

(*c*) 100 g $CaCO_3$ contains oxygen = 48 g

∴ 10 g $CaCO_3$ contains oxygen $= \frac{48}{100} \times 10$

= **4.8 g** **Ans.**

The total weight of calcium, carbon and oxygen in second sample of $CaCO_3$ is 4.0 + 1.2 + 4.8 = **10 g**. This weight is same as the weight of pure sample.

EXAMPLE 7. *In one experiment, 56 mL of hydrogen combines with 28 mL of oxygen to yield water. In second experiment, when 896 mL of hydrogen at NTP are passed over heated ferrosoferric oxide (Fe_3O_4) loses 0.64 g of its weight. Show that these results are in agreement with the law of constant composition (wt. of 22.4 litre of O_2, H_2 at NTP = 32 g, 2 g respectively.*

SOLUTION. First experiment

$$\text{wt. of 56 mL of } H_2 \text{ at N.T.P.} = \frac{56 \times 2}{22400} = 0.005 \text{ g}$$

$$\text{wt. of 28 mL of } O_2 \text{ at N.T.P.} = \frac{28 \times 32}{22400} = 0.04 \text{ g}$$

$$\text{Ratio by wt. of } H_2 \text{ and } O_2 = 0.005 : 0.04 = \frac{0.005}{0.005} : \frac{0.04}{0.005}$$

$$= \mathbf{1 : 8}$$

Second experiment

$$\text{wt. of 896 mL of } H_2 \text{ at N.T.P.} = \frac{896 \times 2}{22400} = 0.08 \text{ g}$$

wt. of oxygen taken away from Fe_3O_4 by 896 ml H_2 (or 0.08 g H_2) at NTP = 0.64 g

$$\text{Ratio by wt. of } H_2 \text{ and } O_2 = 0.08 : 0.64 = \frac{0.08}{0.08} : \frac{0.64}{0.08}$$

$$= 1 : 8$$

Since the ratio by wt. of H_2 and O_2 in both experiments is same, the law of constant composition is proved.

EXAMPLE 8. *56 cm^3 of O_2 gas combines with 112 cm^3 of H_2 to form water. When 336 cm^3 of H_2 are passed over heated cupric oxide, the latter loses 0.24 g of its weight. If all measurements of volume are done at S.T.P., prove that the data illustrates the law of definite proportion.*

SOLUTION. (*i*) 22400 cm^3 O_2 weigh = g.mol. wt. of

$O_2 = 2 \times 16 = 32$ g

$$56 \text{ cm}^3\ O_2 \text{ weigh} = \frac{32}{22400} \times 56 = 0.08 \text{ g}$$

22400 cm^3 H_2 weigh = g.mol. wt. of H_2 = 2g

$$112 \text{ cm}^3 \text{ of } H_2 \text{ weigh} = \frac{2}{22400} \times 112 = 0.01 \text{ g}$$

∴ Ratio by wt. of $H_2 : O_2$ = 0.01 : 0.08 or **1 : 8**

(*ii*) 22400 cm^3 H_2 weigh = g.mol. wt. of H_2 = 2 g

$$336 \text{ cm}^3\ H_2 \text{ weigh} = \frac{2}{22400} \times 336 = 0.03 \text{ g}$$

wt. of oxygen = 0.24 g because H_2 reacts with 'O' of CuO to form Cu and H_2O

$$[CuO + H_2 \longrightarrow Cu + H_2O]$$

$$\therefore \text{Ratio by wt. of } H_2 : O_2 = 0.03 : 0.24 = \frac{0.03}{0.03} : \frac{0.24}{0.03}$$

$$= \mathbf{1 : 8}$$

Since ratio by wt. of H_2 and O_2 (= 1: 8) is same in both experiments, the law of definite proportion is obeyed.

EXAMPLE 9. *Illustrate the law of definite proportions from the following data (i) 0.16 g of sulphur produces 112 mL of SO_2 at NTP (ii) sulphur dioxide obtained by the decomposition of a sulphate contains 50% sulphur. (at. wt. of S = 32, O = 16)*

SOLUTION. First experiment. wt. of sulphur = 0.16 g;

$$\text{wt. of } SO_2 = \frac{\text{g. mol. wt. of } SO_2}{22400 \text{ mL}} \times \text{vol. of } SO_2 \text{ in mL}$$

[g-mol. wt. of SO_2 = 32 + 2 × 16 = 64 g]

$$= \frac{64 \times 112}{22400} = 0.32 \text{ g}$$

∴ wt. of oxygen = 0.32 – 0.16 = 0.16 g

$$\therefore \text{Ratio by wt. of S : O is} = 0.16 : 0.16 = \frac{0.16}{0.16} : \frac{0.16}{0.16}$$

or 1 : 1 ...(1)

Second experiment. wt. of sulphur = 50 g

wt. of oxygen = 100 – 50 = 50 g

$\therefore$ Ratio by wt. of S : O is = 50 : 50

$$= \frac{50}{50} : \frac{50}{50} \text{ or } 1 : 1 \qquad ...(2)$$

Since the ratio by weight of S and O in both experiments is same *i.e.*, 1 : 1, the data illustrates the law of definite proportion.

7.3 LAW OF MULTIPLE PROPORTION

According to this law, *"When two elements, combine to form two or more compounds, the weight of one of the elements that combine with the fixed weight of the other, bear a simple whole number ratio"*.

Example 10. *11 g of one oxide of nitrogen yielded 5.6 litre of nitrogen at N.T.P. 15 g of another oxide of nitrogen yielded same volume of oxygen at N.T.P. Show that the data illustrate the law of multiple proportion.*

Solution. (*a*) **First oxide of nitrogen**

22.4 litre of N_2 weighs = g. mol. wt. of N_2 = 28 g

5.6 litre of N_2 weighs = 28 × 5.6/22.4 = 7 g

(*i.e.* **wt. of nitrogen**)

wt. of oxide of nitrogen = 11 g

$\therefore$ wt. of oxygen = 11 – 7 = 4 g

Ratio by weight of 'N : O' = 7 : 4 ...(A)

(*b*) **Second oxide of nitrogen**

Volume of oxygen at N.T.P = 5.6 litre

22.4 litre of O_2 weighs = g. mol. wt. of O_2 = 32 g

5.6 litre of O_2 weighs = 32 × 5.6/22.4 = 8 g

$\therefore$ wt. of oxygen = 8 g; wt. of oxide of nitrogen = 15 g

$\therefore$ wt. of nitrogen = 15 – 8 = 7 g

Ratio by weight of 'N : O' = 7 : 8 ...(B)

From (A) and (B), keeping the weight of nitrogen (= 7 g) fixed, the ratio by weight of oxygen in both oxides is 4 : 8 or **1 : 2** which is a simple ratio. This proves the law of multiple proportion.

Example 11. *1.27 g of chloride of iron gave 2.87 g of silver chloride and 16.25 g of another chloride of it gave 43.05 g of silver chloride. Show that these results illustrate the law of multiple proportion. (At. wt. Ag = 108 amu, Fe = 56 amu, Cl = 35.5 amu)*

Solution. (*a*) **First chloride of silver**

AgCl ≡ Cl

108 + 35.5 = 143.5 g 35.5 g

143.5 g AgCl contain Cl = 35.5 g

2.87 g AgCl contain Cl = 35.5 × 2.87/143.5 = 0.71 g

$\therefore$ wt. of Cl = 0.71 g

wt. of Ag in silver chloride = 1.27 – 0.71 = 0.56 g

$$\text{Ratio by wt. of Ag : Cl} = 0.56 : 0.71 = \frac{0.56}{0.56} : \frac{0.71}{0.56}$$

$$= 1 : 1.27 \qquad ...(A)$$

(*b*) **Second oxide of silver**

AgCl ≡ Cl

108 + 35.5 = 143.5 g 35.5 g

143.5 g AgCl contain Cl = 35.5 g

43.05 g AgCl contain Cl = 35.5 × 43.05/143.5 = 10.65 g

$\therefore$ wt. of Cl = 10.65 g

wt of Ag in silver chloride = 16.25 – 10.65 = 5.60 g

$$\text{Ratio by weight of Ag : Cl} = 5.6 : 10.65 = \frac{5.6}{5.6} : \frac{10.65}{5.6}$$

$$= 1 : 1.90 \qquad ...(B)$$

Keeping the wt. of Ag in (A) and (B) equal to one fixed, the ratio by wt. of Cl in (A) and (B) is

$$1.27 : 1.90 \text{ or } \frac{1.27}{1.27} : \frac{1.90}{1.27} \text{ or } 1 : 1.5$$

or 1 × 2 : 1.5 × 2 *i.e.*, 2 : 3

(The ratios are multiplied by 2 to get whole number ratios)

This ratio (2 : 3) being simple, the data illustrates the law of multiple proportion.

Example 12. *1.023 g of mercury (II) oxide gave 56.2 mL of oxygen measured at 15° C and 750 mm pressure. 1.895 g of mercury (I) oxide gave 54.1 mL of oxygen at 14° C and 747 mm pressure. Show that these results illustrate the law of multiple proportion.*

Solution. (*a*) **Mercury (II) oxide;** $V_{NTP}(O_2) = 52.57$ mL

$$52.57 \text{ mL of } O_2 \text{ weigh} = \frac{32}{22400} \times 52.57 = 0.075 \text{ g}$$

wt. of mercury = 1.023 – 0.075 = 0.948 g

$$\text{Ratio by wt. of Hg : O} = 0.948 : 0.075 = \frac{0.948}{0.075} : \frac{0.075}{0.075}$$

$$= 12.64 : 1 \qquad ...(A)$$

(*b*) **Mercury (I) oxide;** $V_{NTP}(O_2) = 50.58$ mL

$$50.58 \text{ mL of oxygen weighs} = \frac{32}{22400} \times 50.58 = 0.072 \text{ g}$$

wt. of mercury = 1.895 – 0.072 = 1.823 g

$$\text{Ratio by wt. of Hg : O} = 1.823 : 0.072 = \frac{1.823}{0.072} : \frac{0.072}{0.072}$$

$$= 25.32 : 1 \qquad ...(B)$$

Keeping the wt. of oxygen (= 1) fixed in (A) and (B), the ratio between the weights of mercury is :

$$= 12.64 : 25.32 = \frac{12.64}{12.64} : \frac{25.32}{12.64} = \mathbf{1 : 2}$$

This ratio 1 : 2 being simple, the data illustrates the law of multiple proportion.

Example 13. *Two oxides of a metal contain 31.6% and 48% of oxygen respectively. If the formula of first be M_2O_3, find that of the second.* ***(J & K-CET, 2011)***

Solution.

First oxide	**Second oxide**
oxygen = 31.6%	oxygen = 48%
Metal = 100 – 31.6	Metal = 100 – 48
= 68.4%	= 52%
Formula = M_2O_3	Formula = ?

Let at. wt. of the metal = x amu

$\therefore$ Percentage of metal by weight in M_2O_3

$$= \frac{2 \times x \times 100}{2x + (3 \times 16)} = 68.4 \text{ (given) or}$$

$$x = 51.95$$

At. wt. of metal = 51.95 a.m.u.

Using atomic weight of metal, 51.95, we calculate the emperical formula of metal oxide as follows :

Element	At. wt.	%age	Atomic ratio = %age/At. wt.	Least ratio	Whole no. ratio
Oxygen	16	48	$\frac{48}{16}=3$	**3**	**3**
Metal	51.95	52	$\frac{52}{51.95}=1$	1	1

∴ Formula of the second oxide = MO_3.

Example 14. *Carbon combines with hydrogen to form three compounds X, Y and Z. The percentage of hydrogen in X, Y and Z is 25, 20 and 14.28 respectively. (i) Find the empirical formula of the compound. (ii) What law of chemical combination does this example illustrate ? How ?*

Solution. To calculate empirical formula, we proceed as follows.

Element	At. wt.	% age in compound			Atomic ratio = %age /At. wt.			Least ratio		
		X	Y	Z	X	Y	Z	X	Y	Z
Hydrogen	1	25	20	14.28	$\frac{25}{1}=25$	$\frac{20}{1}=20$	$\frac{14.28}{1}=14.28$	$\frac{25}{6.25}=4$	$\frac{20}{6.67}=3$	$\frac{14.28}{7.14}=2$
Carbon	12	75	80	85.72	$\frac{75}{12}=6.25$	$\frac{80}{12}=6.67$	$\frac{85.72}{12}=7.14$	$\frac{6.25}{6.25}=1$	$\frac{6.67}{6.67}=1$	$\frac{7.14}{7.14}=1$

∴ Empirical formula of X = CH_4, Y = CH_3 and Z = CH_2

The ratio by weight of hydrogen that combine with fixed weight (= 1) of carbon in X, Y and Z is 4 : 3 : 2 which is a simple ratio. So, the law of multiple proportion is illustrated.

Example 15. *(i) A metal M forms two oxides. One of the oxides contains 77.78% of metal while the other one contains 70.0% of the metal. Show that these values are in accordance with the law of multiple proportion.*

(*ii*) *If atomic weight of M is 60, calculate the empirical formula of the oxide containing 70% of the metal, M.*

Solution. (*i*) **First oxide.** wt. of metal = 77.78 g;

wt. of oxygen = 100 – 77.78 = 22.22 g.

Ratio by wt. of metal and oxygen = M : O = 77.78 : 22.22

$$= \frac{77.78}{77.78} : \frac{22.22}{77.78} = \mathbf{1 : 0.2857}$$

(*ii*) **Second oxide.** wt. of metal = 70 g; wt. of oxygen = 100 – 70 = 30 g

∴Ratio by wt. of metal and oxygen = M : O

$$= 70 : 30 = \frac{70}{70} : \frac{30}{70} = \mathbf{1 : 0.4286}$$

Keeping the weight of metal (= 1) fixed, the ratio by weight of oxygen is : 0.2857 : 0.4286

or $$= \frac{0.2857}{0.2857} : \frac{0.4286}{0.2857} = 1 : 1.5$$

$$= 1 \times 2 : 1.5 \times 2 \text{ or } 2 : 3$$

The ratios are multiplied by 2 to get whole number ratio, **2 : 3**.

∴ Law of multiple proportion is obeyed.

(*b*) wt. of metal = 70 g; wt. of oxygen = 100 – 70 = 30 g, at. wt. of M = 60; at wt. of oxygen = 16. To find E.F., we have :

Element	%age	at.wt.	Relative no. of atoms = $\frac{\%\text{ age}}{\text{at. wt.}}$	Simple ratio	Whole no. ratio
M	70	60	$\frac{70}{60}=1.167$	$\frac{1.167}{1.167}=1$	1 × 2 = 2
O	30	16	$\frac{30}{16}=1.875$	$\frac{1.875}{1.167}$ $=1.6 \simeq 1.5$	1.5 × 2 = 3

∴ Empirical formula E.F. = $\mathbf{M_2O_3}$ **Ans.**

Example 16. *Two oxides of a metal contain 27.6 and 30.0 percent of oxygen respectively. If the formula of first be M_3O_4, find that of the second.*

Solution.

First oxide	**Second oxide**
Oxygen = 27.6%	Oxygen = 30.0%
Metal = 100 – 27.6 = 72.4%	Metal = 100 – 30 = 70%
Formula = M_3O_4	Formula = ?
At. wt. of M = x(say)	

$$\%\text{ age by wt. of metal in } M_3O_4 = \frac{3 \times x}{3x + 4 \times 16} \times 100$$

$$= 72.4 \text{ (given)}$$

∴ x = 55.97 = at. wt. of metal

Calculation of empirical formula of second oxide :

Element	%age	at.wt.	Relative no. of atoms = $\frac{\%\text{ age}}{\text{at. wt.}}$	Simple ratio	Whole no. ratio
Oxygen	30	16	$\frac{30}{16}=1.88$	$\frac{1.88}{1.25}=1.5$	$2\times1.5=3$
Metal	70	55.97	$\frac{70}{55.97}=1.25$	$\frac{1.25}{1.25}=1$	$2\times1=2$

∴ E.F. of second oxide = M_2O_3

Example 17. *Metal M and chlorine combine in different proportions to form two compounds A and B. The mass ratio M : Cl is 0.895 : 1 in A and 1.791 : 1 in B. Which law of chemical combination does this example illustrate ?* **(I.I.T. 1969)**

Solution. In compound A, M : Cl

0.895 : 1

In compound B, 1.791 : 1

Ratio between the weights which combine with the fixed weight of chlorine (1 part) is :

$$0.895 : 1.791 \text{ or } 1 : 2$$

which is a simple whole number multiple ratio. Hence this example illustrates the law of multiple proportions.

Example 18. *An element A combines with bromine to form a few compounds. Some of these are given in the following table.*

	Compound, X	*Compound, Y*
(a)	ABr	ABr_2
(b)	ABr	A_2Br
(c)	ABr_3	A_2Br_3
(d)	ABr_2	ABr

The mass ratio of A : Br is 0.4495 : 1 in X and 0.8955 : 1 in Y. Which of the above compounds are correct and which law of chemical combination holds good.

Solution. In compound, *X* and *Y*, keeping the weight of Br(= 1) fixed, the ratio by weight of A is :

$$\text{A(in } X) : \text{A(in } Y) = 0.4495 : 0.8955$$

$$\text{or} \quad = \frac{0.4495}{0.4495} : \frac{0.8955}{0.4495} = 1 : 2 \qquad (1)$$

(*a*) In *X*, ratio by wt. of A : Br is 1 : 1

In *Y*, ratio by wt. of A : Br is 1 : 2 or $\frac{1}{2}:\frac{2}{2}$ or $\frac{1}{2}:1.$

Keeping the wt. of Br (=1) fixed, the ratio of A : A is, $1:\frac{1}{2}$ or 2 : 1.

This ratio does not tally with ratio (1). So, these compounds are not correct.

(*b*) In *X*, ratio by wt. of A : Br is 1 : 1

In *Y*, ratio by wt. of A : Br is 2 : 1.

Keeping the wt. of Br (=1) fixed, the ratio of A : A = 1 : 2. It is in accordance with ratio (1). So, these compounds are correct.

(*c*) In *X*, ratio by wt. of A : Br is 1 : 3

In *Y*, ratio by wt. of A : Br is 2 : 3

Keeping the weight of Br (= 3) fixed, the ratio by wt. of A : A is 1 : 2. It is in accordance with ratio (1). So, these compounds are correct.

(*d*) In *X*, ratio by wt. of A : B is 1 : 2

In *Y*, ratio by wt. of A : B is 1 : 1 or 1 × 2 : 1 × 2 or 2 : 2

Keeping the weight of Br (= 2) fixed, the ratio by wt. of A : A is 1 : 2. It is in accordance with ratio (1). So, the law of multiple proportion is obeyed.

Example 19. *(a) An element M forms two oxides. One of the oxides contains 79.88% element while the other oxide contains 88.81% element. Show that these results obey the law of multiple proportion.*

(b) Find the value of equivalent weight of M in the first oxide. If the formula of first oxide is MO, calculate the atomic weight of M.

Solution. (*a*) **First oxide.** wt. of element = 79.88 g; wt. of oxygen = 100 – 79.88 = 20.12 g.

Ratio by wt. of M : O is : = M : O = 79.88 : 20.12

$$= \frac{79.88}{79.88} : \frac{20.12}{79.88} = \mathbf{1 : 0.25}$$

Second oxide. wt. of element = 88.81 g; wt. of oxygen = 100 – 88.81 = 11. 19 g.

∴ Ratio by weight of M : O is :

$$= \text{M : O} = 88.81 : 11.19$$

$$= \frac{88.81}{88.81} : \frac{11.19}{88.81} = \mathbf{1 : 0.125}$$

Keeping the weight of M(= 1) fixed, the ratio by weight of oxygen

$$= 0.25 : 0.125 = \frac{0.25}{0.125} : \frac{0.125}{0.125}$$

$$= 2 : 1$$

which are simple multiple of each other. So, the data obeys the law of multiple proportion.

(*b*) **For first oxide :** wt. of M = 79.88 g; wt. of oxygen = 100 – 79.88 = 20.12 g; eq. wt. of M = ?, eq. wt. of oxygen = 8. We know that :

$$\frac{\text{wt. of metal}}{\text{wt. of oxygen}} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of oxygen}};$$

$$\frac{79.88 \text{ g}}{20.12 \text{ g}} = \frac{\text{Eq. wt. of metal}}{8}$$

$$\therefore \quad \text{Eq. wt. of metal} = \frac{79.88 \times 8}{20.12} = \mathbf{31.76 \text{ Ans.}}$$

Since first oxide is MO (given) and oxide, O^{2-} is divalent, so valency of M = 2

∴ At. wt. = Eq. wt. × valency

= 31.76 × 2 = **63.52 Ans.**

Example 20. *Two different hydrocarbons were burnt in excess oxygen. One of these weighing 0.052 g and the other weighing 0.016 g produced 95.8 cm^3 of CO_2 and 23.9 cm^3 of CO_2 respectively at 288 K and 755/760 atmospheric pressure. Show that these results are in conformity with the law of multiple proportion.*

Solution. First hydrocarbon (C_xH_y). wt. of C_xH_y = 0.052 g; volume of CO_2 = 95.8 cm^3; mol. wt. of CO_2 = 12 + (2 × 16) = 44 g mol^{-}.

$$P_1 = \frac{755}{760}\text{ atm}, V_1 = 95.8\text{ cm}^3, T_1 = 288\text{ K};$$

at N.T.P., $P_2 = 1$ atm, $V_2 = ?$, $T_2 = 273$ K.

But $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$

or $V_2 = \frac{755}{760}\text{atm} \times \frac{95.8\text{ cm}^3}{288\text{ K}} \times \frac{273\text{ K}}{1\text{ atm}}$

$= 90.2\text{ cm}^3.$

22400 cm^3 CO_2 weigh = g. mol. wt. of CO_2

$= 12 + (2 \times 16) = 44$ g

$90.2\text{ cm}^3\ CO_2$ weigh $= \frac{44\text{ g}}{22400\text{ cm}^3} \times 90.2\text{ cm}^3 = 0.177$ g

$CO_2 \equiv C$

$12 + (2 \times 16) = 44$ g   12 g

44 g CO_2 contain C = 12 g

0.177 g CO_2 contain C $= \frac{12\text{ g}}{44\text{ g}} \times 0.177$ g

= 0.048 g = wt. of carbon.

wt. of hydrogen = wt. of C_xH_y – wt. of C

= 0.052 – 0.048 = 0.004 g

$\therefore$ Ratio by wt. of C : H $= 0.048 : 0.004\text{ g} = \frac{0.048}{0.004} : \frac{0.004}{0.004}$

= **12 : 1** ...(A)

Second hydrocarbon (C_xH_y). wt. of C_xH_y = 0.16 g, volume of CO_2 = 23.9 cm^3;

g.mol. wt. of CO_2 = 12 + (2 × 16) = 44 g.

$$P_1 = \frac{755}{760}\text{ atm}, V_1 = 23.9\text{ cm}^3,$$

T_1 = 288 K;

at N.T.P., P_2 = 1 atm, V_2 = ?, T_2 = 273 K.

We know that, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$; $V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$

$\therefore$ $V_2 = \frac{755}{760}\text{atm} \times \frac{23.9\text{ cm}^3}{288\text{ K}} \times \frac{273\text{ K}}{1\text{ atm}}$

$= 22.5\text{ cm}^3$

22400 cm^3 CO_2 weigh = 44 g

22.5 cm^3 CO_2 weigh $= \frac{44\text{ g}}{22400\text{ cm}^3} \times 22.5\text{ cm}^3$

= 0.044 g

$CO_2 \equiv C$

$12 + (2 \times 16) = 44$ g = 12 g

44 g CO_2 contain C = 12 g

0.044 g CO_2 contain C $= \frac{12\text{ g}}{44\text{ g}} \times 0.044\text{ g} = 0.012$ g

= wt. of C

wt. of hydrogen = wt. of C_xH_y – wt. of C = 0.016 – 0.012 = 0.004 g

$\therefore$ Ratio by wt. of C : H = 0.012 : 0.004

$= \frac{0.012}{0.004} : \frac{0.004}{0.004} =$ **3 : 1** ...(B)

Keeping the wt. of H (= 1) fixed in (A) and (B), the ratio of wts. of C in (A) and (B) is 12 : 3 or 4 : 1 which is a simple multiple ratio. So, these results are in conformity with law of multiple proportion.

Example 21. *On strong heating in presence of H_2, 3.0 g of oxide of a metal produced 0.3776 g water. 3.0 g of the another oxide of the same metal produced 0.6789 g water. Which law of chemical combination is obeyed by the given data ?*

Solution. First oxide. wt. of metal oxide = 3.0 g; wt. of H_2O = 0.3776 g.

$H_2O \equiv 2H$

$(2 \times 1) + 16 = 18$ g $2 \times 1 = 2$g

18 g H_2O contain H = 2.0 g

0.3776 g H_2O contain H $= \frac{2}{18} \times 0.3776\text{ g} = 0.04196$ g

$\therefore$ wt. of oxygen = 0.3776 – 0.04196 = 0.3356 g

wt. of metal = 3 – 0.3356 = 2.6644 g

Ratio by wt. of M : O

$= 2.6644 : 0.3356 = \frac{2.6644}{0.3356} : \frac{0.3356}{0.3356} = 7.94 : 1$ ...(A)

Second oxide. wt. of metal oxide = 3.0 g;

wt. of H_2O = 0.6789 g.

$H_2O \equiv 2H$

$(2 \times 1) + 16 = 18$ g $2 \times 1 = 2$ g

18 g H_2O contain H = 2.0 g

0.6789 g H_2O contain H $= \frac{2.0}{18} \times 0.6789\text{ g} = 0.07543$ g

$\therefore$ wt. of oxygen = 0.6789 – 0.07543 = 0.6035 g

wt. of metal = 3.0 – 0.6035 = 2.3965 g

Ratio by wt. of M : O

$= 2.3965 : 0.6035 = \frac{2.3965}{0.6035} : \frac{0.6035}{0.6035}$

= 3.97 : 1 ...(B)

Keeping the weight of oxygen (= 1) fixed in (A) and (B), the ratio by weight of metal is :

7.94 : 3.97

or $= \frac{7.94}{3.97} : \frac{3.97}{3.97} = 2 : 1$

which is a simple multiple ratio. So, the law of multiple proportion is obeyed.

7.4 LAW OF RECIPROCAL, COMBINING OR EQUIVALENT WEIGHTS

If two elements A and B combine with another element C, they will combine with one another in the same ratio or a multiple or sub-multiple of the ratio in which they combine with constant or fixed weight of C.

Example 22. *Phosphorus (at. mass 31) combines with hydrogen (at.mass = 1) in the mass ratio of 3.1 : 0.3. In water, hydrogen and oxygen (at. mass 16) combine in the mass ratio 0.2 : 1.6.*

(i) From the above data, calculate the mass ratio of phosphorus and oxygen in the oxide of phosphorus.

(ii) Name the law used to calculate this ratio.

(iii) What is the valency of phosphorus in the oxide where the mass ratio of phosphorus to oxygen is 3.1 : 4.

Solution. (*i*) *First compound.* Ratio by wt. of P : H is = $3.1 : 0.3 = \frac{3.1}{0.3} : \frac{0.3}{0.3}$ or $\frac{31}{3} : 1$ ...(1)

(*ii*) *In water* (H_2O). Ratio by wt. of O : H is $= 1.6 : 0.2 = \frac{1.6}{0.2} : \frac{0.2}{0.2}$ or 8 : 1 ...(2)

(*iii*) From (1) and (2), ratio by weight of P : O is = $\frac{31}{3}$: 8 or 31 : 24 **Ans.**

(*iv*) Law used is law of reciprocal proportion

(*v*) Mass ratio of P : O is 3.1 : 4

$\therefore$ No. of P atom = $\frac{\text{wt.}}{\text{at. wt.}} = \frac{3.1}{31} = \frac{1}{10}$

No. of O atom = $\frac{\text{wt.}}{\text{at. wt.}} = \frac{4}{16} = \frac{1}{4}$

Ratio of atoms of P : O is $\frac{1}{10} : \frac{1}{4}$ or 4 : 10 or 2 : 5

$\therefore$ Formula of oxide of phosphorus = P_2O_5

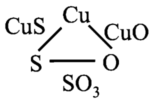
Valency of phosphorus = 5

Example 23. *Copper sulphide contains 66.5% Cu, Copper oxide contains 79.9% Cu and sulphur trioxide contains 40% S. Show that the data illustrates the law of reciprocal proportion.*

Solution. (*a*) In CuS, wt. of Cu = 66.5 g; wt. of S = 100 – 66.5 = 33.5 g

Ratio by wt. of Cu : S is = 66.5 : 33.5 = $\frac{66.5}{66.5} : \frac{33.5}{66.5}$ or 1 : 0.503 ...(1)

(*b*) In CuO, wt. of Cu = 79.9 g



wt. of O = 100 – 79.9 = 20.1 g

Ratio by weight of Cu : O is = 79.9 : 20.1 = $\frac{79.9}{79.9} : \frac{20.1}{79.9}$

or 1: 0.2515 ...(2)

(*c*) In SO_3, wt. of S = 40 g

wt. of O = 100 – 40 = 60 g

Ratio by wt. of S : O in SO_3 = 40 : 60 = 2 : 3 ...(3)

From (1) and (2), keeping the wt. of Cu (= 1) fixed, the ratio by wt. of S : O is

$= 0.503 : 0.2515$

$= \frac{0.503}{0.265} : \frac{0.265}{0.265}$ or 2 : 1 ...(4)

From (3) and (4) we find that the ratios of S and O are related as $\frac{2}{2} : \frac{3}{1}$ or 1 : 3 which is a simple multiple ratio. So, the law of reciprocal proportion is obeyed.

Example 24. *Experiments reveal that (i) 2.50 g of water is formed by the action of 2.22 g of oxygen on hydrogen. (ii) 1.64 g of Mg react with dil. H_2SO_4 to form 1.52 L H_2 at NTP and (iii) 0.92 g Mg on burning forms 1.54 g of MgO. Show that these results obey the law of reciprocal proportion (1 mL of H_2 at NTP weighs 0.00009 g)*

Solution. (*i*) wt. of H_2O = 2.50 g ; wt. of oxygen = 2.22 g.

So, wt of hydrogen = 2.5 – 2.22 = 0.28 g.

So, ratio by wt. of H : O = 0.28 : 2.22 = $\frac{0.28}{0.28} : \frac{2.22}{0.28}$

= 1 : 8 ...(A)

(*ii*) wt. of Mg = 1.64 g ;

volume of H_2 = 1.52 L = 1.52L × $\frac{1000 \text{ mL}}{1 \text{ L}}$

= 1520 mL

wt. of 1 mL H_2 = 0.00009 g

$\therefore$ wt. of 1520 mL H_2 = 1520 × 0.00009 g

= 0.1368 g

$\therefore$ Ratio by wt. of H : Mg : = 0.1368 : 1.64

or $= \frac{0.1368}{0.1368} : \frac{1.64}{0.1368}$

$= 1 : 11.99 \simeq 1 : 12$ ...(B)

(*iii*) wt. of Mg = 0.92 g ; wt. of MgO = 1.54 g.

So, wt. of oxygen = 1.54 – 0.92 = 0.62 g.

So, the ratio by wt. of Mg : O = 0.92 : 0.62 = $\frac{0.92}{0.62} : \frac{0.62}{0.62}$

= 1.5 : 1 or (1.5 × 2) : 1 × 2

or = 3 : 2 ...(C)

Keeping the wt. of H (= 1) fixed , the ratio between Mg and O from (A) and (B) is 12 : 8 *i.e.*, $\frac{12}{4} : \frac{8}{4}$ or 3 : 2. This ratio is same as between Mg and O in (C). So, the law of reciprocal proportion is obeyed.

Example 25. *1.0 g of magnesium combines with 0.3888 g of nitrogen to give Mg_3N_2. In ammonia, there is 82.35% nitrogen. Calculate the volume of hydrogen at 27° C and 750 mm pressure that is expected to be liberated from an acid by 0.6 g of magnesium metal.*

Solution. (*i*) wt. of Mg = 1.0 g ; wt. of nitrogen = 0.3888 g. The ratio by weight of Mg and N is :

Mg : N = 1.0 : 0.3888 = $\frac{1.0}{0.3888} : \frac{0.3888}{0.3888}$

= 2.572 : 1 ...(A)

(*ii*) wt. of nitrogen = 82.35 g

wt. of H in NH_3 = 100 – 82.35 = 17.65 g

Ratio by wt. of H and N is :

H : N = 17.65 : 82.35 = $\frac{17.65}{82.35} : \frac{82.35}{82.35}$

= 0.214 : 1 ...(B)

Keeping the weight of N(= 1) fixed, the ratio by weight of Mg and H is **2.572 : 0.214** ...(C)

(*iii*) wt. of Mg = 0.6 g

From (C), 2.572 g Mg produce H_2 = 0.214 g

0.6 g Mg produce $H_2 = \frac{0.214}{2.572} \times 0.6$ = 0.0499%

But g. mol. wt. of H_2 (= 2 g) produce H_2 at NTP

$= 22400$ mL

$$0.0499 \text{ g } H_2 \text{ produce } H_2 = \frac{22400}{2} \times 0.0499 = 558.9 \text{ mL}$$

$P_1 = 750$ mm, $V_1 = ?$, $T_1 = 27 + 273 = 300$K;

at NTP, $P_2 = 760$ mm, $V_2 = 558.9$ mL, $T_2 = 273$ K;

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

or $$V_1 = \frac{P_2V_2}{T_2} \times \frac{T_1}{P_1} \text{ (Gas law)}$$

$$\therefore \quad V_1 = \frac{760 \text{ mm} \times 558.9 \times 300}{273 \times 750}$$

$= \mathbf{622.4}$ **mL. Ans.**

EXAMPLE 26. *0.252 g of hydrogen combines with 2.0 g of oxygen to form water. 0.108 g of hydrogen combines with 0.5 g of nitrogen to form ammonia. How much oxygen will be needed to combine with 1.5 g of nitrogen to form its oxide.*

SOLUTION. (*i*) $\mathbf{H_2O}$. wt. of hydrogen = 0.252 g ; wt. of oxygen = 2.0 g

$$\therefore \quad \text{Ratio by wt. of H : O} = 0.252 : 2 \text{ or } \frac{0.252}{0.252} : \frac{2}{0.252}$$

$$= 1 : 7.9365 \qquad \text{...(A)}$$

(*ii*) NH_3. wt. of hydrogen = 0.108 g ; wt. of nitrogen = 0.5 g

$\therefore$ Ratio by wt. of H : N = 0.108 : 0.5

or $$\frac{0.108}{0.108} : \frac{0.5}{0.108} = 1 : 4.6296 \text{ g} \qquad \text{...(B)}$$

From (A) and (B), keeping the weight of H (= 1) fixed, the ratio by weight of N : O is 4.6296 : 7.9365

$\therefore$ 4.6296 g nitrogen need oxygen to form oxide = 7.9365 g

$$1.5 \text{ g nitrogen need oxygen to form oxide} = \frac{7.9365}{4.6296} \times 1.5$$

= 2.5714 g Ans.

7.5 GAY LUSSAC'S LAW OF GASEOUS VOLUME

According to this law, whenever gases react together, they do so in volume which bear a simple ratio to one another and also to the volume of products if gaseous. All measurements are done under similar conditions of temperature and pressure.

EXAMPLE 27. *20 mL of ammonia on dissociation gave 30 mL of H_2 and 10 mL of N_2. Which law is illustrated by the data.*

SOLUTION. $2NH_3 (g) \longrightarrow 3H_2 (g) + N_2 (g)$

20 mL 30 mL 10mL

or 2 mL 3 mL 1mL

or 2 vol 3 vol 1 vol.

The reactants and products are gases. The ratio of volume of reactants and products is 2 : 3 : 1 which is simple. So, Gay Lussac's law of gaseous volume is obeyed.

EXAMPLE 28. *Air contains 21% oxygen by volume. Calculate the theoretical volume of air which will be required for burning completely 5 litre of ethylene gas (C_2H_4). All volumes are measured under similar conditions of temperature and pressure.*

SOLUTION. $C_2H_4 (g) + 3O_2 (g) \longrightarrow 2CO_2 (g) + 2H_2O$ (steam)

1 vol 3 vol 2 vol 2 vol

1 litre 3 litre

1 litre C_2H_4 requires O_2 = 3 litre

$$5 \text{ litre } C_2H_4 \text{ require } O_2 = \frac{3}{1} \times 5 = 15 \text{ litre}$$

$$\therefore \quad \text{Volume of air used} = 15 \times \frac{100}{21} = 71.43 \text{ litre}$$

EXAMPLE 29. *2.8 L of Cl_2 was exploded with 3 L of H_2 in a eudiometer tube. What will be the composition of the resulting mixture? All measurements are done under similar conditions of temperature and pressure.*

SOLUTION. Reaction. $Cl_2 + H_2 \longrightarrow 2HCl$

1 vol 1 vol 2 vol

2.8 L 2.8 L 2 × 2.8 L

= 5.6 L

Since 1 vol of Cl_2 reacts with 1 vol of H_2, so only limiting reactant (see chapter, 14) (2.8 L Cl_2) will react completely to form HCl.

$\therefore$ Volume of H_2 left behind = 3 L – 2.8 = 0.2 L

Volume of HCl formed = 5.6 L

Total volume of resulting mixture = 0.2 L + 5.6 L = 5.8 L

Hence 5.8 L mixture will contain 0.2 L H_2 and 5.6 L HCl.

7.6 AIEEE PATTERN EXAMPLES

EXAMPLE 30. *56 cm^3 of oxygen combine with 112 cm^3 of hydrogen to form water : When 56 cm^3 of H_2 is passed over heated cupric oxide, the latter loses 0.04 g of its weight. All measurements are done under similar conditions of temperature and pressure (at. wt., H = 1, O = 16). Which of the following law is obeyed by this data? (A) Gay Lussac's law of gaseous volume (B) Law of constant composition (C) Law of multiple proportion (D) Law of reciprocal proportion.*

SOLUTION. g. mol. wt. of $H_2 = 2 \times 1 = 2$ g ;

g. mol. wt. of $O_2 = 2 \times 16 = 32$ g.

(*i*) 22400 cm^3 H_2 weighs = 2 g

$$112 \text{ cm}^3 \text{ of } H_2 \text{ weighs} = \frac{2}{22400} \times 112 = 0.01 \text{ g}$$

22400 cm^3 of O_2 weighs = 32 g

$$56 \text{ cm}^3 \text{ of } O_2 \text{ weighs} = \frac{32}{22400} \times 56 = 0.08 \text{ g}$$

$\therefore$Ratio by wt. of H_2 and O_2 is : $H_2 : O_2$

0.01 : 0.08

$$\frac{0.01}{0.01} = 1 \quad \frac{0.08}{0.01} = 8 \text{ } i.e.,$$

1 : 8 ratio by wt.

(*ii*) wt. of O_2 = 0.04 g.

$$22400\ cm^3 \text{ of } H_2 \text{ weighs} = 2\ g$$

$$56\ cm^3 \text{ of } H_2 \text{ weighs} = \frac{2}{22400} \times 56 = 0.005\ g$$

$\therefore$ Ratio by wt. of H_2 and O_2 is : $H_2 : O_2$

$$0.005 : 0.04$$

$$\frac{0.005}{0.005} : \frac{0.04}{0.005} \text{ or } \mathbf{1:8}$$

Since the ratio by wt. of H_2 and O_2 in both cases is 1 : 8, the data obeys the law of constant composition. So, the correct result is (*B*).

EXAMPLE 31. *Which one of the following sets of compounds correctly illustrate the law of reciprocal proportions?*

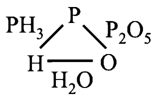
(*a*) P_2O_5, PH_3, H_2O (*b*) $P_2O_5\ PH_3, CO$

(*c*) N_2O_5, NH_3, CO_2 (*d*) N_2O, NH_3, SO_2

(*e*) NO_2, NH_3, SO_3 ***(Kerala PMT, 2011)***

SOLUTION (*a*) At. wt. of P = 31, H = 1, O = 16.

In PH_3, the ratio by wt. of P : H = 31 : 3 or $\frac{31}{3} : \frac{3}{3} = \frac{31}{3} : 1$



In H_2O, the ratio by wt. of O : H = 16 : 2 or $\frac{16}{2} : \frac{2}{2} = 8 : 1$

Keeping the wt. of H (= 1) fixed, the ratio by wt. of P : O = 31/3 : 8 = 31 : 24 ...(1)

In P_2O_5, the ratio by wt. of P : O is (2 × 31) : (5 × 16) or 62 : 80 or 31 : 40 ...(2)

Keeping the wt. of P (= 31) fixed in equations (1) and (2), the ratio of oxygen is 24 : 40 or 3 : 5 which is a simple ratio. So, the correct answer is (*a*). Students are requested to try (*b*), (*c*), (*d*) and (*e*). It will be found that the given data does not relate to the law of reciprocal proportion.

EXAMPLE 32. *Hydrated zinc sulphate contains 22.65% Zn and 43.9% H_2O. If the law of definite proportion is true, the weight of zinc used to produce 7.2 g of crystal would be :*

(*a*) *3.2 g* (*b*) *1.63 g*

(*c*) *0.815 g* (*d*) *None of these*

SOLUTION. % age of Zn = 22.65 ; wt. of crystal = 7.2 g

100 g crystal produce Zn = 22.65 g

$$\therefore \quad 7.2 \text{ g crystal produce Zn} = \frac{22.65}{100} \times 7.2 = 1.63 \text{ g.}$$

So the correct answer is (*b*).

EXAMPLE 33. *An iodine compound on analysis was found to contain iodine and oxygen in the ratio of 127 g and 40 g by weight. If atomic weight of iodine and oxygen are 127 and 16 respectively, the formula of the compound will be :*

(*a*) I_2O_3 (*b*) I_2O_4

(*c*) I_2O_5 (*d*) I_2O

SOLUTION. We know atomic ratio = $\frac{\text{wt. of element}}{\text{At. wt. of element}}$

$$\therefore \quad \text{No. of atoms of I} = \frac{127}{127} = 1\ ;$$

$$\text{No. of atoms of O} = \frac{40}{16} = 2.5$$

$\therefore$ Ratio by wt. of I and O is : I : O

1 : 2.5

or 2 × 1 : 2.5 × 2

= 2 = 5

$\therefore$ Formula of the compound = I_2O_5

So, the correct answer is (*c*).

EXAMPLE 34. *In an experiment, 1.0 g of lime stone ($CaCO_3$) gave 224 cm^3 of CO_2 at NTP and 0.56 g of calcium oxide. These data illustrate the law of :*

(*a*) *Multiple proportion* (*b*) *Reciprocal proportion*

(*c*) *Gaseous volume* (*d*) *Conservation of mass.*

SOLUTION. $$\underset{}{CaCO_3} \longrightarrow \underset{0.56\ g}{CaO} + \underset{22400\ cm^3}{CO_2 \text{ gas}}$$

wt. of $CaCO_3$ = 1.0 g ...(1)

wt. of CaO = 0.56 g

22400 cm^3 CO_2 weighs = g. mol. wt. of CO_2

= 12 + (2 × 16) = 44 g

$$\therefore \quad 224\ cm^3\ CO_2 \text{ weighs} = \frac{44\ g}{22400} \times 224 = 0.44\ g.$$

$\therefore$ wt. of products = 0.56 + 0.44 = 1.0 g

wt. of reactant (= $CaCO_3$) = 1.0 g

Since the weight of reactants is equal to that of products, the law of conservation of mass is obeyed. So, the correct answer is (*d*).

EXAMPLE 35. *A sample of $MgCO_3$ has 28.57 % Mg, 14.29% C and 57.14% oxygen. If the law of constant proportion is true, then the weight of carbon in 2.1 g of $MgCO_3$ from another source will be:*

(*a*) *0.1 g* (*b*) *0.2 g*

(*c*) *0.3 g* (*d*) *0.4 g*

SOLUTION. % age of carbon in $MgCO_3$ = 14.29

Thus : 100 g $MgCO_3$ contain carbon = 14.29 g

$$2.1 \text{ g } MgCO_3 \text{ contain carbon} = \frac{14.29}{100} \times 2.1$$

$$= 0.30\ g.$$

So, the correct answer is (*c*).

EXAMPLE 36. *Two isotopes of ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$ combine with sodium metal to form two samples of sodium chloride. These compound formation obey the law of :*

(*a*) *equivalents* (*b*) *multiple proportion*

(*c*) *constant composition* (*d*) *none of these*

SOLUTION. (*i*) $$\underset{23\ g}{Na} + \underset{35\ g}{{}^{35}Cl} \longrightarrow Na^{35}Cl$$

Ratio by weight of Na and ${}^{35}Cl$ is :

Na : Cl

$$23 : 35; \quad \frac{23}{23} : \frac{35}{23} \quad i.e., \mathbf{1:1.5}$$

(*ii*) $Na + {}^{37}Cl \longrightarrow Na^{37}Cl$

23 g 37 g

Ratio by wt. of Na and Cl is :

$$Na : Cl$$

$$23 : 37 \quad \frac{23}{23} : \frac{37}{23} \quad \textit{i.e.,}\ \mathbf{1 : 1.6}$$

Keeping the weight of Na (= 1) fixed, the ratio between weights of Cl is 1.5 : 1.6 which is neither same nor simple multiple of each other. So, the data does not obey any law. So, the correct answer is (*d*).

Example 37. *8.5 g of silver nitrate react with KCl solution to give 7.15 g silver chloride and 5.05 g KNO_3. If the law of conservation of mass is obeyed, the weight of KCl used will be :*

(a) 1.8 g *(b) 3.7 g*

(c) 2.9 g *(d) 10.6 g*

Solution. Reaction: $AgNO_3 + KCl \longrightarrow AgCl + KNO_3$

$$\underset{8.5\text{ g}}{AgNO_3} + \underset{x\text{ g}}{KCl} \longrightarrow \underset{7.15\text{ g}}{AgCl} + \underset{5.05\text{ g}}{KNO_3}$$

Reactants Products

Since the law of conservation of mass is obeyed ;

The wt. of reactants = wt. of products

∴ $8.5 + x = 7.15 + 5.05$; $x = 7.15 + 5.05 - 8.5 = 3.7$ g.

So, the correct answer is (*b*).

Example 38. *Out of the two oxides formed by a metal, 0.72 g of the lower oxide forms 0.8 g of higher oxide. If the higher oxide contains 80% metal, the data is true for the law of :*

(a) multiple proportion *(b) combining weights*

(c) gaseous volume *(d) constant composition.*

Solution. (*i*) In higher oxide ; wt. of metal = 80 g; wt. of oxygen = 100 – 80 = 20 g

∴ Ratio by wt. of metal and oxygen is :

Metal : Oxygen

$$80 : 20 \text{ or } \frac{80}{80} : \frac{20}{80} : \textit{i.e.,}\ \mathbf{1 : 0.25}$$

(*ii*) Lower oxide.

0.8 g of higher oxide is obtained from lower oxide = 0.72 g

∴ 100 g of higher oxide is obtained from lower oxide

$$= \frac{0.72}{0.8} \times 100 = 90 \text{ g.}$$

Hence, 90 g of higher oxide contains as much metal as 100 g of lower oxide.

So, wt. of metal in lower oxide = 80 g

wt. of oxygen in lower oxide = 90 – 80 = 10 g

Ratio by weight of metal and oxygen in lower oxide is:

Metal : Oxygen

$$80 : 10 \text{ or } \frac{80}{80} : \frac{10}{80} \quad \textit{i.e.,}\ \mathbf{1 : 0.125}$$

Keeping the wt. of metal (= 1) fixed in (*i*) and (*ii*), the ratio by weight of oxygens will be

$$0.25 : 0.125$$

$$\frac{0.25}{0.125} : \frac{0.125}{0.125} \quad \textit{i.e.,}\ \mathbf{2 : 1}$$

which is simple ratio. So, the law of multiple proportion is obeyed. Hence the correct result is (*a*).

Example 39. (*i*) *6.5 g zinc form 8.1 g zinc oxide.*

(ii) 1.3 g zinc produce 448 cm^3 H_2 at NTP

(iii) 2.5 g water is formed when 2.22 g of oxygen combines with hydrogen (wt. of 1 cm^3 H_2 at NTP = 0.00009 g). The above data illustrate the law of :

(a) conservation of mass *(b) multiple proportion*

(c) constant composition *(d) reciprocal proportion*

Solution. (*i*) Wt. of Zn = 6.5 g ;

wt. of oxygen = 8.1 – 6.5 = 1.6 g.

∴ Ratio by wt. of Zn and O is :

$$Zn : O$$

$$6.5 : 1.6$$

$$\frac{6.5}{6.5} : \frac{1.6}{6.5} \quad \textit{i.e.,}\ \mathbf{1 : 0.246.}$$

(*ii*) wt. of Zn = 1.3 g

wt. of 448 cm^3 H_2 = 448 × 0.00009 g

∴ Ratio by wt. of Zn and H_2 is :

$$Zn : H_2$$

$$1.3 : 448 \times 0.00009 \text{ g}$$

$$\frac{1.3}{1.3} : \frac{448 \times 0.00009}{1.3} \quad \textit{i.e.,}\ \mathbf{1 : 0.031}$$

Keeping the wt. of Zn (= 1) fixed in (*i*) and (*ii*) above, the ratio by wt. of H_2 and O_2 is :

$$H_2 : O_2$$

$$0.031 : 0.246$$

$$\text{or} \quad \frac{0.031}{0.031} : \frac{0.246}{0.031} \quad \textit{i.e.,}\ \mathbf{1 : 7.9}$$

(*iii*) wt. of H_2O = 2.5 g ; wt. of O_2 = 2.22 g

∴ wt. of H_2 = 2.5 – 2.22 = 0.28 g

Hence ratio by wt. of H_2 and O_2 is :

$$H_2 : O_2$$

$$0.28 : 2.22 \text{ or } \frac{0.28}{0.28} : \frac{2.22}{0.28} \quad \textit{i.e.,}\ \mathbf{1 : 7.9}$$

Since the ratio of H_2 and O_2 is same, the data obeys the law of reciprocal proportion. So, the correct result is (*d*).

Example 40. *Out of the two unknown hydrocarbons, 0.052 g of one gave 95.8 cm^3 of CO_2. 0.016 g of the other produced 23.9 cm^3 of CO_2. If both experiments were done at 15° C and 755 mm pressure, the data illustrates the law of :*

(a) combining proportion *(b) definite proportion*

(c) multiple proportion *(d) gaseous volume*

Solution. (*i*) **First hydrocarbon:** P_1 = 755 mm, V_1 = 95.8 cm^3, T_1 = 15 + 273 = 288 K; at NTP, P_2 = 760 mm, V_2 = ? T_2 = 273 K. Using gas equation

$$\text{we have} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} ;$$

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} = \frac{755\times 95.8\times 273}{288\times 760}$$

or $V_2 = 90.2\ \text{cm}^3$

$22400\ \text{cm}^3\ CO_2$ weighs = g. mol. wt. of CO_2
= 12 + (2 × 16) = 44 g

$$\therefore\ 90.2\ \text{cm}^3\ CO_2 \text{ weighs} = \frac{44}{22400}\times 90.2 = 0.177\ \text{g}$$

$$\underset{12+(2\times 16)=44\ \text{g}}{CO_2} \equiv \underset{12\ \text{g}}{C}$$

44 g CO_2 contain C = 12 g

$$0.177\ \text{g}\ CO_2 \text{ contain C} = \frac{12}{44}\times 0.177 = 0.048\ \text{g}$$

∴ wt. of hydrogen = 0.052 – 0.048 = 0.004 g

Hence ratio by wt. of C and H is :

$$\begin{array}{c} C : H \\ 0.048 : 0.004 \\ \dfrac{0.048}{0.004} : \dfrac{0.004}{0.004}\ ;\ i.e.,\ \mathbf{12 : 1} \end{array}$$

(*ii*) **Second hydrocarbon.** $P_1 = 755$ mm, $V_1 = 23.9\ \text{cm}^3$, $T_1 = 288$ K ; at NTP., $T_2 = 273$ K, $P_2 = 760$ mm, $V_2 = ?$ Using gas equation,

we have ; $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} = \frac{755\times 23.9\times 273}{288\times 760}$$

or $V_2 = 22.5\ \text{cm}^3$

$22400\ \text{cm}^3\ CO_2$ weighs = g. mol. wt. of CO_2
= 44 g

$$22.5\ \text{cm}^3\ CO_2 \text{ weighs} = \frac{44}{22400}\times 22.5 = 0.044\ \text{g}$$

$$\underset{\substack{12+(2\times 16)\\ =44\text{g}}}{CO_2} \equiv \underset{12\ \text{g}}{C}$$

44 g CO_2 contain C = 12 g

$$0.044\ \text{g}\ CO_2 \text{ contain C} = \frac{12}{44}\times 0.044 = 0.012\ \text{g}$$

∴ wt. of hydrogen = 0.016 – 0.012 = 0.004 g

∴ Ratio by wt. of C and H is :

$$\begin{array}{c} C : H \\ 0.012 : 0.004 \\ \dfrac{0.012}{0.004} : \dfrac{0.004}{0.004} \\ \text{or}\quad \mathbf{3 : 1} \end{array}$$

From (*i*) and (*ii*) keeping the weight of H (= 1) fixed, the ratio by weights of C in both hydrocarbons is 12 : 3 or 4 : 1 which is simple multiple ratio. So, the correct answer is (*c*).

EXAMPLE 41. *3.0 g of ethane (C_2H_6) gave 5.4 g H_2O and 8.8 g CO_2 on complete combustion in oxygen. The data is true for the law of :*

(a) constant composition *(b) multiple proportion*
(c) reciprocal proportion *(d) conservation of mass*

SOLUTION. Reaction $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$ ...(1)

$$\underbrace{3.0\ \text{g}\quad x}_{\text{Reactants}}\qquad \underbrace{8.8\ \text{g}\quad 5.4\ \text{g}}_{\text{Products}}$$

(*i*)
$$\underset{\substack{12+(2\times 16)\\ =44\ \text{g}}}{CO_2} \equiv \underset{\substack{2\times 16\\ =32\ \text{g}}}{2O}$$

44 g CO_2 contain oxygen = 32 g

$$8.8\ \text{g}\ CO_2 \text{ contain oxygen} = \frac{32}{44}\times 8.8 = 6.4\ \text{g}$$

(*ii*)
$$\underset{(2\times 1)+16=18\ \text{g}}{H_2O} \equiv \underset{16\ \text{g}}{O}$$

18 g H_2O contain oxygen = 16 g

$$5.4\ \text{g}\ H_2O \text{ contain oxygen} = \frac{16}{18}\times 5.4 = 4.8\ \text{g}$$

∴ Total weight of oxygen used (= x)
= 6.4 + 4.8 = 11.2 g

Substituting the value of x in (1), we get
3.0 + 11.2 = 8.8 + 5.4
14.2 g = 14.2 g

Since weight of reactants = weight of products, the law of conservation of mass is obeyed. So, the correct result is (*d*).

EXAMPLE 42. *Some results of experiments are given below.*

(a) In phosphorous chloride, P = 22.57%, Cl = 77.43%
(b) In phosphine, P = 91.18 %, H = 8.82%
(c) In hydrogen chloride, H = 2.77%, Cl = 97.23%

The law of combination that obeys the given results is :

(a) conservation of mass
(b) reciprocal proportion
(c) definite proportion
(d) Gay Lussac's law of gaseous volume

SOLUTION. (*a*) In phosphorous chloride, 22.57 g of phosphorus combines with chlorine = 77.43 g

(*b*) In phosphine, 91.18 g of phosphorus combines with hydrogen = 8.82 g

∴ 22.57 g of phosphorus combines with hydrogen

$$= \frac{8.82}{91.18}\times 22.57 = 2.18\ \text{g}$$

Hence, the ratio between the weights of Cl and H which combine with a fixed weight (22.57 g) of phosphorus is 77.43 : 2.18 or 35.5 : 1

(*c*) In HCl, the ratio between the weights of Cl and H is 97.23 : 2.77 or 35.5 : 1.

Since the two ratios between the weights of Cl and H are the same, the example illustrates the law of **reciprocal proportions**.

So, the correct answer is (*b*).

EXAMPLE 43. *'x' g of sulphur and 'y' g of oxygen are allowed to react in a closed vessel so that no solid sulphur is left behind. The ratio of weights of x and y is :*

(a) 2 : 1 *(b)* 1 : 2

(c) 1 : 1 *(d)* 4 : 1

SOLUTION.

$$\underset{32\text{ g}}{S} + \underset{\substack{2\times 16\\=32\text{ g}}}{O_2} \longrightarrow SO_2$$

32 g of S react with oxygen = 32 g

$$\therefore\ x \text{ g of S react with oxygen } = \frac{32}{32}\times x$$

$$= x \text{ g oxygen} \quad ...(1)$$

$$\text{But wt. of oxygen} = y \text{ g (given)} \quad ...(2)$$

∴ From relations (1) and (2), we get

$$x \text{ g} = y \text{ g}$$

$$\text{or} \quad \frac{x}{y} = \frac{1}{1}.$$

Thus ratio of weights of x and y = 1 : 1

So, the correct answer is (*c*).

EXAMPLE 44. *x g of an element A reacts with y g of an element B. Also, y g of element B combines with 2 z g of C. If one gram equivalent of B weighs y g, then the mass ratio in which A and C combine is :*

(a) $x : y$ *(b)* $y : z$

(c) $x : 2z$ *(d)* $y : 2z$

SOLUTION. wt. of $A = x$ g ;

wt. of $B = y$

∴ Ratio by mass of $A : B$ is : $x : y$

$$\frac{x}{y} : \frac{y}{y} \text{ or } \frac{x}{y} : 1 \quad ...(1)$$

Ratio by mass of $B : C$ is : $y : 2z$

$$\frac{y}{y} : \frac{2z}{y} \text{ or } 1 : \frac{2z}{y} \quad ...(2)$$

Keeping the mass of B (= 1) fixed, the ratio by mass of $A : C$ is :

$\frac{x}{y} : \frac{2z}{y}$ or $x : 2z$. So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. When a solution containing 1.5 g of $CuSO_4$ was treated with 0.65 g of zinc metal, 0.635 of copper was precipitated. How much of zinc sulphate will be obtained by evaporating the remaining solution. (**Ans.** 1.115 g)

2. ICl contains 77.8% iodine. KI contains 23.6% K and KCl contains 52% of K. These results obey the law of

(*a*) constant composition

(*b*) reciprocal proportion

(*c*) multiple proportion

(*d*) conservation of mass

3. Illustrate the law of definite proportion from the following data.

(*i*) 0.6 of carbon produces 1120 mL of CO_2.

(*ii*) CO_2 gas obtained from the decomposition of a carbonate contains 27.3% C.

4. When 5 mL of O_2 are treated with 10 mL of H_2, water is formed. When 100 mL of H_2 at N.T.P are passed over heated cupric oxide, the cupric oxide loses 0.072 g of its weight. Show that the results are in agreement with the law of constant composition.

(**Ans.** In both experiments, the ratio by wt. of $H_2 : O_2$ to form H_2O is 1 : 8. So, the law of constant composition is obeyed).

5. Water and hydrogen peroxide contain 11.2% and 5.93% of hydrogen respectively. Show that the data illustrates the law of multiple proportion.

6. Elements *A* and *B* combine to form three different compounds.

(*i*) 0.2 g of A + 0.4 g of B $\longrightarrow$ 0.6 g of compound, X

(*ii*) 6g of A + 24 g of B $\longrightarrow$ 18 g of compound, Y

(*iii*) 20 g of A + 120 g of B $\longrightarrow$ 140 g of compound, Z

Show that the data illustrates the law of multiple proportion.

(**Ans.** Ratio among wts. of B is 1:2:3)

7. Air contains 20.9% oxygen by volume. Calculate the theoretical volume of air which will be required for burning completely 4 litre of methane gas (CH_4). All volumes are measured under similar conditions of temperature and pressure. (**Ans.** 38.27 L)

8. 2.1 g of $NaHCO_3$ when added to 1.5 g of CH_3COOH gave 2.05 g of residue. Find the weight of CO_2 produced. (**Ans.** 1.55 g)

9. Illustrate the law of reciprocal proportion from the following data.

(*i*) In PCl_3, P = 22.57%, Cl = 77.43%

(*ii*) In PH_3, P = 91.18%, H = 8.82%

(*iii*) In HCl, H = 2.77%, Cl = 97.23%.

(**Ans.** Ratio H:Cl = 1:35 in both cases.)

10. Ammonia contains 82.35% nitrogen and 17.65% hydrogen. Water contains 88.9% of oxygen and 11.1% of hydrogen. Nitrogen trioxide contains 63.15% oxygen and 36.85% of nitrogen. Show that the data illustrates the law of chemical combination.

(**Ans.** Ratio of N : O is 1:1.71 in both cases. So, law of reciprocal proportion is obeyed.)

8

CHAPTER

Gaseous State–States of Matter

8.1 SOME RELATED UNITS

I. Pressure, P : *One atmosphere* is the pressure exerted by *exactly 76 cm* (or 760 mm) of mercury at 0ºC (standard gravity, 9.81 ms^{-2}; density, 13.5951 g cm^{-3})

1 atm = 760 torr; 1 torr = 1 mm;

1 atm = 1.01321 bar

$\simeq$ 1 bar (bar is the higher unit of pressure)

C.G.S. unit = dyne cm^{-2}

S.I. unit = Nm^{-2} *i.e.*, Newton $(meter)^{-2}$ = Pascal (Pa).

Pascal is the pressure exerted when a force of one Newton (N) acts on 1 m^2 area. **Newton** is the force that gives mass of 1 kg, an acceleration of 1 ms^{-2}.

1 N = 1 kg ms^{-2}

1 atm = 1.01321×10^6 dyne cm^{-2}

= 1.01321×10^5 N m^{-2} = 101.321×10^3 Pa

= 101.321 kPa $\simeq$ 100 kPa

= 101321 millibar = 14.7 lb.

[$\because$ 1 N m^{-2} = 1 Pa = 10^5 dyne cm^{-2}]

1 bar = 10^5 Pa = 10^5 N m^{-2} = 10^{10} dyne cm^{-2}

1 Pa = 1 kg m^{-} s^{-2}.

II. Volume, V : 1 litre, $L = 1\,dm^3 = 10^{-3}\,m^3 = 10^3\,cm^3$ = 1000 mL or 10^3 mL

III. Temperature, T : (*i*) 273 + tºC = TK

(*ii*) $\dfrac{C}{100} = \dfrac{F-32}{9} = \dfrac{K-273}{100} = \dfrac{R}{4}$.

where C, F, K and R represent celsius, fahrenheit, kelvin and reaumur scales respectively

0ºC = 0 + 273 = **273 K**

IV. STP (standard temperature and pressure) or **NTP** (normal temperature and pressure) are 273 K (or 0ºC) and one atmospheric pressure respectively.

V. Absolute zero = – 273°C = – 273 + 273 = 0 K

VI. Proper units to solve numericals

		C.G.S.	*MKS (S.I)*
Pressure, P	atmosphere, atm.	dyne cm^{-2}	Nm^{-2}
Volume, V	Litre, L	mL or cc or cm^3	m^3
Temperature, T	Kelvin	Kelvin	Kelvin
Mol. wt., M	g mol^{-}	g mol^{-}	kg mol^{-}
Weight, w	g	g	kg
Gas constant, R	0.0821 L atm K^{-} mol^{-}	8.314×10^7 erg K^{-} mol^{-}	8.314 J K^{-} mol^{-}

Other units of R; R = 2 cal K^{-} mol^{-} = 0.002 k cal K^{-} mol^{-} = 5.189×10^{19} eV K^{-} mol^{-} = 0.083 bar L K^{-} mol^{-} = 0.083 bar dm^3 K^{-} mol^{-} = 0.083×10^{-3} m^3 K^{-} mol^{-} = 0.0821×10^{-3} m^3 atm K^{-} mol^{-} = 0.0821 L atm K^{-} mol^{-} = 8.314 J K^{-} mol^{-} = 8.314 Pa m^3 K^{-} mol^{-} = 8.314 Nm K^{-} mol^{-} = 8.314×10^7 erg K^{-} mol^{-}.

VII. At NTP or STP, P = 1 atm = 760 mm; T = 273 K

1 mole of any gas occupies volume at NTP = 22.4 L

Numericals on various gas laws are given below:

8.2 BOYLE'S LAW

At constant temperature, the volume of a fixed mass of a gas is inversely proportional to its pressure.

Mathematically : $V \propto \dfrac{I}{P}$ (T, n are constant) **or** PV **= k,** a constant.

For any two gases : $P_1V_1 = P_2V_2$

EXAMPLE 1. *At constant temperature, 250 mL of* N_2 *at 720 mm and 380 cc of* O_2 *at 650 mm are put together in a 1L flask. Find pressure of mixture.*

SOLUTION. For N_2 : P_1 = 720 mm; $P_2 = pN_2$

V_1 = 250 mL; V_2 = 1000 mL (= 1 L)

$P_1V_1 = P_2V_2$

$$\therefore \quad pN_2 = \frac{P_1V_1}{V_2} = \frac{720 \times 250}{1000} = 180 \text{ mm}$$

For O_2 $\quad P_1 = 650$ mm ; $P_2 = pO_2$

$V_1 = 380$ mL; $V_2 = 1000$ mL (= 1 L)

$$P_1V_1 = P_2V_2 \text{ or } pO_2 = \frac{P_1V_1}{V_2} = \frac{650 \times 380}{1000} = 247 \text{ mm}$$

∴ Total pressure = 180 + 247 = 427 mm **Ans.**

EXAMPLE 2. *A desiccator of internal volume one litre and containing nitrogen at one atmospheric pressure is partially evacuated to a final pressure of 7.6 mm of Hg while the temperature remains constant. What is the volume of gas at this stage.*

(IIT, 1976)

SOLUTION. Internal volume of desiccator is constant *i.e.,* 1L. So, the volume of N_2 gas in desiccator evacuated to a pressure of 7.6 mm of Hg will also be 1 L.

EXAMPLE 3. *A sample of air has volume of 400 dm³ and a pressure of 1.2 bar. What additional pressure is needed to reduce the volume to 150 dm³ at 27°C?*

SOLUTION. Initial pressure, $P_1 = 1.2$ bar; initial volume, $V_1 = 400$ dm³.

Final pressure, P_2 = ?;

Volume = 150 dm³. At constant temperature, 27°C:

$$P_1V_1 = P_2V_2 \text{ (Boyle's law)}$$

$$1.2 \text{ bar} \times 400 \text{ dm}^3 = P_2 \times 150 \text{ dm}^3;$$

$$P_2 = \frac{1.2 \text{ bar} \times 400 \text{ dm}^3}{150 \text{ dm}^3}$$

or $\quad P_2 = 3.2$ bar

∴ Additional pressure required = 3.2 bar – 1.2 = 2 bar **Ans.**

EXAMPLE 4. *A weather balloon having 150 L volume when filled with H_2 gas had a pressure of 1.1 atmosphere. What volume the balloon would have when the balloon rises to 1000 m where the atmospheric pressure is 0.9 atm. Assume that the temperature is constant.*

SOLUTION. Since temperature is constant, it is Boyle's law.

$P_1 = 1.1$ atm, $V_1 = 150$ L; $P_2 = 0.9$ atm, V_2 = ?

$$P_1V_1 = P_2V_2$$

$$1.1 \text{ atm} \times 150 \text{ L} = 0.9 \text{ atm} \times V_2;$$

$$V_2 = \frac{1.1 \text{ atm} \times 150 \text{ L}}{0.9 \text{ atm}} = \mathbf{183.33 \text{ L}} \quad \textbf{Ans.}$$

EXAMPLE 5. *A balloon filled with an ideal gas is taken from the surface of the sea deep to a depth of 100 m. What will be its volume in terms of its original volume ?*

SOLUTION. $\quad P_1$ = Pressure at the surface = *hdg*

$$= 76 \text{ cm} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ cm s}^{-2}$$

$$= 1013961.6 \text{ g cm}^{-1}\text{s}^{-2} \times \frac{1 \text{ dyne}}{\text{g cm s}^{-2}}$$

$$= 1013961.6 \text{ dyne cm}^{-2}.$$

P_2 = Pressure at the required depth

$$= \left[\begin{array}{l} hdg = 100 \text{ m} \times \dfrac{100 \text{ cm}}{1 \text{ m}} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ cm s}^{-2} \\ = 9810000 \text{ g cm}^{-1}\text{s}^{-2} \times \dfrac{1 \text{ dyne}}{\text{g cm s}^{-2}} = 9810000 \text{ dyne cm}^{-2} \end{array}\right]$$

+ P_1 (= 1013961.6 dyne cm^{-2}) = 10823961.6 dyne cm^{-2}.

Applying Boyle's law, we have

$$P_1V_1 = P_2V_2 \quad \text{or} \quad V_2 = \frac{P_1V_1}{P_2}$$

$$\therefore \quad V_2 = \frac{1013961.6 \text{ dyne cm}^{-2} \times V_1}{10823961.6 \text{ dyne cm}^{-2}} = 0.093\, V_1$$

$$\text{or} \quad \frac{V_2}{V_1} = 0.093 \text{ or } V_2 = 0.093\, V_1$$

= 0.093 × 100

= 9.3% of its original volume at the surface.

8.3 CHARLE'S LAW

At constant pressure, the volume of a fixed mass of a gas is directly proportional to the kelvin temperature or absolute temperature.

Mathematically. V ∝ T (P, n are constant) or $\dfrac{V}{T} = k$ *i.e.,* constant.

(*i*) For any two gases : $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

(*ii*) $V \propto T$. But $V \propto \dfrac{1}{\text{density, D}}$. So, $T \propto \dfrac{1}{D}$ or

DT = constant. Also, $D'T'$ = constant.

Hence $\quad DT = D'T'$

EXAMPLE 6. *A student forgot to add a liquid in a round bottomed flask at 25°C. He placed the flask on the flame and recorded its temperature with a pyrometer which was found to be 327°C. Calculate the fraction of air that had gone out of the flask.*

SOLUTION. Since the mouth of flask was open, its pressure is equal to atmospheric pressure which is constant. So, the Charle's law is obeyed.

$T_1 = 25 + 273 = 298$ K, Volume = V_1 ;

$T_2 = 327 + 273 = 600$ K and Volume = V_2.

$$\therefore \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}; \quad \frac{V_1}{V_2} = \frac{T_1}{T_2} = \frac{298 \text{ K}}{600 \text{ K}} = \frac{0.497}{1}$$

$$\therefore \text{Air left in the vessel} = \frac{0.497}{1}$$

Hence volume of air gone out = 1 – 0.497 = 0.503

= 0.503 × 100 = **50.3%** **Ans.**

Type. $\quad D_1T_1 = D_2T_2$

Example 7. *A gas was found to have density 20 at 27° C and 1.0 bar pressure. If pressure remains constant, calculate the temperature at which its density would be 16.*

Solution. Density, $D_1 = 20$;

$$T_1 = 27 + 273 = 300 \text{ K}; T_2 = ?,$$

density, $D_2 = 16$. Since pressure is constant, it is Charle's law.

We know that : $V \propto T$. But $T \propto \frac{1}{D}$. So, $T \propto \frac{1}{D}$ or DT = constant.

Hence $D_1T_1 = D_2T_2$; $T_2 = \frac{D_1T_1}{D_2} = \frac{20 \times 300 \text{ K}}{16} = 375 \text{ K}$

or $\qquad T_2 = 375 - 273 = \mathbf{102°C}$ **Ans.**

Example 8. *A patient is usually given an anesthetic gas at 20°C. But his body temperature is 37.0°C. What would this temperature change do, to 1500 cm^3 of gas if mass and pressure remain unchanged ?*

Solution. Since pressure and mass are constant, the gas obeys Charle's law.

$$V_1 = 1500 \text{ cm}^3, \; T_1 = 20 + 273 = 293 \text{ K},$$
$$T_2 = 37 + 273 = 310 \text{ K}.$$

Thus : $\frac{V_1}{T_1} = \frac{V_2}{T_2}$; $V_2 = \frac{V_1T_2}{T_1} = \frac{1500 \text{ cm}^3 \times 310 \text{ K}}{293 \text{ K}}$

$= 1587 \text{ cm}^3$

$\therefore \qquad \mathbf{V_2 = 1587 \text{ cm}^3}$ **Ans.**

8.4 GAY-LUSSAC'S LAW

At constant volume, the pressure of a fixed mass of a gas is directly proportional to the kelvin temperature or absolute temperature.

Mathematically : $P \propto T$ or $P = KT$ or $\frac{P}{T}$ = a constant.

For any two gases : $\boxed{\frac{P_1}{T_1} = \frac{P_2}{T_2}}$

Example 9. *An iron cylinder contains helium at a pressure of 250 kPa at 300 K. The cylinder can withstand a pressure of 1 × 10^6 Pa. The room in which the cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. (m. pt. of cylinder = 1800 K).* **(Roorkee, 1995)**

Solution. The cylinder will blow up before m.pt. of cylinder (1800 K) if the pressure at 1800 K is greater than 1 × 10^6 Pa. Since the volume of cylinder is constant, the helium gas obeys Gay-Lussac's law.

$$P_1 = 250 \text{ k Pa} = 250 \times 1000 \text{ Pa};$$
$$T_1 = 300 \text{ K}; \; P_2 = ?;$$

T_2 = 1800 K. We know that :

$$\frac{P_1}{T_1} = \frac{P_2}{T_2};$$

$$P_2 = \frac{P_1T_2}{T_1} = \frac{250 \times 1000 \text{ Pa} \times 1800 \text{ K}}{300 \text{ K}}$$

or $\qquad P_2 = 1.5 \times 10^6$ Pa.

Since P_2 (= 1.5 × 10^6 Pa) is greater than 1.0 × 10^6 Pa, the cylinder will blow up before it melts.

Example 10. *A gas cylinder containing cooling gas can withstand a pressure of 14.9 atm. The pressure gauze of the cylinder indicates 12 atm at 27°C. Due to sudden fire in the building its temperature starts rising. At what temperature the cylinder will burst?* **(IIT, 1975)**

Solution. Since volume of cylinder is constant, the gas obeys Gay-Lussac's law.

$$P_1 = 12 \text{ atm}; \; T_1 = 27 + 273 = 300 \text{ K};$$
$$P_2 = 14.9 \text{ atm}; \; T_2 = ?$$
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}; \; T_2 = \frac{P_2T_1}{P_1}$$
$$= \frac{14.9 \text{ atm} \times 300 \text{ K}}{12 \text{ atm}} = 372.5 \text{ K}$$

Example 11. *The internal pressure of a gas maintained in a steel tank is 18 bar. It is desired to increase the pressure by 12%. Calculate the temperature at which the tank must be heated if its initial temperature is 25°C. Write the result in three significant figures.*

Solution. Since the volume of tank is constant, the gas obeys Gay-Lussac's law.

$$P_1 = 18 \text{ bar}, T_1 = 25 + 273 = 298 \text{ K};$$
$$P_2 = \left(18 \times \frac{12}{100}\right) + 18 = 2.16 + 18 = 20.16 \text{ bar};$$
$$T_2 = ?$$
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}; T_2 = \frac{P_2T_1}{P_1} = \frac{20.16 \text{ bar} \times 298 \text{ K}}{18 \text{ bar}} = 333.8 \text{K} \; \textbf{Ans.}$$

or $\quad T_2 = 333.8 - 273 = \mathbf{60.8°C} \qquad [\because t°\text{C} + 273 = T\text{K}]$

which has three significant figures.

8.5 COMBINED GAS LAW

For a fixed mass of a gas, the volume (V) is directly proportional to kelvin temperature (T) and inversely proportional to pressure (P).

Mathematically : $V \propto T/P$ or $V = \frac{kT}{P}$ where k is proportionality constant.

(*a*) For any two gases : $\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$

(*b*) $P \propto \frac{I}{V} \propto D$ or $\mathbf{D \propto P}$ (Boyle's law; $T \propto V \propto \frac{I}{D}$ or $\mathbf{D \propto \frac{I}{T}}$.

Hence D $\propto \frac{P}{T}$ or $\frac{DT}{P}$ = constant. Hence :

$$\boxed{\frac{D_1T_1}{P_1} = \frac{D_2T_2}{P_2}}$$

Example 12. *Calculate the volume of a gas at 37°C and 720 mm pressure if it occupies 22.4 L volume at STP.*

Solution. Given conditions :

$$V_1 = ?, T_1 = 37 + 273 = 310\text{ K},$$

$$P_1 = 720\text{ mm} \times \frac{1\text{ atm}}{760\text{ mm}} = \frac{72}{76}\text{ atm};$$

At STP : $P_2 = 1\text{ atm},\ V_2 = 22.4\text{ L}, T_2 = 273\text{ K}.$

We know that :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ V_1 = \frac{P_2V_2T_1}{P_1T_2}$$

or

$$V_1 = \frac{1\text{ atm} \times 22.4\text{ L} \times 310\text{ K} \times 76}{72\text{ atm} \times 273\text{ K}}$$

$$= \mathbf{26.85\ L} \qquad \textbf{Ans.}$$

Example 13. *112 cm^3 of a gas at NTP was taken to 27°C and 730 mm pressure. Calculate the change in volume of the gas.*

Solution. At NTP :

$$P_1 = 760\text{ mm},\ V_1 = 112\text{ cm}^3,$$

$$T_1 = 273 + 0 = 273\text{ K}$$

At given conditions :

$$P_2 = 730\ mm,\ V_2 = ?,$$

$$T_2 = 27 + 273 = 300\text{ K}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ \text{(gas equation)}$$

$$\therefore \quad V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

$$= \frac{760\text{ mm} \times 112\text{ cm}^3 \times 300\text{ K}}{730\text{ mm} \times 273\text{ K}}$$

$$\simeq \mathbf{128\ cm^3} \qquad \textbf{Ans.}$$

Example 14. *A certain mass of a dry gas has density 28 at 27°C and 760 mm pressure. Calculate the density of gas at 17°C and 72 cm pressure.*

Solution. $\dfrac{D_1T_1}{P_1} = \dfrac{D_2T_2}{P_2}$

$$D_1 = 28,\ T_1 = 27 + 273 = 300\text{ K},$$

$$P_1 = 760\text{ mm};$$

$$D_2 = ?,\ T_2 = 17 + 273 = 290\text{ K},$$

$$P_2 = 72\text{ cm} \times \frac{10\text{ mm}}{1\text{ cm}} = 720\text{ mm}.$$

We know that :

$$\frac{D_1T_1}{P_1} = \frac{D_2T_2}{P_2};$$

$$D_2 = \frac{D_1T_1}{P_1} \times \frac{P_2}{T_2} = \frac{28 \times 300\text{ K} \times 720\text{ mm}}{760\text{ mm} \times 290\text{ K}}$$

or $\quad \mathbf{D_2 = 27.4}$ **Ans.**

Type. $\quad 1\text{ atm} = 1.01325\text{ bar}$

Example 15. *Calculate the density of a gas at NTP if its density at 27°C and 1.8 bar pressure is 5.4 g dm^{-3}.*

Solution. At NTP :

$$D_1 = ?,$$

$$P_1 = 1.0\text{ atm} = 1.01325\text{ bar}; T_1 = 273\text{ K}$$

At given condition :

$$D_2 = 5.4\text{ g dm}^{-3}, P_2 = 1.8\text{ bar};$$

$$T_2 = 27 + 273 = 300\text{ K}.$$

In terms of density :

$$\frac{D_1T_1}{P_1} = \frac{D_2T_2}{P_2};\ D_1 = \frac{D_2T_2}{P_2} \times \frac{P_1}{T_1}$$

$$\therefore \quad D_1 = \frac{5.4\text{ g dm}^{-3} \times 300\text{ K} \times 1.01325\text{ bar}}{1.8\text{ bar} \times 273\text{ K}}$$

$$= \mathbf{3.34\ g\ dm^{-3}} \qquad \textbf{Ans.}$$

8.6 IDEAL GAS EQUATION

It is also called ideal gas law and universal gas law. It states that, the volume of a given amount of a gas is directly proportional to the number of moles of a gas and temperature but is inversely proportional to pressure or V α nT/P.

or $\quad \boxed{V = \dfrac{nRT}{P}}$

where R is a proportionality constant called universal gas constant. Its values are :

$R = 8.314\text{ J mol}^{-}\text{K}^{-} = 0.0821\text{ L atm mol}^{-}\text{ K}^{-} = 2\text{ cal mol}^{-}\text{ K}^{-} = 0.083\text{ bar dm}^3\text{ K}^{-}\text{ mol}^{-}$. **Also see page, 76.**

Different forms of gas equation are :

(*i*) $PV = nRT$

(*ii*) $PM_0 = dRT$ where $d = \dfrac{g}{V}$ *i.e.*, $\dfrac{mass}{volume}$

(*iii*) $PV = \dfrac{g}{M_0}RT$

Example 16. *11.0 g of CO$_2$ gas are introduced in a vessel of 4L capacity at 37°C. Calculate the pressure of the gas in bar in the container.*

Solution.

$$\text{wt. of CO}_2 = 11.0\text{ g};$$

$$\text{mol. wt. of CO}_2 = 12 + (2 \times 16)$$

$$= 44\text{ g mol}^{-}$$

$$\therefore \text{ no. of mol of CO}_2 = \frac{\text{wt.}}{\text{mol. wt}} = \frac{11.0}{44\text{ g mol}^{-}}$$

$$= 0.25\text{ mol}$$

$$P = ?,\ T = 37 + 273 = 310\text{ K},$$

$$V = 4\text{L} = 4 \times 10^{-3}\text{ m}^3$$

$$R = 8.314\text{ Pa m}^3\text{ K}^{-}\text{ mol}^{-}.$$

We know that : $PV = nRT; P = \dfrac{nRT}{V}$

$$= \frac{0.25\text{ mol} \times 8.314\text{ Pa m}^3\text{ K}^{-}\text{ mol}^{-} \times 310\text{K}}{4 \times 10^{-3}\text{ m}^3}$$

or $$P = 161083\text{ Pa} = 161083\text{ Pa} \times \frac{1\text{ bar}}{10^5\text{ Pa}}$$

$$\simeq \mathbf{1.61\ bar} \qquad \textbf{Ans.}$$

EXAMPLE 17. *2.5 mol of a gas occupy 4.5 dm^3 at 2.99 bar. Calculate the temperature of the gas. (R = 0.083 bar dm^3 K$^-$ mol$^-$)*

SOLUTION.

$$
\begin{aligned}
n &= 2.5 \text{ mol}, \ V = 4.5 \text{ dm}^3, \\
P &= 2.99 \text{ bar}, \ T = ? \\
R &= 0.083 \text{ bar dm}^3 \text{ K}^- \text{mol}^-. \\
PV &= nRT; \ T = \frac{PV}{nR} \\
&= \frac{2.99 \text{ bar} \times 4.5 \text{ dm}^3}{2.5 \text{ mol} \times 0.083 \text{ bar dm}^3 \text{ K}^- \text{ mol}^-}
\end{aligned}
$$

or T = **64.8 K** **Ans.**

EXAMPLE 18. *The difference between the mass of displaced air and mass of balloon is called pay load. Find the value of pay load when a balloon of radius 8 m, mass 90 kg is filled with helium at 1.5 bar at 27°C (R = 0.083 bar dm^3 K$^-$ mol$^-$; density of air = 1.2 kg m^{-3}).*

SOLUTION. (*i*)

$$
\begin{aligned}
P &= 1.5 \text{ bar}, \ T = 27 + 273 = 300 \text{ K}, \\
R &= 0.083 \times 10^{-3} \text{ bar m}^3 \text{ K}^-\text{mol}^- \\
r &= 8 \text{ m}; \\
V &= Volume = \frac{4}{3}\pi r^3 = \frac{4}{3}\times\frac{22}{7}\times(8 \text{ m})^3 \\
&= 2145.5 \text{ m}^3 \\
PV &= nRT; \ n = \frac{PV}{RT} \\
&= \frac{1.5 \text{ bar} \times 2145.5 \text{ m}^3 \times 10^3}{0.083 \text{ bar m}^3 \text{ K}^- \text{ mol}^- \times 300 \text{ K}} \\
&= 129.24 \times 10^3 \text{ mol}
\end{aligned}
$$

(*ii*) Mol. wt. of He = 4 g mol$^-$;

∴ Mass of 1 mol of He = 4 g

Mass of 129.24 × 10^3 mol

$$
\begin{aligned}
\text{He} &= 129.24 \times 10^3 \times 4 \text{ g} = 516960 \text{ g} \\
&= 516960 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 516.90 \text{ kg}
\end{aligned}
$$

Mass of filled balloon

= 90 kg + 516.9 kg = 606.9 kg

∴ Pay load = (Mass of displaced air – Mass of balloon) ...(*i*)

Mass of displaced air = volume × density

= 2145.5 m^3 × 1.2 kg m^{-3}

= 2574.6 kg.

∴ Pay load = 2574.6 kg – 606.9 kg

= **1967.7 kg** **Ans.**

EXAMPLE 19. *UF$_6$ (mol. wt., 350 g mol$^-$) was filled in an evacuated bulb of 0.15 m^3 size at 27°C and 2.4 × 10^{-2} atm. pressure. Calculate the mass of UF$_6$ in the bulb if R = 0.082 L atm K$^-$ mol$^-$.*

SOLUTION. wt. of UF$_6$ =?, mol. wt. of UF$_6$ = 350 g mol$^-$.

$$
\therefore \text{ no. of mol. of UF}_6 = n = \frac{\text{wt. (w)}}{\text{Mol. wt.}} = \frac{\text{w}}{350 \text{ g mol}^-}
$$

$$
\begin{aligned}
P &= 2.4 \times 10^{-2} \text{ atm}; \ V = 0.15 \text{ m}^3; \\
T &= 27 + 273 = 300 \text{ K} \\
PV &= nRT \text{ (gas equation)}; \\
\therefore \quad n &= \frac{PV}{RT}
\end{aligned}
$$

$$
\therefore \frac{\text{w}}{350 \text{ g mol}^-} = \frac{2.4\times10^{-2} \text{ atm}\times0.15 \text{ m}^3}{0.0821\times10^{-3} \text{ m}^3 \text{ atm K}^-\text{mol}^- \times 300 \text{ K}}
$$

$[\because \ 1 \text{ L} = 10^{-3}\text{m}^3]$

$$
\therefore \text{w} = \frac{350 \text{ g mol}^- \times 2.4\times10^{-2} \text{ atm}\times0.15 \text{ m}^3}{0.0821\times10^{-3} \text{ m}^3 \text{ atm K}^-\text{mol}^- \times 300 \text{ K}} = \mathbf{51.16 \text{ g}}
$$

EXAMPLE 20. *Calculate the volume of H$_2$ gas at 25°C and 1.2 bar that will be released from the action of 0.2 g aluminium (present in drainex) on sodium hydroxide solution. (at. wt., Al = 27).*

SOLUTION. Reaction :

$$
\underset{2\times27 = 54 \text{ g}}{2\text{Al}} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaAlO}_2 + \underset{3\times22.4\text{L} = 67.2\text{L}}{3\text{H}_2}
$$

54 g Al produce H$_2$ = 67.2 L

$$
0.2 \text{ g Al produce H}_2 = \frac{67.2 \text{ L}}{54 \text{ g}}\times0.2 \text{ g} = 0.249 \text{ L}
$$

$$
\begin{aligned}
P_1 &= 1.0 \text{ bar} = 1.0 \text{ atm}; \\
P_2 &= 1.2 \text{ bar} = 1.2 \text{ atm} \\
V_1 &= 0.249 \text{ L}; V_2 = ?; T_1 = 273 \text{ K}; \\
T_2 &= 25 + 273 = 298 \text{ K} \\
\frac{P_1V_1}{T_1} &= \frac{P_2V_2}{T_2} \text{ (gas equation)} \\
\therefore \quad V_2 &= \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} \\
&= \frac{1 \text{ atm}\times0.249 \text{ L}}{273 \text{ K}}\times\frac{298 \text{ K}}{1.2 \text{ atm}} \\
&= 0.2265 \text{ L}
\end{aligned}
$$

or $V_2 = 0.2265 \text{ L}\times\frac{1000 \text{ mL}}{1\text{L}}$

= **226.5 mL** **Ans.**

EXAMPLE 21. *A vessel of 2.5 dm^3 capacity contains carbon dioxide gas at 101.325 kPa and 27°C. The gas pressure is reduced to 0.1 Pa. If the gas is assumed as an ideal gas :*

(*i*) *Calculate the volume of CO$_2$ gas left behind in the vessel*

(*ii*) *Calculate the amount of CO$_2$ gas and the corresponding number of molecules that are left behind in the vessel.*

(*iii*) *If 2.5 g of O$_2$ is introduced, what will be the pressure of the vessel ?*

SOLUTION. Volume of vessel,

V_1 = 2.5 dm^3; Pressure,

P_1 = 101.325 kPa

$$
\text{Final pressure, } P_2 = 0.1 \text{ Pa} = \frac{0.1}{1000}\text{kPa} = 10^{-4} \text{ kPa};
$$

T = 27 + 273 = 300 K.

(*i*) The volume of CO_2 gas left behind in the flask will be the same *i.e.,* 2.5 dm^3.

(*ii*) We know that $P_2V_1 = nRT$ or $n = \frac{P_2V_1}{RT}$

$\therefore$ Amount of CO_2 gas left behind is given by :

$$n = \frac{10^{-4}\text{kPa} \times 2.5 \text{ dm}^3}{8.314 \text{ kPa. dm}^3\text{K}^{-}\text{mol}^{-} \times 300K}$$

or $n = 1.002 \times 10^{-7}$mol

$$= \frac{1.002 \times 10^{-7} \text{ mol} \times 6.02 \times 10^{23} \text{ molecules}}{1 \text{ mol}}$$

$= 6.03 \times 10^{16}$ molecules

$\therefore$ Amount of CO_2 (g. mol. wt., 44 g)

$$= 1.002 \times 10^{-7} \text{ mol} \times \frac{44 \text{ g}}{\text{mol}} = 44 \times 10^{-7} \text{ g}$$

(*iii*) 2.5 g O_2

$$= \frac{\text{wt. of } O_2}{\text{g. mol. wt. of } O_2} = \frac{2.5}{2 \times 16} = \frac{2.5}{32} \text{ mol}$$

Pressure of the vessel,

$$P = \frac{nRT}{V}$$

$$= \frac{2.5 \text{ mol} \times 8.314 \text{ kPa. dm}^3\text{. K}^{-}\text{mol}^{-} \times 300 \text{ K}}{32 \times 2.5 \text{ dm}^3}$$

= 77.94 kPa.

EXAMPLE 22. *An evacuated glass vessel weighs 50.0 g when empty. It weighs 148.0 g when filled with a liquid of density 0.98 g (mL)⁻ and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.* **(IIT, 1998)**

SOLUTION. wt. of empty vessel = 50 g

wt. of empty vessel + wt. of liquid = 148 g

$\therefore$ wt. of liquid = 148 g – 50 g = 98 g.

Density of liquid = 0.98 g $(mL)^{-}$

$$\therefore \text{Volume of liquid} = \frac{\text{wt.}}{\text{density}} = \frac{98 \text{ g}}{0.98 \text{ g(mL)}^{-}}$$

= 100 mL

= volume of vessel.

wt. of ideal gas + wt. of empty vessel

= 50.5 g

$\therefore$ wt. of ideal gas = 50.5 – 50 = 0.5 g ;

$$P = 760 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} = 1 \text{ atm} ;$$

R = 0.0821 L atm $K^{-}mol^{-}$, T = 300 K.

Mol. wt. of gas = *m*,

$$V = 100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.1 \text{ L}.$$

We know that : $PV = nRT;$

$$PV = \frac{\text{wt.}}{\text{mol. wt}} \times RT$$

$\therefore$ Mol. wt. of ideal gas

$$= \frac{\text{wt.} \times \text{RT}}{\text{PV}}$$

$$= \frac{0.5 \text{ g} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 300 \text{ K}}{1 \text{ atm} \times 0.1 \text{ L}}$$

= 123.15 g mol⁻ **Ans.**

EXAMPLE 23. *Using ideal gas equation, calculate the pressure (in atm.) exerted by 2.0 mol of an ideal gas in a vessel of volume 0.1 m^3 and maintained at 300 K (R = 8.314 J $K^{-}mol^{-}$)*

SOLUTION. P = ?, n = 2.0 mol, V = 0.1 m^3,

R = 8.314 J K^{-} mol^{-} = 8.314 Nm $K^{-}mol^{-}$;

T = 300 K

$$PV = nRT; \quad P = \frac{nRT}{V}$$

$$= \frac{2.0 \text{ mol} \times 8.314 \text{ Nm K}^{-}\text{mol}^{-} \times 300 \text{ K}}{0.1 \text{ m}^3}$$

$\therefore$ P = 49884 N m^{-2} = 49884 Pa

$$= 49884 \text{ Pa} \times \frac{1 \text{ atm}}{101325 \text{ Pa}}$$

= 0.492 atm **Ans.**

[$\because$ N m^{-2} = Pa; 101325 Pa = 1 atm]

Type. Under similar conditions of P and V : $n_1T_1 = n_2T_2$

EXAMPLE 24. *An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find out.*

(*a*) *the temperature at which vessel was heated*

(*b*) *the air escaped out if vessel is heated to 900 K.*

(*c*) *the temperature at which half of the air escapes out.*

(UPSEAT, 1990)

SOLUTION. T_1 = 27°C = 27 + 273 = 300 K,

T_2 = ?

Let initial mole of air at 300 K = *n*

Since 3/5 mole of air goes out at temperature T_2, so:

$$\text{mole of air left at } T_2 = n - \frac{3n}{5} = \frac{2n}{5}$$

(*a*) At similar conditions of *P* and *V* :

$$n_1T_1 = n_2T_2;$$

$$n \times 300 = \frac{2n}{5} \times T_2$$

$$\therefore \quad T_2 = \frac{n \times 300 \times 5}{2n} = \mathbf{750 \ K.}$$

or T_2 = 750 – 273 = 477° C.

(*b*) T_1 = 300 K, $n_1 = n;$ T_2 = 900 K, n_2 = ?

But $n_1T_1 = n_2T_2$. So, $n \times 300$ K

$= n_2 \times 900$ K

$$\therefore \quad n_2 = \frac{n \times 300 \text{ K}}{900 \text{ K}} = \frac{1}{3}n$$

Hence no. of mole of air escaped out

$$= n - \frac{1}{3}n = \frac{2}{3}n = \mathbf{0.67\,n} \quad \textbf{Ans.}$$

(*c*) $T_1 = 300\text{ K},\ n_1 = n\ ;$

$$T_2 = ?\ ,\ n_2 = \frac{n}{2}$$

But $$n_1T_1 = n_2T_2\ ;\ n \times 300\text{ K} = \frac{n}{2} \times T_2$$

$$\therefore \quad T_2 = \frac{n \times 300\text{ K} \times 2}{n} = \mathbf{600\ K} \quad \textbf{Ans.}$$

EXAMPLE 25. *20% N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of equilibrium mixture.* **(Roorkee, 1996)**

SOLUTION. (*i*) No. of mole of

$$N_2O_4 \text{ dissociated} = 20\% = \frac{20}{100} = 0.2$$

$\therefore$ no. of mole of N_2O_4 at equilibrium $= 1 - 0.2 = 0.8$;

$$T = 27 + 273 = 300\text{ K}$$

$$\text{Mol. wt. of } NO_2 = 14 + (2 \times 16) = 46\text{ g mol}^{-}$$

$$\text{Mol. wt. of } N_2O_4 = (2 \times 14) + (4 \times 16) = 92\text{ g mol}^{-}$$

$$P = 760\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} = 1\text{ atm}$$

$$R = 0.0821\text{ L atm K}^{-}\text{ mol}^{-}.$$

Reaction :	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial mol	1		0
Mol at equilibrium	$1 - 0.2$ $= 0.8$		$2 \times 0.2 = 0.4$

$\therefore$ Mol. wt. of mixture

$$= \frac{(0.8 \times 92) + (0.4 \times 46)}{0.8 + 0.4} = \frac{73.6 + 18.4}{1.2} = \frac{92.0}{1.2}$$

$$= \mathbf{76.67\ g\ mol^{-}}$$

(*ii*) $PV = nRT\ ;\quad PV = \dfrac{\text{wt.}}{\text{mol. wt.}} \times RT\ ;$

$$\frac{P \times \text{mol. wt}}{RT} = \frac{\text{wt.}}{\text{volume, } V} = \text{density}$$

$\therefore$ Density at equilibrium

$$= \frac{P \times \text{mol. wt}}{RT} = \frac{1\text{ atm} \times 76.67\text{ g mol}^{-}}{0.0821\text{ L atm K}^{-}\text{mol}^{-} \times 300\text{ K}}$$

$$= \mathbf{3.113\ g\ L^{-}} \quad \textbf{Ans.}$$

EXAMPLE 26. *The density of liquid carbon dioxide at 25°C is 0.89×10^3 kg m^{-3}. How large a cartridge of liquid carbon dioxide must be provided to inflate a life jacket of 5 litre capacity at NTP.*

SOLUTION. Mol. wt. of $CO_2 = 12 + (2 \times 16) = 44$ g mol^{-}

22.4 L CO_2 at NTP. weighs = g. mol. wt. of CO_2 = 44 g

$$5\text{ L } CO_2 \text{ at NTP. weighs} = \frac{44\text{ g}}{22.4\text{ L}} \times 5\text{ L} = 9.82\text{ g}$$

$$\therefore \text{ wt. of } CO_2 = 9.82\text{ g} = 9.82\text{ g} \times \frac{1\text{ kg}}{1000\text{ g}} = 0.00982\text{ kg.}$$

$$\text{Density of } CO_2 = 0.89 \times 10^3\text{ kg m}^{-3}$$

$\therefore$ Volume of cartridge containing 0.00982 kg CO_2

$$= \frac{\text{Mass}}{\text{density}} = \frac{0.00982\text{ kg}}{0.89 \times 10^3\text{ kg m}^{-3}}$$

$$= 1.1 \times 10^{-5}\text{ m}^3$$

$$= 1.1 \times 10^{-5}\text{ m}^3 \times \frac{1000\text{ L}}{1\text{ m}^3} \times \frac{1000\text{ mL}}{1\text{ L}}$$

$$= \mathbf{11\ mL} \quad \textbf{Ans.}$$

EXAMPLE 27. *Calculate the density of a gas in kg m^{-3} at 25°C and 1.1 bar pressure. Molar mass of gas is 48 g mol^{-} amu.*

SOLUTION. $PV = nRT$ (Ideal gas equation);

$$P = 1.1\text{ bar} = 1.1\text{ atm.}$$

$$P = \frac{n}{V} \times RT\ ;\ P = \frac{\text{wt.}}{\text{V}} \times \frac{RT}{\text{mol. wt.}}\ ;$$

$$P = \frac{dRT}{\text{mol. wt.}}$$

$$\therefore \quad d = \frac{P \times \text{mol. wt.}}{RT}$$

$$= \frac{1.1\text{ atm} \times 48\text{ g mol}^{-}}{0.0821\text{ L atm K}^{-}\text{mol}^{-} \times 298\text{ K}}$$

[$\because$ $T = 25 + 273 = 298$ K]

$$= \frac{1.1\text{ atm} \times 48\text{ g mol}^{-}}{0.0821 \times 1000\text{ cm}^3\text{ atm K}^{-}\text{mol}^{-} \times 298\text{ K}}$$

$$= 2.158 \times 10^{-3}\text{ g cm}^{-3}$$

$$d = 2.158 \times 10^{-3} \times 10^3\text{ kg m}^{-3} = \mathbf{2.158\ kg\ m^{-3}} \quad \textbf{Ans.}$$

EXAMPLE 28. *A chemistry student is interested to fill a cylinder of one litre capacity with hydrogen at 25°C and 80 bar pressure. What will be the density of gas in the cylinder in gL^{-}, $g\,(mL)^{-}$ and kg m^{-3}? Also, calculate the volume of H_2 gas under standard conditions of temperature and pressure. (at. wt., H = 1 amu).*

SOLUTION.

(*i*) **Initial conditions**	**Standard conditions**
$P_1 = 80\text{ bar} = 80\text{ atm}$	$P_2 = 1\text{ atm}$
$V_1 = 1\text{ L}$	$V_2 = ?$
$T_1 = 25 + 273 = 298\text{ K}$	$T_2 = 273\text{ K}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (gas equation);} \quad V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$\therefore \quad V_2 = \frac{80\text{ atm} \times 1\text{L}}{298\text{ K}} \times \frac{273\text{ K}}{1\text{ atm}} = \mathbf{73.29\ L} \quad \textbf{Ans.}$$

(*ii*) **To find density of gas :**

Mol. wt. of $H_2 = 2 \times 1 = 2$ g mol^{-}

g mol. wt. of any gas occupies volume at S.T.P. = 22.4 L

$\therefore$ 22.4 L H_2 weigh = 2 g

$$73.29\text{ L } H_2 \text{ weighs} = \frac{2\text{ g}}{22.4\text{ L}} \times 73.29\text{ L} = 6.54\text{ g}$$

Volume = 1 L, mass = 6.54 g

$$\therefore \quad \text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{6.54\text{ g}}{1\text{ L}}$$

$$= \mathbf{6.54\ g\ L^{-}} \quad \textbf{Ans.}$$

$$= \frac{6.54\text{ g}}{1000\text{ mL}} = 0.00654\text{ g (mL)}^{-} \quad \textbf{Ans.}$$

[∵ 1 L = 1000 mL]

$$= \mathbf{6.54\ kg\ m^{-3}} \qquad \textbf{Ans.}$$

[∵ $1L = 10^{-3}\ m^3$; $1g = 10^{-3}$ kg]

EXAMPLE 29. *Calculate the density of CO_2 at 100°C and 800 mm pressure Hg pressure.*

SOLUTION.
$$P = 800\ \text{mm} \times \frac{1\ \text{atm}}{760\ \text{mm}} = \frac{80}{76}\ \text{atm};$$

mol. wt., M of CO_2 = 12 + (2 × 16) = 44 g mol^{-};

$R = 0.0821$ L atm $K^{-}mol^{-}$;

$T = 100 + 273 = 373$ K.

$$\text{We know that}: PV = nRT = \frac{W}{M}RT ; P = \frac{W}{V} \times \frac{RT}{M} = \frac{dRT}{M}$$

$$\therefore \quad d = \frac{MP}{RT} = 44\ \text{g mol}^{-} \times \frac{80\ \text{atm}}{76} \times \frac{1}{0.0821\ \text{L atm K}^{-}\text{mol}^{-} \times 373\ \text{K}}$$

$$= \mathbf{1.512\ gL^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 30. *Calculate the volume occupied by 5.0 g of acetylene gas at 50°C and 740 mm pressure.* **(IIT, 1991)**

SOLUTION. wt. of acetylene, C_2H_2 = 5.0 g ;

mol. wt. of C_2H_2 = (2 × 12) + (2 × 1) = 26 g mol^{-}.

$$n = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{5.0\ \text{g}}{26\ \text{g mol}^{-}} = \frac{5}{26}\ \text{mol};$$

$$P = \frac{740\ \text{mm} \times 1\ \text{atm}}{760\ \text{mm}} = \frac{74}{76}\ \text{atm}$$

$T = 50 + 273 = 323$ K;

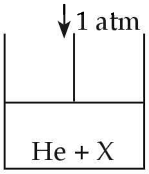
$R = 0.0821$ L atm K^{-} mol^{-}; $V = ?$

$PV = nRT$ (Ideal gas equation)

$$\therefore \quad V = \frac{nRT}{P} = \frac{5}{26}\text{mol} \times \frac{0.0821\ \text{L atm K}^{-}\text{mol}^{-} \times 323\ \text{K} \times 76}{74\ \text{atm}}$$

$$= \mathbf{5.238\ L} \qquad \textbf{Ans.}$$

EXAMPLE 31. *To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.32 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to:* **(IIT-JEE, 2011)**



SOLUTION. (*i*) $P = 0.32$,

$V = ?$,

$n = 0.1$,

$T = 0 + 273 = 273$ K.

$R = 0.0821$

But $PV = n\,RT$; $0.32 \times V$

$= 0.1 \times 0.0821 \times 273$

$\therefore \quad V = (0.1 \times 0.0821 \times 273) / 0.32 = 7L.$

(For He, $n = 0.1$, $P = 0.32$ atm, $V = ?$, $T = 273$K, see above) The unknown compound will not follow ideal gas equation.

EXAMPLE 32. *A cylinder contains H_2 gas at 25°C and 19 atmospheric pressure. This cylinder can hold 2.5 L water at S.T.P. Calculate the number of balloons those can be filled with H_2 gas if diameter of spherical balloon is 19.8 cm.*

SOLUTION. Radius (r) of balloon = $\dfrac{19.8\ \text{cm}}{2} = 9.9$ cm

Volume of sphere or balloon

$$= \frac{4}{3}\pi\, r^3 = \frac{4}{3} \times \frac{22}{7} \times (9.9\ \text{cm})^3 = \mathbf{4066\ cm^3}$$

Capacity of cylinder = 2.5 L = 2.5 × 1000 = 2500 mL = 2500 cm^3

Given conditions	**NTP**
$P_1 = 19$ atm	$P_2 = 1$ atm
$V_1 = 2500\ cm^3$	$V_2 = ?$
$T_1 = 25 + 273 = 298$ K	$T_2 = 273$ K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{(gas equation)}$$

$$\therefore \quad V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{19\ \text{atm} \times 2500\ \text{cm}^3 \times 273\ \text{K}}{298\ \text{K} \times 1\ \text{atm}}$$

$$= 43515\ \text{cm}^3$$

∴ H_2 gas available for filling balloons

$$= 43515\ \text{cm}^3 - 2500\ \text{cm}^3$$

$$= 41015\ \text{cm}^3$$

[∵ 2500 cm^3 is the volume of H_2 gas that will remain in the cylinder]

∴ No. of balloons those can be filled with H_2 gas

$$= \frac{41015\ \text{cm}^3}{4066\ \text{cm}^3} = \mathbf{10} \qquad \textbf{Ans.}$$

EXAMPLE 33. *A flask containing 2 g of an ideal gas X has a pressure of 3 bar at 25°C. When 3 g of another ideal gas y was introduced in the same flask at the same temperature and pressure, the observed pressure was 4.5 bar. Calculate the relationship with their molecular weights.*

(IIT, 1977 modified)

SOLUTION. Mol. wt. of gas $X = M_x$ g mol^{-}; mol. wt. of gas $Y = M_Y$ g mol^{-}; wt. of gas X = 2 g; wt. of gas Y = 3 g

∴ no. of mol of gas

$$X = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{2\ \text{g}}{M_x\ \text{g mol}^{-}} = \frac{2}{M_x}\ \text{mol}$$

$= n_A$ no. of mol of gas

$$Y = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{2\ \text{g}}{M_y\ \text{g mol}^{-}} = \frac{2}{M_y}\ \text{mol} = n_B$$

$PV = nRT$ (gas equation)

∴ For gas X: $P_xV = n_ART$; For gas Y: $P_yV = n_BRT$

$$\therefore \quad \frac{P_xV}{P_yV} = \frac{n_ART}{n_BRT};\ \frac{P_x}{P_y} = \frac{n_A}{n_B} \qquad \ldots (i)$$

$$P_x = 3 \text{ bar};\ P_x + P_y = 4.5 \text{ bar};$$

$$P_y = 4.5 - P_x = 4.5 - 3 = 1.5 \text{ bar}$$

$$n_A = \frac{2}{\mathrm{M}_x}\text{mol};\ n_B = \frac{3}{\mathrm{M}_y} \text{ mol.}$$

Substituting the values in equation (*i*), we get :

$$\frac{3 \text{ bar}}{1.5 \text{ bar}} = \frac{2}{\mathrm{M}_x} \times \frac{\mathrm{M}_y}{3};\ \frac{\mathrm{M}_y}{\mathrm{M}_x} = \frac{3\times 3}{1.5\times 2} = 3$$

or $\quad \mathrm{M}_y = \mathbf{3\ M}_x$. **Ans.**

Example 34. *A sealed room of the dimensions of 2.5 m by 2.5 m by 2.0 m contains 480 g sulphur dioxide at 27°C. Calculate the pressure exerted by the gas. (at. wt., S = 32, O = 16)*

Solution.

(*i*) wt. of SO_2 = 480 g ;

mol. wt. of SO_2 = 32 + (2 × 16) = 64 g mol^{-}

T = 27 + 273 = 300 K ;

R = 0.0821 L atm K^{-} mol^{-}.

Volume of room, V = Length × breadth × height

= 2.5 m × 2.5 m × 2.0 m

$$= 12.5 \text{ m}^3 = 12.5 \text{ m}^3 \times \frac{1000 \text{ L}}{1 \text{ m}^3}$$

= 12500 L.

$$\text{no. of mol of } SO_2,\ n = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{480 \text{ g}}{64 \text{ g mol}^{-}}$$

= 7.5 mol.

$$(ii) \qquad PV = nRT;\ P = \frac{nRT}{V}$$

$$= \frac{7.5 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 300 \text{ K}}{12500 \text{ L}}$$

∴ $\quad$ $\boldsymbol{P}$ **= 1.39 atm** **Ans.**

Example 35. *A sample of unknown liquid is introduced into a container having volume 250 cm^3 and vapourised. The weight of the container increased by 1.34 g. If pressure in the vessel is 770 mm Hg and temperature is 340 K, calculate the molar mass of the liquid.*

Solution. Let molar mass of liquid = M. wt. of liquid = 1.34 g.

∴ no. of mol of liquid

$$= \frac{\text{wt.}}{\text{mol. wt.}} = \frac{1.34 \text{ g}}{\text{M}};$$

$$P = 770 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} = \frac{77}{76} \text{ atm};$$

$$V = 250 \text{ cm}^3 \times \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.25 \text{ L};$$

R = 0.0821 L atm K^{-} mol^{-}, T = 340 K

PV = nRT (gas equation)

$$\frac{77}{76} \text{ atm} \times 0.25 \text{ L}$$

$$= \frac{1.34 \text{ g}}{\text{M}} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 340 \text{ K}$$

$$\therefore \text{M} = \frac{1.34 \text{ g} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 340 \text{ K} \times 76}{77 \text{ atm} \times 0.25 \text{ L}}$$

= 147.7 g mol^{-} **Ans.**

Example 36. *If 0.18 g of hydrogen gas is needed to inflate a balloon to a certain size at 25°C. What mass of gas will be needed to inflate it to the same size at 30°C. Assume that the elasticity of balloon is the same at both the temperatures. (at. wt., H = 1)*

Solution.

(*i*) Mol. wt. of H_2 = 2 × 1 = 2 g mol^{-};

wt. of H_2 = 0.18 g

$$\therefore \text{no. of mol of } H_2 = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{0.18 \text{ g}}{2 \text{ g mol}^{-}}$$

= 0.09 mol = n_1

T_1 = 25 + 273 = 298 K

Under first condition:

$P_1V_1 = n_1RT_1$

= 0.09 mol × R × 298 K ...(*i*)

(*ii*) Mol. wt. of H_2 = 2 × 1 = 2 g mol^{-};

wt. of H_2 = w g

∴ no. of mol of H_2

$$= \frac{\text{wt.}}{\text{mol. wt}} = \frac{\text{w g}}{2 \text{ g mol}^{-}} = \frac{\text{w}}{2} \text{ mol}$$

= 0.5 w mol = n_2

T_2 = 30 + 273 = 303 K

∴ **Under second condition:**

$P_2V_2 = n_2RT_2$

= 0.5 w mol × R × 303 K ...(*ii*)

From equations (*i*) and (*ii*),

$P_1V_1 = P_2V_2$.

So, 0.09 mol × R × 290 K

= 0.5 w mol × R × 303 K

$$\therefore \qquad w = \frac{0.09 \text{ mol} \times R \times 290\text{K}}{0.5 \text{ mol} \times R \times 303 \text{ K}}$$

= 0.17 g **Ans.**

Example 37. *If the pressure of a given mass of a gas becomes one half of its original pressure and simultaneously the volume becomes four times the original volume, what should have happened to the temperature ?*

Solution.

Initial conditions	**Final conditions**
$P_1 = P$ atm	$P_2 = \frac{P}{2}$ atm

$V_1 = VL \qquad V_2 = 4VL$
$T_1 = TK \qquad T_2 = ?$

Using gas equation, we have :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} ; \frac{P\text{ atm} \times VL}{TK} = \frac{P}{2}\text{ atm} \times \frac{4VL}{T_2}$$

$$T_2 = \frac{P}{2}\text{ atm} \times \frac{4VL \times TK}{P\text{ atm} \times VL} = \mathbf{2T\ K} \quad \textbf{Ans.}$$

∴ Temperature in kelvin (K) would become double of the original temperature.

Type. Pressure of dry gas =

= Pressure of moist gas at given temperature, T – Aqueous tension at same temperature T

Or = Pressure of moist gas at a given temperature, T – Pressure of water vapours at the same temperature, T

Example 38. *A gas occupies 100 mL when collected over water at 15°C and 750 mm pressure. It occupies 92 mL in dry state at N.T.P. Find the vapour pressure of water (aqueous tension) at 15°C.*

Solution.

Given conditions	**At N.T.P**
P_1 = 750 mm – p mm	P_2 = 760 mm
V_1 = 100 mL	V_2 = 92 mL
T_1 = 15 + 273 = 288 K	T_2 = 273 K

Using $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} ; \frac{(750-p)\text{ mm} \times 100\text{ mL}}{288\text{ K}} = \frac{760\text{ mm} \times 92\text{ mL}}{273\text{ K}}$$

$(750 \times 100 \times 273) - (100 \times 273\, p) = 760 \times 92 \times 288;$
$20475000 - 27300\, p = 20136960 ;\ 27300\, p = 338040$

$$\therefore \quad p = \frac{338040}{27300} = \mathbf{12.38\ mm} \quad \textbf{Ans.}$$

8.7 AVOGADRO'S LAW

Equal volume (V) of all gases contain equal number of molecules (or moles) (= n) at the same temperature and pressure,

Mathematically : $\frac{V}{n}$ = a constant. It is observed that:

One mole of a gas occupies 22.4 litre volume at NTP or STP *i.e.,* 273 K and 1 atmospheric pressure. It is called **molar volume** of a gas.

Example 39. *Prove that 112 mL of N_2 gas contain same number of molecules as 112 mL of O_2 gas contain under similar conditions of temperature and pressure. Also, name the law which governs this statement.*

Solution. (*i*) 22400 mL of N_2 gas contain molecules = 6.02×10^{23}; 112 mL of N_2 gas contain molecules

$$= \frac{6.02 \times 10^{23}}{22400\text{ mL}} \times 112\text{ mL} = 3.01 \times 10^{21}$$

(*ii*) 22400 mL of O_2 gas contain molecules = 6.02×10^{23}
112 mL of O_2 gas contain molecules

$$= \frac{6.02 \times 10^{23}}{22400\text{ mL}} \times 112\text{ mL} = 3.01 \times 10^{21}$$

Since number of molecules of N_2 gas (= 3.01×10^{21}) are the same as those of O_2 gas (= 3.01×10^{21}), it is in accordance with Avogadro's law which states that equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure.

Example 40. *0.5 mol of H_2 gas occupies 11.2 L volume at N.T.P. Calculate the volume occupied by 0.5 mol of O_2 gas under similar conditions of temperature and pressure. Name the law which helps in solving the problem.*

Solution. (*i*) 0.5 mol of H_2 occupies volume = 11.2 L

$$1\text{ mol of } H_2 \text{ occupies volume} = \frac{11.2}{0.5\text{ mol}} \times 1\text{ mol} = 22.4\text{ L}$$

According to Avogadro's law, $V \propto n$ under similar conditions of temperature and pressure, so
0.5 mol of O_2 will also occupy volume = **11.2 L** **Ans.**

8.8 DALTON'S LAW

Total pressure of a mixture of non-reacting gases is equal to sum of the partial pressures of the individual gases present.

Mathematically : $P = P_1 + P_2 + P_3 + \ldots..$ (V and T are constant)

where P is total pressure. $P_1, P_2, P_3. \ldots..$ are the partial pressures of the gases 1, 2, 3....... and so on. This law follows the application of ideal gas equation $PV = nRT$ separately to each gas of the mixture. If n_1, n_2 and n_3 are the moles of gases 1, 2 and 3 respectively, then

$$P_1 = \frac{n_1RT}{V} ; P_2 = \frac{n_2RT}{V} \text{ and}$$

$$P_3 = \frac{n_3RT}{V}.$$

Hence : Total pressure,

$$P = P_1 + P_2 + P_3$$

or $$P = \frac{(n_1 + n_2 + n_3)RT}{V}.$$

Thus, $$P_1 = \frac{n_1}{n_1 + n_2 + n_3} \times P = x_1P$$

where x_1 = mole fraction of gas, 1

$$P_2 = \frac{n_2}{n_1 + n_2 + n_3} \times P = x_2P$$

where x_2 = mole fraction of gas, 2

$$P_3 = \frac{n_3}{n_1 + n_2 + n_3} \times P = x_3P$$

where x_3 = mole fraction of gas, 3.

Hence, partial pressure of a gas = mole fraction of gas × Total pressure

% age of gas in mixture

$$= \frac{\text{Partial pressure of gas}}{\text{Total pressure}} \times 100$$

Type. Total pressure from partial pressures. Convert all pressures to any same unit.

EXAMPLE 41. *The partial pressure of nitrogen is 110 mm, of helium is 10 cm and of carbon dioxide is 1.2 atmosphere. Calculate the total pressure of gases present in the same closed vessel.*

SOLUTION. P_{N_2} = 110 mm; $P_{He} = 10 \text{ cm} \times \dfrac{10 \text{ mm}}{1 \text{ cm}}$

= 100 mm;

$$P_{CO_2} = 1.1 \text{ atm} \times \frac{760 \text{ mm}}{1 \text{ atm}} = 836 \text{ mm}.$$

∴ Total pressure of gases

= 110 mm + 100 mm + 836 mm

= **1046 mm** **Ans.**

EXAMPLE 42. *A mixture of gases present in a cylinder at 720 mm pressure contains 56% carbon dioxide, 25% oxygen and 19% nitrogen. Calculate the partial pressure of each gas in the mixture.*

SOLUTION.

Partial pressure of $CO_2 = \dfrac{56 \times 720}{100}$ = **403.2 mm** **Ans.**

Partial pressure of $O_2 = \dfrac{25 \times 720}{100}$ = **180 mm** **Ans.**

Partial pressure of $N_2 = \dfrac{19 \times 720}{100}$ = **136.8 mm** **Ans.**

EXAMPLE 43. *7 g of nitrogen and 4 g of oxygen are confined in a total volume of 1.5 litre at 0°C. Calculate the total pressure of gases in the vessel.*

SOLUTION.

(*i*) 1 mol or 28 g N_2 occupy volume at 1 atm pressure and 0°C = 22.4 L

7 g N_2 will occupy volume

$$= \frac{22.4 \text{ L}}{28 \text{ g}} \times 7\text{g} = 5.6 \text{ L}$$

(*ii*) 1 mol or 32 g O_2 occupy volume at 1 atm pressure and 0°C = 22.4 L

4 g O_2 occupy volume

$$= \frac{22.4 \text{ L}}{32 \text{ g}} \times 4 \text{ g} = 2.8 \text{ L}$$

(*iii*) **For N_2:** $P_2 = \dfrac{P_1V_1}{V_2} = \dfrac{1 \text{ atm} \times 5.6 \text{ L}}{1.5 \text{ L}} = 3.73$ atm.

(*iv*) **For O_2:** $P_2 = \dfrac{P_1V_1}{V_2} = \dfrac{1 \text{ atm} \times 2.8 \text{ L}}{1.5 \text{ L}} = 1.87$ atm.

∴ **Total pressure** = 3.73 atm + 1.87 atm

= **5.60 atm.** **Ans.**

EXAMPLE 44. *4 g of O_2 and 2 g of H_2 are introduced into a 1 dm^3 evacuated cylinder at 300 K and sealed. Calculate the pressure. Will the pressure be the same if the cylinder was cubical of the same capacity? (R = 0.083 bar dm^3 K^-mol^-)*

SOLUTION.

(*i*) no. of mol of $O_2 = n(O_2)$

$$= \frac{\text{wt.}}{\text{mol. wt}} = \frac{4}{32} \text{ mol} = 0.125 \text{ mol}.$$

(*ii*) no. of mol of $H_2 = n(H_2)$

$$= \frac{\text{wt.}}{\text{mol. wt.}} = \frac{2 \text{ g}}{2 \text{ g mol}^-} = 1 \text{ mol}$$

(*iii*) **For O_2:** $p(O_2) = \dfrac{n(O_2) \times RT}{V} = 0.125 \text{ mol} \times \dfrac{RT}{V}$

For H_2: $p(H_2) = \dfrac{n(H_2) \times RT}{V} = 1 \text{ mol} \times \dfrac{RT}{V}$

∴ **Total pressure** = $p(O_2) + p(H_2)$

$$= \frac{RT}{V}(0.125 \text{ mol} + 1.0 \text{ mol})$$

$$= \frac{1.125 \text{ mol} \times 0.083 \text{ bar dm}^3 \text{ K}^- \text{ mol}^- \times 300 \text{ K}}{1 \text{ dm}^3}$$

= **28.0 atm** **Ans.**

(*iv*) Since the pressure is independent of the shape of the vessel, the pressure will be the same in the cubical cylinder.

EXAMPLE 45. *A vessel of 4.0 L capacity at S.T.P. contains a gaseous mixture of 8 g oxygen and 112 cm^3 of CO_2 at S.T.P. Calculate the pressure exerted by O_2 and CO_2 gases. Also, calculate the total pressure exerted by the mixed gases.*

SOLUTION.

(*i*) **For O_2:** no. of mol of

$$O_2 = n(O_2) = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{8 \text{ g}}{32 \text{ g mol}^-} = 0.25 \text{ mol}$$

P = ?, V = 4.0 L, R = 0.0821 L atm K^- mol^-;

T = 273 K. $P(O_2) = \dfrac{nRT}{V}$

$$= \frac{0.25 \text{ mol} \times 0.0821 \text{ L atm K}^-\text{mol}^- \times 273 \text{ K}}{4.0 \text{ L}}$$

= **1.4 atm**

(*ii*) **For CO_2:** no. of mol of

$$CO_2 = n(CO_2) = \frac{\text{volume of } CO_2 \text{ at } NTP}{\text{molar volume of } CO_2}$$

$$= \frac{112 \text{ cm}^3}{22400 \text{ cm}^3} = 5 \times 10^{-3} \text{ mol}$$

P = ?; V = 4.0 L; R = 0.0821 L atm K^- mol^-;

T = 273 K; $P(CO_2) = \dfrac{nRT}{V}$

$$= \frac{5 \times 10^{-3} \text{ mol} \times 0.0821 \text{ L atm K}^-\text{mol}^- \times 273 \text{ K}}{4.0 \text{ L}}$$

= **0.028 atm**

(*iii*) Total pressure = $P(O_2) + P(CO_2)$ = 1.4 atm + 0.028 atm = **1.428 atm** **Ans.**

EXAMPLE 46. *400 cm^3 of N_2 maintained at 0.6 bar pressure and 1.5 L of H_2 maintained at 0.5 bar pressure are put together in a 2.0 dm^3 flask. If temperature is kept constant, calculate the pressure of the mixture of gases.*

SOLUTION.

(*i*) **For N_2 :** $P_1 = 0.6$ bar,

$$V_1 = 400\ \text{cm}^3 \times \frac{1\text{L}}{1000\ \text{cm}^3} = 0.4\ \text{L}$$

$$P(N_2) = ?,\ V_2 = 2\ \text{dm}^3 = 2\ \text{L}$$

$$(\because\ 1\ \text{dm}^3 = 1\text{L}).$$

By Boyle's law

$$P_1V_1 = P(N_2)\,V_2;$$

$$\mathbf{P(N_2)} = \frac{P_1V_1}{V_2} = \frac{0.6\ \text{bar} \times 0.4\ \text{L}}{2\ \text{L}}$$

$$= \mathbf{0.12\ bar}$$

(*ii*) **For H_2 :** $P_1 = 0.5$ bar, $V_1 = 1.5$ L; $P(H_2) = ?$,

$$V_2 = 2\ \text{dm}^3 = 2\ \text{L}$$

$$P_1V_1 = P(H_2)V_2 \text{ (Boyle's law). So,}$$

$$P(H_2) = \frac{P_1V_1}{V_2}$$

$$P(H_2) = \frac{0.5\ \text{bar} \times 1.5\ \text{L}}{2\ \text{L}} = \mathbf{0.375\ bar}$$

$\therefore$ **Total pressure** $= P(N_2) + P(H_2)$

$= 0.12$ bar $+ 0.37$ bar

$=$ **0.495 bar** **Ans.**

EXAMPLE 47. *When a mixture of benzene and excess H_2 gas having pressure 60 mm of Hg was passed over nickel catalyst, cyclohexane was formed as follows :*

$$C_6H_6(g) + 3H_2(g) \xrightarrow{Ni} C_6H_{12}(g)$$

The pressure was now observed to be 30 mm of Hg in the same volume at the same temperature. How much fraction of benzene by volume was present in the original mixture.

SOLUTION. Reaction: $\underset{1\ \text{mol}}{C_6H_6(g)} + \underset{3\ \text{mol}}{3H_2(g)} \xrightarrow{Ni} \underset{1\ \text{mol}}{C_6H_{12}(g)}$

Initial state : Pressure of

$C_6H_6 = p_1$ mm; pressure of

$H_2\ (g) = p_2$ mm

$\therefore$ $p_1 + p_2 = 60$ mm ...(*A*)

After completion of reaction.

Pressure due to $C_6H_6\ (g) = 0$

$\therefore$ Pressure due to $H_2(g) = p_2 - 3p_1$; Pressure of due to

$C_6H_{12}\ (g) = p_1$

Total pressure due to H_2 and $C_6H_{12}(g)$

$= P_2 - 3p_1 + p_1 = p_2 - 2p_1$

$\therefore$ $p_2 - 2p_1 = 30$ mm ...(*B*)

Subtracting equation (*B*) from equation (*A*), we get :

$p_1 + p_2 - p_2 + 2p_1 = 60 - 30 = 30$ mm; $3p_1 = 30$ mm

$\therefore$ $p_1 = 10$ mm

Hence fraction of C_6H_6 by volume means fraction of its moles or fraction of pressure

$$= \frac{10}{60} = \mathbf{0.167}$$ **Ans.**

EXAMPLE 48. *Calculate the total pressure in a 10 L 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 for gases. R = 0.082 L atm $K^{-}mol^{-}$.* **(Roorkee, 1997)**

SOLUTION.

(*i*) no. of mol of He $= \dfrac{\text{wt.}}{\text{mol. wt}} = \dfrac{0.4\ \text{g}}{4\ \text{g mol}^{-}} = 0.1$ mol

(*ii*) no. of mol of $O_2 = \dfrac{\text{wt.}}{\text{mol. wt.}} = \dfrac{1.6\ \text{g}}{32\ \text{g mol}^{-}} = 0.05$ mol

(*iii*) no. of mol of $N_2 = \dfrac{\text{wt.}}{\text{mol. wt.}} = \dfrac{1.4\ \text{g}}{28\ \text{g mol}^{-}} = 0.05$ mol

Total no. of mol $= 0.1 + 0.05 + 0.05 = 0.2$;

$T = 27 + 273 = 300$ K

Total pressure,

$$P = \frac{nRT}{V}$$

$$= \frac{0.2\ \text{mol} \times 0.0821\ \text{L atm K}^{-}\text{mol}^{-} \times 300\ \text{K}}{10\ \text{L}}$$

$= 0.492$ atm.

(*iv*) Partial pressure of

He gas $= p_{He} \times$ total pressure

$$= \frac{\text{mol of He}}{\text{Total mol}} \times \text{total pressure}$$

$$= \frac{0.1}{0.2} \times 0.492 = \mathbf{0.246\ atm}$$ **Ans.**

EXAMPLE 49. *A mixture of oxygen and hydrogen gases at 1.5 bar pressure contains 30% by weight of hydrogen. Calculate the partial pressure of hydrogen gas.*

SOLUTION. (*i*) wt. of

$H_2 = 30$g; mol. wt. of $H_2 = 2$ g mol^{-}

$\therefore$ no. of mol of $H_2 =$ wt./mol. wt. $= 30/2$

$=$ **15 mol.**

(*ii*) wt. of $O_2 = 100 - 30 = 70$ g;

mol. wt. of $O_2 = 2 \times 16 = 32$ g mol^{-}

$\therefore$ no. of mol of $O_2 =$ wt./mol. wt. $= 70/32$

$=$ **2.1875 mol.**

Total no. of mol $= 15 + 2.1875 = 17.1875$ mol.

$\therefore$ Partial pressure of

$$H_2 = \frac{n_{H_2}}{\text{Total no. of mol}} \times \text{Total pressure}$$

$$= \frac{15}{17.1875} \times 1.5 = \mathbf{1.31\ bar}$$ **Ans.**

EXAMPLE 50. *A gas occupies 100 cm^3 when collected over water at 15°C and 750 mm pressure. It occupies 92 cm^3 in dry state of S.T.P. Find the aqueous tension (or vapour pressure of water) at 15°C.*

SOLUTION. Let aqueous tension at 15° C = p ;

$P_1 = (750 - \text{p})$ mm, $V_1 = 100\ \text{cm}^3$,

$T_1 = 15 + 273 = 288$ K;

At N.T.P. $P_2 = 760$ mm, $V_2 = 92\ \text{cm}^3$,

$T_2 = 273$ K.

But : $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (gas law)}$$

$$\frac{(750-p)\times 100}{288} = \frac{760\times 92}{273};$$

$$750 - p = \frac{760\times 92\times 288}{273\times 100} = 737.6 \text{ mm}$$

$$\therefore \quad p = 750 - 737.6 = \mathbf{12.4\ mm} \qquad \textbf{Ans.}$$

8.9 GRAHAM'S LAW

(*a*) The rates of diffusion of gases are inversely proportional to the square root of their densities or molecular masses.

Mathematically : $r \propto \left(\frac{1}{d}\right)^{½}$.

For any two gases :

$$\frac{r_1}{r_2} = \left(\frac{d_2}{d_1}\right)^{½} = \left(\frac{2\times d_2}{2\times d_1}\right)^{½} = \left(\frac{M_2}{M_1}\right)^{½}.$$

$$= \left(\frac{M_2}{M_1}\right)^{1/2} \times \frac{P_1}{P_2}$$

Also, $$\frac{r_1}{r_2} = \frac{V_1t_2}{V_2t_1} \qquad \left[\because r = \frac{\text{Volume}}{\text{Time}}\right]$$

where V_1 and V_2 are the volume of gases 1 and 2 and t_1 and t_2 are the times of diffusion of gases 1 and 2 respectively.

(*b*) When a gas is allowed to escape through a pinhole into vacuum or low pressure, the process is called *effusion* (*E*). The rate of effusion of a gas is inversely proportional to its density or molecular mass.

Mathematically : $E \propto \left(\frac{1}{d}\right)^{½}$. Like diffusion of gases, for any two gases :

$$\frac{E_1}{E_2} = \left(\frac{d_2}{d_1}\right)^{½} = \left(\frac{2\times d_2}{2\times d_1}\right)^{½} = \left(\frac{M_2}{M_1}\right)^{½} = \frac{V_1t_2}{V_2t_1}$$

Example 51. *Chlorine gas and H_2S gases have different distinct odours. If both of these gases are simultaneously released in one corner of the laboratory under similar conditions, which gas will be detected first by the students and why?*

Solution.

(*i*) Cl_2 gas. Mol. wt. = 2 × 35.5 = 71 g mol^{-}; rate of diffusion = r_1;

(*ii*) H_2S gas; Mol. wt. = (2 × 1) + 32 = 34 g mol^{-}; rate of diffusion = r_2.

But $$\frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{½};$$

$$\frac{r_1}{r_2} = \left(\frac{34}{71}\right)^{½} = (0.4788)^{½} = 0.692;$$

(Graham's law of diffusion)

$$r_1 = r_2 \times 0.692$$

Thus the rate of diffusion of Cl_2 is less than that of H_2S by the factor 0.692. So, H_2S is a lighter gas and hence diffuses at a faster rate and will be detected first.

Example 52. *The pressure in a bulb dropped from 2000 to 1500 mm of mercury in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio 1:1 at total pressure of 4000 mm of mercury was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 minutes.* **(IIT, 1981)**

Solution. Molar ratio of oxygen : another gas = 1:1; Total pressure = 4000 mm.

Hence, partial pressure of $O_2 = \frac{1}{1+1}\times 4000 = 2000$ mm

Also, partial pressure of another gas = 4000 – 2000 = 2000 mm.

Drop in pressure = 2000 mm – 1500 mm = 500 mm.

Drop in pressure in 47 minutes = 500 mm

$\therefore$ Drop in pressure in 74 minutes = $\frac{500}{47}\times 74$

= 787.2 mm.

(*i*) Pressure of O_2 after 74 minutes = 2000 – 787.2 = **1212.8 mm.**

Mol. wt. of O_2 = 2 × 16 = 32 g mol^{-}

mol. wt. of another gas = 79 g mol^{-}

Rate of diffusion of O_2 and another gas = r_{O_2} and r_n respectively

$$\therefore \quad \frac{r_n}{r_{O_2}} = \left(\frac{M_2}{M_1}\right)^{½} = \left(\frac{32}{79}\right)^{½}$$

$\therefore$ Drop in pressure for the other gas

$$= 787.2 \times \left(\frac{32}{79}\right)^{½} = 787.2 \times (0.405)^{1/2}$$

$$= 787.2 \times 0.6364 = 501 \text{ mm.}$$

(*ii*) Pressure of another gas after 74 minutes = 2000 – 501 = 1499 mm

$$\therefore \quad \text{Molar ratio} = \frac{\text{Mol of another gas}}{\text{Mol of } O_2} = \frac{1499}{1212.8}$$

$$= \mathbf{1.24 : 1} \quad \textbf{Ans.}$$

Type. Use of mole fraction.

Example 53. *The molar volume of liquid benzene [density = 0.877 g (mL)$^{-}$] increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene [density = 0.867 g (mL)$^{-}$] increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has vapour pressure of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.* **(IIT, 1996)**

Solution. Volume = $\frac{\text{mass}}{\text{density}}$;

mol. wt. of C_6H_6 = (6 × 12) + (6 × 1) = 78 g mol^{-}

(*i*) Volume of 1 mol of

$$C_6H_6\,(l) = \frac{\text{mol. wt.}}{\text{density}} = \frac{78 \text{ g mol}^{-}}{0.877 \text{ g (mL)}^{-}}$$

$$= 88.94 \text{ mL}$$

Volume of 1 mol. of

$$C_6H_6\,(g) = 2750 \times 88.94 \text{ mL} = \mathbf{244.58\ L}$$

$$[\because 1 \text{ L} = 1000 \text{ mL}]$$

(*ii*) Mol. wt. of toluene

$$C_7H_8\,(g) = (7 \times 12) + (8 \times 1) = 92 \text{ g mol}^{-}$$

∴ Volume of 1 mol of

$$C_7H_8\,(g) = \frac{92 \text{ g mol}^{-}}{0.867 \text{ g (mL}^{-})} \times 7720 = \mathbf{819.19\ L}$$

$$T = 20 + 273 = 293 \text{ K}$$

(*iii*) Vapour pressure of 1 mol of C_6H_6, $p^o{}_{C_6H_6} = \dfrac{nRT}{V}$

$$= \frac{1 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 293 \text{ K}}{244.58 \text{ L}}$$

$$= \mathbf{0.098\ atm.}$$

(*iv*) Vapour pressure of 1 mol of C_7H_8,

$$p^o{}_{C_7H_8} = \frac{nRT}{V}$$

$$= \frac{1 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 293 \text{ K}}{819.19 \text{ L}}$$

$$= \mathbf{0.029\ atm.}$$

Total pressure

$$= \left(\text{mole fraction of } C_6H_6 \times p^0_{C_6H_6}\right) + \left(\text{mole fraction of } C_7H_8 \times p^0_{C_7H_8}\right)$$

$$\frac{46}{760} = x_{C_6H_6} \times 0.098 \text{ atm} + x_{C_7H_8} \times 0.029 \text{ atm} \qquad \ldots(A)$$

But $x_{C_6H_6} + x_{C_7H_8} = 1.$

So, $x_{C_7H_8} = 1 - x_{C_6H_6}.$

Thus, from equation (*A*), we get $\dfrac{46}{760}$ atm

$$= x_{C_6H_6} \times 0.098 \text{ atm} + (1 - x_{C_6H_6}) \times 0.029 \text{ atm}$$

$$= x_{C_6H_6} \times 0.098 \text{ atm} + 0.029 \text{ atm} - x_{C_6H_6} \times 0.029 \text{ atm}$$

$$0.06 \text{ atm} = x_{C_6H_6}[0.098 \text{ atm} - 0.029 \text{ atm}] + 0.029 \text{ atm}$$

$$0.06 \text{ atm} - 0.029 \text{ atm} = 0.069\, x_{C_6H_6};$$

$$0.031 = 0.069\, x_{C_6H_6}$$

$$\therefore x_{C_6H_6} = \frac{0.031}{0.069} = 0.449$$

∴ Mole fraction of benzene in vapour phase

$$= \frac{0.449}{0.06} \times 0.098 = \mathbf{0.733\ Ans.}$$

Type $\dfrac{r_1}{r_2} = \dfrac{V_1t_2}{V_2t_1} = \left(\dfrac{d_2}{d_1}\right)^{½}$

Example 54. *One litre each of H_2 and N_2 weigh 0.09 g and 1.25 g respectively. Calculate the volume of H_2 that would diffuse through a porous membrane of two square centimeters in area in the same time as 75 mL of N_2 gas.*

Solution.

(*i*) $\mathbf{H_2}$. wt. = 0.09g, Volume = 1L

$$\text{density of } H_2 = \frac{\text{Mass}}{\text{Volume}} = \frac{0.09 \text{ g}}{1 \text{ L}}$$

(*ii*) $\mathbf{N_2}$. wt. = 1.25g, Volume = 1 L,

$$\text{density of } N_2 = \frac{\text{Mass}}{\text{Volume}} = \frac{1.25 \text{ g}}{1 \text{ L}};$$

time for N_2 and $H_2 = t$; Volume of N_2 = 75 mL Volume of H_2 = ?

$$\text{We know that}: \frac{r_{H_2}}{r_{N_2}} = \frac{V_{H_2}}{t} \Big/ \frac{V_{N_2}}{t} = \left(\frac{d_{N_2}}{d_{H_2}}\right)^{1/2}$$

$$\frac{V_{H_2}}{75} = \left(\frac{1.25}{0.09}\right)^{1/2} = (13.89)^{1/2} = 3.727$$

$$\therefore \qquad V_{H_2} = 3.727 \times 75 \text{ mL} = \mathbf{279.5\ mL}\ \ \textbf{Ans.}$$

Example 55. *Calculate the relative rates of diffusion of $^{235}UF_6$ and $^{238}UF_6$ in the gaseous form (F = 19).* **(IIT, 1976)**

Solution. Let rate of diffusion of

$$^{235}UF_6 = r_1$$

$$\text{mol. wt. of } ^{235}UF_6 = 235 + (6 \times 19) = 349 \text{ g mol}^{-}$$

$$\text{rate of diffusion of } ^{238}UF_6 = r_2$$

$$\text{mol. wt. of } ^{238}UF_6 = 238 + (6 \times 19) = 352 \text{ g mol}^{-}$$

$$\frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{1/2};$$

$$\frac{r_1}{r_2} = \left(\frac{352}{349}\right)^{1/2} = (1.0086)^{1/2} = \frac{1.0043}{1}$$

∴ **Ratio of r_1 and r_2 is : $r_1 : r_2$: : 1.0043:1 Ans.**

Example 56. *100 cm^3 of oxygen were confined in a diffusion tube and exposed to air. At equilibirum, 21.0 cm^3 of air was measured in the tube. When same volume of nitrogen gas was placed in the same tube and exposed to air, 19.7 cm^3 of air were measured in the tube at equilibrium. Calculate the molar mass of nitrogen gas.*

Solution. For oxygen.

Mol. wt. of $O_2 = 2 \times 16 = 32 \text{ g mol}^{-}. = M(O_2)$

$$\frac{\text{Rate of diffusion of } O_2}{\text{Rate of diffusion of air}} = \frac{100 \text{ cm}^3}{21.0 \text{ cm}^3} \qquad \ldots(A)$$

For nitrogen : Mol. wt. of nitrogen = M_{N_2} = ?

$$\frac{\text{Rate of diffusion of } N_2}{\text{Rate of diffusion of air}} = \frac{100 \text{ cm}^3}{19.7 \text{ cm}^3} \qquad \ldots(B)$$

Dividing equations (*A*) and (*B*), we get

$$\frac{\text{Rate of diffusion of } O_2}{\text{Rate of diffusion of } N_2} = \frac{100\ \text{cm}^3}{21\ \text{cm}^3} \times \frac{19.7\ \text{cm}^3}{100\ \text{cm}^3} = \frac{19.7}{21}$$

But $\frac{19.7}{21} = \left(\frac{M(N_2)}{M(O_2)}\right)^{1/2}$ (Graham's law of diffusion)

Squaring both sides, we get :

$$\frac{19.7 \times 19.7}{21 \times 21} = \frac{M(N_2)}{32}$$

$$M(N_2) = \frac{19.7 \times 19.7 \times 32}{21 \times 21} = \mathbf{28.2\ g\ mol^{-}\ Ans.}$$

EXAMPLE 57. *40 cm^3 of hydrogen takes 15 minutes to diffuse out of a vessel. Calculate the time in which 25 cm^3 of nitrogen would diffuse through the vessel under similar conditions.*

SOLUTION. For H_2 :

Volume, $V_1 = 40\ \text{cm}^3$; time, $t_1 = 15$ minutes

Mol. wt. of $H_2 = 2 \times 1 = 2\ \text{g mol}^{-}$.

$$\text{So, } r(H_2) = \frac{\text{Volume}}{\text{time}} = \frac{40\ \text{cm}^3}{15\ \text{min.}}$$

For N_2 : Volume, $V_2 = 25\ \text{cm}^3$, time, $t_2 = ?$

mol. wt. of $N_2 = 2 \times 14 = 28\ \text{g mol}^{-}$.

$$\text{So,} \quad r(N_2) = \frac{\text{Volume}}{\text{time}} = \frac{25\ \text{cm}^3}{t_2}$$

$$\text{But} \quad \frac{r(H_2)}{r(N_2)} = \frac{V(H_2)/t(H_2)}{V(N_2)/t(N_2)} = \left(\frac{M(N_2)}{M(H_2)}\right)^{½}$$

$$\therefore \quad \frac{40/15}{25/t_2} = \left(\frac{28}{2}\right)^{½}$$

$$\frac{40}{15} \times \frac{t_2}{25} = (14)^{1/2} = 3.74$$

$$t_2 = \frac{3.74 \times 15 \times 25}{40} = \mathbf{35\ min} \quad \textbf{Ans.}$$

EXAMPLE 58. *115 mL of a certain gas diffuse in the same time as 123 mL of nitrogen under similar conditions. Calculate the molar mass and write the name of the unknown gas (Mol. wt., $H_2 = 2$ g mol^{-}; $Cl_2 = 71$ g mol^{-}; $O_2 = 32$ g mol^{-}).*

SOLUTION. ***Unknown gas :***

V_1 = Volume = 115 mL, time = $t_1 = t$;

mol. wt. of gas = M_1 = ?

N_2 gas : V_2 = Volume = 123 mL; time = $t_2 = t$

mol. wt. of $N_2 = 2 \times 14 = 28\ \text{g mol}^{-}$.

$$\frac{r(\text{unknown gas})}{r(N_2)} = \frac{V_1/t_1}{V_2/t_2} = \left(\frac{M(N_2)}{M_1}\right)^{½}$$

(Graham's law of diffusion)

$$\therefore \quad \frac{115\ \text{mL}/t}{123\ \text{mL}/t} = \left(\frac{28}{M_1}\right)^{½}; \quad \frac{115}{123} = \left(\frac{28}{M_1}\right)^{½}$$

Squaring both sides, we get :

$$\frac{115 \times 115}{123 \times 123} = \frac{28}{M_1};$$

$$M_1 = \frac{123 \times 123 \times 28}{115 \times 115} = 32\ \text{g mol}^{-}$$

$\therefore$ Molar mass of unknown gas = 32 g mol^{-}. This gas is oxygen (O_2) because its molar mass is same as given for O_2 in the question.

Type. To find mol. wt., V.D., and density of a gas.

$$\text{Density of a gas} = \frac{\text{Mol. wt. in g mol}^{-}}{22400\ \text{cm}^3\ \text{mol}^{-}};$$

$$\text{Mol. wt.} = 2 \times \text{V.D.}$$

EXAMPLE 59. *170 cm^3 of sulphur dioxide (SO_2) diffuses in 20 minutes while 180 cm^3 of a sample gas diffuses in 15 minutes. Calculate the molecular weight and density of gas with respect to hydrogen.*

SOLUTION. (*i*) Mol. wt. of

$SO_2 = 32 + (2 \times 16) = 64\ \text{g mol}^{-}$;

Mol. wt. of sample gas,

M (g) = ?

$$\text{We know that :} \quad \frac{r(SO_2)}{r(\text{gas})} = \frac{V_1/t_1}{V_2/t_2} = \left[\frac{M(\text{gas})}{M(SO_2)}\right]^{½}$$

$$\frac{170/20}{180/15} = \left(\frac{M(\text{gas})}{64}\right)^{½};$$

$$\frac{17}{24} = \left(\frac{M(\text{gas})}{64}\right)^{½}$$

Squaring both sides, we get :

$$\frac{17 \times 17}{24 \times 24} = \frac{M(\text{gas})}{64}.$$

$$\mathbf{M\ (gas)} = \frac{17 \times 17 \times 64}{24 \times 24} = \mathbf{32.11\ g\ mol^{-}\ Ans.}$$

$$(ii) \quad \text{V.D.} = \frac{\text{Mol. wt.}}{2} = \frac{32.11}{2} = 16.05\ \text{g mol}^{-}$$

$$(iii) \quad \text{Density} = \frac{\text{Mol. wt. in g mol}^{-}}{22400\ \text{cm}^3\ \text{mol}^{-}}$$

($\because$ 1 mol of a gas occupies volume = 22400 cm^3)

$$= \frac{32.11\ \text{g mol}^{-}}{22400\ \text{cm}^3\ \text{mol}^{-}} = 1.43 \times 10^{-3}$$

$$= \mathbf{0.00143\ g\ cm^{-3}} \quad \textbf{Ans.}$$

EXAMPLE 60. *20 cm^3 of a gaseous hydrocarbon (having same rate of diffusion as N_2) and methane effuse through a hole in 150 minutes while the same volume of nitrogen effuses in 174 minutes under the same conditions. Calculate the contraction in volume if 20 mL of this mixture is exploded with excess of oxygen.*

SOLUTION. Let t_1 = Time of diffusion of N_2 gas;
t_2 = Time of diffusion of hydrocarbon.

$$\frac{t_2}{t_1} = \left(\frac{M_2}{M_1}\right)^{1/2} ; \quad \frac{150}{174} = \left(\frac{M_2}{28}\right)^{1/2}$$

[$\because$ Mol. wt. of $N_2 = 2 \times 14 = 28$ g mol^{-}]

Squaring both sides, we get : $\dfrac{150 \times 150}{174 \times 174} \times 28 = M_2$.

So, $\quad M_2$ **= 20.8.**

Let volume of hydrocarbon = x mL

$$\therefore \quad 20.8 = \frac{x \times 28 + (20 - x) \times 16}{20}$$

$$\left[\begin{array}{l} \because \text{ mol. wt. of methane, } CH_4 \\ \qquad = 12 + (4 \times 1) = 16 \text{ g mol}^{-}; \\ \text{of } N_2 = 2 \times 14 = 28 \text{ g mol}^{-} \end{array}\right]$$

$$20.8 \times 20 = 28x + 320 - 16x$$

$$\therefore \quad 12x = 416 - 320 = 96$$

$$x = \frac{96}{12} = 8$$

$$\therefore \quad x = 8 \text{ mL}$$

Since, mol. wt. of hydrocarbon = mol. wt. of N_2 = 28 g mol^{-},

so, the hydrocarbon will be C_2H_4.

Reaction. $\underset{1 \text{ vol}}{C_2H_4} + 3O_2 \longrightarrow 2CO_2 + \underset{2 \text{ vol}}{2H_2O}$

$\because$ for 1 volume of C_2H_4, contraction in volume of H_2O = 2 volume

$\therefore$ for 8 mL of C_2H_4, contraction in volume of H_2O = 2 × 8 = **16 mL**

Total volume of hydrocarbon + CH_4 (methane) = 20 mL

$\therefore$ 8 mL + volume of CH_4 = 20 mL

$\therefore$ Volume of CH_4 = 20 mL – 8 mL = 12 mL

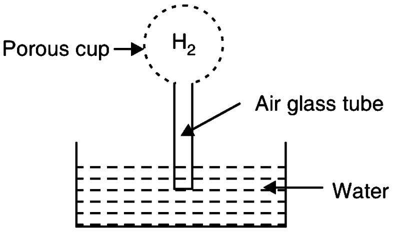
Reaction : $\underset{1 \text{ vol}}{CH_4} + O_2 \longrightarrow CO_2 + \underset{2 \text{ vol}}{2H_2O}$

For 1 volume of CH_4, contraction in volume of H_2O = 2 volume

$\therefore$ For 12 mL of CH_4, contraction in volume of H_2O = 2 × 12 = 24 mL

$\therefore$ Total contraction = 16 mL + 24 mL = **40 mL Ans.**

EXAMPLE 61. *A porous cup was joined to a glass tube which has one end dipped in water as shown in the figure. Explain why water rises in the glass tube?*



SOLUTION. Density of H_2 is less than that of air. Also, $\left(r \propto \dfrac{1}{d}\right)^{1/2}$. So, H_2 gas effuses out of porous cup faster than the air effuses in. As a result, pressure in the cup falls and water is pushed up in the tube by the pressure of air.

EXAMPLE 62. *An unknown saturated hydrocarbon gas effuses out about half as fast as methane. Calculate the molecular formula of the unknown gas.*

SOLUTION.

Mol. wt. of methane (CH_4) = 12 + (4 × 1) = 16 g mol^{-}

Mol. wt. of unknown gas = M

$$\frac{r(\text{unknown gas})}{r_{CH_4}} = \left(\frac{16 \text{ g mol}^{-}}{M}\right)^{1/2} ;$$

$$\frac{1}{2} = \left(\frac{16 \text{ g mol}^{-}}{M}\right)^{1/2} .$$

Squaring both sides, we get :

$$\frac{1}{4} = \frac{16 \text{ g mol}^{-}}{M} ; \; M = 64 \text{ g mol}^{-}.$$

Let molecular formula of unknown saturated hydrocarbon = C_nH_{2n+2}.

Hence (n × 12) + (2n + 2) × 1 = 64;

12n + 2n + 2 = 64; 14n = 62; n = 62/14 ≃ 4.

Hence, formula of hydrocarbon = $C_4H_{2 \times 4 + 2}$ = $\mathbf{C_4H_{10}}$ *i.e.*, **butane.**

EXAMPLE 63. *A gaseous mixture contains H_2 and methane. One litre oxygen effused in 10 minutes while the mixture effused in 5 minutes and 11 seconds. Calculate (i) the density of the mixture and (ii) percentage by volume of each gas in the mixture.*

SOLUTION. (*i*) ***Mixture.***

V_1 = 1L, t_1 = 5 min and 11 sec.
= (5 × 60) + 11 = 311 sec.

(*ii*) $\mathbf{O_2}$ $\quad V_2$ = 1L, t_2 = 10 min = 10 × 60
= 600 sec.

$$\frac{r_{Mix}}{r_{O_2}} = \frac{V_1 t_2}{V_2 t_1} = \left(\frac{d_{O_2}}{d_{mix}}\right)^{1/2} ;$$

$$\frac{1\text{L} \times 600 \text{ sec}}{1\text{L} \times 311 \text{ sec}} = \left(\frac{16}{d_{mix}}\right)^{1/2}$$

$$\frac{600}{311} = \left(\frac{16}{d_{mix}}\right)^{1/2}$$

Squaring both sides, we get : $\dfrac{600 \times 600}{311 \times 311} = \dfrac{16}{d_{mix}}$

$$\therefore \quad d_{mix} = \frac{16 \times 311 \times 311}{600 \times 600} = 4.3 \text{ g L}^{-}$$

(*ii*) Mol. wt. of CH_4 = 12 + (4 × 1) = 16 g mol^{-},
mol. wt. of H_2 = 2 × 1 = 2 g mol^{-}

$\therefore$ V.D. of CH_4 = 16/2 = 8;
V.D. of H_2 = 2/2 = 1

Let % age volume of
CH_4 = a; of H_2 = 100 – a;

$$4.3 = \frac{(a \times 8) + (100 - a) \times 1}{100}$$

$$4.3 \times 100 = 8\,a + 100 - a$$

or $$7\,a = 430 - 100 = 330;$$

$$a = \frac{330}{7} = 47.14\%$$

$\therefore$ % age by volume of

$$CH_4 = \mathbf{47.14\%;}$$

$$H_2 = 100 - 47.14 = \mathbf{52.86\%} \quad \textbf{Ans.}$$

EXAMPLE 64. *100 mL of a gaseous mixture contains 90% unknown gas and 10% carbon monoxide gas. This gaseous mixture effused through an effusiometer in 1 minute and 26 seconds. 100 mL of oxygen (having relative density, 16) effuses through the same effusiometer in 1 minute and 15 seconds. Calculate the density of unknown gas.*

SOLUTION.

(*i*) ***Mixture.*** t_1 = 1 min. 26 sec

= (1 × 60) + 26 = 86 sec,

density = d

V_1 = 100 mL.

(*ii*) $\mathbf{O_2}$. t_2 = 1 min. 15 sec = (1 × 60) + 15

= 75 sec; density = 16

V_2 = 100 mL.

$$\frac{r_{mix}}{r_{O_2}} = \frac{V_1/t_1}{V_2/t_2} = \left(\frac{d_{O_2}}{d_{mix}}\right)^{½};$$

$$\frac{100}{86} \Big/ \frac{100}{75} = \left(\frac{16}{d_{mix}}\right)^{½}$$

$$\frac{75}{86} = \left(\frac{16}{d_{mix}}\right)^{½}$$

Squaring both sides, we get :

$$\frac{75 \times 75}{86 \times 86} = \frac{16}{d_{mix}}$$

$$d_{mix} = \frac{86 \times 86 \times 16}{75 \times 75} = 21.04$$

$$\text{Density of CO} = \frac{\text{Mol. wt.}}{2} = \frac{12 + 16}{2} = 14$$

density of unknown gas = d.

Hence $$21.04 = \frac{(10 \times 14) + (90 \times d)}{100}$$

[$\because$ CO = 10%; unknown gas = 90%]

$$21.04 \times 100 = 140 + 90\,d;$$

$$90\,d = 2104 - 140 = 1964$$

$$d = \frac{1964}{90} = \mathbf{21.82} \quad \textbf{Ans.}$$

EXAMPLE 65. *It was found that a sample of ozonised oxygen diffuses 0.98 times as fast as pure O_2 gas. Calculate the percentage by volume and by weight of ozone in the sample.*

(V.D. of O_2 = 16; O_3 = 24).

SOLUTION. $r_{O_2} = 1, r_{sample} = 0.98;$

mol. wt. of O_2 = 2 × 16 = 32 g mol⁻

Mol. wt. of sample = ?

$$\frac{r_{O_2}}{r_{(sample)}} = \left(\frac{M(sample)}{M\,(O_2)}\right)^{1/2}$$

$$= \left(\frac{M(sample)}{32}\right)^{1/2}$$

$$\frac{1}{0.98} = \left(\frac{M(sample)}{32}\right)^{1/2}.$$

Squaring both sides, we get :

$$\frac{1}{0.98 \times 0.98} = \frac{M(sample)}{32}$$

$$\therefore \quad M\,(sample) = \frac{32}{0.98 \times 0.98} = 33.32 \text{ g mol}^-$$

(*a*) *To find percentage by volume of O_3*

(mol. wt. = 3 × 16 = 48 g mol⁻)

Let volume or mol of

O_3 = a; of O_2 = 100 – a

$$\therefore \quad \frac{a \times 48 + (100 - a) \times 32}{100} = M\,(sample) = 33.32$$

$$48\,a + 3200 - 32\,a = 33.32 \times 100 = 3332;$$

$$16\,a = 3332 - 3200 = 132$$

$$\therefore \quad a = \frac{132}{16} = \mathbf{8.25\ \%} \qquad \textbf{Ans.}$$

(*b*) *To find percentage by weight of O_3 (mol. wt., 48)*

$$\frac{a}{48} + \frac{100 - a}{32} = \frac{100}{M(sample)}$$

$$\frac{a}{48} + \frac{100 - a}{32} = \frac{100}{33.32}$$

or $$32\,a + 4800 - 48\,a = \frac{100 \times 48 \times 32}{33.32} = 4609.84$$

$$-16\,a = -190.16;$$

$$a = \frac{190.16}{16} = \mathbf{11.88\%} \qquad \textbf{Ans.}$$

Type. When quantity of gas in m mol/hour etc. is given.

EXAMPLE 66. *At a particular pressure, helium gas (at. wt., 4) escaped into an evacuated space through a small thin orfice at the rate of 5.2 m mol/hour. Calculate the time that it takes for 12 m mol of SO_2 to leak through a similar orfice if SO_2 were confined at the same pressure. (At. wt. S = 32, O = 16).*

SOLUTION. At. wt. of

He = Mol. wt. of He = 4.0 (given)

Mol. wt. of SO_2 = 32 + 2 (16) = 64.0.

$$\frac{r(\text{He})}{r(\text{SO}_2)} = \left(\frac{\text{M}(\text{SO}_2)}{\text{M}(\text{He})}\right)^{1/2} = \left(\frac{64}{4}\right)^{1/2} = 4.$$

i.e., helium escapes at a rate 4 times as fast as SO_2.

$$\text{Thus : } r(\text{SO}_2) = \frac{r(\text{He})}{4} = \frac{5.2 \text{ m mol}}{\text{hour}} \times \frac{1}{4} = \frac{1.3 \text{ m mol}}{\text{hour}}$$

∴ Time for 12 m mol of SO_2 to leak

$$= 12 \text{ m mol SO}_2 \times \frac{1 \text{ hour}}{1.3 \text{ m mol}}$$

$$= \mathbf{9.23 \text{ hour}} \qquad \textbf{Ans.}$$

EXAMPLE 67. *Pressure in a vessel containing nitrogen dropped from 1000 torr to 800 torr in 47 minutes when N_2 gas leaked through a thin small orfice into a vacuum. When the same vessel was filled with another gas, the above drop in pressure took 72 minutes. Calculate the molecular mass of the second gas. (At. wt., N = 14).*

SOLUTION. Mol. mass of

$$\text{N}_2 = 2 \times 14 = 28 \text{ g mol}^{-}$$

Molecular mass of second gas = M.

$$\frac{r(\text{N}_2)}{r(\text{second gas})} = \left(\frac{t(\text{second gas})}{t(\text{N}_2)}\right)$$

$$= \left(\frac{\text{M}}{\text{M}(\text{N}_2)}\right)^{1/2} \left[\because \frac{r_1}{r_2} = \frac{t_2}{t_1}\right]$$

$$\left(\frac{72 \text{ min}}{47 \text{ min}}\right) = \left(\frac{\text{M}}{28 \text{ g mol}^{-}}\right)^{1/2}.$$

Squaring both sides, we get

$$\frac{72 \times 72}{47 \times 47} = \frac{\text{M}}{28 \text{ g mol}^{-}};$$

$$M = \frac{72 \times 72 \times 28 \text{ g mol}^{-}}{47 \times 47}$$

$$\text{or} \qquad M = \mathbf{65.7 \text{ g mol}^{-}} \qquad \textbf{Ans.}$$

Type. When pressure drop due to effusion is given, use : Rate of pressure drop is directly proportion to rate of effusion.

EXAMPLE 68. *A container contains helium gas (Mol. wt. = 4 g mol^{-}) at 290 K and 1 atmospheric pressure. The gas effuses through a small thin orfice into outer space at such a rate that the pressure drops by 0.28 torr s^{-} (i) if the vessel were filled with CO at the same temperature and pressure, what would be the rate of pressure drop (ii) if the vessel were filled with 15.0 mol % neon, 40.0 mol % nitrogen and 45.0 mol % carbondioxide at a total pressure of 1.0 atmosphere and 290 K, calculate the corresponding rate of pressure drop. (At. wt., He = 4, N = 14, C = 12, O = 16, Ne = 20.2)*

SOLUTION. At. wt. of He = Mol. wt. of He = 4.0 g mol^{-}

mol. wt. of NH_3 = 14 + (3 × 1) = 17 g mol^{-}

mol. wt. of N_2 = 2 × 14 = 28 g mol^{-}

mol. wt. of CO_2 = 12 + (2 × 16) = 44 g mol^{-}

mol. wt. of CO = 12 + 16 = 28 g mol^{-}.

(*i*) We know that rate of effusion is directly proportional to the rate of pressure drop.

$$\text{So;} \quad \frac{r(\text{He})}{r(\text{CO})} = \left(\frac{\text{M(CO)}}{\text{M(He)}}\right)^{1/2}$$

$$= \left(\frac{28 \text{ g mol}^{-}}{4 \text{ g mol}^{-}}\right)^{1/2} = 2.64$$

$$\therefore \quad r(\text{CO}) = \frac{r(\text{He})}{2.64}$$

$$\mathbf{r(CO)} = \frac{0.28 \text{ torr s}^{-}}{2.64} = \mathbf{0.106 \text{ torr. s}^{-}} \quad \textbf{Ans.}$$

(*ii*) The average mol. wt. of the gas is

$$= \left(\frac{15}{100} \times 20.2\right) + \left(\frac{40}{100} \times 28\right) + \left(\frac{45}{100} \times 44\right)$$

$$= 3.03 + 11.2 + 19.8 = 34.03$$

$$\therefore \quad \frac{r(\text{gas})}{r(\text{He})} = \left(\frac{4 \text{ g mol}^{-}}{34.03 \text{ g mol}^{-}}\right)^{1/2};$$

$$r(\text{gas}) = \left(\frac{4}{34.03}\right)^{1/2} \times r(\text{He})$$

$$\therefore \quad r\text{ (gas)} = (0.118)^{½} \times 0.28 \text{ torr. s}^{-}$$

$$= 0.34 \times 0.28 \text{ torr. s}^{-}$$

$$= \mathbf{0.09 \text{ torr. s}^{-}} \qquad \textbf{Ans.}$$

$$\textbf{Type.} \qquad \frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{½} \times \frac{P_1}{P_2};$$

$$r_1 = \frac{w_1}{t_1};\ r_2 = \frac{w_2}{t_2}$$

Partial pressure of a gas α no. of mole, *n*

EXAMPLE 69. *A mixture containing 1.12 litre, D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.1 g of D_2. Calculate the percent by weight of the gases in the second bulb.*

(Roorkee, 1998)

SOLUTION. Mol. wt. of

$$\text{H}_2 = 2 \times 1 = 2 \text{ g mol}^{-};$$

mol. wt. of ${}^2_1\text{D}_2$ = 2 × 2 = 4 g mol^{-}

(*i*) 22.4 L H_2 weighs = g. mol. wt. of

$$\text{H}_2 = 2 \text{ g} = 1 \text{ mol}$$

$$2.24 \text{ L H}_2 \text{ weighs} = \frac{2 \text{ g}}{22.4 \text{ L}} \times 2.24 \text{ L}$$

0.2 g

$$= 0.2\ \text{g} = \frac{0.2\ \text{g}}{2\ \text{g mol}^-} = \mathbf{0.1\ mol}$$

(*ii*) 22.4 L D_2 weighs = g. mol wt. of

D_2 = 4 g = 1 mol.

$$1.12\ \text{L}\ D_2\ \text{weighs} = \frac{4\ \text{g}}{22.4\ \text{L}} \times 1.12\ \text{L}$$

0.2 g

$$= 0.2\ \text{g} = \frac{0.2\ \text{g}}{4\ \text{g mol}^-} = \mathbf{0.05\ mol}$$

When these mol of H_2 and D_2 are placed in a vessel having V and T as constant, their partial pressures will be different. Using P α *n*, we have :

$$\frac{P(D_2)}{P(H_2)} = \frac{0.05\ \text{mol}}{0.10\ \text{mol}} = \mathbf{0.5}$$

(*iii*) wt. of D_2 left in first bulb after diffusion = 0.1 g

wt. of D_2 originally in first bulb = 0.2 g (found above)

∴ wt. of D_2 diffused into second bulb = 0.2 – 0.1 = 0.1 g

wt. of H_2 in second bulb = w(H_2) = ?

$$\frac{r(D_2)}{r(H_2)} = \frac{V(D_2)}{V(H_2)} \times \frac{t(H_2)}{t(D_2)} = \left[\frac{M(H_2)}{M(D_2)}\right]^{1/2} \times \frac{P(D_2)}{P(H_2)}$$

$$\text{Thus,} \quad \frac{w(D_2)}{w(H_2)} \times \frac{t(H_2)}{t(D_2)} = \left(\frac{M(D_2)}{M(H_2)}\right)^{½} \times \frac{P(D_2)}{P(H_2)}$$

$$\left[\begin{array}{l} \because \dfrac{V_1}{t_1} = \dfrac{w_1}{d_1 t_1};\ \dfrac{V_2}{t_2} = \dfrac{w_2}{d_2 t_2};\ \dfrac{V_1 t_2}{t_1 V_2} = \dfrac{d_2 t_1 w_1}{d_1 t_2 w_2} \\ \text{or}\quad \dfrac{V_1 t_2}{V_2 t_1}\ \alpha\ \dfrac{d_2}{d_1}\ \text{or}\ \dfrac{M_2}{M_1} \end{array}\right]$$

$$\frac{0.1}{w(H_2)} \times \frac{t}{t} = \left(\frac{4}{2}\right)^{1/2} \times \frac{1}{2}$$

$$\frac{0.1}{w(H_2)} = (2)^{1/2} \times \frac{1}{2} = 1.4142 \times \frac{1}{2}$$

$$\therefore \quad w\,(H_2) = \frac{2 \times 0.1}{1.4142} = 0.14\ \text{g}$$

∴ Total wt. of D_2 and H_2 in the second bulb

= 0.1 + 0.14 = 0.24 g

∴ % age of D_2 in second bulb

$$= \frac{w(D_2)}{\text{Total wt.}} \times 100 = \frac{0.1 \times 100}{0.24}$$

= **41.67%** **Ans.**

% age of H_2 in second bulb

$$= \frac{w(H_2)}{\text{Total wt.}} \times 100 = \frac{0.14 \times 100}{0.24}$$

= **58.33%** **Ans.**

EXAMPLE 70. *The atomic weight of helium, oxygen and sulphur are 4, 16 and 32 respectively. Helium and sulphur dioxide in equal volumes are contained in a glass vessel. If the gases leak out through a pin hole, what will be the ratio of the rates of escape of helium to that of sulphur dioxide.*

(OJEE, 1980)

SOLUTION. At. wt. of He

= Mol. wt. of He (being mono atomic)

= 4 g mol$^-$

mol. wt. of SO_2 = 32 + (2 × 16) = 64 g mol$^-$.

$$\text{Thus :}\ \frac{r(\text{He})}{r(SO_2)} = \left[\frac{M(SO_2)}{M(\text{He})}\right]^{1/2} = \left(\frac{64}{4}\right)^{1/2}$$

$$= (16)^{½} = \frac{4}{1}$$

∴ Ratio of rate of escape of He : SO_2 = **4 :1** **Ans.**

EXAMPLE 71. *The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl^-$) which is attained at 1200°C is determined by measuring, the rate of effusion through a pin hole. It is observed that at 1.8 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. (at. wt., Kr = 84).* **(IIT, 1995)**

SOLUTION. (*i*) Normal mol. wt. of

Cl_2 = 2 × 35.5 = 71 g mol$^-$

(*ii*) *To find experimental mol. wt. of Cl_2.* Using the formula for rate of effusion of gases, we have:

$$\frac{r(\text{mixture})}{r(Kr)} = \left(\frac{M(Kr)}{M(\text{mix})}\right)^{1/2};\ 1.16 = \left(\frac{84}{M}\right)^{1/2}$$

Squaring both sides, we get :

$$(1.16)^2 = \frac{84}{M};\ M = \frac{84}{1.16 \times 1.16} = 62.426$$

(*iii*) Let α = degree of dissociation of Cl_2. Thus :

$$\begin{array}{lcc} & Cl_2 & \rightleftharpoons\ 2\,Cl^- \\ \text{Initial mol} & 1 & 0 \\ \text{Mol at equilibrium} & 1-\alpha & 2\,\alpha \end{array}$$

Total number of mol. = 1 – α + 2 α = 1 + α

$$\therefore \frac{\text{Normal mol. wt. of } Cl_2}{\text{Experimental mol. wt. of } Cl_2} = 1 + \alpha$$

$$\frac{71}{62.426} = 1 + \alpha;\ \alpha = \frac{71}{62.426} - 1 = 1.137 - 1$$

= 0.137

or α = 0.137 × 100 = **13.7%** **Ans.**

8.10 BOLTZMANN'S CONSTANT, K

The relation $\frac{R}{N}$ is called Boltzmann's constant.

R = gas constant = 8.314 × 10^7 erg K$^-$ mol$^-$ = 8.314 J K$^-$ mol$^-$; N = Avogadro no. = 6.023 × 10^{23} = 1 mol of a substance.

K.E. per **mol** $= \frac{3}{2}\times RT$; **Total K.E. for 'n' mol**

$$= \frac{3}{2}nRT$$

Average K.E. per molecule

$$= \frac{3}{2}\times\frac{R}{N}\times T = \frac{3}{2}\,kT$$

where k = Boltzmann constant $= \frac{R}{N}$

Example 72. *Calculate the total as well as average kinetic energy of 48 g methane molecules at 27°C. ($R = 8.314$ J K^{-} mol^{-}, Boltzmann constant $= 1.38 \times 10^{-23}$ J K^{-} $molecule^{-}$).*

Solution. wt. of CH_4 = 48 g; mol. wt. of CH_4 = 12 + (4 × 1) = 16 g mol^{-}

$$\text{no. of mol, } n = \frac{\text{wt.}}{\text{Mol. wt}} = \frac{48\text{ g}}{16\text{ g mol}^{-}} = 3\text{ mol}$$

$R = 8.314$ J K^{-} mol^{-};

$T = 27 + 273 = 300$ K.

We know that :

(*i*) Total K. E. $= \frac{3}{2}\,nRT = \frac{3}{2}\times 3\text{ mol}\times 8.314\text{J K}^{-}\text{ mol}^{-}\times 300\text{ K}$

= 11223.9 J **Ans.**

(*ii*) Average K.E. per molecule $= \frac{3}{2}\,kT$

$$= \frac{3}{2}\times 1.38\times 10^{-23}\text{ J K}^{-}\text{molecule}^{-}\times 300\text{ K}$$

= 6.21 × 10^{-21} J molecule^{-} **Ans.**

Example 73. *Calculate the root mean square velocity of a mist particle having mass 10^{-10} g at 25°C if kinetic molecular theory attributes an average translational kinetic energy to these mist particles. ($R = 8.314 \times 10^7$ erg K^{-} $mole^{-}$ $= 8.314 \times 10^7$ g cm^2 $s^{-2}K^{-}$ mol^{-}).*

Solution. u_{rms} = ?; T = 25 + 273 = 298 K,

$m = 10^{-10}$g; K.E. of particle $= \frac{1}{2}\,mu^2$

where u is root mean square velocity of mist particles. We know that :

K.E. per molecule,

$$\frac{1}{2}\,mu^2 = \frac{3}{2}\times\frac{RT}{N} \text{ where N} = 6.023 \times 10^{23}$$

$$\therefore \quad u = \left(2\times\frac{3}{2}\times\frac{RT}{Nm}\right)^{1/2}$$

$$= \left(2\times\frac{3}{2}\times\frac{8.314\times 10^7\text{ g cm}^2 s^{-2}\text{K}^{-}\text{mol}^{-}\times 300\text{K}}{6.023\times 10^{23}\text{ mol}^{-}\times 10^{-10}\text{g}}\right)^{1/2}$$

$$= (12.42 \times 10^{-4}\text{ cm}^2\text{s}^{-2})^{½}$$

$\therefore$ u = **3.52 × 10^{-2} cm s^{-}** **Ans.**

Example 74. *Calculate the total and average translation kinetic energy in joule of 3.0 g of ethane at 37° C. (at. wt., C = 12, H = 1)*

Solution. For ethane, C_2H_6, Mol. wt. (= M)

= (2 × 12) + (6 × 1) = 30 g mol^{-};

$R = 8.314 \times 10^7$ g cm^2 s^{-2};

$T = 273 + 37 = 310$ K.

(*i*) $u_{rms} = \left(\frac{3\text{ RT}}{\text{M}}\right)^{½}$

$$= \left(\frac{3\times 8.314\times 10^7\text{ g cm}^2\text{ s}^{-2}\times 310\text{ K}}{30\text{ g mol}^{-}}\right)^{1/2}$$

$= (25.8 \times 10^8\text{ cm}^2\text{ s}^{-2})^{½} = 5.08 \times 10^4$ cm s^{-}

(*ii*) Total K.E. mol^{-} $= \frac{1}{2}$ M U^2

$= \frac{1}{2} \times 30$ g mol^{-} × $(5.08 \times 10^4\text{ cm s}^{-})^2$

$= 3.87 \times 10^{10}$ g cm^2s^{-2} mol^{-}

= 3.87 × 10^{10} erg mol^{-}

Since mol. wt. of C_2H_6 = 30 g mol^{-},

So : 30 g C_2H_6 has K.E. = 3.87 × 10^{10} ergs

∴ 3 g C_2H_6 has

$$\text{K.E.} = \frac{3.87\times 10^{10}\text{ ergs}\times 3\text{ g}}{30\text{ g}}$$

$= 3.87 \times 10^9$ ergs

$= 3.87\times 10^9\text{ ergs}\times\frac{1\text{ J}}{10^7\text{ ergs}}$

= 387 J **Ans.**

(*iii*) Average K.E. per molecule

$$= \frac{\text{K.E. mol}^{-}}{\text{Avogadro no.}} = \frac{3.87\times 10^{10}\text{ erg}}{6.023\times 10^{23}}$$

$= 6.4 \times 10^{-14}$ erg

$= 6.4\times 10^{-14}\text{ erg}\times\frac{1\text{ J}}{10^7\text{ergs}}$

= 6.4 × 10^{-21} J Ans.

Example 75. *The mean kinetic energy of a molecule at 27°C is 6.174 × 10^{-14} erg $molecule^{-}$. Calculate the value of Boltzmann's constant and Avogadro number. ($R = 8.314 \times 10^7$ erg K^{-} mol^{-})*

Solution. $R = 8.314 \times 10^7$ erg K^{-} mol^{-};

Boltzmann constant, k = ?;

Mean (or average)

$K.E.$ = 6.174 ×10^{-14} erg $molecule^{-}$;

$T = 27 + 273 = 300$ K

(*i*) Mean $K.E. = \frac{K.E.\text{ mol}^{-}}{\text{Avogadro no, N}}$

$$= \frac{3}{2}\times\frac{RT}{N} = \frac{3}{2}\times\frac{R}{N}\times T = \frac{3}{2}kT$$

6.174 × 10^{-14} erg $molecule^{-}$

$$= \frac{3}{2}\times k\times 300\text{ K}$$

$$\therefore \quad k = \frac{2\times 6.174\times 10^{-14}\text{ erg molecule}^{-}}{3\times 300\text{ K}}$$

$$= 1.372 \times 10^{-16}\ \text{erg K}^{-}\ \text{molecule}^{-}$$

(*ii*) Avogadro no. $= \dfrac{R}{k}$

$$= \frac{8.314\times10^{7}\ \text{erg K}^{-}\ \text{molecule}^{-}}{1.372\times10^{-16}\ \text{erg K}^{-}\ \text{molecule}^{-}}$$

$$= \mathbf{6.06 \times 10^{23}} \qquad \textbf{Ans.}$$

8.11 PHYSICAL SIGNIFICANCE OF GAS CONSTANT, R

$$R = \frac{PV}{nT} = \frac{\text{Pressure}\times\text{Volume}}{\text{mol}\times\text{Temperature}}$$

$$= \frac{(\text{Force/area})\times\text{Volume}}{\text{mol}\times\text{temperature}}$$

$$= \frac{\text{Force}\times\text{length}}{\text{mol}\times\text{temperature}}$$

$$= \frac{\text{work}}{\text{mol}\times\text{temperature}}$$

Values of *R* in different units. One mole of a gas at NTP (1 atm, 273 K), occupies 22.4L volume.

$$\therefore \quad R = \frac{1\ \text{atm}\times 22.4\ \text{L}}{1\ \text{mol}\times 273\ \text{K}} = 0.0821\ \text{L atm K}^{-}\text{mol}^{-}$$

$$= 8.314 \times 10^{7}\ \text{ergs K}^{-}\ \text{mol}^{-} = 8.314\ \text{J K}^{-}\ \text{mol}^{-}$$

$$= 8.314\ \text{Nm K}^{-}\text{mol}^{-} = 8.314\ \text{k Pa dm}^{3}\ \text{K}^{-}\text{mol}^{-}$$

$$= 8.314\ \text{M Pa cm}^{3}\ \text{K}^{-}\ \text{mol}^{-}$$

$$= 5.189 \times 10^{19}\ \text{ev K}^{-}\ \text{mol}^{-} = 2\ \text{cal K}^{-}\ \text{mol}^{-}$$

$$= 0.002\ \text{k cal K}^{-}\text{mol}^{-}$$

Boltzmann constant,

$$\text{k} = \frac{R}{N} = 1.38\times 10^{-16}\ \text{erg K}^{-}\ \text{mol}^{-}$$

$$= 1.38 \times 10^{-23}\ \text{J K}^{-}\ \text{mol}^{-}$$

8.12 KINETIC MOLECULAR THEORY

Type $\quad m_1u_1^{\,2} = m_2u_2^{\,2}$

Example 76. *Write the postulate (s) of the kinetic molecular theory that can be used to justify (i) Graham's law of effusion (ii) Dalton's law of partial pressures.*

Solution. (*i*) The average translational kinetic energy is directly proportional to absolute temperature.

$$m_1u_1^{\,2} = m_2u_2^{\,2}; \quad \frac{u_1}{u_2} = \left(\frac{m_2}{m_1}\right)^{½} = \left(\frac{M_2}{M_1}\right)^{½}$$

(*ii*) The molecules of each gas are in constant random motion and exert no forces on each other. These forces are necessary to have pressures independent of the presence of other gases.

Example 77. *Ammonia, neon and nitrogen gases, all at the same initial temperature and pressure were expanded adiabetically separately to double of their original volume. Which gas would require the greatest quantity of heat so that the original temperature is restored?*

Solution. The answer is ammonia. This gas has the highest inter molecular forces (due to inter molecular hydrogen bonding in it) and would take the greatest quantity of energy to overcome those forces. Hence NH_3 would take the most heat to restore the original temperature.

Example 78. *The temperature of a tire rises when pumped rapidly. Would this effect be same for air if it is considered ideal?*

Solution. Even if air is ideal, which is not, the compression would cause the temperature to rise. The reason is that energy is expended on the gas in the process. The energy is converted to the kinetic energy of the molecules *i.e.*, heat.

8.13 KINETIC THEORY OF GASES

$\mathbf{PV = \frac{1}{3}mnu^2}$**.** It is called kinetic gas equation. Here; *P* is pressure of a gas; *V* is the volume of the gas; *n* is the number of molecules of the gas while *u* = mean square velocity of molecules

$$= \frac{V_1^2 + V_2^2 + V_3^2 + \text{..........}V_n^2}{n}$$

V_1, V_2, V_3, etc are the velocities of individual molecules. If *N* = number of molecules in a given mass of a gas,

then $\quad PV = \dfrac{1}{3}mNu^2$

$$= \frac{2}{3}N\times\frac{1}{2}mu^2 = \frac{2}{3}N\times K.E_{(av)}$$

where $K.E_{(av)}$ is the average kinetic energy of the **single molecule.**

or $\quad PV = \dfrac{2}{3}N\ KE_{(av)}$

$$PV = \frac{2}{3}E$$

where *E* = total kinetic energy of all the *N* molecules.

Different kinds of velocities.

1. **Average velocity (V_{av}).** It is the arithmatic mean of the various velocities of the molecules. Thus.

$$V_{av} = \frac{V_1 + V_2 + \text{.......}V_n}{n}$$

$$\left[\begin{array}{l}\text{where } V_1, V_2 \text{ etc are the velocities}\\ \text{of individual molecules}\end{array}\right]$$

According to Maxwell,

$$V_{av} = \left(\frac{8RT}{\pi M}\right)^{½} \quad \text{where}$$

M = molecular mass of the gas.

2. **Root mean square velocity, V_{rms}.** It is the square root of the mean of the square of the velocities of all the molecules.

Mathematically :

$$U \text{ or } V_{rms} = \left[\frac{V_1^2 + V_2^2 + \text{......}V_n^2}{n}\right]^{1/2}$$

where V_1, V_2 .... are the velocities of *n* molecules in a gas.

According to Maxwell,

$$U = \left(\frac{3RT}{M}\right)^{1/2}$$

$$= \left(\frac{3PV}{M}\right)^{1/2} = \left(\frac{3P}{d}\right)^{1/2}$$

$$\left[\begin{array}{l}\text{where } d \text{ is the density}\\ \text{of the gas}\end{array}\right]$$

3. **Most probable velocity, V_{mp}.** It is the velocity possessed by the largest number of molecules. According to Maxwell :

$$V_{mp} = \left(\frac{2RT}{M}\right)^{1/2}$$

Relation between average velocity (V_{av}), root mean square velocity (V_{rms}) and most probable velocity (V_{mp}).

(*a*)
$$\frac{V_{av}}{V_{rms}} = \left(\frac{8RT}{\pi M}\right)^{1/2} \times \left(\frac{M}{3RT}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2}$$

$$= \left(\frac{8}{3 \times 3.142}\right)^{1/2} = \mathbf{0.9213}$$

(*b*)
$$\frac{V_{mp}}{V_{rms}} = \left(\frac{2RT}{M}\right)^{1/2} \times \left(\frac{M}{3RT}\right)^{1/2} = \left(\frac{2}{3}\right)^{1/2}$$

$$= \mathbf{0.8165}$$

Example 79. *Calculate V_{mp}, V_{rms} and V_{av} for O_2 gas at 27°C.*

Solution. $T = 27 + 273 = 300$ K;

$R = 8.314 \times 10^7$ g cm^{2}s^{-2} K$^-$ mol$^-$

Mol. wt. of O_2 = $2 \times 16 = 32$ g mol$^-$

$$V_{av} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$= \left(\frac{8 \times 8.314 \times 10^7 \text{ g cm}^2\text{s}^{-2}\text{ K}^- \text{ mol}^- \times 300\text{ K}}{32 \text{ g mol}^- \times 3.142 \times 10^{-3}}\right)^{1/2}$$

$= (198453972)^{1/2} = 44548$ cm s$^-$ $\simeq$ **445.5 m s$^-$** **Ans.**

$$V_{rms} = \frac{V_{av}}{0.9213} = \frac{445.5}{0.9213} = 483.56 \text{ m s}^-$$

$$V_{mp} = V_{rms} \times 0.8165 = 483.56 \times 0.8165$$

$$= 394.82 \text{ m s}^-$$

Example 80. *The r.m.s. velocity of molecules of a gas of density 4 kg m^{-3} and pressure 1.2 × 10^5 Nm^{-2} is :*

(a) 900 ms$^-$ (b) 120 ms$^-$

(c) 600 ms$^-$ (d) 300 ms$^-$ **(Karnataka CET, 2009)**

Solution. P = 1.2×10^5 Nm^{-2};

d = 4 kg m^{-3}, Thus :

r.m.s. velocity $= \sqrt{\frac{3P}{d}}$;

$$V_{rms} = \sqrt{\frac{3 \times 1.2 \times 10^5 \text{ kg ms}^{-2}\text{m}^{-2}}{4 \text{kg m}^{-3}}}$$

$$= \sqrt{9 \times 10^4 \text{m}^2\text{s}^{-2}} = 3 \times 10^2 \text{ ms}^{-1}$$

$$= 300 \text{ ms}^-.$$

So, the correct answer is (*d*).

Example 81. *Spark plugs are not necessary in a diesel engine. Explain.*

Solution. It is because, the compression of the gases heats them above the ignition temperature of the fuel *i.e.,* diesel.

Example 82. *Why Boyle's law cannot be used to calculate the volume of a real gas which is changed from its initial state to its final state by an adiabetic expansion?*

Solution. It is because, the temperature is lowered in this expansion.

Example 83. *Write down the different experimental techniques which can be used to determine absolute zero of temperature.*

Solution. The absolute temperature can be determined from the gas data such as :

(*i*) $PV = nRT$

(*ii*) $\overline{K.E.} = \frac{3}{2}kT$

(*iii*) Electrochemical potential,

$$E = E° - \frac{RT}{nF}$$

$$\ln Q = E° - 2.303 \frac{RT}{nF} \log Q \text{ and}$$

(*iv*) Free energy variation with temperature *i.e.,*

$$\Delta G = \Delta H - T\Delta S.$$

Example 84. *Write the postulates of kinetic molecular theory which are only approximations when applied to real gases.*

Solution. (*i*) The molecules have negligible mass and

(*ii*) There are no intermolecular forces between molecules.

Example 85. *The temperature of a given real gas decreases by 1°C when it is expanded adiabetically into vacuum from its initial 1L volume to final 2L volume. Would the same decrease in temperature takes place if half the given quantity of the same gas were expanded adiabetically into vacuum from 1L to 2L?*

Solution. The gas with less number of mol (*i.e.,* half) will have lower pressure. So, there will be less intermolecular attraction to overcome and hence energy loss from the kinetic energy is lower. So, the temperature drop is less.

Example 86. *Write the relationship between R, the ideal gas law constant and k, the Boltzmann constant.*

Solution. $R = N_A k = 6.02 \times 10^{23} \times k.$

when $R = 8.314$ J K$^-$ mol$^-$ (SI unit)

then
$$k = \frac{8.314 \text{ J K}^-\text{mol}^-}{6.02 \times 10^{23} \text{ molecule}} \times 1 \text{ mol}$$

or $k = 1.381 \times 10^{-23}$ J K$^-$ (molecule)$^-$

In other words, Boltzmann constant,

$$k = \frac{R(i.e.,)\ \text{gas constant}}{\text{Avogadro's number}}$$

EXAMPLE 87. *Calculate (i) the average speed (ii) most probable speed (iii) the mean square speed and (iv) root mean square speed from the following set of speeds of various automobiles; 9 $m\,s^{-}$, 10 $m\,s^{-}$, 1400 $cm\,s^{-}$, 16 $m\,s^{-}$, 16 $m\,s^{-}$.*

SOLUTION. Given speeds in ms^{-} are, 9 ms^{-}, 10 ms^{-}, 1400 $cms^{-} \times \frac{1\ \text{m}}{100\ \text{cm}}$ *i.e.*, 14 ms^{-}, 16 ms^{-} and 16 ms^{-}.

(*i*) Average speed $= \frac{9+10+14+16+16}{5}\ ms^{-}$

$= \mathbf{13\ ms^{-}}$ **Ans.**

(*ii*) Most probable speed = That speed which is the one most often found, here, it is given twice $= 16\ m\,s^{-}$

(*iii*) Mean square speed

$$= \frac{(9)^2+(10)^2+(14)^2+(16)^2+(16)^2}{5}$$

$$= \frac{81+100+196+256+256}{5}\ m^2s^{-2}$$

$= 177.8\ m^2s^{-2}$ **Ans.**

(*iv*) Root mean square velocity $= (177.8\ m^2s^{-})^{½}$ (from (*iii*) above) $= \mathbf{13.3\ ms^{-}}$ **Ans.**

EXAMPLE 88. *Calculate the ratio of (i) average speed to most probable speed and (ii) root mean square speed to most probable speed.*

SOLUTION. Average speed, $U_{avg} = \left(\frac{8kT}{\pi m}\right)^{½}$

Most probable speed, $U_{mp} = \left(\frac{2kT}{m}\right)^{1/2}$

Root mean square velocity, $U_{rms} = \left(\frac{3kT}{m}\right)^{1/2}$

(*i*)

$$\frac{u_{avg}}{u_{mp}} = \left(\frac{8kT}{\pi m}\right)^{1/2} \Big/ \left(\frac{2kT}{m}\right)^{1/2}$$

$$= \left(\frac{4}{\pi}\right)^{1/2} = \left(\frac{4}{3.14}\right)^{1/2} = (1.27)^{1/2}$$

$= \mathbf{1.13}$

(*ii*)

$$\frac{u_{rms}}{u_{mp}} = \left(\frac{3kT}{m}\right)^{1/2} \Big/ \left(\frac{2kT}{m}\right)^{1/2}$$

$$= \left(\frac{3}{2}\right)^{1/2} = (1.5)^{1/2} = \mathbf{1.22}$$

EXAMPLE 89. *Calculate the ratio of average molecular kinetic energy of ${}^{238}UF_6$ to that of H_2 gas at 27°C.*

SOLUTION. The average molecular kinetic energy depends only on T (here $T = 27 + 273 = 300$ K) which is the same for UF_6 and H_2. It does not depend upon the nature of the substance. Thus, the ratio is 1 : 1.

EXAMPLE 90. *Calculate the root mean square velocity of an oxygen molecule at 0°C in S.I. and C.G.S. units.*

SOLUTION.

$T = 0°C + 273 = 273$ K;

$R = 8.314\ J\,K^{-}\,mol^{-}$

mol. wt. (M) of $O_2 = 2 \times 16 = 32 \times 10^{-3}\ kg\ mol^{-}$

(*i*)

$$U_{rms} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$= \left(\frac{3 \times 8.314\ J\,K^{-}mol^{-} \times 273\ K}{32 \times 10^{-3}\ kg\ mol^{-}}\right)^{1/2}$$

$$= \left(\frac{212786\ kg\ m^2\,s^{-2}}{kg}\right)^{1/2}$$

$[\because\ J = kg\ m^2\ s^{-2}]$.

$\therefore \quad U_{rms} = 461.3\ m\ s^{-}$.

This result is in **S.I. units.**

(*ii*) **In C.G.S. Units,** the above result can be used as follows. $461.3\ m\,s^{-} \times \frac{100\ cm}{1\ m}$

$= 46130\ cm\ s^{-}$

Type. $U_{rms} = \left(\frac{3kT}{m}\right)^{½}$

EXAMPLE 91. *Calculate the root mean square velocity of H_2 at 27°C.*

SOLUTION.

Mol. wt. of $H_2 = 2\,u$ where $u = 1.66 \times 10^{-27}$ kg;

$k = 1.381 \times 10^{-23}\ J\ K^{-}$; $J = kg\ m^2\ s^{-2}$.

Thus, $k = 1.381 \times 10^{-23}\ kg\ m^2\ s^{-2}\ K^{-}$.

$T = 27 + 273 = 300$ K.

$$U_{rms} = \left(\frac{3kT}{m}\right)^{½}$$

$$= \left(\frac{3 \times 1.381 \times 10^{-23}\ kg\ m^2\ s^{-2}\ K^{-} \times 300\ K}{2 \times 1.66 \times 10^{-27}\ kg}\right)^{1/2}$$

$\simeq (3.744 \times 10^6\ m^2\ s^{-2})^{½} = \mathbf{1.93 \times 10^3\ m\ s^{-}}$ **Ans.**

Note. When U is to be calculated by using the formula involving 'k', m = mol. wt. × 1.66×10^{-27} kg.

EXAMPLE 92. *Calculate the root mean square velocity of nitrogen at 100°C (i) using the concept of Boltzmann constant, k. ($k = 1.381 \times 10^{-23}\ J\ K^{-}$) and (ii) gas constant, R.*

SOLUTION. $U_{rms} = \left(\frac{3kT}{m}\right)^{½}$ where

$k = 1.381 \times 10^{-23}\ J\ K^{-}$

$T = 100 + 273 = 373$ K,

m = mol. wt. of $N_2 \times 1.66 \times 10^{-27}$ kg

$= (2 \times 14) \times 1.66 \times 10^{-27}$ kg

$= 28 \times 1.66 \times 10^{-27}$ kg

$$U_{rms} = \left[\frac{3 \times 1.381 \times 10^{-23}\ \text{kg m}^2\ \text{s}^{-2}\ \text{K}^{-} \times 373\ \text{K}}{28 \times 1.66 \times 10^{-27}\ \text{kg}}\right]^{½}$$

$[\because\ \text{J} = \text{kg m}^2\ \text{s}^{-2}]$

$= (332474\ \text{m}^2\ \text{s}^{-2})^{½} = \mathbf{576.6\ m\ s^{-}}$ **Ans.**

Second method.

$$U_{rms} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$= \left(\frac{3 \times 8.314 \times 10^7\ \text{erg mol}^{-}\ \text{K}^{-} \times 373\ \text{K}}{28\ \text{g mol}^{-}}\right)^{1/2}$$

$= (3322630714\ \text{g cm}^2\ \text{s}^{-2})^{½}$

$[\because\ \text{erg} = \text{g cm}^2\ \text{s}^{-2}]$

$$= 57642\ \text{cm s}^{-} = 57642\ \text{cm s}^{-} \times \frac{1\ \text{m}}{100\ \text{cm}}$$

$= 576.42\ \text{m s}^{-}$ **Ans.**

EXAMPLE 93. *At what temperature will hydrogen molecules have same root mean square velocity as helium atoms at 291 K ?*

SOLUTION.

Mol. wt. of H_2 = 2 g mol^{-}

mol. wt. of He = at. wt. of He = 4.0 g mol^{-}; T = 291 K.

Both He and H_2 have same root mean square speed, *u*.

For He, $$U = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3R \times 291\ \text{K}}{4\ \text{g mol}^{-}}\right)^{1/2} \quad ...(1)$$

For H_2, $$U = \left(\frac{3RT}{M}\right)^{1/2} = \left(\frac{3R \times \text{T}}{2.0\ \text{g mol}^{-}}\right)^{1/2} \quad ...(2)$$

$$\therefore \quad \left(\frac{291\ \text{K}}{4}\right)^{1/2} = \left(\frac{T}{2}\right)^{1/2}$$

Squaring both sides, we get :

$$\frac{291\ \text{K}}{4} = \frac{T}{2};\ T = \frac{291\text{K} \times 2}{4} = 145.5\ \text{K}\ \textbf{Ans.}$$

EXAMPLE 94. *Calculate the average speed of helium atoms at 300 K.*

SOLUTION. $$U_{av} = \left(\frac{8kT}{\pi m}\right)^{1/2}.$$

Substituting the value of $k = 1.381 \times 10^{-23}$ kg m^2 s^{-2} K^{-}

T = 300 K, π = 3.14

$m = 4.0 \times 1.66 \times 10^{-27}$ kg

($\because$ at. wt. of He = 4)

in the above equation, we get :

$$U_{avg} = \left(\frac{8 \times 1.381 \times 10^{-23}\ \text{kg m}^2\ \text{s}^{-2}\ \text{K}^{-} \times 300\ \text{K}}{3.14 \times 4 \times 1.66 \times 10^{-27}\ \text{kg}}\right)^{1/2}$$

$= (1589671\ \text{m}^2\ \text{s}^{-2})^{1/2} = 1260.8\ \text{m s}^{-}$ **Ans.**

EXAMPLE 95. *Calculate the kinetic energy of a mole of CO gas at 500 K in (i) kcal and (ii) kJ.*

SOLUTION. T = 500 K,

$k = 1.381 \times 10^{-23}$ J K^{-}. We know that:

(*i*) $$\overline{K.E.} = \frac{3}{2}kT$$

$$= \frac{3}{2} \times 1.381 \times 10^{-23}\ \frac{JK^{-}}{\text{molecule}} \times 500\ \text{K}$$

$= 1.04 \times 10^{-20}$ J (molecule)$^{-}$

$$= 1.04 \times 10^{-20}\ J \times \frac{1\ kJ}{1000\ J\ \text{molecule}}$$

$= 1.04 \times 10^{-23}$ *kJ* (molecule)$^{-}$

$= 1.04 \times 10^{-23}$ kJ (molecule)$^{-}$ $\times 6.02 \times 10^{23}$

molecule = 6.26 kJ **Ans.**

(*ii*) 4.184 kJ = 1 k cal.

Hence, $$K.\ E. = 1.04 \times 10^{-23}\text{kJ} \times \frac{1\ \text{k cal}}{4.184\ \text{kJ molecule}}$$

or $$K.\ E. = 2.48 \times 10^{-24}\ \text{k cal (molecule)}^{-} \times \frac{6.02 \times 10^{23}\ \text{molecule}}{1\ \text{mol}}$$

$= 1.49$ k cal mol^{-} **Ans.**

EXAMPLE 96. *At what temperature would the most probable speed of CO gas molecules be thrice at 57°C.*

SOLUTION. T = 57 + 273 = 330 K.

At TK, $$U_{mp} = \left(\frac{2\ kT}{m}\right)^{1/2} \quad ...(1)$$

AT 330 K, $$U_{mp} = 3\left(\frac{2\ k \times 330\ \text{K}}{m}\right)^{1/2} \quad ...(2)$$

From (1) and (2), we get

$$\left(\frac{2\ kT}{m}\right)^{1/2} = 3\left(\frac{2k \times 330\ \text{K}}{m}\right)^{1/2}$$

Squaring both sides, we get :

$$\frac{2kT}{m} = \frac{9 \times 2k \times 330\ \text{K}}{m}$$

$T = 9 \times 330$ K = 2970 K

= 2970 – 273 = 2697°C.

EXAMPLE 97. *Calculate the most probable speed of CO_2 molecules at 27°C, using the concept of gas constant, R.*

SOLUTION. The most probable speed,

$$U_{mp} = \left(\frac{2RT}{M}\right)^{1/2}$$

Where $R = 8.314 \times 10^7$ erg mol^{-} K^{-}

T = 27 + 273 = 300 K,

M of CO_2 = 12 + (2 × 16) = 44 g mol^{-}.

Substituting the values, we get :

$$U_{mp} = \left(\frac{2 \times 8.314 \times 10^7\ \text{erg mol}^{-}\ \text{K}^{-} \times 300\ \text{K}}{44\ \text{g mol}^{-}}\right)^{1/2}$$

$= (1133.7 \times 10^6\ \text{g cm}^2\ \text{s}^{-2})$

$$[\because \ \text{erg} = \text{g cm}^2\ \text{s}^{-2}].$$

Thus, $U_{mp} = 33.67 \times 10^3 \text{ cm s}^{-} = 33670 \text{ cm s}^{-}$ **Ans.**

EXAMPLE 98. *Show that the ideal gas law can be written as $P = 2/3\ \varepsilon$ where ε is kinetic energy per unit volume.*

SOLUTION. $PV = nRT$ (Ideal gas law).

But $n = \dfrac{N}{N_A \text{ i.e., Avogadro's no.}}$

$$\therefore \quad PV = N \times \frac{R}{N_A} \cdot T = N\,kT$$

$$\left[\because \ k = \text{Boltzmann constant} = \frac{R}{N_A}\right]$$

or $$PV = \frac{2}{3}N\left(\frac{3}{2}kT\right) \qquad \left[\because \ \frac{2}{3}\times\frac{3}{2} = 1\right]$$

$$PV = \frac{2}{3}\left(N \times \overline{K.E}\right) = \frac{2}{3} \times \text{total } K.E.$$

or $$P = \frac{2}{3} \times \frac{\text{total } K.E.}{V}$$

Hence $$\mathbf{P = \frac{2}{3}\varepsilon}.$$

EXAMPLE 99. *Calculate the temperature at which O_2 gas molecules will have the same K. E. as N_2 gas molecules at 27°C.*

SOLUTION. The K. E. does not depend upon the identity of the gas but depends only on the absolute temperature. Hence the answer is 27°C or 27 + 273 = **300 K.**

EXAMPLE 100. *For molecules having a given mass, why root mean square speed rather than the average speed has greater significance ?*

SOLUTION. It is because the root mean square speed is directely related to kinetic energy.

EXAMPLE 101. *Explain with a suitable example that the average of the squares of the following set of numbers is different from the square of the average of the numbers: 4, 8, 12, 16.*

SOLUTION. (*i*) Average of the squares

$$= \frac{(4)^2 + (8)^2 + (12)^2 + (16)^2}{4}$$

$$= \frac{16 + 64 + 144 + 256}{4} = \frac{480}{4} = 120.$$

(*ii*) Square of the average of numbers

$$= \left(\frac{4 + 8 + 12 + 16}{4}\right)^2 = \left(\frac{40}{4}\right)^2$$

$$= 100.$$

8.14 KINETIC GAS EQUATION

Type. $PV = \dfrac{1}{3}m\,nU^2$ where U is root mean square velocity.

EXAMPLE 102. *How much pressure will be exerted by 10^{21} molecules of a gas in a container of half litre volume if rms velocity of the molecule is 10^6 cm s^{-} and mass of each molecule is 3.3×10^{-24} g?*

SOLUTION. $U_{rms} = 10^6 \text{ cm s}^{-}$;

$m = 3.3 \times 10^{-24}\text{g};\ n = 10^{21}$

$V = 0.5 \text{ L} = 0.5 \times 10^3 \text{ cm}^3.$

We know that :

$$PV = \frac{1}{3}m\,n\,U_{rms}^2 \text{ (kinetic gas equation)}$$

$$\therefore P = \frac{1}{3V} \times m\,n\,U_{rms}^2$$

$$= \frac{1}{3 \times 0.5 \times 10^3 \text{ cm}^3} \times 3.3 \times 10^{-24} \text{ g} \times 10^{21} \times (10^6 \text{ cm s}^{-})^2$$

$$P = 2.2 \times 10^6 \text{g cm}^{-} \text{ s}^{-2}$$

$$= 2.2 \times 10^6 \text{ g cm}^{-} \text{ s}^{-2} \times \frac{1 \text{ dyne}}{\text{g cm s}^{-2}}$$

$$= \mathbf{2.2 \times 10^{-6} \text{ dyne cm}^{-2}}.$$ **Ans.**

Type. *Average K. E.* $= \dfrac{3}{2} \times nRT$

EXAMPLE 103. *Calculate the average kinetic energy in joules, of the molecules in 8.0 g of methane at 27°C.* **(IIT, 1982)**

SOLUTION. Wt. of

$CH_4 = 8.0$ g ;

mol. wt. of $CH_4 = 12 + (4 \times 1) = 16 \text{ g mol}^{-}$.

$\therefore$ no. of mol, n of

CH_4 = wt./mol. wt. = 8/16 = 0.5 mol.

$R = 8.314 \text{ JK}^{-} \text{ mol}^{-}$;

$T = 27 + 273 = 300$ K.

But : Average $K.\ E. = \dfrac{3}{2} \times nRT$

$$= \frac{3}{2} \times 0.5 \text{ mol} \times 8.314 \text{ JK}^{-} \text{ mol}^{-} \times 300 \text{ K}$$

$$= \mathbf{1870.65\ J}$$ **Ans.**

EXAMPLE 104. *Calculate the root mean square speed, average speed and most probable speed of (a) O_2 at STP (b) ethane at 27°C and 120 mm of Hg (c) O_2 at 17°C (d) O_2 if its density is 0.0081 g $(mL)^{-}$ at 1 atm (e) O_2 if 6.431 g of it occupies 5 litre at 750 mm (f) O_3 at 20°C and 82 cm Hg.* **(IIT, 1985)**

SOLUTION. Mol. wt. of

$O_2 = 2 \times 16 = 32 \text{ g mol}^{-}$;

$R = 8.314 \times 10^7 \text{ g cm}^2 \text{ s}^{-2}$

(*a*) At STP, $T = 273$ K. But

(*i*) $$U_{rms} \text{ for } O_2 = \left(\frac{3RT}{M}\right)^{1/2}$$

$$= \left(\frac{3\times 8.314\times 10^7\ \text{g cm}^2\,\text{s}^{-2}\ \text{mol}^{-}\times 273\ \text{K}}{32\ \text{g mol}^{-}}\right)^{1/2}$$

$= (2127864375\ \text{cm}^2\,\text{s}^{-2})^{1/2} \simeq \mathbf{4.61\times 10^4\ cm\ s^{-}}$ **Ans.**

(*ii*) $U_{mp} = U_{rms}\times 0.8164 = 4.61\times 10^4\times 0.8164$

$= \mathbf{3.76\times 10^4\ cm\ s^{-}}$ **Ans.**

(*iii*) $U_{av} = U_{rms}\times 0.9213 = 4.61\times 10^4\times 0.9213$

$= \mathbf{4.25\times 10^4\ cm\ s^{-}}$ **Ans.**

(*b*) Mol. wt., M of C_2H_6

$= (2\times 12) + (6\times 1) = 30\ \text{g mol}^{-}$

$T = 27 + 273 = 300\ \text{K}$

(*i*) $U_{rms} = \left(\dfrac{3RT}{M}\right)^{1/2}$

$$= \left[\frac{3\times 8.314\times 10^7\ \text{g cm}^2\ \text{s}^{-2}\ \text{mol}^{-}\times 300\ \text{K}}{30\ \text{g mol}^{-}}\right]^{1/2}$$

$\simeq (24.94\times 10^8\ \text{cm}^2\,\text{s}^{-2})^{1/2} = \mathbf{4.99\times 10^4\ cm\ s^{-}}$ **Ans.**

(*ii*) $U_{mp} = U_{rms}\times 0.8164 = 4.99\times 10^4\ \text{cm s}^{-}\times 0.8164$

$= \mathbf{4.07\times 10^4\ cm\ s^{-}}$ **Ans.**

(*iii*) $U_{av} = U_{rms}\times 0.9213 = 4.99\times 10^4\ \text{cm s}^{-}\times 0.9213$

$= \mathbf{4.60\times 10^4\ cm\ s^{-}}$ **Ans.**

(*c*) Mol. wt., M of O_2

$= 2\times 16 = 32\ \text{g mol}^{-};\ T = 273 + 17 = 290\ \text{K}$

(*i*) $U_{rms} = \left(\dfrac{3RT}{M}\right)^{1/2}$

$$= \left[\frac{3\times 8.314\times 10^7\text{g cm}^2\ \text{s}^{-2}\ \text{mol}^{-}\times 290\ \text{K}}{32\ \text{g mol}^{-}}\right]^{1/2}$$

$\simeq (22.6\times 10^8\,\text{cm}^2\,\text{s}^{-2})^{1/2} = \mathbf{4.75\times 10^4\,cm\,s^{-}}$ **Ans.**

(*ii*) $U_{mp} = U_{rms}\times 0.8164 = 4.75\times 10^4\ \text{cm s}^{-}\times 0.8164$

$= \mathbf{3.88\times 10^4\ cm\ s^{-}}$ **Ans.**

(*iii*) $U_{av} = U_{rms}\times 0.9213 = 4.75\times 10^4\ \text{cm s}^{-}\times 0.9213$

$= \mathbf{4.38\times 10^4\ cm\ s^{-}}$ **Ans.**

(*d*) Density of $O_2 = 0.0081\ \text{g (mL)}^{-} = 0.0081\ \text{g cm}^{-3}$;

$P = 1\ \text{atm} = 1\times 76\times 13.6\times 981\ \text{gcm}^{-}\text{s}^{-2}$

(*i*) $U_{rms} = \left(\dfrac{3P}{d}\right)^{1/2}$

$$= \left(\frac{3\times 1\times 76\times 13.6\times 981\ \text{g cm}^{-}\ \text{s}^{-2}}{0.0081\ \text{g cm}^{-3}}\right)^{1/2}$$

$= (3.76\times 10^8\,\text{cm}^2\,\text{s}^{-2})^{1/2} \simeq \mathbf{1.94\times 10^4\,cm\,s^{-}}$ **Ans.**

(*ii*) $U_{mp} = U_{rms}\times 0.8164 = 1.94\times 10^4\ \text{cm s}^{-}\times 0.8164$

$= \mathbf{1.58\times 10^4\ cm\ s^{-}}$ **Ans.**

(*iii*) $U_{av} = U_{rms}\times 0.9213 = 1.94\times 10^4\ \text{cm s}^{-}\times 0.9213$

$= \mathbf{1.79\times 10^4\ cm\ s^{-}}$ **Ans.**

(*e*) wt. of $O_2 = 6.431$ g;

mol. wt., M of $O_2 = 2\times 16 = 32\ \text{g mol}^{-}$

$V = 5\text{L},\ P = 750\ \text{mm}\times\dfrac{1\ \text{atm}}{760\ \text{mm}} = \dfrac{75}{76}\ \text{atm}$

$R = 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-}$

$PV = \dfrac{W}{M}\times RT,\ T = \dfrac{PVM}{WR}$

$$= \frac{75\ \text{atm}\times 5\ \text{L}\times 32\ \text{g mol}^{-}}{76\times 6.431\ \text{g}\times 0.0821\ \text{L atm K}^{-}\text{mol}^{-}}$$

$= 299.05\ \text{K}$

(*i*) $U_{rms} = \left(\dfrac{3RT}{M}\right)^{1/2}$

$$= \left(\frac{3\times 8.314\times 10^7\ \text{g cm}^2\text{s}^{-2}\ \text{mol}^{-}\times 299.05\ \text{K}}{32\ \text{g mol}^{-}}\right)^{1/2}$$

$= (23.3\times 10^8\ \text{cm}^2\ \text{s}^{-2})^{1/2} = \mathbf{4.83\times 10^4\ cm\ s^{-}}$ **Ans.**

(*ii*) $U_{mp} = U_{rms}\times 0.8164 = 4.83\times 10^4\ \text{cm s}^{-}\times 0.8164$

$= \mathbf{3.94\times 10^4\ cm\ s^{-}}$ **Ans.**

(*iii*) $U_{av} = U_{rms}\times 0.9213 = \mathbf{4.45\times 10^4\ cm\ s^{-}}$ **Ans.**

(*f*) Mol. wt., M of

$O_3 = 3\times 16 = 48\ \text{g mol}^{-};\ T = 20 + 273 = 293\ \text{K}$

(*i*) $U_{rms} = \left(\dfrac{3RT}{M}\right)^{1/2}$

$$= \left(\frac{3\times 8.314\times 10^7\ \text{g cm}^2\ \text{s}^{-2}\ \text{mol}^{-}\times 293\ \text{K}}{48\ \text{g mol}^{-}}\right)^{1/2}$$

$= (15.22\times 10^8\ \text{cm}^2\ \text{s}^{-2})^{1/2} = \mathbf{3.9\times 10^4\ cm\ s^{-}}$ **Ans.**

(*ii*) $U_{mp} = U_{rms}\times 0.8164 = 3.9\times 10^4\ \text{cm s}^{-}\times 0.8164$

$= \mathbf{3.18\times 10^4\ cm\ s^{-}}$ **Ans.**

(*iii*) $U_{av} = U_{rms}\times 0.9213 = 3.9\times 10^4\ \text{cm s}^{-}\times 0.9213$

$= \mathbf{3.59\times 10^4\ cm\ s^{-}}$ **Ans.**

EXAMPLE 105. *The average speed at T_1 K and the most probable speed at T_2 K of CO_2 gas is 9×10^4 cm s^{-}. Calculate the value of T_1 and T_2.* **(IIT, 1990)**

SOLUTION. (*i*) Mol. wt., M of

$CO_2 = 12 + (2\times 16) = 44\ \text{g mol}^{-}$

$R = 8.314\times 10^7\ \text{g cm}^2\ \text{s}^{-2}\ \text{mol}^{-}$

Average speed U_{av} at

$$T_1 = \left(\frac{8RT_1}{\pi M}\right)^{1/2}$$

and most probable speed

$$U_{mp}\ \text{at}\ T_2 = \left(\frac{2RT_2}{M}\right)^{1/2}\ \text{are equal for}$$

CO_2 (given)

$$\therefore\quad \left(\frac{8RT_1}{\pi M}\right)^{1/2} = \left(\frac{2RT_2}{M}\right)^{1/2};\ \frac{8RT_1}{\pi M} = \frac{2RT_2}{M};$$

$$\frac{4}{\pi} = \frac{T_2}{T_1} \qquad \text{...(A)}$$

(*ii*) $$U_{mp} = \left(\frac{2RT}{M}\right)^{1/2} ; \qquad 9 \times 10^4 \text{ cm s}^{-}$$

$$= \left(\frac{2\times 8.314\times 10^7 \text{ g cm}^2\text{s}^{-2}\text{ mol}^{-}\ T_2}{44\text{ g mol}^{-}}\right)^{1/2}$$

[∵ Mol. wt. of CO_2 = 12 + (2 × 16) = 44 g mol^{-}]

Squaring both sides, we get : 9×10^4 cm s^{-} × 9×10^4 cms^{-} = $2 \times 8.314 \times 10^7$ cm^2 s^{-2} ×$T_2/44$

$$\therefore \qquad T_2 = \frac{9\times 10^4\times 9\times 10^4\times 44}{2\times 8.314\times 10^7}$$

$$= \mathbf{2143.37\ K} \qquad \textbf{Ans.}$$

Since, $\frac{4}{\pi} = \frac{T_2}{T_1}$ see equation (A),

So, $$\frac{4}{3.142} = \frac{2143.37}{T_1};$$

$$T_1 = \frac{2143.37\times 3.142}{4} = \mathbf{1683.6\ K}\ \textbf{Ans.}$$

Example 106. *The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature.*

(IIT, 2003)

Solution. $$U_{av} = \left(\frac{8RT}{\pi M}\right)^{1/2} \qquad \text{...(A)}$$

$$U_{rms} = \left(\frac{3RT}{M}\right)^{1/2} \qquad \text{...(B)}$$

From equations (A) and (B), we have :

$$\frac{U_{rms}}{U_{av}} = \left(\frac{3RT}{M}\times\frac{\pi M}{8RT}\right)^{1/2} = \left(\frac{3\pi}{8}\right)^{1/2}$$

$$\therefore \qquad U_{rms} = U_{av}\times\left(\frac{3\pi}{8}\right)^{1/2}$$

$$= 400\text{ ms}^{-}\times\left(\frac{3\times 3.142}{8}\right)^{1/2}$$

$$= 400\text{ ms}^{-}\times (1.178)^{1/2}$$

$$= 400\text{ ms}^{-}\times 1.085 = \mathbf{434\ ms^{-}}\ \textbf{Ans.}$$

Example 107. *The average velocity of gas molecules is 425 m/sec. Calculate its most probable velocity (u_{mp}) at the same temperature.*

Solution. Average velocity,

$\bar{v}$ = 425 m s^{-}; Most probable velocity,

u = ?

We know: $$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{1/2}; \quad u_{mp} = \left(\frac{2RT}{M}\right)^{1/2}.$$

Hence, $$\frac{u}{\bar{v}} = \left(\frac{2RT}{M}\times\frac{\pi M}{8RT}\right)^{1/2} = \left(\frac{\pi}{4}\right)^{1/2}$$

$$\therefore \qquad \frac{u}{\bar{v}} = \left(\frac{22}{7\times 4}\right)^{1/2} = (0.7857)^{1/2} = 0.886$$

$$\therefore \qquad u = 0.886\times 425\text{ m s}^{-} = \mathbf{376.55\ m\ s^{-}}\ \textbf{Ans.}$$

8.15 VANDER WAAL EQUATION

vander Waal applied volume correction and pressure correction in ideal gas equation, $PV = nRT$ and introduced the following gas equation, called vander Waal equation.

$$\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

where n is the number of moles of gas. a and b are the vander Waal constants.

Type. $$\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

Example 108. *What will be the pressure exerted by 2 mol of ethane (C_2H_6) gas in a 500 mL vessel at 15°C vusing vander Waal's equation. Also calculate the pressure exerted by an ideal gas equation. (a = 2.253 L^2 atm mol^{-2}; b = 0.04281 L mol^{-})*

Solution. We know,

$$R = 0.0821\text{ L atm K}^{-}\text{ mol}^{-};$$

$$n = 2;\ V = \frac{500}{1000} = 0.5\text{ L}$$

$$T = 15 + 273 = 288\text{ K}.$$

vander Waal equation is given as :

$$\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT.$$

Dividing by $V–nb$ and solving for P, we get :

$$P+\frac{an^2}{V^2} = \frac{nRT}{V-nb} \quad \text{or}$$

$$P = \frac{nRT}{V-nb}-\frac{a\,n^2}{V^2}$$

Substituting the values, we get :

$$P = \frac{2\times 0.0821\times 288}{0.5-(2\times 0.04281)}-\frac{2.253\times 2^2}{(0.5)^2}$$

$$= \frac{47.29}{0.5-0.086}-\frac{9.012}{0.25}$$

$$= \frac{47.29}{0.414}-\frac{9.012}{0.25}$$

$$P = 114.23 - 36.05 = \mathbf{78.18\ atm} \quad \textbf{Ans.}$$

For an ideal gas, $P = \frac{nRT}{V}$.

Substituting the values, we get :

$$P = 2\times 0.0821\times 288/0.5 = \mathbf{94.58\ atm.}$$

Example 109. *In the vander Waal equation ($P + n^2\,a/V^2$) (V-nb) = nRT,*

(*i*) *The constant 'a' and (ii) constant 'b' account for what property of molecules of real gases ?*

Solution. (*i*) '*a*' accounts for intermolecular attraction.

(*ii*) '*b*' accounts for the actual volume of the molecules.

EXAMPLE 110. *Write the expression for the value of P, V and n (of nRT) by using the vander Waal equation,* $(P + n^2a/V^2)(V - nb) = nRT$.

SOLUTION. From $\left(P+\frac{n^2a}{V^2}\right)(V-nb)$

$= nRT$, We have :

(*i*) $$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

(*ii*) $$V = \frac{nRT}{P+\left(n^2a/V^2\right)} + nb$$

(*iii*) Calculate n from $n = \frac{PV}{RT}$ and put this value in vander Waal equation as follows and get 'n' as :

$$n = \left(P+\frac{n^2a}{V^2}\right)\left(\frac{V-nb}{RT}\right)$$

EXAMPLE 111. *Calculate the pressure of 0.5 mol of* CO_2 *gas in a 2.5 L vessel at 25°C (i) with the ideal gas law and (ii) with the vander Waals equation. (For* CO_2, $a = 3.59$ L^2 atm mol^{-2}. $b = 0.0427$ L mol^{-})

SOLUTION. (*i*) Ideal gas equation is

$$PV = nRT.$$

Hence : $$P = \frac{nRT}{V}$$

$$= \frac{0.5 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times (25+273) \text{ K}}{2.5 \text{ L}}$$

= **4.9 atm** **Ans.**

(*ii*) $$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2};$$

$$T = 25 + 273 = 298 \text{ K}$$

$$P = \frac{0.5 \text{ mol} \times 0.0821 \text{ L atm mol}^{-}\text{K}^{-} \times 298 \text{ K}}{2.5 \text{ L} - 0.5 \text{ mol} \times 0.0427 \text{ L mol}^{-}} - \frac{(0.5 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^{-2}}{(2.5 \text{ L})^2}$$

$$= \frac{12.2 \text{ L atm}}{2.5 \text{ L} - 0.021 \text{ L}} - \frac{0.9 \text{ mol}^2\text{L}^2 \text{ atm mol}^{-2}}{6.25 \text{ L}^2}$$

$$= \frac{12.2 \text{ atm}}{2.479} - \frac{0.9 \text{ atm}}{6.25}$$

or $P = (4.9 - 0.1)$ atm $= 4.8$ atm **Ans.**

EXAMPLE 112. *Calculate the volume that 2.5 mol nitrogen would occupy at 45.0 atm pressure and 370 K according to (i) ideal gas law and (ii) vander Waal equation.*

For N_2, a = 1.39 L^2 atm mol^{2-};

b = 0.0391 L mol^{-}.

SOLUTION. (*i*) For ideal gas,

$$V = \frac{nRT}{P}$$

$$= \frac{2.5 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 370 \text{ K}}{45.0 \text{ atm}}$$

$$V = 1.7 \text{ L}$$

(*ii*) For vander Waal equation,

$$V = \frac{nRT}{P+\left(n^2a/V^2\right)} + nb$$

$$\therefore V = \frac{2.5 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 370 \text{ K}}{45.0 \text{ atm} + \frac{(2.5 \text{ mol})^2 \times 1.39 \text{ L}^2 \text{ atm mol}^{-2}}{(1.7 \text{ L})^2}} + 2.5 \text{ mol} \times 0.0391 \text{ L mol}^{-}$$

$$= \frac{75.9 \text{ L atm}}{45.0 \text{ atm} + 3.0 \text{ atm}} + 0.098 \text{ L}$$

$$= \frac{75.9 \text{ L}}{48} + 0.098 \text{ L} = 1.58 \text{ L} + 0.098 \text{ L}$$

or V = **1.68 L** **Ans.**

EXAMPLE 113. *Compare the values of vander Waals constant for* N_2 *and* NH_3. *Why the value of 'a' for* NH_3 *is larger than* N_2 *while the value of 'b' is larger for* N_2 *than* NH_3.

SOLUTION. The vander Waal constant '*a*' is related to intermolecular forces. These forces are higher in NH_3 due to intermolecular hydrogen bonding. The vander Waal constant '*b*' is related to molecular volume. The H-atoms in NH_3 take up practically no volume, and NH_3 is little over half the volume of nitrogen.

EXAMPLE 114. *Find the value of pressure exerted by 4 mol of* CO_2 *gas in a one litre vessel at 37°C. Given* $a = 3.592$ *atm* L^2 mol^{-2}; $b = 0.0427$ L mol^{-}. *Also calculate the pressure if the gas behaves as an ideal gas.*

SOLUTION. (*i*) $P = ?$, $V = 1$ L; $n = 4$;

$a = 3.592$ atm L^2 mol^{-2};

$b = 0.0427$ L mol^{-};

$R = 0.0821$ L atm K^{-} mol^{-}

$T = 37 + 273 = 310$ K.

$$\left(P+\frac{a\,n^2}{V^2}\right)(V-nb)$$

$= nRT$ (vander Waal equation)

$$\therefore \left[P+\frac{3.592 \text{ atm L}^2 \text{ mol}^{-2} \times (4)^2}{(1^2)}\right]$$

$$[1 \text{ L} - (4 \text{ mol} \times 0.0427 \text{ L mol}^{-})]$$

$$= 4 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 310 \text{ K}$$

$$(P + 57.472)(1 - 0.1708) = 101.804$$

$$(P + 57.472) \times 0.8292 = 101.804$$

$$\therefore \quad \boldsymbol{P} = \frac{101.804}{0.8292} - 57.472$$

$$= 122.774 - 57.472$$

= **65.702 atm** **Ans.**

(*ii*) For an ideal gas,

$$PV = nRT \quad \therefore \quad P = \frac{nRT}{V}$$

$$P = \frac{4\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 310\text{ K}}{1\text{ L}}$$

$$= \mathbf{101.804\ atm} \quad \textbf{Ans.}$$

EXAMPLE 115. *Using vander Waal equation, calculate the constant 'a' when 2 mole of a gas confined in a four litre flask exerts a pressure of 11.0 atmosphere at a temperature of 300 K. The value of 'b' is 0.05 litre mol*$^{-}$*.* **(IIT, 1998)**

SOLUTION. Hint. $\left(P + \frac{a\,n^2}{V^2}\right)(V - n\,b)$

$= nRT$ (vander Waal equation).

$$\left(11\text{ atm} + \frac{a \times (2\text{ mol})^2}{(4\text{ L})^2}\right)(4\text{ L} - 2\text{ mol} \times 0.05\text{ L mol}^{-})$$

$$= 2\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 300\text{ K}$$

$$\therefore \quad a = 1.63\text{ atm} \times \frac{4\text{ L}^2}{\text{mol}^2} = \mathbf{6.52\ atm\ L^2\,mol^{-2}} \quad \textbf{Ans.}$$

Type. Using vander Waal equation: $\left(P + \frac{a\,n^2}{V^2}\right)(V - nb)$

$= nRT$

(*i*) Pressure correction

$$= \frac{a\,n^2}{V^2} \text{ where } n = \text{no. of mol} = \frac{\text{wt.}}{\text{Mol. wt.}}$$

(*ii*) Volume correction

$$= n\,b; \text{ where } n = \text{no. of mol} = \frac{\text{wt.}}{\text{Mol. wt.}}$$

EXAMPLE 116. *Find the value of pressure correction and volume correction for 3.5 g* CO_2 *gas kept in 500 cm*^{3} *flask. Given a = 3.6 atm L*^{2} *mol*$^{-2}$*. b = 0.04 L mol*$^{-}$ *for* CO_2 *gas.*

SOLUTION. Wt. of

$CO_2 = 3.5$ g;

mol. wt. of $CO_2 = 12 + (2 \times 16) = 44\text{ g mol}^{-}$

n = no. of mol of

$$CO_2 = \frac{\text{wt. of } CO_2}{\text{Mol. wt. of } CO_2}$$

$$= \frac{3.5\text{ g}}{44\text{ g mol}^{-}}$$

Volume, $V = 500\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = 0.5\text{ L}$

(*i*) Pressure correction

$$= \frac{a\,n^2}{V^2}$$

$$= \frac{3.6\text{ atm L}^2\text{ mol}^{-2} \times (3.5\text{ mol})^2}{(0.5\text{ L})^2 \times (44)^2}$$

$= 0.091$ atm.

(*ii*) Volume correction

$$= nb = \frac{3.5}{44}\text{mol} \times 0.04\text{ L mol}^{-}$$

$$= \mathbf{3.18 \times 10^{-3}\ L} \quad \textbf{Ans.}$$

EXAMPLE 117. *For helium gas, vander Waal constant, b = 0.024 L mol*$^{-}$*. Calculate the molecular diameter of helium gas.*

SOLUTION. 1 mol of He - gas

= Avogadro no.

$N = 6.023 \times 10^{23}\text{ mol}^{-}$

Volume of 1 mol of gas

$$= \frac{4}{3}\pi r^3$$

$b = 0.024\text{ L mol}^{-}$

$$= 0.024\text{ L} \times \frac{1000\text{ cm}^3\text{mol}^{-}}{1\text{ L}}$$

$= 24\text{ cm}^3\text{ mol}^{-}$

We know that : b

$$= 4 \times \begin{bmatrix}\text{Volume occupied by molecules present} \\ \text{in one mol of a gas}\end{bmatrix}$$

$\therefore$ 24 cm^3 mol^{-}

$$= 4 \times N \times \frac{4}{3}\pi r^3 = 4 \times 6.023 \times 10^{23}\text{ mol}^{-} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$\therefore \quad r = \left(\frac{24\text{ cm}^3\text{mol}^{-} \times 3 \times 7}{4 \times 6.023 \times 10^{23}\text{mol}^{-} \times 4 \times 22}\right)^{\frac{1}{3}}$$

$$= \left(2.377 \times 10^{-24}\text{cm}^3\right)^{\frac{1}{3}}$$

Taking logs of both sides, we get :

$$\log r = \frac{1}{3}\left[\log 2.377 + \log 10^{-24}\right]$$

$$= \frac{1}{3}[0.376 - 24]$$

$$= \frac{1}{3} \times -23.624$$

$$= \frac{1}{3} \times -23.624 - 1 + 1 = \frac{1}{3} \times \overline{24}.376$$

$$\log r = \frac{1}{3}\left[\overline{24}.376\right] = \overline{8}.1253\,.$$

Taking antilogs, we get :

r = antilog $\overline{8}$.1253

$= 1.33 \times 10^{-8}$ cm = 1.33 A°.

But Diameter = 2 r.

So, **diameter** = 2 × 1.33 A° = **2.66 A°** **Ans.**

EXAMPLE 118. *Calculate the pressure exerted by one mole of* CO_2 *gas at 273 K if the vander Waals constants a = 3.592 dm*^{6} *atm mol*$^{-2}$*, b = 0.0427 L mol*$^{-}$*. Assume that volume occupied by* CO_2 *is negligible.* **(IIT, 2000)**

Solution. For one mole of a gas :

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \text{ (vander Waal equation)}$$

$$\left(P+\frac{a}{V^2}\right)V = RT \quad [\because \text{ Volume occupied by } CO_2 = 0, \text{ So, } b = 0]$$

or
$$P = \frac{RT}{V}-\frac{a}{V^2}$$

$$= \frac{0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 273 \text{ K}}{22.4 \text{ L}} - \frac{3.592 \text{ L}^2 \text{ atm mol}^{-2}}{(22.4 \text{ L})^2}$$

$$\left[\because \text{ 1 mole of } CO_2 \text{ occupies 22.4 L or 22.4 dm}^3; \text{ 1L = dm}^3\right]$$

$$P = 1 \text{ atm} - 0.0072 \text{ atm} = \mathbf{0.9928 \text{ atm}.}$$

Type. Volume of one molecule of a gas = $\frac{4}{3}\pi r^3$.

Example 119. *vander Waal constant 'b' for N_2 gas is 3.9 × 10^{-2} L mol¯. How close the nuclei of two N_2 molecules come together?*

Solution. We know that :

$$b = 4 \times \text{Avogadro no.} \times \text{Volume of one molecule of } N_2 \quad ...(1)$$

$$b = 3.9\times10^{-2}\text{L mol}^{-} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 39 \text{ mL mol}^{-} = 39 \text{ cm}^3 \text{ mol}^{-}$$

$$\therefore \quad 39 \text{ cm}^3 \text{mol}^{-} = 4 \times 6.023 \times 10^{23} \text{ mol}^{-} \times \left(\frac{4}{3}\pi r^3 \text{ or } \frac{4}{3}\times\frac{22}{7}r^3\right) \quad ...[\text{from (1)}]$$

$$\therefore \quad r = \left(\frac{39 \text{ cm}^3\text{mol}^{-}\times3\times7}{4\times6.023\times10^{23} \text{ mol}^{-}\times4\times22}\right)^{\frac{1}{3}}$$

$$= \left(3.863\times10^{-24}\right)^{\frac{1}{3}} \text{cm}$$

$$= (3.863)^{\frac{1}{3}}\times10^{-8}\text{cm}$$

Taking logs of both sides, we get :

$$\log r = \log\,(3.863)^{\frac{1}{3}}$$

$$\log r = \frac{1}{3}[\log 3.863] = \frac{1}{3}\times0.5869 = 0.1956$$

Taking antilogs, we get :

$$r = \text{antilog } 0.1956\ (\times 10^{-8} \text{ cm})$$

$$= 1.57 \times 10^{-8} \text{ cm}$$

∴ Nuclei of two N_2 molecules come close together

$$= 2r = 2 \times 1.57 \times 10^{-8} \text{ cm}$$

$$= \mathbf{3.14 \times 10^{-8} \text{ cm}} \qquad \textbf{Ans.}$$

Example 120. *Considering N_2 molecule to be spherical in shape and having radius 157 pm calculate (i) volume occupied by one molecule of N_2 gas (ii) % age of empty (or free) space in one mole of this gas at NTP and (iii) comment upon the % age of free space so found.*

Solution. $r = 157 \text{ pm} = 157 \times 10^{-10}$ cm;

Avogadro no., $N = 6.023 \times 10^{23}$ mol¯.

(*i*) Volume occupied by one molecule of

$$N_2 = \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\times\frac{22}{7}\times\left(157\times10^{-10}\text{cm}\right)^3$$

$$= \mathbf{1.62 \times 10^{-23} \text{ cm}^3 \text{ mol}^{-}} \qquad \textbf{Ans.}$$

(*ii*) Volume occupied by Avogadro no. (= 6.023 × 10^{23}) molecules

$$= 6.023\times10^{23}\times1.62\times10^{-23}\text{cm}^3\text{ mol}^{-}$$

$$= 9.76 \text{ cm}^3 \text{ mol}^{-}$$

But 1 mole of any gas at NTP occupies volume

$$= 22400 \text{ cm}^3$$

∴ Volume of empty space

$$= 22400\,\text{cm}^3 - 9.76\,\text{cm}^3 = 22390.24\,\text{cm}^3$$

% age of empty (or free) space

$$= \frac{22390.24}{22400}\times100 = 99.96\%$$

(*c*) 99.96% empty space means that N_2 molecules can move freely in 99.96% of total volume available to the gas. It also means that N_2 gas can be compressed to maximum extent.

Example 121. *Assuming ideal gas behaviour and using density of liquid water at 100°C equal to 0.958 g (mL)¯, find the value of empty space available in one mole of H_2O (g) at 760 mm and 100°C.*

Solution. no. of mol,

$$n = 1; \; T = 100 + 273 = 373 \text{ K}$$

$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-}$$

$$P = 760 \text{ mm}\times\frac{1 \text{ atm}}{760 \text{ mm}} = 1 \text{ atm}$$

V = ?. We know that :

(*i*) $$PV = nRT; \; V = \frac{nRT}{P}$$

$$= \frac{1 \text{ mol}\times0.0821 \text{ L atm K}^{-}\text{mol}^{-}\times373 \text{ K}}{1 \text{ atm}}$$

or $$V = 30.62 \text{ L}$$

(*ii*) Density of

$$H_2O\,(l) = 0.958 \text{ g(mL)}^{-}.$$

Mass of 1 mole of

$$H_2O = (2 \times 1) + 16 = 18 \text{ g}$$

∴ Volume of 1 mole of

$$H_2O\,(l) = \frac{\text{Mass}}{\text{density}}$$

$$= \frac{18\text{ g}}{0.958\text{ g(mL)}^{-}} = 18.79\text{ mL}$$

$$= 18.79\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = 0.01879\text{ L}$$

∴ Percentage of volume occupied by

$$H_2O\text{ (g) molecules} = \frac{0.01879\text{ L}}{30.62\text{ L}} \times 100 = 0.0614$$

Hence, percentage of empty space available

$$= 100 - 0.0614 = \mathbf{99.9386} \qquad \textbf{Ans.}$$

Example 122. *Assuming oxygen molecules as spherical in nature, calculate the average volume available to its molecule in a sample of oxygen gas at N.T.P. Also, calculate the average distance between the neighbouring molecules.*

Solution. (*i*) We know that 1 mole (= 6.02×10^{23} molecules) of every gas occupies 22400 cm^3 volume at N.T.P. Thus:

6.02×10^{23} molecules of oxygen occupy volume = 22400 cm^3

∴ 1 molecule of oxygen occupies volume

$$= \frac{22400\text{ cm}^3}{6.02 \times 10^{23}} = 3.72 \times 10^{-20}\text{cm}^3$$

(*ii*) Volume, $\frac{4}{3}\pi r^3 = 3.72 \times 10^{-20}\text{ cm}^3$

$$\frac{4}{3} \times \frac{22}{7} r^3 = 3.72 \times 10^{-20}\text{ cm}^3$$

$$\therefore \qquad r = \left(\frac{3.72 \times 10^{-20} \times 7 \times 3\text{ cm}^3}{4 \times 22}\right)^{\frac{1}{3}}$$

$$= \left(78.877 \times 10^{-21}\text{ cm}^3\right)^{\frac{1}{3}}$$

$$= (8.877)^{\frac{1}{3}} \times 10^{-7}\text{ cm}$$

Taking logs of $(8.877)^{\frac{1}{3}}$ only to solve $(8.877)^{\frac{1}{3}}$, we get;

$$\log (8.877)^{\frac{1}{3}} = \frac{1}{3}\log 8.877 = \frac{1}{3} \times 0.9483 = 0.3161$$

Taking antilogs, we get :

antilog 0.3161 = 2.07; $r = 2.07 \times 10^{-7}$ cm.

(*iii*) Average distance between neighbouring molecules

$= 2r = 2 \times 2.07 \times 10^{-7}$ cm

$= 4.14 \times 10^{-7}$ cm

$= 41.4 \times 10^{-8}$ cm = **41.4 A°** **Ans.**

8.16 COMPRESSIBILITY FACTOR

Type. Compressibility factor,

$$Z = \frac{PV}{nRT} \text{ where;}$$

$$n = \text{no. of mole} = \frac{\text{wt.}}{\text{Mol. wt.}}$$

Example 123. *7 g of N_2 gas occupies 58.8 mL at 27° and 100 atmospheric pressure. Calculate the compressibility factor of the gas. Also, write the comments on the result so found.*

Solution. wt. of

N_2 gas = 7 g;

mol. wt. of $N_2 = 2 \times 14 = 28$ g mol^{-}

R = 0.0821 L atm K^{-} mol^{-};

T = 27 + 273 = 300 K;

P = 100 atm;

$$V = 58.8\text{ mL} = 58.8\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}}$$

$= 0.0588$ L.

We know that : Compressibility factor,

$$Z = \frac{PV}{nRT}$$

$$Z = \frac{100\text{ atm} \times 0.0588\text{ L}}{0.25\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{mol}^{-} \times 300\text{ K}}$$

$$\left[\because n = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{7\text{ g}}{28\text{ g mol}^{-}} = 0.25\text{ mol}\right]$$

$= 0.955$

Since value of Z is less than 1, $nRT > PV$. So, in order to get $Z = 1$, volume of N_2 must have been more at the same temperature and pressure. Hence N_2 will be more compressible than ideal gas at the same T and P.

Example 124. *Calculate the weight of given real gas having compressibility factor 0.65 and occupies 0.4 L at 40 atm and 27°C. (mol. wt. of gas = 44 g mol^{-})*

Solution. wt. = w g;

Z = 0.65; V = 0.4 L;

P = 40 atm.; T = 27 + 273 = 300 K;

mol. wt. = 44 g mol^{-};

$$n = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{\text{w g}}{44\text{ g mol}^{-}} = \frac{\text{w}}{44}\text{ mole}$$

We know that :

$$Z = \frac{PV}{nRT} = \frac{PV \times 44\text{ mol}^{-}}{wRT}$$

$$\therefore \qquad w = \frac{PV \times 44}{ZRT}$$

$$= \frac{40\text{ atm} \times 0.4\text{ L} \times 44\text{ g mol}^{-}}{0.65 \times 0.0821\text{ L atm K}^{-}\text{mol}^{-} \times 300\text{ K}}$$

$= \mathbf{43.97\text{ g}}$ **Ans.**

Type. vander Waal constant,

$b = 4Nv$

where N = Avogadro's no.,

v = Volume of one molecule of a gas.

Example 125. *Calculate the volume occupied by one mole of steam as compared to that of one mole of water from the following data.*

(*i*) *Density of H_2O (l)= 0.958 g (mL)$^{-}$ at 373 K*

(*ii*) *Value of vander Waal constant, b for steam = 0.0305 L mol^{-}.*

Solution. Mol. wt. of

$$H_2O = (2 \times 1) + 16 = 18 \text{ g mol}^{-}$$

density of H_2O at 373 K

$$= 0.958 \text{ g (mL}^{-}).$$

(*i*) ∴ Volume of 1 mole of

$$H_2O\,(l) = \frac{\text{wt.}}{\text{density}} = \frac{18\text{ g}}{0.958\text{ g}}\text{ mL}$$

$$= \mathbf{18.8\ mL}$$

(*ii*)

$$b = 0.0305 \text{ L mol}^{-}$$

$$= 0.0305 \text{ L mol}^{-} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

$$= 30.5 \text{ mL mol}^{-}$$

But $b = 4\,N\,v$

where v = Volume of 1 molecule of steam and

N = Avogadro no. = 1 mole.

or b = 4 × volume of 1 mole of steam

∴ 30.5 mL mol^{-}

= 4 × volume of 1 mole of steam

∴ Volume of 1 mole of steam

$$= \frac{30.5 \text{ mL}}{4} = 7.625 \text{ mL}.$$

From (*i*) and (*ii*) above, we have :

$$\frac{\text{Volume of 1 mole of steam}}{\text{Volume of 1 mole of } H_2O(l)}$$

$$= \frac{7.625 \text{ mL}}{18.8 \text{ mL}} = 0.4056$$

$$= 0.4056 \times 100 = 40.56\%$$

∴ Volume of 1 mole of steam is 40.56% of the volume of 1 mole of $H_2O(l)$.

Example 126. *A graph is plotted between PV_m along y-axis and P along X-axis, where V_m is the molar volume of a real gas. Find the intercept along the y-axis.* **(IIT, 2004)**

Solution. For 1 mole of a gas, vander Waal equation is :

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b)$$

$$= RT;$$

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \qquad \text{...(A)}$$

For the intercept of PV_m *vs* P at y-axis, P = 0. So, $V_m \to \infty$. Thus by neglecting $\frac{a}{V_m}$ and $\frac{ab}{V_m^2}$ in equation (A), we get :

$$PV_m = RT + Pb. \qquad \text{...(B)}$$

Hence a graph between PV_m *vs* P will give rise to the intercept RT because equation (B) represents an equation of a straight line ($y = mx + c$).

Example 127. *One way of writing the equation of state for real gases is*

$$PV = RT\left[1 + \frac{B}{V} + ...\right]$$

where B is a constant. Derive an approximate expression for B in terms of vander Waals constants a and b. **(IIT, 1997)**

Solution. We know that :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ (vander Waal equation)}$$

or

$$P = \frac{RT}{V-b} - \frac{a}{V^2}.$$

Multiplying throughout by V, we get : $PV = \frac{RTV}{V-b} - \frac{a}{V}$

$$PV = RT\left[\frac{V}{V-b} - \frac{a}{VRT}\right]$$

$$= \left[\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{VRT}\right]$$

$$\left[\because\ \frac{V}{V-b} = \left(\frac{V-b}{V}\right)^{-1} = \left(\frac{V}{V} - \frac{b}{V}\right)^{-1} = \left(1 - \frac{b}{V}\right)^{-1}\right]$$

Since

$$\left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + ...,$$

we have :

$$PV = RT\left[1 + \frac{b}{V} + ... - \frac{a}{VRT}\right]$$

$$= RT\left[1 + \left(b - \frac{a}{RT}\right) \times \frac{1}{V} + ...\right]$$

Now compare with given equation.

$$\therefore \quad B = b - \frac{a}{RT} \qquad \textbf{Ans.}$$

Example 128. *The values of vander Waal constants a and b for a gas are 5.46 atm L^2 mol^{-2} and 0.031 L mol^{-} respectively. Calculate the temperature of the gas whose 20 L volume contain 8 mole of it at 45 atm pressure.*

Solution.

$$\left(P + \frac{a\,n^2}{V^2}\right)(V - nb) = nRT$$

$$\therefore \left[45 \text{ atm} + \frac{5.46 \text{ atm L}^2 \text{ mol}^{-2} \times (8 \text{ mol})^2}{(20 \text{ L})^2}\right]$$

$$[20 \text{ L} - (8 \text{ mol} \times 0.031 \text{ L mol}^{-})]$$

$$= 8 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{mol}^{-} \times T$$

$$(45 \text{ atm} + 0.8736 \text{ atm})\ (20 \text{ L} - 0.248 \text{ L})$$

$$= 0.6568 \text{ L atm K}^{-} \times T$$

$$45.8736 \text{ atm} \times 19.752 \text{ L}$$

$$= 0.6568 \text{ L atm K}^{-} \times T$$

$$\therefore \quad T = \frac{45.8736 \times 19.752 \text{ L atm}}{0.6568 \text{ L atm K}^{-}}$$

$$= \mathbf{1379.6\ K} \qquad \textbf{Ans.}$$

Example 129. *Calculate the number of mole of a real gas that fill a cylinder of 100 litre capacity at 273 K and 100 atm pressure. The compressibility factor for the gas is 0.927.*

Solution.

$$Z = \frac{PV}{nRT};\quad n = \frac{PV}{ZRT}$$

$$= \frac{100 \text{ atm} \times 100 \text{ L}}{0.927 \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 273 \text{ K}}$$

$$\therefore \quad n \simeq 481.3 \qquad \textbf{Ans.}$$

Example 130. *The compressibility factor (Z) for a gas at – 50°C and 800 atm pressure is 1.95. Calculate the molecular weight of the gas (weighing 62.724 kg) present in a cylinder of 100 litre capacity.*

Solution. $Z = 1.95;\ P = 100 \text{ atm};\ V = 100 \text{ L};$

$$n = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{62.724 \text{ kg}}{\text{mol. wt.}}$$

$$= \frac{62.724 \text{ kg}}{\text{mol. wt.}} \times \frac{1000 \text{ g}}{1 \text{ kg}}$$

$$= \frac{62724 \text{ g}}{\text{mol. wt.}};$$

$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-};$$

$$T = -50 + 273 = 223 \text{ K.}$$

We know that : $Z = \frac{PV}{nRT} = \frac{PV}{RT} \times \frac{\text{mol. wt.}}{\text{wt.}}$

$$\therefore \quad \text{Mol. wt.} = \frac{Z \times RT \times \text{wt.}}{PV}$$

$$= \frac{1.95 \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 223 \text{ K} \times 62742 \text{ g}}{800 \text{ atm} \times 100 \text{ L}}$$

$\simeq 28 \text{ g mol}^{-}$ **Ans.**

Example 131. *The compressibility factor for one mole of a vander Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecule is negligible, calculate the vander Waal's constant 'a'.* **(IIT, 2001)**

Solution. Compressibility factor,

$$Z = \frac{PV}{RT};\ 0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$$\therefore \quad V = \frac{0.5 \times 0.0821 \times 273}{100} = 0.1119 \text{ L}$$

If volume of molecules is negligible *i.e.*, *b* is negligible then vander Waal's equation becomes :

$$\left(P + \frac{a}{V^2}\right)(V) = RT \quad \text{or} \quad PV = RT - \frac{a}{V}$$

$$\frac{a}{V} = RT - PV \quad \text{or} \quad a = RTV - PV^2$$

$$\therefore \quad a = (0.0821 \times 273 \times 0.1119) - (100 \times 0.1119 \times 0.1119)$$

$$= \mathbf{1.256 \text{ atm L}^2 \text{ mol}^{-2}}$$

8.17 MOLAR HEAT CAPACITY (C) OF AN IDEAL GAS

It is the amount of heat required to raise the temperature of one mole of a gas through 1°C.

Mathematically :

Molar heat capacity, *C* = specific heat × Mol. wt. of the gas where **specific heat** (sp. heat) of a substance is the amount of heat required to raise the temperature of 1 g of a substance through 1°C.

Unit of sp. heat = cal g¯ K¯.

(*a*) Two values of molar heat are C_p and C_v where :

C_p = Molar heat of a gas at constant pressure and

C_v = Molar heat of a gas at constant volume.

$C_p > C_v$ and

$C_p - C_v = R = 2 \text{ cal K}^{-} \text{mol}^{-}$ or $8.314 \text{ JK}^{-} \text{mol}^{-}$

The ratio $\frac{C_p}{C_v}$ is called **Poisson's ratio, *r*** which helps to get the idea of **atomicity of gases.** *e.g.*,

(1) **For Monoatomic gases,**

$$C_p = 5 \text{ cal};\ C_v = 3 \text{ cal};$$

$$r = \frac{C_p}{C_v} = \frac{5 \text{ cal}}{3 \text{ cal}} = \mathbf{1.67}$$

(2) **For diatomic gases,**

$$C_p = 7 \text{ cal};\ C_v = 5 \text{ cal};$$

$$r = \frac{C_p}{C_v} = \frac{7 \text{ cal}}{5 \text{ cal}} = \mathbf{1.4}$$

(3) **For triatomic gases :**

$$C_p = 8 \text{ cal};\ C_v = 6 \text{ cal};$$

$$r = \frac{C_p}{C_v} = \frac{8 \text{ cal}}{6 \text{ cal}} = \mathbf{1.33}$$

(*b*) Mol. wt. = Atomicity × At. wt.

Type. (*a*) For monoatomic gases, $\frac{C_p}{C_v} = 1.67$

For diatomic gases, $\frac{C_p}{C_v} = 1.4$

For triatomic gases, $\frac{C_p}{C_v} = 1.33$

where $\frac{C_p}{C_v} = r$

= Poisson's ratio

(*b*) $C_p - C_v = R$

(*c*) Mol. wt. = Atomicity × At. wt.

Example 132. *Calculate the molecular weight of a gas having atomic weight 14 and ratio of molar heats at constant pressure and constant volume equal to 1.41.*

Solution. Ratio of molar heat at constant pressure (C_p) and at constant volume (C_v) = 1.41.

Since $\frac{C_p}{C_v} = 1.41$ is for diatomic gases, so atomicity of gas = 2

But Mol. wt. = Atomicity × at. wt.

$= 2 \times 14 = \mathbf{28\ g\ mol^{-}}$ **Ans.**

EXAMPLE 133. *The molar heat of a gas at constant volume is 28.9 J. Calculate the atomicity and molecular weight of the gas if its atomic weight is 16.*

SOLUTION. $C_v = 28.9$ J;

$R = 8.314\ \text{J K}^{-}\ \text{mol}^{-}$. We know that :

$C_p - C_v = R;\ C_p = R + C_v = (8.314 + 28.9)$ J

∴ $C_p = 37.214$ J

(*i*) $$r = \frac{C_p}{C_v} = \frac{37.214\ \text{J}}{28.9\ \text{J}} = 1.29 \simeq 1.3.$$

Since r is 1.3, the gas is triatomic.

Hence, **atomicity of gas** = **3** **Ans.**

(*ii*) Mol. wt. = Atomicity × At. wt.

$= 3 \times 16 = \mathbf{48\ g\ mol^{-}}$ **Ans.**

Type. Molar heat capacity,

C_p or C_v = sp. heat × mol. wt. of gas

EXAMPLE 134. *Find the atomicity of a gas having molar mass 20 and specific heat equal to 0.15.*

SOLUTION. Atomicity of gas = ?; Mol. wt. = 20 g mol^{-}

$R = 2\ \text{cal K}^{-}\ \text{mol}^{-}$; sp. heat = 0.15. We know that :

(*i*) C_v = sp. heat × mol. wt.

$= 0.15 \times 20 = 3$

(*ii*) $C_p - C_v = R;\ C_p - 3 = 2.$

So, $$C_p = 2 + 3 = 5;\ \therefore r = \frac{C_p}{C_v} = \frac{5}{3} = \mathbf{1.67.}$$

Since the value of r is 1.67, the gas is **monoatomic.**

Hence, atomicity of gas = **1** **Ans.**

EXAMPLE 135. *Calculate the atomic weight and molecular weight of a gas if the specific heat of this gas at constant pressure and constant volume are 0.220 and 0.1575 respectively.*

SOLUTION. Let mol. wt. of gas = M; Sp. heat at constant pressure = 0.220,

sp. heat at constant volume = 0.1575. But :

(*i*) C_p = Sp. heat at constant pressure × M

= 0.220 × M = 0.220 M

(*ii*) C_v = Sp. heat at constant volume × M

= 0.1575 × M = 0.1575 M

(*iii*) $C_p - C_v = R$; 0.220 M – 0.1575 M = 2

[∵ R = 2 cal]

∴ 0.0625 M = 2

Hence, $$\mathbf{M} = \frac{2}{0.0625} = \mathbf{32\ g\ mol^{-}}$$ **Ans.**

(*iv*) **To find at. wt.**

$$r = \frac{C_p}{C_v} = \frac{0.22}{0.1575} = 1.4$$

Since r = 1.4 for diatomic gases, so atomicity of gas = 2

(*v*) Mol. wt. = Atomicity × At. wt.

∴ $$\textbf{At. wt.} = \frac{\text{Mol. wt.}}{\text{Atomicity}} = \frac{32}{2} = \mathbf{16}$$ **Ans.**

8.18 BOYLE'S TEMPERATURE, T_b

It is the temperature range at which the real gases obey gas laws.

$$T_b = \frac{a}{bR}$$

where a and b are vander Waal constants while R is the gas constant.

EXAMPLE 136. *Calculate the Boyle's temperature of hydrogen gas if vander Waal constants, a and b are 0.246 L^2 atm mol^{-2} and 0.0267 L mol^{-} respectively.*

SOLUTION. $a = 0.246\ \text{L}^2\ \text{atm mol}^{-2}$;

$b = 0.0267\ \text{L mol}^{-}$;

$R = 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-}$.

$$T_b = \frac{a}{bR}$$

$$= \frac{0.246\ \text{L}^2\ \text{atm mol}^{-2}}{0.0267\ \text{L mol}^{-} \times 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-}}$$

∴ $\mathbf{T_b = 112.2\ K}$ **Ans.**

8.19 CRITICAL CONSTANTS

Critical temperature, T_c. *It is the maximum temperature at which a gas can be liquefied.* Or it is a temperature above which a liquid cannot exist. **Mathematically :**

$$\mathbf{T_c = \frac{8\,a}{27\,Rb}}$$

Critical pressure, P_c. It is the minimum pressure that is required to cause liquefaction at the temperature, T_c. **Mathematically :**

$$\mathbf{P_c = \frac{a}{27\,b^2}}$$

Critical volume, V_c. It is the volume occupied by one mole of gas at critical temperature T_c and critical pressure, P_c. **Mathematically :**

$$\mathbf{V_c = 3\,b.}$$

(*i*) Critical pressure,

$$P_c = \frac{a}{27\,b^2}$$

(*ii*) Critical volume,

$$V_c = 3\,\text{b}$$

(*iii*) Critical temperature,

$$T_c = \frac{8\,a}{27\,Rb}$$

(*iv*)
$$b = \frac{RT_c}{8\,P_c} \qquad \left[\because\ \frac{T_c}{P_c} = \frac{8\,b}{R}\right]$$

where *a* and *b* are the vander Waal's constants and *R* is the gas constant.

Example 137. *The critical pressure and critical temperature of CO_2 gas are 72.9 atm and 304.2 K respectively. Calculate the radius of CO_2 molecule if the gas behaves as a vander Waal gas.*

Solution. $P_c = 72.9$ atm; $T_c = 304.2$ K;

$R = 0.0821$ L atm K^{-} mol^{-};

Avogadro no., $N = 6.023 \times 10^{23}\ mol^{-}$

r = radius of CO_2 molecule.

(*i*) $V_c = 3\,b$;

$$b = \frac{R\,T_c}{8\,P_c}$$

$$\left[\because\ \frac{T_c}{P_c} = \frac{8\,a}{27\,Rb} \times \frac{27\,b^2}{a} = \frac{8\,b}{R}\right]$$

$$\therefore \quad b = \frac{0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 304.2 \text{ K}}{8 \times 72.9 \text{ atm}}$$

$$= 0.0428 \text{ L mol}^{-}$$

$$= 0.0428 \times 1000 \text{ cm}^3 \text{ mol}^{-}$$

(*ii*)
$$b = 4 \times \text{Avogadro no.} \times \frac{4}{3}\,\pi\,r^3$$

$$= 4 \times 6.023 \times 10^{23} \text{mol}^{-} \times \frac{4}{3} \times \frac{22}{7}\,r^3$$

$$\therefore \quad 0.0428 \times 1000 \text{ cm}^3 \text{ mol}^{-} = 4 \times 6.023 \times 10^{23} \text{mol}^{-} \times \frac{4}{3} \times \frac{22}{7}\,r^3$$

$$\therefore \quad r = \left(\frac{0.0428 \times 1000\text{cm}^3 \times 3 \times 7}{4 \times 6.023 \times 10^{23} \times 4 \times 22}\right)^{1/3}$$

$$= (4.2394)^{1/3} \times 10^{-8} \text{ cm} \qquad \text{..... (A)}$$

But
$$\log\,(4.2394)^{\frac{1}{3}} = \frac{1}{3}\,\log 4.2394$$

$$= \frac{1}{3}\,(0.6273) = 0.2091$$

Antilog 0.2091 = 1.618

$$\therefore \quad r = 1.618 \times 10^{-8} \text{ cm}$$

$$= \mathbf{1.618\ A^{\circ}}$$ **Ans.**

Example 138. *A balloon of diameter 20 m weighs 100 kg. Calculate its pay-load, if it is filled with He at 1.00 atm and 27°C. Density of air is 1.2 kg m^{-3}. ($R = 0.082\ dm^3\ atm\ K^{-1}\ mol^{-1}$).* **(Roorkee, 1994)**

Solution. Diameter of balloon = 20 m

$$\text{Radius of balloon} = \frac{20}{2} = 10 \text{ m}$$

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7}(10 \text{ m})^3$$

$$= 4190.47 \text{ m}^3 = 4190.47 \times 10^3 \text{ L}$$

Mass of displaced air

= volume × density

= 4190.47 ×1.2 = 5028.57 kg

Weight of He gas in balloon can be calculated by applying the gas equation,

$$PV = nRT = \frac{m}{M}.\,RT$$

or
$$m_{He} = \frac{PVM_{\text{He}}}{RT} = \frac{1 \times 4190.47 \times 10^3 \times 4}{0.082 \times 300}$$

$$= 681.377 \times 10^3 \text{ g} = 681.377 \text{ kg}$$

Total weight of gas and balloon

= 681.377 + 100 = 781.377 kg

Pay load = Weight of air displaced – Weight of gas and balloon = 5028.57 – 781.377 = 4247.193 kg.

Example 139. *An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to be n-butane with normal boiling point of 0°C.* **(IIT, 1994)**

Solution. Mass of LPG used up

$$= 29.0 - 23.2 = 5.8 \text{ kg} = 5.8 \times 10^3 \text{ g}$$

Molar mass of *n*-butane (C_4H_{10})

$$= (4 \times 12) + (10 \times 1) = 58 \text{ g mol}^{-1}$$

Amount of gas used up

$$= \frac{5.8 \times 10^3 \text{ g}}{58 \text{ g mol}^{-}} = 10^2 \text{ mol}$$

Using ideal gas equation,

$$V = \frac{nRT}{P} = \frac{10^2 \times 0.082 \times 300}{1} = \mathbf{2463\ L}$$

[∵ for normal usage, P = 1 atm]

Example 140. *At room temperature, the following reactions proceed nearly to completion :*

$$2NO + O_2 \longrightarrow 2NO_2 \longrightarrow N_2O_4$$

The dimer, N_2O_4, solidifies at 262 K. A 250 ml flask and a 100 ml flask are separated by a stopcock. At 300 K, the nitric oxide in the larger flask exerts pressure of 1.053 atm and the smaller one contains oxygen at 0.789 atm. The gases are mixed by opening the stopcock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of the dimer, find out the pressure and composition of the gas remaining at 220 K. (Assume the gases to behave ideally). **(IIT, 1992)**

SOLUTION. $2NO + O_2 \longrightarrow 2NO_2 \longrightarrow N_2O_4$

Number of moles of

$$NO = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000}$$

$$= 0.0107$$

Number of moles of

$$O_2 = \frac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.0032$$

Now 2 moles of NO need 1 mole of O_2 for conversion into NO_2.

$\therefore$ 0.0032 moles of O_2 react with

$$NO = 2 \times 0.0032 = 0.0064 \text{ moles}$$

NO left unreacted $= 0.0107 - 0.0064 = 0.0043$ mol

Total volume of the vessels

$$= 250 + 100 = 350 \text{ ml} = \frac{350}{1000} \text{L}$$

$\therefore$ Pressure exerted by NO remaining at 220 K

$$= \frac{nRT}{V}$$

$$= \frac{0.0043 \times 0.0821 \times 220}{350} \times 1000$$

$$= 0.2219 \text{ atm}$$

Number of moles of N_2O_4 at 220 K

$$= 0.0032$$

$\therefore$ Total number of moles at 220 K

$$= 0.0032 + 0.0043 = 0.0075$$

Percentage of NO at 220 K

$$= \frac{0.0043}{0.0075} \times 100 = 57.33\%$$

EXAMPLE 141. *The critical pressure, critical volume and critical temperature of water are 218 atm, 0.0566 L mol*$^{-}$ *and 374°C respectively. Calculate the value of R.*

SOLUTION. $P_c = \frac{a}{27\, b^2}$; $V_c = 3\, b$; $T_c = \frac{8\, a}{27\, Rb}$.

So, $a = 27\, b^2 P_c$; $b = \frac{V_c}{3}$;

$$T_c = 374 + 273 = 647 \text{ K}$$

Hence,

$$R = \frac{8\, a}{27\, T_c b} = \frac{8 \times 27\, b^2 P_c}{27\, T_c b} = \frac{8 \times 27\, b P_c}{27\, T_c}$$

$$= \frac{8 \times 27 \times V_c\, P_c}{3 \times 27\, T_c} = \frac{8}{3}\,\frac{V_c\, P_c}{T_c}$$

$\therefore$

$$R = \frac{8}{3} \times \frac{0.0566 \text{ L mol}^{-} \times 218 \text{ atm}}{647 \text{ K}}$$

$$= \mathbf{0.05086\ L\ atm\ K^{-}\ mol^{-}} \qquad \textbf{Ans.}$$

8.20 INVERSION TEMPERATURE, T_i

It is the temperature below which a gas subjecting to Joule–Thomson effect shows **cooling effect** ($\mu_{J,T} = +\, ve$) and above which it shows heating effect ($\mu_{J,T} = -\, ve$).

Mathematically :

$$T_i = \frac{2\, a}{bR}$$

and $\mu_{J,T}$ is Joule–Thomson co-efficient represented as

$$: \mu_{J,T} = \left(\frac{\delta T}{\delta P}\right)_H$$

Note that $\mu_{J,T}$ for an ideal gas = 0 *i.e.,* zero.

EXAMPLE 142. *Calculate the inversion temperature of CO_2 gas if its vander Waal constants, a and b have the values 3.592 atm L^2 mol^{-2} and 0.0427 L mol^{-} respectively.*

SOLUTION. Inversion temperature,

$$T_i = ?;\ a = 3.592 \text{ atm L}^2 \text{mol}^{-2};$$

$$b = 0.0427 \text{ L mol}^{-}$$

$$R = 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}.$$

We know that :

$$T_i = \frac{2\, a}{bR} = \frac{2 \times 3.592 \text{ atm L}^2 \text{mol}^{-2}}{0.0427 \text{ L mol}^{-} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}}$$

$$= \mathbf{2049.25\ K.} \qquad \textbf{Ans.}$$

8.21 CHANGE IN TRANSLATIONAL K.E. PER MOL

Change in translational K.E. per mol

$$= \frac{3}{2} R\Delta T \text{ where}$$

ΔT = change in temperature; $R = 2$ cal K^{-} mol^{-}

EXAMPLE 143. *Calculate the thermal energy that should be added to 6.65 g of argon in a 15 litre flask to raise its temperature from 25°C to 100°C. (At. wt., Ar = 39.9)*

SOLUTION. Initial temperature

$$= 25 + 273 = 298 \text{ K};$$

Final temperature $= 100 + 273 = 373$ K.

Hence, $\Delta T = 373 \text{ K} - 298 \text{ K} = 75 \text{ K}$

$R = 2$ cal K^{-} mol^{-}.

We know that :

(*i*) Change in translational K.E. per mol

$$= \frac{3}{2} R\, \Delta T$$

$$= \frac{3}{2} \times 2 \text{ cal K}^{-} \text{ mol}^{-} \times 75 \text{ K}$$

$$= 225 \text{ cal mol}^{-}$$

(*ii*) 1 mol of Ar

$$= 1 \text{ g. atom of Ar} = 39.9 \text{ g mol}^{-}$$

Change in translational K.E. for 39.9 g mol^{-} of Ar

$$= 225 \text{ cal mol}^{-}$$

$\therefore$ Change in translational K.E. for 6.65 g of Ar

$$= \frac{225 \text{ cal mol}^{-}}{39.9 \text{ g mol}^{-}} \times 6.65 \text{ g}$$

$$= \mathbf{37.5\ cal} \qquad \textbf{Ans.}$$

8.22 THERMAL EQUILIBRIUM

At thermal equilibrium,

Heat gained = Heat lost

$$n \times C_v \times \Delta T = n \times C_v \times \Delta T$$

where $n = \dfrac{\text{wt.}}{\text{Mol. wt.}}$

For monoatomic gases *e.g.*, He, Ne, Ar etc,

$$C_v = \frac{3}{2}R$$

For diatomic gases, *e.g.*, O_2, N_2 etc,

$$C_v = \frac{5}{2}R$$

EXAMPLE 144. *Nitrogen gas (wt. = 2.8 g) having root mean square (r.m.s) velocity 500 m* s^{-} *and neon gas (wt. = 1.5 g) having r.m.s. velocity 600 m* s^{-} *were mixed in a thermally isolated container. Calculate the r.m.s. velocity of* N_2 *and Ar molecules when thermochemical equilibrium is reached. (at. wt., N = 14; Ne = 20; R = 8.314 kg* $m^2\ s^{-2}$*)*

SOLUTION. (*i*) wt. of

$$N_2 = 2.8 \text{ g; mol. wt. of}$$
$$N_2 = 2 \times 14 = 28 \text{ g mol}^{-}$$

$\therefore$ no. of mol of N_2,

$$n = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{2.8}{28} = \mathbf{0.1\ mol}$$

(*ii*) wt. of neon $= 1.5$ g; at. wt. or mol. wt. of

$$\text{Ne} = 20 \text{ g mol}^{-}$$

$$\therefore \quad \text{no. of mol of Ne} = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{1.5 \text{ g}}{20 \text{ g mol}^{-}}$$
$$= \mathbf{0.075\ mol}$$

(*iii*) U_{rms} of N_2

$$= \left(\frac{3RT}{M}\right)^{1/2};$$

$$500 \text{ m s}^{-} = \left(\frac{3 \times 8.314 \text{ kg m}^2 \text{s}^{-2}\ T}{28 \times 10^{-3} \text{ kg}}\right)^{½}$$

$$\left[\because\ 28 \text{ g} = 28 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 28 \times 10^{-3} \text{kg}\right]$$

Squaring both sides, we get :

$$(500 \text{ m s}^{-})^2 = \frac{3 \times 8.314 \text{ kg m}^2\ \text{s}^{-2} \times T}{28 \times 10^{-3} \text{ kg}};$$

$$250000 \text{ m}^2 \text{s}^{-2} = 890.78 \text{ m}^2 \text{s}^{-2} \times T$$

$$\therefore \quad T = \frac{250000}{890.78}$$

$$= 280.65 \text{ K. K.E. per 0.1 mol}$$

$$N_2 = \frac{3}{2}nRT$$

$$= \frac{3}{2} \times 0.1 \text{ mol} \times 8.314 \text{ JK}^{-} \text{mol}^{-} \times$$
$$280.65 \text{ K} \simeq 700 \text{ J}$$

(*iv*) U_{rms} of Ne $= \left(\dfrac{3\ RT}{M}\right)^{½}$;

$$600 \text{ m s}^{-} = \left(\frac{3 \times 8.314 \text{ kg m}^2 \text{ s}^{-2} \times T}{20 \times 10^{-3} \text{ kg}}\right)^{½}$$

$$\left[\because\ 20 \text{ g} = 20 \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 20 \times 10^{-3} \text{ kg}\right]$$

Squaring both sides, we get : $(600 \text{ m s}^{-})^2$

$$= \frac{3 \times 8.314 \text{ kg m}^2\ \text{s}^{-2} \times T}{20 \times 10^{-3} \text{ kg}}$$

$$360000 \text{ m}^2 \text{s}^{-2} = 1247.1\ T;\ \boldsymbol{T} = \frac{360000}{1247.1} = \mathbf{288.7\ K.}$$

K.E. per 0.075 mol Ne

$$= \frac{3}{2}nRT$$

$$= \frac{3}{2} \times 0.075 \text{ mol} \times 8.314 \text{ J K}^{-} \text{mol}^{-} \times$$
$$288.7 \text{ K} \simeq 270 \text{ J}$$

At equilibrium T becomes constant because Ne molecules provide heat energy to N_2 molecules.

Heat given or taken as equal to $n\ C_v \Delta T$

For monoatomic gases like Ne,

$$C_v = \frac{3}{2}R$$

For diatomic gases like N_2,

$$C_v = \frac{5}{2}R$$

Heat gained by N_2 = Heat lost by Ne; $n\ C_v\ \Delta T$

$$= n\ C_v\ \Delta T$$

$$0.1 \times \frac{5}{2}R \times (T - 280.65)$$

$$= 0.075 \times \frac{3}{2}R \times (288.7 - T)$$

$$0.25\ (T - 280.65) = 0.1125\ (288.7 - T)$$

$$T - 280.65 = \frac{0.1125}{0.25}(288.7 - T)$$

$$= 0.45\ (288.7 - T)$$

$$T - 280.65 = 129.92 - 0.45\ T;$$

$$1.45\ T = 129.92 + 280.65$$

$$\therefore \quad T = \frac{410.57}{1.45} = 283.15 \text{ K}$$

(*i*) $\boldsymbol{U_{rms}}$ **for** $\mathbf{N_2}$ $= \left(\dfrac{3RT}{M}\right)^{1/2}$

$$= \left(\frac{3 \times 8.314 \text{ kg m}^2 \text{s}^{-2} \times 283.15\ K}{28 \times 10^{-3} \text{ kg}}\right)^{1/2}$$

$$= (252226)^{1/2} \text{ ms}^{-}$$

$$= \mathbf{502.2\ ms^{-}}$$ **Ans.**

(*ii*) $\boldsymbol{U_{rms}}$ **for Ne** $= \left(\dfrac{3\text{RT}}{\text{M}}\right)^{1/2}$

$$= \left(\frac{3 \times 8.314 \text{ kg m}^2 \text{ s}^{-2} \times 283.15 \text{ K}}{20 \times 10^{-3} \text{ kg}}\right)^{1/2}$$

$$= (353116)^{1/2} \text{ ms}^{-} = \mathbf{592.2 \text{ ms}^{-}} \textbf{ Ans.}$$

8.23 LAW OF CORRESPONDING STATES

According to this law if two substances have the same reduced temperature and pressure, these will have same reduced volume.

$$\text{Let } \frac{P}{P_c} = \pi, \ \frac{V}{V_c} = \phi \text{ and } \frac{T}{T_c} = \theta.$$

Substituting the values of P, V and T in vander Waal equation

$$\left(P + \frac{a n^2}{V^2}\right)(V - nb) = nRT$$

and replacing the terms P_c, V_c and T_c by vander Waal constants, we get

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta.$$

Example 145. *The critical pressure and critical volume of a hydrocarbon (mol. wt. 16 g mol¯) are 45.6 atm and 0.0988 L mol¯ respectively. Calculate the reduced pressure and reduced volume of the hydrocarbon in a 2 L flask under 4 atmospheric pressure.*

Solution. (*i*)

P_c = 45.6 atm; P = 4 atm;

π = ? = reduced Pressure.

$$\therefore \quad \pi = \frac{P}{P_c} = \frac{4 \text{ atm}}{45.6 \text{ atm}} = \mathbf{0.0877} \quad \textbf{Ans.}$$

(*ii*) V_c = 0.0988 L mol¯;

V = 2 L; ϕ = reduced volume = ?

$$\therefore \quad \phi = \frac{V}{V_c} = \frac{2 \text{ L}}{0.0988 \text{ L}} = \mathbf{20.24} \quad \textbf{Ans.}$$

Example 146. *Calculate the reduced temperature of methane gas having reduced pressure and reduced volume 0.1096 and 50.607 respectively. Also calculate the temperature of the gas if its critical temperature is 190.2 K.*

Solution. We know that : $\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$

$$\therefore \quad \theta = \frac{\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1)}{8}$$

$$= \frac{\left(0.1096 + \frac{3}{(50.607)^2}\right)}{8}$$

[(3 × 50.607) −1]

$$= \frac{(0.1096 + 0.0012)(151.8 - 1)}{8}$$

$$= \frac{0.1108 \times 150.8}{8}$$

$$= 2.088$$

But $\theta = \frac{T}{T_c}$.

So, $T = \theta \times T_c = 2.088 \times 190.2$ K

or T = **397.1 K** **Ans.**

Example 147. *Calculate the reduced pressure of a gas if its reduced temperature and reduced volume are 0.8 and 11.0 respectively.*

Solution.

π = ? θ = 0.8;

ϕ = 11.0. We know that:

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \text{ (Law of corresponding states)}$$

$$\left(\pi + \frac{3}{(11)^2}\right)[(3 \times 11) - 1] = 8 \times 0.8$$

$$\left(\pi + \frac{3}{121}\right)(32) = 6.4;$$

$$\pi = \frac{6.4}{32} - \frac{3}{121} = \frac{(121 \times 6.4) - (3 \times 32)}{32 \times 121}$$

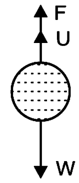
$$\text{or} \quad \pi = \frac{774.4 - 96}{3872} = \frac{678.4}{3872} = \mathbf{0.1752} \textbf{ Ans.}$$

8.24 VISCOSITY

The force existing between the two consecutive layers of fluids due to their velocity gradient is called viscous force. This property of the liquids is called viscosity. Mathematically:

$$F = -\eta A \frac{dV}{dx}$$

Where η is called the co-efficient of viscosity.



Stokes law. Stokes found that the viscous force F acting on the motion of small sphere (of radius, r) of spherical body depends upon the radius r of sphere, velocity v of spherical body and co-efficient of viscosity, η of the fluid. Mathematically:

$$\boldsymbol{F = 6\pi\eta r v.}$$

Terminal velocity. Suppose a sphere of density ρ and radius r, is falling under gravity in a fluid of density ρ'. Following forces act on this falling body.

(*i*) Viscous drag force, F acting upward (*ii*) upthrust U due to buoyancy acting upward and (*iii*) weight, W of the sphere acting vertically downward through the centre of gravity of sphere.

$\therefore$ Net downward force

$= W - (F + U)$.

This force causes the sphere to fall down. When the weight of the sphere is just balanced by the sum of drag force (which increases with increase in velocity of body) and upthrust force, there is no resultant force on the sphere. At this stage, the sphere begins to flow with constant velocity v_0 called terminal velocity which is the maximum velocity of the sphere. Under this condition :

$$F + U = W.$$

Substituting the values of F (= $6\pi\eta r v_0$, Stoke's law), η (= co-efficient of viscosity of medium through which sphere moves) and U (= weight of the fluid displaced, Archimide's principle = $\frac{4}{3}\pi r^3 \rho' g$) and W(= $\frac{4}{3}\pi r^3 \rho g$), we get :

$$6\pi\eta r v_0 + \frac{4}{3}\pi r^3 \rho' g = \frac{4}{3}\pi r^3 \rho g \quad \text{or}$$

$$6\pi\eta r v_0 = \frac{4}{3}\pi r^3 g(\rho - \rho')$$

$$\therefore \quad v_0 = \frac{2}{9}\cdot\frac{r^2(\rho-\rho')g}{\eta}$$

Example 148. *When a liquid having density 0.69 g cm^{-3} was cautiously shaken, an air bubble of 1.2 cm radius started rising at a constant rate of 0.48 cm s^{-} through this liquid. Neglecting density of air, calculate the co-efficient of viscosity of the liquid.*

Solution. Density of liquid,

$$\rho' = 0.69 \text{ g cm}^{-3};$$

radius of air bubble,

$$r = 1.2 \text{ cm; density of air, } \rho = 0;$$

terminal velocity, v_0

$$= -0.48 \text{ cm s}^{-}.$$

Negative sign to v_0 is given because the bubble is moving upward. We know that

$$v_0 = \frac{2}{9}\cdot\frac{r^2(\rho-\rho')g}{\eta}$$

or
$$\eta = \frac{2}{9}\cdot\frac{r^2(\rho-\rho')g}{v_0}$$

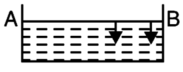
Hence,
$$\eta = \frac{2}{9}\cdot\frac{(1.2)^2(0-0.69)\times 981}{-0.48}$$

$$= \mathbf{451.26 \text{ poise}} \qquad \textbf{Ans.}$$

8.25 SURFACE TENSION, σ

Suppose force F is acting on length l of an imaginary line AB on the surface of a liquid. Then, surface tension, σ is given by the relation,

$$\sigma = \frac{F}{l}.$$



Its units in C.G.S. system = **dyne cm^{-}**; in S.I. system = **N m^{-}**.

Example 149. *A metallic wire ring of radius 2.98 cm radius is rested on a liquid surface and then raised. The pull needed is 2.99 g more before the film breaks than it is after. Calculate the surface tension of the liquid present.*

Solution. By definition, the force due to surface tension = additional pull F of 2.99 g weight.

Thus, Force due to surface tension, $F = \sigma \times$ length of metal wire ring in contact with the liquid $= \sigma \times 2 \times 2\pi r = 4\pi\sigma r$

Thus, $\quad 4\pi\sigma r = 2.99 \times 981$ dyne

or
$$\sigma = \frac{2.99\times 981 \text{ dyne}}{4\pi r \text{ cm}}$$

$$= \frac{2.99\times 981 \text{ dyne}}{4\times 3.142\times 2.98 \text{ cm}}$$

$$= 78.32 \text{ dyne cm}^{-} \ \textbf{Ans.}$$

8.26 AIEEE PATTERN EXAMPLES

Example 150. *If the absolute temperature of a gas is doubled and the pressure is reduced to one half, the volume of gas will :*

(*a*)	*remain unchanged*	(*b*)	*be doubled*
(*c*)	*increase four fold*	(*d*)	*be halved*
(*e*)	*be reduced to one fourth.*		**(Kerala PET, 2005)**

Solution. Let $P_1 = P$, $V_1 = V$ and $T_1 = T$, then

$$P_2 = \frac{P}{2},\ V_2 = ? \text{ and } T_2 = 2T.$$

Applying gas equation, we get :

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

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} = \frac{P\times V\times 2T\times 2}{T\times P} = 4V.$$

So, the correct answer is (*c*).

Example 151. *To what temperature must a neon gas sample be heated to double the pressure, if the initial volume of the gas at 75°C is decreased by 15%?*

(*a*)	*319°C*	(*b*)	*592°C*
(*c*)	*128°C*	(*d*)	*60°C*
(*e*)	*90°C.*		**(Kerala PET, 2005)**

Solution. Let $P_1 = P$, $V_1 = V$ and

$$t_1 = 75 + 273 = 348 \text{ K}.$$

Thus, $\quad P_2 = 2P,\ V_2 = \frac{(100-15)V}{100} = \frac{85V}{100}$ and

$$T_2 = ?.$$

[∵ initial volume is decreased by 15%]

Using gas equation, we have :

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

$$T_2 = \frac{P_2V_2T_1}{P_1V_1} = 2P\times\frac{85V}{100}\times\frac{348 \text{ K}}{P\times V}$$

or
$$T_2 = 591.6 \text{ K} = 591.6 - 273$$

$$= 318.6°\text{C} \simeq \mathbf{319°C}.$$

So, the correct answer is (*a*).

EXAMPLE 152. *2 g of O_2 at 27°C and 760 mm of Hg pressure has volume*

(1) 1.5 *lit.* (2) 2.8 lit.
(3) 11.2 lit. (4) 22.4 lit.

(BCECE, Bihar, 2005)

SOLUTION.
$$P = 760 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} = 1 \text{ atm};$$
$$V = ?$$
$$T = 27 + 273 = 300 \text{ K},$$
$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-}.$$
$$\text{wt. of } O_2 = 2\text{g};$$
$$\text{g. mol. wt. of } O_2 = (2 \times 16) = 32 \text{ g mol}^{-}$$
$$\therefore \text{ no. of mol of } O_2 = n = \text{wt/g. mol.}$$
$$\text{wt} = \frac{2 \text{ g}}{32 \text{ g mol}^{-}} = \frac{1}{16} \text{ mol}$$

By gas equation :
$$PV = nRT; \; V = \frac{nRT}{P}.$$
$$\therefore \quad V = \frac{1}{16}\text{mol} \times \frac{0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 300 \text{ K}}{1 \text{ atm}}$$
$$= 1.5 \text{ L}$$

So, the correct answer is (1).

EXAMPLE 153. *A certain sample of gas has a volume of 0.2 litre measured at 1 atm pressure and 0°C. At the same pressure but 273°C, its volume will be :*

(*a*) 0.4 litres (*b*) 0.8 litres
(*c*) 27.8 litres (*d*) 55.6 litres

(IMS–BHU, 2005)

SOLUTION. Since pressure is the same, it is Charle's law.
$$V_1 = 0.2 \text{ L}, \; T_1 = 0 + 273 = 273 \text{ K};$$
$$V_2 = ? \; T_2 = 273 + 273 = 546 \text{ K}.$$
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}; \; V_2 = \frac{V_1}{T_1} \times T_2$$
$$V_2 = \frac{0.2 \text{ L} \times 546 \text{ K}}{273 \text{ K}} = \mathbf{0.4 \text{ L}}$$

So, the correct answer is (*a*).

EXAMPLE 154. *One mole of monoatomic ideal gas at T (K) is expanded from 1 L to 2 L adiabetically under a constant external pressure of 1 atm. The final temperature of the gas in kelvin is:*

(*a*) T (*b*) $\frac{T}{2^{5/3-1}}$

(*c*) $T - \frac{2}{3 \times 0.0821}$ (*d*) $T + \frac{3}{2 \times 0.0821}$

[IIT – JEE (screening), 2005]

SOLUTION.
$$W_{surr} = \Delta E; \; \Delta E = -P\Delta V;$$
$$n\, C_v \Delta T = -P\Delta V \qquad \text{...(1)}$$

Given : $n = 1 \text{ mol}; \; C_v = \frac{R}{\gamma - 1}; \; \Delta T = T_f - T;$
$$\Delta V = V_2 - V_1 = 2 \text{ L} - 1 \text{ L} = 1 \text{ L}$$

$\therefore$ From relation (1), we have :
$$1 \times \frac{R}{\gamma - 1} \times (T_f - T) = -P\,(V_2 - V_1)$$

or
$$T_f - T = \frac{-P(V_2 - V_1) \times (\gamma - 1)}{R}.$$

Hence,
$$T_f = T - \frac{P(V_2 - V_1) \times (\gamma - 1)}{R}$$
$$\therefore \quad T_f = T - \frac{1(2-1) \times \frac{5}{3} - 1}{0.0821}.$$
$$= T - \frac{2}{3 \times 0.0821}$$

So, the correct answer is (*c*).

EXAMPLE 155. *The ratio of rate of diffusion of helium with respect to methane under similar conditions of constant temperature and pressure is :*

(*a*) 2 (*b*) 0.5
(*c*) 16 (*d*) 4

[IIT–JEE (screening), 2005]

SOLUTION. Molecular weight of
$$CH_4 = 12 + (4 \times 1) = 16 \; amu$$
$$\text{At. wt. of He} = \text{Mol. wt. of He} = 4 \; amu.$$

We know that rate of diffusion (*r*) of gases is inversely proportional to the square root of their molecular weights.

Hence.,
$$\frac{r_{He}}{r_{CH_4}} = \left(\frac{M_{CH_4}}{M_{He}}\right)^{1/2} = \left(\frac{16}{4}\right)^{1/2}$$
$$= (4)^{1/2} = 2.$$

So, the correct answer is (*a*).

EXAMPLE 156. *The average and total kinetic energies of 0.5 mol of an ideal gas at 273 K are respectively in KJ mol^{-} :*

(*a*) 2.5×10^2; 3.9 (*b*) 3.405 ; 1.7025
(*c*) 5.0×10^4; 7.8 (*d*) 6.81 ; 4.08

SOLUTION.
$$R = 8.314 \text{ J K}^{-} \text{mol}^{-};$$
$$T = 273 \text{ K. We know :}$$

(*a*) Average
$$K.E. = \frac{3}{2}RT = \frac{3}{2}[8.314 \text{ JK}^{-} \text{ mol}^{-} \times 273 \text{ K}]$$
$$= 3404.5 \text{ J mol}^{-}$$
$$= \frac{3404.5}{1000} \simeq 3.405 \text{ kJ mol}^{-}.$$

Total *K.E.* of 0.5 mol of gas
$$= 0.5 \text{ mol} \times 3.405 \text{ kJ mol}^{-}$$
$$= 1.7025 \text{ kJ}.$$

Hence, true answer is **(*b*)**.

EXAMPLE 157. *1 mole of a N_2O_4 (g) is kept in a container under 1.0 atmospheric pressure and 27°C. It is heated to 327°C. As a result, 20% of N_2O_4 (g) by mass decomposed to NO_2 (g). The resultant pressure is :*

(*a*) 1 atm (*b*) 1.2 atm
(*c*) 2.4 atm (*d*) 3.6 atm.

[Karnataka, CET, 2012]

Solution. Initial temperature

$$= 27 + 273 = 300 \text{ K}.$$

Final temperature $= 327 + 273 = 600$ K.

$P_1 = 1$ atm; $P_2 = ?$

According to pressure, temperature law :

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{or} \quad \frac{1 \text{ atm}}{300 \text{ K}} = \frac{P_2}{600 \text{ K}}.$$

Thus, $$P_2 = \frac{600}{300} = \mathbf{2\ atm}$$

Let α be the degree of decomposition of N_2O_4 (g). N_2O_4 (g) ionises as :

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$
$$2 - 2\,\alpha \qquad 2\,(2\alpha)$$

Total pressure $= 2 - 2\,\alpha + 4\,\alpha = 2 + 2\,\alpha$.

But, $$\alpha = \frac{20}{100} = 0.2 \text{ (given)}$$

∴ The resultant pressure

$$= 2 + (2 \times 0.2) = 2 + 0.4 = \mathbf{2.4\ atm.}$$

So, the true answer is (*c*).

Example 158. *Hydrogen gas diffuses from two different vessels X and Y. Vessel X has a circular orfice while vessel Y has a square orfice of length equal to the radius of the orfice of vessel X. Assuming same temperature and pressure, the ratio of the rates of diffusion of H_2 gas from vessel X to vessel Y is :*

(*a*) 1 : 1 (*b*) 1 : 2

(*c*) $\frac{1}{\pi}$ (*d*) π.

Solution. Let r = radius of the orfice of vessel X. We know : rate of diffusion is directly proportional to the area of orfice. So :

For gas X, $r_x \propto \pi\, r^2$ ...(*i*); For gas Y, $r_y \propto r^2$ ...(*ii*)

Dividing (*i*) and (*ii*), we get ;

$$\frac{r_X}{r_Y} = \frac{\pi\, r^2}{r^2} \quad \text{or} \quad \frac{r_X}{r_Y} = \pi.$$

So, the correct answer is (*d*).

Example 159. *The molecules of gas X move 3 times faster than those of gas Y at the same temperature. The ratio of the molecular weights $\frac{M_X}{M_Y}$ will be :*

(*a*) 1/10 (*b*) 1/9

(*c*) 1/8 (*d*) 7/1.

Solution. Given

$$\frac{r_X}{r_Y} = 3. \text{ But } \frac{r_X}{r_Y} = \left(\frac{M_Y}{M_X}\right)^{1/2} ; \left(\frac{M_Y}{M_X}\right)^{1/2}$$

$$= \frac{3}{1} \; or \; \left(\frac{M_X}{M_Y}\right)^{1/2} = \frac{1}{3}.$$

Squaring both sides. We get: $\frac{M_X}{M_Y} = \frac{1}{9}$. So, the correct answer is (*b*).

Example 160. *Which of the following statements is false ?*

(*a*) *The difference between rms velocity and mean velocity at any temperature for different gases diminishes as larger and yet larger molar masses are considered.*

(*b*) *The square of the mean velocity of molecules is equal to square of the rms velocity at a certain temperature.*

(*c*) *The ratio of the mean velocity to the rms velocity is independent of temperature.*

(*d*) *The mean K.E. of the gas molecules at any given temperature does not depend on the mean velocity.*

Solution. (*a*) $$V_{av} = \left(\frac{8RT}{\pi M}\right)^{1/2} ; \quad V_{rms} = \left(\frac{3RT}{M}\right)^{1/2}.$$

In both the velocities, molar mass, M is in the denominator. So, (*a*) is true.

(*b*) $$V_{av} = \left(\frac{8RT}{\pi M}\right)$$

$$\therefore \quad V_{av}^2 = \frac{8RT}{\pi M}; \quad V_{rms} = \left(\frac{3RT'}{M}\right)^{1/2}$$

$$\therefore \quad V_{rms}^2 = \frac{3RT'}{M}$$

Thus, $$\frac{8RT}{\pi M} = \frac{3RT'}{M} \quad \text{or} \quad \frac{T}{T'} = \frac{3\pi}{8}$$

or $$T = \frac{3\pi}{8}.T'$$

Since, T is not equal to T' (*b*) is false.

(*c*) $$V_{av} = \left(\frac{8RT}{\pi\, M}\right)^{1/2} ; \; V_{rms} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$\therefore \quad \frac{V_{av}}{V_{rms}} = \left(\frac{8RT}{\pi\, M} \times \frac{M}{3RT}\right)^{1/2} = \left(\frac{8}{3\,\pi}\right)^{1/2}$$

So, V_{av}/V_{rms} is independent of temperature. Thus, (*c*) is true.

(*d*) $$\text{Mean K.E.} = \frac{1}{2}mV^2 \text{ or } \frac{1}{2}mV^2_{rms};$$

$$V_{av} = \left(\frac{8RT}{\pi M}\right)^{1/2};$$

$$V_{rms} = \left(\frac{3RT}{M}\right)^{1/2}.$$

Thus if V_{av} is changed, V_{rms} is also affected.

So, (*d*) is true.

Example 161. *For identical conditions of temperature, the density of a gas A is three times that of gas B but the molar mass of gas B is two times that of gas A. The ratio of pressures of gases A and B is :*

(*a*) 3 (*b*) $\frac{1}{3}$

(*c*) 6 (*d*) $\frac{1}{6}$

Solution. We know, density,

$$d = \frac{PM}{RT} \text{ or } P = \frac{dRT}{M}$$

For gas A, $$P_A = \frac{3dRT}{M_A} \quad ...(i)$$

For gas B, $$P_B = \frac{dRT}{M_B} = \frac{dRT}{2M_A} \quad ...(ii)$$

Dividing (*i*) and (*ii*), we get :

$$\frac{P_A}{P_B} = \frac{3dRT}{M_A} \times \frac{2M_A}{dRT}$$

or $$\frac{P_A}{P_B} = 6.$$

So, the true answer is (*c*).

Example 162. *Density of oxygen will be the highest under one of the following conditions :*

(*a*) *273 K and 2 atm* (*b*) *NTP*

(*c*) *546 K and 1 atm* (*d*) *546 K and 2 atm.*

Solution. Hint. We know, density,

$$d = \frac{PM}{RT}.$$

Since R and M are constant, greater the value of $\frac{P}{T}$, greater will be the density. (*a*) is correct.

Example 163. *The plot of compressibility factor, Z and P at constant temperature helps to predict the behaviour of a gas. The value of Z is greater than one at high temperature and high pressure. This can be easily explained by vander Waal equation when :*

(*a*) *vander Waal constant 'b' is negligible but not 'a'.*

(*b*) *vander Waal constants 'a' and 'b' are negligible.*

(*c*) *vander Waal constants 'a' and 'b' are not negligible.*

(*d*) *vander Waal constant 'a' is negligible but not 'b'.*

Solution. According to vander Waal equation.

$$\left(P + \frac{a\,n^2}{V^2}\right)(V - nb) = nRT \quad ...(1)$$

At high temperature, 'a' can be ignored as the pressure is high. Hence, equation (1) becomes :

$$P\,(V - b) = RT$$

$$\therefore \quad PV - Pb = RT \text{ or } PV = Pb + RT$$

Dividing both sides by RT, we get :

$$\frac{PV}{RT} = \frac{Pb}{RT} + \frac{RT}{RT} \text{ or}$$

$$Z = \frac{Pb}{RT} + 1 \text{ i.e., } Z > 1.$$

So, true statement is (*d*) because constant 'a' is negligible and not 'b'.

Example 164. *Pressure remaining constant, at what temperature, the volume of a gas at 0°C will be double of the volume ?*

(*a*) *100°C* (*b*) *546°C*

(*c*) *273 K* (*d*) *546 K*

(BET, 2003)

Solution. Since pressure is constant, it is Charle's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}.$$

Here $$V_1 = V,\ T_1 = 0 + 273 = 273 \text{ K};$$
$$V_2 = 2V;\ T_2 = ?.$$

Hence, $$\frac{V}{273 \text{ K}} = \frac{2V}{T_2};\ T_2 = 2 \times 273 = 546 \text{ K}.$$

So, the correct answer is (*d*).

Example 165. *$T = 550$ K, $V = 49.8$ litre,*

$n = 2$ mol, then the pressure will be (atm).

(*a*) 2 (*b*) 4

(*c*) 1.5 (*d*) 2.5 **(IMS–BHU, 2003)**

Solution. We know,

$$PV = nRT;$$

$$P = \frac{nRT}{V}.$$

Substituting the values, we get:

$$P = \frac{2 \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 550 \text{ K}}{49.8 \text{ L}}$$

$$= 1.8 \simeq 2.$$

So, the right choice is (*a*).

Example 166. *If rms =1000, then average velocity is :*

(*a*) 920 (*b*) 820

(*c*) 1000 (*d*) 1020

(IMS – BHU, 2003)

Solution. We know

$$V_{av} = 0.92 \times V_{rms}$$

$$\therefore \quad V_{av} = 0.92 \times 1000 = 920.$$

So, the correct answer is (*a*).

Example 167. $\frac{T_A}{M_A} = 4 \times \frac{T_B}{M_B}$, *then* $\frac{V_A}{V_B}$ *is :*

(*a*) *2 : 1* (*b*) 2 : 3

(*c*) *3 : 1* (*d*) *1 : 4*

(I.M.S. – BHU, 2003)

Solution. We know that $V \propto \left(\frac{T}{M}\right)^{1/2}$

Hence, $$\frac{V_A}{V_B} = \left(\frac{T_A}{M_A} / \frac{T_B}{M_B}\right)^{1/2}$$

$$= \left(\frac{4}{1}\right)^{1/2} = \frac{2}{1} \quad \text{or} \quad 2:1$$

$$\left[\because \frac{T_A}{M_A} / \frac{T_B}{M_B} = \frac{4}{1}\text{(given)}\right]$$

So, the correct answer is (*a*).

Example 168. *Iodised table salt contains 7.6×10^{-5} g of KI* *per gram of NaCl. The concentration in ppm of KI is :*

(*a*) *76* (*b*) *152*
(*c*) 500 (*d*) *760*

(JIPMER, Pondicherry, 2000)

SOLUTION. 1 in 10^6 is called as 1 ppm

$\therefore$ 7.6×10^{-5} g $\times 10^6 = 76$ ppm.

So, the correct answer is (*a*).

EXAMPLE 169. *10 litre solution of urea contains 240 g urea. The active mass of urea will be :*

(*a*) *0.02* (*b*) *0.04*
(*c*) *0.2* (*d*) *0.4*

(Karnataka CET, 2000)

SOLUTION. We know that molar concentration of a substance is called its active mass.

10 L of urea solution contains urea

$$= 240 \text{ g}$$

$\therefore$ 1 L of urea solution contains urea

$$= \frac{240 \text{ g}}{10} = 24 \text{ g}.$$

g. mol. wt. of urea, $NH_2CO\ NH_2$

$$= 14 + (2 \times 1) + 12 + 16 + 14 + (2 \times 1)$$
$$= 60 \text{ g}.$$

$\therefore$ No. of mol of urea

$$= \frac{\text{wt. of urea}}{\text{g. mol. wt. of urea}} = \frac{24 \text{ g}}{60 \text{ g}} = 0.4.$$

So, the correct answer is (*d*).

EXAMPLE 170. *What volume of hydrogen gas at 273 K and 1 atmospheric 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*) *22.4 L* (*b*) *89.6 L*
(*c*) *67.2 L* (*d*) *44.8 L*

(AIEEE, 2003)

SOLUTION. Reaction :

$$\begin{array}{ccccccc} 2BCl_3 & + & 3H_2 & \longrightarrow & 2B & + & 6HCl \quad ...(1) \\ & & 3 \times 22.4 \text{ L} & & 2 \times 10.8 \text{ g} & & \end{array}$$

Wt. of boron, B = 21.6 g

From equation (1), we find that :

2×10.8 g boron is obtained by the use of

$$H_2 = 3 \times 22.4 \text{ L}$$

$\therefore$ 21.6 g boron is obtained by the use of

$$H_2 = \frac{3 \times 22.4 \text{ L}}{2 \times 10.8} \times 21.6 = 67.2 \text{ L}$$

So, the correct answer is (*c*).

EXAMPLE 171. *For an ideal gas, number of moles per litre in terms of its pressure P, gas constant R and temperature T is:*

(*a*) $\frac{PT}{R}$ (*b*) $\frac{RT}{P}$
(*c*) $\frac{P}{RT}$ (*d*) *PRT*

(AIEEE, 2002)

SOLUTION. Let no. of moles per litre = n/V

We know that $PV = nRT$

Thus, $$\frac{P}{RT} = \frac{n}{V}$$

Hence, the true answer is (*c*).

EXAMPLE 172. *If 0.44 g of a colourless oxide of nitrogen occupies 224 mL at 1520 mm Hg and 273°C, then the compound is :*

(*a*) *NO* (*b*) NO_2
(*c*) N_2O_3 (*d*) N_2O

SOLUTION. $P_1 = 1520$ mm, $V_1 = 224$ mL,
$T_1 = 273 + 273 = 546$ K

At *N.T.P.*, $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K.

Applying gas equation, we have :

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

Thus, $$V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

Substituting the values, we get :

$$V_2 = \frac{1520 \times 224 \times 273}{760 \times 546} = 224 \text{ mL}.$$

Thus, 224 mL oxide of nitrogen weighs = 0.44 g

$\therefore$ 22400 mL oxide of nitrogen weighs

$$= \frac{0.44}{224} \times 22400 = 44 \text{ g}.$$

$\therefore$ Gram molar mass of oxide of nitrogen = 44

$\therefore$ Gas = N_2O because molar mass of N_2O
$= (2 \times 14) + 16$
$= 44$. So, the correct answer is, (*d*).

EXAMPLE 173. *If the density of air at 298 K and 101.325 kPa is 1.161 kg* m^{-3}*, then the average molar mass of air, assuming air behaves as an ideal gas is :*

(*a*) *18 g* mol^{-} (*b*) *28 g* mol^{-}
(*c*) *32 g* mol^{-} (*d*) *2 g* mol^{-}

SOLUTION. $d = 1.161 \text{ kg m}^{-3}$;
$T = 298$ K;
$R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-} \text{ mol}^{-}$
$P = 101.325 \times 10^3 \text{ kg m}^{-} \text{ s}^{-2}$.

We know, $$PV = nRT\ ;\ PV = \frac{\text{mass}}{\text{molar mass}} \times RT$$

$$\therefore \quad \text{Molar mass} = \frac{\text{mass}}{V} \times \frac{RT}{P} = \frac{d\ RT}{P} \qquad ...(1)$$

Substituting the values in (1), we get :

Molar mass

$$= \frac{1.161 \text{ kg m}^{-3} \times 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-} \text{ mol}^{-} \times 298 \text{ K}}{101.325 \times 10^3 \text{ kg m}^{-} \text{ s}^{-2}}$$

$= 0.028 \text{ kg mol}^{-}$
$= 0.028 \times 1000 \text{ g mol}^{-} = 28 \text{ g mol}^{-}$.

So, the correct answer is, (*b*).

EXAMPLE 174. *Two flasks A and B of 1 L capacity each contains* SO_2 *and* Br_2 *gases respectively maintained at 340 K and pressure of 1.5 atmosphere. If number of* Br_2 *molecules in flask B is N, the total number of atoms in flask A will be :*

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

SOLUTION. Flask *A* contains SO_2 (g) and flask *B* contains Br_2 gas. Both gases have equal volume (= 1L) under similar conditions of temperature (340 K) and pressure (1.5 atm). But, according to Avogadro's law, equal volume of all gases contain equal number of molecules

$\therefore$ No. of SO_2 molecules

= No. of Br_2 molecules = N (given)

One molecule of SO_2(g) contain atoms

= 3 (*i.e.*, one S-atom and two O-atoms)

$\therefore$ N molecules of SO_2(g) contain atoms

= 3 × N = 3 N.

Hence the correct answer is, (*c*).

EXAMPLE 175. *vander Waal's constants a and b for CO_2 gas are 3.592 atm L^2 mol^{-2} and 0.0427 L mol^{-} respectively. The Boyle's temperature for the gas will be :*

(*a*) *84.12 K*	(*b*) *373 K*
(*c*) *1000 K*	(*d*) *1024.6 K*

SOLUTION. Boyle's temperature,

$$T_b = \frac{a}{bR}$$

$$= \frac{3.592 \text{ atm L}^2 \text{ mol}^{-2}}{0.0427 \text{ L mol}^{-} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}}$$

or $T_b = 1024.6$ K

$[\because \text{ R} = 0.0821 \text{ L atm K}^{-} \text{mol}^{-}]$

So, the correct answer is (*d*).

EXAMPLE 176. *vander Waal's constants a and b for hydrogen gas are 0.246 atm L^2 mol^{-2} and 0.0267 L mol^{-} respectively. The value of inversion temperature for the gas will be :*

(*a*) *168.24 K*	(*b*) *84.12 K*
(*c*) *112.2 K*	(*d*) 224.4 K

SOLUTION. $a = 0.246 \text{ atm L}^2 \text{ mol}^{-2}$;

$b = 0.0267 \text{ L mol}^{-}$.

$R = 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}$.

Inversion temperature,

$$T_i = \frac{2a}{bR}$$

$$= \frac{2 \times 0.246 \text{ atm L}^2 \text{ mol}^{-2}}{0.0267 \text{ L mol}^{-} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}}$$

$\therefore$ $T_i = 224.4$ K.

So, the correct answer is (*d*).

EXAMPLE 177. *If the value of critical pressure and critical temperature are 72 atm and 30°C respectively, the value of vander Waal constant 'a' will be :*

(*a*) *0.0432 L mol^{-}*	(*b*) *3.628 L^2 atm mol^{-2}*
(*c*) *0.0216 L mol^{-}*	(*d*) *0.06 atm L^2 mol^{-2}*

SOLUTION. $P_c = 72$ atm; a = ?;

$T_c = 30 + 273 = 303$ K

(*i*) $$P_c = \frac{a}{27\,b^2};$$

$$T_c = \frac{8a}{27bR}; R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-}$$

$$\therefore \quad \frac{T_c}{P_c} = \frac{8a}{27\,bR} \times \frac{27\,b^2}{a} = \frac{8b}{R}.$$

$$\text{So, } b = \frac{T_c\,R}{8\,P_c}$$

$$\therefore \quad b = \frac{303 \text{ K} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}}{8 \times 72 \text{ atm}}$$

$= 0.0432 \text{ L mol}^{-}$

(*ii*) $$P_c = \frac{a}{27\,b^2}.$$

So, $a = 27\,b^2\,P_c$

$= 27 \times (0.0432)^2 \text{ L}^2 \text{ mol}^{-2} \times 72 \text{ atm}$

or $a = 3.628 \text{ L}^2\text{atm mol}^{-2}$.

So, the correct answer is (*b*).

EXAMPLE 178. *The value of vander Waal's constant b for CO_2 gas having critical pressure and critical temperature values 72.9 atm and 31.2°C is :*

(*a*) *0.342 L mol^{-}*	(*b*) *0.342 L^2 atm mol^{-2}*
(*c*) *0.0428 L mol^{-}*	(*d*) *0.0214 L mol^{-}*

SOLUTION. b = ?; $P_c = 72.9$ atm;

$T_c = 31.2 + 273 = 304.2$ K

We know that $$b = \frac{RT_c}{8\,P_c}$$

$$= \frac{0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 304.2 \text{ K}}{8 \times 72.9 \text{ atm}}$$

$\therefore$ $b = 0.0428 \text{ L mol}^{-}$

So, the correct answer is (*c*).

EXAMPLE 179. *A real gas is supposed to obey the gas equation, P(V – b) = nRT at NTP. If one mole of a gas occupies 24 dm^3 volume at NTP, the compressibility factor for the gas will be :*

(*a*) *1.071*	(*b*) 5.8×10^{-3}
(*c*) *2.9×10^{-3}*	(*d*) 2

SOLUTION. We know that compressibility factor,

$$\therefore \quad Z = 1 + \frac{Pb}{nRT} \quad \text{...(A)}$$

Calculation of vander Waal factor, *b*. We know that, at NTP,

P = 1 atm, T = 273 K; P (V – b) = nRT.

So, 1 atm (24 L – b) = 1 mole × 0.0821 L atm K^{-} mol^{-} × 273 K

or 24 L atm – b atm = 22.41 L atm; 24 L – b = 22.41 L

$\therefore$ b = 24 L – 22.41 = 1.59 L.

Substituting the value of *b*, *P*, *n*, *R* and *T* in (*A*), we get:

$$Z = 1 + \frac{1 \text{ atm} \times 1.59 \text{ L}}{1 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 273 \text{ K}}$$

= 1 + 0.071 = 1.071

So, the correct answer is (a).

EXAMPLE 180. *One mole of a real gas occupies 24.7 dm^3 at S.T.P. If the gas obeys the gas equation $P(V-b)=nRT$, the diameter of each gas molecule will be :*

(*a*) *7 A°* (*b*) *1.2198 A°*
(*c*) *3.5 A°* (*d*) *1.75×10^{-8} cm*

SOLUTION. $P = 1$ atm, $V = 24.7\ dm^3$
$= 24.7$ L; $b = ?$; $n = 1$ mole;
$R = 0.0821$ L atm K^{-} mol^{-};
$T = 273$ K at S.T.P.;

Diameter, $d = 2r$

(*i*) $P(V-b) = nRT.$

$$1 \text{ atm } (24.7 \text{ L} - b) = 1 \text{ mole} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 273 \text{ K}$$

$$24.7 \text{ L atm} - b \text{ atm} = 22.41 \text{ L atm}$$

$$\therefore \quad b = 24.7 \text{ L} - 22.41 = 2.29 \text{ L mol}^{-}$$

Also: $b = 4 \times$ Avogadro no. $\times$ volume of one molecule.

$$2.29 \text{ L mol}^{-} = 4 \times 6.023 \times 10^{23} \text{ mol}^{-} \times \frac{4}{3}\pi r^3$$

$$= 4 \times 6.023 \times 10^{23} \text{ mol}^{-} \times \frac{4}{3} \times \frac{22}{7} r^3$$

$$\therefore \quad r = \left(\frac{2.29 \times 1000 \text{ cm}^3 \text{ mol}^{-} \times 3 \times 7}{4 \times 6.023 \times 10^{23} \text{ mol}^{-} \times 4 \times 22}\right)^{\frac{1}{3}}$$

[1 L = 1000 cm^3]

$$r = \left(0.2268 \times 10^{-21} \text{cm}^3\right)^{\frac{1}{3}}$$

$$= (0.2268)^{\frac{1}{3}} \times 10^{-7} \text{cm}.$$

$$\log (0.2268)^{\frac{1}{3}} = \frac{1}{3} \log 0.2268$$

$$= \frac{1}{3}(-0.6443) = -0.2147$$

$$= -0.2147 - 1 + 1 = \bar{2}.7853$$

Taking antilog of $\bar{2}.7853$, we get, 6.099×10^{-2}

$$\therefore \quad r = 6.099 \times 10^{-2} \times 10^{-7} \text{ cm}$$

$$= 6.099 \times 10^{-9} \text{ cm}.$$

$$\text{Diameter} = 2r = 2 \times 6.099 \times 10^{-9} \text{ cm}$$

$$= 1.2198 \times 10^{-8} \text{ cm}$$

$$= 1.2198 \text{ A}°.$$

So, the correct answer is (*b*).

EXAMPLE 181. *The temperature at which 2.5 mol of SO_2 obeying the vander Waal equation will occupy a volume of 12 litre at a pressure of 16 atm is :*

(*a*) *788.69 K* (*b*) *1061.69°C*
(*c*) *273°C* (*d*) *1061.69 K*

(Given $a = 6.71$ atm L^2 mol^{-2}; $b = 0.0564$ L mol^{-})

SOLUTION. $$\left(P + \frac{an^2}{V^2}\right)(V - nb)$$

$$= nRT \text{ (vander Waal equation)}$$

or $$\left[16 \text{ atm} + \frac{6.71 \text{ atm L}^2 \text{ mol}^{-2} \times (3 \text{ mol})^2}{(12 \text{ L})^2}\right]$$

$$[12 \text{ L} - 3 \text{ mol} \times 0.0564 \text{ L mol}^{-}]$$

$$= 3 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times T$$

$$(16 \text{ atm} + 0.4194 \text{ atm})(12 \text{ L} - 0.1692 \text{ L})$$

$$= 3 \text{ mol} \times 0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times T$$

or $$\frac{(16.4194 \text{ atm}) \times 11.8308 \text{ L}}{3 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-}}$$

$$= T; \ \therefore \ T = 788.69 \text{ K}.$$

So, the correct answer is(*a*).

EXAMPLE 182. *The reduced temperature of oxygen at 37°C if critical temperature of this gas is 155 K, will be :*

(*a*) *0.2167* (*b*) *2*
(*c*) *0.5167* (*d*) *48*

SOLUTION. Reduced temperature,

$$T_r = \frac{T}{T_c}$$

Here $T = 37 + 273 = 310$ K; $T_c = 155$ K

$$\therefore \quad T_r = \frac{310 \text{ K}}{155 \text{ K}} = 2.$$

So, the correct answer is (*b*).

EXAMPLE 183. *The reduced pressure of a gas is 0.1604. If critical pressure is 45.6 atm, its pressure will be*

(*a*) *3.5×10^{-3} atm* (*b*) *45.76 atm*
(*c*) *7.31 atm* (*d*) *None of these.*

SOLUTION. $P_c = 45.6$ atm; $P = ?$, $\pi = 0.1604$.

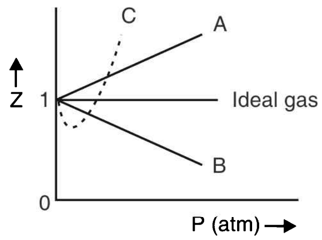
We know that : $\pi = \dfrac{P}{P_c}$; $P = \pi \times P_c$

$= 0.1604 \times 45.6$ atm or $P = 7.31$ atm.

So, the correct answer is (*c*).

EXAMPLE 184. *The given graph represents the variation of Z (compressibility factor = $\dfrac{PV}{nRT}$) versus P, for three real gases A, B and C. Identify the only incorrect statement.*

(*a*) *for the gas A, $a = 0$ and its dependence on P is linear at all pressures.*
(*b*) *for the gas B, $b = 0$ and its dependence on P is linear at all pressures.*
(*c*) *for the gas C, which is typical real gas for which neither a nor b = 0. By knowing the minima and the point of interaction, with Z = 1, a and b can be calculated.*
(*d*) *at high pressure, the slope is positive for all real gases.*



(IIT – JEE, 2006)

SOLUTION. The graph indicates that as the pressure increases, *Z* decreases. It is because at high pressure, when *P* is large, the volume will be small. So, *b* cannot be ignored in comparison to V_m. $\dfrac{a}{V_m^2}$ may however be ignored in comparison to *P* in the vander Waal equation.

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b) = RT$$

So, $P(V_m - b) = RT$

or $PV_m - Pb = RT;\ \frac{PV_m}{RT}-\frac{Pb}{RT}$

$$= \frac{RT}{RT};\ Z-\frac{Pb}{RT} = 1;\ Z=1+\frac{Pb}{RT}$$

Z is greater than 1 and it increases linearly with pressure. So, the false statement is (*b*).

8.27 MISCELLANEOUS EXAMPLES

Example 185. *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, 1992)**

Solution. $p_{H2} + p_g = 6.0$ atm

where p_g is the pressure exerted by the unknown gas.

$$p_{H_2} = \frac{nRT}{V}$$

$$= \frac{0.7\times 0.0821\times 300}{3} = 5.747 \text{ atm.}$$

$\therefore$ $p_g = 6.0 - 5.747 = 0.253$ atm.

Number of moles of unknown gas

$$= \frac{p_g . V}{RT} = \frac{0.253\times 3}{0.0821\times 300} = 0.0308$$

Rate of effusion of H_2

$$= \frac{p_g . V}{RT} = \frac{0.253\times 3}{0.0821\times 300} = 0.0308$$

Rate of effusion of unknown gas

$$= \frac{0.0308}{20} = 0.00154 \text{ mol min}^{-1}$$

According to Graham's Law of effusion

$$\frac{M_g}{M_{H_2}} = \frac{(r_{H_2})^2}{(r_g)^2} = \frac{(0.035)^2}{(0.00154)^2} = 516.5$$

$\therefore$ $M_g = 516.5 \times 2 = 1033 \text{ g mol}^{-1}$

$[\because\ M_{H_2} = 2 \times 1 = 2 \text{ g mol}^{-1}]$

Example 186. *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)**

Solution. Partial pressure of a gas in a mixture = Mole fraction of gas × Total pressure

$$P_{He} = x_{He} \times P = \frac{4}{5}\times 20 = 16 \text{ bar}$$

$$P_{CH4} = x_{CH_4} \times P = \frac{1}{5}\times 20 = 4 \text{ bar}$$

$$r_{He} = \frac{k.P_{He}}{\sqrt{M_{He}}} = \frac{k.16}{\sqrt{4}} = 8k$$

$[\because\ M_{He} = 4 \text{ g mol}^{-1}]$

$$r_{CH_4} = \frac{k.P_{CH_4}}{\sqrt{M_{CH_4}}} = \frac{k\times 4}{\sqrt{16}} = k$$

$\therefore$ Composition of the mixture (He : CH_4) effusing out $= 8k : k = 8 : 1$.

Example 187. *The density of the vapour 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 condition. (a) Determine (i) molecular weight (ii) molar volume (iii) compression factor (Z) of the vapour.*

(b) Which forces among the gas molecules are dominating, the attractive or repulsive ? **(IIT, 2002)**

Solution. (*i*) Rate of effusion $\propto \sqrt{\frac{1}{M}}$

$$\therefore \quad \frac{r_v}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_v}} = \frac{1.33}{1} = \sqrt{\frac{32}{M_v}}$$

$$M_v = \frac{32}{1.33\times 1.33} = \mathbf{18.09\ g}$$

(*ii*) Molar volume $= \frac{\text{Molar mass}}{\text{Density}} = \frac{18.09 \text{g}}{0.36\times 10^3 \text{ g m}^{-3}}$

$= \mathbf{0.05\ m^3}$

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

(*iii*) Compression factor,

$$Z = \frac{PV}{RT} = \frac{1.01\times 10^5 \times 5\times 10^{-2}}{8.314\times 500} = \mathbf{1.22}$$

(*b*) Since Z > 1, hence repulsive forces dominate.

Type: $\frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{1/2} \times \frac{P_1}{P_2}$

Example 188. *One mole of nitrogen gas at 0.8 atm takes 38 sec. to diffuse through a pin hole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound (Xe = 131, F = 19).* **(IIT, 1999)**

Solution. $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$ or $\frac{n_1}{t_1} \times \frac{t_2}{n_2}$

$$= \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

or $\frac{1}{38}\times\frac{57}{1} = \sqrt{\frac{M_g}{28}} \times \frac{0.8}{1.6}$

$$\therefore \quad M_g = 28\times\left[\frac{57}{38}\times\frac{1.6}{0.8}\right]^2;\ \boldsymbol{M_g = 252.}$$

Let the compound is XeF_x.

So, $131 + 19x = 252;\ x = (252 - 131)/19$

Or $x = 121/19 \simeq 6$.

So, molecular formula

$= XeF_6$ **Ans.**

EXAMPLE 189. *Determine the density of H_2S (mol. wt. 34) at 27°C and 2 atm pressure (R = 0.0821 L atm/mol K).* **(BCECE, 1998)**

SOLUTION. According to given data :

$$P = 2 \text{ atm},\ M = 34 \text{ g mol}^{-},$$
$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-},$$
$$T = 27 + 273 = 300 \text{ K}$$

Using the relation,

$$PM = dRT$$
$$d = \frac{PM}{RT} = \frac{2\times 34}{0.0821\times 300}$$
$$= \mathbf{2.76\ g\ L^{-1}}$$

EXAMPLE 190. *In a highly evacuated vessel, there are 3.24×10^9 molecules per cubic centimetre at 27°C. Calculate the pressure.* **(BCECE, 1998)**

SOLUTION. According to ideal gas equation : $PV = nRT$

Here, $P = ?,\ V = 1\times 10^{-3}\text{ L};\ n = \frac{3.24\times 10^{9}}{6.02\times 10^{23}}$

$$T = 27 + 273 = 300 \text{ K};$$
$$R = 0.0821 \text{ atm LK}^{-1}\text{ mol}^{-1}$$
$$P = \frac{nRT}{V} = \frac{3.24\times 10^{9}\times 0.0821\times 300}{6.02\times 10^{23}\times 10^{-3}}$$
$$= \mathbf{1.325 \times 10^{-10}\ atm.}$$

EXAMPLE 191. *The pressure exerted by 12g 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 degree at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V. (Molecular weight of gas = 120).* **(IIT, 1999)**

SOLUTION. According to gas equation : $PV = nRT$

Case I. $$1\times V = \frac{12}{M}\times R(t+273) \qquad ...(i)$$

Case II. $$\left(1+\frac{1\times 10}{100}\right)\times V = \frac{12}{M}\times R(t+283)$$

or $$1.1\ V = \frac{12}{M}\times R(t+283) \qquad ...(ii)$$

From equations (*i*) and (*ii*)

$$\frac{1.1}{1} = \frac{t+283}{t+273}$$

$\therefore$ $1.1\,t + 300.3 = t + 283$ or $0.1\,t = -17.3$

or $t = -173°\text{C} = -173 + 273 = \mathbf{100\ K}$

Also from equation (*i*)

$$1\times V = \frac{12}{120}\times 0.082\times 100 \quad \text{or} \quad V = \mathbf{0.82\ L.}$$

EXAMPLE 192. *What is the difference in pressure between the top and bottom of a vessel 76 cm deep at 27°C when filled with (i) water (ii) mercury ? Density of water at 27°C is 0.990 g cm^{-3} and that of mercury is 13.60 g cm^{-3}.* **(BCECE, 1998)**

SOLUTION. Pressure = height × density × g

Case (*i*). Pressure $= 76 \text{ cm} \times 0.99 \text{ g cm}^{-3} \times 981 \text{ cm s}^{-2}$

$= 7.38 \times 10^4$ dynes cm^{-2}

[$\because$ 1 dyne = g cm s^{-2}]

$$= \frac{7.38\times 10^{4}}{1.013\times 10^{6}} = \mathbf{0.073\ atm.}$$

(1 atm $= 1.013 \times 10^6$ dynes cm^{-2})

Case (*ii*) Pressure $= 76 \text{ cm} \times 13.6 \text{ g cm}^{-3} \times 981 \text{ cm s}^{-2}$

$= 1.013 \times 10^6$ dynes cm^{-2} = **1 atm.**

$\therefore$ Difference of pressure

$= 1 - 0.073 = 0.927$ atm **Ans.**

EXAMPLE 193. *At 300 K and 2.0 atm pressure, gaseous HF has the density 4.87 g L^{-1}. What is its molecular weight ? Account for any discrepency observed in the value ?* **(WBJEE, 2002)**

SOLUTION. According to ideal gas equation,

$$PV = nRT.$$

If *W* and *M* are the weight and molecular weight of the gas, then

$$n = \frac{W}{M}$$

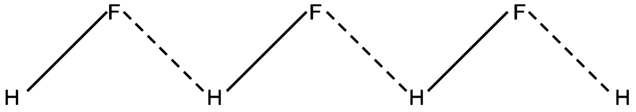
Density of gas, $d = \frac{W}{V};\quad \because\ PV = nRT = \frac{W}{M}RT$

$$M = \frac{W}{V}\cdot\frac{RT}{P} = d\cdot\frac{RT}{P} \qquad \therefore M$$

$$= \frac{4.87 \text{ g L}^{-}\times 0.0821 \text{ L atm K}^{-}\text{mol}^{-}\times 300 \text{ K}}{2 \text{ atm}}$$

= **59.97 g mol^{-} Ans.**

The molecular weight of HF gas calculated from ideal gas equation is much higher than the value calculated from its molecular formula. This is because HF gas is a mixture of HF and its polymer having zig-zag chains of the polymer.



Since the calculated density is the density of the mixture so the molecular weight calculated from this data deviates from the molecular weight calculated from its molecular formula.

EXAMPLE 194. *At temperature, T, and pressure P, two ideal gases A and B are mixed. Show that the density d of the mixture is given by d = $(X_AM_A + X_BM_B)\times\frac{P}{RT}$ where X_A and X_B are the mole fractions and M_A and M_B are the molecular weights of the gases A and B respectively.* **(WBJEE, 2002)**

SOLUTION. Let at temperature *T* and pressure, *P*, n_A moles of *A* and n_B moles of *B* are mixed to form the mixture.

Total number of moles of *A* and *B* present in the mixture, $n = n_A + n_B$

Let the volume of the mixture be *V*

From ideal gas equation,

$$PV = nRT$$

For gas *A*, $PV_A = n_ART$ and $V_A = \frac{n_ART}{P}$

For gas *B*, $PV_B = n_BRT$ and $V_B = \frac{n_BRT}{P}$

Mole fraction, $X_A = \frac{n_A}{n_A+n_B} = \frac{n_A}{n}$;

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

Density of gas, $d = \frac{\text{Mass}}{\text{Volume}}$

$$d = \frac{M}{V} = \frac{n_A.M_A + n_B M_B}{\frac{n_A RT}{P} + \frac{n_B RT}{P}}$$

$$= \frac{P}{RT}\left[\frac{n_A.M_A + n_B.M_B}{n_A + n_B}\right]$$

$$= \frac{P}{RT}\left[\frac{n_A.M_A + n_B M_B}{n}\right]$$

$$= \frac{P}{RT}\left[\frac{n_A}{n}M_A + \frac{n_B}{n}M_B\right]$$

$$d = \frac{P}{RT}[X_A.M_A + X_B M_B]$$

EXAMPLE 195. *An evacuated glass vessel weighs 50 g when empty, 148.0 g when filled with a liquid of density 0.98 g ml^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.* **(IIT, 1998)**

SOLUTION. Weight of liquid

$$= 148.0 - 50.0 = 98.0 \text{ g}$$

$$\text{Density of liquid} = 0.98 \text{ g mL}^{-1}$$

$$\text{Volume of liquid} = \frac{\text{Weight}}{\text{Density}} = \frac{98 \text{ g}}{0.98 \text{ g mL}^{-1}} = 100 \text{ mL}$$

$$\text{Weight of gas} = 50.5 - 50.0 = 0.5 \text{ g}$$

$$\text{Volume} = 100 \text{ mL} = 0.1 \text{ L},$$

$$P = 760 \text{ mm} = 1 \text{ atm}, \quad T = 300 \text{ K}$$

According to ideal gas equation,

$$PV = nRT$$

$$1 \text{ atm} \times 0.1 \text{ L} = \frac{0.5 \text{ g}}{M} \times 0.0821 \text{ L atm K}^{-} \text{mol}^{-} \times 300 \text{ K}$$

$$\therefore \quad M = \frac{0.5 \times 0.0821 \times 300}{0.1}$$

$$= 123.15 \text{ g mol}^{-1}$$

EXAMPLE 196. *A gas bulb of 1 litre capacity contains 2.0 × 10^{21} molecules of nitrogen, exerting a pressure of 7.57 × 10^{3} Nm^{-2}. Calculate the root mean square 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. According to gas equation,

$$PV = nRT; \quad n = \frac{2 \times 10^{21}}{6.02 \times 10^{23}}$$

$$T = \frac{PV}{nR}$$

$$= \frac{7.57 \times 10^3 \text{Nm}^{-2} \times 1 \times 10^{-3} \text{m}^3}{\frac{2 \times 10^{21}}{6.02 \times 10^{23}} \text{mol} \times 8.314 \text{ J(Nm)mol}^{-1}\text{K}^{-1}}$$

= 274.2 K

RMS velocity, $u = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3} \text{kg}}}$

= 494.2 ms^{-1}

$$\left[\begin{array}{l} \because \text{ Mol. wt. of N}_2 = 2 \times 14 = 28 \text{ g} \\ \quad = 28 \text{ g} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 28 \times 10^{-3} \text{ kg} \end{array}\right]$$

Most probable velocity

$$= 0.82 \times u$$

$$= 494.2 \times 0.82 \text{ ms}^{-1} = \mathbf{405.2 \text{ ms}^{-1}}$$

EXAMPLE 197. *56 g of N$_2$ gas are mixed with 44g of CO$_2$ and the pressure of resulting mixture is found to be 303 k Pa. Calculate the partial pressure of N$_2$ and CO$_2$ in the mixture.* **(B.C.E.C.E, 2002)**

SOLUTION. Number of moles of

$$N_2 = \frac{56}{28} = 2$$

Number of moles of

$$CO_2 = \frac{44}{44} = 1$$

Total number of moles of gases in the mixture

$$= 2 + 1 = 3$$

Partial pressure of a gas in the mixture

$$= \frac{\text{Moles of gas}}{\text{Total number of moles}} \times P_{\text{Total}}$$

$$\therefore \quad P_{N_2} = \frac{2}{3} \times 303 = \mathbf{202 \text{ kPa}}$$

$$P_{CO_2} = \frac{1}{3} \times 303 = \mathbf{101 \text{ kPa}}$$

EXAMPLE 198. *Striking a wooden match involves the combustion of P$_4$S$_3$ to produce a white smoke of P$_4$O$_{10}$ and gaseous sulphur dioxide, SO$_2$. Calculate the volume of SO$_2$ that is formed at 27°C and 770 mm Hg pressure from the combustion of 0.0546g P$_4$S$_3$.*

(P = 31, S = 32, O = 16)

(WBJEE, 1993)

SOLUTION. Combustion of P_4S_3 can be represented as :

$$\begin{array}{llll} P_4S_3 & + \; 8O_2 & \longrightarrow & P_4O_{10} + 3\,SO_2 \\ 4 \times 31 + 3 \times 32 & & & 3 \times 22.4 \text{ L at NTP} \\ = 220 \text{ g} & & & = 67.2 \text{ L at NTP} \end{array}$$

$\therefore$ 220 g of P_4S_3 produces

$$SO_2 = 67.2 \text{ L at NTP}$$

0.0546 g of P_4S_3 produces

$$SO_2 = \frac{67.2}{220} \times 0.0546 = 0.0167 \text{ L at NTP}$$

Let this volume be *V* litres at 27°C and 770 mm pressure. Therefore, applying gas equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2};\ \frac{770\times V}{273+27} = \frac{760\times 0.0167}{273}$$

$$V = \frac{760\times 0.0167\times 300}{770\times 273} = 0.0181 \text{ litres}$$

$$= 0.0181\text{L}\times\frac{1000 \text{ mL}}{1\text{L}} = 18.1 \text{ mL}$$

Thus, 0.0546 g P_4S_3 on combustion will produce SO_2 = **18.1 mL.**

Example 199. *A gas filled, freely collapsible balloon, is pushed from the surface of a sea to a depth of 100 m. Assuming the ideal behaviour of gas, approximately what percent of its original volume will balloon finally have ?* **(BCECE, 1998)**

Solution. Pressure = $h\ d\ g$

Pressure at sea level,

$$P_1 = 1 \text{ atm} = 76 \text{ cm of}$$
$$\text{Hg} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$$
$$= 981 \times 1033.6 \text{ dynes cm}^{-2}$$

Pressure at a depth of 100 m,

$$P_2 = 76 \times 13.6 \times 981 + 100 \times 100 \times 1 \times 981$$

$$(\text{density of water} = 1 \text{ g cm}^{-3})$$
$$= 981\ (76 \times 13.6 + 10000)$$
$$= 981 \times 11033.6$$

Let the volume of the balloon at the sea surface be V_1 and volume at the depth of 100 m be V_2

Applying, $P_1V_1 = P_2V_2$

$$981 \times 1033.6 \times V_1 = 981 \times 11033.6 \times V_2$$

$$V_2 = \frac{1033.6}{11033.6}\times V_1$$

$$= \frac{1033.6\times V_1}{11033.6}\times 100 = 9.367\ V_1\%$$

Example 200. *A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 20 atmospheres at 27°C. If the cylinder can hold 2.82 litres of water, calculate the number of balloons that can be filled up.* **(I.I.T., 1987; M.L.N.R., 1991)**

Solution. Let V_1 be the volume of H_2 in the cylinder at NTP. According to gas eqution.

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

$$\therefore \quad \frac{1\times V_1}{273} = \frac{20\times 2.82}{27+273}$$

$$\text{or} \quad V_1 = \frac{20\times 2.82\times 273}{300}$$

$$= 51.324 \text{ L} = 51324 \text{ mL}$$

Volume of H_2 left in the cylinder

= Volume of cylinder

= 2.82 L = 2820 mL

Actual volume transferred to balloons

= 51324 – 2820 = 48504 mL

Radius of balloon (r)

= 21/2 = 10.5 cm

Volume of each balloon

$$= \frac{4}{3}\pi r^3$$

$$= \frac{4}{3} \times 3.142 \times (10.5)^3$$

= 4849.67 = **4850 mL**

Number of balloons which can be filled up

$$= \frac{48504}{4850} = \mathbf{10}$$

Example 201. *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. The distance of P from X is :*

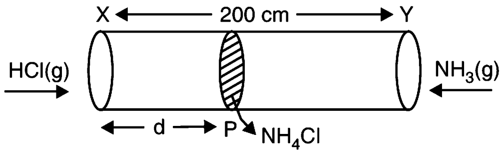
(*a*) *118.88 cm* (*b*) *81.12 cm*

(*c*) *190 cm* (*d*) *none of these*

Solution. Mol. wt. of NH_3

$$= 14 + (3 \times 1) = 17 \text{ g mol}^{-}$$

Mol. wt. of HCl = 1 + 35.5 = 36.5 g mol^{-}



We know that :

$$\frac{r_{\text{HCl}}}{r_{\text{NH}_3}} = \left(\frac{M_{\text{NH}_3}}{M_{\text{HCl}}}\right)^{1/2} = \left(\frac{17}{36.5}\right)^{1/2} = \frac{4.123}{6.042}$$

$$\therefore \quad r_{\text{NH}_3} = 6.042 \text{ if } r_{\text{HCl}} = 4.123.$$

If total length of tube is 6.042 + 4.123 (= 10.165 cm), NH_3 will travel = 6.042 cm

If total length of tube is 200 cm, NH_3 will travel

$$= \frac{6.042}{10.165}\times 200 \text{ cm} = 118.88 \text{ cm}.$$

∴ Distance of P from

$$X = 200 - 118.88 = 81.12 \text{ cm}.$$

So, The correct answer is (*b*).

Example 202. *Find the value of translational energy of gas molecules in a mole of oxygen at 37°C. Also find the average kinetic energy of a single molecule of this gas.*

Solution. (*i*) To find K.E.

(*a*) When $R = 8.314 \times 10^7 \text{ ergs K}^{-}\text{ mol}^{-}$,

$T = 37 + 273 = 310 \text{ K}$,

then $$\text{K.E.} = \frac{3}{2}RT$$

$$= \frac{3}{2} \times 8.314 \times 10^7 \text{ ergs K}^{-}\text{ mol}^{-} \times 310 \text{ K}$$

$$= 3.866 \times 10^{10} \text{ ergs}$$

$$= 3.866 \times 10^{10}\ \text{ergs} \times \frac{1\ \text{J}}{10^{7}\ \text{erg}}$$

$$= 3866\ \text{Joule mol}^{-}$$

(*ii*) When $R = 1.99\ \text{cal K}^{-}\ \text{mol}^{-}$

then $\text{K.E.} = \frac{3}{2}RT$

$$= \frac{3}{2} \times 1.99\ \text{cal K}^{-}\ \text{mol} \times 310\ \text{K}$$

$$= 925.35\ \text{cal mol}^{-}$$ **Ans.**

(*iii*) $1\ \text{mol} = 6.023 \times 10^{23}$ molecules

∴ Average K.E. per molecule

$$= \frac{\text{K.E.}}{6.023 \times 10^{23}\ \text{mol}^{-}}$$

$$= \frac{3866\ \text{J mol}^{-}}{6.023 \times 10^{23}\ \text{mol}^{-}}$$

$$= 6.42 \times 10^{-21}\ \text{J}$$ **Ans.**

EXAMPLE 203. *A sample of 1.4 L gas has density equal to 1.24 kg m^{-3} at 0°C and 760 mm pressure. On compression at 600 atm, the gas occupied 2.61 cm^{3} in violation of Boyle's law. Calculate the final density of the gas.*

SOLUTION. $1\ \text{L} = 10^{-3}\ \text{m}^3,\ 1\ \text{cm}^3 = 10^{-6}\ \text{m}^3.$

So, $2.61\ \text{cm}^3 = 2.61 \times 10^{-6}\ \text{m}^3$

(*i*) wt. of 1.4 L gas = Volume × density

$$= 1.4 \times 10^{-3}\ \text{m}^3 \times 1.24\ \text{kg m}^{-3}$$

$$= 1.736 \times 10^{-3}\ \text{kg}$$

(*ii*) $$\text{New density} = \frac{\text{wt.}}{\text{new volume}} = \frac{1.736 \times 10^{-3}\ \text{kg}}{2.61 \times 10^{-6}\ m^3}$$

$$= \mathbf{665.1\ kg\ m^{-3}}$$ **Ans.**

EXAMPLE 204. *Assuming that dry air contains only N$_2$ and O$_2$ gases and density of air is 1.146 g L^{-} at 740 mm and 27°C, calculate the composition of air by weight if air behaves as an ideal gas.*

SOLUTION. Density of air = 1.146 g L^{-}. So, wt. of air = 1.146 g,

Volume of air = 1 L, $R = 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-}$,

$$P = \frac{740}{760}\ \text{atm},\ T = 27 + 273 = 300\ \text{K}.$$

$$PV = \frac{W}{M} \times RT \quad \text{or} \quad M = \frac{WRT}{PV}$$

$$M = \frac{1.146\ \text{g} \times 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-} \times 300\ \text{K} \times 760}{740\ \text{atm} \times 1\ \text{L}}$$

$$= 28.99\ \text{g mol}^{-}$$

Let a = wt. of N$_2$ present

wt. of O$_2$ present = $(100 - a)$ g; mol. wt. of

$\text{N}_2 = 2 \times 14 = 28\ \text{g mol}^{-}$

mol. wt. of $\text{O}_2 = 2 \times 16 = 32\ \text{g mol}^{-}$

$$\text{Thus, } \frac{a}{28} + \frac{100 - a}{32} = \frac{100}{\text{Mol. wt.}} \text{ or } \frac{100}{28.99}$$

$$32a + 2800 - 28a = \frac{28 \times 32 \times 100}{28.99} = 3090.72;$$

$$4a = 290.72$$

$$a = \frac{290.72}{4} = \mathbf{72.68\ \%}$$

$$= \textbf{\% age of N}_2$$ **Ans.**

∴ % age of O$_2$ = 100 – 72.68 = 27.32% **Ans.**

EXAMPLE 205. *A sealed flask contains 0.01 mol of helium gas and solid ammonium chloride. At 300 K, the pressure inside the flask of helium was 114 mm of mercury. The flask is now heated to 600 K when all the ammonium chloride was decomposed and the final pressure was recorded as 908 mm of mercury. Calculate the partial pressure of HCl if the gases behave like ideal gas.*

SOLUTION. $$\underset{1\ \text{mol}}{\text{NH}_4\text{Cl(s)}} \longrightarrow \underset{1\ \text{mol}}{\text{NH}_3\text{(g)}} + \underset{1\ \text{mol}}{\text{HCl(g)}}$$

Final pressure = 908 mm;

For He : $P_1 = 114\ \text{mm},\ T_1 = 300\ \text{K}$

$P_2 = ?,\ T_2 = 600\ \text{K}.$

Since $$\frac{P_1}{T_1} = \frac{P_2}{T_2};$$

$$P_2 = \frac{P_1T_2}{T_1}$$

$$= \frac{114\ \text{mm} \times 600\ \text{K}}{300\ \text{K}} = 228\ \text{mm}.$$

Final pressure = P of He at 600 K + [P (NH$_3$) + P (HCl)] at 600 K

$$908 = 228 + [P\ (\text{NH}_3) + P\ (\text{HCl})];$$

$$P\ (\text{NH}_3) + P\ (\text{HCl}) = 908 - 228 = 680\ \text{mm}.$$

Since mol of NH$_3$ = mol of HCl

$$\therefore \quad P\ (\text{NH}_3) = \frac{680}{2} = 340\ \text{mm}$$

$$P\ (\text{HCl}) = \mathbf{340\ mm}$$ **Ans.**

EXAMPLE 206. *A gas was filled in a bulb of 2 L capacity and was heated from 25°C to t°C. The gas thus expelled measured 1.2 L at 15°C. If the pressure remained one atmosphere through out the experiment, calculate the value of t. Ignore the expansion of bulb.*

SOLUTION. Let V = Volume of gas coming out at t°C;

$V_1 = 1.2\ \text{L}$

$T_1 = 273 + 15 = 288\ \text{K};$

$V_2 = V,\ T_2 = t + 273.$

We know that : $$\frac{V_1}{T_1} = \frac{V_2}{T_2};\ \frac{1.2\ \text{L}}{288\ \text{K}} = \frac{V}{t + 273};$$

$$V = \frac{1.2\ \text{L}(t + 273)\ \text{K}}{288\ \text{K}} \quad ...(A)$$

Also, $V_1 = 2\ \text{L},\ T_1 = 25 + 273 = 298\ \text{K};$

$V_2 = 2 + V$

$T_2 = t + 273$

Thus : $$\frac{V_1}{T_1} = \frac{V_2}{T_2};\ \frac{2\ \text{L}}{298\ \text{K}} = \frac{(2 + V)\ \text{L}}{(t + 273)\ \text{K}} \quad ...(B)$$

Substituting the value of V from (A) in (B), we get :

$$\frac{2\text{ L}}{298\text{ K}} = \frac{2\text{ L}}{(t+273)\text{ K}} + \frac{1.2\text{L}(t+273)\text{K}}{(t+273)\text{K}\times 288\text{ K}}$$

$$= \frac{2\text{ L}}{(t+273)\text{K}} + \frac{1.2\text{ L}}{288\text{ K}}$$

or $$\frac{1}{149} = \frac{2}{t+273} + \frac{12}{2880};$$

$$\frac{1}{149} - \frac{12}{2880} = \frac{2}{t+273}$$

$$\frac{2880-(12\times 149)}{149\times 2880} = \frac{2}{t+273}; \quad 0.00254 = \frac{2}{t+273}$$

$$t + 273 = \frac{2}{0.00254} = 787.4\text{ K}$$

or $t = 787.4 - 273 = 514.4\text{ K}$ **Ans.**

Example 207. *0.1 L of a mixture contains 72% of methane and rest an unknown gas, A. Due to very fine hole in the vessel 21 mL of the mixture was lost. The remaining mixture contained 68.35% of methane by volume. If all the measurements are done under similar conditions of temperature and pressure, what will be the molecular weight of gas, A ?*

Solution. (*i*) Volume of CH_4 + volume of gas,

$$A = 0.1\text{ L}\times\frac{1000\text{ mL}}{1\text{ L}} = 100\text{ mL}$$

Original volume of

$CH_4 = 72$ mL;

Volume of gas, $A = 100 - 72 = 28$ mL.

If V_1 = volume of CH_4 lost from mixture, then :

Volume of CH_4 left = $72 - V_1$

Volume of mixture left

$= 100 - 21 = 79$ mL

$\therefore$ 79 mL mixture contains

$CH_4 = 72 - V_1$

100 mL mixture contains

$$CH_4 = \frac{72 - V_1}{79}\times 100.$$

Since CH_4 left after effusion is 68.35 mL,

So, $$\frac{72-V_1}{79}\times 100 = 68.35; \; 72 - V_1 = \frac{68.35\times 79}{100} = 54$$

$\therefore$ $V_1 = 72 - 54 = 18$ mL

(*ii*) Let M = mol. wt. of gas, A

mol. wt. of methane,

$CH_4 = 12 + (4 \times 1) = 16\text{ g mol}^{-}$.

Since 21 mL of mixture was lost,

$V_2 = 21 - V_1$

$$\therefore \quad \frac{V_1}{V_2} = \frac{72}{28}\times\left(\frac{M}{16}\right)^{1/2}; \quad \frac{18}{(21-18)=3}$$

$$= \frac{72}{28}\times\left(\frac{M}{16}\right)^{1/2}$$

$$\frac{6\times 28}{72} = \left(\frac{M}{16}\right)^{1/2}$$

Squaring both sides, we get :

$$\frac{6\times 28\times 6\times 28\times 16}{72\times 72} = M \quad\text{or}\quad M = \mathbf{87.1\text{ g mol}^{-}}$$ **Ans.**

Example 208. *Find the volume occupied by 0.42 mol of CO_2 gas at 100 atm and 0°C. If the compressibility factor for CO_2 at 0°C and 100 atm pressure is 0.2005, calculate the above said volume using (i) real gas behaviour and (ii) ideal gas behaviour.*

Solution. V = ? ; $n = 0.42$ mol ;

$R = 0.0821\text{ L atm K}^{-}\text{ mol}^{-}$

$T = 0 + 273 = 273$ K ; $Z = 0.2005$.

(*i*) **For real gas :** $V = Z\times\frac{nRT}{P}$

$\therefore$

$$V = \frac{0.2005\times 0.42\text{ mol}\times 0.0821\text{ L atm K}^{-}\text{ mol}^{-}\times 273\text{ K}}{100\text{ atm}}$$

= 0.01887 L Ans.

(*ii*) **For an ideal gas :**

$$V = \frac{nRT}{P}$$

$$= \frac{0.42\text{ mol}\times 0.0821\text{ L atm K}^{-}\text{ mol}^{-}\times 273\text{ K}}{100\text{ atm}}$$

or V = **0.09414 L** **Ans.**

Example 209. *25 g of each of the following gases are taken at 27°C and 600 mm pressure. Which of these will have the least volume?*

(*a*) HBr (*b*) HCl

(*c*) HF (*d*) HI

(Karnataka CET, 2011)

Solution. $PV = n\,RT$ (ideal gas). If P and T are same for all gases, $V \propto n$ where n = no. of moles = wt./mol. wt. Here weight of all gases is same. Hence $V \propto \frac{1}{\text{mol. wt}}$; Mol. wt. of $HI > HBr > HCl > HF$. So, HI will have least volume.

Example 210. *A vessel of 150 cm^3 volume was filled with xenon gas at 0°C and 0.9 atm pressure. If the radius of xenon atom is 1.3×10^{-8} cm, calculate the fraction of volume occupied by xenon atoms.*

Solution. Number of moles of xenon atoms (= n) *can be found from the relation :*

$$n = \frac{PV}{RT}$$

or $$n = \frac{(0.9\text{ atm})\times\left(150\times 10^{-3}\text{ dm}^3\right)}{\left(0.0821\text{ atm. dm}^3\text{ K}^{-}\text{ mol}^{-}\right)\times 273\text{K}}$$

[0°C = 0 + 273 = 273 K]

$\therefore$ $n = 6.023 \times 10^{-3}$ mol.

$\therefore$ Number of xenon atoms,

$N = 6.023 \times 10^{-3}\text{ mol} \times 6.023 \times 10^{23}\text{ mol}^{-}$

[$\because$ 1 mol = 6.023×10^{23} atoms]

$= 3.63 \times 10^{21}$ atoms.

But volume occupied by atoms

$$= \frac{4}{3}\pi r^3 \times N$$

$$= \frac{4}{3}\times 3.142\times\left(1.3\times10^{-8}\text{ cm}\right)^3\times3.63\times10^{21}$$

$$= 3.34 \times 10^{-3}\text{ cm}^3$$

$\therefore$ Fraction of volume occupied by xenon atoms

$$= \frac{3.34\times10^{-3}}{150}\times100 = 2.23\times10^{-3}\,\%.$$

EXAMPLE 211. *The molar heat capacity of a monoatomic gas, for which the ratio of pressure and volume is one, is :*

(*a*) $\frac{4}{2}R$ (*b*) $\frac{3}{2}R$

(*c*) $\frac{5}{2}R$ (*d*) *zero*

(IIT – JEE, 2006)

SOLUTION. We know that Molar heat capacity for any process,

$$C = C_v + \frac{R}{1-n} \text{ when } PV^n = \text{constant.}$$

In this question, $\frac{P}{V} = 1$ *i.e.,* PV^{-1} = constant.

$$\therefore \quad C = \frac{3}{2}R + \frac{R}{2} = \frac{4R}{2}$$

$$[\because \text{ for monoatomic gas, } C_v = \frac{3}{2}R\,;$$

$$n = -1 \text{ and } 1 - n = 1 - (-1) = 2].$$

So, the correct answer is (*a*).

EXAMPLE 212. *C_v value of helium is always 3R/2 , independent of temperature. The C_v value of H_2 at low temperature and moderate temperature will be respectively.*

(*a*) $\frac{R}{2}, R$ (*b*) $\frac{3R}{2}, \frac{5R}{2}$

(*c*) *2R, 3R* (*d*) $\frac{R}{3}, \frac{2R}{3}$

Explain also in two to three lines.

(IIT, 2003 modified)

SOLUTION. (*i*) Helium gas is **monoatomic.** It has three degrees of freedom corresponding to the three translational motion at all temperatures.

Hence, $C_v = 3\times\frac{R}{2} = \frac{3R}{2}$

(*ii*) H_2 gas molecule is **diatomic.**

At low temperature, its rotational and vibrational contribution = zero.

Hence, $C_v = \frac{3R}{2}$.

At moderate temperature, vibrational contribution,

$$C_v = 2\times\frac{R}{2} = R\,,$$

also becomes dominant and at even higher temperature, vibrational contribution (1 × R) becomes significant also.

So, $C_v = \frac{3R}{2} + R = \frac{5R}{2}$

So, the correct answer is (*b*).

Type. Ideal gas in terms of density :

$$PV = nRT = \frac{m}{M}RT\,; P = \frac{m}{V}\cdot\frac{RT}{M} = \frac{dRT}{M}$$

$\therefore$ Molar mass,

$$M = \frac{dRT}{P}.$$

(*a*) For the same gas at two different temperatures :

$$M = \frac{d_1RT_1}{P_1} \quad ...(i)$$

$$M = \frac{d_2RT_2}{P_2} \quad ...(ii)$$

Dividing (*i*) and (*ii*), we get

$$\frac{d_1RT_1}{P_1} = \frac{d_2RT_2}{P_2}\,;\ \frac{d_1}{d_2} = \frac{P_1T_2}{P_2T_1}$$

(*b*) For two different gases, at same temperature and same density :

$$(i) \quad M_1 = \frac{dRT}{P_1}\,;\quad M_2 = \frac{dRT}{P_2} \quad ...(ii)$$

Dividing (*i*) and (*ii*), we get

$$\frac{M_1}{M_2} = \frac{P_2}{P_1} \quad \text{or} \quad \boldsymbol{M_1P_1 = M_2P_2}$$

EXAMPLE 213. *The density of a gas is 3.8 gL¯ at N.T.P. Find the molar mass of the gas.*

SOLUTION. At N.T.P.,

P = 1 atm, T = 273 K. Density,

d = 3.8 gL¯, R = 0.0821 L atm K¯ mol¯.

We know that : $M = \frac{dRT}{P}$

= 3.8 gL¯ × 0.0821 L atm K¯ mol¯ × 273 K/1 atm

$\therefore$ Molar mass, M = **85.2 g mol¯** **Ans.**

EXAMPLE 214. *Calculate the density of a gas (molar mass = 64 g mol¯) at 740 mm pressure and 55°C.*

SOLUTION. d = ? M = 64 g mol¯,

R = 0.0821 L atm K¯ mol¯,

$$P = \frac{740\text{ mm}}{760\text{ mm}}\text{ atm,}$$

T = 55 + 273 = 328 K. We know that :

$$P = \frac{dRT}{M}\,;$$

$$d = \frac{MP}{RT}$$

$$= \frac{64\text{ g mol}^{-}}{760} \times \frac{740\text{ atm}}{0.0821\text{ L atm K}^{-}\text{ mol}^{-}\times 328\text{ K}}$$

$\therefore$ d = **2.31 gL¯** **Ans.**

EXAMPLE 215. *The density of a gaseous oxide (molar mass, 64 g mol^{-}) at 1.5 atm is the same as that of unknown gas at 3 atm. Calculate the molar mass of the unknown gas at 273 K and name it. (Molar mass, N_2 = 28 g mol^{-}; H_2 = 2 g mol^{-}; O_2 = 32 g mol^{-})*

SOLUTION. Molar mass of gaseous oxide, M_1 = 64 g mol^{-}; P_1 = 1.5 atm; Unknown gas, M_2 = ?; P_2 = 3 atm.

We know that : $d = \frac{MP}{RT}$. At the same temperature and density, for any two gases,

$$M_1P_1 = M_2P_2 \qquad [\because R \text{ is constant}].$$

$$\therefore\ 64 \text{ g mol}^{-} \times 1.5 \text{ atm} = M_2 \times 3 \text{ atm}$$

$$\therefore \qquad M_2 = \frac{64 \text{ g mol}^{-} \times 1.5 \text{ atm}}{3 \text{ atm}}$$

$$= \mathbf{32\ g\ mol^{-}} \qquad \textbf{Ans.}$$

Since given molar mass of O_2 (= 32 g mol^{-}) is the same as calculated above, so, the gas is oxygen.

Type. Effective volume (or excluded volume or co-volume) of a gas molecule, $b = 4v$ where v = actual volume of the gas molecule.

EXAMPLE 216. *Calculate the radius of oxygen atom as well as oxygen molecule if vander Waal's constant 'b' for oxygen is 0.0318 L mol^{-}.*

SOLUTION. We know that, $b = 4v$, where v = volume of oxygen gas molecule. Substituting the values, we get :

$$0.0318 \text{ L mol}^{-} = 4v\ ;$$

$$v = \frac{0.0318 \text{ L mol}^{-}}{4} = 0.00795 \text{ L mol}^{-}$$

$$\text{or} \qquad v = 0.00795 \text{ L mol}^{-} \times \frac{1000 \text{ cm}^3}{1 \text{ L}}$$

$$= 7.95 \text{ cm}^3 \text{ mol}^{-}$$

$$= 7.95 \text{ cm}^3 \text{ mol}^{-} \times \frac{\text{mol}}{6.023 \times 10^{23}}$$

$$= 1.32 \times 10^{-23} \text{ cm}^3$$

$$\text{or} \qquad \frac{4}{3}\pi r^3 = 7.95 \text{ cm}^3$$

(where r = radius of oxygen atom when oxygen molecule is considered spherical)

$$\frac{4}{3} \times \frac{22}{7} \times r^3 = 1.32 \times 10^{-23} \text{ cm}^3$$

$$r^3 = \frac{1.32 \times 10^{-23} \times 3 \times 7}{4 \times 22} \text{ cm}^3 = 3.15 \times 10^{-24} \text{cm}^3$$

$$r = (3.15 \times 10^{-24} \text{ cm}^3)^{1/3}$$

$$= (3.15)^{1/3} \times 10^{-8} \text{ cm}$$

$$= 1.4659 \times 10^{-8} \text{ cm}$$

$$\left[\begin{array}{l} \log r = \log (3.15)^{1/3} \\ \quad = \frac{1}{3} \log 3.15 = \frac{1}{3} \times 0.4983 \\ \quad = 0.1661 \\ \quad r = \text{antilog } 0.1661 = 1.4659 \end{array}\right]$$

$\therefore$ Radius of oxygen atom = 1.4659×10^{-8} cm

Diameter of oxygen molecule = $2r$

$$= 2 \times 1.4659 \times 10^{-8} \text{ cm}$$

$$= \mathbf{2.9318 \times 10^{-8}\ cm} \qquad \textbf{Ans.}$$

EXAMPLE 217. *0.5 mole of each of H_2, SO_2 and CH_4 are kept is a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be :*

(a) $p_{SO_2} > P_{CH_4} > p_{H_2}$ (b) $p_{H_2} > p_{SO_2} > p_{CH_4}$

(c) $p_{H_2} > p_{CH_4} > p_{SO_2}$ (d) $p_{SO_2} > p_{H_2} > p_{CH_4}$

(Karnataka CET, 2009)

SOLUTION. Mol. mass of

$$H_2 = 2 \text{ g mol}^{-};\ CH_4 = 16 \text{ g mol}^{-};$$

$$SO_2 = 32 + (2 \times 16) = 64 \text{ g mol}^{-}.$$

So, order of mol. mass is $SO_2 > CH_4 > H_2$. Also :

$$\text{Rate of diffusion} = \left(\frac{1}{\text{mol.mass}}\right)^{1/2}.$$

So, order of rate of diffusion is $H_2 > CH_4 > SO_2$.

$\therefore$ The order of partial pressure of the gases remaining in the container will be :

$p_{SO_2} > p_{CH_4} > p_{H_2}$. So, the correct answer is (a).

EXAMPLE 218. *A bubble of gas released at the bottom of a lake increases to 8 times its original volume when it reaches the surface. Assuming that atmospheric pressure is equivalent to the pressure exerted by a column of water 10 m height, the depth of the lake is*

(a) 80 m *(b) 90 cm*

(c) 40 m *(d) 10 m*

(e) 70 m

(Kerala PMT, 2011)

SOLUTION. When bubble comes at the surface, its volume increases 8 times. It means, the pressure at the bottom of the lake is 8 times the pressure at the surface. So:

Pressure due to depth of lake = (8 × 10) – 10 = 70 m. So, the correct answer is (*e*).

EXAMPLE 219. *A bubble of air is under water at temperature 15°C and pressure 1.5 bar. If the bubble rises to the surface where the temperature is 25°C and the pressure is 1.0 bar, what will happen to the volume of bubble?*

(a) Volume will become greater by a factor of 1.6.

(b) Volume will become greater by a factor of 1.1.

(c) Volume will become smaller by a factor of 0.70.

(d) Volume will become greater by a factor of 2.5.

(AIPMT, 2011)

SOLUTION. T_1 = 15 + 273 = 288 K; P_1 = 1.5 bar; T_2 = 25 + 273 = 298 K; P_2 = 1 bar; Since $V \propto T/P$ (ideal equation), so $V_1 \propto 288/1.5$ or $V_1 \propto 192$; $V_2 \propto 298/1$. Thus V_2/V_1 = 298/192 = 1.55 ≃ 1.6. So, the correct answer is (*a*).

EXAMPLE 220. *The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas, which of the following is true?*

(*a*) $T_{N_2} = T_{H_2}$ (*b*) $T_{H_2} = \sqrt{7}\ T_{N_2}$

(*c*) $T_{N_2} = 2T_{H_2}$ (*d*) $T_{N_2} = \sqrt{7}\ T_{H_2}$

(Karnataka CET, 2011)

SOLUTION. Let rms velocity of $N_2 = u$. So, rms velocity of $H_2 = u\sqrt{7}$. But rms velocity of gas (say C) = $\left(\frac{3RT}{M}\right)^{1/2}$

$$\therefore \quad \frac{C_{N_2}}{C_{H_2}} = \left(\frac{T_{N_2}}{T_{H_2}} \times \frac{M_{H_2}}{M_{N_2}}\right)^{1/2};$$

$$\left(\frac{u}{u\sqrt{7}}\right)^2 = \left[\left(\frac{T_{N_2}}{T_{H_2}} \times \frac{2}{28}\right)^{1/2}\right]^2$$

[∵ Mol. wt. of $H_2 = 2$; $N_2 = 2 \times 14 = 28$]

$$\therefore \quad \frac{u^2}{7u^2} = \frac{T_{N_2}}{T_{H_2}} \times \frac{1}{14};$$

$$\frac{T_{N_2}}{T_{H_2}} = \frac{14}{7} = 2 \quad \text{or} \quad T_{N_2} = 2\,T_{H_2}.$$

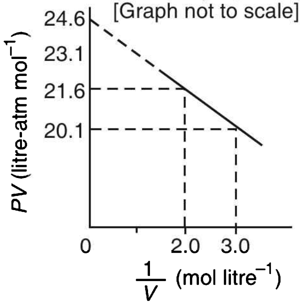
So, the correct answer is (*c*).

EXAMPLE 221. *For one mole of a vander Waals gas when b = 0 and T = 300 K, the PV vs 1/V plot is shown below. The value of the vander Waal's constant, a (atm litre^2 mol^{2-}) is :*

(*a*) 1.0 (*b*) 4.5

(*c*) 1.5 (*d*) 3.0

(IIT-JEE, 2012)



SOLUTION. vander Waal equation is given as:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

But $b = 0$

$$\therefore \quad P + \frac{a}{V} = RT; PV = RT - \frac{a}{V}$$

But $y = mx + c$ (Equation of a straight line)

∴ Intercept, $c = RT$, slope $(m) = -a$. Also:

$$\text{slope} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{20.1 - 21.6}{3 - 2} = -1.5. \text{ Hence } a = +1.5$$

So, the correct answer is (*c*).

EXAMPLE 222. *Equal weights of CH_4 and H_2 are mixed in an empty container at 25°C. The fraction of the total pressure exerted by H_2 is:*

(*a*) 1/9 (*b*) 1/2

(*c*) 8/9 (*d*) 16/17

(W.B. JEE, 2012)

SOLUTION. Let wt. of CH_4 = wt. of H_2 = w g; mol. wt. of $CH_4 = 12 + (4 \times 1) = 16$ g mol^{-}, mol. wt. of $H_2 = (2 \times 1) = 2$ g mol^{-}

$$\therefore \text{ Moles of } H_2 = \frac{w}{2}; \text{ moles of } CH_4 = \frac{w}{16}$$

$$\text{Mole fraction of } H_2 = \frac{w/2}{w/2 + w/16} = \frac{w}{2} \times \frac{16}{9w} = \frac{8}{9}$$

∴ Pressure exerted by H_2 = Total pressure × mole fraction of H_2

= Total pressure × 8/9.

So, the correct answer is (*c*).

EXAMPLE 223. *Equal volumes of two monoatomic gases A and B at same temperature and pressure are mixed. The ratio of specific heats (C_p/C_v) of the mixture will be:*

(*a*) 0.83 (*b*) 1.50

(*c*) 3.3 (*d*) 1.67

(AIPMT, Mains, 2012)

SOLUTION. Value of C_p of mixture of monoatomic gases having same volume = $5/2R$; $C_v = 3/2\,R$

$$\therefore \quad \frac{C_p}{C_v} = \frac{5}{2}R \Big/ \frac{3}{2}R = \frac{5}{3} = 1.67.$$

So, the correct answer is (*d*).

EXAMPLE 224. *A certain gas takes three times as long as to effuse out as helium. Its molecular mass will be :*

(*a*) 27 *u* (*b*) 36 *u*

(*c*) 64 *u* (*d*) 9 *u*

(AIPMT, Mains, 2012)

SOLUTION. For helium, $r_1 = \frac{V_1}{t_1}$; Let for other gas, $r_2 = \frac{V_2}{3t_1}$. If $V_1 = V_2$, $\frac{r_1}{r_2} = \frac{V_1/t_1}{V_1/3t_1} = 3$. But, $\frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{1/2}$

$$\therefore \quad 3 = \left(\frac{M_2}{4}\right)^{1/2}$$

[∵ Mol. wt. (M_1) of helium = at. wt. of He = 4]

Squaring both sides, we get:

$9 = \frac{M_2}{4}$ or $M_2 = 9 \times 4 = 36$ u. So, the correct answer is (*b*).

EXAMPLE 225. *50 mL of each gas A and of gas B takes 150 and 200 seconds respectively for effusing through a pin hole under the similar conditions. If molecular mass of gas B is 36, the molecular mass of gas A will be:*

(*a*) 96 (*b*) 128

(*c*) 32 (*d*) 64

(AIPMT, Pre. 2012)

SOLUTION. For gas *A*, rate of diffusion, $r_1 = \frac{\text{Volume}}{\text{time}} = \frac{50}{150} = \frac{1}{3}$. For gas *B* rate of diffusion, $r_2 = \frac{\text{Volume}}{\text{time}} = \frac{50}{200} = \frac{1}{4}$

Molar mass of *B*, = 36, molar mass of *A* (M_A) = ? We know:

$\frac{r_1}{r_2} = \left(\frac{M_2}{M_1}\right)^{1/2}$; $\frac{1/3}{1/4} = \left(\frac{36}{M_1}\right)^{1/2}$; $\frac{4}{3} = \left(\frac{36}{M_1}\right)^{1/2}$. Squaring both sides, we get, $\frac{16}{9} = \frac{36}{M_1}$; $M_1 = \frac{36 \times 9}{16}$ = **20.25**. So, no answer is correct.

EXAMPLE 226. *For gaseous state, if most probable speed is denoted by C* the average speed by $\bar{C}$ and mean square velocity by C, then for a large number of molecules, the ratios of these speed are:*

(a) $\overset{*}{C} : \bar{C} : C = 1 : 1.225 : 1.128$

(b) $\overset{*}{C} : \bar{C} : C = 1.225 : 1.128 : 1$

(c) $\overset{*}{C} : \bar{C} : C = 1.128 : 1 : 1.225$

(d) $\overset{*}{C} : \bar{C} : C = 1 : 1.128 : 1.225$ **(JEE, Main, 2013)**

SOLUTION. $\overset{*}{C} : \bar{C} : C = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi m}} : \sqrt{\frac{3RT}{M}}$

$$= \sqrt{2} : \sqrt{\frac{8}{3.142}} : \sqrt{3}$$

$$= 1 : 1.128 : 1.225$$

(after dividing above ratios by $\sqrt{2}$)

So, the correct answer is (*d*).

PROBLEMS FOR PRACTICE

1. The volume of a gas at 756 mm pressure is 152 cc. What is the volume at a pressure of 760 mm, the temperature remaining constant. **(OJEE, 1978, DSB, 1978)**

[Hint and Ans.:

$$P_1V_1 = P_2V_2 ;\ (756 \times 152)/760$$
$$= 151.2 \text{ cc } \textbf{Ans.]}$$

2. At a certain place, air sample having a pressure of 1.0 bar and volume 500 dm^3 was taken. What additional pressure is needed to reduce the volume to 150 dm^3 at 27°C.

[Hint and Ans.:

$$P_1V_1 = P_2V_2 ;\quad 1 \times 500 = P_2 \times 150 ;$$
$$P_2 = 3.33 \text{ bar.}$$

Additional pressure required = 3.33 – 1.0 = 2.33 bar **Ans.]**

3. At what temperature will a given volume of a gas at 0°C triple itself, pressure remaining constant?

[Hint and Ans.:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} ;\ \frac{V}{273 \text{ K}} = \frac{3V}{T} ;$$
$$T = 3 \times 273 \text{ K} = 819 \text{ K}$$ **Ans.]**

4. If the temperature of a gas in centigrade is tripled, will its volume be also tripled? Comment.

[Hint and Ans.: Volume is directly proportional to absolute temperature (K) and not to centigrade temperature. Suppose V mL volume is at 27°C or 273 + 27 (= 300 K), the new volume at 3 × 27 = 81°C or 81 + 273 = 354 K will be as:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} ;\ \frac{V}{300 \text{ K}} = \frac{V_2}{354 \text{ K}} ;$$
$$V_2 = \frac{V \times 354 \text{ K}}{300} = 1.18 \text{ V and not 3V.}$$

So, the volume will not be tripled.]

5. A blown up toy balloon at 5°C has volume equal to 420 cm^3. The balloon is distended at 7/8th of its maximum stretching capacity (*i*) will it burst if it is brought into a room at 27°C? (*ii*) calculate the maximum temperature, at which it will burst.

[Hint and Ans.:

Maximum capacity

$$= 420 \times \frac{8}{7} = 480 \text{ mL} ;\ \frac{V_1}{T_1} = \frac{V_2}{T_2} ;\ \frac{420}{5+273}$$
$$= \frac{V_2}{27+273} ;\ \frac{420}{278 \text{ K}} = \frac{V_2}{300 \text{ K}} ;$$
$$V_2 = \frac{(300 \times 420)}{278} = 453.2 \text{ cm}^3.$$

Since 453.2 mL is less than 480 mL, balloon will not burst.

(*ii*) $$\frac{V_1}{T_1} = \frac{V_2}{T_2} ;\ \frac{420}{278} = \frac{480}{T_2} ;$$
$$T_2 = \frac{(480 \times 278)}{420} = 317.7 \text{ K}$$ **Ans.]**

6. The temperature of a given volume of N_2 gas was raised from – 2°C to + 5°C. If the pressure was equal to 755 mm at – 2°C, what would be the new pressure at 8°C assuming the volume to remain constant.

[Hint and Ans.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} ;\ \frac{755}{273 - 2 = 271 \text{ K}} = \frac{P_2}{8 + 273} = 281 \text{ K}$$
$$\therefore \quad P_2 = \frac{(281 \times 755)}{271} = \mathbf{782.86 \text{ mm}}$$ **Ans.]**

7. At 0°C and 760 mm pressure, the densities of N_2 and O_2 gases are 14 and 16 respectively. Calculate the temperature at which O_2 will have the same density as of N_2 at 0°C if pressure remains constant.

[Hint and Ans.:

$$D_1T_1 = D_2T_2 ;\ 16 \times 273 = 14 \times T_2 ;$$
$$T_2 = 312 \text{ K or } 312 - 273 = \mathbf{39°C}$$ **Ans.]**

8. A gas has a volume of 250 cm^3 at 27°C and 740 mm pressure. What will be its volume at standard temperature and pressure?

[Hint and Ans :

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

Standard temperature

$$T_2 = 273 \text{ K} ; P_2 = 760 \text{ mm.}$$

So, $\frac{740 \times 250}{27 + 273 = 300 \text{ K}}$

$$= \frac{760 \times V_2}{273 \text{ K}} ;\ V_2 = \mathbf{221.5 \text{ cm}^3}$$ **Ans.]**

9. Calculate the volume of one mole of oxygen at 27°C and two atmospheric pressure. Molar volume of oxygen at S.T.P. is 22.4 L. **(DBS 1978)**

[Hint and Ans:

But $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\,;\; V_1 = \frac{P_2V_2}{T_2}\times\frac{T_1}{P_1}$$
$$= \frac{1\text{ atm}\times 22.4\text{ L}\times 300\text{ K}}{273\text{ K}\times 2\text{ atm}}$$
$$= \mathbf{12.31\ L}$$ **Ans.]**

10. Two gases *X* and *Y* having molecular weights 60 g mol^{-} and 45 g mol^{-} respectively were enclosed in a vessel. If weight of *X* is 0.5 g and that of *Y* is 0.2 g, calculate the partial pressure of the two gases, if total pressure of mixture is 750 mm. **(AIPMT, 2009 type)**

[Hint and Ans.

no. of mol. of $X = \dfrac{0.5}{60} = 8.3\times 10^{-3}$;

no. of mol. of Y $= \dfrac{0.2}{45} = 4.4\times 10^{-3}$

Total no. of mol. $= 8.3\times 10^{-3} + 4.4\times 10^{-3}$
$= 12.7\times 10^{-3}$

Total pressure = 750 mm ;

$$p_x = \frac{8.3\times 10^{-3}}{12.7\times 10^{-3}}\times 750 = \mathbf{490.16\ mm}\ ;$$

$$p_y = \frac{4.4\times 10^{-3}}{12.7\times 10^{-3}}\times 750$$
$$= \mathbf{259.84\ mm}$$ **Ans.]**

11. A gaseous mixture of O_2 and CO_2 contained in a 5.0 L flask at 300 K exerted a pressure of 6.0 atm. If the quantity of O_2 is 0.2 mol, calculate the partial pressure of each gas.

[Hint and Ans.

$$p_{O_2} = \frac{nRT}{V} = \frac{0.2\times 0.0821\times 300}{5}$$
$= 0.98$ atm. **Ans.**

$p_{CO_2} = 6.0 - 0.98 = 5.02$ atm **Ans.]**

12. The relative rate of diffusion of a gas B as compared to that of a diatomic gas A is 6.5. Find the molecular weight of B, if the atomic weight of A is 36. **(MLNR, 1979)**

[Hints and Ans.

$$\frac{r_A}{r_B} = \left(\frac{M_B}{M_A}\right)^{1/2};\ \frac{1}{6.5} = \left(\frac{M_B}{2\times 36}\right)^{1/2}$$

Squaring both sides, we get,

$$M_B = \frac{72}{(6.5\times 6.5)} = \mathbf{1.70}$$ **Ans.]**

13. Two flasks X and Y have equal volumes. Flask X contains He-gas at 25°C while Y contains equal mass of CH_4 gas at 427°C. Assuming ideal gas behaviour of gases, in which flask and by how many times are the molecules moving with greater speed ?

[Hints and Ans.:

Mol. wt. of He = 4 g mol^{-}, T = 25 + 273 = 298 K

mol. wt. of CH_4 = 12 + (4 × 1) = 16 g mol^{-}

T = 427 +273 = 700 K

For He, $U_{av} = \left(\dfrac{8RT}{\pi M}\right)^{½} = \left(\dfrac{8R\times 298}{\pi\times 4}\right)^{½}$.

For CH_4, $U_{av} = \left(\dfrac{8R\times 700}{\pi\times 16}\right)^{1/2}$.

So, $$\frac{U_{av}\text{ of He}}{U_{av}\text{ of }CH_4} = \left(\frac{2\times 298}{350}\right)^{1/2} = \frac{1.3}{1}$$ or 1.3 : 1**Ans.]**

14. 11.8 L of an unknown gas weighs 16 g under 2.5 atmospheric pressure. Calculate the root mean square velocity of the gas molecules.

[Hints and Ans.:

$$PV = \frac{w}{M}\times RT\ ;$$
$$\frac{T}{M} = \frac{PV}{wR}$$
$$= \frac{2.5\text{ atm}\times 11.8\text{ L}}{16\text{ g}\times 0.0821\text{ L atm K}^{-}\text{mol}^{-}}$$
$$= 22.457\text{ K g}^{-}\text{ mol}$$
$$U_{av} = \left(\frac{8RT}{\pi M}\right)^{½}$$
$$= \left(\frac{\dfrac{8\times 8.314\times 10^{7}\text{ g cm}^2\text{s}^{-2}\text{ K}^{-}\text{ mol}^{-}\times 22.457\text{ g}^{-}\text{ K}}{\text{mol}\times 7}}{22}\right)^{1/2}$$
$$= (47.5\times 10^{8})^{1/2} = 6.89\times 10^{4}\text{ cm s}^{-}$$
$$U_{rms} = U_{av}\times\left(\frac{3\pi}{8}\right)^{1/2}$$
$$= 6.89\times 10^{4}\text{ cm s}^{-}\left(\frac{3\times 22}{7\times 8}\right)^{1/2}$$
$$= 6.89\times 10^{4}\text{ cm s}^{-}\times (1.1786)^{1/2}$$
$$= 6.89\times 10^{4}\text{ cm s}^{-}\times 1.08$$
$$= 74412\text{ cm s}^{-}$$
$$= 74.412\times 10^{3}\text{ cm s}^{-}$$ **Ans.**

or $U_{rms} = U_{av}/0.913$
$= (6.89\times 10^{4}\text{ cm s}^{-})/0.9213$
$= 74.412\times 10^{3}\text{ cm s}^{-}$ **Ans.]**

15. An open vessel at 27°C is heated until three fifth of the air in it has been expelled. Assuming the volume of the vessel remains constant, find the temperature to which the vessel has to be heated. **(IIT, 1977)**

[Hints and Ans. :

$PV = n_1RT_1 = n_2RT_2\,;\ T_2 = T_1n_1/n_2$
$= 300\times 1/0.4 = 750$ K **Ans.]**

16. The density of H_2 at 0°C and 760 mm is 0.00009 g cm^{-3}. Find the root mean square velocity of hydrogen molecules (g = 981 dynes cm^{-2}, density of Hg = 13.5).

[Hint and Ans :

$$U = \left(\frac{3P}{D}\right)^{1/2} = \left(\frac{3hdg}{D}\right)^{1/2}$$

$$= \left(\frac{3 \times 76 \times 13.5 \times 981}{0.00009}\right)^{1/2}$$

$= \mathbf{183166\ cm\ s^{-}}$ **Ans.]**

17. Calculate the temperature at which H_2 gas under 1 bar pressure has the same root mean square velocity as that of oxygen gas at S.T.P.

[Hints and Ans : $U = \left(\frac{3RT}{2}\right)^{1/2} = \left(\frac{3R \times 273}{32}\right)^{1/2}$

where mol. wt. of

$H_2 = 2\ g\ mol^{-}, O_2 = 32\ g\ mol^{-}.$

So, $T = \mathbf{17.06\ K}$ **Ans.]**

18. The vander Waal's constants, *a* and *b* for N_2 gas are 1.39 $litre^2$ atm mol^{-2} and 39.0 mL mol^{-} respectively. Calculate the Boyle's temperature for the gas. (**Ans. 434.1 K)**

[Hint. $T_b = \frac{a}{bR}$ where

$a = 1.39\ L^2\ atm\ mol^{-2};$

$b = \frac{39}{1000}\ L\ mol^{-};$

$R = 0.0821\ L\ atm\ K^{-}\ mol^{-}$**].**

19. The critical temperature of N_2 and O_2 are −147°C and − 118°C respectively. Calculate the ratio of reduced temperature of N_2 and O_2 at 27°C.

[Hints and Ans.

$-147 + 273 = 126K, -118 + 273 = 155K;$

For O_2, $T_{r_1} = 300/155$; For N_2, $T_{r_2} = 300/126$.

So, $\frac{T_{r_1}}{T_{r_2}} = \frac{126}{155} = \mathbf{0.812}$ **Ans.]**

20. If $10^{-4}\ dm^3$ of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established?
(Given: Vapour Pressure of H_2O at 300 K is 3170 Pa ; $R = 8.314\ J\ K^{-1}\ mol^{-1}$)

(*a*) 4.46×10^{-2} mol (*b*) 1.27×10^{-3} mol
(*c*) 5.56×10^{-3} mol (*d*) 1.53×10^{2} mol

[Ans. (b)]

(AIEEE 2010)

21. The density of gas A is twice that of B. Molecular mass of A is half of molecular mass of B. The ratio of partial pressure of A and B is

(*a*) 1/4 (*b*) 1/2
(*c*) 4/1 (*d*) 1/2 **[Ans. (c)]**

(Orissa JEE 2010)

22. An evacuated glass vessel weighs 50 g when empty 144.0 g when filled with a liquid of density 0.47 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. The molar mass of the ideal gas is (Given $R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$)

(*a*) 61.575 (*b*) 130.98
(*c*) 123.75 (*d*) 43.87
(*d*) 87.943 **[Ans. (a)]**

(Kerala PMT, 2010)

23. The *rms* velocity of hydrogen at 300 K is 1.9×10^3 ms^{-1}. The *rms* velocity of oxygen at 1200 K will be

(*a*) $7.6 \times 10^3\ ms^{-1}$ (*b*) $3.8 \times 10^3\ ms^{-1}$
(*c*) $0.95 \times 10^3\ ms^{-1}$ (*d*) $0.475 \times 10^3\ ms^{-1}$

[Ans. (c)]

(Orissa JEE, 2010)

24. What will happen to the volume of a bubble of air found under water in a lake, where the temperature is 15°C and the pressure is 1.5 atm, if the bubble then rises to the surface where the temperature is 25°C and the pressure is 1.0 atm?

(*a*) Its volume will become greater by a factor of 2.5
(*b*) Its volume will become greater by a factor of 1.6
(*b*) Its volume will become grater by a factor of 1.1
(*d*) Its volume will become greater by a factor of 0.70

[Ans. (b)]

(DUMET, 2010)

25. The mass of $2.24 \times 10^{-3}\ m^3$ of a gas is 4.4 g at 273.15 K and 101.325 kPa pressure. The gas may be

(*a*) NO (*b*) NO_2
(*c*) C_3H_8 (*d*) NH_3
(*d*) CH_4 **[Ans. (c)]**

(Kerala PMT, 2010)

26. The vander Waals' constant '*a*' for different gases have been given as:

Gas	O_2	N_2	CH_4	NH_3
a(atm L^2 mol^{-2})	1.36	1.39	2.15	4.17

The gas that can be most easily liquefied is:

(*a*) O_2 (*b*) N_2
(*c*) CH_4 (*d*) NH_3 **[Ans. (d)]**

(Orissa JEE, 2010)

27. By what factor does the average velocity of a gaseous molecule increase when the absolute temperature is doubled?

(*a*) 1.4 (*b*) 2.0
(*c*) 2.8 (*d*) 4.0 **[Ans. (a)]**

(DUMET, 2010)

28. The ratio of rates of diffusion of hydrogen chloride and ammonia gases is

(*a*) 1 : 1.46 (*b*) 1 : 2.92
(*c*) 1.46 : 1 (*d*) 1 : 0.73

[Ans. (a)]

(AMU Engg., 2010)

29. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of *n*?

(*a*) 1 (*b*) 4
(*c*) 3 (*d*) 8 **[Ans. (b)]**

(West Bengal JEE, 2010)

9

CHAPTER

The Mole Concept

9.1 THE MOLE

^{12}C is taken for the comparison of atomic weights of atoms. The same standard is used for all molecular and formula weights. On this basis (atomic weight of carbon = 12 a.m.u.), the value of Avogadro's number (N) is 6.02×10^{23}. **Mole** *is a unit which stands for* 6.02×10^{23} *entities of a substance. In other words, "a mole of a substance is that which contains an Avogadro number* (6.02×10^{23}) *of particles. A gram atom* (*i.e.* atomic weight of an element expressed in grams) of an element contains 6.02×10^{23} atoms while *a gram molecule* (*i.e.* molecular weight of a substance expressed in grams) of a substance contains 6.02×10^{23} molecules of that substance. Hence.

"One mole stands for one gram atom of an element or one gram molecule of a compound". Also, 1 mol = N molecules = g. mol. wt.

Thus (*a*)1 mole of hydrogen atoms
= 1 gram atomic weight of hydrogen (H)
= 1 gram atom of hydrogen = one gram
= 6.02×10^{23} atoms.

(*b*)1 mole of hydrogen molecules
= 1 gram molecular weight of hydrogen (H_2)
= 1 gram molecule of hydrogen
= 2 grams
= 6.02×10^{23} molecules.

Moles, equivalents, millimoles and milliequivalents do not change on dilution.

> **Note.** The Avogadro's number depends upon the basis of the atomic weight scale. Thus it is not a fundamental physical constant. For example, if the atomic weight of carbon were set at 100 U *and not* 12 U, the Avogadro's number would be the number of atoms in 100 grams of carbon which is calculated as:
>
> $$100 \text{ g C} \left[\frac{6.02 \times 10^{23} \text{ atoms}}{12 \text{ g carbon}}\right]$$
>
> $$= 5.01 \times 10^{24} \text{ atoms}$$

Similarly, we can say that

(*i*) One mole of electrons = 6.02×10^{23} electrons

(*ii*) One mole of protons = 6.02×10^{23} protons

(*iii*) One mole of sugar ($C_{12}H_{22}O_{11}$) contains
  (*a*) Carbon atoms = $12 \times 6.02 \times 10^{23} = 7.2 \times 10^{24}$
  (*b*) Hydrogen atoms = $22 \times 6.02 \times 10^{23} = 1.32 \times 10^{25}$
  (*c*) Oxygen atoms = $11 \times 6.02 \times 10^{23} = 6.6 \times 10^{24}$
  (*d*) Sugar molecules = 6.02×10^{23}

(*iv*) One mole of sodium sulphate ($Na_2SO_4 \because 2Na^+ + SO_4^{2-}$) contains
  (*a*) Na^+ ions = $2 \times 6.02 \times 10^{23} = 1.20 \times 10^{24}$
  (*b*) SO_4^{2-} ions or radicals = $1 \times 6.02 \times 10^{23} = 6.02 \times 10^{23}$

We also know that

(*v*) One gram molecular weight (or one gm. mole) of a **gaseous substance** occupy volume equal to 22.4 litre*, 22.4 dm^3, 22400 mL or 22400 c.c. at N.T.P. So:

One gram mole of hydrogen gas (H_2) = 1 gm. mol. wt. of H_2 gas = 2 gram which occupy 22.4 dm^3 or 22.4 L volume at N.T.P.

9.2 SOME IMPORTANT FORMULAE

1. Wt. of an atom of an element

$$= \frac{\text{g. at. wt. of the element}}{6.02 \times 10^{23}}$$

e.g., wt. of an atom of oxygen

$$= \frac{\text{g. at. wt. of oxygen (= 16 g.)}}{6.02 \times 10^{23}}$$

$$= \mathbf{2.7 \times 10^{-23}\ g}$$

2. Wt. of one molecule of a substance

$$= \frac{\text{g. mol. wt. of the substance}}{6.02 \times 10^{23}}$$

***e.g.* wt. of one molecule of oxygen**

---

* Symbol for litre = L; millilitre = mL; gram = g; mole = mol; gram molecular weight = g. mol. wt.; gram atomic weight = g. at. wt.; gram equivalent weight = g. eq. wt.; decimeter cube = dm^3.

$$= \frac{\text{g. mol. wt. of } O_2 (2 \times 16 = 32\text{g})}{6.02 \times 10^{23}}$$

$$= \mathbf{5.3 \times 10^{-23}\ g}$$

3. **Number of atoms of an element in one mole of a compound** = Atomicity** of an element in the compound × 6.02 × 10^{23} atoms
4. **Number of molecules of a substance in one mole of that substance** = 6.02 × 10^{23}
5. **One gram atom of an element** = gram atomic weight of the element which contains 6.02 × 10^{23} atoms = N-atoms = g. at. wt.
6. **x mole A_y molecules = xy mole A atoms**
7. (*a*) No. of moles in x litre of y M solute = xy.
   e.g., 2 L of 0.6 M K_2CO_3 = 2 ×0.6 = 1.2 mol K_2CO_3
   (*b*) For cubic shaped NaCl, the no. of formula units per unit cell = 4.

EXAMPLE. *0.15 mole P_4 molecules*

= 0.15 × 4 mol P atoms

= 0.60 mol P atoms.

7. Weight of one atom of homoatomic gas

$$= \frac{\text{g. mol. wt. of gas}}{\text{Atomicity of gas} \times 6.02 \times 10^{23}}$$

For Example:

(*i*) Wt. of one atom of monoatomic gases like noble gases i.e., He, Ne, Ar, Kr and Xe

$$= \frac{\text{g. mol. wt. of gas}}{1 \times 6.02 \times 10^{23}}$$

> **Note.** g. mol. wt. of noble gas = g. atomic wt. of noble gas

(*ii*) Wt. of one atom of diatomic gases like, H_2, O_2, N_2 etc. $= \dfrac{\text{g. mol. wt. of gas}}{2 \times 6.02 \times 10^{23}}$

(*iii*) Wt. of one atom of triatomic gas like ozone, $O_3 = \dfrac{\text{g. mol. wt. of gas}}{3 \times 6.02 \times 10^{23}}$

8. One mol of a substance

= g. mol. wt. (or mass) of substance

= 6.02 × 10^{23} molecules of that substance

= Atomicity of an element in a substance × 6.02 × 10^{23} atoms of the element in the same substance

= Atomicity of an element in a substance × g. atom

9. One mol. of ionic compound

= Formula mass of that ionic compound

(*a*) No. of cations (or positive radicals) in one mol. of ionic compound

= Valency of anion after dividing by common factor in the compound, if any × [6.02 × 10^{23}]

(*b*) No. of anions (or negative radicals) in one mol. of ionic compound

= Valency of cation after dividing by common factor in the compound, if any × [6.02 × 10^{23}]

9.3 APPLICATIONS OF MOLE CONCEPT

Type. No. of cations and anions.

EXAMPLE 1. *Calculate the number of Zn^{2+} and PO_4^{3-} radicals in one mol. of* $Zn_3(PO_4)_2$.

SOLUTION. The valency 2 of Zn^{2+} and 3 of PO_4^{3-} radicals have no common factor. So:

(*i*) No. of Zn^{2+} ions in one mol. of $Zn_3(PO_4)_2$

= Valency of PO_4^{3-} × 6.02 × 10^{23}

= 3 × 6.02 × 10^{23} = 1.806 × 10^{24} **Ans.**

(*ii*) No. of PO_4^{3-} ions in one mol. of $Zn_3(PO_4)$

= Valency of Zn^{2+} × 6.02 × 10^{23}

= 2 × 6.02 × 10^{23} = 1.204 × 10^{24} **Ans.**

EXAMPLE 2. *Calculate the number of Zn^{2+} and $[Fe(CN)_6]^{4-}$ in one mol. of zinc ferrocyanide.*

SOLUTION. Valency 2 of Zn^{2+} and 4 of $[Fe(CN)_6]^{4-}$ radicals have factor 2 as a comon factor. After dividing both valencies by 2, we get, $Zn^1[Fe(CN)_6]^2$ So:

No. of Zn^{2+} ions in one mole of zinc ferrocyanide

= Valency of $Fe(CN)_6^{4-}$ after dividing by common factor × 6.02 × 10^{23}

= 2 × 6.02 × 10^{23} = 1.204 × 10^{24} **Ans.**

No. of $[Fe(CN)_6]^{4-}$ ions in one mol. of zinc ferrocyanide

= Valency of Zn^{2+} after dividing by common factor × 6.02 × 10^{23}

= 1 × 6.02 × 10^{23} = 6.02 × 10^{23} **Ans.**

EXAMPLE 3. *What is the value of Avogadro's number?*

SOLUTION. Avogadro's number

= 6.02 × 10^{23}.

EXAMPLE 4. *If ^{12}C is taken as the standard for the atomic weights of atoms, write down the standard for the molecular and formula weights of substances.*

SOLUTION. ^{12}C, *i.e.*, the same standard is used for all the atomic, molecular and formula weights.

Type. Value of Avogadro's no. when ^{12}C is not taken as standard.

EXAMPLE 5. *If the atomic weight of carbon is set at 150 U, calculate the value of Avogadro's number.*

SOLUTION. Atomic weight of carbon set at

= 150U

** Atomicity of an element in a compound is equal to number of atoms present in one molecule of the compound. For example, atomicity of hydrogen in C_6H_6 is 6 while in H_2O, it is 2.

g. at. wt. of carbon = 12 g

∴ Number of atoms in 150 g of carbon

$$= 150 \text{ g. C} \times \frac{(6.02 \times 10^{23} \text{ atoms})}{12 \text{ g C}}$$

$$= \mathbf{7.53 \times 10^{24}}$$

Example 6. *Is Avogadro's number a fundamental physical constant?*

Solution. Avogadro's number is not a fundamental physical constant since it depends upon the basis of atomic weight scale.

Example 7. *How many neutrons are present in half a mol. of neutrons?*

Solution. One mole of neutrons

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

$$\therefore \quad \frac{1}{2} \text{ mole of neutrons}$$

$$= \frac{1}{2} \times 6.02 \times 10^{23} \text{ neutrons.}$$

$$= 3.01 \times 10^{23} \text{ neutrons.}$$

Example 8. *How many protons are present in one mole of hydrogen atoms?*

Solution. Number of protons in one atom of hydrogen

= Atomic number (Z) of hydrogen

= 1

∴ Number of protons in one mole (6.02×10^{23} atoms) of hydrogen atoms

$$= 1 \times 6.02 \times 10^{23}$$

$$= 6.02 \times 10^{23} \text{ protons.}$$

Type. Mass or Weight of V mL of a gas at N.T.P.*

$$= \frac{\text{g. mol. wt. of the gas}}{22400 \text{ mL}} \times V \text{ mL}$$

Example 9. *Find the weight of 224 mL of hydrogen gas at N.T.P.*

Solution. The weight of 224 mL of hydrogen gas at N.T.P.

$$= \frac{\text{g. mol. wt. of } H_2}{22400 \text{ mL}} \times 224 \text{ mL}$$

$$= \frac{2\text{g}}{22400 \text{ mL}} \times 224 \text{ mL}$$

$$= \mathbf{0.02 \text{ g}} \qquad \textbf{Ans.}$$

Example 10. *Find the weight of 602 atoms of hydrogen.*

Solution. The weight of 602 atoms of hydrogen

$$= \frac{\text{g. at. wt. of hydrogen}}{6.02 \times 10^{23}} \times 602 \text{ atoms}$$

$$= \frac{1 \text{ g}}{6.02 \times 10^{23} \text{ atoms}} \times 602 \text{ atoms}$$

$$= \mathbf{1.0 \times 10^{-21} \text{ g}} \qquad \textbf{Ans.}$$

Example 11. *Find the weight of 301 molecules of oxygen.*

Solution. The weight of 301 molecules of oxygen

$$= \frac{\text{g. mol. wt. of oxygen}}{6.02 \times 10^{23} \text{ molecules}} \times 301 \text{ molecules}$$

$$= \frac{32 \text{ g}}{6.02 \times 10^{23} \text{ molecules}} \times 301 \text{ molecules}$$

$$= \mathbf{1.6 \times 10^{-20} \text{ g} \quad Ans.}$$

Example 12. *Find the mass of 2.00 × 10^{-2} mol of glucose ($C_6H_{12}O_6$).*

Solution. The mass of 2.00 × 10^{-2} mol of glucose ($C_6H_{12}O_6$)

$$= \frac{\text{g. mol. wt. of } C_6H_{12}O_6}{\text{mol.}} \times 2.00 \times 10^{-2} \text{ mol.}$$

$$= \frac{180 \text{ g}}{\text{mol}} \times 2.00 \times 10^{-2} \text{ mol}$$

$$= \mathbf{0.360} \qquad \textbf{Ans.}$$

Example 13. *Calculate the number of electrons in one mole of methane (CH_4) molecules. (Z for C = 6, H = 1).*

Solution. Number of electrons in a neutral atom

= Atomic number (Z) of the element

One molecule of CH_4 contains

= one atom of carbon + 4 atoms of hydrogen

= 6 + (4 × 1) = 10 protons

= 10 electrons.

∴ One mole (= 6.02×10^{23}) of CH_4 contains

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

$$= \mathbf{6.02 \times 10^{24} \text{ electrons.}}$$

Example 14. *Calculate the number of carbon atoms present in 2.00 × 10^{-4} mol* C_6H_6.

Solution. Number of C-atoms in one mole of C_6H_6

= Atomicity of carbon in C_6H_6 × 6.02×10^{23} atoms

= 6 × 6.02×10^{23} atoms

∴ Number of C-atoms in 2.00 × 10^{-4} mol C_6H_6

$$= 2.00 \times 10^{-4} \times 6 \times 6.02 \times 10^{23} \text{ atoms}$$

$$= \mathbf{7.22 \times 10^{20} \text{ atoms.}}$$

Example 15. *How many moles of* $H_2C_2O_4$ *contain 3.01 × 10^{23} atoms of carbon?*

Solution. Atomicity of carbon in one mole of $H_2C_2O_4$ × 6.02×10^{23} atoms

= 1 mol of $H_2C_2O_4$ of carbon

∴ 2 × 6.02×10^{23} atoms of carbon

---

* *If the volume of gas given as V_1 mL at T_1 K and P_1 pressure, then its volume V_2 is calculated at N.T.P. or S.T.P. (P_2 = 760 mm, T_2 = 273 K) by the relation;

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{or} \quad V_2 = \frac{P_1V_1}{T_1} \times \frac{273}{760}$$

Note. T_1 = t°C + 273.

$$= 1 \text{ mol of } H_2C_2O_4$$

$\therefore$ 3.01×10^{23} atoms of carbon

$$= \frac{1 \text{ mol } H_2C_2O_4}{2 \times 6.02 \times 10^{23}} \times 3.01 \times 10^{23} \text{ atoms of carbon}$$

$$= \mathbf{0.25 \text{ mol } H_2C_2O_4} \qquad \textbf{Ans.}$$

Example 16. *Calculate the number of molecules of nitrogen present in 76 mL of the gas at 20°C and 750 mm pressure.*

Solution. We know that

$$P_1 = 750 \text{ mm}, V_1 = 76 \text{ ml and}$$
$$T_1 = 20 + 273 = 293 \text{ K}$$

At N.T.P., $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K

Using gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}, \text{ We have}$$

Volume V_2 at N.T.P.

$$= \frac{750 \times 76}{293} \times \frac{273}{760} = 69.9 \text{ mL}$$

But 22400 mL of N_2 gas at N.T.P. contain N_2-molecules

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

$\therefore$ 69.9 mL of N_2 gas at N.T.P. contain N_2-molecules

$$= \frac{6.02 \times 10^{23}}{22400 \text{ mL}} \times 69.9 \text{ mL}$$

$$= \mathbf{1.88 \times 10^{21}} \qquad \textbf{Ans.}$$

Example 17. *Calculate the number of moles of each element present in 1.0 mol of each of the following compounds ?*

(a) Al_2O_3 *(b)* $Zn(CH_3COO)_2$

Solution.

(*a*) One mole of Al_2O_3 contains, 2 mol Al and 3 mol O.

(*b*) One mole of $Zn(CH_3COO)_2$ contains, one mol Zn, 4 mol C, 6 mol H and 4 mol O.

Example 18. *How many atoms of hydrogen are present in 10.0 g of* $(NH_4)_2Cr_2O_7$*?*

[at. wt. N = 14, Cr = 52, H = 1, O = 16]

Solution. Wt. of $(NH_4)_2Cr_2O_7 = 10.0$ g

g. mol. wt. of $(NH_4)_2Cr_2O_7 = (2 \times 14) + (8 \times 1) + (2 \times 52) + (7 \times 16) = 252$ g

We know that:

g. mol. wt. of $(NH_4)_2Cr_2O_7$ contain H-atoms

$$= \text{Atomicity of H in } (NH_4)_2Cr_2O_7 \times 6.02 \times 10^{23}$$

Thus: 252 g$(NH_4)_2Cr_2O_7$ contain H-atoms

$$= 8 \times 6.02 \times 10^{23}$$

$\therefore$ 10.0 g$(NH_4)_2Cr_2O_7$ contain H-atom

$$= \frac{8 \times 6.02 \times 10^{23}}{252} \times 10$$

$$= \mathbf{1.91 \times 10^{23}} \qquad \textbf{Ans.}$$

Example 19. *How many molecules of* O_2 *are present in 8.0 g of* O_2*? Also calculate the O-atoms in it.*

Solution. (*a*) Wt. of

$$O_2 = 8.0 \text{ g};$$

g. mol. wt. of O_2 = 32.0 g.

We know that :

g. mol. wt. of O_2 contain O_2 molecules

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

or 32 g O_2 contain O_2 molecules

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

$\therefore$ 8 g O_2 contain O_2 molecules

$$= \frac{6.02 \times 10^{23}}{32} \times 8 = \mathbf{1.51 \times 10^{23}} \qquad \textbf{Ans.}$$

(*b*) 1 molecule of O_2 = 2 atoms of O

$\therefore$ 1.51×10^{23} molecules of

$$O_2 = 2 \times 1.51 \times 10^{23} \text{ atoms of O}$$

$$= \mathbf{3.02 \times 10^{23} \text{ atoms of O.}} \qquad \textbf{Ans.}$$

Example 20. *Calculate grams of* H_2O *present in 5.0 mol of* H_2O.

Solution. H_2O = 5.0 mol.

g.mol.wt. of $H_2O = (2 \times 1) + (1 \times 16) = 18$g.

1 mol. H_2O weighs= g.mol.wt. of H_2O

$$= 18\text{g}$$

$\therefore$ 5.0 mol. H_2O weighs

$$= 5 \times 18 = \mathbf{90 \text{ g.}} \qquad \textbf{Ans.}$$

Example 21. *How many moles of* CH_3COOH *(acetic acid) contain* 6.02×10^{23} *atoms of carbon?*

Solution.

Atomicity of C in $C_2H_4O_2 \times 6.02 \times 10^{23}$ atoms of

$$C = 1 \text{ mol of } C_2H_4O_2$$

$\therefore$ $2 \times 6.02 \times 10^{23}$ atoms of

$$C = 1 \text{ mol } C_2H_4O_2$$

6.02×10^{23} atoms of C

$$= \frac{1 \text{mol} C_2H_4O_2}{2 \times 6.02 \times 10^{23} \text{ atoms}} \times 6.02 \times 10^{23} \text{ atoms}$$

$$= \mathbf{0.50 \text{ mol } C_2H_4O_2} \qquad \textbf{Ans.}$$

Example 22. *How many m mol of manganese are present in 600 mg of manganese? (Mn = 55)*

Solution. mg. mol.wt. of manganese

$$= 1\text{m mol of manganese}$$

55mg of manganese = 1m mol of manganese

$$\therefore 600\text{mg of manganese} = \frac{1\text{m mol manganese}}{55\text{mg}} \times 600 \text{ mg}$$

$$= \mathbf{10.9 \text{ m mol of manganese.}} \quad \textbf{Ans.}$$

Example 23. *Calculate the average weight in kg. of a nitrogen atom. (N = 14.01)*

SOLUTION. g. at. wt. of N

$= 14.01$ g; kg. at. wt. of N $= 14.01 \times 10^{-3}$ kg.

we know that:

6.02×10^{23} atoms of N weigh

$= 14.01 \times 10^{-3}$ kg

$\therefore$ one atom of N weighs

$$= \frac{14.01 \times 10^{-3}\text{ kg}}{6.02 \times 10^{23}\text{ atoms}}$$

$= \mathbf{2.33 \times 10^{-26}}$ **kg/atom** **Ans.**

EXAMPLE 24. *Find the weight of one molecule of ethyl alcohol (C_2H_5OH).*

SOLUTION. g.mol.wt. of C_2H_5OH

$= (2 \times 12) + (6 \times 1) + (16 \times 1) = 46$g.

wt. of one molecule of C_2H_5OH

$$= \frac{\text{g.mol.wt.of } C_2H_5OH}{6.02 \times 10^{23}\text{ molecules}}$$

$$= \frac{46\text{g}}{6.02 \times 10^{23}\text{ molecules}}$$

$= 7.64 \times 10^{-23}$ g/molecule

EXAMPLE 25. *Find the number of mole of sodium atoms that are present in 2.3 g sodium (Na = 23).*

SOLUTION. g. at. wt. of Na

$= 23$ g;

23 g of Na = 1 mole Na atoms

$$2.3 \text{ g of Na} = \frac{1\text{mol Na atoms}}{23\text{g of Na}} \times 2.3\text{g of Na}$$

= 0.1 mol Na atoms **Ans.**

EXAMPLE 26. *How many mol of Ba, Cl and H_2O are contained in 122.0 g $BaCl_2$. $2H_2O$? Also calculate the number of molecules of water of hydration present in the same amount. (Ba = 137, Cl = 35.5, H = 1, O = 16)*

SOLUTION.

(*a*) g. mol. wt. of $BaCl_2$. $2H_2O$

$= (137) + (35.5 \times 2) + 2\,(2 + 16)$

$= 244$ g

244 g $BaCl_2$. $2H_2O$ = 1 mol $BaCl_2$. $2H_2O$

$\therefore$ 122.0 g $BaCl_2$. $2H_2O$

$$= \frac{1\text{mol } BaCl_2.2H_2O}{244\text{g } BaCl_2.2H_2O}$$

$\times$ 122.0 g$BaCl_2$. $2H_2O$

$= 0.50$ mol $BaCl_2$. $2H_2O$

= 0.50 mol Ba, 1.0 mol Cl *and* **1.0 mol $\mathbf{H_2O}$** **Ans.**

(*b*) g. mol. wt. of $BaCl_2$. $2H_2O$

$= 137 + 71 + 36 = 244$ g

244 g $BaCl_2$. $2H_2O$ = 1 mol $BaCl_2$. $2H_2O$

$= 2 \times 6.02 \times 10^{23}$ molecules H_2O

$\therefore$ 122.0 g. $BaCl_2.2H_2O$

$$= \frac{2 \times 6.02 \times 10^{23}\text{ molecules} H_2O}{244\text{g } BaCl_2.2H_2O}$$

$\times$ 122g.$BaCl_2$. $2H_2O$

= 6.02 × $\mathbf{10^{23}}$ molecules $\mathbf{H_2O}$ **Ans.**

EXAMPLE 27. *Find the weight of calcium atoms that contain same number of atoms as 2.4 g of magnesium has. (Mg = 24 , Ca = 40)*

SOLUTION. wt. of Mg= 2.4 g; g. at. wt. of Mg = 24 g

24 g Mg $= 6.02 \times 10^{23}$ Mg atoms

$$2.4 \text{ g Mg} = \frac{6.02 \times 10^{23}\text{ Mg atoms}}{24\text{g Mg}} \times 2.4\text{g Mg}$$

= 6.02 × $\mathbf{10^{22}}$ Mg atoms

$\therefore$ Number of Ca atoms

$= 6.02 \times 10^{22}$

g. at. wt. of

Ca = 40 g = wt. of 6.02×10^{23} Ca atoms

6.02×10^{22} Ca atoms weigh = 40 g

$\therefore$ 6.02×10^{22} Ca atoms weigh

$$= \frac{40\text{g}}{6.02 \times 10^{23}} \times 6.02 \times 10^{22}$$

= 4.0 g **Ans.**

EXAMPLE 28. *How many mol are represented by 21.44 g Ti $S_{1.85}$ (S = 32.00, Ti = 47.90)*

SOLUTION. wt. of

Ti $S_{1.85}$ = 21.44 g

g. mol. wt. of $TiS_{1.85}$ = 47.90 + (32.00 × 1.85) = 107.10

107.10g $TiS_{1.85}$ = 1mol $TiS_{1.85}$

$$21.44 \text{ g } TiS_{1.85} = \frac{1\text{mol } TiS_{1.85}}{107.10\text{g } TiS_{1.85}} \times 21.44\text{g } TiS_{1.35}$$

= 0.2002 mol. of $\mathbf{TiS_{1.85}}$ **Ans.**

EXAMPLE 29. *How many gram atoms are present in 4.0 g of calcium (Ca = 40.0)*

SOLUTION. wt. of Ca= 4.0g; g. at. wt. of Ca = 40.0g.

40.0 g. of Ca = 1 g. atom Ca

$$4.0 \text{ g. of Ca} = \frac{1\text{g.atom Ca}}{40.0\text{g Ca}} \times 4.0\text{g.Ca}$$

= 0.10 g atom Ca **Ans.**

EXAMPLE 30. *One atom of an element X weighs 6.644×10^{-23} g. Calculate the number of gram atoms in 40 kg of it.*

(IIT admission test)

SOLUTION. wt. of

X = 40 kg = 40 × 1000 = 40,000 g.

wt. of one atom of

X $= 6.644 \times 10^{-23}$ g.

1 g. atom of X contain atoms

$= 6.02 \times 10^{23}$

∴ g. atomic weight of

$$X = 6.644 \times 10^{-23} \times 6.02 \times 10^{23} = 40 \text{ g}$$

$$40 \text{ g. } X = 1 \text{ g. atom of } X$$

$$40{,}000 \text{ g. } X = \frac{1 \text{g.atom of } X}{40 \text{g.} X} \times 40{,}000 \text{g.} X$$

$$= \mathbf{1000 \text{ g. atom of } X} \qquad \textbf{Ans.}$$

EXAMPLE 31. *The weight of 350 mL of a diatomic gas at 0°C and 2 atmospheric pressure is 1 g. Calculate the weight of one atom.* **(IIT admission test)**

SOLUTION.

Applying gas equation, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}; \quad \frac{2 \times 350}{273} = \frac{1 \times V_2}{273}$$

∴ $V_2 = 700$ mL

700 mL of a gas weighs

= 1 g (given)

∴ 22400 mL of a gas weighs

$$= \frac{1\text{g}}{700 \text{mL}} \times 22400 = 32\text{g}.$$

= g. mol. wt. of gas.

∴ wt. of one atom of gas

$$= \frac{\text{g.mol.wt.of gas}}{\text{atomicity of gas} \times 6.02 \times 10^{23}}$$

$$= \frac{32\text{g.}}{2 \times 6.02 \times 10^{23}}$$

$$= \mathbf{2.66 \times 10^{-23} \text{ g.}} \qquad \textbf{Ans.}$$

EXAMPLE 32. *Calculate the number of molecules of water present in one drop of water (volume = 0.05 mL) [density of water = 1 g (mL)$^{-}$]*

SOLUTION. wt. of 0.05 mL water

= Volume of water × density of water

= 0.05 mL × 1 g (mL)$^{-}$ = **0.05 g.**

g. mol. wt. of water

(H_2O) = (2 × 1) + 16 = 18 g.

∴ Number of molecules of water

$$= \frac{\text{wt.of water}}{\text{g.mol.wt.of water}} \times 6.02 \times 10^{23}$$

$$= \frac{0.05\text{g}}{18\text{g}} \times 6.02 \times 10^{23}$$

$$= \mathbf{1.67 \times 10^{21}} \qquad \textbf{Ans.}$$

EXAMPLE 33. *If a mole were to contain 1.00 × 10^{24} particles, what would be the mass (i) of a single oxygen molecule and (ii) one mole of oxygen.* **(IIT admission test)**

SOLUTION. (*i*) wt. of one molecule of oxygen

$$= \frac{\text{g.mol.wt.of } O_2}{10^{24}}$$

$$= \frac{32\text{g}}{10^{24}}$$

$$= \mathbf{3.2 \times 10^{-23} \text{ g}} \qquad \textbf{Ans.}$$

(*ii*) g. mol. wt. of O_2 = 32g.

∵ 1 mole = g. mol. wt. = 1.00 × 10^{-24} molecules (given)

∴ 1.00 × 10^{24} molecules of oxygen weigh

= **32 g.** **Ans.**

EXAMPLE 34. *20 mL of N_2 gas contain 1000 molecules at certain temperature and pressure. Find the number of molecules of H_2 gas which occupy 100 mL volume at the same temperature and pressure.*

SOLUTION. According to Avogadro's hypothesis, equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure.

∴ 20 mL of H_2 will contain molecules of

H_2 = 1000

100 mL of H_2 will contain molecules of

$$H_2 = \frac{1000}{20} \times 100 = \mathbf{5000} \qquad \textbf{Ans.}$$

EXAMPLE 35. *Which of the following weighs the most and which one the least ?*

(*i*) *One atom of nitrogen* (*ii*) *One gram of silver*

(*iii*) *10^{23} atoms of sulphur*

(*iv*) *One mole atoms of magnesium*

(*N = 14, Ag = 108, S = 32 and Mg = 24*)

SOLUTION.

(*i*) wt. of one atom of nitrogen

$$= \frac{\text{g.at.wt.of } N_2}{6.02 \times 10^{23}} = \frac{14\text{g}}{6.02 \times 10^{23}}$$

$$= \mathbf{2.33 \times 10^{-23} \text{ g}}$$

(*ii*) wt. of Ag = **1 g.**

(*iii*) 6.02 × 10^{23} atoms of S weigh

= g. at. wt. of S = 32 g.

10^{23} atoms of S weigh

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

= **5.32 g**

(*iv*) one mole atoms of Mg

= g. at. wt. of Mg = **24 g**

Maximum weight

= 24 g = wt. of one mole atoms of Mg

Least weight = 2.33 × 10^{-23} g = wt. of one atom of nitrogen

EXAMPLE 36. *A two litre glass vessel contains nitrogen and water vapours in equimolar proportions at a pressure of 10^{-3} mm mercury at 303 K. Calculate :*

(*i*) *Number of moles of the nitrogen and water vapours present and*

(*ii*) *The total mass of the gaseous mixture*

Find the mass of the gas when the mixture is cooled to –50°C (*R = 0.082*) **(IIT admission test)**

Solution. P = Pressure in atmosphere

$$= \frac{10^{-3}\text{ mm}}{760\text{ mm}} = \frac{10^{-4}}{76}$$

V = Volume in litre = 2

n = Number of moles = ?

$R = 0.082$ L atm K^{-} mol^{-}; $T = 303$ K

We know that : $PV = nRT$; $\frac{10^{-4}}{76} \times 2 = n \times 0.082 \times 303$

$\therefore$ n = **1.058×10^{-7} moles**

Since both N_2 and water vapours are present in equimolar quantities, so we have

$$\text{Nitrogen} = \frac{1.058 \times 10^{-7}}{2} = 0.529 \times 10^{-7} \text{ mole}$$

wt. of nitrogen = 0.529×10^{-7} mole × 28 g./mole

= **1.481×10^{-6} g.**

$$\text{Water vapours} = \frac{1.058 \times 10^{-7}}{2} = \mathbf{0.529 \times 10^{-7}\ mole}$$

wt. of water = 0.529×10^{-7} mole × 18 g./mole

= 0.952×10^{-6} g.

Total mass of mixture

= $(1.481 + 0.952)\ 10^{-6}$ g.

= **2.433×10^{-6} g.**

Since water vapours condense to solid at –50°C, the gas available at –50°C will be nitrogen only. So, the mass of the gas at –50°C will be the mass of nitrogen gas only which is equal to 1.481×10^{-6} g.

Example 37. *What is the number of molecules of CO_2 present that contain 8 g of O_2?* **(PSEB, 1987)**

Solution. $CO_2 \equiv O_2$

$12 + (2 \times 16) = 44$ g $\quad 2 \times 16 = 32$ g

32 g. of O_2 is present in

$CO_2 = 44$ g.

$\therefore$ 8 g. of O_2 is present in

$$CO_2 = \frac{44}{32} \times 8 = 11 \text{ g.}$$

Gram mol. wt. of

$CO_2 = 12 + 2 \times 16 = 44$ g.

= 1 mole CO_2;

= 6.02×10^{23} molecules of CO_2

Thus, 44 g $CO_2 \equiv 6.02 \times 10^{23}$ molecules of CO_2

$$11\text{ g } CO_2 \equiv \frac{6.02 \times 10^{23}}{44} \times 11$$

= **1.505×10^{23} molecules of CO_2**

Ans.

Example 38. (*a*) *How many molecules of CO_2 are present in its molar volume ?*

(*b*) *Calculate the number of molecules and number of atoms present in 11.2 litres of oxygen (O_2) at N.T.P.*

(HP Board, 2007)

Solution. (*a*) Molar volume at N.T.P. = 22.4 L. But molar volume of every gas at N.T.P. contain Avogadro's number of molecules (= 6.02×10^{23}). Hence number of molecules of CO_2 present in its molar volume = **6.02×10^{23}** **Ans.**

(*b*) (*i*) 22.4 L of O_2 gas at N.T.P. contain molecules = 6.02×10^{23}

$\therefore$ 11.2 L of O_2 gas at N.T.P. contain molecules = 6.02

$$\times 10^{23} \times \frac{11.2}{22.4} = \mathbf{3.01 \times 10^{23}}$$ **Ans.**

(*ii*) 22.4 L of O_2 gas at N.T.P. contain O-atoms = Atomicity of $O_2 \times 6.02 \times 10^{23}$ atoms

$\therefore$ 11.2 L of O_2 gas at N.T.P. contain O-atoms

$$= 2 \times 6.02 \times 10^{23} \times \frac{11.2}{22.4} = \mathbf{6.02 \times 10^{23}}$$ **Ans.**

Example 39. *0.01 mole of a compound weighs one gram. Calculate the molecular mass of the compound.* **(PSEB, 1989)**

Solution. We know that one gram molecular mass of a compound is equal to one mole of that compound

Thus : 0.01 mole of a compound weighs

= 1 g.

one mole of a compound weighs

$$= \frac{1}{0.01} \times 1 = \mathbf{100\ amu}$$

$\therefore$ Molecular mass of the compound

= **100 amu.**

Example 40. *Assume that the human body contains 80% water. Calculate the number of molecules of water that are in the body of a person who has a mass of 65 kg.* **(PUPET 1986)**

Solution. wt. of water in human body

$$= 65 \times \frac{80}{100} \text{kg} = 52 \text{ kg or } 52 \times 10^3 \text{ g}$$

g mol. mass of water (H_2O)

= $2 \times 1 + 1 \times 16 = 18$ g.

= 6.02×10^{23} molecules of H_2O

18 g. H_2O contain molecules

= 6.02×10^{23}

52×10^3 g H_2O contain molecules

$$= \frac{6.02 \times 10^{23}}{18\text{ g}} \times 52 \times 10^3 \text{ g}.$$

= **17.39×10^{26}** **Ans.**

Example 41. *From 200 mg of CO_2, 10^{21} molecules are removed. How many moles of CO_2 are left?* **(IIT 1978)**

Solution. wt. of CO_2 = 200 mg = $\frac{200}{1000}$ or **0.2 g**

g. mol. wt. of $CO_2 = 12 + 2 \times 16 = 44$ g.

44 g CO_2 contain molecules

= 6.02×10^{23}

0.2 g CO_2 contain molecules

$$= \frac{6.02 \times 10^{23}}{44\text{ g.}} \times 0.2\text{g} = \mathbf{2.736 \times 10^{21}}$$

Number of CO_2 molecules removed = 10^{21}

$\therefore$ CO_2 molecules left behind

= $2.736 \times 10^{21} - 10^{21} = 10^{21}(2.736 - 1)$

= **$10^{21} \times 1.736$**

6.02×10^{23} molecules of

$$CO_2 = 1 \text{ mole } CO_2$$

1.736×10^{21} molecules of CO_2

$$= \frac{1}{6.02 \times 10^{23}} \times 1.736 \times 10^{21}$$

$$= \mathbf{2.884 \times 10^{-3}\ mol}$$ **Ans.**

EXAMPLE 42. *The atom of an element weighs 6.645×10^{-23} g. Name the element (At. wt. Na = 23, K = 39, Ca = 40).*

SOLUTION. We know that 6.02×10^{23} atoms of an element weigh equal to gram atomic weight of that element. So ;

One atom of an element weighs

$$= 6.645 \times 10^{-23} \text{ g.}$$

6.02×10^{23} atoms of element weighs

$$= 6.645 \times 10^{-23} \times 6.02 \times 10^{23} \text{ g.}$$

$$= 40.00 \text{ g}$$

= g. at. wt. of Ca (given)

∴ Name of the element is **Calcium.**

EXAMPLE 43. *If it requires one second to count one wheat grain, calculate the time (in years) required to count half mole of wheat grains.*

SOLUTION. One mole of wheat grains

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

$$\frac{1}{2} \text{ mole of wheat grains} = 6.02 \times \frac{1}{2} \times 10^{23} \text{ grains}$$

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

Time required to count one wheat grain

= 1 second

Time required to count 3.01×10^{23} wheat grains

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

$$= \frac{3.01 \times 10^{23}}{60 \times 60 \times 24 \times 365} \text{ years}$$

$$= \mathbf{9.54 \times 10^{15}\ years}$$ **Ans.**

EXAMPLE 44. *A glass of juice contains 18 g of glucose ($C_6H_{12}O_6$). Calculate the number of atoms of each kind in one glass of juice. (At. wt. C = 12, H = 1, O = 16)*

SOLUTION. g. mol. wt. of $C_6H_{12}O_6$

$$= 6 \times 12 + 12 \times 1 + 6 \times 16 = 180 \text{ g.}$$

(*a*) 180 g. of $C_6H_{12}O_6$ contain C-atoms

= Atomicity of C × 6.02×10^{23} atoms in $C_6H_{12}O_6$

$$= 6 \times 6.02 \times 10^{23} \text{ atoms}$$

18 g of $C_6H_{12}O_6$ contain C-atoms

$$= \frac{6 \times 6.02 \times 10^{23}}{180} \times 18 \text{ atoms}$$

$$= \mathbf{3.61 \times 10^{23}\ atoms}$$

Since atomicity of 'O' is also six, so 18 gram of glucose would also contain 3.61×10^{23} atoms of oxygen.

(*b*) 180 g. of $C_6H_{12}O_6$ contain H-atoms = Atomicity of H × 6.02×10^{23} atoms in $C_6H_{12}O_6$

∴ 18 g. of $C_6H_{12}O_6$ contain H-atoms

$$= \frac{12 \times 6.02 \times 10^{23}}{180} \times 18 \text{ atoms}$$

$$= \mathbf{7.22 \times 10^{23}\ atoms}$$ **Ans.**

EXAMPLE 45. *Calculate the mass of 2 gram equivalent of K_2CO_3 (At. wt. K = 39, C = 12, O = 16)*

SOLUTION. g. mol. wt. of K_2CO_3

$$= 2 \times 39 + 1 \times 12 + 3 \times 16 = 138 \text{ g}$$

$$K_2CO_3 \rightleftharpoons 2K^+ + CO_3^{2-}$$

∴ Total + ive charge on K^+ ions = 2

∴ One g. equivalent of K_2CO_3

$$= \frac{\text{g. mol. wt. of } K_2CO_3}{\text{Total + ive charge on } K^+ \text{ ions}}$$

$$= \frac{138}{2} \text{g.} = 69 \text{ g.}$$

2 g. equivalent of

$$K_2CO_3 = 2 \times 69 \text{ g.} = \mathbf{138\ g.}$$ **Ans.**

EXAMPLE 46. *Sodium chloride (NaCl) contains 39.32% by weight of sodium. If 1.64 g. of chlorine is mixed with 1.5 g. of sodium, calculate the number of moles of sodium which will combine with chlorine to form sodium chloride.*

(At. wt. Na = 23 amu, Cl = 35.5 amu)

SOLUTION. Percentage of Na in NaCl = 39.32

Percentage of Cl in NaCl

= 100 – 39.32 = 60.68

60.68 g. Cl react with Na

= 39.32 g.

1.64 g. Cl react with Na

$$= \frac{39.32}{60.68} \times 1.64 = 1.06 \text{ g.}$$

Since 1.06 g Na is less than 1.5 g Na (given), so 1.06 g Na will react completely.

g. at. wt of Na = 23 g. = 1 mole of Na

Thus : 23 g. of Na = 1 mole

$$1.06 \text{ g. of Na} = \frac{1.06 \text{ g}}{23 \text{ g}} \text{ mole} = \mathbf{4.6 \times 10^{-2}\ mole}$$ **Ans.**

EXAMPLE 47. *The green colouring matter of plants (chlorophyll) contains 2.68% magnesium by weight. Find the number of magnesium atoms in 10 g. of chlorophyll. (At. wt. Mg = 24 amu)*

SOLUTION. 100 g. chlorophyll contains

Mg = 2.68 g.

10 g. chlorophyll contains Mg

$$= \frac{2.68}{100} \times 10 = 2.68 \times 10^{-1} \text{ g.}$$

g. at. wt. of Mg = 24 g.

24 g. Mg contain Mg-atoms

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

2.68×10^{-1} g Mg contain Mg-atoms

$$= \frac{6.02 \times 10^{23}}{24} \times 2.68 \times 10^{-1}$$

$$= \mathbf{6.72 \times 10^{21}}$$ **Ans.**

9.4. MASS OF 1 a.m.u.

Example 48. *Calculate the mass of one atomic mass unit (1 a.m.u.) is grams.*

Solution. We know that

$$1 \text{ a.m.u.} = \frac{1}{12} \times \text{mass of one carbon atom.}$$

Also, 6.02×10^{23} atoms of carbon weigh

= g. atomic mass of carbon = 12 g.

∴ one atom of carbon weighs

$$= \frac{12}{6.02 \times 10^{23}} \text{ g.}$$

Hence $$1 \text{ a.m.u.} = \frac{1}{12} \times \frac{12}{6.02 \times 10^{23}} = 1.66 \times 10^{-24} \text{ g.}$$

Example 49. *Calculate the number of atoms in each of the following.*

(*i*) *2 g. of helium (He)* (*ii*) *2 a.m.u. of He*

(*iii*) *2 moles of He.* *(He = 4 a.m.u.)*

Solution.

(*i*) Gram atomic mass of He = 4 g.

So, 4 g. of helium contain He-atoms = 6.02×10^{23}

Thus 4 g of He contain He-atoms = 6.02×10^{23}

2 g of He contain He-atoms $= \frac{6.02 \times 10^{23}}{4} \times 2$

$= \mathbf{3.01 \times 10^{23}}$ **Ans.**

(*ii*) Atomic mass of He = 4 a.m.u.

So, 4 a.m.u. of He contain He-atoms = 6.02×10^{23}

2 a.m.u. of He contain He-atoms $= \frac{6.02 \times 10^{23}}{4} \times 2$

$= \mathbf{3.01 \times 10^{23}}$ **Ans.**

(*iii*) 1 mole of He contain He atoms = 6.02×10^{23}

2 moles of He contain He atoms = $6.02 \times 10^{23} \times 2$

$= \mathbf{1.20 \times 10^{24}}$ **Ans.**

Example 50. *A given sample of $AlCl_3$ contains 6.02×10^{21} Al^{3+} ions. Calculate*

(*i*) *Number of formula units*

(*ii*) *Mass of the sample and*

(*iii*) *Number of Cl^- ions.*

(Al = 27 a.m.u., Cl = 35.5 a.m.u.)

Solution. (*i*) *Number of formula units.*

The formula of $AlCl_3$ indicates that one Al^{3+} ion is present in one formula unit.

∴ 6.02×10^{21} Al^{3+} ions are present in formula units

$= 6.02 \times 10^{21}$

Hence number of formula units = $\mathbf{6.02 \times 10^{21}}$ **Ans.**

(*ii*) *Mass of sample.*

1 mole of $AlCl_3$ = 6.02×10^{23} formula units of $AlCl_3$

Thus 6.02×10^{21} formula units of $AlCl_3$ has mass

$$= \frac{133.5}{6.02 \times 10^{23}} \times 6.02 \times 10^{21} = \mathbf{1.335 \text{ g.}}$$

[∵ Molar mass of $AlCl_3$ = 27 + 3 (35.5) = 133.5]

∴ Mass of sample = **1.335 g.**

(*iii*) *Number of Cl^- ions.* The formula of $AlCl_3$ suggests that one Al^{3+} ion is present with three Cl^- ions.

∴ Number of Cl^- ions present with 6.02×10^{21} Al^{3+} ions

$= 3 \times 6.02 \times 10^{21} = \mathbf{1.806 \times 10^{22}}$ **Ans.**

Example 51. *From 6.02×10^{22} molecules of N_2 present in a container, 700 mg. of N_2 are removed. What is the amount of hydrogen (in g) required to convert the remaining nitrogen into NH_3* **(PUCET 1989)**

Solution. (*a*) Mass of nitrogen

= 700 mg/ 1000 = **0.7 g.**

6.02×10^{23} molecules of

N_2 = 1mol of N_2

6.02×10^{22} molecules of

$$N_2 = \frac{1}{6.02 \times 10^{23}} \times 6.02 \times 10^{22}$$

= **0.1 mole of N_2**

Gram molecular mass of

N_2 = 2 × 14 g. = 28 g. = 1 mol of N_2

28 g. N_2 = 1 mol of N_2

$0.7 \text{ g. } N_2 = \frac{1}{28} \times 0.7$ = **0.025 mol of N_2**

∴ Number of moles of N_2 left behind

= 0.1 – 0.025 = **0.075**

(*b*) *To calculate amount of H_2 (in g).* The balanced equation of action of N_2 and H_2 to give NH_3 is :

$$\underset{1 \text{ mol}}{N_2} + \underset{3\text{mol}}{3H_2} \longrightarrow \underset{2\text{mol}}{2NH_3}$$

1 mol of N_2 requires H_2 to convert to NH_3 = 3 mol

0.075 mol of N_2 requires H_2 to convert to NH_3 = 3 × 0.075 mol.

But 1 g. mol of H_2 = 2 g.

∴ 3 × 0.075 g. mol of H_2 = 2 × 3 × 0.075 g.

= **0.45 g**

Ans.

Example 52. *What does a mole represent to a chemist ? Take O_2 as an example.*

Solution. One mole of any substance (say O_2) stands for the following.

(*i*) one gram mole of oxygen

(*ii*) 32 g. of oxygen

(*iii*) 6.02×10^{23} molecules of oxygen

(*iv*) $2 \times 6.02 \times 10^{23}$ atoms of oxygen

(*v*) 2 gram atoms of oxygen

(*vi*) 22.4 litre or 22.4 dm^3 of oxygen at N.T.P.,
(0°C and 760 mm of mercury pressure)

Example 53. *Fill in the blanks for the following reaction.*

$$MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$

(*i*) **Moles** $\frac{1}{2}$ mole + ... $\longrightarrow$ ...... + ...

(*ii*) **Molecules** 6.02×10^{23} + ... $\longrightarrow$ ...... + ...

(*iii*) **Grams** 4.0 g + ... $\longrightarrow$ ...... + ...

Solution. The reaction indicates that one mole of magnesium oxide reacts with two moles of hydrochloric acid to form one mole of magnesium chloride and one mole of water.

(*i*) $\frac{1}{2}$ mole of MgO will react with one mole of HCl to form $\frac{1}{2}$ mole of $MgCl_2$ and $\frac{1}{2}$ mole of water.

(*ii*) 6.02×10^{23} molecules of MgO will react with $2 \times 6.02 \times 10^{23}$ molecules of HCl to give 6.02×10^{23} molecules of $MgCl_2$ and 6.02×10^{23} molecules of water.

(*iii*) 4 g. of MgO will react with 7.3 g. of HCl to form 9.5 g. $MgCl_2$ and 1.8 g. of water.

$$[\because\ 4\text{ g MgO} = \frac{\text{g. mol. wt. of MgO}}{10}$$

$$= \frac{24+16=40}{10};\ \frac{\text{g. mol. wt. of HCl}}{10}$$

$$= \frac{73}{10};\ \frac{\text{g. mol. wt. of } MgCl_2}{10}$$

$$= \frac{95}{10};\ \frac{\text{g. mol. wt. of } H_2O\ (=18)}{10}$$

$$= 1.8]$$

9.5. MISCELLANEOUS APPLICATIONS

Example 54. *^{12}C is the standard for the atomic weights (mass) of atoms. What is the standard for the molecular weight (mass) of molecules and for formula weights?*

Solution. ^{12}**C**. The **same standard** is used for all atomic, molecular and formula weights of substances.

Example 55. *Is Avogadro's number a fundamental physical constant?*

Solution. Avogadro's number is not a fundamental physical constant. It depends on the basis of atomic weight scale. For example, when the basis of atomic weight scale was changed (in 1961) from the naturally occurring mixture of oxygen isotopes at 16.0000 U to ^{12}C, it changed very little, and put the oxygen at 15.9994 U.

Example 56. *One cylinder contains 1.0 g of O-atoms, the other one has 1.0 g of O_2 while the third one has 1.0 g of ozone, O_3. Which one of these contains the greatest number of oxygen atoms and which one has greatest number of molecules?*

Solution. Given

(*i*) 1.0 g. of O atoms (*ii*) 1.0 g. of O_2

(*iii*) 1.0 g. of O_3

We know that :

(*a*) g. at. wt. of O = 6.02×10^{23} atoms of O = 16 g

16 g. of O contain O-atoms = 6.02×10^{23}

$$\therefore\ 1.0\text{ g. of O contain O-atoms} = \frac{6.02\times10^{23}}{16}\text{ atoms of}$$

O = **3.762 × $\mathbf{10^{22}}$ atoms of O**

(*b*) g. mol. wt. of

$$O_2 = \text{Atomicity of O in } O_2 \times 6.02 \times 10^{23}\text{ atoms of O}$$

$$32\text{ g of } O_2 = 2 \times 6.02 \times 10^{23}\text{ atoms of O}$$

$$1.0\text{ g of } O_2 = \frac{2\times6.02\times10^{23}}{32}$$

$$= \mathbf{3.762 \times 10^{22}\ atoms\ of\ O}$$

(*c*) g. mol. wt. of

$$O_3 = \text{Atomicity of O in } O_3 \times 6.02 \times 10^{23}\text{ atoms}$$

$$48.0\text{ g of } O_3 = 3 \times 6.02 \times 10^{23}\text{ atoms}$$

$$1.0\text{ g of } O_3 = \frac{3\times6.02\times10^{23}}{48}\text{ atoms}$$

$$= \mathbf{3.762 \times 10^{22} atoms\ of\ O}$$

From (*a*), (*b*) and (*c*) above, we see that all have same number of atoms of O

(*d*) 1.0 g. sample of O has the largest number of molecules (albeit monoatomic)

Example 57. *How many moles of atoms of each element are present in 1.0 mol of each of the following compounds.*

(*a*) $Ca(C_2H_3O_2)_2$ (*b*) $FeSO_4.7H_2O$

Solution. (*a*) $Ca(C_2H_3O_2)_2 = CaC_4H_6O_4$. 1.0 mol of it contains 1 mol Ca, 4 mol C, 6 mol H and 4 mol O (*b*) $FeSO_4.7H_2O = FeSO_{11}H_{14}$. 1.0 mol of it contains 1 mol Fe, 1 mol S, 11 mol O and 14 mol H.

Type.

$$\text{No. of atoms of the element} = \text{Wt. of compound (g)} \left(\frac{\text{1 mol compound}}{\text{g. mol. wt. of compound}}\right) \left(\frac{\text{no. of moles of element}}{\text{1 mol. compound}}\right) \left(\frac{6.02\times10^{23}\text{ atoms of element}}{\text{mol. element}}\right)$$

Example 58. *How many atoms of oxygen are present in 25.0 g. of $CaCO_3$? (At. wt. Ca = 40, C = 12, O = 16).*

Solution.

no. of atoms of oxygen =

$$\text{wt. of } CaCO_3 \left(\frac{1\text{ mol } CaCO_3}{\text{g. mol. wt. of } CaCO_3}\right) \left(\frac{\text{no. of moles of O}}{\text{1 mol. compound}}\right)$$

$$\left(\frac{6.02\times10^{23}\text{ O-atoms}}{\text{mol of O}}\right)$$

$$= 25.0\text{g}\left(\frac{1\text{ mol CaCO}_3}{100.0\text{ g}}\right)\left(\frac{3\text{ mol}}{1\text{mol CaCO}_3}\right)$$

$$\left(\frac{6.02\times10^{23}\text{ O-atoms}}{\text{mol O}}\right)$$

= **4.52 × 10^{23} O-atoms** **Ans.**

Type.

$$\begin{matrix}\text{No. of molecules}\\ \text{of a substance}\end{matrix} = \begin{matrix}\text{wt. of substance}\\ \text{(g)}\end{matrix}\left(\frac{\text{1 mol substance}}{\begin{matrix}\text{g. mol. wt. of}\\ \text{substance}\end{matrix}}\right)$$

$$\left(\frac{\begin{matrix}6.02\times10^{23}\text{ molecules}\\ \text{of substance}\end{matrix}}{\text{mol. substance}}\right)$$

Example 59. *How many molecules of H_2 are present in 8.5 g. of H_2? (at. wt. H = 1 a.m.u. Or 1U)*

Solution. wt. of

H_2 = 8.5 g ; molecules of H_2 = ?

g. mol. wt. of H_2 = 1 × 2 = 2.0 g. We know that :

$$\begin{matrix}\text{No. of H}_2\\ \text{Molecules}\end{matrix} = \text{wt. of H}_2\left(\frac{1\text{mol H}_2}{\text{g.mol.wt.of H}_2}\right)$$

$$\left(\frac{6.02\times10^{23}\text{ molecules of H}_2}{\text{mol H}_2}\right)$$

$$= 8.5\text{ g}\left(\frac{1\text{mol H}_2}{2.0\text{g}}\right)$$

$$\left(\frac{6.02\times10^{23}\text{ molecules of H}_2}{\text{mol H}_2}\right)$$

= **2.56 × 10^{24} molecules of H_2**

Ans.

Type. To find the number of moles of a substance from the number of atoms of one of the elements present in it. For this, use the following formula.

No. of moles of substances

$$= \left(\frac{\text{Given atoms mol}}{6.02\times10^{23}\text{ atoms}}\right)\left(\frac{\text{1 mol substance}}{\text{no. of moles of element}}\right)$$

Example 60. *How many moles of CH_3COOH contain 6.02 × 10^{23} atoms of hydrogen?*

Solution. CH_3COOH is $C_2H_4O_2$;

Atoms of hydrogen

= 6.02 × 10^{23} Thus : no. of moles of $C_2H_4O_2$

$$= \frac{\text{H atoms mol}}{6.02\times10^{23}\text{ atoms}}\left(\frac{\text{1 mol substance}}{\text{no. of moles of element}}\right)$$

$$= \frac{6.02\times10^{23}\text{ atoms mol}}{6.02\times10^{23}\text{ atoms}}\left(\frac{1\text{mol C}_2\text{H}_4\text{O}_2}{4\text{ mole H}}\right)$$

= **0.25 mol $C_2H_4O_2$** **Ans.**

Example 61. Calculate the number of oxygen atoms that are present in 1.0 mol of Ce_2O_3.

Solution. *Mol of O in Ce_2O_3 = 3; Ce_2O_3 = 1.0 mol. We know.*

$$\begin{matrix}\text{no. of atoms of}\\ \text{required element}\end{matrix} = \begin{pmatrix}\text{no. of mol of}\\ \text{substance}\end{pmatrix}$$

$$\left(\frac{\begin{matrix}\text{no. of mol of}\\ \text{required atom}\end{matrix}}{\text{mol substance}}\right)\left(\frac{6.02\times10^{23}\text{ atoms of element}}{\text{mol element}}\right)$$

no. of O atoms = (1.0 mol Ce_2O_3)

$$\left(\frac{3\text{ mol O}}{\text{mol Ce}_2\text{O}_3}\right)\left(\frac{6.02\times10^{23}\text{ O-atoms}}{\text{mol O}}\right)$$

= **1.81 × 10^{24} O-atoms.** **Ans.**

Example 62. *Calculate the weight of water that is present in 1.50 mol of H_2O. (At. wt. H = 1, O = 16).*

Solution. mol of H_2O = 1.5 ; wt. of H_2O = ? Gram molecular weight of H_2O = (2 × 1) + 16 = 18 g. We know that:

wt. of H_2O = no. of mol of H_2O

$$\left(\frac{\text{g.mol.wt.of H}_2\text{O}}{\text{mol}}\right)$$

$$= (1.50\text{ mol H}_2\text{O})\left(\frac{18\text{g}}{\text{mol}}\right)$$

= **27.0 g** **Ans.**

Type. *To find average weight in kg of atoms of elements. For this purpose, use the following relation.*

Average weight of atom in kg/atom

$$= \frac{\text{At.wt.of element}\times10^{-3}\text{ kg(mol}^-)}{6.02\times10^{23}\text{ atoms(mol}^-)}$$

Example 63. *Calculate the average weight in kg of (a) a nitrogen atom (b) a calcium atom.*

(At. wt. N = 14 u, Ca = 40 u)

Solution. (*a*) At. wt. of nitrogen

= 14 *u*. We know that :

Average weight of N-atom in kg (atom$^-$)

$$= \frac{\text{At.wt.of N}\times10^{-3}\text{ kg(mol}^-)}{6.02\times10^{23}\text{ atoms(mol}^-)}$$

$$= \frac{14\times10^{-3}\text{ kg(mol}^-)}{6.02\times10^{23}\text{ atoms(mol}^-)}$$

= **2.32 × 10^{-26} kg (atom$^-$)** **Ans.**

Example 64. *Calculate the number of m mol of magnesium in 400 mg of magnesium (At. wt. Mg = 24).*

Solution. wt. of

Mg = 400 mg. ;

mg. at. wt. of

Mg = 24 mg. We know that :

Number of m mol of

$$\text{Mg} = \frac{\text{wt. of Mg in mg}}{\text{mg. at. wt. of Mg/m mol of Mg}}$$

∴ Number of m mol of

$$\text{Mg} = \frac{400 \text{ mg Mg}}{24 \text{ mg Mg/m mol Mg}}$$

= 16.67 m mol Mg.

EXAMPLE 65. *Calculate the number of moles of N_2 gas present in 42.5 g of nitrogen.*

(At. wt. N = 14)

SOLUTION. wt. of

N_2 = 42.5 g ; g. mol. wt. of

$N_2 = 2 \times 14 = 28$ g.

We know that :

Number of moles of

$$N_2 = \frac{\text{wt. of } N_2 \text{ (g.)}}{\text{g. mol. wt. of } N_2 \text{ (mol}^{-}\text{)}}$$

$$= \frac{42.5 \text{ g.}}{28 \text{ g. mol}^{-}} = \mathbf{1.52\ mol} \qquad \textbf{Ans.}$$

EXAMPLE 66. *A sample of zirconium bromide, $ZrBr_4$ weighing 10.07 g. was dissolved and the whole combined bromine was precipitated as AgBr. The amount of Ag in AgBr was found to be 10.6 g. Calculate the atomic weight of Zr from the given data. (At. wt. Ag = 108 ; Br = 80)*

SOLUTION. wt. of Ag = 10.6 g. ; At. wt. of Ag = 108 ; at. wt. of Br = 80 ; no. of mol of Br in $ZrBr_4$ = 4 ; wt. of sample = 10.07 g.

(*a*) Mol of $ZrBr_4$

$$= (\text{wt. of Ag}) \left(\frac{1 \text{ mol Ag}}{\text{g. at. wt. of Ag}}\right) \left(\frac{1 \text{ mol Br}}{\text{mol Ag}}\right) \left(\frac{1 \text{ mol } ZrBr_4}{\text{no. of mol Br}}\right)$$

$$= (10.6 \text{ Ag}) \left(\frac{1 \text{ mol Ag}}{108 \text{ g of Ag}}\right) \left(\frac{1 \text{ mol Br}}{\text{mol Ag}}\right) \left(\frac{1 \text{ mol } ZrBr_4}{4 \text{ mol Br}}\right)$$

= 0.0245 mol $ZrBr_4$

(*b*)
$$\frac{\text{wt. of sample (g)}}{\text{no. of mol of } ZrBr_4} = \frac{10.07 \text{ g.}}{0.0245 \text{ mol } ZrBr_4}$$

$= 411.02$ g./mol $ZrBr_4$

∴ At. wt. of Zr = mol. wt. of $ZrBr_4 - 4$ (at. wt. of Br)

$= 411.02 - 4(80) = 411.02 - 320$

$= \mathbf{91.02\ mol^{-}}$ **Ans.**

EXAMPLE 67. *How many mol of atoms are contained in 1.2 g Mg (At. wt. of Mg = 24).*

SOLUTION. wt. of Mg = 1.2 g. ;

g. at. wt. of Mg = 24 g. We know that :

$$\text{Mol of atoms of Mg} = \text{wt. of Mg (g.)} \left[\frac{1 \text{ mol Mg}}{\text{g. at. wt. of Mg}}\right]$$

$$= 1.2 \text{ g Mg} \left(\frac{1 \text{ mol Mg}}{24 \text{ g Mg}}\right)$$

= **0.05 mol Mg.** **Ans.**

EXAMPLE 68. *How many years it would take to spend Avogadro's number of rupees at the rate of 10 lac rupees per second?* **(UP SEAT, 1990, MLNR 1990, ISM Dhanbad 1992)**

SOLUTION. 1 year = 365 days ×

$$\frac{24 \text{ hours}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ hr.}} \times \frac{60 \text{ s}}{1 \text{ min}}$$

Avogadro no. = 6.023×10^{23}

Rupees spent in one second = 10 lac = 10^6

∴ Rupees spent in one year *i.e.,* 365 × 24 × 60 × 60 seconds = $10^6 \times 365 \times 24 \times 60 \times 60$

Thus : $10^6 \times 365 \times 24 \times 60 \times 60$ rupees are spent in years = 1

6.023×10^{23} rupees are spent in years

$$= \frac{1}{10^6 \times 365 \times 24 \times 60 \times 60} \times 6.023 \times 10^{23}$$

= **1. 9099 × 10^{10} Years** **Ans.**

EXAMPLE 69. *The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the mole of NO_2 in 100 g. mixture.* **(MLNR, 1993)**

SOLUTION. (*i*) Mol. wt. of

$NO_2 = 14 + (2 \times 16) = 46$g mol^{-} ;

Mol. wt. of $N_2O_4 = (2 \times 14) + (4 \times 16) = 92$g mol^{-} ;

Mol. wt. of NO_2 = 92 g mol^{-},:

mol. wt. of mixture of NO_2 and

$N_2O_4 = 2 \times$ V.D $= 2 \times 38.3 = 76.6$ g mol^{-}

(*ii*) Let wt. of $NO_2 = x$ g ; wt. of $N_2O_4 = (100 - x)$ g ;

$$\text{no. of mole} = \frac{\text{wt.}}{\text{Mol. wt.}}$$

But no. of mole of NO_2 + no. of mole of N_2O_4 = no. of mole of mixture

$$\frac{x}{46} + \frac{100 - x}{92} = \frac{100}{76.6}$$

$$92x + 4600 - 46x = \frac{100 \times 46 \times 92}{76.6} = 5524.8$$

$46x = 924.8$; $x = 20.1$ g = wt. of NO_2

∴ no. of mole of NO_2 in the mixture

$$= \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{20.1}{46} = \mathbf{0.437} \qquad \textbf{Ans.}$$

EXAMPLE 70. *Calculate molecules of methane, C and H atoms in 25 g methane.* **(MLNR, 1990)**

SOLUTION. (*i*) 1 Mole of methane,

$$CH_4 = \text{g. mol. wt. of } CH_4 = 12 + (4 \times 1)$$
$$= 16 \text{ g}$$

1 mole of CH_4 = 6.023×10^{23} molecules of CH_4.

∴ 16 g CH_4 contain CH_4 molecules

$$= 6.023 \times 10^{23}$$

25 g CH_4 contain CH_4 molecules

$$= \frac{6.023 \times 10^{23} \times 25}{16}$$

$$= \mathbf{9.41 \times 10^{23}} \qquad \textbf{Ans.}$$

(*ii*) 16 g CH_4 contain C-atoms

$$= 6.023 \times 10^{23}$$

25 g CH_4 contain C-atoms

$$= \frac{6.023 \times 10^{23} \times 25}{16}$$

$$= \mathbf{9.41 \times 10^{23}} \qquad \textbf{Ans.}$$

(*iii*) 16 g CH_4 contain H–atoms

$$= 4 \times 6.023 \times 10^{23}$$

25 g CH_4 contain H-atoms

$$= \frac{4 \times 6.023 \times 10^{23}}{16} \times 25$$

$$= \mathbf{3.764 \times 10^{24}} \qquad \textbf{Ans.}$$

EXAMPLE 71. *How many kilogram of S are contained in 1 kg of iron pyrites,* FeS_2*? (at. wt. Fe = 56, S = 32)*

SOLUTION. wt. of FeS_2 = 1 kg = 1000 g; at. wt. of S = 32 g

$$\text{g. mol. wt. of } FeS_2 = 56 + (2 \times 32) = 120 \text{ g}$$

$$120 \text{ g } FeS_2 \equiv 2 \text{ mol S}$$

$$1000 \text{ g } FeS_2 \equiv \frac{2 \text{ mol S}}{120 \text{ g}} \times 1000 \text{ g} = 16.7 \text{ mol}$$

(*a*) no. of mol of S in FeS_2 = 16.7

(*b*) wt. in kg of S = no. of mol of

$$S \left(\frac{\text{g.at.wt.of S}}{\text{mol S}}\right)\left(\frac{1 \text{kg}}{10^3 \text{ g}}\right)$$

$$= 16.7 \text{ mol S} \left(\frac{32 \text{g}}{\text{mol S}}\right)\left(\frac{1 \text{kg}}{10^3 \text{ g}}\right)$$

$$= \mathbf{0.534 \text{ kg S}} \qquad \textbf{Ans.}$$

EXAMPLE 72. *How many atoms of carbon has a young man given to his bride to be, if the engagement ring contains 0.50 carat diamond ? There are 200 mg in a carat.* **(WB JEE 1993)**

SOLUTION. 1 carat of diamond

= 200 mg diamond.

0.5 carat diamond = 0.5 × 200

= 100 mg diamond = 0.1 g

Gram atomic mass of carbon (diamond)

= 12 g = **1 mole**

∴ 12 g diamond contains carbon atoms

$$= 6.023 \times 10^{23}$$

0.1 g diamond contains carbon atoms

$$= \frac{6.023 \times 10^{23}}{12} \times 0.1$$

$$= 5.02 \times 10^{21} \text{ atoms of } ^{12}C$$

∴ **The young man has given 5.02×10^{21} atoms of carbon to his bride to be.**

Type. Finding number of molecules of a substance from a given volume of solution having normality or molarity.

(*a*) 1000 mL of 1 N substance = g. eq. wt. of substance.

(*b*) g. mol. wt. of a substance contain molecules = Avogadro's no. (= 6.023×10^{23})

(*c*) no. of mol of a solute in solution = Molarity × volume in litre.

EXAMPLE 73. *Calculate the number of oxalic acid molecules in 100 mL of 0.02 N oxalic acid solution.* **(Roorkee, 1991)**

SOLUTION. (*i*) Mol. wt. of oxalic acid,

$$H_2C_2O_4 = (2 \times 1) + (2 \times 12) + (4 \times 16)$$
$$= 90 \text{ g mol}^{-}$$

g. mol. wt. of oxalic acid contain molecules

$$= 6.023 \times 10^{23}$$

(*ii*) 1000 mL of 1 N oxalic acid contain oxalic acied

$$= \text{g. eq. wt. of } H_2C_2O_4$$

$$= \frac{\text{Mol.wt.of } H_2C_2O_4}{\text{Basicity of } H_2C_2O_4} = \frac{90}{2} = 45 \text{ g.}$$

∴ 100 mL of 0.02 N oxalic acid contain oxalic acid

$$= \frac{45 \text{ g.}}{1000} \times 100 \times 0.02 = 0.09 \text{ g.}$$

(*iii*) 90 g. $H_2C_2O_4$ contain molecules = 6.023×10^{23}

$$0.09 \text{ g. } H_2C_2O_4 \text{ contain molecules} = \frac{6.023 \times 10^{23}}{90} \times 0.09$$

$$= \mathbf{6.023 \times 10^{20}} \textbf{ Ans.}$$

EXAMPLE 74. *Oxygen and nitrogen are present in a mixture in the ratio 1 : 4 by weight. Calculate the ratio between their molecules.*

SOLUTION. We know that g. mol. wt. of all gases contain 6.023×10^{23} molecules at N.T.P.

Mol. wt. of O_2 = 2 × 16 = 32 g. mol^{-};

mol. wt. of N_2 = 2 × 14 = 28 g. mol^{-}.

Ratio by wt. of

$$O_2 : N_2 = 1 : 4$$

(*i*) 32 g. O_2 contain O_2 molecules

$$= 6.023 \times 10^{23}$$

1 g. O_2 contain O_2 molecules

$$= \frac{6.023 \times 10^{23}}{32} \times 1 = \frac{6.023 \times 10^{23}}{32}$$

(*ii*) 28 g. N_2 contain N_2 molecules

$$= 6.023 \times 10^{23}$$

4 g. N_2 contain N_2 molecules

$$= \frac{6.023 \times 10^{23}}{28} \times 4 = \frac{6.023 \times 10^{23}}{7}$$

From (*i*) and (*ii*), the ratio of molecules of O_2 and N_2 is :

$$\frac{6.023\times10^{23}}{32}:\frac{6.023\times10^{23}}{7}$$

$$= \frac{1}{32}:\frac{1}{7} \text{ or } \mathbf{7:32}$$ **Ans.**

Example 75. *What is the number of atoms in a piece of copper weighing 0.635 g. (at. wt. of Cu = 63.5)*

(CEE (Bihar), 1992)

Solution. g. at. wt. of an element contains atoms

$= 6.023 \times 10^{23}$

g. at. wt. of Cu = 63.5 g. (given)

∴ 63.5 g of Cu contains Cu-atoms

$= 6.023 \times 10^{23}$

0.635 g of Cu contains Cu-atoms

$$= \frac{6.023\times10^{23}}{63.5}\times 0.635$$

$= \mathbf{6.023 \times 10^{21}}$ **Ans.**

Example 76. *Calculate the number of sodium carbonate molecules present is 100 mL of 0.02 M sodium carbonate solution.*

Solution.

No. of mol of Na_2CO_3

= Molarity × Volume in L

$$= 0.02\times\frac{100}{1000} = 2\times10^{-3}$$

1 mol Na_2CO_3 contain Na_2CO_3 molecules $= 6.023 \times 10^{23}$ molecules

2×10^{-3} mol Na_2CO_3 contain Na_2CO_3 molecules

$= 6.023 \times 10^{23} \times 2 \times 10^{-3}$

$= \mathbf{1.205 \times 10^{21}}$ **Ans.**

Example 77. *How many molecules of benzene are there in one litre of benzene? Specific gravity of benzene is 0.88.*

Solution. $$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

∴ Mass of benzene,

C_6H_6 = volume × density

= 1000 mL × 0.88 g (mL)

= 880 g. (∵ 1 L = 1000 mL)

Mol. wt. of $C_6H_6 = (6 \times 12) + (6 \times 1) = 78$ g. mol^-

78 g. of C_6H_6 contain molecules

$= 6.023 \times 10^{23}$

880 g. of C_6H_6 contain molecules

$$= \frac{6.023\times10^{23}}{78\text{g}}\times 880\text{g}$$

$= \mathbf{6.79 \times 10^{24}}$ **Ans.**

Type. *Wt. of an alloy cylinder*

= Volume × denisty = $\pi r^2 h \times d$

Example 78. *Calculate the number of iron atoms in a cylinder of radius 2.1 cm and a length of 8.0 cm. The density of alloy (17% Mo, 71% Fe and 12% Co) is 8.2 g. cm^{-3} (at. wt. of Fe = 56).*

Solution. Wt. of alloy cylinder

= volume × density = $\pi r^2 h \times d$

$$= \frac{22}{7}\ (2.1\text{ cm})^2 \times 8\text{ cm} \times 8.2\text{ g. cm}^{-3}$$

= 909.22 g.

$$\text{wt. of Fe} = \frac{909.22\times71}{100}$$

(∵ alloy contains 71% Fe)

= 645.55 g.

g. at. wt. of Fe (= 56 g) contain Fe atoms

$= 6.023 \times 10^{23}$

∴ 645.55 g. of Fe contain

$$\text{Fe atoms} = \frac{6.023\times10^{23}}{56}\times645.55$$

$= \mathbf{6.943 \times 10^{24}}$ **Ans.**

Example 79. *Calculate the molar volume of oxygen gas having density 1.429 g. L^- at N.T.P.*

Solution. Molar valume of O_2 means volume occupied by 1 mol of a gas, O_2

Mol. wt. of $O_2 = 2 \times 16 = 32$ g. mol^- = 1 mol of O_2

Given 1.429 g of O_2 gas ≡ 1 L at NTP

∴ 32 g. (=1 mol) of

$$O_2 \text{ gas} \equiv \frac{1}{1.429}\times 32\ \text{ L at NTP}$$

$= \mathbf{22.39\ L\ mol^-}$ **Ans.**

Type.

(*a*) $$\textit{Number of mol of compound, } A_xB_y = \left(\begin{matrix}\textit{wt. (in kg) of}\\ \textit{Compound, } A_xB_y\end{matrix}\right)\left(\frac{10^3\text{ g.}}{\text{kg}}\right)\left(\frac{\textit{1 mol compound, } A_xB_y}{\textit{g. mol. wt. of compound, } A_xB_y}\right) = z\ (say)$$

(*b*) *Mol of A = xz ; mol of B = yz.*

Example 80. *How many mol of FeS_2, S and Fe are contained in 1.00 kg iron pyrites, FeS_2 (at. wt. Fe = 56, S = 32).*

Solution. Wt. of FeS_2 = 1.00 kg ;

at. wt. of Fe = 56, S = 32. g. mol^-.

wt. of FeS_2 = 56 + 2 (32) = 56 + 64 = 120 g.

Thus :

(*a*) no. of mol of FeS_2 = wt. in kg of FeS_2

$$\left(\frac{10^3\text{ g.}}{\text{kg}}\right)\left(\frac{1\text{ mol FeS}_2}{\text{g. mol. wt. of FeS}_2}\right)$$

$$= (1.00\text{ kg FeS}_2)\left(\frac{10^3\text{ g.}}{\text{kg}}\right)$$

$$\left(\frac{1\,\text{mol FeS}_2}{120\,\text{g}}\right)$$

$$= 8.33 \text{ mol FeS}_2$$

(*b*) Mol of Fe = 1 × 8.33 = **8.33 mol** **Ans.**

Mol of S = 2 × 8.33 = 16.67 = **16.7 mol.** **Ans.**

The answer is 16.7 and not 16.67 because, the calculations involve multiplication and division. The minimum number of significant figure is 1.00 kg is three. So, answer will also have three significant figures.

Type. *To find weight (in kg) of an element present in a compound when the no. of mol of the compound is given. For this purpose, use the following relation.*

$$\begin{bmatrix}\text{wt. (in kg) of}\\ \text{element}\end{bmatrix} = \begin{bmatrix}\text{no. of mol}\\ \text{of element}\end{bmatrix}$$

$$\left[\frac{\text{g. at. wt. of element}}{\text{mol of element}}\right]\left[\frac{1\text{kg}}{10^3\text{ g.}}\right]$$

Example 81. *Calculate the weight in kg of N that are present in 10 mol of* Ca_3N_2.

Solution. wt. in kg of

$$\text{N} = 2\times 10\text{mol}\times\frac{\text{g. at. wt. of N (= 14 g)}}{\text{mol N}}$$

$$\times\frac{1\text{ kg}}{10^3\text{ g}} = \mathbf{0.28\ kg} \qquad \textbf{Ans.}$$

[∵ 1 mol of Ca_3N_2 contain 2 mol atoms of N].

9.6 AIEEE PATTERN EXAMPLES

EXAMPLES 82. *Number of atoms in 558.5 gram Fe (at. wt. of Fe = 55.85 g* mol^-*) is :*

(*a*) *Half that in 8 g He* (*b*) *Twice that in 60 g carbon*

(*c*) *558.5 ×* 6.023×10^{23} (*d*) 6.023×10^{22}

(AIEEE, 2003)

Solution. At. wt. of

Fe = 55.85 g. mol^- ; wt. of Fe = 558.5 g.

∴ Number of moles of

$$\text{Fe} = \frac{\text{wt. of Fe}}{\text{g. at. wt. of Fe}} = \frac{558.5}{55.85} = 10 \text{ mol.}$$

(*i*) At. wt. of He = 4 g mol^- ; wt. of He = 8g

∴ no. of moles of

$$\text{He} = \frac{8}{4} = 2 \text{ mol; } \frac{1}{2} \text{ of } 2 = 1 \text{ mol}$$

(*ii*) At. wt. of carbon

= 12 g. mol^- ; wt. of carbon = 60 g

∴ no. of moles of carbon

$$= \frac{60\text{ g.}}{12\text{ g. mol}^-} = 5 \text{ mol.}$$

Since twice of no. of moles of carbon (= 5) is 10 which is equal to no. of moles of Fe, the correct answer is (*b*).

Example 83. *The number of potassium atoms required for the preparation of 0.2 M* $KMnO_4$ *are:*

(*a*) 2.408×10^{23} (*b*) 1.408×10^{23}

(*c*) 2.4×10^{22} (*d*) 1.204×10^{23}

Solution. 1 M $KMnO_4$ solution contains K-atoms = 6.02×10^{23}

0.2 M $KMnO_4$ solution contains K-atoms = $0.2\times 6.02\times 10^{23} = 1.204\times 10^{23}$

So, the correct answer is, (*d*).

Example 84. *The number of molecules in 4.49 L of a gas at 0°C and 1 atomspheric pressure is approximately :*

(*a*) 12.06×10^{23} (*b*) 12.06×10^{22}

(*c*) 24.12×10^{22} (*d*) 24.12×10^{23}

Solution. Volume = 4.49 L

22.4 L of a gas at 0°C and 1 atm. pressure contain molecules = 6.02×10^{23}

4.49 L of a gas at 0°C and 1 atm. pressure contain molecules

$$= \frac{6.02\times 10^{23}\times 4.49}{22.4} = 1.206\times 10^{23}$$

$$= \mathbf{12.06\times 10^{22}}$$

So, the correct answer is, (*b*).

Example 85. *The percentage of sodium present is the cereal served in breakfast which is labelled to contain 110 mg of sodium per 100 g of cereal, is :*

(*a*) 2% (*b*) 3%

(*c*) 1% (*d*) 0.11%

Solution. Mass of Na = 110 mg = $\frac{110}{1000}$ g. = 0.11 g.

Total wt. of cereal = 100 g.

$$\therefore \quad \%\text{ age of Na} = \frac{\text{wt. of Na}}{\text{Total wt.}}\times 100 = \frac{0.11\times 100}{100}$$

= 0.11%

So, the correct answer is, (*d*).

Example 86. *The formation of polyethylene from calcium carbide takes place as follows :*

(*i*) $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

(*ii*) $C_2H_2 + H_2 \longrightarrow C_2H_4$

(*iii*) $nC_2H_4 \longrightarrow (-CH_2-CH_2-)_n$.

The amount of polyethylene from 64 kg of CaC_2 *is :*

(*a*) *7 kg* (*b*) *14 kg*

(*c*) *20 kg* (*d*) *28 kg*

Solution. Given reactions are :

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$C_2H_2 + H_2 \longrightarrow C_2H_4$

Add $CaC_2 + 2H_2O + H_2 \longrightarrow Ca(OH)_2 + C_2H_4$

40 + (2 × 12) = 64 kg (2 × 12) + (4 × 1)

= 28 kg

[∵ At. wt. of Ca = 40, C = 12, H = 1]

∴ 64 kg of CaC_2 form C_2H_4 (ethylene) or polyethylene = 28 kg.

So, the correct answer is, (*d*).

EXAMPLE 87. *What amount of isobutylene can be prepared from 37 g of tertiary butyl alcohol by heating with 20%* H_2SO_4 *at 363 K if the yield is 64%?*

(*a*) *1.82 g* (*b*) *18.2 g*
(*c*) *0.182 g* (*d*) *17.92 g*

SOLUTION. The required conversion is :

$$(CH_3)_3COH \longrightarrow (CH_3)_2C = CH_2$$

t. Butyl alcohol — Isobutylene.

$3[12 + (3 \times 1)] + 12 + 16 + 1 = 45 + 12 + 16 + 1 = 74$ g

$2\,[12 + (3 \times 1)] + 12 + 12 + (2 \times 1)) = 30 + 12 + 12 + 2 = 56$ g.

[∵ At. wt. of C = 12, O = 16, H = 1]

Mass of t. butyl alcohol = 37 g.

74 g t. butyl alcohol form isobutylene = 56 g

$$\therefore \text{ 37 g t. butyl alcohol form isobutylene} = \frac{56}{74} \times 37 = 28 \text{ g}$$

$$\therefore \quad \text{Total yield} = \frac{28 \times 64}{100} = \mathbf{17.92\ g} \qquad \textbf{Ans.}$$

So, the correct answer is (*d*).

EXAMPLE 88. *The number of gram atoms of oxygen (atomic mass, 16 a.m.u.) in 8 g of oxygen, is*

(*a*) *0.1* (*b*) *0.3*
(*c*) *0.5* (*d*) *5.0*

SOLUTION. Number of g. atoms of oxygen

$$= \frac{\text{Mass of oxygen in g.}}{\text{g. atomic mass of oxygen}}$$

$$= \frac{8}{16} = \mathbf{0.5} \qquad \textbf{Ans.}$$

So, the correct answer is, (*c*).

EXAMPLE 89. *The number of gram molecules of sulphur dioxide in 16 g of it (S = 32 a.m.u., O = 16 a.m.u.) are :*

(*a*) *0.1* (*b*) *0.13*
(*c*) *5.1* (*d*) *0.25*

SOLUTION. g. molecular mass of SO_2 = Atomic mass of S in g. + 2 × atomic mass of of O in g = 32 + 2 × 16 = 64 g.

∴ Number of g. molecules of

$$SO_2 = \frac{\text{Mass of } SO_2 \text{ in g.}}{\text{Gram molecular mass of } SO_2}$$

$$= \frac{16}{64} = \mathbf{0.25}$$

So, the correct answer is, (*d*).

EXAMPLE 90. *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}

(*CBSE–PMT, 2008 Prelims*)

SOLUTION. The wt. of 6.023×10^{23} molecules of water is equal to g.mol. wt. of H_2O *i.e.,* 18 g

∴ Volume occupied by 6.023×10^{23} molecules of

$$H_2O\ (d = 1 \text{ g cm}^{-3}) = \frac{18\text{ g}}{1\text{ g cm}^{-3}} = 18 \text{ cm}^3$$

Hence volume occupied by 1 molecule of H_2O

$$= \frac{18}{6.023 \times 10^{23}} \simeq 3.0 \times 10^{-23} \text{ cm}^3.$$

So, the correct answer is (*a*).

EXAMPLE 91. *The number of atoms (x) of oxygen present in 88 g of* CO_2 *and (y) the mass of* CO *having same no. of oxygen atoms are :*

(*a*) (*x*) 10^{24} (*y*) *100 g*
(*b*) (*x*) 2.408×10^{24} (*y*) *105 g.*
(*c*) (*x*) 2.408×10^{24} (*y*) *112 g*
(*d*) *None of these.*

SOLUTION. (*a*) O-atoms = ? ; wt. of

CO_2 = 88 g ;

g. mol. wt. of CO_2 = 12 + (2 × 16)

= 44 g. mol$^-$; Mass of CO = ?

No. of oxygen atoms in

$$CO_2 = \begin{bmatrix}\text{Atomicity of}\\ \text{oxygen in } CO_2\end{bmatrix} \times 6.02 \times 10^{23} \text{ atoms}$$

44 g. CO_2 contain oxygen atoms

$= 2 \times 6.02 \times 10^{23}$ atoms

88 g. CO_2 contain oxygen atoms

$$= \frac{2 \times 6.02 \times 10^{23}}{44} \times 88 = 2.408 \times 10^{24}$$

(*b*) [Atomicity of O in CO × 6.02×10^{23} atoms of O = g. mol. wt. of CO

$1 \times 6.02 \times 10^{23}$ atoms of oxygen are present in

CO = 12 + 16 = 28 g mol$^-$

2.408×10^{24} atoms of oxygen are present in

$$CO = \frac{28}{6.02 \times 10^{23}} \times 2.408 \times 10^{24}$$

$$= \mathbf{112\ g.} \qquad \textbf{Ans.}$$

So, the correct answer is (*c*).

EXAMPLE 92. *If we consider that 1/6, in place of 1/12, mass of carbon atom is taken to be the relative atomic mass unit, the mass of one mole of a substance will*

(*a*) *decrease twice*
(*b*) *increase two fold*
(*c*) *remain unchanged*
(*d*) *be a function of the molecular mass of the substance.*

(AIEEE, 2005)

SOLUTION. 1 atomic mass unit (amu) on the scale of 1/6 of C-12 = 2 amu of the scale of 1/12 of C-12. So, numerically, the mass of a substance will become half of the normal scale. So, the correct answer is (*a*).

EXAMPLE 93. *The number of molecules of* CO_2 *present in 44 g of* CO_2 *are :*

(*a*) 6.02×10^{23} (*b*) 3×10^{23}
(*c*) 12×10^{23} (*d*) 3×10^{10}

(BCECE (Bihar), 2005)

Solution. We know g. mol. wt. of any substance contain Avogadro's number of molecules (= 6.02×10^{23}).

g. mol. wt. of CO_2 = 12 + (2 × 16) = 44 g.

∴ 44 g. CO_2 would contain CO_2 molecules
= 6.02×10^{23}.

So, the correct answer is (*a*).

Example 94. *Total number of atoms represented by the compound* $CuSO_4.5H_2O$ *is :*

(*a*) 27 (*b*) 21
(*c*) 5 (*d*) 8

(IMS-BHU, 2005)

Solution. In $CuSO_4$. $5H_2O$: no. of atoms of Cu (= 1) + S (= 1) + O (4 + 5) + H (5 × 2) = 21. So, the correct answer is (*b*).

Example 95. *Number of molecules in one litre of water is close to :*

(*a*) $55.5 \times 6.023 \times 10^{23}$ (*b*) $\frac{18}{23.4} \times 10^{23}$
(*c*) $18 \times 6.023 \times 10^{23}$ (*d*) $\frac{6.023}{23.4} \times 10^{23}$

(Karnataka CET, 2000)

Solution. g. mol. wt. H_2O = (2 × 1) + 16 = 18 g. ;
wt. of 1 L
(= 1000 mL) water = Volume × density
= 1000 mL × 1 g. $(mL)^{-}$ = 1000g.

∴ Molarity of water

$$= \frac{1000\,g.}{18\,g.} = 55.5 \text{ M. But :}$$

1 mol of H_2O contains molecules
= 6.023×10^{23}

∴ 55.5 mol H_2O contain molecules
= $6.023 \times 10^{23} \times 55.5$. So, the correct answer is (*a*).

Example 96. *The molecular mass of hydrogen chloride* (HCl) *having absolute density 1.63 g* L^{-}*, is :*

(*a*) 3.651 g. (*b*) 36.51 g.
(*c*) 18 g. (*d*) 9 g.

Solution. Density in g L^{-} = Mass/vol. in L

∴ Mass = Density is g L^{-} × Vol in L
= 1.63 g L^{-} × 1 L = 1.63 g.

1 L of hydrogen chloride gas weighs
= 1.63 g.

22.4 L of hydrogen chloride gas weighs

$$= \frac{1.63\,g. \times 22.4\,L}{1\,L} = 36.51 \text{ g.}$$

So, the correct answer is, (*b*).

Example 97. *Which has the maximum number of molecules among the molecules?*

(*a*) 44 g CO_2 (*b*) 48 g O_3
(*c*) 8 g H_2 (*d*) 64 g SO_2

[(AIPMT (mains), 2011)]

Solution. 1 mol CO_2 = 12 + (2 × 16) = 44 g; 1 mol O_3 = 3 × 16 = 48 g; 1 mol H_2 = 2 × 1 = 2 g; 1 mol SO_2 = 32 + (2 × 16) = 64 g.

(*a*) 44 g CO_2 ≡ 1 mol; (*b*) 48 g O_3 ≡ 1 mol; (*c*) 2 g H_2 ≡ 1 mol, so, 8 g H_2 ≡ 1/2 × 8 = 4 mol = 4 × 6.02×10^{23} = 24.08×10^{23} molecules. (*d*) 64 g SO_2 ≡ 1 mol. Hence, correct answer is (*c*).

Example 98. *The weight of one litre of an unknown gas is 1.25 g at N.T.P. Which of the following gas pertains to the given data?*

(*a*) N_2 (*b*) N_2O
(*c*) N_2O_2 (*d*) N_2O_4

Solution. Weight of 1 L of gas at
N.T.P. = 1.25 g.

Weight of 22.4 L of gas at
N.T.P. = 1.25 g × 22.4 = 28 g.

We know, at. wt. of
N = 14, O = 16.

So, the mol. wt. of (*a*)
N_2 = 2 × 14 = 28 g. ;
(*b*) N_2O = (2 × 14) + 16 = 44 g.
(*c*) N_2O_2 = (2 × 14) + (2 × 16) = 60.
(*d*) N_2O_4 = (2 × 14) + (4 × 16) = 74.

So, the correct answer is, (*a*).

Example 99. *The measured density of heluim at NTP is 0.1784 g* L^{-}*. The wt. of 1 mol of helium is :*

(*a*) 1 g. mol^{-} (*b*) 2 g. mol^{-}
(*c*) 3 g. mol^{-} (*d*) 4 g. mol^{-}

Solution. 1 mol of He occupies volume
= 22.4 L at NTP.

Given. 1 L He weigh
= 0.1784 g.

$$22.4 \text{ L He weigh} = \frac{0.1784\,g.}{1\,L} \times 22.4\,L$$
$$= 3.996 \simeq \mathbf{4\ g\ mol^{-}} \qquad \textbf{Ans.}$$

So, the correct answer is (*d*).

Example 100. *The minimum molecular weight of insulin containing 3.4% sulphur is :*

(*a*) 941.176 g. mol^{-} (*b*) 4703 g. mol^{-}
(*c*) 10.625 g. mol^{-} (*d*) 106.25 g. mol^{-}

Solution. wt. of sulphur,
S = 3.4 g; mol. wt. of insulin
= 100 g mol^{-} ;
at. wt. of S = 32.

For minimum mol. wt. of insulin, there should be at least one S-atom. Thus :

For 3.4 g S, mol. wt. of insulin
= 100

∴ For 32 g S, mol. wt. of insulin

$$= \frac{100}{3.4} \times 32 = 941.176 \text{ g mol}^{-}$$

So, the correct answer is (*a*).

EXAMPLE 101. *The molar mass of haemoglobin is 89600 g mol⁻. The number of iron atoms per molecule of haemoglobin if the latter contains 0.25% iron by weight are (a) 1 (b) 2 (c) 3 (d) 4.*

SOLUTION. Given. 100 g. haemoglobin contains iron = 0.25 g.

89600 g haemoglobin contains iron

$$= \frac{0.25\,\text{g.}}{100\,\text{g.}} \times 89600\,\text{g} = 224\text{ g.}$$

At. wt. of iron = 56

∴ no. of atoms of Fe per molecule haemoglobin

$$= \frac{224}{56} = 4 \text{ atoms}$$

∴ 1 molecule of haemoglobin contains Fe atoms = 4

So, the correct answer is (*d*).

EXAMPLE 102. *How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mol of oxygen atoms?*

(*a*) 0.02 (*b*) 3.125×10^{-2}

(*c*) 1.25×10^{-2} (*d*) 2.5×10^{-2}

(AIEEE, 2006)

SOLUTION. One mole of $Mg_3(PO_4)_2$ contain 3 mol of Mg atoms, 2 mol of P atoms and 2 × 4 (= 8) mol of oxygen atoms.

8 mol atoms of oxygen are present in

$Mg_3(PO_4)_2$ = 1 mol

0.25 mol atoms of oxygen are present in

$$Mg_3(PO_4)_2 = \frac{1}{8} \times 0.25 = 3.125 \times 10^{-2} \text{ mol.}$$

So, the correct answer is (*b*).

EXAMPLE 103. *How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g HCl ?*

(*a*) 0.011 (*b*) 0.029

(*c*) 0.044 (*d*) 0.333

(CBSE–PMT, 2008 Prelims)

SOLUTION. Reaction.

	PbO +	2HCl	→ $PbCl_2$ +	H_2O
	n	2*n*	*n*	*n*
Molar mass	207 + 16 = 223 g mol⁻	2×[1 + 35.5] = 73 g mol⁻		
No. of mol	$\frac{6.5}{223} = 0.029$	$\frac{3.2}{73} = 0.087$		

Since the value of 0.029 is less than that of 0.087, So PbO is a limiting reactant.

Hence, the correct answer is 0.029 *i.e.*, (*b*).

EXAMPLE 104. *Which one of the following is the lightest?*

(*a*) 0.2 mol of H_2 gas

(*b*) 6.023×10^{22} molecules of nitrogen

(*c*) 0.1 g of silver

(*d*) 0.1 mol of O_2 gas

(*e*) 1 g of water **(Kerala PMT, 2012)**

SOLUTION. (*a*) 1 mol H_2 gas = 1 g. mol. wt. of H_2 gas = 1 × 2 = 2 g

∴ 0.2 mol H_2 gas = 0.2 × 2 = 0.4 g.

(*b*) 6.023×10^{23} molecules of N_2 weigh = 1 g. mol. wt. of N_2 = 2 × 14 = 28 g

$$6.023 \times 10^{22} \text{ molecules of } N_2 \text{ weigh} = \frac{28}{6.023 \times 10^{23}} \times 6.02 \times 10^{22} = 2.8\text{ g.}$$

(*c*) wt. of silver = 0.1 g

(*d*) 1 mol O_2 weighs = g. mol wt. of O_2 = 2 × 16 = 32 g

∴ 0.1 mol O_2 weighs = 32 × 0.1 = 3.2 g

(*e*) wt. of water = 1.0 g. So, the correct answer is (*c*).

EXAMPLE 105. *The total number of electrons in 18 mL water [density, 1 g (m L)⁻] are:*

(*a*) 6.02×10^{23} (*b*) 6.02×10^{25}

(*c*) 6.02×10^{24} (*d*) $6.02 \times 18 \times 10^{23}$

(Karnataka, CET, 2012)

SOLUTION. H (at. no. = 1) has electrons = 1; 8 O has electrons = 8

∴ 1 molecule of H_2O contains electrons = (2 × 1) + 8 = 10.

wt. of 18 mL H_2O = volume × density = 18 mL × 1g (m L)⁻ = 18 g.

1 g. mol. wt. of H_2O (= 18 g) contains electrons = $6.02 \times 10^{23} \times 10 = 6.02 \times 10^{24}$.

So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. The atom of an element weighs 3.986×10^{-23} g. Name the element (At. wt. of H = 1, O = 16, Mg = 24, Na = 23) **[Ans.** Magnesium**]**
2. Potassuim bromide (KBr) contains 32.8% by weight of potassium. If 2.0 g. of bromine is mixed with 1.2 g of potassium, calculate the number of moles of potassium which will combine with bromine to form potassium bromide (At. wt. K = 39 amu, Br = 80 amu). **[Ans.** 2.5×10^{-2} mole**]**
3. Fill in the blanks for the following reaction (At. wt. of Zinc = 65 a.m.u., S = 32 a.m.u., O = 16 a.m.u., H = 1 a.m.u.)

$$ZnO_{(S)} + H_2SO_{4\,(aq)} \longrightarrow ZnSO_{4\,(aq)} + H_2O_{(l)}$$

(1) Moles ...... + ... ⟶ ...... + 2 moles

(2) Grams 8.1 g + ... $\longrightarrow$ ...... + ...

(3) Molecules

3.01×10^{23} + ... $\longrightarrow$ ...... + ...

[Ans. (1) 2 moles, 2moles, 2 moles (2) 9.8 g., 16.1 g., 1.8 g. (3) 3.01×10^{23} each]

4. How many moles of atoms of each element are present in 1.0 mol of (*a*) PF_5 (b) (Fe_2O_3)

[Ans. (*a*) 1 mol P, 5mol F (*b*) 2 mol Fe, 3 mol O]

5. What is the average weight in kg of (*a*) a uranium atom (*b*) a H-atom (At. wt. U = 238.03 u ; H = 1.008 u).**[Ans.** (*a*) 3.95×10^{-25} kg (atom^{-}) (*b*) 1.67×10^{-27} kg (atom^{-})]

6. How many m mol of iron are there in 600 mg of iron? (At. wt. Fe = 55.85). **[Ans.** 10.74 m mol Fe]

7. How many moles of CO_2 gas are there in 2.2 g of CO_2 gas? (At. wt. C = 12, O = 16) **[Ans.** 0.05 mol]

8. How many kilogram of O are contained in 1 kg of aluminium oxide, Al_2O_3? (at. wt. Al = 27, O = 16)

[Ans. 0.47 Kg O]

9. Calculate the number of atoms of oxygen present in 88 g of CO_2. What would be the weight of carbon monoxide having the same number of oxygen atoms?

(Avogadro's constant = 6.023×10^{23} per mole, atomic weight of carbon = 12 g. per mole, Atomic weight of oxygen = 16 g per mole) **[BIT Ranchi, 1991]**

[Ans. 2.409×10^{24} atoms of O ; Wt. of CO having the same number of O atoms = 112 g]

[Hint. 44 g $CO_2 \equiv 2 \times 6.023 \times 10^{23}$ atoms of O; so, 88 g $CO_2 \equiv 2.409 \times 10^{24}$ atoms of O. **Ans.**

6.023×10^{23} atoms of O are present in CO = 28 g (*i.e.*, 1 g. mol. wt.)

$\therefore$ 2.409×10^{24} atoms of O are present in CO = $(28 \times 2.409 \times 10^{24})/6023 \times 10^{23}$ = 112 g **Ans.**

10. How many mol of Zn and P are contained in 1.00 kg of zinc phosphide, Zn_3P_2 (at. wt. Zn = 65 ; P = 31)

[Ans. 3.89 mol Zn_3P_2 ; 11.7 mol Zn ; 7.78 mol P]

11. The molecules present in 5.6 L of sulphur dioxide at STP is

(*a*) 1.5×10^{23}
(*b*) 1.5×10^{-23}
(*c*) 4×10^{23}
(*d*) 0.15×10^{23}

[Ans. (a)]

(JK CET 2010)

12. Which of the following has smallest number of molecules?

(*a*) 11.2 L of O_2 at NTP
(*b*) 8.0 g of O_2
(*c*) 0.1 mole of O_2
(*d*) 2.24×10^4 mL of O_2 **[Ans. (c)]**

(AMU Engg 2010)

13. The number of molecules in 100 ml of 0.02 N H_2SO_4 is

(*a*) 6.02×10^{22}
(*b*) 6.02×10^{21}
(*c*) 6.02×10^{20}
(*d*) 6.02×10^{18}

[Ans. (c)]

(AMU Med 2010)

14. The total number of atoms of all elements present in 1 mole of ammonium dichromate is

(*a*) 19
(*b*) 6.023×10^{23}
(*c*) 114.437×10^{23}
(*d*) 84.322×10^{23}

[Ans. (c)]

(AMU Engg 2010)

15. How much time (in hours) would it take to distribute one Avogadro number of wheat grains if 10^{20} grains are distributed each second?

(*a*) 0.1673
(*b*) 1.673
(*c*) 16.73
(*d*) 167.3
(*e*) 1673 **[Ans. (b)]**

(Kerala PET 2010)

16. The number of atoms in 0.1 mol of triatomic gas is ($N_A = 6.02 \times 10^{23}$)

(*a*) 1.800×10^{22}
(*b*) 6.026×10^{22}
(*c*) 1.806×10^{23}
(*d*) 3.600×10^{22}

[Ans. (c)]

(CBSE PMT 2010)

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

(*a*) 100 g
(*b*) 115 g
(*c*) 110 g
(*d*) 112 g

[Ans. (d)]

18. An electric bulb is filled with 100 cm^3 of argon gas (mass no. 40). The number of atoms of oxygen present in the bulb is:

(*a*) 40
(*b*) 1.0×10^{22}
(*c*) 15
(*d*) 2.7×10^{21}

19. One atom of an element, A weighs 3.01×10^{-23} g. Find the number of gram atoms in 20 kg of it.

[Ans. 1105 g. atoms]

20. The weight of 400 cm^3 of a diatomic gas at 0°C and 2.0 atmospheric pressure is 1 g. Find the weight of one atom.

[Ans. 2.3×10^{-23} g]

10
CHAPTER
The Solid State

10.1 CRYSTAL LATTICE OR SPACE LATTICE

A crystalline solid consists of constituent units called *lattice points* (atoms, ions, molecules). These are arranged in a regular repeating pattern. This pattern of points which describe the arrangement of constituent units (atoms, ions, molecules) in a crystal is called **crystal lattice** or **space lattice**. A space lattice forms the basis of all structures. There are five possible two dimensional lattices while there are 14 possible three dimensional lattices. These are called *Bravais lattices.*

10.2 UNIT CELL

It is the smallest repeating unit in a crystal lattice which when repeated in the direction of its edges by a distance equal to the cell edge, results in the formation of full crystal (Fig. 1).

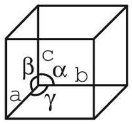


Fig. 1 A unit cell

10.3 SEVEN CRYSTAL SYSTEMS

In a three dimensional lattice, the unit cell is characterised by the lengths *a*, *b*, *c* and the angles α, β, γ. These are known as cell parameters. Based on unit cell parameters, there are seven different types of unit cells called *crystal systems* or *crystal habits*. (Table 1).

Table 1. The Seven Crystal Systems

System	*Axial distances*	*Axial angles*	*Examples*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	NaCl, KCl, CrCl, Zinc blende, Cu, Ag, diamond
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2, White tin, SnO_2
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	$CaCO_3$, $PbCO_3$, Rhombic sulphur, KNO_3, $BaSO_4$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°; \beta \neq 90°$	Monoclinic sulphur, $PbCrO_4$, $CuSO_4.5H_2O$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$	ZnO, graphite
Rhombohedral (or trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$ but less than 120°	As, Sb, Calcite, HgS (Cinnabar), $NaNO_3$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$CuSO_4.\ 5H_2O$, $K_2Cr_2O_7$, H_3BO_3

10.4 CUBIC CRYSTAL SYSTEMS AND NUMBER OF ATOMS IN UNIT CELLS

There are three types of lattices.

10.4.1. Simple or Primitive Cubic Lattices

In this arrangement, the lattice points (atoms, ions or molecules) are present at the 8 corners of the cube. There are 8 atoms at the corners of a cube.

∴ Number of atoms present in each unit cell

$$= (8 \text{ corner atoms}) \times \left[\frac{1}{8} \text{ atom per unit cell}\right] = 1 \text{ atom}$$

∴ A *simple cube has one atom per unit cell.*

10.4.2. Body Centred Cubic Lattice (b.c.c)

In this arrangement, the lattice points (atoms, ions, molecules) are at all the corners as well as at the centre of the cube. Each corner atom is shared by 8 cubes while one atom is present in the body of the cube which is not shared by any other cube.

∴ Number of atoms present at corners per unit cell

$$= 8 \text{ corner atoms} \times \frac{1}{8} \text{ atom per unit cell} = 1 \text{ atom}$$

Number of atoms at body centre = 1

∴ Total number of atoms in b.c.c arrangement = 1 + 1 = 2.

Hence, a body centred cube has two atoms per unit cell.

Note : *Alkali metals are body centred cubic (b.c.c).*

10.4.3. Face Centred Cubic *i.e.*, f.c.c. (or Cubic Close Packed Arrangement *i.e., c.c.p)*

In this arrangement, there are lattice *points (atoms, ions, molecules) at all the corners as well as at the centre of each of the six faces*. Each corner atom is shared by 8 cubes. So, the atom present at each corner contributes $\frac{1}{8}$ to each cube. Also, there are six atoms at the faces of the cube and each atom is shared by two unit cells. So, the atom present at each face contributes $\frac{1}{2}$ to each unit cell.

$\therefore$ Number of atoms present at corners per unit cell

$$= 8 \text{ corners} \times \frac{1}{8} \text{ atom per unit cell} = 1 \text{ atom}$$

Number of atoms present at faces per unit cell

$$= 6 \text{ atoms at the faces} \times \frac{1}{2} \text{ atom per unit cell} = 3 \text{ atoms}$$

$\therefore$ Total number of atoms in f.c.c. (or c.c.p) arrangement

$$= 1 + 3 = 4$$

Example 1. *Find out the number of atoms per unit cell in a face centred cubic structure having only single atoms at its lattice points.* **(CBSE, 2007)**

Solution. See above section 10.4.3. **Ans. is 4.**

Note : *Cu, Al and Ni are face centred cubic (f.c.c.)*

10.4.4. End Face Centred

In this arrangement, points are present at the corners and at the centre of the two ends. It may be noted that end centred unit cell is not encountered in a cubic system *i.e.,* a cubic system has only three types of unit cells.

$$\text{No. of atoms per unit cell} = 8 \text{ corners} \times \frac{1}{8} \text{ atom per unit cell} = 1$$

Such a unit also has points 'only' on the end (two) faces. Since, each point is shared between two unit cells, it contributes to ½ to each unit cell.

$$\therefore \quad \text{No. of atoms per unit cell} = 2 \times \frac{1}{2} = 1$$

$\therefore$ Total number of atoms per unit cell = 1 + 1 = 2

Note : The number of atoms those belong to unit cell are called **lattice sites**.

10.5 STENO'S LAW OF CONSTANCY OF INTERFACIAL ANGLES

According to this law, the angles between the adjacent corresponding faces, called the interfacial angles of the crystals of a particular substance are always the same.

10.6 LAW OF SYMMETRY

According to this law, all crystals of the same substance possess the same elements of symmetry.

Elements of symmetry : Symmetry is a particular regularity observed in the arrangement of objects or their parts on a plane and in space. There are three elements of symmetry.

1. *Centre of symmetry.* Centre of symmetry of a crystal is an imaginary plane within a crystal such that any line drawn through it intersects the surface of the crystal at equal distances in both directions.
2. *Plane of symmetry.* It is an imaginary plane passing through the crystal which can divide crystal into two parts such that one part is the exact mirror image of the other.
3. *Axis of symmetry or axis of rotation.* It is an imaginary line passing through the crystal such that when the crystal is rotated about this line, it presents the same appearance more than once in one complete revolution *i.e.,* in a rotation through 360°.

Example 2. *Calculate the total number of elements of symmetry in a cubic crystal.*

Solution. In a cubic crystal :

(*i*) There are 3 rectangular planes of symmetry + 6 diagonal planes of symmetry. Hence, *total planes of symmetry* = 3 + 6 = 9.

(*ii*) There are three axis of four fold symmetry + 4 axis of three fold symmetry + 6 axis of two-fold axis of symmetry = 3 + 4 + 6 = 13.

(*iii*) Centre of symmetry = 1

$\therefore$ Total number of elements of symmetry = 9 + 13 + 1 = **23.**

10.7 TABLE OF NUMBER OF ATOMS PER UNIT CELL

Following table 2 is given to show total number of atoms per unit cell in different types of cubic unit cells.

Table 2

Unit cell	*No. of atoms at corners*	*No. of atoms in centre*	*No. of atoms at faces*	*Total*
Simple cubic	$8 \times \frac{1}{8} = 1$	0	0	1
Body centred	$8 \times \frac{1}{8} = 1$	1	0	1 + 1 = 2
Face centred	$8 \times \frac{1}{8} = 1$	0	$6 \times \frac{1}{2} = 3$	1 + 3 = 4
End face centred	$8 \times \frac{1}{8} = 1$	0	$2 \times \frac{1}{2} = 1$	1 + 1 = 2

Note : 1. *End centred unit cell* has particles at the centres of end faces in addition to the particles at the corners.

2. The ratio of the number of particles *x* and *y* present per unit cell gives the formula of the compound formed by the combination of *x* and *y*.

3. Edge length, a = shortest distance between A and B atoms of AB type crystal

4. Fraction of an atom or ion that occupies positions in a unit cell is given as follows:

Position in unit cell	**Corner**	**Centre**	**Face**	**Edge**
Fraction in unit cell	$\frac{1}{8}$	1	$\frac{1}{2}$	$\frac{1}{4}$

EXAMPLE 3. *What is the number of atoms per unit cell in a body centred cubic structure ?* **(CBSE, 2007)**

SOLUTION. The number of atoms or lattice points per unit cell (Z) in different cubic unit cells of monoatomic substances can be calculated with the help of the following formula :

$$Z = \frac{n_c}{8} + \frac{n_b}{1} + \frac{n_f}{2} + \frac{n_e}{4}$$

where n_c = number of atoms at the corner.

n_b = number of atoms at the body centre.

n_f = number of atoms at the face centre.

n_e = number of atoms at the edge centre.

For a body centred cubic structure :

$$n_c = 8, n_b = 1, n_f = n_e = 0$$

$$\therefore \quad Z = \frac{8}{8} + \frac{1}{1} + \frac{0}{2} + \frac{0}{4} = 1 + 1 = \mathbf{2\ Ans.}$$

10.8 INTERSTITIAL SITES OR INTERSTITIAL VOIDS

In h.c.p and c.c.p arrangement of spheres, two types of voids (tetrahedral) and (octahedral) are present :

1. **Tetrahedral voids.** The empty space among four spheres having tetrahedral arrangement is called tetrahedral site or void. **Mathematically:**

$$\frac{\text{Radius of sphere that can be fitted in the void } (r)}{\text{Radius of sphere constituting the void (R)}} = \mathbf{0.225}$$

Note : In a close packed structure of ***n*-spheres,** tetrahedral holes or voids = **2*n*.**

2. **Octahedral void.** The vacant space formed by two equilateral triangles with apices in opposite direction is called octahedral void or site **Mathematically :**

$$\frac{\text{Radius of sphere that can be fitted in the void } (r)}{\text{Radius of sphere constituting the void (R)}} = \mathbf{0.414}$$

3. **Octahedral voids.** 1 at body centre and 12 at edge centres. Since contribution of edge centre in unit cell = $\frac{1}{4}$, the no. of voids = 1 + 12 × $\frac{1}{4}$ **= 4**

Note : In a close packed structure of ***n*-spheres,** octahedral holes or voids = ***n*.**

10.9 CO-ORDINATION NUMBER

The number of spheres which touch a given sphere is called the *co-ordination number. For example,* in h.c.p and c.c.p arrangements, *a sphere* which touches 6 other spheres in the same plane, three spheres in the layer above and three spheres in the layer below it, has co-ordination number 12 (= 6 + 3 + 3).

(*i*) **In primitive or simple cubic lattice** unit cell, each particle has **co-ordination number = 6** (*i.e.,* 4 in its own plane + one above + one below).

(*ii*) **In body centred cubic lattice** unit cell, each body centred particle has **co-ordination number 8.** It is because the nearest neighbour of a corner atom is body centred atom. Each body centred atom has 8 corner atoms.

(*iii*) **In face centred cubic lattice** unit cell, each particle has **coordination number 12** *i.e.,* 12 equidistant particles (6 particles in same plane + 3 particles above + 3 particles below it).

Note : 1. Mg, Zn and Be have h.c.p arrangement.

2. Co-ordination number of each sphere in h.c.p and c.c.p arrangement = 12.

3. Stacking pattern

Structure	**Co-ordination number**	**Stacking pattern**
h.c.p.	12	ABABABA...
c.c.p.	12	ABCABCA...

10.10 IONIC RADII

Ionic radius of an ion is the distance from the nucleus of that ion upto which it has its influence in an ionic bond. Considering ions as spheres :

(*a*) Internuclear distance between two ions = Ionic radius of cation + Ionic radius of anion

(*b*) Edge length = 2 (radius of cation + radius of anion)

EXAMPLE 4. *The KBr lattice has a cubic unit cell. The ionic radius of K^+ = 1.33 Å; Br^- = 1.95 A°. Assuming the additivity of ionic radii, calculate the edge length, a.*

SOLUTION. We know edge length,

$a = 2\,(K^+ \text{ radius} + Br^- \text{ radius})$

or $a = 2\,(1.33\ \text{Å} + 1.95\ \text{Å}) = 2\,(3.28\ \text{Å})$

$= \mathbf{6.56\ Å\ Ans.}$

EXAMPLE 5. *Silver iodide crystallises in the c.c.p zinc blende structure. Assuming that iodide ions occupy the lattice points, calculate the fraction of the tetrahedral sites occupied by silver ions.*

SOLUTION. We know that the number of tetrahedral sites per iodide ion, I^- = 2

AgI has c.c.p structure like zinc blende.

∴ Fraction of tetrahedral sites occupied by Ag^+ ion = 50%

Example 6. *Calculate the percentage of void space in a unit cell having fcc arrangement of x and y atoms. x atoms are at the corners, y atoms at the face centres of unit cell and one of the atoms are missing from the corner in each unit cell.*

Solution. Out of 8 corners, one of the atoms is missing in each unit cell. Thus, there are $\frac{7}{8}x$ atoms. There are three face centres. So, there are $3y$ atoms per unit cell. Let a = edge length of the unit cell.

Hence,

$$2r_x + 2r_y = a\sqrt{2}$$

or

$$a = \frac{2(r_x + r_y)}{\sqrt{2}} = \frac{\sqrt{2}\times\sqrt{2}(r_x + r_y)}{\sqrt{2}} =$$

$$= \sqrt{2}(r_x + r_y)$$

Volume of unit cell $= a^3 = \left[\sqrt{2}(r_x + r_y)\right]^3$

Fraction of volume occupied per unit volume of the unit cell i.e.,

$$\text{(packing fraction, PF)} = \frac{\frac{7}{8}\times\left[\frac{4}{3}\pi r_x^3\right] + \left[3\times\frac{4}{3}\pi r_y^3\right]}{\left[\sqrt{2}(r_x + r_y)\right]^3}$$

$$= \frac{\frac{7}{6}\pi r_x^3 + 4\pi r_y^3}{\left[\sqrt{2}(r_x + r_y)\right]^3}$$

Since, $r_y = 0.414\, r_x \quad \left[\because \frac{r_+}{r_-} = 0.414\right]$

We have,

$$\frac{\frac{7}{6}\pi r_x^3 + 4\pi(0.414)^3 r_x^3}{\left(\sqrt{2}\right)^3 (r_x + 0.414 r_x)^3} = \frac{r_x^3\left[\frac{7}{6}\pi + 4\pi\times(0.414)^3\right]}{2\sqrt{2}\, r_x^3[1 + 0.414]^3}$$

$$= \frac{\frac{7}{6}\times 3.142 + 4\times 3.142\times(0.414)^3}{2\times 1.4142(1.414)^3}$$

$$= \frac{3.666 + 0.892}{7.996} = \frac{4.558}{7.996} = 0.57$$

∴ Void space = 1 – packing fraction

= 1 – 0.57 = 0.43

Hence, %age of void space = 0.43 × 100 = **43%**.

Example 7. *How will you prove that void space %age in zinc blende structure is 25% ?*

Solution. Let edge length of the cell = a; radius of cation = r^+; radius of anion = r^-. In zinc blende structure, the anions are in f.c.c. positions and half of the tetrahedral holes are occupied by cations. The number of anions are 4. There are eight tetrahedral holes per unit cell.

But, Face diagonal = $a\sqrt{2}$ **or** $4r = a\sqrt{2}$.

Hence, $a = \frac{4}{\sqrt{2}}r = \frac{\sqrt{2}\times\sqrt{2}\times 2r}{\sqrt{2}} = r\times 2\sqrt{2}$

Volume of unit cell $= a^3 = \left[r\times 2\sqrt{2}\right]^3 = r^3\times 16\sqrt{2}$

$$\text{We know packing fraction} = \frac{4\times\left[\frac{4}{3}\pi r^3\right] + \frac{1}{2}\times 8\times\left[\frac{4}{3}\pi r^3\right]}{r^3\times 16\sqrt{2}}$$

$$= \frac{\pi}{3\sqrt{2}}\left[1 + \left(\frac{r^+}{r^-}\right)^3\right]$$

But, $\frac{r^+}{r^-}$ = 0.225 (for tetrahedral holes)

$$\text{Packing fraction} = \frac{\pi}{3\sqrt{2}}\left[1 + (0.225)^3\right]$$

$$= \frac{3.142}{3\times 1.4142}[1.0114]$$

= 0.749 per unit volume of unit cell.

∴ Void space = 1 − 0.749 = 0.251 per unit volume of unit cell

∴ %age of void space = 0.251 × 100 = 25.1 ≈ **25%**

10.11 SUMMARY OF %AGE OF VOLUME OCCUPIED BY PARTICLES

Unit Cell	*No. of atoms at*			*No. of atoms per unit cell*	*%age of volume occupied by particles*
	Corners	*Centre*	*Face*		
Simple cube	$8\times\frac{1}{8}=1$	0	0	1	52.4%
b.c.c.	$8\times\frac{1}{8}=1$	1	0	2	68%
f.c.c.	$8\times\frac{1}{8}=1$	0	$6\times\frac{1}{2}=3$	4	74%

10.12 SUMMARY OF RADIUS (*r*) OF ATOM, DISTANCE (*d*) BETWEEN NEAREST NEIGHBOURS

Summary of radius (r) of atom; distance (d) between nearest neighbours in different unit cells of pure elements having edge length, a. 'a' is also called **lattice constant**.

Unit Cell	*Distance between nearest neighbours, d or closest distance between atoms = d*	*Radius, r*
Simple cube	a	$\frac{a}{2}$
f.c.c.	$\frac{a}{\sqrt{2}}$	$\frac{a}{2\sqrt{2}}$
b.c.c.	$\frac{a\sqrt{3}}{2}$	$\frac{a\sqrt{3}}{4}$

EXAMPLE 8. *How many unit cells are shared by an atom on the face of a unit cell ?*

SOLUTION. The number of unit cells that are shared by an atom on the face of a unit cell = 2.

EXAMPLE 9. *A compound formed by elements A and B crystallises in the cubic arrangement in which atoms A are at the corners of the cube and atoms B at the face centres. What is the formula of the compound ?*

(a) AB_3, (b) AB (c) A_3B (d) AB_2

(PSEB, 2002, Karnataka, CET, 2009, PSEB, 2013)

SOLUTION.

No. of atoms of A $= 8 \text{ corners} \times \frac{1}{8}$ atom per unit cell $= 1$

No. of atoms of B $= 6 \text{ faces} \times \frac{1}{2}$ atom per unit cell $= 3$

∴ No. of cations and anions in one unit cell = 1 + 3 = 4

∴ Formula of compound = $A_1B_3 = AB_3$

So, correct answer is (*a*)

EXAMPLE 10. *In a crystalline solid, anions C are arranged in cubic close packing. Cation A occupies 50% of the tetrahedral voids and cation B occupies 50% of octahedral voids. What is the formula of solid ?* **(PSEB, 1999 S)**

SOLUTION. Let no. of anions, C = 100. We know that :

In a close packed structure of N spheres, there are 2N tetrahedral sites and N octahedral sites. So,

No. of octahedral voids = 100;
No. of tetrahedral voids = 200

But 50% of both the voids are occupied. Hence, Tetrahedral voids contain A cations = 100

Octahedral voids contain B cations = 50. Hence,

A : B : C is

$100 : 50 : 100$ *i.e.,* $\frac{100}{50} : \frac{50}{50} : \frac{100}{50}$ *i.e.,* $2 : 1 : 2$

∴ Formula of the compound = $\mathbf{A_2B_1C_2}$ **or** $\mathbf{A_2BC_2}$ **Ans.**

EXAMPLE 11. *A cubic solid is made up of two elements P and Q. Atoms Q are present at the corners of the cube and atoms P at the body centre. What is the formula of the compound? What are the co-ordination numbers of P and Q ?*

(CBSE, Sample Paper 1990, HSB Sample Paper, 1991, PSEB., 2002, CBSE, 2013)

SOLUTION. No. of atoms of Q

$= 8 \text{ corners} \times \frac{1}{8}$ atom per unit cell = 1

No. of atoms of P at the body centre = 1.
because contribution of each atom within the body is 1.

∴ Formula of the compound
$= P_1Q_1 = PQ$

Since, the given solid is a body centred cubic solid, both P and Q have co-ordination number equal to **8.**

EXAMPLE 12. *Ferric oxide crystallises in a h.c.p array of oxide ions with two out of every three octahedral voids occupied by ferric ions. What will be the formula of ferric oxide.*

SOLUTION. In h.c.p arrangement of oxide ions, oxide ions are present at every corners of the cube.

∴ No. of oxide ions per unit cell

$= 8 \text{ corners} \times \frac{1}{8}$ atom per unit cell = 1

We know that for every oxide ion, there is one octahedral hole and two out of three are occupied by Fe^{3+} ions.

∴ No. of ferric ions per octahedral void = $\frac{2}{3} Fe^{3+}$

∴ Formula of ferric oxide

= $\mathbf{Fe_{2/3}\,O_1}$ **or** $\mathbf{Fe_2O_3}$ **Ans.**

EXAMPLE 13. *In a cubic type unit cell, atoms of X are at the corners as well as at the centre of a cube. Atoms of Y are at one half faces of the cube. Derive the formula of the compound.* **(PSEB, 2013)**

SOLUTION. No. of atoms of *X*

$= 8 \text{ corners} \times \frac{1}{8}$ atom per unit cell = 1

No. of atoms of *X* at centre = 1.
Hence, total no. of atoms of *X* = 1 + 1 = 2
No. of atoms of *Y*

$= \frac{1}{2}(6 \text{ faces}) \times \frac{1}{2}$ atom per unit cell $= \frac{3}{2}$

∴ Formula of compound = $\mathbf{X_2 \frac{Y_3}{2}}$ **or** $\mathbf{X_4Y_3}$ **Ans.**

EXAMPLE 14. *If three elements P, Q and R crystallise in a cubic lattice with P atoms at the corners, Q atoms at the cube centre and R atoms at the centre of edges of the cube, then write the formula of the compound.* **(PSEB, 2005)**

SOLUTION. No. of P atoms per unit cell

$= 8 \text{ corners} \times \frac{1}{8}$ atom per unit cell = 1

No. of Q atoms per unit cell = 1

No. of R atoms per unit cell = $6 \times \frac{1}{4} = \frac{3}{2}$

∴ Formula of compound = $\mathbf{P_1Q_1R_{3/2}}$ **or** $\mathbf{P_2Q_2R_3}$ **Ans.**

EXAMPLE 15. *In a cubic close packed structure of mixed oxides, the oxide ions are in c.c.p. arrangement. One eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one half the octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxide ?*

SOLUTION. We know that the number of tetrahedral voids for each sphere = 2.

So, the no. of atoms of $A^{2+} = 2 \times \frac{1}{8} = \frac{1}{4}$.

Also, the number of octahedral voids for each sphere = 1

So, the no. of atoms of B^{3+} = $1 \times \frac{1}{2}$.

Hence, the formula of mixed oxide

$$= A_{1/4}B_{1/2}O. \text{ or } AB_2O_4$$

$$[\because \text{Ratio of } \frac{1}{4} : \frac{1}{2} : 1 \text{ is } 1 : 2 : 4]$$

EXAMPLE 16. *In face centred cubic arrangement of A and B atoms, whose A atoms are at the corners of the unit cell and B atoms at the face centres and two atoms are missing from two corners in each unit cell. What is the simplest formula of the compound?*

(a) AB *(b)* AB_2 *(c)* AB_4 *(d)* A_2B_3

(PSEB, 2005, 2012)

SOLUTION. No. of A atoms per unit cell

$$= 6 \text{ i.e., } (8 - 2 = 6) \text{ corners} \times \frac{1}{8} \text{ atom per unit cell}$$

$$= \frac{6}{8} = \frac{3}{4}$$

No. of B atoms per unit cell

$$= 6 \text{ faces} \times \frac{1}{2} \text{ atom per unit cell} = 3$$

Hence, the formula of the compound

$$= A_{3/4}B_3 \text{ or } A_3B_{12} \textit{ i.e., } \mathbf{AB_4}$$

So, the correct formula is (*c*). **Ans.**

EXAMPLE 17. *A unit cell consists of a cube in which there are anions Y at each corner and cations X at the centres of alternate faces of a unit cell. What is the simplest formula of the compound.*

(PSEB, 2002, H.P.B. 2012)

SOLUTION. No. of atoms in a unit cell of *Y*

$$= 8 \text{ corners} \times \frac{1}{8} \text{ atom per unit cell} = 1$$

Also, there are 3*X* atoms present at the centres of 3 alternate faces and each face centred atom is shared by two cubes.

Hence, number of atoms in a unit cell $= \frac{1}{2} \times 3 = \frac{3}{2}$.

Thus, the formula of the compound is

$$\mathbf{X_{3/2}Y_1 \text{ or } X_3Y_2} \quad \textbf{Ans.}$$

EXAMPLE 18. *Calculate the number of atoms in a cube based unit cell having one atom on each corner and two atoms on each body diagonal.* **(CBSE, 1991)**

SOLUTION. No. of atoms per unit cell

$$= 8 \text{ corners} \times \frac{1}{8} \text{ atom per unit cell} = 1.$$

There are four body diagonals having 8 atoms on them and being in the body of the unit cell, are not shared by any other unit cell.

Hence, number of atoms in a cube base unit cell

$$\mathbf{= 1 + 8 = 9} \quad \textbf{Ans.}$$

EXAMPLE 19. *A solid is made up of two elements P and Q. Atoms Q are in c.c.p (or h.c.p.) arrangement while P-atoms occupy all the tetrahedral sites. What is the formula of the compound?* **(PSEB, 2002)**

SOLUTION. No. of tetrahedral sites per sphere

$$= 2 \quad \therefore P = 2$$

The number of atoms in c.c.p arrangement = 8 corners × 1/8 atom per unit cell = 1

So, $Q = 1$

Hence, formula of the compound = $\mathbf{P_2Q}$ **Ans.**

EXAMPLE 20. *In aluminium oxide, the oxide ions are arranged in the hexagonal close packed (h.c.p) arrangement and the aluminium ions occupy 2/3 of the octahedral sites. What is the formula of the oxide ?*

SOLUTION. The number of octahedral sites corresponding to each atom in h.c.p = 1.

∴ no. of oxygen (O) atoms = 1

It is given that 2/3 of the octahedral sites are occupied by aluminium ions. Hence, for each oxide ion, there will be 2/3 aluminium ions. So,

no. of Al atoms = 2/3.

Hence, the formula of the oxide

$$\mathbf{= Al_{2/3}O_1 \text{ or } Al_2O_3} \quad \textbf{Ans.}$$

EXAMPLE 21. *An element crystallised in f.c.c. lattice and the edge of unit cell is 620 pm. Find the nearest neighbour distance and radius of atom of element.* **(AIEEE, 2009, D.B. 2009, CBSE, 2013)**

(a) 157, 113 *(b) 181, 212*

(c) 108, 101 *(d) 438. 4, 219.2* pm

SOLUTION. For f.c.c, neighbour distance,

$$d = \frac{a}{\sqrt{2}} = \frac{620 \text{ pm}}{1.4142} = 438.4 \text{ pm} \quad \textbf{Ans.}$$

For f.c.c., radius of atom,

$$r = \frac{a}{2\sqrt{2}} = \frac{620 \text{ pm}}{2 \times 1.4142} = 219.2 \text{ pm}$$

So, the correct answer is (*d*).

EXAMPLE 22. *An element crystallises in simple cubic or primitive cubic structure. Calculate the radius of atom and distance between nearest neighbours if edge length of unit length is 520 pm.*

SOLUTION. Edge length,

$$a = 520 \text{ pm}$$

For cubic lattice, neighbour distance = *a* = 520 pm

For cubic lattice, radius of atom,

$$r = \frac{a}{2} = \frac{520}{2} = 260 \text{ pm} \quad \textbf{Ans.}$$

EXAMPLE 23. *Calculate the radius of sodium atom if sodium metal crystallises in b.c.c. lattice with the cell edge, a = 4.29Å.* **(IIT, 1994)**

SOLUTION. The body diagonal (Fig. 2) in b.c.c. lattice = $4r$ and $4r = \sqrt{3}.a$ and r = radius of atom, a = edge length.

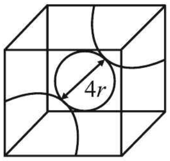


Fig. 2

$$\therefore \qquad r = \frac{\sqrt{3}.a}{4} = \frac{1.732 \times 4.29\text{Å}}{4} = \mathbf{1.86Å} \quad \textbf{Ans.}$$

Note. 1. Total no. of edges in a cube = 12.

2. No. of atoms located at cube edges = $12 \times \frac{1}{4} = 3$
3. A **body diagonal** has two atoms on it. These atoms are not shared by any unit cell because these are present in the body unit cell.

EXAMPLE 24. *Calculate the number of atoms located at cube edges.*

SOLUTION. Total number of edges in a cube = 12

Number of atoms located at cube edges

$$= \mathbf{12 \times \frac{1}{4} = 3} \qquad \textbf{Ans.}$$

EXAMPLE 25. *Gold crystallises in a face centred cubic structure. Calculate the length of the side of the cell if atomic radius of gold is 0.144 nm.*

SOLUTION. Radius (r) of gold atom = 0.144 nm.

For f.c.c. structure,

$$r = \frac{a}{2\sqrt{2}};$$

$$a = 2r\sqrt{2} = 2 \times 0.144 \times 1.4142 \text{ nm}$$

$$= \mathbf{0.407 \text{ nm}} \qquad \textbf{Ans.}$$

EXAMPLE 26. *r_{Na^+} and r_{cl^-} represent radius of Na^+ and Cl^-. If n is the number of NaCl units per unit cell, then give equation, you will use to obtain molar volume.* **(AIPMT,2009)**

SOLUTION. We know that:

Edge length, a, of unit cell of NaCl crystal

$$= 2\,(r_{Na^+} + r_{Cl^-})$$

$\therefore$ Volume (V) of unit cell = a^3

$$= [2(r_{Na^+} + r_{Cl^-})^3 = 8\,(r_{Na^+} + r_{Cl^-}]^3.$$

Volume occupied by one molecule

$$= \frac{8(r_{Na^+} + r_{Cl^-})^3}{n}$$

Volume occupied by one mol molecules

$$= \frac{8(r_{Na^+} + r_{Cl^-})^3 \times N_A}{n}.$$

Where $\quad N_A$ = Avogadro's number = 6.023×10^{23}

$\therefore$ Volume occupied by one mol molecules

$$= \frac{8(r_{Na^+} + r_{Cl^-})^3 \times 6.023 \times 10^{23}}{n}$$

EXAMPLE 27. *CsCl has a b.c.c arrangement and its unit cell edge is 400 pm. Calculate the inter-ionic distance in CsCl.* **(DSB, 1993)**

SOLUTION. Edge length, a = 400 pm

Inter-ionic distance, $d = \dfrac{(a\sqrt{3})}{2}$

Substituting the values, we get,

$$d = \frac{(400 \times 1.732)}{2} = \mathbf{346.4pm} \quad \textbf{Ans.}$$

EXAMPLE 28. *The atomic radius of an ion which crystallises in f.c.c. structure is $\frac{9}{7}$Å. Calculate the lattice constant.*

SOLUTION. Atomic radius,

$$r = \frac{9}{7}\text{Å} = \left(\frac{9}{7}\right) \times 10^{-10}\text{m}$$

Lattice constant,

$$a = ?$$

For f.c.c. structure,

$$r = \frac{a}{(2\sqrt{2})}$$

Substituting the values, we get :

$$\left(\frac{9}{7}\right) \times 10^{-10}\text{m} = \frac{a}{2 \times 1.4142}$$

or

$$a = \left(\frac{9}{7}\right) \times 10^{-10}\text{m} \times 2 \times 1.4142$$

$$= \mathbf{3.6 \times 10^{-10}\, m} \qquad \textbf{Ans.}$$

EXAMPLE 29. *Find (a) radius of NH_4^+ ion and that of Cl^- ion (b) distance between the oppositely charged ions in the NH_4Cl crystal lattice from the given data. NH_4Cl crystallises in a body centred cubic lattice, with a unit cell distance of 3.87Å; radius of Cl^- ion = 181 pm.*

SOLUTION. Given the unit cell distance,

$$a = 3.87 \text{ Å} = 387 \text{ pm}$$

In a b.c.c lattice of NH_4Cl, NH_4^+ and Cl^- ions touch each other along the cross-diagonal of the cube. Thus,

$$2r_{NH_4^+} + 2r_{Cl^-} = a\sqrt{3} \text{ or } 2\left(r_{NH_4^+} + r_{Cl^-}\right)$$

$$= (387 \times 1.732)$$

$$\therefore \qquad r_{NH_4^+} + r_{Cl^-} = \frac{387 \times 1.732}{2} = 335.14\,\text{pm} \qquad \textbf{Ans.}$$

But, $\qquad r_{Cl^-}$ = 181pm (given)

$$\therefore \qquad r_{NH_4^+} = 335.14 - 181 = \mathbf{154.14 \text{ pm}} \qquad \textbf{Ans.}$$

Type. To calculate number of unit cells, using the following relation.

$$\textbf{No. of unit cells} = \frac{\text{Volume of element}}{\text{Volume of unit cell}}$$

$$= \frac{\text{Mass of element}}{(\text{Density of element } \times \text{Volume of unit cell})}$$

$$\text{Where volume of unit cell} = \frac{\text{Mass of unit cell}}{\text{Density of element}}$$

and

Mass of unit cell = Volume × Density

= n (*i.e.*, no. of atoms per unit cell) × mass of atom

EXAMPLE 30. *An element has f.c.c structure and unit cell edge length equal to 400 pm. Calculate the density and number of unit cells for 10 g of the element. (At. wt. of element = 150).*

Solution. The structure is f.c.c. Hence, number (n) of atoms = 4.

$$\text{Edge length} = 400 \text{ pm} = 400 \times 10^{-10} \text{ cm}$$

Thus volume (V) of unit cell

$$= (400 \times 10^{-10} \text{ cm})^3 = 6.4 \times 10^{-23} \text{ cm}^3.$$

$$\text{Density} = \frac{n\text{M}}{\text{N}_\text{A}\text{V}}$$

[M = at. wt. of element; N_A = Avogadro's number]

$$= \frac{4 \times 150 \text{ g mol}^{-}}{6.022 \times 10^{+23} \text{ mol}^{-} \times 6.4 \times 10^{-23} \text{ cm}^3}$$

$$= 15.56 \text{ g cm}^{-3}$$

Volume of 10 g of element

$$= \frac{\text{Mass}}{\text{Density}} = \frac{10 \text{ g}}{15.56 \text{ g cm}^{-3}} =$$

$$= 0.643 \text{ cm}^3$$

Total number of unit cells in 0.643 cm^3

$$= \frac{\text{Volume of element}}{\text{Volume of unit cell}}$$

$$= \frac{0.643 \text{ cm}^3}{6.4 \times 10^{-23} \text{cm}^3} = \mathbf{1.005 \times 10^{22}}$$

Example 31. *Copper crystallises in face centred cubic lattice and has density of 8.930 g* cm^{-3} *at 293 K. Calculate the radius of Cu-atom. (Atomic mass of Cu = 63.55 u,* $N_A = 6.02 \times 10^{23}$ mol^{-}*.)* **(ISC, 2011)**

Solution. For face centred cubic lattice, $n = 4$; density, $d = 8.930 \text{ g cm}^{-3}$, $\text{N}_\text{A} = 6.02 \times 10^{23} \text{ mol}^{-}$; radius of Cu-atom $= a$.

We know that:

$$d = \frac{n\,M}{Na^3 \times 10^{-30}} \text{ g cm}^{-3} \qquad \text{...(1)}$$

Where M = at. wt. of Cu = 63.55 u

$$\therefore\ 8.930 \text{ g cm}^{-3} = \frac{4 \times 63.55\, u \text{ g cm}^{-3}}{6.02 \times 10^{23} \text{ mol}^{-} \times 10^{-30} \times a^3};$$

$$a^3 = \frac{4 \times 63.55 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-} \times 10^{-30} \times 8.930}$$

Or $a^3 = 47285457$. Taking logs of both sides, we get:

$\log a^3 = \log 47285457$; $3 \log a = 7.6747$

$$\therefore\ \log a = \frac{1}{3} \times 7.6747 = 2.5582 \text{ ; } a = \text{antilog } 2.5582$$

$$= \mathbf{361.6 \text{ pm}}$$

When formula (1) is used, the radius is obtained in pm.

Example 32. *How many unit cells are there (a) in a 2.00 g cube shaped ideal crystal of NaCl ? (b) along each edge of this NaCl crystal ?*

Solution. (a) For cubic shaped NaCl, no. of formula units per unit cell = 4;

g mol wt. of NaCl = 23 + 35.5 = 58.5 g mol^{-};

wt. of NaCl = 2.0 g;

N = 6.023 × 10^{23} formula units of NaCl per mol.

Hence,

No. of unit cells

$$= 2.00 \text{ g} \times \frac{1 \text{ mol}}{58.5 \text{ g}} \times \frac{6.023 \times 10^{23} \text{ formula units}}{1 \text{ mol}} \times \frac{1 \text{ unit}}{4 \text{ formu}}$$

$$\times \frac{1 \text{ unit cell}}{4 \text{ formula units}}$$

$$= \mathbf{5.15 \times 10^{21}} \qquad \textbf{Ans.}$$

(b) No. of unit cells along each edge

$$= (5.15 \times 10^{21})^{1/3}.$$

Solving we have :

$$\log (5.15 \times 10^{21})^{1/3} = \frac{1}{3}[\log 5.15 + \log 10^{21}]$$

$$= \frac{1}{3}[0.7118 + 21] = 7.2373$$

Taking antilog, we get 1.73 × 10^7

$\therefore$ No. of unit cells = $\mathbf{1.73 \times 10^7}$ **Ans.**

Example 33. *Aluminium crystallises in a cubic close packed structure. Its metallic radius is 125 ×* 10^{-12} *m. (a) What is the length of the side of the unit cell ? (b) How many unit cells are there in 1.0* m^3 *of aluminium ?* **(CBSE, 2005)**

Solution. (a) Radius, $r = 125 \times 10^{-12}$ m. For a cubic close packed or face centred cubic structure, $r = \dfrac{a}{2\sqrt{2}}$.

$$\text{Hence, Edge length, } a = 2r \times \sqrt{2}$$

$$= 2 \times 125 \times 10^{-12} \text{ m} \times 1.4142$$

$$= \mathbf{3.5355 \times 10^{-10} \text{ m}}$$

(b) Volume of one unit cell = $a^3 = (3.5355 \times 10^{-10})^3 \text{ m}^3$.
Taking logs, we have :

$$\log (3.5355 \times 10^{-10})^3 = 3\,[\log 3.5355 + \log 10^{-10}]$$

$$= 3\,[0.5484 - 10] = 3\,(-10.5484)$$

$$= 3\,(-9.4516) = -28.3548$$

$$= -28 - 1 + 1 - 0.3548$$

$$= \overline{29}.6452$$

Taking antilog, we get, 4.42 × 10^{-29} m^3.

$\therefore$ No. of unit cells in 1 m^3

$$= \frac{1 \text{m}^3}{4.42 \times 10^{-29} \text{m}^3} = \mathbf{2.62 \times 10^{28}} \quad \textbf{Ans.}$$

Example 34. *Calculate the number of unit cells in 1.5* m^3 *of gold metal if radius of gold metal is 0.1018 nm. Gold has f.c.c. structure.*

Solution. Radius,

$$r = 0.1018 \text{ nm} = 0.1018 \times 10^{-9} \text{ m}$$

For f.c.c. structure,

$$r = \frac{a}{2\sqrt{2}};$$

$$a = 2r \times \sqrt{2} = 2 \times 0.1018 \times 10^{-9} \text{ m} \times 1.4142$$

$$= 0.288 \times 10^{-9} \text{ m}$$

∴ Volume of one unit cell

$$a^3 = (0.288 \times 10^{-9})^3 \text{ m}^3$$

$$= 2.39 \times 10^{-29} \text{ m}^3$$

[∵ log $(0.288 \times 10^{-9})^3$ = 3 (log 0.288 + log 10^{-9}) $= 3(-0.5406 - 9) = -9.5406) = -28.6218 = -28 - 1 + 1 - 0.6218 = \overline{29}.3782$. Taking antilog we have 2.38×10^{-29} m^3]

∴ No. of unit cells in 1.5 cm^3

$$= \frac{1.5 \text{ m}^3}{2.39 \times 10^{-29} \text{ m}^3} = \mathbf{6.3 \times 10^{28}} \quad \textbf{Ans.}$$

Type 2. To calculate number of atoms in a unit cell, use the relation :

$$\text{No. of atoms in a unit cell} = \frac{\text{Mass of unit cell}}{\text{Mass of an atom}}$$

Where mass of unit cell = Volume × Density

$$\text{Mass of an atom} = \frac{\text{Atomic mass}}{\text{Avogadro's number} = 6.023 \times 10^{23}}$$

EXAMPLE 35. *An element crystallises into structure which may be described by a cube type of unit cell having one atom on each corner of the cube and two atoms on one of its diagonals. If the volume of this unit cell is 24 × 10^{-24} cm^3 and density of the element is 7.2 g cm^{-3}, calculate the number of atoms present in 200 g of the element.* **(DSB, 1991)**

SOLUTION. No. of atoms present at the corners $= 8 \times \frac{1}{8} = 1$

No. of atoms present on diagonal = 2

∴ Total no. of atoms present in a given unit cell = 1 + 2 = 3

$$\text{But number of unit cells} = \frac{\text{Volume of element}}{\text{Volume of unit cell}}$$

$$= \frac{\text{Mass of element}}{\text{Density of element} \times \text{Volume of unit cell}}$$

$$= \frac{200\text{g}}{7.2 \text{ g cm}^{-3} \times 24 \times 10^{-24} \text{cm}^3} = 1.157 \times 10^{24}$$

∵ No. of atoms present in one unit cell
= 3 (found above)

∴ No. of atoms present in 1.157 × 10^{24} unit cells = 3 × 1.157 × 10^{24} = **3.471 × 10^{24}** **Ans.**

EXAMPLE 36. *What type of unit cell best describes the NaCl crystal lattice ?*

SOLUTION. In the structure of NaCl, either Na$^+$ or Cl$^-$ can be chosen as lattice points. If we choose Cl$^-$ ions, it is observed that simplest cube arrangement contains a Cl$^-$ ion on the centre of each face as well as at the corners of the unit cell. Hence the unit cell is a *face-centred cube.*

EXAMPLE 37. *Calculate the number of formula units of NaCl in the unit cell;* ***or*** *how many ions each of Na$^+$ and Cl$^-$ are there in a unit cell of NaCl ?*

SOLUTION. The unit cell of NaCl is face-centred cube. Hence :

No. of Cl$^-$ ions at 8 corners $= 8 \times \frac{1}{8} = 1$

No. of Cl$^-$ ions at 6 faces $= 6 \times \frac{1}{2} = 3$

No. of Na$^+$ ions along 12 edges $= 12 \times \frac{1}{4} = 3$

No. of Na$^+$ ions at the cube centre = 1

∴ Total no. of Cl$^-$ ions = 1 + 3 = 4 ;

Total no. of Na$^+$ ions = 3 + 1 = 4

Hence, the number of formula units of NaCl in its unit cell = 4.

EXAMPLE 38. *(i) How many sodium ions and chloride ions are present in a unit cell of sodium chloride ?*

(ii) What is the coordination number of sodium and chloride ions in sodium chloride crystals? **(I.S.C., 2007. 2013)**

SOLUTION. (*i*) The total number of ions per unit cell in sodium chloride structure are 8 (**4 Na$^+$** ions and **4 Cl$^-$** ions) while the number of molecules in unit structure of sodium chloride are four.

(*ii*) In sodium chloride structure, each Na$^+$ ion is surrounded by 6 Cl$^-$ ions which are oriented towards the six corners of the regular octahedron. Similarly, each Cl$^-$ ion is surrounded by 6 Na$^+$ ions. Thus, the coordination numbers of Na$^+$ and Cl$^-$ in a NaCl structure are 6 and 6, respectively.

10.13 CALCULATION OF DENSITY OF CRYSTALLINE SOLIDS

Density of a unit cell

$$= \underset{\text{in a unit cell}}{\text{No. of atoms } (n)} \times \frac{\text{at. wt. of atom or mol. wt. of substance}}{6.023 \times 10^{23} \times a^3}$$

Where *a* = edge length of the unit cell

$$\text{or} \quad \text{Density, } \rho \text{ (or } d) = \frac{n \times \text{at. wt. or mol. wt.}}{6.023 \times 10^{23} \times a^3} \quad \text{...(3)}$$

When density is in g cm^{-3} and edge length (*a*) in Å, convert Å into cm where 1Å = 10^{-8} cm. In such a case

$$d \text{ or } \rho \text{ in g cm}^{-3} = \frac{n \times \text{at. wt. or mol. wt.}}{\text{N} \times (a \text{ in cm})^3}$$

Where N = Avogadro's number.

Note : (1) The calculation *i.e.*, $d = \frac{n\text{M}}{\text{N}a^3 \times 10^{-30}}$ g. cm^{-3} is used when edge length '*a*' is taken in pm and density in g cm^{-3}. (2) 1 g cm^{-3} = 1000 kg m^{-3}. (3) 1 pm = 10^{-2} Å = 10^{-10} cm (4) 1 A° = 100 pm

Example 39. *CaO crystallises is one of the cubic systems having edge of 4.80 A°. Calculate the number of* Ca^{2+} *and* O^{2-} *ions that belong to each unit cell. If density of CaO is 3.35 g cm*$^{-3}$*, also calculate the type of cubic system present.*

Solution. Let n = number of molecules per unit cell; a = 4.80 Å = 4.80 × 10^{-8} cm; molar mass, M of CaO = 40 + 16 = 56 g mol^{-}.

$$d = 3.35 \text{ g cm}^{-3}. \text{ But}$$

$$d = \frac{nM}{N_A a^3} \text{ or } n = \frac{d N_A a^3}{M}$$

or

$$n = \frac{3.35 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{ mol}^{-} \times (4.8 \times 10^{-8} \text{cm})^3}{56}$$

$= 3.98 \simeq 4$

∴ Units of CaO present in one unit cell = 4. Hence, no. of Ca^{2+} ions = 4 and number of oxide ions = 4.

Example 40. *A metal crystallises in f.c.c. lattice. If edge length of the cell is 4.077 ×* 10^{-8} *cm and density is 10.56 g cm*$^{-3}$*, calculate the atomic mass of the metal and also name the metal (at. mass of Cu = 63.5 amu, Ag = 107.76 amu, Na = 23 amu).*

Solution. Edge length,

$$a = 4.077 \times 10^{-8} \text{ cm}$$

$$= 4.077 \times 10^{-8} \text{ cm} \times \frac{1 \text{ pm}}{10^{-10} \text{ cm}}$$

$$= 4.077 \times 10^{2} \text{ pm}$$

Density, ρ = 10.56 g cm^{-3}; at. mass, M = ? For f.c.c. structure, n = 4, N = 6.023 × 10^{23}. We know that :

$$\rho = \frac{n\text{M}}{\text{N}a^3 \times 10^{-30}} \text{g cm}^{-3};$$

$$\text{M} = \frac{\rho \text{N} a^3 \times 10^{-30}}{n}$$

or $$\text{M} = \frac{10.56 \times 6.023 \times 10^{23} \times (4.077 \times 10^2)^3 \times 10^{-30}}{4}$$

= 107.76 amu **Ans.**

This value tallies with at. wt. of Ag. So, the metal is silver.

Example 41. *TlCl (thallous chloride) crystallises in either a f.c.c. or simple cubic lattice of* Cl^{-} *ions with* Tl^{+} *ions in the holes. If the edge length and density of the unit cell are 3.85 Å and 9.0 g cm*$^{-3}$ *respectively, what will be the geometry of the unit cell ? (at. wt. Tl = 204.4, Cl = 35.5).*

Solution. Density, ρ = 9.0 g cm^{-3}; n = ?, edge length,

$$a = 3.85 \text{ Å} = 3.85 \text{ Å} \times \frac{100 \text{ pm}}{1\text{Å}} = 385 \text{ pm}, \text{N} = 6.023 \times 10^{23},$$

M = 204.4 + 35.5 = 239.9. We know that :

$$\rho = \frac{n\text{M}}{\text{N}a^3 \times 10^{-30}} \text{g cm}^{-3}; \; n = \frac{\rho \text{N} a^3 \times 10^{-30}}{\text{M}}$$

or $$n = \frac{9.0 \times 6.023 \times 10^{23} \times (385)^3 \times 10^{-30}}{239.9}$$

$= 1.289 = 1$

Since the value of n = 1, the geometry is simple cubic lattice.

Example 42. *Copper metal crystallises into a f.c.c. lattice with edge length 3.61 ×* 10^{-8} *cm. Show that the calculated density is in agreement with its measured value of 8920 kg m*$^{-3}$*. (atomic mass of Cu = 63.5 amu).*

Solution. Density, ρ = 8920 kg m^{-3} = 8920 kg m^{-3} $\times \frac{1000\text{g}}{1 \text{ kg}} \times \frac{10^{-6}\text{cm}^{-3}}{\text{m}^{-3}}$ = 8.92 g cm^{-3}; for f.c.c. structure, n = 4, N = 6.023 × 10^{23} ; edge length, a = 3.61 × 10^{-8} cm $\times \frac{1\text{pm}}{10^{-10}\text{cm}}$ or a = 3.61 × 10^{2} = 361 pm. We know :

$$\rho = \frac{n\text{M}}{\text{N}a^3 \times 10^{-30}} \text{g cm}^{-3}$$

$$= \frac{4 \times 63.5}{6.023 \times 10^{23} \times (361)^3 \times 10^{-30}} = 8.96 \text{g cm}^{-3}$$

$$= 8.96 \text{g cm}^{-3} \times \frac{1\text{kg}}{1000\text{g}} \times \frac{\text{m}^{-3}}{10^{-6}\text{cm}^{-3}}$$

$$= 8960 \text{ kg m}^{-3}$$

This calculated value agrees well with the given value 8920 kg m^{-3}.

Note : 1 g cm^{-3} = 1000 kg m^{-3}

Example 43. *Calculate the atomic radius in nm of bcc niobium metal (atomic mass, 93U, density = 8550 kg m*$^{-3}$ *or 8.55 g cm*$^{-3}$*;* N_A *= 6.023 ×* 10^{23} *mol*$^{-}$*).* **(CBSE 2008)**

Solution. (*i*) Density, ρ = 8550 kg m^{-3} $\times \frac{1000\text{g}}{1 \text{ kg}} \times \frac{10^{-6}\text{cm}^{-3}}{\text{m}^{-3}}$ = 8.55g cm^{-3}, n = 2 (∵ structure is b.c.c), N = 6.023 × 10^{23}, a = ? We know:

$$\rho = \frac{nM}{Na^3 \times 10^{-30}} \text{g cm}^{-3}; \; a = \left(\frac{nM}{N \rho \times 10^{-30}}\right)^{1/3}$$

or $$a = \left(\frac{2 \times 93}{6.023 \times 10^{23} \times 8.55 \times 10^{-30}}\right)^{1/3}$$

$$= (35303267.3)^{1/3} = (35.3 \times 10^6)^{1/3}$$

Taking log of $(35.3 \times 10^6)^{1/3}$,

we have $\frac{1}{3}$ [log 35.3 + log 10^6]

$$= (35303267.3)^{1/3} = (35.3 \times 10^6)^{1/3}$$

$$= \frac{1}{3} [1.5478 + 6 = 7.5478] = 2.5159$$

Taking antilog, we get, 3.28 × 10^{2} pm = **328 pm**. Hence, a **= 328 pm**

For a b.c.c. unit cell,

$$r = a\frac{\sqrt{3}}{4} = \frac{328 \times 1.732}{4}$$

or $r = 142.0 \text{ pm} = 142\,\text{pm} \times \dfrac{10^{-10}\text{cm}}{1\text{pm}} \times \dfrac{1\text{nm}}{10^{-9}\text{cm}}$

$= \mathbf{14.2\ nm}$

$[\because 1 \text{ pm} = 10^{-10} \text{ cm}; 1 \text{ nm} = 10^{-9} \text{ cm}]$.

Also, 1 pm = 10^{-1} nm. Hence 142 pm = 142 × 10^{-1} nm = **14.2 nm** **Ans.**

EXAMPLE 44. *An element (at. mass = 60) having face centred cubic unit cell has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell ? (Avogadro's constant = 6.023 × 10^{23} mol^{-}.)* **(CBSE, 1992, DSB, 1994, PSEB, 1999)**

SOLUTION. For a cubic unit cell *i.e.*, f.c.c., $n = 4$; density $\rho = 6.23$ g cm^{-3}; edge length of unit cell, a = ?, M = 60. We know that :

$$\rho = \frac{nM}{Na^3 \times 10^{-30}} \text{g cm}^{-3}$$

or $$a = \left(\frac{nM}{\rho\, \text{N} \times 10^{-30}}\right)^{1/3}$$

$$= \left(\frac{4 \times 60 \text{g mol}^{-}}{6.23 \text{g cm}^{-3} \times 6.023 \times 10^{23} \text{mol}^{-} \times 10^{-30} \text{cm}^3}\right)^{1/3} \text{pm}$$

$$= (64 \times 10^6)^{1/3} = [4^3 \times (10^2)^3]^{1/3} = 4 \times 10^2$$

or a = **400 pm** **Ans.**

EXAMPLE 45. *Sodium crystallises in the cubic lattice and the edge of the unit cell is 430 pm. Calculate the number of atoms in a unit cell. (Atomic mass of Na = 23.0 amu, density = 0.9623 g cm^{-3}, N_A = 6.023 × 10^{23} mol^{-}.* **(CBSE, 2001)**

SOLUTION. Edge length, a = 430 pm = 430 × 10^{-10} cm

Volume of unit cell = $a^3 = (430 \times 10^{-10} \text{ cm})^3$

$= 79.5 \times 10^{-24} \text{ cm}^3$

Mass of one atom = $\dfrac{\text{At. wt.}}{6.023 \times 10^{23}} = \dfrac{23}{6.023 \times 10^{23}}$

$= 3.82 \times 10^{-23}$ g

Mass of unit cell = Volume × Density

$= 79.5 \times 10^{-24} \text{cm}^3 \times 0.9623 \text{ g cm}^{-3}$

$= 7.65 \times 10^{-23}$ g

∴ No. of atoms in the unit cell

$$= \frac{\text{Mass of unit cell}}{\text{Mass of an atom}}$$

$$= \frac{7.65 \times 10^{-23}\text{g}}{3.82 \times 10^{-23}\text{g}} = 2 \ \textbf{Ans.}$$

EXAMPLE 46. *Calculate the number of carbon atoms in a unit cell of diamond from the following data. Density of diamond = 3.52 g cm^{-3}; volume of unit cell of diamond = 0.0454 nm^3. The unit cell in a diamond crystal belongs to a cubic crystal system but does not correspond to the Bravais lattice. (At. wt. of C = 12 g mol^{-}).*

SOLUTION. Volume of unit cell of diamond = 0.0454 nm^3 = 0.0454 × (10^{-7}cm)^3 = 0.0454 × 10^{-21} cm^3; ρ = 3.52 g cm^{-3}.

But $$\rho = \frac{nM}{N_A V}$$

$$= \frac{n \times 12\text{g mol}^{-}}{6.022 \times 10^{23} \text{mol}^{-} \times 0.0454 \times 10^{-21} \text{cm}^3}$$

or $$3.52 \text{ g cm}^{-3} = \frac{12n\text{g}}{6.022 \times 10^{23} \times 0.0454 \times 10^{-21} \text{cm}^3}$$

∴

$$n = \frac{3.52\text{g cm}^{-3} \times 6.022 \times 10^{23} \times 0.0454 \times 10^{21} \text{cm}^3}{12} \approx 8 \ \textbf{Ans.}$$

EXAMPLE 47. *The density of aluminium (atomic mass = 27) is 2700 kg m^{-3}. If Al has f.c.c. structure, calculate its atomic radius.*

SOLUTION. Density, ρ of aluminium = 2700 kg m^{-3}

Atomic mass of Al = $\dfrac{27}{1000}$kg

For f.c.c. structure, n = 4

Avogadro's number, N = 6.02 × 10^{23}

Volume of unit cell in m^3 = $\boldsymbol{(am)^3 = a^3\ m^3}$

where a = edge length of unit cell. Hence density $\rho = \left(\dfrac{n\text{M}}{\text{Na}^3}\right)$ kg m^{-3}. Substituting the values, we get :

$$2700 = \frac{(4 \times 27)}{(6.02 \times 10^{23} \times a^3 \times 1000)}$$

or $$a^3 = \frac{(4 \times 27)}{(2700 \times 6.02 \times 10^{23} \times 1000)}$$

or $$a^3 = 66.4 \times 10^{-30}$$

∴ $$a = (66.4 \times 10^{-30})^{1/3}$$

or $$a = 4.05 \times 10^{-10}\text{m}.$$

But for f.c.c. structure,

$$r = \frac{a}{2\sqrt{2}}.$$

Substituting the value of 'a', we get,

$$r = \frac{4.05 \times 10^{-10}\text{m}}{(2 \times 1.414)}$$

or $\boldsymbol{r = 1.432 \times 10^{-10}}$ **m** **Ans.**

EXAMPLE 48. *An element of atomic mass 98.5 g mol^{-} occurs in f.c.c. structure. If its unit cell edge length is 5Å and its density is 5.22 g cm^{-3}, what is the value of Avogadro's constant?* **(DSB, 1997 Comptt.)**

SOLUTION. Atomic mass (M) = 98.5 g mol^{-}

For f.c.c. structure, n = 4

Edge length (a) = 5Å = 5 × 100 pm

= 500 pm

Density, ρ = 5.22 g cm^{-3}

Avogadro's number, N = ?

We know, $$\rho = \frac{n\text{M}}{a^3.\text{N}.10^{-30}}$$

or $$\text{N} = \frac{n\text{M}}{a^3.\rho.10^{-30}}$$

Substituting the values, we get :

$$N = \frac{4 \times 98.5}{(500)^3 \times 5.22 \times 10^{-30}} = 6.03 \times 10^{23}\,\text{mol}^{-} \quad \textbf{Ans.}$$

EXAMPLE 49. *An element crystallises in a structure having f.c.c. unit cell of an edge length 200 pm. Calculate the density if 200 g of this element contains 24 × 10^{23} atoms.*

(CBSE, 1991, PSEB, 1995, HPSB, 1998, ISC, 2011)

SOLUTION. Edge length, a = 200 pm;

For f.c.c. unit cell, n = 4

Density, ρ = ?; M = 200 g

No. of atoms, N = 24 × 10^{23}.

We know that : $\rho = \dfrac{nM}{a^3.N.10^{-30}}$

Substituting the values we get :

$$\rho = \frac{(4 \times 200)}{(200)^3 \times 24 \times 10^{23} \times 10^{-30}}$$

or ρ **= 41.67 g cm^{-3}.** **Ans.**

EXAMPLE 50. *The density of chromium metal is 7.2 g cm^{-3}. If the unit cell is cubic with edge length of 289 pm, determine the type of unit cell (simple body centred or face centred). (atomic mass of Cr = 52 amu, N_A = 6.02 × 10^{23} mol^{-}).*

SOLUTION. Density, ρ = 7.2 g cm^{-3}

Edge length, a = 289 pm

Type of unit cell = ? *i.e.*, n = ?; M = 52

N_A = 6.02 × 10^{23}.

We know that : $\rho = \dfrac{nM}{a^3.N.10^{-30}}$

or $n = \dfrac{\rho.a^3.N.10^{-30}}{M}$

Substituting the values, we get :

$$n = \frac{[7.2 \times (289)^3 \times 6.02 \times 10^{23} \times 10^{-30}]}{52} = \mathbf{2.02 \approx 2}$$

Since, n = 2, the type of unit cell = b.c.c.

EXAMPLE 51. *A metal (atomic mass, 50) has a body centred cubic crystal structure. The density of the metal is 5.96 g cm^{-3}. Find the volume of this unit cell.* **(HPSB, 2001, CBSE, 2001)**

SOLUTION. Atomic mass,

M = 50; n = 2

(∵ unit cell is b.c.c.)

Density, ρ = 5.96 g cm^{-3}

Volume of unit cell = a^3 in cm^3

We know that : $\rho = \dfrac{nM}{a^3.N.}$

or $a^3 = \dfrac{nM}{\rho.N.}$

Substituting the values, we get :

$$a^3 = \frac{(2 \times 50)}{5.96 \times 6.02 \times 10^{23}}$$

= 27.8 × 10^{-24} cm^3 **Ans.**

EXAMPLE 52. *Calculate the volume effectively occupied by a single CsCl ion pair in its crystal (density = 3.988 g cm^{-3}) (at. wt., Cs = 132.9, Cl = 35.5).*

SOLUTION. g mol wt. of CsCl = 132.9 + 35.5 = 168.4 g. One g. mol. wt. of CsCl contain ion pairs = 6.02 × 10^{23}. Also,

$$\text{Volume} = \frac{\text{mass}}{\text{density}}.$$

$$\text{So, Volume} = 1\,\text{CsCl unit} \times \frac{168.4\,\text{g}}{6.02 \times 10^{23}\,\text{pairs}} \times \frac{1\text{cm}^3}{3.988\,\text{g}}$$

= 7.014 × 10^{-23} cm^3 **Ans.**

EXAMPLE 53. *KX crystals have f.c.c. structure. What is the distance between K^+ and X^- in a KX crystal if the density of KX is 2.48 g cm^{-3} ? Molar mass of KX = 58 g mol^{-}; N_A = 6.02 × 10^{23} mol^{-}).*

SOLUTION. Molar mass (M) of

KX = 58 g mol^{-}

N = 6.02 × 10^{23} mol^{-}

Edge length = a

Volume of unit cell = a^3, n = 4

(∵ unit cell is f.c.c.)

$$\text{Mass of unit cell} = \frac{58 \times 4}{6.02 \times 10^{23}} = 3.85 \times 10^{-22}\,\text{g}$$

$$\text{Density } (\rho) \text{ of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$2.48\,\text{g cm}^{-3} = \frac{3.85 \times 10^{-22}\text{g}}{a^3}$$

$$\therefore \quad a^3 = \frac{3.85 \times 10^{-22}\text{g}}{2.48\,\text{g cm}^{-3}}$$

or a^3 = 1.55 × 10^{-24} cm^3

or a = (1.55 × 10^{-24}cm^3)$^{1/3}$

= 5.37 × 10^{-8} cm^3 = 537 pm

Edge length (a) of unit cell in

KX = $2(r_{K^+} + r_{X^-})$

$$\therefore \text{ Distance between } K^+ \text{ and } X^- \text{ ions} = \frac{a}{2} = \frac{537}{2}$$

= 268.5 pm **Ans.**

EXAMPLE 54. *An element of atomic mass 50 occurs is bcc structure with a cell edge of 300 pm. Calculate the Avogadro's number if the density is 6.1 g cm^{-3}.* **(HSB, 2002, CBSE, 2009)**

SOLUTION. Atomic mass, M = 50

n = 2 (∵ unit cell is b.c.c.)

Edge length = 300 pm

Avogadro's number, N = ?

Density, ρ = 6.1 g cm^{-3}

We know that, $\rho = \dfrac{nM}{a^3.N.10^{-30}}$

or, $N = \dfrac{(2 \times 50)}{(300)^3 \times 6.1 \times 10^{-30}}$

= 6.07 × 10^{23} **Ans.**

Example 55. *The compound CuCl has ZnS structure and the edge length of its unit cell is 500 pm. Calculate the density [Atomic masses. Cu = 63, Cl = 35.5, Avogadro's number = 6.023 × 10^{23} mol^{-1}].* **(DSB, 1997 : PSEB, 1999, ISC, 2010)**

Solution. For a cubic unit cell,

$$\rho = \frac{nM}{10^{-30} Na^3} \text{g cm}^{-3}$$

where M = molecular mass of CuCl

= 63 + 35.5 = 98.5 g mol^-

N = Avogadro's number

= 6.203 × 10^{23} mol^-

Where '*a*' is in pm. units,

a = edge length of cube = 500 pm

ρ = density = ?

n = number of atoms per unit cell

= 4 (for ZnS)

Substituting the values, we get,

$$\rho = \frac{4 \times 98.5 \text{g mol}^-}{10^{-30} \times 6.02 \times 10^{23} \text{mol}^{-1} \times (500)^3 \text{cm}^3}$$

$$= \frac{394.0 \text{g mol}^-}{10^{-30} \times 6.02 \times 10^{23} \text{mol}^- \times 125 \times 10^6 \text{cm}^3}$$

$$= \mathbf{5.23\ g\ cm^{-3}}$$

Example 56. *Sodium chloride has f.c.c. structure. Its density is 2.163 × 10^3 kg m^{-3}. Calculate (i) each edge of the cube (ii) interplanar spacing in sodium chloride crystals. M_{NaCl} = 58.45 × 10^{-3} kg mol^-.*

Solution. Density, *d* = (2.163 × 10^3) kg m^{-3} = 2163 kg m^{-3}

Edge length, *a* = ?

Interplanar spacing = ?

For f.c.c. structure, *n* = 4

We know, $\rho = \dfrac{nM}{a^3N}$ or $a^3 = \dfrac{nM}{\rho N}$

Substituting the values, we get :

$$a^3 = \left[\frac{(4 \times 58.45 \times 10^{-3}}{2163 \times 6.02 \times 10^{23}}\right]$$

or

$$a = \left[\frac{(4 \times 58.45 \times 10^{-3}}{2163 \times 6.02 \times 10^{23}}\right]^{1/3}$$

= 564 pm **Ans.**

Interplanar spacing $= \dfrac{a}{2} = \dfrac{564}{2} = \mathbf{282\ pm}$ **Ans.**

Example 57. *Sodium chloride crystallises in face centre cubic (f.c.c.) structure. Its density is 2.165 g cm^{-3}. If the distance between Na^+ and its nearest Cl^- ions is 281 pm, find out the Avogadro's number (Na = 23 g mol^-, Cl = 35.5 g mol^-, molar mass of NaCl = 58.5 g mol^-).* **(CBSE, 2004)**

Solution. For f.c.c. structure, *n* = 4; ρ = 2.165 g cm^{-3}; Edge length, *a* = 2 × inter ionic distance = 2 × 281 pm = 562 pm. We know, $\rho = \dfrac{nM}{Na^3 \times 10^{-30}}$; **or** $N = \dfrac{nM}{\rho a^3 \times 10^{-30}}$ when *a* is in pm. Hence,

$$N = \frac{4 \times 58.5 \text{g mol}^-}{2.165 \text{g cm}^{-3} \times (562)^3 \text{cm}^3 \times 10^{-30}}$$

$$= \mathbf{6.09 \times 10^{23}}$$ **Ans.**

Example 58. *The edge length of a unit cell of a metal having molecular weight 75 g/mol is 5Å. It crystallises in cubic lattice. If the density is 2g/cc, then find the radius of the metal atom. (N_A = 6 × 10^{23}). Give the answer in pm.* **(IIT–JEE, 2006)**

Solution. Density, ρ = 2g/cc; *n* = ?, *m* = 75 g mol^-, N_A = 6.023 × 10^{23} mol^-; *a* = 5 × 10^{-8} cm. But,

$$\rho = \frac{nm}{N_A a^3}$$

$$n = \frac{\rho N_A a^3}{m} = \frac{2 \times 6.023 \times 10^{23} \times (5 \times 10^{-8}\text{cm})^3}{75}$$

$$= \frac{2 \times 6.023 \times 10^{23} \times 125 \times 10^{-24}}{75} = 2$$

Since *n* = 2, the element will have b.c.c structure. For b.c.c structure :

$$\text{Atomic radius} = a \times \frac{\sqrt{3}}{4} = 5 \times 10^{-8} \text{cm} \times \frac{1.732}{4}$$

= 2.165 × 10^{-8} cm

$$= 2.165 \times 10^{-8} \text{ cm} \times \frac{1 \text{pm}}{10^{-10} \text{cm}}$$

= 216.5 pm **Ans.**

Example 59. *If Ca crystallises in a f.c.c. unit cell with a = 0.556 nm, find its density if it contain (i) 0.1%. Frankel defect and (ii) 0.1% Schottky defect.*

Solution. For f.c.c. unit cell, Z = 4. In Frankel defect, the atom occupies interstitial position but not the lattice position. So, in this defect case, density does not change. But in case of Schottky defect.

$$Z = 4 \times \left(1 - \frac{0.1}{100}\right) = 3.996. \text{ But density, } d = \frac{ZM}{N \times a^3}$$

(*i*) *a* = 0.556 nm = 0.556 × 10^{-9} m = 0.556 × 10^{-7} cm

∴ For Frankel defect,

$$d = \frac{4 \times 40}{6.023 \times 10^{23} \times (0.556 \times 10^{-7})^3}$$

= 1.5463 g cm^{-3}

(*ii*) For Schottky defect,

$$d = \frac{3.996 \times 40}{6.023 \times 10^{23} \times (0.556 \times 10^{-7} \text{cm})^3}$$

= 1.5448 g cm^{-3} Ans.

10.14 CO-ORDINATION NUMBER AND RADIUS RATIO

Radius Ratio : *In case of ionic* solids, the ratio of radius of cation to radius of anion is called **radius ratio**. Mathematically :

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r^+}{r^-}$$

The relationship between radius ratio (r^+/r^-), coordination number and structural arrangement is given in the following table.

Radius ratio (r^+/r^-)	*Coordination no.*	*Structure*	*Examples*
0.155 – 0.225	3	Triangular	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS, BaS, HgS, CuCl, CuBr, CuI
0.414 – 0.732	6	Octahedral	NaCl, NaBr, KBr, MgO, CaO, MnO
0.732 – 1	8	Cubic	NH_4Br, CsCl, CsBr, CsI, TlBr

EXAMPLE 60. *The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. Predict the structure of Na^+Cl^- and coordination number of cation.*

SOLUTION. Radius of Na^+ ion

= 95 pm; Radius of Cl^- ion = 181 pm

Thus, radius ratio of Na^+ and Cl^- ions

$$= \frac{95}{181} = 0.524\,\text{pm}$$

This value (0.524 pm) falls within the range, 0.414 to 0.732. Hence Na^+Cl^- has octahedral structure and coordination number, **6** **Ans.**

EXAMPLE 61. *Lithium crystallises in b.c.c. structure and the atoms that lie along the body diagonal (the line between opposite corners of the cube) are touching so that body diagonal is four times the radius of the Li-atom. If the edge length of the unit cell is 353 pm, what is the radius of Li-atom ?*

SOLUTION. For b.c.c. structure, body diagonal (d = 2 × distance between nearest neighbours = 2 × ($a\sqrt{3}$ /2)

$$= a\sqrt{3} = 1.732a.$$

But unit edge length, a = 353 pm

So, $d = 1.732 \times 353\,\text{pm} = 611.396\,\text{pm}$

Let, r = radius of Li-atom

Since, $d = 4r$ (given)

Substituting the value of d in $d = 4r$,

we have : 611.396 pm = $4r$.

Hence $$r = \frac{611.396}{4}$$

$\approx$ **152.8** **Ans.**

EXAMPLE 62. *A solid AB has the NaCl structure. If the radius of cation A^+ is 150 pm, calculate the maximum possible value of the radius of the anion, B^-.* **(DSB, 1996)**

SOLUTION. NaCl has octahedral structure. So, its radius ratio value lies between 0.414 to 0.732.

Radius of cation, A^+ = 150 pm

$$\text{Radius of } B^- = \frac{150}{0.414} = 362.3\,\text{pm}$$

$$\text{Radius of } B^- = \frac{150}{0.732} = 204.9\,\text{pm}$$

So, the maximum radius of

B^- = 362.3 pm **Ans.**

EXAMPLE 63. *Calculate the radius ratio, r^+/r^- and the coordination number of Li^+ and F^- ions in LiF crystal structure from the following data. r_{Li^+} = 60 pm; r_{F^-} = 136 pm.* **(CBSE, 1990)**

SOLUTION. Radius of Li^+ = 60 pm

Radius of F^- = 136 pm

Hence,

$$\text{Radius ratio, } \frac{r_{Li^+}}{r_{F^-}} = \frac{60}{136} = 0.441$$

This value (0.441) falls within the range, 0.414 and 0.732. Hence, the coordination number of Li^+ and F^- = **6 each.** **Ans.**

EXAMPLE 64. *Solid X^+Y^- has f.c.c. structure like NaCl. If the radius of cation is 100 pm, what is the radius of anion ?* **(CBSE, 1996)**

SOLUTION. Since X^+Y^- has NaCl structure, X^+ will occupy octahedral void while anion Y^- will occupy c.c.p structure. For octahedral coordination,

$$\frac{r^+}{r^-} = 0.732 \text{ to } 0.414$$

(*i*) $$\frac{r^+}{r^-} = 0.732 \text{ Or } \frac{100\,\text{pm}}{r^-} = 0.732$$

Or $$r^- = \frac{100\,\text{pm}}{0.732} = 136.6\,\text{pm}$$

(*ii*) $$\frac{r^+}{r^-} = 0.414 \text{ Or } \frac{100\,\text{pm}}{r^-} = 0.414$$

Thus, $$r^- = \frac{100\,\text{pm}}{0.414} = 241.5\,\text{pm}$$

So, the radius of anion lies between 136.6 pm to 241.5 pm. **Ans.**

EXAMPLE 65. *The ionic radii of Na^+ and Cl^- are 95 and 181 pm respectively. What is the edge length of the unit cell ?*

SOLUTION. Edge length, $a = 2(r_{Na^+} + r_{Cl^-})$

$= 2\,(95 + 181)$ pm $= 2 \times 276$

= 552 pm **Ans.**

EXAMPLE 66. *What is the distance between Na^+ and Cl^- in a NaCl crystal if its density is 2.165 g cm^{-3} ? NaCl crystallises in the f.c.c. lattice.* **(PSEB, 2001)**

SOLUTION. Distance between Na^+ and Cl^- = $\frac{a}{2}$ = ?

density, ρ = 2.165 g cm^{-3}

mol. wt. of NaCl = 23 + 35.5 = 58.5 = M

n = 4

($\because$ NaCl crystallises in f.c.c. lattice)

We know that,

$$2(r_{Na^+} + r_{Cl^-}) = a$$

Also, $$\rho = \frac{n\text{M}}{a^3.\text{N}.10^{-30}};\quad a^3 = \frac{n\text{M}}{\rho.\text{N}.10^{-30}}$$

Substituting the values, we get :

$$a^3 = \frac{4 \times 58.5}{2.165 \times 6.02 \times 10^{23} \times 10^{-30}}$$

$$\text{Or} \qquad a = \left[\frac{(4\times 58.5)}{2.165\times 6.02\times 10^{23}\times 10^{-30}}\right]^{1/3}$$

$$= 564.17 \simeq 564 \text{ pm}$$

$$\text{But} \quad 2(r_{Na^+} + r_{Cl^-}) = 564 \text{ pm}$$

$$\text{Hence,} \quad r_{Na^+} + r_{Cl^-} = \frac{564}{2}$$

$$= \mathbf{282\ pm} \qquad \textbf{Ans.}$$

EXAMPLE 67. *Lead (II) sulphide crystal has NaCl structure. What is the distance between Pb^{2+} and S^{2-} in PbS if its density is 12.7g cm^{-3} ? (at. mass of Pb = 207).* **(PSEB., 2001, ISC, 2010)**

SOLUTION. Distance between Pb^{2+} and $S^{2-} = \frac{a}{2} = ?$

$$\text{Density, } \rho = 12.7 \text{ g cm}^{-3}$$

$$\text{Mol. wt. (M) of PbS} = 207 + 32 = 239$$

$$n = 4 \quad (\because \text{ PbS has NaCl structure})$$

We know that :

$$2(r_{Pb^{2+}} + r_{S^{2-}}) = a$$

$$\text{Also,} \qquad \rho = \frac{nM}{a^3 . N . 10^{-30}}$$

$$\text{Or} \qquad a^3 = \frac{nM}{\rho N \times 10^{-30}}$$

Substituting the values, we get :

$$a^3 = \frac{(4\times 239)}{12.7\times 6.02\times 10^{23}\times 10^{-30}}$$

$$\text{Or} \qquad a = \left[\frac{(4\times 239)}{12.7\times 6.02\times 10^{23}\times 10^{-30}}\right]^{1/3}$$

$$\text{Or} \qquad a = 500 \text{ pm}$$

$$\text{But,} \quad 2(r_{Pb^{2+}} + r_{S^{2-}}) = 500 \text{ pm}$$

$$\text{Or} \qquad r_{Pb^{2+}} + r_{S^{2-}} = \frac{500}{2} = \mathbf{250\,pm} \qquad \textbf{Ans.}$$

EXAMPLE 68. *A compound X_2Y has ZnS structure. Calculate the edge length of unit cell if its density is 3.4 g cm^{-3}. (At. wt. of X = 32, Y = 35).* **(ISC, 2012)**

SOLUTION. Let a = edge length of unit cell, density, $\rho = 3.4$ g cm^{-3}, molar mass of X_2Y = (2 × 32) + 35 = 99; for ZnS, n = 4. We know :

$$\rho = \frac{nM}{N_A \times a^3} \quad \text{Or} \quad a = \left(\frac{nM}{N_A\rho}\right)^{1/3} = \left[\frac{4\times 99}{6.02\times 10^{23}\times 3.4}\right]^{1/3}$$

$$= (1.9347\times 10^{-22})^{1/3} = 5.78 \times 10^{-8} \text{ cm} = \mathbf{5.78\ Å} \quad \textbf{Ans.}$$

EXAMPLE 69. *In a cubic solid of alkali metal chloride MCl (B.C.C structure), the eight corners are occupied by Cl^-, with a M^+ at the centre and vice-versa. Calculate the radius ratio of M^+ and Cl^-. Given density of MCl = 3.97 g/cc. Also, calculate the distance between the neighbouring M^+ and Cl^-. (At. wt. of M = 133, Cl = 35.5).*

SOLUTION. d = 3.97 g cm^{-3}; mol. wt. = 133 + 35.5 = 168.5 g mol^-; edge length = a. From the given data it is clear that there is one M^+ and one Cl^- *i.e.*, one MCl ion pair. So, n = 1. We know:

$$\rho = \frac{nM}{N_A . a^3}$$

$$\text{Or} \qquad 3.97 = \frac{1\times 168.35}{6.022\times 10^{23}\times a^3}$$

$$\text{Or} \qquad a^3 = \frac{168.35}{3.97\times 6.022\times 10^{23}}$$

$$\therefore \qquad a = \left[\frac{168.35}{3.97\times 6.022\times 10^{23}}\right]^{1/3}$$

$$= 4.13 \times 10^{-8} \text{ cm}$$

$$= 4.13 \text{ Å} = \text{side length of cube}$$

$$\therefore \qquad \text{Diagonal} = a\sqrt{3} = 4.13\times 1.732 = 7.15\,\text{Å}$$

Since MCl has B.C.C structure, with M^+ at centre (of radius r^+) and Cl^- at corner (of radius r^-), we have :

$$2r^+ + 2r^- = 7.15 \text{ Å}$$

$$\text{Or} \qquad 2\,(r^+ + r^-) = 7.15 \text{ Å}$$

$$\text{Or} \qquad r^+ + r^- = \frac{7.15}{2} = 3.57\,\text{Å}$$

∴ Distance between

$$M^+ \text{ and } Cl^- = 3.57 \text{ Å}$$

Suppose two Cl^- ions touch each other. So, length of unit cell,

$$2r^- = 4.13 \text{ Å}$$

$$\textbf{Or} \qquad r^- = \frac{4.13\text{Å}}{2} = \mathbf{2.065Å.}$$

$$\text{Thus,} \qquad r^+ = (r^+ + r^-) - r^- = 3.57 - 2.065$$

$$= 1.505\text{Å}$$

$$\text{Hence,} \qquad \frac{r^+}{r^-} = \frac{1.505}{2.065}$$

$$= \mathbf{0.729Å} \qquad \textbf{Ans.}$$

EXAMPLE 70. *Sodium chloride crystallises in the same type of lattice as KCl. If $\frac{r_{Na^+}}{r_{Cl^-}}$ and $\frac{r_{Na^+}}{r_{K^+}}$ are 0.5 and 0.7 respectively, what will be (a) the density of NaCl to that of KCl and (b) the ratio of the side of the unit cell for KCl to that of NaCl ? (At. wt. Na = 23, Cl = 35.5, K = 39).*

SOLUTION. Let a = edge length of unit cell. Since $\frac{r_{Na^+}}{r_{Cl^-}} = 0.5, r_{Na^+} = 0.5\,r_{Cl^-}$. Since NaCl crystallises in f.c.c. unit cell, $r_{Na^+} + r_{Cl^-} = \frac{a}{2}$.

$$\text{Also,} \qquad \frac{r_{Na^+}}{r_{Cl^-}} = \frac{0.5}{1} \text{ (given)}$$

$$\text{Thus,} \qquad \frac{r_{Na^+} + r_{Cl^-}}{r_{Cl^-}} = \frac{1+0.5}{1} = \frac{1.5}{1} \qquad ...(1)$$

$$\text{But,} \qquad \frac{r_{K^+}}{r_{Na^+}} = \frac{1}{0.7}$$

Thus, $\dfrac{r_{K^+}}{0.5\,r_{Cl^-}} = \dfrac{1}{0.7}$ or $\dfrac{r_{K^+}}{r_{Cl^-}} = \dfrac{0.5}{0.7} = \dfrac{5}{7}$

Hence, $\dfrac{r_{K^+} + r_{Cl^-}}{r_{Cl^-}} = \dfrac{5+7}{7} = \dfrac{12}{7}$ ...(2)

Dividing (1) and (2), we get

$$\frac{\dfrac{(r_{K^+} + r_{Cl^-})}{Cl^-}}{\dfrac{(r_{Na^+} + r_{Cl^-})}{Cl^-}} = \frac{12}{7} \times \frac{1}{1.5} \quad \text{or} \quad \frac{\dfrac{a_{KCl}}{2}}{\dfrac{a_{NaCl}}{2}} = \frac{12}{7 \times 1.5}$$

or $\dfrac{a_{KCl}}{a_{NaCl}} = \dfrac{1.143}{1}$

= ratio of the side of unit cell for KCl to that of NaCl.

But $\rho = \dfrac{nM}{a^3 N_A}$

$\therefore$ For NaCl, $\rho_{NaCl} = \dfrac{n \times 58.5}{a^3_{NaCl} \times N_A}$ ...(3)

[$\because$ Mol. wt. of NaCl = 23 + 35.5 = 58.5]

For KCl, $\rho_{KCl} = \dfrac{n \times 74.5}{a^3_{KCl} \times N_A}$ ...(4)

[$\because$ Mol. wt. of KCl = 39 + 35.5 = 74.5]

Dividing (3) and (4), we get :

$$\frac{\rho_{NaCl}}{\rho_{KCl}} = \frac{a^3_{KCl}}{a^3_{NaCl}} \times \frac{58.5}{74.5} = (1.143)^3 \times \frac{58.5}{74.5}$$

= 1.172 **Ans.**

Example 71. *The crystal of Fe (II) O has cubic structure and density equal to 4 g cm^{-3}. If each edge of the unit cell is 5Å, calculate the number of O^{2-} and Fe^{2+} ions present in each unit cell of iron (II) oxide. (At. wt. Fe = 56, O = 16)*

(MP PET, 2000)

Solution. Density of Fe (II) O = 4 g cm^{-3}; Volume of unit cell = (5Å)^3 = (5 × 10^{-8}cm)^3 = 1.25 × 10^{-22} cm^3. Hence :

Mass of unit cell = Volume × Density

= (1.25 × 10^{-22}cm^3) × (4 g cm^{-3})

= 5 × 10^{-22} g.

$\therefore$Mass of one molecule of

Fe (II) O = $\dfrac{\text{Molar mass in gram}}{\text{Avogadro's number}}$

$= \dfrac{72\,\text{g mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-}} = 1.196 \times 10^{-22}$

[$\because$ Molar mass of FeO = 56 + 16 = 72 g mol^{-}]

Hence number of FeO molecules (*i.e.*, Fe^{2+} and O^{2-} ions each) per unit cell

$= \dfrac{5 \times 10^{-22}}{1.196 \times 10^{-22}}$ **= 4.18 ≈ 4.** **Ans.**

Example 72. *Composition of sample of wurtzite is $Fe_{0.93}O_{1.0}$. What percentage of iron is present in the form of Fe (III) ?*

(HPSB, 2002)

Solution. $Fe_{0.93}O_{1.0}$ is a non-stoichiometric compound and contains mixture of Fe^{2+} and Fe^{3+} ions. Let x atoms of Fe^{3+} ions are present in the compound. This means that xFe^{2+} ions have been replaced by Fe^{3+} ions. No. of Fe^{2+} ions in the compound = 0.93 – x. For electrical neutrality, total positive charge on the compound = total negative charge on the compound

$\therefore$ 2 (0.93 – x) + 3x = 2 or 1.86 + x = 2 or x = 0.14

$\therefore$ %age of Fe^{3+} ion = $\dfrac{(0.14 \times 100)}{0.93}$

= 15.05% **Ans.**

Example 73. *An analysis shows that nickel oxide has the formula $Ni_{0.98}O$. Calculate the fractions of Ni^{2+} and Ni^{3+} present in it.*

Solution. $Ni_{0.98}O$ means that for 98 Ni-atoms, 100 O-atoms are present. Let x = Ni^{2+} ions present out of 98 Ni-atoms.

$\therefore$ No. of Ni^{3+} ions = 98 – x

$\therefore$ Total charge on x Ni^{2+} and (98 – x) Ni^{3+}

= Total charge on 100 O^{2-} ions

$\therefore$ (2 × x) + 3 × (98 – x) = 100 × 2; 2x + 294 – 3x

= 200; or x = 94

$\therefore$ Fraction of Ni present as

Ni^{2+} = (94/98) × 100 = 95.9% and

Fraction of Ni present as

Ni^{3+} = (4/98) × 100 = 4.1%

Example 74. *If NaCl is doped with 10^{-3} mol % SrCl$_2$, what is the concentration of cation vacancies ?* **(CBSE 1986)**

Solution. Doping of NaCl with 10^{-3} mol % SrCl$_2$ means that 100 moles of NaCl are doped with 10^{-3} mol of SrCl$_2$. Thus, one mole of NaCl is doped with SrCl$_2$ $= \dfrac{10^{-3}}{100} = 10^{-5}$ mol. As each Sr^{2+} ion introduces one cation vacancy, therefore, concentration of cation vacancies = 10^{-5} mol/mol of NaCl = 10^{-5} × 6.02 × 10^{23} cation vacancies mol^{-} **= 6.02 × 10^{18} cation vacancies mol^{-}.** **Ans.**

10.15 CRYSTALLOGRAPHIC AXES

In a cubic crystal, the axes selected are the three lines mutually at right angles to each other. The three lines thus selected meeting at a point, are called crystallographic axes. A suitable plane that cuts all the crystallographic axes is called **unit plane.**

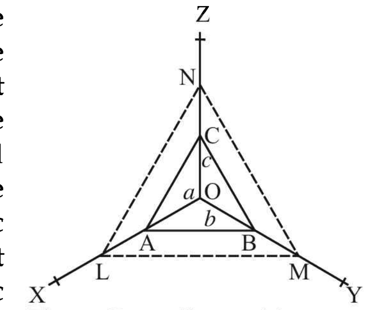


Fig 3. Crystallographic axes

Let OX, OY and OZ are crystallographic axes while ABC is a unit plane that cuts the three axes at A, B and C respectively. Let unit intercepts are OA = a, OB = b and OC = c. The ratio $a : b : c$ is called **axial ratio**. The law of rationality of indices or intercepts were proposed by Hany which states that it is possible to choose along the three crystallographic axes unit distance (a, b, c) not necessarily of the same length such that the intercepts of any face of a crystal along the three crystallographic axes are either equal to unit intercepts (a, b, c) or simply whole number multiples of them *e.g.*, na, $n'b$, $n''c$ *etc., where* n, n', n'' etc., are simple whole numbers. In the Fig. 3, the unit intercepts are a, b and c and the intercepts made by the face LMN are $2a$, $2b$ and $2c$ which are simple whole number multiples of those of the unit plane.

The co-efficients of a, b, c (n, n', n'') are called Weiss indices of plane. These indices are not always simple integral whole numbers and may have fractional values as well as infinity. So, Weiss indices are replaced by **Miller indices.**

10.16 MILLER INDICES

These are a set of integers (h, k, l) which are used to describe a given plane in a crystal. These are obtained by taking the reciprocal of Weiss indices and multiplying throughout by the LCM (least common multiple) in order to make reciprocals as integers. These are the integers which give the ratio of the intercepts of the unit plane to those of the given face *i.e.*, the ratio $\frac{a}{na} : \frac{b}{n'b} : \frac{c}{n'c}$ expressed integers. Miller indices of a face are inversely proportional to the intercepts of that face on the crystallographic axes.

If d_{hkl} represents distances between the parallel planes in a crystal, then for different cubic lattices, these interplanar spacings are given by the relation :

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$ where h, k and l are the miller indices of a plane and a = length of the cube side.

EXAMPLE 75. *Calculate the Weiss and miller indices of crystal planes which cut through the crystal axes at 2a, 3b, c.*

SOLUTION. The unit cell intercepts are a, b, c

Intercepts	$2a$	$3b$	c
Weiss indices	2	3	1
Reciprocal of Weiss indices	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{1}$

LCM of 2, 3, 1 = 6

$\therefore$ Miller indices are : $\frac{1}{2} \times 6 = \mathbf{3};\ \frac{1}{3} \times 6 = \mathbf{2};\ \frac{1}{1} \times 6 = \mathbf{6}.$

So, miller indices are (3, 2, 6).

EXAMPLE 76. *The planes in crystalline solid, intersect the crystal axes as (i) (2a, 2b, 3c), (ii) (a, –2b, 3c). Calculate the Weiss and the miller indices for these planes.*

SOLUTION.

Intercepts	(i) $2a$,	$2b$,	$3c$,
Weiss indices	2	2	3
Reciprocal of Weiss indices	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{3}$

LCM of 2, 2, 3 = 6

Miller indices : $\left(\frac{1}{2} \times 6 = \mathbf{3}; \frac{1}{2} \times 6 = \mathbf{3};\ \frac{1}{3} \times 6 = \mathbf{2}\right)$;

or (3 3 2)

	(ii) a,	$-2b$,	$3c$
	1	-2	3
	$\frac{1}{1}$	$\frac{1}{-2}$	$\frac{1}{3}$

LCM of 1, 2, 3 = 6

Miller indices : $\left(\frac{1}{1} \times 6 = \mathbf{6}; \frac{1}{-2} \times 6 = \bar{\mathbf{3}}; \frac{1}{3} \times 6 = 2\right)$

or $(6\ \bar{3}\ 2)$

EXAMPLE 77. *KCl crystallises with a b.c.c lattice. Calculate the distance between the 110, 200 and 222 planes. The length of the side of the unit cell is 534 pm.*

SOLUTION. We know,

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

$\therefore$ For 110 plane :

$$d_{110} = \frac{534\text{ pm}}{(1^2 + 1^2 + 0^2)^{1/2}} = \frac{534\text{ pm}}{\sqrt{2}(= 1.4142)} =$$

$$\mathbf{= 377.6\ pm}$$

For 200 plane : $d_{200} = \frac{534\text{ pm}}{(2^2 + 0^2 + 0^2)^{1/2}} = \frac{534\text{ pm}}{(4)^{1/2}\ i.e., 2} =$

$$\mathbf{= 267\ pm}$$

For 222 plane : $d_{222} = \frac{534\text{ pm}}{(2^2 + 2^2 + 2^2)^{1/2}} = \frac{534\text{ pm}}{(12)^{1/2}} = 534\text{ pm}$

$= \frac{534\text{ pm}}{3.46} = \mathbf{154.3\ pm}$ **Ans.**

EXAMPLE 78. *In what ratio, the spacings of three planes 100, 110 and 111 of a cubic lattice vary with each other ?*

SOLUTION. We know,

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{1/2}}$$

For 100 plane : $d_{100} = \frac{a}{(1^2 + 0^2 + 0^2)^{1/2}} = \frac{a}{1} = a$

For 110 plane : $d_{110} = \frac{a}{(1^2 + 1^2 + 0^2)^{1/2}} = \frac{a}{\sqrt{2}} = \quad =$

$= \frac{a}{1.4142} = 0.70711a$

For 111 plane : $d_{111} = \frac{a}{(1^2 + 1^2 + 1^2)^{1/2}} = \frac{a}{(3)^{1/2}} = \quad =$

$$= \frac{a}{1.732} = 0.5774a$$

∴ Ratio of

$$d_{100} : d_{110} : d_{111} = a : 0.70711a : 0.5774\,a$$
$$= \mathbf{1 : 0.70711 : 0.5774} \quad \textbf{Ans.}$$

Example 79. *The first order reflection from (100), (110) and (111) faces of sodium chloride using monochromatic X-rays are 5.9°, 8.4° and 5.2° respectively. Predict the crystal structure of sodium chloride.*

Solution. For first order reflection, $n = 1$; Bragg equation, $\frac{n\lambda}{2\sin\theta} = d$. By using Bragg's equation, the ratios of interplanar distances parallel to (100), (110) and (111) planes can be calculated as : $d_{100} : d_{110} : d_{111}$.

$$= \frac{1\times\lambda}{2\sin 5.9} : \frac{1\times\lambda}{2\sin 8.4} : \frac{1\times\lambda}{2\sin 5.2};$$

$$\frac{1}{\sin 5.9} : \frac{1}{\sin 8.4} : \frac{1}{\sin 5.2}$$

$$= \frac{1}{0.103} : \frac{1}{0.146} : \frac{1}{0.0906}$$

$$= 9.709 : 6.849 : 11.038$$

$$= \frac{9.709}{9.709} : \frac{6.849}{9.709} : \frac{11.038}{9.709};$$

$$\mathbf{1 : 0.705 : 1.14} \quad \textbf{Ans.}$$

Example 80. *The interplanar distance in a crystal used for X-ray diffraction is 3.98 Å. Calculate the angle at which second order reflection will take place in an X-ray spectrometer when X-rays of wave length 1.48 Å are diffracted by atoms of a crystal.*

Solution. Using Bragg equation,

we have : $n\lambda = 2d \sin\theta;\ \theta = \sin^{-}\left(\frac{n\lambda}{2d}\right)$

Here $n = 2$ (∵ it is a second order diffraction)

$\lambda = 1.48$Å ; $d = 3.98$Å. Substituting the values,

we get : $\theta = \sin^{-}\left(\frac{2\times 1.48\text{Å}}{2\times 3.98\text{Å}}\right)$

$$= \sin^{-} 0.372 = 21.8°$$

But, 1° = 60′. Hence 0.8° = 60 × 0.8 = 48′

∴ $\theta = \mathbf{21°48'}$ **Ans.**

10.17 STRUCTURE DETERMINATION BY X-RAY DIFFRACTION

When a beam of X-rays strikes a crystal plane composed of regularly arranged atoms or ions, the X-rays get diffracted. Waves from diffracted X-rays may interfere (and destroy each other) or reinforce each other producing constructive interference.

10.17.1. BRAGG'S EQUATION

By analysing the diffraction patterns, the interplanar distance (d) can be determined with the help of Bragg's equation

$$n\lambda = 2d \sin\theta$$

where, n = positive integer (1, 2, 3...) which stands for serial order of diffracted beams. It is called order of reflection. If $n = 1$, $n = 2$ etc., the order of reflection is 1, 2 etc., respectively.

d = Interplanar distance of constituent particles in a crystal.

2θ = Angle between the diffracted beam and the direction of incident X-ray beam

λ = Wave length of X-ray used.

Since interplanar distance varies from crystal to crystal, the type of crystal structure can be established by the use of Bragg's equation.

Note: For values of sin θ, sin¯ θ etc, see appendix (*v*) at the end of the book.

Example 81. *Calculate the angle of diffraction for a first order diffraction from a crystal for which inter planar distance is 0.300 nm and the wavelength of X-rays is 0.1063 nm.*

Solution. Angle of diffraction,

$$\theta = ?\ n = 1$$

Interplanar distance,

$$d = 0.300\,nm = 300 \times 10^{-9} m$$

$$\text{Wavelength, } \lambda = 0.1063\,nm = 0.1063 \times 10^{-9}\,m$$

According to Bragg's equation,

$$n\lambda = 2d \sin\theta$$

$$\text{Or} \quad \sin\theta = \frac{n\lambda}{2d} = \frac{1\times 0.1063\times 10^{-9} m}{2\times 0.300\times 10^{-9} m} = 0.1771.$$

$$\text{Thus,} \quad \theta = \sin^{-} 0.1771;\ \theta = 10.20$$

$$\text{or} \quad 2\theta = \mathbf{20.4°} \quad \textbf{Ans.}$$

Example 82. *A sample of crystalline solid scatters beam of X-rays of wavelength 70.93 pm at an angle of 2θ of 14.66°. If this is a second order reflection (n = 2), calculate the distance between the parallel planes of atoms from which the scattered beam appears to have been reflected.*

Solution. Given; $2\theta = 14.66°$ or $\theta = 7.33°$

$$\text{But,} \quad n\lambda = 2d \sin\theta,\ \lambda = 70.93 \text{ pm}$$
$$= 70.93 \times 10^{-12} m$$

$$\text{Hence,} \quad d = \frac{n\lambda}{2\sin\theta} = \frac{2\times 70.93\times 10^{-12} m}{2\sin 7.33} = \frac{70.93 \quad 10}{}$$

$$= \frac{70.93\times 10^{-12} m}{0.1275}$$

$$= 556.3\times 10^{-12} m = \mathbf{556.3\,pm} \quad \textbf{Ans.}$$

Example 83. *Calculate the wavelength of the X-rays which give a diffraction angle 2θ equal to 16.80° for a first order diffraction in case of a crystal for which interplanar distance is 0.200 nm.*

Solution. Wave length,

$$\lambda = ?\ 2\theta = 16.80° \text{ or } \theta = 8.40°,\ n = 1;$$
$$d = 0.200\,nm = 0.200 \times 10^{-9} m$$

According to Bragg's equation,

$$n\lambda = 2d \sin\theta$$

$$\text{Or} \quad \lambda = \frac{2d \sin\theta}{n}$$

Substituting the values, we get :

$$\lambda = 2 \times 0.200 \times 10^{-9} m \sin 8.40°$$
$$= 2 \times 0.200 \times 10^{-9} m \times 0.1461$$
$$= \mathbf{5.84 \times 10^{-11} m} \qquad \textbf{Ans.}$$

EXAMPLE 84. *A crystalline substance X^+Y^- has NaCl type close packed structure. If Y^- anion has a radius of 250 pm, what will be the ideal radius of cation, X^+. Can a cation A^+ of radius 110 pm be slipped into the tetrahedral hole of the crystal X^+Y^-? Explain also.*

SOLUTION. In a NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions and vice-versa. So, Na^+ ion is placed in an octahedral hole or void.

For octahedral hole,

limiting radius ratio = 0.414

$$\therefore \quad \frac{\text{radius of cation, } r^+}{\text{radius of anion, } R^-} = 0.414; \quad \frac{r^+}{250\,\text{pm}} = 0.414$$

∴ Ideal radius (r^+) of

$$X^+ = 0.414 \times 250 \text{ pm} = \mathbf{103.5\ pm}$$

For a tetrahedral hole, limiting radius ratio = 0.225

$$\therefore \quad \frac{r^+}{R^-} = 0.225\ ; \quad \frac{r^+}{250\,\text{pm}} = 0.225$$

or $\quad r^+ = 0.225 \times 250 \text{ pm} = 56.25 \text{ pm}.$

The ideal radius for cation for tetrahedral hole is 56.25 pm. But the radius of cation A^+ to be slipped in the tetrahedral hole is 110 pm. Since 110 pm radius is much larger than 56.25 pm, A^+ cation cannot be slipped into tetrahedral hole.

Type. When a beam of electrons undergo diffraction by crystals, use, $\lambda = \frac{hc}{eV}$ where $\frac{hc}{e} = 12400 Å$.

EXAMPLE 85. *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 1.54Å.*

(IIT, 1997)

SOLUTION. Potential, $V = ?;\ \frac{hc}{e} = 12400 Å;\ \lambda = 1.54 Å.$

We know,

$$\lambda = \frac{hc}{eV}; V = \frac{hc}{e\lambda}; \quad = \qquad = 8051.9$$

$$V = \frac{12400}{1.54} = 8051.9\,V$$

Or $\quad V = \frac{8051.9}{1000} kV$

$$= \mathbf{8.05\ kV} \qquad \textbf{Ans.}$$

EXAMPLE 86. *The structure of an ionic compound X^+Y^- has ZnS type structure. If radius of X^+ is 100 pm, calculate the ideal radius of Y^-. If radius of X^+ is enlarged by some special technique to 225 pm, in which type of the structure would XY crystallise and what would be its co-ordination number ?*

SOLUTION. (*i*) $r_{X^+} = 100$ pm; $r_{Y^-} = ?$

For the given type of compound :

$$\frac{r_{X^+}}{r_{Y^-}} = 0.225 \text{ (ideal value)}$$

$$\therefore \quad r_{Y^-} = \frac{r_{X^+}}{0.225} = \frac{100\,\text{pm}}{0.225} = 444.4\,\text{pm}$$

(*ii*) New radius of

$$X^+ = 225 \text{ pm}$$

$$\therefore \quad \frac{r_{X^+}}{r_{Y^-}} = \frac{225}{444.4} = 0.5.$$

This value (0.5) corresponds to NaCl type structure. So, co-ordination number will change from 4 to 6.

EXAMPLE 87. *You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bounded by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area ? Sketch the diagram and derive expression for the number of molecules per unit area.*

(IIT, 2003)

SOLUTION. Let a = Length of the side of quadrilateral (Fig. 4).

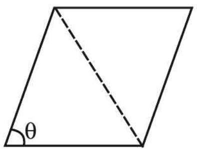


Fig. 4.

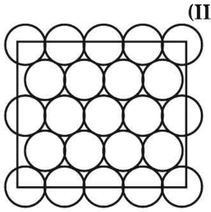


Fig. 5.

$$\therefore \text{ Area of quadrilateral} = 2 \times \frac{1}{2} \times a \times a \times \sin\theta = a^2 \sin\theta$$

In order to have maximum area, $\sin\theta = 1$ *i.e.*, $\theta = 90°$. In other words, quadrilateral must be a square (Fig. 5).

Hence, area of square = $a \times a = a^2$ *i.e.*,

$$\left(40\,\text{mm} \times \frac{1\,\text{cm}}{10\,\text{mm}}\right)^2 = \mathbf{16\ cm}^2.$$

To have maximum number of spheres, the packing should be **h.c.p.**

∴ Maximum number of spheres = 18. But area = 16 cm^2.

$$\therefore \textbf{ Number of spheres per cm}^3 = \frac{\mathbf{18}}{\mathbf{16}} = \mathbf{1.125} \qquad \textbf{Ans.}$$

EXAMPLE 88. *20% of surface sites are occupied by N_2 molecules. The density of surface site is 6.023×10^{14} cm^{-2} and total surface area is 1000 cm^2. The catalyst is heated to 300 K while N_2 is completely desorbed into a pressure of 0.001 atm and volume 2.46 cm^3. Find the number of active sites occupied by each N_2 molecule.*

[IIT–JEE (Mains), 2005]

SOLUTION.

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

Total surface area = 1000 cm^2

∴ Total no. of surface sites = Density of surface site × total surface area

$$= 6.023 \times 10^{14} \text{cm}^{-2} \times 1000 \text{ cm}^2$$
$$= 6.023 \times 10^{17}$$

Sites occupied by N_2 molecule

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

Number of N_2 molecules $= \frac{PV}{RT} \times$ Avogadro's number

where P = 0.001 atm, V = 2.46 cm^3 = 2.46 × 10^{-3} L, T = 300 K, R = 0.0821 L atm $K^{-}mol^{-}$.

∴Number of N_2 molecules

$$= \frac{0.001\,\text{atm} \times 2.46 \times 10^{-3}\text{L} \times 6.023 \times 10^{23}\text{mol}}{0.0821\,\text{L atm K}^{-}\text{mol}^{-} \times 300\,\text{K}}$$

$$= 6.016 \times 10^{16}$$

Hence number of sites occupied by each N_2 molecule

$$= \frac{\text{Sites occupied by N}_2 \text{ molecules}}{\text{Number of N}_2 \text{ molecules}}$$

$$= \frac{\mathbf{1.2046 \times 10^{17}}}{\mathbf{6.016 \times 10^{16}}} \approx \mathbf{2}$$ **Ans.**

EXAMPLE 89. *In face centred cubic (f.c.c) crystal lattice, edge length is 400 pm. Find the diameter of the greatest sphere which can be fit into the interstitial void without distortion of lattice.*

[IIT-JEE (Mains), 2005]

SOLUTION. Let radius of void sphere = *R*; radius of lattice sphere = *r*. In f.c.c lattice, the largest void present is octahedral. So: $r = \frac{\sqrt{2} \times 400}{4} = \frac{1.4142 \times 400}{4} = 141.42\,\text{pm}$

Applying condition for octahedral void, we have :

$$2(R + r) = \text{edge length, } a$$

Hence, $2R = a - 2r$

$$= 400 - 2 \times 141.42 = 400 - 282.84$$
$$= \mathbf{117.16\ pm}$$

∴Diameter of greatest sphere **(= *R*) = 117.16 pm Ans.**

EXAMPLE 90. *Calculate the smallest Cs to Cs inter-nuclear distance equal to length of the side of a cube corresponding to volume (7.014 × 10^{-23} cm^3) of one CsCl ion pair.*

SOLUTION. We know that :

Edge of each cube

$$= \frac{1}{\text{no. of units per centimeter along the edge}} \quad ...(1)$$

Volume of CsCl ion pair = 7.014 × 10^{-23} cm^3

$$\therefore \quad \text{No. of units per cm}^3 = \frac{1}{7.014 \times 10^{-23}} \text{units/cm}^3$$

$$\therefore \text{No. of units/cm along the edge} = \left(\frac{1}{7.014 \times 10^{-23}}\right)^{1/3}.$$

Solving we have,

$$\log\left(\frac{1}{7.014 \times 10^{-23}}\right)^{1/3} = \frac{1}{3}\left[\log 1 - \left(\log 7.014 + \log 10^{-23}\right)\right]$$

$$= \frac{1}{3}[0 - 0.8460 + 23]$$

$$= \frac{1}{3}[22.154] = 7.3847$$

Taking antilog, we get, **2.42 × 10^7.**

Substituting the value in (1), we get :

Edge of each cube

$$= \frac{1}{2.42 \times 10^7 \text{ units/cm}} = 4.13 \times 10^{-8}\text{cm}$$

$$= \mathbf{4.13\ Å}$$ **Ans.**

> **Note:** Body diagonal = Distance between nearest neighbours = $a \times \sqrt{3}$ where a = edge length

EXAMPLE 91. *The unit length, 'a' of potassium that crystallises in b.c.c lattice is 520 pm. Calculate (i) the distance between nearest neighbours, (ii) the distance between next-nearest neighbours, (iii) the number of nearest neighbours that potassium atom has, (iv) the number of next-nearest neighbours that each potassium has, (v) the density of crystalline potassium.*

SOLUTION. (*i*) The distance between nearest neighbours = Body diagonal = $a \times \sqrt{3}$ = 500 pm × 1.732

= **900.6 pm** **Ans.**

(*ii*) The number of nearest neighbours along the diagonal = $\frac{1}{2}$ × Body diagonal = $\frac{1}{2}$ × 900.6 pm

= **450.3 pm Ans.**

(*iii*) 8 *e.g.,* the body centre is next to 8 corners.

(*iv*) 6 because the corners have neighbours along each cell edge *i.e.,* left, right, up, down, in and out.

(*v*) Two potassium atoms per unit cell *i.e.,* 8 corners × $\frac{1}{8}$ = 1; one at the body centre. So, total = 1 + 1 = 2.

$$\text{Their mass} = \frac{2 \times \text{g. at. wt. of K}}{\text{Avogadro no.}} = \frac{2 \times 39\text{g}}{6.023 \times 10^{23}} = \quad \times$$

$$= 1.295 \times 10^{-22}\text{ g}$$

$$\text{Volume} = \left(520\text{pm} \times \frac{10^{-10}\text{cm}}{1\text{pm}}\right)^3 \quad 1.41 \quad 10 \quad \text{cm}$$

$$= 1.41 \times 10^{-22}\text{ cm}^3$$

$$\therefore \quad \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{1.295 \times 10^{-22}\text{g}}{1.41 \times 10^{-22}\text{cm}^3} =$$

$$= \mathbf{0.918\ g\ cm^{-3}}$$ **Ans.**

EXAMPLE 92. *Silver crystallises in face-centred cubic unit cell. Each side of this unit cell has a length of 400 pm. Calculate the radius of the silver atom. (Assume the atoms just touch each other on the diagonal across the face of the unit cell. That is, each face atom is touching the four corner atoms.)*

(I.I.T., 1994; CBSE Board, 2011)

SOLUTION. Let a = Length of unit cell; r = radius of silver atom. Since Ag crystallises in face centred cubic structure, we have: $r = \frac{a}{2\sqrt{2}} = \frac{400}{2 \times 1.4142}$

= **141.42 pm** **Ans.**

> **Note:** Packing fraction
>
> $$= \frac{\text{Volume occupied by atoms in a unit cell}}{\text{Volume of the unit cell}}$$

EXAMPLE 93. *A metallic element crystallises into a lattice containing sequence of layers of ABABAB...Any packing of spheres leaves out voids in the lattice. What percentage by volume of this space is empty space ?* **(IIT, 1996)**

SOLUTION. ABABAB.....type packing means hexagonal close packed (h.c.p) crystalline structure (Fig. 6).

Number of atoms per unit cell = 2

Here $a = b \neq c$ and $\frac{c}{a} = \sqrt{\frac{8}{3}}$

$$\alpha = \beta = 90°$$

and $\gamma = 120°$

$\therefore$ Area of base $= ab \sin y$

$$= a^2 \sin 120°$$

$$= a^2 \times \frac{\sqrt{3}}{2}$$

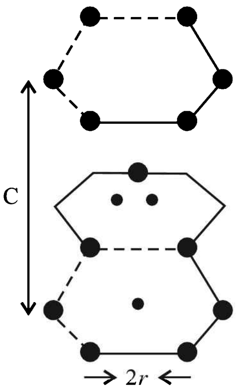


Fig. 6.

$\therefore$Volume of unit cell

=Area of base × height

$$= a^2 \times \frac{\sqrt{3}}{2} \times c$$

$$= a^2 \times \frac{\sqrt{3}}{2} \times \frac{\sqrt{8}}{\sqrt{3}} a = \sqrt{2} a^3$$

Also, here $a = 2r$ or $r = \frac{a}{2}$

$\therefore$Packing fraction

$$= \frac{\text{Volume of atoms in unit cell}}{\text{Volume of the unit cell}}$$

$$= \frac{n \times \frac{4}{3}\pi r^3}{\sqrt{2}a^3} = \frac{n \times \frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{\sqrt{2}a^3}$$

$$= \frac{\pi}{3\sqrt{2}} = \frac{3.142}{3 \times 1.414} = 0.74 = 74\%$$

Percentage of empty space

= 100 – 74 = 26% **Ans.**

EXAMPLE 94. *A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride ?* **(IIT, 1997)**

SOLUTION.

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

Edge length of unit cell $= 0.564 \times 10^{-9}$m

$= 5.64 \times 10^{-10}$ m

$= 5.64 \times 10^{-8}$ cm

Formula of mass of NaCl = 58.5 g mole^{-1}

Number of formula units in unit cell = 4

$$\text{Mass of formula unit} = \frac{58.5}{6.023 \times 10^{23}}$$

$$\therefore \quad \text{Density} = \frac{4 \times 58.5}{6.023 \times 10^{23} \times (5.64 \times 10^{-8})^3}$$

= 2.16 g cm^{-3}. **Ans.**

EXAMPLE 95. *(i) AB crystallizes in a rock salt structure with A : B = 1 : 1. The shortest distance between A and B is $Y^{1/3}$ nm. The formula mass of A and B is 6.023 Y a.m.u. where Y is any arbitrary constant. Find the density in kg m^{-3}.*

(ii) If measured density is 20 kg m^{-3}, identify the type of point defect. **(IIT, 2004)**

SOLUTION. (*i*) For a rock salt structure (F.C.C unit cell), $n = 4$

Edge length = 2 × shortest distance between A and B = $2 \times Y^{1/3}$

$$\text{Density of the crystal AB} = \frac{n \times M}{N_A \times a^3}$$

$$= \frac{4 \times (6.023\text{Y})}{6.023 \times 10^{23} \times (2\text{Y}^{1/3} \times 10^{-9})^3}$$

$= 5 \times 10^3$ g m^{-3} = 5 kg m^{-3}.

Ans.

(*ii*) Since there is a huge difference in theoretically calculated density and observed density, some foreign species occupies interstitial space *i.e.*, there exists a substitution defect.

EXAMPLE 96. *Calculate the miller indices of crystal planes which cut through the crystal axes at*

(i) (2a, 3b, c), (ii) (a, b, c),

(iii) (6a, 3b, 3c), (iv) (2a, 2b, ∞). **(Pb CET, 1997)**

SOLUTION.

Weiss indices	(*i*)	*a*	*b*	*c*	(*ii*)	*a*	*b*	*c*
		2	3	1		1	1	1
Reciprocal of Weiss indices		$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{1}$		1	1	1
LCM		6				1		

Miller indices $\left(\frac{1}{2} \times 6 = 3; \frac{1}{3} \times 6 = 2; \frac{1}{1} \times 6 = 6\right)$ *i.e.,*

(3, 2, 6) (1, 1, 1)

(try (ii) yourself)

Weiss indices	(*iii*)	*a*	*b*	*c*	(*iv*)	*a*	*b*	*c*
		6	3	3		2	2	∞
Reciprocal of Weiss indices		$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$		$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{\infty}$ or 0
LCM		6				2		

Miller indices $\left(\frac{1}{6} \times 6 = 1; \frac{1}{3} \times 6 = 2; \frac{1}{3} \times 6 = 2\right)$ *i.e.,*

(1, 2, 2) (1, 1, 0)

(try(iv)yourself)

EXAMPLE 97. *Chromium metal crystallises with a body centred cubic lattice. The length of unit cell edge is found to be 287 pm. Calculate the atomic radius. What would be the density of chromium in g/cm^3? (at. wt., Cr = 51.99).*

[IIT, (Re Exam) 1997]

SOLUTION. For b.c.c structure, atomic radius,

$$r = \frac{\sqrt{3}}{4}\cdot a$$

Where a, is the edge length;

$$r = \frac{\sqrt{3}\times 287}{4} = \frac{1.732\times 287}{4}$$

$$= 124.27 \text{ pm}$$

Further, density is given by the relation

$$\rho = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{n\times \text{Atomic mass}}{N_0 \times a^3}$$

For b.c.c, $n = 2$; Volume of unit cell

$$= a^3 = (287\text{ pm})^3 = (287\times 10^{-10}\text{ cm})^3$$

$$\rho = \frac{2\times 51.99}{6.023\times 10^{23}\times(287\times 10^{-10}\text{cm})^3}$$

$= \mathbf{7.3\ g\ cm^{-3}}$ **Ans.**

EXAMPLE 98. *A metal crystallises into two cubic planes, face centred cubic (f.c.c) and body centred cubic (b.c.c), whose unit cell lengths are 3.5 and 3.0 Å respectively. Calculate the ratio of densities of f.c.c and b.c.c.* **(III, 1999)**

SOLUTION. $d = \dfrac{n\times \text{M}}{\text{N}a^3}$.

Now for f.c.c, n = 4 and for b.c.c, n = 2

$$\therefore \quad d\,(\text{f.c.c}) = \frac{4\times \text{Atomic mass of metal}}{\text{N}\times(3.5\text{ Å})^3}$$

$$d\,(\text{b.c.c}) = \frac{2\times \text{Atomic mass of metal}}{\text{N}\times(3.0\text{ Å})^3}$$

$$\therefore \quad \frac{d(\text{f.c.c})}{d(\text{b.c.c})} = \frac{4}{2}\times\frac{(3.0)^3}{(3.5)^3} = \mathbf{1.26}$$ **Ans.**

EXAMPLE 99. *The number of molecules in the cubic unit cell of sodium hydrogen diacetate is 24. Find the side length of the unit cell if the density of the compound is 1.4 g/mL.*

SOLUTION. Molar mass of

$$\text{NaH}(\text{CH}_3\text{COO})_2 = 23 + 1 + 2\,[12 + (3\times 1) + 12 + 16 + 16]$$

$$= 142\text{ g mol}^{-}$$

$$\text{Density} = 1.4\text{ g (mL)}^{-}\text{ or } 1.4\text{ g cm}^{-3}$$

Let,side length of unit cell = a;

volume of unit cell = a^3

No. of molecules in the unit cell = 24

$$\therefore \text{Volume of one molecule of the unit cell} = \frac{a^3}{24}$$

$$\therefore \text{Volume per mole} = \frac{a^3}{24}\times 6.02\times 10^{23} \qquad ...(1)$$

Also, volume per mole of sodium hydrogen acetate

$$= \frac{142}{1.4} \qquad ...(2)$$

Equating equations (1) and (2), we get :

$$\frac{a^3}{24}\times 6.02\times 10^{23} = \frac{142}{1.4}$$

$$\therefore \quad a = \left[\frac{142}{1.4}\times\frac{24}{6.02\times 10^{23}}\right]^{1/3}$$

$$= (4.0437\times 10^{-21})^{1/3}$$

Taking logs of both sides, we get :

$$\log a = \log\,(4.0437\times 10^{-21})^{1/3}$$

$$= \frac{1}{3}[\log 4.0437 + \log 10^{-21}]$$

$$= \frac{1}{3}[0.6068 - 21] = \frac{1}{3}\times -20.3932$$

$$= -6.7977 = -6 - 1 + 1 - 0.7977$$

$$= \bar{7}.2023$$

Taking antilog of both sides, we get :

$$a = \text{antilog } \bar{7}.2023$$

$$= 1.593\times 10^{-7} = 15.93\times 10^{-8}\text{ cm}$$

Or $\quad a = 15.93\text{Å}$

Second method. We know,

$$\text{density, } \rho = \frac{n\text{M}}{\text{N}a^3\times 10^{-30}}\text{ g cm}^{-3} \qquad ...(1)$$

Here, $\quad \text{N} = \dfrac{6.02\times 10^{23}}{24}$,

n = 1 for cubic unit cell,

M = 142 g mol^{-}

$\therefore$ From relation (1),

$$a = \left(\frac{n\text{M}}{\text{N}\rho\times 10^{-30}}\right)^{1/3}\text{ pm}$$

Or $$a = \left[\frac{1\times 142\times 24}{6.02\times 10^{23}\times 1.4\times 10^{-30}}\right]^{1/3}$$

$$= (4.0437\times 10^{9})^{1/3}\text{ pm}$$

Taking logs of both sides, we get :

$$\log a = \log\,[4.0437\times 10^{9}]^{1/3}$$

Or $$\log a = \frac{1}{3}[\log 4.0437 + \log 10^{9}]$$

$$= \frac{1}{3}(0.6068 + 9)$$

$$= \frac{1}{3}\times 9.6068 = 3.2023$$

Taking antilog of both sides, we get : a = antilog 3.2023

$$\therefore \quad a = 1.593\times 10^{3}\text{ pm}$$

$$= 1593\text{ pm or } 1593\text{ pm}\times\frac{1\text{Å}}{100\text{ pm}}$$

$= \mathbf{15.93Å}$ **Ans.**

EXAMPLE 100. *A compound made up of elements A and B crystallises in cubic structure. Atoms A are present on the corner as well as face centres where as atoms B are present on edge centres as well as body centre. Find the formula of the compound.*

SOLUTION. (*i*) Contribution of atom A on the corner

$$= 8 \times \frac{1}{8} = 1 \text{ atom}$$

Contribution of atom A on face centres

$$= 6 \times \frac{1}{2} = 3 \text{ atoms}$$

∴ Total number of A atoms

$$= 1 + 3 = 4$$

(*ii*) Contribution of atom B on edge centres

$$= 12 \times \frac{1}{4} = 3$$

Contribution of atom B on body centre

$$= 1 \times 1 = 1$$

∴ Total number of B atoms

$$= 3 + 1 = 4$$

∴ Formula of compound

$$= \mathbf{A_4B_4 \text{ or } AB} \qquad \textbf{Ans.}$$

EXAMPLE 101. *A compound formed by elements X and Y crystallises in the cubic structure where Y atoms are at the corners of cube and X atoms are at alternate faces. What is the formula of the compound ?* **(PSEB, 2002)**

SOLUTION. Contribution of atom Y on the corners

$$= 8 \times \frac{1}{8} = 1 \text{ atom}$$

Since there are three X atoms present at the centre of three alternate faces and each face centred atom is shared by two cubes, so number of atoms of X in a unit cell

$$= \frac{1}{2} \times 3 = \frac{3}{2}$$

∴ Formula of compound

$$= X_{3/2}Y_1 = \mathbf{X_3Y_2} \qquad \textbf{Ans.}$$

EXAMPLE 102. *How many atoms of element does 208 g of element contain if element density is 7.2 g cm^{-3} and it has b.c.c structure with a unit cell edge of 288 pm.* **(PSEB, 2007)**

SOLUTION. For b.c.c, $n = 2$; $\rho = 7.2$ g cm^{-3}; M = ? ; N = 6.02×10^{23}, a = 288 pm. We know that:

$$\rho = \frac{nM}{Na^3 \times 10^{-30}} \text{ g cm}^{-3}$$

$$M = \frac{\rho N a^3 \times 10^{-30}}{n}$$

23

$$M = \frac{7.2 \times 6.02 \times 10^{23} \times (288)^3 \times 10^{-30}}{2}$$

$$\therefore \quad M = 51.77 \text{ g}$$

51.77 g of element contain atoms = 6.02×10^{23}

$$\therefore 208 \text{ g of element contain atoms} = \frac{6.02 \times 10^{23}}{51.77} \times 208$$

$$= \mathbf{2.47 \times 10^{24} \text{ atoms}} \qquad \textbf{Ans.}$$

EXAMPLE 103. *Sodium metal crystallises in b.c.c lattice with the cell edge, a = 4.29 Å. What is the radius of sodium atom ?* **(IIT, 1994, AIPMT, 2009 Modified)**

SOLUTION. For b.c.c. lattice,

$$\text{radius, } r = \frac{a\sqrt{3}}{4} = \frac{4.29\text{Å} \times 1.732}{4}$$

$$\therefore \quad r = \mathbf{1.86Å} \qquad \textbf{Ans.}$$

EXAMPLE 104. *A crystal of Pb (II) sulphide has sodium chloride structure. In this crystal, the shortest distance between the Pb^{2+} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide ?*

SOLUTION. For NaCl type structure (f.c.c.), distance between nearest neighbours,

$$d = \frac{a}{\sqrt{2}} \text{ where } a = \text{edge length}$$

$$\therefore \quad a = d \times \sqrt{2} = 297 \text{ pm} \times 1.4142$$

$$\text{Or} \quad a = 420 \text{ pm} \qquad \textbf{Ans.}$$

EXAMPLE 105. *In a metal oxide, the metal ions occupy two-third of the octahedral voids while oxide ions are arranged in hexagonal close packing. The metal oxide formula will be:*

(a) M_2O *(b)* $M_2O_{1.5}$ *(c)* M_2O_3 *(d)* MO_2

SOLUTION. Number of octahedral holes per sphere = 1. So, number of O-atoms = 1. The number of metal atoms = 1 × 2/3 = 2/3. Thus M : O is 2/3: 1 or 2 : 3. So, the formula is M_2O_3.

EXAMPLE 106. *Calculate the formula of a compound if its structure has sodium atoms at the cube centres, oxygen atoms at the cube edges while tungsten (W) atoms are located at the corners of the unit cell. Also, write the type of the lattice represented by this compound.*

(a) $NaWO_2$ *(b)* $NaWO_3$

(c) Na_2WO_3 *(d)* $NaWO_4$

(AMU, Engg., 2012)

SOLUTION. From the given data, it is clear that the lattice type of the compound is simple cubic.

No. of Na atoms at the cube centre

$$= 1 \times 1 = 1$$

No. of O-atoms at the cube edges

$$= 12 \text{ edges} \times \frac{1}{4} = 3 \text{ edges}$$

No. of W-atoms at the corners of unit cell

3 30

$$= 8 \times \frac{1}{8} = 1$$

∴Formula of compound

$$= Na_1O_3W_1 \quad \textbf{or} \quad \mathbf{NaWO_3} \qquad \textbf{Ans.}$$

So, the correct answer is (*b*).

EXAMPLE 107. *The effective radius of an iron atom is 1.42 Å. It has rock salt structure. Calculate its density. (Fe = 56 a.m.u.).*

SOLUTION. Rock salt structure means f.c.c. structure.

$$\text{For f.c.c. structure, } r = \frac{a}{2 \times \sqrt{2}}.$$

But, $r = 1.42 \text{ Å} = 142 \text{ pm}.$

Hence $142 \text{ pm} = \frac{a}{2 \times 1.4142};$

$a = 142 \times 2 \times 1.4142 \text{ pm} = 401.63 \text{ pm}$

But, $\text{Density}, \rho = \frac{nM}{Na^3 \times 10^{-30}} \text{ g cm}^{-3}$

For f.c.c., $n = 4; \text{M} = 56$

$\therefore \quad \rho = \frac{4 \times 56}{6.02 \times 10^{23} \times (401.63)^3 \times 10^{-30}}$

$= \mathbf{5.74 \text{ g cm}^{-3}}$ **Ans.**

EXAMPLE 108. *The unit cell dimensions of lithium borohydride (molar mass 21.8) are a = 680 pm, b = 440 pm and c = 720 pm. Calculate the density of lithium borohydride if it crystallises in an orthorhombic system with 4 molecules per unit cell.*

SOLUTION. Volume (V) of unit cell

$= a \times b \times c = (680 \times 440 \times 720) \text{ pm}^3$

$= 215{,}424{,}000 \text{ pm}^3$

$= 215{,}424{,}000 \times 10^{-30} \text{ cm}^3$

$[\because 1\text{pm} = 10^{-10} \text{ cm}]$

$n = 4, \text{mol. wt.} = 21.8,$

$\text{Avogadro's number} = 6.023 \times 10^{23}$

$\therefore \quad \text{Density}, \rho = \frac{n \times \text{Mol. wt.}}{\text{Avogadro's number} \times \text{Volume}}$

$= \frac{4 \times 21.8 \text{ g}}{6.023 \times 10^{23} \times 215{,}424{,}000 \times 10^{-30} \text{cm}^3}$

$\text{Density} = 0.672 \text{ g cm}^{-3}$ **Ans.**

EXAMPLE 109. *Solid argon (at. wt. 40) has density 1.65 g cm^{-3}. If argon atom is considered to be a sphere of radius 154 pm, calculate the percent empty space in solid argon.*

SOLUTION.

Radius (r) of Ar $= 154 \text{ pm} = 154 \times 10^{-10} \text{ cm}$

$\therefore$ Volume (V) of one Ar-atom in solid state

$= \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (154 \times 10^{-10} \text{cm})^3$

No. of atoms in 1.65 g Ar

$= \frac{\text{wt. of Ar}}{\text{at. wt. of Ar}} = \frac{1.65 \text{g}}{40 \text{ g}}$

Total volume of all atoms in solid Ar

$= \frac{4}{3} \times \frac{22}{7} \times (154 \times 10^{-10} \text{cm})^3 \quad 1.65$

$\times \frac{1.65}{40} \times 6.023 \times 10^{23}$

$= 0.38 \text{ cm}^3$

Since volume of solid argon

$= 1 \text{ cm}^3$, empty space $= 1 - 0.38$

$= 0.62 \text{ cm}^3$

$\therefore$Percent empty space

$= \frac{1 - 0.38}{1} \times 100 = \mathbf{62\%}$ **Ans.**

10.18 CALCULATION OF RADII OF IONS

Let a = edge length of a cubic cell. The ionic radii for the ion in a crystal lattice can be calculated with the help of Fig. 7. as described below.

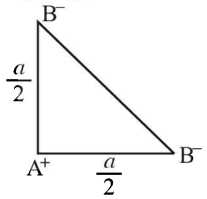


Fig. 7.

$$\text{Radius of anion, B}^- = \frac{\left[\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2\right]^{1/2}}{2}$$

$$= \frac{\left(\frac{2a^2}{4}\right)^{1/2}}{2} = \frac{\boldsymbol{a}}{\mathbf{2\sqrt{2}}}$$

EXAMPLE 110. *In case of LiCl (having cubic NaCl structure), the unit cell cube length is 514 pm. Assuming an ion-anion contact, find the ionic radius of Cl$^-$ ion.*

SOLUTION. In Fig. 8,

$d_{\text{Li}^+ - \text{Cl}^-} = \frac{514 \text{pm}}{2} = 257 \text{ pm}$

$d_{\text{Cl}^- - \text{Cl}^-} = [(257 \text{ pm})^2 + (257 \text{ pm})^2]^{1/2}$

$= [66049 + 66049]^{1/2} = (132098)^{1/2}$

$= \mathbf{363.4} \text{ pm}.$

$\therefore \quad \text{Radius of Cl}^- = \frac{363.4}{2} = \mathbf{181.7 \text{ pm}}$ **Ans.**

Second method. Radius of Cl$^-$

$= \frac{a}{2\sqrt{2}} = \frac{514 \text{pm}}{2 \times 1.4142} = \mathbf{181.7 \text{ pm.}}$

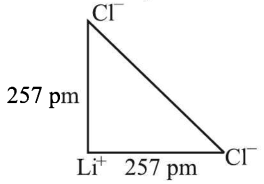
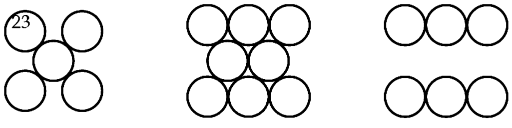


Fig. 8.

EXAMPLE 111. *The figures given below show the location of atoms in three crystallographic planes in a f.c.c. lattice. Draw the unit cell for the corresponding structure and identify these planes in your diagram.* **(IIT, 2000)**



(*i*) (*ii*) (*iii*)

Fig. 9.

SOLUTION.

(*i*) Face plane, (*ii*) Face diagonal plane, (*iii*) Diagonal plane. (Fig. 9)

EXAMPLE 112. *In an unknown solid, oxide ions are arranged in c.c.p. Cations (A) occupy one sixth of the tetrahedral voids while cations (B) occupy one third of the octahedral voids. Calculate the formula of the solid.*

SOLUTION. Let no. of oxide ions = 30. So, octahedral voids = 30 but tetrahedral voids = 2 × 30 = 60. Hence: no. of cations (A) = 1/6 × 60 = 10; no. of cations (B) = 1/3 × 30 = 10

∴ Ratio of A : B : O^{2-} = 10 : 10 : 30 or 1 : 1 : 3. So, the formula of solid = ABO_3.

10.19 AIEEE PATTERN EXAMPLES

EXAMPLE 113. *If three elements A, B and C crystallised in cubic solid lattice with A atoms at corners, B atoms at cube centre and C atoms at the edges, which formula of the compound is expected out of:*

(*a*) ABC_3, (*b*) ABC_2,
(*c*) *ABC*, (*d*) AB_3C.

SOLUTION. (*a*) Atom A is shared by 8 corners. So, effective number of atoms of A per unit cell = $8 \times \frac{1}{8} = 1$.

(*b*) Atom B is present at the cube centre. So, effective number of atoms of B per unit cell = 1.

(*c*) C atoms are present at the edges. 1 atom of C is shared by 4 unit cells. So, effective number of atoms of C per unit cell = $\frac{12}{4} = 3$.

Hence, formula of compound = ABC_3. So, the answer is (*a*).

EXAMPLE 114. *In a face centred cubic lattice, atom A occupies the corner positions and atom B occupies the face centre positions. If one atom of A is missing from face centred points, the formula of the compound is*

(*a*) A_2B (*b*) AB_2
(*c*) A_2B_3 (*d*) A_2B_5 **(AIEEE, 2011)**

SOLUTION. No. of atoms of A = 8 corners × $\frac{1}{8}$ atom per unit cell = 1

No. of atoms of B = (6 – 1) faces × $\frac{1}{2}$ atom per unit cell = 5/2

∴ Formula of compound = $A_1B_{5/2}$ = A_2B_5. So, the correct answer is (*d*).

EXAMPLE 115. *Which one is true in the closest packing of atoms ?*

(*a*) *The size of octahedral void is equal to or smaller or larger to that of the size of tetrahedral void depending on the atomic size.*

(*b*) *The size of octahedral void is equal to that of tetrahedral void.*

(*c*) *The size of octahedral void is larger than that of tetrahedral void.*

(*d*) *The size of octahedral void is smaller than that of tetrahedral void.*

SOLUTION. (*a*) For octahedral void, $\frac{r^+}{r^-} = 0.414$.

So, $r^+ = 0.414\, r^-$ ...(1)

(*b*) For tetrahedral void, $\frac{r^+}{r^-} = 0.225$. So, $r^+ = 0.225\, r^-$ ...(2)

From relations (1) and (2), we find that octahedral void is larger than that of tetrahedral void. So, the true answer is (*c*).

EXAMPLE 116. *The radius of A^+ in ionic compound AB is 0.225 Å. If AB has ZnS structure, the ideal radius of B^- will be*

(*a*) *5.06 pm,* (*b*) *50.6 pm,*
(*c*) *100 pm,* (*d*) *150.6 pm.*

SOLUTION. A^+B^- has ZnS structure. So, it has tetrahedral holes. For tetrahedral holes.

$$\frac{\text{Radius of cation}}{\text{Radius of anion}} = 0.225 \textbf{ Or } \frac{r_{A^+}}{r_{B^-}} = 0.225$$

$$\textbf{Or} \quad \frac{0.225}{r_{B^-}} = 0.225$$

$$\textbf{Or} \quad r_{B^-} = \frac{0.225\text{Å}}{0.225} = 1\text{Å} = 100 \text{ pm}$$

Thus, ideal radius of B^- is 100pm. So, correct answer is (*c*).

EXAMPLE 117. *A substance crystallises to f.c.c lattice having 6Å edge length. If the density of unit cell is 2kg dm^{-3}, the molar mass of substance is :*

(*a*) *51.65 g mol^-* (*b*) *25.8 g mol^-*
(*c*) *76.4 g mol^-* (*d*) *65.04 g mol^-*

SOLUTION. $\rho = 2 \text{ kg dm}^{-3} = \frac{2 \times 1000 \text{ g}}{10^3 \text{cm}^3} = 2 \text{ g cm}^{-3}$. For f.c.c. lattice, *n* = 4; edge length, *a* = 6Å = 6 × 10^{-8} cm. But :

$$\rho = \frac{nM}{N_A a^3}$$

$$\textbf{Or} \quad 2 = \frac{4 \times M}{6.022 \times 10^{23} \times (6 \times 10^{-8})^3}$$

$$\textbf{Or} \quad M = \frac{2 \times 6.022 \times 10^{23} \times (6)^3 \times (10^{-8})^3}{4}$$

$$= \mathbf{65.04 \ g \ mol^-}.$$

So, correct answer is (*d*).

EXAMPLE 118. *Which of the following are true ?*

(*a*) *If all the octahedral voids are occupied by cation A^+ and B^- occupy ccp, the crystal has the same molecular formula AB, if A^+ occupies the alternate tetrahedral voids.*

(*b*) *The coordination number of U : O is in 8 : 4 ratio.*

(*c*) *In closest packing of Q atoms, there are Q-octahedral holes and 2Q tetrahedral holes.*

(*d*) *In h.c.p of O^{2-} ion sapphire (Al_2O_3), the Al^{3+} ions crystallise in 2/3rd of the octahedral void, then the sapphire has Al_2O_3 formula.*

SOLUTION. (*a*) The number of octahedral and tetrahedral voids in c.c.p are 4 and 8 respectively. B^- also occupies ccp. So, total number of B-atoms = 4.

A^+ ions occupy octahedral voids. So, total number of A atoms = 4. So, the ratio of atoms A : B = 4 : 4. Hence the **formula is AB**.

If A^+ occupy alternate tetrahedral voids, total number of A^+ ions = 4 and total number of B^- ions = 4. The ratio of atoms A : B = 4 : 4 or 1 : 1. So the formula of the compound is AB. Hence the correct answer is (*a*).

(*b*) and (*c*). In closest packing, number of tetrahedral holes = 2 × number of octahedral voids. So, (*b*) and (*c*) are correct.

(*d*) For h.c.p of O^{2-} ion, there is one octahedral hole whose 2/3rd part is occupied by Al^{3+} ions. So, the number of Al^{3+} ions per unit cell = $1 \times \frac{2}{3} = \frac{2}{3}\cdot$

Hence, formula of compound is $Al_{2/3}O_1$ or Al_2O_3. So, (*d*) is the correct answer.

EXAMPLE 119. *Which of the following statements are correct?*

(*a*) *The void space in a f.c.c unit cell = 26%.*

(*b*) *The void space in a b.c.c unit cell = 68%.*

(*c*) $r^+ + r^- = \frac{a\sqrt{3}}{2}$ *for CrCl unit cell having edge length, a.*

(*d*) $r^+ + r^- = \frac{a}{2}$ *for NaCl unit cell having edge length, a.*

SOLUTION. (*a*) In f.c.c unit cell, packing fraction = 74%.

∴ Void fraction = 100 – 74 = 26%

Hence, (*a*) is correct.

(*b*) In b.c.c unit cell, packing fraction = 68%.

∴ Void faction = 100 – 68 = 32%

So, (*b*) is not correct.

(*c*) CrCl has b.c.c structure. For b.c.c structure,

$$r^+ + r^- = \frac{a\sqrt{3}}{2}\cdot \text{ Hence } (c) \text{ is correct.}$$

(*d*) NaCl has f.c.c structure. For f.c.c structure,

$$r^+ + r^- = \frac{\text{edge length}}{2} = \frac{a}{2}\cdot$$

So, (*d*) is correct.

EXAMPLE 120. *The edge length of the unit length of NaCl is 552 pm while the radius of Na^+ ion is 95 pm. Calculate the radius of Cl^- ion.*

SOLUTION. Edge length, *a* of NaCl, $2(r^+ + r^-) = 552$ pm

$$\therefore \quad r_{Na^+} + r_{Cl^-} = \frac{552}{2}\text{pm} = 276 \text{ pm}$$

or $\quad 95 \text{ pm} + r_{Cl^-} = 276.$

Hence, $\quad r_{Cl^-} = 276 - 95 = 181$ pm **Ans.**

EXAMPLE 121. *An ionic compound AB crystallises in b.c.c lattice. If its unit cell edge length is 412 pm and radius of B^- is 181 pm, the radius of A^+ is :*

(*a*) *200 pm* (*b*) *175.8 pm*

(*c*) *351.6 pm* (*d*) *100 pm.*

SOLUTION. For b.c.c lattice,

$$2(r_{A^+} + r_{B^-}) = a\sqrt{3}$$

$$\therefore \quad r_{A^+} + r_{B^-} = \frac{a\sqrt{3}}{2} = \frac{412 \times 1.732}{2} = 356.8 \text{ pm}$$

$$r_{A^+} + 181 \text{ pm} = 356.8 \text{ pm}$$

$$\therefore \quad r_{A^+} = 356.8 \text{ pm} - 181 \text{ pm} = \mathbf{175.8\ pm.}$$

So, correct answer is (*b*).

EXAMPLE 122. *A compound has a cubic close packed structure of mixed oxides. Its lattice is made up of oxide ions. If one half of the octahedral holes are occupied by trivalent ions (B^{3+}) and one fifth of tetrahedral holes are occupied by divalent ions (A^{2+}), then the formula of the oxide is :*

(*a*) ABO_8 (*b*) $A_2B_2O_7$

(*c*) $A_3B_3O_3$ (*d*) $A_4B_5O_{10}$

SOLUTION. In cubic close packed structure of mixed oxides, the cations occupy holes while anions occupy primitives of the cube. In c.c.p, there is one octahedral and two tetrahedral voids per anion. So, for one oxygen atom, there is one octahedral and two tetrahedral holes.

(*i*) It is given that one half of the octahedral holes are occupied by B^{3+} ions. So :

$$\text{Number of trivalent cations} = 1 \times \frac{1}{2} = \frac{1}{2}\cdot$$

(*ii*) It is given that one fifth of the tetrahedral holes are occupied by A^{2+} ions. So :

$$\text{Number of divalent cations} = 2 \times \frac{1}{5} = \frac{2}{5}\cdot$$

Hence, the formula of the compound = $A_{2/5}B_{1/2}O_1$

$= A_4B_5O_{10}$

$$\left[\because \frac{2}{5}, \frac{1}{2}, 1 = \frac{4:5:10}{10(\text{LCM})} = 4:5:10\right]$$

EXAMPLE 123. *The solid compound XY has NaCl structure. If the radius of cation is 100 pm, the radius of anion (Y^-) will be :*

(*a*) *275.1 pm* (*b*) *322.5 pm*

(*c*) *241.5 pm* (*d*) *165.7 pm* **(AIPMT, 2011)**

SOLUTION. For NaCl (C.N. = 6), the radius ratio, r^+/r^- = 0.414. But r^+ = 400 pm (given). So, we have :

$$\frac{100}{r^-} = 0.414; \; r^- = \frac{100}{0.414} = 241.5 \text{ pm.}$$

So, the correct answer is (*c*)

EXAMPLE 124. *The number (n) of atoms in a cube when atoms are given on its own diagonal are*

(*a*) *n* (*b*) *2n*

(*c*) *3n* (*d*) *4n*

SOLUTION. No. of atoms per unit cell in a cube when atoms are given on its own diagonal are equal to *n i.e.,* number of atoms present on the diagonal. So, the correct answer is (*a*).

Example 125. *The number of atoms in a cubic based unit cell having one atom on each corner and two atoms on each body diagonal are :*

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

Solution. No. of atoms in a cubic based unit cell = 8 corners $\times \frac{1}{8}$ atom per unit cell = 1.

No. of atoms on diagonal = 2

$\therefore$ Total no. of atoms = 1 + 2 = 3.

So, the correct answer is (*c*).

Example 126. *How many unit cells are present in a cube shaped ideal crystal of NaCl of mass 1.00 g ? (atomic masses, Na = 23, Cl = 35.5).*

(*a*) 1.71×10^{21} *unit cells* (*b*) 2.57×10^{21} *unit cells*
(*c*) 5.14×10^{21} *unit cells* (*d*) 1.28×10^{21} *unit cells*

(AIEEE, 2003)

Solution.

$$\begin{aligned}\text{Molar mass of NaCl} &= 23 + 35.5\\ &= 58.5 \text{ g mol}^{-}\\ \text{Mass of NaCl} &= 1.00 \text{ g.}\\ \text{58.5 g NaCl contain formula units} &= 6.023 \times 10^{23}\\ \therefore \quad \text{1 g NaCl contain formula units} &= \frac{6.023 \times 10^{23}}{58.5}\\ &= 1.029 \times 10^{22}\end{aligned}$$

In a cubic shaped ideal crystal of NaCl:

4 formula units consist of unit cells = 1

$\therefore$ 1.029×10^{22} formula units consist of unit cells

$$= \frac{1}{4} \times 1.029 \times 10^{22}$$
$$= 2.57 \times 10^{21}$$

So, the correct answer is (*b*).

Example 127. *If 'a' stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively :*

(*a*) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$ (*b*) $1a : \sqrt{3}a : \sqrt{2}a$

(*c*) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$ (*d*) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$

(CBSE–PMT, 2008 Prelims)

Solution. For simple cubic system,

$$r^+ + r^- = \frac{a}{2}$$

For body centred cubic system,

$$r^+ + r^- = \frac{a\sqrt{3}}{4}$$

For face centred cubic system,

$$r^+ + r^- = \frac{a}{2\sqrt{2}}$$

Where a = edge length and $r^+ + r^-$ is interatomic distance.

Hence ratio of radii of three will be :

$$\frac{a}{2} : \frac{a\sqrt{3}}{4} : \frac{a}{2\sqrt{2}}.$$

So, the correct answer is, (*c*).

Example 128. *A binary solid (A^+B^-) has a zinc blende structure with B^- ions constituting the lattice and A^+ ions occupying 25% tetrahedral holes. The formula of solid is :*

(*a*) AB_3 (*b*) AB_2
(*c*) AB_4 (*d*) AB

Solution. For a zinc blende structure, the number of B^- ions in a unit cell having 8 corners and six faces = $\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 1 + 3 = 4.$

The number of A^+ ions occupying 25% of tetrahedral holes = $8 \times \frac{25}{100} = 2$. So, the formula of the compound = A_2B_4 or AB_2. So, the correct answer is, (*b*).

Example 129. *Radius ratio of an ionic compound is 0.93. The structure of the ionic compound is of*

(*a*) *NaCl* (*b*) *Cs Cl type*
(*c*) *ZnS type* (*d*) *none of these.*

(Odisha, JEE, 2011)

Solution. Given $r^+/r^- = 0.93$. Since radius ratio range 0.732 to 1.0 represents coordination number 8, so, out of all the given types, coordination number ratio for CsCl is 8 : 8. So, the correct answer is (*b*).

Example 130. *In a solid AB having NaCl structure, A atoms occupy the corners of the cubic unit cell. If all the face centred atoms along one of the axes are removed, then the resultant stoichiometry of the solid is :*

(*a*) *AB* (*b*) A_2B_3
(*c*) A_3B_4 (*d*) A_4B_3

Solution. AB has NaCl structure. A atoms which occupy corners, also occupy face centres. Removal of face centred atoms along one axis means removal of two atoms of A from face centres. Hence :

$$\text{A atoms left per unit cell} = \frac{1}{8} \times 8(\text{corners}) + \frac{1}{2} \times 4(\text{faces}) = 1 + 2 = 3.$$
$$= 1 + 2 = 3.$$

Since B atoms remain the same, so number of B atoms = 4. Hence ratio of A : B atoms = 3 : 4. Hence formula of AB = A_3B_4. So, the correct formula is, (*c*).

Example 131. *The percentage of free space is a body centred unit cell is*

(*a*) 34% (*b*) 28%
(*c*) 30% (*d*) 32%

(CBSE–PMT, 2008 Prelims)

Solution. Packing fraction

$$= \frac{\text{Volume occupied by atoms in a unit cell}}{\text{Volume of unit cell}}$$

For a body centred cubic structure, packing fraction is 0.68 *i.e.*, 0.68 × 100 = 68%.

So, 68% of the unit cell is accupied by atoms and 32% (100 – 68 = 32) is empty space.

So, the correct answer is (*d*).

Example 132. *The number of octahedral sites for sphere in a cubic closest-packed (face-centred cubic) structure are :*

(*a*) *One* (*b*) *Two*

(*c*) *Three* (*d*) *Four*

Solution. In a close-packed structure of *n*-spheres, octahedral sites or voids = *n*. So, the correct answer is (*a*).

Example 133. *An ionic compound has a unit cell constituting of A ions at the corners of a cube and B ions on the centres of the faces of the cube. The empirical formula for this compound will be :*

(*a*) *AB* (*b*) A_2B

(*c*) AB_3 (*d*) A_3B **(AIEEE, 2005)**

Solution. Number of A ions per unit cell = 1

Number of B ions per unit cell = 3

∴ Empirical formula of compound = A_1B_3 or AB_3.

So, the correct answer is (*c*).

Example 134. *Total volume of atoms present in a face centred cubic unit cell of a metal is (r is atomic radius)*

(*a*) $\frac{20}{3}\pi r^3$ (*b*) $\frac{24}{3}\pi r^3$

(*c*) $\frac{12}{3}\pi r^3$ (*d*) $\frac{16}{3}\pi r^3$ **(AIEEE, 2006)**

Solution. For f.c.c, number of atoms present in a unit cell = 4. Hence

$$\text{Volume} = 4\left[\frac{4}{3}\pi r^3\right] = \frac{16}{3}\pi r^3.$$

So, the correct answer is (*d*).

Example 135. *A metal of atomic mass = 75 forms a cubic lattice of edge length 5Å and density 2 g cm*$^{-3}$*. The radius of atom (Avogadro's number,* $N_A = 6 \times 10^{23}$*) is :*

(*a*) *217 pm* (*b*) *100 pm*

(*c*) *217Å* (*d*) *None of these*

(IIT-JEE, 2006)

Solution. $d = 2$ g cm^{-3}, *n* for cubic lattice = ? ; *r* = ? ; *m* = 75; $N_A = 6 \times 10^{23}$, a = 5Å = 5×10^{-8} cm; $a^3 = (5 \times 10^{-8}\ \text{cm})^3$.We know :

$$d = \frac{nm}{N_A a^3} \quad ; \quad n = \frac{dN_A a^3}{m}$$

$$\therefore n = \frac{2\text{g cm}^{-3} \times 6 \times 10^{23}\text{mol}^{-} \times (5 \times 10^{-8}\text{cm})^3}{75\,g\,\text{mol}^{-}} = 2$$

Since *n* = 2, the cubic lattice will be body centred. For b.c.c. lattice, $4r = \sqrt{3}a$ but *a* = 5Å = 5 × 100 pm. Hence.

$$4r = \sqrt{3} \times 5 \times 100\,\text{pm}$$

$$r = \frac{\sqrt{3} \times 500\,\text{pm}}{4} = \frac{1.732 \times 500}{4}\text{pm}$$

Or $r = 216.5\ \text{pm} \simeq 217\ \text{pm}$

So, the correct answer is (*a*).

Example 136. *The following paragraph is for questions (i), (ii) and (iii).*

In hexagonal systems of crystals, a frequently encountered arrangement of atoms is described as a hexagonal prism. Here, the top and bottom of the cell are regular hexagons and three atoms are sandwiched in-between them. A space filling model of this structure, called hexagonal close-packed (hcp), is constituted of a sphere on a flat surrounded in the same plane by six identical spheres as closely as possible. Three spheres are then placed over the first layer so that they touch each other and represent the second layer. Finally, the second layer is covered with a third layer that is identical to the bottom layer in relative position. Assume radius of every sphere to be 'r'. Answer the following :

(*i*) *The number of atoms in this hcp unit cell is :*

(*a*) 4 (*b*) 6

(*c*) 12 (*d*) 17

(*ii*) *The volume of this unit cell is :*

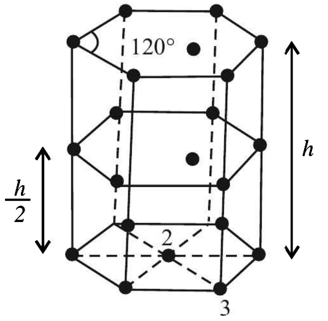
(*a*) $24\sqrt{2}\,r^3$ (*b*) $16\sqrt{2}r^3$

(*c*) $12\sqrt{2}\,r^3$ (*d*) $\frac{64}{3\sqrt{3}}r^3$

(*iii*) *The empty space is this unit cell is :*

(*a*) 74% (*b*) 47.6%

(*c*) 32% (*d*) 26% **(IIT-JEE, 2008)**



Solution. (*i*) Total number of atoms is one unit cell $= \left(12 \times \frac{1}{6}\right) + 3 + \left(2 \times \frac{1}{2}\right) = 6$

So, the correct answer is (*b*).

(*ii*) Height of unit cell = $4r\left(\frac{2}{3}\right)^{1/2}$. Base area = $\frac{6 \times \sqrt{3}}{4(2r)^2}$

$$\text{Volume} = \text{height} \times \text{base area}$$

$$= 4r\left(\frac{2}{3}\right)^{1/2} \times 6 \times \frac{\sqrt{3}}{4}(2r)^2 =$$

$$= 24\sqrt{2}\,r^3$$

So, the correct answer is (*a*).

(*iii*) Packing fraction

$$= \frac{\text{Volume of the atoms in one unit cell}}{\text{Volume of one unit cell}}$$

$$= \frac{6\times\frac{4}{3}\pi r^3}{24\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.74$$

or $0.74 \times 100 = 74\%$

$\therefore$ Empty space = 100 – 74 = 26%

So, the correct answer is (*d*).

Example 137. *Given that the radius of Na^+ ion is 0.95 Å and that of Cl^- ion is 1.81 Å, hence in the close packed lattice of Cl^- ions, Na^+ ions prefer to occupy:*

(a) tetrahedral site	*(b) octahedral site*
(c) cubic site	*(d) trigonal site*

(AMU (medical, 2012))

Solution. r^+ = radius of Na^+ = 0.95 Å, r^- = radius of Cl^- = 1.81 Å.

$\therefore$ Radius ratio, $\frac{r^+}{r^-} = \frac{0.95}{1.81} = 0.524.$ Hence the ions fit in the octahedral site. So, the correct answer is (*b*).

Example 138. *Structure of a mixed oxide is cubic close packed (ccp). The cubic unit cell of mixed oxide is composed of oxide ions. One fourth of the tetrahedral voids are occupied by divalent metal A and the octahedral voids are occupied by a monovalent metal B. The formula of the oxide is:*

(a) ABO_2	(b) A_2BO_2
(c) $A_2B_3O_4$	(d) AB_2O_2

(AIPMT, Mains, 2012)

Solution. Number (N) of atoms in *ccp* = 4 = O^{2-}

$\therefore$ No. of tetrahedral holes = 2 × N = 2 × 4 = 8

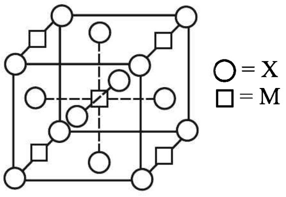
No. of A^{2+} ions = 8 × 1/4 = 2

No. of octahedral voids = No. of B^+ ions = N = 4

Ratio of $O^{2-} : A^{2+} : B^+ = 4 : 2 : 4 = 2 : 1 : 2$

$\therefore$ Formula of oxide = AB_2O_2. So, the correct answer is (*d*).

Example 139. *A compound $M_p X_q$ has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is:*



(a) MX	(b) MX_2
(c) M_2X	(d) M_5X_{14}

(IIT-JEE, 2012)

Solution. Atoms present at the corners = 8X

$\therefore$ No. of atoms that contribute to one unit cell = $8 \times \frac{1}{8} = 1$

Atoms present at the face centres = 6X

$\therefore$ No. of atoms that contribute to one unit cell = $6 \times \frac{1}{2} = 3$

$\therefore$ Total X atoms = 1 + 3 = 4

Atoms present at the edge centres = 4 M

$\therefore$ No. of atoms that contribute to one unit cell = $4 \times \frac{1}{4} = 1$

Atoms present at the body centre = 1 M

$\therefore$ No. of atoms that contribute to one unit cell = 1

$\therefore$ Total M atoms = 1 + 1 = 2

Hence the ratio M : X : : 2 : 4 : : 1 : 2

$\therefore$ Empirical formula = MX_2. So, the correct answer is (*b*).

Example 140. *A metal crystallises with a face-centred cubic lattice. The edge of the unit cell is 408 pm. The diameter of the metal atom is:*

(a) 288 pm	*(b) 408 pm*
(c) 144 pm	*(d) 204 pm*

(AIPMT, Pre. 2012)

Solution. Edge length, *a* = 408 pm. For f.c.c. structure

Radius, $r = \frac{a}{2\sqrt{2}} = \frac{408}{2\times 1.4142} = 144.25 \simeq 144\ pm.$

$\therefore$ Diameter = 2 × 144 = 288 pm. So, the correct answer is (*a*).

Example 141. *Tungsten crystallises in body centred cubic unit cell. If the edge of the unit cell is 316.5 pm, what is the radius of the tungsten atom?* **(CBSE, 2012)**

Solution. For *bcc* structure, radius, $r = \frac{\sqrt{3}}{4} \cdot a$

But *a* = 316.5 pm (given). So, $r = \frac{\sqrt{3}}{4} \times 316.5\ pm$

$$= \frac{1.732 \times 316.5}{4} pm = \mathbf{137.04\ pm} \qquad \textbf{Ans.}$$

Example 142. *Iron has a body centred cubic unit cell dimension of 286.65 pm. The density of iron is 7.874 g cm^{-3}. Use this information to calculate Avogadro's number (at. mass of Fe = 55.845 u)* **(CBSE, 2012)**

Solution. For *bcc*, *Z* = 2 ; *d* = 7.874 g cm^{-3}; *a* = 286.65 pm = 286.65×10^{-10} cm; *M* = 55.845 *u*.

We know:

density, $d = \frac{ZM}{N_A \cdot a^3}$. So;

Avogadro's number, $N_A = \frac{ZM}{d.a^3}$

$$= \frac{2 \times 55.845}{7.874 \times (286.65 \times 10^{-10})^3} = \mathbf{6.02 \times 10^{23}} \qquad \textbf{Ans.}$$

Example 143. *For a crystal of diamond, state:*

(i) The hybridisation of carbon atom.

(ii) The coordination of each carbon atom.

(iii) The type of lattice in which it crystallises.

(iv) The number of carbon atoms present per unit cell.

(ISC, 2012)

Solution. (*i*) C-atom is sp^3–hybridised

(*ii*) Coordination number of each *C*-atom = 4

(*iii*) Cubic lattice

(*iv*) Number of *C*-atoms present per unit cell = 1 i.e., 8 corners × $\frac{1}{8}$ atom per unit cell = 1.

Type (*i*). When density, *d* (in g cm^{-3}), mass or atomic mass, *M* (in g) and edge length, a (in pm) are required, then:

$$d = \frac{MZ}{N_A . a^3 \times 10^{-30}} \text{ g cm}^{-3}$$

(*ii*) When density, *d* (in kg m^{-3}), mass or atomic mass, M (in kg) and edge length, a (in pm) are required, then:

$$d = \frac{MZ}{N_A . a^3 \times 10^{-36}} \text{ kg m}^{-3}$$

(*iii*) Number of atoms, $N_A = \dfrac{MZ}{d\,(\text{in g cm}^{-3}) \times a^3 \times 10^{-30}}$

$$= \frac{MZ}{d\,(\text{in kg } m^{-3}) \times a^3 \times 10^{-36}}$$

(*iv*) 1 *pm* = 10^{-10} cm = 10^{-12} m

EXAMPLE 144. *An element has a body Centered Cubic (bcc) structure with a cell edge of 288 pm. The density of the element is 7200 kg m^{-3}. How many atoms are present in 208 g of the element?*

SOLUTION. Mass of element = 208 g = 208/1000 = 0.208 kg; *d* = 7200 kg m^{-3}; *a* = 288 pm; Z = 2 for bcc.

∴ Number of atoms

$$= \frac{MZ}{d.a^3.10^{-36}} = \frac{0.208 \text{ kg} \times 2}{7200 \text{ kg m}^{-3} \times (288)^3 \times 10^{-36} \text{m}^3}$$

= 2.418 × 10^{24} **Ans.**

EXAMPLE 145. *Lithium forms body centred cubic structure. The length of the side of its unit cell in 351 pm. Atomic radius of the lithium will be:*

(*a*) 300 pm (*b*) 240 pm

(*c*) 152 pm (*d*) 75 pm. **(AIEEE, 2012)**

SOLUTION. Edge length = 351 pm. For bcc stucture :

$$a\sqrt{3} = 4r\,;\quad r = \frac{a\sqrt{3}}{4} = \frac{351 \times 1.732}{4} = 151.98 \simeq 152 \text{ pm.}$$

So, the correct answer is (c).

PROBLEMS FOR PRACTICE

1. A compound P_2Q has wurtzite structure. Calculate its density if edge length of its unit cell is 5.9Å. (At. wt. P = 30, Q = 38) (**Ans.** 3.169 g cm^{-3})
2. Calculate the formula of corundum if its aluminium ions occupy two third of octahedral voids and oxide ions are arranged is hcp. (**Ans.** Al_2O_3)
3. Radii of A^+, B^- and C^- are 1 pm, 1 pm and 2 pm respectively. Find the structure of AB and AC along with volume of unit cell of AB and AC. (**Ans.** AB is b.c.c., volume = 12.32 cm^3; AC is octahedral, volume is 216 pm^3)
4. NaCl unit length is 0.5627 nm and density is 2.164g cm^{-3}. Find the difference of calculated and observed density and calculate % age of Cl^- and Na^+ ions **(Ans. 0.031, 0.775%).**
5. A metal (at. wt. 63.54) has fcc structure. If its atomic radius is 130 pm, find the length, density and volume of its unit cell. Also, calculate the number of atoms that belong to the unit cell.
   (**Ans.** *a* = 367.64 pm, *d* = 8.54 g cm^{-3},
   volume = 4.94 × 10^{-23} cm^3; Z = 4.)
6. An unknown metal crystallises in two phases, i.e., fcc and bcc with unit length of 3.5 and 3Å respectively. Find the ratio of density of fcc and bcc. (**Ans.** 1.259)
7. In a MA crystal, A^- ions form a ccp arrangement while M^+ ions occupy octahedral holes. Find relationship between edge length of unit cells and radii of A^- ions. If *a* = 600 pm, what will be the limiting radii of M^+ and A^-? (**Ans.** r^+/r^- = 0.414 (octahedral); M^+ = 87.84 pm; A^- = 212.164 pm)
8. The second order Bragg diffraction of *X*-rays with λ = 1.0Å from a set of parallel planes in a metal takes place at an angle of 60° (sin 60° = $\sqrt{3}/2$). The distance between the scattering planes in the crystal is :
   (*a*) 0.25Å (*b*) 1.0Å
   (*c*) 1.15Å (*d*) 3.0Å (**Ans.** (*c*))
9. In a compound, AB the ionic radii of A^+ and B^- are 88 pm and 200 pm respectively. The coordination number of A^+ is :
   (*a*) 4 (*b*) 6
   (*c*) 10 (*d*) 10
   [(**Ans.** (*b*)]
10. In the bcc structure of potassium (at. wt. 39), the nearest neighbour distance is 452 pm. Its density will be :
    (*a*) 302.3 kg m^{-3} (*b*) 604.6 kg m^{-3}
    (*c*) 910 kg m^{-3} (*d*) none of these.
    (**Ans.** (*c*))
11. The edge of fcc unit cell is 508 pm. The radius of cation is 110 pm. So, the radius of anion is :
    (*a*) 288 pm (*b*) 144 pm
    (*c*) 433 pm (*d*) 100 pm
    (**Ans.** (*b*))

11

CHAPTER

Eudiometry–Gas Analysis

11.1 SOME ABSORBENTS OF GASES

Absorbent	**Gas or gases absorbed**
Turpentine oil	O_3
Alkaline pyrogallol	CO_2 and O_2
Ferrous sulphate solution	NO
Heated magnesium	N_2
Heated palladium	H_2
Ammonical cuprous chloride	O_2, CO, C_2H_2 or $CH \equiv CH$
Copper sulphate solution	H_2S, PH_3, AsH_3
Conc. H_2SO_4	H_2O *i.e.*, moisture, NH_3
NaOH or KOH solution	CO_2, NO_2, SO_2, X_2, all acidic oxides

11.2 EUDIOMETRY – GAS ANALYSIS

The study of gaseous reactions is done in a eudiometer tube with the help of Gay-Lussac's law and Avogadro's law. Eudiometer tube is a closed graduated tube open at one end. The other end is a closed one which is provided with platinum terminals for passing electricity through the known volume of mixture of gases and known volume of oxygen gas. Volume of CO_2 formed is determined by absorbing in KOH solution, O_2 is determined by dissolving unreacted O_2 in alkaline pyrogallol and water vapours formed are determined by noting contraction in volume caused due to cooling. Eudiometry helps :

(*i*) to study composition of gaseous mixtures

(*ii*) to study volume – volume relationship

(*iii*) to determine molecular formula of gaseous hydrocarbons and

(*iv*) to determine molecular formula of gases

EXAMPLE 1. *A mixture of ethyne (C_2H_2) and H_2 was mixed with 65 mL of O_2 and exploded in a eudiometer tube. On cooling, it was found to have undergone a contraction of 35 mL. When treated with a KOH solution, a further contraction of 34 mL took place and 15 mL of O_2 alone was left behind. Find the percentage composition of ethyne and H_2 in the mixture.*

SOLUTION. Let mixture contains

$$H_2 = x\text{mL and } C_2H_2 = y\text{mL}$$

Reactions

$$\begin{array}{lllll} (i) & 2H_2 & + \quad O_2 & \longrightarrow & 2H_2O \\ & 2\text{Vol} & \quad 1\text{Vol} & & 2\text{Vol (steam)} \\ \text{or} & x\text{mL} & \quad \frac{x}{2}\text{mL} & & \text{Zero (cooled to liquid } H_2O) \end{array}$$

$$\begin{array}{llllll} (ii) & 2C_2H_2 & + \; 5O_2 & \rightarrow 4CO_2 & + & 2H_2O \\ & 2\text{Vol} & \;\; 5\text{Vol} & \;\; 4\text{Vol} & & 2\text{Vol (steam)} \\ \text{or} & y\text{mL} & \;\; \frac{5y}{2}\text{mL} & \;\; 2y\text{mL} & & \text{Zero (cooled to liquid } H_2O) \end{array}$$

KOH solution absorbs CO_2. So, CO_2 produced = 34 mL

O_2 left behind = 15 mL;

O_2 added to mixture = 65 mL

$$\therefore \quad O_2 \text{ used} = 65 - 15 = 50 \text{ mL}$$

But oxygen used according to reactions (*i*) and (*ii*)

$$= \frac{x}{2} + \frac{5y}{2}$$

$$\therefore \quad \frac{x}{2} + \frac{5y}{2} = 50 \qquad ...(iii)$$

Total CO_2 produced,

$$2y = 34 \text{ mL} \qquad ...(iv)$$

From equation (*iv*),

$$y = \frac{34}{2} = 17\text{mL}$$

Substituting the value of y in (*iii*), we get

$$\frac{x}{2} + \frac{5 \times 17}{2} = 50; \frac{x}{2} = 50 - \frac{85}{2} = 7.5 \text{ mL}$$

$$\therefore \quad x = 2 \times 7.5 = 15.0 \text{ mL}$$

Thus, Volume of H_2 = 15.0 mL;

volume of C_2H_2 = 17 mL

$$\therefore \quad \%\text{age of } H_2 = \frac{\text{Vol. of } H_2}{\text{Vol. of } H_2 + \text{Vol. of } C_2H_2} \times 100$$

$$= \frac{15}{15+17} \times 100 = \mathbf{46.88}$$

$$\therefore \quad \%\text{age of } C_2H_2 = 100 - 46.88 = \mathbf{53.12.}$$

EXAMPLE 2. *100 mL of O_2 gas was mixed with 20 mL of a mixture of methane (CH_4) and a gaseous compound of ethyne and exploded in a eudiometric tube. On cooling at room temperature and pressure, 80 mL volume was observed. After treatment with caustic potash solution, a further contraction of 40 mL was observed. Calculate the percentage composition of the mixture as well as the molecular formula of the gaseous compound of ethyne.*

SOLUTION. General formula of homologous series of ethynes is $\mathbf{C_nH_{2n-2}}$. It contains n atoms of C and $2n$–2 atoms of H. Thus :

Reactions

$$\begin{array}{llcccc} (a) & C & + & O_2 & \longrightarrow & CO_2 \\ & n\text{ atoms} & & n\text{ mol} & & n\text{ mol} \\ & 4H & + & O_2 & \longrightarrow & 2H_2O \\ & 4\text{ atoms} & & 1\text{mol} & & 2\text{ mol} \\ & 2n-2\text{ atoms} & & \frac{2n-2}{4}\text{ or }\frac{n-1}{2}\text{mol} & & \\ & & & & & \frac{2n-2}{2}\ i.e., n-1\text{ mol.} \end{array}$$

$$\textbf{or}\quad C_nH_{2n-2} + \left(n + \frac{n-1}{2}\right)\text{mol } O_2 \rightarrow nCO_2 + (n-1)H_2O$$

$$\textbf{or}\quad C_nH_{2n-2} + \frac{3n-1}{2}\,O_2 \rightarrow nCO_2 + (n-1)H_2O \qquad ...(i)$$

Suppose volume of $C_nH_{2n-2} = x$mL

Total volume = 20 mL

$\therefore$ Volume of $CH_4 = (20 - x)$mL.

Using equation (1) :

O_2 used for xmL of C_nH_{2n-2}

$$= x\left(\frac{3n-1}{2}\right)\text{mL}$$

CO_2 formed for xmL of $C_nH_{2n-2} = nx$mL

$$\begin{array}{llcllcl} (b) & CH_4 & + & 2O_2 & \longrightarrow & CO_2 & + 2H_2O \\ & (20\text{–}x)\text{ mL} & & 2\,(20\text{–}x)\text{ mL} & & (20\text{–}x)\text{ mL} & \end{array}$$

Actual volume of O_2 used = 100 – 40 = 60 mL

Actual volume of CO_2 formed = 80 – 40 = 40 mL

$$\therefore O_2\text{ used, } 2\,(20 - x) + \left(\frac{3n-1}{2}\right)x = 60$$

$$i.e.,\ 40 - 2x + \frac{3n-1}{2}x = 60$$

or $80 - 4x + (3n - 1)\,x = 120$

i.e., $-4x + (3n - 1)\,x = 40$

or $-4x + 3nx - x = 40$

or $-5x + 3nx - 40 = 0 \qquad ...(ii)$

CO_2 formed, $20 - x + nx = 40$

or $-x + nx - 20 = 0 \qquad ...(iii)$

Multiplying equation (*iii*) by 3 and subtracting from (*ii*), we get :

$$\begin{array}{rrrcl} -5x & +3nx & -40 & = & 0 \\ -3x & +3nx & -60 & = & 0 \\ + & - & + & & - \\ \hline -2x & & +20 & = & 0 \end{array}$$

$$\textbf{or}\quad -2x = -20 \quad \textbf{or}\quad -x = \frac{-20}{2} \quad \textbf{or}\quad \mathbf{x = 10.}$$

Substituting the value of $x = 10$ in (*iii*), we get :

$-10 + 10\,n - 20 = 0$ **or** $10\,n = 20 + 10 = 30$ **or**

$$n = \frac{30}{10} = \mathbf{3.}$$

Hence the molecular formula of

$$C_nH_{2n-2} = C_3H_{(2\times 3)-2} = \mathbf{C_3H_4}.$$

i.e., **propyne**.

(*c*) Volume of mixture of CH_4 and C_3H_4 = 20 mL

Volume of C_3H_4 = 10 mL

$$\therefore\quad \%\text{age of } C_3H_4 = \frac{\text{Vol. of } C_3H_4}{\text{Total volume}} \times 100$$

$$= \frac{10}{20} \times 100 = \mathbf{50.}$$

$$\therefore\quad \%\text{age of } CH_4 = 100 - 50 = \mathbf{50.}$$

EXAMPLE 3. *30 cm^3 of water gas containing only carbon monoxide and hydrogen in equal proportions by volume, was mixed with 90 mL of air containing 20% by volume of O_2 and exploded. Calculate the composition of the resulting gaseous mixture if all gaseous volumes are measured at room temperature and pressure.*

SOLUTION. Reactions :

$$\begin{array}{llllll} 2H_2 & + & O_2 & \longrightarrow & 2H_2O & ...(i) \\ 2\text{Vol} & & 1\text{Vol} & & \text{Zero (liquid water)} & \\ 2CO & + & O_2 & \longrightarrow & 2CO_2 & ...(ii) \\ 2\text{Vol} & & 1\text{Vol} & & 2\text{Vol} & \end{array}$$

Since water gas contains equal volumes of H_2 and CO, so:

$$\text{Volume of } H_2 = \text{Volume of CO} = \frac{30}{2} = 15\text{mL}$$

(*i*) 2Vol $H_2 \equiv$ 1 Vol O_2 [from equation (*i*)]

$$\therefore\quad 15\text{ mL } H_2 = \frac{1}{2} \times 15 = 7.5\text{ ml } O_2$$

(*ii*) 2Vol CO $\equiv$ 1Vol O_2 [from equation (*ii*)]

$$\therefore\quad 15\text{ mL CO} = \frac{1}{2} \times 15 = 7.5\text{ ml } O_2$$

$\therefore$ Total volume of O_2 used

= 7.5 mL + 7.5 mL = 15 mL

But vol. of O_2 present in 90 mL air

$$= 90 \times \frac{20}{100} = 18\text{mL}$$

$\therefore$ Volume of O_2 remained unused

= 18 – 15 = 3 mL

Volume of N_2 present in air, remained unused

= 90 – 18 = 72 mL

$\because$ 2Vol CO $\equiv$ 2Vol CO_2 [from equation (*ii*)]

$\therefore$ 15 mL CO $\equiv$ 15 mL CO_2

$\therefore$ Volume of CO_2 produced = 15 mL

EXAMPLE 4. *Electric current was passed through 10 mL of ammonia taken in a eudiometer tube. Sparks were allowed to occur till no further increase in volume took place. The volume after sparking was 20 mL. Now 30 mL O_2 gas was introduced and sparking was again continued. The resulting volume was found to be 27.5 mL. If nitrogen and hydrogen are diatomic, vapour density of ammonia is 8.5, then calculate the molecular formula of ammonia if all measurements of volume are done under identical conditions of temperature and pressure.*

SOLUTION. We know that on sparking ammonia, only hydrogen and nitrogen gases are formed. So,

Volume of H_2 + Volume of N_2 = 20 mL

Let, Volume of

H_2 gas $= x$ mL

$\therefore$ Volume of N_2 gas $= (20 - x)$ mL

Volume of O_2 gas added = 30 mL

On sparking H_2 reacts with O_2 to form water as follows:

$$\begin{array}{cccc} 2H_2 & + \quad O_2 & \longrightarrow & 2H_2O \\ 2\text{Vol} & 1\text{Vol} & & \text{Zero (liquid water)} \\ 2x \text{ mL} & x \text{ mL} & & \\ x \text{ mL} & \frac{x}{2} \text{ mL} & & \end{array}$$

$$\text{Contraction in volume} = x + \frac{x}{2} \qquad ...(i)$$

$$\text{Actual contraction} = \text{Vol. of } O_2 \text{ added} + (\text{Vol. of } N_2 + H_2) - 27.5$$

$$= 30 + 20 - 27.5 = 22.5 \qquad ...(ii)$$

Equating equations (*i*) and (*ii*), we get :

$$x + \frac{x}{2} = 22.5$$

or $$\frac{3x}{2} = 22.5$$

or $$3x = 2 \times 22.5 = 45$$

$$\therefore \quad x = \frac{45}{3} = \mathbf{15\ mL}$$

$\therefore$ 10mL of ammonia produces H_2 = 15 mL

10 mL of ammonia produces N_2 = 20 – 15 = 5 mL

Thus 10 mL ammonia produces 15 mL hydrogen and 5 mL nitrogen.

or 10 molecules of ammonia produce 15 molecules of hydrogen and 5 molecules of nitrogen.

$\therefore$ 1 molecule of ammonia produces $\frac{15}{10}$ or $\frac{3}{2}$ molecules of hydrogen and $\frac{5}{10}$ or $\frac{1}{2}$ molecule of nitrogen.

Since hydrogen and nitrogen are diatomic (given), so:

1 molecule of ammonia contains $\frac{3}{2} \times 2$ (= 3) atoms of hydrogen and $\frac{1}{2} \times 2$ (= 1) atom of nitrogen. Hence :

Molecular formula of ammonia = $\mathbf{NH_3}$

$\therefore$ Molecular mass of ammonia = 14 + (3 × 1) = 17

Since, Mol. wt. = 2 × V.D., Mol. wt. = 2 × 8.5 (given) = 17. This mol. wt. is same as found from the formula of NH_3, hence molecular formula of ammonia is NH_3.

EXAMPLE 5. *A vessel having capacity of 2.5 L contains $H_2O(l)$ and $N_2(g)$ at 302 K and one atmospheric pressure. On passing electric current, $H_2O(l)$ splits as $H_2O(l) \rightleftharpoons \frac{1}{2}O_2(g) + H_2(g)$. After the completion of reaction, the resulting pressure is 1.5 atm. If aqueous tension at 302 K is 0.04 atm, calculate the mass of water present in the vessel.*

SOLUTION. Total pressure in the beginning,

$$p_{\text{total}} = p_{N_2} + p_{H_2O}$$

$$H_2O(l) \xrightleftharpoons[\text{Spark}]{\text{Electric}} H_2(g) + \frac{1}{2}O_2(g)$$

$$\begin{array}{cc} 1\text{mol} & \frac{1}{2}\text{ mol} \\ p_{H_2} & \frac{1}{2}p_{O_2} \end{array}$$

$$\therefore \quad p_{\text{total}} = p_{N_2} + p_{H_2} + \frac{1}{2}p_{O_2}$$

$$= p_{N_2} + p_{H_2} + \frac{1}{2}\ p_{H_2}$$

$$\left[\because nH_2 = \frac{1}{2}nO_2 \text{ or } p_{H_2} = \frac{1}{2}p_{O_2}\right]$$

$$p_{\text{total}} = p_{N_2} + \frac{3}{2}p_{H_2} \qquad ...(1)$$

Considering aqueous tension, p_{H_2O} we have :

$$p_{\text{total}} = p_{N_2} + \frac{3}{2}p_{H_2} - p_{H_2O} \qquad ...(2)$$

Substituting the values in (2), we get

$$1.5 = 1 + \frac{3}{2}p_{H_2} - 0.04$$

or $$\frac{3}{2}p_{H_2} = 1.5 - 1 + 0.04 = 0.54 \text{ atm.}$$

or $$p_{H_2} = \frac{(2 \times 0.54)}{3} = 0.36 \text{ atm.}$$

But $$n = \frac{PV}{RT}.$$

Hence, $$n = \frac{0.36 \text{ atm} \times 2.5 \text{ L}}{0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 302 \text{ K}}$$

$$= 0.0363 \text{ mol}$$

From equation (1), we find that $n_{H_2O} = n_{H_2}$. Hence mass of H_2O originally present in the vessel will also be equal to 0.0363 mol.

One mol of H_2O weigh = (2 × 1) + 16 = 18 g

$\therefore$ 0.0363 mol of H_2O weigh = 0.0363 × 18 = **0.6534 g**

Ans.

11.3 COMPOSITION OF GASEOUS MIXTURE

Example 6. *A mixture of Cl_2 gas (2.8 L) and H_2 gas (3L) was exploded in a eudiometer tube. Calculate the composition by volume of the resulting mixture if all measurements are done under similar conditions of temperature and pressure.*

Solution. Reaction :

$$\begin{array}{llll} H_2 & + \; Cl_2 & \longrightarrow & 2HCl \\ 1mol & 1mol & & 2mol \\ 1Vol & 1Vol & & 2Vol \text{ (By Avogadro's Law)} \\ 2.8\,L & 2.8\,L & & 2 \times 2.8 = 5.6L \end{array}$$

1 Volume of Cl_2 reacts with H_2 = 1 Vol

$\therefore$ 2.8 L of Cl_2 react with H_2 = 2.8 L;

Volume of H_2 gas taken = 3 L

Volume of H_2 gas used = 2.8 L

$\therefore$ Volume of H_2 gas left behind = 3L – 2.8 L = 0.2 L **Ans.**

Volume of HCl gas formed = 2 × 2.8 L = 5.6 L **Ans.**

Example 7. *A mixture of 80 mL O_2 and 15 mL CH_4 gases was exploded in a eudiometer tube. The resulting mixture on cooling measured 65 mL, of which 50 mL was unused oxygen. Show that the results obey Gay Lussac's law of gaseous volumes.*

Solution. Reaction : $CH_4 + xO_2 \rightarrow yCO_2 + \underset{\text{steam}}{zH_2O}$.

Th product contains steam which on cooling gives water which has negligible volume. So, the resulting mixture will contain only gases.

Volume of CH_4 = 15 mL;

Volume of O_2 taken = 80 mL

Volume of O_2 left unused = 50 mL

$\therefore$ Volume of O_2 used = 80 – 50 = 30 mL

$\therefore$ Volume of CO_2 formed = 65 – 50 = 15 mL

$$\begin{array}{lccccc} \therefore \text{ Ratio by volume of } & CH_4 & : & O_2 & : & CO_2 \text{ is} \\ & 15 & : & 30 & : & 15 \\ & 1 & : & 2 & : & 1 \end{array}$$

which is a simple whole number ratio. So, Gay Lussac's law is obeyed.

Example 8. *When measured at the same temperature and pressure, hydrogen reacts with oxygen to form water in their volume ratio 2 : 1. Calculate the volume of O_2 gas measured at 137°C and 760 mm pressure that will combine with 100 mL of H_2 at 0°C and 200 mm pressure.*

Solution. Reaction :

$$\begin{array}{lcccc} 2H_2 & + & O_2 & \longrightarrow & 2H_2O \\ 2Vol & & 1Vol & & \end{array}$$

2 volume of H_2 require O_2 = 1 Vol

$\therefore$ 100 mL of H_2 require

$$O_2 = \frac{100}{2} = 50 \text{ mL at } 0°C \text{ and } 200 \text{ mm}$$

$\therefore$ $P_1 = 200$ mm, $V_1 = 50$ mL, $T_1 = 0 + 273 = 273$ K,
$P_2 = 760$ mm, $V_2 = ?$, $T_2 = 137 + 273 = 410$ K.

But, $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (gas equation)}$$

Hence, $$V_2 = \frac{P_1V_1T_2}{P_2T_1}$$

$\therefore$ $$V_2 = \frac{200\,\text{mm} \times 50\,\text{mL} \times 410\,\text{K}}{760\,\text{mm} \times 273\,\text{K}}$$

$= \mathbf{19.76\ mL}$ **Ans.**

Example 9. *20.0 cm^3 of a mixture of CO, CH_4 and He gas was exploded with excess of oxygen in a eudiometer tube at room temperature. After cooling, the volume contraction was found to be 13.0 cm^3. A further contraction of 14.0 cm^3 occurred when the residual gas was treated with KOH solution. Find the composition of the mixture.*

Solution. Let the volume of CO in the mixture = x cm^3

Let the volume of CH_4 in the mixture = y cm^3

$\therefore$ Volume of He in the mixture = $(20 - x - y)$ cm^3

Contraction in volume due to explosion and cooling = 13 cm^3

Also contraction in volume due to absorption in KOH = 14.0 cm^3

$\therefore$ Volume of CO_2 evolved = 14 cm^3

The chemical reactions can be written as :

$$\begin{array}{lcccr} 2CO & + & O_2 & \longrightarrow & 2CO_2 \quad \ldots(i) \\ x\ cm^3 & & \frac{x}{2}\ cm^3 & & x\ cm^3 \end{array}$$

$$\begin{array}{lcccr} \text{Also, } CH_4 & + & 2O_2 & \longrightarrow & CO_2 + 2H_2O \quad \ldots(ii) \\ y\ cm^3 & & 2y\ cm^3 & & y\ cm^3 \end{array}$$

Contraction in volume due to the combustion of CO

$$= x + \frac{x}{2} - x = \frac{x}{2} cm^3$$

Contraction in volume due to the combustion of CH_4

$$y + 2y - y = 2y \ cm^3$$

Total contraction in volume = $\left(\frac{x}{2} + 2y\right) cm^3$

Given that, $\frac{x}{2} + 2y = 13$ ...(*iii*)

Total volume of CO_2 produced = $(x + y)$ cm^3

Also, $x + y = 14$ cm^3 ...(*iv*)

Solving equations (*iii*) and (*iv*), we get

$x = 10.0$ cm^3 and $y = 4.0$ cm^3

Hence,volume of CO in the mixture = 10 cm^3

Volume of CH_4 in the mixture = 4.0 cm^3

$\therefore$ Volume of He in the mixture = 20 – (10 + 4) = **6 cm^3**.

Example 10. *3 litre of a gaseous mixture containing methane and ethane on complete combustion at 25°C produced four litre of carbon dioxide. Calculate the composition of the gas mixture.*

Solution. Volume of methane (CH_4) and ethane (C_2H_6) = 3 L

Volume of CO_2 produced = 4 L

Let volume of CH_4= xL; Volume of C_2H_6 = $(3 - x)$ L

Reactions

$$\begin{array}{lcccccc} (i) & CH_4 & + & 2O_2 & \longrightarrow & CO_2 & + \; 2H_2O \\ & x & & & & x & \end{array}$$

$$\begin{array}{llllll} (ii) & C_2H_6 \ + & \frac{7}{2}O_2 & \longrightarrow & 2CO_2 \ + & 3H_2O \\ & 3-x & & & 2(3-x) & \end{array}$$

Thus, CO_2 produced from both, $x + 2(3-x) = 4$ (given)

$$x + 6 - 2x = 4$$

or $-x = 4 - 6 = -2 \ \therefore \ x = 2\text{ L}$

or Volume of CH_4 = 2L; Volume of $C_2H_6 = 3 - 2 = 1\text{L}$

$$\%\text{age of } CH_4 = \frac{\text{Vol. of } CH_4}{\text{Total volume}} \times 100$$

$$= \frac{2}{3} \times 100 = \mathbf{66.67}$$

$$\%\text{age of } C_2H_6 = 100 - 66.67 = \mathbf{33.33.}$$

Example 11. *A gaseous mixture containing 49.5 mL of hydrogen chloride and H_2 gases was kept in contact with Na/Hg. The volume of mixture decreased to 42 mL. If 99.5 mL of the same mixture is mixed with 49.5 mL of gaseous ammonia and then exposed to water, calculate the final volume. All measurements of volume being done under same conditions of temperature and pressure.* **(IIT, 1972)**

Solution. Volume of H_2 gas + HCl (g) = 49.5 mL. When kept in contact with Na/Hg, only HCl will react with Na as follows :

$$\begin{array}{lllll} 2Na \ + & 2HCl & \longrightarrow & 2NaCl \ + & H_2 \\ & 2\text{Vol} & & & 1\text{Vol} \end{array}$$

Reduction in volume = 2Vol – 1Vol

= 1Vol for 2 Vol of HCl

Actual reduction in volume = 49.5 – 42 = 7.5 mL

$\therefore$ Volume of HCl present in 49.5 mL mixture

$= 7.5 \times 2 = 15$ mL

Volume of $H_2 = 49.5 - 15 = 34.5$ mL

$\therefore$ 99.5 mL of mixture would contain HCl (g)

$= 15 \times 2 = 30$ mL

and $H_2 = 99.5 - 30 = 69.5$ mL

When mixed with NH_3, the reaction will be :

$$\begin{array}{llll} NH_3(g) \ + & HCl(g) & \longrightarrow & NH_4Cl(s) \\ 1\text{Vol} & 1\text{Vol} & & \\ 30\text{ mL} & 30\text{ mL} & & [30\text{ mL } NH_3 \equiv 30\text{ mL HCl}] \end{array}$$

$\therefore$ Residual $NH_3 = 49.5 - 30 = 19.5$ mL

It will also dissolve in H_2O. So, only gas left behind is H_2 gas. Hence :

Residual $H_2 = 99.5 - 30$

= 69.5 mL or final volume

= **69.5 mL**

Example 12. *A gaseous mixture containing one litre of deuterium and same volume of hydrogen at STP were taken in a bulb. This bulb was then connected to another fully evacuated bulb by a stop-cock having a small opening. The stop-cock was opened for a certain time and then closed. The first bulb was now found to contain 0.04 g of hydrogen. Calculate the percentage composition by weight of H_2 and D_2 gases in the second bulb.*

Solution. The weight of H_2 in first bulb = 0.04 g. We know that:

g. mol. wt. of H_2 (= 2g) occupy vol. = 22.4 L

$\therefore$ 0.04 g H_2 will occupy volume,

$$V_1 = \frac{22.4}{2} \times 0.04 = 0.448\text{ L}$$

$\therefore$ Volume of H_2 diffused = 1.0 L – 0.448 L = **0.552 L.**

$\therefore$ Volume of H_2 in second bulb = 0.552 L

22.4 L volume of H_2 weigh = g. mol. wt. of H_2 = 2 g

0.552 L volume of H_2 weigh

$$= \frac{2}{22.4} \times 0.552 = 0.049\text{ g}$$

Let volume of deuterium (D_2) diffused

= V_2; g. mol. wt. of D_2 = 4g.

But,
$$\frac{V_1}{V_2} = \left(\frac{M_{D_2}}{M_{H_2}}\right)^{1/2} = \left(\frac{4}{2}\right)^{1/2}$$

$$= (2)^{1/2} = 1.4142$$

$$\therefore \quad \frac{0.448}{V_2} = 1.4142$$

or
$$V_2 = \frac{0.448}{1.4142} = 0.317\text{ L at NTP}$$

22.4 L of D_2 weigh = g. mol. wt. of D_2 = 4g

$\therefore$ 0.317 L of D_2 weigh

$$= \frac{4}{22.4} \times 0.317\text{ g} = 0.057\text{ g}$$

$\therefore$ Wt. of D_2 in second bulb = 0.057 g;

wt. of H_2 in second bulb = 0.049 g

$$\therefore \quad \%\text{age of } H_2 = \frac{\text{wt. of } H_2}{\text{wt. of } H_2 + \text{wt. of } D_2} \times 100$$

$$= \frac{0.049}{0.049 + 0.057} \times 100$$

$$= \frac{0.049}{0.106} \times 100 = \mathbf{46.23}$$

$$\%\text{age of } D_2 = 100 - 46.23 = \mathbf{53.77.}$$

Example 13. *A gas X weighing 3g was introduced into an initially evacuated flask at 298 K. Its pressure is one atmosphere. Now, 4 g of a gas Y was introduced into it at the same temperature and pressure. The final pressure was found to be 1.8 atmosphere. Calculate the ratio of molecular weights of gases X and Y if both gases behave as ideal gases.* **(IIT 1977)**

Solution. Let mol. wt. of gas X = M_1 and that of gas Y is M_2. wt. of gas X is 3 g and that of gas Y is 4 g. Thus :

No. of moles of gas, X = $\frac{3}{M_1}$;

No. of moles of gas, Y = $\frac{4}{M_2}$

We know that under the same conditions of temperature and volume, the partial pressure of gases is proportional to their molar concentration. Hence :

Initial pressure, $p_1 \propto \dfrac{3}{M_1} \propto 1$ atm

Final pressure, $p_2 \propto \dfrac{3}{M_1}+\dfrac{4}{M_2} \propto 1.8$ atm

Hence, $\dfrac{p_1}{p_2} = \dfrac{1}{1.8}=\dfrac{10}{18}$

or $\dfrac{\dfrac{3}{M_1}}{\dfrac{3}{M_1}+\dfrac{4}{M_2}} = \dfrac{10}{18}$ or $\dfrac{\dfrac{3}{M_1}}{\dfrac{(3M_2+4M_1)}{M_1M_2}} = \dfrac{10}{18}$

or $\dfrac{3}{M_1}\times\dfrac{M_1M_2}{3M_2+4M_1} = \dfrac{10}{18}$ or $\dfrac{3M_2}{3M_2+4M_1} = \dfrac{10}{18}$

or $\dfrac{3M_2+4M_1}{3M_2} = \dfrac{18}{10}$ or $\dfrac{3M_2}{3M_2}+\dfrac{4M_1}{3M_2} = \dfrac{18}{10}$

i.e., $1+\dfrac{4M_1}{3M_2} = \dfrac{18}{10}$ or $\dfrac{4M_1}{3M_2} = \dfrac{18}{10}-1=\dfrac{8}{10}$

or $\dfrac{M_1}{M_2} = \dfrac{8\times 3}{4\times 10}=\dfrac{3}{5}$

$\therefore M_1 : M_2 :: 3 : 5$ **Ans.**

11.4 ANALYSIS OF GASEOUS MIXTURES

Type. Contraction in volume of gaseous mixture due to absorption of CO_2 gas by KOH solution.

EXAMPLE 14. *In a eudiometric experiment, 15 mL of a mixture of N_2, CO and CH_4 was exploded with excess of oxygen gas. The contraction observed was 9.8 mL. When the residual gas was treated with KOH solution, a further contraction of 10.6 mL was observed. Calculate the composition of the original mixture.*

SOLUTION. Volume of N_2 + CO + CH_4 = 15 mL.

Let, Volume of CO = x mL;

Volume of CH_4 = y mL

$\therefore$ Volume of N_2 = $(15 - x - y)$ mL

Reactions

$$\begin{array}{llllll}
(i) & CO & + & \frac{1}{2}O_2 & \longrightarrow & CO_2 \\
 & 1\text{Vol} & & \frac{1}{2}\text{Vol} & & 1\text{Vol} \\
 & x\text{ mL} & & \frac{x}{2}\text{ mL} & & x\text{ mL}
\end{array}$$

$$\begin{array}{llllllll}
(ii) & CH_4 & + & 2O_2 & \longrightarrow & CO_2 & + & 2H_2O \\
 & 1\text{Vol} & & 2\text{Vol} & & 1\text{Vol} & & 2\text{ Vol (steam or} \\
 & & & & & & & \text{zero vol. on} \\
 & y\text{ mL} & & 2y\text{mL} & & y\text{ mL} & & \text{cooling to 0°C)}
\end{array}$$

Original contraction = 9.8 mL. Contraction from reactions (*i*) and (*ii*) is :

$$x + \frac{x}{2} - x + y + 2y - y \textbf{ or } \frac{x}{2} + 2y.$$

Hence $\dfrac{x}{2} + 2y = 9.8$ mL ...(A)

Total contraction due to CO_2 absorption by KOH = 10.6 mL.

Total CO_2 volume formed from reactions (*i*) and (*ii*) is: $x + y$. Hence, $x + y = 10.6$ ...(B)

Multiplying equation (A) by (2) and subtracting equation (B) from it we get :

$$\left[\frac{x}{2}+2y = 9.8\right] \times 2$$

$$\begin{array}{r}
x + y = 10.6 \\
- \quad - \quad - \\
\hline
\end{array}$$

$3y = (2 \times 9.8) - 10.6 = 19.6 - 10.6 = 9.0$

or $y = \dfrac{9}{3}=3$ mL

$\therefore$ **Volume of CH_4 = 3 mL** **Ans.**

Putting $y = 3$ in (B), we get :

$x + 3 = 10.6$

$x = 10.6 - 3 = 7.6$ mL

$\therefore$ **Volume of CO = 7.6 mL** **Ans.**

Volume of N_2 $=15 - x - y = 15 - 7.6 - 3 =$ **4.4 mL Ans.**

EXAMPLE 15. *One litre of a mixture of CO and CO_2 is taken. This mixture is passed through a red hot tube containing red hot charcoal. The volume now becomes 1.6 litres. The volumes are measured under the same conditions. Find the composition of the mixture by volume.* **(IIT, 1980)**

SOLUTION. Volume of CO + CO_2 gas = 1 L = 1000 mL

Let, Volume of CO_2 = x mL

Volume of CO = $(1000 - x)$ mL

Reaction

$$\begin{array}{llllll}
(i) & CO_2 & + & C & \longrightarrow & 2CO \\
 & x\text{ mL} & & \text{(charcoal)} & & 2x\text{ mL}
\end{array}$$

Total volume after reaction = $2x + (1000 - x)$

Thus : $2x + 1000 - x = 1.6$ L $= 1.6 \times 1000 = 1600$ mL;

$x = 1600 - 1000 =$ **600 mL.**

$\therefore$ Volume of CO_2 = 600 mL

Volume of CO = 1000 – 600 = **400 mL** **Ans.**

EXAMPLE 16. *A eudiometer tube contains a mixture of 45% ethane (C_2H_6), 45% H_2 and 10% oxygen. Calculate the additional volume of O_2 gas that would be required for the complete combustion of 300 mL of the given mixture measured at 17°C and 740 mm pressure.*

Also, calculate the amount of potassium nitrate required to get the excess oxygen required.

SOLUTION. C_2H_6 = 45%, H_2 = 45%, O_2 = 10%;

Total volume = 300 mL

(*i*) 100 mL mixture contain C_2H_6 = 45 mL

300 mL mixture contain

$$C_2H_6 = \frac{45}{100}\times 300 = 135\text{ mL}$$

(*ii*) 100 mL mixture contain H_2 = 45 mL

300 mL mixture contain $H_2 = \dfrac{45}{100}\times 300 = 135$ mL

(*iii*) 100 mL mixture contain O_2 = 10 mL

300 mL mixture contain $O_2 = \frac{10}{100} \times 300 = 30\,\text{mL}$

Reactions

$$\begin{array}{lllllll} (i) & C_2H_6 & + & \frac{7}{2}O_2 & \longrightarrow & 2CO_2 & + \; 3H_2O \\ & 1\text{Vol} & & \frac{7}{2}\text{Vol} & & & \end{array}$$

1 mL C_2H_6 need $O_2 = \frac{7}{2}$ mL

135 mL C_2H_6 need $O_2 = \frac{7}{2} \times 135 = 472.5$ mL

$$\begin{array}{llllll} (ii) & 2H_2 & + & O_2 & \longrightarrow & 2H_2O \\ & 2\text{Vol} & & 1\text{Vol} & & \end{array}$$

2mL H_2 need O_2 = 1 mL

135 mL H_2 need $O_2 = \frac{1}{2} \times 135 = 67.5\,\text{mL}$

Total Volume of O_2 required

= 472.5 + 67.5 = 540.0 mL

Volume of O_2 already present

= 30 mL

Volume of O_2 needed more

= 540 – 30 = **510 mL** **Ans.**

Conversion of volume to N.T.P. P_1 = 740 mm; V_1 = 510 mL, T_1 = 17 + 273 = 290 K; At N.T.P., P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

But $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ (gas equation);

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$\therefore \quad V_2 = \frac{740\,\text{mm} \times 510\,\text{mL} \times 273\,\text{K}}{290\,\text{K} \times 760\,\text{mm}}$$

= 467.47 mL

$$KNO_3 \longrightarrow KNO_2 + \frac{1}{2}O_2$$

39 + 14 + (3 × 16) = 101 g $\quad \frac{1}{2} \times 22400 = 11200$ mL

11200 mL O_2 is available from KNO_3 = 101 g

467.47 mL O_2 is available from KNO_3

$= \frac{101}{11200} \times 467.47 =$ **4.2 g** **Ans.**

Example 17. *One litre of O_2 and one litre of H_2 are taken in a vessel of 2 litre capacity at N.T.P. The gases are made to combine by applying an electric spark. Assume that water is formed quantitatively. How many grams of water are formed ? What is the other component present in the vessel and in what weight ? If the vessel is now heated to 100°C what will be the total pressure inside the vessel in mm of Hg (R = 0.082).*

(IIT, 1976)

Solution.

$$\begin{array}{lllll} 2H_2 & + \; O_2 & \longrightarrow & 2H_2O & \ldots(1) \\ 2\text{ Vol} & 1\text{ Vol} & & 2\text{ Vol steam} & \\ 2\text{L} & 1\text{L} & & \text{or zero volume at } 0°\text{C} & \end{array}$$

Given volume of H_2 = 1 L; O_2 = 1 L

From reaction, we see that one litre of H_2 react with $\frac{1}{2}$L of O_2.

$\therefore$ Volume of unreacted $O_2 = 1 - \frac{1}{2} = \frac{1}{2}$L

In reaction :

$$\begin{array}{lllll} H_2 & + & \frac{1}{2}O_2 & \longrightarrow & H_2O \\ 22.4\text{ L} & & & & (2\times1) + 16 = 18\text{g} \end{array}$$

22.4 L H_2 produce H_2O = 18 g

1 L H_2 produce $H_2O = \frac{18}{22.4} \times 1 =$ **0.8036 g**

= wt. of H_2O

Since $\frac{1}{2}$L O_2 has reacted out of 1L, we are left with $1 - \frac{1}{2} = \frac{1}{2}$L O_2

$\therefore$ 22.4 L O_2 weighs = g. mol. wt. of O_2 = 2 × 16 = 32 g

$\frac{1}{2}$L O_2 weighs $= \frac{32}{22.4} \times \frac{1}{2}$

= 0.7143 g

= wt. of other component. Ans.

(*i*) Considering water in the form of steam (100°C), we have :

$$PV = n\text{RT (gas equation)}$$

$$PV = \frac{W}{M}RT; \; P = \frac{W}{MV} \times RT$$

But W = wt. of H_2O = 0.8036g ; V = 2L, M = mol. wt. of H_2O = (2 × 1) + 16 = 18 g

R = 0.082 L atm $K^{-}mol^{-}$, T = 100 + 273 = 373 K.

$$\therefore \quad P = \frac{0.8036\text{g} \times 0.082\text{ L atm K}^{-}\text{mol}^{-} \times 373\text{ K}}{18\text{ g mol}^{-} \times 2\text{L}}$$

= 0.6827 atm **Ans.**

(*ii*) Partial pressure, P_1 due to 0.7143 g O_2 left behind is :

$$P = \frac{WRT}{MV}$$

$$= \frac{0.7143\text{g} \times 0.082\text{ L atm K}^{-}\text{mol}^{-} \times 373\text{ K}}{32\text{ g mol}^{-} \times 2\text{L}}$$

= 0.3414 atm

$\therefore$ Total pressure = 0.6827 atm + 0.3414 atm

= 1.0241 atm.

$= 1.0241\text{ atm} \times \frac{760\text{ mm}}{1\text{ atm}}$

= 778.32 mm **Ans.**

Example 18. *In a eudiometer tube explosion experiment, 30 mL of a mixture of ethyne (C_2H_2) and carbon monoxide was exploded with 45 mL of oxygen gas. The residual gases occupied*

51 mL. When the latter gases were treated with caustic potash, O_2 gas occupied 12 mL. Calculate the composition of the mixture.

SOLUTION. Volume of C_2H_2 + CO gases = 30 mL

Volume of O_2 gas mixed = 45 mL

Let, Volume of CO gas = x mL

Volume of C_2H_2 = $(30-x)$mL

Total volume after combustion = 51 mL

Volume of O_2 left behind = 12 mL

$\therefore$ Volume of CO_2 absorbed when treated with KOH $= 51 - 12 = 39$ mL

Volume of O_2 used $= 45 - 12 = 33$ mL

Reactions

$$\begin{array}{lllllll}
(i)\ CO & + & \frac{1}{2}O_2 & \longrightarrow & CO_2 & & \\
1\ \text{Vol} & & \frac{1}{2}\ \text{Vol} & & & & \\
(ii)\ C_2H_2 & + & \frac{5}{2}O_2 & \longrightarrow & 2CO_2 & + & H_2O \\
1\ \text{Vol} & & \frac{5}{2}\ \text{Vol} & & & &
\end{array}$$

(*a*) 1 mL CO require $O_2 = \frac{1}{2}$ mL

x mL CO require $O_2 = \frac{1}{2} \times x = \frac{x}{2}$ mL

(*b*) 1 mL C_2H_2 require $O_2 = \frac{5}{2}$ mL

$(30 - x)$ mL C_2H_2 require $O_2 = \frac{5}{2} \times (30 - x)$ mL

$\therefore$ Total O_2 used by CO and $C_2H_2 = \frac{x}{2} + \frac{5(30-x)}{2}$

or $\frac{x}{2} + \frac{5(30-x)}{2} = 33$ mL;

$x + 150 - 5x = 2 \times 33 = 66$ mL

$\therefore 4x = 150 - 66 = 84$ mL. Hence $x = \frac{84}{4} = 21$ mL

$\therefore$ Volume of CO gas = x = **21 mL** **Ans.**

Volume of C_2H_2 gas $= 30 - x = 30 - 21 =$ **9 mL** **Ans.**

EXAMPLE 19. *Water gas sample (120 mL) containing CO, H_2 and CO_2 gases was bubbled through caustic potash (KOH) solution. As a result, the sample showed a contraction of 7.08 mL. Out of the residue, 56 mL were taken, mixed with 52 mL O_2 and exploded. The volume left after explosion and cooling was 37 mL. Calculate the composition of water gas.*

SOLUTION. Total Volume of H_2, CO and CO_2 gases $= 120$ mL

Volume of CO_2 (absorbed by KOH) = 7.08 mL

Volume of residual gases (H_2 + CO) $= 120 - 7.08 = 112.92$ mL

Volume of residual gases + Volume of O_2 mixed $= 56 + 52 = 108$ mL

Volume of gases left after explosion $= 108 - 37 = 71$ mL

Reactions (*i*)

$$\begin{array}{lllll}
(i) & CO & + \frac{1}{2}O_2 & \longrightarrow & CO_2 \\
 & 1\ \text{Vol} & \frac{1}{2}\ \text{Vol} & & 1\ \text{Vol} \\
(ii) & H_2 & + \frac{1}{2}O_2 & \longrightarrow & H_2O(l) \\
 & 1\ \text{Vol} & \frac{1}{2}\ \text{Vol} & & \text{Negligible volume}
\end{array}$$

Let, Volume of CO gas in the mixture = x mL

Volume of H_2 gas in the mixture = $(56 - x)$ mL

(*a*) From reaction (*i*), contraction in volume

$= 1 + \frac{1}{2} - 1 = \frac{1}{2}$ Vol

$\therefore$ Contraction due to CO $= \frac{1}{2} \times x = \frac{x}{2}$

(*b*) From reaction (*ii*),

Contraction in volume $= 1 + \frac{1}{2} - 0 = \frac{3}{2}$

$\therefore$ Contraction due to $H_2 = \frac{3}{2} \times (56 - x)$

$\therefore$ Total contraction from (*i*) and (*ii*) :

$\frac{x}{2} + \frac{3(56-x)}{2} = 71$ mL

$x + 168 - 3x = 2 \times 71 = 142;$

$2x = 168 - 142 = 26$ mL

$\therefore x = \frac{26}{2} = 13$ mL. Hence **volume of CO = 13 mL.**

Volume of H_2 gas $= 56 - 13 = 43$ mL

Calculation of CO and H_2 present in 112.92 mL after the removal of CO_2 gas.

(*c*) Volume of CO $= \frac{13}{56} \times 112.92 =$ **26.21 mL** **Ans.**

(*d*) Volume of $H_2 = \frac{43}{56} \times 112.92 =$ **86.71 mL** **Ans.**

Also, Volume of CO_2 found above = **7.08 mL** **Ans.**

EXAMPLE 20. *A mixture of 20 mL of CO, CH_4 and N_2 was burnt in excess of O_2 resulting in the reduction of 13 mL of volume. The residual gas was then treated with KOH solution to show a contraction of 14 mL in volume. Calculate the volume of CO, CH_4 and N_2 in the mixture. All measurements are done at constant pressure and temperature.* **(IIT, 1995)**

SOLUTION. Since KOH absorbs CO_2 gas only, so, volume of CO_2 formed = 14 mL.

Let, Volume of CO = a mL; of CO_2 = b mL; of N_2 = c mL.

$\therefore \quad a + b + c = 20$ mL

$$\begin{array}{lllll}
(i) & CO & + \frac{1}{2}O_2 & \longrightarrow & CO_2 \\
 & 1\ \text{mol} & \frac{1}{2}\ \text{mol} & & 1\text{mol} \\
 & a\ \text{mL} & \frac{a}{2}\ \text{mL} & & a\ \text{mL}
\end{array}$$

Volume of CO = a mL. So, volume of CO_2 = a mL.

$$\begin{array}{llllll} (ii) & CH_4 & + \; 2O_2 & \longrightarrow & CO_2 & + \; 2H_2O \\ & 1 \text{ mol} & 2 \text{ mol} & & 1 \text{ mol} & \\ & b \text{ mL} & 2b \text{ mL} & & b \text{ mL} & \end{array}$$

Volume of CH_4 = b mL; Volume of CO_2 = b mL.

(*iii*) $N_2 + O_2 \longrightarrow$ no action.

(*iv*) Volume of CO_2 formed

$$= \text{Volume of gas absorbed by KOH}$$

$$a + b = 14 \text{ mL} \qquad ...(A)$$

(*v*) Also, volume of O_2 used = $\frac{a}{2} + 2b$ (from equations (*i*) and (*ii*) above)

(*vi*) Reduction in volume, 13 mL = initial volume of CO + CH_4 + N_2 + (Volume of O_2 taken – Volume of O_2 left) – Volume of CO_2 formed – Volume of N_2 (= c).

or $13 \text{ mL} = a + b + c + (\text{volume of } O_2 \text{ used}) - (a + b) - c$

$13 \text{ mL} = \text{Volume of } O_2 \text{ used}$

$13 \text{ mL} = \frac{a}{2} + 2b$ [from equation (*v*)]

or $26 \text{ mL} = a + 4b \qquad ...(B)$

From equations (B) and (A), we have :

$$\begin{array}{r} a + 4b = 26 \\ a + b = 14 \\ - \quad - \quad - \\ \hline \end{array}$$

Subtract, $3b = 12$; $\mathbf{b = 4}$ **mL**

But, $a + b = 14$. So, $a + 4 = 14$; $\mathbf{a} = 14 - 4 =$ **10 mL**

But, $a + b + c = 20$ mL ; $10 + 4 + c = 20$; $c = 6$ mL

$\therefore$ Volume of CO = a = 10 mL **Ans.**

Volume of CH_4 = b = 4 mL **Ans.**

Volume of N_2 = c = 6 mL **Ans.**

11.5 MOLECULAR FORMULA OF GASEOUS HYDROCARBONS

Type. When V mL of hydrocarbon C_xH_y is exploded with O_2 in a eudiometer tube, on cooling, the contraction in volume = $\text{V mL} + \text{V}\left(x + \frac{y}{4}\right) \text{mL} - \text{V}x \text{ mL}$. The reaction is:

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \text{ (zero volume at 0°C)}.$$

Example 21. *20 mL of a gaseous hydrocarbon is exploded with oxygen in a eudiometer tube avoiding excess. On cooling, the volume contracts by 60 mL. Find the formula of the compound if the vapour density of hydrocarbon is 22.*

Solution. Let formula of hydrocarbon = C_xH_y

Volume of hydrocarbon = 20 mL

Contraction in volume = 60 mL

Reactions :

$$\begin{array}{lllll} C_xH_y & + \left(x + \frac{y}{4}\right)O_2 & \longrightarrow & xCO_2 & + \; \frac{y}{2}H_2O \\ 1 \text{ Vol} & \left(x + \frac{y}{4}\right)\text{Vol} & & x \text{ Vol} & \text{Zero volume at 0°C} \\ 20 \text{ mL} & 20\left(x + \frac{y}{4}\right)\text{mL} & & 20\,x \text{ mL} & \end{array}$$

$\therefore$ Contraction in volume, 60 mL

$$\begin{aligned} &= 20 \text{ mL} + 20\left(x + \frac{y}{4}\right) \text{mL} - 20\,x \text{ mL} \\ 60 &= 20 + 20\,x + 5y - 20\,x \\ 5y &= 60 - 20 = 40 \\ y &= \frac{40}{5} = \mathbf{8} \end{aligned}$$

$\therefore$ Hydrocarbon = C_xH_8

Mol. wt. of C_xH_8 = 2 × V.D. = 2 × 22 = 44

$$\begin{aligned} \therefore \; 12 \times x + (8 \times 1) &= 44 \\ 12\,x &= 44 - 8 = 36 \\ x &= \frac{36}{12} = \mathbf{3} \end{aligned}$$

$\therefore$ Formula of hydrocarbon = $\mathbf{C_3H_8}$ **Ans.**

Example 22. *500 mL of a hydrocarbon gas burnt in excess of oxygen yields 2500 mL of CO_2 and 3.0 litres of water vapours, all the volume being measured at the same temperature and pressure. What is the formula of hydrocarbon gas ?* **(IIT, 1974)**

Solution. Volume of hydrocarbon = 500 mL; Volume of CO_2 = 2500 mL; Volume of water vapours = 3L = 3 × 1000 = 3000 mL.

Let the formula of hydrocarbon = C_xH_y

Reactions

$$\begin{array}{lllll} C_xH_y & + \left(x + \frac{y}{4}\right)O_2 & \longrightarrow & xCO_2 & + \; \frac{y}{2}H_2O \\ 1 \text{ Vol} & \left(x + \frac{y}{4}\right)\text{Vol} & & x \text{ Vol} & \frac{y}{2} \text{ Vol} \\ 500 \text{ mL} & 500\left(x + \frac{y}{4}\right)\text{mL} & & 500\,x \text{ mL} & 500 \times \frac{y}{2} \\ & & & & = 250\,y \text{ mL} \\ & & & 2500 \text{ mL} & 3000 \text{ mL} \end{array}$$

$$\begin{aligned} \therefore \quad 500\,x &= 2500 \\ x &= \frac{2500}{500} = \mathbf{5} \end{aligned}$$

$$250\,y = 3000 \; ; \quad y = \frac{3000}{250} = \mathbf{12}$$

$\therefore$ **Formula of hydrocarbon =** $\mathbf{C_5H_{12}}$ **Ans.**

Example 23. *20 mL of a hydrocarbon were exploded in a eudiometric tube with excess of oxygen. On cooling, there was a contraction in volume of 40 mL. The residual gases when bubbled through KOH solution, a further contraction of 30 mL was observed. Calculate the molecular formula of hydrocarbon if all the volumes are measured under similar conditions of temperature and pressure.*

Solution. Volume of hydrocarbon taken = 20 mL.

Since contraction of volume is due to absorption of CO_2 by KOH, so, volume of CO_2 formed = 40 mL.

Let molecular formula of hydrocarbon = C_xH_y

Reactions

$$\begin{array}{llll} C_xH_y \;+ & \left(x+\frac{y}{4}\right)O_2 & \longrightarrow \; xCO_2 \;+ & \frac{y}{2}H_2O \;...(1) \\ 1 \text{ Vol} & \left(x+\frac{y}{4}\right)\text{Vol} & x \text{ Vol} & \text{Zero volume} \\ 20 \text{ mL} & 20\left(x+\frac{y}{4}\right)\text{mL} & 20\,x \text{ mL} & \end{array}$$

∴ Volume of CO_2 formed, $20\,x$ mL = 40 mL (given)

$$\therefore \qquad x = \frac{40}{20} = \mathbf{2}$$

Contraction in volume from reaction (1) is given as :

$$20 \text{ mL} + 20\left(x+\frac{y}{4}\right)\text{mL} - 20\,x \text{ mL} = 30 \text{ mL}$$

$$20 + 20\,x + 5y - 20\,x = 30;$$

$$5y = 30 - 20 = 10$$

$$\therefore \qquad y = \frac{10}{5} = \mathbf{2}$$

Hence molecular formula of hydrocarbon C_xH_y = $\mathbf{C_2H_2}$. *i.e.*, **ethyne**.

EXAMPLE 24. *10 mL of a mixture of gaseous hydrocarbon were burnt completely in 80 mL of O_2 at N.T.P. The remaining gas occupied 70 mL at N.T.P. This volume becomes 50 mL on treatment with KOH solution. What is the empirical formula of the hydrocarbon ?* **(IIT, 1976)**

SOLUTION. Let formula of hydrocarbon = C_xH_y
Volume of hydrocarbon taken = 10mL
Volume of oxygen gas added = 80mL

Reaction of combustion in O_2

$$\begin{array}{llll} C_xH_y \;+ & \left(x+\frac{y}{4}\right)O_2 & \longrightarrow \; xCO_2 \;+ & \frac{y}{2}H_2O \;...(1) \\ 1 \text{ mol} & \left(x+\frac{y}{4}\right)\text{mol} & x \text{ mol} & \frac{y}{2}\text{mol} \end{array}$$

By Avogadro's law

$$\begin{array}{llll} 1 \text{ mL} & \left(x+\frac{y}{4}\right)\text{mL} & x \text{ mL} & \text{Zero mL} \\ & & & \text{at } 0°\text{C} \\ 10 \text{ mL} & 10\left(x+\frac{y}{4}\right)\text{mL} & 10\,x \text{ mL} & \end{array}$$

(*a*) Volume of residual gas (CO_2 + unused O_2) = 70 mL

Since, KOH absorbs whole CO_2 and volume of gas left after KOH treatment is 50 mL, so :

Volume of CO_2 formed = 70 – 50 = 20 mL

From reaction (1),

$$10\,x \text{ mL } CO_2 = 20 \text{ mL } CO_2$$

$$\therefore \qquad x = \frac{20}{10} = \mathbf{2}$$

(*b*) Volume of O_2unused = 50 mL

∴ Volume of O_2 used = 80 – 50 = 30 mL

From equation (1), $10\left(x+\frac{y}{4}\right) = 30;$

$$x + \frac{y}{4} = \frac{30}{10} = 3$$

Substituting the values, we get :

$$2 + \frac{y}{4} = 3\,;\; 8 + y = 3 \times 4\,;\; \mathbf{y = 4.}$$

∴ Molecular formula of hydrocarbon

= C_xH_y = $\mathbf{C_2H_4}$ *i.e.*, **ethylene.**

Type. To determine molecular formula when vapour density of hydrocarbon is given.

EXAMPLE 25. *A gaseous hydrocarbon (V.D. = 15) having volume 10 mL was exploded with excess of O_2. On cooling, a contraction in volume by 25 mL was observed. Calculate the molecular formula of the hydrocarbon.*

SOLUTION. Let the molecular formula of hydrocarbon = C_xH_y

Volume of hydrocarbon taken = 10 mL

Contraction of volume after reaction and cooling = 25 mL

Reaction

$$\begin{array}{llll} C_xH_y \;+ & \left(x+\frac{y}{4}\right)O_2 & \longrightarrow \; xCO_2 \;+ & \frac{y}{2}H_2O \;...(1) \\ 1 \text{ Vol} & \left(x+\frac{y}{4}\right)\text{Vol} & x \text{ Vol} & \text{Zero volume} \\ & & & \text{at } 0°\text{C} \\ 10 \text{ mL} & 10\left(x+\frac{y}{4}\right)\text{mL} & 10\,x \text{ mL} & \end{array}$$

From reaction (1), contraction in volume is given as :

$$10 + 10\left(x+\frac{y}{4}\right) - 10\,x = 25 \text{ (given)}$$

$$10 + 10x + \frac{5y}{2} - 10\,x = 25,\; 10 + \frac{5y}{2} = 25;$$

$$20 + 5y = 50$$

$$\textbf{or} \qquad 5y = 50 - 20 = 30;\; \mathbf{y} = \frac{30}{5} = \mathbf{6}$$

∴ Formula of hydrocarbon = C_xH_6

(*a*) Mol. wt. of C_xH_6 = (12 × *x*) + (6 × 1) = 12 *x* + 6.

(*b*) Mol. wt. = 2 × V.D. (given) = 2 × 15 = 30.

From (*a*) and (*b*)

$$12x + 6 = 30;\; 12\,x = 30 - 6 = 24\,;\; x = 2$$

∴ Molecular formula of hydrocarbon = $\mathbf{C_2H_6}$ **Ans.**

EXAMPLE 26. *0.9 g of a solid organic compound (molecular weight, 90) containing carbon, hydrogen and oxygen, was heated with oxygen corresponding to a volume of 224 mL at S.T.P. After combustion, the total volume of the gases was 560 mL at S.T.P. On treatment with potassium hydroxide, the volume decreased to 112 mL. Determine the molecular formula of the compound.* **(IIT, 1972)**

SOLUTION. Let the formula of organic compound containing C, H and oxygen = $C_xH_yO_z$.

Mol. wt. of $C_xH_yO_z$ = 90

Volume of O_2 added = 224 mL

On combustion, CO_2 and H_2O (zero volume at 0°C) are formed.

So, the residual gas will contain CO_2 and unused O_2.

Since CO_2 gas is absorbed by KOH, the volume of CO_2 formed = 560 – 112 = **448 mL**

Volume of O_2 used = 224 – 112 = 112 mL

(*a*) 22400 mL $CO_2 \equiv$ 1 mol CO_2

$$448 \text{ mL } CO_2 \equiv \frac{1}{22400} \times 448 \text{ mol } CO_2$$

No. of mol. of compound

$$= \frac{\text{wt.}}{\text{mol. wt.}} = \frac{0.9}{90} = 0.01 \text{ mol}$$

$\therefore$ 0.01 mol compound produced CO_2

$$= \frac{448}{22400} \text{mol } CO_2$$

1 mol compound produced CO_2

$$= \frac{448}{22400} \times \frac{1}{0.01} = 2 \text{ mol } CO_2$$

$\therefore$ 2 mol $CO_2 \equiv$ 2 mol C atoms

$\therefore$ Formula of compound

$$= C_2H_yO_z$$

Mol. wt. of $C_2H_yO_z = (2 \times 12) + 1 \times y + 16 \times z$ $= \mathbf{24 + y + 16\,z}$.

Reaction $C_2H_yO_z + \frac{1}{2}O_2 \rightarrow 2CO_2 + \frac{y}{2}H_2O$

Atoms of oxygen involved in the above reaction are :

$$z + 1 = 4 + \frac{y}{2};\; z = 4 + \frac{y}{2} - 1 = 3 + \frac{y}{2}$$

$$\therefore \quad z = 3 + \frac{y}{2} \qquad \text{...(2)}$$

But mol. wt. $24 + y + 16z = 90$

But, $z = 3 + \frac{y}{2}$

Hence : $24 + y + 16\left(3 + \frac{y}{2}\right) = 90$

$$\begin{aligned} 24 + y + 48 + 8y &= 90 \\ 9y &= 90 - 48 - 24 = 18 \\ y &= \frac{18}{9} = \mathbf{2} \end{aligned}$$

Substituting the value of $y = 2$ in (2), we get :

$$z = 3 + \frac{2}{2} = \mathbf{4}$$

$\therefore$ Molecular formula of compound = $C_2H_yO_z$ = $C_2H_2O_4$ **Ans.**

Type. When combustion is done with air.

EXAMPLE 27. *15 mL of a gaseous hydrocarbon required for complete combustion 357 mL of air (21 percent oxygen by volume) and the gaseous products occupied 327 mL (all volumes being measured at N.T.P.). What is the formula of the hydrocarbon ?* **(Rohtak, Pre-Engg/Pre-medical, 1980)**

SOLUTION. (*a*) Let the formula of hydrocarbon = C_xH_y

Volume of C_xH_y = 15 mL

$$\text{Volume of oxygen} = 357 \times \frac{21}{100} = 75 \text{ mL}$$

Reaction

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \quad \text{...(1)}$$

15 mL $\quad 15\left(x + \frac{y}{4}\right)$ mL $\quad 15\,x$ mL $\quad$ Zero volume at 0°C

$\therefore$ Volume of $O_2 = 75 = 15\left(x + \frac{y}{4}\right)$;

$$x + \frac{y}{4} = \frac{75}{15} = 5 \qquad \text{...(2)}$$

(*b*) Residual volume

$$= 327 - (357 - 75) = 327 - 282 = 45 \text{ mL}$$

From reaction, residual volume, $15 + 15\left(x + \frac{y}{4}\right) - 15x = 45$

or $15 + 15x + \frac{15y}{4} - 15x = 45$;

$$15 + \frac{15y}{4} = 45$$

$$\therefore \quad 60 + 15y = 4 \times 45;$$

$$15\,y = 180 - 60 = 120;\; y = \frac{120}{15} = 8$$

Substituting the value of $y = 8$ in (2), we get :

$$x + \frac{8}{4} = 5;\, x + 2 = 5;\, x = 5 - 2 = 3. \text{ Hence :}$$

Formula of C_xH_y = $\mathbf{C_3H_8}$ **Ans.**

EXAMPLE 28. *12 mL of a gaseous hydrocarbon were mixed with 90 mL of oxygen and exploded. After explosion, the volume was 72 mL and after treatment with KOH, which was found to be 36 mL. Determine the molecular formula of the hydrocarbon.*

SOLUTION. Let the formula of hydrocarbon = C_xH_y

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O \quad \text{...(1)}$$

12 mL $\quad 12\left(x + \frac{y}{4}\right)$ mL $\quad 12\,x$ mL $\quad$ Zero volume at 0°C

Volume of hydrocarbon = 12 mL

Volume of O_2 taken = 90 mL

Volume of CO_2 formed = 72 – 36 = 36 mL

$$\therefore \quad 12\,x = 36\,;\, x = \frac{36}{12} = 3;\, \mathbf{x = 3.}$$

Volume of oxygen unused = 36 mL

$\therefore$ Volume of oxygen used = 90 – 36 = 54 mL

From reaction (1), volume of O_2 used,

$$12\left(x + \frac{y}{4}\right) = 54$$

$$12\,x + 3y = 54$$

Substituting the value of $x = 3$ in it, we get :

$$\begin{aligned}(12 \times 3) + 3y &= 54\\ 3y &= 54 - 36 = 18\\ y &= \frac{18}{3} = 6\end{aligned}$$

∴ When $x = 3, y = 6$, the formula of hydrocarbon C_xH_y = $\mathbf{C_3H_6}$ **Ans.**

EXAMPLE 29. *When 2.5 volumes of oxygen were exploded with one volume of a gaseous compound containing carbon, hydrogen and oxygen, two volumes of CO_2 and 2 volumes of steam were formed. All volumes were measured under identical conditions. Derive the formula of the compound from the above data.*

SOLUTION. According to Avogadro's law, equal volume of all gases contain equal number of molecules. Let formula of the compound = $C_xH_yO_z$. Hence :

$$\begin{array}{ccccccc} C_xH_yO_z & + & 2.5\,O_2 & \longrightarrow & 2H_2O & + & 2CO_2\\ \text{1 molecule} & & \text{2.5 molecules} & & \text{2 molecules} & & \text{2 molecules}\end{array}$$

From the equation, it is clear that :

2 molecules of H_2O are produced from hydrogen atoms = 2 × 2 = **4** atoms

2 molecules of CO_2 are produced from carbon atoms = **2**

To find number of oxygen atoms. Consider the oxidation of 'C' and H_2 of the compound in the following reactions:

$$\begin{array}{lcccc} (i)\ 2C & + & 2O_2 & \longrightarrow & 2CO_2\\ & & \text{2 molecules} & & \end{array}$$

2 carbon atoms use oxygen = 2 molecules

$$\begin{array}{lcccc} (ii)\ 2H_2 & + & O_2 & \longrightarrow & 2H_2O\\ \text{4 H atoms} & & \text{1 molecule} & & \end{array}$$

4 hydrogen atoms use oxygen = 1 molecule

Total number of molecules of oxygen used = 2 + 1 = 3

Actual number of molecules of oxygen used by compound = 2.5

∴ 3 – 2.5 *i.e.*, 0.5 molecule or 1 atom (0.5 × 2 = 1, ∵ oxygen is diatomic) of oxygen ($z = 1$) must have been derived from the compound. So, the formula of the compound $C_xH_yO_z$ = $\mathbf{C_2H_4O}$ **Ans.**

EXAMPLE 30. *A sample of gaseous hydrocarbon occupying 1.12 litres at N.T.P., when completely burnt in air produced 2.2 g of CO_2 and 1.8 g water. Calculate the weight of the compound taken and the volume of O_2 at N.T.P. required for its burning. Find the molecular formula of the hydrocarbon.* **(IIT, 1978)**

SOLUTION. Volume of hydrocarbon at N.T.P. = 1.12 L.

(*a*) wt. of CO_2 formed = 2.2 g;

g. mol. wt. of CO_2 = 12 + (2 × 16) = 44 g

44 g CO_2 occupy volume = 22.4 L

2.2 g CO_2 occupy volume = $\frac{22.4}{44} \times 2.2 = 1.12\,\text{L}$

(*b*) wt. of H_2O formed = 1.8g; g. mol. wt. of H_2O = (2 × 1) + 16 = 18 g

18 g steam occupy volume = 22.4 L

1.8 g steam occupy volume = $\frac{22.4}{18} \times 1.8 = 2.24\,\text{L}$

Reaction

$$\begin{array}{ccccccc} C_xH_y & + & \left(x+\frac{y}{4}\right)O_2 & \longrightarrow & xCO_2 & + & \frac{y}{2}H_2O \quad ...(1)\\ 1.12\text{ L} & & 1.12\left(x+\frac{y}{4}\right)\text{L} & & 1.12\,x\text{L} & & 1.12 \times \frac{y}{2}\end{array}$$

$= 0.56\,y\text{L steam}$

(*a*) From equation (1), CO_2 formed 1.12 xL = 1.12 L;

$$x = \frac{1.12}{1.12} = 1 \ \textit{i.e.},\ \mathbf{x = 1.}$$

(*b*) From reaction (1), H_2O (steam) formed,

$$0.56\,y\text{L} = 2.24\text{ L}$$

$$\therefore \quad y = \frac{2.24}{0.56} = 4 \ \textit{i.e.},\ y = 4$$

∴ Formula of hydrocarbon,

$C_xH_y = C_1H_4$ *i.e.*, CH_4 (methane)

(*c*) Volume of O_2 at N.T.P. required = $1.12\left(x+\frac{y}{4}\right)\text{L}$.

Substituting the values of x and y in it, we get :
Volume of O_2 at N.T.P. required

$$= 1.12\left(1+\frac{4}{4}\right)\text{L} = 1.12 \times 2 = \mathbf{2.24\ L}$$

(*d*) To find weight of compound CH_4,

g. mol. wt. of CH_4 = 12 + (4 × 1) = 16 g.

22.4 L CH_4 weighs = 16 g

1.12 L CH_4 weighs = $\frac{16}{22.4} \times 1.12 = = \mathbf{0.8\ g}$ **Ans.**

EXAMPLE 31. *5 mL of a gas containing only carbon and hydrogen were mixed with excess of oxygen (30 mL) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 mL. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 mL, the residual gas being pure oxygen. All the volumes have been reduced to N.T.P. Calculate the molecular formula of hydrocarbon gas.* **(IIT, 1979)**

SOLUTION. Let the formula of hydrocarbon = C_xH_y

Volume of hydrocarbon taken = 5 mL

Volume of oxygen gas added = 30 mL

Reaction

$$\begin{array}{ccccccc} C_xH_y & + & \left(x+\frac{y}{4}\right)O_2 & \xrightarrow[\text{Spark}]{\text{Electric}} & xCO_2 & + & \frac{y}{2}H_2O \quad ...(1)\\ 1\text{ mol} & & \left(x+\frac{y}{4}\right)\text{mol} & & x\text{ mol} & & \frac{y}{2}\text{mol}\end{array}$$

By Avogadro's law

$$\begin{array}{ccccccc} 1\text{ mL} & & \left(x+\frac{y}{4}\right)\text{mL} & & x\text{ mL} & & \text{Zero mL at } 0°\text{C}\\ 5\text{ mL} & & 5\left(x+\frac{y}{4}\right)\text{mL} & & 5x\text{ mL} & & \end{array}$$

(*a*) Volume of residual gas (CO_2 + unused O_2) = 25 mL

Since KOH absorbs whole CO_2 and volume of gas left after KOH treatment is 15 mL, so:

$$\text{Volume of } CO_2 \text{ formed} = 25 - 15 = 10 \text{ mL}$$

$$\text{From reaction (1)}, 5x \text{ mL } CO_2 = 10 \text{ mL } CO_2$$

$$\therefore \quad x = \frac{10}{5} = 2$$

(*b*) Volume of oxygen unused = 15 mL

$$\therefore \quad \text{Volume of oxygen used} = 30 - 15 = 15 \text{ mL}$$

$$\text{From reaction (1)}, \quad 5\left(x + \frac{y}{4}\right) = 15; \; x + \frac{y}{4} = \frac{15}{5} = 3$$

$$\textbf{or} \quad 2 + \frac{y}{4} = 3;$$

$$\frac{y}{4} = 3 - 2 = 1 \text{ or } \boldsymbol{y = 4}$$

$\therefore$ Molecular formula of hydrocarbon C_xH_y = $\mathbf{C_2H_4}$

Ans.

11.6 TO FIND MOLECULAR FORMULA OF GASES

Type. Use of turpentine oil to absorb ozone gas (O_3)

Example 32. *When silent electric discharge was passed through 40 mL oxygen gas, the volume contracted to 36 mL and gases found were oxygen and ozone. When above gases were heated to decompose ozone, the mixture occupied 40 mL volume. In another experiment, the mixture of 36 mL was treated with turpentine oil to absorb ozone, the volume contracted to 28 mL. Derive the formula of ozone from the above data.*

Solution. Volume of oxygen + Ozone = 36 mL

Volume of ozone absorbed by turpentine oil = 36 – 28 = 8 mL

Since 36 mL of mixture of oxygen and ozone on heating converts 8 mL of ozone present to oxygen, the total volume becomes 40 mL

$\therefore$ Vol. of oxygen produced by 8 mL of ozone = 40 – 28 = 12 mL

It is because 36 – 8 = 28 mL of oxygen were already present in the mixture.

$\therefore$ 16 mL of ozone on decomposition gives oxygen

$$= \frac{12}{8} \times 16 = 24 \text{ mL}$$

1 mL of ozone on decomposition gives oxygen

$$= \frac{24}{16} = 1.5 \text{ mL}$$

or 1 molecule of ozone on decomposition gives oxygen= 1.5 molecules

(By Avogadro's law)

But atomicity of oxygen = 2. Hence number of oxygen atoms in 1.5 molecule of oxygen = 1.5 × 2 = 3.

$\therefore$ **Formula of ozone =** $\mathbf{O_3}$ **Ans.**

Example 33. *35 volumes of oxygen were mixed with 25 volumes of a gas in a eudiometer tube and exploded. As a result 25 volume of CO_2 and after absorption by caustic potash, 22.5 volume of oxygen are left behind. Calculate the formula of the gas.*

Solution. Volume of O_2 taken = 35;

Volume of unknown gas = 25;

Volume of CO_2 formed = 25;

Volume of O_2 left behind = 22.5.

Hence volume of used O_2 = 35 – 22.5 = 12.5. Thus:

$$\begin{array}{lcccc} & \text{gas} & + \; \text{oxygen used} & \longrightarrow & CO_2 \text{ gas} \\ & 25 \text{ Volume} & 12.5 \text{ Volume} & & 25 \text{ Volume} \\ & \frac{25}{25} = 1\text{Vol} & \frac{12.5}{25} = \frac{1}{2}\text{Vol} & & \frac{25}{25} = 1\text{Vol } CO_2 \end{array}$$

(after dividing by 25)

$$\begin{array}{lccc} \textbf{or} & 1 \text{ molecule} & \frac{1}{2} \text{ molecule} & 1 \text{ molecule } CO_2 \end{array}$$

(By Avogadro's law)

$\therefore$ 1 molecule of gas + 1 atom of oxygen = 1 molecule CO_2

$\therefore$ 1 molecule of gas = CO_2 – 1 atom of oxygen = **CO** *i.e.*, carbon monoxide.

Example 34. *When 18 mL of H_2 and 10 mL of nitrous oxide gas were exploded in a eudiometer tube, volume after explosion was found to be 18 mL. Now 27 mL of O_2 were added and the mixture was exploded again. Volume after explosion was 15 mL. If all the measurements are done at N.T.P., determine the formula of nitrous oxide.*

Solution. Volume of H_2 added = 18 mL;

Volume of gas added = 10 mL

$\therefore$ Total volume = 18 + 10 = 28 mL

Volume after explosion = 18 mL

$\therefore$ Contraction in volume due to combination of H_2 with oxygen of nitrous oxide = 28 – 18 = 10 mL.

Volume of O_2 added = 27 mL

$\therefore$ Volume of O_2 used to oxidise excess H_2 = 27 – 18 = 9 mL

Contraction due to oxidation of excess H_2 with oxygen = 27 – 15 = 12 mL

Reaction :

$$\begin{array}{cccc} 2H_2 + & O_2 & \longrightarrow & 2H_2O \quad \ldots(1) \\ 2 \text{ Vol} & 1 \text{ Vol} & & \text{Zero volume, being liquid} \end{array}$$

Since H_2O formed has negligible volume and is formed from 2 volume of H_2 and 1 volume of O_2, there is *contraction of volume* = 3.

For contraction of 3 volumes,

Volumes of H_2 present = 2 [see reaction (1)]

For contraction of 12 volumes,

$$\text{Volumes of } H_2 \text{ present} = \frac{2}{3} \times 12 = 8$$

Also, 2 volumes of H_2 use oxygen = 1 volume [reaction (1)]

8 volumes of H_2 use oxygen = $\frac{1}{2}\times 8 = 4$ volumes

∴ Volume of H_2 used to consume O_2 oxygen from nitrous oxide =18 – 8 = 10 mL

Out of 9 volumes of O_2,
oxygen remains unused = 9 – 4 = 5 volume
∴ Residual volume of 15 mL contains
= 5 mL O_2 + 10 mL N_2
From reaction (1), it is clear that :
Volume of H_2 used for 5 vol of O_2 = 10

∴ When 10 volumes of nitrous oxide are reduced with 10 volumes of H_2, we get : 5 vol of O_2 + 10 vol of N_2. In other words :

Nitrous oxide	⟶	Oxygen +	Nitrogen
10 Vol		5 Vol	10 Vol
Using Avogadro's law :			
10 molecules		5 molecules	10 molecules
After dividing by 10 :			
1 molecule		$\frac{5}{10}=\frac{1}{2}$ molecule	1 molecule
		= 1 atom	= two atoms

∴ Formula of nitrous oxide = $\mathbf{N_2O}$ **Ans.**

EXAMPLE 35. *In a silent discharge apparatus, certain volume of oxygen was ozonized. As a result, the volume decreased by 5 mL. On addition of turpentine, the volume further decreased by 10 mL. Calculate the formula of ozone from this data if all the measurements are done under similar conditions of temperature and pressure.*

SOLUTION. Since turpentine absorbs ozone,
Volume of ozone formed = 10 mL
Decrease of volume of oxygen on ozonisation
= Vol of oxygen used – Volume of ozone formed
= 5 mL (given).

∴ Volume of oxygen used = Decrease of volume of O_2 on ozonisation + Volume of ozone formed = 5 + 10
= 15 mL.

∴	Oxygen 15 mL	⟶	Ozone 10 mL
	15 molecules		10 molecules
			(By Avogadro's law)
	$\frac{15}{10}$ or 1.5 molecules		1 molecule
			(After dividing by 10)

Since oxygen is diatomic, 1.5 molecules of oxygen contain 1.5 × 2 = 3 atoms.

∴ 1 molecule of ozone contains oxygen atoms = 3

∴ **Formula of ozone** $= \mathbf{O_3}$.

Type. When Cl_2 gas present in the mixture of gases is absorbed by NaOH solution.

EXAMPLE 36. *30 cm^3 of a mixture of equal volumes of Cl_2 and an oxide of chlorine were heated and then cooled to the room temperature. The resulting constituents occupied 37.5 mL. The resulting mixture was treated with NaOH solution and the volume contracted to 7.5 mL. If oxide of chlorine on heating decomposes quantitatively to O_2 and Cl_2 and all the measurements are done under similar conditions of temperature and pressure, deduce the simplest formula of oxide of chlorine.*

SOLUTION. Total volume of Cl_2 + oxide of chlorine = 30 mL

∴ Volume of Cl_2 = Volume of oxide of chlorine
$= \frac{30}{2} = 15$ mL

Volume of gases after decomposition = 37.5 mL

Volume of products of decomposition of oxide of chlorine = Total volume after decomposition – Volume of Cl_2 originally present = 37.5 – 15 = 22.5 mL.

Since NaOH solution absorbs Cl_2 (and O_2 is left behind):
Volume of products after treatment with NaOH
= 7.5 mL (given)

∴ Vol. of Cl_2 obtained from oxide of chlorine
= 22.5 – 7.5 = 15 mL

∴ 15 mL of chlorine oxide, on decomposition gives 7.5 mL of O_2 and 15 mL of Cl_2. In other words:

Chlorine oxide	⟶	Chlorine	+	Oxygen
15 mL		15 mL		7.5 mL
15 molecules		15 molecules		7.5 molecules

Applying Avogadro's law :
After dividing by 15

$\frac{15}{15}$ = 1 molecule	$\frac{15}{15}$ = 1 molecule	$\frac{7.5}{15}=\frac{1}{2}$ molecule
	= 1 × 2 atoms	$\frac{1}{2}\times 2 = 1$ atom
	= 2 atoms	

It is because chlorine as well as oxygen molecules are diatomic.

∴ One molecule of oxide of chlorine contains 2 atoms of chlorine and one atom of oxygen. Hence **formula of oxide of chlorine =** $\mathbf{Cl_2O}$.

EXAMPLE 37. *The silicon element (at. wt. 28) forms three hydrides which on heating liberate hydrogen gas. The first, second and third hydride respectively liberate twice, thrice and 4 times its volume of hydrogen. Deduce the formula of these hydrides if their respective densities are 16,30.7 and 46.4.*

SOLUTION. (*a*) **First hydride.** Mol. wt. = 2 × V.D = 2 × 16 = 32. This hydride liberates twice its volume of hydrogen. Thus :

First hydride	⟶	Hydrogen
1 Volume		2 Volume
1 molecule		2 molecules
		(By Avogadro's law)
		= 2 × 2 = 4 atoms
		(∵ hydrogen is diatomic)

∴ Formula of hydride = Si_xH_4

Mol. wt. of Si_xH_4 = 32; 28 x + (4 × 1) = 32;

$28\,x = 28;\; x = \frac{28}{28} = 1$

∴ Formula of Si_xH_4 = Si_1H_4 = $\mathbf{SiH_4}$ **Ans.**

(*b*) **Second hydride.** Mol. wt. = 2 × V.D. = 2 × 30.7 = 61.4

Second hydride	⟶ Hydrogen
1 Volume	3 Volume
1 molecule	3 molecules
	= 3 × 2 = 6 atoms

(By Avogadro's law)
(∵ hydrogen is diatomic)

∴ Formula of hydride = Si_xH_6

∴ Mol. wt. of Si_xH_6 = 61.4 ; 28 *x* + (6 × 1) = 61.4 ;

$$28x = 61.4 - 6 = 55.4.$$

Hence $x = \frac{55.4}{28} \approx 2.$

So, formula of hydride = $\mathbf{Si_2H_6}$ **Ans.**

(*c*) **Third hydride.**

Mol. wt. = 2 × V.D. = 2 × 46.4 = 92.8

Third hydride	⟶ Hydrogen
1 Volume	4 Volume
1 molecule	4 molecules
	= 4 × 2 = 8 atoms

(By Avogadro's law)
(∵ hydrogen is diatomic)

∴ Formula of hydride = Si_xH_8

∴ Mol. wt. of Si_xH_8 = 92.8; 28*x* + (8 × 1) = 92.8;

$$28x = 92.8 - 8 = 84.8;$$

$$x = \frac{84.8}{28} \approx 3.$$

Hence formula of hydride = $\mathbf{Si_3H_8}$ **Ans.**

EXAMPLE 38. *A gas (V.D., 17) measuring 75.9 mL when heated with cadmium, the latter was completely consumed to form cadmium sulphide. The residual gas was hydrogen which when passed over red hot cupric oxide yielded 0.061 g water. Derive the formula of the gas (at. wt., Cu = 64, H = 1, O = 16, S = 32).*

SOLUTION. Wt. of H_2O = 0.061 g

Reaction

$$CuO + \underset{22400\text{ mL}}{H_2} \longrightarrow Cu + \underset{(2\times1)+16=18\text{ g}}{H_2O}$$

18 g water is produced from H_2 = 22400 mL

0.061 g water is produced from $H_2 = \frac{22400}{18} \times 0.061$

= 75.9 mL

∴ 75.9 mL of gas combines with Cd to form H_2 gas = 75.9 mL under similar conditions of temperature and pressure. Hence gas contains same volume of hydrogen. So :

1 Vol. of gas contains *x* atoms of sulphur + 1 Vol of hydrogen.

Using Avogadro's law :

1 molecule of gas contains *x* atoms of sulphur + 1 molecule of hydrogen *i.e.*, 2 atoms of hydrogen because hydrogen is diatomic.

∴ Formula of gas = H_2S_x

Mol. wt. of H_2S_x = 2 × V.D. = 2 × 17 = 34

$$(2 \times 1) + 32x = 34; 32x = 34 - 2 = 32; x = \frac{32}{32} = 1.$$

∴ Formula of gas = H_2S_1 = $\mathbf{H_2S}$ **Ans.**

EXAMPLE 39. *At high temperatures, the compound S_4N_4 decomposes completely into N_2 and sulphur vapours. If all measurements are made under the same conditions of temperature and pressure, it is found that for each volume of S_4N_4 decomposed, 2.5 volumes of gaseous products are formed. What is the molecular formula of sulphur ?* **(IIT, 1970)**

SOLUTION. Reaction

$$\underset{1\text{ Vol}}{N_4S_4} \xrightarrow{\text{High temp.}} \underset{2.5\text{ Vol}}{2N_2 + \text{sulphur vapours}}$$

By Avogadro's law

1 molecule 2.5 molecules

2.5 molecules of $2N_2$ + sulphur vapours = 4 atoms of nitrogen (or 2 molecules of N_2 as nitrogen is diatomic) + 0.5 molecule of sulphur vapour. Hence the formula S_4N_4 indicates that :

0.5 molecule of sulphur contains S-atoms = 4

1 molecule of sulphur contains S-atoms = $\frac{4}{0.5} = 8$

∴ Formula of sulphur = $\mathbf{S_8}$ **Ans.**

EXAMPLE 40. *Nine volumes of a gaseous mixture consisting of a gaseous organic compound A and just sufficient amount of oxygen required for complete combustion yielded on burning 4 volumes of CO_2, 6 volumes of water vapours and 2 volumes of N_2, all volumes measured at the same temperature and pressure. If the compound A contained only carbon, hydrogen and nitrogen;*

(*i*) *How many volumes of oxygen are required for complete combustion ?*

(*ii*) *What is the molecular formula of the compound A ?*

(IIT, 1974)

SOLUTION. Reactions involved are:

(*i*)	C	+	O_2	→	CO_2	...(1)
	1 atom		1 Vol		1 Vol	
	1 × 4 = 4 Vol		1 × 4 = 4 Vol		4 Vol (given)	
(By Avogadro's law)	4 atoms of carbon					
(*ii*)	H_2	+	$\frac{1}{2}O_2$	→	$H_2O(g)$	...(2)
	1 Vol		$\frac{1}{2}$ Vol		1 Vol	
	1 × 6 = 6 Vol		$\frac{1}{2} \times 6 = 3$ Vol		6 Vol (given)	
(By Avogadro's law)	6 molecules = 6 × 2 = 12 atoms (∵ hydrogen is diatomic)		3 molecules		6 molecules	

(*iii*) Since no oxygen is used to liberate nitrogen, so 2 Volumes of nitrogen, N_2 (given) correspond to 2 × 2 = 4 atoms of nitrogen.

From reactions (1) and (2),

oxygen present = 4 + 3 = 7 Vol.

Total volume = 9 volume

∴ Vol. of gaseous organic compound

= 9 – 7 = 2 Vol.

Now consider the following overall reaction.

A	+ O_2	→ CO_2	+ H_2O	+ N_2
2 Vol	7 Vol	4 Vol	6 Vol	2 Vol
2 molecules	7 molecules	4 molecules	6 molecules	2 molecules (By Avogadro's law)
1 molecule	$\frac{7}{2}$ molecules	$\frac{4}{2}=2$ molecules = 2 atoms of C	$\frac{6}{2}=3$ molecules = 6 atoms of H	$\frac{2}{2}=1$ molecule = 2 atoms of N

∴ Molecular formula of compound = $C_2H_6N_2$ **Ans.**

Also, volume of O_2 required for complete combustion

$= \frac{7}{2}$ **Ans.**

EXAMPLE 41. *10 mL of a gaseous organic compound containing C, H and O only was mixed with 100 mL of oxygen and exploded under conditions which allowed the water formed to condense. The volume of the gas after explosion was 90 mL. On treatment with potash solution, a further contraction in volume of 20 mL was observed. Given that the vapour density of the compound is 23, deduce the molecular formula. All volume measurements were carried out under the same conditions.* **(IIT, 1977)**

SOLUTION. Let formula of organic compound = $C_xH_yO_z$

Reaction

$$C_xH_yO_z + \left(x+\frac{y}{4}-\frac{z}{2}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O \quad ...(1)$$

$$10\text{ mL} \qquad 10\left(x+\frac{y}{4}-\frac{z}{2}\right) \qquad 10\,x\text{mL} \qquad \frac{10\times y}{2} = 5y\text{ mL}$$

(*a*) Since potash solution (KOH) absorbs CO_2, so volume of CO_2 gas = 20 mL. From reaction (1) :

$$10\,x = 20\,;\ x = \frac{20}{10} = \mathbf{2.}$$

(*b*) Contraction in volume after explosion and cooling as obtained from reaction (1)

$$10 + 10\left(x+\frac{y}{4}-\frac{z}{2}\right) - 10x = 10 + 100 - 90$$

$$= 20 \text{ mL (given)}$$

$$10 + 10\left(2+\frac{y}{4}-\frac{z}{2}\right) - (10 \times 2) = 20$$

$$10 + 20 + \frac{5y}{2} - 5z - 20$$

$$10 + \frac{5y}{2} - 5z = 20$$

$$20 + 5y - 10z = 40$$

$$\mathbf{5y - 10z = 40 - 20 = 20} \quad ...(2)$$

But mol. wt. of $C_xH_yO_z$

or $C_2H_yO_z = (2 \times 12) + (y \times 1) + (16 \times z)$

$= 24 + y + 16z$ Or $24 + y + 16z$

$= 2 \times 23$ (given)

or $y + 16z = 46 - 24 = 22$ ...(3)

From (2) and (3), we have

$5y - 10z = 20$ ...(4)

$y + 16z = 22] \times 5$ ...(5)

Subtracting – – –

$$-90z = -90\ ;\quad z = \frac{90}{90} = \mathbf{1.}$$

Substituting the value of $z = 1$ in (3), we get ;

$y + (16 \times 1) = 22\ y = 22 - 16 = \mathbf{6}$

Since $x = 2$, $y = 6$ and $z = 1$, the molecular formula of $C_xH_yO_z = \mathbf{C_2H_6O}$ **Ans.**

11.7 FINDING EQUIVALENT WEIGHT OF AN ELEMENT

EXAMPLE 42. *An unknown solid element 'E' when burnt in oxygen gas produced a gas which had the same volume as that of the oxygen gas used under the same conditions of temperature and pressure. Calculate the equivalent weight of the element if the vapour density of pure gaseous product is 32.*

SOLUTION. Mol. wt. of gaseous product

= 2 × V.D. = 2 × 32 = 64.

Let x = number of atoms of element, E.

Reaction

$$xE + O_2 \longrightarrow E_xO_2$$

1 Vol 1 Vol (given)

By Avogadro's law :

1 mole 1 mole

(2 × 16) = 32 g 64 g (∵ mol. wt. = 64 given)

64 g of E_xO_2 contain oxygen = 32 g

∴ wt. of element,

E = 64 – 32 = 32 g. We know

$$\frac{\text{wt. of element}}{\text{wt. of oxygen}} = \frac{\text{Eq. wt. of element}}{\text{Eq. wt. of oxygen } (= 8)}$$

∴ Eq. wt. of element

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

$$= \frac{32}{32} \times 8 = \mathbf{8} \quad \textbf{Ans.}$$

11.8 AIEEE PATTERN EXAMPLES

EXAMPLE 43. *The volume of O_2 required for the complete combustion of 120 cm^3 of methane gas in a eudiometer tube will be:*

(*a*) *60cm^3*

(*b*) *120 cm^3*

(*c*) *240 cm^3*

(*d*) *360 cm^3*

SOLUTION. Reaction

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

1 mol 2 mol

22400 cm^3 2 × 22400 cm^3

22400 cm^3 CH_4 need O_2 for complete combustion

$$= 2 \times 22400\ cm^3$$

120 cm^3 CH_4 need O_2 for complete combustion

$$= \frac{2\times 22400\ cm^3}{22400\, cm^3} \times 120 cm^3$$

$$= 240\ cm^3$$

So, the correct answer is (*c*).

Example 44. *The volume of oxygen gas required for the complete combustion of 1.12 litre of ethene at 27°C and 750 mm pressure will be :*

(*a*) *1L*	(*b*) *2L*
(*c*) *2.3 L*	(*d*) *3.03 L*

Solution. Reaction

$$\begin{array}{ccccc} C_2H_4 & + & 3O_2 & \longrightarrow & 2CO_2 + 2H_2O \\ 1\text{ mol} & & 3\text{ mol} & & \\ 22400\text{ mL} & & 3 \times 22400\text{ mL} & & \\ = 22.4\text{ L} & & = 3 \times 22.4\text{ L} & & \end{array}$$

Given : $P_1 = 750$ mm, $V_1 = 1.12$ L, $T_1 = 27 + 273 = 300$ K; at N.T.P; $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K. Using gas equation, we have :

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

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{750\text{ mm} \times 1.12\text{ L} \times 273\text{ K}}{300\text{ K} \times 760\text{ mm}} = 1.01\text{L}$$

22.4 L ethene require O_2 for complete combustion

$$= 3 \times 22.4\text{ L}$$

1.01 L ethene require O_2 for complete combustion

$$= \frac{3 \times 22.4\text{ L}}{22.4\text{ L}} \times 1.01\text{ L} = 3.03\text{ L}$$

So, the correct answer is (*d*).

Example 45. *A mixture of 25 mL nitric oxide and 25 mL of oxygen was sparked in a eudiometer tube. The volume of the gas left behind after treating with KOH solution would be :*

(*a*) *12.5 mL* O_2	(*b*) *25 mL* O_2
(*c*) *2.5 mL* O_2	(*d*) *2.5 mL* NO_2

Solution. Reaction

$$\begin{array}{ccccc} 2NO & + & O_2 & \longrightarrow & 2NO_2 \\ 2\text{ mol} & & 1\text{ mol} & & 2\text{ mol} \\ 2\text{ Vol} & & 1\text{ Vol} & & 2\text{ Vol} \\ 2 \times 22400\text{ mL} & & 22400\text{ mL} & & 2 \times 22400\text{ mL} \end{array}$$

(Avogadro's law)

(*i*) 2 × 22400 mL NO require O_2 for complete combustion = 22400 mL

25 mL NO require O_2 for complete combustion

$$= \frac{22400\text{ mL}}{2 \times 22400\text{ mL}} \times 25\text{ mL}$$

$$= 12.5\text{ mL}$$

∴ Volume of O_2 left behind = Volume of O_2 taken – Volume of O_2 used = 25 – 12.5 = 12.5 mL

Since NO_2 gas formed is completely absorbed by KOH according to the reaction

$$2\,KOH + 2NO_2 \rightarrow KNO_3 + H_2O + KNO_2$$

only O_2 gas is left behind = 12.5 mL.

So, the correct answer is (*a*).

Example 46. *1.0 litre of a mixture of CO and* CO_2 *is taken. This mixture is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litres. If volumes are measured under similar conditions of temperature and pressure, the composition of the mixture CO and* CO_2 *by volume will be respectively :*

(*a*) *600 mL, 400 mL*	(*b*) *400 mL, 600 mL*
(*c*) *300 mL, 200 mL*	(*d*) *200 mL, 300 mL*

Solution. Volume of CO + CO_2 = 1 L = 1000 mL

Let, Volume of CO_2 = xmL

Volume of CO = $(1000 - x)$ mL

$$\textbf{Reaction :}\quad \begin{array}{ccccc} CO_2 & + & C & \longrightarrow & 2CO \\ x\text{mL} & & & & 2x\text{mL} \end{array}$$

After the reaction : Total volume will be :

$$2x + (1000 - x) = 1.6\text{ L} = 1.6 \times 1000 = 1600\text{ mL}$$

$$x = 1600 - 1000 = 600\text{ mL}$$

∴ Volume of CO_2 = 600 mL;

Volume of CO = 1000 – x

= 1000 – 600 = 400 mL.

So, the correct answer is (*b*).

Example 47. *50 mL of gaseous mixture of hydrogen and hydrogen chloride was exposed to sodium amalgam. The volume decreased to 42.5 mL. If 100 mL of the same mixture is mixed with 50 mL of gaseous ammonia and then exposed to water, the final volume will be :*

(*a*) *50 mL*	(*b*) *100 mL*
(*c*) *70 mL*	(*d*) *220 mL*

All measurements are done under similar conditions of temperature and pressure.

Solution.

Volume of H_2 + Volume of HCl(g) = 50 mL

Volume of mixture left after reaction = 42.5 mL

∴ Reduction in volume = 50 – 42.5

= 7.5 mL ...(1)

(*i*) *Na reacts with HCl only.*

$$\begin{array}{ccccc} 2Na + 2HCl & \longrightarrow & 2NaCl & + & H_2 \\ 2\text{ Vol} & & & & 1\text{ Vol} \end{array}$$

2 Volume HCl forms

H_2 = 1 Volume

∴ Reaction in volume of gases is 1 volume (2 – 1 = 1) for 2 volumes of HCl.

∴ Vol. of HCl in 50 mL of mixture

= 2 × 7.5 mL [From equation (1)]

= 15 mL

∴ Vol. of H_2 in 50 mL of mixture

= 50 mL – 15 mL = 35 mL

Volume of H_2 in 100 mL of mixture

$$= \frac{35}{50} \times 100 = 70 \text{ mL}$$

∴ Volume of HCl in the mixture

$$= 100 - 70 = 30 \text{ mL}$$

(*ii*) *Reaction of NH_3 with HCl is :*

$$\begin{array}{ccccc} NH_3 & + & HCl & \longrightarrow & NH_4Cl \\ 1 \text{ Vol} & & 1 \text{ Vol} & & \\ 30 \text{ mL} & & 30 \text{ mL} & & \end{array}$$

Total volume of NH_3 = 50 mL

Volume of NH_3 reacted = 30 mL

∴ Volume of NH_3 left = 50 – 30 = 20 mL

These 20 mL of NH_3 also dissolve in water. Since whole HCl(g) has been consumed, the gas left behind is only H_2.

∴ Final volume = 70 mL

So, the correct answer is (*c*).

EXAMPLE 48. *An organic compound $C_xH_{2y}O_y$ was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H_2O. The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 litres. The water collected during cooling weighed 0.9 g. The vapour pressure of water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. The molecular formula of the compound is :*

(*a*) $C_6H_{12}O_6$ (*b*) $C_5H_{10}O_5$

(*c*) $C_{12}H_{22}O_{11}$ (*d*) $C_2H_2O_4$

(IIT, 1983, modified)

SOLUTION.

Reaction

$$\begin{array}{ccccccc} C_xH_{2y}O_y & + & xO_2 & \longrightarrow & xCO_2 & + & yH_2O \text{ (steam)} \\ 1 \text{ mol} & & x \text{ mol} & & x \text{ mol} & & y \text{ mol} \\ 1 \text{ Vol} & & x \text{ Vol} & & x \text{ Vol} & & y \text{ Vol} \end{array}$$

(Avogadro's law)

(*i*) Volume of O_2 needed in the reaction for combustion = x volume

Volume of O_2 mixed = Twice the volume of O_2 needed
= 2 × x = $2x$ Vol.

∴ Volume of O_2 left unreacted = $2x - x = x$ Vol

Total volume of gases left after combustion
= $x + x = 2x$ volume

∴ $2x$ = 2.24 L (given); **x = 1.12 L.**

(*ii*) 18 g H_2O (= 1 mol steam) ≡ 22.4 L

$$0.9\text{g } H_2O \equiv \frac{22.4 \text{ L}}{18 \text{ g}} \times 0.9 = 1.12 \text{L}$$

∴ ***y* volume = 1.12 L.**

(*iii*) *To find mol. wt. of compound, $C_xH_{2x}O_x$ ($\because x = y$ = 1.12 L)* : We know that :

$$\frac{p° - ps}{p°} = \frac{wM}{mW}$$

where $p° - ps$ = 0.104 mm, $p°$ = 17.5 mm, w = 50 g; M = mol. wt. of H_2O (2 × 1) + 16 = 18g, W = 1000 g; mol. wt. of compound, m = ?. Thus :

$$\frac{0.104 \text{ mm}}{17.5 \text{ mm}} = \frac{50 \text{ g} \times 18 \text{ g}}{m \times 1000 \text{ g}}$$

$$m = \frac{50 \text{ g} \times 18 \text{ g}}{1000 \text{ g}} \times \frac{17.5 \text{mm}}{0.104 \text{ mm}} = 151.4 \text{ g}$$

∴ In $C_xH_{2x}O_x$: = (12 × x) + (1 × $2x$) + (16 × x)

$$= 151.4;\ 30x = 151.4;\ x = \frac{151.4}{30} \simeq 5$$

∴ Molecular formula = $C_5H_{10}O_5$

So, the correct answer is (*b*).

EXAMPLE 49. *An organic compound contains C, H and N. When 9 volumes of a gaseous mixture containing organic compound 'X' and just sufficient quantity of O_2 was exploded, 2 volumes of N_2, 6 volumes of water and 4 volumes of CO_2 were produced. If all measurements are done under similar conditions of temperature and pressure, the molecular formula of the compound X is :*

(*a*) CH_2N (*b*) $C_2H_6N_2$

(*c*) C_3H_7N (*d*) C_5H_5N

SOLUTION. Reactions

$$\begin{array}{ccccc} C & + & O_2 & \longrightarrow & CO_2 \\ 1 \text{ mol} & & 1 \text{ mol} & & 1 \text{ mol} \\ 1 \text{ Vol} & & 1 \text{ Vol} & & 1 \text{ Vol (Avogadro's law)} \\ 4 \text{ Vol} = 4 \text{ atoms} & & 4 \text{ Vol} & & 4 \text{ Vol} \end{array}$$

∴ Volume of O_2 used = **4 volume**; no. of C-atoms = 4

$$\begin{array}{lccccc} (ii) & H_2 & + & \frac{1}{2}O_2 & \longrightarrow & H_2O \\ & 1 \text{ mol} & & \frac{1}{2} \text{ mol} & & 1 \text{ mol} \\ & 1 \text{ Vol} & & \frac{1}{2} \text{ Vol} & & 1 \text{ Vol} \\ & 6 \text{ Vol} = 6 \times 2 = 12 \text{ atoms} & & \frac{1}{2} \times 6 \text{ Vol} = 3 \text{ Vol} & & 6 \text{ Vol} \end{array}$$

∴ Volume of O_2 used
= 3 Volume; no. of H-atoms = 12.

Since no O_2 is used to oxidise N_2, So :

Total volume of O_2 used
= 4 Volume + 3 Volume = 7 Volume

Volume of hydrocarbon 'X' + Volume of O_2
= 9 Volume (given)

∴ Volume of hydrocarbon
'X' = 9 volume – 7 volume = 2 volume.

$$\begin{array}{lccccccccc} (iii) & X & + & 7O_2 & \rightarrow & 4CO_2 & + & 6H_2O & + & N_2 \\ & 2 \text{ Vol} & & 7 \text{ Vol} & & 4 \text{ Vol} & & 6 \text{ Vol} & & 2 \text{ Vol} \\ & 2 \text{ mol} & & 7 \text{ mol} & & 4 \text{ mol} & & 6 \text{ mol} & & 2 \text{ mol (Avogadro's law)} \\ & 1 \text{ mol} & & \frac{7}{2} \text{ mol} & & \frac{4}{2} & & \frac{6}{2} & & \frac{2}{2} \\ & & & & & = 2 \text{ mol} & & = 3 \text{ mol} & & = 1 \text{ mol} \\ & & & & & = 2 \text{ C-atoms} & & = 3 \times 2 & & = 1 \times 2 \\ & & & & & & & = 6 \text{ H atoms} & & = 2 \text{ N atoms} \end{array}$$

∴ Molecular formula of compound
'X' = $C_2H_6N_2$

So, the correct formula is (*b*).

Example 50. *50 cm^3 of a mixture of ethyne (C_2H_2) and methane (CH_4) was mixed with excess of O_2 in a eudiometer tube. After explosion and cooling, the mixture was treated with strong NaOH solution when a reduction of 82.5 cm^3 volume was observed. If all the measurements are done under similar conditions of temperature and pressure, the volume of ethyne in the mixture is :*

(a) 35 cm^3 *(b)* 32.5 cm^3

(c) 65 cm^3 *(d)* 3.5 cm^3

Solution. Volume of $C_2H_2 + CH_4 = 50\ cm^3$ (given)

Let Volume of $CH_4 = x\ cm^3$;

Volume of $C_2H_2 = (50 - x)\ cm^3$.

Since NaOH solution absorbs CO_2,

Volume of CO_2 formed = 82.5 cm^3

Reactions

$$\begin{array}{llllll}
(i) & CH_4 & + \ 2O_2 & \longrightarrow & CO_2 & + \ 2H_2O \\
 & 1\text{ Vol} & 2\text{ Vol} & & 1\text{ Vol} & \\
 & x\text{ mL} & 2x\text{ mL} & & x\text{ mL} & \\
(ii) & 2C_2H_2 & + \ 5O_2 & \longrightarrow & 4CO_2 & + \ 2H_2O \\
 & 2\text{ Vol} & 5\text{ Vol} & & 4\text{ Vol} & \\
 & 2(50-x)\text{ Vol} & & & 4(50-x)\text{ Vol} & \\
 & \text{or } (50-x)\text{ Vol} & & & 2(50-x)\text{ Vol} &
\end{array}$$

From equations (*i*) and (*ii*), we get :

$$x + 2(50 - x) = 82.5\ ;\ x + 100 - 2x = 82.5;$$

$$-x = -17.5;\ x = 17.5\text{ mL}$$

$\therefore$ Volume of $C_2H_2 = 50 - 17.5 = 32.5\ cm^3$.

So, the correct answer is (*b*).

Example 51. *20 mL of methane is completely burnt in 50 mL of oxygen. The volume of the gas left after cooling to room temperature is:*

(a) 80 mL *(b)* 40 mL

(c) 60 mL *(d)* 30 mL

(Karnataka, CET, 2012)

Solution.

$$\begin{array}{ccccccc}
CH_{4(g)} & + & 2O_{2(g)} & \rightarrow & CO_{2(g)} & + & 2H_2O_{(l)} \\
22400\text{ mL} & & 2\times 22400\text{ mL} & & 22400\text{ mL} & &
\end{array}$$

(*i*) 22400 mL CH_4 requires $O_2 = 2 \times 22400$ mL

$$20\text{ mL } CH_4 \text{ requires } O_2 = \frac{2 \times 22400}{22400} \times 20 = 40\text{ mL}$$

$\therefore$ Volume of unused O_2 left behind = 50 – 40 = 10 mL

(*ii*) 22400 mL CH_4 forms $CO_{2(g)}$ = 22400 mL

$$20\text{ mL } CH_4 \text{ forms } CO_{2(g)} = \frac{22400}{22400} \times 20 = 20\text{ mL}$$

$\therefore$ Total volume of gases left behind = 10 + 20 = 30 mL

So, the correct answer is (*d*).

PROBLEMS FOR PRACTICE

1. A mixture of H_2 and acetylene was mixed with 66 cm^3 of O_2 and exploded in a eudiometer tube. On cooling, it was found to have undergone a contraction of 37 cm^3. When treated with a solution of KOH solution, a further contraction of 36 cm^3 took place and 16 cm^3 of O_2 was left behind. Find the %age composition of H_2 and acetylene.

Ans. H_2 = 35.7%; C_2H_2 = 64.3%

2. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in O_2 gives 3.38 g CO_2; 0.69 g H_2O and no other products. A volume of 10 L (measured at N.T.P.) of this welding gas is found to weigh 11.6 g. Calculate the empirical formula of the compound. **Ans.** CH
3. Using the data of question number, 2, find the molar mass of the gas. **Ans.** 26g
4. Using the data of question number, 2, find the molecular formula of the gas. **Ans.** C_2H_2
5. A mixture of bromine gas (3.0 L) and H_2 (3.2 L) was exploded in a eudiometer tube. Calculate the composition by volume of the resulting mixture if all measurements are done under similar conditions of temperature and pressure.

Ans. Volume of H_2 left = 0.2 L; volume of HBr formed = 6L

6. A gaseous mixture contains 48.0 mL of HCl and H_2 gases. It was kept in contact with Na/Hg. The volume of mixture decreased to 40 mL. If 98.0 mL of mixture is mixed with 48 mL of gaseous ammonia and then exposed to water, calculate the final volume. All measurements of volume are done under similar conditions of temperature and pressure.

Ans. Residual H_2 or final volume = 66 mL; Residual NH_3 = 16 mL

7. 250 mL of hydrocarbon gas burnt in O_2 gas yields 1250 mL of CO_2 and 1.5 L water vapours. What is the formula of hydrocarbon if all the volume is measured under similar conditions of temperature and pressure. **Ans.** C_5H_{12}
8. 10 cm^3 of a hydrocarbon were exploded in a eudiometer tube with excess of O_2. On cooling, there was a contraction in volume of 20 cm^3. The residual gases when bubbled through KOH solution, a further contraction of 15 cm^3 was observed. Calculate the molecular formula of the hydrocarbon if all the volumes are measured under similar conditions of temperature and pressure. **Ans.** C_2H_2
9. 7.5 mL of a gaseous hydrocarbon required for complete combustion 178.5 mL air (21% O_2 by volume) and the gaseous products occupied 163.5 mL. Find the formula of hydrocarbon if all measurements of volume are done under similar conditions of temperature and pressure. **Ans.** C_3H_8
10. The volume of oxygen needed for the complete combustion of 112 mL of methane gas in a eudiometer tube is:

(*a*) 112 mL (*b*) 224 mL

(*c*) 336 mL (*d*) 448 mL

Ans. (*b*)

12

CHAPTER

Structure of Atom

12.1 SOME BASIC CONVERSIONS

$$1\text{J} = 1\text{ kg m}^2\text{ s}^{-2} = 10^7\text{ erg.}$$

$$1\text{J} = 1\text{V} \times 1\text{ C}$$

$$1\text{ eV} = 1.6 \times 10^{-19}\text{ J}$$

1 eV = energy of one electron being accelerated by 1V.

x eV = energy of one electron being accelerated by xV.

$1\text{Å} = 10^{-10}\text{ m} = 10^{-8}\text{ cm}; 1\text{ cm}^{-} = 12\text{ J mol}^{-}$

$= 1.99 \times 10^{-23}\text{ J photon}^{-} = 2.86\text{ cal mol}^{-}$

1 Watt = 1 Js^{-}

12.2 RUTHERFORD AND THOMSON MODEL OF ATOM

Example 1. *What was proved by Rutherford's α-particle scattering experiment ?*

Solution. Atoms contain positively charged massive nucleus.

Example 2. *Convert one atomic mass unit (u) to kilogram.*

Solution. We know that 1 mol of ^{12}C has mass

$$= 0.012\text{ kg.}$$

$$1\text{ mol} = 6.02 \times 10^{23}\text{ atoms}$$

There are 6.02×10^{23} atoms in 1 mol, each of mass 12.0 U.

Thus $$12\text{U} = \frac{0.012\text{ kg}}{6.02 \times 10^{23}};$$

$$\mathbf{1U} = \frac{0.012\text{ kg}}{6.02 \times 10^{23} \times 12}$$

$$= \mathbf{1.66 \times 10^{-27}\text{ kg}}$$ **Ans.**

Example 3. *Which experiment disapproved Thomson's model of atom as an intimate mixture of negative and positive particles ?*

Solution. Thomson's model of atom was negated by Rutherford's experiment in which large angle scattering of alpha particles by a metal foil was observed.

Example 4. *Calculate the magnitude of charge on (a) a proton and (b) on the nucleus of a lithium atom. Charge on an electron = 4.8×10^{-10} esu.*

Solution. (*a*) Magnitude of charge on a proton = magnitude of charge on an electron = **4.8×10^{-10} esu.** **Ans.**

(*b*) Nucleus of $_3$Li contains protons = 3

∴ Magnitude of charge on the Li-nucleus

$$= 3 \times 4.8 \times 10^{-10}\text{ esu}$$

$$= \mathbf{1.44 \times 10^{-9}\text{ esu}}$$ **Ans.**

Example 5. *The charge to mass ratio of all the cathode rays is the same but those of positive rays depend on the residual gas in the discharge tube. Why ?*

Solution. Cathode rays are composed of electrons. Electrons may be available from any source, these have same charge/mass ratio. On the other hand, the ions left after the loss of electrons may have same magnitude of charge but their masses are different. So, their charge/mass ratio is different.

Example 6. *Though the charge on α-particles is more than that on β-particles, the β-particles are deflected more than α-particles in a given electric field. Why ?*

Solution. The mass of β-particles is much less than that of α-particles, so their charge/mass ratio is larger than α-particles. Hence β-particles are deflected more than α-particles.

Example 7. *In order to know the radius (R) of a nucleus in cm, the relation used is : $R \approx 1.4 \times 10^{-13} A^{1/3}$ where A = mass number of the atom. Calculate the approximate radius of ^{238}U-nucleus.*

Solution. $A = 238$

Hence, $R = 1.4 \times 10^{-13} (238)^{1/3}$

Taking logs, we get : $\log R$

$$= \log 1.4 + \log 10^{-13} + \log (238)^{1/3}$$

$$\log R = 0.146 - 13 + \frac{1}{3} \times 2.376$$

$$= 0.146 - 13 + 0.792$$

$$= -12.062 = -12 - 1 + 1 - 0.062$$

$$= \overline{13}.938.$$

Taking antilogs we get :

$$\boldsymbol{R} = \text{antilog } \overline{13}.938$$

$$= \mathbf{8.67 \times 10^{-13}\text{ cm}}$$ **Ans.**

Example 8. *The terminal velocity of an oil-droplet in an oil-drop experiment was observed to be 0.98 mm s⁻. The viscosity (η) of air is 1.83 × 10⁻⁵ N.s.m⁻² and density of oil drop is 0.85 g cm⁻³. Calculate the radius as well as mass of the oil-drop.*

Solution. We know,

$$\text{Volume, } V = \frac{4}{3}\pi r^3$$

$$\text{But} \qquad d = \frac{m}{V}$$

$$\text{Hence,} \qquad m = \frac{4}{3}\pi d r^3 \,;$$

$$v = 0.98 \text{ mms}^{-} \times \frac{1\text{m}}{1000\text{mm}}$$

$$= 0.00098 \text{ ms}^{-}$$

$$\text{Velocity,} \qquad v = \frac{mg}{6\pi\eta r} = \frac{\frac{4}{3}\pi r d^3 \times g}{6\pi\eta r} = \frac{2dr^2 g}{9\eta}$$

$$\therefore \qquad \boldsymbol{r} = \left(\frac{9v\eta}{2dg}\right)^{1/2}$$

$$= \left(\frac{9 \times 0.00098 \text{ ms}^{-} \times 1.83 \times 10^{-5} \text{kg m s}^{-2}.\text{ sm}^{-2}}{2 \times 0.85 \times 10^3 \text{kg m}^{-3} \times 9.8 \text{ ms}^{-2}}\right)$$

$[\because\ \text{N} = \text{kg m s}^{-2}]$

$$= (9.688 \times 10^{-12} \text{ m}^2)^{1/2}$$

$$= \mathbf{3.11 \times 10^{-6}\ m} \quad \textbf{Ans.}$$

$$\left(\because d = 0.85 \frac{\text{g}}{\text{cm}^3} = 0.85 \times 10^3 \frac{\text{kg}}{\text{m}^3}\right)$$

$$(ii) \qquad m = \frac{4}{3}\pi d r^3$$

$$= 1.33 \times 3.142 \times 0.85 \times 10^3 \frac{\text{kg}}{m^3}$$

$$\times (3.11 \times 10^{-6}\, m)^3$$

$$= \mathbf{1.068 \times 10^{-13}\ kg} \quad \textbf{Ans.}$$

12.3 CALCULATING RADIUS AND VOLUME OCCUPIED BY AN ATOM

Type. To find the radius and volume occupied by an atom, use :

Mass of one nucleus

$$= \left(\frac{\text{at. wt.}}{\text{Avogadro's no.}}\right)$$

$$= \left[\text{Volume of atom} \left(= \frac{4}{3}\pi r^3\right)\right] \times \text{density.}$$

Example 9. *A metal has density 7.2 g cm⁻³ and atomic weight 54.94. Find the radius as well as volume of the metal atom considering atom as spherical.*

Solution. At. wt. = 54.94;

Avogadro no. = 6.023 × 10²³

$$\text{Volume} = \frac{4}{3}\pi r^3 \,;\ \text{Density} = 7.2 \text{ g cm}^{-3}$$

$$(i) \text{ But, } \frac{\text{At. wt.}}{\text{Avogadro no.}} = \text{Volume} \times \text{Density}$$

$$\frac{54.94}{6.023 \times 10^{23}} = \frac{4}{3}\pi r^3 \times 7.2 \,;$$

$$\frac{54.94}{6.023 \times 10^{23}} = \frac{4}{3} \times \frac{22}{7} \times r^3 \times 7.2$$

$$\therefore \qquad r^3 = \frac{54.94 \times 3 \times 7}{6.023 \times 10^{23} \times 4 \times 22 \times 7.2}$$

$$= 3.02 \times 10^{-24}$$

$$\therefore \qquad r = (3.02)^{1/3} \times (10^{-24}\text{cm}^3)^{1/3}$$

$$= (3.02)^{1/3} \times 10^{-8} \text{ cm}$$

$$\log r = [\log (3.02)^{1/3}] \times 10^{-8}$$

$$\text{or} \qquad \boldsymbol{r} = \mathbf{1.445 \times 10^{-8} cm} \qquad \textbf{Ans.}$$

$$\left[\because \log (3.02)^{1/3} = \frac{1}{3} \log 3.02 = \frac{1}{3} \times 0.48 = 0.16.\right.$$

Taking antilog of both sides, we get : r = anti-log 0.16 = 1.445]

$$(ii) \text{ Volume} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (1.445 \times 10^{-8} \text{cm})^3$$

$$= \frac{4 \times 22 \times 3.017 \times 10^{-24}}{3 \times 7} \text{cm}^3$$

$$= \mathbf{1.26 \times 10^{-23}\ cm^3} \qquad \textbf{Ans.}$$

Example 10. *Calculate the density of matter in the nucleus of fluorine assuming that fluorine atom is a sphere of radius 5 × 10⁻¹³cm. (at. wt. of F = 19).*

Solution. We know that : Mass of one nucleus = Volume × Density

$$\textbf{or} \qquad \frac{\text{At. wt.}}{\text{Avogadro no.}} = \text{Volume} \times \text{Density}$$

$$\frac{19}{6.023 \times 10^{23}} = \frac{4}{3}\pi r^3 \times \text{density}$$

$$\frac{19\text{g}}{6.023 \times 10^{23}} = \frac{4}{3} \times \frac{22}{7} (5 \times 10^{-13} \text{ cm})^3 \times \text{density}$$

$$\therefore \quad \text{Density} = \frac{19\text{g} \times 3 \times 7}{6.023 \times 10^{23} \times 4 \times 22 \times (5 \times 10^{-13} \text{cm})^3}$$

$$= \frac{19 \times 3 \times 7}{6.023 \times 10^{23} \times 4 \times 22 \times 125 \times 10^{-39} \text{cm}^3}$$

$$\textbf{Density} = \mathbf{6.022 \times 10^{13} g\ cm^{-3}} \qquad \textbf{Ans.}$$

12.4 ELECTRON VOLT (eV), FORCE OF ATTRACTION BETWEEN CHARGES ETC.

Type. $1\text{eV} = (1.6 \times 10^{-19}\text{C}) \times 1.0 \text{ V} = 1.6 \times 10^{-19}\text{J}$

$= 23 \text{ k cal mol}^{-} = 96.4 \text{ kJ mol}^{-}$

Example 11. *What is meant by an electron volt (eV) ? Express this energy in (i) J (ii) kJ mol⁻ and (iii) k cal mol⁻.*

Solution. An electron volt is the energy required to move an electronic charge (e) through a potential of exactly one volt (V).

(*i*) $1 \text{ eV} = (1.6 \times 10^{-19}\text{C}) \times 1.0 \text{ V} = 1.6 \times 10^{-19} \text{ J}$

[∵ CV = J]

(*ii*) $1.6 \times 10^{-19}\text{J} \times \frac{1\text{kJ}}{10^3\text{J}} \times \frac{6.023 \times 10^{23}}{\text{mol}} = 96.4 \text{ kJ mol}^-$

[∵ 1 kJ = 10^3J]

(*iii*) $1.6 \times 10^{-19}\text{J} \times \frac{1\text{k cal}}{4184\text{ J}} \times \frac{6.023 \times 10^{23}}{\text{mol}} = 23 \text{ k cal mol}^-$

[∵ 1 k cal = 4184 J]

EXAMPLE 12. *Calculate the force of attraction between an electron (charge = -1.6×10^{-19}C) and a body with a charge +1.0 C on it placed at a distance of 1.5 m apart. (k = 9.0×10^9 Nm^2/C^2).*

SOLUTION.

We know that force of attraction :

$$f = \frac{kq_1q_2}{d^2}$$

$$= \frac{9.0 \times 10^9 \text{Nm}^2}{\text{C}^2} \times \frac{-1.6 \times 10^{-19}\text{C} \times +1.0\text{C}}{(1.5\text{ m})^2}$$

$$\mathbf{f = -6.4 \times 10^{-10} \text{ N}}$$ **Ans.**

EXAMPLE 13. *Calculate the amount of energy released when Na$^+$ and Cl$^-$ ions originally at infinite distance apart are brought close together at a distance of 2.76 Å. Assume that ions act as point charges with 1.6×10^{-19}C (the electronic charge). (k = 9.0×10^9Nm^2/C^2).*

SOLUTION.

$$E = \frac{kq_1q_2}{d}$$

$$= \frac{9.0 \times 10^9 \text{Jm}}{\text{C}^2} \times \frac{1.6 \times 10^{-19}\text{C} \times 1.6 \times 10^{-19}\text{C}}{2.76 \times 10^{-10}\text{m}}$$

$$E = 8.3 \times 10^{-19} \text{ J}$$

$$= 8.3 \times 10^{-19}\text{J} \times \frac{1\text{k cal}}{4184\text{ J}} \times \frac{6.023 \times 10^{23}}{\text{mol}}$$

$$\mathbf{= 119 \text{ k cal mol}^-}$$ **Ans.**

EXAMPLE 14. *Find the value of energy required to move a 2.0×10^{-10} C negatively charged body from infinite distance to a point (i) 0.2 cm from a 1.0 C negatively charged body, (ii) 2.0 cm from a 1.0 C negatively charged body and (iii) from position (ii) to position (i) k = 9.0×10^{11} J cm/C^2.*

SOLUTION. $k = 9.0 \times 10^{11} \text{ J cm/C}^2$

We know that the energy required to move the charged body from infinite distance to a given distance is given as

$$E = \frac{kq_1q_2}{d}\cdot \text{ Hence}$$

(*i*) $E = \frac{kq_1q_2}{d} = 9.0 \times 10^{11} \frac{\text{Jcm}}{\text{C}^2} \times \frac{2.0 \times 10^{-10}\text{C} \times 1.0\text{ C}}{0.2\text{cm}}$

$\mathbf{= 900 \text{ J}}$ **Ans.**

(*ii*) $E = \frac{kq_1q_2}{d} = 9.0 \times 10^{11} \frac{\text{Jcm}}{\text{C}^2} \times \frac{2.0 \times 10^{-10}\text{C} \times 1.0\text{C}}{2.0\text{cm}}$

$\mathbf{= 90 \text{ J}}$ **Ans.**

(*iii*) $\Delta E = 900 \text{ J} - 90 \text{ J} = \mathbf{810 \text{ J}}$ **Ans.**

EXAMPLE 15. *A force of 10^{-6}N exists between two carbon discs (1.5 g each) 1.0 cm apart. If the opposite charges are of equal magnitude, calculate the ratio of excess electrons to total atoms on the negatively charged disc. (k = 9.0×10^9J m/C^2; charge on electron = 1.6×10^{-19}C).*

SOLUTION. We know,

$$f = \frac{kq_1q_2}{d^2}$$

Since $q_1 = q_2 = q$ (say);

$$d = 1 \text{ cm} = \frac{1}{100}\text{m} = 0.01 \text{ m};$$

$$1 \text{ N} = \text{J/m} ; f = \frac{kq^2}{d^2}$$

$$q = \left(\frac{fd^2}{k}\right)^{1/2}$$

$$= \left(\frac{10^{-6} \text{ J/m} \times (0.01 \text{ m})^2}{9 \times 10^9 \text{Jm/C}^2}\right)^{1/2}$$

$$= (1.1 \times 10^{-20} \text{ C}^2)^{1/2}$$

or $q = 1.05 \times 10^{-10}$C on each disc

∴ No. of electrons $= 1.05 \times 10^{-10}\text{C} \times \frac{1 \text{ electron}}{1.6 \times 10^{-19}\text{C}}$

$= 6.6 \times 10^8$ electrons.

No. of atoms $= \frac{1.5 \times 6.023 \times 10^{23} \text{atoms}}{12.0 \text{ g}}$

[∵ at. wt. of C = 12]

$= 7.5 \times 10^{22}$ atoms.

∴ Ratio of electrons and atoms

$$= \frac{6.5 \times 10^8 \text{ electrons}}{7.5 \times 10^{22} \text{atoms}}$$

$$= 8.7 \times 10^{-15} \frac{\text{electrons}}{\text{atom}}$$

Type. Calculation of charge on oil droplets in an oil drop experiment.

EXAMPLE 16. *Following values of charge on the electron were found on oil droplets (in arbitrary units) in an oil drop experiment -1.4×10^{-19}, -2.8×10^{-19} and -3.5×10^{-19}. Calculate the value of the electronic charge that would be indicated by these results (in the same units).*

SOLUTION. The value of the electronic charge that would be indicated from the given results will be the H.C.F. (highest common factor) of these results. The H.C.F. of -1.4×10^{-19}, -2.8×10^{-19} and -3.5×10^{-19} is -0.7×10^{-19}. So, answer is, -0.7×10^{-19}.

Note.(*i*) H.C.F. of 1.4 and 2.8 is 1.4 because 2.8 is divisible by 1.4.

(*ii*) H.C.F. of 1.4 and 3.5 is 0.7 because 0.7 divides both 1.4 and 3.5 in whole numbers.

EXAMPLE 17. *The following charges (in arbitrary units) were found on a number of oil droplets in an oil drop experiment.*

3.14×10^{-14}, 9.42×10^{-14}, 1.727×10^{-13}, 2.512×10^{-13}, 6.28×10^{-14}. Calculate the magnitude of charge on the electron in the same units.

SOLUTION. The magnitude of charge on the electron will be the H.C.F. (highest common factor) of 3.14×10^{-14}, 9.42×10^{-14}, 1.727×10^{-13}, 2.512×10^{-13} and 6.28×10^{-14} which is 1.57×10^{-14}. So, the answer is $\mathbf{1.57 \times 10^{-14}}$.

Type. Effect of magnetic field on electric charge.

EXAMPLE 18. *Is there any effect of a magnetic field on*

(i) an electric charge moving through the field and

(ii) a static electric charge in the field ?

SOLUTION. (*i*) An electric charge in motion generates its own magnetic field. The external magnetic field interacts with the above created magnetic field and creates a force perpendicular to its original direction of motion. (*ii*) None.

EXAMPLE 19. *Will it be possible to perform Millikan's oil drop experiment in an evacuated vessel if it is assumed that the oil is sufficiently non-volatile ? Explain.*

SOLUTION. It is not possible to perform oil drop experiment. It is because the oil droplets must reach a terminal velocity to be able to estimate their weights by Stokes law. Since there is no air, there would be no good way to determine their weights and the force of the electric field would then not be precisely known.

EXAMPLE 20. *The viscosity of air (η) is 1.83×10^{-5} N.s/m^2 and density of oil is 0.85 g cm^{-3}. If the terminal velocity of an oil droplet in an oil drop experiment is 1 mm s^{-}, what would be the radius and mass of the oil droplet ?*

SOLUTION. We know that density,

$$d = \frac{\text{mass}}{\text{volume}} = \frac{m}{\frac{4}{3}\pi r^3}.$$

$$\eta = 1.83 \times 10^{-5}\ \text{N s m}^{-2}$$

$$= 1.83 \times 10^{-5}\ \text{kg m s}^{-2}\ .\ \text{s m}^{-2}$$

Hence $$m = \frac{4}{3}\pi r^3 d \qquad ...(1)$$

$$v = 1\text{mms}^{-} = \frac{1}{1000}\text{ms}^{-} = 10^{-3}\text{ms}^{-}$$

$$d = 0.85\ \text{g cm}^{-3} = 0.85 \times 10^3\ \text{kg. m}^{-3}$$

But, Velocity, $$v = \frac{mg}{6\pi\eta r}$$

Substituting the value of m from equation (1),

we get: $$v = \frac{\frac{4}{3}\pi r^3 dg}{6\pi\eta r} = \frac{2}{9}\frac{r^2 dg}{\eta}$$

Hence :

(*i*) radius,

$$r = \left(\frac{9\eta v}{2dg}\right)^{1/2}$$

$$= \left(\frac{9 \times 1.83 \times 10^{-5}\text{kg ms}^{-2}.\text{sm}^{-2} \times 10^{-3}\text{ms}^{-}}{2 \times 0.85 \times 10^3\text{kg}.\text{m}^{-3} \times 9.8\,\text{ms}^{-2}}\right)$$

$r = (9.88 \times 10^{-12}\ \text{m}^2)^{1/2} = \mathbf{3.14 \times 10^{-6}\ m}$ **Ans.**

(*ii*) $m = \frac{4}{3}\pi r^3 d = \frac{4}{3} \times 3.14 \times (3.14 \times 10^{-6}\ \text{m})^3 \times 0.85 \times 10^3\ \text{kg m}^{-3}$

$m = \mathbf{1.1 \times 10^{-13}\ kg}$ **Ans.**

12.5 ELECTRON, PROTON, NEUTRON, ISOTOPES, ISOBARS, ISOTONES, FRACTIONAL ABUNDANCE OF ELEMENTS

Electron, ${}_{-1}^{0}\text{e}$. It is a subatomic particle having a unit negative charge (-1.602×10^{-19}C *i.e.,* coulomb) and mass (9.11×10^{-31} kg or 9.11×10^{-28}g) which is equal to $\frac{1}{1837}$ of that of hydrogen atom.

Proton. It is a positively charged particle having a unit positive charge ($+1.602 \times 10^{-19}$C *i.e.,* coulomb or 4.8×10^{-10} esu) and mass (1.672×10^{-27} kg or 1.672×10^{-24}g) which is equal to 1837 times the mass of electron.

In atomic mass units (amu), it is 1.007276 on ^{12}C scale where 1 amu = 1.66×10^{-27} kg.

Atomic number (Z). Atomic number of an element is equal to the number of protons present in the nucleus of that element. In a *neutral atom, number of protons = atomic number = number of electrons = number of unit positive charges present in the nucleus.*

Neutron. It is a subatomic particle having no charge but mass equal to 1.675×10^{-27}kg or 1.675×10^{-24} g.

All atoms contain fundamental particles *i.e.,* protons, electrons and neutrons. H-atom contains one proton and one electron. It has no neutron.

Mass number (A) of an atom is equal to sum total of protons and neutrons present in its nucleus *i.e.,*

Mass number = No. of protons + No. of neutrons
= Atomic number (Z) + No. of neutrons

∴ No. of neutrons = A – Z.

Method to represent *the atomic number (Z), mass number (A) and number of neutrons on the symbol of element (say E)* = ${}_{\text{Z}}^{\text{A}}\text{E}_{(\text{A}-\text{Z})}$. So, the symbol of chlorine, ${}_{17}^{35}\text{Cl}_{18}$ represents:

Atomic number = 17, mass number = 35 and number of neutrons = 18.

Isotopes. Isotopes are the atoms of the same element having same atomic number but different mass numbers. *For example,* ${}_{17}^{35}\text{Cl}$ and ${}_{17}^{37}\text{Cl}$ are the isotopes of chlorine atom.

Isobars. Isobars are the atoms of different elements having same mass number but different atomic numbers. *For example,* ${}_{18}^{40}\text{Ar}$ and ${}_{20}^{40}\text{Ca}$ are isobars of each other.

Isotones. Isotones are the atoms of different elements having same number of neutrons *e.g.,* ${}_{33}^{77}\text{As}$ and ${}_{34}^{78}\text{Se}$ have same number of neutrons (= 44) *i.e.*, 77 – 33 = 44 and 78 – 34 = 44.

Atomic mass. *Atomic mass of an element is the average weight of the atomic masses of the natural isotopes.*

(*i*) **Fractional abundance or mole fraction**

$$= \text{Percentage abundance} \times \frac{1}{100}$$

(*ii*) **Atomic mass** = Σ Fractional abundance × mass.

Atomic mass unit (amu). It is exactly equal to $\frac{1}{12}$th of the mass of ^{12}C atom.

$$\textbf{1 a.m.u} = 1.66 \times 10^{-24}\ g = 931.5\ MeV.$$

Type. Mass of one electron

$$= 9.109 \times 10^{-28}\ g = 9.109 \times 10^{-31}\ kg$$

Charge on an electron

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

Mass of one proton

$$= 1.672 \times 10^{-24}\ g = 1.672 \times 10^{-27}\ kg$$

Mass of one neutron

$$= 1.675 \times 10^{-24} g = 1.675 \times 10^{-27}\ kg$$

EXAMPLE 21. *Find mass of 1 mole of protons*

SOLUTION. 1 mole = 6.02×10^{23}

Mass of one proton = 1.672×10^{-24}g

∴ Mass of one mole protons

$$= 1.672 \times 10^{-24}\ g \times 6.02 \times 10^{23}$$

$$= 1.0065\ g$$ **Ans.**

EXAMPLE 22. *Find charge on one mole of electrons*

SOLUTION. 1 mole = 6.02×10^{23}

Charge on one electron

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

Charge on one mole electrons

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

$$= -96440\ \text{coulomb} \simeq -9.64 \times 10^{4}\ C$$

EXAMPLE 23. *Calculate the number of electrons which together weigh one gram.*

SOLUTION. Mass of one electron

$$= 9.109 \times 10^{-28} g$$

9.109×10^{-28} g is the mass of electrons = 1

1 g is the mass of electrons

$$= \frac{1}{9.109 \times 10^{-28}}$$

$$= \mathbf{1.098 \times 10^{27}\ electrons}$$ **Ans.**

EXAMPLE 24. *Boron occurs in nature in the form of two isotopes having mass 10 and 11. Calculate the percentage abundances of two isotopes in a sample of boron having average atomic mass 10.8.*

SOLUTION. Isotopes of boron = ^{10}B and ^{11}B.

Let, total number of moles of ^{10}B and $^{11}B = 1$

Let fractional abundance of $^{10}B = \alpha$;

Fractional abundance of $^{11}B = 1 - \alpha$

But, average atomic mass = [Fractional abundance of ^{10}B × mass of ^{10}B] + [Fractional abundance of ^{11}B × mass of ^{11}B].

$$10.8 = (\alpha \times 10) + (1 - \alpha) \times 11$$

$$= 10\alpha + 11 - 11\alpha$$

or, $\alpha = 11 - 10.8$; $\alpha = 0.2$. Hence $1 - \alpha = 1 - 0.2 = 0.8$

∴ % age abundance of ^{10}B

$$= 0.2 \times 100 = \mathbf{20\%}$$ **Ans.**

% age abundance of ^{11}B

$$= 0.8 \times 100 = \mathbf{80\%}$$ **Ans.**

EXAMPLE 25. *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-JEE, 2009)

SOLUTION. Average atomic mass of Fe = (Fractional abundance of ^{54}Fe × mass of ^{54}Fe) + (Fractional abundance of ^{56}Fe × mass of ^{56}Fe) + (Fractional abundance of ^{57}Fe × mass of ^{57}Fe). Hence :

$$\text{Atomic mass of Fe} = \left(54 \times \frac{5}{100}\right) + \left(56 \times \frac{90}{100}\right)$$

$$+ \left(57 \times \frac{5}{100}\right) = 2.7 + 50.4 + 2.58 = 55.95.$$

So, the correct answer is (*b*).

EXAMPLE 26. *The relative atomic masses of ^{86}Sr ^{87}Sr, and ^{88}Sr are 85.91, 86.91 and 87.91 respectively. Calculate the atomic mass of strontium if a sample of strontium consists of following three isotopes, i.e., ^{86}Sr, ^{87}Sr and ^{88}Sr have natural abundances 9.86 %, 7.58% and 82.56% respectively.*

SOLUTION. Average atomic mass of strontium = [Fractional abundance of ^{86}Sr × Mass of ^{86}Sr] + [Fractional abundance of ^{87}Sr × Mass of ^{87}Sr] + [Fractional abundance of ^{88}Sr × Mass of ^{88}Sr].

$$= \left(\frac{9.86}{100} \times 85.91\right) + \left(\frac{7.58}{100} \times 86.91\right)$$

$$+ \left(\frac{82.56}{100} \times 87.91\right)$$

$$= 8.47 + 6.59 + 72.58$$

$$= \mathbf{87.64}$$ **Ans.**

Type. For a symbol of element $^{A}_{Z}E_{A-Z}$ mass number = A, atomic number = no. of protons = no. of electrons = Z; **no. of neutrons** = A–Z; E = symbol of element or nuclei.

EXAMPLE 27. *Write the complete symbols for the nuclei (or elements) having*

(i) *atomic number 19, mass number, 39; no. of neutrons, 20.*

(ii) *atomic number 4, mass number, 9, no. of neutrons, 5.*

SOLUTION. For an element having symbol $^{A}_{Z}E_{A-Z}$, A = mass no.; Z = at. no.; A–Z = no. of neutrons. Hence :

(*i*) Symbol = $^{39}_{19}K_{20}$ (*ii*) $^{9}_{4}Be_{5}$

EXAMPLE 28. *Calculate the number of protons, neutrons and electrons in the following nuclei.*

(i) $^{138}_{56}Ba$ *(ii)* $^{25}_{12}Mg$

SOLUTION. For an element having symbol $^{A}_{Z}E_{A-Z}$, A = mass no., Z = at. no. = no. of protons = no. of electrons; A – Z = no. of neutrons.

(*i*) $^{138}_{56}Ba$; no. of protons = no. of electrons = 56; no. of neutrons = 138 – 56 = 82 **Ans.**

(*ii*) $^{25}_{12}Mg$; no. of protons = no. of electrons = 12; no. of neutrons = **25 – 12 = 13** **Ans.**

EXAMPLE 29. (*a*) *Atoms may be regarded as comprising of protons, electrons and neutrons. If the mass attributed to a neutron were halved and that attributed to the electron were doubled, calculate the mass of* $^{12}_{6}C$.

(*b*) *When is the number of protons and electrons same in an atom ?* **(HP Board, 2007)**

SOLUTION. (*a*) (*i*) For $^{12}_{6}C$,

mass no. of C = 12 ; no. of protons = 6

But, no. of protons = no. of electrons in a neutral atom.

So, no. of electrons = 6 ; no. of neutrons = 12 – 6 = 6

(*ii*) Mass of neutron = 1.675×10^{-24} g ;

Mass of proton = 1.672×10^{-24} g

$$\therefore \frac{1}{2} \times 6 \text{ neutrons} = 3 \text{ ; no. of protons } = 6$$

$\therefore$ Mass number = no. of neutrons + no. of protons

= 3 + 6 = **9** **Ans.**

The electrons have negligible mass, so that mass is not considered for mass number.

(*b*) In a neutral atom, the number of protons are equal to the number of electrons. For example, in lithium atom (at. no. 7), the number of protons = at. no. So, in Li. atom, the number of electrons are also, 7.

EXAMPLE 30. *The oxide of an element has molar mass equal to 28. Find the total number of electrons in one molecule of the compound. (At. no. C = 6, O = 8).*

SOLUTION. Mass no. of C = 12, O = 16. Molar mass of compound = 28. So, oxide will be CO. At. no. of C = 6, O = 8.

In CO, no. of electrons in C = no. of protons in C = at. no. of C = 6

No. of electrons in O = no. of protons in O = at. no. of O = 8

$\therefore$ Total no. of electrons in CO = 6 + 8 = 14 **Ans.**

EXAMPLE 31. *Calculate the number of electrons in, (i)* $^{23}_{11}Na^{+}$, *(ii)* $^{40}_{20}Ca^{2+}$.

SOLUTION. For a cation $_{Z}E^{+p}$, no. of electrons = Z–p. Hence :

(*i*) no. of electrons in $_{11}Na^{+}$ = 11 – 1 = 10 **Ans.**

(*ii*) no. of electrons in $_{20}Ca^{2+}$ = 20 – 2 = 18 **Ans.**

EXAMPLE 32. *Calculate the number of electrons in,* $_{17}Cl^{-}$

SOLUTION. For an anion $(_{Z}E)^{-p}$, no. of electrons = Z + p. Hence :

no. of electrons in $_{17}Cl^{-}$ = 17 + 1 = 18 **Ans.**

Type. In a molecule, $^{A_1}_{Z_1}L\,^{A_2}_{Z_2}M$ where A_1 and A_2 are the mass numbers of L and M respectively, Z_1 and Z_2 are the atomic number of L and M respectively.

Total no. of protons = total number of electrons

$= Z_1 + Z_2$.

Total no. of neutrons = $(A_1 - Z_1) + (A_2 - Z_2)$

EXAMPLE 33. *Calculate the total number of protons, electrons and neutrons in* PH_3.

SOLUTION. PH_3. At. no. of P = no. of protons of P = no. of electrons of P = 15

3 × at. no. of H (= 1) = 3 × no. of protons of H (= 1) = 3 × no. of electrons of H (= 1) = 3 × 1 = 3.

No. of neutrons of P = Mass no. – at. no. = 31 – 15 = 16

No. of neutrons of 3H = (3 × mass no. of H) – (3 × at. no. of H) = (3 × 1) – (3 × 1) = 0

$\therefore$ Total no. of neutrons in PH_3 = 16 + 0 = **16** **Ans.**

$\therefore$ Total no. of protons = total no. of electrons = **3** **Ans.**

EXAMPLE 34. *Calculate the total number of protons, electrons and neutrons in (i)* NO_3^{-} *(ii)* $S_2O_3^{2-}$, *(at. no., N = 7, O = 8, S = 16, mass no., N = 14, O = 16, S = 32.)*

SOLUTION. (*i*) NO_3^{-}.

(*a*) At. no. of N = no. of protons of N = 7

(*b*) 3 × at. no. of O = 3 × no. of protons of O = 3 × 8 = 24

$\therefore$ Total no. of protons in NO_3^{-} = 7 + 24 = **31** **Ans.**

(*c*) No. of neutrons in N = 14 – 7 = 7

[$\because$ No. of neutrons = (mass no.) – (at. no.)]

3 × no. of neutrons in O = 3 [16 – 8] = 24

$\therefore$ Total number of neutrons in NO_3^{-} = 7 + 24

= **31** **Ans.**

(*d*) no. of electrons in

N = no. of protons in N = 7

3 × no. of electrons in O = 3 × no. of protons in

O = 3 × 8 = 24

$\therefore$ Total no. of electrons in

NO_3^{-1} = 7 + 24 + 1 = **32** **Ans.**

(*ii*) $S_2O_3^{2-}$. (*a*) 2 × at. no. of S

= 2 × no. of protons of S

= 2 × 16 = 32

(*b*) 3 × at. no. of O = 3 × no. of protons of O

= 3 × 8 = 24

$\therefore$ Total no. of protons in

$S_2O_3^{2-}$ = 32 + 24 = **56** **Ans.**

(*c*) 2 × no. of neutrons in S

= 2 (32 – 16) = 32

3 × no. of neutrons in O

= 3 (16 – 8) = 24

∴ Total no. of neutrons in

$S_2O_3^{2-} = 32 + 24 = \mathbf{56}$ **Ans.**

(*d*) 2 × at. no. of S = 2 × no. of electrons of S = 2 × 16 = 32

3 × at. no. of O = 3 × no. of electrons of O = 3 × 8 = 24

∴ Total no. of electrons in $S_2O_3^{2-}$

= 32 + 24 + 2 = **58** **Ans.**

Example 35. *Calculate the total number of protons, electrons and neutrons in (i) NH_4^+, (ii) NO^+ (at. no. N = 7, H = 1, mass no., N = 14, H = 1.*

Solution. $\mathbf{NH_4^+}$.

(*a*) At. no. of N = no. of protons of N = 7

4 × at. no. of H = 4 × no. of protons of H = 4 × 1 = 4

∴ Total no. of protons = 7 + 4 = **11** **Ans.**

(*b*) No. of neutrons in N

= mass no. – at. no. = 14 – 7 = 7

4 × no. of neutrons in H

= 4 × 0 = 0 [∵ no. of neutrons in H = mass no. – at. no. = 1 – 1 = 0]

∴ Total no. of neutrons in

$NH_4^+ = 7 + 0 = 7$

(*c*) No. of electrons in N

= at. no. of N = 7

4 × no. of electrons in H

= 4 × no. of protons in H

= 4 × 1 = 4

∴ No. of electrons in NH_4^{+1}

= 7 + 4 – 1 = 10

Example 36. *Calculate the number of protons and neutrons in an element with mass number, 19 and atomic number, 9.*

Solution. No. of protons = **9** **Ans.**

No. of neutrons = (mass no.) – (at. no.)

= 19 – 9 = **10** **Ans.**

12.6 WAVE LENGTH, FREQUENCY, VELOCITY, WAVE NUMBER, AMPLITUDE, RADIANT ENERGY

Wavelength (λ). It is the distance between two adjacent crests or troughs in a particular wave. Unit is Angstrom, Å.

1Å = 10^{-10}m = 10^{-8}cm

= 10^{-1}nm = 100 pm.

1 micrometer (μ) = 10^{-6}m = 10^{-4}cm

1 millimicron (mμ) = 10^{-9}m = 10^{-7}cm

1 mega meter = 10^{6}m = 10^{8}cm;

1 km = 10^{3}m = 10^{5}cm

1 hectometer = 10^{2}m = 10^{4}cm;

1 decameter = 10 m = 10^{3}cm

1 decimeter = 10^{-1}m = 10 cm; 1 cm = 10^{-2}m

1 mm = 10^{-3}m = 10^{-1} cm

Frequency (υ). It is defined as the number of waves or cycles which pass through a given point in one second. Unit is hertz (Hz) or s^{-}.

Velocity (*c*). It is the distance travelled by a wave in one second. Unit is ms^{-} or cms^{-}.

Relation between velocity (c), wavelength (λ) and frequency (υ) is : c = λυ

For light, c = 3.0 × $10^{8}ms^{-}$ = 3.0 × 10^{10} cms^{-}.

Wave number ($\bar{\upsilon}$). It is the reciprocal of wavelength. It is defined as the number of waves per metre. **Unit is $\mathbf{m^{-}}$**

or $$\bar{\upsilon} = \frac{1}{\lambda}$$

or Wave number $$= \frac{\mathbf{1}}{\mathbf{Wavelength}}$$

Amplitude (a). It is the height of crest or depth of a wave.

Radiant energy. It is the energy transmitted from one body to another in the form of radiations or rays. The decreasing order of various radiant energies is :

Cosmic rays > gamma rays (γ) > X-rays > ultra-violet rays > visible light rays > infra-red rays > microwaves > radio waves > heat.

Type. Velocity (*c*) = Wavelength (λ) × frequency (υ); wave number, $\bar{\upsilon} = \frac{1}{\lambda}$

Example 37. *A radio station broadcasts at a frequency of 14 MHz (megahertz). Calculate the wavelength of the radio-waves put out by the transmitter.*

Solution. υ = 14 MHz = 14 × 10^{6} s^{-}; *c* = 3 × 10^{8} ms^{-};

λ = ? We know that :

$$\lambda = \frac{c}{\upsilon} = \frac{3.0 \times 10^{8}\,ms^{-}}{14 \times 10^{6} s^{-}} = \mathbf{21.4\ m}$$ **Ans.**

Example 38. *A radio-operator broadcasts at a frequency of 1000 kHz. Calculate the wavelength and wave number of these radiowaves.*

Solution. υ = 1000 kHz = 1000 × 1000 s^{-} = $10^{6}s^{-}$;

c = 3.0 × 10^{8} ms^{-}, λ = ?, $\bar{\upsilon}$ = ?.

(*i*) Wavelength,

$$\lambda = \frac{c}{\upsilon} = \frac{3.0 \times 10^{8}\,ms^{-}}{10^{6} s^{-}}$$

$= \mathbf{3.0 \times 10^{2}\ m}$ **Ans.**

(*ii*) $$\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{3.0 \times 10^{2}} = \mathbf{3.3 \times 10^{-3}\ m^{-}}$$ **Ans.**

Example 39. *Calculate the frequency of spectral line of calcium having wavelength of 456 nm.*

Solution. υ = ? *c* = 3.0 × $10^{8}ms^{-}$;

λ = 456 nm = 456 × 10^{-9} m.

But, $$\upsilon = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\,ms^{-}}{456 \times 10^{-9}\,m}$$

$= \mathbf{6.6 \times 10^{14}\ s^{-}}$ **Ans.**

Example 40. *A sunlight has a maximum intensity at a wavelength of about 6.0 × 10^{-7}m. Calculate the wave number of this light.*

Solution. $\lambda = 6.0 \times 10^{-7}\text{m};\ \bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{6.0 \times 10^{-7}\ \text{m}}$

$= 0.16 \times 10^{7}\ \text{m}^{-}$ or $\bar{\upsilon} = \mathbf{1.6 \times 10^{6}\ m^{-}}$

Ans.

Example 41. *The violet to red coloured radiations, making up the visible light have wavelength range 400 nm to 750 nm. Calculate the corresponding range of frequencies.*

Solution. For violet colour, $\lambda = 400\ \text{nm} = 400 \times 10^{-9}\ \text{m}$; $c = 3.0 \times 10^{8}\text{ms}^{-}$; $\upsilon = ?$

We know that : $\upsilon = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\ \text{ms}^{-}}{400 \times 10^{-9}\ \text{m}} = 7.5 \times 10^{14}\ \text{s}^{-}$

For red colour, $\lambda = 750\ \text{nm} = 750 \times 10^{-9}\ \text{m}$;

$c = 3.0 \times 10^{8}\ \text{ms}^{-}; \upsilon = ?.$

We know that : $\upsilon = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\text{ms}^{-}}{750 \times 10^{-9}\text{m}} = 4.0 \times 10^{14}\text{s}^{-}$

So, frequency range = $7.5 \times 10^{14}\text{s}^{-}$ to $4.0 \times 10^{14}\text{s}^{-}$ **Ans.**

12.7 PLANCK'S QUANTUM THEORY

Energy of a body can change by some definite whole number multiple of unit energy as the quantum. Energy of body can increase or decrease by whole numbers 1, 2, 3,...*n* quanta and not in fractions.

1. **Planck's relation.** $E = h\upsilon$ or $E = \frac{hc}{\lambda}$ or $E = hc\bar{\upsilon}$

where E = energy of photon or radiation; **h = Planck's constant = 6.625 × 10^{-27} erg sec = 6.625 × 10^{-34} Js or 3.99 × 10^{-13} kJs mol^{-}**; c = velocity of light = $3.0 \times 10^{8}\text{ms}^{-}$ = $3.0 \times 10^{10}\text{cms}^{-}$, λ = wavelength of the photon or radiation.

2. Total energy of striking photon ($h\upsilon$) = Binding energy or threshold energy ($h\upsilon_0$) + Kinetic energy of the ejected electron $\left(= \frac{1}{2}mv^{2}\right)$

$\therefore$ Kinetic energy of the ejected electron, $\frac{1}{2}mv^{2}$

$= h\upsilon - h\upsilon_0 = h(\upsilon - \upsilon_0)$

where v_0 = threshold frequency.

3. According to Planck's quantum theory :

$$\Delta E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}$$

where ΔE = energy difference between two electronic states.

Type. (*i*) $E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}$, (*ii*) $\Delta E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon}$

Example 42. *The energy difference between two electronic states is 399.1 kJ mol^{-}. Calculate the wavelength and frequency of light emitted when an electron drops from a higher to a lower state. (Planck's constant, h = 6.6262 × 10^{-34} Js).*

Solution. $\upsilon = \frac{\Delta E}{h}$

$= \frac{399.1 \times 1000\ \text{J mol}^{-}}{6.6262 \times 10^{-34} \times 6.023 \times 10^{23}\ \text{Js mol}^{-}}$

$= \mathbf{10^{15}\ s^{-}}$ **Ans.**

(*ii*) $\lambda = \frac{c}{\upsilon} = \frac{3.0 \times 10^{8}\text{ms}^{-}}{10^{15}\text{s}^{-}} = \mathbf{3.0 \times 10^{-7}\ m}$ **Ans.**

Example 43. *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. (Planck's constant, h = 6.624 × 10^{-27} erg.).*

(WB EE, 1990)

Solution. $\Delta E = 35.64 \times 10^{-13}\text{erg}$; $h = 6.624 \times 10^{-27}$ ergs. We know that : $\Delta E = h\upsilon$. So,

$\upsilon = \frac{\Delta E}{h} = \frac{35.64 \times 10^{-13}\,\text{erg}}{6.624 \times 10^{-27}\text{ergs.}}$

$= \mathbf{5.38 \times 10^{14}\ s^{-}}$ **Ans.**

Example 44. *A quanta of light having energy E, has a wavelength equal to 750 nm. Find the wavelength of photon that corresponds to energy 5E.*

Solution. Energy of first light,

$$E_1 = \frac{hc}{\lambda_1} \quad \text{...(A)}$$

Energy of second light,

$$E_2\ (= 5E_1) = \frac{hc}{\lambda_2} \quad \text{...(B)}$$

Dividing equations (*A*) and (*B*), we get

$$\frac{E_1}{E_2} = \frac{hc}{\lambda_1} \times \frac{\lambda_2}{hc} = \frac{\lambda_2}{\lambda_1};\ \frac{E_1}{5E_1} = \frac{\lambda_2}{750\,\text{nm}}$$

Hence, $\lambda_2 = \frac{750\,\text{nm}}{5} = \mathbf{150\ nm}$ **Ans.**

Example 45. *A spectral line having wavelength 450 nm is seen in an atomic emission spectrum. How much does the energy of an electron decrease as this photon is emitted ?*

Solution. $\lambda = 450\ nm = 450 \times 10^{-9}\ \text{m}$,

$h = 6.626 \times 10^{-34}\text{Js}; c = 3.0 \times 10^{8}\ \text{ms}^{-}.$

But $E = \frac{\lambda c}{\lambda}\cdot$

So, $E = \frac{6.626 \times 10^{-34}\,\text{Js} \times 3.0 \times 10^{8}\,\text{ms}^{-}}{450 \times 10^{-9}\,\text{m}}$

$= \mathbf{4.417 \times 10^{-19}\ J}$ **Ans.**

Example 46. *Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol^{-}.* **(Roorkee JEE., 1989, 92)**

Solution. $\lambda = 242\ \text{nm} = 242 \times 10^{-9}\text{m}$,

$c = 3.0 \times 10^{8}\ \text{ms}^{-}, h = 6.626 \times 10^{-34}\ \text{Js}$

1 mole = Avogadro's number

$= 6.023 \times 10^{23}$

We know that : $E = h\upsilon = \frac{hc}{\lambda}\cdot$

$$= \frac{6.626\times10^{-34}\,\text{Js}\times3.0\times10^{8}\,\text{ms}^{-}}{242\times10^{-9}\,\text{m}}$$

$$= 8.21 \times 10^{-19}\,\text{J}$$

Energy required to ionise one Na-atom = 8.21×10^{-19}J

$\therefore$ Energy required to ionise 1 mole or Avogadro's number of Na-atoms

$$= 8.21 \times 10^{-19}\text{J} \times 6.023 \times 10^{23}$$

$$= \mathbf{494488\ J}$$ **Ans.**

EXAMPLE 47. *Calculate the wavelength of a photon associated with one electron volt energy.*

SOLUTION. $\lambda = ?, E = 1\ \text{eV} = 1.602 \times 10^{-19}\text{J};$
$h = 6.626 \times 10^{-34}$ Js. We know

$$E = h\upsilon = \frac{hc}{\lambda};\ c = 3.0 \times 10^{8}\ \text{ms}^{-}.$$

$$\therefore \qquad \lambda = \frac{hc}{E} = \frac{6.626\times10^{-34}\,\text{Js}\times3.0\times10^{8}\,\text{ms}^{-}}{1.602\times10^{-19}\,\text{J}}$$

$$= \mathbf{1.24 \times 10^{-6} m}$$ **Ans.**

EXAMPLE 48. *A gas absorbs a near U.V. photon of wavelength 300 nm and then emitted as 2 photons. One photon is red which has a wavelength of 760 nm. Calculate the wavelength of second photon.*

SOLUTION. λ_1 (U.V. light) = 300 nm = 300×10^{-9}m; λ_2 (red light) = 760 nm = 760×10^{-9}m.

For U.V. light, $E = \dfrac{hc}{\lambda} = \dfrac{hc}{300\times10^{-9}\,\text{m}}$ ...(*i*)

For red light, $E_1 = \dfrac{hc}{\lambda_1} = \dfrac{hc}{760\times10^{-9}\,\text{m}}$ ...(*ii*)

Energy associated with second photon, E_2

Now $E = E_1 + E_2$.

$$\frac{hc}{300\times10^{-9}\,\text{m}} = \frac{hc}{760\times10^{-9}\,\text{m}} + \frac{hc}{\lambda_2}$$

$$\frac{hc}{300\times10^{-9}\,\text{m}} = hc\left[\frac{1}{760\times10^{-9}\,\text{m}} + \frac{1}{\lambda_2}\right]$$

$$\therefore \qquad \frac{1}{\lambda_2} = \frac{1}{300\times10^{-9}\,\text{m}} - \frac{1}{760\times10^{-9}\,\text{m}}$$

$$= \frac{(760\times10^{-9}\,\text{m})-(300\times10^{-9}\,\text{m})}{300\times10^{-9}\,\text{m}\times760\times10^{-9}\,\text{m}}$$

$$= \frac{460\times10^{-9}\,\text{m}}{228{,}000\times10^{-18}\,\text{m}^2}$$

$$\lambda_2 = \frac{228000\times10^{-18}\,\text{m}^2}{460\times10^{-9}\,\text{m}}$$

$$= 4.96 \times 10^{-7}\ \text{m}$$

$$= 4.96 \times 10^{-7}\ \text{m} \times \frac{1\ \text{nm}}{10^{-9}\text{m}}$$

$$= \mathbf{496\ nm}$$ **Ans.**

Type. No. of photons = $\dfrac{\textbf{Given energy}}{\textbf{Energy of one photon}}$

EXAMPLE 49. *Calculate the number of photons of light with a wavelength of 4000 Å that provide one joule of energy.*

SOLUTION. Given energy, E = 1J; λ = 4000 Å = 4000×10^{-10} m, $h = 6.626 \times 10^{-34}$ Js, $c = 3.0 \times 10^{8}$ ms^{-}.

We know that: $E = h\upsilon = \dfrac{hc}{\lambda}$

$$\therefore \qquad E = \frac{6.626\times10^{-34}\,\text{Js}\times3.0\times10^{8}\,\text{ms}^{-}}{4000\times10^{-10}\,\text{m}}$$

$$= 4.9695 \times 10^{-19}\ \text{J}$$

Total number of photons

$$= \frac{\text{Given energy}}{\text{Energy of one photon}}$$

$$= \frac{1\text{J}}{4.9695\times10^{-19}\text{J}} = \mathbf{2.0\times10^{18}}$$ **Ans.**

EXAMPLE 50. *In order to melt one gram of ice, 333 J energy is required. Calculate the number of quanta of infra-red radiation of frequency 4.67 × 10*^{13} *s*$^{-}$ *that must be absorbed in order to melt 3g of ice.*

SOLUTION. Energy required to melt 1 g ice = 333 J

$\therefore$ Energy required to melt 3.0 g of ice

$$= 333 \times 3\ \text{J} = 999\ \text{J}$$

$\upsilon = 4.67 \times 10^{13}$ s^{-}; $h = 6.626 \times 10^{-34}$ Js. We know that :

$$E = h\upsilon = 6.626 \times 10^{-34}\text{Js} \times 4.67 \times 10^{13}\ \text{s}^{-}$$

$$= 3.094 \times 10^{-20}\ \text{J}$$

$\therefore$ Energy provided by one quanta of infra-red radiations $= 3.094 \times 10^{-20}$ J

Hence number of quanta of infra-red radiations

$$= \frac{\text{Given energy}}{\text{Energy of one photon}}$$

$$= \frac{999\,\text{J}}{3.094\times10^{-20}\ \text{J}} = \mathbf{3.229 \times 10^{22}}$$

Ans.

EXAMPLE 51. *The binding energy of electron in a metal is 201 kJ mol*$^{-}$*. Calculate the threshold frequency of the metal.*

SOLUTION. E = 201 kJ mol^{-} = 201 × 1000 J mol^{-}; threshold frequency, υ_0 = ?, $h = 6.626 \times 10^{-34} \times 6.023 \times 10^{23}$ Js mol^{-} [1 mole = 6.023×10^{23}]. But $E = h\upsilon_0$. so,

$$\upsilon_0 = \frac{E}{h} = \frac{201\times1000\,\text{J mol}^{-}}{6.626\times10^{-34}\times6.023\times10^{23}\ \text{Js mol}^{-}}$$

or $\qquad \upsilon_0 = \mathbf{5.0 \times 10^{14}\ s^{-}}$ **Ans.**

EXAMPLE 52. *When an unknown metal was irradiated with light radiations of frequency 2.9 × 10*^{16}*s*$^{-}$*, the photoelectrons emitted have twice the kinetic energy as did the photoelectrons emitted when the same metal was irradiated with light of frequency 1.9 × 10*^{16}*s*$^{-}$*. Calculate the threshold frequency of unknown metal.*

SOLUTION. $\upsilon_1 = 2.9 \times 10^{16}$s^{-}; $\upsilon_2 = 1.9 \times 10^{16}$s^{-}.

We know that : K.E. = $h\upsilon - h\upsilon_0$.

Hence $\quad h\upsilon_1 - h\upsilon_0 = 2\,(h\upsilon_2 - h\upsilon_0)$.

or $\quad h(\upsilon_1 - \upsilon_0) = 2h\,(\upsilon_2 - \upsilon_0)$

$$\upsilon_1 - \upsilon_0 = 2\upsilon_1 - 2\upsilon_0 \text{ or } 2\upsilon_0 - \upsilon_0 = 2\upsilon_2 - \upsilon_1$$

Hence :
$$\upsilon_0 = 2\upsilon_2 - \upsilon_1 = 2 \times 1.9 \times 10^{16}\ s^{-} - 2.9 \times 10^{16}\ s^{-}$$
$$= 3.8 \times 10^{16}\ s^{-} - 2.9 \times 10^{16}\ s^{-}$$
$$= 10^{16}\ s^{-}\ (3.8 - 2.9)$$
$$= \mathbf{9.0 \times 10^{15} s^{-}}$$ **Ans.**

Example 53. *The threshold frequency of silver metal is 1.13 × $10^{17}s^{-}$. Calculate the maximum energy of photoelectrons produced by shining ultraviolet light of wavelength of 15Å on the metal.*

Solution. $\upsilon_0 = 1.13 \times 10^{17}\ s^{-}$; $E = ?$, $\lambda = 15$ Å $= 15 \times 10^{-10}$m; $c = 3.0 \times 10^8$ ms^{-}, $h = 6.626 \times 10^{-34}$ Js.

(*i*)
$$\upsilon = \frac{c}{\lambda} = \frac{3.0 \times 10^{8}\,\text{ms}^{-}}{15 \times 10^{-10}\,\text{m}} = 2.0 \times 10^{17}\ s^{-}$$

(*ii*)
$$\text{K.E.} = h\upsilon - h\upsilon_0 = h(\upsilon - \upsilon_0)$$
$$= 6.626 \times 10^{-34}\ \text{Js}\ (2.0 \times 10^{17}\ s^{-} - 1.13 \times 10^{17}\ s^{-})$$
$$= 6.626 \times 10^{-34}\ \text{Js} \times 0.87 \times 10^{17}\ s^{-}$$

Thus, $\mathbf{K.E. = 5.76 \times 10^{-17}\ J}$ **Ans.**

Example 54. *An electromagnetic radiation of wavelength 656 nm when falls on a metal, electrons are emitted with a kinetic energy of 1.03 × 10^{-19} J. From this data, calculate the following:*

(i) Maximum wavelength to emit photoelectron.

(ii) Minimum energy to remove an electron from the metal

(iii) Threshold frequency (υ_0) of the metal

Solution. $\lambda = 656$ nm $= 656 \times 10^{-9}$m; K.E. $= 1.03 \times 10^{-19}$ J; $h = 6.626 \times 10^{-34}$ Js; $c = 3.0 \times 10^8$ ms^{-}.

(*a*) Energy,
$$E = h\upsilon = \frac{hc}{\lambda}$$

or
$$E = \frac{6.626 \times 10^{-34}\,\text{Js} \times 3.0 \times 10^{8}\,\text{ms}^{-}}{656 \times 10^{-9}\,\text{m}}$$
$$= \mathbf{3.03 \times 10^{-19}\ J = h\upsilon}$$

∴ Energy to remove an electron, $h\upsilon_0$
$$= h\upsilon - \text{K.E.} \qquad [\because \text{K.E.} = h\upsilon - h\upsilon_0]$$
$$= 3.03 \times 10^{-19}\ \text{J} - 1.03 \times 10^{-19}\ \text{J}$$
$$= 10^{-19}\ \text{J}\ (3.03 - 1.03)$$
$$= \mathbf{2 \times 10^{-19}\ J}$$ **Ans.**

(*b*) Calculation of threshold frequency, υ_0.

We know that : $E = h\upsilon_0$

Hence
$$\upsilon_0 = \frac{E}{h} = \frac{2.0 \times 10^{-19}\,\text{J}}{6.626 \times 10^{-34}\,\text{Js}}$$
$$= \mathbf{3.02 \times 10^{14}\ s^{-}}$$ **Ans.**

(*c*)
$$\upsilon_0 = \frac{c}{\lambda} \quad \text{or} \quad \lambda = \frac{c}{\upsilon_0} = \frac{3.0 \times 10^{8}\,\text{ms}^{-}}{3.02 \times 10^{14}\,\text{s}^{-}}$$
$$= 9.93 \times 10^{-7}\ \text{m}$$

∴ Maximum wavelength to emit photoelectron
$$= \mathbf{9.93 \times 10^{-7}\ m}$$ **Ans.**

Example 55. *The threshold wavelength of a metal is 5800 Å. The metal surface is illuminated with a light of wavelength of 2800 Å and the electron is emitted with a certain energy. Calculate the potential required to bring the electron to rest.*

Solution. Energy associated with a light of wavelength
$$2800\ \text{Å} = h\upsilon = h\frac{c}{\lambda}$$

or
$$E = \frac{(6.626 \times 10^{-34}\,\text{Js})(3 \times 10^{8}\,\text{ms}^{-1})}{2800 \times 10^{-10}\,\text{m}}$$
$$= \mathbf{7.099 \times 10^{-19}\ J}$$

Threshold Energy,
$$E_0 = \frac{hc}{\lambda_0}$$
$$= \frac{(6.626 \times 10^{-34}\,\text{Js})(3 \times 10^{8}\,\text{ms}^{-1})}{5800 \times 10^{-10}\,\text{m}}$$
$$= 3.427 \times 10^{-19}\ \text{J}$$
$$\text{K.E.} = \frac{1}{2}mv^2 = E - E_0$$
$$= 7.099 \times 10^{-19}\ \text{J} - 3.427 \times 10^{-19}\ \text{J}$$
$$= 3.672 \times 10^{-19}\,\text{J} = \frac{3.672 \times 10^{-19}\,\text{J}}{1.602 \times 10^{-19}\,\text{J/eV}}$$
$$= 2.292\ \text{eV}$$

Energy required to stop the electron
$$= 2.292\ \text{eV}$$

∴ Potential required to bring the electron to rest
$$= \mathbf{2.292\ eV.}$$

Example 56. *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. Bond energy per molecule
$$= \frac{240 \times 10^{3}\,\text{J}}{6.02 \times 10^{23}}$$
$$= 3.98 \times 10^{-19}\ \text{J/molecule}$$

Energy absorbed,
$$\frac{hc}{\lambda} = \frac{6.62 \times 10^{-34}\,\text{Js} \times 3 \times 10^{8}\,\text{ms}^{-1}}{4500 \times 10^{-10}\,\text{m}}$$
$$= 4.41 \times 10^{-19}\ \text{J}$$

Kinetic energy $= (4.41 \times 10^{-19} - 3.98 \times 10^{-19})$ J
$$= 4.3 \times 10^{-20}\ \text{J}$$

Kinetic energy per atom
$$= \frac{4.3 \times 10^{-20}}{2}\ \text{J} = \mathbf{2.15 \times 10^{-20}\ J}$$

[∵ $I_2 \equiv 2I$ atoms].

Example 57. *A bulb emits light of λ 4500 Å. The bulb is rated as 150 watt and 8% of the energy is emitted as light. How many photons are emitted by the bulb per second ? (h = 6.625 × 10^{-34} Js ; c = 3 × 10^8 ms^{-1}).* **(IIT, 1995)**

Solution. Energy emitted by the bulb $= 150 \times \frac{8}{100}$ J

[1 watt = 1 J s^{-}]

Energy of one photon
$$= \frac{hc}{\lambda} = \frac{6.625 \times 10^{-34} \times 3 \times 10^{8}}{4500 \times 10^{-10}}\ \text{J}$$
$$= 4.42 \times 10^{-19}$$

If n is the number of photons emitted by the bulb, then

$$n \times 4.42 \times 10^{-19}\text{ J} = 150\times\frac{8}{100}\text{ Js}^{-};n=\frac{150\times 8}{100\times 4.42\times 10^{-19}}$$

$$= \mathbf{2.72 \times 10^{19}\ s^{-}}$$

Example 58. *A beam of electrons accelerated through 4.0 V in a tube containing mercury vapours was partly absorbed by the vapours. As a result of absorption, electronic changes occurred within a mercury atom and light was emitted. Calculate the wave number of the emitted light assuming that the full energy of a single incident electron was converted into light.*

Solution. Energy associated with electron beam accelerated through 4V = 4eV = $4 \times 1.602 \times 10^{-19}$ J; $E = hv = hc\bar{\upsilon}$

$$\therefore \quad \bar{\upsilon} = \frac{E}{hc} = \frac{4\times 1.602\times 10^{-19}\text{ J}}{6.626\times 10^{-34}\text{ Js}\times 3\times 10^{8}\text{ ms}^{-1}}$$

$$= 0.3223 \times 10^{7}\text{ m}^{-1}$$

$$= \mathbf{3.223 \times 10^{6} m^{-1} = 32230\ cm^{-1}}$$

Type. $\upsilon = \frac{c}{\lambda}$; $c = 3.0 \times 10^{8}$ ms^{-}; 1Å = 10^{-8}cm = 10^{-10}m; 1μm = 10^{-6}m ; 1 nm = 10^{-9} m.

Example 59. *Calculate the frequencies of light of following wavelengths : (i) 452 nm, (ii) 3.8μm, (iii) 2.0 Å, (iv) 72 m.*

Solution. (*i*)
$$\upsilon = \frac{c}{\lambda} = \frac{3.0\times 10^{8}\text{ ms}^{-}}{452\times 10^{-9}\text{ m}}$$

$= 6.6 \times 10^{14}$ s^{-} = **6.6 × 10^{14} Hz** **Ans.**

(*ii*)
$$\upsilon = \frac{c}{\lambda} = \frac{3.0\times 10^{8}\text{ ms}^{-}}{3.8\times 10^{-6}\text{ m}}$$

[∵ 1μm = 10^{-6}m]

$\upsilon = 7.9 \times 10^{13}$ s^{-} = **7.9 × 10^{13} Hz** **Ans.**

(*iii*)
$$\upsilon = \frac{c}{\lambda} = \frac{3.0\times 10^{8}\text{ ms}^{-}}{2\times 10^{-10}\text{ m}}$$

[∵ 1Å = 10^{-10}m]

$\upsilon = 1.5 \times 10^{18}$ s^{-} = **1.5 × 10^{18} Hz Ans.**

(*iv*)
$$\upsilon = \frac{c}{\lambda} = \frac{3\times 10^{8}\text{ ms}^{-}}{72\text{ m}} = 4.2 \times 10^{6}\text{ s}^{-}$$

= **4.2 × 10^{6} Hz** **Ans.**

Example 60. *Calculate the relationship between the electron volt (eV) and wavelength in nm of the energetically equivalent photon.*

Solution. The frequency (υ) equivalent of 1 eV from Planck equation is given as :

$$\upsilon = \frac{E}{h} = \frac{1.6022\times 10^{-19}\text{ J}}{6.626\times 10^{-34}\text{ Js}}$$

$$= 2.418 \times 10^{14}\text{ s}^{-}$$

But, $\upsilon = \frac{c}{\lambda}$

So, $$\lambda = \frac{3.0\times 10^{8}\text{ ms}^{-}}{2.418\times 10^{14}\text{ s}^{-}} = 1.2407 \times 10^{-6}\text{ m}$$

or $\lambda = 1.2407 \times 10^{-6} \times 10^{9}$ nm = **1240.7 m**

[∵ 1m = 10^{9} nm]

Example 61. *What is equivalent of energy unit 1 cm^{-} in (i) J per photon (ii) kJ per mol of photons (iii) k cal per mol of photons ? (h = 6.62 × 10^{-34} Js).*

Solution. (*i*) We know,

$$E = h\upsilon = \frac{hc}{\lambda} = hc\bar{\upsilon};\bar{\upsilon} = 1\text{ cm}^{-}.$$

$$\therefore \quad E = hc\bar{\upsilon} = 6.62 \times 10^{-34}\text{ Js} \times 3.0 \times 10^{10}\text{ cms}^{-} \times 1\text{ cm}^{-}$$

$$= \mathbf{1.99 \times 10^{-23}\ J}$$

(*ii*) 1 kJ = 10^{3} J; 1 mol of photons = 6.02×10^{23} photons. Hence

$$E = \frac{1.99\times 10^{-23}\text{ J}}{\text{photon}}\times\frac{1\text{ kJ}}{10^{3}\text{ J}}$$

$$\times\ \frac{6.02\times 10^{23}\text{ photon}}{1\text{ mol}}$$

= **1.2 × 10^{-2} kJ mol^{-}** **Ans.**

(*iii*) 1 mol of photons = 6.02×10^{23} photons;

1 k cal = 4184 J

$$\therefore \quad E = \frac{1.99\times 10^{-23}\text{ J}}{\text{photon}}\times\frac{1\text{ k cal}}{4184\text{ J}}$$

$$\times\ \frac{6.02\times 10^{23}\text{ photon}}{1\text{ mol}}$$

= **2.86 × 10^{-3} k cal mol^{-}** **Ans.**

Example 62. *The wavelength of a beam of light is 4.4 μm. Calculate (i) its wave number (ii) its frequency (iii) its wavelength in cm and (iv) the energy of one of its photons. (h = 6.63 × 10^{-34} Js).*

Solution. (*i*)Wave number,

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{4.4\times 10^{-4}\text{ cm}}$$

= **2.27 × 10^{3} cm^{-}** **Ans.**

(*ii*)
$$\upsilon = \frac{c}{\lambda} = \frac{3.0\times 10^{10}\text{ cms}^{-}}{4.4\times 10^{-4}\text{ cm}}$$

= **6.8 × 10^{13} s^{-}** **Ans.**

(*iii*) λ = 4.4 μm = 4.4×10^{-6}m

= $4.4 \times 10^{-6} \times 10^{2}$ cm

= 4.4×10^{-4} cm

(*iv*) $E = h\upsilon = 6.63 \times 10^{-34}\text{ Js} \times 6.8 \times 10^{13}\text{ s}^{-}$

= **4.5 × 10^{-20}J** **Ans.**

Example 63. *One mole of photon, each of frequency 2500s^{-}, would have approximately a total energy of :*

(a) *1 erg* *(b)* *1 joule*

(c) *1 eV* *(d)* *1 MeV*

(West Bengal-JEE, 2009)

Solution. Energy of a photon,

$E = h\upsilon$; $\upsilon = 2500$ s^{-}

So, $E = (6.626 \times 10^{-34} \times 2500)$ J.

Since 1 mole = 6.023×10^{23}

So,Energy of one mol of photons

= $(6.626 \times 10^{-34} \times 2500 \times 6.023 \times 10^{23})$ J

$$= \frac{997}{10^9}\text{J} = \frac{997}{10^9} \times 10^7 \text{ erg} \approx 10 \text{ erg.}$$

So, none of the answer is correct.

Example 64. *Find the value of the period (i.e., time required for one cycle) if the second hand on a watch rotates 60 cycles per hour. Also find the relationship (i) between frequency and period (ii) between their units.*

Solution. Frequency,

$$\upsilon = \frac{60 \text{ cycles}}{\text{hour}} = \frac{60}{h} \times \frac{1h}{60 \text{ min}}$$

$$= 1 \text{ min}^{-} \qquad [\because 1h = 60 \text{ min}]$$

(*i*) Period, $T = \frac{1}{\upsilon} = \frac{1}{1\text{min}^{-}} = 1 \text{ min}$ **Ans.**

(*ii*) Since T and υ are reciprocal of each other, their units will be, for example, s and s^{-} (= Hz) respectively.

Example 65. *Find the wavelength of light (in m, cm and Å) having frequency 45 MHz.*

Solution. (*i*) $\upsilon = 45 \text{ MHz} = 45 \times 10^6 s^{-}$

Hence, $\lambda = \frac{c}{\upsilon} = \frac{3.0 \times 10^8 \text{ms}^{-}}{45 \times 10^6 \text{s}^{-}}$

or $\boldsymbol{\lambda = 6.67 \text{ m}}$ **Ans.**

(*ii*) Since $1 \text{ m} = 100 \text{ cm}; \lambda = 6.67 \times 100 \text{ cm}$

$= 667 \text{ cm.}$

(*iii*) Since $10^{-10}\text{m} = 1 \text{ Å}, 1 \text{ m} = 10^{10} \text{ Å.} = 6.67 \text{ m}$

$= \mathbf{6.67 \times 10^{10}}$ **Å** **Ans.**

Example 66. *Which of the following (a) E = hυ, (b) E = mc^2, (c) diffraction, (d) photoelectric effect and (e) interference, relate to light as wave motion, to light as a stream of particles or to both ?*

Solution. (*a*) both, (*b*) particles, (*c*) wave motion, (*d*) particles, (*e*) wave motion. In $E = h\upsilon$, E refers to the energy of each photon of light while υ refers to the frequency of the wave of light.

Example 67. *What is the shortest and the longest wavelength of visible light ?*

Solution. Shortest wavelength and longest wavelengths of visible light are 4000 Å and 7000 Å respectively.

Example 68. *Calculate (i) J mol⁻ (or J/mol), (ii) ergs (photons)⁻ and (iii) k cal mol⁻ of photons of shortest wavelength of visible light.*

Solution. (*i*) $E = hc\bar{\upsilon}$ ...(*i*)

But, $\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{4000\text{Å}} = \frac{1}{4000 \times 10^{-8}\text{cm}}$

$= 2.5 \times 10^4 \text{ cm}^{-}$

∴ $E = 6.62 \times 10^{-34} \text{ Js} \times 3.0 \times 10^{10} \text{ cms}^{-} \times 2.5 \times 10^4 \text{ cm}$

$= 4.965 \times 10^{-19} \text{ J}$

But, $1 \text{ mol} = 6.023 \times 10^{23}$.

Hence energy in J/mol will be :

$$4.965 \times 10^{-19} \text{ J} \times \frac{6.023 \times 10^{23}}{1 \text{ mol}}$$

$= \mathbf{3.0 \times 10^5 \text{ J mol}^{-}}$ **Ans.**

(*ii*) $1\text{J} = 10^7$ erg; $1 \text{ mol} = 6.023 \times 10^{23}$ photons. Hence from answer (*i*), we have :

Energy in ergs/photon

$$= \frac{3.0 \times 10^5 \times 10^7 \text{erg}}{6.023 \times 10^{23} \text{ photons}}$$

$= 4.97 \times 10^{-12}$ erg/photon.

(*iii*) 4.184 J = 1 cal ; 4.184 × 1000 J = 1 k cal; 4184 J = 1 k cal. Using answer (*i*), we have :

$$\text{Energy in k cal/mol} = \frac{3.0 \times 10^5 \text{J}}{4184 \text{ J}} \text{ k cal}$$

= 71.7 k cal/mol **Ans.**

Example 69. *Experiments reveal that gaseous iodine I_2 (g), dissociates into separate atoms after the absorption of light at wavelengths less than 4995 Å. If each quantum is absorbed by one molecule of I_2, calculate the minimum input, in kJ mol⁻ and k cal mol⁻ required to dissociate I_2 by this photochemical technique. [Avogadro's no. $N_A = 6.022 \times 10^{23}$ mol⁻, $h = 6.626 \times 10^{-34}$ Js].*

Solution. For one mol,

$$E = N_A h\upsilon = \frac{N_A hc}{\lambda}.$$

Substituting the values, we get :

$$E = \frac{6.022 \times 10^{23} \text{mol}^{-} \times 6.626 \times 10^{-34} \text{Js} \times 3.0 \times 10^8 \text{ms}^{-}}{4995 \times 10^{-10} \text{m}}$$

$= 239650 \text{ J mol}^{-}$

$= \frac{239650}{1000} = \mathbf{239.65 \text{ kJ mol}^{-}}$ **Ans.**

But 4.184 kJ = 1 k cal

∴ $E = \frac{239.65 \text{ kJ}}{\text{mol}} \times \frac{1 \text{ k cal}}{4.184 \text{ kJ}}$

$= \mathbf{57.28 \text{ k cal mol}^{-}}$ **Ans.**

Example 70. *Give the distinction between (i) a photon and a quantum and (ii) a photon and a proton.*

Solution. (*i*) A photon is a particle of light energy or a photon is a quantum of light (electromagnetic energy) while a quantum is a bundle of energy of definite magnitude, but not necessarily light energy.

(*ii*) A photon is a particle of light energy while a proton is a positively charged nuclear particle.

Example 71. *Experiments reveal that O_2 undergoes photochemical dissociation into one normal oxygen atom and one oxygen atom, 1.967 eV more energetic than normal. Also, the dissociation of O_2 into two normal oxygen atoms needs 498 kJ mol⁻ O_2. Calculate the maximum wavelength effective for the photochemical dissociation of O_2.*

Solution. 1 eV = 1.6×10^{-19} J. Hence :

Extra energy for excited oxygen atom

$$= 1.967 \text{ eV} \times \frac{1.6 \times 10^{-19} \text{J}}{1 \text{ eV}}$$

$= 3.15 \times 10^{-19} \text{ J}$

But for normal oxygen atom,

$$E = \frac{498\times10^{3}\,\text{J}}{1\ \text{mol O}_2} \times \frac{1\,\text{mol O}_2}{6.02\times10^{23}\,\text{O}_2\ \text{molecules}}$$

$$= 8.27\times10^{-19}\,J$$

∴ Total energy for excited oxygen atom = 3.15×10^{-19} J + 8.27×10^{-19} J = 11.42×10^{-19}

But,

$$\lambda = \frac{hc}{E}$$

$$\lambda = \frac{6.626\times10^{-34}\,\text{J.s}\times3\times10^{8}\,\text{ms}^{-}}{11.42\times10^{-19}\text{J}}$$

$$= \mathbf{1.74\times10^{-7}\ m} = 1.74\times10^{-7}\times\frac{10^{-2}}{10^{-2}}$$

$$= 1.74\times100\times10^{-9}\ \text{m} = \mathbf{174\ nm}\quad \textbf{Ans.}$$

Example 72. *The quantum efficiency of photosynthesis measurement in green plants indicated that 8 quanta of red light at 6850 Å are required to evolve one molecule of oxygen. The average energy storage in the photo-synthetic process is 112 k cal mol⁻ O_2 evolved. Calculate the energy conversion efficiency in the experiment.*

Solution. λ = 6850 Å = 6850 × 10^{-10} m; h = 6.63 × 10^{-34} Js. We know that :

$$E = \frac{hc}{\lambda}$$

Thus,

$$E = \frac{6.63\times10^{-34}\,\text{Js}\times3.0\times10^{8}\,\text{ms}^{-}}{6850\times10^{-10}\,\text{m}}$$

or $E = 2.9\times10^{-19}$ J

8 quanta means, $E = 8\times2.9\times10^{-19}\ \text{J} = 23.2\times10^{-19}$ J

Average energy stored

$$= \frac{112\ \text{k cal}}{\text{mol}}\times\frac{4184\ \text{J}}{1\ \text{k cal}} \times \frac{1\ \text{mol}}{6.02\times10^{23}\ \text{molecules}}$$

$$= 7.78\times10^{-19}\ \text{J/molecule}$$

[∵ 1 k cal = 4184 J; 1 mol = 6.02 × 10^{23} molecules]

∴ Energy conversion efficiency

$$= \left[\frac{7.78\times10^{-19}\text{J}}{\text{molecule}}\times\frac{1}{23.2\times10^{-19}\ \text{J}}\right]\times100$$

$$= \mathbf{33.53\%}\qquad \textbf{Ans.}$$

Example 73. *A yellow coloured spectral line was observed at 5890 Å in the spectrum of a sodium vapour lamp. Calculate the minimum accelerating potential that is required to excite this line in an electron tube containing sodium vapour.*

Solution. $\lambda = 5890\times10^{-10}$m; $c = 3.0\times10^{8}$ ms⁻.

We know that : $E = h\upsilon;\ E = \frac{hc}{\lambda}$

$$E = \frac{6.626\times10^{-34}\,\text{J.s}\times3.0\times10^{8}\,\text{ms}^{-}}{5890\times10^{-10}\,\text{m}}$$

$$= 3.37\times10^{-19}\ \text{J}$$

But, 1 eV = 1.6 × 10^{-19} J

Hence,

$$E = 3.37\times10\text{–}19\text{J}\times\frac{1\ \text{eV}}{1.6\times10^{-19}\text{J}}$$

$$= 2.1\ \text{eV}$$

= 2.1 V × charge on one electron

∴ 2.1 V is needed to accelerate the electron away from the atom.

Example 74. *A white light was passed through sodium vapour and was viewed through a spectroscope. A dark line at 5890 Å was observed. Explain the observation shown above.*

Solution. It means that a light of 5890 Å wavelength has precisely the energy absorbed by the sodium atom to promote its outermost electron from its ground state level to a higher level.

Example 75. *A specific dye when dissolved in water was found to absorb maximum light at 4500 Å. Its maximum fluorescence emission is at 5000 Å. On the average, the number of fluorescence quota is 52% of the number of quanta absorbed. Calculate the percentage of absorbed light that is emitted as fluorescence. Use wavelengths of maximum absorption and emission.*

Solution. (*i*) Energy (E) absorbed by each photon

$$= h\upsilon = \frac{hc}{\lambda}.\ \text{Hence :}$$

$$E = \frac{6.626\times10^{-34}\,\text{Js}\times3.0\times10^{8}\,\text{ms}^{-}}{4500\times10^{-10}\,\text{m}}$$

$$= 4.4\times10^{-19}\ \text{J}$$

(*ii*) Energy (E) emitted by each photon

$$= \frac{hc}{\lambda}$$

$$= \frac{6.626\times10^{-34}\,\text{Js}\times3.0\times10^{8}\,\text{ms}^{-}}{5000\times10^{-10}\,\text{m}}$$

$$= 3.97\times10^{-19}\ \text{J}$$

∴ Energy fraction emitted

$$= \left[\frac{3.97\times10^{-19}\text{J}}{4.4\ \times10^{-19}J}\times\frac{52}{100}\right]\times100$$

$$= \mathbf{46.9\%}\qquad \textbf{Ans.}$$

12.8 PHOTOELECTRIC EFFECT

The minimum energy of light radiations required to remove an electron from the metal surface is called threshold energy. The effect is called photoelectric effect.

The kinetic energy of the ejected photoelectron = Energy of photoelectron–Energy required to remove an electron.

or K.E. = $h\upsilon - h\upsilon_0$, where :

$h\upsilon_0$ = Work function

= Minimum energy of photon to remove an electron

υ_0 = Threshold frequency

υ = Frequency of incident photon

Hence, **K.E.**, $\frac{1}{2}mv^2 = h(\upsilon - \upsilon_0)$

Note.1. Photon behaves as a mechanical particle which can exchange momentum with other particles.

2. Photon is always absorbed or destroyed completely or remains intact.

Example 76. *Find the kinetic energy of an electron liberated from a metal surface by light of wavelength 6.2 × 10^{-8} cm. Threshold energy for the metal is 2.62 × 10^{-9} erg s.; h = 6.63 × 10^{-27} erg s.*

Solution. $\lambda = 6.2 \times 10^{-8}$cm; velocity of light, $c = 3.0 \times 10^{10}$ cms⁻, Frequency, υ = ?, K.E. = ?.

$$\text{We know that : } \upsilon = \frac{c}{\lambda} = \frac{3.0\times10^{10}\,\text{cms}^{-}}{6.2\times10^{-8}\,\text{cm}}$$

$$= 4.84 \times 10^{17}\ \text{s}^{-}$$

$$\therefore \quad \text{K.E.} = h\upsilon - h\upsilon_0$$

$$= [(6.63 \times 10^{-27}\text{erg. s}) \times 4.84 \times 10^{17}\ \text{s}^{-}] - 2.62 \times 10^{-9}\ \text{erg}$$

$$= 3.21 \times 10^{-9}\ \text{erg} - 2.62 \times 10^{-9}\ \text{erg}$$

$$= 0.59 \times 10^{-9}\ \text{erg}$$

$$= \mathbf{5.9 \times 10^{-10}\ erg} \qquad \textbf{Ans.}$$

Example 77. *When ultra-violet light of wavelength 3000 Å was focussed on a metallic surface, photoelectrons were emitted. If photo-electric threshold is 4000 Å, find the de Broglie wavelength of electrons emitted with maximum kinetic energy (K.E.).*

Solution. de Broglie wavelength,

$$\lambda = \frac{h}{mv} \text{ (see section 12.10)} \qquad ...(1)$$

Wavelength of striking photon,

$$\lambda = 3000\ \text{Å} = 3000 \times 10^{-10}\ \text{m}$$

Threshold wavelength,

$$\lambda° = 4000\ \text{Å} = 4000 \times 10^{-10}\ \text{m}$$

We know, K.E. *i.e.*,

$$\frac{1}{2}mv^2 = h\upsilon - h\upsilon_0 \textit{ i.e., } \frac{hc}{\lambda} - \frac{hc}{\lambda°}$$

$$= hc\left(\frac{1}{\lambda} - \frac{1}{\lambda°}\right) = hc\left[\frac{\lambda° - \lambda}{\lambda\lambda°}\right]$$

$$= \frac{6.625\times10^{-34}\text{Js}\times3\times10^{8}\text{ms}^{-}[4000\times10^{-10}\text{m} - 3000\times10^{-10}\text{m}]}{4000\times10^{-10}\text{m}\times3000\times10^{-10}\text{m}}$$

$[\because h = 6.625 \times 10^{-34}$ Js, $c = 3 \times 10^{8}$ m s⁻]

$$= \frac{6.625\times10^{-34}\text{Js}\times3\times10^{8}\text{ms}^{-}\times10^{-10}\text{m}[4000 - 3000]}{4000\times10^{-10}\text{m}\times3000\times10^{-10}\text{m}}$$

$$= \frac{6.625\times10^{-34}\text{Js}\times3\times10^{8}\text{ms}^{-}\times10^{-10}\text{m}\times1000}{12\times10^{6}\text{m}\times10^{-20}\text{m}^2}$$

$$\frac{1}{2}mv^2 = \mathbf{1.6562 \times 10^{-19}\ J}$$

$$mv^2 = 2 \times 1.6562 \times 10^{-19}\ \text{J}$$

$$\text{or} \quad m \times mv^2 = 2 \times 1.6562 \times 10^{-19}\,\text{J} \times \text{m}$$

$$\therefore \quad m^2v^2 = 2 \times 1.6562 \times 10^{-19}\ \text{Jm}$$

$$= 2 \times 1.6562 \times 10^{-19}\text{J} \times 9.109 \times 10^{-31}\ \text{kg}$$

$[\because$ Mass of electron, $m = 9.109 \times 10^{-31}$ kg]

$$= 3.017 \times 10^{-49} = 30.17 \times 10^{-50}\ \text{J kg}$$

$$\therefore \quad mv = (30.17 \times 10^{-50}\ \text{J kg})^{1/2}$$

$$= 5.49 \times 10^{-25}\ (\text{J kg})^{1/2}$$

$$\text{But,} \quad \text{J} = kg\ \text{m}^2\ \text{s}^{-2}$$

$$\text{Hence} \quad mv = 5.49 \times 10^{-25}\ (\text{kg m}^2\text{s}^{-2} \times \text{kg})^{1/2}$$

$$= 5.49 \times 10^{-25}\ \text{kg ms}^{-}$$

Substituting the value of *mv* in (1), we get :

$$\lambda = \frac{h}{mv} = \frac{6.625\times10^{-34}\text{kg m}^2\text{s}^{-}}{5.49\times10^{-25}\text{kg ms}^{-}}$$

$$= \mathbf{1.2 \times 10^{-9}\ m} \qquad \textbf{Ans.}$$

Example 78. *A given sample contains a mixture of fluorine and chlorine gases. Each atom of the sample requires 284 kJ energy for the removal of an electron. The addition of an electron to each atom of the mixture releases 68.89 kJ of energy. If ionisation energies of F and Cl are 27.91 × 10^{-22} kJ and 20.77 × 10^{-22} kJ respectively, calculate the percentage composition of the mixture. Electron affinity of F and Cl are 5.53 × 10^{-22} k J and 5.78 × 10^{-22} k J respectively.*

Solution.

Let number of atoms of fluorine = *a*

Number of atoms of chlorine = *b*

I.E. or energy absorbed by F-atom = 27.91 × 10^{-22} kJ

I.E. or energy absorbed by Cl-atom = 20.77 × 10^{-22} kJ

∴ Total energy absorbed by F and Cl atoms,

$$284\ \text{kJ} = (a \times 27.91 \times 10^{-22} + b \times 20.77 \times 10^{-22})\ \text{kJ} \quad ...(i)$$

Electron affinity or energy released by F-atom = 5.53 × 10^{-22} kJ

Electron affinity or energy released by Cl-atom = 5.78 × 10^{-22} kJ

∴ Total energy released by F and Cl-atoms,

$$68.89\ \text{kJ} = (a \times 5.53 \times 10^{-22} + b \times 5.78 \times 10^{-22})\ \text{kJ} \quad ...(ii)$$

Solving equations (*i*) and (*ii*), we have

$$(27.91a + 20.77\,b) \times 10^{-22} = 284$$

$$(5.53a + 5.78\,b) \times 10^{-22} = 68.89$$

$$\text{or} \quad 27.91a + 20.77b = 284 \times 10^{22} \quad ...(iii)$$

$$5.53a + 5.78b = 68.89 \times 10^{22} \quad ...(iv)$$

Multiplying equation (*iii*) by 5.53 and (*iv*) by 27.91 and subtracting, we get :

$$27.91\,a \times 5.53 + 20.77b \times 5.53 = 284 \times 10^{22} \times 5.53$$

$$5.53\,a \times 27.91 + 5.78\,b \times 27.91 = 68.89 \times 10^{22} \times 27.91$$

$$- \qquad - \qquad -$$

$$114.8581\,b - 161.3198\,b = 1570.52 \times 10^{22} - 1922.7199 \times 10^{22}$$

$$-46.4617\,b = 10^{22}\,(-352.1999)$$

$$\therefore \quad b = \frac{-352.1999\times10^{22}}{-46.4617}$$

$$= 7.58 \times 10^{22} \qquad ...(v)$$

Substituting the value of b from (v) in (iii), we get :

$$27.91 \times a + 20.77 \times 7.58 \times 10^{22}$$

$$= 284 \times 10^{22}$$

$$27.91\,a = 284 \times 10^{22} - 20.77 \times 7.58 \times 10^{22}$$

$$= 284 \times 10^{22} - 157.4366 \times 10^{22}$$

$$= 10^{22}\,(284 - 157.4366)$$

$$= 10^{22} \times 126.5634$$

$$\therefore \quad a = \frac{10^{22} \times 126.5634}{27.91}$$

$$= 4.53 \times 10^{22} \qquad ...(vi)$$

$$a + b = 4.53 \times 10^{22} + 7.58 \times 10^{22}$$

$$= 12.11 \times 10^{22}$$

$$\therefore \quad \text{\%age of } a \text{ i.e., F} = \frac{4.53 \times 10^{22}}{12.11 \times 10^{22}} \times 100 = \mathbf{37.4} \qquad \textbf{Ans.}$$

$$\text{\%age of } b \text{ i.e., Cl} = 100 - 37.4 = \mathbf{62.6} \qquad \textbf{Ans.}$$

EXAMPLE 79. *Two H-atoms were travelling with certain velocity in opposite direction. After head on collision, these end up with zero kinetic energy. Each of these atoms then emitted a photon of wavelength 121.6 nm. Which transition led to this wavelength ? Also, calcualte the velocity of these atoms before collision.* $R_H = 1.09678 \times 10^7 m^{-}$; $M_H = 1.672 \times 10^{-27}$ *kg.*

SOLUTION. Since the wavelength of emitted radiation is 121.6 nm, it will fall in U.V. region of spectrum. So, $n_1 = 1$.

For H-atom, $\bar{\upsilon}$ or $\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ (see section, 12.14)

$$\therefore \quad \frac{1}{121.6 \times 10^{-9}\,\text{m}} = 1.09678 \times 10^7\,\text{m}^{-}\left[\frac{1}{1^2} - \frac{1}{n_2^2}\right]$$

$$= 1.09678 \times 10^7\,\text{m}^{-}\left(\frac{n_2^2 - 1}{n_2^2}\right)$$

$$\therefore \quad n_2^2 = 121.6 \times 10^{-9}\,\text{m} \times 1.09678 \times 10^7\text{m}^{-}\,(n_2^2 - 1)$$

$$n_2^2 = 121.6 \times 10^{-9} \times 1.09678 \times 10^7\,n_2^2 - 121.6 \times 10^{-9} \times 1.09678 \times 10^7$$

$$n_2^2 = 1.33\,n_2^2 - 1.33$$

$$\text{or} \quad n_2^2 - 1.33\,n_2^2 = -1.33$$

$$\therefore \quad n_2^2\,(1 - 1.33) = -1.33 - 0.33\,n_2^2 = -1.33$$

$$\text{or} \quad n_2^2 = \frac{1.33}{0.33} = 4$$

$$\therefore \quad \boldsymbol{n_2} = (4)^{1/2} = \mathbf{2}$$

The energy given out is because of collision. The whole of energy released is in the form of radiant energy.

Determination of velocity, *v*. We know, K.E., $\frac{1}{2}mv^2 = \frac{hc}{\lambda}$

$$\therefore \quad v^2 = \frac{2hc}{m\lambda}$$

$$\text{or} \quad v = \left(\frac{2hc}{m\lambda}\right)^{1/2}$$

Substituting the values, we get :

$$v = \left[\frac{2 \times 6.625 \times 10^{-34}\,\text{kg m}^2 s^{-} \times 3 \times 10^8\,\text{ms}^{-}}{1.67 \times 10^{-27}\,\text{kg} \times 121.6 \times 10^{-9}\,\text{m}}\right]^{1/2}$$

$$= (1{,}957{,}433{,}817)^{1/2}$$

$$= \mathbf{4.42 \times 10^4\ ms^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 80. *Calculate the wavelength and energy of photons of frequency 3.5 MHz. Also, calculate the energy per mole of photons of the same wavelength.*

SOLUTION. Given : frequency, $\upsilon = 3.5$ MHz $= 3.5 \times 10^6$ Hz $= 3.5 \times 10^6$ s^{-}. But,

$$(i) \quad \lambda = \frac{c}{\upsilon} = \frac{3 \times 10^8\,\text{ms}^{-}}{3.5 \times 10^6\,\text{s}^{-}} = 85.7\,\text{m}$$

$$(ii) \quad \text{Energy, } E = h\upsilon = \frac{hc}{\lambda}$$

$$= \frac{6.625 \times 10^{-34}\,\text{Js} \times 3 \times 10^8\,\text{ms}^{-}}{85.7\,\text{m}}$$

$$= 2.3 \times 10^{-27}\,\text{J}$$

(iii) Energy per mole of photon

$$= 6.023 \times 10^{23} \times E$$

$$= 6.023 \times 10^{23} \times 2.3 \times 10^{-27}\,\text{J}$$

$$= \mathbf{1.385 \times 10^{-3}\ J} \qquad \textbf{Ans.}$$

EXAMPLE 81. *A light radiation of wavelength (λ) shines on a metal surface with intensity (I) and the metal emits n electrons per second, of average energy (E). What will be the effect on n and E if (a) λ is doubled and (b) if I is doubled ?*

SOLUTION. We know, $E = \frac{hc}{\lambda}$ *i.e.,* $E \propto \frac{1}{\lambda}\cdot$ If the wavelength of incident light is doubled, the energy of each photon becomes one half and energy of each emitted electron decreases. (b) If the intensity of light is doubled, the number (n) of electrons emitted will be doubled but the average energy (E) will remain the same.

EXAMPLE 82. *It is found that* 7.52×10^{-19} *J energy is needed to just overcome the force of attraction between the electron and Ag-metal surface. Calculate the minimum kinetic energy of the electrons ejected from the above metal which is being irradiated with U.V. light of* 3.6×10^{-8} *m.*

SOLUTION. K.E. $= h\upsilon - h\upsilon_0$, where υ_0 = Threshold frequency ($= 7.52 \times 10^{-19}$ J). Thus :

$$\text{K.E.} = \frac{hc}{\lambda} - h\upsilon_0$$

$$= \left(\frac{6.626 \times 10^{-34}\,\text{Js} \times 3.0 \times 10^8\,\text{ms}^{-}}{3.6 \times 10^{-8}\,\text{m}}\right) - (7.52 \times 10^{-19}\,\text{J})$$

$$\text{or} \quad \text{K.E.} = 5.52 \times 10^{-18}\,\text{J} - 7.52 \times 10^{-19}\,\text{J}$$

$$= 55.2 \times 10^{-19}\,\text{J} - 7.52 \times 10^{-19}\,\text{J}$$

$$\mathbf{K.E. = 47.68 \times 10^{-19}\ J} \qquad \textbf{Ans.}$$

Example 83. *An electron gets excited from the surface of a certain metal with one photon of u.v. light. When two photons of red light having total energy equal to that of one photon of U.V. light, shines on the same metal surface, no photoelectrons were produced. How Einstein's theory of photoelectric effect explains it ?*

Solution. Since the energy of red photons is below the threshold frequency and one electron can interact with one photon, no electron will be produced by red photons.

Example 84. *The threshold frequency (υ_0) of a silver metal is 1.13×10^{17} s^-. Calculate the maximum kinetic energy of the photoelectrons emitted by shining U.V. light of* 16 A° *wavelength on the above metal surface.*

Solution. $\upsilon_0 = 1.13 \times 10^{17} s^-$;

υ = ?. We know, $\upsilon = \dfrac{c}{\lambda}\cdot$ Hence :

$$\upsilon = \frac{3 \times 10^8 \text{ ms}^-}{16 \times 10^{-10} \text{ m}} = 1.875 \times 10^{17} \text{ s}^-$$

$$\therefore \quad \text{K.E.} = h(\upsilon - \upsilon_0)$$

$$= 6.626 \times 10^{-34} \text{Js} \, (1.875 \times 10^{17} - 1.13 \times 10^{17}) \text{ s}^-$$

$$\textbf{K.E.} = 6.626 \times 10^{-34} \text{ Js} \times 0.745 \times 10^{17} \text{ s}^-$$

$$= \mathbf{4.9 \times 10^{-17} \ J} \qquad \textbf{Ans.}$$

Example 85. *What will be the maximum wavelength of light that can be used to eject an electron from a certain metal surface if the energy needed to remove an electron from the said metal is 7.52×10^{-19} J ? ($h = 6.626 \times 10^{-34}$ Js).*

Solution. We know,

$$E = h\upsilon = \frac{hc}{\lambda}\cdot$$

Hence, $\lambda = \dfrac{hc}{E}\cdot$ Substituting the values, we get:

$$\lambda = \frac{6.626 \times 10^{-34} \text{Js} \times 3.0 \times 10^8 \text{ms}^-}{7.52 \times 10^{-19} \text{J}}$$

$$= \mathbf{2.64 \times 10^{-7} \ m} \qquad \textbf{Ans.}$$

Example 86. *When a light radiation of wavelength 2600 Å falls on a metal surface, photoelectric effect takes place. (i) Calculate the energy of quantum at this wavelength in eV and J. (ii) Calculate the wavelength that would be required to produce photoelectrons from the same metal having thrice the kinetic energy of those produced at 2000 Å. ($h = 6.626 \times 10^{-34}$ Js).*

Solution. (*i*) λ = 2600 Å = 2600×10^{-8} m;

$c = 3.0 \times 10^8$ ms$^-$. We know :

$$E = h\upsilon = \frac{hc}{\lambda}$$

$$E = \frac{6.626 \times 10^{-34} \text{Js} \times 3.0 \times 10^8 \text{ms}^-}{2600 \times 10^{-10} \text{m}}$$

or $\quad E = \mathbf{7.64 \times 10^{-19} \ J}$ **Ans.**

(*ii*)

$$\text{K.E.}_{2000} = h\upsilon - h\upsilon_0$$

$$= \frac{hc}{\lambda_{2000}} - \frac{hc}{\lambda_0} = hc\left(\frac{1}{\lambda_{2000}} - \frac{1}{\lambda_0}\right) \quad ...(1)$$

Also,

$$\text{K.E.}_{\text{new}} = h\upsilon - h\upsilon_0$$

$$= \frac{hc}{\lambda_{new}} - \frac{hc}{\lambda_0} = hc\left(\frac{1}{\lambda_{new}} - \frac{1}{\lambda_0}\right) \quad ...(2)$$

Dividing (2) by (1), we get :

$$\frac{\text{K.E.}_{\text{new}}}{\text{K.E.}_{2000}} = \frac{\dfrac{1}{\lambda_{\text{new}}} - \dfrac{1}{2600}}{\dfrac{1}{2000} - \dfrac{1}{2600}};$$

$$\frac{3}{1} = \frac{\dfrac{1}{\lambda_{\text{new}}} - 3.85 \times 10^{-4} \text{ Å}}{1.15 \times 10^{-4} \text{ Å}}$$

$$3 \times 1.15 \times 10^{-40}\text{Å} + 3.85 \times 10^{-4} \text{ Å}$$

$$= \frac{1}{\lambda_{\text{new}}}; \ 7.3 \times 10^{-4}\text{Å} = \frac{1}{\lambda_{\text{new}}}$$

$$\therefore \quad \lambda_{\text{new}} = \frac{1}{7.3 \times 10^{-4}} \text{Å} = 1370 \text{Å}$$

Example 87. *Light of frequency 3.2×10^{16} s^- was made to shine on a metal surface. As a result, the kinetic energy of ejected electrons was found to be twice as those of photoelectrons which were ejected when the light radiations of frequency $2.0 \times 10^{16} s^-$ was made to shine on the same metal. Find the value of υ_0 of this metal.*

Solution. Given

$$\text{K.E}_2 = 2 \text{ KE}_1; \text{K.E.} = h(\upsilon - \upsilon_0);$$

$$\upsilon - \upsilon_0 = \frac{\text{K.E.}}{h}$$

$$\therefore \text{ For K.E}_2, \upsilon_2 - \upsilon_0 = \frac{\text{K.E}_2}{h} \quad ...(1)$$

$$\text{For K.E}_1, \quad \upsilon_1 - \upsilon_0 = \frac{\text{K.E}_1}{h} \quad ...(2)$$

Dividing equations (1) and (2), we get :

$$\frac{\upsilon_2 - \upsilon_0}{\upsilon_1 - \upsilon_0} = \frac{\dfrac{\text{KE}_2}{h}}{\dfrac{\text{KE}_1}{h}} = \frac{2\text{KE}_1}{\text{KE}_1} = 2$$

$$\therefore \quad \upsilon_2 - \upsilon_0 = 2(\upsilon_1 - \upsilon_0);$$

$$\upsilon_2 - \upsilon_0 = 2\upsilon_1 - 2\upsilon_0; \upsilon_0 = 2\upsilon_1 - \upsilon_2.$$

$$\therefore \quad \upsilon_0 = 2(2.0 \times 10^{16} \text{s}^-) - (3.2 \times 10^{16} \text{ s}^-)$$

$$= 0.8 \times 10^{16} \text{ s}^- = \mathbf{8.0 \times 10^{15} s^-} \quad \textbf{Ans.}$$

12.9 CALCULATING IONISATION ENERGY

Type. (*i*) Ionisation energy of an atom or ion say, I having one electron = $Z_I^2 \times E_H$

where Z = at. no. of atom or ion, I ; E_H = First ionisation energy of H (= 13.6 eV where 1 eV = 1.602×10^{-19} J).

(*ii*) 1 watt = 1 Js$^-$

Example 88. *The ionisation energy of hydrogen atom is 13.6 eV. Calculate the ionisation energy of He^+ (i.e., second I.E. of He) and Li^{2+}. (At. no., He = 2, Li = 3).* **(Roorkee, 1986)**

Solution. (*i*) Atomic number (Z) of He = 2; E_H = 13.6 eV. But :

Ionisation energy of monoelectronic,

$$He^+ = Z_{He}^2 \times E_H = (2)^2 \times 13.6 \text{ eV} = \mathbf{54.4\ eV}\ \textbf{Ans.}$$

(*ii*) Atomic number (Z) of Li = 3; $E_H = 13.6$ eV. But :
Ionisation energy of monoelectronic,

$$Li^{2+} = Z_{Li}^2 \times E_H = (3)^2 \times 13.6 \text{ eV}$$

$$= \mathbf{122.4\ eV} \qquad \textbf{Ans.}$$

Example 89. *The ionisation energy of He^+ is 19.6×10^{-18} J atom⁻. Calculate the energy of first stationary state of Li^{2+} (at. no. (Z); He = 2, Li = 3).* **(Roorkee, 1989)**

Solution. Energy of He^+

$$= -\text{I.P. of } He^+ = -19.6 \times 10^{-18} \text{J atom}^{-}$$

(*i*) $$E_{He^+} = E_H \times Z_{He}^2 = E_H \times (2)^2 = 4E_H$$

(*ii*) $$E_{Li^{2+}} = E_H \times Z_{Li}^2 = E_H \times (3)^2 = 9E_H$$

Dividing (*i*) and (*ii*), we get :

$$\frac{E_{Li^{2+}}}{E_{He^+}} = \frac{9E_H}{4E_H} = \frac{9}{4}$$

$$E_{Li^{2+}} = \frac{9}{4} \times E_{He^+}$$

$$= \frac{9}{4} \times -19.6 \times 10^{-18} \text{ J atom}^{-}$$

or $$E_{Li^{2+}} = -4.41 \times 10^{-17} \text{ J atom}^{-} \qquad \textbf{Ans.}$$

Example 90. *The ionisation energy of H-atom is 1.312×10^6 J mol⁻. Calculate the energy required to excite an electron in a H-atom from ground state to the first excited state. (Avogadro's number = 6.022×10^{23} mol⁻).*

Solution. Ionisation energy of H-atom

$$= \frac{1.312 \times 10^6}{10^3} = 1312 \text{ kJ}$$

Energy (E_1) of electron in ground state

$$= \left(\frac{-1312}{1^2}\right) \text{kJ}$$

Energy (E_2) of electron in the first excited state

$$= \frac{-1312 \text{ kJ}}{2^2} = -328 \text{ kJ}$$

Thus, $\Delta E = E_2 - E_1 = -328 - (-1312) = 984 \text{ kJ mol}^{-}$

$$= \left(\frac{984}{6.02 \times 10^{23}}\right) \text{kJ (atom)}^{-}$$

or $$\Delta E = 1.635 \times 10^{-18} \text{ J (atom)}^{-}.$$

Example 91. *Calculate the wavelength of the radiation which excites the electron of hydrogen atom from first shell to the fourth shell. Ionisation energy of hydrogen atom is 1.312×10^3 kJ mol⁻. (Planck's constant = 6.63×10^{-34} kg m²s⁻, velocity of light = 3×10^8 ms⁻. Avogadro's number = 6×10^{23} mol⁻.*

(DSB, 1996)

Solution. Wavelength of radiation, λ = ?

Ionisation energy (I.E.) $= 1.312 \times 10^3 \text{ kJ mol}^{-1}$
$= 1312 \text{ kJ}, c = 3 \times 10^8 \text{ ms}^{-}$

I.E. (E_4) of H-atom in 4th orbit $= -1312 \text{ kJ mol}^{-}/4^2$
$= -82 \text{ kJ mol}^{-}$

I.E. (E_1) of H-atom in first orbit
$= -1312 \text{ kJ mol}^{-}/1^2$
$= -1312 \text{ kJ mol}^{-}$

Hence, $$\Delta E = E_4 - E_1 = -82 - (-1312)$$
$$= 1230 \text{ kJ mol}^{-}$$

The energy released per atom

$$E = \frac{1230 \times 10^3 \text{ J(atom)}^{-}}{6.02 \times 10^{23}}$$

But, $$\Delta E = h\upsilon = \frac{hc}{\lambda}$$

$\therefore$ $$\lambda = \frac{hc}{\Delta E}$$

$$= \frac{(6.63 \times 10^{-34} Js \times 3 \times 10^8 ms^{-} \times 6.02 \times 10^{23})}{1230 \times 10^3 J}$$

$$= \mathbf{7.9 \times 10^{-8}\ m} \qquad \textbf{Ans.}$$

12.10 de BROGLIE EQUATION

Light as well as all material objects like electrons, protons, neutrons, atoms, molecules etc., have dual character *i.e.,* wave as well as particle character. According to de Broglie :

'The wavelength (λ) associated with a particle of mass (m) moving with velocity (v) is given by the relation : $\lambda = \frac{h}{mv}$ *where h is Planck's constant.*

This relation is called **de Broglie equation** and λ is called the **de Broglie wavelength. *mv* is called the momentum of the particle. Thus :**

$$\boldsymbol{\lambda = \frac{h}{\text{momentum}}}$$

h = Planck's constant
$= 6.626 \times 10^{-34}$ Js $= 6.626 \times 10^{-34}$ kg m²s⁻
$= 6.626 \times 10^{-27}$ erg. s
$= 6.626 \times 10^{-27}$ g cm² s⁻
$= 9.52 \times 10^{-14}$ k.cal. s. mol⁻
J = kg m²s⁻²

Kinetic energy. It is the energy due to the motion of a particle. Mathematically :

K.E. = $\frac{1}{2}mv^2$ where m is the mass of the particle and v is the velocity of a particle.

Type. $\lambda = \frac{h}{mv}$

Example 92. (*a*) *A beam of He atoms moves with a velocity of 2×10^3 ms⁻. Find the wavelength of particles constituting the beam. h = (6.625×10^{-34} Js). Atomic mass of He = 4 a.m.u.*

(PSEB, 1999)

(*b*) Write the mathematical expression for the relationship of wavelength (λ) of a moving particle and its momentum (*p*). **(CBSE, 2007)**

Solution. (*a*) Mass (*m*) of He atom

$$= \frac{\text{(gram atomic mass of He)}}{\text{Avogadro's number}}$$

$$= \frac{4}{6.02 \times 10^{23}}$$

$$v = 2 \times 10^{3}\ \text{ms}^{-}$$

Wavelength of particles,

$$\lambda = ?$$

$$h = 6.625 \times 10^{-34}\ \text{kg m}^{2}\text{s}^{-}$$

Thus, $$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}\ \text{kg m}^{2}\text{s}}{\left(\frac{4}{6.02 \times 10^{23}}\right) \times 2 \times 10^{3}\ \text{ms}^{-}}$$

$$= \mathbf{4.98 \times 10^{-14}\ m} \qquad \textbf{Ans.}$$

(*b*) The relationship between wavelength (λ) and momentum (p) of a moving particle can be represented mathematically by de Broglie equation, $\lambda = \frac{h}{p}$

where h is Planck's constant = 6.625×10^{-34} Js.

EXAMPLE 93. *Calculate the wavelength associated with an electron (mass = 9.1×10^{-31} kg) moving with a velocity of 10^{3} ms^{-} ($h = 6.6 \times 10^{-34}$ kg m^{2}s^{-}).* **(PSEB, 2000, CBSE, 1985, DSB, 1992)**

SOLUTION. mass, $m = 9.1 \times 10^{-31}$kg

velocity, $v = 10^{3}\ \text{ms}^{-}$

wavelength, λ = ?

We know, $$\lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34}\ \text{kg m}^{2}\text{s}^{-}}{(9.1 \times 10^{-31}\ \text{kg} \times 10^{3}\ \text{ms}^{-})}$$

$$= \mathbf{7.25 \times 10^{-7}\ m} \qquad \textbf{Ans.}$$

EXAMPLE 94. *Find the de Broglie wavelength of an electron (mass = 9.11×10^{-31} kg) moving at 2% speed of light ($h = 6.625 \times 10^{-34}$ kg m^{2}s^{-}).*

SOLUTION. λ = ? ; $m = 9.11 \times 10^{-31}$ kg

$$v = \frac{(2 \times 3.0 \times 10^{8}\ \text{ms}^{-})}{100};$$

$$h = 6.625 \times 10^{-34}\ \text{kg m}^{2}\text{s}^{-}$$

We know, $$\lambda = \frac{h}{mv} \qquad ...(i)$$

Substituting the value of h, m and v in (*i*), we get

$$\lambda = 6.625 \times 10^{-34}\ \text{kg m}^{2}\ \text{s}^{-}$$

$$\div \left[\frac{(9.11 \times 10^{-31}\ \text{kg} \times (2 \times 3.0 \times 10^{8}\ \text{ms}^{-})}{100}\right]$$

$$= \mathbf{12.1 \times 10^{-10}m} \qquad \textbf{Ans.}$$

EXAMPLE 95. *Calculate the de Broglie wavelength of α-particles moving with a speed of 10^{5} cm s^{-}, (mass of α-particles = 6.6×10^{-27} kg).* **(PSEB, 2000)**

SOLUTION. λ = ?; $v = 10^{5}\ \text{cms}^{-}$

mass of α-particles, $m = 6.6 \times 10^{-27}$ kg;

$h = 6.63 \times 10^{-34}$ kg m^{2}s^{-}

We know, $$\lambda = \frac{h}{mv}$$

Substituting the values, we get :

$$\lambda = \frac{6.63 \times 10^{-34}\ \text{kg m}^{2}\text{s}^{-}}{(6.6 \times 10^{-27}\ \text{kg} \times 10^{3}\ \text{ms}^{-})}$$

$$= \mathbf{10^{-10}\ m\ or\ 10^{-8}\ cm\ or\ 1\text{Å}.\ Ans.}$$

EXAMPLE 96. *Calculate the ratio between the wave length of an electron and a proton, if the proton is moving at half the velocity of the electron (mass of proton = 1.67×10^{-27} kg; mass of electron = 9.11×10^{-28} g).*

SOLUTION. (*i*) For an electron, mass of electron,

$$m_e = 9.11 \times 10^{-28}\text{g} = 9.11 \times 10^{-31}\text{kg}$$

Wavelength = λ_e; velocity of electron = v_e.

(*ii*) For a proton, mass of proton,

$$m_p = 1.67 \times 10^{-27}\ \text{kg}$$

wavelength = λ_p; velocity of proton,

$$v_p = \frac{v_e}{2}$$

For an electron, $$\lambda_e = \frac{h}{m_e}v_e = \frac{h}{(9.11 \times 10^{-31} kg \times v_e)} \qquad ...(i)$$

For a proton, $\lambda p = h/m_p v_p$

$= h/(1.67 \times 10^{-27}\ \text{kg} \times v_e/2)$ ...(*ii*)

Dividing (*i*) and (*ii*), we get :

$$\frac{\lambda_e}{\lambda_p} = \mathbf{9.16 \times 10^{2}} \qquad \textbf{Ans.}$$

EXAMPLE 97. *A tennis ball of mass 6.0×10^{-2} kg is moving with a speed of 62 ms^{-}. Calculate the wavelength associated with this moving tennis ball. Will the movement of this ball exhibit a wave character ? Explain.* **(CBSE, sample paper, 1997)**

SOLUTION. Mass, $m = 6.0 \times 10^{-2}$kg; velocity, $v = 62\ \text{ms}^{-}$

$$\lambda = ?;\ \text{But}\ \lambda = \frac{h}{mv};$$

$$\therefore \qquad \lambda = \frac{(6.6 \times 10^{-34}\ \text{kg m}^{2}\text{s}^{-1})}{(6.0 \times 10^{-2}\ \text{kg} \times 62\ \text{ms}^{-})}$$

or $$\lambda = \mathbf{1.8 \times 10^{-34}} \qquad \textbf{Ans.}$$

The ball will not exhibit wave character because wavelength is extremely small.

EXAMPLE 98. *Calculate the wavelength of 1000 kg of rocket moving with a velocity of 300 km per hour. ($h = 6.625 \times 10^{-34}$ Js).* **(DSB, 1984, 1992; HSB, 1994)**

SOLUTION. λ = ?; m = 1000 kg

$$v = 300\ \text{km hr}^{-}$$

$$= \frac{(300 \times 1000)}{(60 \times 60)} = \left(\frac{250}{3}\right)\text{ms}^{-};$$

$h = 6.625 \times 10^{-34}$ kg m^{2}s^{-} But, $\lambda = \frac{h}{mv}$

Hence, $$\lambda = \frac{(6.625 \times 10^{-34}\ \text{kg m}^{2}\text{s}^{-})}{\left[1000\ \text{kg} \times \left(\frac{250}{3}\text{ms}^{-}\right)\right]}$$

$$= \mathbf{7.95 \times 10^{-39}m} \qquad \textbf{Ans.}$$

Type. (*i*) $\lambda = \frac{h}{mv}$, (*ii*) 1 MeV = 1.602×10^{-6} erg.

EXAMPLE 99. *Calculate the wavelength of α-particles which are associated with an energy 10 MeV (1 MeV = 1.602 × 10^{-6} erg, h = 6.626 × 10^{-27} ergs).* **(PSEB, 1999 S)**

SOLUTION. Wavelength,

$$\lambda = ?;\ \text{Energy}, E = 10\ \text{MeV}$$
$$= 10 \times 1.602 \times 10^{-6}\ \text{erg};$$
$$h = 6.626 \times 10^{-27}\ \text{ergs}.$$

We know, $E = h\upsilon = \frac{hc}{\lambda}$ or $\lambda = \frac{hc}{E}$

Substituting the values, we get :

$$\lambda = \frac{6.626 \times 10^{-27}\ \text{erg.s} \times 3 \times 10^{10}\ \text{cm s}^{-}}{10 \times 1.602 \times 10^{-6}\ \text{erg}}$$
$$= \mathbf{1.24 \times 10^{-31}\ cm} \qquad \textbf{Ans.}$$

EXAMPLE 100. *Electrons with wavelength 12 pm are used for electron diffraction. What is the velocity of these electrons ?*

SOLUTION. $\lambda = 12\ \text{pm} = 12 \times 10^{-12}\text{m}$

∴ mass (m) of electron $= 9.11 \times 10^{-31}$ kg;

$h = 6.63 \times 10^{-34}\ \text{kg m}^2\text{s}^{-}$

velocity of electron, v = ?

But, $\lambda = \frac{h}{mv}$; So, $v = \frac{h}{m\lambda}$

Substituting the values, we get :

$$v = \frac{6.63 \times 10^{-34}\text{kg m}^2\text{s}^{-}}{(9.11 \times 10^{-31}\ \text{kg} \times 12 \times 10^{-12}\text{m})}$$
$$= \mathbf{6.1 \times 10^7\ ms^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 101. *What must be the velocity of a beam of electrons if they are to display a de Broglie wavelength of 100Å (mass of electron = 9.1 × 10^{-31} kg, h = 6.6 × 10^{-34} Js).* **(CBSE, 1987)**

SOLUTION. Velocity of electrons,

v = ? wavelength, λ = 100

Å = 100 × 10^{-10} m; mass of electron,

$m = 9.1 \times 10^{-31}$ kg

We know, $\lambda = \frac{h}{mv}$ ∴ $v = \frac{h}{m\lambda}$

$$= \frac{(6.6 \times 10^{-34}\text{kg m}^2\text{s}^{-})}{(9.1 \times 10^{-31}\text{kg} \times 100 \times 10^{-10}\text{m})}$$

or $v = \mathbf{7.25 \times 10^4\ ms^{-}}$ **Ans.**

EXAMPLE 102. *Calculate the kinetic energy of the moving electron which has a wavelength of 4.8 pm (mass of electron = 9.11 × 10^{-31} kg, h = 6.63 × 10^{-34} Js).* **(PSEB, 1999, 2003)**

SOLUTION. $\lambda = 4.8\ \text{pm} = 4.8 \times 10^{-12}\text{m};$

$h = 6.63 \times 10^{-34}\ \text{kg m}^2\text{s}^{-},$

$m = 9.11 \times 10^{-31}$ kg

But, $\lambda = \frac{h}{mv}$ ∴ $v = \frac{h}{m\lambda}$

$$= \frac{(6.63 \times 10^{-34}\text{kg m}^2\text{s}^{-})}{(9.11 \times 10^{-31}\text{kg} \times 4.8 \times 10^{-12}\text{m})}$$
$$= 0.152 \times 10^9\ \text{ms}^{-}$$

But, K.E. $= \frac{1}{2}mv^2$

Substituting the values of m and v, we get :

$$\text{K.E.} = \frac{1}{2}\ (9.11 \times 10^{-31}\ \text{kg} \times (0.152 \times 10^9)^2\ \text{m}^2\text{s}^{-2}$$
$$= 10.52 \times 10^{-15}\ \text{kg m}^2\text{s}^{-2} = \mathbf{10.52 \times 10^{-15}\ J} \quad \textbf{Ans.}$$

EXAMPLE 103. *The wavelength of a moving body of mass 0.1 mg is 3.31 × 10^{-29} m. Calculate its kinetic energy (h = 6.625 × 10^{-34} kg m^2s^{-}).* **(CBSE, 1989)**

SOLUTION. Hint. Mass of body,

$m = 0.1\ \text{mg} = 0.1 \times 10^{-6}$ kg,

Substituting the values of h, m and λ in equation

$v = \frac{h}{m\lambda}$, we have $v = 200\ \text{ms}^{-}$

∴ $$\text{K.E.} = \frac{mv^2}{2}$$
$$= \frac{(0.1 \times 10^{-6}\text{kg}) \times (200)^2\,\text{m}^2\text{s}^{-2}}{2}$$
$$= \mathbf{2 \times 10^{-3}\ J} \qquad \textbf{Ans.}$$

EXAMPLE 104. *Calculate the wavelength of a particle of mass, m = 6.62 × 10^{-27} kg moving with kinetic energy 7.425 × 10^{-13} J (h = 6.6 × 10^{-34} kg m^2sec^{-}).* **(HPSB, 1993, 2012)**

SOLUTION.

We know, $\text{K.E.} = \frac{mv^2}{2}$ or $v = \left(\frac{2\text{K.E.}}{m}\right)^{1/2}$

$$= \left[\frac{(2 \times 7.425 \times 10^{-13}\text{kg m}^2\text{s}^{-2}}{6.62 \times 10^{-27}\text{kg}}\right]^{1/2}$$
$$= 1.497 \times 10^7\ \text{ms}^{-}$$

But, $\lambda = \frac{h}{mv}$

$$= \frac{6.6 \times 10^{-34}\ \text{kg m}^2\text{s}^{-}}{6.62 \times 10^{-27}\ \text{kg} \times 1.497 \times 10^7\ \text{ms}^{-}}$$
$$= \mathbf{6.66 \times 10^{-15}\ m} \qquad \textbf{Ans.}$$

Type. (*i*) $\lambda = \lambda = \frac{h}{mv}$,

(*ii*) Mass of one molecule of a substance

$$= \frac{\text{g. mol. wt. of substance}}{\text{Avogadro's no. } (= 6.023 \times 10^{23})}$$

EXAMPLE 105. *Calculate the kinetic energy of a CO_2 molecule which has a wavelength of 18 pm.* **(PSEB, 2003)**

SOLUTION. Mass of $CO_2(g)$ molecule

$$= \frac{(44 \times 10^{-3})}{(6.023 \times 10^{23})}\ \text{kg} = 7.3 \times 10^{-26}\ \text{kg}.$$

[∵ mol. wt. of CO_2 =[12 + (2 × 16)] = 44 g = 44 × 10^{-3} kg]

$$\text{K.E.} = \left(\frac{1}{2}\right)mv^2;\ \lambda = \frac{h}{mv} \quad \text{or} \quad v = \frac{h}{m\lambda}$$
$$= (6.6 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-}/(7.3 \times 10^{-26}\ \text{kg} \times 18 \times 10^{-12}\text{m} = 502\ \text{ms}^{-}$$

But, K.E. $= \left(\frac{1}{2}\right)mv^2$

$$= \frac{1}{2} \times 7.3 \times 10^{-26}\,\text{kg} \times 502\,\text{ms}^{-} \times 502\,\text{ms}^{-}$$

$$= 9.2 \times 10^{-21}\,\text{kg m}^2\text{s}^{-2} = \mathbf{9.2 \times 10^{-21}J.} \qquad \textbf{Ans.}$$

EXAMPLE 106. *Calculate the wavelength of a molecule of carbon dioxide molecule moving at a velocity of 440 ms⁻.*

(PSEB, 2000)

SOLUTION. mass (m) of CO_2

$$= \frac{\text{g. mol. wt. of } CO_2}{\text{Avogadro's number}}$$

$$= \frac{44\,g}{6.02 \times 10^{23}} = \frac{44 \times 10^{-3}\,\text{kg}}{6.02 \times 10^{23}}$$

We know, $\lambda = \dfrac{h}{mv}$ ...(*i*)

Substituting the values of h, m and v in

(*i*), we get: $\lambda = \dfrac{(6.6 \times 10^{-34}\text{kg m}^2\text{s}^{-})}{\left[\left(\dfrac{44 \times 10^{-3}\,\text{kg}}{6.02 \times 10^{23}}\right) \times 440\,\text{ms}^{-}\right]}$

$$= \mathbf{2.05 \times 10^{-11}\,m} \qquad \textbf{Ans.}$$

EXAMPLE 107. *Calculate the momentum of a particle which has a de Broglie wavelength of 1Å (h = 6.6 × 10⁻³⁴ Js).*

(PSEB, 1989, HSB, 2000)

SOLUTION. $\lambda = 1\text{Å} = 1 \times 10^{-10}\text{m}$. Momentum, mv = ?

We know, $\lambda = \dfrac{h}{mv}$ Thus, $mv = \dfrac{h}{\lambda}$ ...(*i*)

Substituting the values of h and λ in (*i*), we get,

$$mv = \frac{(6.6 \times 10^{-34}\text{kg m}^2\text{s}^{-})}{10^{-10}\text{m}}$$

$$= \mathbf{6.6 \times 10^{-24}\,kg\,ms^{-}} \qquad \textbf{Ans.}$$

Type. For an electron,

K.E = Charge on e *i.e.*, electron

$(= 1.602 \times 10^{-19}\,\text{C}) \times$ potential difference (V).

EXAMPLE 108. *An electron beam can undergo diffraction by crystals. Through what potential a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å?*

(IIT, 1997)

SOLUTION. For an electron, K.E. $= \frac{1}{2}mv^2$

= charge on electron (e) × potential difference (V) and

$$\lambda = \frac{h}{mv};\ (h = 6.62 \times 10^{-34}\,\text{Js};$$

$$m = 9.108 \times 10^{-31}\,\text{kg};$$

$$\lambda = 1.54 \times 10^{-10} m)\,;\ e = 1.602 \times 10^{-19}\,\text{C}$$

$$v = \frac{h}{m\lambda} \text{ and } v^2 = \frac{h^2}{m^2\lambda^2}$$

But, $\text{K.E.} = \dfrac{1}{2} m \times \dfrac{h^2}{m^2\lambda^2} = eV$

$\therefore$ $V = \dfrac{1 \times h^2}{2 \times m \times \lambda^2 . e}$

$$= \frac{1 \times (6.62 \times 10^{-34})^2}{2 \times 9.108 \times 10^{-31} \times (1.54 \times 10^{-10})^2 \times 1.602 \times 10^{-19}} = \mathbf{63.3\,V.}$$

EXAMPLE 109. *Calculate de Broglie wavelength for a hydrogen atom moving with a velocity of 1900 ms⁻. (atomic mass of H = 1.00797 amu).*

SOLUTION. 1 mol. of H-atoms = 6.023×10^{23} atoms. Atomic mass of hydrogen = 1.00797 amu. Velocity, $v = 1900\,\text{ms}^{-}$.

$$\text{Mass of H-atom} = \frac{1.00797}{6.023 \times 10^{23}} = 1.674 \times 10^{-24}\,\text{g}$$

$$= 1.674 \times 10^{-27}\,\text{kg}$$

But de Broglie wave length,

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}\text{kg m}^2\text{s}^{-}}{1.674 \times 10^{-27}\,\text{kg} \times 1900\,\text{ms}^{-}}$$

$\therefore$ $\lambda = 2.08 \times 10^{-10}\text{m}$ **or** 20.8 nm

$(\because 1\,\text{nm} = 10^{-9}\text{m})$

12.11 ELECTRON DIFFRACTION – de BROGLIE EQUATION

EXAMPLE 110. *Calculate the accelerating potential that must be imparted to a proton beam to give it an effective wavelength of 4 × 10⁻² Å.*

SOLUTION. (*i*) Mass (m) of a proton

$$= \frac{1.008}{6.02 \times 10^{23} \times 10^{3}}\,\text{kg}$$

$$h = 6.62 \times 10^{-34}\,\text{Js}$$

We know : $\lambda = \dfrac{h}{mv};\ v = \dfrac{h}{m\lambda}$

$$= \frac{6.626 \times 10^{-34}\text{Js} \times 6.02 \times 10^{+26}}{1.008\,\text{kg} \times 4 \times 10^{-2} \times 10^{-10}\,\text{m}}$$

$$= 9.9 \times 10^4\,\text{Js kg}^{-}\text{m}^{-}$$

$$= 9.9 \times 10^4\,\text{kg m}^2\text{s}^{-2}.\text{s.kg}^{-}\text{m}^{-}$$

$$= 9.9 \times 10^4\,\text{ms}^{-} \qquad [\text{J} = \text{kg m}^2\text{s}^{-2}]$$

(*ii*) K.E. $= \dfrac{1}{2}mv^2$

$$= \frac{1}{2} \times \frac{1.008}{6.02 \times 10^{26}}\text{kg} \times (9.9 \times 10^4\text{ms}^{-})^2$$

$$= 8.2 \times 10^{-18}\,\text{kg m}^2\text{s}^{-2}$$

$$= 8.2 \times 10^{-18}\,\text{J} \qquad (\because \text{J} = \text{kg m}^2\text{s}^{-2})$$

or $\text{K.E.} = 8.2 \times 10^{-18}\text{J} \times \dfrac{1\text{eV}}{1.6 \times 10^{-19}\text{J}}$

$$= \mathbf{51.3\,eV} \qquad \textbf{Ans.}$$

Since the charge on a proton is of the same magnitude as that of an electron, the potential needed is equal in magnitude to the number of electron volts (= 51.3 eV).

EXAMPLE 111. *Calculate the wavelength of an electron beam when electron diffraction experiment was done using a beam of electrons accelerated by a potential difference of 8.0 kV.*

Solution. Mass of electron = 9.1×10^{-31} kg. In order to find the velocity of the electron, its K.E. $\left(= \frac{1}{2}mv^2\right)$ is equated to its loss of electrical potential energy (= 8.0 keV).

$$\therefore \quad \frac{1}{2}mv^2 = 8 \text{ ke V} = 8 \times 10^3 \text{ eV} \times \frac{1.602 \times 10^{-19}\text{J}}{1\text{eV}}$$

$$(\because\ 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

$$= 1.28 \times 10^{-15} \text{ J} = 1.28 \times 10^{-15} \text{ kg m}^2\text{s}^{-2}$$

$$(\because\ \text{J} = \text{kg m}^2\text{s}^{-2})$$

$$v = \left(\frac{2 \times 1.28 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2}}{\begin{array}{c}\text{Mass of electron } (= m) \\ = 9.1 \times 10^{-31} \text{ kg}\end{array}} \right)^{1/2}$$

$$\therefore \quad v = \left(\frac{2 \times 1.28 \times 10^{-15} \text{kg m}^2\text{s}^{-2}}{9.1 \times 10^{-31}\text{kg}} \right)^{\frac{1}{2}}$$

$$= (28.1 \times 10^{14} \text{ m}^2\text{s}^{-2})^{1/2} = 5.3 \times 10^7 \text{ ms}^{-}$$

But $\lambda = \frac{h}{mv}$ (de Broglie equation). Hence :

$$\lambda = \frac{6.626 \times 10^{-34}\text{kg m}^2\text{s}^{-}}{9.1 \times 10^{-31}\text{kg} \times 5.3 \times 10^7 \text{ms}^{-}}$$

$$= 1.37 \times 10^{-11} \text{ m}$$

$$= 1.37 \times 10^{-11} \text{ m} \times \frac{10^{10}\text{Å}}{1\text{m}}$$

or λ = **0.137 Å** **Ans.**

Example 112. *Derive the expression which shows that de Broglie's hypothesis applied to an electron moving in a circular orbit leads to Bohr's postulate of quantised angular momentum.*

Solution. In a circular orbit, an electron must have its path length equal to whole number multiple of wave lengths for reinforcement to take place. Hence $n\lambda$ must be equal to the path length, $2\pi r$.

$$\therefore \quad 2\pi r = n\lambda\ ;\ \lambda = \frac{2\pi r}{n} \qquad \text{...(1)}$$

$$\text{But} \quad \lambda = \frac{h}{mv} \qquad \text{...(2)}$$

∴ From (1) and (2), we get :

$$\frac{2\pi r}{n} = \frac{h}{mv}; \ mvr = \frac{nh}{2\pi}$$

where, mvr = angular momentum.

Example 113. *An electron in a hydrogen atom, in its ground state absorbs 1.5 times as much energy as the minimum energy needed for it to escape from that atom. Calculate the wavelength of emitted electron.*

Solution. Energy needed to ionise H-atom = 13.6 eV

∴ Energy absorbed = 13.6 eV × 1.5 = 20.4 eV

Energy converted to kinetic energy

$$= 20.4 - 13.6 = 6.8 \text{ eV}$$

$$= 6.8 \times 1.6 \times 10^{-19} \text{ C} \times 1\text{V}$$

$$\simeq 1.09 \times 10^{-18} \text{ CV}$$

$$= 1.09 \times 10^{-18} \text{ J} \qquad [\because \text{CV} = \text{J}]$$

$$\text{But} \quad \text{K.E.} = \frac{1}{2}mv^2$$

$$\therefore \quad v = \left(\frac{2\text{K.E.}}{\text{m}}\right)^{\frac{1}{2}}$$

$$= \left(\frac{2 \times 1.09 \times 10^{-18}\text{J}(= \text{kg m}^2\text{s}^{-2})}{9.1 \times 10^{-31}\text{kg}}\right)^{\frac{1}{2}}$$

$$\text{or} \quad v = (2.4 \times 10^{12} \text{ m}^2\text{s}^{-2})^{1/2}$$

$$= 1.55 \times 10^6 \text{ ms}^{-}$$

$$\text{But,} \quad \lambda = \frac{h}{mv}$$

$$\text{Hence} \quad \lambda = \frac{6.626 \times 10^{-34}\text{kg m}^2\text{s}^{-}}{9.1 \times 10^{-31}\text{kg} \times 1.55 \times 10^6 \text{ms}^{-}}$$

$$= \mathbf{4.7 \times 10^{-10} m} \quad \textbf{Ans.}$$

12.12 HEISENBERG'S UNCERTAINTY PRINCIPLE

According to this principle : *"It is impossible to measure simultaneously, both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty."*

Mathematically :

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \text{ or } (\Delta x) \times (m\Delta V) \geq \frac{h}{4\pi}$$

where

Δx = uncertainty in position of a microscopic particle

Δp = uncertainty in momentum of a microscopic particle

m = mass of the particle; v = velocity of the particle

Example 114. *The uncertainty in the location of an electron using a microscope is found to be 0.1Å. What is the uncertainty involved in the measurement of its velocity ?*

Solution. Mass (m) of an electron

$$= 9.11 \times 10^{-31} \text{ kg};\ \Delta x = 0.1\text{Å}$$

$$= 0.1 \times 10^{-10} \text{ m}$$

$$h = 6.626 \times 10^{-34}\text{Js.}$$

We know, $\Delta x \times m\Delta v = \frac{h}{4\pi}$

$$\therefore \quad \Delta v = \frac{h}{4\pi m \Delta x}$$

$$= \frac{6.62 \times 10^{-34}\text{Js}}{(4 \times 3.14 \times 0.1 \times 10^{-10}\text{m} \times 9.11 \times 10^{-31}\text{kg})}$$

$$= \mathbf{5.79 \times 10^7\ ms^{-}} (\because 1\text{J} = \text{kg m}^2\text{s}^{-2}) \quad \textbf{Ans.}$$

Example 115. *An electron has a velocity of 5×10^6ms^{-} accurate up to 0.002% (or with 0.002% error) Calculate the uncertainty in its position ($m = 9.1 \times 10^{-31}$ kg, $h = 6.62 \times 10^{-34}$ Js).*

Solution. Uncertainty in velocity (Δv) of electron $= 5 \times 10^6 \times \left(\frac{0.002}{100}\right)$ ms^{-} ; uncertainty in position (Δx) of electron = ?.

$$\text{We know : } \Delta x \,.\, m\Delta v = \frac{h}{4\pi} \text{ or } \Delta x = \frac{h}{4\pi m \Delta v} \qquad \text{...}(i)$$

Substituting the values of h, m and Δv in (i), we get

$$\Delta x = \frac{6.62\times10^{-34}\text{kg m}^2\text{s}^{-}}{4\times3.142\times9.1\times10^{-31}\text{kg}\times(5\times10^{6})\times(0.002/100)\text{ms}^{-}}$$

$= 5.79 \times 10^{-7}\text{m}$ **Ans.**

EXAMPLE 116. *Calculate the uncertainty in the position of an electron if the uncertainty in its velocity is 5.7 × 10^5 ms^-. (h = 6.6 × 10^{-34} kg m^2s^-).* **(PSEB, 2002; CBSE, 1999; DSB, 1992)**

SOLUTION. Uncertainty in position of an electron, Δx = ?; uncertainty in velocity, $\Delta v = 5.7 \times 10^5$ ms^-; mass (m) of electron $= 9.1 \times 10^{-31}$ kg; $h = 6.6 \times 10^{-34}$ kg m^2s^-. We know,

$$\Delta x.\ m\Delta v = \frac{h}{4\pi} \quad \textbf{or} \quad \Delta x = \frac{h}{4\pi m\Delta v} \qquad ...(i)$$

Substituting the values of h, π, m and Δv in (i), we get:

$$\Delta x = \frac{6.6\times10^{-34}\text{kg m}^2\text{s}^{-}}{4\times3.142\times9.1\times10^{-31}\text{kg}\times5.7\times10^{5}\text{ms}^{-}}$$

$= \pm 10^{-10}$ **m** **Ans.**

EXAMPLE 117. *Calculate the uncertainty in position of an electron if uncertainty in its velocity is (i) 0.001% (ii) zero.*

SOLUTION. (i) Uncertainty in position of an electron, Δx = ?; uncertainty in its velocity, $\Delta v = 0.001\% = \frac{0.001}{100}$ $= 1 \times 10^{-5}$ ms^-; mass of electron, $m = 9.1 \times 10^{-31}$ kg; $h = 6.6 \times 10^{-34}$ kg m^2s^-. We know :

$$\Delta x\ .\ m\Delta v = \frac{h}{4\pi} \quad \textbf{or} \quad \Delta x = \frac{h}{4\pi m\Delta v} \qquad ...(i)$$

Substituting the values of h, π, m and Δv in (i), we get:

$$\Delta x = \frac{6.6\times10^{-34}\text{kg m}^2\text{s}^{-}}{4\times3.142\times9.1\times10^{-31}\ \text{kg}\times10^{-5}\text{ms}^{-}}$$

$= 5.78\text{m}$ **Ans.**

(ii) When Δv = zero, $\Delta x = \frac{h}{4\pi m\times0}$ = infinity.

EXAMPLE 118. *A proton is accelerated to a velocity of 3 × 10^7 ms^-. If the velocity can be measured with a precision of ± 0.5%, calculate the uncertainty in the position of proton. (h = 6.6 × 10^{-34} Js, mass of proton = 1.66 × 10^{-27} kg).* **(DSB, 2001)**

SOLUTION. Uncertainty in velocity,

$\Delta v = 3 \times 10^7\ \text{ms}^- \times \frac{0.5}{100} = 1.5 \times 10^5\ \text{ms}^-$, uncertainty in position of proton,

Δx = ?; mass (m) of proton $= 1.66 \times 10^{-27}$kg.

We know :

$$\Delta x\ .\ m\Delta v = \frac{h}{4\pi} \quad \textbf{or} \quad \Delta x = \frac{h}{4\pi m\Delta v} \qquad ...(i)$$

Substituting the values of h, π, m and Δv in (i), we get:

$$\Delta x = \frac{6.6\times10^{-34}\text{kg m}^2\text{s}^{-}}{4\times3.142\times1.66\times10^{-27}\text{kg}\times1.5\times10^{5}\text{ms}^{-}}$$

$= 2.11 \times 10^{-13}\text{m}$ **Ans.**

EXAMPLE 119. *Calculate the uncertainty in the velocity of a wagon of mass, 3000 kg whose position while in motion is known to an accuracy of ± 10 pm (h = 6.63 × 10^{-34} kg m^2s^-).* **(CBSE, 1999, HP Board, 2008)**

SOLUTION. Uncertainty in position,

$\Delta x = 10\ \text{pm} = 10 \times 10^{-12}$ m

$= 10^{-11}$m; uncertainty in velocity,

Δv = ?, mass (m) = 3000 kg;

$h = 6.63 \times 10^{-34}$ kg m^2s^-.

$$\text{We know :}\Delta x\ .\ m\Delta v = \frac{h}{4\pi} \quad \textbf{or} \quad \Delta v = \frac{h}{4\pi m\Delta x} \qquad ...(i)$$

Substituting the values of h, m and Δx in (i), we get :

$$\Delta v = \frac{6.63\times10^{-34}\text{kg m}^2\text{s}^{-}}{4\times3.142\times3000\,\text{kg}\times10^{-11}\text{m}}$$

$= 1.76 \times 10^{-27}\ \text{ms}^-$ **Ans.**

EXAMPLE 120. *The uncertainty in the position and velocity of a particle are 10^{-10} m and 5.27 × 10^{-24} ms^- respectively. Calculate the mass of the particle (h = 6.625 × 10^{-34} Js).* **(CBSE, 1989, PSEB, 1991, 2005)**

SOLUTION. Uncertainty in position, $\Delta x = 10^{-10}$m; uncertainty in velocity, $\Delta v = 5.27 \times 10^{-24}$ ms^-. Mass of particle, m = ?. We know :

$$\Delta x\ .\ m\ .\ \Delta v = \frac{h}{4\pi}$$

$$\textbf{or} \qquad m = \frac{h}{4\pi\,\Delta x\Delta v} \qquad ...(i)$$

Substituting the values of h, Δx and Δv in (i), we get :

$$m = \frac{6.625\times10^{-34}\text{kg m}^2\text{s}^{-}}{(4\times3.142\times10^{-10}\text{m}\times5.27\times10^{-24}\text{ms}^{-}}$$

$= 0.1\ \text{kg} = 0.1 \times 1000 =$ **100 g** **Ans.**

EXAMPLE 121. *Calculate the uncertainty in the position of a dust particle with mass equal to 1 mg if the uncertainty in its velocity is 5.5 × 10^{-20}m/s, h = 6.623 × 10^{-34}Js.* **(PSEB, 2006, 2012)**

SOLUTION. Mass (m) of dust particle $= 1\text{mg} \times \frac{10^{-3}\text{g}}{1\text{mg}}\times\frac{10^{-3}\text{kg}}{1\text{g}} = 10^{-6}$ kg; $\Delta v = 5.5 \times 10^{-20}\text{ms}^-$; $h = 6.623 \times 10^{-34}$ Js $= 6.623 \times 10^{-34}$kg m^2s^-; $\pi = \frac{22}{7}$, Δx = ?. We know that :

$$\Delta x\ .\ m\Delta v = \frac{h}{4\pi}; \quad \textbf{or} \quad \Delta x = \frac{h}{4\pi m\Delta v}$$

$$= \frac{6.623\times10^{-34}\text{kg m}^2\text{s}^{-}\times7}{4\times22\times10^{-6}\text{kg}\times5.5\times10^{-20}\text{ms}^{-}}$$

$\therefore \qquad \Delta x = 9.58 \times 10^{-10}\text{m}$ **Ans.**

EXAMPLE 122. *Calculate the uncertainty in velocity of a cricket ball (mass = 150 g) if the uncertainty in its position is of the order of 1Å (h = 6.6 × 10^{-34} kg m^2s^-).* **(PSEB, 2002, 04)**

SOLUTION. Δv = ?, $m = 150\ \text{g} = 150\ \text{g} \times \frac{1\text{kg}}{1000\,\text{g}} = 0.15$ kg; $\Delta x = 1\text{Å} = 10^{-10}$m, $h = 6.6 \times 10^{-34}$kg m^2s^-. We know that :

$$\Delta x \,.\, m\Delta v = \frac{h}{4\pi}$$

$$\therefore \qquad \Delta v = \frac{h}{4\pi\,\Delta x\, m}$$

$$= \frac{6.6\times10^{-34}\,\text{kg m}^2\text{s}^{-}}{4\times3.142\times10^{-10}\,\text{m}\times0.15\,\text{kg}}$$

or $\qquad \Delta v = \mathbf{3.5\times10^{-24}\ ms^{-}}$ **Ans.**

Example 123. *On the basis of Heisenberg's uncertainty principle, show that an electron cannot exist in the nucleus. (Radius of nucleus = 10^{-15}m, h = 6.6 × 10^{-34} Js; m = 9.1 × 10^{-31}kg).*

(PSEB, 1999)

Solution. Radius of nucleus = 10^{-15}m. It means uncertainty in the position of electron = 10^{-15}m **or** $\Delta x = 10^{-15}$m; h = 6.6 × 10^{-34} Js = 6.6 × 10^{-34} kg m^{2}s^{-2}.s = 6.6 × 10^{-34} kg m^{2}s^{-}; mass, m = 9.1 × 10^{-31} kg. But :

$$\Delta x \,.\, m\Delta v = \frac{h}{4\pi} \text{ (Heisenberg's uncertainty principle)}$$

$$\therefore \quad \Delta v = \frac{h}{4\pi\, m\Delta x} = \frac{6.6\times10^{-34}\,\text{kg m}^2\text{s}^{-}}{4\times3.142\times9.1\times10^{-31}\,\text{kg}\times10^{-15}\,\text{m}}$$

$$= 5.76\times10^{10}\ \text{ms}^{-}$$

This velocity (= 5.77 × 10^{10} ms^{-}) is 200 times the velocity of light. Such a velocity for an electron can never be possible because it cannot have velocity greater than the velocity of light. Hence electron cannot exist in the nucleus of an atom.

12.13 BOHR'S MODEL OF ATOM

(*a*) **To calculate E_n is C.G.S. units (erg atom^{-}) :**

$$E_n = \frac{-2\pi^2 me^4Z^2}{n^2h^2} \text{ where } \pi = 3.14,$$

$$m = 9.108\times10^{-28}\text{g}, e = 4.8\times10^{-10}\,\text{esu},$$

$$h = 6.624\times10^{-27}\,\text{ergs and considering}$$

$$\text{erg} = \text{g cm}^2\text{s}^{-2} \text{ and}$$

$$\text{esu} = \text{g}^{1/2}\,\text{cm}^{3/2}\text{s}^{-}, \text{ we have :}$$

$$\mathbf{E_n = -2.173\times10^{-11}\,\frac{Z^2}{n^2}\ erg\ atom^{-}.}$$

(*b*) To calculate E_n in electron volt *i.e.*, eV (atom^{-}) use the relation, $E_n = -\,2.173\times10^{-11}\,\frac{Z^2}{n^2}$ erg atom^{-} × 6.2419 × 10^{11} eV (atom^{-}) [$\because$ 1 erg = 6.2419 × 10^{11} eV). Thus

$$E_n = -13.6\times\frac{Z^2}{n^2}\ \text{eV (atom}^{-})$$

(*c*) To calculate E_n in erg mol^{-} and k cal mol^{-}, use the relations

(*i*) $E_n = -2.173\times10^{-11}\times\frac{Z^2}{n^2}$ erg atom^{-} × 6.023 × 10^{23} atoms mol^{-}

or $\qquad \mathbf{E_n = -13.1\times10^{12} erg\ mol^{-}.}$

(*ii*) $\qquad E_n = -13.1\times10^{12}\,\frac{Z^2}{n^2}$ erg mol^{-}

$$\times\ \frac{\text{k cal}}{4.183\times10^{10}\text{erg}} = \mathbf{\frac{-313.2\,Z^2}{n^2}\ k\ cal\ mol^{-}}$$

Example 124. *Calculate the energy (in C.G.S. units) of an electron in the first orbit of H-atom.*

Solution. For H-atom :

(*i*) $\qquad E_n = -2.173\times10^{-11}\,\frac{Z^2}{n^2}$ erg atom^{-}

$$= -2.173\times10^{-11}\times\frac{(1)^2}{(1)^2}$$

$$\left[\begin{array}{l}\therefore \text{ For H-atom, } Z = 1, \\ \quad \text{no. of orbit, } n = 1\end{array}\right]$$

$$= \mathbf{-2.173\times10^{-11}\ erg\ atom^{-}}$$ **Ans.**

(*ii*) $\qquad E_n = -13.6\times\frac{Z^2}{n^2}$ eV atom^{-}

$$= -13.6\times\frac{(1)^2}{(1)^2}$$

$$= \mathbf{-13.6\ eV\ atom^{-}}$$ **Ans.**

(*iii*) $E_n = -2.173\times10^{-11}\,\frac{Z^2}{n^2}$ erg atom^{-} × 6.023 × 10^{23} atoms mol^{-}

$$= -13.1\times10^{12}\times\frac{(1)^2}{(1)^2}\ \text{erg mol}^{-}$$

$$= \mathbf{-13.1\times10^{12}\ erg\ mol^{-}}$$ **Ans.**

(*iv*) $E_n = -13.1\times10^{12}\,\frac{Z^2}{n^2}$ erg mol^{-} × $\frac{\text{k cal}}{4.183\times10^{10}\text{erg}}$

$$= -313.2\,\frac{Z^2}{n^2}\ \text{k cal mol}^{-}$$

or $\quad E = -313.2\times\frac{(1)^2}{(1)^2} = \mathbf{-313.2\ k\ cal\ mol^{-}}$ **Ans.**

Example 125. *Calculate the energy of an electron in electron volt in the second orbit of Li^{2+} ion.*

Solution. For Li^{2+},

$$Z = 3; n = 2. \text{ We know :}$$

$$E_n = -13.6\times\frac{Z^2}{n^2}\ \text{eV atom}^{-}.$$

Thus : $\qquad E_2 = -13.6\times\frac{(3)^2}{(2)^2}$ eV atom^{-}

$$= \mathbf{-\,30.6\ eV\ atom^{-}}$$ **Ans.**

Type. (*a*) To calculate E_n in **S.I. units** (J atom^{-} and Nm atom^{-}), $\qquad E_n = \frac{-me^4Z^2}{8\varepsilon_0^2n^2h^2}$ where

$$m = 9.108\times10^{-31}\,\text{kg}, e = 1.602\times10^{-19}\text{C},$$

$$\varepsilon_0 = 8.85\times10^{-12}\ \text{C}^2\text{J}^{-}\text{m}^{-};$$

$$h = 6.626\times10^{-34}\text{Js and considering}$$

J = kg m^{2}s^{-2}, we have :

$$E_n = -2.173 \times 10^{-18} \frac{Z^2}{n^2} \text{ kg m}^2\text{s}^{-2}$$

or $$E_n = -2.173 \times 10^{-18} \frac{Z^2}{n^2} \text{ J atom}^-$$

[∵ J = kg m^{2}s^{-2}]

$$= -2.173 \times 10^{-18} \frac{Z^2}{n^2} \text{ Nm atom}^-$$

[∵ J = Nm]

(*b*) To calculate E_n in **S.I. Units** (J mol$^-$ and kJ mol$^-$), use :

$$E_n = -2.173 \times 10^{-18} \times \frac{Z^2}{n^2} \text{ J atom}^-$$

$$= -2.173 \times 10^{-18} \frac{Z^2}{n^2} \text{ J atom}^- \times 6.023 \times 10^{23} \text{ atoms mol}^-$$

or $$E_n = -13.1 \times 10^5 \frac{Z^2}{n^2} \text{ J mol}^-$$

or $$\boldsymbol{E_n} = -13.1 \times 10^5 \times \frac{Z^2}{n^2} \times \frac{1}{10^3} \text{ kJ mol}^-$$

$$\mathbf{= -13.1 \times 10^2 \frac{Z^2}{n^2} \text{ kJ mol}^-}$$

Example 126. *Calculate the energy (in S.I. units) of an electron in the first orbit of He$^+$.*

Solution. (*i*) For He$^+$, Z = 2; n = 1 (given). We know :

$$E_n = -2.173 \times 10^{-18} \frac{Z^2}{n^2} \text{ kg m}^2\text{s}^{-2}$$

$$= -2.173 \times 10^{-18} \times \frac{(2)^2}{(1)^2} \text{ kg m}^2\text{s}^{-2}$$

$= -8.692 \times 10^{-18}$ kg m^{2}s^{-2} **Ans.**

$= -8.692 \times 10^{-18}$ J atom$^-$ **Ans.**

[∵ J = kg m^{2}s^{-2}]

$= -8.692 \times 10^{-18}$ Nm atom$^-$ **Ans.**

[∵ J = Nm]

(*ii*) $$E_n = -2.173 \times 10^{-18} \frac{Z^2}{n^2} \text{ J atom}^- \times 6.023 \times 10^{23} \text{ atoms mol}^-$$

$$= -13.1 \times 10^5 \frac{Z^2}{n^2} \text{ J mol}^-$$

$$= -13.1 \times 10^5 \times \frac{(2)^2}{(1)^2} \text{ J mol}^-$$

$= -52.4 \times 10^5$ J mol$^-$ **Ans.**

Example 127. *Calculate the order of (E_1)H, (E_2)H and(E_3) H where (E_1)H, (E_2)H and (E_3)H represent the energies associated with an electron moving in first, second and third orbit of hydrogen atom.*

Solution. For (E_1)H, (E_2)H and (E_3)H, n = 1, n = 2 and n = 3 respectively. For H-atom, Z = 1.

But $$E_n = -2.173 \times 10^{-11} \frac{Z^2}{n^2} \text{ erg atom}^-.$$

∴ $$(E_1)\text{H} = 2.173 \times 10^{-11} \times \frac{(1)^2}{(1)^2}$$

$$= -2.173 \times 10^{-11} \text{ ergatom}^-$$

$$(E_2)\text{H} = -2.173 \times 10^{-11} \times \frac{(1)^2}{(2)^2}$$

$$= -0.5448 \times 10^{-11} \text{ erg atom}^-$$

$$(E_3)\text{H} = -2.173 \times 10^{-11} \times \frac{(1)^2}{(3)^2}$$

$$= -0.2421 \times 10^{-1} \text{ erg atom}^-$$

∴ Order of energies of (E_1)H, (E_2)H and (E_3)H is (E_1)H < (E_2)H < (E_3)H.

Type. To calculate the radius of nth orbit (r_n) in C.G.S. units, use the relation :

$$r_n = \frac{n^2h^2}{4\pi^2me^2Z}$$ where n = no. of orbit, $h = 6.626 \times 10^{-27}$ ergs., π = 3.14, $m = 9.18 \times 10^{-28}$g, $e = 4.8 \times 10^{-10}$ e.s.u., considering erg = g cm^{2}s$^-$ and e.s.u. = g$^{1/2}$cm$^{3/2}$s$^-$, we have :

$$\mathbf{r_n = 0.529 \times 10^{-8} \times \frac{n^2}{Z} \text{ cm}}$$

$$\mathbf{= 0.529 \times \frac{n^2}{Z} \text{ Å} \quad (\because 1\text{Å} = 10^{-8} \text{ cm})}$$

Example 128. *Calculate Bohr's radius, a_0 or (r_1) H in C.G.S. units.*

Solution. For H-atom, Z = 1. Also, for first orbit, n = 1. We know that :

$$r_n = 0.529 \times \frac{n^2}{Z} \text{ Å}$$

Hence : $$r_1 = 0.529 \times \frac{(1)^2}{(1)} \text{ Å} = \mathbf{0.529 \text{ Å}}$$ **Ans.**

Type. To calculate the radius of nth orbit (r_n) in S.I. units, use the relation :

$$r_n = \frac{n^2h^2\varepsilon_0}{\pi me^2Z}$$ where n = no. of the orbit, h = Planck's constant = 6.626×10^{-34}Js, π = 3.14, $\varepsilon_0 = 8.85 \times 10^{-12}$ C^{2}J$^-$m$^-$, $m = 9.108 \times 10^{-31}$kg = mass of electron, $e = 1.602 \times 10^{-19}$C. Also, considering J = kg m^{2}s$^-$, we have :

$$\mathbf{r_n = 0.529 \times 10^{-10}\text{m} \frac{n^2}{Z}}$$

Example 129. *Calculate Bohr's radius, a_0 or (r_1)H in S.I. units.*

Solution. For H-atom, Z = 1; no. of orbit = n = 1. We know that :

$$r_n = 0.529 \times 10^{-10}\text{m} \frac{n^2}{Z}$$

Hence, $$n_1 = 0.529 \times 10^{-10}\text{m} \times \frac{(1)^2}{1}$$

$$\therefore \quad (r_1)\text{H} = \mathbf{0.529 \times 10^{-10}m} \qquad \textbf{Ans.}$$

EXAMPLE 130. *Calculate the radius of third orbit of H-atom in C.G.S. as well as S.I. units.*

SOLUTION. For H-atom, $Z = 1, n = 3$.

(*a*) *In C.G.S. units.* We know :

$$r_n = 0.529 \times \frac{n^2}{Z}\text{Å} ;$$

$$r_3 = 0.529 \times \frac{(3)^2}{(1)}\text{Å} = 4.761\text{Å}$$

(*b*) *In S.I. units.* we know : $r_n = 0.529 \times 10^{-10}\text{m}\frac{n^2}{Z}$

$$r_3 = 0.529 \times 10^{-10}\text{m}\ \frac{(3)^2}{(1)}$$

$$= \mathbf{4.761 \times 10^{-10}m} \quad \textbf{Ans.}$$

Type. To calculate velocity (v_n) of an electron (in **C.G.S. units**) revolving in *n*th orbit of H-atom and other one electron species like He^+, Li^{2+}, Be^{3+} etc., use the relation :

$$v_n = \frac{2\pi Ze^2}{nh} \qquad ...(1)$$

where $\pi = 3.14, e = 4.8 \times 10^{-10}$e.s.u., $h = 6.626 \times 10^{-27}$erg and considering erg = g cm^{2}s^{-2} and e.s.u. = g$^{1/2}$cm$^{3/2}$s$^-$ and substituting these values in equation (1), we get :

$v_n = 2.183 \times 10^8 \times \frac{Z}{n}cms^-$ where Z = atomic number of element and n = no. of the orbit.

EXAMPLE 131. *Calculate the velocity of an electron (in C.G.S. units) revolving in second orbit of Li^{2+}.*

SOLUTION. For Li, atomic number, $Z = 3$; $n = 2$ (given). We know :

$v_n = 2.183 \times 10^8 \times \frac{Z}{n}$ cms$^-$. Substituting the values, we get :

$$v_2 = 2.183 \times 10^8 \times \frac{3}{1}\ \text{cms}^-$$

$$= \mathbf{6.549 \times 10^8\ cm\ s^-} \qquad \textbf{Ans.}$$

Type. To calculate velocity (v_n) of an electron (in S.I. units) revolving in *n*th orbit of H-atom and other one electron species like He^+, Li^{2+}, Be^{3+} etc., use the relation :

$$v_n = \frac{Ze^2}{2\varepsilon_0 nh} \qquad ...(1)$$

Substituting the value of $e = 1.602 \times 10^{-10}$C, $\varepsilon_0 = 8.85 \times 10^{-12}$C^{2}J$^-m^-$ and $h = 6.626 \times 10^{-34}$Js in equation (1) and considering J = kg m^{2}s^{-2}, we have :

$$\mathbf{v_n = 2.183 \times 10^6 \times \frac{Z}{n}\ ms^-.}$$

EXAMPLE 132. *Calculate the velocity of an electron (in S.I. units) revolving in the third orbit of Be^{3+}.*

SOLUTION. For Be^{3+}, $Z = 4$; $n = 3$ (given). We know :

$$v_n = 2.183 \times 10^6 \times \frac{Z}{n}\ \text{ms}^-$$

Substituting the values, we get :

$$v_3 = 2.183 \times 10^6 \times \frac{4}{3}\ \text{ms}^-$$

$$= \mathbf{2.91 \times 10^6\ ms^-} \qquad \textbf{Ans.}$$

EXAMPLE 133. *Derive an expression to calculate velocity of an electron in nth Bohr orbit of a hydrogen like atoms and then calculate the velocity of an electron in the first orbit of H-atom. Also prove that light (in vacuum) travels about 137 times as fast as the electron in this orbit.*

SOLUTION. We know,

$$\text{K.E.} = \frac{1}{2}mv^2 \qquad ...(1)$$

Also, $$\text{K.E.} = \frac{\text{k}Ze^2}{2r} \qquad ...(2)$$

$$\frac{1}{2}mv^2 = \frac{\text{k}\ Ze^2}{2r}\ ;\ v = \left[\frac{\text{k}\,Ze^2}{mr}\right]^{1/2}$$

But, $$r = \frac{n^2h^2}{4\pi^2\,\text{k}\,me^2}$$

Hence : $$v = \left[\frac{\text{k}\,Ze^2 \times 4\pi^2\text{k}\,me^2}{m \times n^2h^2}\right]^{1/2}$$

$$= \frac{2\pi\,\text{k}e^2(Z)^{1/2}}{nh}$$

For H-atom, $n = 1$ (first orbit), $Z = 1$. So :

(*i*) $$v = \frac{2 \times 3.14 \times 9.0 \times 10^9\text{Jm} \times (1.6 \times 10^{-19}\text{C})^2 \times (1)^{1/2}}{\text{C}^2 \times 1 \times 6.626 \times 10^{-34}\text{Js}}$$

$= 2.18 \times 10^6$ ms$^-$

(*ii*) Velocity of light (*c*) in vacuum

$$= 3.0 \times 10^8\ \text{ms}^- \ \therefore\ \frac{c}{v} = \frac{3.0 \times 10^8\text{ms}^-}{2.18 \times 10^6\text{ms}^-} \simeq 137$$

Hence light travels about 137 times as fast as the electron in the orbit under consideration.

Type. To calculate number of revolutions made by an electron revolving in *n*th orbit of an atom, following relation is used.

In C.G.S. unit, no. of revolutions, $= \frac{v_n}{2\pi r_n}$ ...(1)

Substituting the value of

$$v_n = \left(2.183 \times 10^8 \times \frac{Z}{n}\right)\text{cm s}^- \ \text{and}$$

$$r_n = \left(0.529 \times 10^8 \times \frac{n^2}{Z}\right)\text{cm} \ \text{and}$$

$\pi = 3.14$ in equation (1), we get :

Number of revolutions $= 65.71 \times 10^{14} \times \frac{Z^2}{n^3}s^-$

EXAMPLE 134. *Calculate the number of revolutions made by an electron revolving in third orbit of He^+, in terms of C.G.S. units.*

SOLUTION. In He^+, $Z = 2$; $n = 3$ (given). We know :

No. of revolutions (in C.G.S. units)

$$= 65.71 \times 10^{14} \times \frac{Z^2}{n^3}\,s^{-}$$

Substituting the values, we get :

$$\text{No. of revolutions} = 65.71 \times 10^{14} \times \frac{(2)^2}{(3)^3}\,s^{-}$$

$$= 9.7 \times 10^{14} s^{-}$$

EXAMPLE 135. *Calculate the number of revolutions made by an electron revolving in the second orbit of Be^{3+}.*

SOLUTION. For Be^{3+}, $Z = 4$, $n = 2$. We know that :

No. of revolutions (in S.I. units)

$$= \left(65.71 \times 10^{14} \times \frac{Z^2}{n^3}\right) s^{-}$$

$$= 65.71 \times 10^{14} \times \frac{(4)^2}{(2)^3}\,s^{-}$$

$$= \mathbf{1.31 \times 10^{16} s^{-}} \qquad \textbf{Ans.}$$

Type. To calculate ionisation energy (I.E.) of H-atom and other one electron species (such as He^+, Li^{2+}, Be^{3+} etc.) having atomic number (Z), use the following relation.

In C.G.S. Units, I.E. = $E_\infty - E_1$ where

$$E_n = -\frac{2\pi^2 me^4 Z^2}{n^2 h^2}$$

$$\therefore \quad E_1 = -2.173 \times 10^{-11} Z^2 \text{ erg atom}^{-}$$

$$= -13.1\, Z^2 \text{ erg mol}^{-}$$

$$= \mathbf{-13.6\, Z^2 \text{ eV atom}^{-}}$$

$$E_\infty = \frac{-2\pi^2 me^4 Z^2}{(\infty)h^2} = 0 \text{ (zero).}$$

$$\therefore \quad \text{I.E.} = 0 - E_1 = -E_1$$

Note. I.E. of a given species is the amount of energy required to excite an electron from lowest energy level ($n = 1$) to an energy level having $n = \infty$ *i.e.*, infinity.

EXAMPLE 136. *Calculate the ionisation energy of Li^{2+} (in C.G.S. units) in first orbit.*

SOLUTION. For Li^{2+}, $Z = 3$, we know :

(*i*) $\quad$ I.E. = $E_\infty - E_1 = 0 - E_1 = -E_1$

But, $\quad E_1 = -2.18 \times 10^{-11} Z^2$ erg atom^{-};

$\quad E_3 = -2.173 \times 10^{-11} \times 3^2$ erg atom^{-}

or $\quad E_1 = -1.962 \times 10^{-10}$ erg atom^{-}.

$\therefore \quad$ I.E. = $-E_1 = -(-1.962 \times 10^{-10})$ erg atom^{-}

$\quad$ = **1.962×10^{-10} erg atom^{-}** $\quad$ **Ans.**

(*ii*) $\quad$ I.E. = $-E_1 = -(-13.1 \times 3^2)$ erg mol^{-}

$\quad$ = **117.9 erg mol^{-}** $\quad$ **Ans.**

(*iii*) $\quad$ I.E. = $-E_1 = -(-13.6\, Z^2)$ eV atom^{-}

$\quad$ = 13.6×3^2 eV atom^{-}

$\quad$ = **122.4 eV atom^{-}** $\quad$ **Ans.**

Type. To calculate ionisation energy (I.E.) of H-atom and other one electron species (such as He^+, Li^{2+}, Be^{3+} etc.) having atomic number (Z), use the following relation.

In S.I. units. I.E. = $E_\infty - E_1$ where,

$$E_n = \frac{-me^4 Z^2}{8\varepsilon_0^2 h^2 n^2}$$

$$\therefore \quad E_1 = -2.173 \times 10^{-18} Z^2 \text{ J atom}^{-}$$

$$= -13.1279 \times Z^2 \text{ kJ mol}^{-}$$

$$\simeq -13.1\, Z^2 \text{ kJ mol}^{-}$$

$$E_\infty = \frac{-me^4 Z^2}{8\varepsilon_0^2 h^2 n^2 (\infty)^2} = 0 \quad \textit{i.e.}, \text{ zero.}$$

$$\therefore \quad \textbf{I.E.} = 0 - E_1 = -E_1$$

I.E. of H-like one electron species

$$= \text{I.E. of H-atom} \times Z^2$$

EXAMPLE 137. *Calculate the ionisation energy of He^+ (in S.I. unit).*

SOLUTION. For He^+, $Z = 2$. We know that :

$\quad$ *I.E.* = $E_\infty - E_1 = 0 - E_1 = -E_1$

But $\quad E_1 = -2.173 \times 10^{-18} Z^2$ J atom^{-}

or $\quad E_1 = -2.173 \times 10^{-18} \times (2)^2$

$\quad = -8.692 \times 10^{-18}$ J atom^{-}

$\therefore \quad$ I.E. = $E_1 = -(-8.692 \times 10^{-18})$ J atom^{-}

$\quad$ = **8.692×10^{-18} J atom^{-}** $\quad$ **Ans.**

Also, $\quad E = -13.1279\, Z^2$ kJ mol^{-}

$\quad = -13.1279 \times (2)^2$ kJ mol^{-}

$\quad = -52.5116$ kJ mol^{-}.

$\therefore \quad$ I.E. = $-E_1 = -(-52.5116)$ kJ mol^{-}

$\quad$ = **52.5116 kJ mol^{-}** $\quad$ **Ans.**

Type. To calculate energy of an electron in nth Bohr orbit of hydrogen, use the relation, $E_1 = \dfrac{-ke^2}{2rn^2}$ where r = radius of first orbit, k = 9.0×10^9 J m/C^2, $e = 1.6 \times 10^{-19}$ C, n = number of the orbit.

EXAMPLE 138. *Calculate the energy of an electron in the first Bohr orbit of hydrogen.(r = 0.529 Å).*

SOLUTION. For orbit,

$$\text{let energy} = E_1. \text{ So : } E_1 = \frac{-ke^2}{2rn^2}$$

$$= -\frac{9.0 \times 10^9 \text{Jm}}{\text{C}^2} \times \frac{1.6 \times 10^{-19}\text{C} \times 1.6 \times 10^{-19}\text{C}}{2 \times 0.529 \times 10^{-10}\text{m} \times 1^2}$$

$$\therefore \quad E_1 = -2.18 \times 10^{-18}\text{J} \qquad \textbf{Ans.}$$

Second method. $E_n = -k^2\left(\dfrac{2\pi^2 me^4}{n^2h^2}\right)$.

For $\quad n = 1$ *i.e.*, first orbit,

$$E_1 = -\left(9.0 \times 10^9 \frac{\text{Jm}}{\text{C}^2}\right)^2$$

$$\left[\frac{2\times(3.14)^2\times 9.109\times 10^{-31}\text{kg}\times(1.6\times 10^{-19}\text{C})^4}{(1)^2(6.63\times 10^{-34}\text{Js})^2}\right]$$

$$= -\mathbf{2.17\times 10^{-18}J}$$ **Ans.**

12.14 SPECTRAL LINES

Whenever an electron jumps from higher orbit (n_2) to lower orbit (n_1), radiations of certain wavelengths or frequencies are emitted. As a result, spectral lines corresponding to those wavelengths or frequencies are formed. Similarly when an electron jumps from a lower orbit (n_1) to a higher orbit (n_2), radiations of certain wavelengths or frequencies are absorbed. As a result, spectral lines corresponding to those wavelengths or frequencies are observed. Following relations are used to find the frequency (υ) or wavelength of observed spectral lines.

(*i*) **Frequency** (υ) of spectral line = $\dfrac{E_{n_2}-E_{n_1}}{h}$

(*ii*) $\lambda = \dfrac{c}{\upsilon} = \dfrac{ch}{E_{n_2}-E_{n_1}}$ where h = Planck's constant = 6.626×10^{-34}Js = 3.99×10^{-13} k Js mol$^-$ = 9.52×10^{-14} k cal s mol$^-$. c = Velocity of light = 3.0×10^8 ms$^-$ = 3.0×10^{10} cm s$^-$

E_{n_2} and E_{n_1} are the energies of an electron in higher orbit and lower orbit respectively.

For shortest wavelength in H-spectrum, $n_1 = 1$, $n_2 = \infty$ and $1/\infty$ is zero.

(*iii*) **Wave number** $\bar{\upsilon}$ of spectral line of H-atom

$$= \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

where R = Rydberg constant

$= 109678$ cm$^-$

$= 10.9678\times 10^6$ m$^- \simeq 10.97\times 10^6$ m$^-$

$= 1.097\times 10^7$ m$^-$;

Z = atomic number of element

(*iv*) (*a*) **Frequency,** υ of spectral line of H-atom

$$= RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

where R = Rydberg constant

$= 3.289\times 10^{15}$ s$^-$;

Z = at. no. of element

(*b*) $$\upsilon = RZ^2c\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$ where

$R = 109678$ cm$^-$ and $c = 3.0\times 10^{10}$ cms$^-$

(*v*) Number of lines in the spectrum = $\dfrac{n(n-1)}{2}$

where n is the outermost shell.

Also, no. of spectral lines emitted when electron jumps from n_2 to n_1 = $\mathbf{(n_2-n_1)(n_2-n_1+1)/2}$

(*vi*) (*a*) Total energy (E) of revolving electron in Bohr's orbit = K.E. $\left(=\dfrac{1}{2}mv^2\right)$ + Potential energy $\left(\dfrac{-Ze^2}{r}\right)$

where Z = at. no; e = charge on electron; r = radius of orbit; m = mass of electron; v = velocity of electron.

(*b*) $mv^2 = \dfrac{Ze^2}{r}$

(*vii*) Lyman series, Balmer series, Paschen series, Brackett series and Pfund series fall in the U.V., visible, near I.R., I.R. and I.R. far regions respectively.

(*viii*) For one electron species like hydrogen, He$^+$, Li^{2+} etc., electronic energy in the nth Bohr's orbit.

$$E_n = -\frac{21.76\times 10^{-19}Z^2}{n^2}\text{J}$$

where Z = atomic number of element,

n = no. of the orbit.

$$E_n = -21.76\times 10^{-12}\times\frac{Z^2}{n^2}\text{ erg (atom)}^-$$

$$= -13.6\times\frac{Z^2}{n^2}\text{ eV (atom)}^-$$ where 1 erg $= 6.2419\times 10^{11}$ eV

$$= -313.6\times\frac{Z^2}{n^2}\text{ k cal mol}^-$$

$$= -109700\times\frac{Z^2}{n^2}\text{ cm}^-\text{ atom}^-$$

(*ix*)

Series	*For first line*	*For second line*	*For third line*	*For fourth line*
Lyman	$n_1 = 1, n_2 = 2$	$n_1 = 1, n_2 = 3$	$n_1 = 1, n_2 = 4$	$n_1 = 1, n_2 = 5$
Balmer	$n_1 = 2, n_2 = 3$	$n_1 = 2, n_2 = 4$	$n_1 = 2, n_2 = 5$	$n_1 = 2, n_2 = 6$
Paschen	$n_1 = 3, n_2 = 4$	$n_1 = 3, n_2 = 5$	$n_1 = 3, n_2 = 6$	$n_1 = 3, n_2 = 7$
Brackett	$n_1 = 4, n_2 = 5$	$n_1 = 4, n_2 = 6$	$n_1 = 4, n_2 = 7$	$n_1 = 4, n_2 = 8$
Pfund	$n_1 = 5, n_2 = 6$	$n_1 = 5, n_2 = 7$	$n_1 = 5, n_2 = 8$	$n_1 = 5, n_2 = 9$

(*x*) erg = g cm^{2}s^{-2}

(*xi*) esu = g$^{1/2}$cm$^{3/2}$s$^-$

(*xii*)

Wavelength of radiation absorbed (Å)	*Observed complementary colour*	*Wavelength of radiation absorbed (Å)*	*Observed complementary colour*
4000 – 4500	Yellow-green	5500 – 6000	Violet
4500 – 5000	Yellow, orange	6000 – 6500	Blue
5000 – 5500	Red, purple	6500 – 7000	Green-blue, Blue-green

(*xiii*) Maximum number of spectral lines obtained

$$= \frac{n(n-1)}{2}$$

where n = no. of the maximum orbit.

Type. To calculate the frequency (υ) and wave number ($\bar{\upsilon}$) of spectral line in C.G.S. and S.I. units, use the following relations :

(*i*) **In C.G.S. units,** $\upsilon = 3.283 \times 10^{15} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) s^-$ or Hz.
or $v = 1.09678 \times 10^5 Z^2 cm^- \times c\ (= 3 \times 10^{10}\ cm\ s^-) \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

(*ii*) **In S.I. units,** $\upsilon = 1.09678 \times 10^7\ m^- Z^2 \times C\ (= 3 \times 10^8\ ms^-) \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

(*iii*) **In C.G.S. units,** $\bar{\upsilon} = 1.09678 \times 10^5 \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^-$

(*iv*) **In S.I. units,** $\bar{\upsilon} = 1.09678 \times 10^7 \times Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) m^-$

where Z = at. no. of element.

> **Note.** (*i*) In above cases, n_1 and n_2 are the number of lower orbit and the higher orbit respectively.
> (*ii*) To calculate wavelength (λ) of spectral line, use the relation : $\bar{\upsilon} = \frac{1}{\lambda} = \frac{\upsilon}{c}$

EXAMPLE 139. *What will be the frequency of light emitted for an electron transition from third to the first orbit of the H-atom ? Also, name the region of the spectrum in which this light would appear.*

SOLUTION. $\bar{\upsilon} = \frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^-$ where

$n_1 = 1$, $n_2 = 3$ and $R = 109678\ cm^-$,
$Z = 1$ for H-atom.

Hence. $\frac{1}{\lambda} = 1^2 \times 109678 \left(\frac{1}{1^2} - \frac{1}{3^2}\right) cm^-$

$= 109678 \times \frac{8}{9}\ cm^- = 97491\ cm^-$

But frequency, $\upsilon = c \times \frac{1}{\lambda}$

$= 3.0 \times 10^{10}\ cms^- \times 97491\ cm^-$

or $\upsilon = 2.92 \times 10^{15}\ s^-$

This line falls in the U.V. spectrum of hydrogen. It is a part of Lyman series because it falls to the first orbit from the higher orbit.

EXAMPLE 140. *According to Bohr's theory, the electronic energy of hydrogen atom in the nth Bohr's orbit is given by :*

$$E_n = -\frac{21.76 \times 10^{-19}}{n^2} J$$

Calculate the longest wavelength of light that will be needed to remove an electron from the third orbit of He⁺ ion. **(IIT, 1990)**

SOLUTION. For one electron species like H, He^+, Li^{2+};

$$E_n = -\frac{21.76 \times 10^{-19} Z^2}{n^2} J$$

(*i*) For third orbit ($n = 3$) and for He^+ ($Z = 2$), we have

$$E_3 = -\frac{21.76 \times 10^{-19} \times (2)^2}{(3)^2} J$$

(*ii*) Energy required to remove an electron from third orbit is given as :

$$\Delta E = E_\infty - E_3 = 0 - E_3$$
$$= -\frac{(-21.76 \times 10^{-19} \times 4)}{9} J \quad [\because E_\infty = 0]$$
$$= \frac{21.76 \times 10^{-19} \times 4}{9} J$$

(*iii*) $\Delta E = h\upsilon = \frac{hc}{\lambda}$

$\therefore$ $\lambda = \frac{hc}{\Delta E}$

$= \frac{6.626 \times 10^{-34} Js \times 3.0 \times 10^8 ms^- \times 9}{21.76 \times 10^{-19} \times 4\ J}$

$= 2055 \times 10^{-7}\ m = 2.055 \times 10^{-10} m$

= 2055 Å **Ans.**

EXAMPLE 141. *Calculate the frequency, energy and wavelength of the radiation corresponding to the spectral line of lowest frequency in Lyman series in the spectra of hydrogen atom. Also, calculate the energy for the corresponding line in the spectrum of* Li^{2+}. ($R_H = 1.09678 \times 10^7\ m^-$, $c = 3 \times 10^8\ ms^-$, $h = 6.625 \times 10^{-34}\ Js$). **(Roorkee, 1991)**

SOLUTION. (*i*) $\bar{\upsilon} = \frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) cm^-$ ...(A)

For a spectral line of lowest frequency in Lyman series, $n_1 = 1$ and $n_2 = 2$. Also, $R = 1.09678 \times 10^7\ m^-$.

Substituting the values in equation (A), we get

$\frac{1}{\lambda} = 1.09678 \times 10^7 m^- \times 1^2 \left(\frac{1}{1^2} - \frac{1}{2^2}\right)$

$= 1.09678 \times 10^7\ m^- \left(1 - \frac{1}{4}\right)$

$= 1.09678 \times 10^7 \times \frac{3}{4} m^-$

$\therefore$ $\lambda = \frac{4}{1.09678 \times 10^7 \times 3}$ **m**

= 1.216 × 10⁻⁷ m **Ans.**

(*ii*) Frequency, $\upsilon = \frac{c}{\lambda} = \frac{3 \times 10^8 ms^-}{1.216 \times 10^{-7} m}$

= 2.47 × 10¹⁵ s⁻ **Ans.**

(*iii*) $E = hv$ (Planck's equation)

$= 6.625 \times 10^{-34}\ Js \times 2.47 \times 10^{15} s^-$

= 1.636 × 10⁻¹⁸ J **Ans.**

(*iv*) $$E_{\text{Li}^{2+}} = E_H \times Z_{\text{Li}}^2 = 1.636 \times 10^{-18}\text{J s} \times (3)^2 \quad [\because Z \text{ for Li} = 3]$$

$$= \mathbf{1.4724 \times 10^{-17}J} \qquad \textbf{Ans.}$$

Example 142. *In a H-atom, an electron jumps from energy level 4 to energy level 2. Calculate the wavelength of the spectral line formed. Also, name the colour of the radiation emitted, the region and the series to which the spectral line belongs.*

Solution. $R = 10.97 \times 10^{-6}\ \text{m}^-$, $n_1 = 2$, $n_2 = 4$.

Since electron falls to the second orbit, it will fall in the visible region of Balmer series.

Also: $$\bar{\upsilon} = \frac{1}{\lambda} = 10.97 \times 10^6 \text{m}^- \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2$$

$$\frac{1}{\lambda} = 10.97 \times 10^6 \text{ m}^- \left(\frac{1}{2^2} - \frac{1}{4^2}\right) \times (1)^2$$

$$= 10.97 \times 10^6 \text{ m} \left(\frac{1}{4} - \frac{1}{16}\right)$$

$$= 10.97 \times 10^6 \text{ m}^- \times \frac{3}{16}$$

$$\therefore \quad \lambda = \frac{16}{10.97 \times 10^6 \text{ m}^- \times 3}$$

$$= 4.86 \times 10^{-7} \text{ m} = 486 \times 10^{-9} \text{ m}$$

$$= 486 \text{ nm.}$$

The radiation of this wavelength (= 486 nm) corresponds to bluish green colour.

Example 143. *Calculate the wavelength of second line and the series limit for the Lyman series of hydrogen.*

Solution. (*i*) For second line in the Lyman series,

$$n_1 = 1, n_2 = 3$$

$$\therefore \quad \bar{\upsilon} = \frac{1}{\lambda} = 10.97 \times 10^6 \text{m}^- \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2$$

$$= 10.97 \times 10^6 \text{ m}^- \left(\frac{1}{1^2} - \frac{1}{3^2}\right) \times (1)^2$$

$$= 10.97 \times 10^6 \text{ m}^- \times \frac{8}{9}$$

$$\therefore \quad \lambda = \frac{9}{10.97 \times 10^6 \text{m}^- \times 8}$$

$$= \mathbf{1.026 \times 10^{-7}\ m} \qquad \textbf{Ans.}$$

(*ii*) For series limit in Lyman series, $n_1 = 1$, $n_2 = \infty$

$$\therefore \quad \bar{\upsilon} = 10.97 \times 10^6 \text{m}^- \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right)$$

$$= 10.97 \times 10^6 \text{ m}^- (1-0)$$

$$= 10.97 \times 10^6 \text{m}^-$$

$$\therefore \quad \lambda = \frac{1}{10.97 \times 10^6 \text{m}^-}$$

$$= \mathbf{9.116 \times 10^{-8}\ m} \qquad \textbf{Ans.}$$

Example 144. *What will be the energy emitted when two gram atoms of hydrogen undergo transition giving the spectral lines of lowest energy of visible region of its atomic spectra. Given, $h = 6.625 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms$^-$; $R_H = 1.1 \times 10^7$m$^-$.*

Solution. The given region is visible region. So, for minimum energy transition the H-spectrum would correspond to Balmer series for which $n_1 = 2$, $n_2 = 3$. Hence :

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] Z^2$$

$$= 1.1 \times 10^7 \text{m}^- \left[\frac{1}{2^2} - \frac{1}{3^2}\right] \times (1)^2$$

$$= 1.1 \times 10^7 \text{ m}^- \left(\frac{1}{4} - \frac{1}{9}\right)$$

$$= 1.1 \times 10^7 \text{m}^- \left(\frac{5}{36}\right)$$

$$\therefore \quad \lambda = \frac{36}{1.1 \times 10^7 \times 5} \text{m} = 6.54 \times 10^{-7}\text{m.}$$

Energy, $$E = h\upsilon = \frac{hc}{\lambda}$$

Substituting the values, we get :

$$E = \frac{6.625 \times 10^{-34} \text{Js} \times 3 \times 10^8 \text{ms}^-}{6.54 \times 10^{-7} \text{m}}$$

$$= \mathbf{3.04 \times 10^{-19}\ J}$$

Thus, for 1 gram atom (1 mol) of hydrogen, energy released

$$= 3.04 \times 10^{-19}\text{J} \times 6.02 \times 10^{23}$$

$\therefore$ For 2 gram atoms (2 mol) of hydrogen, energy released

$$= 2 \times 3.04 \times 10^{-19}\text{J} \times 6.02 \times 10^{23}$$

$$= 366016 \text{ J} = \mathbf{366.016\ kJ} \qquad \textbf{Ans.}$$

Example 145. *The wavelength of a certain line in the Balmer series is observed to be 434.1nm. To what value of 'n' does this correspond ?*

Solution. $$\lambda = 434.1 \text{ nm} = 434.1 \times 10^{-9}\text{m};$$

$$R = 10.97 \times 10^6\text{m}^-$$

$$\frac{1}{\lambda} = 10.97 \times 10^6\text{m}^- \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2$$

$$\frac{1}{434.1 \times 10^{-9}\text{m}} = 10.97 \times 10^6\text{m}^- \left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) \times 1^2$$

$$[\because \text{ For Balmer series, } n_1 = 2]$$

$$= 10.97 \times 10^6\text{m}^- \left(\frac{1}{4} - \frac{1}{n_2^2}\right)$$

$$= \frac{1}{434.1 \times 10^{-9}\text{m} \times 10.97 \times 10^6 \text{m}^-}$$

$$= \frac{1}{4} - \frac{1}{n_2^2}; \ \frac{1}{n_2^2} = \frac{1}{4}\ 0.21 = 0.25 - 0.21$$

$$= 0.04 = \frac{4}{100}$$

or $$n_2^2 = \frac{100}{4} = 25;$$

$$(n_2)^2 = (5)^2. \text{ Hence } n_2 = 5 \qquad \textbf{Ans.}$$

Example 146. *The highest wavelength of a spectral line in the atomic spectra of hydrogen is found to be 18751 × 10^{-8} cm. Find the series to which this line belongs (R_H = 109737 cm$^-$).*

Solution. (*i*) $\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{18751\times10^{-8}\text{cm}} = 5333 \text{ cm}^{-}$

(*ii*) For highest wavelength in (*a*) Lyman series, $n_1 = 1$, $n_2 = 2$; (*b*) Balmer series, $n_1 = 2$, $n_2 = 3$; (*c*) Paschen series, $n_1 = 3$, $n_2 = 4$ and so on. Hence :

$$\bar{\upsilon} \text{ for Lyman series} = 109737 \text{ cm}^{-}\left(\frac{1}{1^2}-\frac{1}{2^2}\right) Z^2$$

$$= 109737 \text{ cm}^{-} \times \frac{3}{4} \times 1^2$$

$$= 82302.75 \text{ cm}^{-}$$

$$\bar{\upsilon} \text{ for Balmer series} = 109737 \text{ cm}^{-}\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$$

$$= 109737 \text{ cm}^{-} \times \frac{5}{36}$$

$$= 15241.25 \text{ cm}^{-}$$

$$\bar{\upsilon} \text{ for Paschen series} = 109737 \text{ cm}^{-}\left(\frac{1}{3^2}-\frac{1}{4^2}\right)$$

$$= 109737 \text{ cm}^{-} \times \frac{7}{9\times16}$$

$$= 5334.4 \text{ cm}^{-}$$

Since the value of $\bar{\upsilon}$ for Paschen series (= 5334.4 cm^{-}) is almost same as that of given spectral line (= 5333 cm^{-}), so, the spectral line belongs to Paschen series.

Example 147. *Calculate the wavelength, frequency, wave number and amount of energy in ergs and kilocalories per mole of radiation emitted when an electron jumps from fifth to third orbit in a hydrogen atom. Also, name the region in which the spectral line will appear. ($R = 3.289 \times 10^{15}s^{-}$).*

Solution. (*i*) $n_1 = 3, n_2 = 5$;

$R = 3.289 \times 10^{15}\text{s}^{-}$. We know that :

$$\text{Frequency, } \upsilon = 3.289 \times 10^{15}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{s}^{-} \times Z^2$$

$$= 3.289 \times 10^{15}\left(\frac{1}{3^2}-\frac{1}{5^2}\right)\text{s}^{-} \times 1^2$$

($\because$ Z = 1 for H-atom)

$$\upsilon = 3.289 \times 10^{15}\left(\frac{1}{9}-\frac{1}{25}\right)\text{s}^{-}$$

$$= \frac{3.289\times10^{15}\times16}{9\times25}\text{s}^{-}$$

$$= \mathbf{2.339 \times 10^{14}\ s^{-}} \qquad \textbf{Ans.}$$

(*ii*) $\text{Wavelength, } \lambda = \frac{c}{\upsilon} = \frac{3.0\times10^{10}\text{cms}^{-}}{2.339\times10^{14}\text{s}^{-}}$

$$= \mathbf{1.282 \times 10^{-4}\ cm} \qquad \textbf{Ans.}$$

(*iii*) $\text{Wave number, } \bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{1.282\times10^{-4}\text{cm}}$

$$= \mathbf{7800\ cm^{-}} \qquad \textbf{Ans.}$$

(*iv*) $h = 6.625 \times 10^{-27}\text{erg.s}$

$\therefore$ Energy,

$$E = h\upsilon = 6.625 \times 10^{-27}\text{ erg.s} \times 2.339 \times 10^{14}\text{s}^{-}$$

$$= 1.549 \times 10^{-12}\text{ erg}$$

$$= 1.549 \times 10^{-12}\text{ erg} \times \frac{1\text{k cal atom}^{-}}{4.183\times10^{10}\text{ergs}}$$

$$= 3.7 \times 10^{-23}\text{ k cal atom}^{-} \times \frac{6.023\times10^{23}\text{atoms}}{1\text{mole}}$$

$$= \mathbf{22.28\ k\ cal\ mol^{-}} \qquad \textbf{Ans.}$$

[$\because$ 4.183×10^{10} ergs = 1 k cal;
1 mole = 6.023×10^{23} atoms]

The spectral line will fall into the I.R. region as the electron jumps from fifth to the third orbit.

Example 148. *If the wavelength of the first member of the Lyman series in hydrogen spectrum is 1215.3Å, calculate the wavelength of the first member of the Balmer series in the same spectrum.*

Solution. (*i*) For Lyman series, $\lambda = 1215.3\text{Å} = 1215.3 \times 10^{-8}\text{cm}$; $n_1 = 1, n = 2$.

$$\text{But} \qquad \frac{1}{\lambda} = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)Z^2;$$

$$\frac{1}{1215.3\times10^{-8}\text{cm}} = R\left(\frac{1}{1^2}-\frac{1}{2^2}\right)\times1^2 = \frac{3}{4}R$$

[$\because$ For H, Z = 1]

$$\therefore \qquad R = \frac{4}{3\times1215.3\times10^{-8}\text{cm}}$$

$$= 109712 \text{ cm}^{-}$$

(*ii*) For Balmer series, $n_1 = 2$, $n_2 = 3$. For H-atom, Z = 1. Hence :

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)Z^2;$$

$$\frac{1}{\lambda} = 109712 \text{ cm}^{-}\left(\frac{1}{2^2}-\frac{1}{3^2}\right) \times 1^2$$

$$= 109712 \text{ cm}^{-} \times \frac{5}{4\times9}$$

$$\therefore \qquad \lambda = \frac{4\times9}{5\times109712\text{cm}^{-}} = 6.563 \times 10^{-5}\text{ cm}$$

$$= 6.563 \times 10^{-5}\text{ cm} \times \frac{1\text{Å}}{10^{-8}\text{cm}}$$

$$\mathbf{\lambda = 6563\ Å} \quad \textbf{Ans.}$$

Example 149. *Calculate the velocity (cm s^{-}) of an electron placed in the third orbit of the hydrogen atom. Also, calculate the number of revolutions per second that this electron makes around the nucleus.* **(Roorkee, 1987)**

Solution. (*i*) Velocity of an electron moving in *n*th orbit.

$$v_n = \frac{2\pi e^2}{nh}\text{. Here } n = 3,$$

$$e = 4.8 \times 10^{-10}\text{ esu,}$$

$$h = 6.626 \times 10^{-27}\text{ erg.s}$$

$$\therefore \quad v_n = \frac{2\times 3.142\times(4.8\times 10^{-10}\text{esu})^2}{3\times 6.626\times 10^{-27}\text{erg s}}$$

$$= \frac{2\times 3.142\times(4.8\times 10^{-10}\text{g}^{1/2}\text{cm}^{3/2}\text{s}^{-})^2}{3\times 6.626\times 10^{-27}\text{gcm}^2.\text{s}^{-2}.\text{s}}$$

$$[\because \text{esu} = \text{g}^{1/2}\text{cm}^{3/2}\text{s}^{-};\ \text{erg} = \text{g cm}^2\text{s}^{-2}]$$

$$\simeq 7.28 \times 10^7\text{ cm s}^{-}$$

(*ii*) No. of revolutions per second

$$= \frac{v_n}{2\pi r_n} \text{ where } r_n = \frac{n^2h^2}{4\pi^2 me^2}$$

$$= \frac{v_n\times 4\pi^2 me^2}{2\pi n^2h^2} = \frac{2\pi e^2}{nh}\times\frac{4\pi^2 me^2}{2\pi n^2h^2} = \frac{4\pi^2 me^4}{n^3h^3}$$

$$= \frac{4\times(3.142)^2\times 9.1\times 10^{-28}\text{g}\times(4.8\times 10^{-10}\text{esu})^4}{(3)^3\times(6.626\times 10^{-27}\text{erg.s})^3}$$

$$= \frac{4\times(3.142)^2\times 9.1\times 10^{-28}\text{g}\times(4.8\times 10^{-10}\text{g}^{1/2}\text{cm}^{3/2}\text{s}^{-})^4}{(3)^3\times(6.626\times 10^{-27}\text{g cm}^2.\text{s}^{-2}.\text{s})^3}$$

$= \mathbf{2.42 \times 10^{14}}$ **Ans.**

Example 150. *Calculate the number of spectral lines emitted by atomic hydrogen excited to nth orbit.*

Solution. The number of lines emitted from *n*th orbit are given as : $= 1 + 2 + 3 + \ldots n - 1 = \Sigma n - 1$

$$\text{But} \quad \Sigma n = \frac{n(n+1)}{2}$$

$$\text{Hence,} \quad \Sigma n - 1 = \frac{(n-1)(n-1+1)}{2} = \frac{(n-1)n}{2}$$

$\therefore$ Number of spectral lines emitted by atomic hydrogen from *n*th orbit $= \dfrac{n(n-1)}{2}$

Example 151. *Calculate the number of spectral lines emitted by hydrogen atom excited to 4th energy level.*

Solution. $n = 4$ (given).

Hence number of spectral lines emitted $= \dfrac{n(n-1)}{2}$

$$= \frac{4(4-1)}{2} = \frac{4\times 3}{2} = 6$$ **Ans.**

Example 152. *(i) Calculate the wavelength of radiation needed to excite an electron in Li^{2+} (Z = 3) from first to the 4th orbit. (Ionisation energy of H-atom = 13.6 eV).*

(ii) Calculate the number of spectral lines observed in the emission spectrum of the above excited species.

Solution. (*i*) $Z = 3, n_1 = 1, n_2 = 4, E_n = -13.6\dfrac{Z^2}{n^2}$

Excitation energy, ΔE

$$= E_4 - E_1 = -13.6\, Z^2\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)\text{eV}$$

$$= -13.6 \times 3^2\left(\frac{1}{4^2} - \frac{1}{1^2}\right)\text{eV}$$

$$= -13.6 \times 9\left(\frac{1}{16} - 1\right)$$

$$= -13.6 \times 9 \times \left(-\frac{15}{16}\right)$$

$$= 114.75\text{ eV} = 114.75 \times 1.6 \times 10^{-19}\text{J}$$

$$[\because 1\text{ eV} = 1.6 \times 10^{-19}\text{J}]$$

$$\text{But wavelength, } \lambda = \frac{hc}{\Delta E}$$

$$\text{So,} \quad \lambda = \frac{6.63\times 10^{-34}\text{Js}\times 3\times 10^8\text{ms}^{-}}{114.75\times 1.6\times 10^{-19}\text{J}}$$

$$= 1.08 \times 10^{-8}\text{ m}$$

(*ii*) The number of spectral lines observed

$$= \frac{n(n-1)}{2} \text{ (where } n = 4)$$

$$= \frac{4(4-1)}{2} = \frac{4\times 3}{2} = 6$$ **Ans.**

Example 153. *The energy of the electron in the first Bohr orbit of hydrogen is –2.178 × 10^{-11} erg. Calculate the charge on electron if the radius of Bohr's orbit is 0.529 Å.*

Solution. Total energy (E) of revolving electron

$$= \text{K.E.}\left(= \frac{1}{2}mv^2\right) + \text{P.E.}\left(= \frac{-Ze^2}{r}\right).$$

$$\text{But } mv^2 = Ze^2\text{. So :}$$

$$E = \frac{1}{2}\times\frac{Ze^2}{r} - \frac{Ze^2}{r} = \frac{Ze^2 - 2Ze^2}{2r}$$

$$= -\frac{Ze^2}{2r} \quad \ldots(1)$$

Substituting the values in relation (1), we get :

$$-2.178 \times 10^{-11}\text{ erg} = -\frac{-1\times e^2}{2\times 0.529\times 10^{-8}\text{cm}}$$

$$-2.178 \times 10^{-11}\text{ g cm}^2\text{s}^{-2} = \frac{-e^2}{2\times 0.529\times 10^{-8}\text{cm}}$$

$$\therefore \quad e = (2.178 \times 10^{-11}\text{ g cm}^2\text{s}^{-2} \times 2 \times 0.529 \times 10^{-8}\text{cm})^{1/2}$$

$$= (2.3 \times 10^{-19}\text{ g cm}^3\text{s}^{-2})^{1/2} = (23 \times 10^{-20}\text{ g cm}^3\text{s}^{-2})^{1/2}$$

$$e = 4.8 \times 10^{-10}\text{ g}^{1/2}\text{cm}^{3/2}\text{s}^{-} = 4.8 \times 10^{-10}\text{ esu}$$

$$[\because 1\text{ esu} = \text{g}^{1/2}\text{cm}^{3/2}\text{s}^{-}]$$

$\therefore$ Charge on electron $=$ $\mathbf{4.8 \times 10^{-10}}$ **esu.** **Ans.**

Type. To find maximum number of spectral lines, use the relation :

Maximum no. of spectral lines

$$= \frac{n(n-1)}{2}$$

Example 154. *Calculate the maximum number of lines when an excited electron drops from n = 6 to its ground state in case of a H-atom.*

Solution. $n = 6$. Thus :

Maximum number of spectral lines

$$= \frac{n(n-1)}{2} = \frac{6(6-1)}{2} = \mathbf{15} \qquad \textbf{Ans.}$$

Example 155. *In a hydrogen atom, an electron jumps from a third orbit to the first orbit. Find out the frequency and wavelength of the spectral line. (R = 109678 cm⁻).*

(Roorkee, 1989, 1985)

Solution. $n_1 = 1$, $n_2 = 3$, $R = 109678 \text{ cm}^{-}$; $\lambda = ?$, $\upsilon = ?$; $c = 3 \times 10^{10} \text{ cms}^{-}$. For H-atom, $Z = 1$. We know that :

$$\bar{\upsilon} = \frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \times Z^2$$

$$= 109678 \text{ cm}^{-} \left(\frac{1}{1^2} - \frac{1}{3^2}\right) \times 1^2$$

$$= 109678 \text{ cm}^{-} \times \frac{8}{9}$$

(*i*) $\therefore$

$$\lambda = \frac{9}{109678 \text{ cm}^{-} \times 8}$$

$$= 1.0257 \times 10^{-5} \text{ cm}$$

$$= 1.0257 \times 10^{-5} \text{ cm} \times \frac{1 \text{Å}}{10^{-8} \text{cm}};$$

$$\lambda = \mathbf{1025.7 \text{ Å}} \qquad \textbf{Ans.}$$

(*ii*)

$$\upsilon = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{cm s}^{-}}{1025.7 \times 10^{-8} \text{cm}}$$

$$= \mathbf{2.925 \times 10^{15} s^{-}} \qquad \textbf{Ans.}$$

$[\because 1 \text{Å} = 10^{-8} \text{ cm}]$

Example 156. *Calculate the wavelength in Å of the photon that is emitted when an electron in the Bohr orbit n = 2 returns to the orbit n = 1 in the hydrogen atom. The ionisation potential of the ground state of the hydrogen atom is 2.17 × 10⁻¹¹ erg per atom.* **(IIT, 1982)**

Solution. $\lambda = ?$. We know that for H-atom :

$$E_n = \frac{-2.17 \times 10^{-11} \text{erg atom}^{-}}{n^2}$$

$\therefore$ When $n = 1$, $E_1 = \dfrac{-2.17 \times 10^{-11} \text{erg atom}^{-}}{1^2}$

$= -2.17 \times 10^{-11}$ erg atom⁻ (given)

When $n = 2$, $E_2 = \dfrac{-2.17 \times 10^{-11} \text{erg atom}^{-}}{2^2}$

$$= \frac{-2.17 \times 10^{-11} \text{erg atom}^{-}}{4}$$

$$= -0.542 \times 10^{-11} \text{ erg atom}^{-}$$

$\therefore$ $\Delta E = E_2 - E_1 = (-0.542 \times 10^{-11}$ erg atom⁻$) - (-2.17 \times 10^{-11}$erg atom⁻$)$

$$= 1.628 \times 10^{-11} \text{ erg atom}^{-}$$

But $E = h\upsilon = \dfrac{hc}{\lambda}\cdot$ Hence ;

$$\lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-27} \text{erg.s} \times 3.0 \times 10^{10} \text{cm s}^{-}}{1.628 \times 10^{-11} \text{erg atom}^{-}}$$

$$= 1.221 \times 10^{-5} \text{ cm}$$

$$= 1.221 \times 10^{-5} \text{ cm} \times \frac{1 \text{Å}}{10^{-8} \text{cm}}$$

$$= \mathbf{1221 \text{ Å}} \qquad \textbf{Ans.}$$

Example 157. *What transition in the He⁺ spectrum would have the same wavelength as the first Lyman transition of hydrogen (n = 2 to n = 1) ?*

Solution. At. no. (Z) of He = 2. $R_H = 109678 \text{ cm}^{-}$. Given $n_1 = 1$, $n_2 = 2$. We know that:

$$\bar{\upsilon}_H = \frac{1}{\lambda_H} = 109678 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Z^2$$

$$= 109678 \left(\frac{1}{1^2} - \frac{1}{2^2}\right) \times 1^2 \text{ cm}^{-}$$

$$= 109678 \times \frac{3}{4} \text{cm}^{-}$$

$\therefore$

$$\lambda_H = \frac{4}{109678 \times 3} \text{cm.}$$

As $\Delta E_{He^+} = Z^2 E_H$, similarly, $\lambda_{He^+} = Z_{He}^2 \times \lambda_H$

or $\lambda_{He^+} = (2)^2 \times \dfrac{4}{109678 \times 3} \text{cm};$

$$\frac{1}{\lambda_{He^+}} = \frac{109678 \times 3}{16} \text{cm}^{-}$$

For He⁺, let $n_1 = 2$, $n_2 = ?$. Thus we have :

$$\bar{\upsilon}_{He^+} = \frac{1}{\lambda_{He^+}} = 109678 \left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) \text{cm}^{-}$$

or $\dfrac{109678 \times 3}{16} \text{cm}^{-} = 109678 \left(\dfrac{1}{4} - \dfrac{1}{n_2^2}\right) \text{cm}^{-};$

$$\frac{3}{16} = \frac{1}{4} - \frac{1}{n_2^2}$$

$$\frac{1}{n_2^2} = \frac{1}{4} - \frac{3}{16} = \frac{1}{16} \; ; \; n_2^2 = 16.$$

Hence $n_2 = (16)^{1/2} = 4$.

So, in case of He⁺ spectrum, transition will be from 4 to 2.

Example 158. *In a Balmer series of atomic spectra of hydrogen, there is a spectral line having wavelength 434.4 nm. Calculate the number of higher orbit from which the electron drops to generate this line. (R = 10.97 × 10⁶ m⁻).*

Solution. For Balmer series, $n_1 = 2$, $n_2 = ?$, $\lambda = 434.4$ nm $= 434.4 \times 10^{-9}$m; $R = 10.97 \times 10^{6}$m^{-}. We know that, for H-atom, $Z = 1$. So :

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)Z^2;$$

$$\frac{1}{434.4\times10^{-9}\text{m}} = 10.97 \times 10^{6}\ \text{m}^{-} \left(\frac{1}{2^2}-\frac{1}{n_2^2}\right)\times 1^2$$

or $\dfrac{1}{434.4\times10^{-9}\text{m}\times10.97\times10^{6}\text{m}}$

$$= \frac{1}{4}-\frac{1}{n_2^2};0.21 = \frac{1}{4}-\frac{1}{n_2^2};$$

$$0.21 = 0.25-\frac{1}{n_2^2};\ \frac{1}{n_2^2} = 0.25-0.21=0.04$$

$$= \frac{4}{100}=\frac{1}{25} \quad \therefore n_2 = 5$$ **Ans.**

Example 159. *The energy of the electron in the second and the third Bohr orbits of the hydrogen atom are -5.42×10^{-12} erg and -2.41×10^{-12} erg respectively. Calculate the wavelength of the emitted radiation when the electron drops from the third to the second orbit.* **(IIT, 1981)**

Solution. Energy E_2 of second orbit

$= -5.42 \times 10^{-12}$ erg

Energy E_3 of third orbit $= -2.41 \times 10^{-12}$ erg

Change in energy,

$\Delta E = E_3 - E_2 = -2.41 \times 10^{-12}$ erg $- (-5.42 \times 10^{-12}$ erg$)$

$= 10^{-12}\,(5.42 - 2.41) = 3.01 \times 10^{-12}$ erg

But $\quad \Delta E = \dfrac{hc}{\lambda}$ **or**

Wavelength, $\lambda = \dfrac{hc}{\Delta E}$ ...(*i*)

Substituting the values of Planck's constant, h (= 6.625 × 10^{-27} erg. s.) and velocity of light, c (= 3 × 10^{10} cm s^{-}) in (*i*), we get

$$\lambda = \frac{6.625\times10^{-27}\text{erg.s}\times3\times10^{10}\text{cm s}^{-}}{3.01\times10^{-12}\text{erg}}$$

$= \mathbf{6.6 \times 10^{-5}}$ **cm** **Ans.**

Example 160. *Calculate the energy emitted when electrons in one gm. atom of hydrogen undergo transition giving the spectral lines of lowest energy in the visible region of its atomic spectra.* **(Roorkee, 1993)**

Solution. For visible line spectrum *i.e.*, Balmer series and for minimum energy transition :

We know that $n_1 = 2$ and $n_2 = 3$

[∵ 1st line has minimum energy]

$$\frac{1}{\lambda} = R_{\text{H}}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\times Z^2;$$

$$\frac{1}{\lambda} = 1.097 \times 10^{7}\ \text{m}^{-1}\left[\frac{1}{2^2}-\frac{1}{3^2}\right]\times 1^2$$

or $$\frac{1}{\lambda} = 1.097 \times 10^{7}\ \text{m}^{-1}\left[\frac{1}{4}-\frac{1}{9}\right]$$

$$= 1.097 \times 10^{-7}\text{m}^{-1} \times \frac{5}{36}$$

$$= 0.1524 \times 10^{7}\ \text{m}^{-1} = 1.524 \times 10^{6}\ \text{m}^{-1}$$

$\therefore \quad \lambda = 6.56 \times 10^{-7}$m

Now $$E = \frac{hc}{\lambda} = \frac{6.62\times10^{-34}\text{Js}\times3\times10^{8}\text{ms}^{-1}}{6.56\times10^{-7}\text{m}}$$

$= 3.0274 \times 10^{-19}$J

Energy corresponding to 1gm atom of Hydrogen

$E = 3.0274 \times 10^{-19} \times 6.02 \times 10^{23}$J

$= 18.22 \times 10^{4}$J $= 182.2 \times 10^{3}$J

$=$ **182.2 kJ.**

Example 161. *Estimate the difference in energy between the first and second orbit for a 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 λ = 3.0 × 10^{-8} m ? Which hydrogen atom like species does this atomic number correspond to ?* **(IIT, 1993)**

Solution. (*i*) The expression for the energy difference between two electronic levels is given by

$$\Delta E = hv = h\frac{c}{\lambda} = hc\bar{v} \qquad \text{...}(i)$$

$$\bar{\upsilon} = R_{\text{H}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)Z^2 \qquad \text{...}(ii)$$

$$\therefore \quad \Delta E = hc.R_{\text{H}}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)Z^2 \qquad \text{...}(iii)$$

$Z = 1$ for H-atom

Therefore, energy difference between first and second orbit of H-atom is given by

$$\Delta E = R_{\text{H}}.hc\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

$$= (1.09677 \times 10^{7}\text{m}^{-1})\,(6.626 \times 10^{-34}\text{Js}) \times (3 \times 10^{8}\text{ms}^{-}) \times \left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

$= \mathbf{1.635 \times 10^{-18}J}$

(*ii*) Energy of X-rays of wavelength $\lambda = \dfrac{hc}{\lambda}$

Energy emission for hydrogen like atom during transition from $n = 2$ to $n = 1$ energy state

$= 1.635 \times 10^{-18}Z^2$J

$$\therefore\ 1.635 \times 10^{-18}Z^2\text{J} = \frac{hc}{\lambda}$$

$$= \frac{(6.626\times10^{-34}\text{Js}\times3\times10^{8}\text{ms}^{-1})}{(3\times10^{-8}\text{m})}$$

$$Z^2 = \frac{6.626\times10^{-34}\times3\times10^{8}}{(1.635\times10^{-18})(3\times10^{-8})} = 4$$

$\therefore \quad Z = 2$

(*iii*) The hydrogen atom-like species having atomic number 2 is He^+.

EXAMPLE 162. *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 a spectral transition

$$\frac{1}{\lambda} = R_H Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

∴ For He^+ ion,

$$\text{we have } \frac{1}{\lambda} = R_H.(2)^2\left(\frac{1}{2^2}-\frac{1}{4^2}\right)=\frac{3}{4}R_H \qquad ...(i)$$

Now for hydrogen atom

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \qquad ...(ii)$$

Equating equations (*i*) and (*ii*), we get :

$$\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = \frac{3}{4}$$

Obviously $n_1 = 1$ and $n_2 = 2$. Hence the transition $n = 2$ to $n = 1$ in hydrogen atom will have the same wavelength as the transition, $n = 4$ to $n = 2$ in He^+ species. The transition belongs to Lyman series.

EXAMPLE 163. *Wavelength of high energy transition of H-atoms is 9.21 nm. Calculate the corresponding wavelength of He atoms.* **(IIT, 2003)**

SOLUTION. $$\frac{1}{\lambda} = R_H Z^2\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]$$

$$\therefore \quad \frac{1}{91.2} = R_H\left[\frac{1}{1^2}-\frac{1}{n^2}\right]$$

$$\text{Since} \quad R_H = \text{constant} \ \frac{\lambda_{He}}{\lambda_H} = \frac{Z_H^2}{Z_{He}^2} = \frac{1^2}{2^2} = \frac{1}{4}$$

$$\text{or} \quad \lambda_{He} = \frac{\lambda_H}{4} = \frac{91.2}{4} = \mathbf{22.8\ nm.}$$

EXAMPLE 164. *Calculate the wavelength of the first Lyman line in the spectrum of He^+ and Li^{2+}. Given : wave number of first Balmer line in the H-spectrum = 15200 cm⁻.*

SOLUTION. For first Balmer line

$$n_1 = 2; n_2 = 3,$$

$$\text{wave number } \bar{\upsilon} = R\,Z^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right).$$

$$\text{Given } \bar{\upsilon} = 15200\ \text{cm}^-.$$

$$\therefore \quad 15200\ \text{cm}^- = R \times 1^2\left(\frac{1}{2^2}-\frac{1}{3^2}\right)$$

[∵ For H-atom, $Z = 1$]

$$= R\left(\frac{1}{4}-\frac{1}{9}\right) = R\left(\frac{9-4}{4\times 9}\right) = \frac{5R}{36}$$

$$\therefore \quad R = \frac{15200\,\text{cm}^- \times 36}{5} = 109440\ \text{cm}^-$$

(*i*) Fe He^+, $Z = 2$. Hence $\bar{\upsilon} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$.

$$\bar{\upsilon} = 109440\ \text{cm}^- \times 2^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

[∵ For first Lyman line, $n_1 = 1, n_2 = 2$]

$$\bar{\upsilon} = 109440\ \text{cm}^- \times 4\ (1 - \tfrac{1}{4}\ i.e.,\ \tfrac{3}{4})$$

$$= 328320\ \text{cm}^-$$

$$\text{But } \lambda = \frac{1}{\bar{\upsilon}} \quad \therefore \quad \lambda = \frac{1}{328320\,\text{cm}^-} = 3.046 \times 10^{-6}\ \text{cm}$$

$$= \mathbf{304.6Å}$$ **Ans.**

(*ii*) For Li^{2+}, $Z = 3$. Hence $\bar{\upsilon} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$.

$$\bar{\upsilon} = 109440\ \text{cm}^- \times 3^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

[∵ For first Lyman line, $n_1 = 1, n_2 = 2$]

$$= 109440\ \text{cm}^- \times 9 \times \frac{3}{4}$$

$$= 738720\ \text{cm}^-$$

$$\text{But } \lambda = \frac{1}{\bar{\upsilon}} \quad \therefore \quad \lambda = \frac{4}{738720\,\text{cm}^-} = 1.354 \times 10^{-6}\ \text{cm}$$

$$= \mathbf{135.4Å}$$ **Ans.**

EXAMPLE 165. *In H-atom, the energy of electron in the nth orbit is given as*

$$E_n = -\frac{13.6}{n^2}eV.\ \textit{Show that } E_{(n+1)} - E_n$$

$$= -\frac{13.6}{n^3}eV \times 2 \textit{ for large value of } n.$$

[WBJEE, 2001]

SOLUTION. $$E_{(n+1)} - E_n = \left[-\frac{13.6}{(n+1)^2}-\left(-\frac{13.6}{n^2}\right)\right]\text{eV}$$

$$= \left[\frac{-13.6n^2+13.6(n+1)^2}{n^2(n+1)^2}\right]\text{eV}$$

$$= \left[\frac{-13.6n^2+13.6n^2+13.6+13.6\times 2n}{n^2(n+1)^2}\right]\text{eV}$$

$$= \frac{13.6(2n+1)}{n^2(n+1)^2}\text{eV} = \frac{13.6\times 2n}{n^2(n)^2}\text{eV}$$

(neglecting 1 in comparison to n since $n >> 1$)

$$= \mathbf{\frac{13.6\times 2}{n^3}eV}$$

EXAMPLE 166. *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 bonds is 436 kJ mol⁻¹.* **(IIT, 2000)**

SOLUTION. No. of moles of H_2 gas,

$$n = \frac{PV}{RT} = \frac{1\times 1}{0.0821\times 298} = 0.0409$$

Energy required to dissociate 0.0409 mol H_2 into atoms

$$= 0.0409 \times 436 = \mathbf{17.83\ kJ.}$$

No. of moles of H-atoms

$$= 2 \times 0.0409 = 0.0818$$

$$E_n = -\frac{1312}{n^2}\,\text{kJ mol}^{-1}$$

∴ Energy required for excitation of 0.0818 moles of H atoms from ground state to first excited state

$$= (E_2 - E_1) \times 0.0818\ \text{kJ mol}^{-1}$$

$$= -\left[\left(\frac{-1312}{2^2}\right) - \left(\frac{-1312}{1^2}\right)\right] \times 0.0818\,\text{kJ}$$

$$= \mathbf{80.49\ kJ}$$

Total energy required for excitation of 1 litre H_2 gas

$$= 17.83 + 80.49 = \mathbf{98.32\ kJ.}$$

Type. no. of waves $= \dfrac{\text{circumference of orbit } (2\pi r)}{\text{wave length } \lambda\ (= h/mv)}$

EXAMPLE 167. *Find the number of waves made by Bohr electron in one complete revolution in its third orbit.* **(IIT, 1994)**

SOLUTION. According to Bohr's theory $mvr = \dfrac{nh}{2\pi}$

In the third orbit, $n = 3$; $mvr = 3\left(\dfrac{h}{2\pi}\right)$ ...(*i*)

According to de Broglie expression

$$\lambda = \frac{h}{mv} \qquad ...(ii)$$

Substituting this in equation (*i*), we get :

$$\left(\frac{h}{\lambda}\right)r = 3\left(\frac{h}{2\pi}\right) \text{ or}$$

$$3\lambda = 2\pi r\ (= \text{circumference})$$

Thus, the circumference of third orbit is equal to three times the wavelength of electron *i.e.*, the number of waves made by Bohr electron in one complete revolution is three.

In general, the number of waves made by a Bohr electron in an orbit is equal to its principal quantum number.

EXAMPLE 168. *A gas has atoms identical to hydrogen atoms. Some of its atoms are in the lowest (ground) orbit (x). Some of its atoms are also in a specific upper excited orbit (y). However, no atoms are present into any other orbit. The gas atoms absorb monochromatic light of photon energy (= 2.7 eV) and undergo transition to higher orbits. Subsequently, these gas atoms emit radiations of only six different photons. Some of the emitted photons have energy equal to 2.7 eV, some have less while some have more energy than 2.7 eV.*

(*i*) *Calculate the ionisation energy of the gas atoms.*

(*ii*) *Calculate the minimum and maximum energies of the emitted photons.*

(*iii*) *Calculate the principal quantum number of initially excited level 'y'.*

SOLUTION. (*iii*) Let ground state = n_1 and excited state = n_2, Energy absorbed = 2.7 eV. When electrons fall from higher orbit n_2 to lower orbit, n_1, the six photon energies are emitted.

$$\therefore \quad \Sigma n_2 - 1 = \frac{n_2(n_2-1)}{2} \text{ or } \frac{n_2(n_2-1)}{2} = 6$$

$$\therefore \; n_2^2 - n_2 = 12 \textbf{ or } n_2^2 - n_2 - 12 = 0 \textbf{ or}$$

$n_2^2 - 4n_2 + 3n_2 - 12 = 0$ (using factors)

$\therefore\ n_2(n_2 - 4) + 3(n_2 - 4) = 0$ **or** $(n_2 - 4)(n_2 + 3) = 0$

$\therefore\ n_2 - 4 = 0$ **or** $n_2 = 4$ [When $n_2 + 3 = 0, n_2 = -3$ which is not possible]

∴ Principal quantum number = **4.**

But $\quad E_n = \dfrac{-R_H ch}{n^2}$ for hydrogen like atom

$$\therefore \quad E_4 = \frac{-R_H ch}{4^2} = \frac{-R_H ch}{16};$$

$$E_3 = \frac{-R_H ch}{3^2} = \frac{-R_H ch}{9};$$

$$E_2 = \frac{-R_H ch}{2^2} = \frac{-R_H ch}{4};$$

$$E_1 = \frac{-R_H ch}{1^2} = -R_H ch$$

But $\quad E_4 - E_2 = 2.7$ eV (given)

$\therefore\ E_4 - E_3 < 2.7$ eV and $E_4 - E_1 > 2.7$ eV.

(*i*) We know

$$E_4 - E_2 = 2.7\text{ eV}$$

$$\therefore \quad \frac{-R_H ch}{16} - \left(\frac{-R_H ch}{4}\right) = 2.7\text{ eV}$$

$$\textbf{or} \quad -\frac{R_H ch}{16} + \frac{R_H ch}{4} = 2.7\text{eV}$$

$$\therefore \quad \frac{R_H ch}{4}\left[\frac{1}{4} - 1\right] = 2.7\text{ eV}; \quad \frac{E_1}{4}\left[\frac{-3}{4}\right] = 2.7\text{ eV}$$

$$\frac{-3E_1}{16} = 2.7\text{eV.}$$

$$\text{Hence,} \quad E_1 = \frac{2.7\text{eV} \times 16}{-3} = -14.4\text{eV}$$

∴ Ionisation energy of gas atoms = 14.4 eV.

(*ii*) Minimum energy of emitted photons

$$= E_4 - E_3 = \frac{-E_1}{16} - \left(\frac{-E_1}{9}\right)$$

$$\therefore \quad E_4 - E_3 = \frac{E_1}{9} - \frac{E_1}{16} = E_1\left(\frac{1}{9} - \frac{1}{16}\right)$$

$$= E_1\left(\frac{16-9}{16 \times 9}\right) = E_1 \times \frac{7}{144}$$

$$\therefore \quad E_4 - E_3 = 14.4 \times \frac{7}{144} = 0.7\text{eV.}$$

Maximum energy of emitted photons

$$= E_4 - E_1 = \frac{-E_1}{16} - \left(\frac{-E_1}{1}\right)$$

$$= \frac{E_1}{1} - \frac{E_1}{16} = E_1\left(1 - \frac{1}{16}\right) = E_1 \times \frac{15}{16}$$

$$\textbf{or} \quad E_4 - E_1 = +14.4 \times \frac{15}{16} = +13.5\text{ eV} \qquad \textbf{Ans.}$$

EXAMPLE 169. *Identify each parameter in the following Bohr's energy expression,* $E = -k^2\dfrac{2\pi^2 me^4 Z^2}{n^2h^2}$.

Solution. k = Coulomb's law constant, $\pi = \frac{22}{7}$; m = mass of electron, e = charge on the electron, Z = atomic number of element, n = integer (quantum number) and h = Planck's constant.

Example 170. *What will be the wave lengths of the first line and the series limit for the Balmer series for hydrogen ?*

Solution. (*i*) *For first line* in Balmer series,

$n_1 = 2, n_2 = 3$, we have :

$$\bar{\upsilon} = \frac{1}{\lambda} = 109678\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2\,\text{cm}^{-}$$

$$(\because \text{ For H-atom, Z} = 1)$$

$$\therefore \quad \frac{1}{\lambda} = 109678\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \times 1^2 \times \text{cm}^{-}$$

$$= 109678 \times \frac{5}{36}\,\text{cm}^{-} = 15233\,\text{cm}^{-}$$

$$\therefore \quad \lambda = \frac{1}{15233\,\text{cm}^{-}} = \mathbf{6.56 \times 10^{-5}\ cm\ Ans.}$$

(*ii*) *For series limit* in Balmer series,

$n_1 = 2, n_2 = \infty$, we have :

$$\bar{\upsilon} = \frac{1}{\lambda} = 109678\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2\,\text{cm}^{-}$$

$$= 109678\left(\frac{1}{2^2} - \frac{1}{(\infty)^2}\right) \times 1^2\,\text{cm}^{-}$$

$$\left(\because \frac{1}{\infty} = 0\right)$$

$$\frac{1}{\lambda} = 109678 \times \frac{1}{4}\,\text{cm}^{-} = 27419.5\,\text{cm}^{-}$$

$$\therefore \quad \lambda = \frac{1}{27419.5\,\text{cm}^{-}}$$

$$= \mathbf{3.65 \times 10^{-5}\ cm} \qquad \textbf{Ans.}$$

Example 171. *Express Rydberg constant, R = 109678 cm^{-} into (i) J atom^{-} and (ii) J mol^{-}.*

Solution. (*i*) 1 cm^{-} = 1.99×10^{-23} J atom^{-}.

Hence, 109678 cm^{-} = $109678 \times 1.99 \times 10^{-23}$ J atom^{-}

= $\mathbf{2.18 \times 10^{-18}}$ **J (atom)$^{-}$** **Ans.**

(*ii*) 1 cm^{-} = 12.0 J mol, hence

109678 cm^{-} = 109678×12.0 J mol^{-}

= $\mathbf{1.32 \times 10^{6}}$ **J mol^{-}** **Ans.**

Type. Wave number, $\bar{\upsilon} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{cm}^{-}$ where R = Rydberg constant = 109678 cm^{-}, Z = atomic number of element, n_1 = number of the lower orbit and n_2 = number of the higher orbit.

Example 172. *Assuming that reduced mass effects are neglected,*

(*i*) *Calculate the optical transition in the He$^+$ spectrum that would have the same wavelength as the first Lyman transition of hydrogen i.e., $n_1 = 1$ and $n_2 = 2$.*

(*ii*) *Calculate the second ionisation potential of He.*

(*iii*) *Calculate the radius of first Bohr orbit for He$^+$.*

Solution. (*i*) Number of electrons in $_2He^+ = 2 - 1 = 1$. So, it is a hydrogen like species with $Z = 2$. So, we can apply the following Bohr's equation

$$\bar{\upsilon} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For H-atom, $Z = 1$. For first Lyman series,

$n_1 = 1, n_2 = 2$.

$$\text{Thus :} \quad \bar{\upsilon} = R\,(1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3R}{4};$$

$$\frac{1}{\lambda} = \frac{3R}{4};\ \lambda = \frac{4}{3R} \qquad \text{...(A)}$$

The assumption regarding mass effects is equivalent to considering R for He$^+$ the same as for H. The term Z^2 can just be compensated by increasing n_1 and n_2 by a factor of 2 each. So, $n_1 = 1 \times 2 = 2$; $n_2 = 2 \times 2 = 4$. Hence :

$$\bar{\upsilon} = R(2)^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right);$$

$$= R \times 4 \times \frac{3}{16} = \frac{3R}{4}$$

$$\frac{1}{\lambda} = \frac{3R}{4};\ \lambda = \frac{4}{3R}$$

which is same as found in equation (A). Hence the transition in question will be from $n = 4$ to $n = 2$.

(*ii*) The second ionisation potential of He is same as the ionisation potential for He$^+$. The Bohr equations can be applied to the ground state of He$^+$ for which $n = 1$ and $Z = 2$. Since energy of Bohr level depends upon Z^2 and mass correction of deuterium (^{2}D) is closer to that of He$^+$ than to that for ^{1}H, we have :

I.P. (He$^+$) = $Z^2 \times$ I.P. (^{2}D) = $(2)^2 \times 13.6$ eV

= **54.4 eV** **Ans.**

(*iii*) We know that radius for nth orbit is given as :

$$r_n = \frac{n^2 a_0}{Z}$$

where a_0 = Bohr's radius for first orbit, $Z = 2$, $n = 1$. So,

$$r_1 = \frac{(1)^2 \times 0.529\text{Å}}{2} = \mathbf{0.264\ Å} \qquad \textbf{Ans.}$$

Example 173. *Calculate the energy of a positron in the first Bohr orbit of a H-atom. Assume that such an atom exists.*

Solution. Positron is a positive electron (e^+). The characteristics of a positron are the same as that of the electron (e^-) except for the sign of its charge. It would cause its energy in the atom to be opposite to that of the electron. So, energy of positron is +13.6 eV and not –13.6eV which is the value of an electron.

Example 174. *For deuterium (^2_1H or ^2_1D), the value of Rydberg constant is 109707 cm^{-}. (This value reflects a refinement* *of simple Bohr theory, wherein the orbital radii and Rydberg constant do not depend on electron mass but on the so called reduced mass. The latter mass, in turn, varies slightly with the mass of the nucleus).*

Find (i) shortest wavelength in the absorption spectrum of deuterium (ii) the ionisation potential of deuterium.

Solution. (*i*) R for ${}_1^2\text{H}$ = 109707 cm^{-}. The shortest wavelength transition corresponds to highest frequency and hence to the highest energy ($\because E = h\upsilon$). So, the transition will be from ground state (lowest energy state) for which $\boldsymbol{n = 1}$ to the highest state for which $\boldsymbol{n = \infty}$.

Hence, $$\bar{\upsilon} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)\text{cm}^{-}$$

$$= 109707 \times 1^2\left(\frac{1}{1^2}-\frac{1}{(\infty)^2}\right)\text{cm}^{-}$$

or $$\frac{1}{\lambda} = 109707\,(1-0)\,\text{cm}^{-} = 109707\,\text{cm}^{-}$$

$$\therefore \quad \lambda = \frac{1}{109707\,\text{cm}^{-}} = 9.1152 \times 10^{-6}\,\text{cm}$$

$$= 9.1152 \times 10^{-6}\,\text{cm} \times \frac{10^7\,\text{nm}}{1\,\text{cm}}$$

or λ = **91.152 nm** **Ans.**

(*ii*) In fact, the transition computed in (*i*) above is the ionisation of the atom in the ground state. We know that frequency (υ) equivalent of 1 eV from Planck equation is given as :

$$\upsilon = \frac{E}{h} = \frac{1.6022\times10^{-19}\,\text{J}}{6.626\times10^{-34}\,\text{Js}} = 2.418 \times 10^{14}\,\text{s}^{-}$$

$$\therefore \quad \lambda = \frac{c}{\upsilon} = \frac{3.0\times10^{8}\,\text{ms}^{-}}{2.418\times10^{14}\,\text{s}^{-}} = 1.2407\,\text{m}$$

$$= 1.2407\,\text{m} \times 10^{-6}\,\text{m} \times \frac{10^9\,\text{nm}}{1\text{m}}$$

$$= 1240.7\,\text{nm}.$$

From $v = \dfrac{E}{h}$ and $\lambda = \dfrac{c}{\upsilon}$, we have $\lambda = \dfrac{ch}{E}$; $\lambda E = ch$

or $\lambda E = ch = 1240.7$ nm eV

$$\therefore \quad \text{I.P.} = \frac{1240.7\,\text{nm eV}}{91.152\,\text{nm (from result of }(i)\text{ above)}}$$

$$= 13.61\,\text{eV}$$

This value is a bit greater than that for ${}^1\text{H}$.

Example 175. *The Rydberg constant for deuterium (${}_1^2H$) is 109707 cm⁻. Calculate the radii of first three Bohr orbits.*

Solution. We know, $r = \dfrac{n^2 a_0}{Z}$ where r = radius of the orbit, n = number of the orbit, a_0 = 0.529 Å, Z = atomic number of element = 1 (for ${}_1^2\text{H}$). Hence :

(*i*) For first orbit

$$(n = 1),\ r = \frac{(1)^2\times 0.529\text{Å}}{1} = \mathbf{0.529\ Å} \qquad \textbf{Ans.}$$

(*ii*) For second orbit

$$(n = 2),\ r = \frac{(2)^2\times 0.529\text{Å}}{1} = \mathbf{2.116\ Å} \qquad \textbf{Ans.}$$

(*iii*) For third orbit

$$(n = 3),\ r = \frac{(3)^2\times 0.529\text{Å}}{1} = \mathbf{4.761\ Å} \qquad \textbf{Ans.}$$

Example 176. *Calculate the wave number of first line in the Balmer series of Be^{3+} if wave number of first line in the Balmer series of hydrogen is 15200 cm⁻.*

Solution. Z for Be^{3+} = 4. We know :

$$\Delta E_{\text{Be}} = \Delta E_H \times Z^2;$$

$$\Delta E_{\text{Be}} = 15200\,\text{cm}^{-} \times (4)^2;$$

$$\Delta E_{\text{Be}} = \mathbf{2.43 \times 10^5\ cm^{-}} \qquad \textbf{Ans.}$$

Type. $\lambda = k\left[\dfrac{1}{n_1}-\dfrac{1}{n_2}\right]$ where k = 136.52Å, λ = wavelength of the spectral line, n_1 and n_2 are the number of lower and higher orbits.

Example 177. *On absorbing a photon by H-atom, an electron got excited and reached fifth orbit. When the excited atom returned to its ground state, visible and other quanta were emitted. Radiation of what wavelength must have been emitted ? Explain it.*

Solution. Visible region indicates the fall of electron to the second orbit. After this, the transition 2 → 1 must take place for the atom to return to its ground state (n = 1). Hence:

$$\bar{\upsilon} = 109678\left(\frac{1}{1^2}-\frac{1}{2^2}\right)\text{cm}^{-}$$

$$= 82258\,\text{cm}^{-}$$

or $$\frac{1}{\lambda} = \frac{1}{82258\,\text{cm}^{-}} = 1.22 \times 10^{-5}\,\text{cm}$$

$$= 1.22 \times 10^{-5}\,\text{cm} \times \frac{10^8\,\text{Å}}{1\text{cm}}$$

$$= \mathbf{1220Å} \qquad \textbf{Ans.}$$

Example 178. *At what value of Z (minimum), would a transition from second orbit to the first orbit result in the emission of X-rays ? Also estimate the minimum difference in energy between two Bohr orbits such that an electronic transition would correspond to the emission of an X-ray, if the wavelength of lowest energy X-rays is 4.0 × 10^{-8} m.*

Solution. $\lambda = 4.0 \times 10^{-8}$m. But $E = hv = \dfrac{hc}{\lambda}$

$$= \frac{6.626\times10^{-34}\,\text{Js}\times3\times10^{8}\,\text{ms}^{-}}{4.0\times10^{-8}\,\text{m}}$$

$$\therefore \quad E = 4.97 \times 10^{-18}\,\text{J}$$

But $\Delta E_H = 2.178 \times 10^{-18}\,\text{J}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$= 2.178 \times 10^{-18}\text{J}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$= 2.178 \times 10^{-18}\text{J} \times \frac{3}{4} = 1.63 \times 10^{-18}\text{J}$$

$\therefore$ $\Delta E = \Delta E_H(Z^2)$.

or $Z^2 = \frac{\Delta E}{\Delta E_H} = \frac{4.97 \times 10^{-18}\,\text{J}}{1.63 \times 10^{-18}\,\text{J}} = 3.05$

$\therefore$ $Z = (3.05)^{1/2} \simeq 2$ *i.e.*, helium atom.

Example 179. *Calculate the quotient from the Bohr theory,* $\frac{2\pi^2k^2me^4}{Ch^3}$. *Compare the result so obtained with Rydberg constant (=* $1.09 \times 10^5\ cm^{-}$*).*

Solution. $\frac{2\pi^2k^2me^4}{ch^3}$.

$$= \frac{2 \times (3.14)^2 \times \left(9.0 \times 10^9 \frac{\text{Jm}}{\text{C}^2}\right)^2 \times 9.1 \times 10^{-31}\text{kg} \times (1.6 \times 10^{-19}\text{C})^4}{3.0 \times 10^8\,\text{ms}^{-} \times (6.626 \times 10^{-34}\text{Js})^3}$$

$$= 1.09 \times 10^7\ \text{kg J}^{-}\text{s}^{-2}\text{m} = 1.09 \times 10^7\ \frac{\text{kg s}^{2-}\text{m}}{\text{kg m}^2\text{s}^{2-}}$$

$[\because 1\text{J} = \text{kg m}^2\text{s}^{-2}]$

$$= 1.09 \times 10^7\text{m}^{-} = 1.09 \times 10^7\text{m}^{-} \times \frac{10^{-2}\text{cm}^{-}}{1\text{m}^{-}}$$

$$= 1.09 \times 10^5\ \text{cm}^{-}$$

The above result up to three significant figures is the same as the value of Rydberg constant.

Example 180. *How will you show that radius of first Bohr orbit (a_0) is 0.529 Å with the help of permittivity of free space instead of coloumb's law constant ?*

($\varepsilon_0 = 8.854 \times 10^{-12}\ C^2/Nm^2$, $h = 6.626 \times 10^{-34}Js$).

Solution. We know, $a_0 = \frac{\varepsilon_0 h^2}{\pi me^2}$ where m and e are the mass and charge on the electron.

Hence : $a_0 = \frac{8.854 \times 10^{-12}\text{C}^2}{\text{N.m}^2}$

$$\times \frac{(6.626 \times 10^{-34}\text{Js})^2}{3.14 \times 9.109 \times 10^{-31}\text{kg} \times (1.602 \times 10^{-19}\text{C})^2}$$

$$= \frac{5.29 \times 10^{-11}\text{J}^2\text{s}^2}{\text{Nm}^2 \times \text{kg}} = \frac{5.29 \times 10^{-11}\text{J}^2\text{s}^2}{\text{Nm} \times \text{m} \times \text{kg}}$$

$$= \frac{5.29 \times 10^{-11}\text{J}^2\text{s}^2}{\text{J} \times \text{m} \times \text{kg}} = \frac{5.29 \times 10^{-11}\text{Js}^2}{\text{m} \times \text{kg}}$$

$$= \frac{5.29 \times 10^{-11}\text{kg m}^2\text{s}^{-2} \times \text{s}^2}{\text{m} \times \text{kg}}$$

$$= 5.29 \times 10^{-11}\ \text{m}$$

$$= 5.29 \times 10^{-11}\ \text{m} \times \frac{10^{10}\,\text{Å}}{1\text{m}} = 0.529\ \text{Å}$$

$[\because 1\ \text{Nm} = \text{J};\ \text{J} = \text{kg m}^2\text{s}^{-2}]$

12.15 ELECTRONIC CONFIGURATION OF ELEMENTS

For subsidiary quantum number or azimuthal quantum number (l)* :

The orbital angular momentum (μ or μ_l) of the electron

$$= [l\,(l+1)]^{1/2} \cdot \frac{h}{2\pi} = [l\,(l+1)]^{1/2}\hbar$$

Example 181. *Calculate the orbital angular momentum of an electron in (i) 3s, (ii) 4p, (iii) 5d orbitals.*

Solution. We know that orbital angular momentum

$$(\mu) = (l\,(l+1))^{1/2}\ \frac{h}{2\pi} = [l\,(l+1)]^{1/2}\hbar.$$

(*i*) *For 3s orbital,* $l = 0$.

Thus, $\mu = [0\,(0+1)]^{1/2}\hbar$ = zero. **Ans.**

(*ii*) For 4*p* orbital, $l = 1$.

Thus, $\mu = [1\,(1+1)]^{1/2}\hbar = (2)^{1/2}\hbar$ **Ans.**

(*iii*) For 5*d* orbital, $l = 2$.

Thus, $\mu = [2\,(2+1)]^{1/2}\,\hbar = (6)^{1/2}\hbar$ **Ans.**

Example 182. *Name the orbitals which correspond to following set of quantum numbers.*

(*i*) $n = 2, l = 1, m = -1,$ (*ii*) $n = 3, l = 1, m = \pm 1,$

(*iii*) $n = 3, l = 2, m = \pm 2,$ (*iv*) $n = 4, l = 0, m = 0.$

Solution. (*i*) $2p_x$ or $2p_y$; (*ii*) $3p_x$ or $3p_y$; (*iii*) $3d_{x^2-y^2}$ or $3d_{xy}$; (*iv*) 4*s*.

Example 183. *How many 4s electrons are there in an atom with atomic number, 19?*

Solution. Electronic configuration of element with atomic number, 19 = $1s^22s^22p^63s^23p^64s^1$. Hence, there is one electron in 4s subshell.

Example 184. *A compound of titanium has a magnetic moment of 1.73 BM. Find the electronic configuration of titanium in the compound.*

Solution. We know that, magnetic moment = $[n\,(n+2)]^{1/2}$ where n is the number of unpaired electrons. Thus : $[n\,(n+2)]^{1/2} = 1.73$. Squaring both sides, we get :

$n\,(n+2) = (1.73)^2$ **or** $n^2 + 2n - 2.9929 = 0$

$$n = \frac{-2 \pm \sqrt{2^2 - 4(1 \times -2.9929)}}{2 \times 1}$$

$$\left[\because n = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ for } ax^2 + bx + c = 0\right]$$

$$= \frac{-2 \pm \sqrt{4 + 11.9716}}{2}$$

$$= \frac{-2 + \sqrt{15.9716}}{2}$$

$$= \frac{-2+3.996}{2} = \frac{1.996}{2}$$

$$= .998;\ n \approx 1$$

Thus, titanium ion will have one unpaired electron. Hence, titanium ion having one unpaired electron is $_{22}Ti^{3+}$ having 19 electrons. Its electronic configuration = $1s^22s^22p^63s^23p^63d^1$.

EXAMPLE 185. *Find the velocity (in ms⁻) of electron in first Bohr's orbit of radius a_0. Also, find the de Broglie's wavelength (in m). Find the orbital angular momentum of 2p orbital of hydrogen atom in units of* $\frac{h}{2\pi}$· **[IIT–JEE (mains), 2005]**

SOLUTION. (*a*) For H-atom,

$$Z = 1, n = 1 \text{ i.e., first orbit.}$$

But velocity, $v = 2.18 \times 10^6 \times \frac{Z}{n}\text{ms}^{-}$

$$= 2.18 \times 10^6 \times \frac{1}{1}\text{ms}^{-}.$$

de-Broglie wavelength,

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626 \times 10^{-34}\text{kg m}^2\text{s}^{-}}{9.1 \times 10^{-31}\text{kg} \times 2.18 \times 10^6\text{ms}^{-}}$$

or $\boldsymbol{\lambda = 3.34 \times 10^{-10}}$**m.**

Note: (*i*) Maximum number of electrons in a shell (n) = $2n^2$; for a given value of n, l = 0 to n – 1; for a given value of l, m = –l to 0 to + l; $s = \pm \frac{1}{2}$ for each value of m; **no. of subshells** in a shell (n) = n.

(*ii*) **no. of electrons in a subshell (l) = 2 (2l + 1) = 4l + 2. (CBSE-PMT, 2009)**; no. of orbitals in a subshell (l) = 2l + 1; no. of orbitals in a shell (n) = n^2.

(*b*)Orbital angular momentum

$$= [l(l+1)]^{1/2}.\frac{h}{2\pi}$$

For 2 *p*-orbital l = 1. Hence :

Orbital angular momentum

$$= [(1+1)]^{1/2}.\frac{h}{2\pi} = \mathbf{(2)^{1/2} \times \frac{h}{2\pi}} \quad \textbf{Ans.}$$

EXAMPLE 186. *Give the electronic configuration of the following ions (i) H⁻, (ii) Na⁺, (iii) F⁻, (iv) Mg²⁺.* **(DSB, 1984)**

SOLUTION. (*i*) Number of electrons in $_{11}Na^+$ (= 11 – 1 = 10), $_9F^-$ (= 9 + 1 = 10) and $_{12}Mg^{2+}$ (12 – 2 = 10). Electronic configuration for all these ions is same *i.e.*, $1s^22s^22p^6$.

EXAMPLE 187. *Give the electronic configuration of : (i) scandium (at. no. 21); and chromium (at. no. 24).* **(DSB, 1983)**

SOLUTION. Electronic configuration of $_{21}Sc = 1s^22s^22p^6 3s^23p^63d^14s^2$; electronic configuration of chromium, $_{24}Cr = 1s^22s^22p^63s^23p^63d^54s^1$.

EXAMPLE 188. *What is the maximum number of unpaired electrons in Ca, Cr and Br⁻ ?*

SOLUTION. (*i*) Electronic configuration of

$$_{20}Ca = 1s^22s^22p^63s^23p^64s^2 \text{ i.e., } \overset{4s}{\boxed{\upharpoonleft\downharpoonright}}$$

So, number of unpaired electrons in Ca = zero. (*ii*) Electronic configuration of $_{24}Cr = 1s^22s^22p^63s^23p^63d^54s^1$,

$$\overset{3d}{\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}} \quad \overset{4s}{\boxed{\upharpoonleft}}$$

i.e., six unpaired electrons. (*iii*) Electronic configuration of $_{35}Br^-$ (= 35 + 1 = 36 electrons) = $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$*i.e.*, no unpaired electron.

EXAMPLE 189. *One unpaired electron in an atom contributes a magnetic moment of 1.1 BM. Calculate the magnetic moment of chromium (at. no. 24).* **(CBSE, Sample Paper)**

SOLUTION. Electronic configuration of

$$_{24}Cr = 1s^22s^22p^63s^23p^63d^54s^1$$

$$\text{i.e., } \overset{3d}{\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}} \quad \overset{4s}{\boxed{\upharpoonleft}}$$

i.e., six unpaired electrons. Since, magnetic moment for one unpaired electron = 1.1 B.M. so, magnetic moments for six unpaired electrons = 6 × 1.1 = **6.6 B.M.** **Ans.**

EXAMPLE 190. *Name the tripositive metal ion represented by the configuration (i) $1s^22s^22p^63s^23p^63d^3$, (ii) $1s^22s^22p^63s^23p^6$.* **(CBSE, 1997)**

SOLUTION. (*i*) No. of electrons in metal atom of tripositive ion = 21 + 3 = 24. So, the ion with atomic number 24 is **Cr^{3+}**. (*ii*) No. of electrons in metal atom of tripositive ion = 18 + 3 = 21. So, the ion with atomic number 21 is **Sc^{3+}**.

EXAMPLE 191. *Arrange the following orbitals in order of increasing energy; 5s, 3p, 3d, 5f, 4p, 6s, 6p.*

SOLUTION. $n + l$ values for given orbitals in 5*s* (5 + 0 = 5), 3*p* (= 3 + 1 = 4), 3*d* (= 3 + 2 = 5), 5*f* (= 5 + 3 = 8), 4*p* (= 4 + 1 = 5), 6*s* (= 6 + 0 = 6) and 6*p* (= 6 + 1 = 7). According to aufbau principle, an orbital with less value of $n + l$ has less energy and filled first. Also, for orbitals with same value of $n + l$, the orbital with less value of n has lower energy and filled first. Hence the order of orbitals with increasing energy is, 3*p* < 3*d* < 4*p* < 5*s* < 6*s* < 6*p* < 5*f*.

EXAMPLE 192. *An electron is present in 4f subshell. Give the possible values of its four quantum numbers.*

SOLUTION. For 4*f* subshell, n = 3, l = 3. When l = 3, m = – l to 0 to + l = – 3 to 0 to + 3. So, m = 0, –1, –2, –3, +1, +2 or +3; s = +1/2 or –1/2 for each value of m.

EXAMPLE 193. *What designation is given to an orbital having (i) n = 3, l = 1, (ii) n = 4, l = 0 ?* **(PSEB, 1996)**

SOLUTION. (*i*) When l = 1, it is *p*-subshell. So, the orbital is 3*p*. (*ii*) When l = 0, it is *s*-subshell. So, the orbital is 4*s*. **Ans.**

EXAMPLE 194. *An electron is present in 4s subshell. Find the possible values of n, l and m.*

SOLUTION. For 4*s* subshell, n = 4, l = 0. When l = 0,

$m = -l$ to 0 to $+ l = 0$. So, for an electron, $m = 0$.

EXAMPLE 195. *What values of magnetic quantum number, m are permitted for an electron having angular momentum quantum number value, l = 2 ?* **(CBSE, 1997)**

SOLUTION. $l = 2$ (given). But values of $m = -l$ to 0 to $+l$. Hence $m = -2$ to 0 to $+2$ *i.e.,* $m = -2, -1, 0, +1$ and $+2$.

EXAMPLE 196. *What values are permitted from the angular momentum quantum number l for an electron with principal quantum number, n = 4 ?* **(CBSE, 1997)**

SOLUTION. $n = 4$ (given). When $n = 4$, $l = 0$ to $n-1 = 0$ to $4-1 = 0$ to $3 = 0, 1, 2$ and 3. **Ans.**

EXAMPLE 197. *If n = 3, what are the values of l and m ?* **(AISB, 1980)**

SOLUTION. When $n = 3$, $l = 0$ to $n-1$ or 0 to $3-1$ or 0 to 2 *i.e.,* **0, 1, 2,**. When $l = 2$, $m = -l$ to 0 to $+l = -2$ to 0 to $+2$ *i.e.,* $-2, -1, 0, +1, +2$.

Similarly, when $l = 0, m = 0; l = 1, m = -1, 0, +1$. **Ans.**

EXAMPLE 198. *For a particular atom, the maximum value of 'm' obtained from experiment is +1. What are all the possible values of n, l and m ?*

SOLUTION. Maximum value of $m = +1$. But values of $m = -l$ to 0 to $+1$; $\therefore\ l = 0, + 1$. But $l = 0$ to $n-1$ or $1 = n-1$ or $n = 1 + 1 = 2$. Thus, $n = 2, l = 0, 1; m = -l$ to 0 to $+ l$ or $-1, 0, +1$ **Ans.**

EXAMPLE 199. *An element has atomic number 12. Find out its electronic configuration, name of the element and quantum number of its valence shell electrons.*

SOLUTION. Number of electrons in a neutral atom = at. no. of element = 12. The element with at. no. 12 is **magnesium.**

Electronic configuration = $1s^2 2s^2 2p^6 3s^2$. Quantum numbers of $3s^2$ (*i.e.,* valence electrons) electrons = $n = 3$, $l = 0$, $m = 0$ and $s = +\frac{1}{2}$ and $-\frac{1}{2}$.

EXAMPLE 200. *Calculate total spin and magnetic moment for the atoms of elements having atomic number as 10 and 24.*

SOLUTION.

Atomic number of element	*Electronic configuration of the element*	*No. of unpaired electrons*
10	$1s^2\ 2s^2\ 2p^6$	0
24	$1s^{2'}\ 2s^2\ 2p^6;\ 3s^2\ 3p^{6'}\ 4s^1, 3d^5$	6

We know that :

Total spins for an atom

$$= \pm\frac{1}{2} \times \text{No. of unpaired electrons}$$

Total spins for Neon atom

$$= \pm\frac{1}{2} \times 0 = 0$$

Total spins for chromium atom

$$= \pm\frac{1}{2} \times 6 = \pm 3$$

We also know that : Magnetic moment

$$\mu = \sqrt{n(n+2)}\text{B.M.}$$

where n = No. of unpaired electrons

For neon atom, $\mu = 0$

For chromium atom,

$$\mu = \sqrt{6(6+2)} = \sqrt{48} = 6.93\,\text{B.M.}$$

EXAMPLE 201. *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. We know that, magnetic moment,

$$\mu = \sqrt{n(n+2)}$$

where [n = number of unpaired electrons]

$$1.73 = \sqrt{n(n+2)}$$

$\therefore$ $n = 1$ [After solving we get $n = 1$]

So, vanadium ion contains only one unpaired electron.

But, ${}_{23}\text{V} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$,

so $\text{V}^{4+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

(will have one unpaired electron).

EXAMPLE 202. *Give the various quantum numbers of valence electrons of potassium whose atomic number is 19.* **(OJEE, 1990)**

SOLUTION. Electronic configuration of K is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. Therefore, valence electron is $4s$ electron and its quantum numbers are :

$$n = 4, l = 0, m = 0, s = +1/2 \text{ or } -1/2.$$

EXAMPLE 203. *Write all the quantum numbers for all the electrons with n = 3.* **(Pb CET, 1990)**

SOLUTION. For $n = 3, l = 0, 1$ and 2.

For $l = 0$ (s-subshell), $m = 0$.

$l = 1$ (p-subshell), $m = 1, 0, -1$;

$l = 2$ (d-subshell) $m = 2, 1, 0, -1, -2$

Thus for $n = 3$, there are 9 different orbitals which can accommodate 18 electrons. Quantum numbers for these electrons are :

$$3s\begin{cases} e_1(n=3, l=0, m=0, s=+\frac{1}{2}) \\ e_2(n=3, l=0, m=0, s=-\frac{1}{2}) \end{cases} \quad 3p\begin{cases} e_3(n=3, l=1, m=1, s=+\frac{1}{2}) \\ e_4(n=3, l=1, m=1, s=-\frac{1}{2}) \\ e_5(n=3, l=1, m=0, s=+\frac{1}{2}) \\ e_6(n=3, l=1, m=0, s=-\frac{1}{2}) \\ e_7(n=3, l=1, m=-1, s=+\frac{1}{2}) \\ e_8(n=3, l=1, m=-1, s=-\frac{1}{2}) \end{cases}$$

$$3d\begin{cases} e_9(n=3, l=2, m=2, s=+\frac{1}{2}) \\ e_{10}(n=3, l=2, m=2, s=-\frac{1}{2}) \\ e_{11}(n=3, l=2, m=1, s=+\frac{1}{2}) \\ e_{12}(n=3, l=2, m=1, s=-\frac{1}{2}) \\ e_{13}(n=3, l=2, m=0, s=+\frac{1}{2}) \\ e_{14}(n=3, l=2, m=0, s=-\frac{1}{2}) \\ e_{15}(n=3, l=2, m=-1, s=+\frac{1}{2}) \\ e_{16}(n=3, l=2, m=-1, s=-\frac{1}{2}) \\ e_{17}(n=3, l=2, m=-2, s=+\frac{1}{2}) \\ e_{18}(n=3, l=2, m=-2, s=-\frac{1}{2}) \end{cases}$$

EXAMPLE 204. *An atom of an element has 19 electrons. What is the total number of p-electrons.* **(HP Board, 2007, 2012)**

SOLUTION. Number of electrons = 19

Electronic configuration = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

$\therefore$ Number of p-electrons = 6(of $2p$) + 6(of $3p$)

= **12** **Ans.**

EXAMPLE 205. *Can an electron have the quantum number values as, n = 2, l = 2 and m = +2 ?* **(HP Board, 2007)**

SOLUTION. $n = 2$; values of $l = 0$ to $n - 1 = 0$ to $2 - 1 = 0$ to 1 *i.e.*, 0 and 1. Since for $n = 2$, l has only two values 0 and 1 but not 2, so, electron having $n = 2$ value cannot have $l = 2$ value.

EXAMPLE 206. *Using s, p, d notations, describe orbitals with the following quantum numbers.*

(*i*) $n = 1, l = 0$ (*ii*) $n = 3, l = 2$.

(HP Board, 2007

SOLUTION. (*i*) For $n = 1, l = 0$, it is 1*s* orbital

(*ii*) For $n = 3, l = 2$, it is 3*d* orbital.

EXAMPLE 207. *An electron is present in 4f-subshell. Write the possible values of quantum numbers l and m.*

(HP Board, 2007)

SOLUTION. For 4*f*-subshell, $n = 4, l = 3$. Values of $m = -l$ to 0 to $+l$. Hence, $m = -3$ to 0 to +3 *i.e.*, –3, –2, –1, 0, +1, +2 or +3.

EXAMPLE 208. *How many orbitals are possible in a d-subshell ?* **(HP Board, 2007)**

SOLUTION. For d-subshell, $l = 2$. But :

no. of orbitals in a subshell = $2l + 1 = (2 \times 2) + 1 = 5$. *i.e.* $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}$ and d_{z^2}

EXAMPLE 209. *The number of unpaired electrons in Ni(CO)$_4$ is :*

(*a*) *zero* (*b*) *1*

(*c*) *3* (*d*) *4* **(H.P. Board, 2007)**

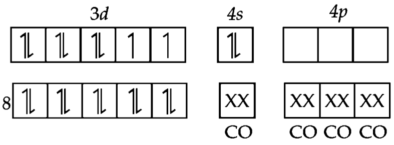
SOLUTION. The oxidation state of Ni in Ni(CO)$_4$ is calculated as :

O.N. of Ni + 4(O.N. of CO)) = 0 ; O.N. of Ni + 4(0) = 0

$\therefore$ O.N. of Ni = 0. At. no. of Ni = 28. Thus :

(*a*) $_{28}$Ni^0 is : (A*r*)^{18}

(*b*) Ni(CO)$_4$ is : (A*r*)^{18}



From the arrangement of electrons in Ni(CO)$_4$, we see that there is no unpaired electron. So, the correct answer is (*a*).

12.16 AIEEE PATTERN EXAMPLES

EXAMPLE 210. *Of the following, the electromagnetic radiation with maximum wavelength is :*

(*a*) *Ultraviolet* (*b*) *Radiowaves*

(*c*) *X-ray* (*d*) *Infra-red* **(BET, 2003)**

SOLUTION. We know, $E = hv = \frac{hc}{\lambda}\cdot$ Hence, $E \propto \frac{1}{\lambda}$ *i.e.*, smaller the wavelength, greater is the energy. The order of increasing wavelength is :

γ-rays < X-rays < U.V. < visible < I.R. < microwave < radiowaves. So, the correct answer is radiowaves. So, the correct answer is (*b*).

EXAMPLE 211. *Radius of second Bohr orbit of H-atom is....... times the first Bohr orbit of H-atom.*

(*a*) *4 times* (*b*) *2 times*

(*c*) *5 times* (*d*) *3 times* **(IMS-BHU, 2003)**

SOLUTION. We know, radius,

$R \propto n^2$; n = no. of the orbit.

$$\therefore \quad \frac{R_1}{R_2} = \frac{(1)^2}{(2)^2} = \frac{1}{4};$$

$R_2 = 4R_1$. So, the correct answer is (*a*).

EXAMPLE 212. *Maximum number of orbitals in h subshell are :*

(*a*) *16* (*b*) *11*

(*c*) *13* (*d*) *10* **(IMS-BHU, 2003)**

SOLUTION. We know that :

Subshell	*s*	*p*	*d*	*f*	*g*	*h*
Value of *l*	0	1	2	3	4	5

$\therefore$ For *h* subshell, $l = 5$. Hence no. of orbitals = $2l + 1$ = $(2 \times 5) + 1 = 11$. So, the correct answer is (*b*).

EXAMPLE 213. *The nitride ion in lithium nitride is composed of :*

(*a*) *10 protons + 10 electrons*

(*b*) *7 protons + 10 electrons*

(*c*) *10 protons + 7 electrons*

(*d*) *7 protons + 7 electrons* **(Karnataka, CET, 2000)**

SOLUTION. Lithium nitride = Li$_3$N. So, the nitride ion is $_7$N^{3-}.

In $_7$N^{3-}, no. of protons = 7; no. of electrons = 7 + 3 = 10. So, the correct answer is (*b*).

EXAMPLE 214. *For azimuthal quantum number, $l = 2$, the maximum number of electrons will be*

(a) 0 (b) 5

(c) 10 (d) 14

SOLUTION. For $l = 2$, $m = -l$ to 0 to $+l$; – 2 to 0 to +2 *i.e.*, –2, –1, 0 + 1 and +2 *i.e.*, five orbitals. Each orbital has 2 electrons. So, maximum number of electrons are, $5 \times 2 = 10$. So, the correct answer is (*c*).

EXAMPLE 215. *In which one of the following orbital diagrams, the Aufbau principle is violated ?*

(a) $\boxed{\upharpoonleft\downharpoonright}\ \boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$ (b) $\boxed{\upharpoonleft\downharpoonright}\ \boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}$

(c) $\boxed{\upharpoonleft}\ \boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}\boxed{\downharpoonright}$ (d) $\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$

SOLUTION. According to Aufbau principle, an orbital with lower energy is filled first. Since in orbital diagram (*c*), lower orbital is not fully filled, so the correct answer is (*c*).

EXAMPLE 216. *The angular momentum of electrons in 3d-orbitals is :*

(a) $\frac{h}{\pi}\left(\frac{2}{3}\right)^{1/2}$ (b) $\frac{h}{\pi}\left(\frac{3}{2}\right)^{1/2}$

(c) 1 (d) $\frac{h}{\pi}$

SOLUTION. Angular momentum in $3d = \frac{h}{2\pi}[l(l+1)]^{1/2}$
For *d*-orbital, $l = 2$. So :

Angular momentum in

$$3d = \frac{h}{2\pi}[2(2+1)]^{1/2} = \frac{h}{2\pi}(6)^{1/2}$$

$$= \frac{h}{\pi}\left(\frac{6}{4}\right)^{1/2} = \frac{h}{\pi}\left(\frac{3}{2}\right)^{1/2}.$$

So, the correct answer is (*b*).

EXAMPLE 217. *Calcium atom has 2, 8, 8, 2 electrons in K, L, M and N energy levels respectively. The number of electron/electrons with $m = 0$, $s = +\frac{1}{2}$ is/are :*

(a) 2 (b) 4

(c) 6 (d) 8

SOLUTION. The electron configuration of Ca-atom = $1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^2\,3s^2 3p_x^2\,3p_y^2 3p_z^2\,4s^2$. We know that the value of $m = -l$ to 0 to $+l$.

Also, $s = +\frac{1}{2}$ and $m = 0$ are to be considered only.

For

1*s*-orbital, ($l = 0$)	$n = 1$	$l = 0$	$m = 0$	$s = +\frac{1}{2}$	one electron
2*s*-orbital, ($l = 0$)	$n = 2$	$l = 0$	$m = 0$	$s = +\frac{1}{2}$	one electron
2*p*-orbital, ($l = 1$)	$n = 2$	$l = 1$	$m = -l$ to 0 to $+ l = -1, 0, +1$; $m = 0$	$s = +\frac{1}{2}$	one electron
3*s*-orbital, ($l = 0$)	$n = 3$	$l = 0$	$m = 0$	$s = +\frac{1}{2}$	one electron
3*p*-orbital, ($l = 1$)	$n = 3$	$l = 1$	$m = -1, 0, +1$, $m = 0$	$s = +\frac{1}{2}$	one electron
4*s*-orbital, ($l = 0$)	$n = 4$	$l = 0$	$m = 0$	$s = +\frac{1}{2}$	one electron

Hence number of electrons with $m = 0$ and $s = +\frac{1}{2}$ only, are six. So, the correct answer is (*c*).

EXAMPLE 218. *According to Bohr theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon?*

(a) $n = 6$ to $n = 1$ (b) $n = 5$ to $n = 4$

(c) $n = 6$ to $n = 5$ (d) $n = 5$ to $n = 3$

(AIPMT, 2011)

SOLUTION. Since energy change, $\Delta E = \left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$ where $n_2 > n_1$, the value of ΔE will be least, if the values of n_1 and n_2 are the highest. Here the highest values are $n_1 = 5$ and $n_2 = 6$, so the correct answer is (*c*)

EXAMPLE 219. *The energy of electron in first Bohr orbit of H-atoms is 13.6 eV. The possible energy value of electron in the excited state of Li^{2+} is:*

(a) –122.4eV (b) 30.6eV

(c) –30.6eV (d) –13.6eV

(WB-JEE, 2011)

SOLUTION. We know that $E_n = (E_1 \times Z^2)/n^2$ ...(*i*)
where Z = atomic number of ${}_3Li^{2+} = 3$, E_1 = energy of first orbit in *H*-atom = 13.6 eV., n = no. of orbit = 2. Substituting the values in (1), we get: $E = -13.6 \times (3)^2/2^2 = -30.6$ eV. So, the correct answer is (*c*)

EXAMPLE 220. *The mass of an electron = 9.1×10^{-28}g. The uncertainty in the position of an electron moving with a velocity of 4.2×10^4 cms⁻ accurate upto 0.011% will be*

(a) 125 cm (b) 12.5 cm

(c) 1.25 cm (d) 0.125 cm

SOLUTION. Uncertainty in position, Δx = ? Uncertainty in velocity = $4.2 \times 10^4 \text{ cm s}^{-} \times \frac{0.011}{100}$, mass, m of electron $= 9.1 \times 10^{-28}$ g, $h = 6.6 \times 10^{-27} \text{g cm}^2\text{s}^{-}$. According to Heisenberg's uncertainty principle,

$$\Delta x \times m\Delta v = \frac{h}{4\pi};$$

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

$$\text{or } \Delta x = \frac{6.6 \times 10^{-27}\,\text{g cm}^2\text{s}^{-} \times 100}{4 \times 3.142 \times 9.1 \times 10^{-28}\,\text{g} \times 4.2 \times 10^4\,\text{cms}^{-} \times 0.011}$$

= 0.125 cm

So, the correct answer is (*d*).

EXAMPLE 221. *The radius of fifth orbit of the hydrogen atom is :*

(*a*) *6.612 Å* (*b*) *13.225 Å*

(*c*) *26.45 Å* (*d*) *none of these*

SOLUTION. In case of H-atom; $n = 5$.

Radius of 5th orbit $= 0.529\, n^2 \text{Å} = 0.529 \times 5^2 \text{Å}$

$= 13.225$ Å

So, the correct answer is (*b*).

EXAMPLE 222. *The wave number of the first line in the Balmer series of hydrogen is 15200 cm*$^{-}$*. The wave number of the first line in the Balmer series of Be*$^{3+}$ *ion is :*

(*a*) *200 cm*$^{-}$ (*b*) *400 cm*$^{-}$

(*c*) *243 Å* (*d*) *2.432 × 10*^{5}*cm*$^{-}$

SOLUTION. At. no. (Z) for Be = 4

As $\Delta E_{Be^{3+}} = \Delta E_H \times Z^2_{Be}$,

Similarly, $\bar{\upsilon}_{Be^{3+}} = \bar{\upsilon}_H \times Z^2_{Be}$ ...(*A*)

We know : $\bar{\upsilon}_H = 15200 \text{ cm}^{-}$ (given). Substituting the value in equation (*A*), we get :

$\bar{\upsilon}_{Be^{3+}} = 15200 \text{ cm}^{-} \times (4)^2 = 2.432 \times 10^5 \text{ cm}^{-}$.

So, the correct answer is (*d*).

EXAMPLE 223. *The increase in distance from the nucleus when an electron in a hydrogen atom is excited from the first to the third orbit is :*

(*a*) *4.232 Å* (*b*) *4.232 nm*

(*c*) *423.2 pm* (*d*) *400 nm*

SOLUTION. $n_1 = 1, n_2 = 3$. Radius of *n*th orbit, $r_n = 0.529\, n^2$Å.

(*i*) When $n = 1, r = 0.529 \times 1^2 \text{Å} = 0.529$ Å

When $n = 3, r = 0.529 \times 3^2 \text{Å} = 4.761$ Å

∴ Increase in distance

$= 4.761 \text{ Å} - 0.529 \text{ Å} = 4.232$ Å

$= 4.232 \text{ Å} \times \frac{100 \text{ pm}}{1\text{Å}} = 423.2$ pm.

So, the correct answers are (*a*) and (*c*).

EXAMPLE 224. *The energy associated with an orbit having radius 16r*$_1$ *where r*$_1$ *is the radius of first orbit if energy associated with an orbit in the hydrogen atom is given by* $E_n = \frac{-13.6}{n^2} eV$*; is :*

(*a*) *–13.6 eV* (*b*) *–27.2 eV*

(*c*) *–0.85 eV* (*d*) *+13.6 eV*

SOLUTION. We know : $r_n = 0.529\, n^2$Å. For first orbit ($n = 1$) : $r_1 = 0.529 \times 1^2 \text{Å} = 0.529$ Å. For orbit under study : $16\, r_1 = 0.529 \times n^2$Å.

$$\therefore \quad \frac{16 r_1}{r_1} = \frac{0.529\, n^2 \text{Å}}{0.529 \text{Å}}; n^2 = 16.$$

But $E_n = \frac{-13.6}{n^2}$eV.

Hence, $E_n = \frac{-13.6}{16}\text{eV} = -0.85\text{eV}$.

So, the correct answer is (*c*).

EXAMPLE 225. *The energy difference between two energy states is 43.56 k cal mol*$^{-}$*. The frequency of light emitted when an electron jumps from higher orbit to lower orbit is*

(*a*) *4.15 × 10*$^{-12}$*s*$^{-}$ (*b*) *4.576 × 10*$^{-14}$*s*$^{-}$

(*c*) *10*$^{-15}$*s*$^{-}$ (*d*) *2.075 × 10*$^{-6}$*s*$^{-}$

(*h = 9.52 × 10*$^{-14}$ *k cal . s. mol*$^{-}$)

SOLUTION. We know that,

$$E = hv\ ; \upsilon = \frac{E}{h}$$

$$= \frac{43.56 \text{ k cal mol}^{-}}{9.52 \times 10^{-14} \text{k cal.s.mol}^{-}}$$

or $\upsilon = 4.576 \times 10^{-14} \text{s}^{-}$. So, the correct answer is (*b*).

EXAMPLE 226. *The energies of an electron in second and third Bohr's orbit of H-atom are –5.42 × 10*$^{-12}$ *erg and –2.41 × 10*$^{-12}$ *erg respectively. The wavelength of the emitted radiation when the electron drops from third to second orbit is :*

(*a*) *60Å* (*b*) *66 Å*

(*c*) *660 Å* (*d*) *6604Å*

(*h = 6.626 × 10*$^{-27}$ *erg s*)

SOLUTION. $E_1 = -5.42 \times 10^{-12}$ erg, $E_2 = -2.41 \times 10^{-12}$ erg

$\therefore \quad \Delta E = E_2 - E_1$

$= -2.41 \times 10^{-12} \text{ erg} - (-5.42 \times 10^{-12} \text{ erg})$

$= 3.01 \times 10^{-12}$ erg

But $\Delta E = h\upsilon = \frac{hc}{\lambda}$

$\therefore \quad \lambda = \frac{hc}{\Delta E}$

$$= \frac{6.626 \times 10^{-27} \text{erg.s} \times 3.0 \times 10^{10} \text{cms}^{-}}{3.01 \times 10^{-12} \text{erg}}$$

$= 6.604 \times 10^{-5}$ cm

$= 6.604 \times 10^{-5}\text{cm} \times \frac{1\text{Å}}{10^{-8}\text{cm}} = \mathbf{6604\ Å}$

($\because$ 1Å = 10^{-8}cm)

So, the correct answer is (*d*).

EXAMPLE 227. *If the energies of two photons are in the ratio of 3:2, their wave lengths will be in the ratio of :*

(*a*) *9 : 4* (*b*) *2 : 3*

(*c*) *1 : 2* (*d*) *3 : 2*

(Karnattka CET, 2011)

SOLUTION. $E \propto 1/\lambda$ (Planck's quantum theory). So, $\frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1}$ or $\frac{3}{2} = \frac{\lambda_2}{\lambda_1}$. Hence $\lambda_1 : \lambda_2 = 2 : 3$. So, the correct answer is (*b*)

EXAMPLE 228. *With the increase in the number of energy levels, the energy difference between different energy levels in atoms :*

(*a*) *remains constant*

(*b*) *decreases for atoms with lower atomic number than with higher atomic number*

(*c*) *decreases*

(*d*) *increases*

Solution.

$$E_1 = \frac{-13.6\,\text{eV}}{1^2} = -13.6\,\text{eV}.$$

$$E_2 = \frac{-13.6\,\text{eV}}{2^2} = -3.4\,\text{eV}$$

$$\therefore \quad E_2 - E_1 = -3.4 - (-13.6) = 10.4\ \text{eV};$$

$$E_3 = \frac{-13.6\,\text{eV}}{3^2} = -1.51\,\text{eV}$$

$$\therefore \quad E_3 - E_2 = -1.51 - (-3.4) = 1.89\ \text{eV}$$

$$E_4 = \frac{-13.6\,\text{eV}}{4^2} = -0.85\,\text{eV}$$

$$\therefore \quad E_4 - E_3 = -0.85 - (-1.51) = 0.66\ \text{eV}$$

Since $E_4 < E_3 < E_2 < E_1$, the true answer is (*c*).

Example 229. *The number of electrons in sulphur atom having $n + l = 3$ are :*

(*a*) 8 (*b*) 6

(*c*) 4 (*d*) 2

Solution. Sulphur ($Z = 16$) has electronic configuration $= 1s^2 2s^2 2p^6 3s^2 3p^4$. $n + l = 3$ is for :

(*i*) $2p$ because in this case, $n = 2, l = 1$. So, $n + l = 2 + 1 = 3$. Number of electrons in $2p$ sub-shell are **6**.

(*ii*) $3s$ because in this case, $n = 3, l = 0$. So, $n + l = 3 + 0 = 3$. Number of electrons in $3s$ sub-shell are **2**. Hence :

Total number of electrons = 6 + 2 = 8. So, true answer is (*a*).

Example 230. *The atom which contains an electron with quantum number $n = 3, l = 2, m = -1, s = -\frac{1}{2}$ is :*

(*a*) Li (*b*) F

(*c*) V (*d*) Na

Solution. The electronic configuration of given atoms is :

$_3\text{Li} = 1s^2 2s^1$; $_9\text{F} = 1s^2 2s^2 2p^5$; $_{23}\text{V} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$; $_{11}\text{Na} = 1s^2 2s^2 2p^6 3s^1$. For $n = 3, l = 2, m = -1$ and $s = -\frac{1}{2}$, the sub-shell is $3d$. Since $3d$ is present in vanadium, V, the correct answer is (*c*).

Example 231. *One of the following atoms that has same number of s electrons as the d-electrons in Cr^{3+} is :*

(*a*) Be (*b*) B

(*c*) C (*d*) Li

Solution. Electronic configuration of given atoms is :

(*a*) $_4\text{Be} = 1s^2 2s^2$. Here *s*-electrons = 2 + 2 = 4

(*b*) $_5\text{B} = 1s^2 2s^2 2p^1$. Here *s*-electrons = 2 + 2 = 4

(*c*) $_6\text{C} = 1s^2 2s^2 2p^2$. Here *s*-electrons = 2 + 2 = 4

(*d*) $_3\text{Li} = 1s^2 2s^1$. Here *s*-electrons = 2 + 1 = 3.

$_{24}\text{Cr}^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$. Here *d*-electrons = 3. Li has three *s*-electrons which are same as are present in Cr^{3+}. So, true answer is (*d*).

Example 232. *The orbital that has two angular nodal planes is :*

(*a*) *f* (*b*) *d*

(*c*) *p* (*d*) *s*

Solution. Angular node = azimuthal quantum number, *l*. For *f*-orbital, $l = 3$; *d*-orbital, $l = 2$; *p*-orbital, $l = 1$; for *s*-orbital, $l = 0$. From above, we see that $l = 2$ for *d*-orbital. So, true answer is (*b*).

Example 233. *The total spin in Fe^{2+} is :*

(*a*) $\pm\frac{1}{2}$ (*b*) ± 1

(*c*) $\pm\frac{3}{2}$ (*d*) ± 2

Solution.

$$_{26}\text{Fe} = (\text{Ar})^{18}\ \overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\quad \overset{4s}{\boxed{\uparrow\downarrow}};$$

$$\text{Fe}^{2+} = (\text{Ar})^{18}\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\quad \overset{4s}{\boxed{}}$$

Fe^{2+} has four unpaired electrons. Thus, total spins for 4 unpaired electrons $= 4 \times \pm\frac{1}{2} = \pm$ **2**. So, the true answer is (*d*).

Example 234. *A gas absorbs a photon of 355 nm and emits two wave lengths. If one of the emissions is at 680 nm, the other is at:*

(*a*) 1035 nm (*b*) 325 nm

(*c*) 743 nm (*d*) 518 nm

(AIEEE, 2011)

Solution. Since $E = h\nu = hc/\lambda$, so, for one wave length, λ_1 and second wave length, λ_2, we have energies E_1 and E_2 respectively.

$$\text{Thus:} \quad E = E_1 + E_2;\ \frac{hc}{\lambda} = \frac{hc}{\lambda_1} + \frac{hc}{\lambda_2};$$

$$\text{or} \quad \frac{1}{\lambda} = \frac{1}{\lambda_1} + \frac{1}{\lambda_2}$$

$$\therefore \quad \frac{1}{355} = \frac{1}{680} + \frac{1}{\lambda_2};\ \frac{1}{\lambda_2} = \frac{1}{355} - \frac{1}{680}$$

$$= \frac{680 - 355}{355 \times 680} = \frac{325}{355 \times 680}$$

$$\text{or} \quad \lambda_2 = \frac{355 \times 680}{325} \simeq 743\ \text{nm}.$$

So, the correct answer is (*c*).

Example 235. *The highest excited state that an unexcited H-atom can reach when these are bombarded with 12.75 eV electron is :*

(*a*) $n = 1$ (*b*) $n = 2$

(*c*) $n = 3$ (*d*) $n = 4$

Solution. We know, $E_1 = -13.6$ eV. After the absorption of 12.75 eV, the energy of electron = –13.6 + 12.75 = –0.85 eV. But $E_n = \frac{E_1}{n^2}\cdot$ Hence : $n^2 = \frac{E_1}{E_n} = \frac{-13.6\,\text{eV}}{-0.85\,\text{eV}} = 16$

or $n = (16)^{1/2} = 4$

Hence, the true answer is (*d*).

Example 236. *The wave number of the shortest wavelength transition in Lyman series of atomic hydrogen will be :*

(a) 3647 Å *(b) 109678 cm*

(c) 9.1 × 10^{-6}cm *(d) 9.1Å*

(Kerala PET, 2010)

Solution. Wave number, $\bar{\upsilon} = RZ^2\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$ ...(1)

R = 109678 cm^{-}, n_1 = 1 (for Lyman series), $n_2 = \infty$; Z = 1 (for H-atom). Substituting the values in (1), we get :

$$\bar{\upsilon} = 109678\ \text{cm}^{-} \times 1^2\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right)$$

$$= 109678\ \text{cm}^{-}(1-0) = 109678\ \text{cm}^{-}$$

or $$\lambda_{\text{shortest}} = \frac{1}{109678\ \text{cm}^{-}} = 9.1 \times 10^{-6}\ \text{cm}.$$

So, the true answer is (*c*).

Example 237. *A body of mass x kg is moving with a velocity of 100 ms⁻. Its de Broglie wavelength is 6.62 × 10^{-35} m. Hence x is (h = 6.62 × 10^{-34} Js) :*

(a) 0.25 kg *(b) 0.15 kg*

(c) 0.2 kg *(d) 0.1 kg*

(Karnataka CET, 2009)

Solution. Given, $\lambda = 6.62 \times 10^{-35}$ m, $h = 6.62 \times 10^{-34}$ Js or kg m^2 s^{-}, v = 100 ms^{-} and mass, $m = x$ kg.

But : $$\lambda = \frac{h}{mv} \text{ (de Broglie equation).}$$

Thus: $$6.62 \times 10^{-35}\ \text{m} = \frac{6.62\times10^{-34}\ \text{kg m}^2\text{s}^{-}}{x\times100\,\text{ms}^{-}}$$

$$\therefore \quad x = \frac{6{,}62\times10^{-34}\text{kg m}^2\text{s}^{-}}{6.62\times10^{-35}\text{m} \times 100\ \text{ms}^{-}}$$

$$= 0.1\ \text{kg}.$$

So, the correct answer is (*d*).

Example 238. *The energy of electron in the first Bohr orbit of H-atom is –13.6 eV. The possible energy value of the excited state (s) for electrons in Bohr orbits of hydrogen is:*

(a) –3.4 eV *(b) –4.2 eV*

(c) –6.8 eV *(d) + 6.8 eV*

(AMU, (engg), 2011)

Solution. Since, $E_n = (-13.6/n^2)$ eV and for first excited state, n = 2, so $E_n = -13.6/(2)^2 = -3.4$ eV. So, the correct answer is (*a*)

Example 239. *When the frequency of light incident on a metallic plate is doubled, the kinetic energy of the emitted photoelectron will be :*

(a) halved *(b) unchanged*

(c) increase but more than double of the previous K.E.

(d) doubled.

Solution. We know, K.E. = $h\upsilon - hv_0$ where h is Planck's constant, υ is frequency of incident light, υ_0 is the threshold frequency and $h\upsilon_0$ is work function. Since work function ($h\upsilon_0$) of the metal remains constant, on doubling the frequency, the energy of photon will be doubled. So, K.E. of photoelectron will be more than the double of what it possessed previously. So, true answer is (*c*).

Example 240. *The light energy required by the interior of human eye to see an object is 10^{-17}J. The number of photons of green light (λ = 550 nm) required to see the object will be :*

(a) 25 *(b) 26*

(c) 28 *(d) 30*

Solution. Required energy, E to see an object = 10^{-17}J. But $E = \frac{nhc}{\lambda}$ where n = number of photons, h is Planck's constant (= 6.625 × 10^{-34} Js), c is velocity of light (= 3 × 10^8ms^{-}) and λ = 550 × 10^{-9}m. Substituting the values, we get

$$10^{-17}\ \text{J} = \frac{n\times6.625\times10^{-34}\text{Js}\times3\times10^{8}\text{ms}^{-}}{550\times10^{-9}\text{m}}$$

$$\therefore \quad n = \frac{10^{-17}\text{J}\times550\times10^{-9}\text{m}}{6.625\times10^{-34}\text{J.s}\times3\times10^{8}\text{ms}^{-}}$$

$$= 27.64 \simeq \mathbf{28}.$$

So, the true answer is (*c*).

Example 241. *The total energy of an electron in a hydrogen like atom in excited state is –3.4eV. If velocity of the electron in nth orbit is 2.18 × 10^6 ms⁻/n, the de Broglie wavelength of the electron will be :*

(a) 3.3 × 10^{-5}cm *(b) 6.67 × 10^{-10}m*

(c) 9.9 × 10^{-15}cm *(d) 16.5 × 10^{-10}m*

Solution. We know, total energy of an electron in nth orbit = $\frac{E_1}{n^2}$ or $-3.4\text{eV} = \frac{-13.6\text{eV}}{n^2}$

$$\therefore \quad n^2 = \frac{-13.6\,\text{eV}}{-3.4\,\text{eV}} = 4$$

Hence $n = (4)^{1/2} = 2$

Velocity of electron

$$= \frac{2.18\times10^{6}\text{ms}^{-}}{n} = \frac{2.18\times10^{6}\text{ms}^{-}}{2}$$

$$= 1.09 \times 10^6\ \text{ms}^{-}$$

According to de Broglie equation :

$$l = \frac{h}{mv} \text{ or}$$

$$l = \frac{6.625\times10^{-34}\text{kg m}^2\text{s}^{-2}}{9.1089\times10^{-31}\text{kg}\times1.09\times10^{6}\text{ms}^{-}}$$

$$= 6.67 \times 10^{-10}\ \text{m}$$

So, correct answer is (*b*).

Example 242. *An electron, a proton and an α-particle have kinetic energies E_1, E_2 and E_3 respectively. If their de Broglie wavelength is same, then :*

(a) $E_1 > E_2 > E_3$ *(b) $E_2 > E_3 > E_1$*

(c) $E_3 > E_1 > E_2$ *(d) $E_1 > E_3 > E_2$*

Solution. $$\text{K.E.} = \frac{1}{2}mv^2 \quad ...(1)$$

and $$\lambda = \frac{h}{mv} \text{ or } v = \frac{h}{m\lambda} \quad ...(2)$$

Substituting the value of v from (2) in (1), we get :

$$\text{K.E.} = \frac{1}{2}\times m \times \frac{h^2}{m^2\lambda^2} = \frac{h^2}{2m\lambda^2}$$

Since mass (m) of electron < mass of proton < mass of α-particles, so, $E_1 > E_2 > E_3$. Thus the correct answer is (a).

Example 243. *The orbital angular momentum for an electron revolving in an orbit is given by* $[l\,(l+1)]^{1/2} \cdot \frac{h}{2\pi}$. *This momentum for an s-electron will be given by :*

(a) $\sqrt{2}\cdot\frac{h}{2\pi}$
(b) $+\frac{1}{2}\cdot\frac{h}{2\pi}$
(c) *zero*
(d) $\frac{h}{2\pi}$

(AIEEE, 2003)

Solution. For an s-electron, $l = 0$. Substituting $l = 0$ in $[l\,(l+1)]^{1/2} \cdot \frac{h}{2\pi}$, we get :

$[0\,(0+1)]^{1/2} \cdot \frac{h}{2\pi} = 0$ *i.e.*, zero. So, the correct answer is (c).

Example 244. *The number of d-electrons retained in* Fe^{2+} *(at. no. of Fe = 26) ion is :*

(a) 6
(b) 3
(c) 4
(d) 5 **(AIEEE, 2003)**

Solution. $_{26}Fe = (Ar)^{18}\ 3d^6 4s^2$. Thus $Fe^{2+} = (Ar)^{18} 3d^6$. So the number of d-electrons retained in Fe^{2+} = 6. So the correct answer is (a).

Example 245. *In Bohr series of lines of hydrogen spectrum, the third line from the red end corresponds to which one the following inter-orbit jumps of the electron for Bohr orbits in an atom of hydrogen ?*

(a) $3 \longrightarrow 2$
(b) $5 \longrightarrow 2$
(c) $4 \longrightarrow 1$
(d) $2 \longrightarrow 5$

(AIEEE, 2003)

Solution. The third line from the red end corresponds to yellow colour as shown below. Hence, $n_2 = 5$.

Violet, Indigo, Blue, Green, Yellow, Orange, Red, (third colour from red is yellow).

Thus *inter-orbit jump* of electron will be from 5 to less than 5. So, the correct answer is, (b).

Example 246. *If uncertainty in position and momentum are equal, then uncertainty in velocity is :*

(a) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$
(b) $\sqrt{\frac{h}{\pi}}$
(c) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$
(d) $\sqrt{\frac{h}{2\pi}}$

(CBSE–PMT, 2008 Prelims)

Solution. $\Delta x \times \Delta p \geq \frac{h}{4\pi}$ (Heisenberg's uncertainty principle)

or $\Delta x \times \Delta p \geq \frac{h}{4\pi}$. Since $\Delta x = \Delta p$ (given);

$\therefore\ (m\Delta v)^2 > \frac{h}{4\pi}$ ($\because \Delta p = m\Delta v$)

or $m^2 \Delta v^2 \geq \frac{h}{4\pi}$ *i.e.*; $\Delta v \geq \frac{1}{2m}\cdot\sqrt{\frac{h}{\pi}}$.

So, the correct answer is (c).

Example 247. *The wave number of first line of Balmer series of hydrogen is 15200* cm^{-}. *The wave number of the first Balmer line of* Li^{2+} *ion is :*

(a) 1.368 cm^{-}
(b) 8631 cm^{-}
(c) 136,800 cm^{-}
(d) $10^2 cm^{-}$

Solution. Atomic number, Z of Li = 3; wave number, $\bar{\upsilon}$ of hydrogen (H) = 15,200 cm^{-}. $_3Li^{2+}$ contains electrons = 1. So, it is hydrogen like species. For hydrogen like species, we have :

Wave number of first Balmer line of Li^{2+} ion = $\bar{\upsilon}_H \times Z^2$ = 15,200 $cm^{-} \times (3)^2$ = 15,200 $cm^{-} \times 9$ = 136,800 cm^{-}. So, the correct answer is (c).

Example 248. *The correct set of four quantum numbers for outermost electron of potassium (Z = 19) is :*

(a) 3, 1, 0, 1/2
(b) 4, 0, 0, 1/2
(c) 3, 0, 0, 1/2
(d) 4, 1, 0, 1/2

(Karnataka CET, 2009)

Solution. Electronic configuration of potassium, K (Z = 19) is $(Ar)^{18}\,4s^1$. Thus, the outermost configuration is $4s^1$. The various quantum numbers for this electron will be, $n = 4, l = 0, m = 0, s = 1/2$ because for $n = 4$, $l = 0$ to $n - l$ *i.e.*, 0 to 3; $m = -l$ to 0 to $+l$, for $l = 0$, $m = 0$; $s = +\frac{1}{2}$ or $-\frac{1}{2}$. So, the correct answer is (b).

Example 249. *The total number of electrons that can be accommodated in all the orbitals having principal quantum number 2 and azimuthal quantum number 1 is :*

(a) 2
(b) 6
(c) 10
(d) 14

Solution. Given, $n = 2$, $l = 1$. So, it is $2p$-subshell. p-subshell has maximum 6 electrons. So, the correct answer is (b).

Example 250. *As found experimentally, the energy of an electron in the first Bohr orbit for hydrogen is –13.6 eV. Which one of the following is possible excited state for electrons in Bohr's orbit of hydrogen ?*

(a) –2.92 eV
(b) +2.92 eV
(c) –3.4 eV
(d) +3.4 eV

Solution. For Bohr's first orbit, $n_1 = 1$. For excited states, $n_2 = 2, 3, 4$ etc. Also, $E_n = -k^2 \frac{2\pi^2 m Z^2 e^4}{n^2 h^2}$. So, excited states have energies; $E_n = \frac{E_1}{n^2}$

$$\therefore \quad \text{For } n = 1,\ E_1 = \frac{-13.6\,\text{eV}}{1^2} = -13.6\,\text{eV}$$

$$\text{For } n = 2,\ E_2 = \frac{-13.6\,\text{eV}}{2^2} = -3.4\,\text{eV}$$

$$\text{For } n = 3,\ E_3 = \frac{-13.6\,\text{eV}}{3^2} = -1.51\,\text{eV}.$$

So, the correct answer is –3.4 eV. Hence answer (*c*) is correct.

EXAMPLE 251. *For H-atom,* $E_n = -R_H\left(\frac{1}{n^2}\right)$ *where* $R_H = 2.178 \times 10^{-18}$*J. The wavelength of the transition from the ground state to the n = 3 state is :*

(*a*) 10^{-7}m (*b*) 1220 Å

(*c*) 10 nm (*d*) 15.0 Å

SOLUTION.

$$\Delta E = 2.178 \times 10^{-18}\,\text{J}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)$$

$$= 2.178 \times 10^{-18}\,\text{J}\left(\frac{1}{1^2}-\frac{1}{2^2}\right)$$

or

$$\Delta E = 2.178 \times 10^{-18}\,\text{J} \times \frac{3}{4} = 1.63 \times 10^{-18}\text{J}$$

But

$$\Delta E = \frac{hc}{\lambda}\cdot \text{ Hence, } \lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.626\times10^{-34}\text{Js}\times3.0\times10^{8}\text{ms}^{-}}{1.63\times10^{-18}\text{J}}$$

or

$$\lambda = 1.22 \times 10^{-7}\text{m}$$

$$= 1.22 \times 10^{-7}\text{m} \times \frac{10^{10}\text{Å}}{1\text{m}} = 1220\text{ Å}.$$

So, the correct answer is (*b*).

EXAMPLE 252. *Least paramagnetic property is shown by :*

(*a*) Fe (*b*) Mn

(*c*) Ni (*d*) Cu **(DCE, 2005)**

SOLUTION. (*a*) $_{26}$Fe = $(\text{Ar})^{18}\,3d^{2+1+1+1+1}\,4s^2$
= 4 unpaired electrons.

(*b*) $_{25}$Mn = $(\text{Ar})^{18}\,3d^{1+1+1+1+1}\,4s^2$ = 5 unpaired electrons.

(*c*) $_{28}$Ni = $(\text{Ar})^{18}\,3d^{2+2+2+1+1}\,4s^2$ = 2 unpaired electrons.

(*d*) $_{29}$Cu = $(\text{Ar})^{18}\,3d^{2+2+2+2+2}\,4s^1$ = one unpaired electron.

Smaller the number of unpaired electrons, lesser will be the paramagnetic property. So, the correct answer will be (*d*).

EXAMPLE 253. *Which of the following is not permissible ?*

(*a*) $n = 4, l = 3, m = 0$ (*b*) $n = 4, l = 2, m = 1$

(*c*) $n = 4, l = 4, m = 1$ (*d*) $n = 4, l = 0, m = 0$

(DCE, 2005, CBSE-PMT, 2009)

SOLUTION. We know that, $l = 0$ to $n–1$ and $m = –l$ to 0 to $+l$.

(*a*) For $n = 4$, $l = 0$ to 4–1 *i.e.*, 3 = 0, 1, 2, 3; $m = –0$ to 0 to 0 = 0. So, (*a*) is possible.

(*b*) For $n = 4$, $l = 0$ to 4–1 = 0, 1, 2, 3; $m = 0$ as shown above. So, (*b*) is possible.

(*c*) For $n = 4$, $l = 0$ to 4–1 = 0, 1, 2, 3. Since l cannot be 4, (*c*) is not possible.

(*d*) For $n = 4$, $l = 0$ to 4–1 = 0, 1, 2, 3; $m = 0$ as shown above. So, (*d*) is possible.

Hence the correct answer is (*c*).

EXAMPLE 254. *The relationship between the energy* E_1 *of the radiation with a wavelength 8000 Å and the energy* E_2 *of the radiation with a wavelength 16,000 Å is :*

(*a*) $E_1 = 6E_2$ (*b*) $E_1 = 2E_2$

(*c*) $E_1 = 4E_2$ (*d*) $E_1 = \frac{1}{2}E_2$

(*e*) $E_1 = E_2$. **(Kerala PET, 2005)**

SOLUTION.

$$E = h\nu = \frac{hc}{\lambda} \text{ or } E \propto \frac{1}{\lambda}$$

∴

$$E_1 = \frac{1}{8{,}000\text{Å}};\ E_2 = \frac{1}{16{,}000\text{Å}};$$

$$\frac{E_1}{E_2} = \frac{16{,}000\text{Å}}{8{,}000\text{Å}} = \frac{2}{1}$$

∴ $E_1 = 2E_2$. So, the correct answer is (*b*).

EXAMPLE 255. *The work function (ϕ) of some metals is listed below. The number of metals which will show photoelectric effect when light of 300 nm wave length falls on the metal is:*

Metal	Li	Na	K	Mg	Cu	Ag	Fe	Pt	W
ϕ(eV)	2.4	2.3	2.2	3.7	4.8	4.3	4.7	6.3	4.75

(IIT-JEE, 2011)

SOLUTION. $h = 6.626 \times 10^{-34}$ J sec; $c = 3 \times 10^8$ cm s^{-};
$\lambda = 300$ nm $= 300 \times 10^{-9}$ cm; 1 ev = 1.6×10^{-19} J. we know:

$$E = \frac{hc}{\lambda};$$

$$E = \frac{6.626\times10^{-34}\text{Js}\times3\times10^{8}\text{cms}}{300\times10^{-9}\text{cm}}$$

or

$$E = \frac{6.626\times10^{-34}\text{J}\times3\times10^{8}}{300\times10^{-9}\times1.6\times10^{-19}}ev$$

$[\because 1\text{ev} = 1.6 \times 10^{-19}\text{ J}]$

$$\simeq 4\text{eV}.$$

If $E_{\text{photon}} \geq \phi$, then and only then photoelectric effect is possible. Thus, Li, Na, K and Mg can show photoelectric effect only. So, the correct answer is these 4 metals.

EXAMPLE 256. *In a multielectron atom, which of the following orbitals described by the three quantum numbers will have the same energy in the absence of magnetic and electric fields ?*

(*a*) $n = 1, l = 0, m = 0$ (*b*) $n = 2, l = 0, m = 0$

(*c*) $n = 2, l = 1, m = 1$ (*d*) $n = 3, l = 2, m = 1$

(*e*) $n = 3, l = 2, m = 0$.

(1) (*a*) and (*b*); (2) (*b*) and (*c*);

(3) (*c*) and (*d*); (4) (*d*) and (*e*). **(AIEEE, 2005)**

SOLUTION. Those orbitals which have the same $(n + l)$ value in the absence of electric and magnetic field will have same energy. So, we have :

(*a*) $n = 1$, $l = 0$; $n + l = 1 + 0 = 1$; (*b*) $n + l = 2 + 0 = 2$; (*c*) $n + l = 2 + 1 = 3$; (*d*) $n + l = 3 + 2 = 5$; (*e*) $n + l = 3 + 2 = 5$. From above we see that (*d*) and (*e*) have same value of $n + l$ (=5). So, the correct answer is (4).

EXAMPLE 257. *The de Broglie wavelength of a ball of mass 10 g moving with a velocity of 10 ms⁻ is: ($h = 6.626 \times 10^{-34}$ Js).*

(a) 6.626×10^{-33} m (b) 6.626×10^{-29} m

(c) 6.626×10^{-31} m (d) 6.626×10^{-36} m

(J and K-CET, 2011)

SOLUTION. $_{24}$de Broglie equation is, $\lambda = h/mv$ where $h = 6.626 \times 10^{-34}$ Js, $v = 10$ ms, $m = 10$ g/1000 = 0.01 kg. Putting the values, we get:

$$\lambda = \frac{6.626 \times 10^{-34}\,\text{kgm}^2\text{s}^-}{0.01\,\text{kg} \times 10\,\text{ms}^-}$$

$$= 6.626 \times 10^{-33}\ \text{m}.$$

So, the correct answer is (*a*)

EXAMPLE 258. *The ratio of charge and mass would be greater for :*

(a) proton (b) electron

(c) neutron (d) alpha particle

(IMS-BHU, 2005)

SOLUTION. $\frac{\text{Charge}}{\text{Mass}}$ for proton,

$$_1\text{H}^+ = \frac{1}{1} = 1;\ \text{electron}, e = \frac{1}{1/1837} = 1837;$$

$$\text{neutron, } {}^0_1n = \frac{0}{1} = \text{zero; alpha, } {}^4\text{He}^{2+} = \frac{2}{4} = 0.5.$$

So, the correct answer is (*b*).

EXAMPLE 259. *The energy of second Bohr orbit of the hydrogen atom is –328 kJ mol⁻, hence the energy of fourth Bohr orbit would be*

(a) –41 kJ mol⁻ (b) –82 kJ mol⁻

(c) –164 kJ mol⁻ (d) –1312 kJ mol⁻

[CBSE–PMT (Prelims), 2005]

SOLUTION. (*a*) For H-atom,

$$Z = 1, n = 2. \text{ But } E_n = -k\left(\frac{Z}{n}\right)^2;$$

$$E_2 = -k\left(\frac{1}{2}\right)^2 = \frac{-k}{4}\cdot \text{ But}$$

$$E_2 = -328\ \text{kJ mol}^-.$$

$$\text{Hence } -328\ \text{kJ mol}^- = \frac{-k}{4} \qquad \textbf{or } k = 4 \times 328$$

$$= 1312\ \text{kJ mol}^-.$$

(*b*) Also, for H-atom,

$$Z = 1 \text{ and } n = 4. \text{ Hence } E_n = -k\left(\frac{Z}{n}\right)^2$$

$$\textbf{or} \qquad E_n = -k\left(\frac{1}{4}\right)^2 = \frac{-k}{16}$$

$$= \frac{-1312\,\text{kJ mol}^-}{16} = -82\ \text{kJ mol}^-.$$

So, the correct answer is (*b*).

EXAMPLE 260. *The number of radial nodes of 3s and 2p orbitals are respectively*

(a) 2, 0 (b) 0, 2

(c) 1, 2 (d) 2, 1

[IIT-JEE (Screening), 2005]

SOLUTION. Number of radial nodes = $n - l - 1$.

(*i*) For 3*s*, $n = 3, l = 0$.
Hence no. of radial nodes = 3 – 0 – 1 = **2**.

(*ii*) For 2*p*, $n = 2, l = 1$.
Hence no. of radial nodes = $n - l - 1 = 2 - 1 - 1 = \mathbf{0}$.

So, the correct answer is (*a*).

EXAMPLE 261. *Given that the mass of electron is 9.11×10^{-31}kg. Planck constant is 6.626×10^{-34}Js. The uncertainty involved in the measurement of velocity within a distance of 0.1Å is :*

(a) 5.79×10^5ms⁻ (b) 5.79×10^6ms⁻

(c) 5.79×10^7ms⁻ (d) 5.79×10^8ms⁻

(CBSE-PMT, 2006)

SOLUTION. $m = 9.11 \times 10^{-31}$kg, $\Delta x = 0.1$ Å $= 0.1 \times 10^{-10}$m; $\Delta v = ?$; $h = 6.626 \times 10^{-34}$Js. But

$$\Delta x \times m\Delta v = \frac{h}{4\pi};\ \Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x \times \text{m}}$$

$$= \frac{6.626 \times 10^{-34}\text{Js} \times 7}{4 \times 22 \times 0.1 \times 10^{-10}\text{m} \times 9.11 \times 10^{-31}\text{kg}}$$

$$= \frac{6.626 \times 10^{-34}\text{kg m}^2\text{s}^{-2}.\text{s} \times 7}{4 \times 22 \times 0.1 \times 10^{-10}\text{m} \times 9.11 \times 10^{-31}\text{kg}}$$

$$= 5.79 \times 10^6\ \text{ms}^-.$$

So, the correct answer is (*b*).

EXAMPLE 262. *[Cr ($H_2O)_6$]Cl (at. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in the chromium metal of the complex is :*

(a) $3d^1{}_{xy}, 3d^1{}_{yz}, 3d^1{}_{zx}$ (b) $3d^1_{x^2-y^2}, 3d^1_{z^2}, 3d^1_{xz}$

(c) $3d^1_{xy}, 3d^1_{x^2-y^2}, 3d^1_{yz}$ (d) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}$.

(C.B.S.E.–PMT, 2006)

SOLUTION. Magnetic moment 3.83 B.M. = $[n\,(n + 2)]^{1/2}$ where n = no. of unpaired electrons. Squaring both sides, we get :

$$(3.83)^2 = \{n(n + 2)^{1/2}\}^2;$$

$$14.67 = n(n + 2) = n^2 + 2n$$

$$\therefore\ n^2 + 2n - 14.67 = 0;$$

$$n = \frac{-2 \pm [(2)^2 - (4 \times 1 \times -14.67)]^{1/2}}{2}$$

$$[\because \text{ For } ax^2 + bx + c = 0; x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}]$$

$$n = \frac{-2 \pm [4 + 58.0]^{1/2}}{2}$$

$$= \frac{-2 \pm 7.9}{2}\ 3\ \textit{i.e.}, \boldsymbol{n = 3}.$$

$$\therefore \qquad \text{Cr}^{3+} = (\text{Ar})^{18}\,3d^3;\ (\text{Ar})^{18} \begin{array}{|c|c|c|c|c|}\hline 1 & 1 & 1 & & \\ \hline \multicolumn{1}{c}{d_{xy}} & \multicolumn{1}{c}{d_{yz}} & \multicolumn{1}{c}{d_{zx}} & \multicolumn{1}{c}{d_{x^2-y^2}} & \multicolumn{1}{c}{d_{z^2}} \end{array}$$

So, the correct answer is (*d*).

EXAMPLE 263. *According to Bohr theory, the angular momentum of an electron in 5th orb(IIT-JEE, 2011) it is :*

(a) $\frac{25h}{\pi}$ (b) $1.0\frac{h}{\pi}$

(c) $10\frac{h}{\pi}$ (d) $2.5\frac{h}{\pi}$

(AIEEE, 2005)

Solution. We know that angular momentum of an electron, $mvr = \frac{nh}{2\pi}\cdot$ Since, $n = 5$, so we have : Angular momentum $= \frac{5h}{2\pi} = 2.5\frac{h}{\pi}\cdot$ So, the correct answer is (*d*).

Example 264. *Which of the following molecules/ions do not contain unpaired electrons ?*

(*a*) O_2^{2-} (*b*) B_2

(*c*) N_2^+ (*d*) O_2

(AIEEE, 2006)

Solution. Electronic configurations of : (*a*) O_2^{2-}.

Total electrons = (2 × 8) + 2 = 18.

$KK\,(\sigma_{2s})2\,(\sigma^*_{2s})^2\,(\sigma^*_{2p_z})^2(\pi_{2p_x})^2 = (\pi_{2p_y})^2(\pi^*_{2p_x})^2 = (\pi^*_{2p_y})^2$

KK represent non-bonding molecular orbitals of 1*s*-orbital.

$\therefore$ O_2^{2-} does not contain any unpaired electron.

(*b*) B_2. $_5B = 1s^22s^22p^1$. Total electrons = 2 × 5 = 10; $KK\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\pi_{2p_x})^1 = (\pi_{2p_y})^1$. So, B_2 contains 2 unpaired electrons.

(*c*) N_2^+. $_7N = 1s^22s^22p^3$; $N^+ = 1s^22s^22p^2$. Total electrons $= 7 + 6 = 13$. $KK\,(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^2 = (\pi_{2p_y})^2 = (\pi_{2p_z})^1$.

So, N_2^+ contains one electron.

(*d*) O_2. $_8O = 1s^22s^22p^4$. Total electrons = 2 × 8 = 16. $KK\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\sigma_{2p_z})^2\,(\pi_{2p_x})^2 = (\pi_{2p_y})^2\,(\pi^*_{2p_x})^1 = (\pi^*_{2p_y})^1\,(\pi^*_{2p_z})^0$. So, O_2 contains 2 unpaired electrons.

So, the correct answer is (*a*).

Example 265. *Uncertainty in the position of an electron (mass = 9.1×10^{-31} kg) moving with a velocity 300 ms⁻ accurate up to 0.001% will be (h = 6.6×10^{-34} Js)*

(*a*) 19.2×10^{-2}m (*b*) 5.76×10^{-2}m

(*c*) 1.92×10^{-2}m (*d*) 3.84×10^{-2}m.

(AIEEE, 2006, AIEEE, 2009)

Solution. According to Heisenberg's uncertainty principle.

$$\Delta x \times \Delta p = \frac{h}{4\pi};\ \Delta x.m\Delta v = \frac{h}{4\pi}$$

$$\therefore \quad \Delta x = \frac{h}{4\pi\, m\Delta v}$$

$$\text{But} \quad \Delta v = \frac{0.001}{100} \times 300 = 0.003\ \text{ms}^-$$

$$\therefore \quad \Delta x = \frac{6.6\times10^{-34}\text{kg m}^2\text{s}^-}{4\times3.142\times9.1\times10^{-31}\text{kg}\times0.003\,\text{ms}^-}$$

$$= 1.92 \times 10^{-2}\ \text{m}.$$

So, the correct answer is (*c*).

Example 266. *Which of the following sets of ions represents a collection of isoelectron species :*

(*a*) $K^+, Cl^-, Ca^{2+}, Sc^{3+}$ (*b*) $Ba^{2+}, Sr^{2+}, K^+, S^{2-}$

(*c*) $N^{3-}, O^{2-}, F^-, S^{2-}$ (*d*) $Li^+, Na^+, Mg^{2+}, Ca^{2+}$

(AIEEE, 2006)

Solution. (*a*) $_{19}K^+ = 19 - 1 = 18$; $_{17}Cl^- = 17 + 1 = 18$; $_{20}Ca^{2+} = 20 - 2 = 18$; $_{21}Sc^{3+} = 21 - 3 = 18$. Each species contains same number of electrons = 18. So, these are isoelectron species. Here 19, 17, 20 and 21 are the atomic numbers of K, Cl, Ca and Sc respectively.

(*b*) $_{56}Ba^{2+} = 56 - 2 = 54$; $_{38}Sr^{2+} = 38 - 2 = 36$; $_{19}K^+ = 19 - 1 = 18$; $_{16}S^{2-} = 16 + 2 = 18$. Since the number of electrons is not same in all species, these are not isoelectronic species.

(*c*) $_7N^{3-} = 7 + 3 = 10$; $_8O^{2-} = 8 + 2 = 10$; $_9F^- = 9 + 1 = 10$; $_{16}S^{2-} = 16 + 2 = 18$. Since the number of electrons in all species is not same, these are not isoelectronic species.

(*d*) $_3Li^+ = 3 - 1 = 2$; $_{11}Na^+ = 11 - 1 = 10$; $_{12}Mg^{2+} = 12 - 2 = 10$; $_{20}Ca^{2+} = 20 - 2 = 18$. Since the number of electrons is not same in all species, these are not isoelectronic species.

So, the correct answer is (*a*).

Example 267. *The diameter of water molecule and that of oxygen atom if (i) oxygen atom occupies half of the volume occupied by water molecule (ii) volume occupied by one molecule of water = 2.989×10^{-23} cm³ (iii) water molecule is assumed to be spherical are respectively :*

(*a*) 2.1 Å, 4.2 Å (*b*) 3.85 Å, 3.056 Å

(*c*) 1 Å, 2 Å (*d*) 7.7 Å, 6.1 Å

Solution. (*i*) To find diameter of water molecule. Since water molecule is spherical:

$$\frac{4}{3}\pi R^3 = \text{Volume of one molecule of water}$$

$$\text{Where,} \quad R = \text{radius of water molecule}$$

$$\therefore \quad \frac{4}{3}\times\frac{22}{7}\times R^3 = 2.989 \times 10^{-23}\ \text{cm}^3$$

$$\therefore \quad R^3 = 2.989\times10^{-23}\,\text{cm}^3\times\frac{3}{4}\times\frac{7}{22}$$

$$= 7.133 \times 10^{-24}\ \text{cm}^3$$

$$\therefore \quad R = (7.133 \times 10^{-24}\ \text{cm}^3)^{1/3}$$

$$= (7.133)^{1/3} \times 10^{-8}\ \text{cm}.$$

$$= 1.925 \times 10^{-8}\ \text{cm}$$

$\therefore$ Diameter of water molecule

$$= 2R = 2 \times 1.925 \times 10^{-8}\ \text{cm}$$

$= 3.85 \times 10^{-8}$ cm = 3.85 Å.

[$\because$ 1 Å = 10^{-8} cm]

To find R :

$$\log R = \log (7.133)^{1/3}$$

$$= \frac{1}{3}\log 7.133$$

$$= \frac{1}{3}\times 0.8533$$

$$= 0.2844$$

$$\therefore \quad R = \text{antilog}\ 0.2844$$

$$= 1.925\ \text{cm}$$

(*ii*) **To find radius of oxygen atom.**

$$\frac{4}{3}\pi r^3 = \frac{1}{2} \times \text{Volume occupied by water molecule}$$

$$\frac{4}{3}\times\frac{22}{7}\times r^3 = \frac{1}{2} \times 2.989 \times 10^{-23}\ \text{cm}^3$$

$$\therefore \quad r^3 = \frac{1}{2}\times\frac{2.989\times10^{-23}\times3\times7}{4\times22}\ \text{cm}^3$$

$$= 3.566 \times 10^{-24}\ \text{cm}^3$$

$$\therefore \quad r = (3.566 \times 10^{-24}\ \text{cm}^3)^{1/3}$$

$$= (3.566)^{1/3} \times 10^{-8}\ \text{cm}$$

$$= 1.528 \times 10^{-8}\ \text{cm.}$$

$$\log r = \log (3.566)^{1/3}$$

$$= \frac{1}{3}\log 3.566$$

∴ Diameter of oxygen atom

$$= 2r = 2 \times 1.528 \times 10^{-8}\ \text{cm}$$

$$= \frac{1}{3}\times 0.5522$$

$$= 0.1841$$

$$\therefore \quad r = \text{antilog } 0.1841$$

$$= 1.528$$

$$= 3.056 \times 10^{-8}\ \text{cm}$$

$$= 3.056\ \text{Å} \quad (\because 1\ \text{Å} = 10^{-8}\text{cm})$$ **Ans.**

So, the correct answer is (*b*).

EXAMPLE 268. *A metal was found to have its threshold frequency equal to* 10^{15} s^{-}. *If the same metal is irradiated with radiations of frequencies* 1.5×10^{15} s^{-} *and* 2.5×10^{15} s^{-} *respectively, the ratio of maximum kinetic energies will be :*

(*a*) 1 : 2 (*b*) 2 : 1

(*c*) 1 : 4 (*d*) 1 : 3

SOLUTION. We know that :

$$\frac{(\text{K.E.})_1}{(\text{K.E.})_2} = \frac{v_1 - v_0}{v_2 - v_0} = \frac{1.5\times10^{15} - 1\times10^{15}}{2.5\times10^{15} - 1\times10^{15}}$$

$$= \frac{0.5}{1.5} = \frac{1}{3}$$

So, the ratio is 1 : 3. Hence, the correct answer is (*d*).

EXAMPLE 269. *The measurement of the electron position is associated with an uncertainty in momentum, which is equal to* 1×10^{-18} *g cm* s^{-}. *The uncertainty in electron velocity is (mass of an electron is* 9×10^{-28} *g) :*

(*a*) 1×10^5 *cm* s^{-} (*b*) 1×10^{11} *cm* s^{-}

(*c*) 1×10^9 *cm* s^{-} (*d*) 1×10^6 *cm* s^{-}

(CBSE–PMT, 2008 Prelims)

SOLUTION. Uncertainty in momentum ($m\ \Delta\ v$)

$$= 10^{-18}\ \text{g cm s}^{-}$$

∴ Uncertainty in velocity,

$$\Delta v = \frac{10^{-18}\text{g cm s}^{-}}{m} = 1.1 \times 10^{+9}\ \text{cm s}^{-}$$

So, the correct answer is (*c*).

EXAMPLE 251. *The isotopic abundance of* ^{12}C *and* ^{14}C *is 98% and 2% respectively. The number of* ^{14}C *isotope in 6.0 g carbon sample will be:*

(*a*) 5.16×10^{21} (*b*) 2.58×10^{21}

(*c*) 2.58×10^{22} (*d*) 5.16×10^{23}

(H.P.B. modified, 2012)

SOLUTION. ^{14}C = 2%. So, weight of ^{14}C in 6.0 g carbon = $\frac{2}{100}\times 6$.

Hence, number of ^{14}C isotopes = $\frac{2\times6\times6.02\times10^{23}}{100\times14}$

$$= 5.16 \times 10^{21}$$

So, the correct answer is (*a*).

EXAMPLE 252. *The ratio of the frequency corresponding to the third line in Lyman series of hydrogen atomic spectrum to that of the first line in Balmer series of* Li^{2+} *spectrum is:*

(*a*) 4/5 (*b*) 5/4

(*c*) 4/3 (*d*) 3/4

(*e*) 3/8

(Kerala PET, 2012)

SOLUTION. (*a*) For H-atom, Z = 1; for Lyman series, $n_1 = 1$ and for third line, $n_2 = 4$; frequency, $v_H = \frac{C}{\lambda} = C.R_H Z^2$

$$\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = CR_H(1)^2\left[\frac{1}{1} - \frac{1}{4^2}\right] = \frac{15}{16} C R_H \quad ...(1)$$

For Li-atom, Z = 3; for Balmer series, $n_1 = 2$, $n_2 = 3$.

$$\text{So: } v_{Li} = CR_H\,(3)^2\left[\frac{1}{2^2} - \frac{1}{3^2}\right] = CR_H \times 9 \times \frac{5}{36} = \frac{5}{4}CR_H \quad ...(2)$$

Dividing equation (1) and (2), we get:

$$\frac{v_{\text{H}}}{v_{\text{Li}}} = \frac{(15/16)\,C.R_H}{(5/4)\,C.R_H} = \frac{15}{16}\times\frac{4}{5} = \frac{3}{4}.$$

So, the correct answer is (*d*).

EXAMPLE 253. *Ratio of area of second orbit to first orbit in an atom is:*

(*a*) 1 : 4 (*b*) 4 : 1

(*c*) 16 : 1 (*d*) 1 : 16

(AFMC, 2014)

SOLUTION. For first orbit, $n = 1$; for second orbit, $n = 2$.

But radius, $r_n = 0.529 \times \frac{n^2}{Z}$ Å. So, $r_n \propto n^2$; Area = $\pi r^2 = \pi n^4$

$$\therefore \quad \frac{\text{Area of second orbit}}{\text{Area of first orbit}} = \frac{\pi\,(4)^2}{\pi\,(1)^4} = \frac{16}{1}$$

∴ Ratio = 16 : 1. So, the correct answer is (*c*).

EXAMPLE 254. *The kinectic energy of an electron in the second Bohr orbit of a hydrogen atom (*a_0 *is Bohr radius):*

(*a*) $h^2/4\pi^2 m a_0^2$ (*b*) $h^2/16\pi^2 m a_0^2$

(*c*) $h^2/32\pi^2 m a_0^2$ (*d*) $h^2/64\pi^2 m a_0^2$

(IIT-JEE, 2012)

SOLUTION. We know that for Bohr orbit angular momentum: $mvr_n = \frac{nh}{2\pi}$ and $v = \frac{nh}{2\pi m r_n}$ ...(*i*)

$$\text{K.E.} = \frac{1}{2}mv^2 \quad ...(ii)$$

Substituting the value of v from (i) in (ii), we get:

$$\text{K.E.} = \frac{1}{2} m \times \frac{n^2h^2}{4\pi^2m^2r_n^2} = \frac{n^2h^2}{8\pi^2mr_n^2} \qquad ...(iii)$$

But $r_n = \frac{a_0n^2}{z^2}\text{Å}; r_n^2 = \frac{a_0^2n^2}{1^2}$. Substituting the value of $n = 2$ and r_n^2 in (iii), we get

$$\text{K.E.} = \frac{(2)^2h^2}{8\pi^2ma_0^2 \times 2^4} = \frac{h^2}{32\,\pi^2ma_0^2}.$$

So, the correct answer is (c).

EXAMPLE 255. *If the first I.E. of H-atom is 13.6 eV, then the second I.E. of the He-atom is:*

(a) *29.2 eV* *(b)* *40.8 eV*

(c) *54.4 eV* *(d)* *108.8 eV*

(W.B.JEE, 2012)

SOLUTION. For H-atom ($Z = 1$), $E_H = \frac{-13.6Z^2}{n^2}$. So, $(E_1)_H = -13.6$ eV. For He^+ ($Z = 2$), $(E_1)_{He^+} = \frac{-13.6Z^2}{n^2} = -13.6 \times \frac{2^2}{1} = -54.4$ eV.

$\therefore$ Second I.E. of the He-atom $= E_\infty - (E_1)_{He^+} = 0 - (-54.4) = +54.4$ eV.

So, the correct answer is (c).

EXAMPLE 256. *The orbital angular momentum of a p-electron is given as:*

(a) $\frac{h}{\sqrt{2\pi}}$ *(b)* $\sqrt{3}\,.\frac{h}{2\pi}$

(c) $\sqrt{\frac{3h}{2\pi}}$ *(d)* $\sqrt{6}\,\frac{h}{2\pi}$

(AIPMT, Mains, 2012)

SOLUTION. For p-electron, $l = 1$.

Orbital angular momentum (m) $= \sqrt{l\,(l+1)}.\frac{h}{2\pi}$

$$\therefore\ m = \sqrt{1\,(1+1)}.\frac{h}{2\pi}\ (\because l = 1).$$

$$\text{So, } m = \frac{\sqrt{2}h}{2\pi} = \frac{h}{\sqrt{2}\,.\,\pi}\ [\because \sqrt{2} \times \sqrt{2} = 2]$$

EXAMPLE 257. *The energy of an electron is given by $E = -2.178 \times 10^{-18}$ J (Z^2/n^2). The wave length of light required to excite an electron in a hydrogen atom from level n = 1 to n = 2 will be: (h = 6.62×10^{-34} Js, c = 3.0×10^8 ms⁻)*

(a) *2.816×10^{-7} m* *(b)* *6.500×10^{-7} m*

(c) *8.500×10^{-7} m* *(d)* *1.214×10^{-7} m*

(JEE Main, 2013)

SOLUTION. $E = 2.178 \times 10^{-18}\,Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

$$= 2.178 \times 10^{-18} \times 1^2\left(\frac{1}{(2)^2} = \frac{1}{1^2}\right) = -2.178 \times 10^{-18}\left(\frac{1}{4} - 1\right)$$

$$= -2.178 \times 10^{-18}\left(\frac{-3}{4}\right) = 1.6335 \times 10^{-18}\text{ J}$$

$$\text{But } E = \frac{hc}{\lambda}.\ \text{So, } \lambda = \frac{hc}{E} = \frac{6.62 \times 10^{-34}\text{ Js} \times 3 \times 10^8\text{ m}}{1.6335 \times 10^{-18}\text{ J}}$$

$= 12.14 \times 10^{-8}$ m

or $\lambda = 1.214 \times 10^{-7}$ m. So the Correct answer is (4).

PROBLEMS

1. Calculate the number of protons which together weigh two grams.

[**Hint.** $2/1.672 \times 10^{-24}$) (**Ans.** 1.196×10^{24} protons)

2. Calculate the charge on one mole of neutrons.

[**Ans.** zero]

3. Find the value of electrons and neutrons in (i) ${}^{19}_{9}\text{F}$ and ${}^{40}_{18}\text{Ar}$ atoms.

[**Ans.** (i) 9, 10; (ii) 18, 22]

4. An oxide of an element has molecular mass 30. Find the total number of electrons in one molecule of the compound (at. no., N = 7, O = 8)

[(**Hint.** Compound is NO) **Ans.** 15

5. Calculate the total number of electrons, protons and neutrons in (i) NH_3, (ii) CN^-, (iii) Hg_2^{2+} (at. no., N = 7, H = 1, C = 6, Hg = 80; mass no., N = 14, H = 1, C = 12, Hg = 200)

[**Ans.** (i) 10, 10, 7; (ii) 14, 13, 13; (iii) 158, 160, 240]

6. Find the kinetic energy of the electron emitted when light of frequency 2.0×10^{15} Hz is hit on a metal surface which has a threshold frequency equal to 10^{15} Hz.

[(**Hint.** K.E. $= h(\upsilon - \upsilon_0) = 6.63 \times 10^{-34}$ Js $\times [(2-1) \times 10^{15}$ Hz] **Ans. 6.63×10^{-19}J**

7. Calculate the velocity of an electron (in C.G.S. units) revolving in the first orbit of H-atom.

Ans. 2.183×10^8cm s⁻

8. Calculate the velocity of an electron (in S.I. units) revolving in the second orbit of H-atom.

[**Hint and Ans.** $v_2 = 2.183 \times 10^6 \times \frac{1}{2}$ ms⁻ = **1.0915×10^6 ms⁻]**

9. Calculate the number of revolutions made by an electron revolving in first orbit of H-atom, in terms of C.G.S. units. [**Ans.** 65.71×10^{14}s⁻]

10. Calculate the ionisation energy of H-atom in C.G.S. units in first orbit.

[**Ans.** 2.173×10^{-11} erg atom⁻; 13.1 erg mol⁻; 13.6 eV atom⁻]

11. Calculate the ionisation energy of H-atom (in S.I. unit) in first orbit.

[**Ans.** 2.173×10^{-18} J atom⁻; 13.1 kJ mol⁻]

12. Number of atoms present in 4.25 g of NH_3 is:

(a) 6.023×10^{23} *(b)* $4 \times 6.023 \times 10^{23}$

(c) 1.7×10^{24} *(d)* $4.25 \times 6.023 \times 10^{23}$

(AFMC, 2010)

Ans. (*a*)

13. If 1 *mL* of H_2O contains 20 drops, then no. of molecules in a drop of water are:

(a) 6.023×10^{23} *(b)* 1.376×10^{26}

(c) 1.344×10^{18} *(d)* 4.346×10^{20}

(AFMC, 2010)

Ans. (*c*)

14. Total number of atoms of all elements present in one mole of ammonium dichromate are:

(a) 19 *(b)* 6.023×10^{23}

(c) 114.437×10^{23} *(d)* 84.322×10^{22}

Ans. (*c*)

15. Which of the following orbitals will have the probability of finding the electron in the *yz*-plane?

(a) p_x *(b)* p_y

(c) p_z *(d)* d_{yz}

(West Bengal, 2010)

Ans. (*d*)

16. What is the maximum number of spectral lines obtained when the excited electrons of a hydrogen atom in $n = 5$, drop to ground state?

(a) 10 *(b)* 5

(c) 12 *(d)* 15

(JK CET, 2010)

Ans. (*a*)

17. The wave number of the spectral line in the emission spectrum of H_2 will be equal to 8/9 times the Rydberg constant if the elctron jumps from:

(a) $n = 3$ to $n = 1$ *(b)* $n = 10$ to $n = 1$

(c) $n = 9$ to $n = 1$ *(d)* $n = 2$ to $n = 1$

(Karnatka, CET, 2010)

Ans. (*a*)

18. A 600 W mercury lamp emits monochromatic radiation of wavelength 331.3 nm. How many photons are emitted from the lamp per second? ($h = 6.626 \times 10^{-34}$ *Js*; velocity of light = 3×10^8 ms^-)

(a) 1×10^{19} *(b)* 1×10^{20}

(c) 1×10^{22} *(d)* 1×10^{23}

(Kerala, PET, 2010)

Ans. (*d*)

19. The energy required to break one mol of Cl—Cl bonds in Cl_2 is 242 k J mol^-. The largest wavelength of light capable of breaking a single Cl–Cl bond is: ($c = 3 \times 10^8$ ms^- and $N_A = 6.02 \times 10^{23}$ mol^-).

(a) 700 nm *(b)* 494 nm

(c) 594 nm *(d)* 640 nm

(AIEEE, 2010)

Ans. (*b*)

20. Ionisation energy of He^+ is 19.6×10^{-18} J $atom^{-1}$. The energy of first stationary state ($n = 1$) of Li^{2+} is

(a) -2.2×10^{-15} J $atom^{-1}$ *(b)* 8.82×10^{-17} J $atom^{-1}$

(c) 4.41×10^{-16} J $atom^{-1}$ *(d)* -4.41×10^{-17} J $atom^{-1}$

(AIEEE, 2010)

Ans. (*d*)

21. Which of the following sets of quantum numbers represents the 19th electron in chromium ($Z = 24$)?

(a) 4,0,0, 1/2 *(b)* 4, 1, –1, 1/2

(c) 3, 2, 2, 1/2 *(d)* 3, 2, –2, 1/2

(AMU, 2010)

Ans. (*a*)

13

CHAPTER

Periodic Properties and Chemical Bonding

13.1 TO PREDICT PERIOD, GROUP AND BLOCK OF ELEMENTS

Type. *To predict* the period, group and block of an element in the *periodic* table, following points will help.

(*i*) Write the electronic configuration of the concerned element.

(*ii*) **No. of period** = Highest number of shell in the electronic configuration of element.

(*iii*) **No. of group.** (*a*) For **s-block elements,** group no. = no. of valence electrons (ns)

(*b*) **For p-block elements,** group no. = 10 + no. of valence electrons (ns and np). 10 is added because 10 elements are present in d-block prior to p-block elements.

(*c*) **For d-block elements,** group no. = no. of electrons in (n – 1) d and ns shell.

> **Note.** No. of groups in s-block = 2, *p*-block = 6, *d*-block = 10.

(*iv*) **Name of block** = name of sub-shell in which last electron of the element is filled.

> **Note.** No. of elements in first, 2nd, 3rd, 4th, 5th, 6th, and 7th period are 2, 8, 8 18, 18, 32 and 26 (incomplete) respectively.

EXAMPLE 1. *Write the number of period, group and block to which an element with at. no. 24 belongs.*

SOLUTION. Electron configuration of element with at. no. 24 = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

(*a*) Highest number of shell in the electron configuration = 4

∴ **No. of period = 4** **Ans.**

(*b*) **Name of block** = name of sub-shell in which last electron of the element is filled.

= d-block

(∵ last electron enters in 3 *d*). **Ans.**

(*c*) Element with at. no. 24 belongs to *d*-block.

∴ **group number** = no. of electrons in (n – 1) *d* and ns shell *i.e.,*

$3d^5$ (*i.e.,* 4 – 1 = 3) and $4s^1$

= 5 + 1 = **6** **Ans.**

EXAMPLE 2. *Name the period, group and block to which an element with at. no. 20 belongs.*

SOLUTION. (*i*) Electron configuration of element with at. no. 20.

= $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

(*a*) No. of period = highest no. of shell

= **4 (of 4s)** **Ans.**

(*b*) Name of block = name of sub-shell in which last electron of the element is filled.

= **s-block Ans.**

(*c*) Group no. = no. of electrons in ns shells

= **2** **Ans.**

EXAMPLE 3. *The chemical formula of the higher oxide of an element (X) is XO_3. The name of element if the hydride of this element contains 1.543% hydrogen is :*

(at. wt., S = 32, Se = 78.96, Te = 127.6)

SOLUTION. Since the higher oxides are formed by group 16 elements, **X** will be either *S*, *Se* or *Te* and not oxygen which can not extend its octet.

% age of *H* in XH_2 = 1.543

∴ % age of *X* in XH_2 = 100 – 1.543 = 98.457%

Atomic ratio of *X* and *H* in XH_2 = 1 : 2 ...(1)

Let *A* = atomic mass of element, *X*

Atomic ratio of *X* and *H*

$$= \frac{98.457}{A} : \frac{1.543}{1} \qquad ...(2)$$

From (1) and (2), we get :

$$\frac{1}{2} = \frac{\dfrac{98.457}{A}}{1.543/1}; \ 98.457 \times 2 = 1.543\,A$$

$$\therefore \qquad A = \frac{98.457 \times 2}{1.543} = 127.6$$

So, the name of the element is tellurium.

13.2 CALCULATING BOND LENGTH IN MOLECULES

Tpye. Bond length in a molecule = Covalent radius of one atom + Covalent radius of second atom

Note. H_2 molecule is unique. Its observed (or experimental) bond length is greater than the sum total of their covalent radii. It is because there is no inner electron cloud. In other covalent molecules, the proton **buries** itself in the surrounding electrons, causing a bit smaller effective radius.

Example 4. *Calculate the bond length in SCl_2 molecule. (covalent radius of S = 1.04 A°, Cl = 0.99A°).*

Solution. Bond length S – Cl = Covalent radius of S + Covalent radius of Cl

= 1.04 A° + 0.99 A° = **2.03 A° Ans.**

Example 5. *Calculate the bond length in H_2. Compare this value with the observed value of 0.75 A°. Explain the discrepancy, if any. (covalent radius of H = 0.28 A°).*

Solution. Bond length H–H = 2 × covalent radius of H = 2 × 0.28 A° = 0.56 A°.

This bond length (0.56 A°) is less than the observed value (0.75 A°). It is because there is no inner electron cloud in H-atom ($1s^1$) and experimental covalent radius of hydrogen being determined using molecules other than H_2.

Example 6. *The H–O bond distance in H_2O is 0.94 A°. Calculate the single bond covalent radius of O. (covalent radius of H = 0.28 A°).*

Solution. Radius of O atom = Internuclear distance – Radius of H- atom = 0.94 A° – 0.28 A° = **0.66 A°** **Ans.**

Tpye. Molecular length in a molecule = Sum total of radii of all the atoms in the molecule

Example 7. *Calculate the molecular length of acetylene molecule (covalent radius of H – is 0.28 A°, C – is 0.77 A°, C ≡ is 0.61 A°).*

Solution. Acetylene is C_2H_2 i.e., H–C ≡ C – H.

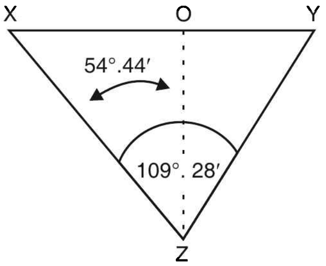
∴ Molecular length of C_2H_2 = covalent radii of (H –) + (– C) + (C≡) + (≡C) + (C –) + (– H) = 0.28 A° + 0.77 A° + 0.61 A° + 0.61 A°+ 0.77 A° + 0.28 A° = **3.32 A°** **Ans.**

Example 8. *Assuming that all the four bonds of any carbon atom are directed towards the four corners of a tetrahedron, calculate the distance between the terminal carbons in propane, C_3H_8. The C-C single bond length = 154 pm.*

Solution. Let central C- atom in C_3H_8 is at Z and other C- atoms are at X and Y.

∴ XY = 2 (XO)

= 2 (XZ sin 54° 44′)



= 2 (154 pm) × sin 54.73°

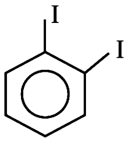
= 2 × 154 pm × 0.816

= **251 pm** **Ans.**

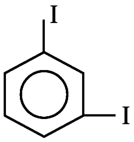
Note. Tetrahedral angle is 109° 28′.
Also, 60′ =100°. So, 44′ = (100/60) × 44 = 73°.

EXAMPLE 9. *Calculate the iodine-iodine distance in each of the three isomers (i.e., o, m and p) of diiodobenzene having adjacent C-C distance equal to 140 pm. Assume that the ring is a regular hexagon, each C-I bond lie on a line through the centre of the hexagon and also assume the additivity of covalent radii in the C-I bond (covalent radius I = 133 pm, – C = 77 pm).*

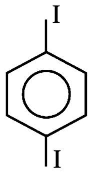
Solution. The three isomers of diiodobenzene are :



o-Diiodobenzene

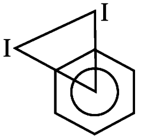


m-Diiodobenzene

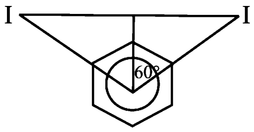


p-Diiodobenzene

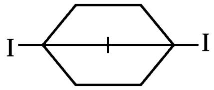
Since the compound contains regular hexagon, the lines from the centre to two adjacent apices form an equilateral triangle.



(*a*)



(*b*)



(*c*)

The distance from the centre of hexagon to I- atom = Distance from centre of hexagon to any of its corner + covalent radius (–C) + covalent radius (I) = 140 pm + 77 pm + 133 pm = 350 pm.

This distance (350 pm) is also, the side of the equilateral triangle.

∴ *in* (*a*) : The distance from one adjacent iodine to another iodine = **350 pm.** **Ans.**

In (*b*) Half of I - I distance $= 350 \text{ pm} \times \frac{\sqrt{3}}{2}$.

Hence Full I - I distance $= 350 \text{ pm} \times \frac{\sqrt{3}}{2} \times 2$

= 350 pm × 1.732

= **606.2 pm.** **Ans.**

In (*c*) I - I distance = 2 × 350 pm = **700 pm. Ans.**

Example 10. *All the B - I bonds in BI_3 are at 120° to each other. Calculate the covalent radius of boron if distance between iodine atoms is 354 pm. Assume that all the B - I bonds are single bonds. Covalent radius of I - atom = 133 pm.*

SOLUTION.

Distance,

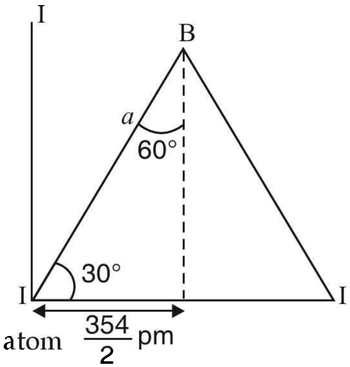
$$a = d_{B-I} = \frac{\frac{354\text{ pm}}{2}}{\text{Sin }60}$$

$$a = \frac{177\text{ pm}}{0.866} \simeq 204\text{ pm.}$$

∴ Radius of boron atom

= 204 pm – radius of I - atom

= 204 pm – 133 pm = **71 pm** **Ans.**



13.3 IONISATION ENTHALPY (OR IONISATION ENERGY, I.E.) OR IONISATION POTENTIAL (I.P.)

First ionisation enthalpy. First I.E. of an element is the amount of energy required to remove an electron from a neutral gaseous atom to form a unipositive gaseous ion.

Second ionisation enthalpy. It is the amount of energy required to remove an electron from a unipositive gaseous ion to form a dipositive gaseous ion.

Third ionisation enthalpy. It is the amount of energy required to remove an electron from a dipositive gaseous ion to form a tripositive gaseous ion.

Third IE_3 > Second IE_2 > First IE_1

Type. Energy required to convert x mol of an element A to A^+ (g)

$= x \times IE_1$ of element, A

Use. $1\text{ eV (atom)}^{-} = 6.023 \times 10^{23}\text{ eV (mol)}^{-}$

$= 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\text{ J mol}^{-}$

EXAMPLE 11. *How much energy will be needed to convert 2.5 mol of Li atoms in the gaseous state to form Li (g)? First I.P of Li = 5.41 eV.*

SOLUTION. I.P. of Li $= 5.41\text{ eV atom}^{-}$

$$\times \frac{6.023\times10^{23}\times1.602\times10^{-19}\text{ J mol}^{-}}{1\text{ eV atom}^{-}}$$

$= 522 \times 10^{3}\text{ J mol}^{-}$

∴ Energy needed to convert 2.5 mol Li (s) to Li (g)

$= 2.5\text{ mol} \times 522 \times 10^{3}\text{ J mol}^{-}$

= **1305 kJ** **Ans.**

EXAMPLE 12. *The first and second ionisation energies of magnesium are 740 kJ mol⁻ and 1450 kJ mol⁻ respectively. Calculate the percentage composition of the final mixture if one gram of Mg - atom (at. wt., = 24 amu) absorbs 50 kJ energy in its vapour phase.*

SOLUTION. wt. of

Mg = 1 g; at. wt. of Mg = 24 a.m.u.

Thus :no. of mol of Mg atoms

$$= \frac{\text{wt.}}{\text{at.wt.}} = \frac{1}{24} = 0.04167$$

Reactions: $\text{Mg} \xrightarrow[\text{First I.E.}]{740\text{ kJ}} \text{Mg}^{+} \xrightarrow[\text{second I.E.}]{1450\text{ kJ}} \text{Mg}^{2+}$

(*i*) For Mg to Mg^+ : Energy required to ionise 0.04167 mol Mg to Mg^+

$= 0.04167 \times 740\text{ kJ} = 30.84\text{ kJ}$

Energy left behind = 50.0 – 30.84 = 19.16 kJ

(*ii*) For Mg^+ to Mg^{2+} : 1450 kJ ionise mol of Mg^+ to Mg^{2+} = 1

19.16 kJ ionise mol of Mg^+ to Mg^{2+}

$$= \frac{1}{1450} \times 19.16 = 0.01321\text{ mol}$$

∴ mol of Mg^+ left behind

= 0.04167 – 0.01321 = 0.02846 mol

(*iii*) % age composition of Mg^+

$$= \frac{0.02846}{0.04167}\times100 = \mathbf{68.3\%}$$ **Ans.**

% age composition of Mg^{2+}

$$= \frac{0.01321}{0.04167}\times100\,' = \mathbf{31.7\%}$$ **Ans.**

13.4 ELECTRON GAIN ENTHALPY (OR ELECTRON AFFINITY)

The enthalpy change when an electron is added to a neutral gaseous atom to form a uninegative gaseous ion is called **first electron affinity** or **first electron gain enthalpy**, (Δ_{eg} H). It is measured in k cal mol⁻ or kJ mol⁻.

Second electron gain enthalpy (or second electron affinity). The enthalpy change when an electron is added to a uninegative gaseous ion to form a dinegative gaseous ion is called second electron gain enthalpy or second electron affinity.

In the first electron affinity of a gaseous atom, **Δ H = – ive** because energy is released when an electron is added to a neutral gaseous atom. In the **second electron affinity** of a gaseous atom, **Δ H = + ive** because energy has to be supplied to overcome the electrostatic force of repulsion between negatively charge electron to be added and the uninegative charge already present on uninegative gaseous ion. e.g.,

$O(g) + e^- \longrightarrow O^-(g) + 142\text{ kJ mol}^-$. Thus first electron affinity of O = –142 kJ mol⁻

$O^-(g) + e^- + 702\text{ kJ mol}^- \longrightarrow O^{2-}(g)$. Thus second electron affinity of O = +702 kJ mol⁻

EXAMPLE 13. *Calculate the energy in kJ and k cal released when 7.1 g of chlorine are completely converted to Cl^- (g) ion. The electron gain enthalpy of Cl (g) is –3.7 eV.*

SOLUTION. $Cl(g) + e^- \longrightarrow Cl^-(g) + 3.7\text{ eV}$

Energy released from

35.5 g Cl (g) = 3.7 eV

∴ Energy released from 7.1 g.

$$\text{Cl (g)} = \frac{3.7}{35.5}\times7.1 = 0.74\text{ eV}$$

(*a*) 1 eV = 96.5 kJ

∴ 0.74 eV = 96.5 × 0.74 = 71.41 kJ **Ans.**

(*b*) 1 eV = 23.064 k cal

0.74 eV = 23.064 × 0.74 = **17.07 k cal** **Ans.**

EXAMPLE 14. *Calculate the amount of energy released when 3.55 g of chlorine atoms are converted to Cl^- (g) ion. First electron affinity of Cl = – 349 kJ mol⁻. (at. wt. of Cl = 35.5)*

SOLUTION. no. of mol of Cl atoms

$$= \frac{\text{wt. of Cl}}{\text{at. wt. of Cl}} = \frac{3.55\text{g.}}{35.5\text{g.}} = 0.1 \text{ mol}$$

Energy released for 1 mol of Cl atoms = 349 kJ

Energy released for 0.1 mol of Cl atoms = 349 × 0.1

= **34.9 kJ** **Ans.**

EXAMPLE 15. *Find the value of ΔH in kJ mol⁻ for the reaction*

$$K(g) + F(g) \longrightarrow K^+(g) + F^-(g)$$

Given :Electron affinity of

$F = -3.48$ eV (atom)⁻; I.P. of

K = 4.3 eV (atom)⁻

SOLUTION. $K(g) + 4.3 \text{ eV (atom)}^- \longrightarrow K^+(g)$

$$F(g) + e^-(g) \longrightarrow F^-(g) + 3.48 \text{ eV (atom)}^-$$

$\therefore$ ΔH (molecule)⁻ = *I.P.* + *E.A* = + 4.3 eV – 3.48 eV

= 0.82 eV

1 mol = 6.023×10^{23} molecule

$\therefore$ ΔH mol⁻ = $0.82 \times 6.023 \times 10^{23}$ eV

$$= 0.82 \times 6.023 \times 10^{23} \text{ eV} \times \frac{1.602 \times 10^{-19} \times 10^{-3} \text{ kJ}}{1 \text{ eV}}$$

= **79.12 kJ** **Ans.**

EXAMPLE 16. *When half of the Avogadro number of A atoms transfer electron to its other half, 390 kJ energy has to be added. When these A^- are subsequently converted to A^+, 700 kJ energy has to be added. Find the value of I.P. and E.A. of A.*

SOLUTION. Let N = Avogadro's no. = 6.023×10^{23}

(*i*) $A \longrightarrow A^+ + e^-\,;\Delta H = I.P_1 = a$ eV

(*ii*) $A + e^- \longrightarrow A^-\,;\Delta H = -EA_1 = -b$ eV

$$\therefore \quad a \times \frac{N}{2} - b \times \frac{N}{2} = \frac{390 \times 10^3}{1.602 \times 10^{-19}} \text{ eV}$$

$$\left[\because 390 \text{ kJ} = 390 \times 10^3 \text{ J};\; 1 \text{ ev} = 1.602 \times 10^{-19} \text{ J}\right]$$

$$\therefore \quad \frac{N}{2}(a-b) = \frac{390 \times 10^3}{1.602 \times 10^{-19}} \text{ eV};$$

$$a - b = \frac{2 \times 390 \times 10^3}{1.602 \times 10^{-19} \times N}$$

$$\therefore \quad a - b = \frac{2 \times 390 \times 10^3}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}}$$

$$= 8.08 \text{ eV.} \qquad ...(1)$$

(*ii*) $X^- - 2e^- \longrightarrow \mathbf{X^+}\,;\Delta H = +EA_1 = +b$ eV

$X \longrightarrow X^+ + e^-\,;\quad \Delta H = +IP_1 = +a$ eV

$$\therefore \quad a \times \frac{N}{2} + b \times \frac{N}{2} = \frac{700 \times 10^3}{1.602 \times 10^{-19}} \text{ eV}$$

$[\because 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}]$

$$\therefore \quad a + b = \frac{700 \times 10^3 \times 2}{1.602 \times 10^{-19} \times 6.023 \times 10^{23}} \text{eV}$$

$$= 14.5 \text{ eV} \qquad ...(2)$$

Adding (1) and (2), we get

$a - b + a + b$ = 8.08 eV + 14.5 eV;

$2a$ = 22.58

$$\therefore \quad a = \frac{22.58}{2} = \mathbf{11.29 \text{ eV}}$$

b = 14.5 – 11.29 = **3.21 eV**

$[\because a + b = 14.5 \text{ eV}]$

EXAMPLE 17. *Calculate the number of atoms of fluorine and chlorine gases present in a mixture of fluorine and chlorine with the help of following data.*

(*i*) Addition of an electron to each atom of the sample releases a total energy of 68.8 kJ

(*ii*) Removal of an electron from each atom of the sample aquire a total energy of 284 kJ.

(*iii*) Electon affinity (EA) of fluorine = 5.53×10^{-22} kJ mol⁻.

(*iv*) E.A. of chlorine = 5.78×10^{-22} kJ mol⁻.

(*v*) Ionisation energy (I.E.) of fluorine = 27.91×10^{-22} kJ mol⁻.

(*vi*) I.E. of chlorine = 20.77×10^{-22} kJ mol⁻.

SOLUTION. Suppose the ratio of F and Cl atoms = $a : b$

(*i*) I.E. *i.e.*, Energy required to remove one electron each from F and Cl in the mixture = $(a \times 27.91 \times 10^{-22}) + b \times 20.77 \times 10^{-22} = 284$ kJ ...(*A*)

(*ii*) E.A. i.e., energy released when one electron is added to F and Cl of the mixture = $a \times -5.53 \times 10^{-22} + b \times -5.78 \times 10^{-22} = -68.8$ kJ ...(*B*)

Solving equations (*A*) and (*B*), we get :

$27.91 \times 10^{-22}\,a + 20.77 \times 10^{-22}\,b = 284$ ...(*A*)

$-5.53 \times 10^{-22}\,a - 5.78 \times 10^{-22}\,b = -68.8$ ...(*B*)

Multiplying equation (*A*) with -5.53×10^{-22} and equation (*B*) with 27.91×10^{-22} and subtracting, we get

$27.91 \times 10^{-22} \times -5.53 \times 10^{-22}\,a + 20.77 \times 10^{-22} \times -5.53 \times 10^{-22}\,b = 284 \times -5.53 \times 10^{-22}$

$-5.53 \times 10^{-22} \times 27.91 \times 10^{-22}\,a - 5.78 \times 10^{-22} \times 27.91 \times 10^{-22}\,b = -68.8 \times 27.91 \times 10^{-22}$

$$\begin{array}{rcl} -114.8581 \times 10^{-44}\,b & = & -1570.52 \times 10^{-22} \\ -161.3198 \times 10^{-44}\,b & = & -1920.208 \times 10^{-22} \\ + & & + \qquad \text{(subtracting)} \\ \hline 46.4617 \times 10^{-44}\,b & = & 349.688 \times 10^{-22} \end{array}$$

$$\therefore \quad b = \frac{349.688 \times 10^{-22}}{46.4617 \times 10^{-44}}$$

$= \mathbf{7.5 \times 10^{22}}$

= **no. of chlorine atoms.** **Ans.**

Substituting the value of (*b*) in equation (*A*), we get :

$$27.91 \times 10^{-22} a + 20.77 \times 10^{-22} \times 7.5 \times 10^{22}$$

$$= 284\ 27.91 \times 10^{-22} a + 155.775$$

$$= 284, 27.91 \times 10^{-22} a$$

$$= 284 - 155.775$$

$$= 128.225$$

$$\therefore \quad a = \frac{128.225}{27.91 \times 10^{-22}}$$

$$= 4.6 \times 10^{22}$$

= no. of fluorine atoms. **Ans.**

EXAMPLE 18. *What is the value of electron gain* enthalpy *of Na^+ if I.E. of Na = 5.1 eV?*

(a) *–5.1 eV*

(b) *–10.2 eV*

(c) *+ 2.55 eV*

(d) *+ 10.2 eV*

(AIPMT, 2011)

SOLUTION. Given: $Na \rightarrow Na^+ + \bar{e}$; IE_1, *i.e.*, $\Delta H = +5.1$ eV

$\therefore$ $Na^+ + \bar{e} = Na$; $\bar{e}$-gain enthalpy, $\Delta H = -5.1$ eV.

So, the correct answer is (*a*).

13.5 ELECTRONEGATIVITY

Electronegativity of an element is the relative tendency (or power) of an element in a molecule to attract the shared pair of electrons towards itself.

Linus Pauling related the electonegativity difference ($X_A - X_B$) between two atoms *A* and *B* (forming a bond) to the bond energies (*B.E.*) of the molecules as :

(*a*) $X_A - X_B = 0.102$

$$\left[\text{B.E. of AB} - \frac{1}{2}(\text{B.E.}(A-A) + \text{B.E.}(B-B))\right]^{1/2} \text{ kJ mol}^-$$

When bond energies are given in **kJ mol⁻**

(*b*) $X_A - X_B = 0.208$

$$\left[\text{B.E. of AB} - \{\text{B.E.}(A-A) \times \text{B.E.}(B-B)\}^{1/2}\right]^{1/2} \text{ k cal mol}^-$$

When bond energies are given in **k cal mol⁻**.

EXAMPLE 19. *Calculate the electronegativity of fluorine from the bond energy of ClF (255.224 kJ mol⁻) if electronegativity of Cl = 3.2; bond energies of Cl_2 and F_2 are 243 and 158 kJ mol⁻ respectively.*

SOLUTION. According to Pauling :

$$X_F - X_{Cl} = 0.102 \left[\text{BE of ClF} - \frac{(\text{BE of } Cl_2 + \text{BE of } F_2)}{2}\right]^{1/2}$$

because bond energy is given in kJ mol⁻

$$\therefore \quad X_F = X_{Cl} + 0.102 \left[255.224 - \frac{243 + 158}{2}\right]^{1/2}$$

$$= 3.2 + 0.102\,[255.224 - 200.5]^{1/2}$$

$$= 3.0 + 0.102 \times (54.724)^{1/2}$$

$$= 3.2 + (0.102 \times 7.397)$$

$$= 3.2 + 0.75 = \mathbf{3.95}$$

Ans.

EXAMPLE 20. *Calculate the electronegativity of chlorine from the bond energy of HCl (103.2 k cal mol⁻) if electronegativity of H = 2.1, bond energies of H – H and Cl – Cl are 104.2 k cal mol⁻ and 58 k cal mol⁻ respectively.*

SOLUTION. We know that

$$X_{Cl} - X_H = 0.208\,[\text{BE of HCl} - \{\text{BE }(H-H) \times \text{BE }(Cl-Cl)\}^{1/2}]^{1/2} \text{ k cal mol}^-$$

X represents electronegativity.

$$\therefore \quad X_{Cl} = X_H + 0.208\,[103.2 - (104.2 \times 58)^{1/2}]^{1/2}$$

$$= 2.1 + 0.208\,[103.2 - 77.74]^{1/2}$$

$$= 2.1 + 0.208 \times (25.46)^{1/2}$$

$$= 2.1 + (0.208 \times 5.046)$$

$$= 2.1 + 1.05 = \mathbf{3.15}$$

Ans.

EXAMPLE 21. *Electronegativity of nitrogen atom as available from tables in literature is 3.0. Calculate the value of electronegativity of nitrogen from the bond energies of bonds N – F = 56 k cal mol⁻, F – F = 37.8 k cal mol⁻ and N – N = 32 k cal mol⁻. Electongegativity of F = 4.0. Compare the calculated value with tabulated value and suggest a reason for the difference if any.*

SOLUTION. Since bond energies are given in k cal mol⁻, we have :

$$X_F - X_N = 0.208\,[\text{BE of }(N-F) - \{\text{BE }(N-N) \times \text{BE }(F-F)\}^{1/2}]^{1/2}$$

$$4.0 - X_N = 0.208\,[56 - \{32 \times 37.8\}^{1/2}]^{1/2}$$

$$= 0.208\,[56 - (1209.6)^{1/2}]^{1/2}$$

$$= 0.208\,[56 - 34.78]^{1/2}$$

$$= 0.208\,(21.22)^{1/2} = 0.208 \times 4.6 = 0.96$$

$$\therefore \quad X_N = 4 - 0.96 = \mathbf{3.04}$$

The calculated value of electronegativity of *N* (= 3.04) is different from that of tabulated value (= 3.0) because the tabulated value is an average value from many compounds.

EXAMPLE 22. *Calculate the electronegativity of fluorine from the following data.*

$E_{H-H} = 104.2$ *k cal mol⁻*, $E_{F-F} = 36.6$ *k cal mol⁻*, $E_{H-F} = 134.6$ *k cal mol⁻* **(UP SEAT, 1996)**

SOLUTION. *We know that electronegativity of H = 2.1. Since bond energy is given in k cal mol⁻, so :*

$$X_F - X_H = 0.208\,[BE_{H-F} - \{BE_{H-H} \times BE_{F-F}\}^{1/2}]^{1/2}$$

$$X_F - 2.1 = 0.208\,[134.6 - \{104.2 \times 36.6\}^{1/2}]^{1/2}$$

$$X_F = 2.1 + 0.208\,[134.6 - (3813.72)^{1/2} \text{ i.e., } 61.76]^{1/2}$$

$$= 2.1 + 0.208 \times (72.84)^{1/2}$$

$$= 2.1 + (0.208 \times 8.53) = 2.1 + 1.77$$

$$= \mathbf{3.87}$$

Ans.

EXAMPLE 23. *Using Allred-Rochow equation, calculate the electronegativity of Zn atom from the following data.*

Covalent radius of Zn = 1.25 A°, at. no., Z = 30 and screening constant, σ = 25.65.

SOLUTION. According to Allred-Rochow :

Electronegative (x) of

$$\text{Zn} = \frac{0.359 \times \text{Zeff}}{r^2 \text{ (in A°)}} + 0.744 \qquad ...(1)$$

where Z_{eff} = (At. no., Z) – (Screening constant, σ)

$= 30 - 25.65 = 4.35$

Substituting the values in (1), we get :

Electronegativity of Zn

$$= \frac{0.359 \times 4.35}{(1.25)^2} + 0.744$$

$= 0.999 + 0.744 =$ **1.743** **Ans.**

13.6. ELECTRONEGATIVITY AND PERCENTAGE IONIC CHARACTER

Type : Electronegativity difference and percentage ionic character. Different methods to calculate percentage ionic character in a bond are given below. If X_A and X_B represent the electronegativities of atoms A and B and $X_B > X_A$, then :

(*i*) According to Hanny and Smyth : % age ionic character $= 16\ (\Delta x) + 3.5\ (\Delta x)^2$

Where $\Delta x = X_B - X_A$

(*ii*) According to Pauling

(*a*) % age ionic character

$= 18\ (X_B - X_A)^{1.4}$

(*b*) % age ionic character

$= [1 - e^{-0.25\,(X_B - X_A)}] \times 100$

Where $e = 2.732$.

EXAMPLE 24. *Arrange HCl, HBr and HI in the increasing order of their percentage ionic character. The electronegativity of H, Cl, Br and I are 2.1, 3.0, 2.8 and 2.4 respectively.*

SOLUTION. (*a*) For HCl, % age ionic character

$= 16\ (\Delta x) + 3.5\ (\Delta x)^2$

Where $\Delta x = X_{Cl} - X_H = 3.0 - 2.1 = 0.9$

∴ % age ionic character

$= 16\ (0.9) + 3.5\ (0.9)^2 =$ **17.235**

(*b*) For HBr, % age ionic character

$= 16\ (\Delta x) + 3.5\ (\Delta x)^2$

Where $\Delta x = X_{Br} - X_H = 2.8 - 2.1 = 0.7$

∴ % age ionic character

$= 16\ (0.7) + 3.5\ (0.7)^2 =$ **12.9**

(*c*) For HI, % age ionic character

$= 16\ (\Delta x) + 3.5\ (\Delta x)^2$

Where $\Delta x = X_I - X_H = 2.4 - 2.1 = 0.3$

∴ % age ionic character

$= 16\ (0.3) + 3.5\ (0.3)^2 =$ **5.1**

∴ Increasing order of ionic character

= HI < HBr < HCI.

EXAMPLE 25. *Calculate the percentage ionic character of Si–H bond in SiH_4 assuming the Pauling's electronegativity value of Si and H to be 1.8 and 2.1 respectively.*

SOLUTION. According to Pauling

% age ionic character

$= 18\ (X_B - X_A)^{1.4} = 18\ (2.1 - 1.8)^{1.4}$

$= 18\ (0.3)^{1.4}$

∴ Log (% age ionic character)

$= \text{Log } 18\ (0.3)^{1.4}$

$= \log 18 + 1.4 \log 1.3$

$= 1.2552 + 1.4\ (-0.5228)$

$= 1.2552 - 0.7319 = 0.5233.$

Taking antilog of both sides, we get :

% age ionic character

= antilog 0.5233 = **3.34%.** **Ans.**

EXAMPLE 26. *Calculate the percent ionic character in H–F bond if the electronegativities of H and F are 2.1 and 4.0 respectively.*

SOLUTION. We know that, % age ionic character

$= [1 - e^{-0.25\,(X_B - X_A)}] \times 100$

Electronegativity of H

$= 2.1, F = 4.0;\ X_B - X_A$

$= 4.0 - 2.1$

$= 1.9;\ e = 2.732$

∴ % age ionic character

$= [1 - (2.732)^{-0.25\,(1.9)}] \times 100$

$= [1 - (2.732)^{-0.475}] \times 100$

$= [1 - 0.620] \times 100 = 0.38 \times 100$

$= 38\%$

To get value of $(2.732)^{-0.475}$:

Let $x = (2.732)^{-0.475}$

Taking logs of both sides, we get :

$\log x = \log (2.732)^{-0.475}$

$= -0.475 \log 2.732$

$= -0.475 \times 0.4365$

$= -0.2073$

$= -0.2073 + 1 - 1$

$= \bar{1}.7927$

∴ $x = \text{anti log } \bar{1}.7927$

$= 0.620$

13.7 CALCULATING BOND ANGLE IN MOLECULES

Type. To calculate bond angle in a molecule, use the relation : $\mu = (\mu_1^2 + \mu_2^2 + 2\mu_1 \mu_2 \cos \alpha)^{1/2}$ where μ, μ_1 and μ_2 are the dipole moments of molecule, one bond and second bond respectively. α = Bond angle of the molecule.

EXAMPLE 27. *The experimental bond angle in water molecule is 105° while O–H bond distance in this molecule is 94 pm. Calculate the charge on oxygen atom if dipole moment of molecule is 1.84 D.*

SOLUTION. There are two O–H bonds in HOH molecule. Let dipole moment of OH –bond = x. Dipolemoment of HOH = 1.84 D. Distance, $d = 94$ pm $= 94 \times 10^{-10}$ cm.

$$\mu\,(H_2O) = [\mu^2_{OH} + \mu^2_{OH} + 2\mu^2_{OH}\cos 105°]^{1/2}$$
$$= [x^2 + x^2 + 2x^2 \cos 105°]^{1/2}$$
$$1.84 = [2x^2\,(1 + \cos 105°)]^{1/2}$$
$$= [2x^2\,(1 - 0.2588)]^{1/2} = (1.4824\,x^2)^{1/2}$$
$$1.84 = 1.2175\,x$$
$$\therefore \quad x = \frac{1.84}{1.2175} = 1.51 \text{ debye}$$

Or $\mu_{O\text{–}H} = 1.51 \times 10^{-18}$ esu cm

[∵ 1 Debye = 10^{-18} esu cm]

Also, μ_{OH} = Charge (δ) × distance (d)

$$\therefore \quad \text{Charge, } \delta = \frac{\mu_{OH}}{d} = \frac{1.51\times10^{-18}\text{ esu cm}}{94\times10^{-10}\text{ cm}}$$

$$= \mathbf{1.606 \times 10^{-10}\ esu} \qquad \textbf{Ans.}$$

13.8 CONDITION TO FORM IONS IN SOLUTION

Type. If hydration energy, ΔH_h (i.e., energy released during hydration) is greater than ionisation energy, ΔH ionisation (i.e., energy used during ionisation), the compound splits into ions. In other words :

Ions are formed if ΔH (hydration) > ΔH (ionisation)

Example 28. *Anhydrous* $AlCl_3$ *is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution. (Ionisation energy for* $AlCl_3$ *= 5137 kJ mol⁻ ;* ΔH *(hydration) for* Al^{3+} *= –4655 kJ mol⁻ ;* ΔH *(hydration) for* Cl^- *= –381 kJ mol⁻).* **(IIT, July 1997)**

Solution. Reaction : $AlCl_3 + aq \longrightarrow AlCl_3\,(aq)$; $\Delta H = ?$

We know that : ΔH = Energy released during hydration + Energy used during ionisation

$$= [-4665 + (3 \times -381)] + 5137$$
$$= -4665 - 1143 + 5137$$
$$= -5808 + 5137 = -671 \text{ kJ}$$

Since ΔH (hydration), 5808 > ΔH (ionisation), 5137, $AlCl_3$ will split into ions, Al^{3+} and $3Cl^-$. Also, ΔH is –ve (= – 671 kJ), the ionisation will take place.

13.9 EXTRA IONIC RESONANCE ENERGY

Type. Extra ionic resonance enegy of *AB* molecule = [Bond energy of *AB* molecule] – [Bond energy of *A–A* × bond energy of *B–B*]$^{1/2}$

Example 29. *Calculate the extra ionic resonance energy in HI molecule. Bond energies of HI, H–H and I–I are 71, 104.2 and 36 k cal mol⁻ respectively.*

Solution. We know that :

Extra ionic resonance energy in HI molecule = [Bond energy of H–I] – [Bond energy of H–H × bond energy of I–I]$^{1/2}$ = 71 – [104.2 × 36]$^{1/2}$ = 71 – 61.2 = 9.8 k cal.

13.10 DIPOLE MOMENT

Dipole moment (μ) of a molecule is *equal to the product of its net positive or negative charge and distance between the charges.*

Mathematically, $\mu = e \times d$

where e = net +ive or –ive charge and is of the order of 10^{-10} esu.

d = Distance between the charges and is of the order of 10^{-8} cm

∴ μ has a value of the order of 10^{-10} esu × 10^{-8} cm *i.e.,* **10^{-18} esu cm.**

This quantity is called a **Debye** *i.e., D.* (unit of dipole moment)

In **C.G.S. units, charge on an electron = 4.8 × 10^{-10} esu cm.**

In SI units, charge on an electron

= 1.602 × 10^{-19} coulomb (*C*)

In SI units, μ = 1.602 × 10^{-19} C × 10^{-10} m

= 1.602 × 10^{-29} Cm.

So, **in SI units,** *dipole moment is expressed* in **C.m** *i.e.,* **coulomb metre** while in C.G.S. units, dipole moment is expressed in **esu cm** (*i.e.,* **electrostatic unit centimeter**).

Note.(*i*) **In C.G.S units, 1 *D* = 10^{-18} (esu of charge) cm.**

(*ii*) Esu is defined as **1 *C*** *i.e.,* coulomb = **2.998 × 10^9 esu.**

(*iii*) **In SI units** :1 *D* = 10^{-18} esu cm

$$\times \frac{1\,C}{2.998\times10^{9}\text{ esu}} \times \frac{1\text{ m}}{10^{2}\text{ cm}}$$

1 *D* = 3.336 × 10^{-30} C. m.

(*iv*) Since charge on an electron (*e*)

= 4.8 × 10^{-10} esu

∴ Fraction of an electronic charge

$$= \frac{\text{Charge, } \delta\ (= \frac{\mu}{d})}{4.8\times10^{-10}\text{ esu/e}}$$

Example 30. *A diatomic molecule has a dipole moment of 0.38 D. If its bond distance is 1.61 A°, calculate the fraction of an electronic charge, e, that exists on each atom.*

Solution. μ = dipole moment = 0.38

D = 0.38 × 10^{-18} esu. cm.

d = 1.61 A° = 1.61 × 10^{-8} cm

$$\therefore \quad \text{charge, } \delta = \frac{\mu}{d} = \frac{0.38\times10^{-18}\ esu.cm}{1.61\times10^{-8}\ cm}$$

= 2.36 × 10^{-11} esu.

∴ Fraction of electronic charge

$$= \frac{2.36\times10^{-11}\ esu}{4.8\times10^{-10}\ esu/e}$$

[∵ charge on an electron (*e*) = 4.8 × 10^{-10}esu]

= 0.049

Or = 0.049 × 100 = **4.9%** **Ans.**

Example 31. *The dipole moment of a diatomic molecule is 1.2 D. Calculate its value in SI units.*

SOLUTION. $1\ D = 10^{-18}$(esu of charge). cm

$$\therefore \quad 1.2\ D = 1.2 \times 10^{-18}\ \text{esu.cm} \times \frac{1C}{2.998\times 10^{9}\ \text{esu}} \times \frac{1\text{m}}{10^{2}\ \text{cm}}$$

$$= 4.0 \times 10^{-30}\ \text{C.m.}$$

i.e., coulomb metre.

Type. To find % age ionic character in *A–B* molecule, use the following relations.

(*i*)*Calculated dipole moment of*

$A - B$ (μ_{AB}) = Charge on electron in coulomb (*C*) × *A–B* bond length in metre (*m*)

= (1.602×10^{-19} C) × (bond length in metre)

(*ii*) *% age ionic character*

$$= \frac{\mu_{A-B}\ \text{(experimental) in C.m.}}{\text{calculated } \mu_{AB} \text{ in C.m.}} \times 100$$

Or (*i*) *Calculated dipole moment*

AB (μ_{AB}) = Charge on electron in esu × *A*–B bond length in cm

= 4.8×10^{-10} esu cm × bond length in cm

(*ii*) *% age ionic character*

$$= \frac{\mu_{AB}\ \text{(experimental) in esu cm}}{\mu_{AB}\ \text{(calculated) in esu cm}} \times 100$$

See section, 13.13

EXAMPLE 32. *0.5 N_0 atoms of $(A)_g$ are converted to $(A^+)_g$ by energy, ΔH_1 and 0.5 N_0 atoms of $(A)_g$ are converted to $(A^-)_g$ by energy, ΔH_2. Calculate ionisation energy (I. E.) and electron affinity (E. A.) of $(A)_g$.*

SOLUTION. Suppose *I. E.* of $(A)_g$ per atom = *I* and *E. A.* of $(A)_g$ per atom = $-E$.

(*i*) $(A)_g + I \longrightarrow (A^+)_g + 1\ e^-$

$\therefore$ Energy needed to ionise 0.5 N_0 atoms of $(A)_g$

$= 0.5\ N_0 I$

Thus : $\quad 0.5\ N_0 I = \Delta H_1$ ...(1)

Or $\quad I = \dfrac{\Delta H_1}{0.5 N_0}$

(*ii*) $(A)_g + e^- \longrightarrow (A^-)_g + E$

$\therefore$ Energy released by 0.5 N_0 atoms of $(A)_g$

$= -0.5\ N_0 E$

Thus $0.5\ N_0 I - 0.5\ N_0 E$

$= \Delta H_2$ ...(2)

Substituting the value of $0.5\ N_0 I$ from (1) in (2), we get:

$\Delta H_1 - 0.5\ N_0 E = \Delta H_2$

Or $\quad -0.5\ N_0 E = \Delta H_2 - \Delta H_1 \quad \therefore \quad -E = \dfrac{\Delta H_2 - \Delta H_1}{0.5 N_0}$

$\therefore$ Ionisation energy

$= \dfrac{\Delta H_1}{0.5 N_0}$ atom$^-$ **Ans.**

Electron affinity $= \dfrac{\Delta H_2 - \Delta H_1}{0.5 N_0}$ atom$^-$ **Ans.**

13.11 PREDICTING TYPE OF HYBRIDISATION

Tips to predict the type of hybridisation of central atom in a molecule or ion.

1. Add the number of valence electrons of all the atoms present in the given molecule or ion.
2. In case of a cation, subtract number of electrons equal to the charge on cation and in case of an anion, add number of electrons equal to the charge on the anion.
3. (*i*) If the result obtained in step 2 is less than 8, divide it by 2 and find the sum of the quotient and remainder.

   (*ii*) If the result obtained in step 2 lies between 9 and 56, divide it by 8 and find the first quotient (Q_1). Divide the remainder R_1 (if any) by 2 and find the quotient (Q_2). Add all the quotients and the final remainder (R_2).

Let the final result obtained in (*i*) or (*ii*) be *X*. The type of hybridisation is decided by the value of *X* as follows :

Value of *X*	2	3	4	5	6	7
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

EXAMPLE 33. *Find the type of hybridisation of N in NH_4^+*

SOLUTION. NH_4^+. ${}_7N = 1s^2\ 2s^2 2p^3$; ${}_1H = 1s^1$

Total valence electrons $= 5 + (4 \times 1) = 9$

Total electrons in NH_4^+ $= 9 - 1 = 8$; $\dfrac{8}{2}$

$= 4\ (Q_1) + R_1\ (0); X = 4$

$\therefore$ Hybridisation = sp^3 **Ans.**

EXAMPLE 34. *Find the type of hybridisation of S in SO_4^{2-}.*

SOLUTION. SO_4^{2-}. ${}_{16}S = (Ne)^{10}\ 3s^2\ 3p^4$;

${}_8O = 1s^2\ 2s^2\ 2p^4$

Total valence electrons $= 6 + (6 \times 4) = 30$

Total electrons in SO_4^{2-} $= 30 + 2 = 32$;

$\dfrac{32}{8} = 4(Q_1) + 0(R_1);\ X = 4 + 0 = 4$

$\therefore$ Hybridisation = sp^3 **Ans.**

EXAMPLE 35. *Find the type of hybridisation of O in H_2O.*

SOLUTION. H_2O. ${}_8O = 1s^2\ 2s^2\ 2p^4$; ${}_1H = 1$

$\therefore$ Total valence electrons in H_2O

$= (2 \times 1) + 6 = 8$;

$\dfrac{8}{2} = 4(Q_1) + R_1(0);\ X = 4 + 0 = 4$

$\therefore$ Hybridisation = sp^3

13.12 BOND ORDER

Bond order. It is defined as the number of covalent bonds in a molecule.

Bond order $= \frac{N_b - N_a}{2}$ where N_a and N_b are the number of electrons in antibonding and bonding molecular orbitals.

(*a*) The molecular orbital (M.O.) electronic configurations (also electron configurations) of molecules upto N_2 i.e., H_2, He_2, Li_2, Be_2, B_2, C_2 and N_2 are in the order :

$$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^2$$
$$= (\pi_{2py})^2 (\pi_{2pz})^2 (\pi^*_{2px})^2$$
$$= (\pi^*_{2py})^2 (\sigma^*_{2pz})^2$$

(*b*) The M.O. electronic configurations for molecules O_2, F_2 and Ne_2 are :

$$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2pz})^2 (\pi_{2px})^2$$
$$= (\pi_{2py})^2 (\pi^*_{2px})^2 = (\pi^*_{2py})^2 (\sigma^*_{2pz})^2$$

(*c*) While filling electrons in molecular orbitals, each M.O. should contain one electron first and then pairing takes place.

(*d*) Firstly find total number of electrons in a given molecule or ion and then fill them in the increasing order of their energies shown in (*a*) and (*b*) above.

EXAMPLE 36. *Write the molecular orbital electron configuration of*

(i) H_2^- *(ii)* He_2^+

(iii) N_2 *(at. no., H = 1, He = 2; N = 7)*

SOLUTION. (*i*) no. of electrons in H_2^-

$$= (2 \times \text{at. no. of H}) + 1$$
$$= (2 \times 1) + 1 = 3$$

∴ M.O. electron configuration of

$$H_2^- = (\sigma_{1s})^2 (\sigma^*_{1s})^1$$

(*ii*) no. of electrons in

$$He_2^+ = (2 \times \text{at. no. of He}) - 1$$
$$= (2 \times 2) - 1 = 3$$

∴ M.O. electron configuration of

$$He_2^+ = (\sigma_{1s})^2 (\sigma^*_{1s})^1$$

(*iii*) no. of electrons in

$$N_2 = (2 \times \text{at. no. of N}) = 2 \times 7 = 14$$

∴ M.O. electron configuration of

$$N_2 = (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^2$$
$$= (\pi_{2py})^2 (\sigma_{2pz})^2$$

EXAMPLE 37. *Find the bond order in* B_2 *molecule. (at. no. of B = 5).*

SOLUTION. no. of electrons in

$$B_2 = (2 \times \text{at. no. of B}) = 2 \times 5 = 10$$

∴ M.O. electron configuration of

$$B_2 = (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^1$$
$$= (\pi_{2py})^1$$

∴ Bond order $= \frac{N_b - N_a}{2} = \frac{6-4}{2} = \mathbf{1}$ **Ans.**

EXAMPLE 38. *Find the bond order in* O_2 *molecule.*

(CBSE, 2007)

SOLUTION. $_8O = 1s^2\, 2s^2\, 2p^4$

∴ Total number of electrons in O_2 molecule

$$= 2 \times 8 = 16$$

These 16 electrons occupy different molecular orbitals (M.O.) in the increasing order of their energies. Thus

Electron configuration of O_2 molecule

$$= KK\, (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2pz})^2$$
$$(\pi_{2px})^2 = (\pi_{2py})^2 (\pi^*_{2px})^1 = (\pi^*_{2py})^1$$

$$\therefore \text{Bond order} = \frac{\text{no. of electron in bonding M.O.} - \text{no. of electrons in antibonding M.O.}}{2}$$

$$= \frac{8-4}{2} = 2$$ **Ans.**

13.13 AIEEE PATTERN EXAMPLES

EXAMPLE 39. *Experimental dipole moment of HBr is 0.263 × 10^{-29} C. m. If bond length of H–Br is 1.41 A°, the percentage of ionic character in H–Br is :*

(a) 5.8% *(b) 11.63%*

(c) 23.26% *(d) 90%*

SOLUTION. Dipole moment of HBr = Charge on electron is coulomb (*C*) × H–Br bond length in metre (*m*).

$$= (1.602 \times 10^{-19}\ \text{C}) \times (1.41 \times 10^{-10}\ \text{m})$$
$$= 2.26 \times 10^{-29}\ \text{C.m.}$$

$$\%\ \text{age ionic character} = \frac{\mu\,(\text{experimental})}{\mu\,(\text{calculated})} \times 100$$

$$= \frac{0.263 \times 10^{-29}\ \text{C.m}}{2.26 \times 10^{-29}\ \text{C.m}} \times 100 = 11.63\%.$$

So, the correct answer is (*b*).

EXAMPLE 40. *The dipole moment of HF molecule is 1.91 D and bond distance is 0.92 A°. The fractional charge δ on H and F in HF bond respectively is :*

(a) + 0.43, –99.57 *(b) –0.43, +99.57*

(c) +0.43, –0.43 *(d) 4.3%, –4.3%*

SOLUTION. Dipole moment = Charge × distance

$$\therefore \text{Charge} = \frac{\text{Dipole moment}}{\text{distance}}$$

$$= \frac{1.91\,D}{0.92\,A^\circ} = \frac{1.91 \times 10^{-18}\ \text{esu cm}}{0.92 \times 10^{-8}\ \text{cm}}$$

$$= 2.08 \times 10^{-10}\ \text{esu}$$

∴ Fraction of electron charge, δ

$$= \frac{\text{Calculated charge}}{\text{Electronic charge}},$$

$$= \frac{2.08\times10^{-10}\text{esu}}{4.8\times10^{-10}\text{ esu/e}} = 0.43$$

$\therefore \quad \delta_{H}^{+} = +0.43; \delta_{F}^{-} = -0.43$

So, the correct answer is (*c*).

EXAMPLE 41. *The percentage ionic character of C–H bond in CH_4 assuming the Pauli's electronegativity value of C and H to be 2.5 and 2.1 respectively is :*

(*a*) 3.34%	(*b*) 6.68%
(*c*) 4.99%	(*d*) 6.96%

SOLUTION. Electronegativity of

$$C = 2.5, H = 2.1.$$

So, $\Delta X = 2.5 - 2.1 = 0.4$. We know :

$$\%\text{ age ionic character} = 16\,(\Delta x) + 3.5\,(\Delta x)^2$$
$$= 16 \times 0.4 + 3.5\,(0.4)^2$$
$$= 6.4 + 0.56 = 6.96\%$$

So, the correct answer is (*d*).

EXAMPLE 42. *The dipole moment of KCl is 3.336×10^{-29} coulomb metre 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,

$$\mu = 3.336 \times 10^{-29} \text{ coulomb metre}$$

Interatomic distance, $d = 2.6 \times 10^{-10}$ m; charge, δ = ?

(*a*) $\mu = \delta \times d$

So, $$\delta = \frac{\mu}{d} = \frac{3.336\times10^{-29}\text{ coulomb metre}}{2.6\times10^{-10}\text{ m}}$$
$$= 1.283 \times 10^{-19} \text{ coulomb.}$$

Since 1.602×10^{-19} coulomb charge is present on each ion :

∴ % age ionic character

$$= \frac{1.283\times10^{-19}\text{ coulomb}}{1.602\times10^{-19}\text{ coulomb}}\times100$$
$$= 80.09\%$$

(*b*) $\mu = \delta \times d$

$$= 1.602 \times 10^{-19} \text{ coulomb} \times 2.6 \times 10^{-10} \text{ m}$$

μ = **4.1652×10^{-29} coulomb metre** **Ans.**

EXAMPLE 43. *The covalent radius of double bonded oxygen atoms in CO_2 is :*

(*a*) 0.98 A°	(*b*) 0.32 A°
(*c*) 0.49 A°	(*d*) 4.9 A°

if oxygen to oxygen distance is 2.323 A° and (C=) covalent radius is 0.67 A°.

SOLUTION. Let covalent radius of double bonded oxygen atoms = *a*

In $\quad O = C = O$:

covalent radius of (O=) + (=C) + (C=) + (=O) = *a* + 0.67 A° + 0.67 A° + *a* = 2*a* + 1.34 A°

$$\therefore \quad 2a + 1.34 = 2.323; a = \frac{2.323 - 1.34}{2}\text{ A°}$$

Or $a = 0.4915 \simeq 0.49$ A°

= covalent radius of (O=)

So, the correct answer is (*c*).

EXAMPLE 44. *The mass fraction of hydrogen in a compound of group 14 element is 0.25. The chemical formula of the hydride of this element is :*

(*a*) CH_4	(*b*) SiH_4
(*c*) SiH_6	(*d*) C_2H_6

(at. wt., C = 12, Si = 28, H = 1)

SOLUTION. Let element of group 14 is *A* and its mass number is B. Since valency of group 14 element is 4, so its formula is AH_4. Mass fraction of hydrogen in

$$AH_4 = \frac{4\times1}{B+4}$$

Hence $$\frac{4}{B+4} = 0.25 \text{ (given)}; 4 = 0.25\,B + 4 \times 0.25$$

Or $0.25\,B = 4 - 1 = 3.$

So, $$B = \frac{3}{0.25} = 12 \quad (= \text{at. wt. of } C)$$

∴ Chemical formula of AH_4 = **CH_4**.

So, the correct answer is (*a*).

EXAMPLE 45. *The number of period to which an element with atomic number 21 belongs is :*

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

SOLUTION. (*i*) Electron configuration of element with at. no. 21

$$= 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$$

Number of period = Highest shell present in the electronic configuration of the element = **4**

So, the correct answer is (*d*).

EXAMPLE 46. *If the molecule of HCl was totally polar, the expected value of dipole moment is 6.12 D (debye), but the experimental value of dipole moment was 1.03 D. Calculate the percentage ionic character.*

(*a*) 17	(*b*) 83
(*c*) 50	(*d*) zero

(*e*) 90. **(Kerala PET, 2005)**

SOLUTION. We know that :

% age of ionic character

$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}}\times100$$

$$= \frac{1.03}{6.12}\times100 = 16.83 \simeq 17\%.$$

So, the correct answer is (*a*).

EXAMPLE 47. *The number of π electrons present in 2.6 g of ethyne are :*

(a) N_A (b) $2N_A$

(c) $0.4\,N_A$ (d) $4\,N_A$

if N_A = Avogadro's number.

SOLUTION. Ethyne is $CH \overset{\pi}{\underset{\pi}{\equiv}} C$. There are two π-bonds in ethyne. One bond contains 2 electrons. So, there are 2 × 2 i.e., 4π electrons is one molecule of ethyne.

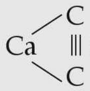
Mol. wt. of $CH \equiv CH$ = 12 + 1 + 12 + 1 = 26 = 1 mol of $CH \equiv CH$

∴ 26 g. $CH \equiv CH$ contain π electrons = 4 × N_A

2.6 g. $CH \equiv CH$ contain π electrons

$$= \frac{4\,N_A \times 2.6}{26} = 0.4\,N_A$$

So, the correct answer is (*c*).

Note. The same number of π electrons will be present in 6.4 g of calcium carbide, CaC_2 or  (mol. wt. = 64).

EXAMPLE 48. *Energy needed to convert 5.75 g Na-atom in gaseous state to form Na^+ (g) is :*

(a) 2829 kJ (b) 28.29 kJ

(c) 123 kJ (d) 282.9 kJ

(Ist I. E. of Na = 492 kJ mol⁻ ; mass no. of Na = 23)

SOLUTION. No. of mol of Na

$$= \frac{\text{wt. of Na}}{\text{At. wt. of Na}} = \frac{5.75\text{ g.}}{23\text{ g.}}$$

= 0.25 mol.

Energy required to convert 1 mol Na to Na^+ (g)

= 492 kJ

Energy required to convert 0.25 mol Na to Na^+ (g)

= 492 × 0.25 kJ

= 123 kJ.

So, the correct answer is (*c*).

EXAMPLE 49. *The electron affinity of Cl when 1.0g of Cl-atom is converted to Cl^- (g) liberate 9.83 kJ energy is :*

(a) –349 kJ (b) +349 kJ

(c) 35.5 kJ (d) –35.5 kJ

SOLUTION. $Cl\,(g) + 1e^- \longrightarrow Cl^-\,(g)$

1 g of Cl-atoms liberate energy

= 9.83 kJ

∴ 35.5 g of Cl-atoms liberate energy

= 9.83 × 35.5 = 349 kJ

∴ Electron affinity of Cl

= –349 kJ

So, the correct answer is (*a*)

EXAMPLE 50. *The value of first ionisation potential of potassium atom if Δ H for the gaseous phase reaction:*

$$K\,(g) + F\,(g) \longrightarrow K^+\,(g) + F^-\,(g)$$

is 0.82 eV (atom)⁻ and first electron affinity of F is 3.48 eV (atom)⁻, is :

(a) 2.15 eV atom⁻ (b) 4.30 eV atom⁻

(c) 1.0 eV mol⁻ (d) –4.3 eV atom⁻

SOLUTION. We know Δ H

$= I.\,P_1 + E.\,A_1$

$0.82\text{ eV (atom)}^- = I.\,P_1 + (-3.48\text{ eV atom}^-)$

∴ $I.\,P_1 = 0.82 + 3.48 = 4.30\text{ eV atom}^-$.

So, the correct answer is (*b*).

EXAMPLE 51. *The energy released in the following reaction.*

$$He^{2+} + 2e^- \longrightarrow He$$

if I. P. of H and He atoms are 13.6 eV and 24.6 eV respectively, is :

(a) –29.8 eV (b) –79 eV

(c) +29.8 eV (d) +59.6 eV

SOLUTION. $I.\,P_1$ of He = 24.6 eV; $I.\,P_1$ of H = 13.6 eV.

$He^{2+} + e^- \longrightarrow He^+;\ \Delta H = a$ eV (say)

$He^+ + e^- \longrightarrow He\ ;\ \Delta H = b$ eV (say)

Adding $He^{2+} + 2e^- \longrightarrow He;\ \Delta H = (a + b)$ eV.

But $I.\,P_1$ of He^+ = $I\,P_1$ of $H \times (Z_{He})^2$ = 13.6 eV × $(2)^2$

= 13.6 eV × 4 = 54.4 eV

∴ a = –54.4 eV

Also, $He^+ + e^- \longrightarrow He$, $I\,P_1$ = 24.6 eV

∴ b = **–24.6 eV.**

∴ Energy released = $a + b$ = –54.4 – 24.6 = –79.0 eV

So, the correct answer is (*b*).

EXAMPLE 52. *87.75 kJ mol⁻ energy is absorbed to convert 2.0g O^- (g) to O^{2-} (g). The second electron gain enthalpy of oxygen will be :*

(a) 7.02 kJ (b) 70.2 kJ

(c) 702 kJ (d) 0.702 kJ

SOLUTION. $\underset{16\text{ g.}}{O^-\,(g.)} + e^- + \underset{x\text{kJ}}{EA} \longrightarrow O^{2-}\,(g)$

Electron gain enthalpy for 2 g. O^- (g.) = 87.75 kJ

Electron gain enthalpy for 16 g. O^- (g.) = $\frac{87.75}{2} \times 16$

= 702 kJ.

So, the correct answer is (*c*).

EXAMPLE 53. *The electronegativity of sulphur as calculated with the help of electronegativity of H = 2.1, bond energies of H–S, H–H and S–S bonds as 81, 104.2 and 49 k cal mol⁻ respectively, is:*

(a) 1.46 (b) 2.3

(c) 3.2 (d) 2.74

SOLUTION. Since bond energies are given in k cal mol⁻, we have :

$$\begin{aligned} X_S - X_H &= 0.208\,[BE \text{ of (S–H)} - \{BE\text{ (H–H)} \\ &\quad \times BE\text{ (S–S)}\}^{½}]^{½} \\ X_S &= X_H + 0.208\,[81 - \{104.2 \times 49\}^{1/2}]^{1/2} \\ &= 2.1 + 0.208\,[81 - 71.45]^{1/2} \\ X_S &= 2.1 + (0.208 \times 3.09) \\ &= 2.1 + 0.64 = \mathbf{2.74} \end{aligned}$$

So, the correct answer is (*d*).

EXAMPLE 54. *The energy absorbed by each molecule (A_2) of a substance is 4.4×10^{-19} J and bond energy per molecule is 4.0×10^{-19} J. The kinetic energy of the molecule per atom will be :*

(*a*) 2.2×10^{-19} J (*b*) 2.0×10^{-19} J

(*c*) 4.0×10^{-20} J (*d*) 2.0×10^{-20} J

(CBSE– PMT, 2009)

SOLUTION. Energy absorbed by each molecule = 4.4×10^{-19} J

Energy required to break the bond = 4.0×10^{-19} J.

So, the remaining energy will be converted into kinetic energy = $(4.4 \times 10^{-19} - 4.0 \times 10^{-19})$ J = 0.4×10^{-19} J (molecule)⁻ = 4.0×10^{-20} J (molecule)⁻.

So, the kinetic energy per atom = $(4.0 \times 10^{-20})/2$ J = 2.0×10^{-20} J

($\because$ the molecule A_2 is diatomic)

So, the correct answer is (*d*).

EXAMPLE 55. *The dipole moment of a diatomic molecule having charge 1.2×10^{-19} coulomb and distance between the charges in the molecule as 1.6 A° is :*

(*a*) 0.96×10^{-30} coulomb metre

(*b*) 1.92×10^{-29} coulomb metre

(*c*) 1.92×10^{-10} coulomb metre

(*d*) 3.84×10^{-27} coulomb cm

SOLUTION. Charge, $\delta = 1.2 \times 10^{-19}$ coulomb ;

$$\begin{aligned} d &= 1.6 \text{ A°} = 1.6 \times 10^{-8} \text{ cm} \\ \text{Dipole moment, } \mu &= \delta \times d\,; \\ \mu &= 1.2 \times 10^{-19} \text{ coulomb} \\ &\quad \times 1.6 \times 10^{-8} \text{ cm} \\ \therefore \quad \mu &= 1.92 \times 10^{-27} \text{ coulomb cm} \\ &= \frac{1.92 \times 10^{-27} \text{ coulomb cm} \times 1 \text{ metre}}{100 \text{ cm}} \\ &= 1.92 \times 10^{-29} \text{ coulomb metre} \end{aligned}$$

So, the correct answer is (*b*).

EXAMPLE 56. *The bond length in CO is 1.128 A°. What will be the bond length of CO in $Fe(CO)_5$?*

(*a*) 1.158 A° (*b*) 1.128 A°

(*c*) 1.178 A° (*d*) 1.118 A°

(IIT JEE, 2006)

SOLUTION. In $Fe(CO)_5$, Fe-atom makes back bonding to CO. Thus Fe–CO bonding creates a synergic effect. So, Fe–CO bond strength increases. This causes shortening of Fe–CO bond.

So, the correct answer is (*d*).

EXAMPLE 57. *The species having bond order different from that in CO is :*

(*a*) NO^- (*b*) NO^+

(*c*) CN^- (*d*) N_2**(at. no. N = 7, O = 8, C = 6)**

(IIT – JEE 2007)

SOLUTION. no. of electrons in

$$\begin{aligned} \text{CO} &= \text{at. no. of C + at. no. of O} \\ &= 6 + 8 = 14 \end{aligned}$$

M.O. electron configuration of

$$\begin{aligned} \text{CO} &= (\sigma_{1s})^2\,(\sigma^*_{1s})^2\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\pi_{2px})^2 \\ &= (\pi_{2py})^2\,(\sigma_{2pz})^2. \end{aligned}$$

$$\therefore \quad \text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 4}{2} = 3$$

(*a*) no. of electrons in NO^- = 7 + 8 + 1 = 16. So, M.O. electron configuration of NO^-

$$= (\sigma_{1s})^2\,(\sigma^*_{1s})^2\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\sigma_{2pz})^2\,(\pi_{2px})^2$$

$$= (\pi_{2py})^2\,(\pi^*_{2px})^1 = (\pi^*_{2py})^1$$

$$\therefore \quad \text{Bond order} = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

(*b*) no. of electrons in NO^+ = 7 + 8 – 1 = 14. Its bond order will also be 3 as shown for 14 electrons in CO above.

(*c*) no. of electrons in CN^- = 6 + 7 + 1 = 14

(*d*) no. of electrons in N_2 = 2 × 7 = 14

In both (c) and (d), no. of electrons are same as in CO. So, their bond order is 3. Hence, the correct answer is (*a*).

EXAMPLE 58. *Among the following, the paramagnetic compound is :*

(*a*) Na_2O_2 (*b*) O_3

(*c*) N_2O (*d*) KO_2*(at. no., O = 8)*

(IIT, JEE, 2007)

SOLUTION. (*a*) In O_2^{2-} (peroxide), no. of electrons

$$= (2 \times 8) + 2 = 18$$

$\therefore$ M.O. electron configuration of O_2^{2-}

$$= (\sigma_{1s})^2\,(\sigma^*_{1s})^2\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\sigma_{2pz})^2\,(\pi_{2px})^2$$

$$= (\pi_{2py})^2\,(\pi^*_{2px})^2 = (\pi^*_{2py})^2\,(\sigma^*_{2pz})^0.$$

This configuration has no unpaired electron. So, it is not paramagnetic.

(*b*) In O_3, the number of electrons = 3 × 8 = 24.

All the electrons are paired. So, it is diamagnetic .

(*c*) In N_2O, the number of electrons = (2 × 7) + 8 = 22. All electrons are paired. So, it is diamagnetic.

(*d*) O_2^- (superoxide). no. of electrons = (2 × 8) + 1 = 17

M.O. electron configuration

$= (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2pz})^2 (\pi_{2px})^2$

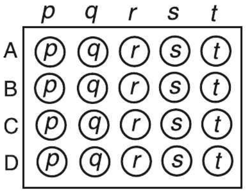
$= (\pi_{2py})^2 (\pi^*_{2px})^2 = (\pi^*_{2py})^1$.

Since, there is one unpaired electron, KO_2 is paramagnetic. Magnetic moment, $\mu = [n(n+2)]^{1/2} = [1(1+2)]^{1/2} = (3)^{1/2} =$ **1.732 B.M**. So, the correct answer is (*d*).

EXAMPLE 59. *Match each of the diatomic molecules in column I with its property/properties in column II*

Column I		*Column II*	
(A)	B_2	*p*	Paramagnetic
(B)	N_2	*q*	Undergoes oxidation
(C)	O_2^-	*r*	Undergoes reduction
(D)	O_2	*s*	Bond order ≥ 2
		t	Mixing of s and *p* orbitals

The statements in column I are labelled A, B, C and D. While the statements is column II are labelled p, q, r, s and t. Any statement given in column I can have correct matching with one or more statement (s) in column II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example. If the correct matches are A-p, s and t; B-q, and r; C-p and q and D-s and t; then the correct darkening of bulbs will look like as given in Fig. 1. **(IIT-JEE, 2009)**



	p	q	r	s	t
A	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ
B	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ
C	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ
D	ⓟ	ⓠ	ⓡ	ⓢ	ⓣ

Fig. 1.

SOLUTION. Molecular electron configurations of B_2, N_2, O_2^- and O_2, having total electrons, 10, 14, 17 and 16 respectively, are given below.

(*i*) $B_2 = (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^1 = (\pi_{2py})^1$; Bond order B.O = [$\bar{e}$s in bonding orbital – $\bar{e}$s in anti-bonding. MO] ÷ 2 = (6 – 4)/2 = 1

Due to two unpaired electrons, it is paramagnetic

(*ii*) $N_2 = (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^2 = (\pi^*_{2y})^2 (\sigma_{2pz})^2$;

B.O = (10 –4)/2 = 3. Due to all $\bar{e}$s paired, it is diamagnetic.

(*iii*) $O_2^- (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2pz})^2 (\pi_{2px})^2$

$= (\pi_{2py})^2 (\pi^*_{2px})^2 = (\pi^*_{2py})^1$; = (10 –7)/2 = 1.5. Due to one unpaired electron, it is paramagnetic.

(*iv*) $O_2 = (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2pz})^2 (\pi_{2px})^2$

$= (\pi_{2py})^2 (\pi^*_{2px})^1 = (\pi^*_{2py})^1$; B.O = (10 –6)/2 = 2.

Due to the presence of two unpaired electrons, it is paramagnetic. Thus, the answer is: *A* – (*p*, *r*, *t*); *B* – (*s*, *t*); *C* – (*p*, *q*); *D* – (*p*, *q*, *s*).

EXAMPLE 60. *The percentage of π-character in the orbitals forming P–P bonds in P_4 is :*

(*a*) 25	(*b*) 33
(*c*) 50	(*d*) 75

(IIT–JEE, 2007)

SOLUTION. ${}_{15}P = (Ne)^{10}\,\underbrace{3s^2\;3px^1\;3py^1\;3pz^1}$. In P_4, the P–P bond is formed by $sp^3 - sp^3$ hybridised orbital overlapping. Thus, the % age of π-character in $s^1p^3 - s^1p^3$ bonds

$$= \frac{3}{1+3} \times 100 = 75$$

So, the correct answer is (*d*).

EXAMPLE 61. *Four diatomic species are listed below in different sequences. Which of these represents the correct order of their increasing bond order :*

(*a*) $C_2^{2-} < He_2^+ < NO < O_2^-$

(*b*) $He_2^+ < O_2^- < NO < C_2^{2-}$

(*c*) $O_2^- < NO < C_2^{2-} < He_2^+$

(*d*) $NO < C_2^{2-} < O_2^- < He_2^+$

(CBSE-PMT, 2008 Prelims)

SOLUTION.

(*i*) no. of electrons in $C_2^{2-} = (2 \times 6) + 2 = 14$. So, its M.O. electron configuration $= (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^2 = (\pi_{2py})^2 (\sigma_{2pz})^2$. Its bond order = (10 – 4) / 2 = **3**.

(*ii*) no. of electrons in $He_2^+ = (2 \times 2) - 1 = 3$. So, its M.O. electron configuration = $(\sigma^*_{1s})^2 (\sigma^*_{1s})^1$. Bond order $= \frac{(2-1)}{2} = \mathbf{\frac{1}{2}}$.

(*iii*) no. of electrons is NO = 7 + 8 = 15. So, its M.O. electron configuration

$= (\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px})^2$

$= (\pi_{2py})^2 (\sigma_{2pz})^2 (\pi^*_{2px})^1$. Bond order

$= \frac{(10-5)}{2} = \mathbf{2.5}$.

(*iv*) no. of electrons in O_2^- = (2 × 8) + 1 = 17. Its M.O. electron configuration

$$= (\sigma_{1s})^2 (\overset{*}{\sigma}_{1s})^2 (\sigma_{2s})^2 (\overset{*}{\sigma}_{2s})^2 (\sigma_{2pz})^2 (\pi_{2px})^2$$

$$= (\pi_{2py})^2 (\overset{*}{\pi}_{2px})^2 = (\overset{*}{\pi}_{2py})^1.$$

$$\text{Bond order} = \frac{(10-7)}{2} = \mathbf{1.5}.$$

Since $\frac{1}{2} < 1.5 < 2.5 < 3$ bond order, the correct answer is (*b*).

Example 62. *Hybridisation of contral atom in NF_3 is:*

(*a*) sp^3 (*b*) sp

(*c*) sp^2 (*d*) d^2sp^3

(West Bengal JEE, 2009)

Solution. The general formula to find the type of hybridisation in a given type of compounds is:

$X = \frac{1}{2}(V + M + A - C)$ where V = number of electrons in valence shell; M = number of monovalent atoms; A = charge on anion and C = charge on cation. Central atom, $_7N$ ($1s^2\,2s^2\,2p^3$) has 5 (*i.e.*, 2 of 2*s* + 3 of 2*p*) valence electrons; no. of monovalent atoms in NF_3 = 3. Thus; $x = \frac{1}{2}(5 + 3 + 0 - 0) = 4$. Hence, type of hybridisation is sp^3 ($\therefore$ 1 + 3 = 4). So, the correct answer is (*a*).

Example 63. *The percentage of p-character of the hybrid orbitals in graphite and diamond are respectively:*

(*a*) 33 and 25 (*b*) 50 and 75

(*c*) 67 and 75 (*d*) 33 and 75

(Karnataka, CET, 2012)

Solution. (*i*) Carbon in graphite is s^1p^2 hybridised.

$$\therefore \text{ \% age of } p\text{-character} = \frac{2}{1+2} \times 100 \simeq 66.66 \simeq 67\%.$$

(*ii*) Carbon is diamond is s^1p^3 hybridised.

$$\therefore \text{ \% age of } p\text{-character} = \frac{3}{1+3} \times 100 = 75\%$$

So, the correct answer is (*c*).

Example 64. *For the reaction, $A + 2B \rightarrow C$, 5 mol of A and 8 moles of B will produce:*

(*a*) 5 mole of C (*b*) 4 mole of C

(*c*) 8 mole of C (*d*) 13 mole of C

(PSEB, 2012, modified)

Solution.	A	+	2B	→	C
	5 mol		8 mol		0
Moles present	5 mol		4 mol		0
			[∵ 2B = 8, so B = 4]		
Moles left	5 – 4 = 1		4 – 4 = 0		4

[B is a limiting reactant because its moles (= 4) are less than those of A (= 5)].

So, the correct answer is (*b*).

Example 65. *When $Al(OH)_3$ (= 0.78g) was dehydrated to get Al_2O_3 which reacted with 60 milliequivalents of HCl. The equivalents of $AlCl_3$ formed are:*

(*a*) 5.0×10^{-1} (*b*) 3×10^{-2}

(*c*) 2 (*d*) 2.5

(Haryana Board, 2012 modified)

Solution. Equivalent = milli equivalents/1000

$$\text{Milliequivalent} = \frac{wt. \times 1000}{Mol.\ wt./\text{ valance factor}}$$

Mol. wt. of Al $(OH)_3$ = 27 + 3 (16 + 1) = 78 g mol⁻ valance of Al^{3+} = 3

$\therefore$ Milliequivalents of $AlCl_3$ formed = 30

Or Equivalents of $AlCl_3$ formed = $\frac{30}{1000} = 3 \times 10^{-2}$

So, the correct answer is (*b*).

Example 66. *0.02 mole of $KHCO_3$ will react with how many equivalents of $Ca(OH)_2$:*

(*a*) 0.1 eq. (*b*) 0.01 eq.

(*c*) 0.04 eq. (*d*) 0.02 eq.

(H.P.B, 2012 modified)

Solution. For a complete reaction, the number of equivalents of all the reactants involved should be the same. Since the valency factor of Na^+ in $NaHCO_3$ is 1, so its 0.02 mole = its 0.02 equivalent. So, number of equivalents of $Ca(OH)_2$ must be 0.02. The correct answer is thus, (*d*).

Example 67. *The first ionisation potential of Na is 5.1 V. The value of electron gain evthalpy of Na^+ will be:*

(*a*) –5.1 eV (*b*) – 10.2 eV

(*c*) + 2.55 eV (*d*) – 2.55 eV.

(JEE, Main, 2013)

Solution. We know that :

Electron gain enthalpy = – Inonisation potential

$\therefore$ Electron gain enthalpy = – 5.1 eV.

So, the correct answer is (1).

PROBLEM

1. Which one of the following ion has electronic configuration [Ar] $3d^6$?

(*a*) Fe^{3+} (*b*) Co^{3+}

(*b*) Ni^{3+} (*c*) Mn^{3+}

(CBSE Med, 2010)

Ans. = (*b*)

2. The atom/ion that has the highest number of unpaired electrons is

(*a*) Mg^{2+} (*b*) F

(*c*) Ti^{3+} (*d*) S^{2-}

(Kerala PMT 2010)

Ans. = (*c*)

3. The electronegativity difference between two atoms A and B is 1.0. Calculate the % age ionic character of AB bond. **Ans.** = 22.2%

4. Calculate the extra ionic resonance energy in the HCl molecule from the following data. Bond energies of HCl, H–H and Cl–Cl are 103.2, 104.2 and 58 k cal mol$^-$ respectively. **Ans.** 77.7 k cal mol$^-$

5. Find the type of hybridisation in the following :

(*i*) N in NH_3 (*ii*) N in NO_2^-

(*iii*) N in NO_3^- (*iv*) C in CO_3^{2-}

Ans. (*i*) sp^3 (*ii*) sp^2 (*iii*) sp^2 (*iv*) sp^2

6. Calculate the percent ionic character in Br-Cl if the electronegativity values of Br and Cl are 2.8 and 3.0 respectively. **Ans.** 3.34

7. Calculate the value of ΔH in kJ mol$^-$ for the reaction

$$K(g) + Cl(g) \rightarrow K^+(g) + Cl^-(g).$$

Electron affinity of Cl = –3.7 eV atom$^-$ and I.P. of K =4.3 eV atom$^-$. **Ans.** = 57.86 kJ.

8. Calculate the amount of energy needed to convert 3 mol of K-atoms to K(g). First I.P. of K = 4.3 eV (atom$^-$). **Ans.** 1244.7 × 10^3 J)

9. Calculate the bond length in H-Cl molecule (covalent radius of H = 0.28 Å, Cl = 0.99 Å). **Ans.** 1.2 7Å

10. Write the number of period to which the element with atomic number 19 belongs. **Ans.** 4

14

CHAPTER

Stoichiometry–Limiting Reactants

14.1 STOICHIOMETRY.

A balanced chemical equation exactly tells the number of molecules (or mol), weights of reactants and products, and in case of gases, it tells the volume of reactants and products. At N.T.P. or S.T.P., one mol of every gas occupies 22.4 L or 22.4 dm^3 or 22400 mL or 22400 cm^3 volume. Following examples are given for understanding under different heads.

14.2 WEIGHT -WEIGHT RELATIONSHIP.

Various steps to solve such problems are :

(*i*) Write the balanced chemical reaction.

(*ii*) Write the number of mol or g. mol. wt of the substances given and substances to be found or calculated.

(*iii*) Use unitary method to find the unknown.

In case of gravimetric analysis, we relate the weight of a substance or weights of substances with general reaction involving n_1, n_2, n_3, n_4 moles of A, B, C and D substances respectively, *i.e.*, $n_1A + n_2B \longrightarrow n_3C + n_4D$. In case of gaseous substance, 1 mol of a gas occupies 22.4 L volume at N.T.P. or S.T.P. One gram mol of a substance weighs equal to its gram atomic weight or gram molecular weight (or mass).

$$\underset{n_1\text{ mol}}{n_1A\text{ (s)}} + \underset{n_2\text{ mol}}{n_2B\text{ (s)}} \longrightarrow \underset{n_3\text{ mol}}{n_3C\text{ (s)}} + \underset{n_4\text{ mol or }n_4 \times 22.4\text{ L.}}{n_4D\text{ (g).}}$$

$\therefore$ n_1 mol $A \equiv n_2$ mol $B \equiv n_3$ mol $C \equiv n_4$ mol D or 22.4 n_4 L or 22400 mL × n_4

EXAMPLE 1. *A partially dried sample of clay on analysis was found to contain 45% silica and 9% water. The original clay contained 14% water. Calculate the % age of silica in the original sample.*

SOLUTION. Partially dried clay = 45% SiO_2 + 9% H_2O

$\therefore$ % age of impurity in clay = 100 – (45 + 9) = 46

Also, $\dfrac{\text{wt. of } SiO_2}{\text{wt. of impurity}} = \dfrac{45}{46}$

Let % age of SiO_2 = x ;

% age of impurity = $86 - x$

[$\because$ 100 – 14 = 86]

$\therefore$ $\dfrac{x}{86-x} = \dfrac{45}{46}$ **Or** $46\,x = 45(86 - x)$

or $46\,x = 3870 - 45\,x$ **Or** $46\,x + 45\,x = 3870$

$\therefore$ $91\,x = 3870$ **Or** $x = 3870/91 = 42.53\%$

or % age of silica in the sample

= **42.53%** **Ans.**

EXAMPLE 2. *What weight of H_2 will be produced from the action of 3.25 g pure zinc on excess of caustic soda solution. (At. wt., Zn = 65, H = 1)?*

SOLUTION. $\underset{65\text{ g}}{Zn} + 2NaOH \longrightarrow Na_2ZnO_2 + \underset{2\text{ g}}{H_2}$

65 g Zn produce H_2 = 2 g

3.25 g Zn produce H_2 = $\dfrac{2\text{ g}}{65} \times 3.25$ = **0.1 g Ans.**

EXAMPLE 3. *A solution of nitric acid of specific gravity 1.48, contains 65% nitric acid. Calculate the weight of this solution that is theoretically required to dissolve 4.0 g of magnesium oxide (At. wt., Mg = 24, O = 16, H = 1, N = 14).*

SOLUTION. Reaction.

$$\underset{\substack{24 + 16\\ = 40\text{ g}}}{MgO} + \underset{\substack{2\,[1 + 14 + (3 \times 16)]\\ = 126\text{ g}}}{2HNO_3} \longrightarrow Mg(NO_3)_2 + H_2O$$

To find wt. of 100% HNO_3 to dissolve 4.0 g MgO.

40 g MgO require HNO_3 to dissolve

= 126 g

4 g MgO require HNO_3 to dissolve

= $\dfrac{126}{40} \times 4$ = 12.6 g

$\therefore$ wt. of 65% HNO_3 of sp. gr 1.48 required

= $12.6 \times \dfrac{100}{65} \times 1.48$ = **28.69 g Ans.**

EXAMPLE 4. *A commercial sample of H_2SO_4 (96 % H_2SO_4, density = 1.81 g cm^{-3}) was treated with 20.8 g of $BaCl_2$. Calculate the volume of acid used to react completely with $BaCl_2$ to form $BaSO_4$ ppt. (At. wt., Ba = 137, Cl = 35.5, H = 1, S = 32, O = 16)*

Solution. *Reaction.*

$$\begin{array}{ccc} BaCl_2 + & H_2SO_4 \longrightarrow & BaSO_4\downarrow + 2HCl \\ 137 + (2 \times 35.5) & (2 \times 1) + 32 & 137 + 32 \\ & + (4 \times 16) & + (4 \times 16) \\ = 208\text{ g} & = 98\text{ g} & = 233\text{ g} \end{array}$$

(*i*) 208 g $BaCl_2$ form $BaSO_4$ = 233 g

$$20.8\text{ g } BaCl_2 \text{ form } BaSO_4 = \frac{233}{208} \times 20.8\text{ g}$$

$$= \mathbf{23.3\ g} \qquad \textbf{Ans.}$$

(*ii*) $$\text{wt. of 100\% } H_2SO_4 = \frac{98 \times 20.8}{208} = 9.8\text{ g}$$

$$\text{wt. of 96\% } H_2SO_4 = \frac{9.8 \times 100}{96}$$

$$\text{volume of 96\% } H_2SO_4 = \frac{\text{wt.}}{\text{density}}$$

$$= \frac{9.8 \times 100}{96} \times \frac{1}{1.81}$$

$$= \mathbf{5.64\ mL} \qquad \textbf{Ans.}$$

Example 5. *When 2.0 g of a mixture of anhydrous sodium carbonate and baking soda (sodium bicarbonate) was strongly heated, loss in weight was found to be 0.124 g. Calculate the percentage composition of the mixture. (At. wt., Na = 23, C = 12, O = 16).* **(IIT, 1977)**

Solution. Reaction

(*i*) $Na_2CO_3 \xrightarrow{\text{Heat}}$ no action

$$\begin{array}{lccc} (ii)\ 2NaHCO_3 & \longrightarrow & Na_2CO_3 + & CO_2 + H_2O \\ 2[23 + 1 + 12 & & 2\,(23) + 12 & \\ + (3 \times 16)] = 168\text{ g} & & + 3(16) = 106\text{ g} & \end{array}$$

From reactions, it is clear that loss in weight 168 g – 106 g (= 62 g) corresponds to 168 g $NaHCO_3$. Hence :

For loss in wt. 62 g, wt. of $NaHCO_3$ = 168 g

For loss in wt. 0.124 g, wt. of $NaHCO_3$

$$= \frac{168}{62} \times 0.124 = 0.336\text{ g}$$

$$\therefore \text{ \% age of } NaHCO_3 = \frac{\text{wt. of } NaHCO_3}{\text{Total weight}} \times 100$$

$$= \frac{0.336}{2.0} \times 100 = \mathbf{16.8\%} \qquad \textbf{Ans.}$$

$$\text{\% age of } Na_2CO_3 = 100 - 16.8 = \mathbf{83.2\%} \qquad \textbf{Ans.}$$

EXAMPLE 6. *3.36 g of a mixture of dry sodium carbonate and sodium bicarbonate containing 75% of the latter was heated until there was no more loss in weight. Calculate the volume of CO_2 evolved at N.T.P.*

Solution. $$\text{wt. of } NaHCO_3 = 3.36 \times \frac{75}{100} = 2.52\text{ g.}$$

Since Na_2CO_3 does not decompose on heating, CO_2 gas is evolved only from $NaHCO_3$.

$$\begin{array}{lcl} \text{Thus,}\quad 2NaHCO_3 & \longrightarrow & Na_2CO_3 + CO_2 + H_2O \\ 2[23 + 1 + 12 + (3 \times 16)] = 168\text{ g} & & \qquad 22400\text{ mL} \end{array}$$

168 g $NaHCO_3$ produce CO_2 = 22400 mL

$$2.52\text{ g } NaHCO_3 \text{ produce } CO_2 = \frac{22400}{168} \times 2.52$$

$$= \mathbf{336\ mL} \qquad \textbf{Ans.}$$

Example 7. *How many g each of Na_2CO_3 and water are required to prepare 250 g of a 23.2 % by weight solution of Na_2CO_3? (At. wt., Na = 23, C = 12, O = 16).*

Solution. 23.2% Na_2CO_3 solution means,

wt. of Na_2CO_3 = 23.2 g, wt. of solution = 100 g.

100 g solution contain Na_2CO_3 = 23.2 g

$$250\text{ g solution contain } Na_2CO_3 = \frac{23.2}{100} \times 250 = 58\text{ g}$$

$\therefore$ wt. of Na_2CO_3 required = 58 g ;

wt. of H_2O = 250 – 58

= **192 g** **Ans.**

Example 8. *Calculate the wieght of $CrCl_3.\ 6H_2O$ required to prepare 1.0 L of a solution containing 26 g Cr^{3+} per litre. (At. wt., Cr = 52, Cl = 35.5, H = 1, O = 16)*

Solution.

$$\begin{array}{lcl} CrCl_3.\ 6H_2O & \longrightarrow & Cr^{3+} + 3Cl^- + 6H_2O \\ 52 + (3 \times 35.5) + 6\,[(2 \times 1) + 16] = 266.5\text{ g} & & 52\text{ g} \end{array}$$

52 g Cr^{3+} is present in $CrCl_3.\ 6H_2O$ = 266.5 g

$$26\text{ g } Cr^{3+} \text{ is present in } CrCl_3.6H_2O = \frac{266.5}{52} \times 26$$

$$= 133.25\text{ g}$$

Example 9. *Assuming that only one of the chlorines present in a bleaching powder ($CaOCl_2$) is liberated as chlorine, find the percentage of available chlorine (at wt., Ca = 40, O = 16, Cl = 35.5).*

Solution. Given : $CaOCl_2 \equiv$ one Cl (as required)

$$\begin{array}{cc} 40 + 16 + (2 \times 35.5) & 35.5\text{ g} \\ = 127\text{ g} & \end{array}$$

$\therefore$ % age of available chlorine

$$= \frac{\text{wt. of chlorine}}{\text{wt. of compound}} \times 100$$

$$= \frac{35.5}{127} \times 100 = \mathbf{27.95}\ \textbf{Ans.}$$

14.3 SUCCESSIVE REACTIONS IN WEIGHT–WEIGHT RELATIONSHIP.

Example 10. *Calculate the weight of $MgCO_3$ that is required to get enough CO_2 which may convert 5.3 g of sodium carbonate into sodium bicarbonate (at. wt., Na = 23, C = 12, O = 16; Mg = 24).*

Solution.

$$\begin{array}{rcl} MgCO_3 & \longrightarrow & MgO + CO_2 \\ Na_2CO_3 + CO_2 + H_2O & \longrightarrow & 2NaHCO_3 \\ MgCO_3 + Na_2CO_3 + H_2O & \longrightarrow & MgO + 2NaHCO_3 \end{array}$$

$$\begin{array}{ll} 24 + 12 + (3 \times 16) & (2 \times 23) + 12 + 3 \times 16 \\ = 84\text{ g} & = 106\text{ g} \end{array}$$

To convert 106 g Na_2CO_3,
$MgCO_3$ required = 84 g
To convert 5.3 g Na_2CO_3,

$MgCO_3$ required $= \frac{84}{106}\times 5.3 = \mathbf{4.2\ g}$ **Ans.**

EXAMPLE 11. *What weight of potassium permanganate (96% pure) in dil H_2SO_4 is needed to produce so much oxygen which could oxidise 1.8 g of oxalic acid to CO_2 and H_2O. (mol. wt. 90 g mol⁻¹)? (at. wt., K = 39, Mn = 55, O = 16)*

SOLUTION.

$$\begin{array}{rcl} 2KMnO_4 + 3H_2SO_4 & \longrightarrow & K_2SO_4 + 2MnSO_4 \\ & & + 3H_2O + 5O \\ H_2C_2O_4 + O & \longrightarrow & 2CO_2 + H_2O\ ] \times 5 \\ \hline 2KMnO_4 + 3H_2SO_4 + 5H_2C_2O_4 & \longrightarrow & K_2SO_4 + 2MnSO_4 \\ 2\,[39 + 55 + (4\times 16)] \quad 5\times 90 & & + 8H_2O + 10CO_2 \\ = 316\text{ g} \qquad = 450\text{ g} & & \end{array}$$

450 g oxalic acid, $H_2C_2O_4$ need $KMnO_4$
= 316 g

1.8 g oxalic acid need $KMnO_4$

$$= \frac{316}{450}\times 1.8 = \mathbf{1.264\ g}$$

Since $KMnO_4$ is 96% pure ;
The wt. of $KMnO_4$ required

$$= 1.264\times\frac{100}{96} = \mathbf{1.317\ g} \qquad \textbf{Ans.}$$

14.4 WEIGHT-VOLUME RELATIONSHIP.

Various steps to solve such problems are :

(*i*) Write the balanced chemical reaction.

(*ii*) Write the number of mol or g. mol. wt (Or 22.4L or 22.4 dm³ or 22400 mL or 22400 cm³ for each mol of a gas) of the substances given and substances to be found or calculated.

(*iii*) Use unitary method to find the unknown.

(*iv*) Convert the volume of the given gas to N.T.P. or S.T.P by using the relation $P_1V_1/T_1 = P_2V_2/T_2$ where P_2 = 760 mm, T_2 = 273 K.

EXAMPLE 12. *When one gram of $KClO_3$ was heated under a particular condition, following reaction took place and O_2 gas evolved at N.T.P. was 150 mL.*

(a) $2KClO_3 \longrightarrow 2KCl + 3O_2$.

When the conditions were changed, for the remaining $KClO_3$, following reaction took place.

(b) $4KClO_3 \longrightarrow 3KClO_4 + KCl$.

Calculate the percent by weight of $KClO_4$ in the residue.

SOLUTION. (*a*)

$$\begin{array}{cccc} 2KClO_3 & \longrightarrow\ 2KCl & + & 3O_2 \\ 2\text{ mol} & 2\text{ mol} & & 3\text{ mol} \\ 2[39 + 35.5 + (3\times 16)] & 2(39 + 35.5) & & \\ = 245\text{ g} & = 149\text{ g} & & = 3\times 22400\text{ mL} \end{array}$$

Volume of oxygen gas evolved = 150 mL

3 × 22400 mL O_2 gas is formed from $KClO_3$ = 245 g

150 mL O_2 gas is formed from $KClO_3$

$$= \frac{245\times 150}{3\times 22400}\text{ mL} = 0.547\text{ g}$$

$$\begin{array}{lccc} (b)\ 4KClO_3 & \longrightarrow\ 3KClO_4 & + & KCl \\ 4\text{ mol} & 3\text{ mol} & & 1\text{ mol} \\ 4[39 + 35.5 & 3[39 + 35.5 & & = 39 + 35.5 \\ + (3\times 16)] & + (4\times 16)] & & = 74.5\text{ g} \\ = 4\times 122.5 & 3\times 138.5 & & \\ = 490\text{ g} & = 415.5\text{ g} & & \end{array}$$

Weight of $KClO_3$ undergoing second reaction
= 1.0 – 0.547 g = 0.453 g

Thus : 490 g $KClO_3$ form
$KClO_4$ = 415.5 g

$$0.453\text{ g }KClO_3\text{ form }KClO_4 = \frac{415.5}{490}\times 0.453 = 0.38\text{ g}.$$

∴ wt. of $KClO_4$ = 0.38 g

The residue contains $KClO_4$ and KCl.

∴ % age by wt. of $KClO_4$ in the residue

$$= \frac{\text{wt. of }KClO_4}{\text{wt. of }KClO_4 + \text{wt. of }KCl}\times 100 \quad ...(1)$$

(*c*) **Wt. of KCl from reaction (*a*).**

245 g $KClO_3$ ≡ 149 g KCl

$$0.547\text{ g }KClO_3 \equiv \frac{149}{245}\times 0.547 = 0.33\text{ g}$$

(*d*) **Wt. of KCl from reaction (*b*).**

490 g $KClO_3$ ≡ 74.5 g KCl

$$0.453\text{ g }KClO_3 \equiv \frac{74.5}{490}\times 0.453 = 0.069\text{ g}.$$

∴ Total wt. of KCl = 0.33 + 0.069 = 0.399 g.

Substituting the values of $KClO_4$ and KCl in reaction (*1*), we have :

% age by wt. of $KClO_4$ in the residue

$$= \frac{0.38}{0.38 + 0.399}\times 100$$

$$= \frac{0.38}{0.779}\times 100 = \mathbf{48.78} \qquad \textbf{Ans.}$$

EXAMPLE 13. *How many litres of oxygen at NTP are required to burn completely 2.2 g of propane, C_3H_8?* **(IIT, 1976)**

SOLUTION. *Reaction.*

$$\begin{array}{ccccccc} C_3H_8 & + & 5O_2 & \longrightarrow & 3CO_2 & + & 4H_2O \\ (3\times 12) + (8\times 1) & & 5\times 22.4\text{ L} & & & & \\ = 44\text{ g} & & & & & & \end{array}$$

44 g C_3H_8 require O_2 = 5 × 22.4 L

$$2.2\text{ g }C_3H_8\text{ require }O_2 = \frac{5\times 22.4}{44}\times 2.2 = \mathbf{5.6\ L} \qquad \textbf{Ans.}$$

EXAMPLE 14. *2.5 g of a sample of sodium bicarbonate when strongly heated give 310 cc of CO_2 measured at 27°C and 760 mm pressure. Calculate the percentage purity of sample.*

SOLUTION. (*i*)

$$\underset{\substack{2[23+1+12+(3\times16)] \\ 168\text{ g}}}{2NaHCO_3} \longrightarrow Na_2CO_3 + \underset{22400\text{ cc.}}{CO_2} + H_2O$$

(*ii*) $P_1 = 760$ mm, $V_1 = 310$ cc, $T_1 = 27 + 273 = 300$ K, at N.T.P., $P_2 = 760$ mm, $V_2 = ?$ $T_2 = 273$ K. We know that :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2}$$

$$= \frac{760\times310\times273}{300\times760} = 282.1 \text{ c.c.}$$

(*iii*) 22400 c.c. of CO_2 is formed from $NaHCO_3 = 168$ g

282.1 c.c. of CO_2 is formed from $NaHCO_3$

$$= \frac{168}{22400}\times282.1 \text{ g}$$

∴ % age purity of

$$NaHCO_3 = \frac{\text{wt. of } NaHCO_3}{\text{Total wt.}}\times100$$

$$= \frac{168\times282.1}{22400}\times\frac{100}{2.5} = \mathbf{84.63\%}\ \textbf{Ans.}$$

EXAMPLE 15. *Calculate (i) the wt. of MnO_2 and (ii) volume of hydrochloric acid of specific gravity 1.12 and containing 40 percent HCl by weight, needed to produce 1.78 litres of chlorine gas at S.T.P. according to the reaction*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

(*at. wt., Mn = 55, O = 16, H = 1, Cl = 35.5*) **(IIT, 1977)**

SOLUTION. Volume of Cl_2 at S.T.P. = 1.78 L

$$\underset{\substack{55+(2\times16) \\ =87\text{ g}}}{MnO_2} + \underset{\substack{4(1+35.5) \\ =146\text{ g}}}{4HCl} \longrightarrow MnCl_2 + \underset{22.4\text{ L}}{Cl_2} + 2H_2O$$

(*i*) 22.4 L Cl_2 is produced from MnO_2 = 87 g

$$1.78 \text{ L } Cl_2 \text{ is produced from } MnO_2 = \frac{87}{22.4}\times1.78$$

$$= \mathbf{6.913\ g}\ \textbf{Ans.}$$

(*ii*) 22.4 L Cl_2 is produced from HCl = 146 g

$$1.78 \text{ L } Cl_2 \text{ is produced from HCl} = \frac{146}{22.4}\times1.78$$

$$= 11.6 \text{ g}$$

sp. gr. of HCl = 1.12

$$\text{wt. of 40\% HCl} = 11.6\times\frac{100}{40}$$

$$= 29 \text{ g}$$

$$\therefore \quad \text{Volume of HCl} = \frac{\text{Mass}}{\text{sp.gr.}}$$

$$= \frac{29}{1.12}$$

$$= \mathbf{25.9\ mL}\ \textbf{Ans.}$$

EXAMPLE 16. *0.5 kg of coal contain 65% carbon and 35% incombustible matter. Calculate the volume of air at 37°C and 720 mm pressure that would be required to burn completely the coal. Air contains 20% oxygen by volume.*

SOLUTION. wt. of coal

$$= 0.5 \text{ kg} = 0.5\text{ kg}\times\frac{1000\text{ g}}{1\,kg} = 500 \text{ g}$$

$$\therefore \quad \text{wt. of carbon} = 500\text{ g}\times\frac{65}{100} = 325 \text{ g}$$

Reaction :

$$\underset{12\text{ g}}{C} + \underset{22.4\text{ L}}{O_2} \longrightarrow CO_2$$

12 g C need O_2 = 22.4 L

$$325 \text{ g C need } O_2 = \frac{22.4\text{ L}}{12\text{ g}}\times325\text{ g} = 606.67 \text{ L}$$

∴ Volume of O_2 = 606.67 L

$P_1 = 720$ mm, $V_1 = ?$, $T_1 = 37 + 273 = 310$ K ;

$P_2 = 760$ mm, $V_2 = 606.67$ L,

$T_2 = 273$ K. So :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_1 = \frac{P_2V_2}{T_2}\times\frac{T_1}{P_1}$$

$$= \frac{760\text{ mm}\times606.67\text{ L}\times310\text{ K}}{273\text{ K}\times720\text{ mm}}$$

∴ $V_1 = 727.16$ L

∴ Volume of air required

$$= 727.16 \text{ L}\times\frac{100}{20} = \mathbf{3635.8\ L}\ \textbf{Ans.}$$

EXAMPLE 17. *The solubility of slaked lime at 20°C is 1.26 g L^{-}. At 20°C and 720 mm pressure, CO_2 was passed into 75 mL limewater. Calculate the volume of CO_2 required (i) to give maximum milkiness and (ii) to make the milkiness clear. (at. wt., Ca = 40, H = 1, O = 16)*

SOLUTION. (*i*) 1000 mL lime water contains

$Ca(OH)_2$ = 1.26 g

$$75 \text{ ml lime water contains } Ca(OH)_2 = \frac{1.26\text{ g}}{1000\text{ mL}}\times75 \text{ ml}$$

$$= 0.0945 \text{ g.}$$

Reaction (*i*)

$$\underset{\substack{40+2(16+1) \\ =74\text{ g}}}{Ca(OH)_2} + \underset{22400\text{ mL}}{CO_2} \longrightarrow CaCO_3 + H_2O$$

74 g $Ca(OH)_2$ need CO_2

= 22400 mL

0.0945 g $Ca(OH)_2$ need CO_2

$$= \frac{22400}{74}\times0.0945 = 28.6 \text{ mL}$$

$P_1 = 720$ mm, $V_1 = ?$,

$T_1 = 20 + 273 = 293$ K ;

at N.T.P., $P_2 = 760$ mm, $V_2 = 28.6$ mL,

$T_2 = 273$ K.

So,

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

or

$$V_1 = \frac{P_2V_2}{T_2}\times\frac{T_1}{P_1} = \frac{760\times28.6\times293}{273\times720}$$

$$= 32.4 \text{ mL}$$

∴ Volume of CO_2 to get maximum milkiness

= **32.4 mL Ans.**

(*ii*)

$$\begin{array}{rcl} Ca(OH)_2 + CO_2 & \longrightarrow & CaCO_3 + H_2O \\ CaCO_3 + H_2O + CO_2 & \longrightarrow & Ca(HCO_3)_2 \\ \text{excess} & & \text{(clear solution)} \end{array}$$

$$\begin{array}{cccc} Ca(OH)_2 + & 2CO_2 & \longrightarrow & Ca(HCO_3)_2 \\ 1\text{ mol} & 2\text{ mol} & & \\ 74\text{ g} & = 2 \times 22400\text{ mL} & & \end{array}$$

Since for 74 g $Ca(OH)_2$, 22400 mL CO_2 is required to get maximum milkiness and 2 × 22400 mL CO_2 is required to get clear solution, so :

Volume of CO_2 to get clear solution = 2 × [volume of CO_2 for maximum milkiness]

$= 2 \times 32.4$ mL $=$ **64.8 mL Ans.**

EXAMPLE 18. *Calculate the amount of NaCl formed by passing 2.24 L of Cl_2 gas at 25°C and 770 mm pressure into cold dilute* NaOH *solution and* (*ii*) *hot strong* NaOH *solution.*

SOLUTION.

$$\begin{array}{llcl} (i) & 2NaOH + Cl_2 & \longrightarrow & NaCl + NaClO + H_2O \\ & \quad 22.4\text{ L} & & 23 + 35.5 = 58.5\text{ g} \\ (ii) & 6NaOH + 3Cl_2 & \longrightarrow & 5NaCl + NaClO_3 + 3H_2O \\ & \quad 3 \times 22.4\text{ L} & & 5\,(23 + 35.5) \\ & & & = 5 \times 58.5 \end{array}$$

$P_1 = 770$ mm, $V_1 = 2.24$ L, $T_1 = 25 + 273 = 298$ K ; at NTP, $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K:

But $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$\therefore \quad V_2 = \frac{770\text{ mm} \times 2.24\text{ L} \times 273\text{ K}}{298\text{ K} \times 760\text{ mm}}$$

$= 2.079$ L

(*i*) But 22.4 L Cl_2 form NaCl = 58.5 g

$$\therefore \quad 2.079\text{ L } Cl_2 \text{ form NaCl} = \frac{58.5\text{ g}}{22.4\text{ L}} \times 2.079\text{ L}$$

$=$ **5.43 g Ans.**

(*ii*) 3 × 22.4 L Cl_2 form NaCl = 5 × 58.5 g

$$2.079\text{ L } Cl_2 \text{ form NaCl} = \frac{5 \times 58.5}{3 \times 22.4} \times 2.079$$

$=$ **9.05 g Ans.**

EXAMPLE 19. I*n an experiment when 845 cm³ of oxygen at S.T.P., was passed through an ozoniser, the resulting volume was found to be 750 cm³ at N.T.P. The resulting ozonised oxygen when passed through KI solution, iodine was liberated. Calculate the weight of iodine formed. (at. wt., I = 127).*

SOLUTION. Total volume of O_2 at NTP = 845 cm³.

$$3O_2 \longrightarrow 2O_3 \quad ...(1)$$

Let volume of O_3 in 750 cm³

$= x$ cm³.

So, volume of O_2 = $(750 - x)$ cm³

From equation (*1*), 2 × 22400 cm³

$O_3 = 3 \times 22400$ cm³ O_2

$$x\text{ cm}^3\ O_3 = \frac{3 \times 22400}{2 \times 22400} \times x$$

$$= \frac{3x}{2}\text{ cm}^3\ O_2$$

$$\therefore \quad \frac{3x}{2} + (750 - x) = 845\ ;\ 3x + 2(750 - x) = 2 \times 845\ ;$$

$$3x + 1500 - 2x = 1690\ ;\ x = 1690 - 1500 = 190\text{ cm}^3$$

∴ Volume of ozone = 190 cm³

Reaction

$$\begin{array}{ccccc} 2KI + H_2O + & O_3 & \longrightarrow 2KOH + & I_2 & + O_2 \\ & 22400\text{ cm}^3 & & 2 \times 127\text{ g} & \end{array}$$

22400 cm³ O_3 produce I_2 = 2 × 127 g

$$190\text{ cm}^3\ O_3 \text{ produce } I_2 = \frac{2 \times 127}{22400} \times 190$$

$=$ **2.1545 g Ans.**

EXAMPLE 20. *One gram of an alloy of aluminium and magnesium reacts with excess hydrochloric acid to form aluminium chloride, magnesium chloride and hydrogen. The hydrogen collected over mercury at 0°C, occupied 1200 mL at 699 mm. What is the composition of the alloy? (Al = 27, Mg = 24)* **(IIT, 1971)**

SOLUTION. Let wt. of Al

$= x$ g ; wt. of Mg = $(1 - x)$ g.

$P_1 = 699$ mm, $V_1 = 1200$ mL,

$T_1 = 0 + 273 = 273$ K.

At N.T.P., $P_2 = 760$ mm, $V_2 = ?$ $T_2 = 273$ K.

So, $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}\ \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{699\text{ mm} \times 1200\text{ mL}}{273\text{ K}} \times \frac{273\text{ K}}{760\text{ mm}}$$

$= 1103.68$ mL

$$\begin{array}{lcccc} (i) \quad 2\,Al & + \ 6HCl & \longrightarrow & 2AlCl_3 & + \ 3H_2 \\ 2 \times 27 = 54\text{ g} & & & & 3 \times 22400\text{ mL} \end{array}$$

54 g Al produces H_2 = 3 × 22400 mL

$$x\text{ g Al produces } H_2 = \frac{3 \times 22400}{54} \times x\text{ mL} \quad ...(A)$$

$$\begin{array}{lcl} (ii)\ Mg + 2HCl & \longrightarrow & MgCl_2 + H_2 \\ \quad 24\text{ g} & & \quad 22400\text{ mL} \end{array}$$

24 g Mg produces H_2 = 22400 mL

$$(1 - x)\text{ g Mg produces } H_2 = \frac{22400}{24} \times (1 - x)\text{ g}$$

$$= \frac{22400\,(1 - x)}{24}\text{ g} \quad ...(B)$$

∴ From equations (*A*) and (*B*), we have :

$$\frac{3 \times 22400x}{54} + \frac{22400\,(1 - x)}{24} = 1103.68$$

or $$\frac{3x}{54} + \frac{(1 - x)}{24} = \frac{1103.68}{22400}\ ;$$

$$(3x \times 24) + 54\,(1 - x) = \frac{54 \times 24 \times 1103.68}{22400}$$

$$72x + 54 - 54x = 63.68\ ;\ 18x = 9.86;$$

$$x = \frac{9.86}{18} = 0.5477 \text{ g}$$

$$\therefore \quad \%\text{ age of Al} = \frac{\text{wt. of Al}}{\text{Total wt.}} \times 100$$

$$= \frac{0.5477}{1} \times 100 = \mathbf{54.77\%\ Ans.}$$

$$\%\text{ age of Mg} = 100 - 54.77 = \mathbf{45.23\%}\ \ \textbf{Ans.}$$

EXAMPLE 21. *A mixture of* NaI *and* NaCl *when treated with excess of* H_2SO_4*, gave* Na_2SO_4 *whose weight is the same as the weight of original mixture. Calculate the percentage composition of the mixture (at. wt., Na = 23, I = 127, Cl = 35.5, O = 16, S = 32)*

SOLUTION. Let total weight of NaI and NaCl = 1.0 g.

Let wt. of NaI = x g ; wt. of NaCl = $1 - x$

Reactions

$$\begin{array}{rcl} (i)\quad H_2SO_4 & \longrightarrow & SO_2 + H_2O + O \\ 2NaI + H_2SO_4 + O & \longrightarrow & Na_2SO_4 + H_2O + I_2 \\ \hline 2NaI + 2H_2SO_4 & \longrightarrow & SO_2 + Na_2SO_4 + 2H_2O + I_2 \\ 2\,(23 + 127) & & (2 \times 23) + 32 + (4 \times 16) \\ = 300 \text{ g} & & = 142 \text{ g} \end{array}$$

300 g NaI form Na_2SO_4 = 142 g

$$x \text{ g NaI form } Na_2SO_4 = \frac{142}{300} \times x = \frac{142x}{300} \text{ g}$$

$$\begin{array}{rcl} (ii)\quad H_2SO_4 & \longrightarrow & SO_2 + H_2O + O \\ 2NaCl + H_2SO_4 + O & \longrightarrow & Na_2SO_4 + Cl_2 + H_2O \\ \hline 2NaCl + 2H_2SO_4 & \longrightarrow & SO_2 + Na_2SO_4 + Cl_2 + H_2O \\ 2\,(23 + 35.5) & & (2 \times 23) + 32 + (4 \times 16) \\ = 117.0 \text{ g} & & = 142 \text{ g} \end{array}$$

117 g NaCl form Na_2SO_4 = 142 g

$$(1 - x) \text{ g NaCl form } Na_2SO_4 = \frac{142}{117} \times (1 - x) \text{ g}$$

wt. of Na_2SO_4 + wt. of Na_2SO_4 = 1 (supposed)
from NaI from NaCl

$$\frac{142\,x}{300} + \frac{142\,(1 - x)}{117} = 1;142 \times 117x + (300 \times 142)$$

$$-(300 \times 142)\,x = 300 \times 117\,16614x + 42600$$

$$-42600x = 300 \times 117\ ;$$

$$16614x + 42600 - 42600x = 35100$$

Or $25986x = 7500$;

$$x = \frac{7500}{25986} = 0.2886 \text{ g}$$

$$= \text{wt. of NaI}$$

$$\therefore \quad \%\text{ age of NaI} = \frac{\text{wt. of NaI}}{\text{Total wt.}} \times 100$$

$$= \frac{0.2886}{1} \times 100$$

$$= \mathbf{28.86\%} \qquad \textbf{Ans.}$$

$$\%\text{ age of NaCl} = 100 - 28.86$$

$$= \mathbf{71.14\%} \qquad \textbf{Ans.}$$

EXAMPLE 22. *How many kilogram of potassuim chlorate will be needed to get sufficient oxygen to oxidise completely 1250 cm*^{3} *of a gaseous mixture containing 40%* C_2H_2 *and 60% carbon monoxide at 17°C and 740 mm pressure? (At. wt., K = 39, Cl = 35.5, O = 16)*

SOLUTION. P_1 = 740 mm, V_1 = 1250 cm^3, T_1 = 17 + 273 = 290 K ; at. N.T.P., P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

$$\text{But :} \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} \text{ (gas law)}$$

$$\therefore \quad V_2 = \frac{740 \text{ mm} \times 1250 \text{ cm}^3 \times 273 \text{ K}}{290 \text{ K} \times 760 \text{ mm}}$$

$$= 1145.76 \text{ cm}^3$$

$$\text{Volume of } C_2H_2 = 1145.76 \times \frac{40}{100} = 458.3 \text{ cm}^3$$

$$\text{Volume of CO} = 1145.76 \times \frac{60}{100} = 687.46 \text{ cm}^3$$

$$\begin{array}{lllcl} (i) & & KClO_3 & \longrightarrow & KCl + 3O] \times 5 \\ & & C_2H_2 + 5O & \longrightarrow & 2CO_2 + H_2O] \times 3 \\ \hline 5KClO_3 & + & 3C_2H_2 & \longrightarrow & 5KCl + 6CO_2 + 3H_2O \\ 5[39 + 35 + (3 \times 16)] & & & & \\ = 612.5 \text{ g} & & 3 \times 22400 \text{ cm}^3 & & \end{array}$$

3 × 22400 cm^3 C_2H_2 need

$KClO_3$ = 612.5 g

458.3 cm^3 C_2H_2 need

$$KClO_3 = \frac{612.5}{3 \times 22400} \times 458.3 = 4.177 \text{ g}$$

$$\begin{array}{lllcl} (ii) & KClO_3 & & \longrightarrow & KCl + 3O \\ & [CO + O & & \longrightarrow & CO_2] \times 3 \\ \hline KClO_3 & + & 3CO & \longrightarrow & KCl + 3CO_2 \\ 39 + 35.5 + (3 \times 16) & & 3 \times 22400 \text{ cm}^3 & & \\ = 122.5 \text{ g} & & & & \end{array}$$

3 × 22400 cm^3 CO need

$KClO_3$ = 122.5 g

687.46 cm^3 CO need

$$KClO_3 = \frac{122.5 \times 687.46}{3 \times 22400} = 1.253 \text{ g}$$

∴ Total wt. of $KClO_3$ required = 4.177 + 1.253 = **5.43 g**

Ans.

EXAMPLE 23. *Calculate the volume of phosphine gas formed at 27°C and 740 mm pressure from the decomposition of 16.2 g of phosphonium iodide with NaOH. (at. wt., P = 31, H = 1, I = 127)*

SOLUTION. Hint.

$$\begin{array}{lcl} PH_4I + NaOH & \longrightarrow & NaI + PH_3\uparrow + H_2O \\ 31 + (4 \times 1) + 127 & & \qquad\quad 22400 \text{ mL} \\ = 162 \text{ g} & & \end{array}$$

162 g PH_4I form PH_3 = 22400 mL

$$\therefore\ 16.2 \text{ g } PH_4I \text{ form } PH_3 = \frac{(22400 \times 16.2)}{162} = 2240 \text{ mL.}$$

Convert this volume at (27 + 273) K and 740 mm to NTP, yourself. **Ans. 2.528 L.**

14.5 VOLUME - VOLUME RELATIONSHIP.

Various steps to solve such problems are :

(*i*) Write the balanced chemical equation.

(*ii*) Write the number of mol and "22.4 L or 22.4 dm^3 or 22400 mL or 22400 cm^3 volume" for each mol of the gas under the gas given and gas to be found (or calculated).

(*iii*) Use the unitary method to find the unknown.

(*iv*) Convert the volume of the given gas to N.T.P. or S.T.P. by using the relation, $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$ where P_2 = 760 mm, T_2 = 273 K.

(*v*) Use Avogadro's law which states that "equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure".

EXAMPLE 24. *Heavy water, D_2O dissociates as follows :*

$$2D_2O \longrightarrow 2D_2 + O_2$$

Calculate its volumetric composition.

SOLUTION. *Reaction.*

$$\begin{array}{ccccc} 2D_2O\,(g) & \longrightarrow & 2D_2\,(g) & + & O_2\,(g) \\ 2\text{ mol} & & 2\text{ mol} & & 1\text{ mol} \\ 2\text{ Vol} & & 2\text{ Vol} & & 1\text{ Vol} \end{array}\Bigg]\text{ Avogadro's law}$$

$$\underbrace{2\text{ Vol} \quad 1\text{ Vol}}_{= 3\text{ Vol}}$$

(*i*) 3 Vol gaseous product has

$$D_2 = 2\text{ Vol}$$

100 Vol gaseous product has

$$D_2 = \frac{2}{3}\times 100 = 66.66$$

(*ii*) 3 Vol gaseous product has

$$O_2 = 1\text{ Vol}$$

100 Vol gaseous product has

$$O_2 = \frac{1}{3}\times 100 = 33.33$$

∴ Volumetric composition of D_2O is

$$D_2 : O_2$$
$$66.66 : 33.33$$

or $\frac{66.66}{33.33} : \frac{33.33}{33.33}$ or **2 : 1** **Ans.**

EXAMPLE 25. *One litre of a mixture of* CO *and* CO_2 *is taken. This is passed through a tube containing red hot charcoal. The volume now becomes 1.6 litre. The volumes are measured under same conditions. Find the composition of the mixture by volume.* **(I.I.T., 1980)**

SOLUTION. Volume of CO + volume of

$$CO_2 = 1\text{ L} = 1000\text{ mL}$$

Let volume of CO = x mL ; Volume of

$$CO_2 = (1000 - x)\text{ mL}$$

Out of CO and CO_2, only CO_2 is reduced by charcoal. Thus :

$$\begin{array}{ccc} CO_2 + C & \longrightarrow & 2CO \\ 1\text{ mol} & & 2\text{ mol} \\ 1\text{ Vol} & & 2\text{ Vol} \end{array}\Bigg]\text{ Avogadro's law}$$

(*i*) 1 mL CO_2 forms CO
= 2 mL

$(1000 - x)$ mL CO_2 forms CO = $\frac{2}{1}\times 1000 - x = 2000 - 2x$

∴ Total volume of

$$CO = x\text{ mL} + (2000 - 2x)\text{ mL}$$
$$= (2000 - x)\text{ mL}$$

Thus : $2000 - x = 1.6\text{ L} = 1.6\text{ L}\times\frac{1000\text{ mL}}{1\text{ L}}$

$$= 1600\text{ mL}$$

∴ $x = 400$ mL

= volume of CO in the mixture **Ans.**

Vol of CO_2 in the mixture

= 1000 – 400 = **600 mL** **Ans.**

EXAMPLE 26. *A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are –1423 and –891 kJ mol^{-} at 25°C.* **(IIT, 1991)**

SOLUTION. Volume of C_2H_4 + volume of

$$CH_4 = 3.67\text{ L}$$

Let Volume of $C_2H_4 = x$ L ; volume of

$$CH_4 = (3.67 - x)\text{ L}$$

Reaction.

$$\begin{array}{ccc} C_2H_4 + 3O_2 & \longrightarrow & 2CO_2 + 2H_2O \\ 1\text{ mol} & & 2\text{ mol} \\ 1\text{ Vol} & & 2\text{ Vol} \end{array}\Bigg]\text{ Avogadro's law}$$

(*i*) 1 L of C_2H_4 produce CO_2 = 2 L

x L of C_2H_4 produce CO_2 = $2x$ L

(*ii*)

$$\begin{array}{ccc} CH_4 + 2O_2 & \longrightarrow & CO_2 + 2H_2O \\ 1\text{ mol} & & 1\text{ mol} \\ 1\text{ Vol} & & 1\text{ Vol} \end{array}$$

1 L CH_4 produce CO_2 = 1 L

$(3.67 - x)$ L CH_4 produce CO_2 = $(3.67 - x)$ L

∴ $2x + 3.67 - x = 6.11$ (given) ;

$x = 6.11 - 3.67 = 2.44$ L

∴ Volume of C_2H_4 = 2.44 L ;

Volume of CH_4 = 3.67 – 2.44 = 1.23 L

(*iii*) Volume of CH_4 per litre of mixture

$$= \frac{1.23}{3.67} = 0.335\text{ L}$$

Volume of C_2H_4 per litre of mixture

$$= \frac{2.44}{3.67} = 0.665\text{ L}$$

(*iv*) For one mol of any gas:

V_1 = ?, $T_1 = 25 + 273 = 298$ K : at N.T.P.,

$V_2 = 22.4$ L, $T_2 = 273$ K

$$\therefore \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2}\ ;\ V_1 = \frac{V_2\,T_1}{T_2}$$

$$= \frac{22.4\,\text{L} \times 298\,\text{K}}{273\,\text{K}} = \mathbf{22.45\ L}$$

(*v*) For22.45 L, heat produced by

C_2H_4 = 1423 kJ

For 0.665 L, heat produced by

$$C_2H_4 = \frac{1423}{24.45} \times 0.665 = 38.7\ \text{kJ}$$

For 24.45 L, heat produced by

CH_4 = 891 kJ

For 0.335 L, heat produced by

$$CH_4 = \frac{891}{24.45} \times 0.335 = 12.2\ \text{kJ}$$

$\therefore$ Total heat produced

= 38.7 + 12.2 = **50.9 kJ** **Ans.**

EXAMPLE 27. *Upon mixing 45.0 mL of 0.25 M lead nitrate solution with 25.0 mL of 0.1 M chromic sulphate solution, precipitation of lead sulphate takes place. How many lead sulphate moles are formed? Also calculate the molar concentration of the species left behind in the final solution. Assume that lead sulphate is completely insoluble.* **(IIT, 1983)**

SOLUTION.

(*i*) $\text{Pb(NO}_3)_2 \rightarrow \text{Pb}^{2+} + 2\text{NO}^-_3$

1 mol 1 mol 2mol

Mol of $\text{Pb(NO}_3)_2$ = Molarity × volume in litre

$$= 0.25 \times \frac{45}{1000} = 0.01125$$

$\therefore$ Mol of Pb^{2+} ions = 1 × 0.01125 = 0.01125

Mol of 2NO_3^- ions = 2 × 0.01125 = **0.02250**

(*ii*) $\text{Cr}_2(\text{SO}_4)_3 \longrightarrow 2\text{Cr}^{3+} + 3\text{SO}_4^{2-}$

1 mol 2 mol 3 mol

Mol of $\text{Cr}_2(\text{SO}_4)_3$ = Molarity × Volume in litre

$$= 0.1 \times \frac{25}{1000} = 0.0025$$

$\therefore$ Mol of 2Cr^{3+} = 2 × 0.0025 = **0.0050**

Mol of 3SO_4^{2-} = 3 × 0.0025 = **0.0075**

Since number of mol of SO_4^{2-} ions are less than those of Pb^{2+} ions, so, all the SO_4^{2-} ions would react to form PbSO_4

$\therefore$ no. of mol of Pb^{2+} ions left behind

= 0.01125 – 0.0075 = **0.00375**

no. of mol of NO_3^- ions left

= **0.0225**

Total volume of solution

= 45 + 25 = 70 mL

$\therefore$ Molar concentration of Pb^{2+} ions left

$$= \frac{0.00375}{70} \times 1000 = \mathbf{0.05357\,M} \quad \textbf{Ans.}$$

Molar concentration of NO_3^- ions left

$$= \frac{0.00375 \times 1000}{70} = \mathbf{0.3214\,M} \quad \textbf{Ans.}$$

Molar concentration of Cr^{3+} ions left

$$= \frac{0.005}{70} \times 1000 = \mathbf{0.07143\ M} \quad \textbf{Ans.}$$

EXAMPLE 28. *A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 litres at 1.0 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O. Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture.* **(IIT, 1995)**

SOLUTION. n = no. of mol of O_2 = ?, P = 1 atm, V = as from data, T = 400 K, R = 0.0821 L atm K^- mol^-.

But $\quad PV = nRT$. So, $n = \dfrac{PV}{RT}$ ...(*1*)

Let volume of C_2H_6 = x L ; Volume of C_2H_4 = (40 – x) L

(*i*) $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

1 mol $\frac{7}{2}$ mol

1 L $\frac{7}{2}$ L

1 L C_2H_6 require $O_2 = \frac{7}{2}$ L;

x L C_2H_6 require $O_2 = (\frac{7}{2}x)$ L ...(*2*)

(*ii*) $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

1 mol 3 mol

1 L 3 L

1 L C_2H_4 require O_2 = 3 L

(40 – x) L C_2H_4 require O_2 = 3 (40 – x) L

= 120 – 3x ... (*3*)

$\therefore$ Total volume of O_2 from (*2*) and (*3*)

$$= \frac{7}{2}x + 120 - 3x = V$$

Substituting this value of V in (*1*), we get

$$n = \frac{1\,\text{atm} \times \left(\frac{7x}{2} + 120 - 3x\right)\text{L}}{0.0821\,\text{L atm K}^- \text{mol}^- \times 400\,\text{K}}\ \text{mol}$$

But1mol O_2 weighs

= 2 × 16 = 32 g

$$\therefore \quad \text{wt. of } O_2 = \frac{\frac{7x}{2} + 120 - 3x}{0.0821 \times 400} \times 32\,\text{g}\ ;$$

$$130\ \text{g (given)} = \frac{\frac{7x}{2} + 120 - 3x}{32.84} \times 32\,\text{g}\ ;$$

$$130 \times 32.84 = \left(\frac{7x}{2} + \frac{120}{1} - \frac{3x}{1}\right) \times 32$$

$$130 \times 32.84 \times 2 = (7x + (2 \times 120) - 2\,(3x)) \times 32$$

$$= (7x + 240 - 6x) \times 32 \quad \frac{8538.4}{32}$$

$$= x + 240\ ;\ 266.825 = x + 240\ ;$$

x = 26.825 = Volume of C_2H_6

(*iii*) % age $C_2H_6 = \dfrac{26.825}{40} \times 100$ = **67.6%** **Ans.**

% age of C_2H_4 = 100 – 67.06 = **32.94%** **Ans.**

EXAMPLE 29. *Calculate the percentage of free sulphur trioxide in an oleum bottle labelled as 107%* H_2SO_4.

SOLUTION. (*i*) *To calculate wt. of* H_2O *in oleum.* 107% oleum means that 107 g oleum on dilution gives 107 g of pure H_2SO_4.

Thus Wt. of H_2O = 107 – 100 = 7 g

$$\begin{array}{lccc} \text{Reaction :} & H_2O & + \quad SO_3 & \longrightarrow H_2SO_4 \\ & (2\times 1)+16 & 32+(3\times 16) & \\ & =18\text{ g} & =80\text{ g} & \end{array}$$

18 g H_2O react with

SO_3 = 80 g

7 g H_2O react with

$$SO_3 = \frac{80}{18}\times 7 = 31.1\text{ g}$$

It means100 g oleum contains

SO_3 = 31.1 g

or % age of free SO_3 in oleum

= **31.1%**

EXAMPLE 30. *Four volumes of a mixture of gaseous organic liquid 'X' including three volumes of oxygen which are required for its complete combustion, form on burning two volume of carbon dioxide and three volume of water, all being measured at the same temperature and pressure. Calculate the molecular formula of X if it contains only carbon, hydrogen and oxygen.*

SOLUTION. Given :
$$\begin{array}{lccc} X + 3O_2 & \longrightarrow & 2CO_2 & +\ 3H_2O \\ 4\text{ volume} & & 2\text{ Vol} & 3\text{ Vol} \\ 4\text{ mol} & & 2\text{ mol} & 3\text{mol} \end{array}$$

Hence $X + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

Total oxygen atoms present in the product are

(2 × 2) + (3 × 1) = 7

Total oxygen atoms present on the reactant side

= 3 × 2 = 6

∴ no. of oxygen atoms present in

X = 7 – 6 = 1

no. of mol of X = Total no. of mol of reactants – no. of mol of O_2

= 4 – 3 = 1

So, one mol of compound X will contain 2 atoms of C, 6 atoms of H and one atom of O. Hence molecular formula of X = $\mathbf{C_2H_6O}$. **Ans.**

EXAMPLE 31. *25 cm*^{3} *of* CO *at N.T.P. were mixed with 150 cm*^{3} *of air (containing 21%* O_2 *by volume) at 25°C and 740 mm pressure and the mixture was exploded. Find the volume of the residual gases at 37°C and 750 mm pressure.*

SOLUTION. (*i*) For air.

P_1 = 740 mm, V_1 = 150 cm^3,

T_1 = 25 + 273 = 298 K.

At N.T.P. P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

But
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ or } V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2}$$

$$= \frac{740\text{ mm}\times 150\text{ cm}^3\times 273\text{ K}}{298\text{ K}\times 760\text{ mm}}$$

= 133.8 cm^3

∴ Volume of air at N.T.P.

= 133.8 cm^3

∴ Volume of O_2 at N.T.P.

$$= 133.8\times\frac{21}{100} = \mathbf{28.1\ cm^3}$$

Volume of N_2 at N.T.P.

= volume of air (O_2 + N_2) – Vol of O_2 = 133.8 – 28.1 = **105.7 cm^3**

(*ii*) $2CO + O_2 \longrightarrow 2CO_2$

2 Vol 2 Vol

2 cm^3 2 cm^3

2 cm^3 CO form CO_2 = 2 cm^3

$$25\text{ cm}^3\text{ CO form } CO_2 = \frac{2}{2}\times 25 = 25\text{ cm}^3$$

(*iii*) $2CO + O_2 \longrightarrow 2CO_2$

2 Vol 1 Vol

2 cm^3 1 cm^3

2 cm^3 CO use O_2 = 1 cm^3

$$25\text{ cm}^3\text{ CO use } O_2 = \frac{1}{2}\times 25 = 12.5\text{ cm}^3$$

∴ Volume of unused O_2 left behind

= 28.1 – 12.5 = 15.6 cm^3

∴ Total volume of residual gases

= Vol of CO_2 + Vol of N_2 + Vol of unused O_2 = 25 + 105.7 + 15.6 = **146.3 cm^3**

(*iv*) Conversion of 146.3 cm^3 volume to N.T.P.

P_1 = 750 mm, V_1 = ?, T_1 = 37 + 273 = 310 K ; at N.T.P., P_2 = 760 mm, V_2 = 146.3 cm^3, T_2 = 273 K. But :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_1 = \frac{P_2V_2}{T_2}\times\frac{T_1}{P_1}$$

$$= \frac{760\text{ mm}\times 146.3\text{ cm}^3\times 310\text{ K}}{273\text{ K}\times 750\text{ mm}}$$

Or V_1 = **168.3 cm^3** **Ans.**

14.6 MISCELLANEOUS EXAMPLES.

EXAMPLE 32. *When sodium carbonate is heated with slaked lime, sodium hydroxide is formed. Calculate the amount of sodium hydroxide when :*

(*i*) 20 mg of sodium carbonate is heated with slaked lime.

(*ii*) Half kg of slaked lime is heated with sodium carbonate.

SOLUTION.

$$\begin{array}{cccc} Na_2CO_3 & + \quad Ca(OH)_2 & \longrightarrow & 2NaOH + CaCO_3 \\ 1\text{ mol} & 1\text{ mol} & & 2\text{ mol} \\ (2\times 23)+12+(3\times 16) & 40+2(16+1) & & 2(23+16+1) \\ =106\text{ mg} & =74\text{ mg} & & =80\text{ mg} \\ =106\text{ g} & =74\text{ g} & & =80\text{ g} \end{array}$$

$$\frac{1}{2}\text{ kg} = \frac{1}{2}\times 1000\text{ g} = 500\text{ g}.$$

(*i*) 106 mg Na_2CO_3 forms

$NaOH = 80$ mg

∴ 20 mg Na_2CO_3 forms

$$NaOH = \frac{80}{106}\times 20 \simeq \mathbf{15.0\ mg}$$ **Ans.**

(*ii*) 74 g of $Ca(OH)_2$ form

$NaOH = 80$ g

∴ 500 g of $Ca(OH)_2$ form

$$NaOH = \frac{80}{74}\times 500 \simeq \mathbf{54\ g}$$ **Ans.**

Example 33. *Calculate the weight of sodium carbonate formed by heating 8.4 g of baking soda of 90% purity. (Na = 23, C = 12, O = 16, H = 1)*

Solution. Wt. of pure $NaHCO_3$ (baking soda)

$$= 8.4\times\frac{90}{100} = 7.56\text{ g}$$

$$\begin{array}{ccc} 2NaHCO_3 & \longrightarrow & Na_2CO_3 + CO_2 + H_2O \\ 2\,(23+1+12+3(16)) & & 2\,(23)+12+3(16) \\ = 168\text{ g} & & = 106\text{ g} \end{array}$$

168. g $NaHCO_3$ form

$Na_2CO_3 = 106$ g

7.56 g $NaHCO_3$ form

$$Na_2CO_3 = \frac{106}{168}\times 7.56 = \mathbf{4.77\ g}$$ **Ans.**

Example 34. I*n order to convert fluorine into its useful compound, CaF_2, 150 kg of fluorine was fed into the plant containing 75×10^2 kg lime. Calculate the percentage utilization of lime to get CaF_2. (At. wt., F = 19, Ca = 10, O = 16)*

Solution.

$$\begin{array}{ccccc} CaO & + & F_2 & \longrightarrow & CaF_2 + \frac{1}{2}O_2 \\ 40+16 & & 2\times 19 & & \\ = 56\text{ g} & & = 38\text{ g} & & \\ = 56\text{ Kg} & & = 38\text{ Kg} & & \end{array}$$

38 kg F_2 require lime

(CaO) = 56 kg

150 kg F_2 require lime

$$(CaO) = \frac{56}{38}\times 150\text{ kg}$$

∴ % age of CaO utilized

$$= \frac{\text{wt. of CaO used}}{\text{Total wt. of CaO added}}\times 100$$

$$= \frac{56\times 150}{38}\times\frac{1}{75\times 10^2}\times 100$$

$$\approx \mathbf{2.95\%}$$ **Ans.**

Example 35. *Calculate the amount of H_2SO_4 containing 92% H_2SO_4 by weight to prepare 2 kg of HNO_3 containing 36% HNO_3 by weight. HNO_3 is prepared from $NaNO_3$ and H_2SO_4. (At. wt., H = 1, N = 14, O = 16, S = 32)*

Solution.

$$\begin{array}{ccc} 2NaNO_3 + H_2SO_4 & \longrightarrow & Na_2SO_4 + 2HNO_3 \\ 1\text{ mol} & & 2\text{ mol} \\ (2\times 1)+32+(4\times 16) & & 2\,[1+14+(3\times 16)] \\ = 98\text{ g or } 98\text{ kg} & & = 126\text{ g or } 126\text{ kg} \end{array}$$

Wt. of HNO_3 in 2 kg

$$HNO_3 = \frac{2\times 36}{100} = 0.72\text{ kg}$$

126 kg HNO_3 require $H_2SO_4 = 98$ kg

∴ 0.72 kg HNO_3 require

$$H_2SO_4 = \frac{98}{126}\times 0.72 = 0.56\text{ kg}$$

∴ wt. of HNO_3 formed from 92%

$$H_2SO_4 = \frac{0.56\times 100}{92} = \mathbf{0.61\ kg}$$ **Ans.**

Example 36. *5.0 g of common salt is heated with excess of conc. H_2SO_4 and MnO_2. Cl_2 gas so evolved when passed through KI solution, evolved I_2 gas. Calculate the weight of I_2 evolved and MnO_2 used (At. wt., I = 127, Mn = 55, O = 16, Na = 23).*

Solution.

$$\begin{array}{ccc} 2NaCl + 3H_2SO_4 + MnO_2 & \longrightarrow & 2NaHSO_4 + MnSO_4 \\ & & + 2H_2O + Cl_2 \\ Cl_2 + 2KI & \longrightarrow & 2KCl + I_2 \\ \hline 2NaCl + 3H_2SO_4 + 2KI & \longrightarrow & 2NaHSO_4 + MnSO_4 \\ + MnO_2 & & + 2H_2O + 2KCl + I_2 \\ 2\,(23+35.5) \quad 55+(2\times 16) & & 2\times 127 = 254\text{ g} \\ = 117.0\text{ g} \quad = 87\text{ g} & & \end{array}$$

(*a*) 117 g common salt (NaCl) require,

$MnO_2 = 87$ g

∴ 5 g NaCl require MnO_2

$$= \frac{87}{117}\times 5 = \mathbf{3.7\ g}$$ **Ans.**

(*b*) 117 g NaCl produced

$I_2 = 254$ g

∴ 5 g NaCl produced I_2

$$= \frac{254}{117}\times 5 = \mathbf{10.85\ g}$$ **Ans.**

Example 37. *A sample of hydrated magnesium sulphate weiging 0.123 g was dissolved in water and the solution was treated with excess of barium nitrate solution. As a result, 0.1165 g of* $BaSO_4$ *was obtained. Calculate the percentage loss in weight when the hydrated salt is ignited to constant weight of* $BaSO_4$. *(At. wt., Ba = 137, S = 32, O = 16, Mg = 24)*

Solution.

$$\begin{array}{ccc} MgSO_4.\,xH_2O + Ba(NO_3)_2 & \longrightarrow & BaSO_4 + Mg(NO_3)_2 \\ 1\text{ mol} & & 1\text{ mol} \\ = Y\text{ g (say)} & & 137+32+(4\times 16) = 233\text{ g} \end{array}$$

0.1165 g $BaSO_4$ is produced from

$MgSO_4.\,xH_2O = 0.123$ g

∴ 233 g $BaSO_4$ is produced from

$$MgSO_4.\,xH_2O = \frac{0.123}{0.1165}\times 233$$

$= 246\text{ g} = 1\text{ mol}$

$= \text{g. mol. wt. of } MgSO_4.\,xH_2O.$

$\therefore$ wt. of H_2O in $MgSO_4.\,xH_2O$

$= 246 - (\text{g. mol. wt. of } MgSO_4)$

$= 246 - [24 + 32 + (4 \times 16)] = 126\text{ g}$

$\therefore$ % age loss of H_2O

$$= \frac{\text{wt. of } H_2O}{\text{Total wt.}} \times 100 = \frac{126}{246} \times 100$$

$= \mathbf{51.22\%}$ **Ans.**

EXAMPLE 38. *A mixture of two oxides* (MO *and* M_3O_4) *when heated in air to a constant weight gained 4.5 % in its weight. Calculate the percentage of each oxide in the sample.* (*at. wt. M = 56, O = 16*). MO *and* M_3O_4 *on heating give* M_2O_3.

SOLUTION. Let wt. of mixture = 1 g ;

wt. of MO $= x$ g ; wt. of $M_3O_4 = 100 - x$ g

Reaction. (*i*) $2MO + \frac{1}{2}O_2 \longrightarrow M_2O_3$

$2\,(56 + 16) = 144\text{ g}$ $\qquad (2 \times 56) + (3 \times 16) = 160\text{ g}$

(*ii*) $2M_3O_4 + \frac{1}{2}O_2 \longrightarrow 3M_2O_3$

$2\,[(3 \times 56) + (4 \times 16)] = 464\text{ g}$ $\qquad 3\,[(2 \times 56) + (3 \times 16)] = 480\text{ g}$

(*a*) 144 g MO form M_2O_3 = 160 g

$$\therefore \quad x\text{ g MO form } M_2O_3 = \frac{160}{144} \times x\text{ g} = \frac{10x}{9}\text{ g}$$

(*b*) 464 g M_3O_4 form M_2O_3 = 480 g

$$\therefore \quad 100 - x\text{ g } M_3O_4 \text{ form } M_2O_3 = \frac{480}{464} \times (100 - x)\text{ g}$$

$$= \frac{30\,(100 - x)}{29}$$

Original wt. of mixture = 100 g

Wt. of mixture after gaining 4.5% of its weight

$= 100 + 4.5 = 104.5\text{ g}$

$$\therefore \frac{10x}{9} + \frac{30\,(100 - x)}{29} = 104.5 ;$$

$290x + 270\,(100 - x) = 29 \times 9 \times 104.5$

$290x + 27000 - 270x = 27274.5 ;$

$$x = \frac{27274.5 - 27000}{20} = 13.725\text{ g}$$

$$\therefore \quad \%\text{ age of MO} = \frac{13.725}{100} \times 100 = 13.725\% ;$$

% age of $M_3O_4 = 100 - x = 100 - 13.725$

$= \mathbf{86.275\%}$ **Ans.**

EXAMPLE 39. *A mixture of lead monoxide* (PbO) *and lead dioxide* (PbO_2) *was found to contain 90% lead. How much percent of* PbO *and* PbO_2 *are present in the given mixture?* (*at. wt., Pb = 207, O = 16*)

SOLUTION. Let wt. of PbO

$= x$ g ; wt. of $PbO_2 = (100 - x)$ g.

g. mol. wt. of PbO = 207 + 16 = 223 g ;

g. mol. wt. of PbO_2 = 207 + (2 × 16) = 239 g

(*i*) $PbO \equiv Pb$ (223 g, 207 g) $\qquad$ (*ii*) $PbO_2 \equiv Pb$ (239 g, 207 g)

(*a*) 223 g PbO contain

Pb = 207 g

$$x\text{ g PbO contain Pb} = \frac{207}{223} \times x\text{ g}$$

(*b*) 239 g PbO_2 contain

Pb = 207 g

(100 – *x*) g PbO_2 contain

$$\text{Pb} = \frac{207}{239} \times (100 - x) ;$$

$$\text{Total wt. of Pb} = \frac{90}{100} \times 100 = 90\text{ g}$$

$$\therefore \quad 90 = \frac{207x}{223} + \frac{207\,(100 - x)}{239} ;$$

$90 \times 223 \times 239 = 207 \times 239x + 207 \times 223\,(100 - x)$

$4796730 = 49473x + 4616100 - 46161x ;$

$3312x = 180630 ; x = 54.5 = \text{PbO} ;$

$PbO_2 = 100 - x = 100 - 54.5 = 45.5$

$\therefore$ PbO = 54.5% ; PbO_2 = **45.5 %** **Ans.**

EXAMPLE 40. *A given sample of HCl contains 35% HCl by weight. Calculate the amount of this acid that is sufficient to react with 8.4 g of magnesium carbonate (at. wt., Mg = 24, C = 12, H = 1, Cl = 35.5).*

SOLUTION. $MgCO_3 + 2HCl \longrightarrow MgCl_2 + CO_2 + H_2O$

$24 + 12 + (3 \times 16) = 84\text{ g}$ $\qquad 2\,(1 + 35.5) = 73\text{ g}$

84 g $MgCO_3$ react with

HCl = 73 g

$\therefore$ 8.4 g $MgCO_3$ react with

$$\text{HCl} = \frac{73}{84} \times 8.4 = 7.3\text{ g}$$

$\therefore$ wt. of 35% HCl for complete reaction

$$= \frac{7.3 \times 100}{35} = \mathbf{20.86\text{ g}}$$ **Ans.**

EXAMPLE 41. *Calculate the amount of sulphur* (*S*) *that should be burnt in air to remove oxygen as* SO_2 *from 250 g of air. Also, calculate the weight of residual gases in it. Air contains 23% by weight of oxygen gas. (at. wt., S = 32, O = 16).*

SOLUTION. wt. of O_2 in 250 g of air

$$= \frac{250 \times 23}{100} = 57.5\text{ g}$$

$S + O_2 \longrightarrow SO_2$

32 g $\qquad 2 \times 16 = 32$ g

32 g of O_2 combine with sulphur

= 32 g

$\therefore$ 57.5 g of O_2 combine with sulphur

$$= \frac{32}{32} \times 57.5 = 57.5\text{ g}$$

$\therefore$ wt. of sulphur = 57.5 g

wt. of residual gases (N_2, CO_2 etc)

$= 250 - 57.5 = \mathbf{192.5\text{ g}}$ **Ans.**

EXAMPLE 42. *Pyrolusite (an ore of manganese) contains MnO_2 = 89%, SiO_2 and other inert substances = 7% while rest is water. The ore is ignited till constant weight is obtained. Calculate the % age of Mn in the given ore if MnO_2 changes to Mn_3O_4 quantitatively. (at. wt., Mn = 55, O = 16)*

SOLUTION. Let wt. of ore

$$= 100 \text{ g} \; ; \text{ wt. of } MnO_2 = 89 \text{ g}$$

wt. of SiO_2 + inert substances

$$= 7 \text{ g.}$$

Water, however, evaporates on ignition.

$$\begin{array}{ccc} 3MnO_2 & \longrightarrow & Mn_3O_4 + O_2 \\ 3\,[55 + (2 \times 16)] & & (3 \times 55) + (4 \times 16) \\ = 261 \text{ g} & & = 229 \text{ g} \end{array}$$

261 g MnO_2 forms Mn_3O_4

$$= 229 \text{ g}$$

89 g MnO_2 forms Mn_3O_4

$$= \frac{229}{261} \times 89 = 78.1 \text{ g}$$

unchanged inert substances

$$= 7 \text{ g}$$

$\therefore$ Total residue = 78.1 + 7 = 85.1 g

$\therefore$ % age of Mn_3O_4 in the ignited ore

$$= \frac{78.1}{85.1} \times 100 = \mathbf{91.8\%} \qquad \textbf{Ans.}$$

EXAMPLE 43. *When 16.8 g of white solid x was heated, 4.4 g of acid gas A that turned lime water milky was driven off to-gether with 1.8 g of a gas B, which condensed to a colourless liquid. The solid of that remained, dissolved in water to give an alkaline solution which with excess barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving off carbon dioxide. Identify A, B and x. Write down equations for the thermal decomposition of x.* **(Roorkee, 1984)**

SOLUTION. Since gas evolved is acidic and turned lime water milky, the solid will be $NaHCO_3$ and not Na_2CO_3 because it does not decompose on heating.

$$\begin{array}{ccccccc} 2NaHCO_3 & \longrightarrow & Na_2CO_3 & + & CO_2 & + & H_2O \\ 2\,[23 + 1 + 12 + (3 \times 16)] & & & & 12 + (2 \times 16) & & (2 \times 1) + 16 \\ = 168 \text{ g} & & & & = 44 \text{ g} & & = 18 \text{ g} \end{array}$$

(*a*) 168 g of x form gas A = 44 g

$$\therefore \; 16.8 \text{ g of } x \text{ form gas } A = \frac{44}{168} \times 16.8 = 4.4 \text{ g.}$$

Hence, gas A is CO_2.

(*b*) 168 g of x form gas B = 18 g

$$\therefore \; 16.8 \text{ g of } x \text{ form gas } B = \frac{18}{168} \times 16.8 = 1.8 \text{ g.}$$

Hence gas B is H_2O.

Reactions involved are :

(*i*) $\underset{\text{gas } A}{Ca(OH)_2 + CO_2} \longrightarrow CaCO_3 + H_2O$

(*ii*) $H_2O\,(g) \longrightarrow \underset{\text{Colourless liquid, } B}{H_2O\,(l)}$

(*iii*) $Na_2CO_3 + 2H_2O \longrightarrow \underset{\text{Alkaline solution}}{2NaOH} + H_2CO_3$

(*iv*) $BaCl_2 + H_2CO_3 \longrightarrow \underset{\text{White ppt.}}{BaCO_3\downarrow} + 2HCl$

EXAMPLE 44. *A mixture contains* NaCl *and an unknown chloride* MCl. (*i*) *1 g of this is dissolved in water. Excess of acidified* $AgNO_3$ *solution is added to it and 2.567 g of a white precipitate is obtained.* (*ii*) *1 g of the original mixture is heated to 300°C. Some vapours came out which are absorbed in acidified* $AgNO_3$ *solution and 1.341 g of a white precipitate is obtained. Find out the molecular weight of the compound.* **(IIT, 1980)**

SOLUTION. Let wt. of MCl = x g ;

wt. of NaCl = $(1 - x)$ g

Mol. wt. of MCl = m (say)

$$(i) \quad \begin{array}{ccccc} MCl + AgNO_3 & \longrightarrow & AgCl & + & MNO_3 \\ m & & 108 + 35.5 = 143.5 \text{ g} & & \end{array}$$

m g MCl form AgCl = 143.5 g

$$\therefore \quad x \text{ g MCl form AgCl} = \frac{143.5}{m} \times x \text{ g}$$

$$(ii) \quad \begin{array}{ccc} NaCl + AgNO_3 & \longrightarrow & AgCl + NaNO_3 \\ 23 + 35.5 & & 108 + 35.5 \\ = 58.5 \text{ g} & & = 143.5 \text{ g} \end{array}$$

58.5 g NaCl form AgCl = 143.5 g

$$(1 - x) \text{ g NaCl form AgCl} = \frac{143.5(1-x)}{58.5} \text{ g}$$

$$\therefore \quad \frac{143.5x}{m} + \frac{143.5(1-x)}{58.5} = 2.567 \qquad \ldots(1)$$

(*c*) When vapours from heated MCl are passed through $AgNO_3$ solution, precipitate of AgCl is formed.

$$\therefore \quad \frac{143.5\,x}{m} = 1.341 \text{ g (given)} \qquad \ldots(2)$$

Subtracting equation (*2*) from (*1*), we get :

$$\frac{143.5(1-x)}{58.5} = 2.567 - 1.341 = 1.226 \; ;$$

$$143.5 - 143.5x = 58.5 \times 1.226$$

$$143.5x = 143.5 - 71.7 = 71.8 \; ;$$

$$x = \frac{71.8}{143.5} = 0.5$$

Substituting the value of x (= 0.5) in (*2*), we get :

$$\frac{143.5 \times 0.5}{m} = 1.341 \; ;$$

$$m = \frac{143.5 \times 0.5}{1.341} = \mathbf{53.5}$$

$\therefore$ Mol. wt. of MCl = 53.5

EXAMPLE 45. *A 0.51 g sample of an ore contains Na_2O and K_2O. The ore when treated with HCl yielded the respective chlorides of the metals which weighed 0.12 g. The solution of these chlorides gave 0.242 g of AgCl. Calculate the percentage of Na_2O and K_2O in the ore (at. wt., Ag = 108, Cl = 35.5, Na = 23, K = 39).*

Solution. Hint.

$$(a)\quad \underset{(2\times 23)+16\,=\,62\text{ g}}{Na_2O} + 2HCl \longrightarrow \underset{2(23+35.5)\,=\,117\text{ g}}{2NaCl} + H_2$$

$$\underset{(2\times 39)+16\,=\,94\text{ g}}{K_2O} + 2HCl \longrightarrow \underset{2(39+35.5)\,=\,149\text{ g}}{2KCl} + H_2O$$

$$(b)\quad \underset{23+35.5\,=\,58.5\text{ g}}{NaCl} + AgNO_3 \longrightarrow \underset{108+35.5\,=\,143.5\text{ g}}{AgCl\downarrow} + NaNO_3$$

$$\underset{39+35.5\,=\,74.5\text{ g}}{KCl} + AgNO_3 \longrightarrow \underset{108+35.5\,=\,143.5\text{ g}}{AgCl\downarrow} + KNO_3$$

Try yourself

Ans. $Na_2O = 2.16\%$; $K_2O = 12.25\%$

Example 46. *During photosynthesis, one gram of green algae absorbs 0.0047 mol of CO_2 per hour. Assuming that all the carbon atoms of CO_2 are converted to starch, how much time it would take for the algae to increase its mass by 65%. (at. wt., C = 12, H = 1, O = 16).*

Solution. Photosynthesis reaction is :

$$\underset{6\text{ mol}}{6nCO_2} + 5nH_2O \xrightarrow[h\nu]{\text{Chlorophyll}} \underset{\substack{\text{starch}\\(6\times 12)+(10\times 1)+(5\times 16)\,=\,162\text{ g}}}{nC_6H_{10}O_5} + 6nO_2$$

$$\text{Mass of starch} = 65\,\% = \frac{65}{100} = 0.65\text{ g}$$

(a) 162 g starch is formed from

$$CO_2 = 6\text{ mol}$$

0.65 g starch is formed from

$$CO_2 = \frac{6}{162}\times 0.65 = 0.024\text{ mol}$$

(b) time to consume 0.0047 mol

$$CO_2 = 1\text{ hour}$$

Time to consume 0.024 mol

$$CO_2 = \frac{1}{0.0047}\times 0.024 \simeq \textbf{5.11 hours Ans.}$$

Example 47. *Equivalent weights of two metals M_1 and M_2 are 104 and 32 respectively. When 8 g of the mixture of their anhydrous nitrates was heated strongly, a constant weight of 4.4 g of the oxides was recorded. Calculate the percentage of M_1 in the mixture.*

Solution. Let wt. of nitrate of metal $M_1 = a$ g ;

wt. of nitrate of metal $M_2 = b$ g

$$\therefore \quad a + b = 8 \qquad \ldots(1)$$

$$(a)\ \text{Eq. wt. of nitrate } (NO_3^-) = \frac{\text{Mol. wt. of } NO_3^-}{\text{valency of } NO_3^-} = \frac{14+(3\times 16)}{1} = 62$$

$$\therefore\ \text{Eq. wt. of nitrate of } M_1 = 104 + 62 = 166$$

$$(b)\ \text{Eq. wt. of oxide } (O^{2-}) = \frac{\text{At. wt. of } O^{2-}}{\text{Valency of } O^{2-}} = \frac{16}{2} = 8$$

$$\therefore\ \text{Eq. wt. of oxide of } M_1 = 104 + 8 = 112$$

(c) Eq. wt. of nitrate (NO^-_3) = 62 (found above)

$\therefore$ Eq. wt. of nitrate of $M_2 = 32 + 62 = 94$

(d) Eq. wt. of oxide (O^{2-}) = 8 (found above).

$\therefore$ Eq. wt. of oxide of $M_2 = 32 + 8 = 40$

(e) 166 g of nitrate of M_1 form oxide = 112 g

$$\therefore\ a\text{ g of nitrate of } M_1 \text{ form oxide} = \frac{112a}{166}$$

(f) 94 g of nitrate of M_2 form oxide = 40 g

$$b\text{ g of nitrate of } M_2 \text{ form oxide} = \frac{40b}{94}\text{ g}$$

$$\therefore \quad \frac{112a}{166} + \frac{40b}{94} = 4.4 \ \text{(Total wt. of oxides)} \qquad \ldots(2)$$

From equation (1), $b = 8 - a$. Substituting the value of b in (2), we get :

$$\frac{112a}{166} + \frac{40(8-a)}{94} = 4.4\,;$$

$$112 \times 94a + 40 \times 166\,(8 - a) = 4.4 \times 166 \times 94$$

$$10528a + 53120 - 6640a = 68657.6\,;$$

$$3888a = 15537.6$$

$$\therefore \quad a = \left(\frac{15537.6}{3888}\right) \simeq 3.99\text{ g}$$

$$= \text{wt. of nitrate of } M_1$$

$$\text{wt. of nitrate of } M_2 = b = 8 - 3.99 = 4.01\text{ g}$$

166 g of nitrate of M_1 contain M_1 = 104 g

$$3.99\text{ g of nitrate of } M_1 \text{ contain } M_1 = \frac{104}{166}\times 3.99\text{ g}$$

$$\therefore \quad \%\text{ age of } M_1 = \frac{104\times 3.99}{166}\times\frac{100}{8}$$

$$= \textbf{31.26\% Ans.}$$

Type. One mol of every gas at N.T.P. or S.T.P. occupies 22.4 L or 22.4 dm^3 or 22400 cm^3 volume.

Example 48. *How much magnesium metal will be needed to evolve 336 cm³ of dry hydrogen at 27°C and 700 mm pressure from a solution of dil. H_2SO_4 ? Also, calculate the weight and volume of chlorine that will be required to combine with hydrogen. (at. wt., Mg = 24, H = 1, Cl = 35.5)*

Solution. (a) $P_1 = 700$ mm ; $V_1 = 336\ cm^3$;

$T_1 = 27 + 273 = 300$ K

At. N.T.P. $P_2 = 760$ mm ; $V_2 = ?$; $T_2 = 273$ K

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ \text{(gas equation)}$$

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2}\,;$$

$$V_2 = \frac{700\times 336\times 273}{300\times 760} = 281.62\ cm^3$$

$$\underset{24\text{ g}}{Mg} + H_2SO_4 \longrightarrow MgSO_4 + \underset{22400\ cm^3}{H_2}$$

22400 cm^3 H_2 is produced from Mg = 24 g

$$281.62\ cm^3\ H_2 \text{ is produced from Mg} = \frac{24}{22400}\times 281.62$$

$$= \textbf{0.3 g Ans.}$$

(*b*)
$$\underset{22400\ \text{cm}^3}{H_2} + \underset{\substack{2 \times 35.5 \\ = 71\ \text{g} = 22400\ \text{cm}^3}}{Cl_2} \longrightarrow 2HCl$$

$$22400\ \text{cm}^3\ H_2 \text{ combine with } Cl_2 = 71\ \text{g}$$

$$\therefore 281.62\ \text{cm}^3\ H_2 \text{ combine with } Cl_2 = \frac{71}{22400} \times 281.62$$

$$= \mathbf{0.89\ g}\ \ \textbf{Ans.}$$

(*c*)
$$22400\ \text{cm}^3\ H_2 \text{ combine with } Cl_2 = 22400\ \text{cm}^3$$

$$\therefore 281.62\ \text{cm}^3\ H_2 \text{ combine with } Cl_2 = \frac{22400}{22400} \times 281.62$$

$$= \mathbf{281.62\ cm^3}\ \ \textbf{Ans.}$$

EXAMPLE 49. *A gaseous mixture containing 40 mL of laughing gas and nitric oxide was mixed with equal volume of hydrogen gas and exploded. As a result, 25 mL of nitrogen gas was formed. Calculate the volume of each gas in the original gaseous mixture.*

SOLUTION. Let volume of laughing gas,

$$N_2O = x\ \text{mL};$$

volume of NO gas = $(40 - x)$ mL

(*i*) $$\underset{x\ \text{mL}}{N_2O} + H_2 \longrightarrow \underset{x\ \text{mL}}{N_2} + H_2O$$

(*ii*) $$\underset{(40 - x)\ \text{mL}}{NO} + H_2 \longrightarrow \underset{\left(\frac{40 - x}{2}\right)\ \text{mL}}{\frac{1}{2}\ N_2} + H_2O$$

Total volume of N_2 gas formed = 25 mL.

$$\text{Hence}: x + \frac{40 - x}{2} = 25\ ;\ 2x + 40 - x = 50\ ;$$

$$x = 10\ \text{mL}$$

$$\therefore \text{Volume of } N_2O \text{ gas} = x = \mathbf{10\ mL} \quad \textbf{Ans.}$$

$$\text{Volume of NO gas} = 40 - 10 = \mathbf{50\ mL} \quad \textbf{Ans.}$$

EXAMPLE 50. *Calculate the volume of one normal HCl required to decompose 0.29 g of manganese carbonate completely. Also, calculate the volume of CO_2 gas at N.T.P. liberated.* (*at. wt., Mn = 55, C = 12, O = 16, H = 1, Cl = 35.5*).

SOLUTION.

$$\underset{\substack{55 + 12 + (3 \times 16) \\ = 115\ \text{g}}}{MnCO_3} + \underset{\substack{2\,(1 + 35.5) \\ = 73\ \text{g}}}{2HCl} \longrightarrow MnCl_2 + \underset{22400\ \text{mL}}{CO_2} + H_2O$$

(*a*)
$$115\ \text{g}\ MnCO_3 \text{ require HCl} = 73\ \text{g}$$

$$\therefore 0.29\ \text{g}\ MnCO_3 \text{ require HCl} = \frac{73}{115} \times 0.29 = 0.184\ \text{g}$$

(*b*)
$$\text{Strength of HCl} = \text{Normality} \times \text{Eq. wt.}$$

$$= 1 \times 36.5 = 36.5\ \text{g L}^-$$

Thus : 36.5 g HCl is present in solution

$$= 1000\ \text{mL}$$

$\therefore$ 0.184 g HCl is present in solution

$$= \frac{1000}{36.5} \times 0.184 = 5\ \text{mL}$$

(*c*) 115 g $MnCO_3$ produce CO_2 gas

$$= 22400\ \text{mL}$$

$\therefore$ 0.29 g $MnCO_3$ produce CO_2 gas

$$= \frac{22400}{115} \times 0.29 = \mathbf{56.5\ mL} \quad \textbf{Ans.}$$

Type. To calculate volume of gases when specific gravity of substance is given. Use the relation, volume

$$= \frac{\text{wt}}{\text{sp. gr.}}.$$

EXAMPLE 51. *40 mL of dil. H_2SO_4 (sp. gr. 1.3) of 42% purity when treated with magnesium produced H_2 gas. Calculate the volume of H_2 gas at N.T.P. (at. wt., Mg = 24, H = 1, S = 32, O = 16)*

SOLUTION.

$$\underset{24\ \text{g}}{Mg} + \underset{\substack{(2 \times 1) + 32 + (4 \times 16) \\ = 98\ \text{g}}}{H_2SO_4} \longrightarrow MgSO_4 + \underset{22.4\ \text{L}}{H_2}$$

(*a*) volume occupied by 100 g H_2SO_4 (sp. gr. 1.3)

$$= \frac{\text{Mass}}{\text{sp. gr.}} = \frac{100}{1.3} = 76.92\ \text{mL}$$

76.92 mL H_2SO_4 contain pure

$$H_2SO_4 = 42\ \text{g}$$

$\therefore$ 40 mL H_2SO_4 contain pure

$$H_2SO_4 = \frac{42}{76.92} \times 40 = 21.84\ \text{g}.$$

(*b*) 98 g H_2SO_4 liberate H_2 gas at

N.T.P. = 22.4 L

$\therefore$ 21.84 g H_2SO_4 liberate

$$H_2 \text{ gas} = \frac{22.4}{98} \times 21.84 = 4.99\ \text{L}$$

$\therefore$ Volume of H_2 liberated at

N.T.P. = **4.99 L** **Ans.**

EXAMPLE 52. *When 20.02 g of a white solid X is heated, 4.4 g of an acid gas A and 1.8 g of a neutral gas B are evolved, leaving behind a solid residue Y of weight 13.8 g. A turns lime water milky and B condenses into a liquid which changes anhydrous copper sulphate blue. The aqueous solution of Y is alkaline to litmus and gives 19.7 g of a white precipitate Z with barium chloride solution. Z gives carbon dioxide with an acid. Identify A, B, X, Y and Z.*

SOLUTION. (*a*) Acid gas *A* turns lime water milky. So, it should be CO_2 gas.

(*b*) Neutral gas *B* changes anhydrous copper sulphate blue. So, *B* should be H_2O.

(*c*) Aqueous solution of *Y* is alkaline to litmus. So,it should be alkali metal bicarbonate. This solution gives white ppt. *Z* with $BaCl_2$ solution and *Z* also gives CO_2 with acid. So, the reactions can be written as :

$$\underset{X}{2MHCO_3} \longrightarrow \underset{Y}{M_2CO_3} + \underset{A}{CO_2} + \underset{B}{H_2O}$$

$$\underset{Y}{M_2CO_3} + BaCl_2 \longrightarrow \underset{Z}{BaCO_3\downarrow} + 2MCl$$

$$\begin{array}{ccccccc} \therefore\ 2MHCO_3 & \longrightarrow & M_2CO_3 & + & CO_2 & + & H_2O \\ 2\,[m+1+12 & & 2m+12+ & & 12+(2 & & (2\times 1) \\ +\,(3\times 16)] & & (3\times 16) & & \times\, 16) & & +\,16 \\ =2\,(m+16) & & =2\,m+60 & & =44\text{ g} & & =18\text{ g} \\ 20.02\text{ g} & & 13.8\text{ g} & & 4.4\text{ g} & & 1.8\text{ g} \end{array}$$

Here m = at. wt. of metal, M.

(*d*) 44 g CO_2 is formed from

$$MHCO_3 = 2\,(m+61)$$

4.4 g CO_2 is formed from

$$MHCO_3 = \frac{2(m+61)\times 4.4}{44} = \frac{m+61}{5}$$

$$\therefore \quad \frac{m+61}{5} = 20.02\,;$$

$$m = (20.02\times 5)-61 = 39.1\text{ g}$$

So, at. wt. of metal M is 39.1. So, the alkali metal M will be potassium.

EXAMPLE 53. *In order to take a photograph, a photographer used a flash bulb having 25 mL of O_2 at a pressure of 775 mm at 27°C. If the metal wire flashed is of Al metal and it converted to its oxide during the flash process, calculate the minimum weight of Al wire required for maximum efficiency purpose. (at. wt., Al = 27, O = 16)*

SOLUTION. (*a*) $P_1 = 775$ mm, $V_1 = 25$ mL,

$T_1 = 27 + 273 = 300$ K

At N.T.P., $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K.

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

$$\text{or} \quad V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} \quad \text{(gas equation)}$$

$$\therefore \quad V_2 = \frac{775\times 25\times 273}{300\times 760} = 23.2\text{ mL}$$

We know that g. mol. wt. of a gas occupies 22400 mL volume at N.T.P.

$\therefore$ 22400 mL of O_2 weighs at N.T.P. = 32 g

23.2 mL of O_2 weighs at N.T.P. $= \frac{32}{22400}\times 23.2$

$= 0.033$ g.

(*b*)

$$\begin{array}{ccccc} 4\,Al & + & 3O_2 & \longrightarrow & 2Al_2O_3 \\ 4\times 27 & & 3\,(2\times 16) & & \\ =108\text{ g} & & =96\text{ g} & & \end{array}$$

96 g O_2 oxidise Al = 108 g

0.033 g O_2 oxidise Al $= \frac{108}{96}\times 0.033$ = **0.037 g** **Ans.**

EXAMPLE 54. *Calculate the percent of CaO in a 9.0 g mixture of CaO and BaO which needs 95 mL of 2.65 M HCl for complete reaction. (At. wt., Ca = 40, Ba = 137, O = 16)*

SOLUTION.

$$\begin{array}{ccccc} CaO & + & 2HCl & \longrightarrow & CaCl_2 + H_2O \\ 40+16 & & 2\,(1+35.5) & & \\ =56\text{ g} & & =73\text{ g} & & \end{array}$$

$$\begin{array}{ccccc} BaO & + & 2HCl & \longrightarrow & BaCl_2 + H_2O \\ 137+16 & & 2\,(1+35.5) & & \\ =153\text{ g} & & =73\text{ g} & & \end{array}$$

Let wt. of CaO = x g;

wt. of BaO = $(9-x)$ g

(*a*) 56 g CaO need HCl = 73 g

x g CaO need HCl $= \frac{73x}{56}$ g.

(*b*) 153 g BaO need HCl = 73 g

$(9-x)$ g BaO need HCl $= \frac{73(9-x)}{153}$ g

To find wt. of HCl used.

(*c*)

$$\text{Molarity of HCl} = \frac{\text{wt. of HCl}}{\text{g mol. wt. of HCl}} \times \frac{1000}{\text{Vol. of HCl in mL}}$$

$$2.65 = \frac{\text{wt. of HCl}}{36.5}\times\frac{1000}{95}\,;$$

$$\text{wt. of HCl} = \frac{2.65\times 36.5\times 95}{1000} = 9.19\text{ g}$$

$$\therefore \quad \frac{73x}{56}+\frac{73(9-x)}{153} = 9.19;$$

$$73\times 153x + 56\times 73\,(9-x) = 9.19\times 56\times 153$$

$$11169\,x + 36972 - 4088x = 78739.9;$$

$$7081x = 41767.9$$

$$\therefore \quad x = \text{wt. of CaO} = \frac{41767.9}{7081}$$

$$= 5.9\text{ g}$$

$\therefore$ % age of CaO $= \frac{5.9}{9}\times 100$ = **65.5%** **Ans**

EXAMPLE 55. *A given sample of coal contains pollution causing impurity pyrites, FeS_2. What volume of 5.5 M NaOH would be required to react with the SO_2 gas formed from the combustion of 10^3 kg of coal containing 0.06% by mass of pyrites impurity. (at. wt., Fe = 56, S = 32, O = 16, Na = 23, H = 1).*

SOLUTION. (*i*)

$$\begin{array}{ccc} 2FeS_2 + 5O_2 & \longrightarrow & 4SO_2 + 2FeO \\ 2\,[56+(2\times 32)] & & 4\,[32+(2\times 16)] \\ =240\text{ g} & & =256\text{ g} \end{array}$$

10^3 kg $= 10^3\times 1000 = 10^6$ g.

Wt. of 10^6 g coal containing 0.06% by mass of pyrites (FeS_2) impurity

$$= \frac{10^6\times 0.06}{100} = 600\text{ g}$$

(*ii*) 240 g FeS_2 liberate SO_2 = 256 g

600 g FeS_2 liberate SO_2 $= \frac{256}{240}\times 600 = 640$ g

(*iii*)

$$\begin{array}{ccc} 2NaOH + SO_2 & \longrightarrow & Na_2SO_3 + H_2O \\ 2\,(23+16+1)32 + (2\times 16) & & \\ =80\text{ g} \quad =64\text{ g} & & \end{array}$$

64 g SO_2 react with NaOH = 80 g

640 g SO_2 react with NaOH $= \frac{80}{64}\times 640 = 800$ g

$$\text{no. of mol of NaOH} = \frac{\text{wt.}}{\text{g. mol. wt}}$$

$$= \frac{800}{40} = 20\text{ mol}$$

For NaOH : $M_1V_1 = M_2V_2$

$$20 \times 1\text{ L} = 5.5 \times V_2$$

$$\therefore \quad V_2 = \frac{20}{5.5} = \mathbf{3.6\ L} \qquad \textbf{Ans.}$$

Type. Use of gas equation, $PV = nRT$ for calculating volume of gases produced.

EXAMPLE 56. *Calculate the volume of 4.0 M* HNO_3 *that is needed to react completely with 12.0 g of brass alloy (10% Zn + 90% Cu) according to following reactions.*

$$4Zn + 10H^+ (aq) + NO_3^- (aq) \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$$

$$Cu + 4H^+ (aq) + 2NO_3^- (aq) \longrightarrow Cu^{2+} + 2NO_2 (g) + 2H_2O.$$

Also, find the volume of NO_2 *gas produced at 27°C and 1.0 atmospheric pressure. (At. wt., Cu = 63.5, Zn = 65, N = 14, O = 16)*

SOLUTION. wt. of Zn $= \dfrac{12 \times 10}{100} = 1.2$ g

$$\text{wt. of Cu} = \frac{12 \times 90}{100} = 10.8 \text{ g}$$

(*a*) $4Zn + 10H^+ (aq) + NO_3^- (aq) \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O.$

4 × 65 10 mol
= 260 g

260 g Zn require HNO_3 = 10 mol

$$\therefore 1.2 \text{ g Zn require } HNO_3 = \frac{10}{260} \times 1.2 = 0.046 \text{ mol.}$$

(*b*) $Cu + 4H^+ (aq) + 2NO_3^- (aq) \longrightarrow Cu^{2+} + 2NO_2 (g) + 2H_2O$

63.5 g 4 mol 2 mol

63.5 g Cu require HNO_3 = 4 mol

$$10.8 \text{ g Cu require } HNO_3 = \frac{4 \times 10.8}{63.5} = 0.68 \text{ mol}$$

$$\therefore \quad \text{Total mol of } HNO_3 = 0.046 + 0.68 = 0.726 \text{ mol.}$$

For HNO_3 $M_1V_1 = M_2V_2$

$$0.726 \times 1\text{ L} = 4 \times V_2;$$

$$V_2 = \frac{0.726 \times 1\text{L}}{4} \simeq 0.182 \text{ L}$$

or $V_2 = 0.182 \times 1000 =$ **182 mL** **Ans.**

(*c*) **For NO_2**

63.5 g Cu form NO_2 gas = 2 mol

$$10.8 \text{ g Cu form } NO_2 \text{ gas} = \frac{2}{63.5} \times 10.8 = 0.34 \text{ mol}$$

∴ no. of mol of NO_2 $(= n) = 0.34$; V = ?, R = 0.0821 L atm K^- mol^- ; $T = 27 + 273 = 300$ K. We know :

$$PV = nRT \; ; \; V = \frac{nRT}{P}$$

$$V = \frac{0.34 \text{ mol} \times 0.0821 \text{ L atm K}^- \text{ mol}^- \times 300 \text{ K}}{1 \text{ atm}}$$

$$\simeq \mathbf{8.37\ L} \qquad \textbf{Ans.}$$

EXAMPLE 57. *Vinegar contains acetic acid. When 8.0 g of a certain vinegar was titrated with 0.2 M of* NaOH, *25.6 mL of a base have to be added to reach the equivalence point. Calculate the percent by mass of acetic acid in this sample of vinegar. (at. wt., C = 12, O = 16, H = 1).*

SOLUTION.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Acetic acid 1 mol
1 mol

g. mol. wt. of CH_3COOH = 12 + (3 × 1) + 12 + 2 (16) + 1 = 60 g

No. of m. mol of NaOH used = Molarity × volume in mL = 0.2 × 25.6 = 5.12 m mol

$$\therefore \text{ no. of mol of NaOH used} = \frac{5.12}{1000} \text{ mol}$$

Since 1 mol CH_3COOH ≡ 1 mol NaOH (See equation above), so :

$$\frac{5.12}{1000} \text{ mol of NaOH} \equiv \frac{5.12}{1000} \text{ mol of } CH_3COOH$$

$$\therefore \quad \text{wt. of } CH_3COOH = \frac{5.12}{1000} \text{ mol} \times 60 \text{ g mol}^-$$

$$(\because \text{ g. mol. wt. of } CH_3COOH = 60 \text{ g})$$

$$\therefore \quad \% \text{ age of } CH_3COOH = \frac{5.12 \times 60}{1000} \times \frac{100}{8}$$

$$= \mathbf{3.84\%\ CH_3COOH}$$

Ans.

Type. To find mass of a substance dissolved in x mL of a solution, proceed as follows :

1000 mL of 1 M solution weigh = g. mol. wt. of substance

∴ x mL of y M solution weigh
= (g. mol. wt $x \times y$)/ 1000

EXAMPLE 58. *When 45 mL of HCl was titrated with 0.312 M NaOH, 39.7 mL of NaOH was used to get equivalence point. Calculate the molarity of HCl solution. Also, find the mass of HCl that could be dissolved in 75 mL of solution. (At. wt., H = 1, Cl = 35.5)*

SOLUTION. (*a*) $HCl + NaOH \longrightarrow NaCl + H_2O$

Using molarity equation :

$$M_1V_1 \text{ (acid)} = M_2V_2 \text{ (base)}$$

$$M_1 \times 45 = 0.312 \times 39.7$$

$$\therefore \quad M_1 = \mathbf{0.275\ M} \qquad \textbf{Ans.}$$

(*b*) To find mass of 0.725 M HCl in 75 mL solution.

1000 mL of 1 M HCl weigh = 36.5 g

[∵ g. mol. wt. of HCl = 1 + 35.5 = 36.5 g]

$$\therefore 75 \text{ mL of } 0.275 \text{ M HCl weigh} = \frac{36.5}{1000} \times 75 \times 0.275$$

$$= \mathbf{0.75\ g} \qquad \textbf{Ans.}$$

Type. Molarity of a solution $= \dfrac{\text{no. of mol of ion}}{\text{volume in litre}}$

$$= \frac{\text{no. of m. mol of ion}}{\text{volume in mL}}$$

Where no. of m. mol = Molarity × Volume in mL

Example 59. *When excess of* H_2S *gas was passed through 1.0 L of 0.1 M* $Cd(NO_3)_2$ *solution, yellow precipitate of* CdS *is formed.* $Cd^{2+} + H_2S \longrightarrow CdS + 2H^+$. *Calculate the mass of* CdS *and concentration of* H^+ *ions in the solution. (At. wt., Cd = 112.4, S = 32)*

Solution.

$$\begin{array}{lcccc} (a)\ Cd^{2+} & + & H_2S \longrightarrow & CdS\downarrow & + \quad 2H^+ \\ 1\text{ mol or }112.4\text{ g} & & & 112.4+32 & 2\text{ mol} \\ & & & =144.4\text{ g} & \end{array}$$

$$\begin{aligned} \text{Volume of } Cd^{2+} \text{ solution} &= 1.0\text{ L} = 1 \times 1000 \\ &= 1000\text{ mL.} \\ \text{molarity} &= 0.1\text{ M} \\ 1000\text{ mL of 1 } M\ Cd^{2+} &= \text{g. mol. wt. of} \\ Cd^{2+} &= 112.4\text{ g} \\ 1000\text{ mL of 0.1 } M\ Cd^{2+} &= \frac{112.4 \times 1000 \times 0.1}{1000} \\ &= 11.24\text{ g} \\ \text{Thus : } 112.4\text{ g } Cd^{2+} \text{ form CdS} &= 144.4\text{ g} \\ 11.24\text{ g } Cd^{2+} \text{ form CdS} &= \frac{144.4}{112.4} \times 11.24 \\ &= \mathbf{14.44\ g} \qquad \textbf{Ans.} \end{aligned}$$

$$\begin{aligned} (b) 1\text{ mol of } Cd^{2+} \text{ form } H^+ \text{ ions} &= 2\text{ mol} \\ 0.1\text{ mol of } Cd^{2+} \text{ form } H^+ \text{ ions} &= \frac{2}{1} \times 0.1 \\ &= 0.2\text{ mol } H^+ \text{ ions.} \\ \therefore \quad \text{Molarity, } M \text{ of } H^+ \text{ ions} &= \frac{\text{no. of mol of } H^+ \text{ ions}}{\text{vol of } H^+ \text{ ions in litre}} \\ &= \frac{0.2\text{ mol}}{1.0\text{ L}} \\ &= \mathbf{0.2\ M\ H^+\ ions.} \qquad \textbf{Ans.} \end{aligned}$$

Example 60. *Calculate the concentration of* $K_4Fe(CN)_6$ *that should be used so that 36.0 mL of the solution titrates 125 mg of* Zn *dissolved by forming* $K_2Zn_3[Fe(CN)_6]_2$ *(At. wt., Zn = 65)*

Solution.

$$\begin{array}{ccccc} K_2Zn_3[Fe(CN)_6]_2 & \equiv & 3Zn & \equiv & 2[Fe(CN)_6] \\ 1\text{ mol} & & 3\text{ mol} & & 2\text{ mol} \\ \text{Or } 1\text{ m. mol} & & 3\text{ m. mol} & & 2\text{ m. mol} \end{array}$$

$$\begin{aligned} \text{wt. of Zn} &= 125\text{ mg} \\ \text{Thus, } \quad \text{no. of m. mol of Zn} &= \frac{125\text{ mg}}{\text{mg. mol. wt. of Zn}} \\ &= \frac{125\text{ mg}}{65\text{ mg}} \end{aligned}$$

We know that :

$$\begin{aligned} 3\text{ m. mol of Zn} &\equiv 2\text{ m. mol of } K_4Fe(CN)_6 \\ \therefore \quad \frac{125}{65}\text{ m. mol of Zn} &= \frac{2}{3} \times \frac{125}{65}\text{ m. mol of } K_4Fe(CN)_6 \\ \therefore \text{ Molarity, M of } K_4Fe(CN)_6 &= \frac{\text{no. of m.mol}}{\text{volume in mL}} \\ &= \frac{2 \times 125}{3 \times 65} \times \frac{1}{36} \\ &= \mathbf{0.0356\ M} \qquad \textbf{Ans.} \end{aligned}$$

Example 61. *How many millilitre of 0.5 M* H_2SO_4 *are needed to dissolve 0.5 g of copper (II) carbonate ? (at. wt., Cu = 63.5, C = 12, O = 16)* **(IIT, 1999)**

Solution. Reaction

$$\begin{array}{ccccc} CuCO_3 & + & H_2SO_4 & \longrightarrow & CuSO_4 + CO_2 + H_2O \\ 63.5 + 12 + (3 \times 16) & & (2 \times 1) + 32 + (4 \times 16) & & \\ = 123.5\text{ g} & & = 98\text{ g} & & \end{array}$$

$$\begin{aligned} 1000\text{ mL of 1 M } H_2SO_4 &= \text{g. mol. wt. of } H_2SO_4 \\ &= (2 \times 1) + 32 + (4 \times 16) = 98\text{ g} \\ V\text{ mL of 0.5 M } H_2SO_4 &= \frac{98}{1000} \times V \times 0.5\text{ g } H_2SO_4 \\ \text{But} \qquad 98\text{ g } H_2SO_4 &\equiv 123.5\text{ g } CuCO_3 \\ \therefore \quad \frac{98 \times V \times 0.5}{1000}\text{ g } H_2SO_4 &\equiv \frac{123.5}{98} \times \frac{98 \times V \times 0.5}{1000} \\ &= \frac{123.5 \times V \times 0.5}{1000}\text{ g} \\ \text{Hence} \quad \frac{123.5 \times V \times 0.5}{1000} &= 0.5\text{ g (given)} \\ \therefore \qquad V &= \frac{1000}{123.5} = \mathbf{8.1\ mL} \qquad \textbf{Ans.} \end{aligned}$$

14.7 LIMITING REACTANT

The reactant which is completely used and determines the amount of product formed is called limiting reactant.

Steps to know limiting reactant. (1) Write the number of mol [and/or wt.] of each reactant in a balanced equation. e.g:

$$\begin{array}{ccc} CH_4 + 2O_2 & \longrightarrow & CO_2 + 2H_2O \\ 1\text{ mol} \quad 2\text{ mol} & & \end{array}$$

2. Write the given number of mol (or wt.) (as in the given data) of reactant/reactants

$$\begin{array}{lccccc} & CH_4 & + & 2O_2 & \longrightarrow & CO_2 + 2H_2O \\ & 1\text{ mol} & & 2\text{ mol} & & \\ \text{Given data (say)} & 0.5\text{ mol} & & 1.5\text{ mol} & & \end{array}$$

3. Calculate the number of mol (or wt.) of other reactants with the help of mol in balanced equation and one of the reactants.

$$\begin{array}{lccccc} & CH_4 & + & 2O_2 & \longrightarrow & CO_2 + 2H_2O \\ & 1\text{ mol} & & 2\text{ mol} & & \\ \text{Given data (say)} & 0.5\text{ mol} & & 1.5\text{ mol} & & \end{array}$$

$$\left.\begin{array}{l} \text{Calculate value of } O_2 \\ \text{from 0.5 mol } CH_4 \\ \text{(reactant)} \end{array}\right] \begin{array}{cc} 0.5 & 1.0 \\ \text{mol} & \text{mol} \end{array} \left[\begin{array}{l} \because 1\text{ mol } CH_4 \equiv 2\text{ mol } O_2 \\ 0.5\text{ mol } CH_4 \equiv \frac{2}{1} \times 0.5 = 1.0 \end{array}\right.$$

$$\left.\begin{array}{r} \text{(given data) - (calculated} \\ \text{data)} \end{array}\right] 0.5 - 0.5 = 0 \quad \overset{1.5-1.0}{=0.5}$$

4. Reactant with less value of difference, is the limiting reactant. So, in above example, CH_4 (value = zero which is less than + 0.5 in O_2) is the limiting reactant.

Example 62. *How will you recognise whether the given problem is of limiting quantities or not ?*

Solution. The problem will concern with limiting quantities if quantities of two or more reactants are given.

EXAMPLE 63. *When 0.2 mol of* Fe_2O_3 *was heated with 1.1 mol of* CO, *following reaction took place.*

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Determine the limiting reactant.

SOLUTION.

Fe_2O_3	+	$3CO$	$\longrightarrow$	$2Fe + 3CO_2$
1 mol		3 mol		[Mol in balanced equation]
0.2 mol		1.1 mol		[mol in the given data]
0.2 mol		0.6 mol		[Calculated value of CO from 0.2 mol Fe_2O_3.

∵ 1 mol $Fe_2O_3 \equiv 3$ mol CO

$$0.2 \text{ mol } Fe_2O_3 = \frac{3}{1} \times 0.2 = 0.6]$$

0.2 - 0.2	1.1 - 0.6	
= Zero	= +0.5	[Difference : Given Value – Calculated Value].

Since difference value of Fe_2O_3 (= 0) is less than that of CO (= + 0.5), Fe_2O_3 is a limiting reactant.

EXAMPLE 64. *8.0 g of Al was heated with 14.0 g of* Cl_2 *to form* Al_2Cl_6*. Which one is the limiting reactant in this process? (At. wt. Al = 27, Cl = 35.5)*

SOLUTION.

2Al	+	$3Cl_2$	$\longrightarrow$	Al_2Cl_6
2 mol		3 mol		(Mol in balanced equation)
2 × 27		3 × (2 × 35.5)		(wt. in balanced equation)
= 54 g		= 213 g		
8.0 g		14.0 g		(Wt. in the given data)
8.0 g		31.6 g		(Calculated value of Cl_2 from 8.0 g of Al.)
8.0 – 8.0		14.0 – 31.6		
= 0		= –17.6 g		∵ 54 g Al ≡ 213 g Cl_2

$$\therefore \ 8 \text{ g Al} = \frac{213}{54} \times 8 = 31.6\text{g}$$

[Difference = Given value – Calculated value]

Since difference value of Cl_2 (–17.6 g) is less than Al value (= zero), Cl_2 is the limiting reactant.

EXAMPLE 65. *390 g of* SO_2 *were treated with 170 g* O_2 *and 120 g water to form* H_2SO_4 *with the help of following reaction.*

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4$$

Find out the limiting reactant and wt. of other reactants left behind. (At. wt., S = 32, O = 16, H = 1)

SOLUTION.

$2SO_2$	+	O_2	+	$2H_2O$	$\longrightarrow$	$2H_2SO_4$
2 mol		1 mol		2 mol		(Mol in balanced equation)
2 [32 + (2 × 16)] = 128 g		2 × 16 = 32 g		2 (1 × 1 + 16) = 36 g		(Wt. in balanced equation)
390 g		170 g		120 g		(wt. in the given data)
						(Calculated value of O_2 and H_2O from 390 g SO_2)
390 g		97.5 g		109.7 g		

(*i*) 128 g. $SO_2 \equiv 32$ g O_2

$$\because \quad 390 \text{ g } SO_2 \equiv \frac{32}{128} \times 390 \equiv 97.5 \text{ g}$$

(*ii*) 128 g $SO_2 \equiv 36$ g H_2O

$$390 \text{ g } SO_2 \equiv \frac{36}{128} \times 390 = 109.7 \text{ g}$$

390 – 390	170 – 97.5	120 – 109.7	Defference: Given– Calculated Value Value
= 0 g	= 72.5 g	= 10.3 g	

Since difference value of SO_2 (= 0) is the least value among SO_2, O_2 and H_2O, the SO_2 is the limiting reactant. Wt. of O_2 and H_2O left behind are 72.5 g and 10.3 g respectively.

EXAMPLE 66. *How many g of copper will be replaced from 2.0 L of 2.5 M* $CuSO_4$ *solution by 47.25 g aluminium metal ? (At. wt., Cu = 63.5, Al = 27)*

SOLUTION. no. of mol of

$CuSO_4$ = Molarity × Volume in litre

$$= \frac{2.5 \text{ mol}}{\text{L}} \times 2.0 \text{ L} = 5.0 \text{ mol}$$

$$\text{no. of mol of Al} = \frac{47.25 \text{ g}}{27 \text{ g}} = 1.75 \text{ mol.}$$

2 Al	+	$3\,CuSO_4$	$\longrightarrow$	$Al_2(SO_4)_3 + 3Cu$
				3 × 63.5 = 190.5 g
2 mol		3 mol		(Data from balanced equation)
1.75 mol		5 mol		(Given data)
1.75 mol		2.625 mol		[Calculated value of $CuSO_4$ from 1.75 mol Al.

∴ * Only 2.625 mol $CuSO_4$ will react

∵ 2 mol Al ≡ 3 mol $CuSO_4$

Hence : 3 mol $CuSO_4$ form Cu = 190.5 g

$$\therefore \quad 1.75 \text{ mol Al} = \frac{3}{2} \times 1.75 = 2.625 \text{ mol}]$$

$$2.625 \text{ mol } CuSO_4 \text{ form Cu} = \frac{190.5}{3} \times 2.625$$

= **166.7 g** **Ans.**

* **Second method.** Difference. Given value – Calculated value

Al = 1.75 – 1.75 = 0 (zero)

mol; $CuSO_4$ = 5 – 2.625 = +2.375 mol

∴ Limiting reactant = Al (having least difference)

Hence 2 mol Al displace Cu = 190.5 g

$$1.75 \text{ mol Al displace Cu} = \frac{190.5}{2} \times 1.75$$

= **166.7 g** **Ans.**

EXAMPLE 67. *When solutions containing 2.0 g* Na_2SO_4 *and 3.0 g* $BaCl_2$ *are mixed to-gether, what will be the amount of* $BaSO_4$ *produced ? (At. wt., Na = 23, S = 32, O = 16, Ba = 137, Cl = 35.5)*

SOLUTION.

$BaCl_2$	+	Na_2SO_4	$\longrightarrow$	$BaSO_4 + 2NaCl$
137+ (2 × 35.5)		(2 × 23) + 32		137 + 32 + (Data from balanced equation)

= 208 g + (4 × 16) = 142 g (4 × 16) = 233 g

3.0 g 2.0 g (Given data)

3.0 g 2.05 g (Calculated data of Na_2SO_4 from 3.0 g $BaCl_2$)

3.0 − 3.0 = 0 2.0 − 2.05 =− 0.5

$\because$ 208 g $BaCl_2$ ≡ 142 g Na_2SO_4

$\therefore$ 3 g $BaCl_2$ = $\frac{142}{208} \times 3$ = 2.05 g]

Difference : Given value – Calculated value

Since the difference value of Na_2SO_4 (= –0.5) is less than that of $BaCl_2$ (= 0), Na_2SO_4 is a limiting reactant.

Hence :142 g Na_2SO_4 form $BaSO_4$ = 233 g

$\therefore$ 2.0 g Na_2SO_4 form $BaSO_4$ = $\frac{233}{142} \times 2$

= **3.28 g** **Ans.**

EXAMPLE 68. *How many g of* Cu_2S *will be formed when 95.0 g of* Cu *is heated with 48 g of sulphur ? (At. wt., Cu = 63.5, S = 32)*

SOLUTION.

$2Cu + S \longrightarrow Cu_2S$

2 × 63.5 32 g (2 × 63.5) + 32

(Data from balanced equation)

= 127.0 g = 159 g

95.0 g 48 g (Given data)

95.0 g 23.9 g [Calculated data of S from 95.0 g Cu.

$\because$ 127 g Cu ≡ 32 g S

$\therefore$ 95 g Cu ≡ $\frac{32}{127} \times 95 = 23.9$ g]

95 – 95 = 0 48 – 23.9 = 24.1 g

[Difference : Given value – Calculated value]

Limiting reactant

Cu is limiting reactant because its difference value is least.

Hence, we have :

127 g Cu form Cu_2S = 159 g

$\therefore$ 95 g Cu form Cu_2S = $\frac{159}{127} \times 95$ = **118.9 g** **Ans.**

EXAMPLE 69. *Calculate the masses of* P_4O_6 *and* P_4O_{10} *that would be produced by the combustion of 3.0 g of* P_4 *in 3.0 g of oxygen, leaving no* O_2 *or* P_4*. (At. wt., P = 31, O = 16)*

SOLUTION. (*1*)

$P_4 + 3O_2 \longrightarrow P_4O_6$

1 mol 3 mol 1 mol (Data from balanced equation)

4 × 31 3 (2 × 16) (4 × 31) + (6 × 16)

= 124 g = 96 g = 220 g

= 3.0 g 3.0 g (Given data)

3.0 g 2.32 g [Calculated data of O_2 from 3.0 g P_4]

3.0 – 3.0 3.0 – 2.32 $\because$ 124 g P_4 = 96 g O_2

= 0 g = 0.68 g $\therefore$ 3 g P_4 = $\frac{96}{124} \times 3 = 2.32g$]

P_4 is limiting reagent because its difference value (= 0) is least as compared to 0.68 g of O_2. Hence:

124 g P_4 forms P_4O_6 = 220 g

3.0 g P_4 forms P_4O_6 = $\frac{220 \times 3.0}{124} = 5.32\ g$

(2) $P_4O_6 + 2O_2 \longrightarrow P_4O_{10}$

(4×31)+(6×16) 2(2×16) (4×31)+(10×16)

= 220 g = 64 g = 284 g

5.32 g 0.68 g [See part (1)]

5.32 g 1.548 g

[$\because$ 220 g P_4O_6 ≡ 64 g O_2

5.32 g P_4O_6 = $\frac{64}{220} \times 5.32 = 1.548g$]

5.32 – 5.32 0.68 – 1.548

= 0 g = – 0.868 g Least value

[Difference = Given value – Calculated value]

Since difference value for O_2 is less than that of P_4O_6 value (= 0), O_2 is the limiting reactant.

Hence: 64 g O_2 ≡ 284 g P_4O_{10}

0.68 g O_2 = $\frac{284}{64} \times 0.68$ = **3.02 g** **Ans.**

Total wt. of P_4O_6 = 5.32 g

Wt. of P_4O_6 used to form P_4O_{10} = 3.02 g

Now 284 g P_4O_{10} ≡ 220 g P_4O_6

3.02 g P_4O_{10} ≡ $\frac{220}{284} \times 3.02 = 2.34$ g

$\therefore$ Wt. of P_4O_6 used to form P_4O_{10} = 2.34 g

$\therefore$ Wt. of P_4O_6 actually formed = 5.32 – 2.34

= **2.98 g** **Ans.**

EXAMPLE 70. *A 49.5 g of zinc piece was put into a 100 L vessel containing 2.9 g* $Ag^+ L^-$*. (a) Which reactant reacted completely ? (b) How much of the other substance remained unreacted ? (At. wt., Ag = 108 ; Zn = 65)*

SOLUTION. $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$

1 mol 2 mol 2 mol 1 mol

65 g 2 × 108 = 216 g 2 × 108 65 g

(Data from balanced equation)

49.50 g $\frac{2.9\,g}{L} \times 100\,L$ = 216 g

(Given Data)

= 290 g

49.5 g 164.5 g [Calculated data of Ag^+ from 49.5 g Zn.

$\because$ 65 g Zn ≡ 216 g Ag

$\therefore$ 49.5 g Zn = $\frac{216}{65} \times 49.5$ = 164.5 g]

49.5 – 49.5 290.0 – 164.5

Difference = Given Value – Calculated value

= zero   = 125.5 g

The difference value of Zn (= 0) being less than that of Ag^+ (= 125.5 g), so, Zn is a limiting reactant and would react completely.

Thus, 65 g Zn react with Ag^+ = 216 g

$\therefore$ 49.5 Zn react with Ag^+ = $\frac{216\text{ g}}{65\text{ g}} \times 49.5$ g

= **164.5 g** **Ans.**

(*b*) Excess of Ag^+ left behind = 290 – 164.5 = **125.5 g.**

EXAMPLE 71. *When 50.0 g of chlorobenzene were treated with 50.0 g of chloral, D.D.T. insecticide was formed by the following reaction.*

$$2C_6H_5Cl + CCl_3CHO \longrightarrow (C_6H_4Cl)_2CH.CCl_3 + H_2O$$

Chlorobenzene *Chloral* *D.D.T.*

Assuming that the reaction goes to completion without any losses, calculate the amount of this insecticide formed. (At. wt., C = 12, Cl = 35.5, H = 1, O = 16)

SOLUTION.

$2C_6H_5Cl$ +	CCl_3CHO ⟶	$(C_6H_4Cl)_2CHCCl_3 + H_2O$	
2 mol	1 mol	1 mol	
2 [(6 × 12) + 5 + 35.5] = 225 g	12 + (3 × 35.5) + 12 + 1 + 16 = 147.5 g	2[(6 × 12) + (4 × 1) + 35.5] + 12 + 1 + 12 + (3 × 35.5) = 354.5 g	[Data of balanced equation]
50 g	50 g		[Given data]
50 g	32.8 g		[Calculated data for CCl_3CHO from 50.0 g C_6H_5Cl

$\because$ 225 g $C_6H_5Cl \equiv$ 147.5 g CCl_3CHO

$\therefore$ 50 g $C_6H_5Cl \equiv \frac{147.5}{225} \times 50$ = 32.8g]

50 – 50   50 – 32.8

Difference : Given value – Calculated value

= 0 g   = 17.2 g

Since difference value of C_6H_5Cl (= 0) is less than that of CCl_3CHO, C_6H_5Cl is a limiting reagent.

225 g C_6H_5Cl form D.D.T. = 354.5 g

50 g C_6H_5Cl form D.D.T. = $\frac{354.5}{225} \times 50$ = **78.8 g Ans.**

EXAMPLE 72. *When a mixture of 2.2 tons of* Cl_2 *and 1.5 tons of* CS_2 *is passed through a hot reaction tube, following reaction took place.* $3Cl_2 + CS_2 \longrightarrow CCl_4 + S_2Cl_2$. *(a) Calculate the weight of* CCl_4 *that could be prepared from the limiting reactant. (b) Which of the reactants is in excess and how much ? (At. wt., C = 12, S = 32, Cl = 35.5)*

SOLUTION. Note. Ratio of tons is the same as the ratio for g. So, solve the question using, g.

CS_2 +	$3Cl_2$ ⟶	$CCl_4 + S_2Cl_2$	
1 mol	3 mol	1 mol	
12 + (2 × 32) = 76 g	3 (2 × 35.5) = 213 g	12 (4 × 35.5) = 154 g	[Data of the balanced chemical equation.]
1.5 g	2.2 g		(Given data)
1.5 g	4.2 g		(Calculated data for Cl_2 from 1.5 g CS_2)

(*i*) 76 g $CS_2 \equiv$ 213 g Cl_2

1.5 g $CS_2 \equiv \frac{213}{76} \times 1.5$ = 4.2 g

1.5 – 1.5   2.2 – 4.2

Difference : Given value – Calculated value

= 0 g   = –2.0 g

Since difference value of Cl_2 (= –2.0 g) is less than that of CS_2 (= 0), so, Cl_2 is the limiting reactant while CS_2 is in excess.

(*a*) 213 g Cl_2 reacts with CS_2 = 76 g

$\therefore$ 2.2 g Cl_2 reacts with CS_2 = $\frac{76}{213} \times 2.2$ = 0.78 g

$\therefore$ wt. of CS_2 in excess = 1.5 – 0.78 = 0.72 g

= **0.72 ton** **Ans.**

(*b*) 213 g Cl_2 form CCl_4 = 154 g

$\therefore$ 2.2 g Cl_2 form CCl_4 = $\frac{154}{213} \times 2.2$ = 1.59 g

= **1.59 ton** **Ans.**

14.8 TYPICAL EXAMPLES

EXAMPLE 73. *Air contains 20% oxygen by volume. What volume of air is required to produce 10 litres of* CO_2 *?*

(BCECE, 2000)

SOLUTION. Formation of CO_2 is represented by the equation

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$$

1 vol.   1 vol.

1 volume of O_2 produces one volume of CO_2. Hence for producing 10 litre of CO_2, 10 litre of oxygen will be needed.

Now 20 litre of oxygen is present in air = 100 L

$\therefore$ 10 litre of oxygen is present in air = $\frac{100}{20} \times 10$

= 50 L

EXAMPLE 74. *4.00 g of powder known to contain only copper, zinc and aluminium was treated with excess of warm dilute hydrochloric acid until reaction was complete. The undissolved material after filtration, washing and drying weighed 1.50 g. The filtered solution and washings were treated with ammonium chloride solution and ammonium hydroxide in slight excess. A colourless precipitate was produced. After filtration, washing, drying and ignition to constant weight, it left a product weighing 2.55 g. Calculate the percentage composition of original powder (Al = 27, O = 16).* **(WBJEE, 1994)**

SOLUTION. Reactions involved are :

$Cu + HCl \longrightarrow$ No reaction

$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$

$$AlCl_3 + 3NH_4OH \xrightarrow{NH_4Cl} \underset{\text{White ppt.}}{Al(OH)_3} + 3NH_4Cl$$

$$2Al(OH)_3 \xrightarrow{\text{Ignition}} \underset{\text{(residue)}}{Al_2O_3} + 3H_2O$$

Thus, material left undissolved after treatment with dil. HCl is copper metal.

$\therefore$ Weight of Cu metal in the mixture = 1.5 g

Weight of Zn and Al in the mixture = 4 – 1.5 = 2.5 g

White ppt. obtained after treatment with NH_4Cl and NH_4OH is $Al(OH)_3$ and the residue obtained after ignition of $Al(OH)_3$ is Al_2O_3.

$\therefore$ Weight of Al_2O_3 = 2.55 g

$Al_2O_3 \equiv 2Al$

27 × 2 + 3 × 16 = 102 g = 2 × 27 = 54 g

Thus 102 g of Al_2O_3 contains Al = 54 g

$$2.55 \text{ g of } Al_2O_3 \text{ contains Al} = \frac{54}{102} \times 2.55 = 1.35 \text{ g}$$

$\therefore$ Weight of Al in the mixture = 1.35 g ;

Weight of Zn in the mixture = 2.5 – 1.35 g = 1.15 g

In 4 g of mixture, Al = 1.35 g

$$\therefore \text{Percentage of Al} = \frac{1.35}{4} \times 100 = 33.75 ;$$

$$\text{Percentage of Zn} = \frac{1.15}{4} \times 100 = 28.75$$

$$\text{Percentage of Cu} = \frac{1.50}{4} \times 100 = 37.5$$

Example 75. *2.00g of a mixture of sodium carbonate and sodium bicarbonate lose 0.248 g when heated to 300 C. Calculate the %age of* Na_2CO_3 *in the mixture.*

Solution. The relevant chemical reaction is :

$2NaHCO_3$	$\longrightarrow$	Na_2CO_3 +	H_2O +	CO_2
2 mol			1 mol	1 mol
168 g			18 g	44 g

Loss of wt. must be on account of evolution of H_2O and CO_2

Wt. lost by heating 168 g of $NaHCO_3$ = 18 + 44 = 62 g

$\therefore$ 62 g wt. is lost by heating = 168 g $NaHCO_3$

$$\therefore 0.248 \text{ g wt. will be lost by heating} = \frac{168 \times 0.248}{62} = 0.672 \text{ g of } NaHCO_3$$

$\therefore$ 2.0 g of sample contains = 0.672 g $NaHCO_3$

$\therefore$ 2.00 g of sample contains 2 – 0.672 = 1.328 g of Na_2CO_3

Thus, the %age of Na_2CO_3 in the mixture

$$= \frac{1.328}{2} \times 100 = 66.4$$

Hence, sample contains **66.40%** Na_2CO_3

Example 76. *What weight of* AgCl *will be precipitated when a solution containing 4.77 g of* NaCl *is added to a solution of 5.77 g of* $AgNO_3$. *(Na = 23, Cl = 35.5, Ag = 107.9).*

(IIT, 1978)

Solution. Reaction :

NaCl +	$AgNO_3$	$\longrightarrow$	$AgCl\downarrow$ + $NaNO_3$
23 + 35.5	108 + 14 + (3 × 16)		108 + 35.5
= 58.5 g	= 170 g		= 143.5 g
Or 1 mol	Or 1 mol		

Given no. of mol. $\frac{4.77}{58.5} = 0.08$; $\frac{5.77}{170} = 0.03$ mol

1 mol NaCl = 1 mol $AgNO_3$

0.08 mol NaCl = 0.08 mol $AgNO_3$

Calculated no. of mol.	0.08	0.03
Given mol – Calculated mol	0.08 – 0.08 = zero	0.03 – 0.08 = –0.05

So, $AgNO_3$ is a limiting reactant because its difference value (= – 0.05) is least and is responsible to form AgCl ppt. Thus :

170 g $AgNO_3$ form AgCl = 143.5 g

$$5.77 \text{ g } AgNO_3 \text{ form AgCl} = \frac{143.5}{170} \times 5.77 = \mathbf{4.87\ g} \quad \textbf{Ans.}$$

14.9 AIEEE PATTERN EXAMPLES

Example 77. *According to the reaction* $Ag^+ + 2CN^- \longrightarrow Ag(CN)_2^-$, *40 mL of 0.225 M* $AgNO_3$ *solution is needed to react with exact 55 mL of NaCN solution. The concentration of NaCN solution will be :*

(*a*) *0.180 M* (*b*) *0.1635 M*

(*c*) *0.327 M* (*d*) *0.72 M*

Solution.

Ag^+ +	$2CN^-$	$\longrightarrow$	$Ag(CN)_2^-$
1 mol	2 mol		
Or 1 m. mol	2 m. mol		

(*a*) no. of m. mol of Ag^+ = molarity × volume in mL = 0.225 × 40 = 9 m.mol

From the reaction, it is clear that :

1 m. mol of Ag^+ react with CN^- = 2 m. mol

$\therefore$ 9 m. mol of Ag^+ react with CN^- = 2 × 9 = 18 m. mol

Volume of NaCN solution = 55.0 mL.

$$\therefore \text{Molarity, M of } CN^- = \frac{\text{no. of mol of } CN^-}{\text{Volume of } CN^- \text{ in mL}} = \frac{18 \text{ m.mol}}{55 \text{ mL}} = 0.327 \text{ M}$$

So, the correct answer is (*c*),

Example 78. *Volume of 0.2 M* $BaCl_2$ *required to precipitate all the* SO_4^{2-} *ions from 15 mL of a solution containing 90 g of* Na_2SO_4 *per litre will be :*

(*a*) *32 mL* (*b*) *20 mL*
(*c*) *16 mL* (*d*) *8 mL*
(*At. wt., Ba = 137, Cl = 35.5, S = 32, O = 16, Na = 23*)

Solution. $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$

1 mol 1 mol

(2 × 23) + 32 + (4 × 16)

= 142 g

(*a*) no. of mol of

$$Na_2SO_4 = \frac{\text{wt.}}{\text{g.mol.wt}} = \frac{90}{142}\text{ mol};$$

$$\text{Volume} = 10\text{ mL} = \frac{10}{1000}\text{ L.}$$

∴ Molarity, M of Na_2SO_4

$$= \frac{90}{142}\times\frac{10}{1000} = \frac{9}{1420}\text{ M}$$

From the equation, it is clear that :

1 mol of Na_2SO_4 react with $BaCl_2$

= 1 mol

$$\therefore \frac{M_1V_1\text{ (of BaCl}_2)}{M_2V_2\text{ (of Na}_2\text{SO}_4)} = \frac{\text{No. of mol of BaCl}_2}{\text{No. of mol of Na}_2\text{SO}_4}$$

$$\frac{0.2 \times V_1}{\frac{9}{1420}\times 1\text{ L}} = \frac{1}{1}$$

$$\therefore \quad V_1 = \frac{9}{1420}\times\frac{1}{0.2}\text{ L} = 0.032\text{ L}$$

$$= 0.032 \times 1000 = 32\text{ mL.}$$

So, the correct answer is (*a*).

Example 79. *A 35.0 mL of sodium chloride solution is treated with excess of $AgNO_3$ solution. As a result, 1.1 g of AgCl precipitate is formed. The molar concentration of NaCl is :*

(*a*) *0.44 M* (*b*) *0.22 M*
(*c*) *0.11 M* (*d*) 0.011 M
(*At. wt. Ag = 108, Cl = 35.5*)

Solution.

(*a*) $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

1 mol 1 mol 1 mol

108 + 35.5

= 143.5 g

143.5 g AgCl is formed from

NaCl = 1 mol

∴ 1.1 g AgCl is formed from

$$NaCl = \frac{1}{143.5}\times 1.1 = 7.7\times10^{-3}\text{ mol}$$

(*b*) Volume of NaCl= 35 mL = $\frac{35}{1000}$ = 0.035 L.

We know that :

$$\text{Molarity of NaCl} = \frac{\text{no. of mol of NaCl}}{\text{Volume in L}}$$

$$= \frac{7.7\times10^{-3}}{0.035} = 0.22\text{ M.}$$

So, the correct answer is (*b*).

Example 80. *When 6.3 g of sodium bicarbonate are added to 30.0 g of acetic acid solution, the residual solution is found to weigh 33. g. The mass of carbon dioxide released in the reaction is:*

(*a*) *3.0 g* (*b*) *0.91 g*
(*c*) *1.91 g* (*d*) *3.3 g* **J and K-CET, 2011**

Solution. Reaction :

$NaHCO_3 + CH_3COOH \longrightarrow CH_3COONa + CO_2 + H_2O$

Mol. wts. (g mol⁻):

84 80 44

Given.

6.3 g 30 g 33 g

Since 84 g $NaHCO_3$ forms, CO_2 = 44 g

6.3 g $NaHCO_3$ forms CO_2 = (44 × 6.3)/84 = 3.3 g

So, the correct answer is (*d*).

Example 81. *The volume of a 0.5 M H_2SO_4 required to react completely with 25 mL of 0.1 M NaOH will be :*

(*a*) *25 mL* (*b*) *5.2 mL*
(*c*) *50 mL* (*d*) *2.5 mL*

Solution.

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$ ...(1)

2 mol 1 mol

2 m. mol 1 m. mol

$$\frac{M_1V_1\text{ (NaOH)}}{M_2V_2\text{ (H}_2\text{SO}_4)} = \frac{\text{no. of mol of NaOH}}{\text{no. of mol of H}_2\text{SO}_4};$$

$$\frac{0.1\times2.5}{0.5\times V_2} = \frac{2}{1};\ V_2 = \frac{0.1\times25}{0.5\times2} = \mathbf{2.5\ mL}$$

So, the correct answer is (*d*).

Example 82. *Volume of 4.0 M* HCl *required to react completely with 25.2 g sodium bicarbonate is :*

(*a*) 0.75 L (*b*) 0.075 mL
(*c*) 75 mL (*d*) 7.5 mL
(*At. wt., Na = 23, H = 1, C = 12, O = 16*)

Solution.

$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$ ...(1)

1 mol 1 mol

23 + 1 + 12 + (3 × 16)

= 84 g

no. of mol of

$$NaHCO_3 = \frac{\text{wt. of NaHCO}_3}{\text{g. mol. wt. of NaHCO}_3}$$

$$= \frac{25.2\text{ g}}{84\text{ g}} = 0.3\text{ mol}$$

From equation (*1*), we see that :

1 mol of $NaHCO_3$ react with

HCl = 1 mol

∴ 0.3 mol of $NaHCO_3$ react with

HCl = 0.3 mol.

∴ Volume of HCl in litre

$$= \frac{\text{no. of mol of HCl}}{\text{Molarity of HCl}} = \frac{0.3}{4}$$

$$= 0.075\ \text{L}$$

$$= 0.075 \times 1000 = 75\ \text{mL.}$$

So, the correct answer is (*c*).

EXAMPLE 83. *Volume of 4.0 M H_2SO_4 required to react completely with 25.2 g of sodium bicarbonate is :*

(*a*) *37.5 mL* (*b*) *0.375 L*

(*c*) *3.75 mL* (*d*) *4 mL*

(*At. wt., Na = 23, H = 1, C = 12, O = 16*)

SOLUTION.

$$\underset{2\ \text{mol}}{2NaHCO_3} + \underset{1\ \text{mol}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2CO_2 + H_2O \quad ...(1)$$

$$\text{no. of mol of } NaHCO_3 = \frac{\text{wt. of } NaHCO_3}{\text{g. mol. wt. of } NaHCO_3}$$

$$= \frac{25.2}{84} = 0.3\ \text{mol}$$

From equation (*1*), we see that :

$$2\ \text{mol of } NaHCO_3 \text{ react with } H_2SO_4 = 1\ \text{mol}$$

$$\therefore\ 0.3\ \text{mol of } NaHCO_3 \text{ react with } H_2SO_4 = \frac{1}{2} \times 0.3$$

$$= 0.15\ \text{mol}$$

$\therefore$ Volume of H_2SO_4 in litre

$$= \frac{\text{no. of mol of } H_2SO_4}{\text{Molarity of } H_2SO_4}$$

$$= \frac{0.15}{4.0} = 0.375\ \text{L}$$

$$= 0.0375 \times 1000 = 37.5\ \text{mL.}$$

So, the correct answer is (*a*).

EXAMPLE 84. *Considering the reaction, Zn + $H_2SO_4 \longrightarrow ZnSO_4 + H_2$ as quantitative, the volume of 2.0 M H_2SO_4 required to react with 13.0 g of zinc is :*

(*a*) *50 mL* (*b*) *25 mL*

(*c*) *30 mL* (*d*) *100 mL*

(*At. wt. Zn = 65*)

SOLUTION.

$$\underset{\substack{1\ \text{mol} \\ 65\ \text{g}}}{Zn} + \underset{1\ \text{mol}}{H_2SO_4} \longrightarrow ZnSO_4 + H_2 \quad ...(1)$$

$$\text{no. of mol of Zn} = \frac{\text{wt. of Zn}}{\text{g. at. wt. of Zn}} = \frac{13}{65} = 0.2\ \text{mol}$$

From reaction (1), it is clear that :

1 mol of Zn require

$$H_2SO_4 = 1\ \text{mol}$$

$\therefore$ 0.2 mol of Zn require

$$H_2SO_4 = 0.2\ \text{mol.}$$

$\therefore$ Volume of H_2SO_4 in litre

$$= \frac{\text{no. of mol of } H_2SO_4}{\text{molarity of } H_2SO_4}$$

$$= \frac{0.2}{2} = 0.1\ \text{L}$$

$$= 0.1 \times 1000\ \text{mL} = 100\ \text{mL}$$

So, the correct answer is (*d*).

EXAMPLE 85. *The final concentration of HCl if 0.15 mol HCl is added to a beaker containing 1.6 L of 1.75 M HCl and enough water to give a final volume of 3.5 L, is :*

(*a*) *0.84 M* (*b*) *0.42 M*

(*c*) *0.21 M* (*d*) *0.2 M*

SOLUTION. (*a*) Original concentration of HCl = 0.15mol.

(*b*) no. of mol of HCl

$$= \text{Molarity} \times \text{Volume in litre}$$

$$= 1.75 \times 1.6 = 2.8\ \text{mol}$$

$\therefore$ Total number of mol of HCl

$$= 0.15 + 2.8 = 2.95$$

$$\therefore \text{Molarity of HCl} = \frac{\text{no. of mol}}{\text{Volume in litre}}$$

$$= \frac{2.95}{3.5} = 0.84\ \text{M.}$$

So, the correct answer is (*a*).

EXAMPLE 86. *The weight of* Na_2CO_3 *that is required to prepare 250 cm³ of a solution containing 5.0 mg of* CO_3^{2-} *per cm³ is :*

(*a*) *8.84 g* (*b*) *4.42 g*

(*c*) *6.66 g* (*d*) *2.2 g*

(*At. wt., Na = 23, C = 12, O = 16*)

SOLUTION.

$$1\ \text{cm}^3\ CO_3^{2-} \text{ weighs} = 5.0\ \text{mg}$$

$$\therefore \quad 250\ \text{cm}^3 \text{ of } CO_3^{2-} \text{ weigh} = 5 \times 250\ \text{mg}$$

$$= \frac{5 \times 250}{1000}\ \text{g} = 1.25\ \text{g}$$

$$\text{g. mol. wt. of } CO_3^{2-} = 12 + 3(16) = 60\ \text{g.}$$

$$\therefore \quad \text{no. of mol of } CO_3^{2-} = \frac{1.25}{60}\ \text{mol}$$

$$\underset{\substack{2(23) + 12 + 3(16) \\ = 106\ \text{g}}}{Na_2CO_3} \longrightarrow 2Na^+ + \underset{1\ \text{mol}}{CO_3^{2-}}$$

$$1\ \text{mol } CO_3^{2-} \text{ is from } Na_2CO_3 = 106\ \text{g}$$

$$\frac{1.25}{60}\ \text{mol } CO_3^{2-} \text{ is from } Na_2CO_3 = \frac{106}{1} \times \frac{1.25}{60} = 2.2\ \text{g}$$

So, the correct answer is (*d*).

EXAMPLE 87. *The molarity of the original H_3PO_4 solution if 18.0 mL of H_3PO_4 solution is required to completely neutralise 35.0 mL of 0.045 M $Ba(OH)_2$ is :*

(*a*) *5.8 M* (*b*) *0.058 M*

(*c*) *1.58 M* (*d*) *2 M*

SOLUTION.

$$\underset{\substack{3\ \text{mol} \\ 3\ \text{m. mol}}}{3Ba(OH)_2} + \underset{\substack{2\ \text{mol} \\ 2\ \text{m. mol}}}{2H_3PO_4} \longrightarrow Ba_3(PO_4)_2 + 6H_2O \quad ...(1)$$

$$\frac{M_1V_1\ (H_3PO_4)}{M_2V_2 \text{ of } Ba\ (OH)_2} = \frac{\text{no. of mol of } H_3PO_4}{\text{no. of mol of } Ba(OH)_2}$$

$$\frac{M_1 \times 18}{0.045 \times 35} = \frac{2}{3}$$

$$\therefore \quad M_1 = \frac{2 \times 0.045 \times 35}{18 \times 3} = 0.058\ \text{M}$$

So, the correct answer is (*b*).

Example 88. *The molar concentration of MnO_4^- ions in a solution containing 18.75 g $Ba(MnO_4)_2$ per 500 mL of the given solution is :*

(*a*) *0.1 M* (*b*) *0.2 M*
(*c*) *0.3 M* (*d*) *0.4 M*

(*At. wt., Ba = 137, Mn = 55, O = 16*)

Solution. $Ba(MnO_4)_2 \rightleftharpoons Ba^{2+} + 2MnO_4^-$ ...(1)

$137 + 2[55 + (4 \times 16)]$ 2 mol

$= 375$ g **Or** 1 mol

(*a*) 500 mL solution contains

$Ba(MnO_4)_2 = 18.75$ g

$\therefore$ 1000 mL (= 1 L) solution contains

$$Ba(MnO_4)_2 = \frac{18.75}{500} \times 1000 = 37.5\ \text{g}$$

$\therefore$ no. of mol of $Ba(MnO_4)_2$

$$= \frac{37.5}{375} = 0.1\ \text{mol L}^-$$

(*b*) 1 mol $Ba(MnO_4)_2$ contains

MnO^-_4 ions = 2 mol

0.1 mol $Ba(MnO_4)_2$ contains

$$MnO^-_4 \text{ ions} = \frac{2}{1} \times 0.1 = 0.2\ \text{M}.$$

So, the correct answer is (*b*).

Example 89. *The weight of* $AgNO_3$ *required to prepare 250 mL of a solution containing 50 mg of* $AgNO_3$ *per mL will be :*

(*a*) *1.5 g* (*b*) *11.5 g*
(*c*) *12.5 g* (*d*) *25 g*

Solution. 1 mL solution contains

$AgNO_3 = 50$ mg

250 mL solution contain

$$AgNO_3 = 50 \times 250\ \text{mg} = \frac{50 \times 250}{1000}\ \text{g} = 12.5\ \text{g}$$

So, the correct answer is (*c*).

Example 90. *How many g of concentrated nitric acid, containing 37.9% HNO_3 by weight, will contain, 6.0 g HNO_3 ?*

(*a*) *6.6 g* (*b*) *13.2 g*
(*c*) *19.8 g* (*d*) *15.83 g*

Solution. 37.9 g HNO_3 is present in solution

= 100 g

$\therefore$ 6.0 g HNO_3 is present in solution

$$= \frac{100}{37.9} \times 6 = 15.83\ \text{g}$$

So, the correct answer is (*d*).

Example 91. *The mass of anhydrous HCl in 8.0 mL concentrated HCl [density, 1.19 g (mL)$^-$] containing 37.9% HCl by weight will be :*

(*a*) *3.6 g* (*b*) *7.2 g*
(*c*) *2.7 g* (*d*) *36 g*

Solution. Density = 1.19 g (mL$^-$). Thus :

1 mL HCl weighs = 1.19 g

$\therefore$ 8 mL HCl weigh = 1.19 × 8 = 9.52 g

Solution contain HCl by weight

$$= 37.9\% = \frac{37.9}{100} = 0.379$$

$\therefore$ Mass of anhydrous HCl in 9.52 g conc.

HCl = 9.52 × 0.379

= 3.6 g.

So, the correct answer is (*a*).

Example 92. *The volume of conc. H_2SO_4 [density, 1.84 g (mL)$^-$] containing 98% H_2SO_4 by weight, that would contain 25 g pure H_2SO_4 will be :*

(*a*) *1.29 mL* (*b*) *1.39 mL*
(c) *13.9 mL* (*d*) *9.15 mL*

Solution. Density = 1.84 g (mL)$^-$. Thus :

1 mL solution has mass = 1.84 g.

$$\text{This solution contains pure. } H_2SO_4 = \frac{98}{100} \times 1.84 = 1.8\ \text{g}$$

Hence, 25 g pure H_2SO_4 is contained in solution

$$= \frac{25}{1.8} \times 1\ \text{mL solution} = 13.9\ \text{mL solution.}$$

So, the correct answer is (*c*).

Example 93. *The extent to which a solution of concentration 30 mg NaCl per mL be diluted to yield one mL of concentration of 12 mg NaCl per mL is :*

(*a*) *5 mL* (*b*) *0.5 mL*
(*c*) *0.4 mL* (*d*) *2.5 mL*

Solution. Let V_2 = volume to which 1 mL of original solution should be diluted. We know that amount of solute does not change with dilution. Also :

Concentration, C_1 × Volume, V_1 = Concentration, C_2 × Volume, V_2

$$\therefore \quad 30\ \text{mg (mL)}^- \times 1\ \text{mL} = 12\ \text{mg (mL)}^- \times V_2$$

$$\therefore \quad V_2 = \frac{30}{12} = 2.5\ \text{mL}$$

Hence each mL of the original solution should be diluted to 2.5 mL. So, the correct answer is (*d*).

Example 94. *The volume of conc. H_2SO_4 (density, 1.84 g/cm^3) containing 98% H_2SO_4 by weight that should be diluted with water to prepare 50 cm^3 acid of 25% strength (density = 1.14 g/cm^3) is :*

(*a*) *7.9 cm^3* (*b*) *9.7 cm^3*
(*c*) *25 cm^3* (*d*) *3.95 cm^3*

Solution. Mass of H_2SO_4 per cm^3 of 98% acid

$$= \frac{98}{100} \times 1.84\ \text{g/cm}^3 = 1.8\ \text{g/cm}^3$$

Mass of H_2SO_4 per cm^3 of 25% acid

$$= \frac{25}{100} \times 1.14 \text{ g/cm}^3$$

$$= 0.285 \text{ g/cm}^3.$$

We know that :

Concentration, C_1 × Volume, V_1

$= $ Concentration, C_2 × Volume, V_2

or $1.8 \text{ g/cm}^3 \times V_1 = 0.285 \text{ g.cm}^{-3} \times 50 \text{ cm}^3$

$$\therefore \qquad V_1 = \frac{0.285}{1.8} \times 50 \text{ cm}^3$$

$= 7.9 \text{ cm}^3$ of concentrated acid.

So, the correct answer is (*a*).

Example 95. *The volume of dil. HCl (density 1.11 g/mL) and 18% HCl by weight and containing 8.0 g HCl, will be :*

(*a*) *30 mL* (*b*) *1.29 mL*

(*c*) *40 mL* (*d*) *30.3 mL*

Solution. Mass of

HCl = 8.0 g ; density = 1.11 g/mL.

$$\text{But} \qquad \text{Volume} = \frac{\text{Mass}}{\text{density}} = \frac{8}{1.11} \text{ mL.}$$

$$\therefore \text{Volume of 18\% HCl} = \frac{8}{1.11} \times \frac{100}{18} = 40.0 \text{ mL.}$$

So, the correct answer is (*c*).

Type. To find mass of a solution when its density and % age by weight is given.

Example 96. *An ammonia solution (density 0.928 g/mL) containing 19% ammonia by weight was obtained when* $NH_3(g)$ *was passed through water. The mass of ammonia per cm*^{3} *will be:*

(*a*) *4.88 g* (*b*) *0.18 g*

(*c*) *0.09 g* (*d*) *2.44 g*

$$\textbf{Solution. } \text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{or} \qquad \text{Mass} = \text{density} \times \text{Volume}$$

$$= \frac{0.928 \text{ g}}{\text{mL}} \times 1 \text{ mL}$$

or Mass = 0.928 g.

NH_3 solution = 19% NH_3 by weight. Thus :

100 g solution contain ammonia

= 19 g

0.928 g solution contain ammonia

$$= \frac{19}{100} \times 0.928 = 0.18 \text{ g/mL.}$$

So, the correct answer is (*b*).

Example 97. *You are provided with 90 cm*^{3} *of pure water at 4°C. The volume of a solution of* HNO_3 *(density, 1.11 g/cm*^{3}*) and containing 19%* HNO_3 *by weight that could be prepared is:*

(*a*) *10 cm*^{3} (*b*) *100 cm*^{3}

(*c*) *50 cm*^{3} (*d*) *111 cm*^{3}

Solution. 19% HNO_3 by weight means :

Wt. of HNO_3 solution = 100 g ;

wt. of HNO_3 = 19 g ;

wt. of H_2O = 100 – 19 = 81 g.

Density of water at 4°C = 1 g/cm^3.

∴ Wt. of 90 cm^3 water = 90 × 1 = 90 g

(*a*) 81 g water is present in solution = 100 g

$$\text{90 g water solution is present in solution} = \frac{100}{81} \times 90$$

$$= 111 \text{ g.}$$

Density of solution = 1.11 g cm^3.

Thus 1.11 g solution is present in volume = 1 cm^3

$$\text{111 g solution is present in volume} = \frac{1}{1.11} \times 111$$

$$= 100 \text{ cm}^3.$$

So, the correct answer is (*b*).

Type. To find density of a solution when its density and % age by volume is given.

Example 98. *The butter–fat present in one litre milk (weight = 1.032 kg) is 4% by volume. If the density of this fat is 865 kg/m*^{3}*, the density of fat-free skimmed milk will be :*

(*a*) *2494 kg m*$^{-3}$ (*b*) *1038.9 kg m*$^{-3}$

(*c*) *1.249 g m*$^{-3}$ (*d*) *2076.8 kg m*$^{-3}$

$$\textbf{Solution. } \text{Density} = \frac{\text{Mass}}{\text{Volume}} ;$$

Mass = density × Volume

$$= 865 \text{ kg m}^{-3} \times \frac{4}{100} \text{ m}^3 = 34.6 \text{ kg}$$

Or Mass of butter fat = 34.6 kg.

∴ Mass of skimmed milk

$$= \frac{1.032 \text{ kg}}{\text{litre}} \times 10^3 \text{ L} - (34.6 \text{ kg})$$

$= 997.4$ kg.

$$\text{Volume} = \frac{100 - 4}{100} = 0.96 \text{ m}^3.$$

∴ Density of fat-free skimmed milk

$$= \frac{\text{Mass}}{\text{Volume}} = \frac{997.4 \text{ kg}}{0.96 \text{ m}^3}$$

$= 1038.9 \text{ kg m}^{-3}$

So, the correct answer is (*b*).

Example 99. *The weight of* NaCl *required to make 50.0 mL of an aqueous solution containing 60.0 mg Na*$^+$ *per mL will be*

(*a*) *76 g* (*b*) *0.076 g*

(*c*) *7.6 g* (*d*) none of these

(*at. wt., Na = 23, Cl = 35.5*)

$$\textbf{Solution.} \quad \begin{array}{lcl} NaCl & \rightleftharpoons & Na^+ + Cl^- \\ 23 + 35.5 & & 23 \text{ g} \\ = 58.5 \text{ g} & & \end{array} \qquad ...(1)$$

$$\text{1 mL solution contains } Na^+ = 60 \text{ mg} = \frac{60}{1000} \text{ g}$$

$$\text{50 mL solution contain } Na^+ = \frac{60}{1000} \times 50 = 3 \text{ g}$$

From equation (*1*):

23 g Na^+ are available from NaCl = 58.5 g

$$\therefore 3 \text{ g } Na^+ \text{ are available from NaCl} = \frac{58.5}{23} \times 3 = 7.6 \text{ g.}$$

So, the correct answer is (*c*).

EXAMPLE 100. *The volume of 90% ethanol by weight (density 0.799 g/cm³) that is used to prepare 175 cm³ of 35% ethanol by weight (density = 0.91 g/cm³) will be :*

(*a*) *62.74 cm³*	(*b*) *31.37 cm³*
(*c*) *77.5 cm³*	(*d*) *38.75 cm³*

SOLUTION. (*a*) Volume = 175 cm³ ; density = 0.91 g/cm³; ethanol = 35% *i.e.,* 35 g ethanol in 100 g solution.

$$\therefore \text{Mass of 35\% ethanol} = \text{density} \times \text{volume} \times \frac{35}{100}$$

$$= \frac{0.91 \text{g}}{\text{cm}^3} \times 175 \text{ cm}^3 \times \frac{35 \text{ g}}{100 \text{ g}}$$

$$= 55.7 \text{ g}$$

(*b*) $$\text{Mass of ethanol} = \text{density} \times \text{volume} \times \frac{90}{100}$$

or $$\text{Volume} = \frac{\text{Mass of ethanol} \times 100}{90 \times \text{density}}$$

$$= \frac{55.7 \text{ g} \times 100 \times \text{cm}^3}{90 \times 0.799 \text{ g}}$$

$$= 77.5 \text{ cm}^3$$

So, the correct answer is (*c*).

EXAMPLE 101. *The weight of $BaCl_2$. $2H_2O$ and water that must be weighed to make 50.0 g of a solution that is 7% $BaCl_2$ is :*

(*a*) *45.9g ; 4.1 g* H_2O	(*b*) *4.1 g ; 45.9 g* H_2O
(*c*) *5.7 g ; 44.3 g* H_2O	(*d*) *44.3 g ; 5.7 g* H_2O

(*At. wt., Ba = 137, Cl = 35.5, H = 1, O = 16*)

SOLUTION. g. mol. wt. of

$$BaCl_2.2H_2O = 137 + (2 \times 35.5) + 2\,[(2 \times 1) + 16]$$

$$= 244 \text{ g.}$$

7% $BaCl_2$ solution means, 7 g $BaCl_2$ in 100 g solution.

$$\begin{array}{lcl} BaCl_2.\,2H_2O & \longrightarrow & BaCl_2 \quad + \quad 2H_2O \\ 244 \text{ g} & & 137 + (2 \times 35.5) \\ & & = 208 \text{ g} \\ 1 \text{ mol} & & 1 \text{ mol} \end{array}$$

(*a*) 100 g solution contain $BaCl_2$ = 7 g

$$\text{50 g of solution contain } BaCl_2 = \frac{7}{100} \times 50$$

$$= 3.5 \text{ g}$$

(*b*) 208 g $BaCl_2$ is present in $BaCl_2$. $2H_2O$ = 244 g

$$3.5 \text{ g } BaCl_2 \text{ is present in } BaCl_2.\,2H_2O = \frac{244}{208} \times 3.5$$

$$= 4.1 \text{ g}$$

$\therefore$ Wt. of $BaCl_2$. $2H_2O$ = 4.1 g

$\therefore$ Wt. of water = 50 – 4.1

= 45.9 g.

So, the correct answer is (*b*).

Type. Volume (V_1) × concentration (C_1) = Volume (V_2) × concentration (C_2)

EXAMPLE 102. *The volume in mL of a solution of concentration 75 mg* Mn^{2+} *per mL needed to prepare 0.75 L of solution of concentration 15 mg* Mn^{2+} *per mL will be :*

(*a*) *3750 mL*	(*b*) *37.50 mL*
(*c*) *250 mL*	(*d*) *150 mL*

SOLUTION. V_1 = ?, C_1 = 75 mg (mL^-) ;

V_2 = 0.75 L = 0.75 × 1000 = 750 ml ;

C_2 = 15 mg $(\text{mL})^-$.

We know : $$C_1V_1 = C_2V_2 \; ; \; V_1 = \frac{C_2V_2}{C_1} \; ;$$

$$V_1 = \frac{15 \text{ mg (mL)}^- \times 750 \text{ mL}}{75 \text{ mg (mL)}^-}$$

or V_1 = 150 mL.

So, the correct answer is (*d*).

EXAMPLE 103. *The extent to which a solution containing 60 mg* KCl *per mL be diluted to give a solution of concentration 10 mg* KCl *per mL will be :*

(*a*) *4 times*	(*b*) *5 times*
(*c*) *6 times*	(*d*) *600 times*

SOLUTION. V_1 = 1 mL, C_1 = 60 mg $(\text{mL})^-$;

V_2 = ?, C_2 = 10 mg $(\text{mL})^-$. We know :

$$C_1V_1 = C_2V_2 \; ; \; V_2 = \frac{C_1V_1}{C_2}$$

$$= \frac{60 \text{ mg (mL)}^- \times 1 \text{ mL}}{10 \text{ mg (mL)}^-}$$

or V_2 = 6. So, the correct answer is (*c*).

EXAMPLE 104. *The volume of 0.25 M H_2SO_4 required to produce 51.0 g H_2S by the reaction, $8KI + 5H_2SO_4 \longrightarrow 4K_2SO_4 + H_2S + 4I_2 + 4H_2O$, is :*

(*a*) *25 L*	(*b*) *30 L*
(*c*) *0.57 L*	(*d*) *7.5 L*

(*At. wt., H = 1, S = 32*)

SOLUTION. Reaction.

$$\begin{array}{ccccc} 8KI + 5H_2SO_4 & \longrightarrow & 4K_2SO_4 + & H_2S & + 4I_2 + 4H_2O \\ \text{5 mol} & & & (2 \times 1) + 32 & \\ & & & = 34 \text{ g} & \end{array}$$

34 g H_2S is formed from

$$H_2SO_4 = 5 \text{ mol}$$

51 g H_2S is formed from

$$H_2SO_4 = \frac{5}{34} \times 51 = 7.5 \text{ mol}$$

But number of mol of

$$H_2SO_4 = \text{Molarity} \times \text{Volume in litre}$$

$$\therefore \quad 7.5 \text{ mol} = 0.25 \text{ mol L}^- \times \text{volume in litre}$$

$$\text{or Volume in litre} = \frac{7.5 \text{ mol}}{0.25 \text{ mol L}^-} = \mathbf{30.0\ L}$$

So, the correct answer is (*b*).

EXAMPLE 105. *The amount of Th^{4+} that requires 40.0 mL of 0.045 M $H_2C_2O_4$ to precipitate it as $Th(C_2O_4)_2$ is :*

(*a*) *1.8 mg* (*b*) *17.2 mg*
(*c*) *10.45 mg* (*d*) *209 mg.*

(*At. wt., Th = 232*)

SOLUTION. Reaction.

$$\underset{\substack{1\text{ m. mol}\\232\text{ mg}}}{Th^{4+}} + \underset{2\text{ m. mol}}{2C_2O_4^{2-}} \longrightarrow Th(C_2O_4)_2;\ [H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}]$$

Number of m. mol of

$$H_2C_2O_4 = \text{Molarity} \times \text{Volume in mL}$$
$$= 0.045 \times 40 = 1.8 \text{ m. mol.}$$

From equation, we have :

$\therefore$ 2 m. mol of $H_2C_2O_4$ react with Th^{4+}

$$= 232 \text{ mg}$$

$\therefore$ 1.8 m. mol of $H_2C_2O_4$ react with Th^{4+}

$$= \frac{232}{2} \times 1.8 = 209 \text{ mg.}$$

So, the correct answer is (*d*).

EXAMPLE 106. *The mass of $(NH_4)_2CO_3$ that contain 0.5 mol of NH_4^+ is :*

(*a*) *48 g* (*b*) *24 g*
(*c*) *12 g* (*d*) *None of these.*

(*At. wt., N = 14, H = 1, C = 12, O = 16*)

SOLUTION. g. formula weight of $(NH_4)_2CO_3$ = 2 [14 + (4 × 1)] + 12 + (3 × 16) = 96 g

$$\underset{\substack{1\text{ mol}\\96\text{ g}}}{(NH_4)_2CO_3} \rightleftharpoons \underset{2\text{ mol}}{2NH_4^+} + CO_3^{2-}$$

2 mol NH_4^+ are available from

$$(NH_4)_2CO_3 = 96 \text{ g}$$

0.5 mol NH_4^+ are available from

$$(NH_4)_2CO_3 = \frac{96}{2} \times 0.5 = \mathbf{24\ g}$$

So, the correct answer is (*b*).

EXAMPLE 107. *A mixture of $CaCl_2$ and NaCl weighting 4.44g is treated with sodium carbonate solution to precipitate all the calcium ions as calcium carbonate. The calcium carbonate so obtained is heated strongly to get 0.56g of CaO. The percentage of NaCl in the mixture is: (atomic mass of Ca = 40]*

(*a*) *31.5* (*b*) *75*
(*c*) *25* (*d*) *40.2*

Karnataka CET, 2011

SOLUTION. Wt. of CaO = 0.56g. Reaction is:

$$\underbrace{\underset{x}{CaCl_2} + \underset{y}{NaCl}}_{= 4.44\text{ g}} \xrightarrow{Na_2CO_3} CaCO_3 \xrightarrow{\text{Heat}} \underset{0.56\text{g}}{CaO} + CO_2\uparrow$$

Since moles of Ca in $CaCl_2$ = moles of Ca in $CaCO_3$

Also moles of Ca in $CaCO_3$ = moles of Ca in CaO

$$\therefore \quad \frac{x}{111} = \frac{0.56}{56}$$

[$\therefore$ Mol. wt. of $CaCl_2$ = 40 + (2 × 35.5) = 111 g mol^{-}; mol. wt. of CaO = 40 + 16 = 56g mol^{-}]

$$\therefore \quad x = \frac{111 \times 0.56}{56} = 1.11\text{g}$$

Given wt. of NaCl + wt. of $CaCl_2$ = 4.44g

$\therefore$ $y + 1.11 = 4.44; y = 4.44 - 1.11 = 3.33$g. Hence

%age of NaCl = 3.33 × 100/4.44

= 75%. So, the correct answer is (*b*)

EXAMPLE 108. *100 g $CaCO_3$ is treated with 1 litre of 1NHCl. What would be the weight of CO_2 liberated after the completion of the reaction.*

(*a*) *5.5 g* (*b*) *11 g*
(*c*) *22 g* (*d*) *33 g*
(*e*) *44 g*

(Kerala PET, 2005)

SOLUTION. Reaction.

$$\underset{\substack{40+12+(3\times16)\\=100\text{ g}}}{CaCO_3} + \underset{2\text{ N}}{2HCl} \longrightarrow CaCl_2 + \underset{\substack{12+(2\times16)\\=44\text{ g}}}{CO_2} + H_2O$$

100 g $CaCO_3$ with 2 N HCl gives CO_2 = 44 g

100 g $CaCO_3$ with 1 N HCl gives CO_2 = $44 \times \frac{1}{2}$ = 22 g.

So, the correct answer is (*c*).

EXAMPLE 109. *The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by Hall process is :*

(*a*) *270 kg* (*b*) *540 kg*
(*c*) *90 kg* (*d*) *180 kg*

(*at. mass, Al = 27*) **[CBSE - PMT (Prelims), 2005]**

SOLUTION. Reaction.

$$\underset{3\times12=36\text{ g}}{3C} + \underset{\text{(from bauxite)}}{2Al_2O_3} \longrightarrow \underset{4\times27=108\text{ g}}{4Al} + 3CO_2$$

Al required = 270 kg = 270 × 1000 = 270,000 g.

108 g Al is available by using carbon

= 36 g

270,000 g Al is available from using carbon

$$= \frac{36}{108} \times 270{,}000 = 90{,}000 \text{ g}$$
$$= \frac{90{,}000}{1000} = 90 \text{ kg.}$$

So, the correct answer is (*c*).

EXAMPLE 110. *How many grams of CaO are required to neutralise 852 gm of P_4O_{10} (at. wt., P = 31, O = 16, Ca = 40).*

[IIT, – JEE (mains), 2005]

SOLUTION. Reaction.

$$\underset{\substack{6\,(40+16)\\=336\text{ g}}}{6CaO} + \underset{\substack{(4\times31)+(10\times16)\\=284\text{ g}}}{P_4O_{10}} \longrightarrow 2Ca_3(PO_4)_2$$

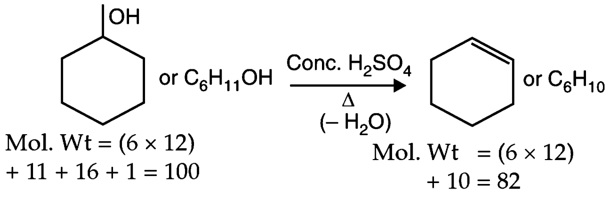
284 g P_4O_{10} neutralise CaO $= 336$ g

852 g P_4O_{10} neutralise CaO $= \frac{336}{284}\times 852$ **=1008g Ans.**

EXAMPLE 111. *Cyclohexanol is dehydrated to cyclohexene on heating with conc. H_2SO_4. If the yield of the reaction is 60%, the amount of cyclohexene obtained from 80 g of cyclohexanol will be:*

(*a*) *0.4 g* (*b*) *3.936 g*
(*c*) *393.6 g* (*d*) *39.36 g*

SOLUTION.



100 g $C_6H_{11}OH$ form $C_6H_{10} = 82$ g

80 g $C_6H_{11}OH$ form $C_6H_{10} = \frac{82}{100}\times 80 = 65.6$ g

$\therefore$ Exact yield of $C_6H_{10} = 65.6\times\frac{60}{100} = 39.36$ g

So, the correct answer is (*d*).

EXAMPLE 112. *The volume in litre of CO_2 produced at NTP when 8.4 g of 80% pure sodium bicarbonate is heated completely is :*

(*a*) *1.792 L* (*b*) *0.896 L*
(*c*) *0.448 L* (*d*) *0.224 L*

SOLUTION. 100 g $NaHCO_3$ contain pure $NaHCO_3 = 80$ g

$\therefore$ 8.4 g $NaHCO_3$ contain pure

$$NaHCO_3 = \frac{80}{100}\times 8.4 = 6.72 \text{ g}$$

$$\underset{\substack{2\,[23+1+12+(3\times 16)]\\ =168\text{ g}}}{2NaHCO_3} \longrightarrow Na_2CO_3 + \underset{22.4\text{ L}}{CO_2} + H_2O$$

168 g $NaHCO_3$ produce $CO_2 = 22.4$ L

6.72 g $NaHCO_3$ produce $CO_2 = \frac{22.4\text{ L}}{168\text{ g}}\times 6.72\text{ g}$

$= 0.896$ L

So, the correct answer is (*b*).

EXAMPLE 113. *10 g of hydrogen and 64g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be:*

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

(CBSE-PMT, 2009)

SOLUTION. Reaction:

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

g. mol. wt.	2g	16 g	2 + 16 = 18 g
	1 mol	0.5 mol	1 mol

Thus: 2g H_2 = 1 mol, so 10g $H_2 = 1/2 \times 10 = 5$ mol
16 g O_2 = 0.5 ml, so 64 g $O_2 = (0.5/16)\times 64 = 2$ mol

We see that in this reaction, oxygen is the limiting reagent because 2 mol value is less than 5 mol value. So, the amount of water produced will depend on oxygen. Hence:

0.5 mol O_2 gives H_2O = 1 mol

2 mol O_2 gives H_2O = $(1/0.5)\times 2 = 4$ mol.

So, the correct answer is (*b*)

EXAMPLE 114. *20.0 kg of $N_2(g)$ and 3.0 kg of $H_2(g)$, are mixed to produce $NH_3(g)$. The amount of NH_3 (g) formed is:*

(*a*) *17 kg* (*b*) *34 kg*
(*c*) *20 kg* (*d*) *3 kg*
(*e*) *23 kg*

(Kerala PMT, 2011)

SOLUTION. Mol. wt. of $N_2 = 2\times 14 = 28$ g mol⁻; mol. wt. of $H_2 = 2\times 1 = 2$g mol⁻; mol. wt. of $NH_3 = 14 + (3\times 1) = 17$ g mol⁻. The given equation is:

$$N_2 + 3H_2 \longrightarrow 2NH_3 \quad ...(1)$$

	28 kg	3 × 2 = 6 kg	2 × 17 = 34 kg
or	14 kg	3 kg	17 kg

Since the data shown in equation (1) pertains to 3.0 kg of H_2 and in the question also, 3.0 kg of H_2 reacts to form NH_3, so H_2 is a limiting reactant. So, amount of NH_3 formed will be 17 kg. Hence, the correct answer is (*a*)

PROBLEMS FOR PRACTICE

1. If 1.5 moles of oxygen combine with Al to form Al_2O_3, the mass of Al in g [Atomic mass of Al = 27] used in the reaction is
(*a*) 2.7 (*b*) 54
(*c*) 40.5 (*d*) 81
(*e*) 27 **Ans.** (*b*)
(Kerala PMT 2010)

2. One kilogram of a sea water sample contains 6 mg of dissolved O_2. The concentration of O_2 in the sample in ppm is
(*a*) 0.6 (*b*) 6.0
(*c*) 60.0 (*d*) 16.0
(*e*) 32.0 **Ans.** 6ppm
(Kerala PMT 2010)

3. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of Na^+ and CO_3^{2-}ions are respectively (molar mass of Na_2CO_3 = 106 g mol^{-1})

(*a*) 0.477 M and 0.477 M
(*b*) 0.955 M and 1.910 M
(*c*) 1.910 M and 0.955 M
(*d*) 1.90 M and 1.910 M **Ans.** (*b*)

(C.B.S.E PMT 2010)

4. Calculate the amount of silver chloride formed by mixing 5.0 g of NaCl with solution containing 20 g of silver nitrate.

Ans. 12.26 g

5. Calculate the volume of CO_2 gas formed from the action of 8.4 g $NaHCO_3$ on excess of HCl.

Ans. 2240 mL

6. Write the limiting reactant in the reaction between 3.31 g Pb $(NO_3)_2$ and solution of one gram NaCl

Ans. NaCl

7. The volume of 0.4M H_2SO_4 required to neutralise 20 mL of 0.2 N $Ca(OH)_2$ is :

(*a*) 3 mL (*b*) 4 mL
(*c*) 5 mL (*d*) 6 mL

Ans. (*c*)

8. Considering the reaction $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$ quatitative, the volume of 0.4 M H_2SO_4 used to react with 2.4 g Mg is:

(*a*) 0.25 L (*b*) 1.5 L
(*c*) 2.0 L (*d*) none of these

Ans. (*a*)

9. Calculate the weight of sodium chloride formed in g when 100 g HCl is treated with 100 g Na_2CO_3. Also, find the weight of reagent left unreacted.
(At. wt., Na = 23, C = 12, O = 16, N = 14, H = 1).

[**Ans.** 110 g NaCl ; 31.1 g HCl in excess]

10. Calculate the weight of potassium chloride formed when 1.8 g of potassium is heated with 2.8 g of Cl_2. (At. wt., K = 39, Cl = 35.5). [**Ans.** wt. of KCl = 3.427 g]

11. The weight of $Al_2(SO_4)_3 . 18H_2O$ required to make up 50.0 mL of aqueous solution of concentration 30.0 mg Al^{3+} per mL will be :

(*a*) 18.5 g (*b*) 1.85 g
(*c*) 0.185 g (*d*) 0.0185 g

(at. wt., Al = 27, S = 32, O = 16, H = 1).

[Hint

$$Al_2(SO_4)_3 . 18H_2O \longrightarrow 2Al^{3+}$$

$(2 \times 27) + 3(32 + 64) + 18(2 \times 1 + 16)$ $\quad$ $2 \times 27 = 54$ g

$= 666$ g

$$\therefore \text{ Wt. of } Al_2(SO_4)_3 . 18H_2O = 50 \times \frac{30}{1000} \times \frac{666}{54} = 18.5 \text{ g.}$$

[**Ans.** (*a*)]

15

CHAPTER

Thermodynamics–Thermochemistry

15.1 THERMODYNAMICS

Broadly speaking, thermodynamics involves all kinds of energy changes (heat, work etc) accompanying a process.

15.2 THERMODYNAMIC PROCESS.

It is an operation with the help of which a change from one state to another state is brought about. The various opertions include :

1. **Isothermal process ($\Delta T = 0, \Delta E = 0$).** It is a process in which the temperature of the system remains constant. Constant temperature is attained by the use of **thermostatic bath.** *i.e.*, **"$\Delta T = 0$ and $\Delta E = 0$ or $\Delta U = 0$".**
2. **Adiabetic process ($q = 0$).** It is a process in which no exchange of heat takes place between the system and the surroundings. It is achieved by **"insulating the whole system".**
3. **Isochoric process ($\Delta V = 0$).** It is a process in which the volume of the system remains constant throughout the study of the system.
4. **Isobaric process ($\Delta P = 0$).** It is a process in which the pressure of the system remains constant throughout the study of the system.
5. **Cyclic process ($\Delta H = 0, \Delta E$ or $\Delta U = 0$).** It is a process in which the initial state of the system is reachieved after a number of operations.
6. **Reversible process.** It is a slow process which can be reversed when it is carried out in the opposite direction. The driving force is infinitesimally greater than the opposing force. *Maximum work is obtained in this process.*
7. **Irreversible process.** It is a unidirectional fast process in which the driving force is much different from opposing force. The *net work obtained is much less than the maximum work.* If work is carried out at constant pressure, *P*, it is irreversible work.

Heat. It is a '*measure of quantity of energy*' that gets transferred from one body to another one as a result of temperature difference between them.

Temperature. It is a '*measure of intensity of energy*'. It is concerned with the energy possessed by an individual particle.

15.3 Internal energy (U or E).

Sum total of all types of energies (translational, rotational, vibrational, potential, kinetic, coulombic etc) possessed by a substance under given conditions of *T*, *P* and *V* is called internal energy of the substance. Since energies like translational, rotational etc. cannot be accurately known, exact or absolute value of *U* cannot be determined. It is a **state function** and is **independent of path.** Hence, change in internal energy, ΔU of two states can be studied only where

$$\Delta U = U_2 - U_1$$

15.4 WORK (W)

Mathematically: Work = Intensity factor × Capacity factor

Where capacity factor represents '*extent for which work* is done and intensity factor represents, '*measure of force against which work is done,*

Thus : Mechanical work = $F \times d$

Other types of work are :

(*A*) **Electrical work** = Potential difference (E) × quantity of current (Q) = $\mathbf{E \times Q}$

(*B*) **Work of expansion** = Pressure × change in volume = $\mathbf{P \times \Delta V}$

Note. (*a*) $W = -$ *ive* if work is done **by** the system.
(*b*) $W = +$ *ive* if work is done **on** the system.

General expression of $P\Delta V$ work is :

$$W = -P\Delta V.$$

For expansion, $\Delta V = V_2 - V_1 = +$ ***ive*** because V_2 (final volume) > V_1 (initial volume)

$\therefore \quad W = -P(+\Delta V) = -P\Delta V = -$ ***ive***.

Hence work for expansion is – *ive i.e.,* work done by the system is negative.

For compression, $\Delta V = V_2 - V_1 = -$ *ive* because

V_2 (final volume) < V_1 (initial volume)

$$\therefore \qquad W = -P(-\Delta V) = +P\Delta V = +\ ive.$$

Hence work for compression is + *ive i.e.,* work done on the system is positive.

Units of work. (*i*) **Newton m** *i.e.,* ***N m*** or Joule (SI units)

(*ii*) **Dyne cm** or erg (C.G.S. units)

(*iii*) calorie where 1 calorie = 4.184 J = 4.184×10^7 erg.

(*C*) **Gravitational work** = mg. h *i.e.,* gravitational force (*mg*) × height (*h*).

15.5 ENTHALPY (H) OR HEAT CONTENT

The total heat content of a system is called enthalpy of the system. Like internal energy (*U*), it is a *state function* and is *independent of path.* Mathematically :

$$H = U + PV$$

Like *U*, we can study only change in enthalphy (ΔH) where :

$$\Delta H = H_2 - H_1$$

ΔH and ΔU are related as :

$$\boldsymbol{\Delta H = \Delta U + P\Delta V}$$

15.6 FIRST LAW OF THERMODYNAMICS

According to this law *'the sum total of mass and energy of an isolated system remains constant'*. Mathematically, for an **infinitesimal change :**

$$\boldsymbol{dq = dU - dW}$$

where dq = heat added to the system.

dU = change in internal energy.

$-dW$ = work done by the system.

For finite change : $q = \Delta U - W$ **or** $q = \Delta E - W$

or $\boldsymbol{\Delta U = q + W}$ **or** $\boldsymbol{\Delta E = q + W}$

15.7 APPLICATIONS OF FIRST LAW OF THERMODYNAMICS

We know that : $\Delta U = q + W$ (First law of thermodynamics) ...(1)

(*A*) **For an isothermal process,**

$\Delta T = 0$ and $\Delta U = 0$

$\therefore$ From (1), we have : $0 = q + W$ or $\boldsymbol{q = -W}$

i.e., heat added, q = work done by the system, $-W$.

(*B*) **For an adiabatic process,** $q = 0$

$\therefore$ From (1), we have : $\Delta U = 0 + W$ or $\Delta U = W$

or $-\Delta U = -W$

i.e., work done by the system ($-W$) is done at the cost of its internal energy ($-\Delta U$).

(*C*) **For an isochoric process,** $\Delta V = 0$

$\therefore$ From (1), we have : $\Delta U = q_v + P\Delta V$

$[\because W = P\Delta V]$

$\therefore$ $\Delta U = q_v + P \times 0$ or $\Delta U = q_v$.

It means that :

Internal energy ΔU increases when heat (q_v) is added at constant volume.

(*D*) **For a cyclic process,** $\Delta U = 0$

$\therefore$ From (1), we have : $0 = q + W$ or $\boldsymbol{q = -W}$

Isobaric process (ΔP = 0). Consider increase in volume of the system from V_1 to V_2 at constant pressure. Here work done (W) by the system is negative (*i.e.,* $-P\Delta V$)

$$\therefore \qquad W = -P\Delta V$$

$$\text{But} \qquad q_p = \Delta U - W;\ q_p = \Delta U - (-P\Delta V);$$

$$q_p = \Delta U + P\Delta V$$

$$\text{Also,} \qquad \Delta U = U_2 - U_1$$

$$\begin{aligned} \text{Hence,} \qquad q_p &= U_2 - U_1 + P(V_2 - V_1) \\ &= U_2 - U_1 + PV_2 - PV_1 \\ &= U_2 + PV_2 - U_1 - PV_1 \\ &= U_2 + PV_2 - (U_1 + PV_1) = H_2 - H_1 \end{aligned}$$

$$[\because H = U + PV]$$

$$\therefore \qquad \boldsymbol{q_p = \Delta H}$$

Hence heat absorbed (q_p) at constant pressure increases the enthalpy of the system.

For an insulated container, $\boldsymbol{q = 0}$

15.8 WORK DONE IN ISOTHERMAL REVERSIBLE PROCESS (ΔT = 0 AND ΔU = 0)

Total work done during expansion from volume V_1 to V_2 is :

$$\int dw = \int_{V_1}^{V_2} -PdV = \int_{V_1}^{V_2} -\frac{nRT}{V}dV \quad [\because PV = nRT]$$

$$W_{rev} = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\frac{V_2}{V_1}$$

$$= -2.303\,nRT\log\frac{V_2}{V_1}$$

$$\text{Also,} \qquad W_{rev} = -\ 2.303\,nRT\log\frac{P_1}{P_2}$$

$$\left[\because \boldsymbol{P_1V_1 = P_2V_2;\ \frac{P_1}{P_2} = \frac{V_2}{V_1}}\right]$$

15.9 WORK DONE IN ADIABETIC REVERSIBLE PROCESS (dq =0).

$$dU = dq + dW \quad \text{[First law of thermodynamics]}$$

$$\therefore \qquad dU = 0 + dW \quad \textbf{or} \quad dU = dW \ \therefore\ nC_v dT = dW$$

where C_v = heat capacity at constant volume

$$\textbf{or} \qquad dW = nC_v dT;\ dW = n\frac{R}{\gamma - 1}.dT$$

$$\left[\because C_p - C_v = R;\ \frac{C_p}{C_v} - \frac{C_v}{C_v} = \frac{R}{C_v};\ \gamma - 1 = \frac{R}{C_v};\ C_v = \frac{R}{\gamma - 1}\right]$$

$$\therefore \int dW = \frac{nR}{\gamma - 1}\int_{T_1}^{T_2} dT \quad [\gamma = \text{Poisson's ratio} = C_p/C_v]$$

$$\therefore \quad W_{rev} = \frac{nR}{\gamma - 1}(T_2 - T_1)$$

(*i*) If $T_2 > T_1$, $W_{rev} = +$ *ive i.e.,* work done on the system

(*ii*) If $T_2 < T_1$, $W_{rev} = -$ *ive i.e.,* work done by the system.

Some useful results of adiabetic expansion are :

(*a*) PV^{γ} = constant (*b*) $V^{\gamma-1}T$ = constant

(*c*) $P^{1-\gamma}T^{\gamma}$ = constant

15.10 SIGN CONVENSIONS

For *endothermic reactions* (*i.e.,* heat is absorbed), Δ*H is positive.* For exothermic reactions (*i.e.,* heat is evolved), Δ*H* is negative.

15.11 STANDARD STATES.

The *heat of formation of elements in their standard* states is zero. Conditions of standard states are given in the following table.

State	Standard state
Gas	Ideal gas at one atmospheric pressure and the given temperature
Liquid	Pure liquid at one atmospheric pressure and the given temperature
Solid	Stable crystalline state at one atmospheric pressure and the given temperature (*e.g.,* red form of phosphorus, diamond form of carbon etc.)

Standard states are represented by Δ*E*° or Δ*H*° at a given temperature.

15.12 DIFFERENT TYPES OF REACTIONS

(*a*) **Enthalpy of formation.** *It is the enthalpy change when one mole of a substance is formed from its constituent elements.* For exmple :

$$\underset{2\text{ mol}}{2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)}; \ \Delta H = -571.66 \text{ kJ}$$

or $H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = \dfrac{-571.66}{2}$

1 mol

$= -285.83$ kJ mol⁻

(*b*) **Enthalpy of combustion.** *It is the enthalpy change when one mole of a substance is burnt in oxygen.* For example, the enthalpy of combustion of one mole of methane (CH_4) is 890.36 kJ mol⁻.

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; ΔH $= -890.36$ kJ mol⁻

(*c*) **Enthalpy of transition.** *It is the enthalpy change when one mole of a substance is transformed from one allotropic form to another allotropic form.* For example:

C (graphite) $\longrightarrow$ C (diamond); ΔH = 1.9 kJ mol⁻ 1 mole

(*d*) **Enthalpy of hydration.** *It is the enthalpy change when one mole of a partially hydrated or anhydrous salt combines with a requisite number of moles of water to form a specific hydrate.* For example, the enthalpy of hydration of anhydrous copper sulphate is 18.69 k cal mol⁻.

$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s)$; ΔH $= -18.69$ k cal mol⁻.

(*e*) **Enthalpy of neutralisation.** *It is the enthalpy change when one equivalent of an acid is neutralised by a base in dilute solution.* Its value is constant. for example:

(*a*) For the neutralisation of any strong acid by a strong base, ΔH = – 13.7 k cal because in dilute solutions, these dissociate complelety into ions.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; ΔH $= -13.7$ k cal.

(*b*) For the neutralisation of weak acids and weak bases, the heat of neutralisations are different because these are not dissociated completely and during dissociation some heat is absorbed. Thus, the total heat evolved during neutralisation will be less than 13.7 k cal. For example :

$\underset{\text{Weak acid}}{HCN} + NaOH \longrightarrow NaCN + H_2O$; ΔH $= -2.9$ k cal.

Heat of neutralisation, ΔH = – 2.9 k. cal.

Heat of ionisation, ΔH = – 2.9 + 13.7 = 10.8 k cal.

15.13 LAW OF THERMOCHEMISTRY – HESS'S LAW OF CONSTANT HEAT SUMMATION.

Hess's law of constant heat summation. The enthalpy change during a chemical reaction will be the same whether the reaction takes place in one step or several steps.

Example 1. *In the following case,*

$$\begin{tikzcd} A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"'] & D \\ B \arrow[r, "\Delta H_2"] & C \arrow[u, "\Delta H_3"'] \end{tikzcd}$$

express Δ*H in terms of* ΔH_1, ΔH_2 *and* ΔH_3.

Solution. According to Hess's law :

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

15.14 ΔU = q + W (FIRST LAW OF THERMODYNAMICS)

W = + *ive* if work is done on the system

W = – *ive* if work is done by the system

q = + *ive* if heat is added to the system

q = – *ive* if heat is lost to the surrounding.

EXAMPLE 2. *What will be the internal energy change when 50 J heat is added to the system and 15 J work is done on the system ?*

SOLUTION. We know that :

$$\Delta U = q + W \text{ [First law of thermodynamics]}$$
$$W = +15\text{ J} \text{ [}\because \text{ work is done on the system]}$$
$$q = 50\text{ J.}$$

Substituting the values, we get :

$$\Delta U = 50 + 15 = \mathbf{65\ J}$$ **Ans.**

Type. When a gas expands in vacuum, $P_{ext} = 0$ and the process is irreversible.

Use $W = -P_{ext}(V_2 - V_1)$.

EXAMPLE 3. *How much work will be done when one mol of a gas is allowed to expand freely into vacuum?*

SOLUTION. For a gas which expands in vacuum,

P_{ext} = 0 and the process is irreversible

But, $W = -P_{ext}(V_2 - V_1)$.

So, $W = -0\,(V_2 - V_1) = 0$ **Ans.**

EXAMPLE 4. *Calculate the amount of work done when one mole of an ideal gas present in a vessel of 2 litre capacity at one atmospheric pressure is allowed to enter into an evacuated vessel of 10 litre capacity.* **(PSEB, 1995 S)**

SOLUTION. The expansion has taken place in an evacuated vessel.

Thus external pressure, $P = 0$.

But, work, $W = P \times \Delta V;\ W = 0 \times \Delta V$

$= 0$ *i.e.*, zero **Ans.**

Type. (*i*) Change in internal energy,

$$\Delta U = q + W$$

(*ii*) Work, $W = P \times \Delta V;\ W = P(V_2 - V_1)$

EXAMPLE 5. *A system absorbs 150 joules of heat and performs work equal to 80 joules. Calculate the change in the internal energy of the system.*

SOLUTION. Heat absorbed, $q = 150$ J

Work done by the system $= -W = -80$ J

But, $\Delta U = q + W$ (first law of thermodynamics)

$\therefore$ $\Delta U = 150 + (-80) = \mathbf{70\ J}$

Ans.

EXAMPLE 6. *A system having internal energy U_1 was supplied 120 joule energy. As a result, 65 joule of work was done on the system to change its state. Calculate (i) The energy of the system in the new state and (ii) Change in the internal energy of the system.*

SOLUTION. $q = +120\text{ J};\ W = +65\text{ J};\ U_1$ = internal energy

But, $\Delta U = q + W$ (first law of thermodynamics)

$= +120 + (+65) = +185$ J

Also, $\Delta U = U_2 - U_1$;

$\therefore$ $U_2 = \Delta U + U_1 = \mathbf{(185 + U_1)\ J}$ **Ans.**

EXAMPLE 7. *Calculate the time for which a 100 watt electric heater must operate to evaporate 50 g sample of benzene at its boiling point. Given, standard enthalpy of vaporisation of benzene equal to 30.8 kJ mol^{-} (Power = energy/time; 1 W = 1 J s^{-})*

SOLUTION. Mol. wt. of benzene, C_6H_6

$= (6 \times 12) + (6 \times 1) = 78\text{ g mol}^{-}$

(*i*) 78 g benzene require heat for vaporisation

$= 30.8$ kJ

50 g benzene require heat for vaporisation

$$= \frac{30.8}{78} \times 50 = 19.74\text{ kJ}$$

(*ii*) 100 watt heater gives energy

$= 100\text{ J s}^{-}$ $[\because 1\text{ W} = 1\text{ J s}^{-}]$

$\therefore$ Time required to get 19.74 kJ energy

$$= \frac{19.74\text{ kJ}}{100\text{ J s}^{-}} \times \frac{1000\text{ J}}{1\text{ kJ}}$$

$$= 197.4\text{ s} = 197.4\text{ s} \times \frac{1\text{ min.}}{60\text{s}}$$

$= \mathbf{3.29\ minutes}$ **Ans.**

Type. For gases which are allowed to expand against a constant external pressure, use the relations :

$$\boldsymbol{W = -P_{ext}(V_2 - V_1)}$$

$$\text{Litre atmosphere} = \frac{1.987 \times 4.184}{0.0821}\text{ J} = \frac{1.987}{0.0821}\text{ calorie}$$

$$= \frac{8.314}{0.0821}\text{ J}$$

EXAMPLE 8. *One mole of an ideal gas is expanded isothermally against a constant pressure of 3 atmosphere from 10 L to 35 L. Calculate the work done during change in energy and heat absorbed during the process.* *(.I.S.C., 2010)*

SOLUTION. Since work done by the system is negative, the work done, $W = -P\Delta V$ where $\Delta V = 35 - 10 = 25\ L$; P = 3 atmosphere. So:

$$W = -3\text{ atm.} \times 25\ L = -75\ L\text{ atm.}$$
$$= -75 \times 101.3\text{ J} = -7597.5\text{ J}$$

For isothermal process, $\Delta U = 0$ $[\because 1\ L\text{ atm.} = 101.3\text{ J}]$

According to first law of thermodynamics,

$$\Delta U = q + W$$

$\therefore$ $0 = q - 7597.5\text{ J}$ or $q = 7597.5$ J.

Since, q is positive, the reaction is **endothermic.**

EXAMPLE 9. *Calculate the work done by a system when one mol of a gas occupying 2 L volume is allowed to expand to 10 L volume against an external pressure of one atmosphere.*

SOLUTION. Since the gas is allowed to expand against the external pressure, the work done is negative and is irreversible.

$\therefore$ $W_{irr} = -P_{ext}(V_2 - V_1) = -1\text{ atm} \times (10 - 2)$

$\text{L} = -8\text{ L atm}$

$$= -8 \times \frac{1.987 \times 4.184}{0.0821}\text{ J} = \mathbf{-810.1\ J}$$ **Ans.**

Example 10. *At 3 atmospheric pressure and 273 K, 1.5 L of H_2 gas was allowed to expand isothermally at constant pressure of one atmosphere till pressure of the gas became one atmosphere. Calculate the work of expansion of H_2 gas.*

Solution. $P_1 = 3\text{ atm},\ V_1 = 1.5\text{ L},\ T = 273\text{ K}$

$P_2 = 1\text{ atm},\ V_2 = ?;$

At constant temperature, T

$$P_1V_1 = P_2V_2;\ 3 \times 1.5 = 1 \times V_2;\ V_2 = 4.5\text{ L}$$

External pressure being different from that of H_2 pressure, W is irreversible and negative.

So, $W = -P_{ext}(V_2 - V_1) = -1\,(4.5 - 1.5)$

$= -3\text{ L atm}$

$$= -3 \times \frac{1.987 \times 4.184}{0.0821}\text{ J} = \mathbf{303.78\ J}$$

Ans.

15.15 GRAVITATIONAL WORK = mgh

where mass, $m = \text{Volume} \times \text{density} = \pi r^2 l \times d$

and $g = 980\text{ cm s}^{-2}$

Example 11. *A simple electric device system raises a column of a liquid of radius 7.0 mm through 50 cm. Calculate the work done by the system (density of liquid is 1.1 g cm^{-3})*

Solution. Since work is done by the system, it is negative

i.e., $W = -\text{mgh};\ r = 5\text{ mm} = \frac{5}{10}\text{ cm}$

$= 0.5\text{ cm};$

$l = 50\text{ cm};\ d = 1.1\text{ g cm}^{-3}$

We know mass, $m = \text{Volume} \times \text{density}$

$= \pi r^2 l \times d$

$= \frac{22}{7} \times (0.5\text{ cm})^2 \times 50\text{ cm}$

$\times 1.1\text{ g cm}^{-3} = 43.2\text{ g}$

Since the centre of mass of column lies half-way along its length l, the centre of mass is raised to the height,

$$h = \frac{l}{2} = \frac{50}{2} = \mathbf{25\ cm.}$$

Also, $g = 980\text{ cm s}^{-2}$.

Hence, $W = -\text{mgh} = -43.2\text{ g} \times 980\text{ cm s}^{-2}$

$\times 25\text{ cm} = -1{,}058{,}400\text{ g cm}^2\text{ s}^{-2}$

$= -1{,}058{,}400\text{ erg.}$

$[\because\ \text{g cm}^2\text{ s}^{-2} = \text{erg}]$

$$= \frac{-1{,}058{,}400}{10^7}\text{ J} = \mathbf{1.0584 \times 10^{-1}\ J}$$

Ans.

Example 12. *A system consisting of a gas is fitted with a frictionless and weightless piston. When it absorbs 500 J heat from its surrounding, the gas expands against a constant pressure of one atmosphere from 3 L to 4.35 L volume. Calculate the change in the internal energy of the system.*

Solution. $P = 1\text{ atm};\ \Delta V = V_{final} - V_{initial}$

$= 4.5 - 3 = 1.5\text{ L}$

Since work is done by the system to push the piston upward, W is negative.

So, $W = P\Delta V = -1\text{ atm} \times 1.5\text{ L} = -1.5\text{ L atm}$

$$= \frac{-1.5 \times 1.987 \times 4.184}{0.0821}\text{ J}$$

$$\left[\because\ \text{L atm} = \frac{1.987 \times 4.184}{0.0821}\text{ J}\right]$$

But, $\Delta U = q + W$ (First law of thermodynamics)

$$\therefore\quad \Delta U = 500\text{ J} - \frac{1.5 \times 1.987 \times 4.184}{0.0821}$$

$\text{J} = 500\text{ J} - 151.89$

$= \mathbf{348.11\ J}$ **Ans.**

Type. (*i*) Work done by a heater

= current 'C' in ampere × no. of volts (V) × time (t) in seconds

= Enthalpy change, ΔH

(*ii*) $\Delta H = \Delta U + P\Delta V = \Delta U + \Delta n_{(g)}RT$

Example 13. *In order to evaporate 1.578 g of water, one ampere current from a 6 V supply was passed for 10 minutes. If water boils under a pressure of 1.0 atmosphere, what will be the enthalpy change and molar internal change at the boiling point (100°C).*

Solution. Work done by the heater

$= CVt = 1\text{ amp} \times 6\ V \times 10 \times 60\text{ s}$

$= 3600\text{ amp. Volt. s} = 3600\text{ J} = \Delta H$

Wt. of H_2O = 1.578 g; g. mol. wt. of H_2O

$= (2 \times 1) + 16 = 18\text{ g.}$

$\therefore$ no. of mol of H_2O

$$= \frac{1.578}{18} = 0.0877$$

$\therefore$ Molar enthalpy of vaporisation

$$= \frac{\Delta H}{n_{H_2O}} = \frac{3600\text{ J}}{0.0877} = 41{,}049\text{ J}$$

$= 41.049\text{ k J mol}^{-} = \Delta H'$

But, $\Delta H' = \Delta U + P\Delta V = \Delta U + \Delta n_g RT = \Delta U + 1\,RT$

$[\because\ \text{for } H_2O\,(l) \rightleftharpoons H_2O(g),\ \Delta n_g = 1\text{ mol}]$

$\therefore\quad \Delta U = \Delta H' - RT = 41.049\text{ k J mol}^{-} - 1 \times 8.314$

$\times 10^{-3}\text{ k J mol}^{-}\text{ K}^{-} \times (100 + 273)\text{ K}$

$= 41.049\text{ k J mol}^{-} - 3.1\text{ k J mol}^{-}$

$= \mathbf{37.95\ k\ J\ mol^{-}}$ **Ans.**

Example 14. *The enthalpy change (ΔH) for the reaction*

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

is – 92.38 k J at 298 K. What is ΔE or ΔU at 298 K ?

(PSEB, 2006)

Solution. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

$\Delta n(g)$ = no. of mol of products – no. of mol of reactants

$$\begin{aligned}
&= 2 - (1 + 3) = -2\\
\Delta H &= -92.38 \text{ k J} = -92.38 \times 1000 \text{ J}\\
&= -92380 \text{ J};\\
\Delta U &= ?;\ R = 8.314 \text{ J K}^{-} \text{mol}^{-};\\
T &= 298 \text{ K}.
\end{aligned}$$

We know that : $\Delta H = \Delta U + \Delta n(g)\, RT$

$$\begin{aligned}
\therefore \quad \Delta U &= \Delta H - \Delta n(g)\, RT\\
&= -92380 \text{ J mol}^{-} - (-2) \times 8.314 \text{ J K}^{-} \text{mol}^{-} \times 298 \text{ K}\\
&= -92380 \text{ J mol}^{-} + 4955.1 \text{ J mol}^{-}\\
&= -87424.8 \text{ J mol}^{-}\\
\Delta U &= \mathbf{-87.425 \text{ J mol}^{-}} \ \textbf{Ans.}
\end{aligned}$$

EXAMPLE 15. *Heat of combustion of CH_4 (g) at constant volume is measured in a bomb calorimeter at 298 K and found to be – 885389 J mol¯. Find the value of enthalpy change.* **(P.S.E.B., 2006)**

SOLUTION. Reaction:

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

$$\begin{aligned}
\Delta n(g) &= \text{no. of mol of gaseous products} - \text{no. of mol of gaseous reactants}\\
&= 1 - (1 + 2) = -2\\
\Delta U &= -885389 \text{ J mol}^{-};\ \Delta H = ?;\ R = 8.314 \text{ J K}^{-} \text{mol}^{-}\\
T &= 298 \text{ K}\\
\Delta H &= \Delta U + \Delta n(g)\, RT\\
&= -885389 \text{ J mol}^{-} + (-2) \times 8.314 \text{ J K}^{-} \text{mol}^{-} \times 298 \text{ K}\\
\Delta H &= -885389 \text{ J mol}^{-} - 4955.1 \text{ J mol}^{-}\\
&= -890{,}344.1 \text{ J mol}^{-}\\
\text{or} \quad \Delta H &= -890344.1 \text{ J mol}^{-} \times \frac{1 \text{ k J}}{1000 \text{ J}}\\
&= -890.3441 \text{ k J mol}^{-} \quad \textbf{Ans.}
\end{aligned}$$

EXAMPLE 16. *When one mol of an allotropic form of a compound A (density 2.45 g cm^{-3}) changes to its another form B (density 2.81 g cm^{-3}), internal energy change was found to be 190 J. Calculate the enthalpy change when the pressure is 1.1 bar and mol. wt. of compound is 84.*

SOLUTION. $P = 1.1 \text{ bar} = 1.1 \times 10^5\ Pa;$

$$\begin{aligned}
V_B &= \frac{\text{mass}}{\text{density}} = \frac{84}{2.81};\ V_A = \frac{\text{mass}}{\text{density}} = \frac{84}{2.45}\\
\text{So,} \quad \Delta V &= V_B - V_A\\
&= \frac{84}{2.81} - \frac{84}{2.45}\\
&= \frac{84 \times 2.45 - 84 \times 2.81}{2.81 \times 2.45}\\
&= \frac{205.8 - 236.04}{2.81 \times 2.45} = -30.24 \text{ cm}^3 \text{ mol}^{-}\\
&= -30.24 \times 10^{-6} \text{ m}^3 \text{ mol}^{-}\\
\Delta U &= 190 \text{ J mol}^{-}\\
\therefore \quad \Delta H &= \Delta U + P\Delta V;\ \Delta H = 190 \text{ J mol}^{-} + 1.1 \times 10^5\ Pa \text{ (or Nm}^{-2}) \times (-30.24 \times 10^{-6}) \text{ m}^3 \text{ mol}^{-}\\
&= 190 \text{ J mol}^{-} - 3.33 \text{ Nm mol}^{-}\\
&= 190 \text{ J mol}^{-} - 3.33 \text{ J mol}^{-}\\
&[\because\ 1 \text{ Nm} = 1 \text{ J}] = \mathbf{186.67 \text{ J mol}^{-}} \ \textbf{Ans.}
\end{aligned}$$

EXAMPLE 17. *In an insulated container 1 mol of a liquid, molar volume 100 mL is at 1 bar. Liquid is steeply taken to 100 bar, when volume of liquid decreases by 1 mL. Find ΔH and ΔU for the process.* **(IIT, 2004)**

SOLUTION. Molar volume of liquid at 1 bar pressure

$$= 100 \text{ mL} = V_1$$

molar volume of liquid at 100 bar pressure

$$= 100 - 1 = 99 \text{ mL} = V_2$$

Since the change in pressure is very large, it is irreversible process.

So, work is negative.

$$\begin{aligned}
W &= -P\,(V_2 - V_1)\\
&= -100 \text{ bar } (99 - 100) \text{ mL}\\
&= +100 \text{ bar mL}
\end{aligned}$$

The container being isolated,

$$\begin{aligned}
q &= 0.\\
\text{But,} \quad \Delta U &= q + W.\\
\text{So,} \quad \Delta U &= 0 + 100 \text{ bar mL} = \mathbf{100 \text{ bar mL}}\\
\text{Also,} \quad \Delta H &= \Delta U + P\Delta V;\\
\Delta H &= \Delta U + (P_2V_2 - P_1V_1)\\
\mathbf{\Delta H} &= 100 + (100 \times 99 - 1 \times 100)\\
&= 100 + 9800\\
&= \mathbf{9900 \text{ bar mL}} \ \textbf{Ans.}
\end{aligned}$$

15.16 WORK REQUIRED TO HEAT n mol OF A SUBSTANCE

Type. Work (W) required to heat n mol of a substance

$$= n \times C \times \Delta T$$

where C = sp. heat of a substance

and W = work done by a system $= -P_{ext} \times \Delta V;$

ΔT = Change in temperature

Final temperature = Initial temperature + ΔT

EXAMPLE 18. *One mol of water (sp. heat 4.184 J g¯ K¯) at 15°C was heated by performing work to expand an ideal gas from 2 dm^3 to 4 dm^3 against a constant external pressure of 2.2 atmosphere. Calculate the final temperature of water.*

SOLUTION. g. mol. wt. of H_2O = $(2 \times 1) + 16 = 18$ g.

$$C = 4.184\ \text{J g}^{-}\ \text{K}^{-}$$
$$= 4.184 \times 18\ \text{J mol}^{-}\ \text{K}^{-};$$
$$n = 1\ \text{mol}$$
$$\Delta T = ?$$

Since work has been done against external pressure, it is negative as well as irreversible.

So : $W = -P_{ext}.\ \Delta V = -2.2\ \text{atm} \times (4-2)\ \text{dm}^3$ or L

$$= -4.4\ \text{L atm} = -4.4 \times \frac{1.987 \times 4.184}{0.0821}\ \text{J}$$
$$\left[\because\ 1\ \text{L atm} = \frac{1.987 \times 4.184}{0.0821}\ \text{J}\right]$$
$$= -445.55\ \text{J}$$

Since work is used to heat 1 mol of water,

$$W = n \times C \times \Delta T$$
$$= 1\ \text{mol} \times 4.184 \times 18\ \text{J mol}^{-}\ \text{K}^{-} \times \Delta T$$
$$445.55\ \text{J} = 1\ \text{mol} \times 4.184 \times 18\ \text{J mol}^{-}\ \text{K}^{-} \times \Delta T$$
$$\therefore \quad \Delta T = \frac{445.55\ \text{J}}{4.184 \times 18\ \text{J}}\ \text{K} = 6.05\ \text{K}$$

$\therefore$Final temperature

$$= (15 + 273)\ \text{K} + \Delta T = 288\ \text{K} + 6.05\ \text{K}$$

= 294.05 K **Ans.**

EXAMPLE 19. *A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm.The work done during expansion is used to heat 10 mol of water of temperature 290 K. Calculate final temperature of water. Specific heat of water = 4.184 J g^{-} K^{-}.*

(Roorkee, 1993)

SOLUTION. g. mol. wt. of H_2O = $(2 \times 1) + 16 = 18$ g

$$C = 4.184\ \text{J g}^{-}\ \text{K}^{-}$$
$$= 4.184 \times 18\ \text{J mol}^{-}\ \text{K}^{-}$$
$$n = 10\ \text{mol};\ \Delta T = ?$$

Since work has been done against external pressure, it is negative as well as irreversible.

So : $W = -P_{ext} \times \Delta V = -3$ atm $\times (5-3)\ \text{dm}^3$ or L $= -6$ L atm

$$= -6 \times \frac{1.987 \times 4.184}{0.0821}\ \text{J}$$
$$\left[\because\ 1\ \text{L atm} = \frac{1.987 \times 4.184}{0.0821}\ \text{J}\right]$$
$$= -607.57\ \text{J}$$

Since work is used to heat 10 mol of water

$$W = n \times C \times \Delta T = 10\ \text{mol} \times 4.184 \times 18\ \text{J mol}^{-}\ \text{K}^{-} \times \Delta T$$
$$607.57\ J = 10\ \text{mol} \times 4.184 \times 18\ \text{J mol}^{-}\ \text{K}^{-} \times \Delta T$$
$$\therefore \quad \Delta T = \frac{607.57\ \text{J}}{10\ \text{mol} \times 4.184 \times 18\ \text{J}}\ \text{K} = 0.81\ \text{K}$$

$\therefore$ Final temperature = 290 K + 0.81 K

= 290.81 K **Ans.**

15.17 WORK FOR ISOTHERMAL REVERSIBLE PROCESS

For isothermal reversible process, work,

$$W = -2.303\, nRT \log \frac{V_2}{V_1}$$
$$= -2.303\, nRT \log \frac{P_1}{P_2}$$
$$n = \text{no. of mol} = \frac{\text{wt.}}{\text{mol. wt.}},$$
$$R = 8.314\ \text{J K}^{-}\ \text{mol}^{-}$$
$$T = t°C + 273$$

EXAMPLE 20. *Calculate the maximum work done when 64 g of oxygen gas occupying volume of 7 litres is expanded isothermally and reversibly to 14 litres at 27°C. (R = 1.987 cal deg^{-} mol^{-}).*

(ISC, 2008)

SOLUTION. Wt. of oxygen = 64 g; mol. wt of O_2 = 32 g mol^{-}.

So, $$''O_2 = \frac{64\,\text{g}}{32\,g\,\text{mol}^{-1}} = 2$$

$$R = 1.987\ \text{cal deg}^{-}\ \text{mol}^{-},$$
$$T = 27 + 273$$
$$= 300\ \text{K};\ V_1 = 7\ \text{L},$$
$$V_2 = 14\ \text{L}.$$

We know that : $$W = -2.303\ \text{nRT} \log \frac{V_2}{V_1}$$

(for isothermal and reversible process)

$$= -2.303 \times 2\ \text{mol} \times 1.987\ \text{cal deg}^{-}\ \text{mol}^{-} \times 300\ \text{K} \log \frac{14}{7}\ \text{i.e., } 2$$
$$= -2.303 \times 2 \times 1.987 \times 300 \times 0.301\ \text{cal} = \mathbf{-826.4\ cal}$$

EXAMPLE 21. *10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L.Calculate q, W, ΔU and ΔH for this process. R = 2.0 cal K^{-} mol^{-}, log 10^2 = 0.30, at. wt. of Ar = 40.*

(Roorkee, 1997)

SOLUTION. (*a*) $$n = \text{no. of mol of Ar} = \frac{\text{wt.}}{\text{at. wt}} = \frac{10}{40}$$
$$= 0.25\ \text{mol}$$
$$R = 2.0\ \text{cal K}^{-}\ \text{mol}^{-};\ T = 27 + 273$$
$$= 300\ \text{K}$$
$$V_1 = 10\ \text{L},\ V_2 = 5\text{L}$$

We know that : $$W = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$\left[-2.303 \times 0.25\ \text{mol} \times 2\ \text{cal K}^{-}\ \text{mol}^{-} \times 300\ \text{K} \log \frac{5}{10}\ i.e., 0.5\right]$$
$$= -2.303 \times 0.25 \times 2\ \text{cal} \times 300 \times -0.30$$
$$W = 103.635\ \text{cal.}$$

(*b*) For isothermal reversible process, **ΔU = 0.**

(*c*) But, $\Delta U = q + W$ (First law of thermodynamics)

$\therefore \quad 0 = q + W;\ 0 = q + 103.635$ cal;

$q =$ **–103.635 cal** **Ans.**

(*d*) When temperature is constant, it is Boyle's law *i.e.,*

$P_1V_1 = P_2V_2$

or $\quad PV =$ a constant.

But : $\quad \Delta H = \Delta U + \Delta (PV)$;

$\mathbf{\Delta H} = 0 + \Delta (0) = \mathbf{0}$ **Ans.**

EXAMPLE 22. *One mol of an ideal gas undergoes reversible isothermal expansion from an initial volume V_1 to final volume 10 V_1 and does 10 kJ of work. The initial pressure was 1×10^7 Pa. (a) Calculate V_1 (b) if there were 2 mol of gas, what must its temperature have been ?* **(Roorkee, 2001)**

SOLUTION. (*a*) no. of mol of ideal gas,

$n = 1,\ R = 8.314\ \text{J K}^{-}\text{mol}^{-},\ T = ?$

$P_1 = 10^7\ \text{Pa};\ V_1 = V_1,\ V_2 = 10\ V_1.$

If temperature is constant, it is Boyle's law.

So : $\quad P_1V_1 = P_2V_2$

$10^7\ \text{Pa} \times V_1 = P_2 \times 10\ V_1$

$$P_2 = \frac{10^7}{10} = 10^6\,Pa$$

For isothermal reversible process, work done by the system is negative.

$W = -10\ \text{kJ} = -10 \times 10^3 = -10000\ \text{J}$

But , $\quad W = -2.303\ n\,RT \log \dfrac{P_1}{P_2}$

$$-10000\ \text{J} = -2.303 \times 1 \times 8.314\ \text{J K}^{-}\text{mol}^{-} \times T \log \frac{10^7}{10^6} \text{ or } 10$$

$$\therefore \quad T = \frac{-10000\ \text{J}}{-2.303 \times 1 \times 8.314\ \text{J} \times 1}\ \text{K}$$

$[\because \log 10 = 1]$

$T = 522.27$ K

Calculation of V_1. We know

$P\,V = n\,RT$ for one mol of a gas

$\therefore \quad 10^7\,Pa \times V_1 = 1 \times 8.314\ Pa\ \text{m}^3\ \text{K}^{-} \times 522.27\ \text{K}$

$$V_1 = \frac{8.314\ Pa\ m^3}{10^7\ Pa} \times 522.27$$

$= 4.43 \times 10^{-4}\ \text{m}^3.$

(*b*) Temperature for 2 mol of a gas

$$= \frac{522.27\ \text{K}}{2} = \mathbf{261.14\ K} \qquad \textbf{Ans.}$$

EXAMPLE 23. *Calculate q, W, ΔU and ΔH for the isothermal reversible expansion of one mol of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K.*

(Roorkee, 2000)

SOLUTION. (*a*) n = no. of mol of ideal gas = 1 mol

$R = 8.314\ \text{J K}^{-}\text{mol}^{-};\ T = 273$ K,

$P_1 = 1.0$ bar,

$P_2 = 0.1$ bar.

For isothermal reversible expansion, work is negative.

So : $\quad W = -2.303\ nRT \log \dfrac{P_1}{P_2}$

$$= -2.303 \times 1\ \text{mol} \times 8.314\ \text{J K}^{-}\text{mol}^{-} \times 273\ \text{K} \times \log \frac{1.0}{0.1}$$

$\mathbf{W} = -2.303 \times 8.314\ \text{J} \times 273 \times \log 10$

$= -2.303 \times 8.314 \times 273 \times 1\ \text{J}$

$=$ **– 5227.2 J** **Ans.**

(*b*) For expansion, at constant temperature, $\Delta T = 0$

$\therefore \quad \mathbf{\Delta U} = n \times C_v \times \Delta T = 1 \times C_v \times 0$

$= \mathbf{0}$ (for one mol) **Ans.**

(*c*) $\quad \Delta U = q + W$ (First law of thermodynamics)

$\therefore \quad 0 = q + W;\ q = -W$

$\mathbf{q} = -(-5227.2\ \text{J}) = \mathbf{+\,5227.2\ J}$ **Ans.**

(*d*) At constant temperature, according to Boyle's law :

$P_1V_1 = P_2V_2$ or PV = a constant.

But, $\quad \Delta H = \Delta U + \Delta (PV) = \mathbf{0}$ **Ans.**

$[\because \ \Delta U = 0].$

EXAMPLE 24. *For the reaction $2CO + O_2 \longrightarrow 2CO_2$, $\Delta H = -560$ kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 litre. They completely form two moles of CO_2, and 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 atm = 0.1 kJ).*

(I.I.T – JEE, 2006)

SOLUTION. $\quad \Delta H = -560$ kJ;

$\Delta P = (40 - 70)\ \text{atm} = -30$ atm

$= -30 \times 0.1\ \text{kJ} = -3$ kJ

$[\because \ 1\ \text{atm} = 0.1\ \text{kJ}]$

$\Delta U = ?$

We know that :

$\Delta H = \Delta U + V\Delta P;\ \Delta U = \Delta H - V\Delta P$

$= -560\ \text{kJ} - [1 \times -3\ \text{kJ}]$

or $\quad \Delta U = -560\ \text{kJ} + 3\ \text{kJ} =$ **– 557 kJ** **Ans.**

EXAMPLE 25. *Two mol of a perfect gas undergo the following processes.*

(*a*) *a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L)*

(*b*) *a reversible isochoric change of state from (1.0 atm, 40.0 L) to 10.5 atm, 40.0 L)*

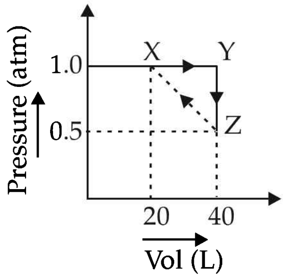
(*c*) *a reversible isothermic compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)*

(*i*) *Sketch with labels each of the processes on the same P – V diagram*

(*ii*) *Calculate the total work (w) and the total heat change (q) involved in the above processes*

(*iii*) *What will be the values of ΔU, ΔH and ΔS for the overall process.* **(IIT, 2002)**

Solution. XY = Isobaric expansion
YZ = Isochoric change
ZX = Isothermal compression



Since the process is cyclic,

$$\Delta U = 0;$$
$$\Delta S = 0 \text{ and } \Delta H = 0$$

Total work, $W = W_{X \longrightarrow Y} + W_{Y \longrightarrow Z} + W_{Z \longrightarrow X}$ ...(1)

$$V_Y = 40 \text{ L}, \; V_X = 20 \text{ L};$$
$$W_{Y \longrightarrow Z} = 0; \; V_Z = 40 \text{ L}$$
$$W_{Z \longrightarrow X} = 2.303\, P_X V_Y \log \frac{V_Z}{V_X}$$
$$[\because \; nRT = P_X V_Y]; \; n = 1$$

Substituting the values in (1), we get :

$$W = -P(V_Y - V_X) + 0 + 2.303 \times P_X V_Y \log \frac{V_Z}{V_X}$$
$$= -1 \text{ atm } (40 - 20) \text{ L} + 0 + 2.303 \times 1 \text{ atm} \times 20 \text{ L} \log \frac{40}{20} \; i.e., 2$$
$$= -20 \text{ L atm} + 46.06 \text{ L atm} \times 0.301$$
$$= -20 + 13.86 = -6.14 \text{ L atm}$$
$$W = \frac{-6.14 \times 8.314}{0.0821} \text{ J} = \mathbf{-621.78\ J} \quad \textbf{Ans.}$$
$$[\because \; 1 \text{ L atm} = \frac{8.314}{0.0821} \text{ J}]$$

Also, for a cyclic process,

$$q = -W = -(-621.78 \text{ J}) = \mathbf{+621.78\ J} \quad \textbf{Ans.}$$

15.18 CLAUSIUS – CLAPEYRON EQUATION

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

ΔH_v = Latent heat of vaporisation.

Example 26. *The vapour pressures exerted by an organic liquid at 30°C and 60°C are respectively 1.53 × 10^4 Pa and 5.2 × 10^4 Pa. How much will be the mean latent heat of vaporisation within 30°C and 63°C range ?*

Solution.` $T_1 = 30 + 273 = 303$ K; $T_2 = 60 + 273 = 333$ K,
$P_1 = 1.53 \times 10^4$ *Pa*, $P_2 = 5.2 \times 10^4$ *Pa*;
$R = 8.314$ J K^{-} mol^{-}; $\Delta H_v = ?$

According to clausius – clapeyron equation :

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \frac{(T_2 - T_1)}{T_1 T_2} \quad \textbf{or}$$

$$\Delta H_v = \left(2.303 \log \frac{P_2}{P_1}\right) \times \frac{R \times T_1 T_2}{T_2 - T_1}$$
$$= 2.303 \log \frac{5.2 \times 10^4}{1.53 \times 10^4} \times \frac{8.314 \times 303 \times 333}{333 - 303 = 30}$$
$$= 2.303 [\log 5.2 - \log 1.53] \times 27962.48$$
$$= 2.303 [0.716 - 0.1847$$
$$= 0.5313] \times 27962.48 \text{ J} = 34214 \text{ J}$$
$$\Delta H_v = \mathbf{34.214\ k\ J} \quad \textbf{Ans.}$$

Type. $\left(\frac{\delta H}{\delta T}\right)_P = C_p = \frac{\Delta H}{\Delta T}$ (for one mol)

$\therefore$ $\Delta H = n\, C_p \Delta T$ (for n mol)

where C_p = heat capacity at constant pressure.

Example 27. *The whole material (e.g., chairs, tables, roof, walls etc) present in a drawing room are completely insulated and hence donot absorb heat. If 30 persons are sitting in this room lose energy at the average of 120 watt, how much time will it take to raise the temperature of air in room from 15°C at 1 atm to 30°C. Given $C_p = \frac{7}{2}R$, dimensions of room as 8 × 4 × 2.5 m^3 and no heat is lost to the surrounding.*

Solution.

1 watt = 1 J s^{-}. no. of watt = 120.

So, heat released by 30 persons

$$= 30 \times 120 \text{ J s}^{-}.$$
$$T_1 = 15 + 273 = 288 \text{ K},$$
$$T_2 = 30 + 273 = 303 \text{ K}.$$

So, $\Delta T = 303 - 288 = \mathbf{15\ K}$

V = Volume of air
= Length × breadth × height
= $8 \times 4 \times 2.5 = 80 \text{ m}^3 = 80 \times 10^6 \text{ cm}^3$

$PV = nRT.$

So, n = no. of mol of air = $\frac{PV}{RT}$

$$= \frac{1 \text{ atm} \times 80 \times 10^6 \text{ cm}^3}{0.0821 \times 10^3 \text{cm}^3 \text{ atm K}^{-}\text{mol}^{-} \times 288 \text{ K}}$$
$$= 3383.4 \text{ mol}$$

We know that : for 1 mol $\left(\frac{\delta H}{\delta T}\right)_p$

$$= C_p = \frac{\Delta H}{\Delta T}$$

$\therefore$ For n mol,

$$\Delta H = n\, C_p \Delta T = 3383.4 \times \frac{7}{2} R \times 15 \text{ K}$$
$$= 3383.4 \text{ mol} \times \frac{7}{2} \times 8.314 \text{ J K}^{-}\text{mol}^{-} \times 15 \text{ K}$$
$$= 1476803 \text{ J}$$

= heat needed to heat room at 30°C

30 × 120 J heat is released in time = 1 sec

1476803 J heat is released in time = $\frac{1476803 \times 1}{30 \times 120}$

= 410.2 seconds Ans.

Type (*i*)
$$q_p\,(=\Delta H) = n\,C_p\,\Delta T;$$
$$C_p - C_v = R \quad \text{and} \quad \gamma - 1 = \frac{R}{C_v}$$

(*ii*)
$$\Delta U = q + w$$

Example 28. *Calculate the value of ΔU and W for 1 mol of an ideal gas ($\gamma = 1.4$) to which 100 J heat is supplied at constant pressure.*

Solution. Since heat is supplied at constant pressure,

$$q_p = \Delta H.$$

So,
$$\Delta H = n \times C_p \times \Delta T \qquad \text{...(1)}$$
$$\Delta H = 100\text{ J (at constant pressure)}$$
$$\gamma - 1 = \frac{R}{C_v};\ 1.4 - 1 = \frac{R}{C_v};\ C_v = \frac{R}{0.4} = \frac{5}{2}R.$$

But,
$$C_p - C_v = R$$
$$\therefore \quad C_p = R + C_v = R + \frac{5}{2}R = \frac{7}{2}R.$$

Substituting the values in (1),

We get :
$$100\text{ J} = n \times \frac{7}{2}R \times \Delta T$$
$$\therefore \quad \Delta T = \frac{2 \times 100\text{ J}}{n\,R \times 7} = \frac{200\text{ J}}{7\,n\,R} \qquad \text{...(2)}$$

Also,
$$W = -\,n\,R\,\Delta T$$

or
$$\mathbf{W} = -\,n\,R \times \frac{200\text{ J}}{7\,n\,R} = -\frac{200\text{ J}}{7}$$
$$= \mathbf{-\,28.56\ J} \qquad \textbf{Ans.}$$

But,
$$\Delta U = q + w$$
$$\Delta \mathbf{U} = 100\text{ J} - 28.56\text{ J} = \mathbf{71.44\ J} \quad \textbf{Ans.}$$

Example 29. *A NCC cadet was asked to shoot at a wooden block (1.5 kg) with a lead bullet (18.0 g) which travels with the velocity of 450 m s^{-}. Calculate the final temperature of the wooden block if the initial temperature of bullet as well as the wooden block were at 15°C. (Heat capacity of Pb = 0.03 k cal (kg)$^{-}$ K^{-}; of wood = 0.5 k cal (kg)$^{-}$ K^{-}).*

Solution.

$$\text{wt. of bullet} = 18.0\text{ g} \times \frac{1\text{ kg}}{1000\text{ g}}$$
$$= 0.018\text{ kg};\ u = 450\text{ m s}^{-}$$
$$\therefore \quad K.E.\text{ of bullet} = \frac{1}{2}m\,u^2$$
$$= \frac{1}{2} \times 0.018\text{ kg} \times (450\text{ m s}^{-})^2$$
$$= 1822.5\text{ kg m}^2\text{ s}^{-2} = 1822.5\text{ J}$$
$$[\because\ 1\text{ J} = \text{kg m}^2\text{s}^{-2}]$$
$$K.E. = 1822.5\text{ J} \times \frac{1\text{ k cal}}{4.184 \times 1000\text{ J}}$$
$$= \mathbf{0.4356\ k\ cal}$$

But,
$$K.E\,(= q) = m\,S\Delta T$$
$$\therefore \quad \Delta T = \frac{K.E}{m.S} \qquad \text{...(1)}$$

But,
$$m\,S = m\,S\text{ for wooden block} + m\,S\text{ for bullet}$$
$$= (1.5\text{ kg} \times 0.5\text{ k cal (kg)}^{-}\text{ K}^{-}) + 0.018\text{ kg} \times 0.03\text{ k cal (kg)}^{-}\text{ K}^{-}$$
$$m\,S = 0.75\text{ k cal K}^{-} + 0.00054\text{ k cal K}^{-}$$
$$= 0.75054\text{ k cal K}^{-}$$

Substituting the value of *K.E.* and *m S* in (1), we get :

$$\Delta T = \frac{0.4356\text{ k cal}}{0.75054\text{ k cal K}^{-}} = 0.58\text{ K}$$

Initial temperature

$$= 15 + 273 = 288\text{ K}$$

$\therefore$**Final temperature**

$$= 288 + 0.58 = \mathbf{288.58\ K} \qquad \textbf{Ans.}$$

Example 30. *20.0 g of ammonium nitrate (NH_4NO_3) when dissolved in 125 g of water in a coffee-cup calorimeter, the temperature falls from 296.5 K to 286.4 K. Find the value of q for the calorimeter. (Treat heat capacity of water as the heat capacity of the calorimeter and its content).*

Solution. Mass of ammonium nitrate

$$= 20.0\text{ g}$$
$$\text{Mass of water } (m) = 125\text{ g}$$
$$\text{Fall of temperature } \Delta T = 286.4 - 296.5 = -\,10.1\text{ K}$$

Heat capacity of the calorimeter,

$$C = 4.18\text{ J g}^{-1}\text{ K}^{-1}$$

Thus,
$$q = mC.\,\Delta T = 125\text{ g} \times 4.18\text{ Jg}^{-1}\text{ K}^{-1} \times (-\,10.1\text{ K})$$
$$= \mathbf{5277\ J.} \qquad \textbf{Ans.}$$

Example 31. *A gas expands from a volume of 3.0 dm^3 to 5.0 dm^3 against a constant external pressure of 3.0 atm. The work done during expansion is used to heat 10.0 mole of water at temperature 290 K. Calculate the final temperature of water (specific heat of water = 4.184 g^{-1} K^{-1}).*

(Roorkee, 1993)

Solution. Initial volume

$$(V_1) = 3\text{ dm}^3 = 3 \times 10^{-3}\text{m}^3 = 3L$$
$$\text{Final volume } (V_2) = 5\text{ dm}^3 = 5 \times 10^{-3}\text{ m}^3 = 5L.$$
$$\text{Pressure (constant)} = 3\text{ atm} = 3 \times 1.01 \times 10^5\text{ Nm}^{-2}$$
$$\therefore \quad \text{Work done} = P\,(V_2 - V_1) = 3 \times 1.01 \times 10^5\,(5 - 3) \times 10^{-3}\text{ Nm}$$
$$= 3.03 \times 10^2 \times 2 = 6.06 \times 10^2\text{ J}$$

This work is used to heat water at 290 K to a temperature say TK.

$$\text{Specific heat of water} = 4.184\text{ Jg}^{-1}\text{ K}^{-1}$$
$$\text{Weight of water } (m) = \text{No. of moles} \times \text{Mol. wt}$$
$$= 10 \times 18 = 180\text{ g}$$

Heat required to raise the temperature by

$$\Delta T = \text{mass} \times \text{Specific heat} \times \text{Rise in temp.}$$
$$= m \times C_v \times \Delta T = 180 \times 4.184 \times (T - 290)\text{ JK}^{-1}$$

$$\therefore\quad 6.06 \times 10^2\ \mathrm{J} = 180 \times 4.184 \times (T - 290)\ \mathrm{JK^{-1}}$$

$$(T-290) = \frac{6.06 \times 10^2}{180 \times 4.184}\ \mathrm{K} = 0.804\ \mathrm{K}$$

$$\therefore\quad T = 290 + 0.804\ \mathrm{K} = \mathbf{290.804\ K}$$

Type. ΔH or $q_p = n\,C_p\,\Delta T;\ C_p - C_v = R$

$$\Delta S = \int_{T_1}^{T_2} \frac{n\,C_p dT}{T} = n\,C_p ln\,\frac{T_2}{T_1}$$

$$= 2.303\,n\,C_p \log\frac{T_2}{T_1}$$

EXAMPLE 32. *Find the value of* ΔH, ΔU *and* ΔS *for one mol of an ideal gas* ($C_v = \frac{5}{2}R$) *that is heated at constant pressure from 27°C to 77°C.*

SOLUTION. $C_p - C_v = R;$

$$C_p = R + C_v = R + \frac{5}{2}R = \frac{7R}{2}$$

$$T_1 = 27 + 273 = 300\ \mathrm{K};$$

$$T_2 = 77 + 273 = 350\ \mathrm{K}$$

$$\Delta T = 350 - 300 = 50\ \mathrm{K}$$

$$R = 1.987\ \mathrm{cal\ K^{-}\ mol^{-}};\ n = 1\ \mathrm{mol}$$

(*a*) ΔH (or q_p) $= n \times C_p \times \Delta T$

$$= 1\ \mathrm{mol} \times \frac{7}{2}R \times 50\ \mathrm{K}$$

$$q_p\ (= \Delta H) = 1\ \mathrm{mol} \times \frac{7}{2}$$

$$\times\ 1.987\ \mathrm{cal\ K^{-}\ mol^{-}} \times 50\ \mathrm{K}$$

$$= \mathbf{347.725\ cal} \qquad \textbf{Ans.}$$

(*b*) Work done, $W = -P\,(V_2 - V_1)$

$$= -P\left[\frac{nRT_2}{P} - \frac{nRT_1}{P}\right]$$

$$\left[\because\ PV = nRT;\ V = \frac{nRT}{P}\right]$$

$$= -P \times \frac{nR}{P}[T_2 - T_1]$$

$$= -nR[T_2 - T_1]$$

$$W = -1\ \mathrm{mol} \times 1.987\ \mathrm{cal\ K^{-}\ mol^{-}}$$

$$(350 - 300 = 50)\ \mathrm{K}$$

$$= \mathbf{-99.35\ cal} \quad [\because\ n = 1\ \mathrm{mol}]$$

(*c*) $\Delta U = q + W$

(First law of thermodynamics)

$$\Delta U = 347.725\ \mathrm{cal} + (-99.35)\ \mathrm{cal}$$

$$= \mathbf{248.375\ cal} \qquad \textbf{Ans.}$$

(*d*) **To find ΔS**

$$dS = \frac{dq_{rev}}{T};\ dS = \frac{nC_pdT}{T}$$

$$\left[\because\ dq_{rev} = \frac{nC_pdT}{T}\right]$$

or

$$\Delta S = \int_{T_1}^{T_2} \frac{n\,C_pdT}{T}$$

$$= n\,C_p \int_{T_1}^{T_2} \frac{dT}{T} = n\,C_p \log_e \frac{T_2}{T_1}$$

$$= 2.303\,n\,C_p \log\frac{T_2}{T_1}$$

$$= 2.303 \times \mathrm{mol} \times \frac{7}{2}R \log\frac{350}{300}$$

$$= 2.303 \times 1\ \mathrm{mol} \times \frac{7}{2}$$

$$\times\ 1.987\ \mathrm{cal\ K^{-}\ mol^{-}}$$

$$[\log 350 - \log 300]$$

$$= 16.02\,[2.544 - 2.477 = 0.067]\ \mathrm{cal\ K^{-}}$$

$$\Delta S = \mathbf{1.07\ cal\ K^{-}} \qquad \textbf{Ans.}$$

15.19 ENDOTHERMIC REACTIONS

Such reactions which are accompanied by the absorption of heat energy are called endothermic reactions. In such reactions, enthalpy of products (H_P) is greater than that of reactants (H_R). so, ΔH is positive

$$\therefore\quad \Delta H = H_P - H_R = +\ \mathrm{ve}$$

Exothermic reactions. Such reactions which are accompanied by the evolution of heat energy are called exothermic reactions. In such reactions, enthalpy of products (H_P) is less than that of reactants (H_R). So, ΔH is negative

$$\therefore\quad \Delta H = H_P - H_R = -\ \mathrm{ve}.$$

EXAMPLE 33. *Classify the following reactions in endothermic and exothermic reactions.*

(*i*) $C(s) + H_2O(g) + 131.4\ kJ \longrightarrow CO(g) + H_2(g)$

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5\ kJ$

(*iii*) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O\ (l);$

$\Delta H = -\,2876\ kJ$ (*iv*)

$SnO_2(s) + 2C(s) \longrightarrow Sn(s) + 2CO\ (g);\ \Delta H = +\,360\ kJ$

SOLUTION. (*i*) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g);$

$$\Delta H = +\,131.4\ \mathrm{kJ}$$

Since ΔH is positive, reaction is endothermic.

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -\,393.5\ kJ.$

Since ΔH is negative, reaction is exothermic.

(*iii*) $C_4H_{10}(g) + \frac{13}{2}\ O_2(g) \longrightarrow 4CO_2(g) + 5H_2O;$

$$\Delta H = -\,2876\ \mathrm{kJ}.$$

Since ΔH is negative, reaction is exothermic.

(*iv*) $SnO_2(s) + 2C(s) \longrightarrow Sn(s) + 2CO(g);$

$$\Delta H = +\,360\ \mathrm{kJ}.$$

Since ΔH is positive, reaction is endothermic.

15.20 SOME IMPORTANT HINTS TO SOLVE NUMERICAL PROBLEMS ON HESS'S LAW OF CONSTANT HEAT SUMMATION

1. To calculate **heat of formation,** the required equation should be written in terms of the

formation of **ONE MOLE** of a substance. For example, the heat of formation of one mole of ethyl alcohol (C_2H_5OH), benzene (C_6H_6), acetic acid (CH_3COOH), potassium hydroxide (KOH) etc can be written as :

(*i*) $2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow \underset{1\ \text{mol}}{C_2H_5OH}$; $\Delta H = ?$

(*ii*) $6C + 3H_2 \longrightarrow \underset{1\ \text{mol}}{C_6H_6}$; $\Delta H = ?$

(*iii*) $2C + 2H_2 + O_2 \longrightarrow \underset{1\ \text{mol}}{CH_3COOH}$; $\Delta H = ?$

(*iv*) $K + \frac{1}{2}O_2 + \frac{1}{2}H_2 \longrightarrow \underset{1\text{mol}}{KOH}$; $\Delta H = ?$

2. To calculate **heat of combustion,** the required equation should be written by adding O_2 gas in the **one mole** of the substance whose heat of combustion is required. For example :

(*a*) If substance is hydrocarbon, the product will be CO_2 and H_2O. For example :

$$\underset{1\ \text{mole}}{C_6H_6} + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O;\ \Delta H = ?$$

(*b*) If substance is an element or a compound (other than hydrocarbon), treat **one mole** of the element or compound with oxygen to form oxide. For example :

(*i*) $\underset{1\ \text{mol}}{NO} + \frac{1}{2}O_2 \longrightarrow NO_2$

(*ii*) $\underset{1\ \text{mol}}{N_2} + O_2 \longrightarrow 2NO$

(*iii*) $\underset{1\ \text{mol}}{Al} + \frac{3}{4}O_2 \longrightarrow \frac{1}{2}Al_2O_3$

(*iv*) $\underset{1\ \text{mol}}{S} + \frac{3}{2}O_2 \longrightarrow SO_3$

(*v*) $\underset{1\ \text{mol}}{S} + O_2 \longrightarrow SO_2$

3. Any integer such as 2, 3, 4 etc × aq = aq (but not 2 aq, 3 aq, 4 aq etc).

15.21 ENTHALPY OF FORMATION ($\Delta_f H$)

The enthalpy (heat) change when one mole of a substance is formed from its elements is called enthalpy of formation e.g., for the reaction, $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; $\Delta H = -572$ kJ, the value of $\Delta_f H = -572/2 = -286$ kJ mol^{-}.

EXAMPLE 34. *The enthalpy of formation of NH_3 is –46 kJ mol^{-}. The enthalpy change for the reaction:*

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g) \text{ is:}$$

(*a*) + 23 kJ (*b*) + 92 kJ

(*c*) + 46 kJ (*d*) + 184 kJ

Karnataka CET, 2009

SOLUTION. Given: Enthalpy of formation of one mol of NH_3 is:

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3;\ \Delta H = -46 \text{ kJ}$$

or for the reaction, $NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$;

$$\Delta H = +46 \text{ kJ}$$

∴ Enthalpy change for 2 mol NH_3 *i.e.,*

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g);$$

ΔH will be 2 ×+ 46 = 92 kJ.

So, the correct answer is (*b*)

EXAMPLE 35. *Calculate the heat of formation of acetic acid from the following data.*

(*i*) *Heat of formation of CO_2 is – 94.0 k cal mol^{-}*

(*ii*) *Heat of formation of H_2O is – 68.3 k cal mol^{-}*

(*iii*) *Heat of combustion of 2 CH_3COOH = – 417.4 k cal*

SOLUTION. Required equation is to form one mol of CH_3COOH is :

$$2C + 2H_2 + O_2 \longrightarrow CH_3COOH;\quad \Delta H = ? \qquad ...(A)$$

Given. Writing for the formation of one mol of CO_2 and H_2O and the combustion of one mole of CH_3COOH, we have :

(*i*) $C + O_2 \longrightarrow CO_2$; $\Delta H = -94.0$ k cal

(*ii*) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$; $\Delta H = -68.3$ k cal

(*iii*) $CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O$

$$\Delta H = \frac{-417.4}{2} = -208.7 \text{ k cal}$$

In order to get equation (*A*), we have, 2 × equation (*i*) + 2 × equation (*ii*) – equation (*iii*)

$$\begin{aligned} 2C + 2O_2 + 2H_2 + O_2 &\longrightarrow 2CO_2 + 2H_2O \\ -CH_3COOH - 2O_2 &\qquad -2CO_2 - 2H_2O \\ \text{or}\quad 2C + 2H_2 + O_2 &\longrightarrow CH_3COOH \end{aligned}$$

$\Delta H = \mathbf{-115.9\ k\ cal}$ **Ans.**

ΔH in k cal

(*i*) $2 \times -94 = -188$

(*ii*) $2 \times (-68.3) = -136.6$

(*iii*) $-(-208.7) = +208.7$

$$\therefore \quad \Delta H = -188 - 136.6 + 208.7 = -115.9 \text{ k cal}$$

EXAMPLE 36. *Calculate the heat of formation of anhydrous aluminium chloride, Al_2Cl_6 from the following data.*

(*i*) $2Al(s) + 6HCl(aq) \longrightarrow Al_2Cl_6(aq) + 3H_2(g)$;

$$\Delta H = -240.0 \text{ k cal.}$$

(*ii*) $H_2(g) + Cl_2(g) \xrightarrow{\quad} 2HCl(g);\ \Delta H = -44.0$ k cal.

(*iii*) $HCl(g) + aq \xrightarrow{\quad} HCl(aq);\ \Delta H = -17.5$ k cal.

(*iv*) $Al_2Cl_6(s) + aq \xrightarrow{\quad} Al_2Cl_6(aq);\ \Delta H = -153.7$ k cal.

SOLUTION. The required equation is :

$$2Al(s) + 3Cl_2(g) \xrightarrow{\quad} Al_2Cl_6(s);\ \Delta H = ? \qquad ...(A)$$

In order to get equation (*A*), we have, equation (*i*) + 3 × equation (*ii*) + 6 × equation (*iii*) – equation (*iv*)

$$\begin{array}{rcl} 2Al(s) + 6HCl(aq) + & \xrightarrow{\quad} & Al_2Cl_6(aq) + 3H_2(g) \\ 3H_2(g) + 3Cl_2(g) + & & + 6HCl(g) \\ 6HCl(g) + aq - Al_2Cl_6(s) & & + 6HCl(aq) \\ - aq & & - Al_2Cl_6(aq) \\ \text{or} \quad 2Al(s) + 3Cl_2(g) & \xrightarrow{\quad} & Al_2Cl_6(s) \\ \Delta H & = & \mathbf{-323.3\ k\ cal} \end{array}$$

Ans.

ΔH in k cal

(*i*) – 240

(*ii*) 3 × – 44 = – 132

(*iii*) 6 × – 17.5 = – 105.0

(*iv*) – (– 153.7) = + 153.7

$\therefore$ ΔH = – 240 – 132 – 105 + 153.7

= – 323.3 k cal

Heat (enthalpy) of formation. It is the enthalpy change when **one** mole of a substance is formed from its elements. If one mole of a substance is formed from its elements in their standard states *i.e.,* 25°C and one atmospheric pressure, then enthalpy change is called standard enthalpy of formation, ΔH_f°.

Type. Heat of formation of a compound is equal in magnitude but opposite in sign to the heat of dissociation of that compound at a given temperature and pressure.

EXAMPLE 37. $H_2(g) + ½\, O_2(g) \xrightarrow{\quad} H_2O(l);$ $\Delta H = -890.36$ *k J mol⁻. What will be the value of ΔH for the dissociation of one mole of liquid water?*

SOLUTION. $H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{\quad} H_2O(l)$

$$\Delta H = -890.36 \text{ k J mol}^{-}$$

$$\therefore \qquad H_2O(l) \xrightarrow{\quad} H_2(g) + \frac{1}{2}O_2(g)$$

$$\Delta H = +890.36 \text{ k mol}^{-}$$

or $(\Delta H_{diss})H_2O = +890.36$ k J mol⁻ **Ans.**

EXAMPLE 38. *Calculate the heat of formation of anhydrous KOH from the following data.*

(*i*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 68.4$ *k cal*

(*ii*) $K(s) + H_2O(l) + aq \longrightarrow KOH(aq) + \frac{1}{2}H_2(g) + 98.1$ *k cal*

(*iii*) $KOH(s) + aq \longrightarrow KOH(aq) + 13.3$ *k cal.*

SOLUTION. The required equation is :

$$K(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) \longrightarrow KOH(s);$$

$$\Delta H = ? \qquad ...(A)$$

Given : (*i*) $H_2(g) + \frac{1}{2}O_2(g) \xrightarrow{\quad} H_2O(l);$

$$\Delta H = -68.4 \text{ k cal}$$

(*ii*) $K(s) + H_2O(l) + aq \xrightarrow{\quad} KOH(aq) + \frac{1}{2}H_2(g);$

$$\Delta H = -98.1 \text{ k cal}$$

(*iii*) $KOH(s) + aq \xrightarrow{\quad} KOH(aq);\ \Delta H = -13.3$ k cal.

In order to get equation (*A*),
we have, equation (*ii*) + equation (*i*) – equation (*iii*)

$$\begin{array}{rcl} K(s) + H_2O(l) + aq + & \longrightarrow & KOH(aq) + \frac{1}{2}H_2(g) \\ H_2(g) + \frac{1}{2}O_2(g) & & + H_2O(l) \\ - KOH(s) - aq & & - KOH(aq) \\ \text{or} \quad K(s) + \frac{1}{2}O_2(g) + \frac{1}{2}H_2(g) & \longrightarrow & KOH(s); \\ \Delta H & = & \mathbf{-153.2\ k\ cal} \end{array}$$

Ans.

ΔH in k cal

(*ii*) 98.1

(*i*) 68.4

(*iii*) – (– 13.3) = + 13.3

$\therefore$ ΔH = – 98.1 – 68.4 + 13.3

= – 153.2 k cal

EXAMPLE 39. *The heats of formation of CO_2 and H_2O are 97.0 and 68.4 k cal. If the heat of combustion of benzene, C_6H_6 is 783.4 k cal, calculate the heat of formation of benzene.*

SOLUTION. Required equation is :

$$6C + 3H_2 \xrightarrow{\quad} C_6H_6;\ \Delta H = ? \qquad ...(A)$$

Reactions. (*i*) $C + O_2 \xrightarrow{\quad} CO_2;\ \Delta H = -97$ k cal

(*ii*) $H_2 + \frac{1}{2}O_2 \xrightarrow{\quad} H_2O;\ \Delta H = -68.4$ k cal

(*iii*) $C_6H_6 + \frac{15}{2}O_2 \xrightarrow{\quad} 6CO_2 + 3H_2O;$

$$\Delta H = -783.4 \text{ k cal}$$

In order to get equation (*A*),
we have, 6 × equation (*i*) + 3 × equation (*ii*) – equation (*iii*)

$$\begin{array}{rcl} 6C + 6O_2 + 3H_2 + \frac{3}{2}O_2 & \longrightarrow & 6CO_2 + 3H_2O \\ - C_6H_6 - \frac{15}{2}O_2 & & - 6CO_2 - 3H_2O \\ \text{or} \quad 6C + 3H_2 & \longrightarrow & C_6H_6 \\ \Delta H & = & \mathbf{-3.8\ k\ cal} \end{array}$$

Ans.

ΔH in k cal

(*i*) 6 × – 97 = – 582

(*ii*) 3 × – 68.4 = – 205.2

(*iii*) – (– 783.4) = + 783.4

$\therefore$ ΔH = – 582 – 205.2 + 783.4 = – 3.8 k cal

EXAMPLE 40. *The standard enthalpy of formanation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ are 52, –394 and –286 kJ mol⁻ respectively. Then the amount of heat evolved by burning 7.0g of $C_2H_4(g)$ is:*

(*a*) *1412 kJ* (*b*) *9884 kJ*
(*c*) *353 kJ* (*d*) *706 kJ*

(HP Board, 2007, J and K-CET, 2011)

Solution. From the given data:

(*i*) $2C(s) + 2H_2(g) \longrightarrow C_2H_4(g); \Delta H = 52 \text{ kJ}$

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H = -394 \text{ kJ}$

(*iii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H = -286 \text{ kJ}$

Required equation is:

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g); \quad \Delta H = ? \qquad ...(1)$$

In order to get equation (1), we have:

– equation (*i*) + 2 × equation (*ii*) + 2 × equation (*iii*).

$$\begin{aligned} \therefore\ & -2C(s) - 2H_2(g) && \\ & + 2C(s) + 2O_2(g) \longrightarrow && -C_2H_4(g) + 2CO_2(g) \\ & + 2H_2(g) + O_2(g) && + 2H_2O(l) \\ \text{or } & C_2H_4(g) + 3O_2(g) \longrightarrow && 2CO_2(g) + 2H_2O(g); \\ & (2 \times 12) + (4 \times 1) = 28\text{g} && \Delta H = -1412 \text{ kJ} \end{aligned}$$

28g $C_2H_4(g)$ liberate heat = 1412 kJ

7.0g $C_2H_4(g)$ liberates heat = $\frac{1412}{28} \times 7 = 353$ kJ.

So, the correct answer is (*c*).

ΔH in kJ

(*i*) -52

(*ii*) $2 \times -394 = -788$

(*iii*) $2 \times -286 = -572$

Total $\Delta H = -1412$ kJ

Example 41. *Calculate the standard enthalpy change for the reaction:*

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g).$$

Given that $\Delta_f H°$, for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are –393.5, –110.5 and –244.8 kJ mol^{-} respectively. **ISC, 2011**

Solution. To form $CO_2(g)$, $CO(g)$ and $H_2O(g)$, we have:

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g); \Delta H = -393.5 \text{ kJ mol}^{-}$

(*ii*) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g); \quad \Delta H = -110.5 \text{ kJ mol}^{-}$

(*c*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \quad \Delta H = -244.8 \text{ kJ mol}^{-}$

Given: $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g), \quad \Delta H = ? \qquad ...(A)$

In order to get equation (A), we have:

– equation (*i*) + equations (*ii*) + equation (*iii*). So, we have:

ΔH in kJ mol^{-}

(*i*) $-(-393.5) = +393.5$

(*ii*) -110.5

(*iii*) -244.8

Total; $\Delta H = +38.2$ kJ mol^{-}.

$$\begin{aligned} & -C(s) - O_2(g) + C(s) + \tfrac{1}{2}O_2(g) \longrightarrow && -CO_2(g) \\ & + H_2(g) + \tfrac{1}{2}O_2(g) && + CO(g) \\ & && + H_2O(g) \end{aligned}$$

Or $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g);$

$\Delta H = +38.2 \text{ kJ mol}^{-}$ **Ans.**

Example 42. *Calculate the heat of formation of ethyl acetate from ethyl alcohol and acetic acid, given the heat of combustion of ethyl alcohol is 34.0 k cal, of acetic acid is 21.0 k cal and of ethyl acetate is – 55.4 k cal.*

Solution. The required equation is :

$$C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O; \quad \Delta H = ? \qquad ...(A)$$

Reactions of heat of combustion are :

(*i*) $C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O; \quad \Delta H = -34.0 \text{ k cal}$

(*ii*) $CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O; \quad \Delta H = -21.0 \text{ k cal}$

(*iii*) $CH_3COOC_2H_5 + 5O_2 \longrightarrow 4CO_2 + 4H_2O; \quad \Delta H = -55.4 \text{ k cal.}$

In order to get equation (A),
we have equation (*i*) + equation (*ii*) – equation (*iii*)

$$\begin{aligned} & C_2H_5OH + 3O_2 + CH_3COOH \longrightarrow && 2CO_2 + 3H_2O \\ & + 2O_2 - CH_3COOC_2H_5 - 5O_2 && + 2CO_2 + 2H_2O \\ & && - 4CO_2 - 4H_2O \end{aligned}$$

or $C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O$

$\Delta H = 0.4$ k cal **Ans.**

ΔH in k cal

(*i*) -34

(*ii*) -21

(*iii*) $-(-55.4) = +55.4$

$\Delta H = -34 - 21 + 55.4$
$= 0.4$ k cal

Example 43. *Calculate the heat of formation of KCl from the following data.*

(*i*) $KOH(aq) + HCl(aq) \longrightarrow KCl(aq) + H_2O; \quad \Delta H = -13.7 \text{ k cal}$

(*ii*) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \ \Delta H = -68.4 \text{ k cal}$

(*iii*) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 + aq \longrightarrow HCl(aq); \quad \Delta H = -39.3 \text{ k cal}$

(*iv*) $K + \frac{1}{2}O_2 + \frac{1}{2}H_2 + aq \longrightarrow KOH(aq); \quad \Delta H = -116.5 \text{ k cal}$

(*v*) $KCl + aq \longrightarrow KCl(aq); \ \Delta H = +4.4 \text{ k cal}$

Solution. The required equation is :

$$K + \frac{1}{2}Cl_2 + aq \longrightarrow KCl(aq); \ \Delta H = ? \qquad ...(A)$$

In order to get equation (*A*), we have, equation (*iv*) + equation (*iii*) – equation (*v*) + equation (*i*) – equation (*ii*).

$$\begin{array}{ll} K + \frac{1}{2}O_2 + \frac{1}{2}H_2 + aq + \frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow & KOH(aq) \\ & + HCl(aq) \\ + aq - KCl - aq + KOH(aq) & - KCl(aq) \\ + HCl(aq) - H_2 - \frac{1}{2}O_2 & + KCl(aq) + H_2O \\ & - H_2O \\ \text{Or} \quad K + \frac{1}{2}Cl_2 + aq \longrightarrow & KCl; \\ \Delta H = -105.5 \text{ k cal} & \text{Ans.} \end{array}$$

ΔH in k cal

(*iv*) – 116.5

(*iii*) – 39.3

(*v*) – 4.4

(*i*) – 13.7

(*ii*) – (– 68.4) = + 68.4

$\Delta H = -116.5 - 39.3 - 4.4 - 13.7 + 68.4 = -105.5$ k cal

15.22 $\Delta E = \Delta H - \Delta n_{(g)}RT$

ΔE = ΔH – ΔnRT where ΔE and ΔH are the enthalpies of a reaction at constant volume and constant pressure respectively; Δn = no. of mole of gaseous products – no. of mol of gaseous reactants; R = 0.002 k cal; T = t°C + 273.

Example 44. *Calculate the heat of formation of ethanol at constant volume from the following data at 27°C.*

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -94$ k cal

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -68.3$ k cal

(*iii*) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);$ $\Delta H = -326.7$ k cal

Solution. The required equation is :

$$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l); \quad \Delta H = ? \quad ...(A)$$

In order to get equation (*A*), we have, 2 × equation (*i*) + 3 × equation (*ii*) – equation (*iii*)

$$\begin{array}{ll} 2C(s) + 2O_2(g) + 3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow & 2CO_2(g) + 3H_2O(l) \\ - C_2H_5OH(l) - 3O_2(g) & - 2CO_2(g) - 3H_2O(l) \\ \text{or } 2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow & C_2H_5OH(l) \\ \Delta H = -66.2 \text{ k cal} & \end{array}$$

Enthalpy at constant volume = ΔE = ?

ΔH in k cal

(*i*) 2 × – 94

(*ii*) 3 × – 68.3

(*iii*) – (– 326.7)

∴ ΔH = – 188 – 204.9 + 326.7 = – 66.2 k cal.

But, ΔH = ΔE + ΔnRT

[Δn = (no. of mol of gaseous products – no. of mol of gaseous reactants in reaction A

$= 0 - \frac{1}{2} - 3 = -3\frac{1}{2}$ or -3.5]

∴ $-66.2 = \Delta E + (-3.5) \times (2 \times 10^{-3}$ k cal$) \times (27 + 273)$ K

[∵ R = 2×10^{-3} k cal; T = 27 + 273 = 300 K]

∴ $\Delta E = -66.2 + 3.5 \times 2 \times 10^{-3} \times 300$

$= -66.2 + 2.1 = -64.1$ k cal **Ans.**

15.23 HEAT OF REACTION

Example 45. *Calculate the heat of reaction for the formation of benzene from acetylene at 25°C according to the equation.*

$$3C_2H_2 \longrightarrow C_6H_6$$

Given the heats of combustion for 2 moles each of benzene and acetylene respectively are –1598.7 k cal and –620.1 k cal.

Solution. Required equation is :

$$3C_2H_2 \longrightarrow C_6H_6;\ \Delta H = ? \quad ...(A)$$

Reactions.

$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$;

2 mol ΔH = –1598.7 k cal

∴ (*i*) $C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$

1 mol $\Delta H = \frac{-1598.7}{2} = -799.35$ k cal

Also, $2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$;

2 mol ΔH = –620.1 k cal

∴ (*ii*) $C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$;

1 mol $\Delta H = \frac{-620.1}{2} = -310.05$ k cal

In order to get equation (*A*),
we have, 3 × equation (*ii*) – equation (*i*).

$$\begin{array}{ll} 3C_2H_2 + \frac{15}{2}O_2 - C_6H_6 - \frac{15}{2}O_2 \longrightarrow & 6CO_2 + 3H_2O \\ & -6CO_2 - 3H_2O \\ \text{or} \quad 3C_2H_2 \longrightarrow & C_6H_6 \\ \Delta H = -130.80 \text{ k cal} & \text{Ans.} \end{array}$$

ΔH in k cal

(*ii*) 3 × – 310.05 = – 930.15

(*i*) – (–799.35) = +799.35

ΔH = –930.15 + 799.35

= –130.80 k cal

Example 46. *Calculate $\Delta_f H°$ for the chloride ions from the following data.*

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g);$$

$$\Delta_f H° = -92.4 \text{ kJ}$$

$$HCl(g) + nH_2O \longrightarrow H^+(aq) + Cl^-(aq)$$

$\Delta H_{298} = -74.8\ kJ;\ \Delta_f H^\circ\ (H^+)aq = 0.0 kJ$

(Roorkee entrance, 1992)

Solution. The required equation is :

$$\frac{1}{2}\ Cl_2(g) + e^- + nH_2O \longrightarrow Cl^-(aq)\ ;$$

$$\Delta_f H^\circ = ? \qquad ...(A)$$

Given. (*i*) $\frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) \longrightarrow HCl(g)\ ;$

$\Delta_f H^\circ = -92.4$ kJ

(*ii*) $HCl(g) + nH_2O \longrightarrow H^+(aq) + Cl^-(aq)\ ;$

$\Delta H_{298} = -74.8$ kj

(*iii*) $\frac{1}{2}\ H_2(g) + nH_2O \longrightarrow H^+(aq) + e^-\ ;\ \Delta_f H^\circ = 0$

In order to get equation (*A*), we have,

equation (*i*) + equation (*ii*) – equation (*iii*)

$$\begin{array}{lcl} \frac{1}{2}\ H_2(g) + \frac{1}{2}\ Cl_2(g) & \longrightarrow & HCl(g) \\ + HCl(g) + nH_2O & & + H^+(aq) + Cl^-(aq) \\ -\frac{1}{2}\ H_2(g) - nH_2O & & -H^+(aq) - e^- \end{array}$$

Or $\frac{1}{2}\ Cl_2(g) + e^- + nH_2O \longrightarrow Cl^-(aq); \Delta_f H^\circ$

$= -167.2$ kJ **Ans.**

ΔH in kJ

(*i*) – 92.4

(*ii*) – 74.8

(*iii*) 0

ΔH = –92.4 – 74.8 = – 167.2 kJ.

Example 47. *Determine the enthalpy of reaction.*

$$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$$

at 25°C, using the given enthalpy of combustion values under standard conditions.

Compound	$H_2(g)$	$CH_4(g)$	$C_2H_6(g)$	*C(graphite)*
$\Delta_c H^\circ (kJmol^-)$	–285.8	–890.0	–1560.0	–393.5

The standard enthalpy of formation of $C_3H_8(g)$ is –103.8 kJ mol$^-$ **(IIT 1992)**

Solution. Required equation is :

$C_3H_8(g) + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)\ ;\ \Delta H = ?$ ...(*A*)

Given. (*i*) $C(graphite) + O_2(g) \longrightarrow CO_2(g)\ ;$

$\Delta_c H^\circ = -393.5$ kJ

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\ ;\ \Delta_c H^\circ = -285.8$ kJ

(*iii*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)\ ;$

$\Delta_c H^\circ = -890$ kJ

(*iv*) $C_2H_6(g) + \frac{7}{2}\ O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)\ ;$

$\Delta_c H^\circ = -1560$ kJ

(*v*) $3C\ (graphite) + 4H_2(g) \longrightarrow C_3H_8(g)\ ;$

$\Delta_r H^\circ = -103.8$ kJ

In order to get equation (*A*), we have, 5 × equation (*ii*) + 3 × equation (*i*) – equation (*v*) – equation (*iv*) – equation (*iii*)

$$\begin{array}{lcl} 5H_2(g) + \frac{5}{2}\ O_2(g) + 3C(graphite) & \longrightarrow & 5H_2O(l) + 3CO_2(g) \\ + 3O_2(g) - 3C(graphite) - 4H_2(g) & & - C_3H_8(g) - 2CO_2(g) \\ - C_2H_6(g) - \frac{7}{2}\ O_2 - CH_4(g) - 2O_2(g) & & - CO_2(g) - 2H_2O(l) \\ \text{or } C_3H_8(g) + H_2(g) & \longrightarrow & C_2H_6(g) + CH_4(g) \end{array}$$

$\Delta_r H^\circ = -55.7$ kJ

ΔH in kJ

(*ii*) 5 × –285.8 = – 1429

(*i*) 3 × –393.5

= – 1180.5

(*v*) – (–103.8) = +103.8

(*iv*) (– 1560) = + 1560

(*iii*) – (– 890) = + 890

∴ ΔH = –1429 – 1180.5

+ 103.8 + 1560

+ 890

= –55.7 k J

15.24 HEAT OF COMBUSTION

Example 48. *Calculate heat of combustion of glucose from the following data.*

(*i*) $C(graphite) + O_2(g) \longrightarrow CO_2(g)\ ;$

$\Delta H = -395.0\ kJ$

(*ii*) $H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l)\ ;$

$\Delta H = -269.4\ kJ$

(*iii*) $6C(graphite) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6(s)\ ;$

$\Delta H^\circ = -1169.8\ kJ$

Solution. The required equation is :

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)\ ;$$

$$\Delta H = ? \qquad ...(A)$$

In order to get equation (*A*), we have, – equation (*iii*) + 6 × equation (*i*) + 6 × equation (*ii*)

$$\begin{array}{lcl} -6C(graphite) - 6H_2(g) - 3O_2(g) & \longrightarrow & -C_6H_{12}O_6(s) \\ +6C(graphite) + 6O_2 & & + 6CO_2(g) \\ + 6H_2(g) + 3O_2(g) & & + 6H_2O(l) \\ \text{or} \quad C_6H_{12}O_6(s) + 6O_2(g) & \longrightarrow & 6CO_2(g) + 6H_2O(l); \end{array}$$

$\Delta H = -2816.6$ kJ **Ans.**

ΔH in kJ

(*iii*) –(–1169) = + 1169

(*i*) 6 × – 395 = –2370

(*ii*) 6 × –269.4

= –1616.4

∴ ΔH = –2370 – 1616.4

+ 1169

= –2816.6 k J

EXAMPLE 49. *Calculate the enthalpy change for the reaction:* $C_{(graptite)} + 2H_2(g) \longrightarrow CH_4(g)$. Given that:

(*i*) $C_{(graptite)} + O_2(g) \longrightarrow CO_2(g); \Delta_f H° = -393.5\text{ kJ mol}^{-}$

(*ii*) $H_2(g) + 0.5\ O_2(g) \longrightarrow H_2O(l); \Delta_f H° = -285.8\text{ kJ mol}^{-}$

(*iii*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);$
$\Delta_f H° = -890.3\text{ kJ mol}^{-}$ **(ISC, 2010)**

SOLUTION. The required equation is:

$C_{(graptitie)} + 2\ H_2(g) \longrightarrow CH_4(g); \Delta_f H° = ?$ ...(A)

In order to get equation (A) from equations (*i*), (*ii*) and (*iii*), we have; equation (*i*) + 2 × equation (*ii*) – equation (*iii*). Thus:

$$\begin{aligned} C_{graptite} + O_2(g) + 2H_2(g) + O_2(g) &\longrightarrow CO_2(g) + 2H_2O(l) \\ -CH_4(g) - 2O_2(g) &\qquad -CO_2(g) \end{aligned}$$

or $\quad Cgraptite + 2H_2(g) \longrightarrow CH_4(g);$

$\Delta_f H° = -74.8\text{ kJ mol}^{-}$ **Ans.**

$$\begin{aligned} [\because \Delta_f H° &= -393.5 \\ &\quad - 2\,(285.8) \\ &\quad -(-890.3)\text{ kJ mol}^{-} \\ &= -74.8\text{ kJ mol}^{-}] \end{aligned}$$

EXAMPLE 50. *Calculate the enthalpy of combustion of ethylene at 298 K and one atmospheric pressure. Given that enthalpy of formation of* $CO_2(g)$, $H_2O(l)$ *and* C_2H_4 *are –393.7 kJ/mol, –241.8 kJ/mol and +52.3 kJ/mol respectively.* **(HP Board, 2007)**

SOLUTION. *Required equation is :*

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)\ ;$

$\Delta H = ?$ ...(A)

Given : (*i*)$C(s) + O_2(g) \longrightarrow CO_2(g)\ ;$

$\Delta H = -393.7\text{ kJ mol}^{-}$

(*ii*) $H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l)\ ;$

$\Delta H = -241.8\text{ kJ mol}^{-}$

(*iii*) $2C(s) + 2H_2(g) \longrightarrow C_2H_4(g)\ ;$

$\Delta H = +52.3\text{ kJ mol}^{-}$

In order to get equation (A), we have :

2 × equation (i) + 2 × equation (ii) – equation (iii)

$$\begin{aligned} 2C(s) + 2O_2(g) &\longrightarrow 2CO_2(g) + 2H_2O(l) \\ + 2H_2(g) + O_2(g) &\qquad - C_2H_4(g) \\ - 2C(s) - 2H_2(g) & \end{aligned}$$

Or $\quad C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$

$\Delta H = -1323.3\text{ kJ mol}^{-}$ **Ans.**

ΔH in kJ mol^{-}

(*i*) $2 \times -393.7 = -787.4$

(*ii*) $2 \times -241.8 = -483.6$

(*iii*) $-(+52.3) = -52.3$

$\therefore \Delta H = -787.4 - 483.6 - 52.3$

$= -1323.3\text{ kJ mol}^{-}$

EXAMPLE 51. *Find the amount in kg of water at 20°C that is needed to convert into steam at 100°C by burning 1 L of ethene (of 70% efficiency) measured at NTP. The enthalpy of combustion of ethene is –337 k cal. Latent heat of vaporisation of water is 540 k cal g*$^{-}$.

SOLUTION. Rise in temperature

= 100°C – 20°C = 80°C

Let wt. of water = Wg

Heat required to raise temperature of 1 kg of H_2O through 1°C = 1 k cal.

Heat required to raise temperature of W g of H_2O from 20°C to 100°C

= W × 80 k cal

Heat required to convert W g of water at 100°C to Wg steam at 100°C

= W × 540 k cal.

(*a*) $\therefore$ Total heat needed

= 80W + 540W = 620W k cal.

(*b*) **Given** $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l);$

22.4 L

$\Delta H = -337$ k cal

For 22.4 L $C_2H_4(g)$, heat liberated

= 337 k cal

For 1L $C_2H_4(g)$, heat liberated

$$= \frac{337}{22.4} = 15.04\text{ k cal}$$

For 1L $C_2H_4(g)$ of 70% efficiency, heat liberated

$$= 15.04 \times \frac{70}{100} = 10.53\text{ k cal}$$

From (*a*) and (*b*), 620 W

= 10.53 k cal

$$W = \frac{10.53}{620} = \mathbf{0.017\ kg}$$ **Ans.**

EXAMPLE 52. *A person requires on an average, 2900 k cal of energy to lead a normal life. If the person is to live on cane sugar only, how many kilogram of cane sugar* ($C_{12}H_{22}O_{11}$) *would be required for survival. The heats of formation of cane sugar,* $H_2O(l)$ *and* $CO_2(g)$ *are –503.3, –68.3 and –94 k cal mol*$^{-}$ *respectively.*

SOLUTION. The required equation is :

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)\ ;$

$\Delta H = ?$ ...(A)

The given equations are :

(*i*) $12C(s) + 11H_2(g) + \frac{11}{2}O_2(g) \longrightarrow C_{12}H_{22}O_{11}(s)\ ;$

$\Delta H = -530.3$ k cal.

(*ii*) $C(s) + O_2(g) \longrightarrow CO_2(g)\ ;$

$\Delta H = -94$ k cal.

(*iii*) $H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l)\ ;$

$\Delta H = -68.3$ k cal

In order to get equation (*A*), we have : 12 × equation (*ii*) +11 × equation (*iii*) – Equation (*i*)

$$\therefore \quad 12C(s) + 12O_2(g) + 11H_2(g) + \frac{11}{2}O_2(g) - 12C(s) - 11H_2(g) - \frac{11}{2}O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l) - C_{12}H_{22}O_{11}(s)$$

or $C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$

$; \Delta H = -1349$ k cal.

g. mol. wt. of $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 × 16)

= 342 g

$= \dfrac{342}{1000} = 0.342$ kg.

Cane sugar required to produce 1349 k cal energy

= 0.342 kg

Cane sugar required to produce 2900 k cal energy

$= \dfrac{0.342 \times 2900}{1349}$

= **0.735 kg**

ΔH values

(*ii*) 12 × –94 = – 1128 k cal

(*iii*) 11 × –68.3 = –751.3 k cal

(*i*) +530.3 k cal

$\therefore \Delta H = -1128 - 751.3 + 503.3$

$= -1349$ k cal

Example 53. *Air contains 21% of oxygen by volume. The air exhaled by a person contains 16.1% of oxygen by volume. A person breathes 15 times a minute and air inhaled per breath is 450 mL. The temperature of inhaled and exhaled air is 298 K. Suppose whole of the oxygen is used for the combustion of sucrose in the body, calculate the amount of sucrose burnt per day in the body and the amount of heat produced. ΔH (combustion) for sucrose is –5645 kJ mol*$^{-}$.

Solution. 1 day = 24 hours = 24 × 60 = 1440 minutes.

(*i*) 100 mL of inhaled air contains oxygen = 21 mL

∴450 mL air contains oxygen

$= \dfrac{21 \times 450}{100} = 94.5$ mL

(*ii*) 100 mL of exhaled air contains oxygen

= 16.1 mL

450 mL of exhaled air contains oxygen

$= \dfrac{16.1 \times 450}{100} = 72.45$ mL

∴Volume of oxygen actually inhaled

= 94.50 – 72.45

= 22.05 mL per minute

∴Volume of oxygen inhaled in 1440 minutes at the rate of 15 breaths per minute

= 15 × 1440 × 22.05 = 476280 ml

$= \dfrac{476280}{1000}$ L = 476.28 L

But, $PV = nRT$

Or $n = \dfrac{PV}{RT}$

Where n = number of moles of oxygen inhaled per day

$$\therefore \quad n = \frac{1\,\text{atm} \times 476.28\,\text{L}}{0.0821\,\text{L atm K}^{-}\text{mol}^{-} \times 298\,\text{K}}$$

= 19.467 mol.

Combustion of sucrose ($C_{12}O_{22}O_{11}$) in O_2 is given as :

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$;

1 mol = 342 g   12 mol   ΔH = –5645 kJ

(*a*) 12 mol O_2 is needed to burn sucrose = 1 mol

19.467 mol O_2 is needed to burn sucrose

$= \dfrac{19.467}{12} = 1.622$ mol

= 1.622 × 342 g = **554.7 g.**

(*b*) Heat evolved to burn 1 mol $C_{12}H_{22}O_{11}$ = –5645 kJ

Heat evolved to burn 1.622 mol $C_{12}H_{22}O_{11}$ = –5645 × 1.622 = **–9156.19 kJ**

Example 54. *An LPG cylinder contains 11.2 kg of n-butane. A family requires 19,000 kJ of energy per day for cooking purpose. Calculate the time in days the cylinder will work if enthalpy of combustion of n-butane is –2658 kJ.*

Solution. g. mol. wt. of n-butane, C_4H_{10} = (4 × 12) + (10 × 1) = 58 g.

Combustion of n-butane is represented as :

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g) ;$$

$$\Delta H = -2658 \text{ kJ}$$

Wt. of n–butane = 11.2 kg = 11.2 × 1000 = 11200 g

58 g n-butane produce heat

= 2658 kJ

∴ 11200 g n-butane will produce heat

$= \dfrac{2658}{58} \times 11200 = 513268.97$ kJ

19,000 kJ heat is needed for days = 1

∴ 513268.97 kJ heat is needed for days

$= \dfrac{513268.97}{19{,}000} = 27$ days **Ans.**

Example 55. *You are given the following data.*

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\,;\ \Delta H = -68.3$ *k cal*

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)\,;\ \Delta H = -57$ *k cal.*

Calculate the amount of heat needed to convert 1g $H_2O(l)$ *to 1g* $H_2O(g)$*. Also, calculate the enthalpy of vaporisation for water.*

Solution. The required equation is :

$$H_2O(l) \longrightarrow H_2O(g)\ ;\ \Delta H = ? \quad ...(A)$$

Given : (*i*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)\ ;\ \Delta H = -68.3$ k cal

(*ii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)\ ;\ \Delta H = -57$ k cal.

In order to get equation (A), we have ; Equation (*ii*) –Equation (*i*).

$$\begin{array}{llcl} \text{Thus :} & H_2(g) + \frac{1}{2} O_2(g) & \longrightarrow & H_2O(g) \\ & -H_2(g) - \frac{1}{2} O_2(g) & & -H_2O(l) \\ \text{or} & H_2O(l) & \longrightarrow & H_2O(g)\ ; \\ & (2 \times 1) + 16 = 18\ g & & \end{array}$$

ΔH = **11.3 k cal** **Ans.**

18 g $H_2O(l)$ needs enthalpy of vaporisation = 11.3 k cal

∴ 1 g $H_2O(l)$ needs enthalpy of vaporisation

$$= \frac{11.3}{18} = \mathbf{0.628\ k\ cal} \qquad \textbf{Ans.}$$

Example 56. *Calculate the heat produced by burning 2m^3 of methane gas measured under normal conditions from the following data. Standard heat of formation of CH_4, H_2O and CO_2 in kJ mol^{-} are –76.2, –241.6 and –394.8 respectively.*

Solution. Required equation is :

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O\ ;\ \Delta H = ?\ ...(A)$$

Given : (*i*) $C + 2H_2 \longrightarrow CH_4\ ;\ \Delta H = -76.2$ kJ

(*ii*) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O\ ;\ \Delta H = -241.6$ kJ

(*iii*) $C + O_2 \longrightarrow CO_2\ ;\ \Delta H = -394.8$ kJ

In order to get equation (A), we have :

Equation (*iii*) +2 × Equation (*ii*) –Equation (*i*)

$$\begin{array}{lrcl} & C + O_2 + 2H_2 + O_2 & \longrightarrow & CO_2 + 2H_2O \\ & -C - 2H_2 & & -CH_4 \\ \text{or} & CH_4 + 2O_2 & \longrightarrow & CO_2 + 2H_2O\ ; \\ & 1\ \text{mol} & & \Delta H = -801.8\ \text{kJ} \\ & = 22.4 \times 10^{-3}\ m^3 & & \end{array}$$

ΔH values

(*iii*) –394.8 kJ

(*ii*) 2 × (–241.6) kJ = –483.2 kJ

(*i*) +76.2 kJ

$$\therefore\ \Delta H = -394.8 - 483.2 + 76.2 = -801.8\ \text{kJ}$$

22.4×10^{-3} m^3 CH_4 gives energy on burning = 801.8 kJ

∴ 2 m^3 CH_4 gives energy on burning

$$= \frac{801.8\,\text{kJ} \times 2\,\text{m}^3}{22.4 \times 10^{-3}\,\text{m}^3} = 71589.3\,\text{kJ} \quad \textbf{Ans.}$$

Example 57. *From the following data, calculate the heat of reaction for the hydrogenation of ethyne to ethene at constant volume at 298 K.*

(*i*) *Enthalpy of combustion of ethyne = –1299.6 kJ mol^{-}*

(*ii*) *Enthalpy of combustion of ethene = – 1410.8 kJ mol^{-}*

(*iii*) *Enthalpy of formation of water = – 285.8 k J mol^{-}*

Solution. Hint. Required equation is :

$$\begin{array}{ccccl} C_2H_2 & + & H_2 & \longrightarrow & C_2H_4\ ;\ \Delta H = ? \end{array}$$

Find ΔH = –174.6 kJ.

1 mol 1 mol 1 mol

But heat of reaction at constant volume = ΔE

$$\begin{aligned} \text{Hence, we have } \Delta H &= \Delta E + \Delta nRT \\ \text{or} \qquad \Delta E &= \Delta H - \Delta nRT \\ &= -174.6\ \text{kJ} - (-1)\ \text{mol} \times 8.314 \\ &\quad \times 10^{-3}\ \text{kJK}^{-}\text{mol}^{-} \times 298\text{K} \\ \Delta E &= -174.6\ \text{kJ} + 2.48 \\ &= \mathbf{-172.2\ kJ} \qquad \textbf{Ans.} \end{aligned}$$

Example 58. *$\Delta H_f°$ for $Ca^{2+}(aq)$, CO_3^{2-} (aq) and $CaCO_3(s)$ are –129.80, –161.65 and –288.5 k cal mol^{-} respectively. Find the enthalpy change when infinitely dilute solutions of Na_2CO_3 and $CaCl_2$ are mixed to-gether.*

Solution. Since the solutions are very dilute, so Na_2CO_3 and $CaCl_2$ are 100% ionised. The reaction can be written as :

$$Na_2CO_3(aq) + CaCl_2(aq) \longrightarrow CaCO_3(s) + 2NaCl(aq)$$

$$\text{or } CO_3^{2-}(aq) + Ca^{2+}(aq) \longrightarrow CaCO_3(s)\ ;\ \Delta H = ?$$

$$\begin{aligned} \therefore \qquad \Delta H &= \Sigma H°\,(\text{products}) - \Sigma H°\,(\text{reactants}) \\ &= H°\,[CaCO_3(s)] - [H°\,\{CO_3^{2-}(aq)\} \\ + H°\,Ca^{2+}(aq)] &= -288.5\ \text{k cal} - (-161.65 - 129.8) \\ \text{k cal} &= -288.5 + 161.65 + 129.8\ \text{k cal} \\ \Delta H &= \mathbf{+2.95\ k\ cal} \qquad \textbf{Ans.} \end{aligned}$$

Example 59. *The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are –76.2, – 394.6 and –241.8 kJ mol^{-1}, respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal conditions.*

(Roorkee, 1990)

Solution. Required equation :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)\ ;\ \Delta H° = ?$$

$$\begin{aligned} \Delta H° &= \Delta H°(\text{Products}) - \Delta H°(\text{reactants}) \\ &= \Delta H°(CO_2) + 2\,[\Delta H°(H_2O)] - \Delta H°(CH_4) \\ &\quad - 2[\Delta H°\,(O_2)] \\ &= -394.8 + 2x - 241.6 - (-76.2) - 2 \times 0 \\ &\qquad [\because\ \Delta H° \text{ of elements like } O_2 = 0] \\ &= -394.8 - 483.2 + 76.2 = -801.8\ \text{kJ mol}^{-} \end{aligned}$$

But, 1m^3 = 1000 dm^3 ; 1L = 1 dm^3. Also :

1 mol or 22.4 L or 22.4 dm^3 of CH_4 produce heat

= 801.8 kJ mol^{-}

∴ 1000 dm^3 of CH_4 produce heat

$$= \frac{801.8}{22.4} \times 1000 = \mathbf{35794.6\ kJ\ mol^{-}} \qquad \textbf{Ans.}$$

Example 60. *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 k cal/mol respectively. Calculate ΔH°298 for the reaction.

$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$ **(IIT 1982)**

Solution. ΔH°298 for the reaction :

$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$

$= \Delta H°(\text{products}) - \Delta H°(\text{reactants})$

$= [\Delta_f H° \text{ of } CO_{2(g)} + 4\Delta_f H° \text{ of } HCL_{(g)}]$

$-[\Delta_f H° CCl_{4(g)} + 2\Delta_f H° \text{ of } H_2O_{(g)}]$

$= [-94.1 + 4 \times (-22.1)] - [-25.5 + 2(-57.8)]$

$= -182.5 + 141.1 =$ **–41.4 k cal.**

Example 61. *Calculate the enthalpy of decomposition of $CaCO_3$ into CaO and CO_2. The ΔH of formation ($\Delta_f H°$) are –288.5 k cal/mol for $CaCO_3$, –151.9 k cal/mol for CaO and –94.0 k cal/mol for CO_2.* **(BCECE 1998)**

Solution. The required equation is :

$CaCO_3 \longrightarrow CaO + CO_2;\ \Delta_r H° = ?$

$\Delta_f H° = \Sigma\, \Delta H°_f(\text{products}) - \Sigma\, \Delta H°_f(\text{reactants})$

$= \Delta_f H°\,(CaO) + \Delta H°_f\,(CO_2) - \Delta_f H°(CaCO_3)$

$= (-151.9 - 94.0 + 288.5)$ k cal = **42.6 k cal**

Example 62. *Metabolism of glucose provides energy for our growth and body function. In this process CO_2 and H_2O are produced as metabolites. An overall reaction for this complex process is given as :*

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

If 856 g of $C_6H_{12}O_6$ is consumed by the body over a certain period, what is the mass of CO_2 produced?

[Molar mass of CO_2 = 44.01 g ; molar mass of $C_6H_{12}O_6$ = 180.2 g]

Solution. According to the given data,

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

180.2 g $\quad$ 6 × 44.01 = 264.06 g

180.2 g of glucose produce

$CO_2 = 264.06$ g

856 g of glucose produce

$CO_2 = \dfrac{264.06 \times 856}{180.2} =$ **1254.3 g**

Example 63. *An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilises 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of water is 44 kJ/mole.* **(IIT 1989)**

Solution. Energy given to athlete = 1560 kJ

Energy utilised by athlete $= 1560 \times \dfrac{50}{100}$

= 780 kJ

Excess energy = 1560 – 780

= 780 kJ

Enthalpy of evaporation of water = 44 kJ/mole

∴ 44 kJ of energy is used in the perspiration of water = 18 g

780 kJ of energy is used in the perspiration of water

$= \dfrac{18}{44} \times 780 =$ **319 g**

Example 64. *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 isomerisation of cyclopropene to propene is –33.0 kJ mol^{-1}.*

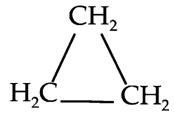
(IIT 1998)

Solution. According to the given data :

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta_f H° = -393.5$ kJ

(*ii*) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l);\ \Delta_f H° = -285.8$ kJ

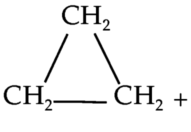
(*iii*) $3C(s) + 3H_2(g) \longrightarrow C_3H_6(g);\ \Delta_f H° = +20.42$ kJ



$\longrightarrow C_3H_6(g);\ \Delta_f H° = -33.0$ kJ

(*iv*) cyclopropane $\quad$ Propene

The required equation is :

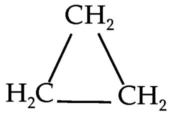


$+ \frac{9}{2} O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l)\ \Delta H = ?$ ...(*A*)

In order to get equation (A), we have equation 3 × (*i*) + 3 × (*ii*) + (*iv*) – (*iii*)

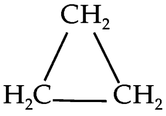
$3C(s) + 3O_2(g) + 3H_2(g) + \frac{3}{2} O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l) + C_3H_6(g) - C_3H_6(g)$

\+



$-3C(s) - 3H_2(g)$

or



$+ \frac{9}{2} O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l)$

ΔH° = –2091.32 kJ **Ans.**

ΔH° in kJ

(*i*) 3 × –393.5 = –1180.5

(*ii*) 3 × –285.8 = –857.4

(*iv*) –33

(*iii*) –20.42

∴ ΔH° = –1180.5 – 857.4 – 33 – 20.42

= –2091.32 kJ

Example 65. *Diborane is a potential rocket fuel which undergoes combustion according to the reaction :*

$B_2H_6 + 3O_2 \longrightarrow B_2O_{3(s)} + 3H_2O_{(g)}$

From the following data, calculate the enthalpy change for the combustion of diborane.

(*i*) $2B_{(s)} + \left(\frac{3}{2}\right) O_{2(g)} \longrightarrow B_2O_{3(s)};\ \Delta_f H° = -1273$ kJ mol^{-1}

(*ii*) $H_{2(g)} + \left(\frac{1}{2}\right) O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta_f H° = -286\ kJ\ mol^{-1}$

(*iii*) $H_2O_{(l)} \longrightarrow H_2O_{(g)}$; $\Delta_f H° = 44\ kJ\ mol^{-1}$

(*iv*) $2B(s) + 3H_{2(g)} \longrightarrow B_2H_{6(g)}$; $\Delta_f H° = 36\ kJ\ mol^{-1}$

(IIT 2000)

SOLUTION. The required equation is :

$B_2H_{6(g)} + 3O_{2(g)} \longrightarrow B_2O_{3(g)} + 3H_2O_{(g)}$; $\Delta_f H° = ?$ ...(A)

In order to get equation (A),

we have equation (*i*) + (3 × (*ii*)) + (3 × (*iii*)) – (*iv*)

ΔH in kJ mol^{-}

(*i*) –1273

(*ii*) 3 × –286 = –858

(*iii*) 3 × 44 = 132

(*iv*) –36

∴ ΔH = –1273 – 858 + 132 – 36 = –2035 kJ mol^{-}

$$2B_{(s)} + \frac{3}{2}O_{2(g)} + 3H_{2(g)} + \frac{3}{2}O_{2(g)} \longrightarrow B_2O_{3(s)} + 3H_2O_{(l)}$$
$$+ 3H_2O_{(l)} - 2B_{(s)} - 3H_{2(g)} \qquad + 3H_2O_{(g)} - B_2H_{6(g)}$$

or $B_2H_{6(g)} + 3O_{2(g)} \longrightarrow B_2O_{3(s)} + 3H_2O_{(g)}$

ΔH° = –2035 kJ mol^{-} **Ans.**

EXAMPLE 66. *Determine the heat change in the reaction of one mole of Fe_2O_3 with Al to produce white hot molten iron and Al_2O_3 from the following data.* **(Pb PMT 1981)**

(*i*) $2Al + \frac{3}{2}O_2 \longrightarrow Al_2O_3$; ΔH = – 400 k cal

(*ii*) $2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3$; ΔH = – 200 k cal

SOLUTION. The required thermochemical equation is :

$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$; ΔH = ? ...(A)

In order to get equation (A),

we have, equation (*i*) – equation (*ii*)

$$2Al + \frac{3}{2}O_2 - 2Fe - \frac{3}{2}O_2 \longrightarrow Al_2O_3 - Fe_2O_3$$

or $Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$;

ΔH = – 200 k cal mol^{-} **Ans.**

EXAMPLE 67. *A gas mixture of 3.67 litres of ethylene and methane on complete combustion at 25°C produces 6.11 litres of CO_2. Find out the amount of heat evolved on burning one 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. Combustion of C_2H_4 and CH_4 is represented as :

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

1 Vol. 2 Vol.

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

1 Vol. 1 Vol.

Let V litre be the volume of CH_4 in the mixture.

The volume of C_2H_4 in the mixture

= (3.67 – V) L

Volume of CO_2 formed = V + 2 (3.67 – V)

= 6.11 L (given)

or V + 7.34 – 2V = 6.11 L

or V = 7.34 – 6.11 = 1.23 L

∴ Vol of CH_4 at 25°C = **1.23 L**

Vol. of C_2H_4 at 25°C = 3.67 – 1.23 = **2.44 L**

Vol. of CH_4 in 1 L of gas mixture

$$= \frac{1.23}{3.67}\ L$$

Vol. of C_2H_4 in 1 L of gas mixture

$$= \frac{2.44}{3.67}$$

Vol. of 1 mol. of any gas at 25°C and 1 atm

$$= \frac{22.4}{273} \times 298 = \mathbf{24.45\ L}$$

Heat evolved due to the combustion of CH_4

$$= \frac{1.23 \times 891}{3.67 \times 24.45}\ kJ = 12.213\ kJ$$

Heat evolved due to the combustion of C_2H_4

$$= \frac{2.44 \times 1423}{3.67 \times 24.45}\ kJ = 38.694\ kJ$$

Total heat evolved = 12.213 + 38.694 kJ = 50.907 kJ

EXAMPLE 68. *You are provided with the following thermochemical equation involving the combustion of ethylene gas, C_2H_4,*

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$;

ΔH = – 337 kcal.

Assuming 65% efficiency, calculate the weight of water at 293 K that can be converted into steam by burning 1 m^3 of C_2H_4 gas measured at N.T.P. Heat of vaporisation of water at 293 K and 373 K are one k cal kg^{-} and 540 k cal kg^{-} respectively.

SOLUTION. Given reaction is :

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$;

1 mol ΔH = – 337 k cal

= 22.4 L = 22.4 × 10^{-3} m^3

22.4 × 10^{-3} m^3 C_2H_4 = 1 mol C_2H_4

$$1\ m^3\ C_2H_4 = \frac{1\ m^3}{22.4 \times 10^{-3}\ m^3}\ mol = 44.6\ mol.$$

ΔH for 1 mol C_2H_4 = – 337 k cal.

∴ ΔH for 44.6 mol C_2H_4

= – 337 × 44.6 = – 15030 k cal.

Due to 65% efficiency of C_2H_4,

$$\text{useful heat} = \frac{-15030 \times 65}{100} = 9769.5\ k\ cal$$

For 293 K and 373 K conditions, we have :

$H_2O(l, 293\ K) \longrightarrow H_2O(l, 373\ K)$;

ΔH = 1 kcal kg^{-} K^{-} × (373 – 293 K)

= 80 kcal kg^{-}

$H_2O(l, 373\ K) \longrightarrow H_2O(l, 373\ K)$;

$$\Delta H = 540 \text{ k cal kg}^{-}$$

$$\therefore \quad \text{Total } \Delta H = 80 \text{ k cal kg}^{-} + 540 \text{ k cal kg}^{-}$$

$$= 620 \text{ k cal kg}^{-}$$

Hence amount of water converted into steam

$$= \frac{\text{Total heat available}}{\text{Total heat required per kg}}$$

$$= \frac{9769.5}{620} = \mathbf{15.76\ kg} \qquad \textbf{Ans.}$$

15.25 BOND ENERGIES

(*a*) **Bond dissociation energy.** *The energy required to break a particular bond in a gaseous molecule is called bond dissociation energy.* But when a chemical bond is formed, energy is released. For example, consider the following reactions.

$$H-O-H(g) \longrightarrow H(g) + O(g)\ ;\ \Delta H = 498 \text{ kJ}$$

$$O-H(g) \longrightarrow O(g) + H(g)\ ;\ \Delta H = 430 \text{ kJ}$$

In above type of cases, bond energy is expressed as the average of the bond dissociation energies of different similar bonds

$$\therefore \quad \Delta H_{O-H} = \frac{498 + 430}{2} = 464 \text{ kJ mol}^{-}$$

Hence, **bond energy** is the average amount of energy required to break one mole bonds of that type in gaseous substances. Hence :

(*b*) Bond energies help to calculate bond energies of specific bond in the molecule and to calculate standard enthalpy of reactions.

(*c*) ΔH = B.E. of reactants – B.E. of products.

Example 69. *Calculate the O – H bond energy in the hydroxyl radical, if heat of formation for the reactions at 25°C are given below :*

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g) - 10.06 \text{ k cal}$$

$$H_2(g) \longrightarrow 2H(g) - 104.18 \text{ k cal}$$

$$O_2(g) \longrightarrow 2O(g) - 118.22 \text{ k cal}$$

(IIT, 1981)

Solution. The required equation is :

$$O-H(g) \longrightarrow O(g) + H(g)\ ;$$

$$\Delta H = ? \qquad \text{...(A)}$$

Given (*i*) $\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)\ ;$

$$\Delta H = +\ 10.06 \text{ k cal}$$

(*ii*) $H_2(g) \longrightarrow 2H(g)\ ;$

$$\Delta H = +\ 104.18 \text{ k cal}$$

(*iii*) $O_2(g) \longrightarrow 2O(g)\ ;$

$$\Delta H = +\ 118.22 \text{ k cal}$$

In order to get equation (A), we have;

$\frac{1}{2}$ × equation (*ii*) + $\frac{1}{2}$ × equation (*iii*) – equation (*i*)

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H(g) + O(g)$$

$$-\frac{1}{2}H_2(g) - \frac{1}{2}O_2(g) - OH(g)$$

or $O-H(g) \longrightarrow O(g) + H(g)\ ;$

$$\Delta H = \mathbf{101.14\ k\ cal} \qquad \textbf{Ans.}$$

ΔH in k cal

(*ii*) $\frac{1}{2} \times 104.18 = 52.09$

(*iii*) $\frac{1}{2} \times 118.22 = 59.11$

(*i*) $-(+\ 10.06) = -\ 10.06$

$$\Delta H = 52.09 + 59.11 - 10.06 = 101.14 \text{ k cal}$$

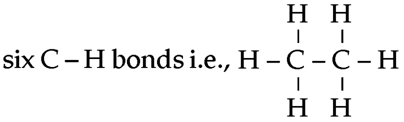
Example 70. *Given:*

$$C_2H_6(g) \longrightarrow 2C(g) + 6H(g);$$

$$\Delta H = 712 \text{ k cal.}$$

The C – C bond energy is 112 k cal. What is the C – H bond energy?

(*a*) 88 k cal	(*b*) 12 k cal
(*c*) 50 k cal	(*d*) 100 k cal **(Orissa, JEE, 2011)**

Solution. C_2H_6 has six C – H bonds i.e.,  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

Given ΔH = 712 k cal. But C – C bond energy is 112 k cal.

$$\therefore \text{ C – H bond energy} = \frac{712-112}{6} = 600 \text{ k cal} = 100 \text{ k cal.}$$

So, the correct answer is (*d*)

Example 71. *Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol⁻ respectively. Enthalpy of formation of HCl is :*

(*a*) –93 kJ mol⁻	(*b*) 245 kJ mol⁻
(*c*) 93 kJ mol⁻	(*d*) –245 kJ mol⁻

(CBSE–PMT, 2008 Prelims)

Solution. Reaction : H—H + Cl – Cl → 2H—Cl

$$\therefore \quad \Delta H_{\text{reaction}} = \Sigma\, BE_{\text{reactants}} - \Sigma\, BE_{\text{products}}$$

$$= (BE_{H-H} + BE_{Cl-Cl}) - (2\ BE_{H-Cl})$$

$$= 434 + 242 - 2(431)$$

$$= 434 + 242 - 862 = \mathbf{-186\ kJ}$$

But heat of formation is the amount of enthalpy absorbed or evolved when one mol of a substance is directly obtained from its constituent elements

$$\therefore \text{ Enthalpy of formation of one mol of HCl} = -\frac{186}{2}$$

i.e., – 93 kJ.

So, the correct answer is (*a*).

15.26 CALCULATING RESONANCE ENERGY

Example 72. *Calculate the heat of formation and resonance energy of isoprene C_5H_8 [$CH_2 = CH - C\ (CH_3) = CH_2$] from the following data if heat of combustion of C_5H_8 into CO_2 and*

H_2O is –3186 kJ mol^{-}. Bond energies of C – C, C = C and C – H bonds are 348, 413 and 615 kJ respectively. Heat of atomisation of hydrogen and carbon are 435.8 and 718.4 kJ mol^{-}.

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $H_1 = -393.5$ kJ mol^{-}

(*ii*) $H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$; $H_2 = -285.84$ kJ mol^{-}

SOLUTION. $\Delta H_f\ [CO_2(g)] = -393.5$ kJ ; $\Delta H_f\ [H_2O(l)] = -285.84$ kJ. Combustion of isoprene, C_5H_8 is given as :

$$C_5H_8(g) + 7O_2(g) \longrightarrow 5\,CO_2(g) + 4H_2O(l)\ ;\quad \Delta H = -3186 \text{ kJ mol}^{-}$$

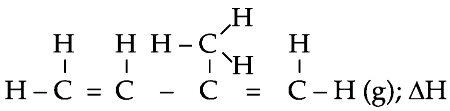
$$\therefore \quad \Delta H = [5\Delta H_f CO_2(g) + 4\Delta H_f H_2O(l) - \Delta H_f C_5H_8(g) - 7 \times \Delta H_f O_2(g)]$$

$$-3186 = 5(-393.5) + 4(-285.84) - \Delta H_f C_5H_8(g) - 0$$

$$\therefore \quad \Delta H_f C_5H_8(g) = +3186 - 1967.5 - 1143.36 = 75.14 \text{ kJ}$$

Heat of formation of $C_5H_8(g)$ can be represented as :

5C(s) + 4H – H (g)



$$\longrightarrow H-\overset{\displaystyle H}{\underset{}{C}}=\overset{\displaystyle H}{C}-\overset{\displaystyle H-C\begin{smallmatrix}H\\H\end{smallmatrix}}{C}=\overset{\displaystyle H}{C}-H\ (g);\ \Delta H = ?$$

ΔH = Bond energy of reactants – Bond energy of products.

$$\therefore \quad \Delta H\ C_5H_8(g) = [5\ \Delta HC(s) - C(g) + 4\ \Delta H_{H-H}] - [2\ \Delta H_{C-C} + 2\ \Delta H_{C=C} + 8\ \Delta H_{C-H}]$$

$$= [5\ (718.4 + 4\ (435.8)] - [2\ (348) + 2\ (413) + 8\ (615)]$$

$$= 3592 + 1743.2 - 696 - 826 - 4920$$

$$= \mathbf{-1106.8\ kJ}$$

∴Resonance Energy

$$= \text{Actual } \Delta H_f C_5H_8(g) - \text{Theoretical } \Delta H_f C_5H_8(g) = 75.14 - (-1106.8)$$

$$= 1181.94 \textbf{ kJ mol}^{-} \qquad \textbf{Ans.}$$

Note. Also, see examples, 75 and 144.

EXAMPLE 73. *Calculate the heat of formation of acetone from the following data.*

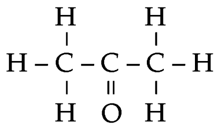
Heat of atomisation in kcal mol^{-} of C = 170.9 ; O = 59.6, H = 52.1. Average bond energies in k cal of C – C = 80, C = O is 81 and C – H = 99.

SOLUTION. Required equation is :

$$3C(s) + 3H_2(g) + ½O_2(g) \longrightarrow CH_3COCH_3(g);\ \Delta H = ?$$

Acetone

or



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

ΔH = Bond energy of reactants – Bond energy of products

$$= [3\ \Delta H_{C(s) \to C(g)} + 3\ \Delta H_{H-H} + 1/2\ \Delta H_{O2}] - [6\ \Delta H_{C-H} + \Delta H_{C=O} + 2\ \Delta H_{C-C}]$$

$$= [(3 \times 170.9) + (6 \times 52.1) + 59.6] - [(6 \times 99) + 81 + (2 \times 80)]$$

$$= 512.7 + 312.6 + 59.6 - 594 - 160 - 81$$

$$= \mathbf{49.9\ k\ cal\ mol^{-}}$$

EXAMPLE 74. *Calculate the bond enthalpies of C ≡ N and C – C bonds from the following data.*

(*i*) *Heat of formation of methyl cyanide, CH_3CN = 87.86 kJ mol^{-}*

(*ii*) *Bond enthalpy of C – H bond = 414.22 kJ mol^{-}*

(*iii*) *Heat of formation of C_2H_6 = – 83.68 kJ mol^{-}*

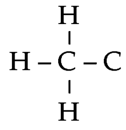
(*iv*) *Enthalpy of dissociation of nitrogen = 945.58 kJ mol^{-}*

(*v*) *Enthalpy of dissociation of hydrogen = 435.14 kJ mol^{-}*

(*vi*) *Heat of sublimation of graphite = 719.65 kJ mol^{-}*

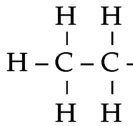
SOLUTION. Formation of CH_3CN is given below.

$$2C(s) + \tfrac{3}{2}H-H\ (g) + \tfrac{1}{2}N \equiv N(g)$$



$$\longrightarrow H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-C \equiv N(g);\ \Delta H = 87.86 \text{ kJ mol}^{-} \qquad ...(i)$$

In the given question, the enthalpy of C–C bond is not given. So, to find it, we use the following equation for the formation of C_2H_6.



$$2C(s) + 3H-H\ (g) \longrightarrow H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H;\ \Delta H = -83.68 \text{ kJ}$$

$$\therefore \quad \Delta H = [2\ \Delta H_{C(s) \to C(g)} + 3\ \Delta H_{H-H}] - [\Delta H_{C-C} + 6\ \Delta H_{C-H}]$$

$$-83.68 = (2 \times 719.65) + 3\ (435.14) - \Delta H_{C-C} - (6 \times 414.22)$$

$$-83.68 = 1439.30 + 1305.42 - \Delta H_{C-C} - 2485.32$$

$$\Delta H_{C-C} = 1439.30 + 1305.42 - 2485.32 + 83.68 = 343.08 \text{ kJ}$$

From equation (*i*), we have :

$$\Delta H = [2\ \Delta H_{C(s) \to C(g)} + 3/2\ \Delta H_{H-H} + 1/2\ \Delta H_{N \equiv N}] - [\Delta H_{C-C} + \Delta H_{C \equiv N} + 3\ \Delta H_{C-H}]$$

$$87.86 = (2 \times 719.65 + \left(\frac{3}{2} \times 435.14\right) + \frac{1}{4}\ (945.58) - 343.08 - \Delta H_{C \equiv N} - 3\ (414.22)$$

$$87.86 = 1439.30 + 652.71 + 472.79 - 343.08 - \Delta H_{C \equiv N} - 1242.66$$

$$\therefore \quad \Delta H_{C \equiv N} = 1439.30 + 652.71 + 472.79 - 343.08 - 1242.66 - 87.86 = \mathbf{891.2\ kJ\ mol^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 75. *Calculate the resonance energy of N_2O from the following data :*

$$\Delta_f H° \text{ of } N_2O = 82 \text{ kJ mol}^{-1}$$

Bond energy of N ≡ N, N = N, O = O and N = O bonds is 946, 418, 498 and 607 kJ mol^{-1} respectively. **(Roorkee, 1991)**

Solution. Formation of N_2O may be represented as

$$N \equiv N + \frac{1}{2}\ O = O \longrightarrow N^- = N^+ = O$$

In the above reaction,

$$\begin{aligned} N &= N \text{ bond is broken,} \\ \Delta_{diss}H° &= 946 \text{ kJ} \\ O &= O \text{ bond is broken,} \\ \Delta_{diss}H° &= 498 \text{ kJ} \\ N &= N \text{ bond is formed,} \\ \Delta_f H° &= -418 \text{ kJ} \\ N &= O \text{ bond is formed,} \\ \Delta_f H° &= -607 \text{ kJ} \end{aligned}$$

∴ $\Delta_f H°$ for N_2O = Bond energy (reactants) – bond energy (products)

$$\therefore \quad \Delta_f H° \text{ for } N_2O = 946 + \frac{1}{2} \times 498 - 418 - 607$$

$$= \mathbf{170\ kJ\ mol^{-1}}$$

Experimental value of $\Delta_f H°$ for N_2O

$= 82$ kJ mol^{-}

∴ Resonance energy of N_2O

$= 170 - 82 =$ **88 kJ mol^{-}**

Example 76. *The polymerisation of ethylene to linear polyethylene is represented by the reaction.*

$$nCH_2 = CH_2 \longrightarrow (-CH_2 - CH_2 -)_n$$

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 polymerisation per mole of ethylene at 298 K. **(IIT 1994)**

Solution. Polymerisation of ethylene is represented as

$$nCH_2 = CH_2 \longrightarrow (-CH_2 - CH_2 -)_n$$

During the polymerisation of ethylene, C = C double bond breaks and two CH_2 groups are linked with single bonds. In the whole polymer unit, the number of single bonds formed per mole of ethylene are two.

Energy absorbed due to dissociation of one C = C double bond = 590 kJ mol^{-1}

Energy released due to the formation of two C–C single bonds = 2 × 331 = 662 kJ mol^{-1}

∴ΔH(polymerisation)

$$= \left[\begin{array}{l}\text{Energy absorbed due} \\ \text{to dissociation of one} \\ \text{C = C bond}\end{array}\right] - \left[\begin{array}{l}\text{Energy released} \\ \text{due to formation} \\ \text{of two C - C} \\ \text{single bonds}\end{array}\right]$$

= (590 – 662) kJ mol^{-} = – 72 kJ mol^{-} **Ans.**

Example 77. Calculate the heat of reaction, $HC \equiv CH(g) + H_2(g) \longrightarrow H_2C = CH_2(g)$, if the bond energies of C = C, H – H, C ≡ C and C – H bonds are 147, 104, 160.86 and 99 k cal respectively. **(BCECE 2004)**

Solution. $HC \equiv CH(g) + H_2(g) \longrightarrow H_2C = CH_2(g)$. The reaction involves breaking of H – H bond, C ≡ C triple bond and making of a C = C double bond and two C – H bonds.

$$\begin{aligned} \therefore\ \Delta_r H &= \Sigma B.E_{(Reactants)} - \Sigma B.E._{(Products)} \\ &= [B.E.\ 2(C-H) + B.E.\ (C \equiv C) + B.E.\ (H-H)] \\ &\quad - [B.E.\ (C = C) + B.E.\ 4(C-H)] \\ &= B.E.\ (C \equiv C) + B.E.\ (H-H) - 2B.E.\ (C-H) - \\ &\quad B.E.\ (C = C) \\ &= 160.86 + 104 - 2 \times 99 - 147 \\ &= 264.86 - 345 = \mathbf{-80.14\ k\ cal} \end{aligned}$$

Example 78. *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. According to the given data :

(*i*) $S_{(s)} + 3F_{2(g)} \longrightarrow SF_6\ ;\ \Delta H = -1100$ kJ

(*ii*) $S_{(s)} \longrightarrow S_{(g)}\ ;\ \Delta_f H° = 275$ kJ

(*iii*) $\frac{1}{2} F_{2(g)} \longrightarrow F_{(g)}\ ;\ \Delta_f H° = 80$ kJ

Required equation is :

$$SF_6(g) \longrightarrow S(g) + 6F(g)\ ;\ \Delta H° = ?$$

To get this equation, we can proceed as follows :

Equation (*ii*) + 6 × (*iii*) – (*i*)

$$\begin{aligned} S(s) + 3F_2(g) - S(s) &\longrightarrow S(g) + 6F(g) \\ -3\,F_2(g) \quad &\qquad -SF_6(g) \end{aligned}$$

$$\text{or} \qquad SF_6(g) \longrightarrow S(g) + 6\ F)g)\ ;$$

$$\begin{aligned} \Delta H° &= 1855 \text{ kJ } mol^{-} \\ \text{Total S – F bonds in } SF_6 &= 6 \\ \therefore\ \text{Average bond energy} &= \frac{1855}{6} \\ &= \mathbf{309.16\ kJ\ mol^{-}}\ \textbf{Ans.} \end{aligned}$$

ΔH° in kJ mol^{-}

(*ii*) 275

(*iii*) 6 × 80 = 480

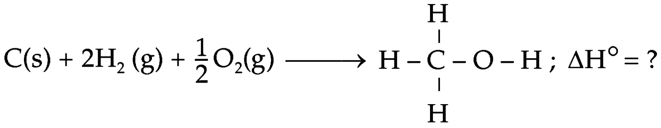
(*i*) – (– 1100) = +1100

∴ ΔH° = 275 + 480 + 1100 = 1855 kJ mol^{-}

Example 79. *Compute the heat of formation of liquid methyl alcohol in kilo joules per mole, using the following data. Heat of vaporization of liquid methyl alcohol = 38 kJ mol^{-1}. Heat of formation of gaseous atoms from the elements in their standard states ; H, 218 kJ/mol ; C, 715 kJ/mol ; O, 249 kJ/mol.*

Average bond energies : C – H, 415 kJ/mol, C – O, 356 kJ/mol ; O – H, 463 kJ mol^{-} **(IIT 1997)**

Solution. The required equation is :



$$C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-O-H\ ;\ \Delta H° = ? \qquad ...(A)$$

Given :

(*i*) $C_{(s)} \longrightarrow C_{(g)}\ ;\ \Delta H° = 715$ kJ mol^{-}

(*ii*) $\frac{1}{2} H_{2(g)} \longrightarrow H_{(g)}\ ;\ \Delta H° = 218$ kJ mol^{-}

(*iii*) $\frac{1}{2} O_{2(g)} \longrightarrow O_{(g)}\ ;\ \Delta H° = 249$ kJ mol^{-}

(*iv*) $CH_3OH(l) \xrightarrow{\quad\quad} CH_3OH(g)$; $\Delta H = 38$ kJ mol^{-}

$\therefore$ $\Delta H°$ = Bond energy of reactants – bond energy of products.

= B.E. [(*i*) + 4 × (*ii*) + (*iii*) – (*iv*)] – [B.E. (3 × C – H) + (1 × C – O) + (1 × O – H)]

= [715 + (4 × 218) + 249 – 38] – [(3 × 415) + 356 + 463]

= 715 + 872 + 249 – 38 – 1245 – 356 – 463 = – 266 kJ

Note. CH_3OH contains three C – H, one C – O and one O – H bonds.

Example 80. *Using the data (all values are in kilocalories per mole at 25°C) given below, calculate the bond energy of C – C and C – H bonds.*

$\Delta H°$ combustion (ethane) = – 372.0; $\Delta H°$ combustion
(propane) = – 530.0; $\Delta H°$ for (graphite)
C(g) = 172.0; Bond energy of H – H
bond = 104.0
$\Delta H°_f$ of $H_2O_{(l)}$ = – 68.0
$\Delta H°_f$ of $CO_{2(g)}$ = – 94.0 **(IIT 1990)**

Solution. According to the given data :

(*i*) $C_2H_{6(g)} + \frac{1}{2}O_{2(g)} \xrightarrow{\quad\quad} 2CO_2 + 3H_2O$

$\Delta H = -372$ kcal/mole

(*ii*) $C_3H_8(g) + 5O_2(g) \xrightarrow{\quad\quad} 3CO_2 + 4H_2O$

$\Delta H = -530.0$ kcal/mole

$\Delta H = \Sigma\Delta H°_f(\text{Products}) - \Sigma H°_f(\text{Reactants})$

(For C_2H_6)

$\therefore$ $-372 = -2 \times 94 - 3 \times 68 - \Delta H°_f$ of C_2H_6

$\therefore$ $\Delta H°_f(C_2H_6) = 372 - 188 - 204 = -20$ k cal/mole

-530.0 kcal/mole $= -3 \times 94.0 - 4 \times 68.0 - \Delta H°_f$ (For C_3H_8)

$\therefore$ $\Delta H°_f(C_3H_8) = -282 - 272 + 530$

$= -24$ k cal/mole

$\therefore$ $2C_{(s)} + 3H_{2(g)} \xrightarrow{\quad\quad} C_2H_6$; $\Delta H = -20$ kcal ...(1)

and $3C_{(s)} + 4H_{2(g)} \xrightarrow{\quad\quad} C_3H_8$; $\Delta H = -24$ kcal ...(2)

ΔH = Bond energy of reactants – Bond energy of products.

Now let C – C bond strength be *a* kcal and C – H bond strength be *b* kcal.

For (1) $-20 \text{ kcal} = -(a + 6b) + 3 \times 104 + 2 \times 172$

or $a + 6b = (312 + 344 + 20)$ kcal

or $a + 6b = 676$ kcal ...(3)

For (2) $-24 \text{ kcal} = -(2a + 8b) + 4 \times 104 + 3 \times 172$

or $2a + 8b = (416 + 516 + 24)$ kcal;

or $2a + 8b = 956$ kcal ...(4)

Multiplying (3) by 2, we get

$2a + 12b = 1352$ kcal ...(5)

Subtracting equation (4) from (5), we get :

$4b = 396$ or $b = 99$ kcal.

Substituting this value of (*b*) in (*4*), we get, *a* = **82 kcal.**

15.27. HEAT OF HYDRATION

Type. Heat of hydration of solution of anhydrous compound

= Heat of hydration of anhydrous compound + Heat of solution of hydrated compound

Example 81. *The heat of solution of $BaCl_2.2H_2O$ is + 2.1 k. cal and the heat of hydration of barium chloride is – 7.03 k cal. What is the heat of solution of anhydrous barium chloride ?*

Solution. *Reactions.*

(*i*) $BaCl_2.2H_2O(s) + aq \longrightarrow BaCl_2.2H_2O\,(aq)$;

$\Delta H = 2.1$ k cal.

(*ii*) $BaCl_2(s) + 2H_2O \longrightarrow BaCl_2.2H_2O(s)$;

$\Delta H = -7.03$ k cal.

The required equation is :

$BaCl_2(s) + 2H_2O + aq \longrightarrow BaCl_2.2H_2O(aq)$;

$\Delta H = ?$ ...(*A*)

In order to get equation (A), we have, equation (*i*) + equation (*ii*).

$$\begin{aligned} BaCl_2.2H_2O_{(s)} + aq + &\longrightarrow BaCl_2.2H_2O(aq) \\ BaCl_2(s) + 2H_2O \quad &\quad + BaCl_2.2H_2O(s) \end{aligned}$$

or $BaCl_2(s) + 2H_2O + aq \longrightarrow BaCl_2.2H_2O(aq)$

$\Delta H = $ **– 4.93 k cal** **Ans.**

ΔH in k cal

(*i*) + 2.1

(*ii*) – 7.03

$\Delta H = +2.1 - 7.03 = -4.93$ k cal

or Heat of hydration of solution of anhydrous $BaCl_2(s)$

= Heat of hydration of anhydrous $BaCl_2(s)$ + Heat of solution of $BaCl_2.2H_2O(s)$

= – 7.03 + 2.1 = **– 4.93 k cal** **Ans.**

Example 82. *The heat of solution of hydrated barium chloride ($BaCl_2.2H_2O$) and anhydrous barium chloride ($BaCl_2$) are + 8.8 kJ and – 20.6 kJ respectively. Calculate heat of hydration of $BaCl_2$ to $BaCl_2.2H_2O$.* **(HP Board, 2007)**

Solution. *Required equation is :*

$BaCl_2 + 2H_2O \xrightarrow{\quad\quad} BaCl_2.2H_2O$; $\Delta H = ?$ ...(A)

Reactions.

(*i*) $BaCl_2.2H_2O + aq \longrightarrow BaCl_2.2H_2O(aq)$;

$$\Delta H = +8.8 \text{ kJ}$$

(*ii*) $BaCl_2 + 2H_2O + aq \longrightarrow BaCl_2.2H_2O(aq)$;

$$\Delta H = -20.6 \text{ kJ}$$

In order to get equation (A), we have, equation (*ii*) – equation (*i*)

$$\begin{array}{lcl} BaCl_2 + 2H_2O + aq & \longrightarrow & BaCl_2.2H_2O(aq) \\ -BaCl_2.2H_2O - aq & & -BaCl_2.2H_2O\ (aq) \\ \text{or} \quad BaCl_2 + 2H_2O & \longrightarrow & BaCl_2.2H_2O\ ; \\ \Delta H & = & \mathbf{-29.4\ kJ} \end{array}$$

Ans.

ΔH in kJ

(*ii*) – 20.6

(*i*) – (+ 8.8) = – 8.8

$$\Delta H = -20.6 - 8.8 = -29.4 \text{ kJ}$$

EXAMPLE 83. *On dissolving 100 g anhydrous $CuSO_4$ in water, the heat evolved amounted to 9900 cal. The same amount of crystalline $CuSO_4.5H_2O$ on dissolving absorbed 1100 cal of heat. Calculate the heat of hydration of $CuSO_4$ into $CuSO_4.5H_2O$ (at. wt., Cu = 63.5 g mol^{-}, S = 32 g mol^{-}, O = 16 g mol^{-}).*

SOLUTION. Required equation is :

$$CuSO_4 + 5H_2O \longrightarrow CuSO_4.5H_2O\ ;\ \Delta H = ? \quad ...(A)$$

(*a*)Mol. wt. of $CuSO_4$

$$= 63.5 + 32 + (4 \times 16) = 159.5 \text{ g mol}^{-}$$

Heat evolved to dissolve 100 g $CuSO_4$ in water

$$= 9900 \text{ cal.}$$

Heat evolved to dissolve 159.5 g $CuSO_4$ in water

$$= \frac{9900 \text{ cal}}{100 \text{ g}} \times 159.5 \text{ g}$$

$$= 15790.5 \text{ cal.}$$

(*b*)Mol. wt. of $CuSO_4.5\ H_2O$

$$= 63.5 + 32 + (4 \times 16) + 5$$

$$[(2 \times 1) + 16] = 249.5 \text{ g mol}^{-}$$

Heat absorbed to dissolve 100 g $CuSO_4.5H_2O$ in

$$H_2O = 1100 \text{ cal}$$

Heat absorbed to dissolve 249.5 g $CuSO_4.5\ H_2O$ in

$$H_2O = \frac{1100 \text{ cal}}{100 \text{ g}} \times 249.5 \text{ g} = 2744.5 \text{ cal}$$

Reactions.

(*i*) $CuSO_4 + 5H_2O + aq \longrightarrow CuSO_4(aq)$;

$$\Delta H = -15790.5 \text{ cal}$$

(*ii*) $CuSO_4.5H_2O + aq \longrightarrow CuSO_4(aq)$;

$$\Delta H = -2744.5 \text{ cal}$$

In order to get equations (A), we have,
equation (*i*) – equation (*ii*)

$$\begin{array}{lcl} CuSO_4 + 5H_2O + aq & \longrightarrow & CuSO_4(aq) \\ -CuSO_4.5H_2O - aq & & -CuSO_4(aq) \\ \text{or} \quad CuSO_4 + 5H_2O & \longrightarrow & CuSO_4.5H_2O\ ; \\ \Delta H & = & -18.535 \text{ k cal} \end{array}$$

Ans.

ΔH in k cal

(*i*) – 15790.5

(*ii*) – (+ 2744.5) = – 2744.5

$$\begin{aligned} \Delta H &= -15790.5 - 2744.5 \\ &= -18{,}535 \text{ cal} = \text{ k cal} \\ &= -18.535 \text{ k cal} \end{aligned}$$

EXAMPLE 84. *The enthalpy of solution of anhydrous $CuSO_4$ and hydrated $CuSO_4.5H_2O$ are – 67.0 kJ and 12 kJ mol^{-} respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4.5H_2O$*

SOLUTION. Required equation is :

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O\ ;\ \Delta H = ? \quad ...(A)$$

Given. (*i*) $CuSO_4(s) + aq \longrightarrow CuSO_4(aq)$;

$$\Delta H = -67 \text{ kJ}$$

(*ii*) $CuSO_4.5H_2O + aq \longrightarrow CuSO_4(aq) + 5H_2O$;

$$\Delta H = 12 \text{ kJ}$$

In order to get equation (A),
we have equation (*i*) – equation (*ii*)

$$\begin{array}{lcl} CuSO_4(s) + aq & \longrightarrow & CuSO_4(aq) - CuSO_4(aq) \\ -CuSO_4.5H_2O - aq & & -5H_2O(l) \\ \text{or} \quad CuSO_4(s) + 5H_2O & \longrightarrow & CuSO_4.5H_2O\ ; \\ \Delta H & = & -79.0 \text{ kJ} \end{array}$$

Ans.

EXAMPLE 85. *The enthalpy of solution of sodium chloride is 4 kJ mol^{-} and its enthalpy of hydration of ions is –784 kJ mol^{-}. Then the lattice enthalpy of NaCl (in kJ mol^{-}) is*

(a) *+ 788* *(b)* *+ 4*
(c) *+ 398* *(d)* *+ 780*

Kerala PMT, 2011

SOLUTION. $\Delta H_{solution} = \Delta H_{hydration} + \Delta H_{lattice}$
Substituting the values, we get:
$4 \text{kJ mol}^{-} = -784 \text{ kJ mol}^{-} + \Delta H_{lathice}$; $\Delta H_{lattice} = 4 - (-784) = +788 \text{ kJ mol}^{-}$. So, the correct answer is (*a*)

15.28 ENTHALPY (HEAT) OF VAPORISATION, $\Delta_{vap}H°$.

It is defined as the enthalpy change when one mole of a liquid is converted into vapours at its boiling point. e.g.,

$$H_2O(l) \longrightarrow H_2O(g)\ ;\ \Delta_{vap}H° = 40.79 \text{ kJ}$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}, \text{ where } \Delta S \text{ is the entropy change.}$$

EXAMPLE 86. *When a swimmer came out of a pool, he was found to contain 72 g of water on his body. Calculate the amount of heat required to evaporate this water if enthalpy of vaporisation of water = 40.79 kJ mol^{-}.*

SOLUTION. $H_2O(l) \longrightarrow H_2O(g)$;

$$(2 \times 1) + 16 = 18 \text{ g}$$

$$\Delta_{vap}H° = 40.79 \text{ kJ mol}^{-}$$

Heat of evaporation for 18 g water

$$= 40.79 \text{ kJ}$$

Heat of evaporation for 72 g water

$$= \frac{40.79 \text{ kJ}}{18 \text{ g}} \times 72 \text{ g} = 163.16 \text{ kJ} \textbf{ Ans.}$$

EXAMPLE 87. *Calculate the enthalpy change when 7.8 g of benzene (C_6H_6) vaporizes at its normal boiling point. $\Delta_{vap}H^\circ$ for benzene = 30.8 kJ mol$^-$.*

SOLUTION. $C_6H_6(l) \longrightarrow C_6H_6(g)$;

$\Delta_{vap}H^\circ = 30.8 \text{ kJ mol}^-$

$(6 \times 12) + (6 \times 1) = 78 \text{ g} = 1$ mol 78 g of C_6H_6 has

$\Delta_{vap} H^\circ = 30.8 \text{ kJ mol}^-$

$\therefore$7.8 g of C_6H_6 has

$$\Delta_{vap} H^\circ = \frac{30.8 \text{ kJ}}{78} \times 7.8 = \mathbf{3.08 \text{ kJ}} \qquad \textbf{Ans.}$$

EXAMPLE 88. *Calculate the enthalpy of vaporisation per mole for ethanol. Given ΔS, 109.8 JK$^-$ mol$^-$ and boiling point of ethanol, 78.5°C.* **(CBSE, 1989)**

SOLUTION. $\Delta S_{vap} = 109.8 \text{ JK}^- \text{ mol}^-$; $\Delta H_{vap} = ?$,

$T = 273 + 78.5 = 351.5$ k

We know that : $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T}$; $\Delta H_{vap} = \Delta S_{vap} \times T$

$\therefore \quad \Delta H_{vap} = 109.8 \text{ JK}^- \text{ mol}^- \times 351.5 \text{ K}$

$= 38594.7 \text{ J mol}^- = 38.595 \text{ kJ mol}^-$

EXAMPLE 89. *For The reaction, $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ at 373 K and one atmospheric pressure:*

(a) $\Delta E = 0$ *(b)* $\Delta H = T\Delta S$

(c) $\Delta H = \Delta E$ *(d)* $\Delta H = 0$

(Karnataka CET, 2009)

SOLUTION. Given: Liquid water and water gas at 373 K and one atmospheric pressure are in equilibrium. So, $\Delta G = 0$. Since, $\Delta G = \Delta H - T\Delta S$, so $0 = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$. So, the correct answer is (*b*).

15.29 ENTHALPY OF HYDROGENATION OF ALKENES.

Required equation is : alkene + 2H $\longrightarrow$ Alkane ;

$\Delta H = ?$

EXAMPLE 90. *Calculate the enthalpy of hydrogenation of $C_2H_4(g)$ when the enthalpy of formation of $C_2H_6(g)$ and $C_2H_4(g)$ are – 20.2 k cal and 12.5 k cal respectively.* **(IIT, 1989)**

SOLUTION. The required equation is :

$C_2H_4(g) + 2H(g) \longrightarrow C_2H_6(g)$; $\Delta H = ?$ ...(A)

Given (*i*) $2C(s) + 6H(g) \longrightarrow C_2H_6(g)$;

$\Delta H = -20.2$ k cal

(*ii*) $2C(s) + 4H(g) \longrightarrow C_2H_4(g)$;

$\Delta H = 12.5$ k cal

In order to get equation (A), we have equation (*i*) – equation (*ii*)

$2C(s) + 6H(g) \longrightarrow C_2H_6(g)$

$-2C(s) - 4H(g) \qquad -C_2H_4(g)$

Or $C_2H_4(g) + 2H(g) \longrightarrow C_2H_6(g)$;

$\Delta H = -20.2 - 12.5 = -32.7$ k cal **Ans.**

EXAMPLE 91. *Calculate the heat of hydrogenation of cyclohexene from the following data.*

The standard enthalpy of combustion of cyclohexane (C_6H_{12}), C_6H_{10} and H_2 in kJ mol$^-$ are – 3920, –3800 and – 241 respectively.

SOLUTION. The required equation is :

$C_6H_{10} + H_2 \longrightarrow C_6H_{12}$; $\Delta H = ?$ ...(A)

Given. (*i*) $C_6H_{12} + 9O_2 \longrightarrow 6CO_2 + 6H_2O$;

$\Delta H = -3920$ kJ

(*ii*) $C_6H_{10} + \frac{17}{2} O_2 \longrightarrow 6CO_2 + 5H_2O$;

$\Delta H = -3800$ kJ

(*iii*) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$; $\Delta H = -241$ kJ

In order to get equation (A) we have equation (*ii*) + equation (*iii*) – equation (*i*)

$C_6H_{10} + \frac{17}{2} O_2 + H_2 \longrightarrow 6CO_2 + 5H_2O + H_2O$

$+ \frac{1}{2} O_2 - C_6H_{12} - 9O_2 \qquad -6CO_2 - 6H_2O$

Or $C_6H_{10} + H_2 \longrightarrow C_6H_{12}$;

$\Delta H = \mathbf{-121 \text{ kJ}}$ **Ans.**

ΔH in kJ

(*ii*) – 3800

(*iii*) – 241

(*i*) – (– 3920) = 3920

$\therefore \quad \Delta H = -3800 - 241 + 3920 = -121$ kJ

15.30 ENTHALPY (HEAT) OF NEUTRALISATION

It is defined as the change in enthalpy when one gram equivalent of an acid is neutralised by a base or vice – versa, in dilute solution. The enthalpy of neutralisation of all strong acids with strong bases is – 57.1 kJ or –13.7 k cal.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; $\Delta_n H^\circ = -57.1$ kJ

1 g. eq. 1 g. eq.

> **Note.** The enthalpy of neutralisation of 'strong acids with weak bases and vice versa' and of weak acids with weak bases is always less than 57.1 kJ.

EXAMPLE 92. *Given that $H^+(aq) + OH^-(aq) \longrightarrow H_2O$ + 57.1 kJ. Calculate the heat evolved when (i) 0.5 mol of HCl solution is neutralised by 0.5 mol of NaOH solution (ii) 0.5 mol of HNO_3 is mixed with 0.25 mol KOH (iii) 300 cm^3 of 0.2 M HCl solution is mixed with 200 cm^3 of 0.1 M K OH solution.*

SOLUTION. (*i*) 0.5 mol HCl ≡ 0.5 mol of H^+ ions

0.5 mol NaOH ≡ 0.5 mol of OH^- ions

$\therefore$ Heat released = 0.5 × 57.1 = 28.55 kJ **Ans.**

(*ii*) 0.5 mol of HNO_3 ≡ 0.5 mol of H^+ ions

0.25 mol of KOH ≡ 0.25 mol of OH^- ions

But 0.25 moles of OH^- ≡ 0.25 mole of H^+ ions

and hence 0.5 – 0.25 = 0.25 mol of H^+ ions remain unreacted

$\therefore$ Heat released = no. of mole reacted × + 57.1

= 0.25 × 57.1 = 14.275 kJ

(*iii*) 1000 cm^3 of 0.2 M HCl ≡ 0.2 mol H^+ ions

$$300\ cm^3 \text{ of } 0.2\ M\ HCl = \frac{0.2}{1000} \times 300$$

$= 0.06$ mol H^+ ions ...(1)

1000 cm^3 of 0.1 M KOH ≡ 0.1 mol OH^-

$$200\ cm^3 \text{ of } 0.1\ M\ KOH = \frac{0.1}{1000} \times 200$$

$= 0.02$ mol OH^- ions ...(2)

From (1), (2), we have

$\therefore$ 0.02 mol OH^- ions ≡ 0.02 mol H^+ ions

$\therefore$ Heat released = 0.02 × 57.1 = 1.142 kJ

EXAMPLE 93. *Given that $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$; $\Delta H = -57.1$ kJ. Calculate the heat evolved when 200 cm^3 of 0.2 M H_2SO_4 is mixed with 400 cm^3 of 0.1 M NaOH solution.*

SOLUTION. (*i*) 1000 cm^3 of 0.2 M H_2SO_4 = 0.2 × 2 mol H^+ ions

$$\therefore \quad 200\ cm^3 \text{ of } 0.2\ M\ H_2SO_4 = \frac{0.2 \times 2}{1000} \times 200$$

$= 0.08$ mol H^+ ions

(*ii*) 1000 cm^3 of 0.1 M NaOH = 0.1 M OH^- ions

$$\therefore \quad 400\ cm^3 \text{ of } 0.1\ M\ NaOH = \frac{0.1}{1000} \times 400$$

$= 0.04$ mol OH^- ions

From (*i*) and (*ii*), we have :

0.04 mol H^+ ions = 0.04 mol OH^- ions while rest of H^+ ions (= 0.08 – 0.04 = 0.04 mol) remain unreacted.

$\therefore$ Heat released = 0.04 × 57.1 = **2.284 kJ** **Ans.**

Type (*i*) Normality of acid = Molarity × basicity of acid

(*ii*) Normality of base = Molarity × acidity of base

(*iii*) Heat of neutralisation

$$= \frac{\text{Total heat}(q)\text{ produced}}{\text{Volume of acid or base}} \times \frac{1000}{\text{normality of acid or base}}$$

EXAMPLE 94. *The amount of heat released when 20 mL of 0.5 M NaOH is mixed with 100 ml of 0.1 M HCl is x kJ. The heat of neutralisation is:*

(*a*) *–100 x kJ mol⁻* (*b*) *–50 x kJ mol⁻*

(*c*) *+ 100 x kJ mol⁻* (*d*) *+ 50 x kJ mol⁻*

WB-JEE, 2011

SOLUTION. Normality of NaOH = Molarity × acidity = 0.5 × 1 = 0.5 N. Total heat (*q*) produced = *x* kJ. But:

$$\text{Heat of neutralisation} = \frac{q}{\text{Vol. of acid or base}} \times 1000 \times \frac{1}{\text{normality of acid or base}} = \frac{x}{20} \times 1000 \times \frac{1}{0.5} = 100\ x \text{ kJ}$$

mol⁻. Since heat is liberated, heat of neutralisation = – 100 *x* kJ mol⁻. So, the correct answer is (*a*).

EXAMPLE 95. *On neutralisation, 75 mL of semi-normal sulphuric acid with the same volume of caustic soda of the same strength at 25°C in a Dewar flask, the temperature rose to 28°C. The water equivalent of flask being 21.125 g, calculate the heat of neutralisation.*

SOLUTION. Water equivalent = 21.125 g, specific heat of water = 1 cal g^- $°C^-$; rise in temperature = 28 – 25 = 3°C.

(*i*) *Amount of heat taken up by the calorimeter* = water equivalent × sp. heat of water × rise in temperature

= 21.125 g × 1 cal g^- $°C^-$ × 3°C

= **63.375 cal.**

(*ii*) Volume of N/2 H_2SO_4 = 75 mL ;

Volume of N/2 NaOH = 75 mL

$\therefore$ Total volume of solution = 75 + 75 = 150 mL

$\therefore$ Wt. of solution (mainly water) = volume × density of water

$$= 150\ mL \times \frac{1\ g}{mL}$$

= 150 g

Sp. heat of water = 1 cal g^- $°C^-$; rise in temperature = 3°C

$\therefore$ Amount of heat taken up by solution = Amount of solution (mainly water × sp-heat of water × rise in temperature =150 g × 1 cal g^- $°C^-$ × 3°C = 450 calories.

(*iii*) Total heat taken up by calorimeter and solution

= 63.375 cal + 450 cal = 513.375 cal

(*iv*) 75 mL of N/2 H_2SO_4 produce heat

= 513.375 cal

1000 mL of 1 N H_2SO_4 produce heat

$$= \frac{513.375\ cal \times 2 \times 1000\ mL}{75\ mL}$$

$$= 13690\ cal = 13690\ cal \times \frac{1\ k\ cal}{1000\ cal}$$

= **13.69 k cal** **Ans.**

EXAMPLE 96. *The heat of neutralisation of NaOH and NH_4OH by HCl are – 13.7 k cal and – 12.3 k cal respectively. Calculate the heat of dissociation of NH_4OH.*

SOLUTION. (*i*) $NaOH + HCl \longrightarrow NaCl + H_2O$;

$\Delta H = -13.7$ k cal

(*ii*) $NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$;

$\Delta H = -12.3$ k cal

The required equation is :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- ;\ \Delta H = ? \quad ...(A)$$

In order to get equation (A), we have,

equation (*ii*) – equation (*i*)

$$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$$

$$-NaOH - HCl \qquad -NaCl - H_2O$$

or $NH_4OH + NaCl \longrightarrow NH_4Cl + NaOH$

or $NH_4OH + Na^+ + Cl^- \longrightarrow NH_4^+ + Cl^- + Na^+ + OH^-$

or $NH_4OH \longrightarrow NH_4^+ + OH^-$;

$\Delta H = +1.4$ **k cal** **Ans.**

ΔH in k cal

(*ii*) – 12.3

(*i*) – (– 13.7) = + 13.7

$\Delta H = -12.3 + 13.7 = +1.4$ k cal

Example 97. *50 mL of 1 M KOH and 50 mL of 1 M HCl both having same temperature were mixed in a calorimeter (heat capacity is almost negligible). A temperature rise of 6.3°C was recorded. In another experiment, the HCl acid was replaced by 50 mL of 1M HCOOH. The temperature rise was recorded as 4.9°C. Calculate the enthalpy of ionisation of HCOOH.*

Solution. Total volume of mixed solution = 50 mL + 50 mL = 100 mL.

To find molarity of mixed solution

Mixed solution Original solution

$$M_1V_1 = M_2V_2$$

$$M_1 \times 100 = 1 \times 50;$$

$$\therefore \quad M_1 = \frac{50}{100} = 0.5\text{ M}$$

∴ 100 mL of 0.5 M solution produce heat

= 100 × 6.3 = 630 cal.

1000 mL of 1 M solution produce heat

$$= \frac{630}{100} \times \frac{1000}{0.5} = 12600\text{ cal.}$$

In second experiment

100 mL of 0.5 M solution produce heat

= 100 × 4.9 cal

1000 mL of 1 M solution produce heat

$$= \frac{100 \times 4.9}{100} \times \frac{1000}{0.5}$$

= 9800 cal

∴Heat of ionisation

= (12,600 – 9,800) cal = 2800 cal

= **2.8 k cal** **Ans.**

15.31. ENTHALPY (HEAT) OF SOLUTION

(Heat) of solution : *It is the enthalpy change when one mole of a solute is dissolved in large excess of solvent so that on further dilution, no heat change occurs.* For example :

In the reaction

$$NaCl_{(s)} + aq \longrightarrow NaCl_{(aq)}; \ \Delta H = 5.0\text{ kJ}$$

the enthalpy (heat) of solution is 5.0 kJ

Integral enthalpy (heat) of Solution. It is defined as the enthalpy change when one mole of a solute is dissolved in a **specific amount of solvent.**

Example 98. *Calculate the integral heat of sulphuric acid solution in the following.*

(*i*) $H_2SO_4(l) + H_2O(l) \longrightarrow H_2SO_4(aq)$;

$\Delta_{sol}H° = -30.5$ kJ

(*ii*) $H_2SO_4(l) + 10H_2O(l) \longrightarrow H_2SO_4(aq)$;

$\Delta_{sol}H° = -68.0$ kJ.

Solution. Since integral heat of solution is the enthalpy change when one mole of a solute is dissolved in a specific amount of solvent, so :

(*i*) In $H_2SO_4(l) + H_2O(l)$ *i.e.*, one mole $\longrightarrow H_2SO_4(l)$, the integral heat of solution = 30.5 kJ **Ans.**

(*ii*) In $H_2SO_4(l) + 10H_2O(l)$ *i.e.*, 10 mole $\longrightarrow H_2SO_4$(aq), the integral heat of solution is 68.0 kJ **Ans.**

15.32. VARIATION OF HEAT OF REACTION WITH TEMPERATURE–KIRCHOFF'S EQUATION.

The heat of a reaction depends on temperature. Heat of reaction, ΔH (or ΔE) and temperature, T are related by **Kirchoff's equation** as given below

(a) $$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}; \ \Delta C_v = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$$

Where, ΔC_p = (Molar heat capacity of products) – (molar heat capacity of reactants) at constant pressure.

ΔC_v = (Molar heat capacity of products) – (molar heat capacity of reactants) at constant volume.

Example 99. *The molar heat capacities of $H_2(g)$, $O_2(g)$ and $H_2O(l)$ are respectively 6.62 cal, 6.76 cal and 18 cal. If heat of formation of water at 298 K is – 68.4 k cal, calculate its value at 95°C.*

Solution. $T_1 = 298$ K, $T_2 = 273 + 95 = 368$ K;

$\Delta H_2 = ?$

Reaction $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$;

$$\Delta H_1 = -68.4\text{ k cal.}$$

$$\Delta C_p = C_p(\text{products}) - C_p(\text{reactants})$$

$$= C_p(H_2O) - \left[C_p(H_2) + \frac{1}{2}C_p(O_2)\right]$$

$$= 18 - \left[6.62 + \frac{1}{2}(6.76)\right]$$

$$= 18 - 6.62 - 3.38 = 8\text{ cal}$$

$$= 8\text{ cal} \times \frac{1\text{ k cal}}{1000\text{ cal}} = 0.008\text{ k cal.}$$

We know, $$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}.$$

Substituting the values, we get :

$$0.008\text{ k cal} = \frac{\Delta H_2 - (-68.4)\text{ k cal}}{(368 - 298)\ i.e., 70}$$

$$\therefore \quad \Delta H_2 = (0.008\text{ k cal} \times 70) - 68.4\text{ k cal}$$

$$= 0.56 - 68.4 = -67.84\text{ k cal}$$ **Ans.**

Example 100. *The heat of reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 300 K was found to be 91.97 kJ. What will be the heat of reaction at 323 K ? The molar heat capacities at constant pressure and 300 K for nitrogen, hydrogen and ammonia are 28.46, 28.33 and 37.08 JK^{-1} mol^- respectively.*

Solution. The heat of reaction at 300K, $\Delta H_1 = 91.97$ kJ

ΔC_p for the reaction can be calculated. The reaction involved is :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

ΔC_p = (2 × molar heat capacity of NH_3) – (molar heat capacity of N_2 + 3 × molar heat capacity of H_2)

$$\begin{aligned} &= (2 \times 37.08) - (28.46 + 3 \times 28.33) \\ &= 74.16 - (28.46 + 84.99) \\ &= 74.16 - 113.45 = -39.29\ JK^{-1} \\ &= -39.29 \times 10^{-3}\ kJK^{-1} \end{aligned}$$

Applying the relation :

$$\begin{aligned} \Delta H_2 - \Delta H_1 &= \Delta C_p (T_2 - T_1) \\ \Delta H_2 &= \Delta H_1 + \Delta C_p (T_2 - T_1) \\ &= -91.97 + (-39.29)(323 - 300) \times 10^{-3} \\ &= -91.97 + (-39.29)(23) \times 10^{-3} \\ &= -91.97 - 0.904 = -92.87\ kJ \end{aligned}$$

EXAMPLE 101. *The molar heat capacities (C_p) for $H_2O(s)$ and $H_2O(l)$, are 37.7 and 75.3 $JK^{-1}\ mol^{-1}$, respectively. The enthalpy of the fusion process $H_2O(s, -10°C) = H_2O\ (l, -10°C)$ is 5.63 kJ mol^-. Calculate the enthalpy of fusion of ice at 0°C, assuming that the molar heat capacities are independent of temperature in the range – 10 to 0°C.*

SOLUTION.

$$\begin{aligned} \Delta C_p &= C_{p(\text{water})} - C_{p(\text{ice})} \\ &= 75.3 - 37.7 = 37.6\ J \\ &= 37.6 \times 10^{-3}\ kJ \end{aligned}$$

According to Kirchoff's equation.

$$\frac{\Delta H_2 - \Delta H_1}{(T_2 - T_1)} = \Delta C_p$$

or $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

or $\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$

Now ΔH_1 (enthalpy of fusion at – 10°C) = 5.63

$$\begin{aligned} T_1 &= -10°C = 273 - 10 = 263\ K, \\ T_2 &= 0°C = 0 + 273 = 273\ K \end{aligned}$$

$$\therefore \quad \begin{aligned} \Delta H_2 &= [5.63 + (273 - 263) \times 37.6 \times 10^{-3} kJ \\ &= (5.63 + 0.376)\ kJ = \mathbf{6.006\ kJ} \end{aligned}$$

15.33. CALORIMETRIC CALCULATIONS.

Enthalpy change of a system or reaction (exothermic or endothermic) can be measured in a closed and insulated vessel called calorimeter. The experimental procedure is called calorimetry.

Heat of combustion at constant volume (ΔE). It is measured with the help of **bomb calorimeter.**

Heat of solution and heat of neutralisation. These are measured with the help of Dewar flask or thermos flask with perfect insulation, calorimetrically.

Some important terms used in calorimetric calculations.

1. **Water equivalent of calorimeter.** I*t is the amount of water that requires the same amount of heat as is required by the calorimeter to raise its temperature through 1°C. It is usually expressed in gram.*
2. **Heat capacity or thermal capacity (C).** *It is the amount of heat required to increase the temperature of a calorimeter through 1°C. It is usually expressed is* **kJK$^-$** *or* ***k cal*** *°C$^-$, $C = \dfrac{\delta q}{dT}$.*
3. **Specific heat.** *It is the amount of heat required to raise the temperature of 1 gram of a substance through 1 K or 1°C. It is an intensive property. The specific heat of water =* **1 calorie g$^-$ °C$^-$,** *or has unit = Jg$^-$ °C$^-$.*
4. **Relation** among, heat capacity, water equivalent and specific heat is :

   Heat capacity = Water equivalent × Specific heat

Principle of calorimetry : Heat gained = Heat lost *i.e.*, heat evolved or absorbed during a chemical change in a calorimeter is equal to the amount of heat gained or lost by the calorimeter and its contents.

5. **Amount of heat taken up by calorimeter**

   = [Heat capacity of calorimeter] × [Rise in temperature]

   = Water equivalent × sp. heat × rise in temperature.
6. **Heat of combustion at constant pressure (ΔH) is given as :**

$$\Delta H = \Delta E\ (\text{or}\ \Delta U) + \Delta nRT$$

Where ΔE = heat of combustion at constant volume ; Δ*n* = (no. of mol of gaseous products) – (no. of mol of gaseous reactants) ; R = 0.002 k cal or R = 8.314 $JK^-\ mol^-$; T = Temperature in kelvin = t°C + 273

15.34. TYPES OF HEAT CAPACITIES

EXAMPLE 102. *When 2.516 g of a pure sample of graphite is burnt completely in a calorimeter, whose heat capacity (including water) is 2000 cal °C$^-$, it causes the temperature of its calorimeter to rise from 25°C to 34.85°C. Determine the heat of combustion of carbon.*

SOLUTION. Heat of combustion of carbon at constant pressure, ΔH = ?

Reaction $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$;

1 mol = 12 g. 1 mol 1 mol; $\Delta n = 1 - 1 = 0$

(*i*) wt. of graphite = 2.516 g ; rise in temperature = 34.85 – 25 = 9.85°C

Heat capacity of calorimeter = 2000 cal °C$^-$

∴ Amount of heat taken up by the calorimeter

= Heat capacity of calorimeter × rise in temperature

= 2000 cal °C$^-$ × 9.85°C = 19700 cal.

(*ii*) *To find ΔE i.e., heat of combustion at constant volume.*

2.516 g graphite produce heat = 19700 cal

∴12 g graphite produce heat

$$= \frac{19700}{2.516} \times 12 = 93959\ \text{cal}$$

$$= 93959 \text{ cal} \times \frac{1 \text{ k cal}}{1000 \text{ cal}}$$

$$= 93.959 \text{ k cal}$$

$$\therefore \quad \Delta E = -93.959 \text{ k cal.}$$

(*iii*) $\Delta H = \Delta E + \Delta n RT$

$$= -93.959 \text{ k cal} + 0 \times RT$$

$$= -93.959 \text{ k cal}$$ **Ans.**

15.35. BOMB CALORIMETER

Such a calorimeter which is used to determine the enthalpies of combustion is called bomb calorimeter. In this calorimeter :

$$\text{Heat exchange} = Z \times \Delta T$$

Where : Z = Heat capacity of calorimeter

ΔT = Rise in temperature or change in temperature

Heat changes at constant pressure (ΔH) and heat changes at constant volume (ΔE) are related as :

$$\Delta H = \Delta E + \Delta n RT$$

Where Δn = (Number of moles of products) – (number of moles of reactants)

To find internal energy change (ΔU) at constant volume; use the relation :

$$\mathbf{\Delta U = Z \times \Delta T \times \frac{M}{m}}$$

Where m = mass of the substance taken

M = Molecular mass of the substance.

EXAMPLE 103. *In a constant volume calorimeter, 3.5 g 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⁻, the numerical value for the enthalpy of combustion of the gas in kJ mol⁻ is:*

IIT-JEE, 2009

SOLUTION. Since the combustion takes place at constant volume, the energy released ΔU will be given as :

$$\Delta U = Z \times \Delta T \times \frac{M}{m} \quad \text{...(1)}$$

Where Z = heat capacity of the calorimeter

$= 2.5 \text{ kJ K}^{-}$

ΔT = change in temperature

$= 298.45 - 298.0 = 0.45 \text{ K}$

M = molar mass of gas = 28g mol^{-}

m = mass of the substance = 5.3 g

Substituting the values in (1), we get :

$$\Delta U = 2.5 \text{ kJ K}^{-} \times 0.45 \text{ K} \times \frac{28 \text{ g mol}^{-}}{5.3 \text{ g}}$$

$$= 9.0 \text{ kJ mol}^{-}$$ **Ans.**

EXAMPLE 104. *A sample of an unknown hydrocarbon compound weighing 0.661 g was ignited in a bomb calorimeter. The rise in temperature was found to be 3°C. Calculate the molar mass of the hydrocarbon if 4000 kJ energy was liberated. Heat capacity of calorimeter = 11.3 kJ °C⁻.*

SOLUTION. Since the combustion takes place at constant volume, the energy released ΔU (= 4000 kJ mol⁻) is given as : $\Delta U = Z \times \Delta T \times \frac{M}{m}$ ...(1)

Substituting the values in (1), we get :

$$4000 \text{ kJ mol}^{-} = 11.3 \text{ kJ °C}^{-} \times 3\text{°C} \times \frac{M}{0.661 \text{ g}}$$

$$\therefore \quad M = \frac{4000 \text{ kJ mol}^{-} \times 0.661 \text{ g}}{11.3 \text{ kJ °C}^{-} \times 3\text{°C}}$$

$$= 77.99 \simeq 78 \text{ g mol}^{-}$$ **Ans.**

15.36. HEAT CAPACITY

Type. (*i*) Heat capacity = Sp. heat × mass of the substance

(*ii*) **Energy or Heat absorbed or evolved**

= Specific heat × mass of substance × change in temperature

= Heat capacity × change in temperature

EXAMPLE 105. *When 4.6 g of a gold ring was heated, its temperature rose from 298 K to 305 K. Calculate the amount of heat absorbed if specific heat of gold is 0.129 J g⁻ °C⁻.*

SOLUTION. Rise in temperature

$$= 305 \text{ K} - 298 \text{ K} = 7 \text{ K} = 7\text{°C}.$$

Heat absorbed = Sp. heat × mass of gold × rise in temperature.

$$= 0.129 \text{ J g}^{-} \text{°C}^{-} \times 4.6 \text{ g} \times 7\text{°C}$$

$$= \mathbf{4.15 \text{ J}}$$ **Ans.**

EXAMPLE 106. (*a*) *Calculate the energy required to raise the temperature of 15.0 g of silver from 27°C to 227°C if specific heat of silver is 0.235 J g⁻ °C⁻.*

(*b*) *What mass of iron (sp. heat 0.45 J g⁻ °C⁻) can be heated through the same temperature difference when provided with the same amount of energy ?*

SOLUTION. (*a*) Rise in temperature

= 227°C – 27°C = 200°C. Mass of silver = 15.0 g; sp. heat = 0.235 J g⁻ °C⁻

∴ Energy needed = Sp. heat × mass × rise in temperature = $0.235 \text{ J g}^{-} \text{°C}^{-} \times 15.0 \text{ g} \times 200\text{°C}$

= 705 J

(*b*) Sp. heat of iron = 0.45 Jg⁻ °C⁻;

mass = ? ; rise is temperature

= 227°C – 27°C = 200°C

But energy = Sp. heat × mass × rise in temperature; 705 J = $0.45 \text{ Jg}^{-} \text{°C}^{-} \times \text{mass} \times 200\text{°C}$

$$\therefore \quad \text{Mass of iron} = \frac{705 \text{ J}}{0.45 \text{ J g}^{-} \text{°C}^{-} \times 200\text{°C}}$$

$$= 7.8 \text{ g}$$ **Ans.**

EXAMPLE 107. *Calculate the amount of energy absorbed by* *heating 120.0 g of water from 25°C to 35°C. Sp. heat of water is 4.18 J g^{-} $°C^{-}$.*

SOLUTION. Mass of water = 120.0 g ; rise in temperature = 35°C – 25°C = 10°C ; sp. heat = 4.18 J g^{-} $°C^{-}$.

Heat absorbed = Sp. heat × mass × rise in temperature.

$= 0.418\ Jg^{-}\ °C^{-} \times 120.0\ g \times 10°C$

$= 5016\ J$

$$= 5016\ J \times \frac{1\ kJ}{1000\ J} = 5.016\ kJ \quad \textbf{Ans.}$$

Type. Mass of solution

= Volume × density

EXAMPLE 108. *A student mixed 50.0 cm^3 of 1 M H Cl at 25°C (density = 1.02 g cm^{-3}) with 50.0 cm^3 of 1 M NaOH at 25°C (density = 1.04 g cm^{-3}) and stirred thoroughly. The temperature of the mixture rose to 31.9°C. Calculate the heat evolved if specific heat of water is 4.18 J g^{-} $°C^{-}$.*

SOLUTION. Mass of solution

= volume × density

Mass of 50 cm^3 HCl $= 50\ cm^3 \times 1.02\ g\ cm^{-3} = 51.0$ g Mass of 50 cm^3 NaOH $= 50\ cm^3 \times 1.04\ g\ cm^{-3} = 52.0$ g

∴ Total mass of solution

= 51.0 g + 52.0 g = 103.0 g.

Rise in temperature = 31.9°C – 25°C = 6.9°C

∴ Heat evolved = Sp. heat × mass of substance × rise in temperature

$= 4.18\ J\ g\ °C^{-} \times 103.0\ g \times 6.9°C$

$$= 2970.7\ J = 2970.7\ J \times \frac{1\ kJ}{1000\ J}$$

= 2.9707 kJ **Ans.**

EXAMPLE 109. *0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of the calorimeter system is 17.7 kJ K^{-1}.* **(Roorkee 1994)**

SOLUTION. Thermal capacity of the calorimeter system

$= 17.7\ kJ\ K^{-1}$

Rise in temperature of calorimeter system = 0.5°C

Amount of heat energy required to raise the temperature of calorimeter system by

0.5° = 17.7 × 0.5 = 8.85 kJ

Thus 0.16 g CH_4 on combustion produces heat

= 8.85 kJ

Heat liberated by 1 mol CH_4 on combustion

$$= \frac{8.85}{0.16} \times 16 = 885\ kJ$$

[∵ g. mol. wt. of $CH_4 = 12 + (4 \times 1) = 16$ g]

∴ Heat of combustion at constant volume,

ΔE = **– 885 kJ**

Now ΔH = ΔE + Δ*n*RT

$$\underset{1\ mol}{CH_{4(g)}} + \underset{2\ mol}{2O_{2(g)}} \longrightarrow \underset{1\ mol}{CO_{2(g)}} + 2H_2O_{(l)}\ (\text{at } 27°C)$$

Δ*n* = 1 – (1 + 2) = –2

∴ ΔH = ΔE – 2RT

$= -885 + (-2)(8.31 \times 10^{-3} \times 300)$

$= -885 - 4.986 = -889.986\ kJ\ mol^{-1}$

Hence, heat of combustion at constant pressure,

ΔH = **– 889.986 kJ**

Type: Heat Q = no. of mol (*n*) × molar heat capacity (C in JK^{-} mol^{-}) × change in temperature (ΔT in K)

EXAMPLE 110. *Molar heat capacity of aluminium is 25 JK^{-} mol^{-}. The heat necessary to raise the temperature of 54 g of aluminium (atomic mass 27 g mol^{-}) from 30°C to 50°C is:*

(a) 1.5 kJ *(b)* 0.5 kJ
(c) 1.0 kJ *(d)* 2.5 kJ
(e) 2.0 kJ **Kerala PET, 2011**

SOLUTION. Molar heat capcity, C = 25 JK^{-} mol^{-}; Heat needed to raise temperature of Al from 30°C to 50°C = Q; ΔT = 50°C – 30°C = 20°C or 20 K; no. of mols (*n*) of Al = wt./at. wt. = 54/27 = 2. But:

Q = nCΔT; Q = 2 mol × 25 JK^{-} mol^{-} × 20 K = 1000 J or Q = (1000/1000) kJ = 1.0 kJ

Note: ΔT = (50 + 273) K^{-} (30 + 273)K = 20 K

So, the correct answer is (*c*)

15.37. ENTHALPY (HEAT) OF FUSION, Δ_{FUS} H°

It is defined as the enthalpy change which takes place when one mole of a solid substance is converted into its liquid state at its melting point. Δ_{fus} H° represents enthalpy of fusion in the standard state *i.e.*, 298 K and one atmospheric pressure.

EXAMPLE 111. *When 2.5 g sodium metal in liquid state solidifies, 289 joules of heat is released. Calculate the enthalpy of fusion of sodium. (atomic mass of Na = 23 g mol^{-})*

SOLUTION. Reaction $\underset{23\ g\ mol^{-}}{Na(l)} \longrightarrow Na(s)$; ΔH° = ?

On solidification of 2.5 g Na(*l*), heat produced = 289 J

On solidification of 23.0 g Na(*l*), heat produced

$$= \frac{289\ J}{2.5\ g} \times 23.0\ g = 2658.8\ J$$

$$= 2658.8\ J \times \frac{1\ kJ}{1000\ J}$$

= **2.6588 kJ** **Ans.**

EXAMPLE 112. *What is the entropy change for the conversion of one g of ice to water at 273 K and one atmospheric pressure? (ΔH_{fusion} = 6.025 KJ mol^{-}).* **(P.S.E.B., 1999 S, 2012)**

SOLUTION. Entropy of fusion, ΔS_{fusion} = ? ; enthalpy of fusion, ΔH_{fusion} = 6.025 kJ mol^{-} = 6.025 × 1000 J mol^{-} ; T = 273 K. We know, $\Delta S_{fusion} = \Delta H_{fus}/T$. Substituting the values, we get : ΔS_{fusion} = (6.025 × 1000)/273 = 22.07 J mol^{-}. But g-mol.wt. of water, H_2O or ice = (2 × 1) + 16 = 18 g. So, ΔS_{fusion} of 18 g ice = = 22.07 J. Hence ΔS_{fusion} of 1g ice = 22.07/18 = 1.226 $JK^{-}g^{-}$. **Ans.**

EXAMPLE 113. *The latent heat of fusion of sodium at 371 K* *is 2.636 kJ. Calculate the entropy change (i) per gram atom (ii) per gram accompanying the fusion of sodium.*

Solution. g atomic weight of sodium = gram atom = 23 g ;

ΔH_f of sodium = 2.636 kJ = 2.636 × 1000 = 2636J ;

T = 371 K ;

we know, $\Delta S_f = \Delta H_f / T$.

So, (*i*) ΔS_f = 2636 J/371 K = 7.105 JK^{-}.

(*ii*) ΔS_f per gram accompanying the fusion of sodium

$= 7.105\ JK^{-}/23 = 0.3089\ JK^{-}$. **Ans.**

15.38 ENTROPY CHANGE OF VAPORISATION

Type. $\Delta S_v = \dfrac{\Delta H_v}{T}$

Example 114. *Calculate the enthalpy of vaporisation per mole for ethanol. Given ΔS = 109.8 JK¯ mol¯ and boiling point of ethanol is 78.5°C.* **(AISB 1989)**

Solution. Enthalpy of vaporisation, ΔH_v = ? ;

ΔS_v = 109.8 $JK^{-}\ mol^{-}$.

B.pt. of ethanol = 78.6°C

or T = 273 + 78.5 = 351.5 K.

We know, $\Delta S_v = \Delta H_v / T$.

or $\Delta H_v = \Delta Sv \times T$.

Substituting the values, we get.

$\Delta H_v = (109.8\ JK^{-} \times 351.5\ K)$

$= 38594\ J\ mol^{-}$

$= 38594/1000 = 38.594\ kJ\ mol^{-}$ **Ans.**

Example 115. *Diethyl ether boils at 35°C at 1 atmospheric pressure. If its heat of vaporisation is 6.5 kcal, calculate its entropy at boiling point.* **(ISC, 2008)**

Solution. Boiling point of diethyl ether

= 35 + 273 = 308 K;

ΔH_{vap} = 6.5 kcal = 6.5 × 1000 cal = 6500 cal

$$\therefore\ \Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{6500\ cal\ mol^{-}}{308\ K}$$

$= 21.1\ cal\ K^{-}\ mol^{-}$ **Ans.**

Example 116. *Calculate the entropy change involved in the vaporisation of water at 373 K to vapour at the same temperature (latent heat of vaporisation = 2.275 kJ/g.)*

(Haryana school board, 1995)

Solution. g. mol. wt. of water (H_2O = (2 × 1) + 16 = 18 g. So, molar enthalpy of vaporisation (ΔH_V) of H_2O = 18 × 2.275 kJ ; entropy of vaporisation, ΔS_v = ? ; T = 373 K. We know, $\Delta S_V = \Delta H_V/T$. Substituting the values we get : ΔS_V = 18 × 2.275 kJ/373

or ΔS_V = 18 × 2.275 × 1000 J/373

$= 109.78\ JK^{-}\ mol^{-}$ **Ans.**

Example 117. *$\Delta S_{(vap)}$ of acetone is 93.0 J/K/mole. If boiling point of acetone is 56°C, calculate the heat required for the vaporisation of 1 g of acetone.* **(HP Board, 2007, 2012)**

Solution. For entropy change of vaporisation :

$$\Delta S_{(vap)} = \frac{\Delta H}{T} \qquad ...(i)$$

$\Delta S_{(vap)} = 93.0\ J\ K^{-}\ mol^{-}$;

T = 56 + 273 = 329 K

Molar mass of acetone, CH_3COCH_3 = 12 + (3 × 1) + 12 + 16 + 12 + (3 × 1) = 58 g mol^{-}

Substituting the values of ΔS and T in equation (*i*), we get :

$$93\ JK^{-}\ mol^{-} = \frac{\Delta H}{329\ K}\ ;\ \Delta H = 93\ JK^{-}\ mol^{-} \times 329$$

K = 30597 J mol^{-}

ΔH for 1 mol (= 58 g) acetone = 30597 J

$$\Delta\ H \text{ for 1 g acetone} = \frac{30597\ J}{58} = 527.5\ J$$ **Ans.**

Example 118. *Calculate the standard molar entropy change for the reaction,*

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2\,(aq) + H_2(g)$$

$\Delta S^{\ominus}_m = 41.42\ JK^{-} mol^{-};\ \Delta S^{\ominus}_m\,(H_2O)$

$= 69.96\ JK^{-} mol^{-};\ \Delta S^{\ominus}_m\ [Ca(OH)_2\,(aq)]$

$= -\,74.5\ JK^{-}\ mol^{-}\ ;\ \Delta S^{\ominus}_m\ (H_2)$

$= 130.6\ JK^{-}\ mol^{-}$.

Solution. We know, $\Delta_r S^{\ominus}_m = \Sigma S^{\ominus}$ (products) – $\Sigma S^{\ominus}$ (Reactants).

$\therefore\ \Delta_r S^{\ominus}_m = -74.5 + 130.6 - 41.42 - (2 \times 69.96)$

$JK^{-}\ mol^{-} = (-\,74.5 + 130.6 - 41.42 - 139.92)$

$\mathbf{JK^{-}\ mol^{-} = -\,125.24\ JK^{-}\ mol^{-}}$ **Ans.**

Example 119. *For the reaction $A(s) \longrightarrow B(s) + C(s)$, calculate the entropy change at 298K and 1 atmosphere if absolute entropies (JK¯ mol¯) are A = 130, B = 203 and C = 152.*

[DSB, 1991]

Solution. We know

$\Delta S° = \Sigma\, S°$ (products – $\Sigma\, S°$ (reactants)

$= (S°_B + S°_C) - S°_A$

= (203 + 152) – 130 = 355 – 130

= 225 $JK^{-}\ mol^{-}$

Example 118. *2 moles of an ideal gas at 27°C expand reversibly from 2 litres to 20 litres. Find the entropy change for the reaction.* **(ISC, 2007)**

Solution. We know that, entropy change,

$$\Delta S = \frac{q_1}{T} = \frac{2.303\ nRT\ \log \dfrac{V_2}{V_1}}{T}$$

or $\Delta S = 2.303\ nR \log \dfrac{V_2}{V_1}$. But V_1 = 2L,

V_2 = 20L ; n = 2 ; R = 8.314 J $K^{-}\ mol^{-}$.

$\therefore\ \Delta S = 2.303 \times 2 \times 8.314\ JK^{-} \log \dfrac{20}{2}$

$= 2.303 \times 2 \times 8.314\ JK^{-} \times 1$

or $\Delta S = 38.29\ JK^{-}$ **Ans.**

15.39 GIBB'S FREE ENERGY CHANGE

Type. (*i*) $\Delta G° = \Sigma\, \Delta_f G°$ (products) – $\Sigma\, \Delta_f G°$ (reactants) (*ii*) Δ_f G° for elements (*e.g.*, C, S etc) and diatomic homonuclear molecules like H_2, N_2, O_2 = zero.

EXAMPLE 119. *Calculate the standard free energy change for the following reaction at 298 K.*

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

Given $\Delta_f G°$ for $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 0, 0 and – 16.66 kJ mol^{-} respectively.

SOLUTION. $\Delta G° = \Sigma\, \Delta_f G°\ \text{(Products)} - \Sigma\, \Delta_f G°\ \text{(Reactants)}$

$\Delta G° = 2 \times \Delta_f G°\ (NH_3) - [\Delta_f G°\ (N_2) + 3\Delta_f G°\ (H_2)]$

$= (2 \times -16.66 - 0 - 0)$ kJ $= -33.32$ kJ

Ans.

EXAMPLE 120. *Silane, SiH_4 burns in air forming $SiO_2(s)$, and $H_2O(g)$ according to the reaction,*

$$SiH_4(g) + 2O_2(g) \longrightarrow SiO_2(s) + 2H_2O(g).$$

Calculate the value of Δ_r G°, given that :

$\Delta_f G°\ (SiH_4)\ (g) = 52.3\ kJ\ mol^{-}$; $\Delta_f G°\ (SiO_2)_s = 805\ kJ\ mol^{-}$; $\Delta_f G°\ (H_2O)_g = -225.6\ kJ\ mol^{-}$

SOLUTION. We know

$\Delta_r G° = \Sigma\, \Delta_f G°\ \text{(Products)} - \Sigma\, \Delta_f G°\ \text{(Reactants)}$

or $\Delta_r G° = \Delta_f G°\ (SiO_2) + 2\Delta_f G°\ (H_2O) - \Delta_f G°\ (SiH_4) - 2\Delta_f G°\ (O_2)$

$= -805 + 2\,(-228.6)$ **kJ** $- 52.3 - 2(0)$ **kJ**

$= -805 - 457.2 - 52.3$ **kJ** $=$ **– 1314.5 kJ** **Ans.**

EXAMPLE 121. *Calculate the standard free energy change for the formation of methane at 298K*

C(graphite) + $2H_2(g) \longrightarrow CH_4(g)$. Given that :

	C (graphite)	$H_2(g)$	$CH_4(g)$
$\Delta_f H°$ (kJ mol^{-})	0	0	– 74.81
S° (JK^{-} mol^{-})	5.70	130.7	186.3

SOLUTION. We know

$\Delta G° = \Delta H° - T\Delta S°$. Substituting the values we get :

$\Delta G° = [\Sigma\, \Delta H°\ \text{(Products)} - \Sigma\, \Delta H°\ \text{(Reactants)} - T\,[\Sigma\, S°\ \text{(Products)} - \Sigma\, S°\ \text{(Reactants)}]$

$= \Delta H°\ (CH_4) - \Delta H°C\ \text{(graphite)} - 2\Delta H°\ (H_2) - 298\ [S°\ (CH_4) - S°\ C\ \text{(graphite)} - 2S°\ (H_2)]$

$= -74.81\ \text{kJ} - 0 - 0 - 298\ [186.3 - 5.70 - 2\,(130.7)\ \text{J}]$

$= -74.8 \times 1000\ \text{J} - 298\ (186.3 - 5.70 - 261.4)\ \text{J}$

$= -74810 - (-24078.4)$

$= -50731.6\ \text{J} \approx 50.7\ \text{kJ}$ **Ans.**

EXAMPLE 122. *Show that the reaction CO(g) + $\frac{1}{2}$ $O_2(g) \longrightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when the standard entropy change is – 0.094 kJ mol^{-} K^{-}. The standard Gibb's free energies of formation for CO_2 and CO are – 394.4 and – 137.2 kJ mol^{-} respectively.* **(IIT, 2000)**

SOLUTION. $CO(g) + \frac{1}{2}\ O_2(g) \longrightarrow CO_2(g)$

$\Delta_r G° = \overset{\circ}{G}_f\ \text{(products)} - \overset{\circ}{G}_f\ \text{(reactants)}$

$= \overset{\circ}{G}_f\ (CO_2) - \left[\overset{\circ}{G}_f(CO) + \frac{1}{2}\overset{\circ}{G}_f(O_2)\right]$

$= -394.4 - \left[-137.2 + \frac{1}{2} \times 0\right]$

$= -394.4 + 137.2 = -257.2$ kJ

Since $\Delta_r G°$ is negative, the reaction is spontaneous.

But $\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$-257.2\ \text{kJ} = \Delta_r H° - (300\ \text{K} \times -0.094\ \text{kJ})$

$= \Delta_r H° + 28.2\ \text{kJ}$

$\Delta_r H° = -257.2\ \text{kJ} - 28.2\ \text{kJ} = -285.4\ \text{kJ}.$

Since $\Delta_r H°$ is negative, the reaction is exothermic

EXAMPLE 123. *When l-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 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 :*

$$B \rightleftharpoons A,\ \Delta G°_1 = ?$$

$$B \rightleftharpoons C,\ \Delta G°_2 = ?$$

From the calculated values of $\Delta G°_1$ and $\Delta G°_2$, indicate the order of stability of A, B and C. Write a reasonable reaction mechanism sharing all intermediates leading to A, B, C.

(IIT 2001)

SOLUTION. The equilibrium involved is

1-pentyne	$\rightleftharpoons$	2-pentyne	$\rightleftharpoons$	1, 2–pentadiene
(A)		(B)		(C)
1.3%		95.2%		3.5%

(*i*) Calculation of $\Delta G°_1$ and $\Delta G°_2$

$$(Keq)_1 = \frac{(A)_{eq}}{(B)_{eq}} = \frac{1.3}{95.2} = 1.366 \times 10^{-2}$$

$\Delta G°_1 = -2.303\ RT\ \log\ (\boldsymbol{keq})_1$

$= -2.303 \times 8.314 \times (273 + 175 = 448) \times \log\ (1.366 \times 10^{-2})$

$= 15991\ \text{J mol}^{-1}$

For the equilibrium B $\rightleftharpoons$ C, we have

$$(K_{eq})_2 = \frac{[C_{eq}]}{[B_{eq}]} = \frac{3.5}{95.2} = 3.676 \times 10^{-2}$$

$\therefore \quad \Delta G°_2 = -2.303\ [RT\ \log\ (keq)_2]$

$\therefore \quad = -2.303 \times 8.314 \times 448\ \log\ (3.676 \times 10^{-2})$

$= 12304\ \text{J mol}^{-}$

(*ii*) Calculation of order of stability

Stability of a compound is related to its free energy of formation. Higher positive value of ΔG_f means less stability and vice versa.

For the equilibrium B $\rightleftharpoons$ A

$\Delta G°_1 = \Delta G°_f(A) - \Delta G_f°\ (B)$

or $\Delta G°_f(A) = \Delta G°_1 + \Delta G°_f\ (B)$

$= \Delta G°_f(B) + 15991\ \text{J mol}^{-1}$

Similarly, for the equilibrium B $\rightleftharpoons$ C

$$\begin{aligned} \Delta G°_2 &= \Delta G°_f(C) - \Delta G°_f(B). \\ \text{or} \quad \Delta G°_f(C) &= \Delta G°_f(B) + \Delta G°_2 \\ &= \Delta G°_f(B) + 12304 \text{ J mol}^{-1} \end{aligned}$$

But $\Delta G°_f$ of a compound is equal to its G°

[∵ For elements, G° is taken as zero]

Thus standard free energies of A, B, C are in the order $A > C > B$

∴ Order of stabilities is $B > C > A$

This also follows from the percentage of A, B and C in the equilibrium mixture.

EXAMPLE 124. (*i*) *The reaction* $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ *is carried out at 298 K and 20 bar. 5 mol each of* N_2O_4 *and* NO_2 *are taken initially.*

Given : $\Delta_f G°\ N_2O_4 = 100$ *kJ mol*$^{-1}$

$\Delta_f G° NO_2 = 50$ *kJ mol*$^{-1}$

Find ΔG for reaction at 298 K under given conditions.

(*ii*) *The reaction proceeds at an initial pressure of 20 bar. Find the direction in which the reaction proceeds to achieve equilibrium.* **(IIT 2004)**

SOLUTION. (*i*) Standard Gibb's free energy change for the reaction,

$$\begin{aligned} N_2O_4(g) &\rightleftharpoons 2NO_2(g) \\ \Delta G° &= \Delta_f G°\,(\text{products}) - \Delta_f G°\,(\text{reactants}) \\ &= 2 \times 50 - 100 = 0 \\ \Delta G° &= -2.303\, RT \log K_p = 0 \\ \therefore \quad K_p &= 1 \\ \text{Initially, } P_{N_2O_4} &= P_{NO_2} = 10 \text{ bar} \\ \text{So} \quad Q_p(\text{initial}) &= \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{100}{10} = 10 \end{aligned}$$

Initial Gibb's free energy of the above reaction is given by

$$\begin{aligned} \Delta G &= \Delta G° + 2.303\, RT \log Q_p \\ \Delta G &= 0 + 2.303 \times 8.314 \times 298 \log 10 \\ &= 5.705 \times 10^3 \text{ J mol}^{-1} = 5.705 \text{ kJ mol}^{-1} \end{aligned}$$

(*ii*) Since initial Gibbs free energy change for the reaction is positive, so the reverse reaction will take place.

15.40 ΔG = ΔH – TΔS

Type. (*i*) $\Delta G = \Delta H - T\Delta S$

(*ii*) If ΔG is negative, the reaction is feasible or spontaneous.

(*iii*) If ΔG is positive, the reaction is not feasible or is non-spontaneous.

EXAMPLE 125. *The values of ΔH and ΔS for a reaction are* -10.5×10^3 *J mol*$^{-}$ *and* + 31 *JK*$^{-}$ *mol*$^{-}$ *respectively. Decide whether the reaction is spontaneous at 298 K.* **(PSEB, 2000)**

SOLUTION. $\Delta G = \Delta H - T\Delta S$. Substituting the values, we get $\Delta G = -10.5 \times 10^3 \text{ J} - 298\,(31) \text{ J} = -10500 - 9238 = -19738$ J. Since, ΔG is negative, reaction is spontaneous.

EXAMPLE 126. *The decomposition of* Fe_2O_3 *is a non-spontaneous process*

$$2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g)\ ;$$
$$\Delta_r G^{\ominus} = +\,1487 \text{ kJ mol}^{-}$$

Show that the reduction of Fe_2O_3 *by CO can be made spontaneous by coupling with the following reaction :*

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)\ ;$$
$$\Delta_r G^{\ominus} = -\,514 \text{ kJ mol}^{-}$$ **(CBSE, 2007)**

SOLUTION. *Given :* (*i*) $2Fe_2O_3(s) \longrightarrow 4Fe(s) + 3O_2(g);$

$\Delta_r G^{\ominus} = +\,1487$ *kJ mol*$^{-}$

(*ii*) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)\ ;$

$\Delta_r G^{\ominus} = -\,514$ *kJ mol*$^{-}$

Required equation :

$$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2\ ;$$
$$\Delta_r G^{\ominus} = \ ? \qquad \ldots(A)$$

In order to get equation (A), we have :

$\frac{1}{2}$ × *equation (i)* + $\frac{3}{2}$ × *equation (ii)*

$$Fe_2O_3(s) + 3CO(g) + \frac{3}{2}O_2(g) \longrightarrow 2Fe(s) + \frac{3}{2}O_2(g) + 3CO_2(g)$$

Or $$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)\ ;$$
$$\Delta_r G^{\ominus} = -\,27.5 \text{ kJ mol}^{-}$$

$\Delta_r G^{\ominus}$ in kJ mol^{-}

(*i*) $\frac{1}{2} \times 1487 = 743.5$

(*ii*) $\frac{3}{2} \times -514 = -771.0$

$$\begin{aligned} \therefore \quad \Delta r\, G° &= 743.5 - 771.0 \\ &= -\,27.5 \text{ kJ mol}^{-} \end{aligned}$$

Since $\Delta_r G^{\ominus}$ is negative, the reduction of $Fe_2O_3(s)$ with CO(g) is feasible.

EXAMPLE 127. *For a reaction* $M_2O(s) \longrightarrow 2M(s) + \frac{1}{2}O_2(g)$, *ΔH = 30 kJ mol*$^{-}$ *and ΔS = 0.07 kJK*$^{-}$ *mol*$^{-}$ *(at 1 atm). Calculate upto which temperature will the reaction be not spontaneous ?*

SOLUTION. ΔH = 30 kJ mol^{-} = 30 × 1000 = 30,000 J mol^{-} ; ΔS = 0.07 k JK^{-} mol^{-} = 0.07 × 1000 = 70 JK^{-} mol^{-} ; T = ?.

We know that : $\Delta S = \frac{\Delta H}{T}$ or $T = \frac{\Delta H}{\Delta S}$

Substituting the values, we get :

$$T = \frac{30{,}000 \text{ Jmol}^{-}}{70 \text{ JK}^{-}} = 428.57 \text{ K} \quad \textbf{Ans.}$$

EXAMPLE 128. *Calculate the free energy change on dissolving one mole of sodium chloride at 25°C. Lattice energy = + 777.8 kJmol*$^{-}$ *; hydration energy of NaCl = – 774.1 kJ mol*$^{-}$ *; ΔS at 25°C = 43 JK*$^{-}$ *mol*$^{-}$*.* **(DSB 1984)**

SOLUTION. Free energy change, ΔG = ?

lattice energy = 777.8 kJ mol^{-} ;

hydration energy = – 774.1 kJ mol^{-}

Hence, $\Delta H = 777.8 - 774.1 = 3.7 \text{ kJ mol}^{-}$

$= 3.7 \times 1000 = 3700 \text{ J mol}^{-}$;

$\Delta S = 43 \text{ JK}^{-}\text{mol}^{-}$; $T = 25 + 273 = 298$ K.

Using Gibb's Helmholtz equation, $\Delta G = \Delta H - T\Delta S$,

we have ; $\Delta G = 3700 - (298 \times 43)$

$= -9114 \text{ J mol}^{-} = \dfrac{-9114}{1000}$

$= -9.114 \text{ kJ mol}^{-}$ **Ans.**

Example 129. *Calculate the free energy change for the reaction, $C_{(graphite)} + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -300$ kJ/mole; $\Delta S = 3 \text{ JK}^{-} \text{mol}^{-}$ at 300 K. Predict whether the reaction is spontaneous or not at 300 K.* **(HP Board, 2007, ISC, 2009)**

Solution. We know that; $\Delta G = \Delta H - T\Delta S$. Substituting the values, we get:

$\Delta G = -300 \times 1000 \text{ J} - 300 \times 3 \text{ J} = -300\,[1000 + 3] = -300,900 \text{ J} = -300.9 \text{ kJ mol}^{-}$.

Since ΔG is negative, the reaction is feasible.

Example 130. *ΔH and ΔS for the vaporisation of water at one atmospheric pressure are 40.63 kJ mol⁻ and 108.8 JK⁻ mol⁻ respectively. Calculate the temperature at which the free energy change for this transformation will be zero. Predict giving reasons the sign of free energy change (ΔG) above this temperature.*

Solution. $\Delta H = 40.63 \text{ kJ mol}^{-} \times \dfrac{1000 \text{ J}}{1 \text{ kJ}}$

$= 40630 \text{ J mol}^{-}; \Delta S = 108.8 \text{ JK}^{-}\text{mol}^{-}$;

$T = ?$

We know that $\Delta G = \Delta H - T\Delta S$;

$0 = 40630 \text{ J mol}^{-} - T \times 108.8 \text{ J K}^{-}\text{mol}^{-}$

$\therefore \quad T = \dfrac{40630}{108.8} \text{ K} = 373.4 \text{ K}$

At temperature greater than 373.4 K, $T\Delta S > \Delta H$.

So, ΔG is negative.

Type. (*i*) $\Delta G = 0$ *i.e.*, zero at equilibrium.

(*ii*) $\Delta G = \Delta H - T\Delta S$

Example 131. *ΔH_{Vap} for water is 40.73 kJ mol⁻ and ΔS_{vap} is 109 JK⁻mol⁻. Calculate the temperature at which liquid water will be in equilibrium with water vapours.* **(CBSE 2000 S)**

Solution. For equilibrium, $\Delta G = 0$

We know, $\Delta G = \Delta H - T\Delta S$.

Substituting the values, we get :

$0 = 40.73 \text{ kJ} - T\,(109 \text{ J})$

$= 40.73 \times 1000 \text{ J} - 109 \text{ TJ}\}$

or $109\,T = 40730$ **or** $T = \dfrac{40730}{109}$

= 373.67 K **Ans.**

Example 132. *For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, $\Delta H = -95.4$ kJ and $\Delta S = -193.3 \text{ JK}^{-}$. Calculate the temperature at which the free energy change will be zero. Predict the nature of reaction at a temperature above it.*

Solution. $\Delta H = -95.4 \text{ kJ} = -95.4 \times 1000$

$= -95400 \text{ J}$; $\Delta S = -193.3 \text{ JK}^{-}$,

$T = ?$; $\Delta G = 0$.

According to Gibb's Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

Substituting the values, we get :

$0 = -95400 \text{ J} - (T \times 198.3 \text{ JK}^{-})$

or $95400 \text{ J} = 198.3 \text{ TJK}$

or $T = \dfrac{95400 \text{ J}}{198.3 \text{ JK}^{-}} = 481.09 \text{ K}$ **Ans.**

Since, ΔG is positive, the reaction is non–spontaneous.

Example 133. *Given below are the standard Gibb's energy changes for two reactions at 1773 K*

$$C + O_2 \longrightarrow CO_2 \,;\ \Delta_r G^{\ominus} = -380 \text{ kJ mol}^{-}$$

$$2C + O_2 \longrightarrow 2CO \,;\ \Delta_r G^{\ominus} = -500 \text{ kJ mol}^{-}$$

Discuss the possibility of reducing Al_2O_3 with carbon at this temperature

$$4Al + 3O_2 \longrightarrow 2Al_2O_3 \,;$$

$$\Delta_r G^{\ominus} = -22500 \text{ kJ mol}^{-}$$ **(CBSE, 2007)**

Solution. Given : (*i*) $C + O_2 \longrightarrow CO_2$;

$\Delta_r G^{\ominus} = -380 \text{ kJ mol}^{-}$

(*ii*) $2C + O_2 \longrightarrow 2CO$; $\Delta_r G^{\ominus} = -500 \text{ kJ mol}^{-}$

(*iii*) $4Al + 3O_2 \longrightarrow 2Al_2O_3$; $\Delta_r G^{\ominus} = -22500 \text{ kJ mol}^{-}$

Required equation :

$Al_2O_3 + 2C \longrightarrow 2Al + CO + CO_2$; $\Delta_r G^{\ominus} = ?$ ...(A)

In order to get equation (A), we have :

$-\dfrac{1}{2} \times$ equation (*iii*) + equation (*i*) + $\dfrac{1}{2} \times$ equation (*ii*)

$$-2Al - \frac{3}{2} O_2 + C + O_2 \longrightarrow -AL_2O_3 + CO_2 + CO + C + \frac{1}{2} O_2$$

Or $Al_2O_3 + 2C \longrightarrow 2Al + CO + CO_2$;

$\Delta_r G^{\ominus} = +10620 \text{ kJ mol}^{-}$

$\Delta_r G^{\ominus}$ in kJ mol⁻

(*iii*) $-\dfrac{1}{2} \times -22500 = +11250$

(*i*) -380

(*ii*) $\dfrac{1}{2} \times -500 = -250$

$\Delta_r G^{\ominus} = 11250 - 380 - 250$

$= +10620 \text{ kJ mol}^{-}$

Since the value of $\Delta_r G^{\ominus}$ is positive, Al_2O_3 cannot be reduced with carbon.

Example 134. *At 0°C ice and water are in equilibrium and $\Delta H = 6.00$ kJ/mole for the process*

$$H_2O(s) \rightleftharpoons H_2O(l)$$

what will be the ΔS and ΔG for the conversion of ice to liquid water ? **(HP Board, 2007)**

Solution. (*i*) At equilibrium, $\Delta G = 0$ **Ans.**

But $\Delta G = \Delta H - T\Delta S$; $0 = 6 \text{ kJ} - 273 \text{ K}\,\Delta S$

$[\because 0°C + 273 = 273 \text{ K}]$

$$\therefore \quad 273\text{ K}\,\Delta S = 6\text{ kJ} \;;\; \Delta S = \frac{6\text{ kJ mol}^-}{273\text{ K}}$$

$$\therefore \quad \Delta S = \mathbf{0.012198\ kJ\ K^-\ mol^-} \qquad \textbf{Ans.}$$

EXAMPLE 135. *The value of $\Delta_f G°$ for $NH_3(g)$ at 298 K is – 16.6 kJ mol^- Calculate the equilibrium constant, K_p for the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ at 298 K.*

SOLUTION. $\Delta_f G°$ for 1 mol

$$NH_3(g) = -16.6\text{ kJ mol}^- = -16.6 \times 1000 = -16600\text{ J mol}^-$$

So, $\Delta_f G°$ for 2 mol

$$NH_3(g) = 2 \times -16600 = -33200\text{ J mol}^-$$

[∵ The reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$ involves 2 moles of NH_3].

We know that :

$$\Delta_f G° = -2.303\text{ RT}\log K_p$$

Or
$$\log K_p = \frac{\Delta_f G°}{-2.303\text{ RT}}$$

where R = 8.314 JK^- mol^- and T = 298 K.

Substituting the values, we get

$$\log K_p = \frac{-33200}{(-2.303 \times 8.314 \times 298)} = 5.8186$$

$$\therefore \quad K_p = \text{antilog } 5.8186 = \mathbf{6.6 \times 10^5} \qquad \textbf{Ans.}$$

EXAMPLE 136. *If the standard free energy change for a reaction is zero, what is the value of equilibrium constant for the reaction?* **ISC, 2010**

SOLUTION. We know, $\Delta G° = 2.303\text{ RT}\log kp$

or $0 = -2.303\text{ RT}\log kp;\ \log kp = 0;$

$kp = \log 10$. Hence $kp = 1$ **Ans.**

EXAMPLE 137. *Calculate $\Delta_r G°$ for the conversion of oxygen to ozone, $\frac{3}{2}O_2(g) \longrightarrow O_3(g)$ at 298 K if K_p for the conversion is 2.47×10^{-29}.*

SOLUTION. $T = 298\text{ K},\ K_p = 2.47 \times 10^{-29},$

$R = 8.314\text{ JK}^-\text{ mol}^-\ ;\ \Delta_r G° = ?$

We know, $\Delta_r G° = -2.303\text{ RT}\log K_p$.

Substituting the values, we get,

$$\begin{aligned}\Delta_r G° &= -2.303 \times 8.314\text{ JK}^-\text{ mol}^- \times 298\text{ K}\log 2.47 \times 10^{-29}\\ &= -5705.8\,[\log 2.47 - 29\log 10]\\ &= -5705.8\,[0.3927 - 29]\\ &= -5705.8 \times -28.6 = 163185\text{ J}\\ &= 163.185\text{ kJ}\end{aligned}$$ **Ans.**

EXAMPLE 138. *Calculate the equilibrium constant for the following reaction at 298 K and 1 atomspheric pressure. C(graphite) + $H_2O(l) \longrightarrow CO(g) + H_2(g)$. $\Delta_f H°$ at 298 K for : $H_2O(l)$ = – 286.0 kJ mol^- ; CO(g) = – 110.5 kJ mol^- ; ΔS° at 298 K for the reaction = 252.6 JK^- mol^-. Gas constant, R = 8.31 JK^- mol^-.* **(CBSE 1996)**

SOLUTION. Equilibrium constant, K = ?.

Reaction. $C(\text{graphite}) + H_2O(l) \longrightarrow CO(g) + H_2(g)$.

$$\begin{aligned}\Delta_f H°\text{ for }H_2O\,(l) &= -286\text{ kJ mol}^-;\\ CO(g) &= -110.5\text{ KJmol}^-;\\ \Delta S° &= 252.6\text{ JK}^-;\ T = 298\text{ K}.\\ \Delta_f H° &= \Delta_f H°\,(\text{Products}) - \Delta_f H°\,(\text{reactants})\end{aligned}$$

Or
$$\begin{aligned}\Delta_f H° &= \Delta_f H°\,[CO(g) + H_2(g)] - \Delta_f H°\,[C(\text{graphite}) + H_2O(l)]\\ &= -110.5 + 286 - 0 = -175.5\text{ kJ}\\ &= 175500\text{ J}\end{aligned}$$

Substituting the values in equation :

$\Delta G = \Delta H - T\Delta S$, we have :

$$\begin{aligned}\Delta G &= 175.5 \times 1000\text{ J mol}^- - (298 \times 252.6\text{ JK}^-\text{ mol}^-)\\ &= 175500 - 75274.8 = 100225.2\text{ J}\end{aligned}$$

But, $\Delta G = -2.303\text{ RT}\log K$.

Substituting the values, we get :

$$100225.2 = -2.303 \times 8.31 \times 298\log K$$

Or
$$\log K = \frac{100225.2}{(-2.303) \times 8.31 \times 298} = -17.5738$$

Hence, $K = \text{antilog of } -17.5738 = 2.66 \times 10^{-18}$ **Ans.**

EXAMPLE 139. *(a) Integral heat of solution (ΔH) for 1 mole of KCl dissolved in 50 moles of water is + 17.89 kJ. When one mole of KCl is dissolved in 200 moles of water, ΔH is 18.615 kJ. Calculate the heat of dilution.*

(b) A reaction with $\Delta G°_r < 1$ always has an equilibrium constant value greater than 1. Why ? **(CBSE, 2007)**

SOLUTION. Given :

(*a*) (*i*) $KCl(s) + 50H_2O \longrightarrow KCl\,(50H_2O)$;

$\Delta H_1 = +17.891\text{ kJ}$

(*ii*) $KCl(s) + 200H_2O \longrightarrow KCl\,(200H_2O)$;

$\Delta H_2 = +18.615\text{ kJ}$

$$\therefore \text{Heat of dilution} = \Delta H_2 - \Delta H_1 = 18.615 - 17.891 = \mathbf{0.724\ kJ} \qquad \textbf{Ans.}$$

(*b*) We know that,

$$\Delta G° = -2.303\text{ RT}\log K$$

If K = 1, then
$$\Delta G° = -2.303\text{ RT}\log 1 = -2.303\text{ RT} \times 0 = 0$$

So, if the value of ΔG° is negative *i.e.*, ΔG° < 0, the value of K must be greater than 1.

Type. (*i*) $\Delta G = \Delta H - T\Delta S$

(*ii*) If ΔG value is negative, reaction will be feasible or spontaneous.

EXAMPLE 140. *The enthalpy change for the reaction, $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$ is 32.0 kJ mol^- and ΔS = 0.08 kJ K^- mol^- (at atm). Calculate the temperature at which*

ΔG is equal to zero. Also predict the direction of the reaction at a temperature below this calculated temperature. **(PSEB 1995 S)**

SOLUTION. $\Delta H = 32.0\ kJ\ mol^{-} = 32 \times 1000 = 32000\ J\ mol^{-}$; $\Delta S = 0.08\ kJ = 0.08 \times 1000 = 80\ JK^{-}\ mol^{-}$; $T = ?\ \Delta G = 0$.

According to Gibb's Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

Substituting the values, we get :

$$0 = (32000 - (T \times 80)$$

Or $$T = \frac{32000}{80} = 400\ K.$$

Ans. The reaction will not be spontaneous below this temperature.

EXAMPLE 141. *Enthalpy change and entropy change of a chemical reaction at 25°C are 177.0 kJ and 160.4 JK⁻ respectively. Calculate energy change of the reaction and predict whether the reaction is spontaneous or non-spontaneous.* **(ISC, 2007)**

SOLUTION. $\Delta H = 177\ kJ = 177 \times 1000 = 177{,}000\ J$; $\Delta S = 160.4\ J\ K^{-}$; $T = 25 + 273 = 298\ K$. We know that :

$$\Delta G = \Delta H - T\Delta S$$
$$= 177{,}000\ J - 298 \times 160.4\ J$$
$$= 177{,}000 - 47799.2$$
$$= 129200.8\ J = 129.2008\ kJ$$

Since ΔG is positive, the reaction is non-spontaneous.

EXAMPLE 142. *At what temperature does the reduction of lead oxide to lead by carbon becomes spontaneous? PbO + C $\longrightarrow$ Pb(s) + CO(g).. For the reaction, ΔH and ΔS at 25°C are 108.4 kJ mol⁻ and 190 JK⁻ mol⁻ respectively.*

(CBSE 2001 ; PSEB 2002)

SOLUTION. $\Delta H = 108.4\ kJ\ mol^{-} = 108.4 \times 1000 = 108400\ J\ mol^{-}$; $\Delta S = 190\ JK^{-}$; $T = ?$

We know $\Delta S = \dfrac{\Delta H}{T}$ Thus, $T = \dfrac{\Delta H}{\Delta S}$

Substituting the values, we get :

$$T = \frac{108400\ J\ mol^{-}}{190\ JK^{-}\ mol^{-}} = 570.5\ K \quad \textbf{Ans.}$$

EXAMPLE 143. *The engine of a halicopter (weighing 500 kg) runs with a fuel constituent (mol. wt., 114) which has 35% efficiency. How much volume of fuel [heat of combustion, 1500 k cal mol⁻; density, 0.71 g (mL)$^{-1}$] will be used to fly the halicopter up to 500 m (g = 9.8 m s^{-2}).*

SOLUTION. m = mass of halicopter

$$= 500\ kg \times \frac{1000\ g}{1\ kg} = 5 \times 10^5\ g.$$

$$g = 9.8\ m\ s^{-2} = 9.8 \times 100\ cm\ s^{-2} = 980\ cm\ s^{-2}$$
$$h = 500\ m = 500 \times 100 = 5 \times 10^4\ cm$$

$\therefore$ Work needed to lift halicopter = mgh

$$= 5 \times 10^5\ g \times 980\ cm\ s^{-2} \times 5 \times 10^4\ cm$$
$$= 2.45 \times 10^{13}\ g\ cm^2\ s^{-2} = 2.45 \times 10^{13}\ erg$$

$[\because 1\ erg = 1\ g\ cm^2\ s^{-2}]$

$$= \frac{2.45 \times 10^{13}}{4.184 \times 10^7}\ cal$$

$[\because 1\ cal = 4.184 \times 10^7\ erg]$

$$= 585,564\ cal = 585.564\ k\ cal$$

Efficiency of fuel

= 35%

$\therefore$ Work obtained from 1 mol fuel

$$= \frac{1500\ k\ cal \times 35}{100} = 525\ k\ cal$$

525 k cal work is obtained from fuel

= 1 mol = 114 g

585.564 k cal work is obtained from fuel

$$= \frac{114}{525} \times 585.564 = 127.15\ g$$

$\therefore$ Volume of fuel required

$$= \frac{\text{Mass of fuel}}{\text{density of fuel}} = \frac{127.15\ g}{0.71\ g(mL)^{-}}$$

= **179 mL** **Ans.**

EXAMPLE 144. *(a) Calculate the resonance energy of C_6H_6 using Kekule formula for C_6H_6 from the following data.*

(i) $\Delta_f H°$ for C_6H_6 = – 358.5 kJ mol

(ii) Bond energy of C—H, C—C, C = C and H—H bonds in kJ mol⁻ respectively are 490, 340, 620 and 436.9.

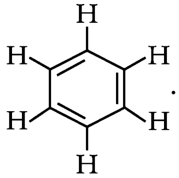
(iii) Heat of atomisation of C = 716.8 kJ mol⁻.

(b) In the production of water gas, the reaction involved is:

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)\ ;$$
$$\Delta_r H° = +\ 131.4\ kJ\ mol^{-}$$

For this reaction, $\Delta_r S°$ is + 134 JK⁻ mol⁻. Find out the spontaneous feasibility of this reaction at (i) 25°C (ii) 1000°C.

(CBSE, 2007)

SOLUTION. (*a*) C_6H_6 is  . It has 3 C—C, 3C = C, and 6 C—H bonds.

Reaction : $6C(s) + 3H - H(g) \longrightarrow C_6H_6$;

$$\Delta H_{exp.} = -358.5\ kJ$$
$$\Delta H_{cal.} = [\text{B.E. of reactants}] - [\text{B.E. of products}]$$
$$= [6C_{s \to g} + 3H\text{–}H] - [3C\text{–}C + 3C = C + 6\ C\text{–}H]$$
$$= (6 \times 716.8) + (3 \times 436.9) - [(3 \times 340) + (3 \times 620) + (6 \times 490)]$$
$$= 4300.8 + 1310.7 - 1020 - 1860 - 2940 = -298.5\ kJ$$

$\therefore$ Resonance energy $= \Delta H_{exp} - \Delta H_{cal}$

$$= -358.5 - (-208.5)$$
$$= -358.5 + 208.5$$

= **– 150 kJ mol⁻** **Ans.**

(*b*) We know that : $\Delta G° = \Delta H° - T\Delta S°$

$$\Delta H° = +131.4 \text{ kJ mol}^{-};$$

$$\Delta S° = +134 \text{ J} \times \frac{1 \text{ kJ}}{1000\ J} \text{ K}^{-} \text{mol}^{-}$$

$$= 0.134 \text{ kJ K}^{-} \text{mol}^{-}$$

(*i*) 25°C = 25 + 273 = 298 K

(*ii*) 1000°C = 1000 + 273 = 1273 K

(*a*) At 25°C : $\Delta G° = \Delta H° - T\Delta S°$

$= 131.4 \text{ kJ mol}^{-} - (298 \text{ K} \times 0.134 \text{ kJ}$

$\text{K}^{-} \text{mol}^{-}) = 131.4 - 39.932$

$=$ **91.468 kJ mol⁻** **Ans.**

Since $\Delta G°$ is positive, reaction is not feasible

(*b*) At 1000°C : $\Delta G° = \Delta H° - T\Delta S°$

$= 131.4 \text{ kJ mol}^{-} - (1273 \text{ K} \times 0.134 \text{ kJ}$

$\text{K}^{-} \text{mol}^{-}) = 131.4 - 170.582 = -39.182 \text{ kJ mol}^{-}$

Since $\Delta G°$ is negative, the reaction is feasible.

EXAMPLE 145. *Calculate the efficiency of a steam engine which operates between 373 K and 573 K. What is the minimum heat which must be withdrawn from the reservoir to obtain 171.52 Joules of work ?*

SOLUTION. $T_1 = 373 \text{ K}, T_2 = 573 \text{ K}$

$$\text{Efficiency } (\eta) = \frac{T_2 - T_1}{T_2} = \frac{573 - 373}{573} = 0.35 = 35\%$$

Work to be done = 171.52 J

Heat to be withdrawn from the reservoir,

$$q_2 = \frac{W_{max}}{\eta} = \frac{171.52}{0.35} = \mathbf{490.0\ J}$$

15.41 CALORIFIC VALUES OF FOODS AND FUELS

The amount of heat energy released by the complete combustion of ***one gram*** *of fuel or food is called the calorific value of fuel or food.*

EXAMPLE 146. *Calculate the calorific value of octane (C_8H_{18}), a component of gasoline with the help of following reaction.*

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l);$$
$$\Delta H = -10{,}920 \text{ kJ}.$$

(at. wt., C = 12, H = 1)

SOLUTION. Reaction

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l);$$
$$\Delta H = -10{,}920 \text{ kJ}$$

2[(8 × 12) + (18 × 1)] = 228 g

228 g of C_8H_{18} produce heat = 10920 kJ

$\therefore$ 1 g of C_8H_{18} produce heat

$$= \frac{10920}{228} \text{ kJ} = \mathbf{47.89\ kJ} \qquad \textbf{Ans.}$$

EXAMPLE 147. *The heat produced in the combustion of glucose is given below.*

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g);$$
$$\Delta H = -2840 \text{ kJ}$$

How much energy is needed to produce 0.90 g of glucose for the reverse reaction ? (at. wt., C = 12, H = 1, O = 16)

SOLUTION.

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g);$$
$$\Delta H = -2840 \text{ kJ}$$

(6 × 12) + (12 × 1) + (6 × 16)

= 180 g

180 g glucose produce heat = 2840 kJ

$$\therefore 0.9 \text{ g of glucose produce heat} = \frac{2840}{180} \times 0.9$$

$$= \mathbf{14.2\ kJ} \qquad \textbf{Ans.}$$

EXAMPLE 148. *The bacterial fermentation of animal refuse produces gobar gas which mainly contains methane gas. The latter gas on combustion gives following products.*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g);$$
$$\Delta H = -809 \text{ kJ}$$

If a village contains 50 families and each family needs 15,000 kJ of energy per day, how much gobar gas will be needed per day for this purpose if methane gas present in gobar gas is 75% by weight?

SOLUTION. Energy consumed per day by 50 families

= 50 × 15,000 kJ = 750,000 kJ

Reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g);$$
$$\Delta H = -809 \text{ kJ}$$

12 + (4 × 1) = 16 g

809 kJ energy is produced from

CH_4 = 16 g

750,000 kJ energy is produced from

$$CH_4 = \frac{16}{809} \times 750{,}000 \text{ g}$$

But CH_4 present is 75% by weight.

$$\therefore \text{Wt. of gobar gas} = \frac{16}{809} \times 750{,}000 \times \frac{100}{75} \text{ g}$$

$$= \frac{16}{809} \times \frac{750{,}000 \times 100}{1000 \times 75}$$

$$= \mathbf{19.78\ kg} \qquad \textbf{Ans.}$$

EXAMPLE 149. *Calculate the number of mol and volume (in litre) of propane at N.T.P. to heat 100 kg of water from 20°C to 60°C. ($\Delta_c H$ (propane) = – 2050 kJ, sp. heat for water = 4.184 × 10^{-3} kJg⁻ °C⁻).*

SOLUTION.

(*i*) $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O + 2050 \text{ kJ}$

Propane

1 mol

$$\text{Mass } (m) \text{ of water} = 100 \text{ kg} = 100 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}}$$

$\Delta T = 60 - 20 = 40°C$;

sp. heat of water, C = $4.184 \times 10^{-3} \text{ kJg}^{-} \text{°C}^{-}$

$\therefore$ Heat energy required to heat water,

$$Q = m \times C \times \Delta T$$

$$= 100 \times 1000 \text{ g} \times 4.184 \times 10^{-3}$$

$$\text{kJ g}^{-}\ ^\circ\text{C}^{-} \times 40^\circ\text{C} = 16736 \text{ kJ}$$

(*ii*) 2050 kJ heat is produced from propane = 1 mol

16736 kJ heat is produced from propane

$$= \frac{1}{2050} \times 16736 = 8.16 \text{ mol}$$

(*iii*)1 mol propane at N.T.P.

$$= 22.4 \text{ L}$$

8.16 mol propane at N.T.P.

$$= 22.4 \times 8.16 = \mathbf{182.784\ L}$$ **Ans.**

EXAMPLE 150. *Supposing that all the energy required by a healthy human being is met only by the carbohydrates, in the form of glucose, calculate the amount of carbohydrates (in mass) needed by the healthy human being. Given, enthalpy of combustion of glucose = 2840 kJ ; energy needed per day by human being = 9500 kJ.*

SOLUTION. Molar mass of glucose,

$$C_6H_{12}O_6 = (6 \times 12) + (12 \times 1) + (6 \times 16)$$

$$= 180 \text{ g mol}^{-}$$

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g) + 2840 \text{ kJ}$$

2840 kJ energy is produced from glucose = 180 g

9500 kJ energy is produced from glucose

$$= \frac{180}{2840} \times 9500 \text{ g} = \mathbf{602.1\ g}$$ **Ans.**

EXAMPLE 151. *A sample of coal contains 75% carbon. When it is burnt in insufficient oxygen, 70% carbon is converted to CO_2 while the rest is converted to carbon monoxide.*

$$C(s) + O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta H = -394 \text{ kJ}$$

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)\ ;\ \Delta H = -111 \text{ kJ}$$

(*i*) *Calculate the heat generated when 5.0 kg of this coal sample is burnt in an oven.*

(*ii*) *Calculate the percent heat loss in heating value when coal is burnt in insufficient oxygen.*

(*iii*) *Calculate the heat evolved if coal sample is burnt in sufficient O_2 to form completely CO_2 gas.*

SOLUTION. Wt. of coal = 5.0 kg.

So, wt. of carbon in coal

$$= 5 \times \frac{75}{100}\,' = 3.75 \text{ kg.}$$

Wt. of carbon converted to

$$CO_2 = 3.75 \text{ kg} \times \frac{70}{100} = 2.625 \text{ kg}$$

$$= 2.625 \times 1000 = 2625\text{g}$$

Wt. of carbon converted to

$$CO = 3.75 \text{ kg} \times \frac{(100-70)}{100}$$

$$= 3.75 \text{ g} \times \frac{30}{100}$$

$$= 1.125 \text{ kg} = 1.125 \times 1000 = 1125 \text{ g}$$

$$\underset{12\text{ g}}{C} + O_2 \longrightarrow CO_2\ ;\ \Delta H = -394 \text{ kJ}$$

$$\underset{12\text{ g}}{C} + \frac{1}{2} O_2 \longrightarrow CO\ ;\ \Delta H = -111 \text{ kJ}$$

(*i*)(*a*) 12 g carbon produce heat = 394 kJ

$$2625 \text{ g carbon produce heat} = \frac{394}{12} \times 2625$$

$$= 86187.5 \text{ kJ}$$

(*b*) 12 g carbon produce heat = 111 kJ

$$1125 \text{ g carbon produce heat} = \frac{111}{12} \times 1125$$

$$= 10406.25 \text{ kJ}$$

∴ Total heat produced = 86187.5 kJ + 10406.25 kJ

$$= 96593.75 \text{ kJ}$$ **Ans.**

(*iii*) Total wt. of carbon = 3.75 × 1000

$$= 3750 \text{ g}$$

12 g carbon produce heat = 394 kJ

$$3750 \text{ g carbon produce heat} = \frac{394}{12} \times 3750$$

$$= 123{,}125 \text{ kJ}$$ **Ans.**

(*ii*) % age loss in heating value, when heated in presence of insufficient O_2

$$= \frac{123{,}125 - 96593.75}{123{,}125} \times 100$$

$$= \frac{26531.25 \times 100}{123{,}125}$$

$$= 21.55\%$$ **Ans.**

EXAMPLE 152. *A woman wants to lose her weight by 1.1 kg. She takes diet equivalent to 9000 kJ per day and expends energy in all forms to a total of 10,000 kJ per day. Calculate the change in internal energy per day. Also, calculate the number of days, she would take to lose 1.1 kg weight if energy lost was stored as sucrose (1632 kJ per 100 g). Ignore water loss.*

SOLUTION. Wt. to be lost

$$= 1.1 \text{ kg} = 1.1 \text{ kg} \times \frac{1000 \text{ g}}{1 \text{ kg}}$$

$$= 1100 \text{ g.}$$

Energy taken by woman

$$= 9000 \text{ kJ}$$

Energy consumed in doing work

$$= 10{,}000 \text{ kJ}$$

∴ Change in internal energy per day

$$= 10{,}000 - 9000 = 1000 \text{ kJ}$$

Loss in energy for 100 g sucrose

$$= 1632 \text{ kJ per day}$$

Loss in energy for 1100 g sucrose

$$= \frac{1632}{100} \times 1100 = 17952 \text{ kJ per day.}$$

$\therefore$ Number of days required to lose 1100 g weight

$$= \frac{17952}{1000} \text{ days} = 17.952 \text{ days} \quad \textbf{Ans.}$$

15.42 BORN-HABER CYCLE

A cyclic process called Born-Haber prcess is helpful to calculate lattice energy (Uo) in terms of thermo-chemical quantities like ionisation energy (I.E.), electron affinity (E.A.), sublimation energy (S), dissociation energy (D), heat of formation, ΔH_f.

(*i*) For M X type compounds (e.g., NaCl, K Br etc) :

$$\Delta H_f = S + \frac{1}{2} D + I.E. + E.A. + Uo$$

(*ii*) For M X_2 type compounds (e.g., MgF_2, SiO_2 etc) :

$$\Delta H_f = S + D + I.E. + 2E.A. + Uo$$

Where Uo is the lattice energy. Lattice energy is the energy released when oppositely charged ions get attracted by strong electrostatic force of attraction to form one mole of a substance.

Example 153. *Calculate the heat of formation of NaCl from the following data.*

Lattice energy (Uo) of NaCl = – 773.95 kJ mol$^-$ *; enthalpy of dissociation (D) of* Cl_2 *= 225.9 kJ mol*$^-$ *; ionisation energy (I.E.) of potassium = 489.5 kJ mol*$^-$ *; electron affinity (E.A.) of chlorine = – 351.4 kJ mol*$^-$ *and sublimation energy (S) of potassium = 108.7 kJ mol_.*

Solution. Using Born-Haber cycle, we have :

$$\begin{tikzcd}
\text{Na(s)} + \frac{1}{2}Cl_2(g) \arrow[d, "+S(+)"'] \arrow[dr, phantom, ""] \arrow[rr, "\Delta H_f"] & & \text{NaCl(s)} \\
\text{Na(g)} \quad \text{Cl(g)} \arrow[d, "+I.E.(+) \quad E.A.(—)"'] & & \\
\text{Na}^+(g) \quad \text{Cl}^-(g) \arrow[uurr, "Uo\ (—)"'] & &
\end{tikzcd}$$

$$\downarrow +\tfrac{1}{2}D(+)$$

We know that : $\Delta H_f = S + \frac{1}{2} D + I.E + E.A. + Uo$ ...(1)

Substituting the values in equation (1), we get :

$$\Delta H_f = 108.7 + \frac{1}{2}(225.9) + 489.5$$
$$+ (–351.4) + (–773.95)$$
$$= – 414.2 \text{ kJ mol}^-$$

Hence heat of formation of

$$\text{NaCl} = – 414.2 \text{ kJ mol}^-. \qquad \textbf{Ans.}$$

Example 154. *Calculate the lattice energy of* MgF_2 *from the following data.*

(*i*) *Heat of sublimation of magnesium = 146.4 kJ mol*$^-$ (*ii*) *dissociation energy of fluorine = 158.8 kJ mol*$^-$ (*iii*) *ionisation energy of magnesium = 2186.0 kJ mol*$^-$ (*iv*) *electron affinity of fluorine = – 332.6 kJ mol*$^-$ (*v*) *Heat of formation of magnesium fluoride = – 1096.5 kJ mol*$^-$*.*

Solution. In case of MX_2 type compounds like MgF_2, we have :

$$\Delta H_f = S + D + I.E. + 2\,(E.A. \text{ of } F_2) + Uo \qquad ...(1)$$

Substituting the values in equation (1), we have :

$$– 1096.5 = 146.4 + 158.8 + 2186.0 + 2(–332.6) + Uo$$

$$\therefore \qquad Uo = – 1096.5 – 146.4 – 158.8 – 2186 + 665.2$$

$$\mathbf{Uo = – 2922.5\ kJ\ mol^-} \qquad \textbf{Ans.}$$

Example 155. *You are provided with the following data for argon chloride (ArCl). Predict whether ArCl will be formed or not ?*

$$Ar(g) + \frac{1}{2} Cl_2(g) \longrightarrow ArCl(g)$$

Lattice energy of ArCl = – 703.0 kJ ; I.E. of Ar = 1526.3 kJ ; heat of dissociation of Cl_2 *= – 243.0 kJ ; E.A. of chlorine = – 348.3 kJ ; enthalpy of sublimation of Ar = 243 kJ.*

Solution. We know that for MX type compounds like ArCl, we have :

$$\Delta H_f = S + \frac{1}{2} D + IE + EA + Uo \qquad ...(1)$$

Substituting the values, we get :

$$\Delta H_f = [243 + \frac{1}{2}(–243) + (1526.3) + (–348.3) –703]kJ$$
$$= [243 – 121.5 + 1526.3 – 348.3 – 703] \text{ kJ}$$
$$= + 596.5 \text{ kJ}$$

Since ΔH_f is positive, the reaction is endothermic. So, the formation of ArCl is not favoured.

Example 156. *Find the electron affinity (EA) of iodine with the help of following data (in k cal mol*$^-$*).* ΔH_f *(NaI) = – 68.8 ; U (NaI) = – 165.4 ;* ΔH *(S) of Na = 25.9 ;* ΔH *(diss)* (I_2) *= 51.0 ; I.E. (Na) = 118.4.*

Solution. We know that :

$$\Delta H_f(\text{NaI}) = \Delta H\,(S)\,\text{Na} + \frac{1}{2}\Delta H\,(\text{diss})\,(I_2) + IE\,(\text{Na}) + EA\,(I) + U\,(\text{NaI})$$

Substituting the values, we get :

$$– 68.8 = 25.9 + \frac{1}{2}(51) + 118.4 + EA\,(I) –165.4$$

$$\therefore \qquad EA\,(I) = 165.4 – 68.8 – 25.9 – 25.5 – 118.4$$

$$EA\,(I) = – 73.2 \text{ k cal mol}^- \qquad \textbf{Ans.}$$

Type. (*i*) To calculate proton affinity (PA) of a base X (*e.g.*, NH_3), the reaction used is :

$$X(g) + H^+(g) \longrightarrow XH^+(g)\ ;\ \Delta H = PA$$

(*ii*) $\qquad \Delta H_f = \Delta H\,(\text{diss}) + IE + EA + PA + Uo$

Example 157. *Calculate the proton affinity of ammonia in the following reaction :*

$$NH_3(g) + H^+ \longrightarrow NH_4^+(g)\ ;\ \Delta H = PA$$

Given : ΔH_f *of* $NH_4^+ = -144.5$ *kJ mol⁻ ;*

$Uo = -648.5$ *kJ mol⁻ ;* $IE = 1311.6$ *kJ mol⁻ ;*

$EA = -347.2$ *kJ mol⁻ ;*

$\Delta H\ (diss) = 430.9$ *kJ*

Solution. We know that :

$$\Delta H_f = \Delta H\ (\text{diss}) + \text{IE} + \text{EA} + \text{PA} + \text{Uo}$$

Substituting the values, we get

$$-144.5 = 430.9 + 1311.6 - 347.2 + \text{PA} - 648.5$$

$$\therefore \quad \text{PA} = -144.5 - 430.9 - 1311.6 + 347.2 + 648.5$$

Or $\quad$ **PA = – 891.3 kJ mol⁻** $\quad$ **Ans.**

15.43 AIEEE PATTERN EXAMPLES

Example 158. *5 mol of* $N_2(g)$ *at 5 atmospheric pressure contained in a 100 L cylinder absorbed 30.26 kJ of heat when it expanded to 200 L at 2 atmospheric pressure. The change in the internal energy of* N_2 *gas is :*

(*a*) *+ 20.26 J* $\quad$ (*b*) *+ 20.26 kJ*

(*c*) *– 20.26 kJ* $\quad$ (*d*) *10 kJ*

Solution. $V_1 = 100$ L ; $V_2 = 200$ L ; $P = 2$ atm

$$\therefore \quad \text{Work, } W = -P(V_2 - V_1)$$

$$= -2 \text{ atm } (200 - 100) \text{ L}$$

$$= -200 \text{ L atm} = -200 \times 101.30 \text{ J}$$

$$[\because 1 \text{ L atm} = 101.30 \text{ J}]$$

$$= -20260 \text{ J} = -20260 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$= -20.26 \text{ kJ}$$

Heat absorbed, $q = 30.26$ kJ

But $\quad \Delta U = q + W$ (first law of thermodynamics)

$$\therefore \quad \Delta U = 30.26 \text{ kJ} + (-20.26 \text{ kJ}) = +10 \text{ kJ}$$

So, the correct answer is (*d*).

Example 159. *A frictionless and weightless piston was fitted into a cylinder containing a gas. This gas was allowed to expand from one litre to 5 litre against a constant pressure of one atmosphere. In doing so, 200 J of heat was absorbed from the surrounding. The change in the internal energy of the system is:*

(*a*) *+ 205.2 J* $\quad$ (*b*) *+ 205.2 kJ*

(*c*) *– 205.2 kJ* $\quad$ (*d*) *– 405.2 J*

Solution. $V_1 = 1\text{L}$, $V_2 = 5\text{L}$; $\Delta V = 5 - 1 = 4\text{L}$;

$P = 1$ atm ; $q = 200$ J

Since work done by the system is negative, so :

$$W = -P\Delta V = -1 \times 4 \text{ L atm} = -4 \text{ L atm}$$

$$= -4 \times 101.3 \text{ J} [\because 1 \text{ L atm} = 101.3 \text{ J}]$$

$$= -405.2 \text{ J}$$

But $\quad \Delta U = q + W$ (First law of thermodynamics)

$$= (200 - 405.2) \text{ J} = -205.2 \text{ J}$$

So, the correct answer is (*c*).

Example 160. *When 50 J heat is supplied to a system, the increase in internal energy of the system is 38 J. The work done by the system is :*

(*a*) *98 J* $\quad$ (*b*) *+ 12 J*

(*c*) *– 12 J* $\quad$ (*d*) *none of these*

Solution. $\Delta U = q + W$ (First law of thermodynamics)

$$q = +50 \text{ J}, \ \Delta U = 38 \text{ J}$$

Substituting the values, we get

$$38 = 50 + W; \ W = 38 - 50 = -12 \text{ J}$$

So, the correct answer is (*c*).

Example 161. *An electric motor generates 20 kJ energy per second as mechanical work. If 1.5 kJ heat is lost to the surrounding, the change in internal energy of the motor will be*

(*a*) *+ 21.5 kJ* $\quad$ (*b*) *– 21.5 kJ*

(*c*) *+ 18.5 kJ* $\quad$ (*d*) *30 kJ*

Solution. $\Delta U = q + W$ (First law of thermodynamics)

$W = -20$ kJ [as energy is lost from the system, W is – ive]

$q = -1.5$ kJ [q is – ive as heat is lost]

Substituting these values, we have :

$$\Delta U = -1.5 - 20 = -21.5 \text{ kJ}.$$

So, the correct answer is (*b*).

Example 162. *2 mol of a gas is allowed to expand freely in vacuum. The work done during the process will be :*

(*a*) *2 kJ* $\quad$ (*b*) *zero kJ*

(*c*) *– 2 kJ* $\quad$ (*d*) *4 kJ*

Solution. Since the gas expands freely in vacuum, it is an irreversible process and $P_{\text{ext}} = 0$. So :

$$W = -P_{\text{ext}}(V_2 - V_1) = -0\,(V_2 - V_1)$$

$$= 0 \ \textit{i.e.}, \text{ zero}$$

So, the correct answer is (*b*).

Example 163. *On supplying 250 J heat to a gas, its 2L volume at N.T.P. becomes 2.2 L at one atmosphere. The change in its internal energy would be :*

(*a*) *302 J* $\quad$ (*b*) *272.75 J*

(*c*) *229.75 J* $\quad$ (*d*) *292.75 J*

Solution. Work done at constant P is negative and irreversible.

$$\therefore \quad W = -P(V_2 - V_1)$$

$$= -1 \text{ atm } (2.2 - 2) \text{ L} = -0.2 \text{ L atm}$$

$$= -0.2 \times \frac{1.987 \times 4.184}{0.0821} \text{ J} = -20.25 \text{ J}$$

$$\left(\because 1 \text{ L atom} = \frac{1.987 \times 4.184}{0.0821} \text{ J}\right)$$

But, $\quad \Delta U = q + W$; $\Delta U = 250 \text{ J} - 20.25$

$$= 229.75 \text{ J}.$$

So, the correct answer is (*c*).

EXAMPLE 164. *The work done to expand isothermally 1.6 g oxygen at 27°C and 5 atmospheric pressure, against a constant external pressure of one atmosphere, is :*

(*a*) *99.76 J* (*b*) *– 49.88 J*

(*c*) *49.88 J* (*d*) *– 99.76 J*

SOLUTION. no. of mol of O_2,

$$n = \frac{\text{wt.}}{\text{mol. wt}} = \frac{1.6}{32} = 0.05;$$

$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-};$$

$$T = 27 + 273 + 300 \text{ K.}$$

(*i*) For O_2, initially,

$$P_1V_1 = nRT$$

$$5 \text{ atm} \times V_1 = 0.05 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{mol}^{-} \times 300 \text{ K}$$

$$\therefore \quad V_1 = \frac{0.05 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 300 \text{ K}}{5 \text{ atm}}$$

$$= 0.2463 \text{ L}$$

(*ii*) For O_2, finally,

$$P_2V_2 = n\text{RT}$$

$$1 \text{ atm} \times V_2 = 0.05 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{mol}^{-} \times 300 \text{ K}$$

$$\therefore V_2 = \frac{0.05 \text{ mol} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 300 \text{ K}}{1 \text{ atm}}$$

$$= 1.2315 \text{ L}$$

Since work is done against constant pressure, P, it is irreversible and also negative.

Thus : $W = -P(V_2 - V_1)$

$= -1 \text{ atm } (1.2315 - 0.2463)$

$\text{L} = -0.9852 \text{ L atm}$

$$= -0.9852 \times \frac{1.987 \times 4.184}{0.0821} \text{ J}$$

$= \mathbf{-99.76 \text{ J}}$

So, the correct answer is (*d*).

EXAMPLE 165. *4 g of H_2 gas at 310 K and 10 atm pressure was allowed to expand isothermally against a constant pressure of 1 atm. The ΔU value for this gas is :*

(*a*) *zero* (*b*) *2.0*

(*c*) *1.0* (*d*) *– 1.0*

SOLUTION. When a gas is allowed to expand isothermally, ΔU = 0 for such an isothermal process.

So, the correct answer is (*a*).

EXAMPLE 166. *When work done by a system was 10 J, the increase in the internal energy of the system was 30 J. The heat 'q' supplied to the system was :*

(*a*) *– 40 J* (*b*) *+ 20 J*

(*c*) *40 J* (*d*) *– 20 J*

SOLUTION. $W = -10 \text{ J} \; ; \; q = ? \; ; \; \Delta U = +30 \text{ J}$

But $\Delta U = q + \text{W}$

[First law of thermodynamics]

$30 = q - 10 \; ; \; q = 30 + 10 = 40 \text{ J}$

So, the correct answer is (*c*).

EXAMPLE 167. *The work done when 10 g of zinc reacts with dil H_2SO_4 in a* ***closed vessel*** *of fixed volume is :*

(*a*) *10 J* (*b*) 1.0 J

(*c*) *zero J* (*d*) *none of these*

SOLUTION. $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2(g)$

The H_2 gas produced cannot drive the atmosphere back because in a closed vessel of fixed volume,

$$\Delta V = 0. \text{ So, } W = -P\Delta V = -P \times 0 = 0$$

So, the correct answer is (*c*).

EXAMPLE 168. *The work done when 6.5 g of zinc reacts with dil. HCl is an* ***open beaker*** *at 298 K is :*

(*a*) *– 495.52 J* (*b*) *247.76 J*

(*c*) *– 247.76 J* (*d*) *– 123.88 J*

(AMU, medical, 2012)

SOLUTION. $Zn + 2HCl \longrightarrow ZnCl_2 + H_2(g)$ ...(1)

1 mol 1 mol

Since H_2 gas drives back the atmosphere in an open beaker, work is done by the gas which is negative.

$$\therefore \quad W = -P_{\text{ext}} \times \Delta V$$

Since initial volume = zero, so ΔV = Final volume – initial volume; ΔV = Final volume

But $$\Delta V = \frac{nRT}{P_{\text{ext}}}$$

$$\therefore \quad \text{W} = -P_{\text{ext}} \times \frac{nRT}{P_{\text{ext}}} = -nRT$$

n = no. of mol of

$$\text{Zn} = \frac{\text{wt. of Zn}}{\text{at. wt. of Zn}} = \frac{6.5}{65} = \frac{1}{10}$$

From equation (1),

$$1 \text{ mol of Zn} \equiv 1 \text{ mol of } H_2; \; \frac{1}{10} \text{ mol of}$$

$$\text{Zn} \equiv \frac{1}{10} \text{ mol of } H_2$$

$$\therefore \quad W = -nRT;$$

$$W = -\frac{1}{10} \text{ mol} \times 8.314 \text{ JK}^{-} \text{mol}$$

$$\times 298 \text{ K} = -247.76 \text{ J}$$ **Ans.**

So, the correct answer is (*c*).

EXAMPLE 169. *The work done in heating one mol of an ideal gas as constant pressure from 15°C to 25°C is :*

(*a*) *1.987 cal* (*b*) *198.7 cal*

(*c*) 9.935 cal (*d*) *19.87 cal*

SOLUTION. $T_1 = 15 + 273 = 288 \text{ K} \;;$

$T_2 = 25 + 273 = 298 \text{ K}$

We know that : $PV_1 = nRT_1$ and $PV_2 = nRT_2$

Hence $$V_1 = \frac{nRT_1}{P} \text{ and } V_2 = \frac{nRT_2}{P}$$

$$\therefore \quad V_2 - V_1 = \frac{nRT_2}{P} - \frac{nRT_1}{P} \text{ i.e.,}$$

$$V_2 - V_1 = \frac{nR}{P}(T_2 - T_1)$$

Or $\Delta V = \frac{nR}{P}(T_2 - T_1)$

But, $W = -P\Delta V = -P \times \frac{nR}{P}(T_2 - T_1)$

$= -nR\,(T_2 - T_1)$

∴ $W = -1 \text{ mol} \times 1.987 \text{ cal K}^{-} \text{mol}^{-}$

$\times (298 - 288) \text{ K} = 19.87 \text{ cal}$

So, the correct answer is (*d*).

EXAMPLE 170. *One mol of a gas was expanded isothermally and reversibly at 17°C from 2 atm to some other pressure P. If 200 cal work is used in causing reversible isothermal expansion then final pressure P will be :*

(*a*) *2.84 atm* (*b*) *1.42 atm*

(c) *4.26 atm* (*d*) *none of these*

SOLUTION. $W = -200 \text{ cal}, n = 1 \text{ mol},$

$R = 1.987 \text{ cal K}^{-} \text{mol}^{-},$

$T = 17 + 273 = 290 \text{ K},$

$P_1 = 2 \text{ atm}, P_2 = P = ?.$

We know that for reversible isothermal expansion.

$$W = -2.303\, n\text{RT} \log \frac{P_1}{P_2}$$

$$-200 \text{ cal} = -2.303 \times 1 \text{ mol} \times 1.987 \text{ cal K}^{-} \text{mol}^{-} \times 290 \text{ K} \log \frac{2}{P_2}$$

$$\therefore \quad \log \frac{2}{P_2} = \frac{-200}{-2.303 \times 1.987 \times 290} = 0.15$$

$$\log 2 - \log P_2 = 0.15; \log P_2 = \log 2 - 0.15$$
$$= 0.301 - 0.15 = 0.151$$

∴ $\boldsymbol{P_2} = \text{antilog } 0.151 \simeq \mathbf{1.42 \text{ atm.}}$

So, the correct answer is (*b*).

EXAMPLE 171. *At 17°C, 1.5 mol of a perfect gas was compressed reversibly and isothermally from a pressure of 2.02 × 10^3 Nm^{-2} to 8.08 × 10^4 Nm^{-2}. The value of work done and that of free energy would be.*

(*a*) *13.38 kJ, 6.69 kJ* (*b*) *13.38 kJ, 13.38 kJ*

(*c*) *13.38 kJ, – 13.38 kJ* (*d*) *– 13.38 kJ, + 13.38 kJ*

SOLUTION. (*a*) $n = 1.5 \text{ mol}, T = 17 + 273 = 290 \text{ K},$

$R = 8.314 \text{ J K}^{-} \text{mol}^{-},$

$P_1 = 2.02 \times 10^3 \text{ Nm}^{-2},$

$P_2 = 8.08 \times 10^4 \text{ Nm}^{-2}.$

For isothermal reversible process, work done is negative.

So : $W = -2.303\, n\text{RT} \log \frac{P_1}{P_2}$

$$= -2.303 \times 1.5 \text{ mol} \times 8.314 \text{ JK}^{-} \text{mol}^{-} \times 290 \text{ K} \log \frac{2.02 \times 10^3}{8.08 \times 10^4}$$

$$= -8329 \text{ J}\left(\log \frac{1}{40.4}\right)$$

$$= -8329 (\log 1 - \log 40.4) \text{ J}$$

$$\boldsymbol{W} = -8329(0 - 1.6064) = +13379.7 \text{ J}$$

$$= \mathbf{13.38 \text{ kJ}}$$

(*b*) We know W_{rev} is a measure of free energy change, ΔG.

So : $-\Delta G = -W_{rev} = -W_{max}$

∴ $\Delta G = +13.38 \text{ kJ}$

So, the correct answer is (*b*).

EXAMPLE 172. *Air (sp. heat at room temperature and 1 atm = 0.71 $Jg^{-}K^{-}$; density = 1.22 × 10^{-6} kg cm^{-3}) present in a room (dimensions 6 × 5 × 4 m^3) got heated up when a bulb of 500 watt was switched on for 10 minutes, The increase in room temperature if heat capacity of four walls and roof is 60 × 10^3 J K^{-} is :*

(*a*) *183 K* (*b*) *1.83 K*

(*c*) *213 K* (*d*) *715 K*

SOLUTION. 1 Watt = 1Js^{-} ; Volume of room = 6 × 5 × 4 m^3 = 120 m^3 = 120 × 10^6 cm^3 ; wt. of air in room = volume × density = 120 × 10^6 cm^3 × 1.22 × 10^{-6} kg cm^{-3} = 120 × 10^6 × 1.22 × 10^{-6} × 10^3 g = 146400 g

Heat given out by bulb

$$= 500 \text{ watt} \times (10 \times 60) \text{ s}$$
$$= 500 \text{ Js}^{-} \times 600 \text{ s} = 3 \times 10^5 \text{ J}$$
$$[\because 1 \text{ watt} = 1 \text{ Js}^{-}]$$

Heat gained by (walls + roof)

$$= 60 \times 10^3 \text{ J K}^{-} (\Delta T)$$

Heat gained by air = 0.71 $\text{Jg}^{-}\text{ K}^{-}$ × 146400 g × ΔT

But Heat given out by bulb

= Heat gained by (walls + roofs)

+ Heat gained by air

$$3 \times 10^5 \text{ J} = 60 \times 10^3 \text{ J K}^{-}(\Delta T) + 0.71 \times 146400$$
$$\text{J K}^{-} \times \Delta T\; 3 \times 10^5 \text{ J} = \Delta T\,[60 \times 10^3 + 0.71 \times 146400]$$
$$\text{J K}^{-} = 163944 \text{ JK}^{-} \times \Delta T$$

$$\therefore \quad \Delta T = \frac{3 \times 10^5 \text{ J}}{163944 \text{ J K}^{-}} = \mathbf{1.83 \text{ K}}$$

So, the correct answer is (*b*).

EXAMPLE 173. *If specific heat, heat of fusion and heat of vaporisation of water are 1 cal g^{-}, 80 cal g^{-} and 540 cal g^{-} respectively then heat required to convert 5.0 g of ice at 0°C to steam at 100°C would be nearly :*

(*a*) *7.53 J* (*b*) *7.53 kJ*

(*c*) *15.06 kJ* (*d*) *30.12 kJ*

SOLUTION. $\Delta H_{fusion} = 5 \text{ g} \times 80 \text{ cal g}^{-} = 400 \text{ cal}$

$\Delta H_{vaporisation} = 5 \text{ g} \times 540 \text{ cal g}^{-} = 2700 \text{ cal}$

$\Delta H_{heating} = ms\Delta T$

$= 5 \text{ g} \times 1 \text{ cal g}^{-} \times [(100 + 273)$

$-(0 + 273) = 100]$

$= 500 \text{ cal}$

∴ $\Delta H_{total} = \Delta H_{fusion} + \Delta H_{vaporisation} + \Delta H_{heating}$

$= 400 \text{ cal} + 2700 \text{ cal} + 500 \text{ cal}$

$$= 3600 \text{ cal}$$

$$= 3600 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}}$$

$$= 15062.4 \text{ J} \simeq 15.06 \text{ kJ}.$$

So, the correct answer is (*c*).

Example 174. *The entropy change for cooling 1.6 g of an organic compound (mol. wt. 32, molar heat capacity at constant pressure, 59 J K^{-} mol^{-}) from 1000 K to 800 K is :*

(*a*) *– 0.7375 J K^{-}*
(*b*) *1.4750 J K^{-}*
(*c*) *0.3688 J K^{-}*
(*d*) *none of these*

Solution. We know

$$\Delta S = \frac{\Delta H}{T} \qquad ...(1)$$

$$\Delta T = 1000 - 800 = 200 \text{ K}$$

ΔH for cooling the organic compound

$$= mS\Delta T$$

$$= \frac{1.6}{32} \text{ mol} \times 59 \text{ J K}^{-} \text{mol}^{-} \times 200 \text{ K}$$

$$= 590 \text{ J}$$

∴ $\Delta H = -590\text{J}$ because cooling is an exothermic process $T = 800$ K

Substituting the values in (1), we get :

$$\Delta S = \frac{-590 \text{ J}}{800 \text{ K}} = -0.7375 \text{ J K}^{-}$$

So, the correct answer is (*a*).

Example 175. *The entropy change to expand 2 mol of an ideal gas at 27°C, reversibly 6 times of its initial volume is :*

(*a*) *14.9 JK^{-}*
(*b*) *29.8 JK^{-}*
(*c*) *44.77 JK^{-}*
(*d*) *20 JK^{-}*

Solution. Let $V_1 = V$. So, $V_2 = 6V$; $n = 2$ mol,

$$R = 8.314 \text{ JK}^{-} \text{mol}^{-},$$

$$T = 27 + 273 = 300 \text{ K}.$$

We know that : $\Delta S = \frac{q_1}{T}$ *i.e.*, $\Delta S = \dfrac{2.303\, nRT \log \frac{V_2}{V_1}}{T}$

$$= \frac{2.303 \times 2 \text{ mol} \times 8.314 \text{ JK}^{-}\text{mol}^{-} \times 300 \text{ K} \log \frac{6V}{V} \textit{ i.e.}, 6}{300 \text{ K}}$$

$$= 38.29 \times 0.7782 \text{ JK}^{-} \simeq 29.8 \text{ JK}^{-}$$

So, the correct answer is (*b*).

Example 176. *The entropy change during heating of 50 g water (sp. heat = 4200 J kg^{-} K^{-}) from 20°C to 40°C will be :*

(*a*) *13.83 JK^{-}*
(*b*) *– 13.83 JK^{-}*
(*c*) *27.66 JK^{-}*
(*d*) *55.32 JK^{-}*

Solution. Mass (*m*) of water

$$= 100 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = \frac{1}{10} \text{kg} \text{ ; sp.heat}$$

$$= 4200 \text{ J kg}^{-}\text{K}^{-},$$

$$T_1 = 20 + 273 = 293 \text{ K} ;$$

$$T_2 = 40 + 273 = 313 \text{ K}.$$

We know that : $\Delta S = 2.303 \text{ m} \times \text{Cp} \log \frac{T_2}{T_1}$

$$\therefore \quad \Delta S = 2.303 \times \frac{1}{10} \text{ kg} \times 4200 \text{ Jkg}^{-} \text{K}^{-} \log$$

$$= 967.26 \, [\log 313 - \log 293]$$

$$= 967.26 \, [2.4955 - 2.4669]$$

$$= 967.26 \times 0.0286 \text{ J K}^{-} = 27.66 \text{ J K}^{-}$$

So, the correct answer is (*c*).

Example 177. *The heat capacities of water and pressure cooker metal are 1k cal(kg)$^{-}$K^{-} and 0.09 k cal(kg)$^{-}$ K^{-} respectively. The actual heat required to raise the temperature of water (750 g) from 27°C to 110°C in this cooker weighing 5 kg is :*

(*a*) *58.59 k cal*
(*b*) *55.59 k cal*
(*c*) *1.2 k cal*
(*d*) *117.18 k cal*

if 85% heat is delivered to water and the cooker.

Solution. Mass (*m*) of water

$$= 750 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.75 \text{ kg},$$

$$T_1 = 27 + 273 = 300 \text{ K},$$

$$T_2 = 110 + 273 = 383 \text{ K} ;$$

$$\Delta T = 383 - 300 = 83 \text{ K}$$

Mass (*m*) of pressure cooker

$$= 5 \text{ kg} ;$$

∴ Heat (ΔH) required to heat water and cooker

$$= \underset{\text{(water)}}{mS\Delta T} + \underset{\text{(Pressure cooker)}}{m'S\Delta T}$$

$$= 0.75 \text{ kg} \times 1 \text{ k cal(kg)}^{-}\text{K}^{-} \times 83 \text{ K} + [5 \text{ kg} \times 0.09 \text{ k cal(kg)}^{-}\text{K}^{-} \times 83 \text{ K}]$$

$$= 62.25 \text{ k cal} + 37.35 \text{ k cal}$$

$$= 99.6 \text{ k cal}$$

Since 85% heat is delivered to water and cooker :
Actual amount of heat needed

$$= \frac{99.6 \times 100}{85} = 117.18 \text{ k cal}$$

So, the correct answer is (*d*).

Example 178. *One end of a rope is tied to a 40 kg weight while the second end is coupled with an electric generator. A labourer lifts the weight up to 3 metre and then allows it to fall. As a result, the electric generator generates equal amount of electric work. The standard free energy change for the reaction*

$$Al_2O_3(s) + 6Na(s) \longrightarrow 3Na_2O(s) + 2Al(s)$$

is 451 kJ mol^{-} of Al_2O_3. The number of times the weight is lifted and dropped to produce 13.5 g aluminium will be

(*a*) *144*
(*b*) *432*
(*c*) *288*
(*d*) *28*

if g = 9.8 ms^{-2}

Solution. $Al_2O_3(s) + 6Na(s) \longrightarrow 3Na_2O(s) + \underset{2 \times 27 = 54 \text{ g}}{2Al(s)}$

To produce 54 g Al, $\Delta G° = 451$ kJ

To produce 13.5 g Al, $\Delta G^\circ = \frac{451}{54} \times 13.5 = \mathbf{112.75\ kJ}$

Let Q = heat produced when 40 g falls through 3 m distance (h)

$$
\begin{aligned}
\text{But} \quad Q &= mgh \\
&= 40\ \text{kg} \times 9.8\ \text{ms}^{-2} \times 3\ \text{m} \\
&= 392\ \text{kg m}^2\text{s}^{-2} = 392\ \text{J} \\
&\qquad [\because \text{kg m}^2\text{s}^{-2} = 1\ \text{J}]
\end{aligned}
$$

$$
\begin{aligned}
\text{Hence, no. of lifting and falling} &= \frac{\Delta G^\circ}{Q} \\
&= 112.75\ \text{kJ} \times \\
\frac{1000\ \text{J}}{1\ \text{kJ}} \times \frac{1}{392\ \text{J}} &= 287.6 \simeq \mathbf{288}
\end{aligned}
$$

Thus, the labourer is to lift the 40 kg for 288 times. So, the correct answer is (*c*).

EXAMPLE 179. *One mole of an ideal gas is allowed to expand reversibly and adiabatically from temperature of 27°C. If the work done during the process is 3 kJ, the final temperature will be equal to ($C_v = 20\ JK^{-}$).*

(*a*) *100 K* (*b*) *150 K*

(*c*) *295* (*d*) *26.85°C*

(Karnataka, CET, 2000)

SOLUTION. For an adiabetic change,

$$
\begin{aligned}
\Delta E &= q + W \text{ and } q = 0. \\
W &= -3\ \text{kJ} = -3 \times 1000 = -3000\text{J} \\
\text{Hence,} \quad \Delta E &= 0 + (-3000)\ \text{J} = \mathbf{-3000\ J} \\
\text{But,} \quad \Delta E &= nC_v\,(T_2 - T_1). \\
\textbf{Given:} \quad n &= 1,\ T_1 = 27 + 273 = 300\ \text{K} \\
\therefore \quad -3000\ \text{J} &= 1 \times 20\ \text{JK}^{-}\,(T_2 - 300)\,; \\
\frac{-3000\ \text{J}}{20\ \text{JK}^{-}} + 300\ \text{K} &= T_2 \\
\textbf{Or} \quad T_2 &= -150\ \text{K} + 300\ \text{K} = 150\ \text{K}
\end{aligned}
$$

So, the correct answer is (*b*).

EXAMPLE 180. *The heat of neutralisation of a strong acid with a strong base is given by ΔH due to the reaction*

(*a*) $HCN + KOH \longrightarrow KCN + H_2O$

(*b*) $H^+ + H_2O \longrightarrow H_3O^+$

(*c*) $H^+ + OH^- \longrightarrow H_2O$

(*d*) $O_2 + 2H_2 \longrightarrow 2H_2O$

SOLUTION. Whenever, a strong acid (say HCl) reacts with a strong base (say NaOH), salt and water are formed. The process is called neutralisation. As a result, heat (Q) is produced.

$$
\underset{\text{Strong Base}}{NaOH} + \underset{\text{Strong Acid}}{HCl} \longrightarrow \underset{\text{Salt}}{NaCl} + \underset{\text{Water}}{H_2O} + \underset{\text{Heatevolved}}{Q\ kJ}
$$

In the above reaction, H^+ of acid reacts with OH^- of base to form water. ΔH = – Q kJ. Thus the correct answer is (*c*).

EXAMPLE 181. *At constant temperature and pressure, one of the following statements is correct for the reaction,*

$$CO(g) + \frac{1}{2}\,O_2(g) \longrightarrow CO_2(g).$$

(*a*) $\Delta H < \Delta E$ (*b*) $\Delta H > \Delta E$

(*c*) $\Delta H = \Delta E$ (*d*) *None of these.*

SOLUTION. For the reaction.

$$
\underset{1\ \text{mol}}{CO(g)} + \underset{\frac{1}{2}\ \text{mol}}{\frac{1}{2}\,O_2(g)} \longrightarrow \underset{1\ \text{mol}}{CO_2(g)}
$$

Δn = Number of moles of products – number of moles of reactants

$$= 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}\ \text{mol}$$

$$
\begin{aligned}
\text{We know,} \quad \Delta H &= \Delta E + \Delta nRT \\
\Delta H &= \Delta E - \frac{1}{2}RT \text{ or } \Delta H + \frac{1}{2}RT = \Delta E
\end{aligned}
$$

Thus, ΔH < ΔE. So, the correct answer is (*a*).

EXAMPLE 182. *At constant volume and at 298 K, the heat of combustion of sucrose [$C_{12}H_{22}O_{11}(s)$] is – 1348.9 kcal mol⁻. If steam is produced during the combustion, the heat of reaction at constant pressure will be :*

(*a*) *– 1355.46 kcal* (*b*) *+ 1355.46 k cal*

(*c*) *– 1342.344 k cal* (*d*) *+ 1342.344 kcal*

SOLUTION. The given reaction for combustion is :

$$
\underset{\text{12 mol}}{C_{12}H_{22}O_{11}(s) + 12O_2(g)} \longrightarrow \underset{\text{12 mol}}{12CO_2(g)} + \underset{\text{11 mol}}{11H_2O(g)};\quad \Delta H = -1348.9\ \text{k cal}
$$

∴ Δn = Number of moles of products – Number of moles of reactants

$$
\begin{aligned}
&= (12 + 11) - 12 = 11\ \text{mol} \\
\Delta H &= \text{Heat of reaction at constant pressure} \\
\Delta E &= \text{Heat of reaction at constant volume;} \\
R &= 0.002\ \text{k cal};\ T = 298\ \text{K.}
\end{aligned}
$$

$$
\begin{aligned}
\text{But } \Delta H &= \Delta E + \Delta nRT \\
&= -1348.9 + (11 \times 0.002 \times 298) = -1348.9 + 6.556 \\
&= -1342.344\ \text{k cal}
\end{aligned}
$$

So, the correct answer is (*c*).

EXAMPLE 183. *The enthalpy change involved in the oxidation of glucose is – 2880 kJ mol⁻. 25% of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, the maximum distance that a person will be able to walk after eating 120 g of glucose is :*

(*a*) *48 K.M.* (*b*) *4.8 K.M.*

(*c*) *24 K.M.* (*d*) *12 K.M.*

SOLUTION. The given equation is :

$$
\underset{\substack{(6 \times 12) + (12 \times 1) + (6 \times 16) \\ = 180\ \text{g}}}{C_6H_{12}O_6(s)} + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l);
$$

Heat available for muscular work

$$= 2880 \times \frac{25}{100} = 720\ \text{kJ}$$

180 g glucose supplies heat for muscular work
$= 720$ kJ

∴ 120 g glucose will supply heat for muscular work

$$= \frac{720}{180} \times 120 = 480 \text{ kJ}$$

100 kJ energy is needed to walk distance = 1 kilometer
480 kJ energy is needed to walk distance

$$= \frac{1}{100} \times 480 = 4.8 \text{ kilometer}$$

So, the correct answer is (*b*).

Example 184. *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*) *Zero*	(*b*) *40 kJ*
(*c*) *> 40 kJ*	(*d*) *< 40 kJ*

(AIEEE, 2003)

Solution. The process under study is cyclic process. For a cyclic process, the net change in internal energy is **zero** because the change in internal energy does not depend on the path, whether it is reversible or irreversible. So, the correct answer is (*a*).

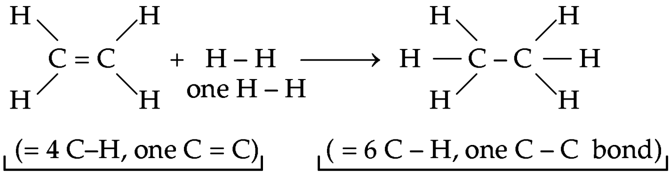
Example 185. *If at 298 K, the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 43 kJ mol⁻, the value of enthalpy change for the reaction :*

$H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ *at 298 k will be :*

(*a*) *– 125 kJ*	(*b*) *+ 250 kJ*
(*c*) *– 250 kJ*	(*d*) *+ 125 kJ*

(AIEEE, 2003, CBSE-PMT 2009)

Solution. The given reaction can be written as :



$$\begin{aligned}\therefore (4 \times 414) + 615 + 435 &= (6 \times 414) + 347\\ &= 1656 + 615 + 435 = 2706 \text{ kJ}\\ &= 2484 + 347 = 2831 \text{ kJ}\\ \therefore \text{ Energy change} &= (\text{Energy of reactants})\\ &\quad - (\text{Energy of products})\\ &= 2706 - 2831 = -125 \text{ kJ.}\end{aligned}$$

So, the correct answer is, (*a*).

Example 186. *The heat of combustion of solid benzoic acid at constant volume is – 312.30 kJ at 27°C. The heat of combustion at constant pressure is :*

(*a*) *100 – R*	(*b*) *200 – 2R*
(*c*) *– 312.3 – 150R*	(*d*) *321.3 + 150R*

Solution. Reaction.

$$\underset{1 \text{ mol}}{C_6H_5COOH(s)} + \underset{\frac{15}{2}\text{ mol}}{\frac{15}{2}O_2(g)} \longrightarrow \underset{7 \text{ mol}}{7CO_2(g)} + 3H_2O(l)$$

$$\begin{aligned}\Delta n_g &= n_p - n_R = 7 - (15/2) = -0.5 \text{ mol;}\\ q_v &= -312.3 \text{ kJ}\\ \text{But} \quad q_p &= q_v + \Delta n_g RT \qquad \text{...(1)}\\ q_p &= -312.3 + (-0.5) \times R \times\\ &\quad (273 + 27 \textit{ i.e.,} \ 300 \text{ K})\\ &= -312.3 - 150 \text{ R}\end{aligned}$$

So, the correct answer is, (*c*).

Example 187. *Based on the first law of thermodynamics, which one of the following is correct?*

(*a*) *For an isothermal process,* $q = +w$
(*b*) *For an isochoric process,* $\Delta u = -q$
(*c*) *For an adiabetic process,* $\Delta u = -w$
(*d*) *For a cyclic process,* $q = -w$

Karnataka CET, 2011

Solution. $\Delta u = q + w$ (First law of thermodynamics). For a cyclic process, $\Delta U = 0$. Hence $0 = q + w$ or $q = -w$

So, the correct answer is (*d*)

Example 188. *If a gas absorbs 200 J of heat and expands by 500 cm*^{3} *against a constant pressure of* $2 \times 10^{+5}$ Nm^{-2}*, then change in internal energy is :*

(*a*) *– 100 J*	(*b*) *+ 100 J*
(*c*) *– 200 J*	(*d*) *+ 200 J*

(10^{-3} m^3 = 1L, 1 L atm = 100 J)

Solution. $q = +200$ J ; P = 10^5 Nm^{-2} = 1 atm ;

$$\Delta V = 500 \text{ cm}^3 = \frac{500}{1000} = 0.5 \text{ L}$$

Change in internal energy,

$$\begin{aligned}\Delta E &= q + W \text{ or } \Delta E = q + (-P\Delta V)\\ \therefore \quad \Delta E &= +200 \text{ J} + (-2 \text{ atm.} \times 0.5 \text{ L})\\ &= 200 \text{ J} - 1 \text{ L atm}\\ &= 200 \text{ J} - 100 \text{ J} \ (\because 1 \text{ L atm} = 100 \text{ J})\\ &= 100 \text{ J}\end{aligned}$$

So, the correct answer is, (*b*).

Example 189. *Work done on a system when one mole of an ideal gas at 500 K is compressed isothermally and reversibly to 1/10th of its original volume. (R = 2 cal).*

(*a*) *1 kJ*	(*b*) *2.303 kJ*
(*c*) *4.606 kJ*	(*d*) *2.303 J*

Solution. $T = 500$ K ; no. of moles, $n = 1$;

$$\frac{V_2}{V_1} = \frac{1}{10} \ ; \ \text{R} = 2 \text{ cal}$$

We know that for an isothermal process ;

$$\text{Work, } W = -2.303 \, n\text{RT} \log \frac{V_2}{V_1}$$

$$= -2.303 \times 1 \times 2 \times 500 \log \frac{1}{10}$$
$$= -2303 \log 10^{-1}$$
$$= (-)(-1)\ 2303 \log 10 \text{ J}$$
$$= \frac{2303 \times 1}{1000} = 2.303 \text{ kJ}$$

So, the correct answer is, (*b*).

EXAMPLE 190. *The amount of heat evolved when 500 cm^3 of 0.1 M HCl is mixed with 200 cm^3 of 0.2 M NaOH is:*

(*a*) *1.292 kJ* (*b*) *2.292 kJ*
(*c*) *0.292 kJ* (*d*) *22.9 kJ*

(Karnataka, CET, 2011)

SOLUTION. No. of moles of HCl = $\frac{500 \times 0.1}{1000}$ = 0.05 mol H^+ ions. No. of moles of NaOH = $\frac{200 \times 0.2}{100}$ = 0.04 mol OH^- ions. From the no. of moles, it is clear that 0.04 mol H^+ ions will neutralise 0.04 mol of OH^- ions and form 0.04 mol H_2O. Amount of heat evolved when 1 mol of H_2O is formed = 57.32 kJ

∴ Amount of heat evolved when 0.04 mol of H_2O is formed = 0.04 × 57.32 = 2.2928 kJ. So, the correct answer is (*b*)

EXAMPLE 191. *For hypothetical reaction,*

$$\frac{1}{2} A_2 + \frac{3}{2} B_2(g) \longrightarrow AB_3(g)\ ;\ \Delta H = -20 \text{ kJ}.$$

If standard entropies of A_2, B_2 and $AB_3(g)$ are 60, 40 and 50 JK^- mol^- respectively. The above reaction will be at equilibrium at :

(*a*) *300 K* (*b*) *400 K*
(*c*) *500 K* (*d*) *10 K*

(Kerala, PET, 2012)

SOLUTION. $\Delta H = -20 \text{ kJ} = -20 \times 1000 \text{ J}$
$= -20{,}000 \text{ J}$

Entropies in JK^- mol^- are,

$$S_{A2} = 60,\ S_{B2} = 40,\ S_{AB3} = 50$$

Thus, for reaction, $\frac{1}{2} A_2(g) + \frac{3}{2} B_2(g) \longrightarrow AB_3(g)$;

$$\Delta S = S_P - S_R$$
$$= (50) - \left[\left(\frac{1}{2} \times 60\right) + \left(\frac{3}{2} \times 40\right)\right]$$
$$= 50 - [30 + 60]$$
$$= 50 - 90 = -40 \text{ JK}^- \text{ mol}^-$$

At equilibrium, $\Delta H = T\Delta S$

Hence, $T = \frac{\Delta H}{\Delta S}$

∴ $T = \frac{-20{,}000\ J}{-40 \text{ JK}^-} = 500 \text{ K}$

So, the correct answer is, (*c*).

EXAMPLE 192. *The enthalpy of vaporisation of benzene is + 35.3 kJ mol^- at its boiling point of 80°C. The entropy change in the transition of vapour to liquid at its boiling point is... J mol^- K^-*

(*a*) *–100* (*b*) *+ 100*
(*c*) *+ 342* (*d*) *– 342*

Karnataka CET, 2011

SOLUTION. $\Delta H_{(\text{Vaporisation})}$ of benzene = 35.3 × 1000 J mol^-

Boiling point, $T_b = 80 + 273 = 353$ K

But $\Delta S_{\text{Vap}} = \frac{\Delta H_{\text{Vap}}}{T_b} = \frac{35.3 \times 1000}{353} = 100 \text{ J mol}^- \text{K}^-$. Thus,

ΔS (condensed) $= -\Delta S_{\text{Vap}} = -100 \text{ J mol}^- \text{ K}^-$

So, the correct answer is (*a*)

EXAMPLE 193. *If for $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$, ΔH_1 is enthalpy of reaction and for $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$, ΔH_2 is the enthalpy of reaction, then :*

(*a*) $\Delta H_1 > \Delta H_2$ (*b*) $\Delta H_2 > \Delta H_1$
(*c*) $\Delta H_1 = \Delta H_2$ (*d*) $\Delta H_1 + \Delta H_2 = 0$

SOLUTION. We know when $H_2O(g)$ condenses to $H_2O(l)$, heat is evolved *i.e.*,

$$H_2O(g) \longrightarrow H_2O(l) + \text{heat}$$

It means ΔH_1 of $H_2O(l)$ is less than of ΔH_2 for $H_2O(g)$. In other words, $\Delta H_2 > \Delta H_1$

So, the correct answer is (*b*).

EXAMPLE 194. *One mole of an ideal gas expanded freely and isothermally at 300 K from 5 litre to 10 litre. If $\Delta E = 0$, the ΔH is :*

(*a*) *1* (*b*) *2*
(*c*) *3* (*d*) *zero*

SOLUTION. Since the gas expands freely and isothermally (*i.e.*, at constant temperature), $\Delta H = 0$. So, the correct answer is, (*d*).

EXAMPLE 195. *Two moles of an ideal gas at 2 atmospheric pressure and 27°C is compressed isothermally to half its volume by external pressure of 4 atmosphere. The work done is :*

(*a*) *2.345 kJ* (*b*) *2.456 J*
(*c*) *4.985 kJ* (*d*) *7 kJ*

SOLUTION. no. of moles, $n = 2$; P = 2 atm. ; R = 0.082 L atm. $(\text{deg})^-$ mol^- ; T = 27 + 273 = 300 K

We know, $PV = nRT$

Hence : $V = \frac{nRT}{P}$

Substituting the values, we get :

$$V = \frac{2 \times 0.082 \times 300}{2} = 24.60 \text{ L}$$

Since gas is compressed isothermally to half its volume,

so : $V = 24.6 \times \frac{1}{2} = 12.3 \text{ L}$

But work, $W = -P_{ext}(V_2 - V_1)$

Thus, we have, $W = -4$ atm (12.3 L)

[∵ External pressure = 4 atm.]

$= -49.2$ atm L

$= 49.2$ L atm

[∵ Work done is positive]

$= 49.2 \times 101.32$ J = 4985 J = 4.985 kJ

So, the correct answer is, (*c*).

Example 196. *$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$; $\Delta H = -270.6$ kJ mol^{-} K^{-} ; $\Delta S = -139.0$ J*

(*i*) *Is the reaction favoured by entropy, enthalpy both or none ?*

(*ii*) *Find ΔG if $T = 300$ K.* **(CBSE 2005)**

Solution. (*i*) $C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$.

The reaction is favoured by enthalpy because ΔH is negative which shows spontaneous process.

(*ii*)
$$\Delta G = \Delta H - T\Delta S\,;$$
$$\Delta G = -270.6 \times 1000\text{ J} - 300\,(-139)\text{ J}$$
$$= -270600\text{ J} + 41700 = -228900\text{ J}$$
$$= \mathbf{-228.9\ kJ} \qquad \textbf{Ans.}$$

Example 197. *For equilibrium reaction, value of Gibb's free energy change is*

(*a*) > 0 (*b*) < 0

(*c*) $= 0$ (*d*) $\neq 0$

(DCE, 2005)

Solution. At equilibrium, $\Delta H = T\Delta S$

Since : $\Delta G = \Delta H - T\Delta S$;

$\Delta G = \Delta H - \Delta H = 0$

So, the correct answer is (*c*).

Example 198. *The sublimation energy of $I_2(s)$ is 57.3 kJ/mol and the enthalpy of fusion is 15.5 kJ/mol. The enthalpy of vaporisation of I_2 is :*

(*a*) *41.8 kJ/mol* (*b*) *− 41.8 kJ/mol*

(*c*) *72.8 kJ/mol* (*d*) *− 72.8 kJ/mol*

(DCE, 2005)

Solution. $I_2(s) \longrightarrow I_2(g)$; $\Delta H_1 = +57.3$ kJ mol^{-}

$I_2(s) \longrightarrow I_2(l)$; $\Delta H_2 = +15.5$ kJ mol^{-}

∴ Enthalpy of vaporisation of

I_2 = ΔH of sublimation − (ΔH of fusion)

= 57.3 − 15.5 = +41.8 kJ mol^{-}

So, the correct answer is (*a*).

Example 199. *For the reaction, $2H_2 + O_2 \longrightarrow 2H_2O$, $\Delta H = -571$. Bond energy of H − H = 435, O = O = 498, then calculate the average bond energy of O − H bond using the above data.*

(*a*) *484* (*b*) *− 484*

(*c*) *271* (*d*) *− 271*

(DCE, 2005)

Solution. Reaction $2H_2 + O_2 \longrightarrow 2H_2O$; $\Delta H = -571$

We know that :ΔH(reaction) = Bond energy of reactants − bond energy of products

∴ $-571 = 2 \times \text{B.E}(H_2) + \text{B.E.}(O_2) - (2 \times \text{B.E. of } H_2O)$

$-571 = 2 \times 435 + 498 - 2 \times \text{B.E. of } H_2O$;

$-571 = 870 + 498 - 2\text{ B.E. }(H_2O)$

$2 \times \text{B.E. of } H_2O = 870 + 498 + 571 = 1939$

∴B.E. of H_2O or H − O − H

$$= \frac{1939}{2} = 969.5$$

$$\therefore \text{B.E. of OH bond} = \frac{969.5}{2} = 484.75 \simeq 484$$

So, the correct answer is (*a*).

Example 200. *The values of ΔH and ΔS for a reaction are respectively 30 kJ mol^{-} and 100 JK^{-} mol^{-}. Then the temperature, above which the reaction will become spontaneous is:*

(*a*) *300 K* (*b*) *30 K*

(*c*) *100 K* (*d*) *300°C*

(J and K– CET, 2011)

Solution. ΔH = 30 kJ mol^{-} = 30 × 1000 = 30,000 J mol^{-}; ΔS = 100 J K^{-} mol^{-}. But at equilibruim, T = ΔH/ΔS

∴ T = 30,000/100 = 300 K. So, the correct answer is (*a*)

Example 201. *ΔH and ΔS for a reaction are + 30.558 kJ mol^{-} and 0.066 kJK^{-} mol^{-} at 1 atm pressure. The temperature at which free energy change is equal to zero and the nature of the reaction below this temperature are :*

(*a*) *483 K, spontaneous*

(*b*) *443 K, non–spontaneous*

(*c*) *443 K, spontaneous*

(*d*) *463 k, non–spontaneous*

(*e*) *463 K, spontaneous* **(Kerala PET, 2005)**

Solution. ΔH = + 30.558 kJ mol^{-} ;

ΔS = 0.066 kJK^{-} mol^{-} ; ΔG = 0

We know : $\Delta G = \Delta H - T\Delta S\,; 0 = +30.558 - T \times 0.066$

Or $$T = \frac{30.558}{0.066} = 463\text{ K}$$

If $(dG)_{T,P} = 0$, the sign '=' refers to a reversible process *i.e.*, non-spontaneous. So, the correct answer is (*d*).

Example 202. *What would be the heat released when an aqueous solution containing 0.5 mole of HNO_3 is mixed with 0.3 mol of OH^- (enthalpy of neutralisation = − 57.1 kJ) ?*

(*a*) *28.5 kJ* (*b*) *17.13 kJ*

(*c*) *45.7 kJ* (*d*) *1.7 kJ*

(*e*) *2.85 kJ* **(Kerala PET, 2005)**

Solution. $\underset{0.5\text{ M}}{HNO_3} \rightleftharpoons \underset{0.5\text{ M}}{H^+} + NO_3^-$; $[OH^-] = 0.3$ M

Concentration of $[OH^-]$ being less (= 0.3 M) than that of $[H^+]$ (= 0.5), so, 0.3 mol of OH^- ions will neutralise 0.3 mol of H^+ ions to form water.

∴ Heat evolved = 0.3 × 57.1 kJ = **17.13 kJ.**

So, the correct answer is (*b*).

Example 203. *If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and*

ΔH_f *for the formation of XY is – 200 kJ mol*$^-$. *The bond dissociation energy of* X_2 *will be :*

(*a*) *100 kJ mol*$^-$ (*b*) *200 kJ mol*$^-$
(*c*) *300 kJ mol*$^-$ (*d*) *400 kJ mol*$^-$

(AIEEE, 2005)

Solution. Since the bond dissociation energies of XY, X_2 and Y_2 are is the ratio 1 : 1 : 0.5, so, let the bond dissociation energies of XY, X_2 and Y_2 are x, x and $x/2$ respectively.

$$\therefore \quad \frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY\ ;\ \Delta H_f = -200 \text{ kJ mol}^-$$

$\therefore$ ΔH(reaction) = (Sum of bond dissociation energies of reactants) – (sum of bond dissociation energies of products)

$$\therefore \quad \Delta H(\text{reaction}) = \frac{1}{2}\Delta H_{X_2} + \frac{1}{2}\Delta H_{Y_2} - \Delta H_{XY}$$

$$-200 \text{ kJ mol}^- = \frac{x}{2} + \frac{0.5x}{2} - x\ ;$$

$$2 \times -200 \text{ kJ mol}^- = x + 0.5\,x - 2\,x;$$

$$-0.5\,x = -400 \text{ kJ mol}^-$$

$$\therefore \quad x = \frac{400}{0.5} = 800 \text{ kJ mol}^-$$

> **Note.** The correct option was not given in the original question paper.

Example 204. *Consider the reaction,* $N_2 + 3H_2 \rightleftharpoons 2NH_3$ *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 are true ?*

(*a*) $\Delta H = 0$ (*b*) $\Delta H = \Delta U$
(*c*) $\Delta H < \Delta U$ (*d*) $\Delta H > \Delta U$ **(AIEEE, 2005)**

Solution. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$

1 mol 3 mol 2 mol

$$\Delta n = n_P - n_R = 2 - (1 + 3) = -2$$

But, $\Delta H = \Delta U + \Delta nRT$

$\therefore$ $\Delta H = \Delta U + (-2)RT = \Delta U - 2RT$

Or $\Delta H + 2RT = \Delta U$

Hence $\Delta H < \Delta U$

So, the correct answer is (*c*).

Example 205. *Which of the following is always negative for exothermic reaction ?*

(*a*) ΔH (*b*) ΔS
(*c*) ΔG (*d*) *None of these.*

(BCECE, Bihar, 2005)

Solution. ΔH is always negative for an exothermic reaction. So, the correct answer is (*a*).

Example 206. *The entropy values (in JK*$^-$ *mol*$^-$*) of* $H_2(g)$ *= 130.6 ;* $Cl_2(g)$ *= 223.0, HCl(g) = 186.7 at 298 K and 1 atm pressure. Then entropy change for the reaction.*

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \text{ is}$$

(*a*) *+ 540.3* (*b*) *+ 727.3*
(*c*) *– 166.9* (*d*) *+ 19.8*

(IMS-BHU, 2005)

Solution. $S°H_2(g) = 130.6, S°\,Cl_2(g) = 223.0, S°\,HCl(g) = 186.7$ in JK$^-$mol$^-$.

Hence entropy change for the reaction

$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ will be

$$\Delta S° = S°(\text{Products}) - S°(\text{reactants})$$
$$= 2 \times S°\,[HCl(g)] - [S°\,H_2(g) + S°\,Cl_2(g)]$$
$$= (2 \times 186.7) - (130.6 + 223) = 373.4 - 353.6$$
$$= 19.8 \text{ JK}^- \text{mol}^-$$

So, the correct answer is (*d*).

Example 207. *The half-cell reaction for the corrosion are :*

$$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O\ ;\ E° = 1.23 \text{ V}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe(s)\ ;\ E° = -0.44 \text{ V}$$

Find $\Delta G°$ *(in kJ) for the overall reaction*

(*a*) *– 76* (*b*) *– 322*
(*c*) *– 161* (*d*) *– 152*

(IIT – JEE screening, 2005)

Solution. Reactions. $Fe(s) \rightleftharpoons Fe^{2+} + 2e^-\ ;\ \Delta G_1^°$

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightleftharpoons H_2O(l)\ ;\ \Delta G_2^°$$

$$Fe(s) + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O\ ;\ \Delta G_1^°$$

Using the relation,

$$\Delta G° = -nFE°$$
$$\Delta G_1^° = -nFE° = -2 \times 96500 \text{ C} \times 0.44 \text{ V}$$
$$= -84920 \text{ CV} = -84920 \text{ J}\ [\because\ 1 \text{ CV} = 1 \text{ J}]$$
$$\Delta G_2^° = -nFE° = -2 \times 96500 \text{ C} \times 1.23 \text{ V}$$
$$= -237390 \text{ J}$$
$$\Delta G_3^° = \Delta G_1^° + \Delta G_2^°$$
$$\therefore \Delta G_3^° = (-84920 - 237390) \text{ J} = -322310 \text{ J}$$

$$\text{Or } \Delta G_3^° = -322310 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -322.31 \text{ kJ} \simeq -322 \text{ kJ}$$

So, the correct answer is (*b*).

Example 208. *For the reaction,* $2Al_2O_3(s) \longrightarrow 4Al(s) + 3O_2(g)$, $\Delta H = +3340$ *kJ, the enthalpy of formation of* $Al_2O_3(s)$ *is :*

(*a*) *+ 1670 kJ* (*b*) *– 3340 kJ*
(*c*) *– 1670 kJ* (*d*) *+ 3340 kJ*

(JIPMER-Pondichery, 2005)

Solution. *Given reaction :*

$$2Al_2O_3(s) \longrightarrow 4Al(s) + 3O_2(g)\ ;$$
$$\Delta H = +3340 \text{ kJ} \qquad \text{...(1)}$$

Required equation :

$$2Al(s) + \frac{3}{2}O_2(g) \longrightarrow Al_2O_3(s)\ ;$$
$$\Delta H = ? \qquad \text{...(A)}$$

In order to get equation (A), we have, $-\frac{1}{2}$ equation (1)

$$-Al_2O_3(s) \longrightarrow -2Al(s) - \frac{3}{2}O_2(g)$$

Or $2Al(s) + \frac{3}{2} O_2(g) \longrightarrow Al_2O_3(s)$;

$$\Delta H = -1670 \text{ kJ}.$$

So, the correct answer is (*c*)

EXAMPLE 209. *Consider the following processes.*

$$\tfrac{1}{2}A \longrightarrow B \qquad \Delta H \ (kJ/mol^{-}) \ +150$$

$$3B \longrightarrow 2C + D \qquad -125$$

$$E + A \longrightarrow 2D \qquad +350$$

For $B + D \longrightarrow E + 2C$, *ΔH will be:*

(*a*) *525 kJ mol*$^{-}$ (*b*) *–175 kJ mol*$^{-}$

(*c*) *–325 kJ mol*$^{-}$ (*d*) *325 kJ mol*$^{-}$

(AIPMT, 2011)

SOLUTION.

(*i*) $1/2\,A \longrightarrow B$; $\Delta H = +150$ kJ mol^{-}

(*ii*) $3B \longrightarrow 2C + D$; $\Delta H = -125$ kJ mol^{-}

(*iii*) $E + A \longrightarrow 2D$; $\Delta H = +350$ kJ mol^{-}

In order to get equation, $B + D \longrightarrow E + 2C$, we have: +[2 × equation, (*i*)] + equation, (*ii*) – equation, (*iii*), Thus:

$$+A + 3B - E - A \longrightarrow +2B + 2C + D - 2D$$

$$\text{or } 3B - 2B + 2D - D \longrightarrow E + 2C$$

$$\text{or } B + D \longrightarrow E + 2C; \Delta H = -175 \text{ kJ mol}^{-}.$$

So, the correct answer is (b)

$$\left[\because \Delta H = +(2 \times 150) + (-125) - 350 = +300 - 125 - 350 = -175 \text{ kJ mol}^{-}\right]$$

EXAMPLE 210. *For the reaction,* $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$, *ΔH is equal to*

(*a*) $\Delta U + 5RT$ (*b*) $\Delta U + 6RT$

(*c*) ΔU (*d*) $\Delta U - 5RT$

(SCRA, 2000)

SOLUTION. For the reaction :

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l),$$

$$\Delta n = 6 \text{ mol} - 6 \text{ mol} = \text{zero}$$

$$6 \text{ mol} \qquad 6 \text{ mol}$$

But, $\Delta H = \Delta U + \Delta nRT$

So, $\Delta H = \Delta U + 0 \times RT$; $\Delta H = \Delta U$

So, the correct answer is (*c*).

EXAMPLE 211. *Given,* $H_2 \longrightarrow 2H(g); \Delta H° = 104$ *k cal;*

$$F_2(g) \longrightarrow 2F(g);$$

$$\Delta H° = 37.8 \text{ k cal and :}$$

$$H_2(g) + F_2(g) \longrightarrow 2HF(g);$$

$\Delta H° = -124$ *k cal, the value of* $\Delta H°$ *for*

$$H(g) + F(g) \longrightarrow HF(g) \text{ will be :}$$

(*a*) *130 k cal* (*b*) *131 k cal*

(*c*) *132.9 k cal* (*d*) *– 132.9 k cal*

SOLUTION. The reaction may be written as :

$$H-H(g) + F-F(g) \longrightarrow 2H-F(g);$$

$$\Delta H = -124 \text{ k cal}$$

ΔH° = Σ B.E. of reactants – Σ B.E. of products.

– 124 = [B.E. of H – H + B.E. of F – F] – 2[B.E. of H – F]

– 124 = (104 + 37.8) – 2 × H – F

∴ B.E. of 2H – F = 104 + 37.8 + 124 = 265.8 k cal

∴ Bond energy (B.E) of one H – F bond

$$= \frac{265.8}{2} = 132.9 \text{ k cal}$$

Or $\Delta H° = -132.9$ k cal.

Hence the correct answer is (*d*).

EXAMPLE 212. *In a fuel cell, methanol is used as a fuel and oxygen gas is used as an oxidiser. The reaction is:*

$$CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l).$$

At 298 K, standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ *and* $CO_2(g)$ *are –166.2, –237.2 and –394. 4 kJ mol*$^{-}$ *respectively. If standard enthalpy of combustion of methanol is –726 kJ mol*$^{-}$*, efficiency of fuel cell will be:*

(*a*) *80%* (*b*) *87%*

(*c*) *9%* (*d*) *97%*

(AIEEE, 2009)

SOLUTION. Given reaction; $CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; $\Delta H = -726$ kJ mol.$^{-}$

$$\Delta G_f^{\circ}\,[CH_3OH(l)] = -166.2 \text{ kJ mol}^{-};$$

$$\Delta G_f^{\circ}\,[H_2O(l)] = -237.2 \text{ kJ mol}^{-};$$

$$\Delta G_f^{\circ}\,[CO_2(g)] = -394.4 \text{ kJ mol}^{-}. \text{ Also:}$$

$$\Delta G^{\circ}_{\text{reaction}} = \Sigma\Delta G_f^{\circ}(\text{products}) - \Sigma\Delta G_f^{\circ}(\text{reactants}) = [-394.4 + 2 \times (-237.2)] - (-166.2) = -702.6 \text{ kJ}$$

$$\therefore \quad \% \text{ efficiency} = \frac{\Delta G}{\Delta H} \times 100 = \frac{702.6}{-726} \times 100 = 97$$

So, correct answer is (*d*)

EXAMPLE 213. *For a given reaction,* $C_7H_8(l) + 9O_2(g) \longrightarrow 7CO_2(g) + 4H_2O(l)$, *the calculated and observed heats of reaction are respectively 232 and 50.4 kJ mol*$^{-}$*. The resonance energy for it will be :*

(*a*) *160 kJ mol*$^{-}$ (*b*) *+ 172.2 kJ mol*$^{-}$

(*c*) *+ 182.2 kJ mol*$^{-}$ (*d*) *– 182.2 kJ mol*$^{-}$

SOLUTION. We know that :

Resonance energy = ΔH°(observed) – ΔH°(calculated) ...(1)

Substituting the values, we get :

Resonance energy = 50.4 – 232.6 = – 182.2 kJ mol^{-}

So, the correct answer is (*d*).

EXAMPLE 214. *Heat capacity of liquid water at constant pressure,* C_p *is 18 cal deg*$^{-}$ *mol*$^{-}$*. The value of heat capacity of water at constant volume,* C_v *is approximately :*

(*a*) *18 cal deg^{-} mol^{-}*
(*b*) *16 cal deg^{-} mol^{-}*
(*c*) *10.8 cal deg^{-} mol^{-}*
(*d*) *cannot be predicted.* **(IIT-JEE, 2006)**

Solution. We know that $C_p - C_v = 2$ cal deg^{-} mol^{-} ;

So $C_v = C_p - 2 = 18 - 2 = 16$ cal deg^{-} mol^{-}

So, the correct answer is (*b*).

Example 215. *The direct conversion of A to B is difficult. Hence it is carried out by the following shown path :*

ΔS ($A \to C$) = 50 e.u., ΔS ($C \to D$) = 30 e.u., ΔS ($B \to D$) = 20 e.u ; where e.u. is entropy unit. Then ΔS ($A \to B$) is :

(*a*) *+ 100 e.u.* (*b*) *+ 60 e.u.*
(*c*) *– 100 e.u.* (*d*) *– 60 e.u.*

(IIT-JEE, 2006)

Solution. ΔS (A $\to$ C) = 50 e.u.

ΔS (C $\to$ D) = 30 e.u.

ΔS (B $\to$ D) = 20 e.u.

Or ΔS (D $\to$ B) = – 20 e.u.

$\therefore$ ΔS (A $\to$ B) = 50 + 30 – 20 = 60 e.u.

So, the correct answer is (*b*).

Example 216. *Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?*

(*a*) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$
(*b*) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
(*c*) $C(s) + 2H_2O(g) \longrightarrow 2H_2(g) + CO_2(g)$
(*d*) $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

(CBSE-PMT, 2006)

Solution. We know that

$$\Delta H = \Delta E + \Delta n(g)RT.$$

So, $\Delta H = \Delta E$, when $\Delta n(g) = 0$

(*a*) $\underset{2\text{ mol}}{2\,CO(g)} + \underset{1\text{ mol}}{O_2(g)} \longrightarrow \underset{2\text{ mol}}{2CO_2(g)}$;

$$\Delta n(g) = 2 - (2 + 1) = -1 \text{ mol}$$

(*b*) $\underset{1\text{ mol}}{H_2(g)} + \underset{1\text{ mol}}{Br_2(g)} \longrightarrow \underset{2\text{ mol}}{2HBr(g)}$;

$$\Delta n(g) = 2 - (1 + 1) = 0$$

(*c*) $C(s) + \underset{2\text{ mol}}{2H_2O(g)} \longrightarrow \underset{2\text{ mol}}{2H_2(g)} + \underset{1\text{ mol}}{CO_2(g)}$;

$$\Delta n(g) = 2 + 1 - 2 = +1 \text{ mol}$$

(*d*) $\underset{1\text{ mol}}{PCl_5(g)} \longrightarrow \underset{1\text{ mol}}{PCl_3(g)} + \underset{1\text{ mol}}{Cl_2(g)}$;

$$\Delta n(g) = (1 + 1) - 1 = 1 \text{ mol}$$

Since $\Delta n(g) = 0$ for (*b*),

$\Delta H = \Delta E$. So, the correct answer is (*b*).

Example 217. *The enthalpy and entropy change for the reaction $Br_2(l) + Cl_2(g) \longrightarrow 2Br\,Cl(g)$ are 30 kJ mol^{-} and 105 J mol^{-} respectively. The temperature at which the reaction will be in equilibrium is :*

(*a*) *300 K* (*b*) *285.7 K*
(*c*) *273 K* (*d*) *450 K* **(CBSE-PMT, 2006)**

Solution. Reaction. $Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$

$$\Delta H = 30 \text{ kJ mol}^{-};$$
$$\Delta S = 105 \text{ J mol}^{-}$$
$$= 105 \text{ J mol}^{-} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$
$$= 0.105 \text{ kJ mol}^{-};\ T = ?$$

We know that : $\Delta S = \dfrac{\Delta H}{T}$;

$$T = \frac{\Delta H}{\Delta S} = \frac{30 \text{ kJ mol}^{-}}{0.105 \text{ kJ mol}^{-}} = 285.7 \text{ K}$$

So, the correct answer is (*b*).

Example 218. *What is the unit of $\overset{\circ}{S}_m$ of the following ?*

(*a*) *cal K^{-} mol^{-}* (*b*) *k cal mol^{-}*
(*c*) *k joule K^{-} mol* (*d*) *calorie K^{-}*

(Gujrat CET, 2006)

Solution. Usually molar heat capacity is represented as Cm but here it is represented as $\overset{\circ}{S}_m$.

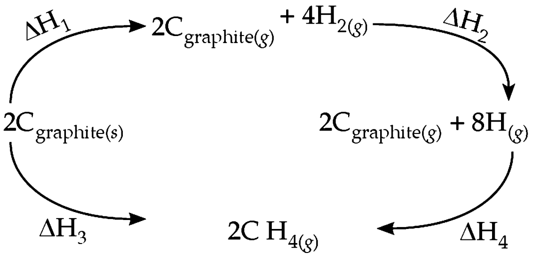
Molar heat capacity

$$\overset{\circ}{S}_m = \frac{\text{Heat absorbed}}{(\text{mol. wt.}) \times \text{temperature difference}}$$

$$\therefore \text{ Unit of } \overset{\circ}{S}_m = \frac{\text{cal}}{\text{mol} \times \text{K}} = \text{cal mol}^{-}\text{ K}^{-}.$$

So, the correct answer is (*a*).

Example 219.



Find out (i) heat of formation of CH_4 in terms of ΔH_1, ΔH_2 etc.

(*ii*) *Heat of sublimation of C (graphite) in terms of ΔH_1, ΔH_2 etc.*

(*iii*) *Heat of dissociation of H_2 in terms of ΔH_1, ΔH_2 etc*

[AIEEE, 2006, AIPMT, 2009]

Solution. From the given graph, we see that:

(*i*) Heat of formation of $CH_4 = \dfrac{\Delta H_3}{2}$ or $\dfrac{\Delta H_1 + \Delta H_2 + \Delta H_4}{2}$ because 2 mol of CH_4 are given and we need 1 mol CH_4 for calculation.

(*ii*) Heat of sublimation of $C_{graphite}$ *i.e.*, $C_{graphite(s)} \longrightarrow C_{graphite(g)} = \dfrac{\Delta H_1}{2}$, because 2 mol of graphite are given and we need 1 mol of it for calculation.

(*iii*) Heat of dissociation of H_2; $4H_2(g) \longrightarrow 8H_{(g)}$. So, for 1 mol H_2, heat of dissociation = $\Delta H_2/4$.

Ans.

EXAMPLE 220. *The enthalpy changes for the following processes are listed below.*

$Cl_2(g) = 2\,Cl(g)$; 242.3 kJ mol$^-$

$I_2(g) = 2I(g)$: 151.0 kJ mol$^-$

$ICl(g) = I(g) + Cl(g)$; 211.3 kJ mol$^-$

$I_2(s) = I_2(g)$; 62.76 kJ mol$^-$

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy for $ICl(g)$ is :

(*a*) – 14.6 kJ mol$^-$ (*b*) – 16.73 kJ mol$^-$

(*c*) + 16.73 kJ mol$^-$ (*d*) + 244.8 kJ mol$^-$

(AIEEE, 2006)

SOLUTION. We know that :

$$\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \longrightarrow ICl(g)$$

$$\therefore \Delta H_{ICl(g)}$$

$$= \left[\frac{1}{2}\Delta H_{I_2(s)\to I_2(g)} + \frac{1}{2}\Delta H_{I-I} + \frac{1}{2}\Delta H_{Cl-Cl} - \left[\Delta H_{I-Cl}\right]\right]$$

$$= \left[\frac{1}{2}\times 62.76 + \frac{1}{2}\times 151 + \frac{1}{2}\times 242.3\right] - 211.3$$

$$= 31.38 + 75.5 + 121.15 - 211.3 = +\,16.73 \text{ kJ mol}^-$$

So, the correct answer is (*c*).

EXAMPLE 221. *($\Delta H - \Delta U$) for the formation of carbon monoxide (CO) from its elements at 298 K is :*

(*a*) – 1238.78 J mol$^-$ (*b*) 1238.78 J mol$^-$

(*c*) – 2477.57 J mol$^-$ (*d*) 2477.57 J mol$^-$

(AIEEE, 2006)

SOLUTION. We know that :

$\Delta H - \Delta U = \Delta n(g)RT$. For the reaction

$$C(g) + \frac{1}{2}O_2(g) \longrightarrow CO(g);$$

1 mol ½ mol 1 mol

$$\Delta n(g) = 1 - \left(1 + \frac{1}{2}\right) = \frac{-1}{2}\text{ mol}$$

$$\therefore \quad \Delta H - \Delta U = -\frac{1}{2} \times 8.314 \text{ JK}^- \text{mol}^- \times 298 \text{ K}$$

$$= -\,1238.78 \text{ J mol}^-$$

So, the correct answer is (*a*).

EXAMPLE 222. *For the reaction*

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)\,;\ \Delta H = -\,560 \text{ kJ mol}^-$$

In one litre vessel at 500 K, the initial pressure is 70 atm and after the reaction, it becomes 40 atm at constant volume of one litre. All the above gases show significant deviation from ideal behaviour (1 L atm = 0.1 kJ). The change in internal energy will be :

(*a*) + 10 kJ mol$^-$ (*b*) – 530 kJ mol$^-$

(*c*) – 106 kJ mol$^-$ (*d*) + 106 kJ mol$^-$

(IIT JEE modified, 2006)

SOLUTION. $2CO + O_2 \longrightarrow 2CO_2$; $\Delta H = -\,560$ kJ mol$^-$

But $\Delta H = \Delta U + \Delta n(g)RT = \Delta U + \Delta(PV)$

$= \Delta U + V(P_2 - P_1)$

$\therefore \quad -\,560 = \Delta U + 1(40 - 70) = \Delta U - 30$

$\therefore \quad \Delta U = -\,560 + 30 = -\,530$ kJ mol$^-$

So, the correct answer is (*b*).

EXAMPLE 223. *On the basis of following thermochemical data ($\Delta_f G°\ H^+_{(aq)} = 0$)*

$$H_2O(l) \longrightarrow H^+_{(aq)} + OH^-_{(aq)}\,;\ \Delta H = 57.32 \text{ kJ}.$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -286.2 \text{ kJ}$$

the value of enthalpy of formation of OH^- ion at 25°C is:

(*a*) –22.88 kJ (*b*) –228.88 kJ

(*c*) + 288.88 kJ (*d*) –343.52 kJ

(AIEEE, 2009)

SOLUTION. Given $H_2O(l) \longrightarrow H^+_{(aq)} + H^-_{(aq)}$;

$\Delta H = 57.32$ kJ ...(1)

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$

$\Delta H = -286.2$ kJ ...(2)

Required equation is:

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H^+_{(aq)} + H^-_{(aq)}$ ...(3)

In order to get equation (3), we have equation (1) + equation (2) Thus:

$$H_2O(l) \longrightarrow H^+_{(aq)} + OH^-_{(aq)}\,;\ \Delta H = 57.32 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -286.2 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H^+_{(aq)} + OH^-_{(aq)}\,;\ \Delta H = -228.88 \text{ kJ}$$

So, the correct answer is (*b*)

EXAMPLE 224. *The standard heats of formation of CH_4, H_2O and CH_3OH are –76, –242 and –266 kJ mol$^-$ respectively. The enthalpy change for the following reaction is:*

$$CH_3OH(l) + H_2(g) \longrightarrow CH_4(g) + H_2O(l).$$

(*a*) –4 kJ/mole (*b*) –556 kJ/mole

(*c*) –318 kJ/mole (*d*) –52 kJ/mole

Orissa JEE, 2009

SOLUTION. Given:

(*i*) $C + 2H_2(g) \longrightarrow CH_4(g);$

$\Delta H_1 = -76$ kJ mol$^-$

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);$

$\Delta H_2 = -242$ kJ mol$^-$

(*iii*) $C + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l);$

$\Delta H_3 = -266$ kJ mol$^-$

Required equation is:

$CH_3OH(l) + H_2(g) \longrightarrow CH_4(g) + H_2O(l);\ \Delta H_4 = ?$ (A)

In order to get equation (A), we have, equation (*i*) + equation (*ii*) –equation (*iii*). Thus:

$$C + 2\,H_2(g) + H_2(g) + \frac{1}{2}\,O_2(g) - C - 2H_2(g) - \frac{1}{2}\,O_2 \longrightarrow$$

$CH_4(g) + H_2O(l) - CH_3OH(l)$; ΔH_1 (= –76 –242 + 266) kJ mol^{-}

$\therefore$ $CH_3OH(l) + H_2(g) \longrightarrow CH_4(g) + H_2O$; $\Delta H_4 = -52$ kJ mol^{-}.

So, the correct answer is (*d*)

EXAMPLE 225. *Write the mathematical expression for the first law of thermodynamics. One mole of an ideal gas is expanded isothermally against a constant pressure of 3 atm from 10 litres to 35 litres. Calculate the work done, change in internal energy and heat absorbed during the process.* **(ISC, 2009)**

SOLUTION. First law of thermodynamics; $\Delta E = q + w$.

But $q = \Delta E + P\Delta V$ (for pressure–volume work)

$= \Delta E + P(V_2 - V_1)$.

For isothermal process,

$\Delta E = 0$. So, $q = w = P(V_2 - V_1)$

$= 3\,(35 - 10) = 75$

$\therefore$ $q = 75 \times 101.3$ J = 7597. 5 J;

$q = w$; $\Delta E = 0$. **Ans.**

EXAMPLE 226. *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) and pentane (g) respectively. The value of E^0_{cell} for the pentane-oxygen fuel cell is :*

(*a*) *1.0968 V* (*b*) *0.0968 V*

(*c*) *1.968 V* (*d*) *2.0968 V*

(CBSE–PMT, 2008 Prelims)

SOLUTION. Reaction :

$$\Delta C_5H_{12}\,(g) + 8O_2\,(g) \longrightarrow 5CO_2\,(g) + 6\,H_2O\,(l)$$

$$\therefore \quad \Delta G^\circ = \Sigma G^0_{products} - \Sigma G^0_{reactants}$$

$$= [-(-394.4 \times 5) + (-237.2 \times 6)] - [(-8.2) + (8 \times 0)]$$

$$= -3387.5 \text{ kJ}$$

($\because \Delta G^\circ$ of elementary substances = 0)

The complete cell reaction for the fuel cell is :

$$C_5H_{12}\,(g) + 8O_2\,(g) \longrightarrow 5CO_2(g) + 6H_2O\,(l)$$

which is obtained by combining the following two half-cell reactions.

$C_5H_{12}\,(g) + 10H_2O(l) \longrightarrow 5CO_2\,(g) + 32H^+ + 32\,e^-$ and $8O_2\,(g) + 32\,H^+ + 32e^- \longrightarrow 16H_2O\,(l)$

Here, no. of electrons exchanged = 32 *i.e.*, $n = 32$

But $\Delta G^\circ = -nFE^\circ$; -3387.5×10^3 J $= -32 \times 96500$ J/V $\times E^\circ$

$$\therefore \quad E^\circ = \frac{-3387.5 \times 10^3}{-32 \times 96500} V = 1.0968\ V.$$

So, the correct answer is (*a*).

EXAMPLE 227. *For the process*

$H_2O(l)$ (1 bar, 373 K) $\longrightarrow$ $H_2O(g)$ (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–JEE, 2007)**

SOLUTION. (*i*) We know that at a given temperature (373 K) and given pressure (1 bar), the change is taking place at the boiling point. So, the liquid-gas or vapour system virtually remains at **equilibrium**. So, **ΔG = 0.**

(*ii*) For a change from liquid (less random) to gaseous state (more random), the randomness increases. So, $\Delta S > 0$.

So, the correct answer is (*a*).

EXAMPLE 228. *Find out internal energy change for the reaction, A(l) $\longrightarrow$ A(g) at 373 K. Heat of vaporisation is 40.66 kJ/mol and R = 8.3 J mol^{-} K^{-}* **(AIPMT, 2009)**

SOLUTION. For the reaction, $A(l) \longrightarrow A(g)$, $\Delta ng = n_p - n_R = 1 - 0 = 1$. But $\Delta H = \Delta E + \Delta ng\,RT$. Substituting the values, we get: 40.66×1000 J mol^{-} = $\Delta E + 1 \times 8.3$ J mol^{-} K^{-} $\times$ 373 K

$\therefore$ ΔE = 40660 J mol^{-} –3095.9 J mol^{-} = 37564. J mol^{-} = 37564.1 J mol^{-}/1000 = 37.56 kJ mol^{-} **Ans.**

EXAMPLE 229. *The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is*

(*a*) *38.3 J mol^{-} K^{-}* (*b*) *35.8 J mol^{-} K^{-}*

(*c*) *32.3 J mol^{-} K^{-}* (*d*) *42.3 J mol^{-} K^{-}*

(AIEEE, 2011)

SOLUTION. The entropy change, ΔS for an isothermal reaction is given as:

$$\Delta S = 2.303\, n\, R \log \frac{V_2}{V_1}$$

$$\Delta S = 2.303 \times 2 \text{ mol} \times 8.314 \text{ JK}^{-} \text{mol}^{-} \log \left[\frac{100}{10} = 10\right]$$

[$\because$ n = 2]

$$\Delta S = 2.303 \times 2 \times 8.314 \text{ JK}^{-} \times 1 = 38.3 \text{ JK}^{-}$$

So, the correct answer is (*a*).

EXAMPLE 230. *The standard enthalpies of combustion of $C_6H_{6(l)}$, $C_{(graphite)}$ and $H_{2(g)}$ respectively are – 3270 kJ mol^{-}, – 394 kJ mol^{-} and – 286 kJ mol^{-}. What is the standard enthalpy of formation of $C_6H_{6(l)}$ in kJ mol^{-}.*

(*a*) *– 48* (*b*) *+ 48*

(*c*) *– 72* (*d*) *+ 480*

(*e*) *– 74* **(Kerala PET, 2012)**

SOLUTION. Required equation : $6C + 3H_2 \longrightarrow C_6H_6$; ΔH = ? ...(A)

Given (*i*) $C_6H_6 + 15/2\,O_2 \longrightarrow 6CO_2 + 3H_2O$

(*ii*) $C + O_2 \longrightarrow CO_2$

(*iii*) $H_2 + 1/2O_2 \longrightarrow H_2O$

In order to get equation (A), we have:

6 × equation (*i*) + 3 × equation (*ii*) – Equation (*i*).

$$6C + 6\,O_2 + 3H_2 + 3/2O_2 \longrightarrow 6CO_2 + 3H_2O - 6CO_2 - C_6H_6 - 15/2O_2 \qquad - 3H_2O$$

$\therefore$ $6\,C + 3H_2 \longrightarrow C_6H_6$; $\Delta H = 48$ kJ mol^{-}. So, the correct answer is (*b*).

ΔH in kJ mol^{-}

(*i*) – 3270

(*ii*) – 394 × 6 = – 2364

(*iii*) – 286 × 3 = – 858

$\therefore$ $\Delta H = -2364 - 858 + 3270 = 48.$

Example 231. *Choose the reaction in which ΔH is not equal to ΔU.*

(*a*) $C(gr) + O_2 \rightarrow CO_2(g)$

(*b*) $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

(*c*) $2\,C(g) + H_2(g) \rightarrow C_2H_2(g)$

(*d*) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

(*e*) $N_2(g) + O_2(g) \rightarrow 2NO(g)$ **(Kerala PET, 2012)**

Solution. We know, $\Delta H = \Delta U + \Delta n(g)\,RT$

So, if $\Delta n(g) = 0$, $\Delta H = \Delta U$. So, $\Delta n(g)$ should not be equal to zero. Δn = no. of mol of products (g) – no. of mol of reactants (g)

(*a*) $\Delta n(g) = 1 - 1 = 0$ (*b*) $\Delta n(g) = 1 - (1+1) = -1$

(*c*) $\Delta n(g) = 1 - 1 = 0$ (*d*) $\Delta n(g) = 2 - (1+1) = 0$

(*e*) $\Delta n(g) = 2 - (1+1) = 0$

So, the correct answer is (*b*).

Example 232. *Calculate the work done (in joules) when 0.2 mole of an ideal gas at 300 K expands isothermally and reversibly from an initial volume of 2.5 litres to the final volume of 25 litres.*

(*a*) 996 (*b*) 1148

(*c*) 11.48 (*d*) 897

(*e*) 114.8 **(Kerala PMT, 2012)**

Solution. Moles of ideal gas, $n = 0.2$, $T = 300$ K, volume, $V_1 = 2.5$ L, $R = 8.314$ JK^{-} mol^{-}.

Work done in reversible isothermal manner is:

$$W = -2.303\,n\,RT \log V_2/V_1$$

$$= -2.303 \times 0.2 \text{ mol} \times 8.314 \text{ JK}^{-}\text{ mol}^{-} \times 300 \text{ K} \log \frac{25}{2.5}$$

$= -1148$ J log 10 = – 1148 J × 1 = – 1148 J. So, the correct answer is (*b*).

Example 233. *The Gibb's energy for the decomposition of Al_2O_3 at 500°C is as follows:*

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2\ ;\ \Delta G = +\,960 \text{ kJ mol}^{-}$$

The potential difference needed for the electrolytic reduction of Al_2O_3 at 500°C is atleast:

(*a*) 4.5 V (*b*) 3.0 V

(*c*) 2.5 V (*d*) 5.0 V

(AIPMT, Mains, 2012)

Solution. We know $E° = -\dfrac{\Delta G}{nF}$ ...(1)

$\Delta G = +960$ kJ mol^{-} = 960 × 1000 J mol^{-}; F = 96500 coulomb

For $\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2$

Total no. of Al-atoms in $Al_2O_3 = \frac{2}{3} \times 2 = \frac{4}{3}$; $Al^{3+} + 3e^{-} \rightarrow Al$

Since for one Al-atom, electron change = 3

$\therefore$ For $\frac{4}{3}$ Al-atoms, electron change = $\frac{4}{3} \times 3 = 4$; So, $n = 4$

Substituting the respective values in equation (1), we get:

$$E° = -\frac{960 \times 1000}{4 \times 96500} = -2.48\ V \simeq 2.5\ V.$$

So, the correct answer is (*c*).

Example 234. *Using the data provided, calculate the multiple bond energy (kJ mol^{-}) of a C ≡ C is C_2H_2. That energy is (take the bond enrgy of C – H bond as 350 kJ mol^{-}):*

$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$; $\Delta H = 225$ kJ mol^{-} ...(*i*)

$2C(s) \longrightarrow 2\,C(g)$; $\Delta H = 1410$ kJ mol^{-} ...(*ii*)

$H_2(g) \longrightarrow 2\,H(g)$; $\Delta H = 330$ kJ mol^{-} ...(*iii*)

(*a*) 1165 (*b*) 837

(*c*) 865 (*d*) 815

(IIT-JEE, 2012)

Solution. The required equation is:

$C_2H_2(g) \longrightarrow 2\,C(g) + 2\,H(g)$; $\Delta H = ?$ ...(A)

In order to get equation (A), we have equation (*ii*) + equation (*iii*) – equation (*i*). Thus:

$$2\,C(s) + H_2(g) - 2\,C(s) - H_2(g) \longrightarrow 2\,C(g) + 2H(g) - C_2H_2(g)$$

Or $C_2H_2(g) \longrightarrow 2\,C(g) + 2\,H(g)$; $\Delta H = 1515$ kJ mol^{-}

Equation (A) involves the breaking of two C – H bonds and one C ≡ C bond. Hence:

1515 = (2 × 350) + C ≡ C bond energy

$\therefore$ C ≡ C bond energy = 1515 – 700 = 815 kJ mol^{-}. So, the correct answer is (*d*).

ΔH values in kJ mol^{-}

(*ii*) 1410 (*iii*) 330

(*i*) – 225

$\therefore$ $\Delta H = 1515$ kJ mol^{-}; C_2H_2 is H – C ≡ C – H.

Example 235. *The equilibrium constant of a reaction is 0.008 at 298 K. The standard free energy change of the reaction at the same temperature is:*

(*a*) + 11.96 kJ (*b*) – 11.96 kJ

(*c*) – 5.43 kJ (*d*) – 8.46 kJ

(Karnataka, CET, 2012)

Solution. $T = 298$ K, $R = 8.314$ JK^{-} mol^{-}, $K_c = 0.008$

$$\therefore\ \Delta G° = -2.303\,RT \log K_c = [-2.303 \times 8.314 \text{ JK}^{-}\text{ mol}^{-} \times 298 \text{ K} \log 0.008]$$

$$= -2.303 \times 8.314 \times 298 \times -2.097$$

$= +11965$ J mol^{-} = 11.96 kJ mol^{-}.

So, the correct answer is (*a*).

EXAMPLE 236. *Enthalpy of combustion of carbon to CO_2 is – 393.52 kJ mol^{-}. The heat released on the formation of 11 g of CO_2 from carbon and dioxygen is:*

(a) 35.77 kJ *(b)* 98.38 kJ
(c) 1574.08 kJ *(d)* 393.52 kJ

(J&K – CET, 2012)

SOLUTION. $C + O_2 \rightarrow \underset{1\text{ mol}}{CO_2}$; $\Delta H = -393.52$ kJ mol^{-}

= 12 + (2 × 16) = 44 g

Heat produced due to the formation of 44 g CO_2
= 393.52 kJ

∴ Heat produced due to the formation of 11 g CO_2

$$= \frac{393.5 \times 11}{44} = 98.38 \text{ kJ}$$

So, the correct answer is (*b*).

EXAMPLE 237. *A gas expands from a volume of 1 m^3 to a volume of $2m^3$ against an external pressure of 10^5 Nm^{-2}. The work done by the gas will be:*

(a) 10^5 kJ *(b)* -10^2 kJ
(c) 10^2 J *(d)* 10^3 J

(Karnataka, CET, 2012)

SOLUTION. Since gas is allowed to expand against the external pressure, the work done is negative and irreversible

$$\therefore W_{irr} = -P_{ext}(V_2 - V_1) = -10^5 \text{ Nm}^{-2} (2\text{m}^3 - 1\text{m}^3)$$
$$= -10^5 \text{ Nm}^{-2} \times \text{m}^3$$

$= -10^5$ J $= -10^5 \times 10^{-3}$ kJ $= -10^2$ kJ. So, the correct answer is (*b*).

EXAMPLE 238. *The enthalpy of fusion of water is 1.435 k cal/mol. The molar entropy change for the melting of ice at 0°°C is:*

(a) 10.52 cal/(mol K) *(b)* 21.04 cal/(mol K)
(c) 5.260 cal/(mol K) *(d)* 0.526 cal/(mol K)

(AIPMT, Pre. 2012)

SOLUTION. Given $\Delta H_f = 1.435$ k cal mol^{-}, $T_f = 0 + 273 = 273$ K

$$\text{But entropy change, } \Delta S = \frac{\Delta H_f}{T_f} = \frac{1.435 \times 1000 \text{ cal/mol}}{273 \text{ K}}$$

= 5.26 cal/(mol K)

So, the correct answer is (*c*).

EXAMPLE 239. *Standard enthalpy of vaporisation $\Delta_{vap} H°$ for water at 100°C is 40.66 kJ mol^{-}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-}) is :*

(a) + 37.56 *(b)* – 43.76
(c) + 43.76 *(d)* + 40.66

(AIPMT, Pre. 2012)

SOLUTION. $\Delta_{vap} H° = 40.66$ kJ mol^{-}; $T = 100 + 273 = 373$ k; ΔE = ?

For $\underset{1\text{ mol}}{H_2O(l)} \rightleftharpoons H_2O(g)$, $\Delta n(g) = 1 - 0 = 1$. $R = 8.314$ JK^{-} mol^{-}.

$\Delta H = \Delta E + \Delta n(g)$ RT

Or $\Delta E = \Delta H - \Delta n(g)$ RT

= 40.66 × 1000 J mol^{-} – (1 × 8.314 JK^{-} mol^{-} × 373 K)

= 40660 J mol^{-} – 3101.12 = 37558.88 J mol^{-} = 37.56 kJ mol^{-}

So, the correct answer is (*a*).

EXAMPLE 240. *A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: (R = 8.314 J/mol K, (ln 7.5 = 2.01)*

(1) *q* = – 208 J, *w* = – 208 J
(2) *q* = – 208 J, *w* = + 208 J
(3) *q* = + 208 J, *w* = + 208 J
(4) *q* = + 208 J, *w* = – 208 J **(JEE, Main, 2013)**

SOLUTION. $n = 0.04$ mol, $V_1 = 50.0$ mL, $V_2 = 375$ mL

T = 37 + 273 = 310 K, R = 8.314 J K^{-} mol^{-}, ln 7.5 = 2.01.

We know that for the said process:

$w = -nRT \ln V_2/V_1$; $w = -0.04$ mol × 8.314 J mol^{-} K^{-} × 310 K ln 375/50.

∴ $w = -0.04 \times 8.314 \times 310 \times (\ln 7.5)$ J

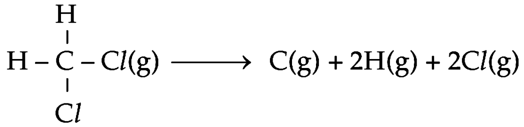
$= -0.04 \times 8.314 \times 310 \times 2.01$ J $\simeq -208$ J

Since energy is absorbed, $q = + 208$ J.

So, the correct answer is (4).

PROBLEM FOR PRACTICE

1. Calculate ΔH of the reaction



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-Cl(g) \longrightarrow C(g) + 2H(g) + 2Cl(g)$$

The average bond energies of C – H bond and C – Cl bond are 416 kJ and 325 kJ mol^{-} respectively.

[Dhanbad 1991]

Ans. 1482 kJ

2. Calculate the enthalpy change when 4.76 g of CO vaporize at its boiling point. $\Delta_{vap}H°$ of CO = 6.04 kJ mol^{-}

[**Ans.** 1.0268 kJ) (At. wt., C = 12, O = 16]

3. (*i*) A normal family requires 2.0×10^4 kJ of energy per day for domestic use. If a gas cylinder contains 14.0 kg butane, calculate the number of days in which the cylinder would last ? (heat of combustion of butane = 2658 kJ mol^{-}).

(*ii*) If 30% of the gas escapes without combustion, calculate the number of days in which the same cylinder would last.

[**Ans.** (*i*) 32 days ; (*ii*) 22.5 days]

4. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 k cal/mole respectively. Calculate the energy of formation of HCl(*g*). **IIT 1985**

Ans. – 22 kcal

5. The molar heat of formation of $NH_4NO_3(s)$ is – 367.54 kJ and those of $N_2O(g)$ and $H_2O(l)$ are + 81.46 kJ and – 285.78 kJ respectively at 25°C and 1.0 atmospheric pressure.
Calculate ΔH and ΔE of the reaction. **[Roorkee 1986]**
Ans. ΔH = – 122.56 kJ ; ΔE = – 125.04 kJ

6. When two moles of ethylene are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation, ΔH_f for C_2H_6, ΔH_f for CO_2 and H_2O are – 395 and – 298.6 kJ respectively. **[Roorkee 1988]**
Ans. – 83.5 kJ

7. Calculate $\Delta H°_{298}$ for the reaction
$2Li(s) + 2H_2O(l) \longrightarrow 2Li^+(aq) + 2OH^-(aq) + H_2(g)$
Given that the standard enthalpies of formation of $Li^+(aq)$, $OH^-(aq)$ and $H_2O(l)$ are – 278.5, – 228.9 and – 285.8 kJ mol$^-$ respectively (all at 298 K).
Ans. –443.2 kJ mol$^-$

8. The molar enthalpies of fusion of ice and vaporization of water are 6 kJ/mole and 44 kJ/mole. Calculate the molar enthalpy of sublimation of ice. **[Pb CET 1989]**
Ans. 50 kJ mol$^-$

9. Calculate the lattice energy of potassium bromide from the following data.
ΔH(sub) K = + 89.95 kJ mol$^-$; ΔH(diss) Br_2 = 220 kJ mol$^-$; IP(K) = + 418.4 kJ mol$^-$; EA(Br) = –341.4 kJ mol$^-$; ΔH(form) KBr = – 392 kJ mol$^-$
Ans. 669.65 kJ mol$^-$

10. The experimental lattice energy of SnO_2 is – 1159.5 kJ mol$^-$. Find the heat of formation of SnO_2 from the following data.
$D(O_2)$ = 454.3 kJ mol$^-$; S(Sn) = 291.6 kJ mol$^-$; $E(O^{2-})$ = + 63.9 kJ mol$^-$; $I(Sn^{4+})$ = 8991.4 kJ mol$^-$
[Hint. ΔH_f = ΔH(sub) + ΔH(diss) + IP + 2EA + Uo ;]
Ans. ΔH_f = – 586.4 kJ mol$^-$

11. As $O_2(l)$ is cooled at 1 atm pressure, it freezes to form solid I at 54.5 K. At a lower temperature, solid I rearranges to solid II, which has a different crystal structure. Thermal measurements show that for the phase transition of solid I to solid II, ΔH = –743.1 J mol^{-1}. At what temperature are solids I and II in equilibrium?
(*a*) 2.06 K (*b*) 31.5 K
(*c*) 43.7 K (*d*) 54.4 K
Ans. (*c*) **[DUMET 2010]**

12. Enthalpy of vaporization of benzene is + 35.3 kJ mol^{-1} at its boling point, 80°C. The entropy change in the transition of the vapour to liquid at its boling point (in JK^{-1} mol^{-1}) is
(*a*) –441 (*b*) –100
(*c*) + 441 (*d*) + 100
Ans. (*b*) **[Karnataka CET 2010]**

13. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 kJ mol^{-1} respectively. For the reaction:

$$\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightleftharpoons XY_3; \Delta H = -30 \text{ kJ}$$

to be at equilibrium, the temperature should be
(*a*) 500 K (*b*) 750 K
(*c*) 1000 K (*d*) 1250 K
Ans. (*b*) **[CBSE PMT 2010]**

14. When water is cooled to ice, its entropy
(*a*) increases (*b*) decreases
(*c*) remains same (*d*) becomes zero
Ans. (*b*) **[JK CET 2010]**

15. The standard enthalpy of formation of H_2(g) and Cl_2(g), HCl(g) are 218 kJ mol$^-$, 121.68 kJ mol$^-$and 92.3 kJ mol$^-$ respectively. Calculate standard enthalpy change in kJ for

$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \longrightarrow HCl(g)$$

(*a*) + 431.99 (*b*) –262.14
(*c*) –431.99 (*d*) + 247.37
Ans. (*b*) **[JK CET 2010]**

16. The amount of heat evolved when 500 cm^3 of 0.1 M HCl is mixed with 200 cm^3 of 0.2 NaOH is
(*a*) 2.29 kJ (*b*) 1.292 kJ
(*c*) 0.292 kJ (*d*) 3.392 kJ
Ans. (*a*) **[Karnataka CET 2010]**

17. Calculate the standard enthalpy change (in kJ mol^{-1}) for the reaction, $H_2(g) + O_2(g) \longrightarrow H_2O_2(g)$, given that, bond enthalpies of H — H, O = O, O — H and O — O (in kJ mol^{-1}) are respectively 438, 498, 464, and 138
(*a*) –130 (*b*) –65
(*c*) + 130 (*d*) –334
(*e*) + 334
Ans. (*a*) **[Kerala PET 2010]**

18. The standard enthalpy of formation of NH_3 is –46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_2 is – 712 kJ mol^{-1}, the average bond enthalpy of N – H bond in NH_3 is
(*a*) + 1056 kJ mol^{-1} (*b*) –1102 kJ mol^{-1}
(*c*) –964 kJ mol^{-1} (*d*) + 352 kJ mol^{-1}
Ans. (*d*) **[AIEEE, 2010]**

19. A certain reaction is at equilibrium at 82°C and the enthalpy change for this reaction is 21.3 kJ. The value of ΔS (in JK^{-1} mol^{-1}) for the reaction is
(*a*) 55.0 (*b*) 60.0
(*c*) 68.5 (*d*) 120.0
(*e*) 80.0
Ans. (*b*) **[Kerala PET 2010]**

20. Calculate the amount of work done when one mole of an ideal gas present in a vessel of 3L capacity at one atmospheric pressure is allowed to enter into an evacuated vessel of 5L capacity.
Ans. zero

16

CHAPTER

Oxidation and Reduction

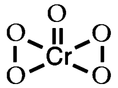
16.1. OXIDATION NUMBER (O.N.)

Oxidation number of an atom in the combined state, is the number of electrons, it has gained or lost in becoming *bonded to other* elements.

Or It is the residual charge which an atom has or appears to have when all other atoms are removed from it as ions.

Rules to determine oxidation number of an atom. General rules to determine O.N. of an atom are given in the following table.

S. No.	Type	Oxidation number (O.N.)
1.	Element in uncombined state. e.g., N_2, P_4, S_8 etc.	Zero i.e. 0
2.	(*i*) Hydrogen in H_2	0
	(*ii*) Hydrogen in metal hydrides like NaH, CaH_2	–1
	(*iii*) Hydrogen in compounds other than metal hydrides e.g., H_2O, NH_3 etc.	+1
3.	For simple ions, O.N. = charge on ion e.g.,	
	(*i*) Cl^-, Br^-, I^-, N_3^-,	–1
	(*ii*) S^{2-}, O^{2-}	–2
	(*iii*) N^{3-}, P^{3-}	–3
	(*iv*) Na^+, K^+	+1
	(*v*) Ca^{2+}, Zn^{2+}	+2
	(*vi*) Al^{3+}, As^{3+}	+3
4.	For compounds of a metal with a non-metal, metal has positive O.N. and non-metal has negative, O.N. e.g., in Na^+Cl^-	
	(*i*) O.N. of Na^+	+1
	(*ii*) O.N. of Cl^-	–1
5.	(*i*) O.N. of alkali metals like Li^+, Na^+	+1
	(*ii*) O.N. of alkaline earth metals, like Be^{2+}, Mg^{2+}	+2
6.	(*i*) Oxygen in O_2	Zero, i.e.; 0
	(*ii*) Oxygen in super oxides like KO_2	–½
	(*iii*) Oxygen in O_2F_2	+1
	(*iv*) Oxygen in OF_2	+2

	(*v*) (a) Oxygen in peroxides like Na_2O_2, H_2O_2, Ba_2O_2	–1
	(*vi*) For compounds containing peroxide linkages [e.g., CrO_5] *i.e.*,  (two peroxide linkages and one oxygen linkage) O.N. of each O-atom in each peroxide linkage is taken as (= – 1)	–1
	(*vii*) Oxygen in compounds other than shown from (*i*) to (*vi*) above i.e., such as H_2O, SO_2 etc.	–2
7.	(A) For coordinate bonds between dissimilar atoms, in which the (*i*) donor atom is **less electronegative than** acceptor atom, then	
	(a) O.N. of donor atom	+2
	(b) O.N. of acceptor atom	–2
	(*ii*) if donor atom is **more electronegative** than acceptor atom, then **neglect** the contribution of coordinate bond.	0
	Also, the contribution of coordinate bond between same atoms = zero.	
	(B) In case of compounds containing covalent and coordinate bonds, for each covalent bond between two dissimilar atoms, assign an O.N. of +1 to less electronegative atom.	
8.	For compounds containing C, H and O O.N. = $\frac{2n_o - n_H}{n_c}$ where n_O, n_H and n_C are the number of O, H and C atoms in the compound	
9.	For ions containing C, H and O O.N. = $\left(\frac{2n_o - n_H}{n_c}\right)$ + charge on ion/n_C	
10.	For compounds containing C and H only O.N. of H is taken as +1	
11.	For compounds containing C, H and halogen O.N. of halogen is taken as –1; H = +1	

16.2. OXIDATION STATE

Oxidation state and oxidation number are two different terms. The oxidation state of an element is its oxidation number per atom separately. Oxidation state of an element is equal to oxidation number when it occurs only once in a compound but it is not equal to its oxidation number when it occurs more than once in a compound. For example :

Oxidation state as well as oxidation number of N in NO_3^- = +5 but average oxidation number of N in NH_4NO_3 is +1 but +1 is not the oxidation state of N in NH_4NO_3.

16.3. DIFFERENCE BETWEEN OXIDATION STATE AND OXIDATION NUMBER

EXAMPLE 1. *Calculate the oxidation number of N in NH_4NO_3. Also comment on the oxidation states of N in this compound.*

SOLUTION. $NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^-$

The oxidation state of an element is its oxidation number per atom separately. Oxidation state of an element is equal to its oxidation number when it occurs only once in a compound. Thus :

(*i*) NH_4^+. Oxidation state of N + 4(oxidation state of H) = +1; oxidation state of N + 4 (+ 1) = + 1; **oxidation state of** N = + 1 – 4 = – **3** **Ans.**

(*ii*) NO_3^-. Oxidation state of N+3(oxidation state of O) = –1

∴ Oxidation state of N + 3 (–2) = –1; **Oxidation state of N** = –1 + 6 = **+5** **Ans.**

(*iii*) $\mathbf{NH_4NO_3}$. O.N. of N+4(O.N. of H) + O.N. of N + 3(O.N. of O) = 0

O.N. of N + 4 (+1) + O.N. of N + 3 (–2) = 0; 2 (O.N. of N) = –4 + 6 = +2

∴ O.N. of N = +2/2 = **+1** **Ans.**

EXAMPLE 2. *Calculate the oxidation num ber of the underlined atom.*

(*i*) $K\underline{Mn}O_4$ (*ii*) $\underline{Cr}_2O_7^{2-}$

(*iii*) P in $\underline{P}O_4^{3-}$ **(HP Board, 2007, CBSE, PMT, 2009)**

SOLUTION.

(*i*) **$KMnO_4$.** O.N. of K + O.N. of Mn + (4 × O.N. of O) = 0 ; + 1 + O.N. of Mn + 4(–2) = 0

∴ O.N. of Mn = + 7 **Ans.**

(*ii*) **$Cr_2O_7^{2-}$.** 2 × O.N. of Cr + 7 × O.N. of O = –2; 2 × O.N. of Cr +7 (– 2) = –2

∴ O.N. of Cr = (– 2 + 14)/2 = **+ 6 Ans.**

(*iii*) **PO_4^{3-}.** O.N. of P + 4 × O.N. of O = –3; O.N. of P + 4(–2) = –3

∴ O.N. of P = –3 + 8 = **+5** **Ans.**

EXAMPLE 3. *Calculate the oxidation number of two* Cl*–atoms in bleaching powder,* $CaOCl_2$*:*

SOLUTION. $CaOCl_2$ is written as, Ca(OCl)Cl.

(*i*) **O.N. of Cl in OCl^-.**

O.N. of O + O.N. of Cl = –1; –2 + O.N. of Cl = –1

∴ O.N. of Cl = –1 + 2 = **+1 Ans.**

(*ii*) **O.N. of Cl in Ca(OCl)Cl.**

O.N. of Ca + O.N. of OCl^- + O.N. of Cl = 0

+2 + (–1) + O.N. of Cl = 0.

Hence O.N. of Cl = –2 + 1 = **–1 Ans.**

Hence oxidation numbers of two Cl–atoms in $CaOCl_2$ are **+1 and –1** as shown above.

16.4. OXIDATION NUMBER (O.N.) OF METAL ATOM OR ION IN CO-ORDINATION COMPOUNDS OR COMPLEX COMPOUNDS.

In order to calculate the oxidation number of metal atom or ion in a complex compound, the following oxidation number of ligands should be used.

1. **Zero oxidation number :**

Ligands with name	**Ligands with name**
CO (carbonyl)	NO (nitrosyl)
CS (thiocarbonyl)	NH_3 (ammine)
H_2O (aqua, new), aquo (old)	$(C_6H_5)_3P$ (triphenyl phosphine)
C_5H_5N (pyridine)	$NH_2CH_2CH_2NH_2$ (en or ethylene diamine)
C_2H_4 (ethene or ethylene)	

2. **–1 oxidation number**

Ligands with name	**Ligands with name**
CN^- (cyano)	N_3^- (azido)
F^- (fluoro); (fluorido, new)	N_2^- (amido)
Cl^- (chloro); (Chlorido, new)	
Br^- (bromo); (bromido, new)	OH^- (hydroxo)
I^- (iodo); (iodido, new)	H^- (hydrido)
NO_2^- (nitro); (nitrito-N, new)	HS^- (mercapto)
ONO^- (nitrito – O)	CH_3COO^- (acetato)
SCN^- (thiocyanato)	NCS^- (isothiocyanato)

3. **–2 oxidation number :**

Ligands with name	**Ligands with name**
S^{2-} (sulphido or thio)	O^{2-} (oxo)
SO_4^{2-} (sulphato)	O_2^{2-} (peroxo)
NH^{2-} (imido)	CO_3^{2-} (carbonato)
$C_2O_4^{2-}$ (oxalato)	

4. **+1 oxidation number :**

Ligands with name	**Ligands with name**
NO^+ (nitrosonium)	$[NH_2 - NH_3]^+$ (hydrazinium)
NO_2^+ (nitronium)	

> **Note :** In negatively charged complex ions, the name of the metal ends with – ate.

EXAMPLE 4. *Calculate the oxidation number of Fe in* $K_4Fe(CN)_6$ *:* **(M.L.N.R. 1986)**

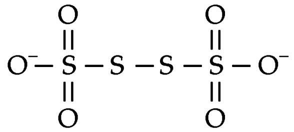
SOLUTION.

$K_4Fe(CN)_6$. 4 × O.N. of K + O.N. of Fe +6 × O.N. of CN = 0;

4 × (+1) + O.N. of Fe + 6(–1) = 0

∴ O.N. of Fe = +6–4 = **+2 Ans.**

EXAMPLE 5. *The oxidation states of S-atoms in* $S_4O_6^{2-}$ *from left to reight respectively are:*



$$O^- - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - S - S - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - O^-$$

(*a*) +6, 0, 0, +6 (*b*) +3, +1, +1, + 3

(*c*) +5, 0, 0, +5 (*d*) +4, +1, +1, 4

(Orissa JEE, 2009, Kerala PMT, 2010)

SOLUTION. Oxidation state (O.S) of left S-atom = +1 (from O^-) + 4 (from +2 of each = O) + 0 (from – S atom) = +5. So, the correct answer is (c).

EXAMPLE 6. *Find the oxidation number of Cr in the complex* $[Cr(NH_3)_3(H_2O)_3]Cl_3$ *and write its IUPAC name.*

SOLUTION. $[Cr(NH_3)_3(H_2O)_3]Cl_3$

O.N. of Cr + 3 × O.N. of NH_3 + 3 × O.N. of H_2O + 3 × O.N. of Cl^- = 0

O.N. of Cr + (3 × 0) + (3 × 0) + (3 × –1) = 0;

O.N. of Cr = + 3 – 0 – 0 = **+3** **Ans.**

IUPAC name is, triamminetriaquachromium (III) chloride.

EXAMPLE 7. *Write the IUPAC name of* $K[Co(CN)(CO)_2(NO)]$ *and calculate the oxidation number of cobalt in this complex.*

SOLUTION.

$K[Co(CN)(CO)_2(NO)]$ is potassium dicarbonylcyanonitrosylcobaltate (0). In this complex :

O.N. of K + O.N. of Co + O.N. of CN^- + 2 (O.N. of CO) + O.N. of NO = 0 + 1 + O.N. of Co + (–1) + 2(0) + 0 = 0.

Hence, O.N. of Co = +1 –1 = **0** ***i.e.*, zero Ans.**

EXAMPLE 8. *The oxidation state of* Fe *in brown ring complex,* $[Fe(H_2O)_5(NO)^+]SO_4$ is:

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

SOLUTION. In $[Fe(H_2O)_5(NO^+)]SO_4$:

(IIT, 1987 Orissa JEE, 2008, Karnataka CET, 2009, Odisha JEE, 2012)

O.N. of Fe + 5(O.N. of H_2O) + O.N. of $(NO)^+$ + O.N. of SO_4^{2-}

$$= 0;$$

$$\text{O.N. of Fe} + 5(0) + 1 - 2 = 0;$$

$$\text{O.N. of Fe} = +2 - 1 = \mathbf{+1}$$ **Ans.**

16.5. OXIDATION NUMBER OF AN ELEMENT CANNOT BE MORE THAN THE NUMBER OF UNPAIRED ELECTRONS PRESENT IN ITS EXCITED STATE.

Example 9. *What is the maximum oxidation number of sulphur in its compounds?*

Solution. At no. of S = 16, $_{16}S = (Ne)^{10}\ 3s^2 3p^4$. $_{16}S(\text{excited}) = (Ne)^{10}\ 3s^1\ 3p_x^1\ 3p^1_y\ 3p_z^1\ 3d^{1+1}$

No. of unpaired electrons in the excited state of S = 6

∴ Maximum oxidation number of 'S' in its compounds = 6 **Ans.**

Example 10. *Calculate the oxidation number of 'S' in* SF_4.

Solution. $_9F = (He)^2\ 2s^2 2p_x^2 2p_y^2 2p_z^1$. So, F-atom has one unpaired electron. To form SF_4, S - atom should have four unpaired electrons [$_{16}S$ (excited to get 4 unpaired electrons $= (Ne)^{10}\ 3s^2 3p_x^1 3p^1_y 3p_z^1 3d^1$].

So, oxidation number of

S in SF_4 = **4** **Ans.**

16.6. COMPOUNDS CONTAINING C, H AND O

Type. For compounds containing C, H and O;

$$\text{O.N. of C} = \frac{2N_O - N_H}{N_C}$$

Where N_O, N_H and N_C are the number of O, H and C atoms present in the compound.

Example 11. *Calculate the oxidation number of carbon in* HCOOH.

Solution. HCOOH = CH_2O_2. No. of C - atoms = 1; H–atoms = 2; O-atoms = 2. We know

$$\text{O.N. of C} = \frac{2N_O - N_H}{N_C}$$

$$= \frac{(2\times 2)-(2)}{1}$$

$$= 4 - 2 = \mathbf{+2}$$ **Ans.**

16.7. IONS CONTAINING C, H AND O

Type. For ions containing C, H and O, O.N. of carbon

$$= \frac{2n_O - n_H + (\text{charge on ion})}{n_C}$$

where n_O, n_H and n_C are the number of O, H and C atoms in the ion.

Example 12. *Calculate the oxidation number of 'C' in* HCO_3^-.

Solution. In HOC_3^-, number of O-atoms = 3; H-atoms = 1; C-atoms = 1 and charge = –1. We know.

$$\text{O.N. of C in } HCO^-_3 = \frac{2N_O - N_H + (\text{charge on ion})}{N_C}$$

$$= \frac{(2\times 3) - 1 + (-1)}{1} = \mathbf{+4}$$ **Ans.**

16.8. COMPOUNDS CONTAINING CO-ORDINATE OR DATIVE BOND

In case of compounds having covalent and co-ordinate bonds, for each covalent bond between two dissimilar atoms, assign an oxidation number of +1 to less electronegative element.

In case of co-ordinate covalent bonds, two cases arise:

(*i*) For co-ordinate bonds between same atoms or dissimilar atoms in which the donor atom is less electronegative than the acceptor atom, assign an oxidation number of +2 to the donor atom and –2 to the acceptor atom.

(*ii*) If the donor atom is more electronegative than the acceptor atom, neglect the contribution of the co-ordinate bond. For example, in $\mathrm{H - N \overset{=}{\rightarrow} C}$, the contribution of co-ordinate bond is neglected because N atom is more electronegative than the acceptor atom.

Thus O.N. of C in $\mathrm{\overset{+1}{H} - \overset{x}{C} \equiv \overset{-3}{N}}$ is +2 and that of N in $\mathrm{\overset{+1}{H} - \overset{-3}{N} \overset{=}{\rightarrow} \overset{x}{C}}$, is –3 and that of C is +2.

Example 13. *Calculate the oxidation number of 'C' and N in* (*i*) $\mathrm{H - N \overset{=}{\rightarrow} C}$ and (*ii*) $\mathrm{H - C \equiv N}$

Solution. (*i*) Given $\mathrm{H - N \overset{=}{\rightarrow} C}$. In this compound, donor atom 'N' is more electronegative (electronegativity = 3) than carbon (electronegativity = 2.5). So, the contribution of coordinate bond (→) is zero. Let O.N. of C = x; O.N. of H = +1; N = –3.

Hence in $\mathrm{H - N \overset{=}{\rightarrow} C}$,

$$\text{O.N. of H} + \text{O.N. of N} + \text{O.N. of C} = 0$$

$$+1 - 3 + x = 0$$

or $$x = +3 - 1 = +2$$

∴ O.N. of C in the given compound = +2

Also, in $\mathrm{H - N \overset{=}{\rightarrow} C}$, O.N. of H (= +1) + O.N. of N + O.N. of C (= +2) = 0.

So, O.N. of N = – 1 – 2 = **– 3** **Ans.**

(*ii*) In H – C ≡ N, let O.N. of C = x; O.N. of H = +1; N = –3.

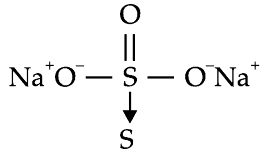
Hence in H – C ≡ N, we have :

O.N. of H + O.N of C + O.N. of N = 0 +1 + x – 3 = 0 or x = +2.

Thus O.N. of C in the given compound = +2

Example 14. *Calculate the oxidation number of S in* $Na_2S_2O_3$

Solution. The structure of $Na_2S_2O_3$ is



$$\mathrm{Na^{+}O^{-} - \underset{\underset{S}{\downarrow}}{\overset{\overset{O}{\|}}{S}} - O^{-}Na^{+}}$$

Since the atoms bonded by coordinate bond are the same (*i.e.* S), the contribution by coordinate bond is zero.

(*i*) The O.N. of one 'S' atom acting as acceptor in coordinate bond = **–2** **Ans.**

(*ii*) Let the O.N. of second S-atom = x. Thus in $Na_2S_2O_3$:

$2 \times (+1) \;+\; 3 \times (-2) \;+\; x \;+\; 1 \times (-2) \;=\; 0$

(For Na) (For O-atoms) (For acceptor, S-atom)

$+2 - 6 + x - 2 = 0$

or $x = -2 + 6 + 2$

$= \mathbf{+6}$ **Ans.**

(*iii*) O.N. of S in $Na_2S_2O_3$ can be calculated by **conventional method** as follows.

Let O.N. of S = x. Thus in $Na_2S_2O_3$:

$2 \times (+1) \;+\; 2x \;+\; 3 \times (-2) = 0$ or $2 + 2x - 6 = 0$

(For Na) (For oxygen)

$2x = 6 - 2 = +4$

or $x = \mathbf{+2}$

∴ O.N. of S by conventional method

= +2.

This value is average of the two values (–2 and + 6) found from its structure. The value +2 is wrong because the two S-atoms in $Na_2S_2O_3$ are in different oxidation states. When $Na_2S_2O_3$ is treated with dil. H_2SO_4, one S-atom is precipitated while the other gets converted to SO_2.

16.9. COMPOUNDS CONTAINING PEROXIDE LINKAGE

Type. *For compounds* containing peroxide linkage (–O– O–) or linkages, O.N. of each O-atom in the peroxide linkage is taken as (–1). In order to predict whether a compound contains a peroxide linkage or not, calculate the O.N. of central atom by conventional method. If the maximum number of unpaired electrons in the excited state of central atom, are **less** than the calculated oxidation number of central atom, then the compound is expected to have a peroxide linkage, otherwise not.

Example. 15. *Calculate the oxidation state of S in (i)* H_2SO_5 *and (ii)* $S_2O_8^{2-}$ *ion.* **(J and K, 2009)**

SOLUTION. $_{16}S$ (excited) = $(Ne)^{10}\,3s^1\,3p_x^1\,3p_y^1\,3p_z^1\,3d^{1+1}$. There are maximum 6 unpaired electrons. So, maximum oxidation state of S should be 6.

(*i*) **In** $\mathbf{H_2SO_5}$, let us calculate oxidation state of 'S' by conventional method. Let O.N. of S = x. So, in H_2SO_5 :

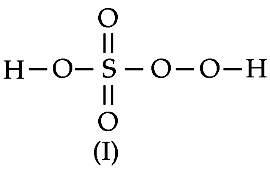
$2 \times (+1) + x + 5 \times (-2) = 0; \; 2 + x - 10 = 0$

(For H) (For oxygen)

or $x = +10 - 2 = +8$

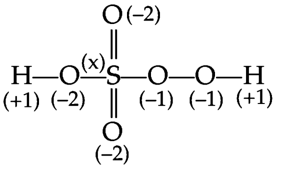
Since +8 > +6, so H_2SO_5 will have a peroxide linkage.

Structure of H_2SO_5 is shown as (I). The O.N. of S can be calculated by chemical method. Thus we have :



$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-H$

(I)



$\underset{(+1)}{H}-\underset{(-2)}{O}-\overset{\overset{O(-2)}{\|}}{\underset{\underset{\underset{(-2)}{O}}{\|}}{S^{(x)}}}-\underset{(-1)}{O}-\underset{(-1)}{O}-\underset{(+1)}{H}$

or $+1 - 2 + x - 2 - 2 - 1 - 1 + 1 = 0$

∴ $x = -1 + 2 + 2 + 2 + 1 + 1 - 1$

$= +6$

∴ O.N. of 'S' in H_2SO_5 = **+ 6** **Ans.**

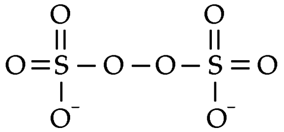
(*ii*) **In** $\mathbf{S_2O_8^{2-}}$, let us calculate O.N. of 'S' by conventional method. Let O.N. of S = x. So, in $S_2O_8^{2-}$:

$2x + 8 \times (-2) = -2;$

$2x = -2 + 16 = \mathbf{+14}$

or $x = +7$

Since +7 > + 6 (maximum no. of unpaired electrons in S),

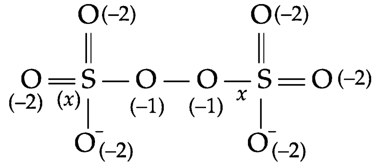


$O=\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{S}}=O$

(II)

so, $S_2O_8^{2-}$ will have a peroxide linkage. Structure of $S_2O^{2-}{}_8$ is shown as (II).

The O.N. of S can be calculated by chemical method. Thus, we have :



$\underset{(-2)}{O}=\overset{\overset{O(-2)}{\|}}{\underset{\underset{O^-(-2)}{|}}{S^{(x)}}}-\underset{(-1)}{O}-\underset{(-1)}{O}-\overset{\overset{O(-2)}{\|}}{\underset{\underset{O^-(-2)}{|}}{S^{x}}}=O(-2)$

or $-2 + x - 2 - 2 - 1 - 1 + x - 2 - 2 - 2$

$= -2$ i.e.; charge on ion.

$2x = -2 + 2 + 2 + 2 + 1 + 1 + 2$

$+ 2 + 2 = 12$

∴ $x = +12/2 = \mathbf{+6.}$

So, the O.N. of S in $S_2O_8^{2-}$

= **+6 Ans.**

Example 16. *Calculate the oxidation number of chromium in* CrO_5.

Solution. $_{24}Cr = (Ar)^{18}\ \overset{3d}{\boxed{\uparrow\,|\uparrow\,|\uparrow\,|\uparrow\,|\uparrow}}\ \ \overset{4s}{\boxed{\uparrow}}$

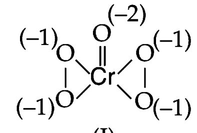
Cr-atom has six unpaired electrons. So, its maximum oxidation state is six.

(*i*) **Conventional method.** $\mathbf{CrO_5}$.

O.N. of Cr + 5(O.N. of O) = 0

O.N. of Cr + 5(–2) = 0

Hence O.N. of Cr = +10



(I)

Since +10 > + 6 (maximum number of unpaired electrons in Cr-atom), CrO_5 will have a peroxide linkage. Structure of CrO_5 is (I).

$\therefore$ O.N. of Cr $-1-1-1-1-2 = 0$ (see structure I)

or O.N. of Cr $= 1+1+1+1+2$

$= +6$ **Ans.**

Type. *For compounds* containing C and H, oxidation number of H *is taken as +1.*

Type. *For compounds containing* C, H and halogen, *O.N. of H is taken as +1* and that of halogen *is taken as –1.* Similarly, for the compounds containing C and halogens, O.N. of halogen is taken as –1.

Example 17. *Calculate the oxidation, number of carbon in (i)* $CHCl_3$ *(ii)* CCl_4

SOLUTION. (*i*) $CHCl_3$.

Let O.N. of C $= x$. Thus, in $CHCl_3$:

x + O.N. of H + 3 % (O.N. of Cl) $= 0$

Or $x + 1 + 3(-1) = 0$

$\therefore$ $x = +3 - 1 = +2$

So, O.N. of C in $CHCl_3$ $=$ **+2 Ans.**

(*ii*) CCl_4.

Let O.N. of C $= x$. Thus, in CCl_4 :

$x +$ 4(O.N. of Cl) $= 0$;

Or $x + 4(-1) = 0$

$x = +4$

Hence, O.N. of C in CCl_4 $=$ **+4** **Ans.**

Type. *The compound,* in which the element *is in the highest* oxidation state will act as an oxidant *only and cannot* act as a reducing agent. It is because *the oxidation number* of that element cannot be further raised. The compound in which the element is not in the highest oxidation state can act as a reducing agent.

Example 18. *Which of the following compound can act as oxidising agent and which one can act as a reducing agent? (i)* SO_3, *(ii)* H_2S

Solution. $_{16}S$ (excited state) $= (Ne)^{10}\ 3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^{1+1}$. The maximum number of unpaired electrons = 6 (one in 3s, three in 3p and two in 3d). So, its maximum oxidation state = 6.

(*i*) SO_3. let O.N. of S $= x$.

So, x + 3(O.N. of O) $= 0$

or $x + 3(-2) = 0$;

$x = +6$

Since O.N. of S in SO_3 (= 6) is maximum, hence SO_3 will act as oxidising agent.

(*ii*) In H_2S. Let O.N. of S $= x$.

So, $2 \times$ O.N. of H $+ x = 0$

or $2 \times (+1) + x = 0$;

$x = -2$

Since, maximum oxidation number of S is 6 as explained in (*i*) above and in H_2S, it is –2, so H_2S will not act as an oxidising agent but can act as a reducing agent. The oxidation state of S can not be lowered below –2. So, H_2S can not act as oxidant.

16.10. OXIDATION

It is a process in which the oxidation *number of* an element or ion increases by the loss of *one or more* electrons. For example, consider the following *reactions.*

(*i*) $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$

(*ii*) $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

In reaction (*i*), the oxidation of Fe^{2+} to Fe^{3+} takes place by the loss of one electron. In reaction (*ii*), the oxidation of Sn^{2+} to Sn^{4+} takes place by the loss of two electrons.

Exampe 19. *Write the element or ion which has undergone oxidation in the following reactions.*

(*i*) $Zn \longrightarrow Zn^{2+} + 2e^-$

(*ii*) $Cu^{2+} + 2e^- \longrightarrow Cu$

Solution. (*i*) Zn has undergone oxidation to Zn^{2+} by the loss of two electrons (*ii*) No ion is oxidised.

16.11. REDUCTION

It is a process in which the oxidation *number of an* element/ion decreases by the gain of one *or more electrons.* For example, consider the following reactions.

(*i*) $Ag^+ + 1e^- \longrightarrow Ag$

(*ii*) $Mg^{2+} + 2e^- \longrightarrow Mg$

In reaction (*i*), the reduction of Ag^+ to Ag takes place by the gain of one electron. Here the oxidation number of Ag has decreased from + 1 to zero (Ag^0). In reaction (*ii*), the reduction of Mg^{2+} to Mg takes place by the gain of two electrons. Here, oxidation number of Mg has decreased from +2 to zero (Mg^0).

Example 20. *Write the element/ion which has undergone reduction in the following reactions.*

(*i*) $K^+ + 1e^- \longrightarrow K$

(*ii*) $Cd \longrightarrow Cd^{2+} + 2e^-$

Solution. In reaction (*i*) K^+ is reduced to K by the gain of one electron. Here oxidation number of K has decreased from + 1 to zero (K^0). In reaction (*ii*), Cd is not reduced because its oxidation number has increased from zero (Cd^0) to + 2 (in Cd^{2+}).

16.12. OXIDANT OR OXIDISING AGENT

An oxidant is a substance (element/ion) whose oxidation number decreases by the gain of one or more electrons. For example, in the change

$$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$$

Fe^{3+} is oxidant because its oxidation number decreases from +3 to +2 (in Fe^{2+})

Example 21. *Write the name of the element/ion which acts as an oxidant in the following reactions.*

(*i*) $Zn \longrightarrow Zn^{2+} + 2e^-$

(*ii*) $Br_2 + 2e^- \longrightarrow 2Br^-$

Solution. Out of above two reactions, Br_2 in reaction (*ii*) acts as an oxidant because it gains two electrons to form 2 Br^-. Also, oxidation number of Br_2 decreases from zero ($Br^0{}_2$) to – 1 (in Br^-).

16.13. REDUCTANT OR REDUCING AGENT

A reductant is a substance (element/ion) whose oxidation number increases by the loss of one or more electrons. For example, in the change

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$$

Fe^{2+} is reductant because its oxidation number increases from +2 to +3 (in Fe^{3+}).

EXAMPLE 22. *Write the name of the element/ion which acts as a reducing agent in the following change.*

(*i*) $Mg \longrightarrow Mg^{2+} + 2e^-$

(*ii*) $Cu^{2+} + 2e^- \longrightarrow Cu$

SOLUTION. In reaction (*i*), Mg acts as a reducing agent because its oxidation number increases from zero (Mg^0) to +2(Mg^{2+}). In reaction (*ii*), Cu^{2+} is not a reductant because its oxidation number decreases (and not increases) from +2 (in Cu^{2+}) to zero (in Cu^0).

16.14. REDOX REACTION

A reaction in which one substance is oxidised while the other one is reduced is called redox reaction. For example:

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

In this reaction, Zn is oxidised to Zn^{2+} because its oxidation number has increased from zero (Zn^0) to +2(Zn^{2+}). Here Cu^{2+} is reduced to Cu because its oxidation number has decreased from +2 (in Cu^{2+}) to zero (in Cu^0).

16.15. METHOD TO KNOW THE OXIDANT AND THE REDUCTANT IN A REDOX REACTION

Different steps to know the oxidant and the reductant are given below and explained by taking the equation

$$H_2S + Br_2 \longrightarrow HBr + S$$

(*i*) Write the equation in the ionic form but do not balance it.

$$H^+ + S^{-2} + Br_2 \longrightarrow H^+ + Br^- + S$$

(*ii*) Ignore the common ions on both the sides.

$$S^{-2} + Br_2 \longrightarrow Br^- + S$$

(*iii*) Write the oxidation number of elements in step (*ii*).

$$S^{-2} + Br^0_2 \longrightarrow Br^- + S^0$$

(*iv*) Look at an element on the reactant side whose oxidation number is more than the same element on the product side. This element on the reactant side is the oxidant.

In the equation of step (*iii*), Br_2 *is the oxidant* because the oxidation number (zero) is more than that of Br(–1) on the product side.

(*v*) Look at an element on the reactant side whose oxidation number is less than the same element on the product side. This element on the reactant side is the reductant.

In the equation of step (*iii*), S^{-2} *is the reductant* because its oxidation number (–2) is less than that of S (zero) on the product side.

16.16. METHOD TO KNOW THE OXIDATION NUMBER CHANGE IN A REDOX REACTION

Different steps to know the oxidation number change in a redox reaction are given below and explained by taking the equation,

$$H_2S + Br_2 \longrightarrow HBr + S$$

(*i*) Write the equation in the ionic form but do not balance it.

$$H^+ + S^{2-} + Br_2 \longrightarrow H^+ + Br^- + S.$$

(*ii*) Ignore the common ions on both the sides.

$$S^{-2} + Br_2 \longrightarrow Br^- + S.$$

(*iii*) Write the oxidation number of elements in step (*ii*) at their top.

$$S^{-2} + Br^0_2 \longrightarrow Br^{-1} + S^0. \qquad \text{..... (1)}$$

(*iv*) *Find the oxidation number change.*

(*a*) *For oxidation process* (in which oxidation number increases).

$$\text{Oxidation number change} = \begin{bmatrix} \text{O.N. of an element on product side} - \text{O.N. of same element on reactant side} \end{bmatrix} \times \begin{bmatrix} \text{Number of atoms of that element on the reactant side} \end{bmatrix}$$

O.N. change for S^{-2}_1 to S^0 in equation (1)

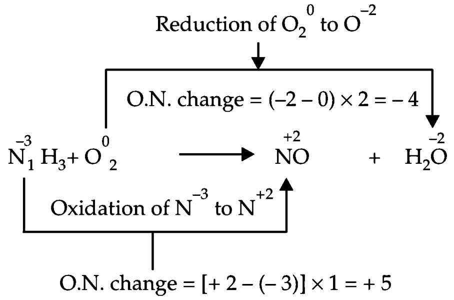
$$= [0 - (-2) \times 1 = +2\,]$$

(*b*) *For reduction process* (in which O.N. decreases). The O.N. change is found by the same method as shown in step (*a*) above e.g. O.N. change for Br_2^0 to Br^{-1} in equation (1).

$$= (-1 - 0) \times 2 = -2$$

16.17 METHOD TO BALANCE THE REDOX REACTION BY OXIDATION NUMBER CHANGE METHOD

Different steps for balancing the change in O.N. are given below and explained by taking the following equation.



... (A)

(*i*) Multiply the molecule of the oxidant (on the reactant side) with the O.N. change for the oxidation process.

(*ii*) Multiply the molecule of the reductant (on the reactant side) with the O.N. change for the reduction process.

Thus the reaction (A) changes to

$$4NH_3 + 5\,O_2 \longrightarrow NO + H_2O \qquad ...(B)$$

(*iii*) Do not change the number of molecules of the reactants at all (e.g., 4 of NH_3 and 5 of O_2).

(*iv*) Make the number of atoms (whose O.N. has changed) of different elements on the product side equal to the number of atoms of the same elements on the reactant side e.g., the reaction (B) becomes.

$$4NH_3 + 5\,O_2 \longrightarrow 4NO + 6H_2O$$

Here, the number of N-atoms, H-atoms and O-atoms on the reactant side are equal to N-atoms, H-atoms and O-atoms on the product side e.g., 4, 12 and 10 respectively.

EXAMPLE 23. *Write the name of the oxidant and reducing agent in the following redox reaction.*

$$F_2 + 2KCl \longrightarrow 2KF + Cl_2$$

SOLUTION. Writing oxidation number of elements in the given substances, we have:

$$F_2^0 + 2K^+\,Cl^- \longrightarrow 2K^+F^-\,Cl_2^0$$

(*i*) F_2 *is an oxidant* because its oxidation number has decreased from zero ($F^0{}_2$) to – 1 (F^-) in the redox reaction.

(*ii*) Cl^- *(or KCl) is a reducing agent* because its oxidation number has increased from –1 (Cl^-) to zero ($Cl^0{}_2$).

EXAMPLE 24. *Which one of the following reactions is a redox reaction and why?*

(*i*) $Ag^+\,Cl^- \rightarrow Ag\,Cl$ (*ii*) $SO_2 + H_2S \rightarrow S + H_2O$

SOLUTION. (*i*) Writing oxidation number of each element, we have :

$$Ag^+ + Cl^- \longrightarrow Ag^+Cl^-$$

Here the oxidation number of neither Ag^+ nor Cl^- has undergone any change. So, it is not a redox reaction.

(*ii*) Writing oxidation number of each element, we have :

$$S^{+4}O^{-2}_2 + H^{+1}_2S^{-2} \longrightarrow S^0 + H^{+1}_2O^{-2}$$

In this reaction, oxidation number of S (in SO_2) has decreased from +4 to zero (in S^0). Also, oxidation number of S (in H_2S) has increased from –2 to zero (in S^0). So, it is a redox reaction.

EXAMPLE 25. *Balance the following reaction by oxidation number change method.*

$$NaClO \longrightarrow NaClO_3 + NaCl$$

SOLUTION. In NaClO;

O.N. of Na + O.N. of Cl + O.N. of O = 0;

+ 1 + O.N. of Cl + (–2) = 0

So, O.N. of Cl = + 2 – 1 = + 1

In $NaClO_3$: O.N. of Na + O.N. of Cl + 3 (O.N. of O) = 0;

+ 1 + O.N. of Cl + 3 (– 2) = 0.

So, O.N. of Cl = + 6 – 1 = + 5

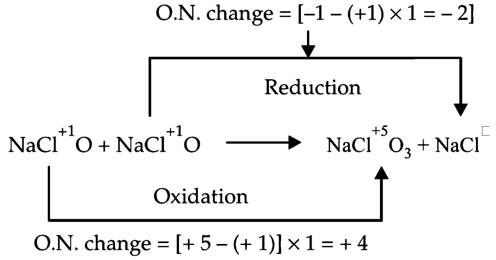
In NaCl :

O.N. of Na + O.N. of Cl = 0;

+ 1 + O.N. of Cl = 0

∴ O.N. of Cl = 0 – 1 = – 1.

Thus we have :



Multiply first NaClO with 2 *i.e.*, O.N. change during reduction and second NaClO with 4 *i.e.*, O.N. change during oxidation. So, we have :

$$\therefore\ 2NaClO + 4NaClO \longrightarrow NaClO_3 + NaCl$$

Balancing Na, Cl and O atoms on product side without changing 2 and 4 co-efficients of reactants, we have :

$$2NaClO + 4NaClO \longrightarrow 2NaClO_3 + 4NaCl$$

$$\text{or}\quad NaClO + 2NaClO \longrightarrow NaClO_3 + 2NaCl$$

EXAMPLE 26. *Balance the following reaction by oxidation number change method.*

$$HNO_2 \longrightarrow HNO_3 + NO + H_2O.$$

SOLUTION. In HNO_2 ;

O.N. of H + O.N. of N + 2 (O.N. of O) = 0;

+ 1 + O.N. of N + 2(–2) = 0

So, O.N. of N = +4 – 1 = +3

In HNO_3;

O.N. of H + O.N. of N + 3 (O.N. of O) = 0;

+ 1 + O.N. of N + 3(–2) = 0

So, O.N. of N = +6 – 1 = +5

In NO;

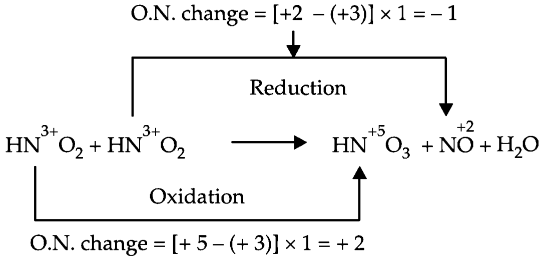
O.N. of N + O.N. of O = 0;

O.N. of N + (–2) = 0

So, O.N. of N = +2

$$\text{O.N. change} = \begin{bmatrix}\text{O.N. of N on the} & - & \text{O.N. of N on the}\\ \text{product side} & & \text{reactant side}\end{bmatrix} \times \begin{matrix}\text{no. of atoms}\\ \text{of N on the}\\ \text{reactant side}\end{matrix}$$

of N on th



Multiply first HNO_2 with 1 *i.e.*, O.N. change during reduction and second NaClO with 2 *i.e.*, O. N. change during oxidation. So, we have :

$$HNO_2 + 2HNO_2 \longrightarrow HNO_3 + NO + H_2O$$

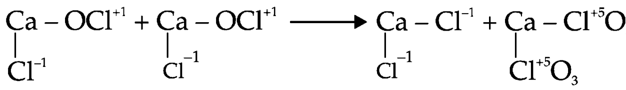
Balancing H, N and O atoms on the product side without changing the co-efficients 1 and 2 on reactant side, we have :

$$HNO_2 + 2HNO_2 \longrightarrow HNO_3 + 2NO + H_2O.$$

Example 27. *Balance the following reaction by oxidation number change method.*

$$\underset{\text{Bleaching powder}}{CaOCl_2} \longrightarrow CaCl_2 + CaClO_3$$

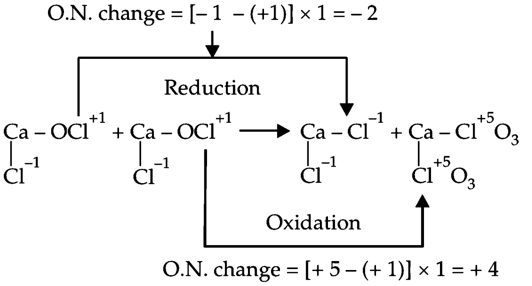
Solution. Reaction



$$\underset{Cl^{-1}}{Ca} - OCl^{+1} + \underset{Cl^{-1}}{Ca} - OCl^{+1} \longrightarrow \underset{Cl^{-1}}{Ca} - Cl^{-1} + \underset{Cl^{+5}O_3}{Ca} - Cl^{+5}O_3$$

$CaOCl_2$ is written as Ca(OCl)Cl. The oxidation number of Cl in OCl^- = +1 and of Cl in Ca(OCl)Cl = –1. For calculation see example 3.

Hence,



In ClO_3^-,

O.N. of Cl + 3(O.N. of O) = –1;

O.N. of Cl + 3(–2) = –1

∴ O.N. of Cl = –1 + 6 = +5

Multiplying first $CaOCl_2$ with 4 *i.e.,* O.N. change during oxidation and second $CaOCl_2$ with 2 *i.e.,* O.N. change during reduction, we have :

$$4CaOCl_2 + 2CaOCl_2 \longrightarrow CaCl_2 + Ca(ClO_3)_2$$

Balancing Ca, O and Cl atoms on the product side without changing co-efficients on reactant side, we have :

$$4CaOCl_2 + 2CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$$

or

$$6CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$$

16.18. REACTIONS INVOLVING NEUTRAL MEDIUM

Example 28. *Balance the following chemical equation by the oxidation number (O.N.) change method.*

$$C_6H_6 + O_2 \longrightarrow CO_2 + H_2O$$

Solution.

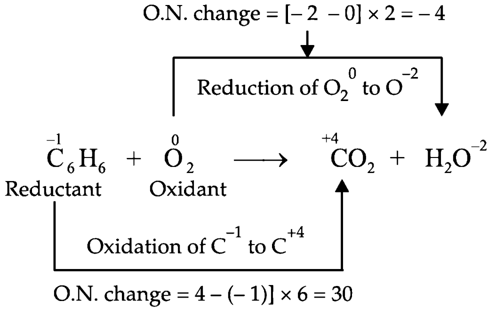
(*i*) Write the skeleton equation with O.N. of each element at its top.

$$\overset{-1}{C}_6\overset{+1}{H}_6 + \overset{0}{O}_2 \longrightarrow \overset{+4}{C}O_2 + \overset{+1}{H}_2O^{-2}$$

(*ii*) Ignore the O.N. of all such elements on the reactant and product side whose O.N. is the same. Retain the oxidation number of the rest elements. Thus, we have

$$\overset{-1}{C}_6H_6 + \overset{0}{O}_2 \longrightarrow \overset{+4}{C}O_2 + H_2O^{-2}$$

(*iii*) Write the O.N. change of two elements *i.e.* oxidant and reductant



...(A)

(*iv*) (*a*) Multiply the molecule of the oxidant (on the reactant side) with the O.N. change (= 30) for the oxidation process.

(*b*) Multiply the molecule of the reductant (on the reactant side) with the O.N. change (= 4) for the reduction process.

Thus the equation (A) becomes :

$$4C_6H_6 + 30O_2 \longrightarrow CO_2 + H_2O. \qquad \text{... (B)}$$

(*v*) Do not change the number of molecules of reactants at all (*e.g.* 4 of C_6H_6 and 30 of O_2). Now, make the number of atoms of such elements on the product and reactant side equal, whose O.N. has changed. Thus the equation (B) becomes :

$$4C_6H_6 + 30O_2 \longrightarrow 24CO_2 + 12H_2O.$$

Dividing throughout by 2, we get

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O.$$

Example 29. *Balance the following chemical equation by the oxidation number (O.N.) change method.*

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

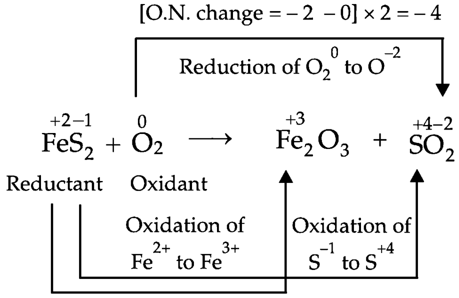
Solution. (*i*) Write the skeleton equation with O.N. of each element at its top.

$$\overset{+2}{Fe}S_2^{-1} + \overset{0}{O}_2 \longrightarrow \overset{+3}{Fe}_2O_3 + \overset{+4}{S}O_2$$

(*ii*) Ignore the O.N. of such elements on the reactant and product side whose O.N. is the same. Retain the oxidation number of the rest elements. Thus, we have

$$Fe^{+2}S_2^{-1} + O_2^0 \longrightarrow \overset{+3}{Fe}_2O_3 + \overset{+4}{S}O_2^{-2}$$

(*iii*) Write the O.N. change of three elements (Fe^{+2}, S^{-1}, O_2^0) *i.e. one oxidant (O_2) and two reductants (Fe^{+2}, S^{-1})*



...(A)

(*i*) Oxidation of Fe^{+2} to Fe^{+3}

O.N. change = [+3 −2] × 1 = 1

(*ii*) Oxidation of S^{-1} to S^{+4}

O.N. change = [4 − (− 1)] × 2 = 10

∴ Total O.N. change = 1 + 10 = 11

(*iii*) (*a*) Multiply the molecule of the oxidant (on the reactant side) with the O.N. change (= 11) for the oxidation process.

(*b*) Multiply the molecule of the reductant (on the reactant side) with the O.N. change (= 4) for the reduction process.

Thus, the equation (A) becomes

$$4FeS_2 + 11O_2 \longrightarrow Fe_2O_3 + SO_2 \qquad \text{... (B)}$$

(*iv*) Do not change the number of molecules of reactants at all (*e.g.* 4 of FeS_2 and 11 of O_2). Now make the number of atoms of such elements on the product and reactant side equal, whose O.N. has changed. Thus, equation (B) becomes

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2 \qquad \text{... (B)}$$

16.19. REACTIONS INVOLVING ACIDIC MEDIUM

Different steps to balance such reactions are given below by taking the following equations.

Example 30. *Balance the following equation by oxidation number change method.*

$$Cr_2O_7^{-2} + C_2O_4^{-2} \longrightarrow Cr^{+3} + CO_2$$

(*acidic medium*)

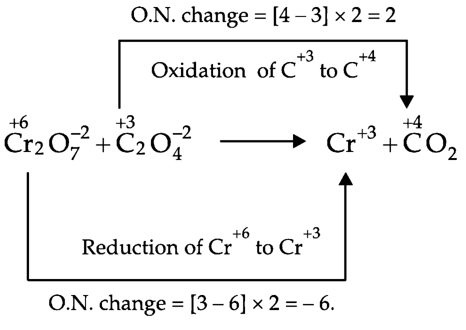
Solution. (*i*) To write the O.N. of each element at its top.

$$\overset{+6}{Cr_2}\,O_7^{-2} + \overset{+3}{C_2}\,O_4^{-2} \longrightarrow \overset{+3}{Cr} + \overset{+4}{C}O_2^{-2}$$

(*ii*) To ignore the O.N. of such elements which do not undergo any O.N. change.

$$\overset{+6}{Cr_2}\,O_7^{-2} + \overset{+3}{C_2}\,O_4^{-2} \longrightarrow \overset{+3}{Cr} + \overset{+4}{C}O_4$$

(*iii*) To find the change in oxidation number (O.N.)



...(A)

(*iv*) (a) Multiply the molecule of the oxidant $Cr_2O_7^{-2}$ (on the reactant side) with the O.N. change (=2) for the oxidation process.

(b) Multiply the molecule of the reductant $C_2O_4^{-2}$ (on the reactant side) with the O.N. change (= 6) for the reduction process.

Thus the equation (A) changes to

$$2Cr_2O_7^{-2} + 6C_2O_4^{-2} \longrightarrow Cr^{3+} + CO_2 \qquad \text{... (B)}$$

(*v*) Do not change the number of molecules of reactants at all (*e.g.* 2 of $Cr_2O_7^{-2}$ and 6 of $C_2O_4^{-2}$). Except O and H, make the number of atoms of such elements on the product and reactant side equal whose O.N. has changed. Thus, the reaction (B) becomes

$$2Cr_2O_7^{-2} + 6C_2O_4^{-2} \longrightarrow 4Cr^{+3} + 12CO_2 \qquad \text{... (C)}$$

(*vi*) Balance the oxygen* atoms (see foot note)

$$2Cr_2O_7^{-2} + 6C_2O_4^{-2} \longrightarrow 4Cr^{3+} + 12CO_2 + 14H_2O.$$

(*vii*) Balance the hydrogen atoms (see foot note on page 364)

$$2Cr_2O_7^{-2} + 6C_2O_4^{-2} + 28H^+ \longrightarrow 4Cr^{+3} + 12CO_2 + 14H_2O.$$

Dividing throughout by 2, we get

$$Cr_2O_7^{-2} + 3C_2O_4^{-2} + 14H^+ \longrightarrow 2Cr^{+3} + 6CO_2 + 7H_2O.$$

Example 31. *Balance the following equation by oxidation number change method*

$$MnO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$$

(*acidic medium*)

Solution.

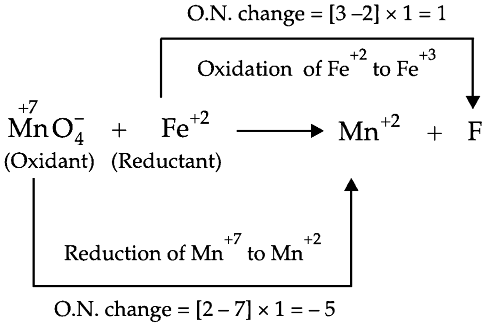
(*i*) To write the oxidation number (O.N.) of each element at its top.

$$\overset{+7}{Mn}O_4^- + \overset{+2}{Fe} \longrightarrow \overset{+2}{Mn} + Fe^{+3}$$

(*ii*) To ignore the O.N. of such elements which do not undergo any O.N. change

$$\overset{+7}{M}nO_4^- + Fe^{+2} \longrightarrow Mn^{+2} + Fe^{+3}$$

(*iii*) To Find the change in O.N.



...(A)

(*iv*) (*a*) Multiply the molecule of the oxidant (on the reactant side) with the O.N. change (= 1) for the oxidation process.

(*b*) Multiply the molecule of the reductant (on the reactant side) with the O.N. change (= 5) for the reduction process.

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*Balancing of oxygen atoms. It is done by adding one H_2O molecule, two H_2O molecules and so on, to the side which is deficient in one oxygen atom, two oxygen atoms and so on respectively.

Thus, the equation (A) changes to

$$MnO_4^- + 5Fe^{+2} \longrightarrow Mn^{+2} + 5Fe^{+3} \quad \text{... (B)}$$

(*v*) Do not change the number of molecules of reactants at all (*e.g.* 1 of MnO_4^- and 5 of Fe^{+2}). Except O and H, make the number of atoms of such elements on the product and reactant side equal, whose O.N. has changed. Thus, the reaction (B) becomes :

$$MnO_4^- + 5Fe^{+2} \longrightarrow Mn^{+2} + 5Fe^{+3}$$

(*vi*) Balance the oxygen atoms (See foot note on page 363)

$$MnO_4^- + 5Fe^{+2} \longrightarrow Mn^{+2} + 5Fe^{+3} + 4H_2O$$

(*vii*) Balance the H-atoms* (See foot note below).

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

EXAMPLE 32. *Balance the following chemical equations (involving acids) by the oxidation number change method.*

(A) $MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(B) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$

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(C) $K_2Cr_2O + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + CO_2 + H_2O$

SOLUTION.

(A) $MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

(*a*) Write the equation in the ionic form but do not balance it.

$$MnO_2 + H^+ + Cl^- \longrightarrow Mn^{+2} + Cl^- + Cl_2 + H_2O$$

(*b*) Write the oxidation number of all the elements in step (*a*) at their top.

$$\overset{+4}{Mn}\overset{-2}{O_2} + H^+ + Cl^- \longrightarrow Mn^{+2} + Cl^- + \overset{0}{Cl_2} + \overset{+1}{H_2}O^{-2}$$

(*c*) Retain (*i*) H^+ (of acidic medium on reactant side) and (*ii*) O.N. of those elements which undergo O.N. change. Ignore the rest oxidation numbers. Thus, we have

$$\overset{+4}{Mn}O_2 + H^+ + Cl^- \longrightarrow Mn^{+2} + Cl^- + \overset{0}{Cl_2} + H_2O.$$

(*d*) Ignore the ions on the reactant and product side whose O.N. does not change. Thus, we have

$$Mn^{+4}O_2 + H^+ + Cl^- \longrightarrow Mn^{+2} + \overset{0}{Cl_2} + H_2O.$$

(*e*) Write the oxidation number change of the oxidant and reductant.

Reduction of $\overset{+4}{Mn}$ to $\overset{+2}{Mn}$

O.N. change = [+ 2 – (+ 4)] × 1 = – 2

$$\overset{+4}{Mn}O_2 + H^+ + Cl^- \longrightarrow \overset{2+}{Mn} + \overset{0}{Cl_2} + H_2O$$

Oxidation of Cl^- to Cl_2

O.N. change = [0 – (– 1)] × 1 = +1

(*f*) Balance the change in the oxidation number.

$$MnO_2 + H^+ + 2Cl^- \longrightarrow Mn^{+2} + Cl_2 + H_2O$$

(*g*) Balance the oxidant and the reductant on both sides *atomically* (except 'O' and 'H') without changing the number of ions and molecules of the reactants.

$$MnO_2 + H^+ + 2Cl^{-1} \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$$

(*h*) Balance the oxygen atoms (see foot note on page, 363).

$$MnO_2 + H^+ + 2Cl^- \longrightarrow Mn^{+2} + Cl_2 + H_2O + H_2O$$

$$MnO_2 + H^+ + 2Cl^- \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$$

(*i*) Balance the H-atoms (see foot note on page, 364)

$$MnO_2 + H^+ + 3H^+ + 2Cl^- \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$$

or $MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$

or $MnO_2 + 2HCl + 2H^+ \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$

(*j*) Change all the H^+-ions into acid molecules (see foot note on page, 364)

$$MnO_2 + 2HCl + 2HCl \longrightarrow Mn^{+2} + Cl_2 + 2H_2O$$

(*k*) Substituting the atoms/ions ignored in step (d), we get,

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

(*B*) **Hint.** $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO_2 + H_2O$

Thus, we have

$$\overset{0}{Zn} + H^+ + \left[N^{+5}O_3\right]^- \longrightarrow Zn^{+2} + [NO_3]^- + N^{+4}O_2 + H_2O$$

$$Zn + 4HNO_3 \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$ **Ans.**

(C) **Hint.** $K_2Cr_2O_7 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + CO_2 + H_2O$

Thus, we have

$$Cr_2^{+6}O_7 + C_2^{+3}O_4^{-2} + H^+ \longrightarrow Cr^{+3} + C^{+4}O_2 + H_2O$$

$$K_2Cr_2O_7 + 3H_2C_2O_4 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 6CO_2 + 7H_2O$$ **Ans.**

16.20. REACTIONS INVOLVING ALKALINE MEDIUM

Different steps to balance such reactions are given below by taking the following equations.

EXAMPLE 33. *Balance the following equation by oxidation number (O.N.) change method.*

$$Zn + NO_3^- \longrightarrow ZnO_2^{-2} + NH_3$$

(*alkaline medium*)

**Balancing of H-atoms.* It is done by adding one H^+-ion, two H^+-ions, and so on to the side which is deficient in one H-atom, two H-atoms and so on respectively.

Change all H^+ions into acid molecules. It is done :

(*i*) By changing one H^+-ion, two H^+-ions and so on into 1 HNO_3 or 1 HCl, $2HNO_3$ or 2HCl and so on respectively if the reaction involves HNO_3 or HCl.

(*ii*) By changing $2H^+$-ions, $4H^+$-ions and so on into H_2SO_4, $2H_2SO_4$ and so on respectively if the reaction involves H_2SO_4.

Solution. (*i*) To write the O.N. of each element at its top.

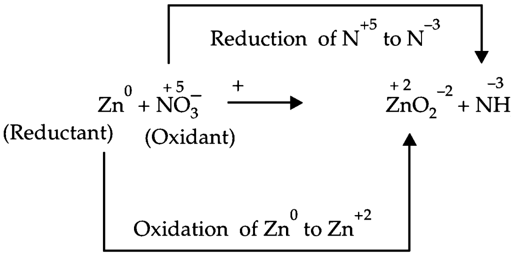
$$Zn^0+\left[\overset{+5}{N}\overset{-2}{O_3}\right]^- \longrightarrow \left[\overset{+2}{Zn}\overset{-2}{O_2}\right]^{-2}+N^{-3}H_3$$

(*ii*) To ignore the O.N. of such elements which do not undergo any O.N. change.

$$Zn^0+\overset{+5}{N}O_3^- \longrightarrow \overset{+2}{Zn}O_2^{-2}+\overset{-3}{N}H_3$$

(*iii*) To find the change in O.N.

O.N. change = − 3 – [(+ 5)] × 1 = − 8



...(A)

O.N. change = [2 – 0] × 1 = 2

(*iv*) (*a*) Multiply the molecule of the oxidant (on the reactant side) with the O.N. change (= 2) for the oxidation process.

(*b*) Multiply the molecule of the reductant (on the reactant side) with the O.N. change (= 8) for the reduction process. Thus, the equation (*A*) changes to

$$8Zn + 2NO_3^- \longrightarrow ZnO_2^{2-} + NH_3. \quad ...(B)$$

(*v*) Do not change the number of molecules of reactant at all (e.g. 8 of Zn and 2 of ZnO_2^{-2}). Except O and H, make the number of atoms of such elements on the product and reactant side equal, whose O.N. has changed. Thus the equation (B) becomes.

$$8Zn + 2NO_3^- \longrightarrow 8ZnO_2^{2-} + 2NH_3.$$

(*vi*) Balance the oxygen atoms* (see foot note).

$$8Zn + 2NO_3^- + 10H_2O \longrightarrow 8ZnO_2^{-2} + 2NH_3$$

(*vii*) Balance the H-atoms** (see foot note).

$$8Zn + 2NO_3^- + 10H_2O + 14OH^- \longrightarrow 8ZnO_2^{-2} + 2NH_3 + 14H_2O$$

Or $8Zn + 2NO_3^- + 14OH^- \longrightarrow 8ZnO_2^{-2} + 2NH_3 + 4H_2O$

Dividing through out by 2, we get

$$4Zn + NO_3^- + 7OH^- \longrightarrow 4ZnO_2^{-2} + NH_3 + 2H_2O.$$

16.21. BALANCING OF REDOX REACTIONS BY ION-ELECTRON (HALF REACTION) METHOD

It is another convenient method for balancing oxidation reduction reactions. In this method, the given reaction is split up into two halves ; one equation describes the oxidation while the other one describes the reduction. The two half reactions are balanced separately and then added in such a way that the electron produced in oxidation half reaction are completely used up in the reduction half reaction. The different steps involved for balancing the equation by this method are :

(*i*) *Write skeleton equation in net ionic form.*

(*ii*) *Identify the species that undergo a change in oxidation numbers.*

(*iii*) *Write two partial equations, one representing oxidation and the other, reduction.*

(*iv*) *Balance each half reaction as follows :*

(*a*) *First of all balance the atoms of elements that are oxidised or reduced.*

(*b*) *Balance the atoms of elements other than oxygen and hydrogen.*

(*c*) *Balance oxygen atoms by adding a H_2O molecule for each oxygen atom on the side deficient in oxygen. (See page 363).*

(*d*) *For balancing hydrogen atoms :*

1. *in case of reactions taking place in acidic medium, add a H^+ ion for each H atom, on the side deficient in hydrogen. (See page, 364).*
2. *in case of reactions taking place in basic medium, add a H_2O molecule for each H atom, on the side deficient in hydrogen and an equal number of OH^- ions on the opposite side. (See page 365.)*

(*v*) *Add the required number of electrons to balance the charges.*

(*vi*) *Mulitply two half reactions by suitable numbers so that the number of electrons lost in a half reaction will be equal to the number of electrons gained in the other half of reaction.*

(*vii*) *Add the two half reactions. The resulting equation will be a balanced equation.*

Now we will balance some redox reactions using the ion-electron method.

Example 34. *Balance the following equation by ion electron method.*

$$KMnO_4 + FeSO_4 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$$

Solution. (*i*) The skeleton equation in the ionic form can be written as :

$$K^+ + MnO_4^- + Fe^{2+} + SO_4^{2-} + H^+ + SO_4^{2-} \longrightarrow Fe^{3+} + SO_4^{2-} + Mn^{2+} + SO_4^{2-} + K^+ + SO_4^{2-} + H_2O$$

On cancelling the common K^+ and SO_4^{2-} ions on both the sides, net ionic equation is :

---

*Balance the oxygen atoms by the same method as shown under "balancing equations involving acidic medium, page 363.

***Balance the H–atoms.* (For alkaline solution only). It is done by adding one *H_2O* molecule, two H_2O molecules and so on to the side which is deficient of one H-atom, two H-atoms and so on respectively. Also, at the same time add an equal number of OH^--ion. (i.e. one OH^-–ion, $2OH^-$-ions and so on respectively) on the other side.

$$MnO_4^- + Fe^{2+} + H^+ \longrightarrow Fe^{3+} + Mn^{2+} + H_2O$$

(*ii*) Now writing two half reactions as :

Oxidation half reaction :

$$Fe^{2+} \longrightarrow Fe^{3+}$$

(O.N. increases from 2 to 3)

Reduction half reaction :

$$(Mn^{+7}O_4)^- \longrightarrow Mn^{2+}$$

[O.N. of Mn decreases from 7to 2]

(*iii*) Now the equations are balanced atomically as :

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

(*iv*) To balance charges, add electrons.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad ...(1)$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(2)$$

(*v*) In order to balance the electrons lost during oxidation half reaction with electrons gained during reduction half reaction, multiply (1) by 5.

Then we get $5Fe^{2+} \longrightarrow 5Fe^{3+} + 5e^- \quad ...(3)$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(4)$$

(*vi*) On adding equations (3) and (4), we get the balanced equation as :

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

or balanced equation in the molecular form after substituting cancelled common ions of step (*i*) is :

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + 2KMnO_4 + 8H_2O + K_2SO_4$$

Example 35. *Balance the following reaction by ion-electron method.*

$$P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$$

(basic medium)

Solution. $P_4 + OH^- \longrightarrow PH_3 + H_2PO_2^-$

(*i*) oxidation half-reaction

$$P_4 \longrightarrow 4H_2PO_2^-$$

Balancing O-atoms, we have :

$$P_4 + 8H_2O \longrightarrow 4H_2PO_2^-$$

Balancing of H-atoms in basic medium. Add H_2O molecules to the side short of H-atoms and add same number of OH^- ions on the other side. (See foot note on page 365)

$$P_4 + 8H_2O + 8OH^- \longrightarrow 4H_2PO_2^- + 8H_2O + 4e^-$$

Or $P_4 + 8OH^- \longrightarrow 4H_2PO_2^- + 4e^-$

(*ii*) $P_4 \longrightarrow 4PH_3$

(Reduction half reaction)

Balancing H-atoms in basic medium by the method shown above, we have :

$$P_4 + 12H_2O + 12e^- \longrightarrow 4PH_3 + 12OH^-$$

From equations (*i*) and (*ii*), we have :

$$P_4 + 8OH^- \longrightarrow 4H_2PO_2^- + 4e^-\,] \times 3$$
$$P_4 + 12H_2O + 12e^- \longrightarrow 4PH_3 + 12OH^-$$
$$4P_4 + 12H_2O + 12OH^- \longrightarrow 4PH_3 + 12OH^-$$

Or $P_4 + 3H_2O + 3OH^- \longrightarrow PH_3 + 3H_2PO_2^-$

(after dividing by common factor, 4)

(*i*) An oxidising agent or oxidant gains electrons while a reducing agent loses electrons.

(*ii*) Stronger reducing agents have least $\overset{o}{E}$ (reduction) value while stronger oxidising agents have higher E° (reduction) value and vice-versa.

Example 36. *On the basis of following $\overset{o}{E}$ values, the strongest oxidising agent is :*

$$[Fe\,(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + \bar{e}\,;$$
$$\overset{o}{E} = -0.35V$$
$$Fe^{2+} \longrightarrow Fe^{3+} + \bar{e}\,;\ \overset{o}{E} = -0.77V$$

(*a*) $[Fe(CN)_6]^{4-}$ (*b*) Fe^{2+}

(*c*) Fe^{3+} (*d*) $[Fe(CN)_6]^{3-}$

(CBSE Med, 2008)

Solution. (*i*) $[Fe(CN)_6]^{3-} + \bar{e} \longrightarrow [Fe(CN)_6]^{4-}$; $\overset{o}{E}$ (reduction) = +0.35 V

(*ii*) $\underset{\text{oxidant}}{Fe^{3+}} + \bar{e} \longrightarrow Fe^{2+}$; $\overset{o}{E}$ (reduction) = +0.77V

Since stronger oxidising agent has higher $\overset{o}{E}$ (reduction) value, so Fe^{3+} is stronger oxidising agent. So, correct answer is (c)

Example 37. *Balance the following reaction by ion-electron method.*

$$NaOH + Br_2 \longrightarrow NaBr + NaBrO_3 + H_2O$$

(basic medium)

Solution. Writing the above reaction in ionic form.

$$OH^- + Br_2 \longrightarrow Br^- + BrO_3^- + H_2O$$

(*i*) Oxidation half reaction.

$$Br_2 \longrightarrow 2BrO_3^-$$

Balancing oxygen atoms, we have (See foot note on page 363)

$$Br_2 + 6H_2O \longrightarrow 2BrO_3^-$$

Balancing H-atoms and charges, we have (See foot note on page 365)

$$Br_2 + 6H_2O + 12OH^- \longrightarrow 2BrO_3^- + 12H_2O + 10e^-$$

(*ii*) **Reduction half-reaction.**

$$Br_2 + 2e^- \longrightarrow 2Br^-$$

From equations (*i*) and (*ii*), we have;

$$Br_2 + 6H_2O + 12OH^- \longrightarrow 2BrO_3^- + 12H_2O + 10e^-$$
$$Br_2 + 2e^- \longrightarrow 2Br^-\ ] \times 5$$

Add $6Br_2 + 12OH^- \longrightarrow 10Br^- + 2BrO_3^- + 6H_2O$

or $3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$

(after dividing by common factor, 2)

or $3Br_2 + 6NaOH \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$

Example 38. *Balance the following reaction in acidic medium by ion–electron method.*

$$MnO_4^- + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$$

Solution. (*i*) The skeleton ionic equation is :

$$MnO_4^- + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$$

(*ii*) Now write two half reactions as

Oxidation half reaction :

$$(C_2^{3+}O_4)^{2-} \longrightarrow 2C^{+4}O_2$$

[O.N. of C increases from 3 to 4]

Reduction half reaction :

$$(Mn^{7+}O_4)^{-} \longrightarrow Mn^{2+}$$

[O.N. of Mn decreases from 7 to 2]

(*iii*) Now the equations are balanced atomically (for O and H atoms)

$$(C_2O_4)^{2-} \longrightarrow 2CO_2$$

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

(*iv*) To balance charges, add electrons.

$$(C_2O_4)^{2-} \longrightarrow 2CO_2 + 2e^- \quad ...(1)$$

$$(MnO_4)^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad ...(2)$$

(*v*) In order to balance the electrons lost during oxidation half reaction with electrons gained during reduction half reaction, multiply (1) by 5 and (2) by 2. Then we have,

$$5(C_2O_4)^{2-} \longrightarrow 10CO_2 + 10e^- \quad ...(3)$$

$$2(MnO_4)^- + 16H^+ + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O \quad ...(4)$$

(*vi*) On adding equations (3) and (4), we get the balanced equation as :

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Example 39. *In the disproportionate reaction*

$$3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$$

the equivalent mass of the oxidising agent is : (molar mass) of $HClO_3$ = 84.45).

(*a*) *16.89*	(*b*) *32.22*
(*c*) *84.45*	(*d*) *28.15*
(*e*) *29.7*	**(Kerala, PET, 2011)**

Solution. We know that, equivalent mass = Molar mass/oxidation number change. ...(1)

(*i*) Oxidation no. of Cl in $HClO_3$.
O.N. of H + O.N. of Cl + 3 × O.N. of O = 0; + 1 + x + 3(–2) + 0; x = +5

(*ii*) O.N. of Cl in Cl_2 = 0. So, O.N. change = 5 – 0 = 5

∴ Equivalent mass = Molar mass/O.N. change = 84.45/5 i.e., 16.89

So, the correct answer is (*a*).

16.22. AIEEE PATTERN EXAMPLES

Example 40. *When* $KMnO_4$ *acts as an oxidising agent and ultimately forms* MnO_4^-, MnO_2, Mn_2O_3, Mn^{2+}, *then the number of electrons transferred in each case respectively is :*

(*a*) *3, 5, 7, 1*	(*b*) *1, 5, 3, 7*
(*c*) *4, 3, 1, 5*	(*d*) *1, 3, 4, 5,* **(AIEEE, 2002)**

Solution. The oxidation state of Mn in different given compounds and ions can be written as follows along with the electrons involved.

$$\begin{tikzcd}
\overset{+4}{MnO_2} & \overset{+7}{KMnO_4} \arrow[l, "-3e^-"'] \arrow[r, "-1e^-"] \arrow[dl, "-4e^-"] \arrow[dr, "-5e^-"] & Mn^{+6}O_4^{-2} \\
\overset{+3}{Mn_2O_3} & & Mn^{2+}
\end{tikzcd}$$

The number of electrons transferred in MnO_4^{-2}, MnO_2, Mn_2O_3 and Mn^{+2} are 1, 3, 4 and 5.

So, the correct answer is, (*d*).

Example 41. *In alkaline medium,* ClO_2 *oxidises* H_2O_2 *to* O_2 *and itself gets reduced to* Cl^-. *How many moles of* H_2O_2 *are oxidised by 1 mole of* ClO_2 ?

(*a*) *1.0*	(*b*) *1.5*
(*c*) *2.5*	(*d*) *3.5*
(*e*) *5.0*	**(Kerala PET, 2005)**

Solution. (*a*) $ClO_2 \longrightarrow Cl^-$

$$ClO_2 + 4H_2O \longrightarrow Cl^- + 2H_2O + 4OH^-$$

$$\text{or} \quad ClO_2 + 2H_2O + 5e^- \longrightarrow Cl^- + 4OH^- \quad ...(1)$$

(*b*) $H_2O_2 \longrightarrow O_2$

$$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^- \quad ...(2)$$

$$\text{Thus: } ClO_2 + 2H_2O + 5e^- \longrightarrow Cl^- + 4OH^- \;] \times 2$$

$$H_2O_2 + 2OH^- \longrightarrow O_2 + 2H_2O + 2e^- \;] \times 5$$

Adding

$$2ClO_2 + 5H_2O_2 + 2OH^- \longrightarrow 2Cl^- + 5O_2 + 6H_2O$$

2 mol   5 mol

$$\therefore \quad 2 \text{ mol } ClO_2 \equiv 5 \text{ mol } H_2O_2$$

$$1 \text{ mol } ClO_2 \equiv \frac{5}{2} \text{ or } 2.5 \text{ mol } H_2O_2$$

So, the correct answer is (*c*).

Example 42. *The oxidation state of chromium in the final product formed by the reaction between KI and acidified potassium dichromate solution is :*

(*a*) +4	(*b*) +6
(*c*) +2	(*d*) +3 **(AIEEE, 2005)**

Solution. Reaction.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

So, oxidation state of Cr in the product is +3. The correct answer is (*d*).

Example 43. *Oxidation number of S in* SO_4^{2-} *is :*

(*a*) +6	(*b*) +3
(*c*) +2	(*d*) –2

(BCE C.E, Bihar, 2005, CBSE – PMT, 2009)

Solution. Oxidation number (O.N.) of S in SO_4^{2-} is found as :

$$\text{O.N. of S} + 4 \text{ (O.N. of O)} = -2$$

$$\text{O.N. of S} + 4(-2) = -2$$

$$\text{O.N. of S} - 8 = -2$$

$$\text{O.N. of S} = -2 + 8 = +6.$$

So, the correct answer is (*a*).

Example 44. *Oxidation state of oxygen in potassium superoxide is :*

(*a*) *–1/2*	(*b*) *–1*
(*c*) *–2*	(*d*) *0* **(BET, 2003)**

Solution. Potassium superoxide= KO_2

∴ Oxidation state of K + 2 × oxidation state of O = 0

∴ +1 + (2 × oxidation state of O) = 0

$\therefore$ Oxidation state of oxygen $= \dfrac{-1}{2}$

So, the correct answer is (*a*).

Example 45. *Which one of the following equations represents oxidation phenomenon?*

(*a*) $Cl^{\circ} \longrightarrow Cl^{\circ}$

(*b*) $Sn^{++++} \longrightarrow Sn^{++}$

(*c*) $Fe^{++} \longrightarrow Fe^{+++}$

(*d*) $Cu^{++} \longrightarrow Cu^{\circ}$

(SCRA, 2000)

Solution. Oxidation is a process which involves increase in the oxidation number by the loss of electron/electrons in a redox reaction. Out of above answers, (*c*) is correct because the oxidation number of Fe^{++} increases to +3 (Fe^{+++}) by the loss of one electron. $Fe^{++} \longrightarrow Fe^{+++} + 1e^-$.

Example 46. *In the reaction,* $2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$

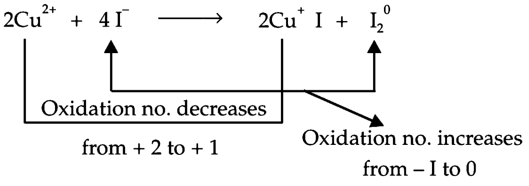
(*a*) Cu^{2+} *is oxidant and* I^- *reductant*

(*b*) Cu^{2+} *is reductant and* I^- *oxidant*

(*c*) *both* Cu^{2+} *and* I^- *are reductants*

(*d*) *both* Cu^{2+} *and* I^- *are oxidants* **(SCRA, 2000)**

Solution. An oxidant is that whose oxidation number decreases in a redox reaction. Also, a reductant is that whose oxidation number increases in a redox reaction. Considering the given reaction, we have :



Here Cu^{2+} is oxidant as its oxidation number decreases from +2 to +1. Also, I^- is reductant because its oxidation number increases from –1 to 0 *i.e.*, zero. So, the correct answer is (*a*).

Example 47. *Sulphur dioxide functions both as an oxidising and as a reducing agent. In which one of the following reactions, it is an oxidising agent ?*

(*a*) $PbO_2 + SO_2 \xrightarrow{Heat} PbSO_4$

(*b*) $SO_2 + H_2O \longrightarrow H_2SO_3$

(*c*) $3Fe + SO_2 \longrightarrow 2FeO + FeS$

(*d*) $2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$ **(SCRA, 2000)**

Solution. An oxidant is that whose oxidation number decreases in a redox reaction by gain of an electron or electrons. Writing oxidation number of sulphur atoms in the given answers, we have :

(*a*) $PbO_2 + S^{4+}O_2 \longrightarrow PbS^{6+}O_4$

(*b*) $S^{4+}O_2 + H_2O \longrightarrow H_2S^{+4}O_3$

(*c*) $3Fe + S^{4+}O_2 \longrightarrow 2FeO + FeS^{2-}$

(*d*) $2NaOH + S^{4+}O_2 \longrightarrow Na_2S^{4+}O_3 + H_2O$

From above, we see that the oxidation number of sulphur decreases from +4 to –2 in reaction (*c*). So, in this reaction, SO_2 acts as an oxidant. Thus, the correct answer is (*c*).

Example 48. *The oxidation number of carbon in carbon suboxide is :*

(*a*) +2/3

(*b*) +4/3

(*c*) +4

(*d*) –4/3

Solution. Carbon suboxide is C_3O_2. Let oxidation number (O.N.) of C is x ;

O.N. of O $= -2$

Thus, in C_3O_2, we have

$3x + 2(-2) = 0$; $3x = +4$; $x = +4/3$

So, the correct answer is (*b*).

Example 49. *Which of the following reactions involve neither oxidation, non reduction ?*

(*a*) $CrO_4^{-2} \longrightarrow Cr_2O_7^{-2}$

(*b*) $Cr \longrightarrow CrCl_3$

(*c*) $Na \longrightarrow Na^+$

(*d*) $2SO_3^{-2} \longrightarrow S_4O_6^{-2}$

Solution. Considering that oxidation involves increase in oxidation number while reduction involves decrease in oxidation number, in a redox reaction, we have :

(*a*) $Cr^{+6}O_4^{-2} \longrightarrow Cr_2^{+6}O_7^{-2}$

(*b*) $Cr^0 \longrightarrow Cr^{+3}Cl_3$

(*c*) $Na^0 \longrightarrow Na^+$

(*d*) $2S_2^{+2}O_3^{-2} \longrightarrow S_4^{2.5}O_6^{-2}$

From above, we find that in reaction (*a*), neither the oxidation number of Cr increases nor decreases from +6. So, the correct answer is (*a*).

Example 50. *In rhombic sulphur, the oxidation number, atomicity and valency of sulphur are:*

(*a*) *0, 2, 8*

(*b*) *0, 8, 2*

(*c*) *2, 8, 2*

(*d*) *2, 1, 8*

Solution. Rhombic sulphur is S_8. So, the oxidation number of S in $S_8 = 0$; Atomicity = 8 and valency = 2

So, the correct answer is (*b*).

Example 51. *The oxidation state of phosphorus in cyclotrimetaphosphoric acid is*

(*a*) +3

(*b*) +5

(c) –3

(*d*) +2

(*e*) –2 **(Kerala PMT, 2011)**

Solution. Cyclotrimetaphosphoric acid is $(HPO_3)_3$. or $H_3P_3O_9$. Let x = oxidation state of phosphorus. Thus:

(3 × O.N. of H) + (3 × O.N. of P) + (9 × O.N. of O) = 0;

$(3 \times +1) + (3x) + 9(-2) = 0$

Or $+3 + 3x - 18 = 0$; $3x = 15$

or $x = +5$.

So ,the correct answer is (*b*)

Example 52. *Oxidation states of the metal in the minerals haematite and magnetite, respectively, are :*

(*a*) *II, III in haematite and III is magnetite*

(*b*) *II, III in haematite and II is magnetite*

(*c*) *II, in haematite and II, III is magnetite*

(*d*) *III, in haematite and II, III is magnetite*

(IIT-JEE, 2011)

Solution. (i) in haematite (Fe_2O_3), oxidation number of Fe(x) is :

$$2x + 3(-2) = 0; \quad 2x = +6; x = 6/2 = +3$$

(*ii*) Magnetite (Fe_3O_4) is an equimolar mixture of FeO and Fe_2O_3.

Thus, oxidation number of Fe(x) is FeO is :

$$x + 1 \times (-2) = 0; \quad x = +2.$$

The oxidation number of Fe(x) in Fe_2O_3 is + 3 (see ii above). So, correct answer is (*d*)

Example 53. *The substance that acts as a reductant in the following reaction*

$$3Ni + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Ni^{2+} + 2Cr^{3+} + 7H_2O, \text{ is :}$$

(*a*) $Cr_2O_7^{2-}$ (*b*) Ni
(*c*) H_2O (*d*) H^+

Solution. Let oxidation state of Cr in $Cr_2O_7^{2-} = x$

$$\therefore \quad 2x + 7(-2) = -2; \; 2x = 12; \; x = +6$$

From the given equation, we have :

$$3Ni^\circ + \overset{6+}{Cr_2}\overset{-2}{O_7^{2-}} + 14H^+ \longrightarrow 3Ni^{2+} + 2Cr^{3+} + 7H_2O$$

Since oxidation state of Ni has increased from zero to +2, Ni will act as a reductant. So, the correct answer is (*b*).

Example 54. For the redox reaction :

$$MnO_4^- + Fe^{2+} + H^+ \longrightarrow Mn^{2+} + Fe^{3+} + H_2O$$

the correct stoichiometric co-efficients of MnO_4^-, Fe^{2+} and H^+ are :

(*a*) *2, 4, 6* (*b*) *1, 3, 14*
(*c*) *1, 5, 8* (*d*) *1, 8, 5*

Solution.

$$\begin{aligned} MnO_4^- + 8H^+ + 5e^- &\longrightarrow Mn^{2+} + 4H_2O \\ Fe^{2+} &\longrightarrow Fe^{3+} + e^- \;] \times 5 \end{aligned}$$

$$\text{Adding } MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \quad ...(1)$$

$\therefore$ Correct stoichiometric co-efficients of MnO_4^-, Fe^{2+} and H^+ in the reaction (1) are, 1, 5, 8. So, the correct answer is (*c*).

Example 55. *The oxidation number of* N *in hydrazine is :*

(*a*) *+2* (*b*) *0*
(*c*) *–1* (*d*) *–2*

Solution. Hydrazine is $\mathbf{N_2H_4}$:

$$\begin{aligned} \text{In } N_2H_4;\; 2 \times \text{O.N. of N} + 4 \times \text{O.N. of H} &= 0;\; 2 \times \text{O.N. of N} + 4(+1) = 0 \\ \therefore \quad \text{O.N. of N} &= -4/2 = -2 \end{aligned}$$

So, the correct answer is (*d*).

Example 56. *The change in oxidation number of carbon in the reaction ignoring +ve or –ve sign in*

$$MnO_4^- + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2 \text{ is :}$$

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

Solution. In $C_2O_4^{2-}$:

$$\begin{aligned} 2(\text{O.N. of C}) + 4(\text{O.N. of O}) &= -2 \\ 2(\text{O.N. of C}) + 4(-2) &= -2;\; \text{O.N. of C} = \frac{(-2+8)}{2} = +3 \end{aligned}$$

$$\begin{aligned} \textbf{In } \mathbf{CO_2}: \text{ O.N. of C} + 2(\text{O.N. of O}) &= 0;\; \text{O.N. of C} + 2(-2) = 0 \\ \therefore \quad \text{O.N. of C} &= +4 \end{aligned}$$

$$\text{Change in O.N.} = \left[\text{O.N. of C on product side} - \text{O.N. of C on reactant side}\right]$$

$$\begin{aligned} &\times \text{ no. of atoms of C on reactant side} \\ &= [+4 - (+3)] \times 2 \\ &= +2 \text{ or } 2 \end{aligned}$$

So, the correct answer is (*c*).

Example 57. *The electron change in the acidic medium in the following reaction :*

$$C_2O_4^{-2} \longrightarrow CO_2 \text{ is :}$$

(*a*) *2* (*b*) *3*
(*c*) *4* (*d*) *5*

Solution.

$$C_2O_4^{2-} \longrightarrow CO_2$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

So, the electron change is 2. Hence the correct answer is (*a*).

Example 58. *A metal ion* M^{3+} *after loss of three electrons in a reaction will have an oxidation number equal to :*

(*a*) *zero* (*b*) *+2*
(*c*) *+3* (*d*) *+6* **(CPMT, 1980, 83, 84)**

Solution.

$$M^{3+} \longrightarrow M^{6+} + 3e^-$$

(Balanced equation)

So, M^{3+} after the loss of three electrons forms M^{6+} having oxidation number, 6. So, the correct answer is (*d*).

Example 59. *The oxidation numbers of* Si *in* $Be_3Al_2Si_6O_{18}$ *and* U *in* UO_2SO_4 *are respectively:*

(*a*) *+6, +4* (*b*) *+4, +6*
(*c*) *+2, +3* (*d*) *+3, +2*

Solution. In $\mathbf{Be_3Al_2Si_6O_{18}}$:

$$3(\text{O.N. of Be}) + 2(\text{O.N. of Al}) + 6(\text{O.N. of Si}) + 18(\text{O.N. of O}) = 0$$

$$\begin{aligned} 3(+2) + 2(+3) + 6(\text{O.N. of Si}) + 18(-2) &= 0;\; +6 + 6 + 6(\text{O.N. of Si}) - 36 = 0 \\ \text{O.N. of Si} &= \frac{36-6-6}{6} = +4 \end{aligned}$$

$$\text{In } UO_2SO_4: \text{ O.N. of U} + 2(\text{O.N. of O}) + \text{O. N. of } SO_4^{2-} = 0$$

$$\therefore \quad \text{O.N. of U} + 2(-2) + (-2) = 0;\; \text{O.N. of U} - 4 - 2 = 0$$

∴ O.N. of U = +4 +2 = +6

So, the correct answer is (*b*)

EXAMPLE 60. *Oxidation number of* O in O_3 *is :*

(*a*) 3 (*b*) –2

(*c*) zero (*d*) –6

SOLUTION. Oxidation number of O in O_3 is zero. So, the correct answer is (*c*).

Example 61. *The oxidation number of* H *in* CaH_2 *is :*

(*a*) +2 (*b*) –2

(*c*) +1 (*d*) –1

SOLUTION. In CaH_2 : O.N. of Ca + 2 (O.N. of H) = 0; 2 + 2 (O.N. of H) = 0; O.N. of H = –2/2 = –1

So, the correct answer is (*d*).

EXAMPLE 62. *The oxidation number of nitrogen in* N_3H *is:*

(*a*) +1/2 (*b*) +3

(*c*) –1 (*d*) –1/3 **(NCERT, 1981)**

SOLUTION. **N_3H.** 3 (O.N. of N) + O.N. of H = 0 ; 3 (O.N. of N) +1 = 0

So, O.N. of N = –1/3

So, the correct answer is (*d*).

EXAMPLE 63. *Oxidation number of oxygen in potassium peroxide is :*

(*a*) zero (*b*) –1/2

(*c*) –1 (*d*) –2

(AIIMS, 1984, MLNR, 1985)

SOLUTION. Potassium peroxide is K_2O_2.

2 (O.N. of K) + 2 (O.N. of O) = 0 ; 2 (+1) + 2 (O.N. of O) = 0

∴ O.N. of O = –2/2 = –1

So, the correct answer is (*c*).

EXAMPLE 64. *Oxidation number of* Mn *in* $KMnO_4$ *is :*

(*a*) +7 (*b*) –7

(*c*) +1 (*d*) –1

(CPMT, 82, 83, EAMCET, 1992,93)

SOLUTION. **$KMnO_4$:** O.N. of K + O.N. of Mn+ 4 (O.N. of O) = 0

+ 1 + O.N. of Mn+4 (–2) = 0

So, O.N. of Mn = +8 – 1 = +7

So, the correct answer is (*a*).

EXAMPLE 65. *The oxidation state of molybdenum in its oxo complex species* $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$ *is :*

(*a*) 2 (*b*) 3 (*c*) 4 (*d*) 5

(IIT, 1991)

SOLUTION. **$[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$:**

2 (O.N. of Mo) + 4 (O.N. of O) + 2 (O.N. of C_2H_4) + 2 (O.N. of H_2O) = –2

2 (O.N. of Mo) + 4(–2) + (2 × 0) + 2(0) = – 2 ; O.N. of Mo = (– 2 + 8)/2 = + 3

So, the correct answer is (*b*).

EXAMPLE 66. *Oxidation state of chlorine in perchloric acid is :*

(*a*) – 1 (*b*) 0 (*c*) – 7 (*d*) + 7

[EAMCET, 1989]

SOLUTION. Perchloric acid = $HClO_4$.

O.N. of H + O.N. of Cl + 4 (O.N. of O) = 0;

+ 1 + O.N. of Cl + 4 (– 2) = 0

∴ O.N. of Cl = – 1 + 8 = + 7.

So, the correct answer is (*d*)

EXAMPLE 67. *The oxidation number of carbon in* CH_2O *is:*

(*a*) –2 (*b*) +1 (*c*) 0 (*d*) +4

[IIT 1982, EAMCET, 1985, MLNR 1990]

SOLUTION. **CH_2O** : For compounds containing C, H and O :

$$\text{O.N. of C} = \frac{2N_O - N_H}{N_C}$$

where N_O, N_H and N_C are the number of atoms of O, H and C respectively

$$\therefore \quad \text{O.N. of C} = \frac{2(1)-(2)}{1} = \frac{2-2}{1} = \frac{0}{1} = 0$$

So, the correct answer is (*c*).

EXAMPLE 68. *Oxidation state of oxygen in hydrogen peroxide is :*

(*a*) –1 (*b*) +1

(*c*) 0 (*d*) –2

[Delhi PMT, 1984, CPMT, 1984, MLNR, 1994]

SOLUTION. Hydrogen peroxide, H_2O_2

2 (O.N. of H) + 2 (O.N. of O) = 0 ;

2(+1) +2 (O.N. of O) = 0

∴ O.N. of O = (0 –2)/2 = –1

So, the correct answer is (*a*).

EXAMPLE 69. *The oxidation state of* Cr *is* $K_2Cr_2O_7$ is :

(*a*) +6 (*b*) –7

(*c*) +2 (*d*) –2

(EAM CET 1986, CPMT, 1981, 85, 90, BHU 1988, AFMC, 1991, CEE Karnataka 1992)

SOLUTION. **$K_2Cr_2O_7$:**

2 (O.N. of K) + 2 (O.N. of Cr) + 7 (O.N. of O) = 0 ;

2(+1) + 2(O.N. of Cr) + 7(–2) = 0;

O.N. of Cr = (14 – 2)/2 = + 6.

So, the correct answer is (*a*).

EXAMPLE 70. *The oxidation number of carbon in* $C_6H_{12}O_6$ *is :*

(*a*) +6 (*b*) –6 (*c*) 0 (*d*) +4

(CEE Karnataka, 1992)

SOLUTION. For compounds containing C, H and O :

$$\text{O.N. of C} = \frac{2N_O - N_H}{N_C}$$

Where N_O, N_H and N_C are the number of atoms of O, H and C in the given compound.

So, In $C_6H_{12}O_6$. O.N. of C $= \dfrac{2(6)-12}{6} = \dfrac{12-12}{6} = 0$

So, the correct answer is (*c*).

Example 71. *Oxygen has an oxidation state of +2 in :*

(*a*) H_2O_2 (*b*) H_2O

(*c*) OF_2 (*d*) SO_2 **(Delhi PMT, 1983)**

Solution. $\mathbf{H_2O_2}$: 2 (O.N. of H) + 2 (O.N. of O) = 0 ; 2(+1) + 2 (O.N. of O) = 0

∴ O.N. of O $= -2/2 = -1$

$\mathbf{H_2O}$. 2 (O.N. of H) + O.N. of O = 0; 2(+1)+O.N. of O = 0

∴ O.N. of O $= -2$

$\mathbf{OF_2}$. O.N. of O + 2 (O.N. of F) = 0 ; O.N. of O + 2(–1) = 0

∴ O.N. of O = +2

So, the correct answer is (*c*).

Example 72. *In which of the following compounds, transition metal is in oxidation state of zero ?*

(*a*) $[Co(NH_3)_6]Cl_2$ (*b*) $[Fe(H_2O)_4SO_4]$

(*c*) $Ni(CO)_4$ (*d*) $[Fe(H_2O)_3](OH)_2$

Solution. $\mathbf{[Co(NH_3)_6]Cl_2}$:

O.N. of Co + 6 (O.N. of NH_3) + 2 (O.N. of Cl) = 0 ; O.N. of Co + 6(0) + 2(–1) = 0

∴ O.N. of Co = +2

$\mathbf{[Fe(H_2O)_4SO_4]}$: O.N. of Fe + 4 (O.N. of H_2O) + O.N. of SO_4^{2-} = 0 ;

O.N. of Fe + 4(0) + (-2) = 0

So, O.N. of Fe = +2

$\mathbf{Ni(CO)_4}$: O.N. of Ni + 4 (O.N. of CO) = 0 ; O.N. of Ni + 4(0) = 0

So, O.N. of Ni = 0

$\mathbf{[Fe(H_2O)_3](OH)_2}$: O.N. of Fe + 3 (O.N. of H_2O) + 2 (O.N. of OH^-) = 0 ;

O.N. of Fe + 3(0) + 2(–1) = 0 ; O.N. of Fe + 0 – 2 = 0

So, O.N. of Fe = +2

So, the correct answer is (*c*).

Example 73. *The oxidation number of phosphorus in* $Ba(H_2PO_2)_2$ *is :*

(*a*) +3 (*b*) +2

(*c*) +1 (*d*) –1 **(IIT, 1990)**

Solution. $\mathbf{Ba(H_2PO_2)_2}$:

O.N. of Ba + 2[(2 × O.N. of H) + 2 (O.N. of P) + 2 (O.N. of O)] = 0 ;

+2 + 2[2(+1) + 2 (O.N. of P) +2(–2)] = 0

So, O.N. of P $= (-2 -4 + 8)/2$
$= +1$

So, the correct answer is (*c*).

Example 74. *Which of the following chemical reactions depicts the oxidising behaviour of* H_2SO_4 *?*

(*a*) $2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

(*b*) $Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

(*c*) $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

(*d*) $2PCl_5 + H_2SO_4 \longrightarrow 2POCl_3 + 2HCl + SO_2Cl_2$

(AIEEE, 2006)

Solution.

(*a*) $2H^+I^- + H_2S^{6+}O_4 \longrightarrow \overset{o}{I}_2 + S^{4+}O_2 + 2H_2O$

In this reaction, the oxidation number of S in (H_2SO_4) has decreased from +6 to +4 (in SO_2). So, H_2SO_4 acts as an oxidant.

(*b*) $Ca(OH)_2 + H_2S^{6+}\,O_4 \longrightarrow CaS^{6+}\,O_4 + 2H_2O$

In this reaction, the oxidation number of S in H_2SO_4 and $CaSO_4$ is same (= +6). So, H_2SO_4 does not act as an oxidant.

(*c*) $NaCl + H_2S^{6+}\,O_4 \longrightarrow NaHS^{6+}\,O_4 + HCl$

In this reaction, the oxidation number of S in H_2SO_4 and $NaHSO_4$ is same (= +6). So, H_2SO_4 does not act as an oxidant.

(*d*) $2PCl_5 + H_2S^{+6}O_4 \longrightarrow 2POCl_3 + 2HCl + S^{6+}O_2Cl_2$

In this reaction, the oxidation number of S in H_2SO_4 and SO_2Cl_2 is same (= +6). So, H_2SO_4 does not act as an oxidant. So, the correct answer is (*a*).

Example 75. *Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is :*

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

(ITT–JEE, 2007)

Solution. In the given titration, potassium dichromate ($K_2Cr_2O_7$) oxidises Fe^{2+} of Mohr's salt ($FeSO_4\,(NH_4)_2SO_4.6H_2O$) solution. So, the reaction will be :

$$Cr_2O_7^{2-} \longrightarrow 6Fe^{2+} + 2Cr^{3+} + 7H_2O$$

no. of moles 1 6

∴ no. of moles of Mohr's salt required per mole of dichromate ($Cr_2O_7^{2-}$) is 6. So, the correct answer is (*d*).

Example 76. *The number of moles of* MnO_4^- *required to oxidise one mol 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*

(CBSE–PMT, 2008 Prilims)

Solution. Reaction :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-] \times 5$$

$$\overline{2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10\,CO_2}$$

Moles : 2 5

5 mol of $C_2O_4^{2-}$ are oxidised by $MnO_4^- = 2$ mol

1 mol of $C_2O_4^{2-}$ is oxidised by $MnO_4^- = 2/5 = 0.4$ mol

So, the correct answer is (*d*).

EXAMPLE 77. *Oxidation state of iron in [Fe $(H_2O)_5$ NO] SO_4 is :*

(*a*) + 1 (*b*) + 2

(*c*) + 3 (*d*) + 4 **(Odisha JEE, 2012)**

SOLUTION. See example, 8.

[Ans. (*a*)]

EXAMPLE 78. *The number of moles of acidified $KMnO_4$ required to oxidise one mole of ferrous oxalate (FeC_2O_4) is:*

(*a*) 5 (*b*) 3

(*c*) 0.6 (*d*) 1.5 **(AFMC, 2012)**

SOLUTION. The reaction is:

$2\,KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O] \times 3$

$2FeC_2O_4 + 3H_2SO_4 + 3O \longrightarrow Fe_2(SO_4)_3 + 4CO_2 + 3H_2O] \times 5$

Add: $6\,KMnO_4 + 10\,FeC_2O_4 + 24H_2SO_4 \longrightarrow 3\,K_2SO_4 + 6\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 20CO_2 + 24H_2O$ ...(1)

To get one mol of Fe C_2O_4,

divide equation (1) by 10, we get

$$\underset{0.6\text{ mol}}{\frac{6}{10}KMnO_4} + \underset{1\text{ mol}}{FeC_2O_4} + \frac{24}{10}H_2SO_4 \longrightarrow \frac{3}{10}K_2SO_4 + \frac{6}{10}MnSO_4 + \frac{5}{10}Fe_2(SO_4)_3 + \frac{20}{10}CO_2 + \frac{24}{10}H_2O.$$

So, one mol of FeC_2O_4 is oxidised by $KMnO_4$ = 0.6 mol. So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. Calculate the oxidation number of C in CH_3OH **(Ans.** –2)

2. Calculate the oxidation state of 'C' in $H_3C_2O^-_2$ i.e., acetate ion. (**Ans.** zero)

   [**Hint.** O.N. of C = $\frac{(2\times 2)-3+(-1)}{2} = 0$

3. Find O.N. of C in (i) C_2H_6 (ii) $C_2\ H_4$ (iii) C_4H_{10}.(**Ans.** (i) – 3 (ii) –2 (iii) –2.5)

4. Balance the following equation (basic medium) by oxidation number change method.

   $$CrO_4^{-2} + SO_3^{-2} \longrightarrow Cr(OH)_4^- + SO_4^{-2}$$

   [**Ans.** $2CrO_4^{-2} + 3SO_3^{-2} + 5H_2O \longrightarrow 2Cr(OH)_4^- + 3SO_4^{-2} + 2OH^-]$

5. Balance the following equations by ion electron method.

   (*i*) $Cr_2O_7^{2-} + NO_2^- \longrightarrow Cr^{3+} + NO_3^-$ (in acidic medium)

   (*ii*) $I^- + MnO_4^- \longrightarrow I_2 + MnO_2$ (in basic medium)

   (*iii*) $Br_2 + NaOH \longrightarrow NaBrO + NaBr + H_2O$

   (*iv*) $ClO_3^- + SO_2 \longrightarrow ClO_2 + HSO_4^-$ (acidic medium)

   Ans. (*i*) $Cr_2O_7^{2-} + 3NO_2^- + 8H^+ \longrightarrow 2Cr^{3+} + 2NO_3^- + 4H_2O$

   (*ii*) $6I^- + 2MnO_4^- + 4H_2O \longrightarrow 3I_2 + 2MnO_2 + 8OH^-$

   (*iii*) $Br_2 + 2NaOH \longrightarrow NaBrO + NaBr + H_2O$

   (*iv*) $SO_2 + 2ClO_3^- + H^+ \longrightarrow HSO_4^- + 2ClO_2$

6. Oxidation state of S in H_2SO_4 is.

   (*a*) +2 (*b*) +4

   (*c*) +6 (*d*) +7

   [Ans. (*c*); AMU Med; 2010]

7. Oxidation number of iodine in IO_3^-, IO_4^-, KI and I_2 respectively are:

   (*a*) –1, –1, 0, +1 (*b*) +3, +5, +7, 0

   (*c*) +5, +7, –1, 0 (*d*) –1, –5, –1, 0

   [Kerala PMT, 2008; Ans. (*c*)]

8. Given E°Ag^+/Ag = 0.80 V; E° Cu^{2+}/Cu = 0.34 V. Which out of Ag^+ and Cu^{2+} is stronger oxidising agent ? (**Ans.** Ag^+)

9. Given E°Zn^{2+}/Zn = –0.76 V; E°Cu^{2+}/Cu = + 0.34 V. Which out of Zn and Cu is better reducing agent? (**Ans.** Zn)

10. The number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acidic medium will be:

    (*a*) 0.6 mol (*b*) 0.4 mol

    (*c*) 7.5 mol (*d*) 0.2 mol

    (CBSE Med; 2008) [Ans. (*a*)]

11. In the redox reaction

    $x\,KMnO_4 + NH_3 \rightarrow y\,KNO_3 + MnO_2 + KOH + H_2O$

    (*a*) $x = 4, y = 6$ (*b*) $x = 8, y = 6$

    (*c*) $x = 3, y = 8$ (*d*) $x = 8, y = 3$

    (DUMET, 2009) Ans. (d)

12. Oxidation state of Hg in Hg_2Cl_2 is:

    (*a*) 0 (*b*) 1

    (*c*) –1 (*d*) 2 **[Ans. (*b*)]**

13. Oxidation number of P in PO_4^{3-}, S in SO_4^{2-} and Cr in $Cr_2O_7^{2-}$ are respectively.

    (*a*) +3, +6 and +5 (*b*) –3, + 6 and + 6

    (*c*) +5, +3 and +6 (*d*) +5, +6 and +6

    (Orissa JEE, 2009). Ans. (*d*).

14. Which of the following species can function both as oxidising as well as reducing agent?

    (*a*) Cl^- (*b*) ClO_4^-

    (*c*) ClO^- (*d*) MnO_4^-

    (*e*) NO_3^- **(Kerala PET, 2010) Ans. (*c*)**

15. Oxidation state of Fe in Mohr's salt is:

    (*a*) +1 (*b*) + 2

    (*c*) + 3 (*d*) + 4

    [Odisha JEE, 2009; Ans. (*b*)]

17
CHAPTER

Solution–Concentration

17.1. CONCENTRATION

The amount of solute dissolved in a given volume of solvent (or solution) (or for gases, the molar proportion in a gas) is called its concentration. For solution, it may be expressed in grams per litre (*i.e.*, g L^{-}), moles per cubic metre (mol m^{3-}) or moles per cubic decimetre (litre) *i.e.*, mol. dm^{3-}. A solution containing only a small proportion of the dissolved substance is called **dilute** while the one containing a high proportion is said to be **concentrated**.

17.2. METHODS TO EXPRESS CONCENTRATION

Different methods to express concentration of a solution are described below

1. **Mass (or weight) percentage.** *It is the mass in grams of a component per 100 grams of solution.* It is independent of temperature. For a solution containing two components A and B :

Mass percent of component,

$$A = \frac{\text{Mass of } A\,(\text{g})}{\text{Mass of } A\,(\text{g}) + \text{Mass of } B\,(\text{g})} \times 100$$

Mass percent of component,

$$B = \frac{\text{Mass of } B\,(\text{g})}{\text{Mass of } A\,(\text{g}) + \text{Mass of } B\,(\text{g})} \times 100$$

$$\%\text{ age by weight} = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

EXAMPLE 1. *Calculate the mass percentage of water in 10% KNO_3 solution.*

SOLUTION. Mass of KNO_3 = 10 g ;

Mass of water = 100 – 10 = 90 g

$$\therefore \text{ Mass percent of water } = \frac{90\,(\text{g})}{10\,\text{g} + 90\,\text{g}} \times 100 = \mathbf{90\%}$$

2. **[Weight or Mass/volume] percentage.** *It is the amount of solute in grams that is present in 100 mL of the solution.* Mathematically :

% by volume or (Mass/volume) percentage

$$= \frac{\text{Mass of solute (g)}}{\text{Volume of solution in mL}} \times 100$$

EXAMPLE 2. *What do you understand by 10% (weight/volume) solution of potassium chloride?*

SOLUTION. 10% (wt./volume) solution of KCl means that 10 g of KCl are present in 100 mL of the solution.

3. **Parts per million (ppm).** *It is the number of parts of a component per million parts of a solution.* Mathematically :

$$\text{ppm of a component} = \frac{\text{Mass of the component (g)}}{\text{Total mass of solution (g)}} \times 10^6$$

This concentration unit is used for substances which are present in extremely small quantity in solution or air etc.

EXAMPLE 3. *Calculate the parts per million of SO_2 gas in 250 mL water (density 1 g cm^{-3}) containing 5×10^{-4} g of SO_2 gas.*

SOLUTION. Mass of SO_2 gas

$= 5 \times 10^{-4}$ g ;

Mass of H_2O = Volume × Density

$= 250\ \text{cm}^3 \times 1\ \text{g cm}^{-3} = 250$ g.

∴ Parts per million of SO_2 gas

$$= \frac{5 \times 10^{-4}\ \text{g}}{250\ \text{g}} \times 10^6 = \mathbf{2}$$ **Ans.**

4. **Volume percentage.** In case of liquids dissolved in liquids, the concentration is usually expressed in volume percentage. *It is defined as the volume of component per 100 parts by volume of the solution.* For a solution containing two liquids A and B.

Volume percentage of

$$A = \frac{\text{Volume of } A}{\text{Volume of } A + \text{Volume of } B} \times 100.$$

The solution of liquid solute (in mL or cm^3) present per mL (or cm^3) of solution is called **volume fraction.**

$$\%\text{ by strength} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

EXAMPLE 4. *What do you understand by (i) 30% (volume/volume) solution of methyl alcohol in water (ii) 30% (volume/volume) solution of ethyl alcohol in methyl alcohol ?*

Solution. (*i*) 30% (vol/vol) solution of methyl alcohol in water means that this solution contains 30 mL methyl alcohol and 70 mL (100 – 30 = 70 mL) of water.

(*ii*) 30% (vol/vol) solution of ethyl alcohol in methyl alcohol means that this solution contains 30 mL ethyl alcohol and 70 mL (100 – 30 = 70 mL) of methyl alcohol.

Example 5. *Calculate the percentage composition in terms of mass of solution obtained from 200 g of a 30% and 300 g of a 45% solution by mass.*

Solution. Total mass of solution

$$= 200 + 300 = 500 \text{ g}$$

Mass of solute in 200 g of 30% solution

$$= \frac{200 \times 30}{100} = 60 \text{ g}$$

Mass of solute in 300 g of 45% of solution

$$= \frac{300 \times 45}{100} = 135 \text{ g}$$

Total mass of solute

$$= 60 + 135 = 195 \text{ g}$$

Total mass of solvent

$$= 500 - 195 = 305 \text{ g}$$

$$\therefore \ \% \text{ age of solute} = \frac{195}{500} \times 100 = \mathbf{39\%} \qquad \textbf{Ans.}$$

$$\therefore \% \text{ age of solvent} = \frac{305}{500} \times 100 = \mathbf{61\%} \qquad \textbf{Ans.}$$

Example 6. *Concentrated nitric acid used as laboratory reagent is usually 69% by mass of nitric acid. Calculate the volume of the solution which contains 23 g nitric acid. The density of concentrated acid is 1.41 g cm^{-3}.* **(HPSB, 1993 S)**

Solution. Given HNO_3 is 69% by mass ;
density of HNO_3 = 1.41 g cm^{-3}. Thus :

(*i*) 69 g HNO_3 is present in conc.

$$HNO_3 = 100 \text{ g}$$

23 g HNO_3 is present in conc.

$$HNO_3 = \frac{100}{69} \times 23 = 33.33 \text{ g}.$$

(*ii*) Volume of solution required

$$= \frac{\text{Mass}}{\text{Density}} = \frac{33.33}{1.41} = \mathbf{23.6 \text{ mL}} \ \textbf{Ans.}$$

Example 7. *What volume of 95% H_2SO_4 (density, 1.85 g cm^{-3}) and what mass of water must be added to prepare 100 cm^3 of 15% solution of H_2SO_4 (density, 1.1 g cm^{-3}) by weight.*

Solution. H_2SO_4 solution to be prepared = 100 cm^3 of 15% solution ;

Mass of water to be added

= ? Thus :

(*i*) Wt. of H_2SO_4 in 100 cm^3 of 15%

$$H_2SO_4 = \frac{\text{Wt. of acid}}{\text{Volume of acid given} (=100/d)} \times \text{Volume of acid to be prepared}$$

$$= \frac{15}{(100/1.1)} \times 100 = \mathbf{16.5 \text{ g}}$$

(*ii*) Volume of 95%

$$H_2SO_4 = \frac{100 \text{ g}}{D} = \frac{100 \text{ g}}{1.85 \text{ g cm}^{-3}} = \mathbf{54.05 \text{ cm}^3}$$

Volume of 95% H_2SO_4 in 16.5 g acid

$$= \frac{54.05}{95} \times 16.5 = \mathbf{9.4 \text{ cm}^3}.$$

(*iii*) Mass of 100 mL of 15% acid

= 100 × density (*d*)

= 100 × 1.1 = 110 g

Mass of 9.4 cm^3 of 95% acid

= volume × density

= 9.4 × 1.85 = **17.4 g.**

Mass of water to be added

= 110 – 17.4 = **92.6 g** **Ans.**

Also see example 10.

Example 8. *A 6.9 M solution of KOH contains 30% KOH by weight. Calculate the density of the solution (At. wt., K = 39, O = 16, H = 1).*

Solution. Wt. of KOH

= 30% by wt. ;

g. mol. wt. of KOH

= 39 + 16 + 1 = 56 g ; density = ?

We know that : Molarity

$$= \frac{\text{Wt. of KOH (g)}}{\text{g. mol. wt. of KOH}} \times \frac{1000}{\text{Volume of solution in mL}}.$$

$$6.9 = \frac{w}{56} \times \frac{1000}{1000} \ ; \ w = 56 \times 6.9$$

= 386.4 g

∴ Actual weight of KOH

= (386.4 × 100)/30 = 1288 g

Hence density of solution

$$= \frac{\text{Mass of solution}}{\text{Volume of solution}} = \frac{1288}{1000}$$

$$= \mathbf{1.288 \text{ g(mL)}^{-}} \qquad \textbf{Ans.}$$

Example 9. *Calculate the volume of concentrated H_2SO_4 of relative density 1.84 and containing 98% H_2SO_4 by mass that would contain 40 g of pure H_2SO_4.*

Solution. Wt. of 98% H_2SO_4 = Wt of $H_2SO_4 \times \frac{100}{98}$

$$= 40 \times \frac{100}{98} = \left(\frac{4000}{98}\right) \text{g}$$

Density of H_2SO_4 = 1.84.

$$\text{Thus volume of } H_2SO_4 = \frac{\text{Mass}}{\text{Density}} = \frac{4000}{(98 \times 1.84)}$$

$$= \mathbf{22.2 \text{ mL.}} \qquad \textbf{Ans.}$$

Example 10. *What volume of 95% sulphuric acid (density 1.85 g/cm^3) and what mass of water must be taken to prepare 100 cm^3 of 15% solution of sulphuric acid (density, 1.10 g/cm^3).* **(DSB 1989)**

Solution. (*i*) Molarity of 95% H_2SO_4

$$= \frac{\text{Mass of } H_2SO_4 \times \text{Density} \times 1000}{\text{Mol. mass of } H_2SO_4 \times \text{Mass of solution}}$$

$$= \frac{95 \times 1.85 \times 1000}{98 \times 100} = 17.93 \text{ M}$$

(*ii*) Molarity of 15% H_2SO_4

$$= \frac{15 \times 1.1 \times 1000}{98 \times 100} = 1.68 \text{ M.}$$

Applying molarity equation,

$$M_1V_1 = M_2V_2 \text{ we have } V_1 = \frac{M_2V_2}{M_1} \text{ ;}$$

Or $$V_1 = \frac{1.68 \times 100}{17.93} = \mathbf{9.4\ cm^3.\ Ans.}$$

(*iii*) Volume of water added

$$= V_1 \times \frac{M_1 - M_2}{M_2} = 9.4 \times \frac{17.93 - 1.68}{1.68}$$

$$= 90.9 \text{ mL.}$$

Hence, mass of water = volume × density

$$= 90.9 \text{ mL} \times 1.0 \text{ g/cm}^3$$

$$= \mathbf{90.9\ g\ \ Ans.}$$

Example 11. *Density of pure ethyl alcohol is 0.785 g cm^{-3}. The density of its solution in water (10% by volume) is 0.9866 g cm^{-3}. Calculate the percentage by weight of the solution.*

Solution. (*i*) Volume of ethyl alcohol = 10 cm^3; Density = 0.785 g cm^{-3}

$$\therefore \text{ Weight of ethyl alcohol} = \text{Vol.} \times \text{Density}$$

$$= 10 \text{ cm}^3 \times 0.785 \text{ g cm}^{-3}$$

$$= 7.85 \text{ g}$$

(*ii*) Volume of solution = 100 cm^3 ;

Density = 0.9866 g cm^{-3}

$$\therefore \text{ Weight of solution} = \text{Vol.} \times \text{Density}$$

$$= 100 \text{ cm}^3 \times 0.9866 \text{ g cm}^{-3}$$

$$= 98.66 \text{ g}$$

Hence, percent by weight

$$= \frac{\text{Wt. of ethyl alcohol}}{\text{Wt. of solution}} \times 100$$

$$= \frac{7.85}{98.66} \times 100 = \mathbf{7.95\%}$$

Ans.

17.3. NORMALITY (N)

It is the number of gram equivalent of a solute dissolved per litre of the given solution. It can be calculated with the help of following relations.

$$\textbf{Normality } (N) = \frac{\text{No. of g. equivalent of a solute}}{\text{Volume of the solution in litre}}$$

∴ **Unit of normality = eq. L^{-}**

Where **no. of gram equivalent**

$$= \frac{\text{Wt. (in g) of solute}}{\text{g. eq. wt. of solute}}$$

$$= \text{Normality} \times \text{Volume of solution in litre}$$

Also, $$\textbf{Normality} = \frac{\text{Wt. of solute (in g)}}{\text{g. eq. wt. of solute}} \times \frac{1000 \text{ (mL) L}^{-}}{\text{Volume of solution in mL}}$$

$$= \frac{\text{No. of milli equivalent}}{\text{Volume of solution in mL}}$$

Where : **no. of milli equivalent or**

$$\textbf{m.eq.} = \frac{\text{Wt. (in g) of solute}}{\text{g. eq. wt. of solute}} \times 1000$$

$$= \text{Normality} \times \text{Volume of solution in mL}$$

Also, **one milli equivalent**

$$= 10^{-3} \text{ equivalent}$$

Also, **Normality**

$$= \frac{\text{Strength of solution in gL}^{-}}{\text{g. eq. wt. of solute}}$$

Some common representations of normality solutions include :

$\frac{N}{2}$ = Seminormal , 1 N = one normal

$\frac{N}{5}$ = Pentinormal , 5 N = Penta normal

$\frac{N}{10}$ = Decinormal , 10 N = Decanormal

$\frac{N}{100}$ = Centinormal.

Type. $$\text{Normality } (N) = \frac{\text{Wt. of solute (in g)}}{\text{g. eq. wt. of solute}} \times \frac{1000 \text{ (mL) L}^{-}}{\text{Volume of solution in mL}}$$

Example 12. *Calculate the normality of sodium carbonate solution, 5.3 g of which have been dissolved per 0.1 L of solution.*

Solution. Volume = 0.1 L = 0.1 × 1000 mL

= 100 mL or 100 cm^3

Wt. of Na_2CO_3 = 5.3 g ;

g. eq. wt. of $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$

$$= \frac{\text{Mol. wt. of } Na_2CO_3}{\text{Total + ve or -ve charge}}$$

$$= \frac{(2 \times 23) + 12 + (3 \times 16)}{2} = 53$$

$$\therefore \text{ Normality } (N) = \frac{\text{Wt. of } Na_2CO_3}{\text{g. eq. wt. of } Na_2CO_3} \times \frac{1000 \text{ cm}^3\text{L}^{-}}{\text{Volume of solution in mL or cm}^3}$$

$$= \frac{5.3 \text{ g}}{53 \text{ g eq}^{-}} \times \frac{1000 \text{ cm}^3\text{L}^{-}}{100 \text{ cm}^3}$$

= **1 N or 1 eq. L^{-}** **Ans.**

Type. Normality (N)

$$= \frac{\text{No.of g.equivalent of a solute}}{\text{Volume of the solution in litre}}$$

Example 13. *2.0g of metal carbonate is neutralised completely by 100 mL of 0.1 N HCl. The equivalent weight of metal carbonate is: (a) 50 (b) 100 (c) 150 (d) 200* **(WB-JEE, 2011)**

Solution. Mass of metal carbonate,

W = 2.0 g. Let E = equivalent weight of metal.

But:

Number of gram equivalent of

$$\text{HCl} = \frac{\text{Normality} \times \text{Volume}}{1000}$$

$$= \frac{0.1 \times 100}{1000} = 0.01.$$

But no. of g equivalent of metal carbonate = no. of g. equivalent of HCl

$$\therefore \quad \frac{W}{E} = 0.01;\ E = \frac{W}{0.01} = \frac{2}{0.01} = 200$$

So, the correct answer is (*d*).

Example 14. *Calculate the normality of NaOH solution containing 0.1 g equivalent of it in half-litre of its solution.*

Solution. no. of g. equivalent

$$= 0.1,\ \text{volume} = \frac{1}{2}\ \text{L} = 0.5\ \text{L}$$

$$\therefore \quad \text{Normality} = \frac{\text{No.of g. equivalent of NaOH}}{\text{Volume in litre}}$$

$$= \frac{0.1}{0.5} = \frac{1}{5} = \mathbf{0.2\ N} \qquad \textbf{Ans.}$$

Type. No. of milli equivalent

= Normality ×

volume of solution in mL

Also no. of milli equivalent

$$= \frac{\text{Wt.of solute(in g)} \times 1000}{\text{g.eq.wt}}$$

Example 15. *Calculate the number of milliequivalent of KOH present in its solution containing 5.6 g of it. (at. wt., K = 39, O = 16, H = 1).*

Solution. wt. of KOH = 5.6 g; g. eq. wt. of KOH

= 39 + 16 + 1 = 56 g.

No. of milliequivalent of KOH

$$= \frac{5.6}{56} \times 1000 = \mathbf{100} \qquad \textbf{Ans.}$$

Type. $\quad \text{Normality} = \dfrac{\text{Strength in gL}^-}{\text{g.eq.wt.of solute}}$

Example 16. *Calculate the normality of H_2SO_4 containing 2 g per 100 mL of its solution.*

Solution. Normality = ? ; g. eq. wt. of H_2SO_4

$(H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-})$

$$= \frac{(2 \times 1) + 32 + (4 \times 16)}{2} = 49$$

100 mL H_2SO_4 contain H_2SO_4 = 2 g

1000 mL (= 1 L) H_2SO_4 contain H_2SO_4

$$= \frac{2}{100} \times 1000 = 20\ \text{gL}^-$$

$$\text{Normality} = \frac{\text{Strength in gL}^- \text{ of } H_2SO_4}{\text{g.eq.wt.of } H_2SO_4}$$

$$= \frac{\mathbf{20}}{\mathbf{49}}\ \mathbf{eq.\ L^-} \qquad \textbf{Ans.}$$

17.4. NORMALITY OF A SOLUTION CONTAINING MIXTURE OF SOLUTES, e.g., ACIDS OR MIXTURE OF BASES

Let normality of mixtre = N_r. Then. $N_1V_1 + N_2V_2 + \ldots.. = N_rV_r$ where $V_r = V_1 + V_2 + \ldots..$; $N_1V_1 = N_2V_2$ where N_1 and N_2 are the normalities of solutes *e.g.*, acid or base (*1*) and acid or base (*2*) respectively ; V_1 and V_2 are the volumes of acid or base (*1*) and acid or base (*2*) respectively.

Example 17. *Calculate the normality of a solution obtained by mixing 10 mL of N/5* HCl *and 30 mL of N/10* HCl.

Solution. Total Volume V_r of mixture

= 10 mL + 30 mL = 40 mL.

$$\text{But} \qquad N_1V_1 + N_2V_2 = N_rV_r$$

$$\therefore \quad \left(\frac{1}{5} \times 10\right) + \left(\frac{1}{10} \times 30\right) = N_r(40);$$

$$2 + 3 = N_r \times 40.$$

$$\text{So :} \qquad N_r = \frac{5}{40} = \mathbf{0.125\ N} \qquad \textbf{Ans.}$$

Example 18. *Calculate the normality of a solution obtained by mixing 0.01 L of $\frac{N}{10}$ NaOH and 40 mL of seminormal KOH solution.*

Solution. Total Volume (V_r) of mixed solution

$$= \left(0.01\text{L} \times \frac{1000\ \text{mL}}{1\ \text{L}}\right) + 40\ \text{mL}$$

$$= 10\ \text{mL} + 40\ \text{mL} = 50\ \text{mL}$$

$$\text{Now} \qquad N_1V_1 + N_2V_2 = N_rV_r$$

$$\frac{1}{10} \times 10 + \frac{1}{2} \times 40 = N_r \times 50;\ 1 + 20 = N_r \times 50.$$

$$\therefore \qquad N_r = \frac{21}{50} = \mathbf{0.42\ N} \quad \textbf{Ans.}$$

Example 19. *What will be the normality of a solution obtained by mixing 200 mL of 1.0 N NaOH and 100 mL of pure water ?*

Solution. Total volume after mixing

= 200 mL + 100 mL = 300 mL

Given solution (NaOH) Dilute solution

$$N_1V_1 = N_2V_2 \quad \text{(Normality equation)}$$

$$1.0 \times 200 = N_2 \times 300$$

$$200 = 300N_2;\ N_2 = \frac{200}{300} = \mathbf{0.67\,N} \quad \textbf{Ans.}$$

17.5. NORMALITY AFTER MIXING OF IDENTICAL ACIDS OR BASES HAVING DIFFERENT NORMALITIES

Example 20. (*a*) *What volume of* $\frac{N}{2}$ *and* $\frac{N}{10}$ H_2SO_4 *must be mixed to prepare 5 litres of* $\frac{N}{5}$ H_2SO_4? *(b) Calculate volume of 0.1 N NaOH that should be mixed with 0.2 N NaOH to prepare 2 L of 0.125 N NaOH.*

Solution. Let Volume of $\frac{N}{2}$ $H_2SO_4 = x$ litre

$$\text{Volume of } \frac{N}{10}\ H_2SO_4 = 5 - x \text{ litre}$$

Using normality equation for mixture solution, we have

$$N_1V_1 + N_2V_2 = N_rV_r$$

$$N_r = \text{resulting normality}$$

$$V_r = \text{resulting volume.}$$

$$\frac{1}{2}\times x + \frac{1}{10}\times 5 - x = \frac{1}{5}\times 5$$

$$\frac{x}{2} + \frac{5-x}{10} = 1$$

$$\frac{5x+5-x}{10} = 1;\ 4x + 5 = 10$$

$$\therefore \quad 4x = 10 - 5 = 5$$

$$\text{or} \quad x = \frac{5}{4} = 1.25 \text{ litre}$$

$$\therefore \quad \text{Volume of } \frac{N}{2}\ H_2SO_4 = 1.25 \text{ litre}$$

$$\text{Volume of } \frac{N}{10}\ H_2SO_4 = 5 - 1.25 = 3.75 \text{ litre.}$$

(*b*) Let Volume of 0.1 N NaOH = x L ;

Volume of 0.2 N NaOH = $(2 - x)$ L

Using normality equation for mixture solution, we have :

$$N_1V_1 \ + \ N_2V_2 = N_rV_r$$

where N_r = resulting normality, V_r = resulting volume

$$0.1 \times x + 0.2 \times (2 - x) = 0.125 \times 2$$

$$0.1x + 0.4 - 0.2x = 0.25;$$

$$0.1x = 0.15\ ;\ x = 1.5,$$

$$\therefore \quad \text{Volume of 0.1 N NaOH} = 1.5 \text{ L ;}$$

Volume of 0.2 N NaOH = 2 − 1.5 = **0.5 L Ans.**

17.6. MOLARITY (M)

It is the number of mol of solute dissolved per litre of the given solution. The molarity of a solution can be calculated with the help of following relations.

$$\textbf{Molarity } (M) = \frac{\text{No. of g. mol of solute}}{\text{Volume of solution in litre}}$$

$\therefore$ **Unit of molarity = g mol L^{-}**

$$\text{Where, } \textbf{No. of g. mol} = \frac{\text{Wt. (in g) of solute}}{\text{Gram mol. wt. of solute}}$$

= Molarity × Volume of solution in litre

$$\text{Also,} \quad \textbf{molarity } (M) = \frac{\text{Wt. of solute (in g)}}{\text{g. mol. wt. of solute}} \times \frac{1000 \text{ cm}^3\text{L}^{-}}{\begin{pmatrix}\text{Volume of solution in} \\ \text{mL or c.c. or cm}^3\end{pmatrix}}$$

$$= \frac{\text{no. of millimol}}{\text{Volume of solution in mL}}$$

Where, **No. of millimol**

$$= \frac{\text{Wt. (in g) of solute}}{\text{g. mol. wt. of solute}} \times 1000$$

= Molarity × Volume of solution in mL

Also, **one millimol = 10^{-3} mol**

$$\text{Also,} \quad \textbf{molarity } (M) = \frac{\text{Strength of solution is gL}^{-}}{\text{g. mol. wt. of solute}}$$

$$\text{Also,} \quad \textbf{molarity } (M) = \frac{\text{Normality} \times \text{Eq. wt.}}{\text{Mol. wt.}}$$

$$\text{and} \quad \textbf{molarity } (M) = \frac{\textbf{Normality}}{\textbf{Valence factor}}.$$

Demal (D). It is another unit to express concentration of a solution. It is equal to molar concentration at 273 K. 1 D represents one mole of solute present in 1 L solution at 273 K.

Example 21. *Calculate the molarity of soduim carbonate solution, 5.3 g of which have been dissolved per 250 mL of the given solution. (At. wt., Na = 23, C = 12, O = 16)*

Solution. g. mol. Wt. of Na_2CO_3

$$= (2 \times 23) + 12 + (3 \times 16) = 106 \text{ g ;}$$

$$\text{Wt. of } Na_2CO_3 = 5.3 \text{ g ;}$$

$$\text{Volume} = 250 \text{ mL.}$$

$$\text{We know : } \textbf{Molarity} = \frac{\text{Wt. of } Na_2CO_3}{\text{g. mol. wt of } Na_2CO_3} \times \frac{1000 \text{ cm}^3\text{L}^{-}}{\text{Volume of solution in mL or cm}^3}$$

$$= \frac{5.3 \text{ g}}{106 \text{ g. mol}^{-}} \times \frac{1000 \text{ cm}^3\text{L}^{-}}{250 \text{ cm}^3}$$

= **0.2 M or 0.2 mol L^{-}** **Ans.**

Example 22. *What will be the molarity of NaOH solution containing 2 g of it in half-litre of the solution ? (Na = 23, O = 16, H = 1)*

Solution. Hint. Molarity $= \dfrac{2.0 \text{ g}}{40 \text{ g mol}^{-} \times 0.5 \text{ L}}$

$= \dfrac{2 \times 2}{40}$ = **0.1 M** **Ans.**

Type. no. of millimol $= \dfrac{\text{Wt. (in g) of solute}}{\text{g. mol. wt. of solute}} \times 1000$

EXAMPLE 23. *How many millimol are present in 0.56 g of KOH ? (at. wt., K = 39, O = 16, H = 1)*

SOLUTION. wt. of KOH = 0.56 g,

g. mol. wt. of KOH = 39 + 16 + 1 = 56 g. mol^{-}

$$\text{Thus : No. of millimol} = \frac{\text{wt.(in g) of KOH}}{\text{g.mol.wt.of KOH}} \times 1000$$

$$= \frac{0.56}{56} \times 1000 = \mathbf{10} \ \textbf{Ans.}$$

$$\textbf{Type.} \quad \textbf{Molarity } (M) = \frac{\text{Strength of solution in gL}^{-}}{\text{g.mol.wt.of solute}}$$

EXAMPLE 24. *Calculate the mol. wt. of NaOH if its 0.5 M solution contains 20 g NaOH per litre.*

SOLUTION. Molarity = 0.5 M,

Strength = 20gL^{-}.

$$\text{We know : Molarity} = \frac{\text{Strength in gL}^{-}}{\text{g.mol.wt.of NaOH}} ;$$

$$0.5 \text{ g mol L}^{-} = \frac{20 \text{ gL}^{-}}{\text{g.mol.wt}}$$

$$\therefore \quad \text{g. mol. wt} = \frac{20 \text{ gL}^{-}}{0.5 \text{ mol L}^{-}} = 40 \text{ g mol}^{-}$$

$$\therefore \quad \text{Mol. wt. of NaOH} = \mathbf{40 \ g. \ mol^{-}} \ \textbf{Ans.}$$

17.7. CALCULATING MOLARITY OF SOLUTION CONTAINING DIFFERENT ACIDS OR DIFFERENT BASES OR DILUTED WITH WATER

Molarity of a solution containing mixture of solutes, e.g., acids or bases. Let molarity of mixture = M_r. Then $M_1V_1 + M_2V_2 + ... = M_r V_r$ where $V_r = V_1 + V_2 + ...$, $M_1V_1 = M_2V_2$ where M_1 and M_2 are the molarities of solutes e.g., acids or bases (1) and acid or base (2) respectively, V_1 and V_2 are the volumes of solutes *e.g.*, acid or base (*1*) and acid or base (*2*) respectively.

For *x* mol acid + *y* mol base → Products

$$\frac{M_1 \times V_1 \text{ (acid)}}{M_2 \times V_2 \text{ (Base)}} = \frac{x}{y}$$

EXAMPLE 25. *Calculate the molarity of a solution obtained by mixing 300 mL of 0.5 M* NaOH *and 200 mL of 0.2 M* KOH *solution.*

SOLUTION. Total volume of mixture

= 300 mL + 200 mL = 500 mL

$$\text{Now} \quad M_1V_1 + M_2V_2 = M_rV_r$$

$$(0.5 \times 300) + (0.2 \times 200) = M_r \times 500 ; \ 150 + 40 = 500 M_r$$

$$\therefore \quad M_r = \frac{190}{500} = \mathbf{0.38 \ M} \quad \textbf{Ans.}$$

EXAMPLE 26. *What will be the molarity of the mixed acid solution obtained by mixing 150 mL of 0.2 M HCl and 300 mL of 0.25 M H_2SO_4 ?* **(JEE, Main, 2013)**

SOLUTION. Total volume of mixed solution

= 150 + 300 = 450 mL

$$\text{Now} \quad M_1V_1 + M_2V_2 = M_rV_r$$

$$(0.2 \times 150) + (0.25 \times 300) = M_r \times 450 ;$$

$$30 + 75 = 450 M_r$$

$$\therefore \quad M_r = \frac{105}{450} = \mathbf{0.23 \ M} \quad \textbf{Ans.}$$

EXAMPLE 27. *Calculate the molarity of a solution obtained by mixing 250 mL of 0.5 M NaOH and 150 mL of water.*

SOLUTION. Total volume of mixed dilute solution

= 250 + 150 = 400 mL

Now Given solution of NaOH Dilute solution

$$M_1V_1 = M_2V_2$$

$$0.5 \times 250 = M_2 \times 400 ; \ 125 = 400 M_2$$

$$\therefore \quad M_2 = \frac{125}{400} = \mathbf{0.3125 \ M} \quad \textbf{Ans.}$$

EXAMPLE 28. *Calculate the molarity of 0.1 N Na_2CO_3 (Na = 23, C = 12, O = 16).*

SOLUTION. Molarity = ? ; normality = 0.1 ; eq. wt. of Na_2CO_3 ($Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$)

$$= \frac{\text{Mol.wt.of } Na_2CO_3}{\text{Total + ve or -ve charge}}$$

$$= \frac{(2 \times 23) + 12 + (3 \times 16)}{2} = \frac{106}{2} = 53$$

$$\therefore \quad \textbf{Molarity} = \frac{\text{Normality} \times \text{Eq.wt.}}{\text{Mol.wt.}}$$

$$= \frac{0.1 \times 53}{106} = \mathbf{0.05 \ M} \quad \textbf{Ans.}$$

EXAMPLE 29. *The density of 10% by mass of KCl solution is 1.06 g cm^{-3}. Calculate the molarity of the solution. (at. wt., K = 39, Cl = 35.5)*

$$\textbf{SOLUTION. } (i) \text{ Volume} = \frac{100 \text{ g}}{\text{density}} = \frac{100 \text{ g}}{1.06 \text{ g cm}^{-3}}$$

$$= 94.34 \text{ cm}^3$$

(*ii*) Wt. of KCl = 10 g ; g. mol. wt. of KCl

= 39 + 35.5 = 74.5 g

$$\therefore \quad \textbf{Molarity} = \frac{\text{wt.(in g)}}{\text{g.mol.wt.}} \times \frac{1000}{\text{vol in cm}^3}$$

$$= \frac{10}{74.5} \times \frac{1000}{94.34} = \mathbf{14.2 M} \ \textbf{Ans.}$$

EXAMPLE 30. *What volume of water should be added to 400 mL of 0.5 M HCl so as to get a 0.2 M solution ?*

SOLUTION. Let vol. of water added = V_1 mL.

Total volume after adding water = *V* mL.

$$\text{Thus volume of water added} = \text{Volume of solution} \times \frac{M_1 - M_2}{M_2}$$

Where M_1 (= 0.5) and M_2 (= 0.2) are the molarities of given HCl solution.

$$\text{So,} \quad \text{Volume of water added} = \frac{400(0.5 - 0.2)}{0.2}$$

$$= \mathbf{600 \ mL} \quad \textbf{Ans.}$$

EXAMPLE 31. *A bottle of commercial sulphuric acid (density 1.787 g mL^{-}) is labelled as 86% by weight. What is the molarity of acid ? What volume of acid has to be used to make 1 L of 0.2 M H_2SO_4?* **(IIT 1979)**

SOLUTION. (*i*) Molarity of H_2SO_4

$$= \frac{\text{Wt.of } H_2SO_4 \text{ in 1L solution}}{\text{mol.wt.of } H_2SO_4}.$$

But wt. of given H_2SO_4 per litre

$$= \text{Strength} \times \text{Density} \times 1000$$

$$= \frac{86}{100} \times 1.787 \times 1000$$

$$= 1536.82 \text{ g.}$$

Also, mol wt. of H_2SO_4 = (2 × 1) + 32 + (4 × 16) = 98.

Hence, molarity of $H_2SO_4 = \frac{1536.82}{98}$ = **15.68 M Ans.**

(*ii*) Volume (V_1) of acid (15.68 M) required to prepare 1000 mL (V_2) of molarity (M_2), 0.2 M. Applying, molarity equation,

$$M_1V_1 \text{ (acid)} = M_2V_2 \text{ (acid).}$$

$$\therefore \quad 15.68 \times V_1 = 0.2 \times 1000$$

Or $$V_1 = 0.2 \times \frac{1000}{15.68}$$

= **12.75 mL** **Ans.**

EXAMPLE 32. *Equal volumes of two solutions contain 50 gram of sodium chloride and 50 gram of potassium chloride respectively. Are their molarities equal ?* **(HP Board, 2008)**

SOLUTION. Mol. wt. of NaCl = 23 + 35.5 = 58.5 g mol^{-}; mol. wt. of KCl = 39 + 35.5 = 74.5 g mol^{-}; wt. of NaCl = wt. of KCl = 50 g. Let each solution has volume = 100 mL. We know that:

$$(i) \text{ Molarity of NaCl} = \frac{\text{wt. of NaCl}}{\text{g. mol. wt. of NaCl}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{50 \text{ g}}{58.5 \text{ g mol}^{-}} \times \frac{1000}{100 \text{ mL}} = 8.54$$

$$(ii) \text{ Molarity of KCl} = \frac{\text{wt. of KCl}}{\text{g. mol. wt. of KCl}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{50 \text{ g}}{74.5 \text{ g mol}^{-}} \times \frac{1000}{100 \text{ mL}} = 6.71$$

From the values of molarity of NaCl and KCl, it is clear that the molarities of both solutions is not same.

EXAMPLE 33. *How many millilitre of concentrated sulphuric acid of density 1.84 g mL^{-} containing 98% H_2SO_4 by mass are required to make (a) 4 litres of 1 N solution and (b) 200 mL of 0.25 M solution.*

SOLUTION.

(*a*) g. Eq. wt. of H_2SO_4

$$= \frac{(2 \times 1) + 32 + (4 \times 16)}{2}$$

= 49 g.

To find wt. of H_2SO_4, we have :

$$1 = \frac{\text{wt.of } H_2SO_4 \times 1000}{\text{g.eq.wt.of } H_2SO_4 \times 1000}$$

$$= \frac{\text{wt. of } H_2SO_4 \times 1000}{49 \times 1000}$$

Or wt. of H_2SO_4 = 49 g.

To find wt. of H_2SO_4 (*W*) required to prepare 4 L of 1 N H_2SO_4, we have :

$$1 = \frac{\text{wt.of } H_2SO_4 \times 1000}{\text{g.eq.wt.of } H_2SO_4 \times 4000 \text{ mL}}$$

$$= \frac{\text{wt. of } H_2SO_4 \times 1000}{49 \times 4000}$$

Or wt. of H_2SO_4 = **196 g.**

Since acid is 98%, thus amount of acid

$$= \frac{196 \times 100}{98} = 200 \text{ g.}$$

Thus, Volume (mass/density) of 98% H_2SO_4

$$= \frac{200}{1.84} = \textbf{108.7 mL}$$ **Ans.**

(*b*) g. mol. wt. of H_2SO_4

= (2 × 1) + 32 + (4 × 16) = 98 g

0.25 M H_2SO_4 = 0.25 × 98 = 24.5 g H_2SO_4.

To prepare 200 mL of 0.25 M H_2SO_4, wt. of H_2SO_4 required is :

$$0.25 = \frac{\text{wt. of } H_2SO_4 \times 1000}{\text{g. mol. wt. of } H_2SO_4 (= 98) \times \text{vol. of sol. in mL}}$$

$$\therefore \quad \text{wt. of } H_2SO_4 = \frac{0.25 \times 98 \times 200}{1000} = 4.9 \text{ g}$$

$$\therefore \quad \text{wt. of 98\% } H_2SO_4 = \frac{4.9 \times 100}{10 \times 98} = 5 \text{ ;}$$

$$\text{Volume of } H_2SO_4 = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{4.9}{1.84} = \textbf{2.72 mL}$$ **Ans.**

EXAMPLE 34. *Concentrated sulphuric acid has a density of 1.9 g/mL and is 99% H_2SO_4 by weight. Calculate the molarity of H_2SO_4 in this acid.* **(CBSE, 1993)**

SOLUTION.

$$\text{Volume of 100 g} H_2SO_4 = \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.9} = 52.63 \text{ mL;}$$

g. mol. mass of H_2SO_4

= (2 × 1) + 32 + + (4 × 16) = 98 g.

We know that :

$$\text{Molarity} = \frac{\text{mass of } H_2SO_4 \times 1000}{\text{g.mol.mass of } H_2SO_4 \times \text{vol. of sol. in mL}}$$

$$= \frac{99 \times 1000}{98 \times 52.63} = \mathbf{19.19\ M} \qquad \textbf{Ans.}$$

EXAMPLE 35. *How many grams of sodium hydroxide pellets containing 12% moisture are required to prepare 60 litres of 0.5 N solution ?*

SOLUTION. Hint.

$$\text{Normality} = \frac{\text{wt. of NaOH} \times 1000}{\text{g.eq.wt. of NaOH} \times \text{volume of sol. in mL}}$$

$$\text{Or} \qquad 0.5 = \frac{\text{wt. of NaOH} \times 1000}{40 \times 60{,}000}$$

Thus, wt. of NaOH = 1200 g.

Thus NaOH containing 12% moist

$$\text{NaOH} = \frac{1200 \times 100}{100 - 12 = 88} = \mathbf{1363.6\ g\ \ Ans.}$$

EXAMPLE 36. *What volume of* $\frac{N}{2}$ *and* $\frac{N}{10}$ H_2SO_4 *must be mixed to prepare 5 litres of* $\frac{N}{5}$ H_2SO_4*?*

SOLUTION. Let vol. of $\frac{N}{2}$ $H_2SO_4 = V_1$;

vol. of $\frac{N}{10}$ $H_2SO_4 = 5 - V_2$

Total normality after mixing

$$= \left(\frac{N_1V_1 + N_2V_2}{V_1 + V_2}\right)$$

$$\textbf{Or} \qquad \frac{1}{5} = \frac{[(1/2 \times V_1) + 1/10(5 - V_1)]}{5}$$

$$\textbf{or} \qquad 1 = \frac{V_1}{2} + \frac{1}{2} - \frac{V_1}{10}$$

Thus, $V_1 = 1.25$ L and $V_2 = 5 - 1.25$

= **3.75 L** **Ans.**

Type. Normality × Eq. wt

= Molarity × mol. wt.

EXAMPLE 37. *Calculate the normality of solution obtained by mixing 100 mL of 0.2 N KOH and 100 mL of 0.1 M* H_2SO_4*.*

SOLUTION. Total volume of solution (V_1 + V_2) = 100 + 100 = 200 mL.

(*i*) Normality due to KOH

$$= \frac{N_1V_1}{V_1 + V_2} = \frac{0.2 \times 100}{200} = 0.1\text{ N}$$

(*ii*) Molarity due of H_2SO_4

$$= \frac{M_1V_1}{V_1 + V_2} = \frac{0.1 \times 100}{200} = \frac{1}{20}\text{ M}$$

∴ Normality of H_2SO_4

$$= \frac{\text{Molarity} \times \text{Mol.wt. of } H_2SO_4}{\text{Eq.wt.}}$$

$$= \frac{\left(\frac{1}{20}\right) \times 98}{49}$$

= 0.1 N

[∵ Eq. wt. of H_2SO_4 = Mol. wt./2]

Total normality after mixing

= 0.1 – 0.1 = **zero** **Ans.**

EXAMPLE 38. *Commercially available concentrated hydrochloric acid contains 38% HCl by mass and has density 1.19 g* cm^{-3}*. Calculate the molarity of this solution.* **(PSEB, 2000)**

SOLUTION. Volume of 100 g HCl

$$= \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{100\text{ g}}{1.19\text{ g cm}^{-3}} = 84.03\text{ cm}^3 ;$$

g. mol. wt of HCl = 1 + 35.5 = 36.5 g.

We know that,

$$\text{molarity} = \frac{\text{mass of HCl} \times 1000}{\text{g.mol.wt. of HCl} \times \text{vol. of HCl in mL}}$$

$$= \frac{38 \times 1000}{36.5 \times 84.03} = \mathbf{12.39\ M.} \qquad \textbf{Ans.}$$

EXAMPLE 39. *Calculate the volume of a 0.1 M HCl that are needed to react completely with 1 g of a mixture of* $NaHCO_3$ *and* Na_2CO_3 *containing equimolar amounts of both.*

SOLUTION. Mol. wt. of $NaHCO_3$

$= 23 + 1 + 12 + (3 \times 16) = 84\text{ g mol}^{-}$;

mol. wt of Na_2CO_3 = (2 × 23) + 12 + (3 × 16)

= 106 g. mol^{-};

Let no. of mol of $NaHCO_3$

= no. of mol of Na_2CO_3 = *a*

wt. of $NaHCO_3$ + Na_2CO_3 = 1 g ;

Hence, (*a* × 84) + (*a* × 106)

= 1 g ; 190*a* = 1 g ;

$$a = \frac{1}{190} = 0.00526\text{ mol}$$

Reactions.

$$\underset{\substack{1\text{ mol}\\0.00526\text{ mol}}}{NaHCO_3} + \underset{\substack{1\text{ mol}\\0.00526\text{ mol}}}{HCl} \longrightarrow NaCl + CO_2 + H_2O$$

$$\underset{\substack{1\text{ mol}\\0.00526\text{ mol}}}{Na_2CO_3} + \underset{\substack{2\text{ mol}\\2 \times 0.00526\ =\ 0.01052\text{ mol}}}{2HCl} \longrightarrow 2NaCl + CO_2 + H_2O$$

∴ For HCl : 0.00526 + 0.01052 = 0.1 mol L^{-} × volume ;

0.01578 mol = 0.1 mol L^{-} × volume

$$\therefore \qquad \text{Volume} = \frac{0.01578\text{ mol}}{0.1\text{ mol L}^{-}}$$

$$= \frac{0.01578}{0.1}\text{ L}$$

$$= \frac{0.01578\text{ L}}{0.1} \times \frac{1000\text{ mL}}{1\text{ L}}$$

157.8 mL Ans.

EXAMPLE 40. *Calculate the molarity of water in pure water (density of water = 1 g/c.c.) Or Calculate the molarity of water if its density is 1000 kg/m^3*

(IIT, 1976; 2003, BCECE, 2000, PSEB, 1999)

SOLUTION. g. mol. wt. of water (H_2O)

$$= (2 \times 1) + 16 = 18 \text{ g.}$$

$$\text{Density of water} = \frac{1000 \text{ kg}}{\text{m}^3} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{\text{m}^3}{10^6 \text{cc}} = 1 \text{ g/cc}$$

$$\text{Wt. of water} = \text{Volume} \times \text{density}$$

$$= 1000 \text{ mL} \times \frac{1 \text{ g}}{\text{mL}}$$

$$= 1000 \text{ g}$$

Volume of water in mL = 1000 mL.

We know : Molarity

$$= \frac{\text{wt. of water (g)}}{\text{g. mol. wt. of water}} \times \frac{1000 \text{ mL. L}^{-}}{\text{volume of water in mL}}$$

$$= \frac{1000}{18} \times \frac{1000}{1000} = \mathbf{55.5 \text{ M}} \quad \textbf{Ans.}$$

Type. $$\text{Molarity} = \frac{\text{no. of millimol}}{\text{volume of solution in mL}}$$

EXAMPLE 41. *Determine the molarity of a solution containing 3 millimoles of solute in 30 mL of solution.*

SOLUTION. Number of millimoles of solute = 3;

Volume of solution = 30 mL.

We know that :

$$\text{Molarity} = \frac{\text{no.of millimoles of solute}}{\text{volume of solution in mL}}$$

$$= \frac{3}{30} = \mathbf{0.1 \text{ M}} \qquad \textbf{Ans.}$$

EXAMPLE 42. *Derive a relation for volume of water to be added to dilute V_1 cm^3 of a solution (molarity, M_1 or normality, N_1) to a solution (molarity, M_2 or normality, N_2) having volume, V_2 cm^3.*

SOLUTION. (*i*) **Molarity equation :**

Initial solution = Final solution

$$M_1V_1 = M_2V_2 \qquad \therefore \; V_2 = \frac{M_1V_1}{M_2}$$

$$\text{or} \quad V_2 - V_1 = \frac{M_1V_1}{M_2} - V_1 = V_1\left[\frac{M_1}{M_2} - 1\right]$$

$$= V_1\left[\frac{M_1 - M_2}{M_2}\right]$$

$\left[\text{After subtracting } V_1 \text{ from both sides}\right]$

(*ii*) **Normality equation :**

Initial solution = Final solution

$$N_1V_1 = N_2V_2$$

$$\therefore \quad V_2 = \frac{N_1V_1}{N_2}$$

$$\text{or} \quad V_2 - V_1 = \frac{N_1V_1}{N_2} - V_1 = V_1\left[\frac{N_1}{N_2} - 1\right]$$

$$= V_1\left[\frac{N_1 - N_2}{N_2}\right]$$

[After subtracting V_1 from both sides]

where, $V_2 - V_1$ = Volume of water to be added to V_1 cm^3 to get V_2 cm^3

EXAMPLE 43. *What volume of water should be added to 400 mL of 0.5 M HCl so as to get 0.2 M solution ?*

SOLUTION. Volume (V_2) of water to be added = ?;

volume of HCl = V_1 = 400 mL;

molarity of HCl (M_1) = 0.5 M;

solution to be prepared = M_2 = 0.2 M.

Using molarity equation, $M_1V_1 = M_2V_2$

we have : Given acid = Required acid

$$M_1V_1 = M_2V_2$$

$$0.5 \times 400 = 0.2 \times V_2$$

$$\therefore \quad V_2 = (0.5 \times 400)/0.2$$

$$= 1000 \text{ mL}$$

Hence, volume of water to be added

$$= 1000 - 400$$

$$= \mathbf{600 \text{ mL}} \qquad \textbf{Ans.}$$

Second method. Volume of water to be added

$$= V_1\left(\frac{M_1 - M_2}{M_2}\right)$$

$$= 400\left(\frac{0.5 - 0.2}{0.2}\right)$$

$$= 400 \times \frac{0.3}{0.2}$$

$$= \mathbf{600 \text{ mL}} \qquad \textbf{Ans.}$$

EXAMPLE 44. For rules only.

SOLUTION. (*i*) *x N* solute solution contains solute = *x* × g. eq. wt. of solute. *e.g.*, 0.5 N H_2SO_4 contain H_2SO_4 = 0.5 × eq. wt. of H_2SO_4 [= (2 × 1) + 32 + (4 × 16)]/2 *i.e.*, 49] = 0.5 × 49 = **24.5 g.**

(*ii*) *x N* solution of solute *Ay Bz* contain total ionic strength (total molarity of all ions) = *xy* + *xz*. *e.g.*, 0.1 N solution of Na_3PO_4 and 0.2 N $Al_2(SO_4)_3$ contain total ionic strength = 0.1 × 3 (of Na^+) + 0.1 × 1 (of PO_4^{3-}) + 0.2 × 2 (of Al^{3+}) + 0.2 × 3 (of SO_4^{2-}) = 0.3 + 0.1 + 0.4 + 0.6 = 1.4 M.

(*iii*) For such solute solutions, having same molarity if solutes undergo 100% ionisation, the normality of that solution will be maximum whose number of ions are maximum in solution. For example, out of

1 M H_2SO_4 ($H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$, having 3 mole ions; 2 of H^+ and 1 of SO_4^{2-}), and 1 M H_3PO_4 ($H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$, having 4 mole ions; 3 of H^+ and one of PO_4^{3-}), the normality of 1 M H_3PO_4 will be more than that of 1 M H_2SO_4.

(*iv*) *x M* solute solution contains solute = *x* × g. mol. wt. of solute e.g., 0.5 M H_2SO_4 contain H_2SO_4 = 0.5 × Mol.

wt. of H_2SO_4 (= (2 × 1) + 32 + (4 × 16) = 98 g mol^{-}) = 0.5 × 98 = 49 g.

(*v*) *x M* solution of solute *Ay Bz* contain ionic strength (total molarity of all ions) = *xy* + *xz*. *e.g.*, total ionic strength or total molarity of all ions in a solution containing 0.1 M $ZnSO_4$ and 0.2 M $Al_2(SO_4)_3$ = 0.1 × 1(of Zn^{2+}) + 0.1 × 1 (of SO_4^{2-}) + 0.2 × 2 (of Al^{3+}) + 0.2 × 3 (of SO_4^{2-}) = 0.1 + 0.1 + 0.4 + 0.6 = 1.2 M.

17.8. MOLALITY (m)

It is the number of mol of the solute dissolved per 1000 g (= one kilogram) of the solvent. It is temperature independent. The molality of a solution can be calculated with the help of following relations.

(*a*) **Molality (*m*)**

$$= \frac{\text{weight of solute(g)} \times 100\,\text{g.kg}^{-}}{\text{g.mo.wt.of solute} \times \text{wt.of solvent(g)}}$$

Where Wt. of solvent

$$= \begin{pmatrix} \text{volume} & \times & \text{density} \\ \text{of solution} & & \text{of solution in} \\ \text{(mL)} & & \text{g (mL)}^{-} \end{pmatrix} - (\text{wt.of solute})$$

$$\textbf{or } m = \frac{\text{weight of solute (g)}}{\text{g.mol.wt.of solute} \times \text{weight of solvent (kg)}}$$

$$= \frac{\text{Number of moles of solute} \times 1000\text{ g. kg}^{-}}{\text{weight of solvent (g)}}$$

$$= \frac{\text{Moles of solute}}{\text{wt. of solvent in kg}}$$

$$= \frac{\text{Number of millimoles of solute}}{\text{weight of solvent (g)}}$$

$$\text{Also molality (m)} = \frac{\text{Mole fraction of solute}}{\text{Mole fraction of solvent}} \times \frac{1000}{\text{Mol. wt. of solvent}}$$

∴ **Unit of molality = mol kg^{-}**

Where, **1 millimole = 10^{-3} mole**

$$= \frac{\text{Number of gram of solute in 1000 g solvent}}{\text{g.mol.wt.of solute}}$$

(*b*) **Relation between molarity (*M*) and molality (*m*).** It is represented as follows :

$$d = M\left[\frac{1}{m} + \frac{M_1}{1000}\right]$$

Where *d* is density of solution in g $(\text{mL})^{-}$; *M* is molarity of solution ; *m* = molality of solution and M_1 is molecular mass of solute.

Example 45. *Derive a relation among molarity (M), molality (m) and density (d) of a solution if molecular weight of the solute is M_1.*

Solution. Let wt. of solute = *a* g ;

wt. of solvent = *W*g

and volume of solution = *V* mL

$$\therefore \quad \text{Molarity}, M = \frac{\text{wt.}}{\text{Mol.wt}} \times \frac{1000}{\text{volume in mL}}$$

$$= \frac{a}{M_1} \times \frac{1000}{V} \quad ...(i)$$

$$\text{Molality}, m = \frac{\text{Wt.}}{\text{Mol.wt.}} \times \frac{1000}{\text{wt. of solvent}}$$

$$\frac{a}{M_1} \times \frac{1000}{W} \quad ...(ii)$$

$$\text{Density}, d = \frac{\text{wt}}{\text{volume}} = \frac{a+W}{V} \quad ...(iii)$$

$$\text{From equation } (i), \quad a = \frac{MM_1V}{1000}$$

$$\text{From equation } (ii), \quad W = \frac{1000a}{mM_1} \quad ...(iv)$$

Substituting the value of a in (*iv*), we get :

$$\boldsymbol{W} = \frac{1000 \times MM_1V}{1000 \times mM_1} = \frac{MV}{\mathbf{m}} \quad ...(v)$$

$$\text{But} \quad d = \frac{a+w}{V} \text{ [from equation } (iii)] \quad ...(vi)$$

Substituting the values of a and *W* in equation (*vi*), we get :

$$dV = \frac{MM_1V}{1000} + \frac{MV}{m}$$

$$\text{Or} \quad d = \frac{MV\left[\frac{M_1}{1000} + \frac{1}{m}\right]}{V}$$

$$= M\left[\frac{1}{m} + \frac{M_1}{1000}\right]$$

$$\text{Or} \quad d = \boldsymbol{M\left[\frac{1}{m} + \frac{M_1}{1000}\right]} \quad \textbf{Ans.}$$

Example 46. *An antifreeze solution [density 1.072 g (mL)⁻] is prepared by dissolving 222.6 g of ethylene glycol in 200 g of water. Calculate the molarity and molality of solution with respect to ethylene glycol.* **(CBSE, 2007)**

Solution. (*i*) Mol. wt. of ethylne glycol, $C_2H_4(OH)_2$

= (2 × 12) + (4 × 1) + 2 (16 + 1)

= 62 g mol^{-};

wt. of glycol = 222.6 g ;

wt. of solvent water = 200 g

$$\therefore \quad \text{Molality} = \frac{\text{wt. in g}}{\text{Mol.wt. in g. mol}^{-}} \times \frac{1000\text{ g. kg}^{-}}{\text{wt.of solvent in g}}$$

$$= \frac{222.6\text{ g}}{62\text{ g. mol}^{-}} \times \frac{1000\text{ g. kg}^{-}}{200\text{ g}}$$

= **17.95 m** or **17.95 mol kg^{-}** **Ans.**

(*ii*) Total mass of solution

$$= 222.6 + 200 = 422.6 \text{ g},$$

$$\text{Density} = 1.072 \text{ g(mL)}^{-}$$

∴ Volume of solution

$$= \frac{\text{Mass}}{\text{density}} = \frac{422.6 \text{ g}}{1.072 \text{ g(mL)}^{-}}$$

$$= \mathbf{394.2 \text{ mL}}$$

$$\therefore \quad \text{Molarity} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{volume of solution}}$$

$$= \frac{222.6 \text{ g}}{62 \text{ g. mol}^{-}} \times \frac{1000 \text{ cm}^3\text{L}^{-}}{394.2 \text{ cm}^3}$$

$$= \mathbf{9.1 \text{ M}} \text{ or } \mathbf{9.1 \text{ mol L}^{-}\text{Ans.}}$$

Example 47. *Calculate the number of grams of ethanol in 1000 g of water if the molality of aqueous solution of ethanol is 1.54 m.*

Solution. Hint.

$$\text{Molality} = \frac{\text{Wt. of } C_2H_5OH \times 1000}{\text{g. mol. wt. of } C_2H_5OH \times \text{wt. of ethanol}}$$

$$\text{Or} \quad 1.54 = \frac{W \times 1000}{46 \times 1000} \quad \text{Or} \quad W = \mathbf{70.84 \text{ g.}} \quad \textbf{Ans.}$$

Type.

$$\text{Molality} = \frac{\text{wt. of solute (in g)}}{\text{g. mol. wt. of solute}} \times \frac{1000}{\text{wt. of solvent}}$$

Where wt. of solvent

$$= \left[\begin{matrix}\text{wt. of solution } [(=\text{volume in mL} \\ \times \text{density in g (mL)}^{-}]\end{matrix}\right] - \text{wt. of solute (in g)}$$

Example 48. *How many grams of acetone must be dissolved in 2.5 kg of water to make 1.60 m solution ?*

Solution.

$$\text{Molality} = \frac{\text{wt. of acetone} \times 1000}{\text{g. mol. wt. of acetone} \times \text{wt. of solvent}}$$

$$\text{Or} \quad 1.6 = \frac{\text{wt. of acetone} \times 1000}{58 \times 2500}$$

$$\therefore \text{ Wt. of acetone} = \frac{58 \times 25 \times 1.6}{10} = \mathbf{232 \text{ g}} \quad \textbf{Ans.}$$

Example 49. *A 20% aqueous solution of a substance with mol. wt. 49 g mol*$^{-}$ *has a density 0.98 g cm*$^{-3}$*. Calculate the molality of the solution.*

Solution. Wt. of substance

$$= 20 \text{ g} ; \text{ mol. wt} = 49 \text{ g mol}^{-};$$

Wt. of solution = volume of solution × density of solution

$$= 100 \text{ cm}^3 \times 0.98 \text{ cm}^{-3} = 98 \text{ g}$$

$$\therefore \quad \text{Wt. of solvent} = \text{wt. of solution} - \text{wt. of solute}$$

$$= 98 - 20 = 78 \text{ g}$$

$$\therefore \quad \text{Molality } (m) = \frac{\text{wt.}}{\text{g. mol. wt}} \times \frac{1000}{\text{wt. of solvent}}$$

$$= \frac{20}{49} \times \frac{1000}{78} = \mathbf{5.23 \text{ m} \ \ \text{Ans.}}$$

Example 50. *A sample of drinking water was found to be contaminated with chloroform and the level of contamination was found to be of the order of 12 ppm by mass. (i) Express it in terms of mass (ii) Determine the molality of chloroform in water sample.*

Solution. (*i*) 12 ppm indicates 12 g of chloroform in 10^6 g of solution.

∴ % age of chloroform

$$= \frac{12}{10^6} \times 100 = 1.2 \times 10^{-3} \%$$

(*ii*) Molar mass of chloroform $CHCl_3$

$$= 12 + 1 + (3 \times 35.5) = 119.5 \text{ g mol}^{-}$$

Mass of $CHCl_3$ = 12 g;

Mass of solvent (H_2O) in 10^6 g solution = $(10^6 - 12)$ g

$$\simeq 10^6 \text{ g} = 10^6 \text{ g}$$

$$\therefore \quad \text{Molality} = \frac{\text{wt. of } CHCl_3}{\text{mol. wt. of } CHCl_3} \times \frac{1000}{\text{wt. of solvent in g}}$$

$$= \frac{12}{119.5} \times \frac{1000}{10^6}$$

$$= \mathbf{1.004 \times 10^{-4} \text{ m}} \quad \textbf{Ans.}$$

Example 51. *A sugar syrup of weight 214.2 g contains 34.2 g of sugar* ($C_{12}H_{22}O_{11}$)*. Calculate the molal concentration of sugar in the syrup. (At. wt. C = 12, H = 1, O = 16).*

(IIT 1988, HPSB 1993)

Solution. Hint.

Molal concentration or

$$\text{molality } (m) = \frac{\text{wt. of sugar (g)}}{\text{g. mol. wt. of sugar}} \times \frac{1000}{\text{wt. of solvent}}$$

$$\textbf{Or} \quad m = \frac{34.2}{342} \times \frac{1000}{214.2 - 34.2 = 180}$$

$$= \mathbf{0.556 \text{ m}} \quad \textbf{Ans.}$$

Example 52. *The molality and molarity of a sulphuric acid solution are 94.13 and 11.12 respectively. Calculate the density of the solution (At. wt., H = 1, S = 32, O = 16).*

Solution.

$$\text{Density} = \text{Molarity}\left[\frac{1}{\text{Molality}} + \frac{\text{g. mol. wt. of } H_2SO_4}{1000}\right]$$

$$= 11.12\left[\frac{1}{94.13} + \frac{98}{1000}\right]$$

$$= 11.12\left[\frac{1000 + (98 \times 94.13)}{94130}\right]$$

Density = 1.2079 g (mL)$^{-}$ **Ans.**

For details, see example 45.

Example 53. *A 2% solution of sodium chloride* (NaCl) *is prepared. Calculate the molality of the solution. (At. wt., Na = 23, Cl = 35.5).*

SOLUTION.

$$\text{Molality } (m) = \frac{\text{wt.of NaCl(g)}}{\text{g.mol.wt.of NaCl}} \times \frac{1000}{\text{wt.of solvent, water}}$$

$$\text{Molality} = \frac{2}{58.5} \times \frac{1000}{100-2=98} = \mathbf{0.35\ m} \qquad \textbf{Ans.}$$

EXAMPLE 54. *Calculate the molality of one litre solution of 93%* H_2SO_4 *(W/vol). The density of solution is 1.84 g(mL)*$^{-}$.

SOLUTION. (*i*) 100 mL solution contains H_2SO_4 = 93 g

1000 mL solution contains H_2SO_4

= (93 × 1000)/100 = **930 g**

(*ii*) Wt. of solution = volume × density

= 1000 × 1.84 = **1840 g**

(*iii*) Wt. of solvent, water

= wt. of solution – wt. of solute

= 1840 – 930 = 910 g.

(*iv*) $$\text{Molality} = \frac{\text{wt.of } H_2SO_4 \text{(g)}}{\text{g.mol.wt.of } H_2SO_4} \times \frac{1000}{\text{wt.of solvent}}$$

$$= \frac{930 \times 1000}{98 \times 910}$$

Molality = **10.43 m** **Ans.**

EXAMPLE 55. *Calculate the molality of a solution obtained by mixing equal volumes of 30% by weight of* H_2SO_4 *[d = 1.218 g(mL)*$^{-}$*] and 70% by weight* H_2SO_4 *[d = 1.61 g(mL)*$^{-}$*]. Also, calculate the molarity of the solution if its density is 1.425 g(mL)*$^{-}$.

SOLUTION. Let volume of solution = 1000 mL

(*i*) *For 30% by weight of* H_2SO_4.

$$d = \frac{\text{Mass}}{\text{Volume}} \quad \text{Or} \quad 1.218 = \frac{\text{Mass}}{1000}$$

or Mass = 1.218 × 1000 = 1218 g

∴ Mass of 1000 mL H_2SO_4 solution

= 1218 g

Mass of 30% H_2SO_4 in 1000 mL solution

= (1218 × 30)/100 = 365.4 g

∴ Mass of solvent, water

= 1218 – 365.4 = **852.6 g**

(*ii*) *For 70% by weight of* H_2SO_4:

$$d = \frac{\text{Mass}}{\text{Volume}} \quad \text{Or} \quad 1.61 = \frac{\text{Mass}}{1000}$$

or Mass = 1.61 × 1000 = 1610 g

∴Mass of 1000 mL H_2SO_4 solution

= 1610 g

Mass of 70% H_2SO_4 in 1000 mL solution

= (1610 × 70)/100 = **1127 g**

∴Mass of solvent, water

= 1610 – 1127 = **483 g.**

Hence, total mass of solvent

= 852.6 + 483 = 1335.6 g

(*iii*) *Molality of 30%* H_2SO_4

$$= \frac{\text{wt.of } H_2SO_4 \text{(g)}}{\text{g.mol.wt.of } H_2SO_4} \times \frac{1000}{\text{wt.of solvent}, H_2O}$$

$$= \frac{365.4}{98} \times \frac{1000}{1335.6} = \mathbf{2.79\ m}$$

(*iv*) Molality of 70% H_2SO_4

$$= \frac{\text{wt.of } H_2SO_4 \text{(g)}}{\text{g.mol.wt.of } H_2SO_4} \times \frac{1000}{\text{wt.of solvent}, H_2O}$$

$$= \frac{1127}{98} \times \frac{1000}{1335.6} = \mathbf{8.61\ m}$$

∴ Total molality = 2.79 + 8.61 = **11.4 m** **Ans.**

(*v*) **Calculation of molarity.** We know :

$$\text{Density} = \text{Molarity}\left[\frac{1}{\text{molality}} + \frac{\text{Mol.wt.of } H_2SO_4}{1000}\right]$$

Substituting the values in the above relation, we have :

$$1.425 = \text{Molarity}\left[\frac{1}{11.4} + \frac{98}{1000}\right]$$

$$= \text{Molarity}\left[\frac{1000 + (98 \times 11.4)}{11400}\right]$$

$$\therefore \quad \text{Molarity} = \frac{1.425 \times 11400}{2117.2} = \mathbf{7.67\ m} \quad \textbf{Ans.}$$

EXAMPLE 56. *18 g of glucose (molar mass, 180 g mol*$^{-}$*) is dissolved in water to give 500 cm*^{3} *of its aqueous solution. What is the molarity of solution ? What additional data is required to calculate the molality of the solution ?*

SOLUTION.

We know that : Molarity of solution

$$= \frac{\text{wt. of solute} \times 1000}{\text{g. mol. mass of solute} \times \text{volume of solution in cm}^3}$$

$$\therefore \text{ Molarity of solution} = \frac{18 \times 1000}{180 \times 500} = \mathbf{0.2\ M} \qquad \textbf{Ans.}$$

Density of solution is required to calculate molality.

EXAMPLE 57. *The density of a 3M* $Na_2S_2O_3$ *solution is 1.25 g(mL)*$^{-}$*. Calculate the molalities of* Na^+ *and* $S_2O_3^{2-}$ *ions and % age by mass of* $Na_2S_2O_3$. **(IIT, 1983)**

SOLUTION. (*i*) Total mass of $Na_2S_2O_3$ solution

= Vol of solution × Density of solution

= 1000g × 1.25 g(mL)$^{-}$ = 1250 g

Wt. of 3M $Na_2S_2O_3$ in 1000 mL solution

= 3 × Mol. wt of $Na_2S_2O_3$ (158)

= 474g

$$\left[\because \text{Mol. wt. of } Na_2S_2O_3 = (2 \times 23) + (2 \times 32) + (3 \times 16) = 158 \text{ g mol}^{-}\right]$$

$$\therefore \quad \% \text{ of } Na_2S_2O_3 = \frac{\text{wt. of } Na_2S_2O_3}{\text{Total wt of solution}} \times 100$$

$$= \frac{474}{1250} \times 100 = 37.92\%$$

(*ii*) To find molality of Na^+ ions.

Mass of Na^+ ions in 3M $Na_2S_2O_3$

$$= 6 \times 158 \text{g} \quad \left[\begin{array}{l}\because 3\text{M } Na_2S_2O_3 \text{ contain} \\ Na^+ \text{ ions} = 3 \times 2 = 6\end{array}\right]$$

$\therefore$ Molality of Na^+ ions

$$= \frac{6 \times 158}{158} \times \frac{1000}{\text{wt of solvent}}$$

$$(= 1250 - 474 = 776 \text{ g})$$

$$= \frac{6 \times 158}{158} \times \frac{1000}{776} = 7.73 \text{ m}$$

(*iii*) To find molality of $S_2O_3^{2-}$

Mass of $S_2O_3^{2-}$ in 3 M $Na_2S_2O_3$

$$= 3 \times 158 \text{ g} \quad \left[\begin{array}{l}\because 3\text{M } Na_2S_2O_3 \text{ contain} \\ S_2O_3^{2-} \text{ ions} = 3 \times 1 = 3\end{array}\right]$$

Molality of $S_2O_3^{2-}$

$$= \frac{3 \times 158}{158} \times \frac{1000}{\text{wt of solvent} = 776 \text{ g}} = \mathbf{3.865 \text{ m.}}$$

17.9 FORMALITY (F)

The number of gram formula weight of an ionic compound dissolved per litre of the given solution gives the formality (F) of that solution. In order to calculate the formality of an ionic compound, following relation is used.

Formality (*F*)

$$= \frac{\text{wt. of ionic substance}}{\text{g. formula weight of the ionic compound}} \times \frac{1000}{\text{volume of the solution in mL}}$$

$$= \frac{\text{wt. of ionic compound}}{\text{g. formula wt. of the ionic compound} \times \text{Volume of the solution in litre}}$$

Also, Formality (*F*)

$$= \frac{\text{Strength of solution in gL}^{-}}{\text{g. formula weight of ionic compound}}$$

Since ionic compounds do not lose molecules because these have definite lattice containing cations and ions, their formula weight is used as molecular weight.

Example 58. *Calculate the formality of* NaCl *solution, 5.85 g of which have been dissolved to form 250 mL of the given solution.* (*At, wt., Na = 23, Cl = 35.5*).

Solution. Hint. Formality,

$$F = \frac{\text{wt. of NaCl}}{\text{g. formula wt. of NaCl}} \times \frac{1000}{\text{volume of NaCl solution in mL}}$$

$$= \frac{5.85}{58.5} \times \frac{1000}{250} = \mathbf{0.4 \text{ F}} \qquad \textbf{Ans.}$$

Type. Formality

$$= \frac{\text{Strength of solution in gL}^{-}}{\text{g. formula weight of ionic compound}}$$

Example 59. *What will be the formality of* KNO_3 *solution having strength equal to 2.02 g per litre ?* (*At. wt., K = 39, N = 14, O = 16*).

Solution. Hint. Strength of KNO_3 = 2.02 gL^{-} ;

g. formula weight of KNO_3

$$= 39 + 14 + (3 \times 16) = 101 \text{ g.}$$

We know that :

$$\text{Formality of } KNO_3 = \frac{\text{Strength in gL}^{-}}{\text{g. formula wt. of } KNO_3}$$

$$= \frac{2.02}{101} = \mathbf{0.02 \text{ F}} \qquad \textbf{Ans.}$$

Example 60. *What weight of* KCl *is needed to prepare 100 mL of its 0.05 F solution ?* (*at. wt., K = 39, Cl = 35.5*).

Solution.

$$\text{Formality} = \frac{\text{wt.}}{\text{g. formula wt.}} \times \frac{1000}{\text{volume of solution in mL}};$$

$$0.05 = \frac{W}{74.5} \times \frac{1000}{100}$$

$$W = \frac{0.05 \times 74.5 \times 100}{1000} = \mathbf{0.3725 \text{ g}} \quad \textbf{Ans.}$$

17.10. MOLE FRACTION

The mole fraction of a component, A in a solution is the ratio of the number of moles of that component, A to the total number of moles of all the components (A + B + C .....) in the solution. It is temperature independent. For example, if a solution contains n_A, n_B, n_C ..... moles of components *A*, *B* and *C* ..... respectively, then :

(*i*) Mole fraction of *A*,

$$x_A = \frac{n_A}{n_A + n_B + n_C + \ldots\ldots}$$

Where

$$n_A = \frac{\text{weight of A(g)}}{\text{g. mol. wt. of A}}$$

$$n_B = \frac{\text{weight of B(g)}}{\text{g. mol. wt. of B}};$$

$$n_C = \frac{\text{weight of C(g)}}{\text{g. mol. wt. of C}}$$

(*ii*) Mole fraction of *B*,

$$x_B = \frac{n_B}{n_A + n_B + n_C + \ldots\ldots}$$

(*iii*) Mole fraction of *C*,

$$x_C = \frac{n_C}{n_A + n_B + n_C + ...}$$

Adding above relations (*i*), (*ii*) and (*iii*), we have :

$$x_A + x_B + x_C = \frac{n_A}{n_A + n_B + n_C} + \frac{n_B}{n_A + n_B + n_C} + \frac{n_C}{n_A + n_B + n_C}$$

Or $$x_A + x_B + x_C = \frac{n_A + n_B + n_C}{n_A + n_B + n_C} = 1$$

From above we conclude that sum total of mole fractions of all the components present in a solution is equal to one.

Example 61. *A sugar syrup of weight 214.2 g contains 34.2 g of sugar (mol. wt.* $C_{12}H_{22}O_{11} = 342$*). Calculate the mole fraction of sugar in the syrup.* **(IIT 1988, HPSB 1993)**

Solution. Wt. of solute (sugar)

= 34.2 g ;

Wt. of sugar solution

= 214.2 g ;

Wt. of solvent (water)

= 214.2 − 34.2 = 180 g ;

g. mol. wt. of sugar = 342 g

Number of moles of sugar,

$$n_1 = \frac{\text{wt.of sugar}}{\text{g.mol.wt.of sugar}} = \frac{34.2}{342} = 0.1$$

Number of moles of solvent, water,

$$n_2 = \frac{\text{wt.of } H_2O}{\text{g.mol.wt.of } H_2O} = \frac{180}{18} = 10$$

∴ Total number of moles

= 0.1 + 10 = 10.1

∴ Mole fraction of sugar

$$= \frac{n_2}{n_1 + n_2} = \frac{0.1}{10.1} = \mathbf{0.0099} \quad \textbf{Ans.}$$

Example 62. *A 5.2 molal aqueous solution of methyl alcohol,* CH_3OH*, is supplied. What is the mole fraction of methyl alcohol in the solution?*

(*a*) 0.100 (*b*) 0.190 (*c*) 0.086 (*d*) 0.050 **(AIEEE, 2011)**

Solution. n = no. of mol of solute = 5.2;

no. of mol. of solvent, N = wt./mol wt of

H_2O = 1000/18 = 55.5

So, mole fraction of solute,

$$x = \frac{n}{n + N} = 5.2/5.2 + 55.5$$

= 5.2/60.7 = **0.086** **Ans**

Example 63. *Calculate the molality of sulphuric acid solution if mole fraction of water in sulphuric acid solution is 0.85.*

Solution. Molality of H_2SO_4 = ? ; n_1 = number of moles of H_2O and n_2 = number of moles of H_2SO_4. Molality of H_2SO_4 means the number of moles of H_2SO_4 present in 1000 g of water ; g. mol. wt. of water (H_2O) = (2 × 1) + 16 = 18 g.

Mole fraction of H_2O in solution = 0.85

Mole fraction of H_2SO_4 in solution

= 1 − 0.85 = 0.15

n_1 = no. of moles of H_2O

$$= \frac{\text{wt.of } H_2O \text{(in g)}}{\text{g.mol.wt.of } H_2O}$$

$$= \frac{1000}{18} = 55.55;$$

n_2 = no. of moles of H_2SO_4 = ?

But

mole fraction of $H_2SO_4 = \dfrac{n_2}{n_1 + n_2}$ $\quad \therefore 0.15 = \dfrac{n_2}{55.55 + n_2}$

or 0.15 (55.55 + n_2) = n_2 or $n_2 = 0.15 n_2 + 8.3325$.

or n_2 = 9.8

∴ Molality = **9.8 m** **Ans.**

$$\text{or Molality of } H_2SO_4 = \frac{x_{H_2SO_4}}{x_{H_2O}} \times \frac{1}{\text{Mol. wt. of } H_2O} \times 1000$$

$$= \frac{1 - 0.85 = 0.15}{0.85} \times \frac{1}{18} \times 1000 = 9.8\text{m}$$

Example 64. *A solution contains 25% water, 25% ethanol* (C_2H_5OH) *and 50% acetic acid* (CH_3COOH) *by mass. Calculate the mole fraction of each component. (At, wt., C = 12, H = 1, O = 16).* **(DSB 1983, 1989; HSB 1994)**

Solution. (*i*) Wt. of H_2O = 25 g ;

g. mol. wt of H_2O = 18 g

∴ No. of moles of H_2O = 25/18 = **1.39**

(*ii*) Wt. of C_2H_5OH = 25 g ;

g. mol. wt. of C_2H_5OH

= (2 × 12) + (5 × 1) + 16 +1 = 46 g

∴ No. of moles of C_2H_5OH

= 25/46 = **0.54**

(*iii*) Wt. of CH_3COOH = 50 g ;

g. mol. wt. of CH_3COOH

= 12 + (3 × 1) + 12 + 2 (16) + 1 = 60 g

∴ No. of moles of CH_3COOH

= 50/60 = **0.83**

∴ Total number of moles of "$H_2O + C_2H_5OH + CH_3COOH$" = 1.39 + 0.54 + 0.83 = **2.76**

$$\therefore \text{ Mole fraction of } H_2O = \frac{\text{no.of moles of } H_2O}{\text{Total no.of moles}}$$

$$= \frac{1.39}{2.76} = \mathbf{0.503} \quad \textbf{Ans.}$$

$$\text{Mole fraction of } C_2H_5OH = \frac{\text{no. of moles of } C_2H_5OH}{\text{Total no. of moles}}$$

$$= \frac{0.54}{2.76} = \mathbf{0.196} \quad \textbf{Ans.}$$

Mole fraction of CH_3COOH

$$= \frac{\text{no. of moles of } CH_3COOH}{\text{Total no. of moles}}$$

$$= \frac{0.83}{2.76} = \mathbf{0.301} \qquad \textbf{Ans.}$$

EXAMPLE 65. *One litre of an aqueous solution contains 15 g of a solute of molecular mass 150. If the density of the solution is 1.005 g cm^{-3}, calculate the mole fraction of the solute.*

SOLUTION. Wt. of solution

$$= \text{volume} \times \text{density} = 1000 \times 1.005$$
$$= 1005 \text{ g}$$

Wt. of solute = 15 g ;

wt. of solvent = 1005 – 15 = 990 g.

No. of moles of solute

$$= \frac{\text{wt. of solute (in g)}}{\text{g.mol.wt. of solute}} = \frac{15}{150}$$
$$= 0.1 \text{ mole}$$

No. of moles of solvent,

$$\text{water} = \frac{\text{wt. of water (in g)}}{\text{g.mol.wt. of water}} = \frac{990}{18} = 55$$

Total number of moles = 0.1 + 55 = 55.1

$\therefore$ Mole fraction of solute

$$= \frac{0.1}{55.1} = \mathbf{0.00181} \qquad \textbf{Ans.}$$

Mole fraction of water

$$= \frac{55}{55.1} = \mathbf{0.099819} \qquad \textbf{Ans.}$$

EXAMPLE 66. *The density of a 3M sodium thiosulphate ($Na_2S_2O_3$) solution is 1.2 g per mL. Calculate the mole fraction of sodium thiosulphate (At. wt., Na = 23, S = 32, O = 16)* **(IIT, 1983)**

SOLUTION. g. mol. wt. of $Na_2S_2O_3$ = (2 × 23) + (2 × 32) + (3 × 16) = 158 g.

(*i*) Mass of $Na_2S_2O_3$ = Molarity × Mol. mass

= 3 × 158 = 474 g.

(*ii*) Mass of solvent water

$$= \begin{bmatrix} \text{volume of} \times \text{density of} \\ \text{solution} \quad \text{solution} \end{bmatrix} - \text{wt. of } Na_2S_2O_3$$

$$= (1000 \times 1.25) - 474$$
$$= 1250 - 474 = 776 \text{ g.}$$

(*iii*) Number of moles of $Na_2S_2O_3$

$$= \frac{\text{wt. of } Na_2S_2O_3 \text{ (in g)}}{\text{g.mol.mass of } Na_2S_2O_3} = \frac{474}{158} = 3$$

Number of moles of water

$$= \frac{\text{wt. of } H_2O \text{ (in g)}}{\text{g.mol.wt. of } H_2O} = \frac{776}{18} = 43.1$$

$\therefore$ Mole fraction of $Na_2S_2O_3$

$$= \frac{3}{3 + 43.1} = \mathbf{0.065} \qquad \textbf{Ans.}$$

EXAMPLE 67. *Derive a relation between molarity (M) and mole fraction (x_2) of solute.*

SOLUTION. Let M_1 = molar mass of solvent; M_2 = molar mass of solute; d = density of solution in g cm^{-3}; M = Molarity of solution; x_2 = mole fraction of solute.

We know that, mole fraction,

$$x_2 = \frac{M}{\frac{1000\,d - MM_2}{M_1} + M}$$

$$= \frac{MM_1}{1000\,d - MM_2 + MM_1}$$

$$\frac{x_2}{1} = \frac{MM_1}{1000\,d + M(M_1 - M_2)}$$

$$\frac{x_2}{x_1 + x_2} = \frac{MM_1}{1000\,d + M(M_1 - M_2)}$$

$[\because x_1 + x_2 = 1]$

$$\text{Or} \quad \frac{x_1 + x_2}{x_2} = \frac{1000\,d + M(M_1 - M_2)}{MM_1}$$

$$= \frac{1000\,d}{MM_1} + \frac{M(M_1 - M_2)}{MM_1}$$

$$\text{Or} \quad \frac{x_1}{x_2} + 1 = \frac{1000\,d}{MM_1} + \frac{M_1 - M_2}{M_1};$$

$$\frac{x_1}{x_2} = \frac{1000\,d}{MM_1} + \frac{M_1 - M_2}{M_1} - \frac{1}{1}$$

$$\text{Or} \quad x_1 MM_1 = MM_1 x_2 - M_2 x_2 M + 1000\,d\,x_2 - MM_1 x_2$$

$\therefore$ $M\,(x_1M_1 + x_2M_2) = 1000\,d\,x_2$.

$$\text{Hence,} \quad M = \frac{1000\,d\,x_2}{x_1M_1 + x_2M_2} \qquad \textbf{Ans.}$$

EXAMPLE 68. *Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 46% ethanol by mass.* **(HPSB, 1996)**

SOLUTION. Wt of ethyl alcohol, C_2H_5OH = 46 g ;

g. mol. wt. of C_2H_5OH = (2 × 12) + (5 × 1) + 16 + 1

= 46 g ;

wt. of water H_2O = 100 – 46 = 54 g ;

g. mol. wt. of H_2O = (2 × 1) + 16 = 18 g

No. of moles (n_1) of C_2H_5OH

$$= \frac{\text{mass}}{\text{g.mol.mass}} = \frac{46}{46} = 1.0\,;$$

no. of moles (n_2) of H_2O

$$= \frac{\text{mass}}{\text{g.mol.mass}} = \frac{54}{18} = 3.0$$

Total no. of moles (N) of C_2H_5OH and H_2O = 1 + 3 = 4

Hence,

$$\text{mole fraction of } C_2H_5OH = \frac{n_2}{N} = \frac{1}{4} = \mathbf{0.25} \qquad \textbf{Ans.}$$

EXAMPLE 69. *Density of an aqueous solution of* NaCl *marked 10% (w/w) is 1.071 g* mL^{-}*. What is its molality and molarity ? Also, what is the mole fraction of each component in solution ?*

SOLUTION. (*i*) wt. of NaCl = 10 g ;

wt. of solvent water = 100 – 10 = 90 g ;

g. mol. wt. of NaCl = 23 + 35.5 = 58.5 g.

$$\text{molality}, m = \frac{\text{wt. of solute} \times 1000}{\text{g. mol. wt. of solute} \times \text{wt. solvent}}$$

$$= \frac{10 \times 1000}{58.5 \times 93.3} = \mathbf{1.9\ m} \qquad \textbf{Ans.}$$

$$\text{volume of solution} = \frac{\text{Mass}}{\text{density}} = \frac{100}{1.071} = 93.3 \text{ mL.}$$

We know that : Molarity of solution

$$= \frac{\text{wt. of solute} \times 1000}{\text{g. mol. wt. of NaCl} \times \text{volume of solution in mL}}$$

$$= \frac{10 \times 1000}{58.5 \times 93.3} = \mathbf{1.83\ M} \qquad \textbf{Ans.}$$

(*iii*) n_1 = no. of moles of NaCl

$$= \frac{\text{wt. of NaCl}}{\text{g. mol. wt. of NaCl}}$$

$$= \frac{10}{58.5} = 0.17$$

n_2 = no. of moles of H_2O

$$= \frac{\text{wt. of } H_2O}{\text{g. mol. wt. of } H_2O}$$

$$= \frac{90}{18} = 5$$

Total no. of moles of NaCl and H_2O

= 0.17 + 5 = 5.17

∴ Mole fraction of NaCl

$$= \frac{n_1}{n_1 + n_2} = \frac{0.17}{5.17} = \mathbf{0.03} \qquad \textbf{Ans.}$$

Mole fraction of H_2O

= 1 – 0.03 = **0.97** **Ans.**

EXAMPLE 70. *Calculate the mole fraction of an unknown solute in 2.0 m aqueous solution.*

SOLUTION. Number of mol of solute = 2.0 (given)

$$\text{Number of mol. of water} = \frac{\text{wt. of water } (H_2O)}{\text{g. mol. wt. of } H_2O\,(=18)}$$

$$= \frac{1000}{18} = 55.6$$

Total no. of mol = 2.0 + 55.6 = 57.6

∴ Mole fraction of solute

$$= \frac{\text{mol of solute}}{\text{Total mol}} = \frac{2}{57.6}$$

= **0.0347** **Ans.**

EXAMPLE 71. *Derive a relation between molality (m) and mole fraction of solute,* x_2*.*

SOLUTION. Molality, *m* means, *m* mol of solute in 1000 g of solvent which is equal to $1000/M_1$ mol where M_1 = molar mass of the solvent.

$$\therefore \text{ Mole fraction, } x_2 = \frac{m}{m + \frac{1000}{M_1}} = \frac{mM_1}{mM_1 + 1000}$$

$$\text{Or} \qquad \frac{1}{x_2} = \frac{mM_1 + 1000}{mM_1} = \frac{mM_1}{mM_1} + \frac{1000}{mM_1}$$

$$= 1 + \frac{1000}{mM_1}$$

$$\frac{1}{x_2} - 1 = \frac{1000}{mM_1}; \frac{1 - x_2}{x_2} = \frac{1000}{mM_1}$$

$$\text{Or} \qquad \frac{x_1}{x_2} = \frac{1000}{mM_1} \qquad \left[\begin{array}{l} \because\ x_1 + x_2 = 1 \\ \therefore\ x_1 = 1 - x_2 \end{array}\right]$$

$$\text{Hence,} \qquad m = \frac{1000 \times x_2}{x_1 M_1}$$

EXAMPLE 72. *Molarity of* H_2SO_4 *is 0.8 and its density is 1.06 gm/cm*^{3}*. What will be its concentration in terms of molality and mole fraction?* **(CBSE, 2005)**

SOLUTION.

(*i*) wt. of solvent = wt. of solution – wt. of solute

= 1060 – 78.4 = 981.6 g

But

$$\text{density} = \text{Molarity}\left[\frac{1}{\text{molality}} + \frac{\text{mol. wt. of solute}}{1000}\right]$$

$$\therefore \qquad 1.06 = 0.8\left[\frac{1}{\text{molality}} + \frac{98}{1000}\right]$$

Molality = **0.814** **Ans.**

(*ii*) Mole fraction of H_2SO_4

$$= \frac{\text{mol of } H_2SO_4}{\text{mol of } H_2SO_4 + \text{mol of } H_2O}$$

$$= \frac{0.8}{0.8 + \frac{981.6}{18(=\text{mol. wt. of } H_2O)}}$$

$$= \frac{0.8}{0.8 + 54.5} = \frac{0.8}{55.3} = \mathbf{0.014} \qquad \textbf{Ans.}$$

EXAMPLE 73. *The mole fraction of* CH_3OH *in an aqueous solution is 0.02 and its density is 0.994 g cm*$^{-3}$*. Calculate the molarity and molality of this solution. (At. wt., C = 12, H = 1, O = 16).*

SOLUTION. g. mol. wt. of

CH_3OH = 12 + (3 × 1) + 16 + 1 = 32 g ;

g. mol. wt. of

H_2O solvent = (2 × 1) + 16 = 18 g ;

$$\text{density} = \frac{0.994\text{ g}}{\text{cm}^3} \times \frac{1000\text{ cm}^3}{1\text{ L}}$$

$$= 0.994 \times 1000 \text{ gL}^{-}$$

Let solution contains $CH_3OH = a$ mol;

Solution contains $H_2O = b$ mol

Total no. of mol of CH_3OH, and

$$H_2O = (a + b) \text{ mol.}$$

$\therefore$ Mole fraction of CH_3OH, x_{CH_3OH}

$$= \frac{a}{a+b}; \frac{a}{a+b} = \frac{0.02}{1} \text{ (given)}$$

Or $$\frac{a+b}{a} = \frac{1}{0.02}; \frac{a}{a}+\frac{b}{a} = 50;$$

$$1+\frac{b}{a} = 50; \frac{b}{a} = 50-1 = \frac{49}{1}$$

$$\therefore \quad a = 1; b = 49$$

(*i*) Molality of solution

$$= \frac{\text{mole fraction of solute}, CH_3OH}{\text{mole fraction of solvent}, H_2O} \times \frac{1000}{\text{Mol.wt.of solvent}, H_2O}$$

$$= \frac{1}{49} \times \frac{1000}{18} = \mathbf{1.13\ m} \qquad \textbf{Ans.}$$

(*ii*) $$\text{Molarity} = \frac{\text{Mol of solute}}{\text{Volume of solution in litre}} \quad ...(1)$$

Volume of solution

$$= \frac{\text{Total mass of } CH_3OH \text{ and } H_2O}{\text{density in gL}^{-}}$$

$$= \frac{32a+18b}{0.994 \times 1000} \text{ L} = \frac{32a+18b}{994}$$

Substituting this value in equation (1), we get

$$\text{Molarity} = \frac{a \times 994}{32a+18b} = \frac{1 \times 994}{(32 \times 1)+(18 \times 49)}$$

$$= \frac{994}{32+882} = \frac{994}{914} = \mathbf{1.0875\ M} \quad \textbf{Ans.}$$

EXAMPLE 74. *A solution has been prepared by dissolving 20 g of 1, 1-dibromoethane* ($C_2H_4Br_2$) *and 60 g of 1, 2-dibromopropane* ($C_3H_6Br_2$). *The vapour pressure of pure* $C_2H_4Br_2$ *and* $C_3H_6Br_2$ *at 360 K is 173 mm Hg and 127 mm Hg respectively. Calculate the partial pressures of* $C_2H_4Br_2$ *and* $C_3H_6Br_2$ *each and also the total pressure of the solution at 360 K. Also calculate the mole fraction of* $C_3H_6Br_2$ *in solution with 50 : 50 mole mixture in the vapour, and also find the composition of the vapour in equilibrium with the above solution and express as mole fraction of* $C_2H_4Br_2$.

SOLUTION. (*i*) Molar mass of $C_2H_4Br_2$ $(= M_1) = (2 \times 12) + (4 \times 1) + (2 \times 80) = 188 \text{ g mol}^{-}$

Molar mass of $C_3H_6Br_2$ $(= M_2)$

$$= (3 \times 12) + (6 \times 1) + (2 \times 80)$$
$$= 202 \text{ g mol}^{-}$$

Moles of $C_2H_4Br_2$,

$$n_1 = \frac{\text{wt.}}{\text{mol.wt.}} = \frac{20}{188} = 0.106$$

Moles of $C_3H_6Br_2$,

$$n_2 = \frac{\text{wt.}}{\text{mol.wt.}} = \frac{60}{202} = 0.297$$

Mole fraction of $C_2H_4Br_2$

$$= \frac{n_1}{n_1+n_2} = \frac{0.106}{0.106+0.297}$$

$$= 0.263 = x_A \text{ (say)}$$

Mole fraction of $C_3H_6Br_2$

$$= 1 - 0.263 = 0.737 = x_B \text{ (say)}$$

$$\text{Total pressure, } P = \overset{\circ}{p}_A x_A + \overset{\circ}{p}_B x_B$$

$$= (173 \times 0.263) + (127 \times 0.737)$$
$$= 45.5 + 93.6 = 139.1 \text{ mm Hg.}$$

$\therefore$ Partial pressure of $C_2H_4Br_2 = 45.5$

Partial pressure of $C_3H_6Br_2 = 93.6$

(*ii*) Mole fraction of $C_2H_4Br_2$ in the vapour

$$= \frac{\text{Partial pressure of } C_2H_4Br_2}{\text{Total pressure}}$$

$$= \frac{45.5}{139.1} = \mathbf{0.327} \qquad \textbf{Ans.}$$

(*iii*) In vapour phase, $^{n}C_2H_4Br_2 : {}^{n}C_3H_6Br_2 = 50 : 50$

$$\therefore \text{ Mole fraction of } C_2H_4Br_2 = \frac{50}{50+50} = \mathbf{0.5} \qquad \textbf{Ans.}$$

Mole fraction of $C_3H_6Br_2 = 1 - 0.5 = \mathbf{0.5}$ **Ans.**

EXAMPLE 75. *4.5 g of* KBr *is dissolved in 1000 g of water. Calculate the normality, molarity, molality and mole fraction of the solution if the density of the solution is 0.988 g per c.c. (K = 39, Br = 80).*

SOLUTION.

(*i*) $$\text{Mole of KBr} = \frac{\text{wt.}}{\text{Mol.wt}} = \frac{4.5}{119} = 0.0378$$

[Mol wt. of KBr = 39 + 80 = 119]

$$\text{Molality} = \frac{\text{mole}}{\text{wt.of solvent in g}} \times 1000$$

$$= \frac{0.0378 \times 1000}{1000} = \mathbf{0.0378\ m.} \quad \textbf{Ans.}$$

(*ii*) Volume of solution

$$= \frac{\text{wt. in g}}{\text{density in g (c.c)}^{-}} = \frac{(1000+4.5)\text{ g}}{0.988 \text{ g (c.c)}^{-}}$$

$$= 1016.7 \text{ c.c} = \frac{1016.7}{1000} = 1.0167 \text{ L}$$

$$\text{Molarity} = \frac{\text{no.of mol}}{\text{vol.of solution in L}} = \frac{0.0378}{1.0167}$$

$$= \mathbf{0.0372\ M} \qquad \textbf{Ans.}$$

(*iii*) Since for KBr,

mol. wt. = Eq. wt.,

hence normality = **0.0372 N** **Ans.**

(*iv*) Density of water = $1\ g\ (c.c)^{-}$

Hence, $1000\ g\ H_2O = \dfrac{1000\,g}{1g(c.c.)^{-}} = 1000\ c.c\ H_2O$

$$\text{mol. of water} = \frac{\text{wt.of } H_2O}{\text{mol.wt.of } H_2O} = \frac{1000}{18} = 55.55$$

$$\therefore \quad \text{Total mol.} = \text{mol. of KBr} + \text{mol. of } H_2O$$

$$= 0.0372 + 55.55 = 55.5372$$

∴ Mole fraction of KBr

$$= \frac{\text{mol.of KBr}}{\text{Total moles}} = \frac{0.0372}{55.5372}$$

$$= \mathbf{6.69 \times 10^{-4}}$$ **Ans.**

17.11. HENRY'S LAW

According to this law, the amount of gas dissolved at equilibrium in a given quantity of a liquid is proportional to the pressure of the gas in contact with the liquid. This law is obeyed if no chemical reaction takes place between the gas and the liquid and solution should not be concentrated. Mathematically:

Partial pressure of a gas, p_{gas} = (Henry's law constant, K_H) × (mole fraction of the gas, x_{gas}.)

Example 76. *If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 k bar.*

Solution. According to Henry's law, $P_{N_2} = K_H \times x_{N_2}$ *i.e.*, $x_{N_2} = \dfrac{P_{N_2}}{K_H}$

$$= 0.987\ \text{bar}/76.48 \times 10^3\ \text{bar} = 1.29$$

Mole fraction of N_2 in H_2O,

$$x_N = 1.29\ ;$$

Mass of 1 litre water = 1000 g

No. of moles (n) of water in 1 litre

$$= \frac{1000}{18} = 55.5$$

If n represents the number of moles of N_2 in solution,

$$x_{N_2} = \frac{n\,\text{mol}}{n\,\text{mol} + 55.5\ \text{mol}} \approx \frac{n}{55.5};$$

$$\frac{n}{55.5} = 1.29$$

$$\therefore \quad n = 1.29 \times 55.5\ \text{mol} = 71.6\ \text{mol}$$

$$= 71.6\ \text{mol} \times 1000\ \text{m mol}/1\ \text{mol}$$

$$= \mathbf{0.71\ m\ mol}$$ **Ans.**

Example 77. *1 litre of water under a nitrogen pressure of 1 bar dissolves 2×10^{-5} kg of nitrogen at 293 K. Calculate Henry's law constant.*

Solution. (*i*) Mass of one litre water = 1000 g ;

g. mol. mass of

$$H_2O = (2 \times 1) + 16 = 18\ g.$$

Hence no. of moles (n_1) of water

$$= \frac{1000\,g}{18\,g} = \mathbf{55.5}$$

(*ii*) Wt. of $N_2 = 2 \times 10^{-5}$ kg

$$= \frac{2 \times 10^{-5}}{1000} = 2 \times 10^{-2}\ g\ ;$$

g. mol. mass of $N_2 = 2 \times 14 = 28$ g.

Hence no. of moles of N_2 (n_2)

$$= \frac{\text{wt.of } N_2\ (g)}{\text{g.mol.mass of } N_2}$$

$$= \frac{2 \times 10^{-2}}{28} = 7.14 \times 10^{-4}$$

Hence total no. of moles $(n_1 + n_2) = 55.5 + 7.14 \times 10^{-4}$

(*iii*) Mole fraction of N_2,

$$x_{N_2} = \frac{n_2}{(n_1 + n_2)} = \frac{7.14 \times 10^{-4}}{55.5 + 7.14 \times 10^{-4}}$$

$$= 1.286 \times 10^{-5}$$

According to Henry's law : P_{N_2} = Henry constant (K_H) × mole fraction of N_2 *i,e.* x_{N_2}

Substituting the values, we get :

$$1\ \text{bar} = K_H \times 1.286 \times 10^{-5}$$

Or $$K_H = \frac{1\,\text{bar}}{1.286 \times 10^{-5}}$$

$$= 77760\ \text{bar} \approx \mathbf{77.7\ k\ bar}$$ **Ans.**

Example 78. *The Henry's law constant for CO_2 in water at 298 K is 1.67 k bar. Calculate the solubility of CO_2 at 298 K when the pressure of CO_2 is one bar.*

Solution. (*i*) According to Henry's law, P_{CO_2}

= Henry's constant, K_H × mole fraction of $CO_2 (x_{CO_2})$

Given that $P_{CO_2} = 1$ bar ;

$$K_H = 1.67 \times 1000\ \text{bar} = 1670\ \text{bar}.$$

Substituting the values in

$P_{CO_2} = K_H \times x_{CO_2}$, we have :

$1\ \text{bar} = 1670\ \text{bar} \times x_{CO_2}$ Or $x_{CO_2} = \mathbf{1/1670}$

(*ii*) Mass of 1000 mL

$$H_2O = 1000\ g\ ;$$

g. mol. mass of

$$H_2O = (2 \times 1) + 16 = 18\ g.$$

Hence, no. of moles of H_2O,

$$n_1 = \frac{\text{wt}(g)}{\text{g.mol.mass of } H_2O} = \frac{1000\,g}{18\,g}$$

$$= \mathbf{55.5}$$

$$\text{But } x_{CO_2} = \frac{\text{moles of } CO_2\ (n_2)}{\underset{CO_2\ (n_2)}{\text{Total no.of moles of}} + \underset{(n_1 = 55.5)}{\text{no.of moles of } H_2O}}$$

Substituting the values, we get :

$$\frac{1}{1670} = \frac{n_2}{n_2 + 55.5} \quad \text{Or } n_2 + 55.5 = 1670n_2$$

$$\text{Or} \quad 1670n_2 - n_2 = 55.5 \quad \text{Or} \quad 1669n_2 = 55.5$$

$$\text{Or} \quad n_2 = \frac{55.5}{1669} = \mathbf{3.32 \times 10^{-2}\ mol\ L^{-}} \ \textbf{Ans.}$$

EXAMPLE 79. *Find the value of vapour pressure of acetone in a solution of acetone in chloroform. Mole fraction of acetone is 0.14 while Henry's law constant for the solution is 0.2 bar.*

SOLUTION. Let x_2 and p_2 are the mole fraction and partial pressure of solute (acetone) respectively.

But $p_2 = K_H x_2$ (Henry's law, K_H = Henry's law constant)

$\therefore$ $p_2 = 0.2 \text{ bar} \times 0.14 = \mathbf{0.028\ bar}$ **Ans.**

17.12. MILLIEQUIVALENTS (m. eq) OF A SALT PRESENT IN *x* ML OF '*Y*' MOLAR SOLUTION

= Volume in mL × molarity × $n = xyn$

where n = no. of mol of ion × oxidation state of ion.

EXAMPLE 80. *Calculate the milliequivalents of* $Ca_3(PO_4)_2$ *in 250 mL of 0.25 M of its solution.*

SOLUTION. $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

$\therefore$ n = (no. of mol of Ca^{2+}) × (oxidation state of Ca^{2+})

$= 3 \times 2 = 6$

Molarity = 0.25 M ; volume = 250 mL

$\therefore$ No. of milliequivalents of $Ca_3(PO_4)_2$

= n × molarity × volume in mL

$= 6 \times 0.25 \times 250 = \mathbf{375}$ **Ans.**

Type. Equivalents of a salt present in x mL of y molar solution

$$= \frac{\text{volume}(x) \text{ in mL} \times \text{molarity} \times n}{1000}$$

$$= \frac{xyn}{1000}$$

EXAMPLE 81. *Calculate the number of equivalents of* $ZnSO_4$ *in 100 mL of 0.25 M solution.*

SOLUTION. $ZnSO_4 \rightleftharpoons \underset{1\text{ mol}}{Zn^{2+}} + SO_4^{2-}$

$\therefore$ n = (no. of mol of Zn^{2+}) × (oxidation state of Zn^{2+})

$= 1 \times 2 = 2$

$\therefore$ No. of equivalents of

$$ZnSO_4 = \frac{n \times \text{molarity} \times \text{volume in mL}}{1000}$$

$$= \frac{2 \times 0.25 \times 100}{1000} = \mathbf{0.05} \quad \textbf{Ans.}$$

17.13. NORMALITY × EQ. WT = MOLARITY × MOL. WT.

EXAMPLE 82. *Calculate the normality of M/20* Na_2CO_3 *solution. (At. wt. of Na = 23, C = 12, O = 16).* **(BET, 2003)**

SOLUTION. Mol. wt. of

$Na_2CO_3 = (2 \times 23) + 12 + (3 \times 16)$

= 106 a.m.u.

Eq. wt. of Na_2CO_3

$$= \frac{\text{Mol. wt. of } Na_2CO_3}{\text{Total + ive or ive charge in } Na_2CO_3}$$

$$= \frac{106}{2} = 53$$

Molarity = M/20

Normality × Eq. wt. = Molarity × Mol. wt.

$$\text{Normality} \times 53 = \frac{1}{20} \times 106$$

$$\therefore \quad \text{Normality} = \frac{1}{20} \times \frac{106}{53} = \frac{1}{10} \quad \textbf{Ans.}$$

EXAMPLE 83. *What is the molality and molarity of 13% solution by weight of* H_2SO_4 *? Its density is 1.02 g* cm^{-3}.

SOLUTION. Wt. of H_2SO_4 = 13 g ;

wt. of H_2O solvent = 100 – 13 = 87 g

g. mol. wt. of

$H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98$ g ;

Density = 1.02 g cm^{-3}

$$(i) \quad \text{Molality}, m = \frac{\text{wt. of } H_2SO_4}{\text{g. mol. wt. of } H_2SO_4} \times \frac{1000}{\text{wt. of solvent}, H_2O}$$

$$= \frac{13}{98} \times \frac{1000}{87} = \mathbf{1.52} \quad \textbf{Ans.}$$

$$(ii) \quad \text{Molarity}, \quad M = \frac{\text{wt. of } H_2SO_4}{100} \times \frac{1000 \times \text{density}}{\text{g. mol. wt. of } H_2SO_4}$$

$$= \frac{13}{100} \times \frac{1000 \times 1.02}{98} = \mathbf{1.35} \quad \textbf{Ans.}$$

EXAMPLE 84. *The solutions A and B are 0.1 and 0.2 molar in a substance. If 100 ml of A is mixed with 25 ml of B and there is no change in volume, find the final molarity of the solution.* **(Pb PMT, 1993)**

SOLUTION. Volume of solution

$A = V_1 = 100$ ml

Volume of solution

$B = V_2 = 25$ ml

Total volume of solutions

A and B = 100 + 25 = 125 ml

For solution A, using molarity equation, we have

Original Solution **Solution after mixing**

$M_1V_1 = M_2V_2$; $0.1 \times 100 = M_2 \times 125$

$$\therefore \quad M_2 = \frac{0.1\times 100}{125} = 0.08$$

For solution *B*, using molarity equation, we have

Original Solution **Solution after mixing**

$$M_3V_3 = M_4V_4;\ 0.2 \times 25 = M_4 \times 125$$

$$\therefore \quad M_4 = \frac{0.2\times 25}{125} = 0.04$$

∴ Total molarity = 0.08 + 0.04 = 0.12 M.

Example 85. *An aqueous solution containing 0.10 g* KIO_3 *(formula wt. = 214.0) was treated with an excess of KI solution. The solution was acidified with* HCl. *The liberated* I_2 *consumed 15.0 ml of thiosulphate solution to decolourise the blue starch iodine complex. Calculate the molarity of the sodium thiosulphate solution.*

Solution. The reactions involved are :

$$KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3I_2 + 3H_2O$$

or
$$\underset{1\text{ mol}}{IO_3^-} + \underset{5\text{ moles}}{5I^-} + 6H^+ \longrightarrow \underset{3\text{ moles}}{3I_2} + 3H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

or
$$\underset{1\text{ mol}}{I_2} + \underset{2\text{ mol}}{2S_2O_3^{2-}} \longrightarrow S_4O_6^{2-} + 2I^-$$

From the reaction, it is obvious that

(*i*) 1 mole KIO_3 and 5 moles of KI liberate 3 moles of I_2

(*ii*) 1 mole of KIO_3 liberate 1/2 or 0.5 mole of I_2 *i.e.* 0.5 + 2.5 mol = 3 mol

(*iii*) 5 moles of KI leberate 5/2 or 2.5 moles of I_2

(*iv*) 1 mole of KIO_3 reacts with 5 moles of KI.

(*v*) 1 mole of I_2 reacts with 2 moles of sodium thiosulphate.

Number of moles of KIO_3 present in solution

$$= \frac{0.1}{214} = 0.00047$$

Number of moles of I_2 liberated by 0.00047 moles of KIO_3

$$= \frac{1}{2}\times 0.00047 = 0.000235$$

Number of moles of KI reacting with 0.00047 moles of KIO_3

$$= 5 \times 0.00047 = 0.00235.$$

Number of moles of I_2 liberated from 0.00235 moles of I^-

$$= \frac{5}{2}\times\frac{1}{5}\times 0.00235 = 0.001175$$

Total number of moles of I_2 produced

$$= 0.00235 + 0.001175 = 0.00141.$$

Since 1 mole of I_2 reacts with 2 moles of sodium thiosulphate, the number of moles of thiosulphate used

$$= 2 \times 0.00141 = 0.00282$$

Since 45 mL of solution contains 0.00282 moles of sodium thiosulphate, 1000 mL of solution contains

$$= \frac{0.00282}{45}\times 1000 = 0.063 \text{ moles}$$

∴ Molarity of sodium thiosulphate

= **0.063 M**

17.14. NUMBER OF MILLIEQUIVALENTS

$$\text{No. of milliequivalents} = \frac{\text{wt.(in g)}}{\text{g.Eq.wt}} \times 1000 = \text{Normality}$$
of solution × volume in mL

Example 86. *Calculate the number of milliequivalents of 20 mL of 0.2 N* Na_2CO_3 *solution.*

Solution. Normality of solution

= 0.2 N ; Volume of solution = 20 mL

∴ No. of milliequivalent of Na_2CO_3 solution.

= Normality of solution × Volume in mL

= 0.2 × 20 = **4** **Ans.**

Type. Number of gram equivalent of a substance

$$= \frac{\text{wt.(in g) of substance}}{\text{g.Eq.wt.of substance}}$$

= *n* × (no. of mol of substance)

'*n*' has the same meaning as shown in the type 'relation between normality and molarity for acids, bases and salts' given in section, 17.16.

Example 87. *Calculate the number of gram equivalents present in 4.0 g of sodium hydroxide.*

Solution. Wt. of NaOH = 4.0 g ;

g. Eq. wt. of NaOH = 23 + 16 + 1 = 40 g.

∴ No. of gram equivalents of

$$\text{NaOH} = \frac{\text{wt.of NaOH}}{\text{g.Eq.wt.of NaOH}} = \frac{4.0}{40}$$

= **0.1** **Ans.**

Example 88. *Calculate the number of gram equivalents of* H_2SO_4 *present, in its 0.5 mol.*

Solution. $H_2SO_4 \rightleftharpoons \underset{n=2}{2H^+} + SO_4^{2-}$

∴ No. of gram equivalents of

H_2SO_4 = *n* × no. of mol of

H_2SO_4 = 2 × 0.5 = **1.0** **Ans.**

Type. Number of millimol of a substance

$$= \frac{\textbf{wt. of substance}}{\textbf{g. mol. wt. of substance}} \times \mathbf{1000}$$

Example 89. *How many millimol of sodium chloride are present in 5.85 g of sodium chloride (At. wt., Na = 23, Cl = 35.5).*

Solution. Wt of NaCl = 5.85 g ; g. mol. wt. of NaCl = 23 + 35.5 = 58.5 g.

∴ No. of millimol of

$$\text{NaCl} = \frac{\text{wt.of NaCl}}{\text{g.mol.wt.of NaCl}}\times 1000$$

$$= \frac{5.85\text{g}}{58.5\text{g}}\times 1000 = \mathbf{100}$$ **Ans.**

EXAMPLE 90. *Calculate the weight of* K_2CO_3 *present in 20 millimol of it.* (*At. wt., K = 39, C = 12, O = 16*).

SOLUTION. No. of millimol of $K_2CO_3 = 20$; wt. of K_2CO_3 = ?

g. mol. wt. of

$$K_2CO_3 = (2 \times 39) + 12 + (3 \times 16)$$
$$= 78 + 12 + 48 = 138 \text{ g.}$$

We know, no. of millimol of

$$K_2CO_3 = \frac{\text{wt.of } K_2CO_3}{\text{g.mol.wt.of } K_2CO_3} \times 1000$$

$$20 = \frac{\text{wt.of } K_2CO_3}{138} \times 1000$$

$$\therefore \quad \text{wt. of } K_2CO_3 = \frac{20 \times 138}{1000} = \mathbf{2.76\ g} \qquad \textbf{Ans.}$$

Type. Number of gram mol

$$= \frac{\text{wt.of substance in g}}{\text{g.mol.wt.of substance}}$$

EXAMPLE 91. *Calculate the number of gram mol in 1.03 g of sodium bromide* (*At. wt. Na = 23, Br = 80*).

SOLUTION. Wt. of NaBr = 1.03 g ;

g. mol. wt. of NaBr = 23 + 80 = 103 g.

∴ no. of gram mol of

$$\text{NaBr} = \frac{\text{wt.of NaBr(g)}}{\text{g.mol.wt.of NaBr}} = \frac{1.03}{103}$$
$$= \mathbf{0.01} \qquad \textbf{Ans.}$$

17.15. NUMBER OF MOL AND MILLIMOL

Type. (*i*) Number of mol = Molarity × Volume of solution in litre

(*ii*) Number of millimol *i.e.*, m. mol = Molarity × Volume of solution in mL

EXAMPLE 92. *What does 2.5 M* NaOH *solution mean ?*

SOLUTION.
$$2.5 \text{ M NaOH} = \frac{2.5 \text{ mol NaOH}}{\text{L}}$$
$$= 2.5 \text{ mol NaOH/L}$$
$$= \frac{2.5 \text{ m.mol NaOH}}{\text{mL}}$$
$$= 2.5 \text{ m. mol NaOH/mL}$$

EXAMPLE 93. *What is meant by 25 mL of 1.5 M* HCl *solution ?*

SOLUTION. 25 mL of 1.5 M HCl solution means that this solution contains :

(*i*) no. of mol of

$$\text{HCl} = (\text{Molarity of HCl}) \times (\text{volume of solution in litre})$$
$$= \frac{1.5 \text{ mol}}{\text{L}} \times \frac{25 \text{ L}}{1000}$$
$$\text{L} = \mathbf{0.0375\ mol} \qquad \textbf{Ans.}$$

(*ii*) no. of m. mol. of

HCl = (Molarity of HCl) × (volume of HCl in mL)

$$= \frac{1.5 \text{ m.mol}}{\text{mL}} \times 25 \text{ mL}$$
$$= \mathbf{37.5\ m.\ mol} \qquad \textbf{Ans.}$$

17.16. NORMALITY = *n* × MOLARITY, WHERE *n* = MOL. WT./EQ WT. OR

n = (no. of mol of cation in one mol of salt) × (oxidation state of cation)

EXAMPLE 94. *Calculate the normality of 1.2 M* H_2SO_4.

SOLUTION. We know that normality = *n* × Molarity

$$\text{Where} \quad n = \frac{\text{Mol.wt}}{\text{Eq.wt.}}$$

$$\text{For} \quad H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

(*i*) 2 mol

(*ii*) oxidation state of $H^+ = 1$

$$\therefore \quad n = 2 \times 1 = 2$$

∴ Normality of

$$H_2SO_4 = n \times \text{Molarity}$$
$$= 2 \times 1.2 = \mathbf{2.4\ N} \qquad \textbf{Ans.}$$

EXAMPLE 95. *Calculate the normality of 2.5 M* $Al(OH)_3$.

SOLUTION. $Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

(*i*) 1 mol

(*ii*) oxidation state of $Al^{3+} = +3$

$$\therefore \quad n = 1 \times 3 = 3$$

$$\text{But} \quad \text{Normality} = n \times \text{Molarity}$$
$$= 3 \times 2.5 = \mathbf{7.5\ N} \qquad \textbf{Ans.}$$

EXAMPLE 96. *Calculate the normality of 0.5 M* $Ca_3(PO_4)_2$.

SOLUTION. $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$

(*i*) 3 mol

(*ii*) oxidation state of $Ca^{2+} = +2$

$$\therefore \quad n = 3 \times 2 = 6$$

$$\text{But} \quad \text{Normality} = n \times \text{molarity}$$
$$= 6 \times 0.5 = \mathbf{3.0\ N} \qquad \textbf{Ans.}$$

EXAMPLE 97. *What is the normality of 0.5 M aqueous solution of tribasic acid ?* **(PSEB, 2006)**

SOLUTION. For tribasic acid,

$$n = 3 \text{ ; Molarity} = 0.5 \text{ M}$$

$$\text{But} \quad \text{Normality} = \text{Molarity} \times n$$

$$\text{Thus} \quad \textbf{Normality} = 0.5 \times 3 = \mathbf{1.5\ N} \qquad \textbf{Ans.}$$

EXAMPLE 98. *Calculate the amount of barium phosphate in 250 mL of 0.15 M solution.* (*At. wt., Ba = 137, P = 31, O = 16*).

SOLUTION. Barium phosphate ionises as :

$$Ba_3(PO_4)_2 \rightleftharpoons 3Ba^{2+} + 2PO_4^{3-}$$

(*i*) 3 mol

(*ii*) oxidation state of $Ba^{2+} = +2$

$$\therefore \quad n = 3 \times 2 = 6$$

∴ No. of m. eq. of

$$Ba_3(PO_4)_2 = (\text{volume in mL}) \times (\text{molarity}) \times n$$
$$= 250 \times 0.15 \times 6 = 225.$$

$$\text{But} \quad \text{no. of m. eq.} = \frac{\text{wt.of solute}}{\text{g.eq.wt.of solute}} \times 1000$$

$$225 = \frac{\text{wt.of solute}}{100.1} \times 1000$$

$$\therefore \quad \text{Wt. of solute} = \frac{225 \times 100.1}{1000}$$

$$= \mathbf{22.52\ g} \qquad \textbf{Ans.}$$

$$\because \quad \text{Eq. wt. of } Ba_3(PO_4)_2 = \frac{\text{Mol. wt. of } Ba_3(PO_4)_2}{n}$$

$$= \frac{(3 \times 137) + (2 \times 31) + 2(4 \times 16)}{n}$$

$$= \frac{601}{6} = 100.1$$

17.17. CALCULATING NORMALITY OR MOLARITY OF AN OXIDANT OR REDUCTANT IN A REDOX REACTION

Type. *To find normality or molarity of an oxidant or reductant in a redox reaction, use the relation :*

Normality of *x* M oxidant or reductant = [Molarity (*x*)] × no. of electrons lost or gained

Example 99. *Calculate the normality of 0.01 M* $K_2Cr_2O_7$ *(oxidant) solution.*

Solution. For

$$K_2Cr_2O_7 : Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

no. of electrons gained = 6

Molarity = 0.01 M (given).

Hence : Normality = Molarity × no. of electrons gained.

$= 0.01 \times 6 = \mathbf{0.06\ N}$ **Ans.**

Example 100. *Calculate the molarity of 0.05 N oxalic acid (reductant) solution.*

Solution. For

$$H_2C_2O_4 \text{ (oxalic acid)} : C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

no of electrons lost = 2

Hence : Normality = Molarity × No. of electrons lost

0.05 = Molarity × 2

$$\therefore \quad \text{Molarity} = \frac{0.05}{2} = \mathbf{0.025\ M} \qquad \textbf{Ans.}$$

17.18. CALCULATING NO. OF MILLIEQUIVALENTS OR NORMALITY OF AN OXIDANT OR REDUCTANT

Type. No. of milliequivalents of *x*M oxidant or reductant = Normality × volume in mL

Where Normality = Molarity × no. of electrons lost or gained

Example 101. *Calculate the number of milliequivalents of 20 mL of 0.02 M* $KMnO_4$ *(oxidant) solution.*

Solution.

$$\text{For } KMnO_4 : MnO_4^- + 8\,H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

No. of electrons gained = 5 ;

molarity = 0.02 M

But Normality = Molarity × no. of electrons gained

∴ Normality = 0.02 × 5

= 0.1 N

∴ No. of milliequivalent of $KMnO_4$ = Normality × volume in mL

$= 0.1 \times 20 = 2$ **Ans.**

17.19. CALCULATING NUMBER OF MILLIMOL OF *x* M OXIDANT OR REDUCTANT

Type. No. of millimol of *x* M oxidant or reductant

$$= \text{no. of milli equivalents} \times \frac{\text{Eq. wt}}{\text{Mol. wt}}$$

Where no. of milli equivalents

= Normality × Volume in mL

Where Normality

= Molarity × No. of electrons lost or gained.

Second method. No. of millimol

= Molarity × Volume in mL

Example 102. *Calculate the number of millimol of 25 mL of 0.02 M* $K_2Cr_2O_7$ *(oxidant) solution.*

Solution. For

$$K_2Cr_2O_7 : Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

No. of electrons gained = 6;

molarity = 0.02 M

∴ Normality = Molarity × No. of electrons gained.

= 0.02 × 6 = 0.12 N

Hence no. of milli equivalent of $K_2Cr_2O_7$

= Normality × Volume in mL

$= 0.12 \times 25 = \mathbf{3.0}$

Also, Eq. wt. of

$$K_2Cr_2O_7 = \frac{\text{Mol. wt.}}{\text{no. of electrons gained}} = \frac{\text{Mol. wt.}}{6}$$

$$\text{But no. of millimol} = \text{no. of milli equivalent} \times \frac{\text{Eq. wt.}}{\text{Mol. wt.}}$$

$$= 3.0 \times \frac{\text{Mol. wt.}}{6} \times \frac{1}{\text{mol. wt.}}$$

$= \mathbf{0.5}$ **Ans.**

Second method. No. of millimol of 25 mL of 0.02 M $K_2Cr_2O_7$

= Molarity × Volume in mL

= 0.02 × 25 = **0.5 millimol Ans.**

Type. Normality × Volume in mL

= no. of milli equivalents

Or Normality × Volume in litre

= no. of equivalents

$$1 \text{ Equivalent} = \frac{\text{no. of milli equivalents}}{1000}$$

EXAMPLE 103. *Calculate the normality of* HCl *having 25 milliequivalents in 1.5 litre.*

SOLUTION. 1.5 L = 1.5 × 1000 mL = 1500 mL

Normality × volume in mL

= no. of milliequivalents

$$\text{Normality} \times 1500 = 25 \therefore \text{Normality} = \frac{25}{1500} = \frac{N}{60}$$ **Ans.**

EXAMPLE 104. *Upon heating a litre of* $\frac{N}{2}$ *HCl solution, 2.675 g hydrogen chloride is lost and the volume of the solution shrinks to 750 ml. Calculate (i) the normality of the resulting solution and (ii) the number of milliequivalents of HCl in 100 mL of the final solution.* **(IIT, 1975)**

SOLUTION. Eq. wt. of

HCl = Mol. wt. of HCl = 36.5

Normality = number of gram equivalents litre^{-1}

$$= \frac{\text{Mass in gL}^{-1}}{\text{Gram equivalent wt.}}$$

$\therefore$ Mass of HCl in 1L of $\frac{N}{2}$

$$\text{HCl} = \frac{1}{2} \times 36.5 = 18.25 \text{ g}$$

Weight of HCl lost on heating

= 2.675 g

Weight of HCl left in solution

= 18.25 – 2.675 = 15.575 g

Number of gram equivalent in 15.575 g

$$\text{HCl} = \frac{15.575}{36.5} = 0.4267 \text{ eq.}$$

Volume of the solution left after heating

$$= 750 \text{ mL} = \frac{750}{1000} = 0.75 \text{ L}$$

$\therefore$ Normality of solution

$$= \frac{\text{No. of gram equivalents}}{\text{Volume in litres}}$$

$$= \frac{0.4267}{0.75} = 0.569 \text{ N}$$

Number of meq. = (Volume in mL) × (Normality)

$\therefore$ No. of meq. in 100 mL of final solution

= 100 × 0.569 = **56.9 meq.** **Ans.**

Type. No. of equivalents

$$= \begin{bmatrix} \text{no. of mol} \times \text{(no. of mol of cation in one mol} \\ \text{of substance} \times \text{oxidation state of cation)} \end{bmatrix}$$

$\therefore$ Normality

$$= \frac{\begin{bmatrix} \text{no. of mol} \times \text{(no. of mol of cation in one mol} \\ \text{of substance} \times \text{oxidation state of cation)} \end{bmatrix}}{\text{volume in litre (or vol in mL/1000)}}$$

EXAMPLE 105. *Calculate the normality of* $\frac{1}{5}$ *mol of* H_2SO_4 *in 250 mL of the solution.*

SOLUTION. $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

(*i*) mol = 2

(*ii*) oxidation state of $H^+ = 1$

Volume = 250 ml

$$\text{No. of mol} = \frac{1}{5}$$

We know that Normality

$$= \frac{\begin{bmatrix} \text{no. of mol} \times \text{(no. of mol of cation in one mol} \\ \text{of } H_2SO_4 \times \text{oxidation state of cation)} \end{bmatrix}}{\text{vol in mL}} \times 1000$$

$$= \frac{1}{5} \times (2 \times 1) \times \frac{1000}{250} = \mathbf{1.6}$$ **Ans.**

17.20. MOLARITY = NORMALITY/ [NO. OF MOL OF CATION IN ONE MOL OF ACID, BASE OR SALT × OXIDATION STATE OF CATION]

EXAMPLE 106. *Calculate the molarity of N/20* Na_2CO_3 *solution. (at. wt. Na = 23, C = 12, O = 16).*

SOLUTION. $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$

(*i*) mol = 2

(*ii*) oxidation state of $Na^+ = 1$

$\therefore$ Molarity

$$= \frac{\text{Normality}}{\text{no. of mol of cation Na}^+ \text{ in one mol of } Na_2CO_3 \times \text{oxidation state of cation, Na}^+}$$

$$= \frac{1}{20 \times 2 \times 1} = \frac{1}{40} = 0.025 \text{ M}$$

17.21. MISCELLANEOUS EXAMPLES

EXAMPLE 107. *8.0575 × 10^{-2} kg of Glauber's salt is dissolved in water to obtain 1dm^3 of a solution of density 1077.2 kg m^{-3}. Calculate the molality, molarity and mole fraction of* Na_2SO_4 *in the solution.* **(IIT JEE, 1994)**

SOLUTION. (*i*) Formula mass of Glauber's salt, $Na_2SO_4.10H_2O$

= (2 × 23) + 32 + (4 × 16) + 10

[(2 × 1) + 16] = 322 g mol^{-}

wt. of Glauber's salt

$$= 8.0575 \times 10^{-2} \text{ kg} \times \frac{1000 \text{ g}}{1 \text{kg}}$$

= 80.575 g

$\therefore$ no. of mol of Glauber's salt

$$= \frac{\text{wt.}}{\text{mol. wt.}} = \frac{80.575 \text{ g}}{322 \text{ g mol}^{-}} = 0.25 \text{mol}$$

(*ii*) Density of solution

$$= 1077.2 \text{kg m}^{-3} \times \frac{1000 \text{ g}}{1 \text{kg}} \times \frac{1 \text{dm}^{-3}}{1000 \text{m}^{-3}}$$

$= 1077.2 \text{ g dm}^{-3}$

Volume of solution

$= 1 \text{ dm}^3$

$\therefore$ Mass of 1dm^3 solution

$= \text{Volume} \times \text{Density}$

$= 1 \text{ dm}^3 \times 1077.2 \text{ g dm}^{-3}$

$= 1077.2 \text{ g}$

Formula mass of

$Na_2SO_4 = (2 \times 23) + 32 + (4 \times 16)$

$= 142 \text{ g mol}^-$

$\therefore$ Mass of Na_2SO_4 in dm^3 solution

$= \text{no. of mol} \times \text{formula mass}$

$= 0.25 \text{ mol} \times 142 \text{ g mol}^- = 35.5 \text{ g}$

$\therefore$ Mass of solvent in 1 dm^3 solution

$= 1077.2 - 35.5 = 1041.7 \text{ g}$

$= 1.0417 \text{ kg}$

(*ii*) $$\text{Molality} = \frac{\text{no.of mol}}{\text{wt.of solvent in kg}} = \frac{0.25 \text{mol}}{1.0417 \text{ kg}}$$

$= 0.24 \text{ mol kg}^- = \mathbf{0.24\ m}$ **Ans.**

(*iii*) $$\text{Molarity} = \frac{\text{no.of mol}}{\text{volume of solution in dm}^3}$$

$$= \frac{0.25 \text{mol}}{1\text{dm}^3}$$

$= \mathbf{0.25\ mol\ dm^{-3}}$ **Ans.**

(*iv*) Mole fraction of Na_2SO_4=

$$\frac{\text{no. of mol of } Na_2SO_4}{\text{no. of mol of } Na_2SO_4 + \text{no. of mol of solvent, } H_2O}$$

But No. of mol of

$$H_2O = \frac{\text{wt.of } H_2O \text{ in g}}{\text{mol.wt.of } H_2O \text{ in g mol}^-}$$

$$= \frac{1041.7 \text{ g}}{18 \text{ g mol}^-} = 57.87 \text{ mol}$$

$\therefore$ Mole fraction of

$$Na_2SO_4 = \frac{0.25 \text{ mol}}{(0.25 + 57.87) \text{ mol}} = \frac{0.25}{58.12}$$

$= 4.3 \times 10^{-3} = \mathbf{0.0043}$ **Ans.**

EXAMPLE 108. *10 mL of* HCl *solution gave 0.1435 g of* AgCl *when treated with excess of* $AgNO_3$. *Find the normality of the acid solution. (Ag = 108)* **(WB JEE, 2003)**

SOLUTION.

$$\underset{\substack{(1+35.5)\\ = 36.5 \text{ g}}}{HCl} + \underset{\text{(excess)}}{AgNO_3} \longrightarrow \underset{\substack{(108+35.5)\\ = 143.5 \text{ g}}}{AgCl} + HNO_3$$

143.5 g of AgCl is obtained from HCl = 36.5 g

0.1435 g of AgCl is obtained from HCl = $\frac{36.5}{143.6}$ × 0.1435 g

36.5 g of HCl = 1 gram equivalent of HCl

$$\therefore \quad \frac{36.5 \times 0.1435}{143.5} \text{g of HCl}$$

$$= \frac{36.5 \times 0.1435}{143.6 \times 36.5}$$

$$= \frac{1}{1000} \text{ g equivalent}$$

$\therefore$ 10 mL of HCl contains HCl = $\frac{1}{1000}$ g equivalent

1000 mL of HCl contains HCl = $\frac{1}{10}$ g equivalent

Hence, Strength of HCl solution = 0.1 g eq. L^{-1}

$\therefore$ Normality of HCl solution = 0.1 N

EXAMPLE 109. *Calculate the (a) molarity (b) normality of the phosphoric acid solution (sp. gravity 1.426 and containing 60% by weight of pure* H_3PO_4*). Atomic mass of P = 31.* **(BCECE, 2004)**

SOLUTION.

Weight of H_3PO_4 in 100 g solution

= 60 g;

Weight of water = 100 − 60 = 40 g

(*a*) *Calculation of molarity*

Molecular mass of

$H_3PO_4 = 3 \times 1 + 31 + 4 \times 16$

$= 98 \text{ g mol}^-$

Moles of H_3PO_4 in 60 g

$$= \frac{60}{98} = 0.612$$

Volume of 100 g solution

$$= \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.426} = 70.13 \text{ mL}$$

$$\text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in mL}} \times 1000$$

$$= \frac{0.612}{70.13} \times 1000 = 8.73 \text{ M}$$

(*b*) *Calculation of normality*

$$\text{Eq. wt. of } H_3PO_4 = \frac{\text{Mol.wt.}}{\text{Basicity}} = \frac{98}{3}$$

Normality = Molarity × Basicity = 8.73 × 3

= 26.19 N

$$\text{Alternatively, } N = \frac{\text{No. of gram equivalents}}{\text{Volume of solution (mL)}} \times 1000$$

$$= \frac{60 \times 3 \times 1000}{98 \times 70.13} = \mathbf{26.19\ N.}$$

EXAMPLE 110. *The Henry's law constant for the solubility of* N_2 *gas in water at 298 K is 1.0 × 10^5 atm. The mole fraction of* N_2 *in air is 0.8. The number of moles of* N_2 *from air dissolved in 10 moles of water at 298 K and 5 atm is*

(*a*) 4.0×10^{-4} (*b*) 4.0×10^{-5}
(*c*) 5.0×10^{-4} (*d*) 4.0×10^{-6}

(IIT-JEE, 2009)

Solution. Henry's law constant, $K_H = 1.0 \times 10^5$ atm; mole fraction of N_2, $x_{N_2} = 0.8$; partial pressure of N_2, p_{N_2} = ?; no. of moles of N_2, n_{N_2} = ? P = 5 atm. We know that:

$$p_{N_2} = x_{N_2} \times P = 0.8 \times 5 \text{ atm} = 4.0 \text{ atm}$$

But, $p_{N_2} = x_{N_2} \times K_H$

$$\therefore \quad 4 = x_{N_2} \times 1.0 \times 10^5;$$

$$x_{N_2} = \frac{4}{1.0 \times 10^5} = 4 \times 10^{-5}$$

no. of mol of

H_2O, n_{H_2O} = 10; no. of mol of N_2, n_{N_2} = ?

$$\therefore \quad x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}};$$

$$4 \times 10^{-5} = \frac{n_{N_2}}{10 + n_{N_2}} \simeq \frac{n_{N_2}}{10}$$

$$\therefore \quad n_{N_2} = 4 \times 10^{-5} \times 10^1 = 4 \times 10^{-4}.$$

So, the correct answer is (*a*).

Example 111. *What concentration of nitrogen should be present in a glass of water at room temperature? Assume a temperature of 25°C, a total pressure of 1 atmosphere and mole fraction of nitrogen in air of 0.78 [K_H of nitrogen = 8.42×10^{-7} M/mm Hg].* **(DB, 2009)**

Solution.

$$p_{N_2} = 1 \text{ atm};$$

$$p_{N_2} = K_H \times x_{N_2} \text{ (Henry's law)}$$

$$\therefore \text{ mole fraction; } x_{N_2} = p_{N_2}/K_H = 1/8.42 \times 10^{-7}$$

$$\text{But} \quad x_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{H_2O}} = \frac{n_{N_2}}{n_{H_2O}};$$

$$n_{N_2} = x_{N_2} \times n_{H_2O}$$

$$\text{or} \quad n_{N_2} = \frac{1}{8.42 \times 10^{-7}} \times 55.5$$

$$= 6.59 \times 10^7 \text{ mol}$$

$$\left\{\because n_{H_2O} = \frac{1000}{\text{mol. mass of } H_2O = 18} = 55.5 \text{ mol}\right\}$$

$\therefore$ Concentration of

$$N_2 \text{ in } H_2O = 6.59 \times 10^7 \text{ mol L}^{-}$$

Example 112. *Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of solution is:*

(*a*) 1.78 M (*b*) 2.00 M
(*c*) 2.05 M (*d*) 2.22 M **(IIT-JEE, 2011)**

Solution. *Wt. of water = 1000 g; wt of urea = 120 g. So, total wt. of solution = 1000 + 120 = 1120 g. Also, total volume of solution in mL = Mass/density = 1120/1.15 = 973.91 mL*

$$\text{Molarity, } M = \frac{\text{Wt.} \times 1000}{\text{Mol. wt.} \times \text{Vol of solution}}$$

$$= \frac{120 \times 1000}{60 \times 973.91} = 2.05 \text{ M}$$

So, the correct answer is (*c*).

Example 113. *When a gas is bubbled through water at 298 K, a very dilute solution of the gas is obtained. Henry's law constant for the gas at 298 K is 100 k bar. If the gas exerts a partial pressure of 1 bar, the number of millimoles of the gas dissolved in one litre of water is:*

(a) 0.555 *(b) 5.55*
(c) 0.0555 *(d) 55.5*
(e) 5.55×10^{-4} **(Kerala PMT, 2012)**

Solution. Given: partial pressure of gas, p = 1 bar; K_H = 100 *k* bar = 100×10^3 bar. But $p = K_H \times$ mole fraction. So:

$$\text{Mole fraction} = p/K_H = \frac{1 \text{ bar}}{100 \times 1000 \text{ bar}} = 10^{-5}$$

Weight of water = 1 L = 1000 mL = 1000 g; mol. wt. of $H_2O = (2 \times 1) + 16 = 18 \text{ g mol}^{-}$

$\therefore$ Moles of water = wt./Mol. wt. = 1000/18 = 55.5.

Let x = moles of gas dissolved. So:

Mole fraction, $10^{-5} = \dfrac{x}{55.5 + x}$. Since x is very small as compared to 55.5, it is neglected from the denominator.

$\therefore$ $10^{-5} = \dfrac{x}{55.5}$ or $x = 55.5 \times 10^{-5}$ moles $= 55.5 \times 10^{-5} \times 10^3$ milli moles $= 55.5 \times 10^{-2}$ milli moles = 0.555 milli moles. So, the correct answer is (*a*).

Example 114. *29.2 % (w/w) HCl stock solution has a density of 1.25 g/mL. The molecular weight of HCl is 36.5 g mol⁻. The volume (mL) of stock solution required to prepare a 200 mL solution of 0.4 M HCl is:*

(a) 2 *(b) 4*
(c) 6 *(d) 8*

(IIT-JEE, 2012)

Solution. Volume of HCl solution

$$= \frac{\text{Mass}}{\text{density}} = \frac{100 \text{ g}}{1.25 \text{ g(mL)}^{-}} = 80 \text{ mL}$$

wt. of HCl = 29.2 g; Mol. wt. of HCl = 36.5 g mol^{-}

$$\therefore \text{Molarity} = \frac{\text{wt.}}{\text{mol wt.}} \times \frac{1000}{\text{vol in mL}} = \frac{29.2}{36.5} \times \frac{1000}{80} = 10 \text{ M}$$

Using the relation: $M_1V_1 = M_2V_2$, we have

$$10 \times V_1 = 0.4 \times 200\ ;\ V_1 = 8$$

So, the correct answer is (*d*).

Example 115. *Two solutions of HCl, A and B have concentrations of 0.5 N and 0.1 M respectively. The volume of solutions A and B required to make 2 litre of 0.2 N HCl are:*

(a) 0.5 L of A + 1.5 L of B
(b) 1.5 L of A + 0.5 L of B
(c) 1.0 L of A + 1.0 L of B
(d) 0.75 L of A + 1.25 L of B

(AMU,Engg. 2012)

Solution. Total volume = 2 L. Let volume of $A = xL$. So, volume of $B = (2 - x)$ L. Since HCl is a monobasic acid, its normality is equal to its molarity. We know:

$$M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$$

$$0.5\,x + 0.1\,(2 - x) = 0.2\,(x + 2 - x)\,;\ 0.5\,x + 0.2 - 0.1\,x = 0.4$$

or $0.4\,x = 0.2$; $x = 0.5$ L

$\therefore$ Volume of $A = 0.5$ L and volume of $B = 2 - 0.5 = 1.5$ L

So, the correct answer is (*a*).

Example 116. *0.3 mole of $Ba(OH)_2$ is mixed with 0.6 mole of H_2SO_4. The number of moles of $BaSO_4$ formed will be:*

(a) 0.1	*(b) 0.2*
(c) 0.3	*(d) 0.4*

Solution. We know that equivalent of Ba $(OH)_2$ = Equivalent of H_2SO_4

Since equivalent pertains to normality and mole pertain to molarity and normality = Molarity × valence factor. Hence,

Equivalent of $Ba(OH)_2 = 0.3 \times 2 = 0.6$; Equivalent of $H_2SO_4 = 0.6 \times 2 = 1.2$. Since 0.6 value is less than 1.2, $Ba(OH)_2$ is a limiting reactant. Hence:

Moles of $BaSO_4$ = Equivalent of $BaSO_4$/Valence factor $= 0.6/2 = 0.3$

So, the correct answer is (*c*).

Example 117. *The density of a 3 M sodium thiosulphate ($Na_2S_2O_3$) solution is 1.25 g/mL. Calculate the percent by weight of sodium thiosulphate.*

(a) 12.64%	*(b) 37.92%*
(c) 0.87%	*(d) 63.21%*

(AMU, Engg. 2012)

Solution. Wt. of $Na_2S_2O_3$ solution = Volume × density $= 1000 \times 1.25 = 1250$ g

$$\text{Molarity} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Vol. of solution in mL}}$$

[$\because$ Mol. wt. of $Na_2S_2O_3 = 2 \times 23 + 2 \times 32 + 3 \times 16 = 158$]

$$3 = \frac{wt.}{158} \times \frac{1000}{1000};\ \text{wt.} = 3 \times 158 = 474\text{ g}$$

$$\therefore\ \%\text{ age by wt. of } Na_2S_2O_3 = \frac{474}{1250} \times 100 = 37.92.$$

So, the correct answer is (*b*).

Example 118. *The mole fraction of methanol in its 4.5 molal aqueous solution is:*

(a) 0.250	*(b) 0.125*
(c) 0.100	*(d) 0.075*
(e) 0.055	

(Kerala PET, 2012)

Solution. Let methanol = x mol; water = y mol.

$\therefore$ Mass of water = y × mol. wt. of H_2O (= 18) = 18 y.

$$\therefore\ \text{Molality, } 4.5 = \frac{x}{18\,y} \times 1000;\ \frac{x}{y} = \frac{4.5 \times 18}{1000} = 0.081$$

Mole fraction of methanol =

$$\frac{x}{x+y} = \frac{x/x}{(x/x)+(y/x)} = \frac{1}{1+y/x}$$

$$= \frac{1}{1+\dfrac{1}{0.081}} = \frac{0.081}{1.081} = 0.075$$

So, the correct answer is (*d*).

Example 119. *The density of a solution prepared by dissolving 120 g of urea (molar mass 60 u) in 1000 g of water is 1.15 g. $(mL)^{-}$. The molarity of this solution is:*

(a) 1.78 M	*(b) 1.02 M*
(c) 2.05 M	*(d) 0.50 M*

(AIEEE, 2012)

Solution. Mass of solvent = 1000 g; mass of solute = 120 g.

$\therefore$ Mass of solution = 1000 + 120 = 1120 g; density = 1.15 g $(mL)^{-}$.

$\therefore$ Volume of solution = Mass/density = 1120/1.15

$$\text{Molarity} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{120}{60} \times \frac{1000}{1120} \times 1.15 = 2.05\text{ M.}$$

So, the correct answer is (*c*).

Example 120. *The weight of oxalic acid that will be required to prepare a 1000 mL (N/20) solution is:*

(a) (126/100)g	*(b) (63/40)g*
(c) (63/20)g	*(d) (126/20)g*

(W.B.-JEE, 2012)

Solution. Mol. wt. of oxalic acid, $H_2C_2O_4.\ 2H_2O$ = $(2 \times 1) + (2 \times 12) + (4 \times 16) + 2\,[(2 \times 1) + 16] = 126\text{ g mol}^{-}$; Eq. wt. of oxalic acid = Mol. wt./charge on cation = $\dfrac{126}{2} = 63$. But:

$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{vol in mL}}$$

$$\frac{1}{20} = \frac{w}{63} \times \frac{1000}{1000};\ w = \frac{63}{20}.$$

So, the correct answer is (*c*).

Example 121. *The vapour pressures of two liquids A and B in their pure state are in the ratio 1 : 2. A binary solution of A and B contains A and B in the mole proportion of 1 : 2. The mole fraction of A in the vapour phase of the solution will be:*

(a) 0.33 *(b)* 0.2 *(c)* 0.25 *(d)* 0.52

(Karnataka, CET, 2012)

Solution. Moles of $A = 1$; moles of $B = 2$; Total moles $= 1 + 2 = 3$.

But:

Mole fraction of A

$$= \frac{\text{mol of A}}{\text{mol of A} + \text{mol of B}} = \frac{1}{1+2} = \frac{1}{3} = 0.33.$$

Thus, the correct answer is (*a*).

Example 122. *500 cm^3 of 0.5 N HCl solution was heated till its volume left behind was 300 mL, 1.5 g of HCl. The normality of residual solution is:*

(a) 0.764 *(b)* 0.22

(c) 1.1 *(d)* 1.528 **(J and K, 2012)**

Solution. Total milliequivalents of HCl

$$= \text{Normality} \times \text{volume}$$
$$= 0.5 \times 500 = 250.$$

$$\text{Milliequivalents of HCl given out} = \frac{1.5}{36.5} \times 500 = 20.54$$

$\therefore$ Milliequivalents of HCl left behind $= 250 - 20.54 = 229.46$

$$\therefore \text{ New normality} = \frac{229.46}{300} = 0.764.$$

So, correct answer is (*a*).

Example 123. *Calculate the percentage of free SO$_3$ in 119% sulphuric acid by weight.* **(H.P.B. 2013)**

Solution. SO_3 dissolves in H_2SO_4 to give oleum ($SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$). 119% H_2SO_4 weight means that (119 – 100 = 19 g) i.e., 19g water when added to 100 g of H_2SO_4 sample, will combine with free SO_3 in the oleum to give only 100% H_2SO_4.

$\therefore$ Percentage of free SO_3 in the given sample of oleum

$$= \frac{80(119-100)}{18} = 84.4\%$$

[$\because$ Mol. wt. of $SO_3 = 32 + (3 \times 16) = 80$ g mol^{-},
of $H_2O = (2 \times 1) + 16 = 18$ g mol^{-}.

Example 124. *Calculate the number of spectral lines emitled in a spectrum when an electron jumps from 4th orbit to second orbit.* **(Haryana Board, 2013)**

Solution. Number of spectral lines in a spectrum

$$= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}. \text{ Here } n_2 = 4, n_1 = 2.$$

$$\therefore \text{ Number of spectral lines} = \frac{(4-2)(4-2+1)}{2}$$
$$= 2 \times 3/2 = \mathbf{3} \textbf{ Ans.}$$

Note. For an atom of principal qucmtum number, n

(*i*) There are number of non-spherical nodes = l.
(*ii*) There are 'n–l–1' radial nodes or spherical nodes
(*iii*) There are 'l' angular nodes
(*iv*) There are total 'n – 1' nodes.

PROBLEMS FOR PRACTICE

1. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, the molar concentration of Na^+ ion and CO_3^{2-} ion are respectively (molar mass of Na_2CO_3 = 106 g mol^{-})
   (*a*) 0.955 M and 1.910 M
   (*b*) 1.910 M and 0.955 M
   (*c*) 1.90 M and 1.910 M
   (*d*) 0.477 M and 0.477 M **Ans (*b*)** **(CBSE PMT, 2010)**
2. Insulin contains about 0.08% by weight of sulphur. What would be the approximate molecular mass of insulin if one sulphur atom is present in a molecule of insulin ?
   (*a*) 40,000 (*b*) 2560
   (c) 20,000 (*d*) 25600
   Ans. (*a*) **(AIIMS, 2010)**
3. 112.0 mL of NO_2 was liquefied, the density of the liquid being 1.15 g (mL)$^{-}$. Calculate the volume and number of molecules in the liquid NO_2.
   (*a*) 0.10 mL, 3.01×10^{22} (*b*) 0.20 mL, 3.01×10^{21}
   (*c*) 0.20 mL, 6.02×10^{23} (*d*) 0.40 mL, 6.02×10^{21}
   Ans. (*b*)
4. Calculate the density of a 6.9 M solution of KOH in water that contain 30% by weight of KOH (at. wt., K = 39, O = 16, H = 1). (**Ans.** 1.288 g (mL^{-})
   Mol. wt. of KOH = 56 g mol^{-} ;
   Wt. of 6.9 mol KOH = 6.9 × 56 = 386.4 g.
   386.4 g KOH is present in solution
   $$= \frac{100 \times 386.4}{30} = 1288 \text{ g};$$
   $$\text{Density} = \frac{1288 \text{ g}}{1000 \text{ mL}} = \mathbf{1.288 \text{ g (mL)}^{-} \text{ Ans.}}]$$
5. Calculate the molality of potassium carbonate solution which is formed by dissolving 2.5 g of it in one litre solution. (density of solution = 0.85 g (mL)$^{-}$) **Ans.** 0.02 m **(PSEB 1992)**
   Mass of solution = 1000 × 0.85 = 850 g ;
   wt. of solvent = 850 – 2.5 = 847.5 g
   $$\therefore \quad m = \frac{2.5}{138(=\text{mol.wt.of } K_2CO_3)} \times \frac{1000}{847.5}$$
   $$= \mathbf{0.02m}$$

6. The density of 10% by mass of KCl solution in water is 1.06 g $(mL)^{-}$. Calculate the molarity and molality of the solution. **Ans.** 1.49 m, 1.42 m

(PSEB 2001, 2003)

wt. of KCl = 10 g ;

wt. of water = 100 – 10 = 90 g

mol. wt. of KCl = 39 + 35.5 = 74.5 g mol^{-},

$$\text{volume of solution} = \frac{100}{1.06} = 94.33 \text{ mL.}$$

$$\text{So,} \quad \text{molality} = \frac{10}{74.5} \times \frac{1000}{90} = \mathbf{1.49\ m.\ Ans.}$$

$$\text{molarity} = \frac{10}{74.5} \times \frac{1000}{94.33} = \mathbf{1.42\ m.\ Ans.}$$

7. Calculate the moles of methanol in 5L of its 2 m solution if the density of solution is 0.981 kgL^{-} (molar mass of CH_3OH = 32 g mol^{-}). (**Ans.** 9.22 mol)

(CBSE, 2002)

Mass of 5 L solution = 5 L × 0.981 kgL^{-} = 4.905 kg

$$= 4.905 \text{ Kg} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 4905 \text{ g.}$$

Mass of 2 m solution

= Mass of solvent + mass of solute

= 1000 g + (2 × 32) = 1064 g

1064 g solution contain

CH_3OH = 2 mol.

Hence 4905 g solution contain

$$CH_3OH = \frac{2 \times 4905}{1064} = \mathbf{9.22\ mol} \qquad \textbf{Ans.}$$

8. Calculate the mole fraction of rectified spirit (95% ethyl alcohol by mass.)

Ans. $x_{C_2H_5OH} = 0.882$; $x_{H_2O} = 0.118$ **(PSEB, 1998)**

Mol wt. of C_2H_5OH = 46 g mol^{-}, that of H_2O = 18, wt. of water = 100 – 95 = 5 g, wt. of C_2H_5OH = 95 g

Ans. $x_{C_2H_5OH} = 0.882$, $x_{H_2O} = 0.118$

9. The partial pressure of a gaseous hydrocarbon over a saturated solution containing 3.28×10^{-2} g of the hydrocarbon is one bar. Calculate the partial pressure of gas if the solution contains 2.5×10^{-2} g of the gas. (**Ans.** 0.762 bar)

$$\frac{m_1}{p_1} = \frac{m_2}{p_2};$$

$$\frac{3.28 \times 10^{-2}}{1 \text{atm}} = \frac{2.5 \times 10^{-2} \text{g}}{p_2}$$

So, p_2 = **0.762 bar Ans.**

10. Mole fraction of a given sample of I_2 and C_6H_6 is 0.2. The molality of iodine in C_6H_6 is :

(*a*) 0.32 (*b*) 3.2

(*c*) 0.032 (*d*) 0.48

Ans. 3.2. (BHU, 2010)

Note. (*i*) For a strong acid, pH = – log $[H_3O^+]$ = – log [N]

(*ii*) For a strong base, pOH = – log $[OH^-]$ = – log [N]

Where 'N' represents normality of a strong acid or strong base.

(*iii*) If *x meq.* of an acid and *y meq.* of a base are mixed,

(Where *meq.* = N × V in mL ; *N* = M × acidity or baricity, then;

$$\text{N (acid) left} = \frac{x - y}{V \text{ in } mL}; \ \text{N (base) left} = \frac{y - x}{V \text{ in } mL}$$

18

CHAPTER

Solution–Colligative Properties

18.1 COLLIGATIVE PROPERTIES

The colligative properties of a dilute solution are such properties which depend upon the number of solute particles present in a known volume of a given solvent. These do not depend upon the nature (*e.g.*, composition, constitution etc) of the solute. Following are the colligative properties,

(*i*) Relative lowering in vapour pressure.
(*ii*) Elevation in boiling point.
(*iii*) Depression in freezing point.
(*iv*) Osmotic pressure.

1. Relative lowering of vapour pressure. For a binary solution of a **non-volatile solute** in a volatile solvent:

Lowering of vapour pressure = $p_A{}^o - p_s$ and

Relative lowering of vapour pressure $= \dfrac{p_A^o - p_s}{p_A^o}$

where $p_A{}^o$ = vapour pressure of pure solvent.

ps = vapour pressure of solution;

$p_s < p_A{}^o$

where p_s or p (solution) = $p_A{}^o \, x_A$

where x_A = mole fraction of solvent.

Raoult's law. According to this law, relative lowering of vapour pressure is equal to mole fraction of solute, x_B. Thus :

$$\frac{p_A^o - p_s}{p_A^o} = x_B$$

$$= \frac{\text{no. of mol of solute}(n_2)}{\text{no. of mol of solute}(n_2) + \text{no. of mol of solvent}(n_1)}$$

$$\frac{p_A^o - p_s}{p_A^o} = \frac{n_2}{n_1 + n_2} \qquad \text{...(1)}$$

For very dilute solutions, n_2 being very small, it can be neglected. Thus :

$$\frac{p_A^o - p_s}{p_A^o} = x_B = \frac{n_2}{n_1} \qquad \text{...(2)}$$

Let W_1 = wt. of solvent;

M_1 = mol. wt. of solvent

W_2 = wt. of solute;

M_2 = mol. wt. of solute

$$\therefore \quad n_1 = \frac{W_1}{M_1};\ n_2 = \frac{W_2}{M_2}$$

Substituting these values in (2), we get :

$$\frac{p_A^o - p_s}{p_A^o} = \frac{W_2 / M_2}{W_1 / M_1} = \frac{W_2\ M_1}{W_1\ M_2} \qquad \text{...(3)}$$

18.2 RAOULT'S LAW AND DALTON'S LAW OF PARTIAL PRESSURES COMBINED

According to Dalton's law of partial pressure, total pressure, P is given by $P = p_A + p_B$ when vapours of a liquid behave as ideal gas. P_A and p_B represent partial pressure of components A and B respectively **Or** $P = x_A P_A{}^o + x_B P_B{}^o$. Since $x_B = 1 - x_A$.

Hence $P = x_A P_A{}^o + (1 - x_A)\, P_B{}^o$

Or $\boldsymbol{P = P_B{}^o + (P_A{}^o - P_B{}^o)\, x_A}$

EXAMPLE 1. *An ideal solution was prepared by mixing 40g of methyl alcohol and 60g of ethyl alcohol. If vapour pressure of methyl alcohol and ethyl alcohol respectively are 88.7 and 44.5 mm Hg, then find the total pressure of the solution.*

SOLUTION. Mol. wt. of methyl alcohol, $CH_3OH = 12 + 3 + 16 + 1 = 32$ g mol$^-$

Mol. wt. of ethyl alcohol,

$C_2H_5OH = (2 \times 12) + (5 \times 1) + 16 + 1$

$= 46$ g mol$^-$

Number of moles of

$$CH_3OH = \frac{\text{wt}}{\text{mol. wt}} = \frac{40\text{g}}{32\text{g mol}^-}$$

$= 1.25$ mol

Number of moles of

$$C_2H_5OH = \frac{\text{wt}}{\text{mol. wt}} = \frac{60\text{g}}{46\text{g mol}^-}$$

$= 1.30$ mol

x_A(= mole fraction of CH_3OH)

$$= \frac{1.25}{1.25+1.30} = \frac{1.25}{2.55} = 0.49$$

x_B(= mole fraction of C_2H_5OH) = 1 – 0.49 = 0.51

Total pressure of solution,

$$P = x_A P_A^{\,o} + x_B P_B^{\,o}$$
$$= (0.49 \times 88.7) + 0.51(44.5)$$
$$= 43.46 + 22.69$$
$$= \mathbf{66.15\ mm\ Hg\ Ans.}$$

18.3 COMPOSITION OF VAPOURS AND DALTON'S LAW OF PARTIAL PRESSURES

When liquids and their vapours are in mutual equilibrium, their composition is not necessarily same. It is because the vapour pressure should be richer in more volatile component. It is confirmed as follows. Let y_A and y_B be the mole fractions of components *A* and *B* in **vapour phase** respectively. If mixture of vapours behave as ideal gas, then :

$$y_A = \frac{p_A}{P} \quad \text{and} \quad y_B = \frac{p_B}{P}$$

Or $$y_A = \frac{x_A p_A^o}{p_B^o + (p_A^o - p_B^o)x_A}$$

and $$y_B = 1 - y_A$$

Example 2. *The mole fraction of toluene in a benzene – toluene solution is 0.6. Calculate the composition of the vapour which is in equilibrium at 30°C (p^o_{tol} = 37.0 torr; p^o_{benz} = 119.0 torr).*

Solution. We know total pressure,

$$P = x_A P_A^{\,o} + x_B P_B^{\,o}.$$

Hence, $$P = x_{\text{Benz}}\, p^o_{\text{Benz}} + x_{\text{tol}}\, p^o_{\text{tol}}$$
$$= 0.4 \times 119 + 0.6 \times 37$$
$$[\because x_{\text{benz}} = 1 - x_{\text{tol}} = 1 - 0.6 = 0.4]$$
$$= 47.6 + 22.2 = 69.8 \text{ torr.}$$

Using the relation for Dalton's law for mole fractions in vapour phase, we have :

$$y_{\text{benz}} = \frac{P_{\text{benz}}}{P} = \frac{47.6}{69.8} = 0.682 \textbf{ Ans.}$$
$$y_{\text{tol}} = 1 - 0.682 = \mathbf{0.318} \quad \textbf{Ans.}$$

18.4 CONDENSATION OF VAPOURS OF SOLUTION

Consider a solution containing liquids A and B. If the vapours of this solution are condensed, the composition of the liquids A and B in this condensate (say C) will remain same. If this condensate C is changed into vapours, we get vapours of A and B again. Now condense these vapours to get condensate, D. It is found that the composition of liquids A and B in D will again be the same.

Example 3. *Consider an ideal solution containing two liquids A and B. On heating to 90°C, the vapour pressures exerted by A and B are 200 and 150 mm Hg respectively. If the vapours above the ideal solution consisting of 1 mole of A and 1 mole of B are condensed and the condensate heated to 90°C again, vapours are again formed. If these are again condensed to a liquid, X, calculate the vapour pressure of A in the vapours of liquid, X.*

Solution. We know $P = x_A P_A^{\,o} + x_B P_B^{\,o}$ (Raoult's law).

Or $P = (x_A \times 200) + x_B(150) = 200x_A + 150x_B$

Since, vapours above solution contain one mole of *A* and one mole of *B*, mole fraction of *A* ($=x_A$) = mole fraction of *B* ($=x_B$) = $\frac{1}{1+1}$ = **0.5.**

Hence $$0.5 = \frac{200x_A}{P} \qquad ...(i)$$

$$0.5 = \frac{150x_B}{P} \qquad ...(ii)$$

Also, $x_A + x_B = 1$ Or $x_B = 1 - x_A$

Dividing (*i*) and (*ii*), we get,

$$\frac{0.5}{0.5} = \frac{\dfrac{200x_A}{P}}{\dfrac{150x_B}{P}} \text{ Or } 200\,x_A = 150\,x_B$$

$$\therefore \quad 200x_A = 150(1 - x_A)$$
or $$200\,x_A = 150 - 150\,x_A$$
$$\therefore \quad 350\,x_A = 150 \text{ or } \boldsymbol{x_A} = \frac{150}{350} = \mathbf{0.43};$$

$$\boldsymbol{x_B} = 1 - 0.43 = \mathbf{0.57}$$

Substituting the values of x_A and x_B in P = 200 x_A + 150 x_B.

We get $$\mathbf{P} = 200 \times 0.43 + 150 \times 0.57$$
$$= 86 + 85.5 = \mathbf{171.5\ mm.}$$

After condensation, in the condensate,

$$x'_A = 0.5 \text{ and } x'_B = 0.5.$$

Hence : $$P' = 0.5 \times 200 + 0.5 \times 150$$
$$= 100 + 75 = 175 \text{ mm.}$$

Let y_A and y_B are the mole fractions of *A* and *B* in vapour phase of condensate. Then

$$y_A = \frac{PA}{P'} = \frac{100}{175} = 0.57$$

$$y_B = 1 - 0.57 = 0.43$$

When the vapours are again condensed, liquid *X* is obtained. Let x''_A and x''_B are the mole fractions of *A* and *B* in liquid *X*.

Then, $$x''_A = 0.57 \text{ and } x''_B = 0.43.$$

Hence, $$P'' = 0.57 \times 200 + 0.43 \times 150$$
$$= 114 + 64.5 = 178.5 \text{ mm Hg.}$$

Thus, mole fraction of A in vapour phase of the second condensate will be :

$$y''_A = \frac{114}{178.5} = \mathbf{0.64\ Ans.}$$

18.5 CALCULATION OF VAPOUR PRESSURE OF WATER ABOVE A SOLUTION

Example 4. *Calculate the vapour pressure of water above sodium sulphate solution (density = 1.041 gcm*$^{-3}$*) having molarity, 0.411M(*$p^0_{H_2O}$ *= 23.80 mm Hg).*

Solution. Molar mass of

$$Na_2SO_4 = (2 \times 23) + 32 + (4 \times 16) = 142$$

$$\therefore \quad \text{Mass of } Na_2SO_4 = \text{molarity} \times \text{molar mass}$$

$$= 0.411 \times 142 = 58.36 \text{ g}$$

Mass of 1L (= 1000 mL) of solution

$$= \text{vol.} \times \text{density}$$

$$= 1000 \times 1.041 \text{ g.} = 1041 \text{ g.}$$

Mass of water in 1L solution

$$= 1041 - 58.36 = 982.64 \text{ g}$$

$$= \frac{982.64}{\text{Mol. wt. of } H_2O} = \frac{982.64}{18}$$

$$= 54.59 \text{ mol.}$$

Considering Na_2SO_4 to be completely ionised :

$$\underset{1 \text{ mol}}{Na_2SO_4} \rightleftharpoons \underset{2 \text{ mol}}{2Na^+} + \underset{1 \text{ mol}}{SO_4^{2-}} = 3 \text{ mol } i.e., 2 + 1 = 3 \text{ mol}$$

the total amount of solute species in solution

$$= 3 \times 0.411 = 1.233 \text{ mol}$$

Hence, mol fraction of water in solution

$$= \frac{54.59}{54.59 + 1.233} = \mathbf{0.978}$$

Thus, **vapour pressure of water above solution** = 0.978 × 23.80 = **23.28 mm Hg**

18.6 DETERMINATION OF MOL. WT. (M_2) OF SOLUTE

From equation (3) section 18.1, we have :

$$\frac{p°_A - p_s}{p°_A} = \frac{W_2 M_1}{W_1 M_2}$$

or

$$M_2 = \frac{W_2 M_1 p°_A}{W_1 (p°_A - p_s)}$$

Example 5. *The vapour pressure of a pure liquid A at 300 K is 150 torr. The vapour pressure of this liquid in a solution with a liquid B is 105 torr. Calculate the mole fraction of A in the solution if the mixture obeys Raoult's law.*

Hint. V.P. of pure liquid, A $p°_A$ = 150 torr; V.P. of liquid B in solution, p_s = 105 torr. Let mole fraction of solute B = x_B. Using Raoult's law $x_B = (P°_A - ps)/P°_A = (150–105)/150 = 0.3$. Hence mole fraction of solvent A = 1–0.3 = 0.7 **Ans.**

Example 6. *At 20°C, acetone has a vapour pressure of 162 torr; water's vapour pressure at 20°C is 17.5 torr. What is the vapour pressure of each component above a solution having 50 mol percent acetone and 50 mol percent water. Also calculate the total pressure if the solution is ideal.*

Hint. Mole fraction of acetone, CH_3COCH_3 = 50/100 = 0.5; mole fraction of water, H_2O = 50/100 = 0.5. Let p_{s_1} and p_{s_2} be the pressures of acetone and water in solution. Thus (*i*) for acetone, ($p°$ acetone $-p_{s_1}$)/$p°$ = 0.5 **Or** (162–p_{s_1})/162 = 0.5. Hence p_{s_1} = 81 torr. **Ans.** (*ii*) for water, ($p°$ water – p_{s_2})/$p°$ = 0.5 **Or** (17.5–p_{s_2})/17.5 = 0.5 **Or** p_{s_2} = 8.75 torr. **Ans.** Hence total pressure = 81 + 8.75 = 89.75 torr. **Ans.**

Example 7. *The vapour pressure of pure liquid A is 70 torr, at 27°C. It forms an ideal solution with another liquid B. The mole fraction of B is 0.2 and total pressure of the solution is 84 torr at 27°C. Find the vapour pressure of pure liquid B at 27°C.*

Solution. $P°_A = 70$ torr. $x_B = 0.2$.

But $x_A + x_B = 1$.

So, $x_A = 1 - x_B = 1 - 0.2 = 0.8$

$$p_A = P°_A x_A = 70 \times 0.8 = 56 \text{ torr}$$

Total pressure, $p_A + p_B = 84$ torr.

So, $p_B = 84 - p_A = 84 - 56 = 28$ torr.

$\therefore \quad p_B = p°_B \times x_B$

or

$$p°_B = \frac{p_B}{x_B} = \frac{28}{0.2} = 140 \textbf{ torr. Ans.}$$

Type. Calculation of lowering in V.P. ($p° - p_s$), relative lowering in V.P. $\left(\frac{p° - p_s}{p°}\right)$, molecular wt. of solute (M_B) and mole fraction of solvent (x_A). For a non-volatile solute.

Method (*i*) $\quad x_B = \left(\frac{p° - p_s}{p°}\right)$

(*ii*) **P** solution of non-volatile solute = $P°_A x_A$

Example 8. *The vapour pressure of water at 298 K is 23.75 mm of Hg. Calculate the vapour pressure at the same temperature over 5 % aqueous solution of urea (*NH_2CONH_2*).*

Solution. Hint. $\quad x_B = \frac{p° - p_s}{p°}$

where, $\quad x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A}$

Mol. wt. of NH_2CONH_2 = 14 + (2 × 1) + 12 + 16 + 14 + (2 × 1) = 60 g mol$^-$

$$\therefore \quad \frac{W_B M_A}{M_B W_A} = \frac{p° - p_s}{p°}$$

or

$$\frac{5 \times 18}{60 \times 95} = \frac{23.75 - p_s}{23.75}$$

$$\therefore \quad p_s = 23.375 \text{ mm.}$$

Example 9. *Vapour pressure of water at 293 K is 17.54 mm Hg and the vapour pressure of a solution of 108 g of a compound in 1000 g of water at the same temperature is 17.34 mm Hg. Calculate the molar mass of solute.*

Solution. $\quad x_B = \frac{p° - p_s}{p°}$

or

$$\frac{W_B M_A}{M_B W_A} = \frac{p° - p_s}{p°}$$

or $$\frac{108\times 18}{1000\times M_B} = \frac{17.54-17.34}{17.54}$$

Thus, $M_B = 170.49$ **Ans.**

EXAMPLE 10. *The vapour pressure of water at 293 K is 17.54 mm Hg and lowering of vapour pressure of urea solution is 0.07 mm Hg. Calculate relative lowering of vapour pressure (ii) Vapour pressure of solution (iii) mole fraction of urea and water.*

SOLUTION.

(*i*) $p^o_{H_2O} = 17.54$ mm,

$p^o - p_s$ = lowering in V.P. = 0.07 mm

Relative lowering in V.P.,

$$\frac{p^o-p_s}{p^o} = \frac{0.07}{17.54} = 0.00399$$

(*ii*) V.P of solution,

p_s = V.P. of solvent – lowering of V.P.

= 17.54 – 0.07 = 17.47mm

(*iii*) $x_B = \dfrac{p^o-p_s}{p^o}$ ∴ $x_{\text{urea}} = 0.00399$

(*iv*) $x_{H_2O} = 1 - x_{\text{urea}}$ *i.e.,* $x_A = 1 - x_B$

= 1 – 0.00399 = 0.99601 **Ans.**

EXAMPLE 11. *Two liquids A and B form an ideal solution. At 300 K, vapour pressure of solution containing 1 mol of A and 3 mol of B is 550 mm of Hg. At the same temperature, if one more mol of B is added to the mixture, the vapour pressure of the solution is increased by 10 mm. The vapour pressure of A and B in the pure state, will be respectively.*

(*a*) 200 and 300
(*b*) 300 and 400
(*c*) 400 and 600
(*d*) 500 and 600

(AIEEE, 2009)

SOLUTION. First solution.

$$P = p^0_A x_A + p^0_B x_B$$

$$550 = \left(p^0_A\times\frac{1}{1+3}\right)+\left(p^0_B\times\frac{3}{1+3}\right)$$

$$\left[\begin{array}{l}\therefore x_A = \dfrac{n_1}{n_1+n_2} = \dfrac{1}{1+3}\\[2mm] x_B = \dfrac{n_2}{n_1+n_2} = \dfrac{3}{1+3}\end{array}\right]$$

Or $550 = p^0_A\times 0.25 + p^0_B\times 0.75$ ...(1)

Second Solution. $P = p^0_A x_A + p^0_B x_B$

where $P = 550 + 10 = 560$ torr.

$$560 = \left(p^0_A\times\frac{1}{4+1}\right)+p^0_B\left(\frac{4}{4+1}\right)$$

$$\left(\because x_A = \frac{n_1}{n_1+n_2} = \frac{1}{4+1};\ x_B = \frac{n_2}{n_1+n_2} = \frac{4}{4+1}\right)$$

Or $560 = p^0_A\times 0.2 + p^0_B\times 0.8$ ...(2)

Total number of mol in first solution

= 1 + 3 = 4

Total number of mol in second solution

= 1 + (3+1) = 5

Multiplying equation (1) by 4 and (2) by 5 and subtracting, we get :

$$\begin{array}{rl} 2200 = p^0_A\times 1 + p^0_B\times 3 & ...(3)\\ 2800 = p^0_A\times 1 + p^0_B\times 4 & ...(4)\\ - \quad\ \ - \qquad\quad - & \\ \hline \end{array}$$

– 600mm = $-p^0_B$ **or** p^0_B = 600mm. **Ans.**

Substituting p^0_B = 600 mm in (3), we get :

$2200 = p^0_A + 3\times 600;$

$p^0_A = 2200 - 1800 = 400$ mm **Ans.**

So, the correct answer is (*c*)

EXAMPLE 12. *The vapour pressure in mm (Hg) of a $CH_3OH - C_2H_5OH$ binary solution, P at a certain temperature is represented by the equation, P = 254 – 119x where x is the mole fraction of C_2H_5OH. Find the vapour pressure of pure components.*

SOLUTION. We know that

$$P = p^o_{CH_3OH}\times x_{CH_3OH} + p^o_{C_2H_5OH}\times x_{C_2H_5OH}$$

$$P = p^o_{CH_3OH}\times(1 - x_{C_2H_5OH}) + p^o_{C_2H_5OH}\times x_{C_2H_5OH}$$

$$= p^o_{CH_3OH} - p^o_{CH_3OH}\times x_{C_2H_5OH} + p^o_{C_2H_5OH}\times x_{C_2H_5OH}$$

$$P = p^o_{CH_3OH} - x_{C_2H_5OH}\,[p^o_{CH_3OH} - p^o_{C_2H_5OH}] \quad ...(1)$$

But $P = 254 - 119x$ ...(2) given.

comparing equations (1) and (2) we get

$p^o_{CH_3OH} = 254$ mm ...(3)

$p^o_{CH_3OH} - p^o_{C_2H_5OH} = 119;\ 254 - p^o_{C_2H_5OH} = 119$

∴ $p^o_{C_2H_5OH} = 254 - 119 =$ **135 mm** **Ans.**

EXAMPLE 13. *What is the mass of non-volatile solute (molar mass, 60) that needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25% ? What will be the molality of the solution ?* **(ISC, 2010)**

SOLUTION. Molar mass of non-volatile solute = 60 g mol^{-}; molar mass of H_2O = 18g mol^{-}; mass of water = 100 g.

Let mass of non-volatile solute dissolved = (*a*) g.

∴ mol of non-volatile solute = $a/60$;

mol of H_2O = 100/18 = 5.55

Let vapour pressure of pure solvent = 1 atm.

∴ Decrease in V.P. = 1 × 25/100 = 0.25 atm.

V.P. of solution = 1.0 – 0.25 = 0.75 atm.

But mole fraction, $x_B = (p^o_A - p_A)/p^o_A$.

Thus : $$\frac{a/60}{(a/60)+5.55} = \frac{1-0.75}{1};$$

$$\frac{a/60}{(a/60)+5.55} = 0.25;$$

$$0.25\,(a/60 + 5.55) = a/60$$

$$\therefore \qquad \frac{a}{60} = 1.3875 + \frac{0.25a}{60};$$

$$\therefore \qquad \frac{a}{60} - \frac{0.25a}{60} = 1.3875$$

$$\text{Or} \qquad \frac{0.75a}{60} = 1.3875.$$

$$\text{Hence,} \qquad a = \frac{1.3875 \times 60}{0.75} = 111\text{g } \textbf{Ans}$$

Example 14. *Methanol and ethanol form nearly ideal solution at 300 K. A solution is made by mixing 32g methanol and 23g ethanol. Calculate the partial pressure of its constituents and total pressure of the solution. (at 300 K, p (CH_3OH) = 90 mm Hg, p(C_2H_5OH) = 51 mm Hg.* **(AISB 1991, PSEB, 2002)**

Hint. (*i*) Wt. of methanol, CH_3OH = 32 g.; g. mol. wt. of CH_3OH = 12 + (3 × 1) + 16 +1 = 32g; So, no. of moles of CH_3OH = 32/32 = 1.0. (*ii*) wt. of ethyl alcohol, C_2H_5OH = 23 g; g. mol. wt. of C_2H_5OH = (2 × 12) + (5 × 1) + 16 + 1 = 46g; so, no. of moles of C_2H_5OH = 23/46 = 0.5 (*a*) mole fraction of CH_3OH x_{CH_3OH}= 1/1+0.5 = 0.67 (*b*) mole fraction of C_2H_5OH $x_{C_2H_5OH}$ = 0.5/1+0.5 = 0.33. (*c*) Applying Raoult's law, partial V.P. of C_2H_5OH in solution = 90 × 0.67 = 60.3 mm; partial v.p. of C_2H_5OH in solution. = 51 × 0.33 = 16.83 mm **Ans.**

Example 15. *Calculate the mass of a non-volatile solute (molecular mass 40), which should be dissolved in 114 gm octane to reduce its vapour pressure to 80%.* **(HP Board, 2008)**

Solution. $P_s = \frac{80}{100}P°$; W_B = wt. of solute = ?; mol. wt. of solute, M_B = 40 g mol^{-}; wt. of solvent; W_A = 114 g mol^{-}; g. mol. wt. (M_A) of octane (C_8H_{18}) = (8 × 12) + (18 × 1) = 114 g mol^{-}. We know that :

$$\frac{P° - P_s}{P_s} = \frac{W_B}{M_B} \times \frac{M_A}{W_A};$$

$$\frac{P° - \frac{80}{100}P°}{\frac{80}{100}P°} = \frac{W_B \times 114}{40 \times 114}$$

$$\frac{P°\left(1 - \frac{80}{100}\right)}{P°\left(\frac{80}{100}\right)} = \frac{W_B}{40}; \frac{20}{100} \times \frac{100}{80} \times 40 = W_B;$$

$$W_B = 10\text{g} \qquad \textbf{Ans.}$$

Example 16. *The vapour pressure of pure benzene at 25°C is 639.7 mm Hg and the vapour pressure of a solution of solute in benzene at the same temperature is 631.9 mm Hg. Calculate the molality of the solution.* **(MLNR, 1989)**

Hint. p^o = 639.7 mm; p_s = 631.9 mm; molality, *m* = ?. According to Raoult's law, $(p^o - p_s)/p^o$ = mole fraction of solute = moles of solute/(moles of solute + moles of solvent) = [moles of solute/moles of solvent] when solution is very dilute. Hence, $(p^o - p_s)/p^o$ = moles of solute/moles of water solvent; **Or** (639.7 – 631.9)/639.7 = moles of solute/moles of solvent. **Or** 0.0122 × moles of solvent = moles of solute **Or** [0.0122 × 1000/78] = moles of solute. But molality = (moles of solute × 1000)/wt. of solvent, benzene, C_6H_6 (mol. wt., 78 g mol^{-}) = 1000 g = [(0.0122 × 1000/78)] 1000/1000 = 0.156 m or mol kg^{-}. **Ans.**

Example 17. *Vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solute weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of the solute ?* **(IIT, 1990 ISC, 2011)**

Hint. p^o = 640 mm, p_s = 600 mm.; wt. of non-volatile solute = 2.175*g*; wt. of solvent, benzene = 39*g*; mol. mass (M) of solute = ? ; g. mol. mass of solvent, C_6H_6 = (6 × 12) + (6 × 1) = 78*g*; no. of moles (n_2) of solute = wt/mol. mass = 2.175/M; no. of moles (n_1) of solvent C_6H_6 = wt./mol. mass = 39/78 = 0.5. According to Raoult's law, $(p^o - p_s)/p^o$ = mole fraction of solute = no. of moles of solute/(no. of moles of solute + no. of moles of solvent). Thus, (640 –600)/640 = (2.175/M)/(2/175/M) + 0.5 **Or** (40/640)= (2.175/M) / (2.175/M) + 0.5. **Or** 4M (0.5 + 2.175/M) = 2.175 × 64 **Or** 2M + 8.7 = 139.2 **Or** M = 65.25 **Ans.**

Example 18. *The vapour pressure of carbon tetrachloride at 30°C is 142 mm (Hg). 0.5 g of a non-volatile organic solute of molecular mass 65 is dissolved in 100 ml of carbon tetrachloride. What would be the vapour pressure of the solution ? Density of carbon tetrachloride is 1.58 g/ml.*

Hint. Wt. of solute = 0.5g; g. mol. wt. of solute = 65g; g. mol. wt. of solvent CCl_4 = 12 + (4 × 35.5) = 154 g; density of CCl_4 = 1.58 *g* (*mL*)$^{-}$. Mass of solvent CCl_4 = volume × density; 100 mL × 1.58 g (mL)$^{-}$ = 158 g. p^o = 142 mm. p_s = ?; n_1 = no. of moles of solvent = wt./mol. wt. = 158/154; n_2 = no. of moles of solute = wt/mol. wt. = 0.5/65 = 7.69 × 100^{-3}; n_1 = no. of moles of solvent = wt/mol. wt. = 158/154 = 1.026. We know $(p^o - p_s)/p^o = n_2/n_1 + n_2$. Substituting the values, we get, $(142 - p_s)$ /142 = (7.69 × 10^{-3}/(1.026 + 7.69 × 10^{-3} **Or** $(142 - p_s)/142$ = 7.44 × 10^{-3} or $142 - p_s$ = 142 × 7.44 × 10^{-3} = 1.056 or p_s = 142 – 1.056 = 140.94 mm. **Ans.**

Example 19. *Calculate the vapour pressure at 295 K of a 0.1 M solution of urea ($NH_2CO\ NH_2$, molar mass = 60). The density of solution may be taken as lg cm^{-3}. The vapour pressure of pure water at 295 K is 20 mm.*

Hint. P^o = 20 mm, *ps* = ? Wt. of urea, NH_2CONH_2 = 0.1 × 60 = 6 g; g. mol. wt. of NH_2CONH_2 = 14 + (2×1) + 12 + 16 + 14 + (2 × 1) = 60g. Wt. of water, H_2O = 1000 – 6 = 994 g; g. mol. wt. of H_2O = (2 × 1) + 16 = 18g; no. of moles (n_2) of solute, NH_2CONH_2 = 6/60 = 0.1; no. of moles (n_1) of solvent, H_2O = 994/18. = 55.2. Thus, mole fraction of solute, urea = $n_2/n_1 + n_2$ = 0.1/(0.1 + 55.2) = 0.1/55.3 = 1/553. We know, $(p^o - p_s)/p^o$ = mole fraction of solute; **Or** (20 – *ps*) /20 = 1/553 **Or** 20 – p_s = 20/553 = 0.036; **Or** *ps* = 20 – 0.036 = 19.96 mm **Ans.**

Example 20. *The vapour pressure of pure water at 30°C is 31.80 mm of Hg. How many grams of urea (mol. mass 60) should be dissolved in 100 g of water to lower the vapour pressure by 0.25 mm of Hg.* **(PSEB, 2001)**

Hint. Vapour pressure of pure water, $p^o = 31.80$ mm, wt. of urea = w_2 = ?, mol. mass of urea, $M_2 = 60$; wt. of solvent water, $W_1 = 100$ g; mol. mass (M_1) of water, H_2O = (2 × 1) + 16 = 18; lowering of vapour pressure, $p^o - p$ = 0.25 mm. We know that :

$(p^o - p/p^o) = (W_2 \times M_1)/M_2 \times W_1$. Substituting the values, we get; 0.25/31.8 = (W_2 × 18)/60 × 100. **Or** W_2 = 0.25 × 60 × 100/31.8 × 18 = 2.62g. **Ans.**

EXAMPLE 21. *15 g of glucose is added to 250 g of water at 293 K. If the vapour pressure of water at 293 K is 17.535 mm, calculate the lowering of vapour perssure of water at 293 K.*

Hint. Wt. of glucose, $C_6H_{12}O_6$ = 15 g; g. mol. wt. of $C_6H_{12}O_6$ = 180g; Wt. of water, H_2O = 250 g; g. mol. wt. of H_2O = 18g ; p^o H_2O = 17.535 mm. n_1 = no. of moles of solvent, H_2O = wt./mol. wt. = 250/18 = 13.88; n_2 = no. of moles of solute, glucose = wt./mol. wt. = 15/180 = 0.083. We know, $(p^o - p_s)/p^o = n_2/n_1 + n_2$. **Or** lowering of vapour pressure $(p^o - p_s) = p^o\,(n_2/n_1 + n_2)$. Substituting the values, we get,

$$p^o - p_s = 17.535(0.083)/(13.88 + 0.083)$$
$$= 17.535 \times 5.94 \times 10^{-3}$$
$$= \mathbf{0.104}\ \textit{mm} \qquad \textbf{Ans.}$$

EXAMPLE 22. *The vapour pressure of a dilute aqueous solution of glucose is 750 mm Hg at 373K. Calculate (i) molality and (ii) mole fraction of solute.*

SOLUTION. (*a*) $p^o_{H_2O}$ at 373 K = 760 mm; p_s = 750 mm.
We know mole fraction of glucose,

$$x_{glucose} = \frac{p^o - ps}{p^o} = \frac{760 - 750}{760}$$
$$= \frac{10}{760} = \frac{1}{76}$$

Also, $$x_{H_2O} = 1 - \frac{1}{76} = \frac{75}{76}$$

(*b*) Molality, $$m = \frac{\text{mole fraction of solute}}{\text{mole fraction of solvent}} \times \frac{1000}{\text{mol. wt. of solvent, } H_2O\ (=18)}$$
$$= \frac{\frac{1}{76}}{75/76} \times \frac{1000}{18}$$
$$= \frac{1}{76} \times \frac{76}{75} \times \frac{1000}{18}$$
$$= 0.74\ \text{m} \qquad \textbf{Ans.}$$

18.7 RAOULT'S LAW AND VAPOUR PRESSURE LOWERING

EXAMPLE 23. *At 28°C, the vapour pressure of water is 28.35 torr. Calculate the vapour pressure at 28°C of a solution prepared by dissolving 68g of cane sugar ($C_{12}H_{22}O_{11}$) in 1000 g of water. (At. wt. C = 12 , H = 1, O = 16).*

SOLUTION. g. mol. mass of $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 × 16) = 342 g : g mol. mass of H_2O = (2 ×1) + 16 = 18g.

∴ No. of moles of

$$C_{12}H_{22}O_{11} \text{ in } 68\ g = \frac{68\ g}{342\ g\ mol^{-}}$$
$$= 0.2\ mol\ C_{12}H_{22}O_{11}$$

No. of moles of

$$H_2O \text{ in } 1000g = \frac{1000\ g}{18\ g\ mol^{-}}$$
$$= 55.55\ mol\ H_2O$$

Total number of moles

$$= 0.2 + 55.55$$
$$= 55.75 \text{ mole.}$$

Mole fraction of

$$C_{12}\,H_{22}O_{11} = \frac{0.2}{55.75} = 0.0036;$$

mole fraction of $$H_2O = \frac{55.55}{55.75} = 0.9964.$$

First method. Vapour pressure depression = D*p* = (vapour pressure of pure solvent) (mole fraction of solute) = (28.35 torr.) (0.0036) = 0.10 torr.

Vapour pressure of solution = (28.35 – 0.10) torr = 28.25 torr.

Second method. Vapour pressure of solution = (vapour pressure of pure solvent) (mole fraction of solvent) = (28.35 torr.) (0.9964) = 28.25 torr.

EXAMPLE 24. *The vapour pressure in torr. of methyl alcohol-ethyl alcohol solutions at 40°C is represented by P = 119x + 135, where x is the mole fraction of methyl alcohol. Calculate the vapour pressures of the pure components at this temperature.*

SOLUTION. If $x = 0, p = 119 \times 0 + 135$ = 135 torr. = vapour pressure of ethyl alcohol.

If $x = 1, p = (119 \times 1) + 135 = 254$ torr. = vapour pressure of methyl alcohol.

EXAMPLE 25. *The vapour pressure of a pure liquid solvent A is 0.80 atm. When a non-volatile substance B is added to the solvent, its vapour pressure drops to 0.60 atm. Calculate the mole fraction of component B in the solution.*

SOLUTION. We know

$$P = p^o \times x_A;$$

∴ $$x_A = \frac{P}{p^o} = \frac{0.60\ atm}{0.80\ atm} = \mathbf{0.75}$$

But $$x_A + x_B = 1$$

∴ $$x_B = 1 - x_A = 1 - 0.75 = \mathbf{0.25}$$

EXAMPLE 26. *Calculate the lowering of the vapour pressure due to the solute in a 1.0 m aqueous solution at 100°C.*

SOLUTION. Lowering of vapour pressure,

$$p^o - ps = \frac{p^o n_2}{n_1} \qquad \text{......(1)}$$

$$n_1 = \frac{\text{wt. of } H_2O}{\text{g.mol. wt. of } H_2O} = \frac{1000\text{g}}{18\text{g}};$$

$$n_2 = 1$$

(∵ solution = 1.0 m)

Substituting the value of n_1 and n_2 in equation (1), we get :

Lowering of vapour pressure

$$= \frac{(1\ \text{atm})(1.0\ \text{mol})}{1000\ \text{g} / 18\ \text{g mol}^{-}}$$

$$= \mathbf{0.018\ atm}$$ **Ans.**

Example 27. *The vapour pressure of methyl alcohol, CH_3OH at 298K is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapour pressure of CH_3OH is 23.0 torr at 298 K.*

Solution. According to Raoult's law, the vapour pressure of solution p_s = vapour pressure of pure solvent, p° × mole fraction of solvent, x. Thus :

$$p_s = p^o x$$

or $$x = \frac{p_s}{p^o} = \frac{96.0\ \text{torr}}{23.0\ \text{torr}} = \mathbf{0.240\ Ans.}$$

Example 28. *At 298K, the vapour pressure of pure ethyl alcohol is 44 torr. and that of pure benzene is 100 torr. Assuming ideal behaviour, calculate the vapour pressure at 298K of a solution which contains 10.0g of each substance (At. wt., C = 12, H = 1, O = 16).*

Solution. Wt. of benzene, C_6H_6 = 10.0 g; g. mol. wt. of $C_6H_6 = (6 \times 12) + (6 \times 1) = 78$ g; wt. of ethyl alcohol, C_2H_5OH = 10.0g; g. mol. wt. of $C_2H_5OH = (2 \times 12) + (5 \times 1) + 16 + 1$ = 46.0g. Thus : No. of moles of $C_6H_6 = \frac{10}{78}$ =0.128; No. of moles of $C_2H_5OH = \frac{10}{46} = 0.217$

$$x_{C_6H_6} = \frac{0.128}{0.128 + 0.217} = 0.371;$$

$$x_{C_2H_5OH} = 1 - 0.371 = 0.629$$

$$\therefore \quad P_{C_6H_6} = p^{o}_{C_6H_6} x_{C_6H_6} = (100)\ (0.371) = 37.1\ \text{torr.};$$

$$P_{C_2H_5OH} = p^{o}_{C_2H_5OH}\, x_{C_2H_5OH} = (44)\ (0.629) = 28\ \text{torr.}$$

∴ Total pressure = 37.1 + 28 = 65.1 torr.

Example 29. *The vapour pressure of pure benzene, C_6H_6 is 268 torr. at 323 K. How many mol of non-volatile solute per mole of benzene are required to prepare a solution of benzene having 167.0 torr. vapour pressure at 323 K.*

Solution. p^{o}_{benz} = 268 torr; p_s = 167.0 torr; $x_{\text{benz.}}$ = ? ; x (non-volatile solute) = ? ; no. of mol of non-volatile solute = ?. According to Raoult's law :

$$p_s = p^{o}_{\text{benz}} x_{\text{benz}}$$

or $$x_{\text{benz}} = \frac{p_s}{p^{0}_{benz}} = \frac{167.0\ \text{torr}}{268.0\ \text{torr}} = \mathbf{0.623}$$

But x_{benz} + x (non-volatile solute) = 1

∴ x (non-volatile solute) = 1– 0.623 = **0.337.** Thus there are 0.377 mol of solute per 0.623 mol of benzene :

$$\frac{0.377\ \text{mol solute}}{0.623\ \text{mol benzene}} = \mathbf{0.605\ mol\ solute/mol\ benzene.}$$ **Ans.**

Example 30. *What weight of the non-volatile solute urea (NH_2CONH_2) needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25% ? What will be the molality of the solution ?* **(PSEB, 2011)**

Solution. (*i*) Vapour pressure of pure solvent = p°
Vapour pressure of solution = p

Wt. of solute, w_2 = ?; wt. of solvent, w_1 = 100g; mol. wt. of solute, NH_2CONH_2, $M_2 = 14 + (2 \times 1) + 12 + 16 + 14 + (2 \times 1) = 60$ g mol‾; mol. wt. of solvent, $H_2O = (2 \times 1) + 16$ = 18 g mol‾. We know that :

$$\frac{p^\circ - p}{p^\circ} = \frac{w_2 / M_2}{w_2 / M_2 + w_1 / M_1} \qquad \text{...(1)}$$

(Raoult's law)

Vapour pressure of solution,

$$p = p^\circ \times \text{mole fraction}$$

$$= p^\circ \times \frac{(100 - 25)}{100} = \frac{3}{4} p^\circ$$

Substituting the values in (1), we get :

$$\frac{p^\circ - \frac{3}{4} p^\circ}{p^\circ} = \frac{w_2 / 60}{(w_2 / 60) + \frac{100}{18}};$$

$$\frac{p^\circ \left(1 - \frac{3}{4}\right)}{p^\circ} = \frac{w_2 / 60}{(w_2 / 60) + 5.55};$$

$$\frac{1}{4} = \frac{w_2 / 60}{(w_2 / 60) + 5.55};$$

$$\frac{w_2}{60} + 5.55 = \frac{w_2}{60} \times 4 \ \text{ or } \ \frac{w_2}{15}$$

$$\therefore \quad 15\left(\frac{w_2}{60} + 5.55\right) = w_2;\ \frac{w_2}{4} + 83.25 = w_2;$$

$$w_2 - \frac{w_2}{4} = 83.25$$

Or $\frac{3}{4} w_2 = 83.25$. Hence $\boldsymbol{w_2}$ **= 111g. Ans**

(*ii*) $$\text{Molality} = \frac{\text{wt. of urea}}{\text{mol. wt. of urea}} \times \frac{1}{\text{wt. of water in kg}}$$

$$= \frac{111g}{60 \text{ g mol}^{-}} \times \frac{1}{\frac{100}{1000}\text{kg}}$$

$$= 18.52 \text{ mol kg}^{-} = \mathbf{18.52 \text{ m Ans.}}$$

Example 31. *The vapour pressure of pure benzene at a certain temperature is 200 mm Hg. At the same temperature, the vapour pressure of a solution containing 2g of non-volatile non-electrolytic solid in 78 g. of benzene is 195 mm Hg. What is the molecular weight of the solid ?* **(MLNR 1992)**

Solution. Vapour pressure of solvent, $p^{\circ} = 200$ mm; v.p. of solution, $p = 195$ mm; wt. of solute, $w_2 = 2$g; wt. of solvent, $w_1 = 78$ g; mol. wt. of solute, $M_2 = ?$, mol. wt. M_1 of solvent, $C_6H_6 = (6 \times 12) + (6 \times 1) = 78\text{g mol}^{-}$. We know that :

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{w_2 / M_2}{w_1 / M_1} = \frac{w_2\, M_1}{w_1\, M_2}$$

(Raoult's law)

$$\therefore \quad \frac{200 \text{ mm} - 195\text{mm}}{200\text{mm}} = \frac{2g \times 78g \text{ mol}^{-}}{78g \times M_2};$$

$$\frac{5}{200} = \frac{2g \text{ mol}^{-}}{M_2}$$

$$\therefore \quad M_2 = 2 \text{ g mol}^{-} \times \frac{200}{5}$$

$$= \mathbf{80 \text{ g mol}^{-}} \qquad \textbf{Ans.}$$

18.8 OSTWALD–WALKER'S DYNAMIC METHOD

This method is based on the measurement of relative lowering of vapour pressure $(p^{\circ} - p_s)/p^{\circ}$ where p° and p_s are the vapour pressures of pure solvent and solution respectively. The apparatus consists of bulbs *A* (filled with solution) and bulbs *B* (filled with pure solvent) and $CaCl_2$ U - tube to absorb vapours carried by air). A current of dry air is drawn through the apparatus. Air carries vapours of solvent from solution as well as of pure solvent. Amount of vapours carried by air from solution and pure solvent are proportional to the vapour pressure p_s and $(p^{o} - p_s)$ respectively. As a result, there is loss in weight of solution and pure solvent. From these losses in weights, the molecular weight of the solute can be determined.

Let w_2 = Loss in wt. in bulbs, *A*.

Thus $w_2 \propto p_s$ ...(1)

w_1 = Loss in wt. in bulbs, *B*.

Thus $w_1 \propto p^{\circ} - p_s$ ...(2)

Adding (1) and (2), we get, $w_1 + w_2 \propto p^{\circ}$ ...(3)

Hence from relations (2) and (3), we get :

$$\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{w_1}{w_1 + w_2}$$

$$= \frac{\text{Loss in wt. in A}}{\text{Loss in wt. in A + B}}$$

$$= \frac{\text{Loss of wt. in A}}{\text{Gain in CaCl}_2 \text{ U-tube}}$$

Where $\frac{p^{\circ} - p_s}{p^{\circ}}$ = relative lowering in vapour pressure

But $$\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{w_2\, M_1}{w_1\, M_2}$$

where M_1 and M_2 are the molar masses (or mol. wt.) of solvent and solute respectively.

Example 32. *A current of dry air is passed through a solution containing 38g of solute in 100 g of water and then through water. The loss in weight of water was 0.0551 g and the total weight of water absorbed in H_2SO_4 tube was 2.2117g. Calculate the molecular weight of the dissolved solute.*

Solution. Loss in wt. of solvent water = 0.0551 g = w_1

Gain in weight by H_2SO_4 tube = 2.2117 g.

M_1 = Mol. wt. of solvent, $H_2O = (2 \times 1) + 16 = 18 \text{ g mol}^{-}$

W_2 = wt. of solute = 38 g ; W_1 = wt. of solvent = 100 g

M_2 = mol. wt. of solute = ? we know

$$\frac{p^{o} - p_s}{p^{o}} = \frac{W_2\, M_1}{W_1\, M_2}$$

$$= \frac{\text{Loss in wt. of solvent}}{\text{Gain in wt. by H}_2\text{SO}_4 \text{ tube}}$$

$$\therefore \quad \frac{38 \text{ g} \times 18 \text{ g mol}^{-}}{100 \text{ g } M_2} = \frac{0.0551 \text{ g}}{2.2117 \text{ g}};$$

$$M_2 = \frac{38 \times 18 \times 2.2117}{100 \times 0.0551}$$

$$= \mathbf{274.6 \text{ g mol}^{-}. \text{ Ans}}$$

Example 33. *In a Walker-Ostwald experiment, dry air is drawn through a solution of 26.66 g of a substance in 200 g of water and then through water alone. The loss in weight of the solution is 1.949 g and that of water is 0.087 g. Calculate the molecular weight of the dissolved substance.*

Solution. Loss in wt. of solvent, water = 0.087 g.

Loss in wt. of solution = 1.949 g

∴ Total loss is wt. of solvent and solution

= 0.087 + 1.949 = 2.036 g

M_1 = mol. wt. of $H_2O = (2 \times 1) + 16 = 18 \text{ g mol}^{-}$;

M_2 = mol. wt. of solute = ?

W_2 = wt. of solute = 26.66 g ;

W_1 = wt. of solvent = 200 g.

But $$\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{W_2\, M_1}{M_2\, W_1}$$

$$= \frac{\text{Loss in wt. of solvent}}{\text{Loss in wt. of solvent + loss in wt. of solution}}$$

$$\therefore \quad \frac{26.66 \text{ g} \times 18 \text{ g mol}^{-}}{M_2 \times 200\, g} = \frac{0.087\, g}{2.036\, g};$$

$$M_2 = \frac{26.66 \times 18 \times 2.036\ g\ \text{mol}^-}{200 \times 0.087}$$

$$M_2 = \mathbf{56.15\ g\ mol^-}.\ \textbf{Ans.}$$

18.9 ELEVATION IN BOILING POINT (ΔT_b)

The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric (or external) pressure. The difference between the boiling point of the solution (containing a non-volatile solute) and that of the pure solvent is called the 'elevation in boiling point' (ΔT_b). Thus $\Delta T_b = T_b - T_b^\circ$ where T_b and T_b° are the boiling points of solution and pure solvent respectively. It is independent of the nature of solute added.

Molal elevation (or ebbulioscopic) constant (K_b) of a solvent is defined as the elevation in boiling point [produced by dissolving 1 g mol of a solute in 1000 g (or 1 kg) of solvent] when molality of a solution is one. **Mathematically** :

(*a*) $\Delta T_b = K_b \times m$ where m = molality of the solution.

$$\textbf{Unit of } K_b = \frac{^oC}{m}$$

$$\text{or} \quad \frac{K}{m} = \frac{^oC}{\text{mol/kg}} \quad \text{or} \quad \frac{K}{\text{mol/kg}}$$

$$= \frac{0°\text{C kg}}{\text{mol}} \quad \text{or} \quad \frac{K\ \text{kg}}{\text{mol}}$$

$$= {}^\circ\text{C kg mol}^- \quad \text{or} \quad \text{K kg mol}^-$$

$$\textbf{Unit of } \Delta T_b = {}^\circ C \quad \text{or} \quad K.$$

Unit of wt. of solvent

$$= \text{kg } [e.g., w_1 g \times \frac{10^{-3}\ \text{kg}}{1\,\text{g}}$$

$$= 10^{-3}\, w_1\ \text{kg} = \frac{w_1}{1000}\text{kg}$$

Unit of wt. of solute = *g*. **Unit of mol. wt. or molar mass** = *g* mol$^-$

(*b*) $$\Delta T_b = K_b \times m$$

$$\Delta T_b\ (\textbf{in}\ ^oC) = \frac{k_b\left(\text{in } ^\circ\text{C kg mol}^-\right) \times W_2\ (\text{in g})}{M_2 \text{ in g mol}^- \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

Or $$\Delta T_b\ (\textbf{in } K) = \frac{k_b\ (\text{in K kg mol}^-) \times W_2\ (\text{in g})}{M_2 \text{ in g mol}^- \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

Also: $\Delta T_b = T_b$ (b. pt. of solution) $- T_b^\circ$ (b. pt of solvent)

(*c*) The value of Δb is same in°*C* and *K* units.

(*d*) The value of b.pt. is not same in °*C* and *K* units.

(*e*) If Δb is in °*C* (say 2°*C*), then b.pt. = 100 + 2 = 102°*C* ($\because$ b.pt. of H_2O = 100°*C*)

(*f*) If Δb is in *K* (say 2*K*), then b.pt. = 373 + 2 = 375*K*.

Molecular elevation constant (k_b). It is defined as the elevation in boiling point of a solvent produced by the dissolution of 1 g mol of any solute (non-volatile, non-electrolyte) in 100 g of the solvent.

Example 34. *A solution containing 0.5126 g of naphthalene (mol. wt. 128.17) in 50 g of CCl_4 yields a b.p. elevation of 0.402°C while a solution of 0.6216 g of an unknown solute in the same wt. of the solvent gives a b.p. elevation of 0.647°C. Find the mol. wt. of the unknown solute.*

Solution. Wt. of solute, W_2 = 0.5126 g ; wt. of solvent, W_1 = 50 g; ΔT_b = 0.402°C ; wt. of unknown solute, w_2 = 0.6216 g ; wt. of solvent w'_1 = 50 g ; $\Delta T'_b$ = 0.647°C. We know that :

(*i*) **For naphthalene.**

$$\Delta T_b\ (^\circ\text{C}) = \frac{K_b\ (\text{in } ^\circ\text{C kg mol}^-) \times W_2\ (\text{in g})}{M_2 \text{ in g mol}^- \times \left(\dfrac{W_1\,\text{g}}{1000}\right) \text{kg}}$$

$$0.402^\circ\text{C} = \frac{K_b \times 50\ \text{g}}{128.17\ \text{g mol}^- \times \dfrac{50}{1000}\text{kg}}\ ;$$

$$K_b = \frac{0.402^\circ C \times 128.17\ \text{g mol}^- \times 50}{1000 \times 50\ \text{g}}\ \text{kg}$$

or $$K_b = 5.025\ \text{K kg mol}^-$$

(*ii*) **For unknown solute.**

$$\Delta T_b (^\circ\text{C}) = \frac{K_b\ (\text{in } ^\circ\text{C kg mol}^-) \times W_2\ (\text{in g})}{M_2 \times \left(\dfrac{W_1\,\text{g}}{1000}\right) \text{kg}}$$

$$0.647^\circ\text{C} = \frac{5.025\ ^\circ\text{C kg mol}^- \times 0.6216\ \text{g}}{M_2 \times \dfrac{50}{1000}\text{kg}}$$

$$M_2 = \frac{5.025\ ^\circ\text{C kg mol}^- \times 0.6216\ \text{g} \times 1000}{0.647^\circ C \times 50\ \text{kg}}$$

$$= \mathbf{96.55\ g\ mol^-} \qquad \textbf{Ans.}$$

Type. Boiling point of water solution = 373 + ΔT_b.

Example 35. *What is the boiling point of a solution containing 18 g of glucose in 100 g of H_2O? Molal elevation constant of water = 0.52 K/m.*

Solution. Wt. of glucose = 18 g ; wt. of solvent, water = 100 g. mol. wt. of glucose ($C_6H_{12}O_6$) = (6 × 12) + (12 × 1) + (6 × 16)) = 180 g mol$^-$ K_b = 0.52 K/m = 0.52 K kg mol$^-$.

$$\Delta T_b\ (\text{in K}) = \frac{K_b\ (\text{in } K \text{ kg mol}^-) \times W_2 \text{ in g}}{M_2 \text{ in g mol}^- \times \left(\dfrac{W_1\,\text{g}}{1000}\right) \text{kg}}$$

$$= \frac{0.52\,K \text{ kg mol}^- \times 18\ \text{g} \times 1000}{180\ \text{g mol}^- \times 100\ \text{kg}}$$

$$= 0.52\,K$$

$\therefore$ Boiling point of water solution

= (373 + 0.52) *K* = 373.52 *K* **Ans.**

Type. To find molecular formula of an element, use :

$$\text{Number of atoms} = \frac{\text{g . mol . wt}}{\text{g . at. wt}}$$

Example 36. *On dissolving 3.24 g of sulphur in 40 g benzene, the boiling point of solution was higher than that of benzene by 0.81 K. K_b value for benzene is 2.53 K kg mol^-. What is the molecular formula of sulphur ? (atomic mass of sulphur = 32 g mol^-)* **(DSB, 2000)**

Solution. Wt. of sulphur, W_2 = 3.24 g ; wt. of solvent, benzene, W_1 = 40 g

$$\Delta T_b = 0.81\text{ K} ; K_b = 2.53\text{ K kg mol}^-;$$

mol. wt. of S, M_2 = ?

$$\Delta T_b = \frac{K_b \times W_2}{M_2 \times \left(\frac{W_1\text{ g}}{1000}\right)\text{kg}};$$

$$0.81\text{ K} = \frac{2.53\,K\text{ kg mol}^- \times 3.24\text{ g}}{M_2 \times \frac{40}{1000}\text{kg}}$$

$$\therefore \quad M_2 = \frac{2.53\,K\text{ kg mol}^- \times 3.24\text{ g} \times 1000}{0.81\,K \times 40\text{ kg}}$$

$$= 253\text{ g mol}^-$$

∴ No. of atoms of sulphur per molecule

$$= \frac{\text{Mol. wt}}{\text{at. wt}} = \frac{253\text{ g mol}^-}{32\text{ g mol}^-} \simeq 8$$

∴ Molecular formula of sulphur = $\mathbf{S_8}$. **Ans.**

Type. To find K_b and mol. wt. of solute when latent heat of vaporisation of solvent (L_v) is given, use the relation :

(*i*) $K_b = \dfrac{R\,(T_b^o)^2}{1000 \times L_v}$; R = 2 cal. $\text{degree}^-\,\text{mol}^-$ = 2 cal $K^-\,\text{mol}^-$;

L_v = 540 cal g^-

(*ii*) $L_v = \dfrac{\Delta H_{\text{vap}}}{M}$ where ΔH_{vap} = molar enthalpy of vaporisation ; M = molar mass of solvent.

Example 37. *A solution of 1.35 g of a non-volatile solute in 72.3 mL of water boils at 0.162°C higher than the boiling point of water. Calculate the molecular weight of the substance. Latent heat of vaporisation of water is 540 cal g^- ; R = 2 cal. $\text{degree}^-\,\text{mol}^-$.*

Solution. R = 2 cal $\text{degree}^-\,\text{mol}^-$; T_b^0 = 100 + 273 = 373 K; T_b = 373 + 0.162 = 373.162 K.; ΔT_b = 373.162 – 373 = 0.162 K. ; L_v = 540 cal $g^-\,\text{mol}^-$. wt. of solute, W_2 = 1.35 g.

We know that :

(*i*) $$K_b = \frac{R\,(T_b^o)^2}{1000 \times L_v} = \frac{2\text{ cal K}^-\text{ mol}^- \times (373)^2\text{ K}^2}{1000 \times 540\text{ cal g}^-}$$

$$= 0.515\text{ K.g. mol}^-$$

(*ii*) wt. of solvent water = volume × density

$$= 72.3\text{ mL} \times 1\text{ g (mL)}^- = 72.3\text{ g}$$

$$\Delta T_b = \frac{K_b \times W_2}{M_2 \times W_1\text{ in g}};$$

$$0.162\text{ K} = \frac{0.515\text{ K . g mol}^- \times 1.35\text{ g}}{M_2 \times 72.3\text{ g}} \times 1000$$

$$\therefore \quad M_2 = \frac{0.515\,K\text{. g mol}^- \times 1.35\text{ g} \times 1000}{0.162\,K \times 72.3\text{ g}}$$

$$= 59.36\text{ g mol}^-$$ **Ans.**

Type. No. of molecules = no. of mol × 6.023 × 10^{23}

Example 38. *An aqueous solution of glucose boils at 100.01°C. The molal elevation constant for water is 0.5 K kg mol^-. What is the number of glucose molecules in the solution containing 100 g of water.*

Solution. T_b = 100.01°C, T_b^o = 100°C ; ΔT_b = 100.01 – 100 = 0.01°C (or K); K_b = 0.5 K/m ; no. of mol = ?. We know that :

(*i*) $\Delta T_b = K_b \times$ molality ;

$$\text{molality} = \frac{\Delta T_b}{K_b} = \frac{0.01\,K}{0.5\,K\text{ kg mol}^-} = 0.02\text{ m}$$

$$= 0.02\text{ mol kg}^-.$$

But Molality,

$$m = \text{no. of mol} \times \frac{1}{\left(\frac{\text{wt. of solvent in g}}{1000}\right)\text{kg}}$$

$$0.02\text{ mol kg}^- = \text{no. of mol} \times \frac{1}{\left(\frac{100}{1000}\right)\text{kg}}$$

$$\text{no. of mol} = 0.02\text{ mol kg}^- \times \frac{100}{1000}\text{kg} = 0.002\text{ mol}$$

∴ no. of molecules

$$= 0.002\text{ mol} \times \frac{6.023 \times 10^{23}\text{ molecules}}{1\text{ mol}}$$

$$= \mathbf{1.205 \times 10^{21}}$$ **Ans.**

Example 39. *Compute the boiling point of a solution containing 24.0 g of an organic compound (molar mass 58.0 g mol^-) and 600 g of water, when the barometer shows the boiling point of water at 99.725°C. (K_b = 0.513°C kg mol^-).*

Solution. Hint.

$$\Delta T_b = \frac{K_b \times W_2}{M_2 \times W_1\text{ in kg}}$$

$$= \frac{0.513°\text{C kg mol}^- \times 24\text{ g}}{58\text{ g mol}^- \times \frac{600}{1000}\text{kg}}$$

$$= \frac{0.513°\text{C kg mol}^- \times 24\text{ g} \times 1000}{58\text{ g mol}^- \times 600\text{ kg}}$$

$$= 0.354°\text{C}$$

∴ b.p. of solution = b.p. of water + ΔT_b

= 99.725°C + 0.354°C = **100.079°C** **Ans.**

Example 40. *3.50 g of a pure hydrocarbon was dissolved in 90.0 g acetone to form a solution. The boiling point of pure acetone was observed to be 55.95°C and of solution, 56.50°C. If molal boiling point constant of acetone is 1.71°C kg mol^-, calculate the approximate molecular mass of the hydrocarbon.*

Solution. $\Delta T_b = (56.50 - 55.95)°\text{C} = 0.55°\text{C}$; $K_b = 1.71°\text{C}$ kg mol¯. wt. of solute, w_2 = 3.5 g ; wt. of solvent, w_1 = 90 g ; we know that :

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$0.55°\text{C} = \frac{1.71°\text{C kg mol}^{-} \times 3.5\text{ g}}{M_2 \times \frac{90}{1000}\text{ kg}}$$

$$\therefore \qquad M_2 = \frac{1.71°\text{C kg mol}^{-} \times 3.5\text{ g} \times 1000}{0.55°\text{C} \times 90\text{ kg}}$$

$$= \textbf{120.9 g mol}^{-}\textbf{ Ans.}$$

Example 41. *A solution prepared by dissolving 288 g of a non-volatile stoichiometric compound (having composition $C_nH_{2n}O_n$) in 90 g of water boils at 101.24°C at 1.0 atmospheric pressure. Calculate the molecular formula of the compound (K_b = 0.512°C/m).*

Solution. Boiling point of pure water = 100°C; wt. of solute, W_2 = 288 g ; boiling point of solution = 101.24°C ; molar mass of solute, M_2 = ? ; $\Delta T_b = (101.24 - 100)°\text{C} = 1.24°\text{C}$. wt. of water solvent (water), W_1 = 90 g ; K_b = 0.512°C/m = 0.512°C kg mol¯ we know that :

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$1.24°\text{C} = \frac{0.512°\text{C kg mol}^{-} \times 288\text{ g}}{M_2 \times \frac{90}{1000}\text{ kg}}$$

$$\therefore \qquad M_2 = \frac{0.512°\text{C kg mol}^{-} \times 288\text{g} \times 1000}{1.24°\text{C} \times 90\text{ kg}}$$

$$= 1321.3\text{ g mol}^{-}$$

Suppose n = 1 in the given formula $C_nH_{2n}O_n$. Then the corresponding formula will be CH_2O and empirical formula weight will be 12 + (2 × 1) + 16 *i.e.*, 30. Hence, n = 1321.3/30 ≃ 44. Hence :

Molecular formula = $(CH_2O)_{44}$ = $\mathbf{C_{44}H_{88}O_{44}}$ **Ans.**

Example 42. *An unknown compound contains 40 % carbon, 6.7 % hydrogen and 53.3 % oxygen. If 5 % aqueous solution of this solute boils at 100.15°C, calculate the molecular weight of the solute (K_f for solvent = 0.512°C/m, At. wt. of C = 12, H = 1, O = 16)*

Solution. To find empirical formula (E.F.) of the solute.

Element	*At.wt.*	*% age*	*Relative no. of atoms = % age/ at. wt.*	*Simple ratio*	*Whole no. ratio*
C	12	40	40/12 = 3.33	$\frac{3.33}{3.33} = 1$	1
H	1	6.7	6.7/1 = 6.7	$\frac{6.7}{3.33} = 2.01$	2
O	16	53.3	53.3/16 = 3.33	$\frac{3.33}{3.33} = 1$	1

∴ E.F. of solute = CH_2O

E.F. wt of solute = 12 + (2 × 1) + 16 = 30 g . B. pt. of H_2O = 100.0°C. We know, $\Delta T_b = (100.15 - 100)°\text{C} = 0.15°\text{C}$; $\Delta T_b = K_b m$

∴ **m** = $\Delta T_b/K_b$ = 0.15°C/(0.512°C/m) = **0.29 m** = 0.29 mol/kg H_2O. Wt. of solute = 5.0 g ; wt. of solvent = 100 – 5 = 95 g = (95/1000) kg = 0.095 kg.

∴ g mol. wt. of solute

$$= \frac{\text{wt. of solute (in g)}}{\text{molality} \times \text{wt. of solvent in kg}}$$

$$= \frac{5.0\text{ g}}{(0.29\text{ mol / kg } H_2O)(0.095\text{ kg } H_2O)}$$

$$= 181.5\text{ g/mol.}$$

But molecular formula

$$= \left(\frac{\text{g. mol. wt.}}{\text{g. E.F. wt.}}\right) \times \text{E.F}$$

$$= \left(\frac{181.5\text{ g/mol}}{30\text{ g/mol}}\right) \times CH_2O$$

$$= 6 \times CH_2O = \mathbf{C_6H_{12}O_6} \qquad \textbf{Ans.}$$

Type. When K_b value for 100 g solvent is given, then convert this value to °C (or K) kg mol¯ by multiplying K_b value by 100 g/1000 because division by 1000 gives value in kg. This will give molal elevation constant (K_b).

Example 43. *Calculate the boiling point of a solution containing 0.456 g of camphor (mol. wt. = 152) dissolved in 35.4 g of acetone (b.pt. = 56.3°C) if the molecular elevation per 100 g of acetone is 17.2°C.*

Solution. wt. of solute, W_2 = 0.456 g ; wt. of solvent, $W_1 = 35.4\text{ g} = \frac{35.4}{1000}\text{kg}$; mol. wt. of solute, M_2 = 152 g mol¯ ; $K_b = 17.2°\text{C}\ (100\text{ g mol}^{-}) = 17.2°\text{C} \times \left(\frac{100}{1000}\text{kg mol}^{-}\right)$ $= 17.2 \times \frac{1}{10}$ °C kg mol¯ = 1.72°C kg mol¯

We know that

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$= \frac{1.72\ °\text{C kg mol}^{-} \times 0.456\text{ g}}{152\text{ g mol}^{-} \times \frac{35.4}{1000}\text{ kg}}$$

$$\textbf{or} \qquad \Delta T_b = \frac{1.72°\text{C kg mol}^{-} \times 0.456\text{ g} \times 1000}{152\text{ g mol}^{-} \times 35.4\text{ kg}}$$

$$= 0.146\ °\text{C}$$

$$\textbf{or} \qquad \Delta T_b = \frac{100\ K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in g}}$$

$$= \frac{100 \times 17.2°\text{C g mol}^{-} \times 0.456\text{ g}}{152\text{ g mol}^{-} \times 35.4\text{ g}}$$

$$= 0.146\ °\text{C}$$

∴ Boiling point of solution

$$= 56.3°\text{C} + 0.146°\text{C} = \mathbf{56.446°C} \quad \textbf{Ans.}$$

Example 44. *The boiling point of chloroform was raised by 0.325°C when 0.5141 g of anthracene was dissolved in 35 g of chloroform. Calculate the molecular weight of anthracene. (K_b = 39.0 per 100 g of chloroform)*

Solution. wt. of solute, W_2 = 0.5141 g ; wt. of solvent, $W_1 = \frac{35}{1000}$ kg = 0.035 kg ; ΔT_b = 0.325°C ; K_b = 39°C (100 g mol^{-}) = 39°C × $\frac{100}{1000}$ kg mol^{-} = 3.9°C kg mol^{-}; mol. wt. of anthracene, M_2 = ?

We know that

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$M_2 = \frac{K_b \times W_2 \text{ in g}}{\Delta T_b \times W_1 \text{ in kg}}$$

Or

$$\boldsymbol{M_2} = \frac{3.9\ °\text{C kg mol}^{-} \times 0.5141 \text{ g}}{0.325\ °\text{C} \times 0.035 \text{ kg}}$$

$$= \mathbf{176.26\ g\ mol^{-}}$$

Example 45. *A solution containing 0.7269 g of camphor (mol. wt. 152) in 32.0 g of acetone (b.pt. = 56.3°C) boiled at 56.85°C. What are the molal, molecular elevation constant and latent heat of vaporisation ?*

Solution. Since we have to find molecular elevation constant and molal elevation constant, so we have :

(*i*) T_b = (273 + 56.85) K = 329.85 K; T_b^o = 273 + 56.3 = 329.3 K ; ΔT_b = 329.85 K – 329.3 K = 0.55 K.

Wt. of solute = 0.7269 g ;

wt. of solvent = 32 g = $\frac{32}{1000}$ kg = 0.032 kg. K_b = ?

We know that :

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$K_b = \frac{\Delta T_b \times M_2 \times W_1 \text{ in kg}}{W_2 \text{ in g}}$$

$$\therefore \quad K_b \text{ (molal)} = \frac{0.55 \text{ K} \times 152 \text{ g mol}^{-} \times 0.032 \text{ kg}}{0.7269 \text{ g}}$$

$$= [3.68 \text{ K kg mol}^{-}]$$

(*ii*) But molecular elevation constant (K_b)

$$= \frac{\Delta T_b \times M_2 \times W_1 \text{ in g}}{W_2 \text{ in g} \times 100}$$

$$\therefore \quad K_b = \frac{0.55 \text{ K} \times 152 \text{ g mol}^{-} \times 32 \text{ g}}{0.7269 \text{ g} \times 100}$$

$$= \mathbf{36.8\ K.\ g.\ mol^{-}} \quad \textbf{Ans.}$$

(*iii*)

$$K_b = \frac{R\,(T_b^o)^2}{L_v \times 100}\,;\; L_v = \frac{R\,(T_b^o)^2}{K_b \times 100}$$

$$= \frac{2 \text{ cal K}^{-} \text{ mol}^{-} \times 329.3 \text{ K} \times 329.3 \text{ K}}{36.8 \text{ K g mol}^{-} \times 100}$$

$$= 58.9 \text{ cal g}^{-}.$$

Example 46. *The boiling point of acetone is 56.38°C. A solution of 0.564 g of a compound in 8.6 g of acetone boiled at 56.75°C. What is the molecular weight of this compound ? (molecular elevation for acetone = 16.7 K. g mol^{-})*

Solution. T_b^o = 56.38 + 273 = 329.38 K,

T_b = 273 + 56.75 = 329.75 K

∴ ΔT_b = 329.75 – 329.38 = 0.37 K. wt. of solute = 0.564 g; wt. of sovent, W_1 = 8.6 g ; mol. wt. of compound, M_2 = ?

Since the value of K_b is given in molecular elevation *i.e.,* per 100 g solvent (and not in molar elevation), we use the following relation :

$$K_b \text{ value for 1000 g solvent} = 16.7 \times \frac{100}{1000}$$

$$= 1.67 \text{ K kg mol}^{-}$$

$$\therefore \quad \Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$\therefore \quad M_2 = \frac{K_b \times W_2 \text{ in g}}{\Delta T_b \times W_1 \text{ in kg}}$$

$$\boldsymbol{M_2} = \frac{1.67 \text{ K kg mol}^{-} \times 0.564 \text{ g}}{0.37 \text{ K} \times \frac{8.6}{1000} \text{ kg}}$$

$$= \mathbf{296\ g\ mol^{-}} \quad \textbf{Ans.}$$

Type. To find molal elevation constant, K_b (and not molecular elevation constant), when latent heat of vaporisation (L_v) is given, following relation is used.

$$K_b = \frac{MR\,(T_b^o)^2}{\Delta_{vap} H \times 1000} = \frac{R\,(T_b^o)^2}{\frac{\Delta_{vap} H}{M} \times 1000}$$

$$= \frac{R\,(T_b^o)^2}{L_v \times 1000}$$

where M = Molar mass of solvent;

R = a gas constant = 2 cal K^{-} mol^{-}

$\Delta_{vap} H$ = Molar enthalpy of vaporisation of solvent ; T_b^o = boiling point of solvent.

L_v = Latent heat of vaporisation of solvent in cal g^{-}

Example 47. *Latent heat of vaporisation of water is 540 cal g^{-} and its boiling point is 100°C. Find the molar elevation constant of water when 1 mol of solute is dissolved in 1000 g of water.*

Solution. L_v = 540 cal g^{-} ; T_b^o = 100 + 273 = 373 K .

We know that :

$$K_b = \frac{R\,(T_b^o)^2}{L_v \times 1000}$$

$$= \frac{2 \text{ cal K}^{-} \text{ mol}^{-} \times (373 \text{ K})^2}{540 \text{ cal g}^{-} \times \dfrac{1000 \text{ g}}{\text{kg}}}$$

$$K_b = \frac{2 \text{ cal K}^{-} \text{ mol}^{-} \times 373 \text{ K} \times 373 \text{ K}}{540 \text{ cal g}^{-} \times 1000 \text{ g. kg}^{-}}$$

$$= 0.515 \text{ K. kg. mol}^{-}$$

EXAMPLE 48. *Calculate the boiling point of a solution prepared by adding 15.0 g of NaCl to 250 g of water (K_b for water = 0.512 K kg mol⁻); molar mass of NaCl = 58.44 g mol⁻).*

(PSEB, 1998, 2000, CBSE, 2011)

SOLUTION. ΔT_b = ?; K_b = 0.512 K kg mol⁻; mol. wt. (M_2) of NaCl = 58.44 g mol⁻; Wt. of solvent (W_1) in kg = 250/1000 kg = 0.25 kg; wt. of solute = W_2 = 15.0 g

$$\Delta T_b = \frac{K_b \text{ (in K kg mol}^{-}) \times W_2 \text{ in g}}{M_2 \text{ in g mol}^{-} \times W_1 \text{ in kg}}$$

$$= \frac{0.512 \text{ K kg mol}^{-} \times 15\text{g}}{58.44 \text{ g mol}^{-} \times 0.25 \text{ kg}}$$

$$= 0.526 \text{ K.}$$

∴ Boiling point = 373 K + 0.526 K = 373.526 K **Ans.**

or B. Pt. = 100°C + 0.526°C = 100.526 °C

EXAMPLE 49. *For a solution of 3.795 g of sulphur in 100 g CS_2, the boiling point was 319.81 K. For pure CS_2, the boiling point is 319.45 K and the latent heat of vaporisation is 351.87 Jg⁻. What is the molar mass and formula of sulphur in CS_2.*

SOLUTION. Wt. of solute (S), W_2 = 3.795 g ; wt. of solvent (CS_2), W_1 = 100 g = 100/1000 = 0.1 kg ;

ΔT_b = 319.81 K – 319.45 K = 0.36 K; L_v = 351.87 J g⁻ ; R = 8.314 J K⁻ mol⁻ ; molar mass of S = ? , formula of S = ?

(*i*) $$K_b = \frac{R\,(T_b^o)^2}{1000\, L_v}$$

$$= \frac{8.314 \text{ J K}^{-} \text{ mol}^{-} \times (319.45 \text{ K})^2}{(1000 \times 351.87 \text{ J}) \text{ kg}^{-}}$$

$$= 2.41 \text{ K kg mol}^{-}$$

(*ii*) $$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$0.36\, K = \frac{2.41 \text{ K kg mol}^{-} \times 3.795 \text{ g}}{M_2 \times 0.1 \text{ kg}}$$

$$\therefore \quad M_2 = \frac{2.41 \text{ K kg mol}^{-} \times 3.795 \text{ g}}{0.36 \text{ K} \times 0.1 \text{ kg}}$$

$$= 254 \text{ g mol}^{-}$$

At. wt. of sulphur = 32 g mol⁻

∴ Number of atoms per molecule of sulphur

$$= \frac{254 \text{ g mol}^{-}}{32 \text{ g mol}^{-}} \simeq 8$$

∴ **Molecular formula of sulphur = S_8 Ans.**

EXAMPLE 50. *Calculate the molar mass of a substance, 1.3 g of which when dissolved in 169 g of water gave a solution boiling at 100.025 °C at a pressure of 1 atm. (K_b for water = 0.52 K kg mol⁻).* **(PSEB, 2000)**

SOLUTION. Hint.

$$\Delta T_b = (373.025 - 373)\, K = 0.025\, K$$

$$M_2 = \frac{K_b \times W_2 \text{ in g}}{\Delta T_b \times W_1 \text{ in kg}}$$

$$= \frac{0.52 \text{ K kg mol}^{-} \times 1.3 \text{ g}}{0.025 \text{ K} \times 0.169 \text{ kg}}$$

or M_2 = **160 g mol⁻** **Ans.**

EXAMPLE 51. *The boiling point of water is 100 °C and it becomes 100.52°C if 3 g of a non - volatile solute is dissolved in 20 ml of it. Calculate the molecular weight of the solute. (k_b for water is 0.52 K/m)* **(PSEB 2000, DSB 1992, HP Board, 2007)**

SOLUTION. Wt. of solute, W_2 = 3 g ; wt. of solvent water = volume in mL × density in g (mL)⁻ = 20 mL × 1 g (mL)⁻ = 20 g = $\frac{20}{1000}$ kg = 0.02 kg ; mol. wt. of solute, M_2 = ? , K_b = 0.52 K/m = 0.52 K kg mol⁻. T_b = 273 + 100.52 K = 373.52 K, T_b^o = 273 + 100 K = 373 K ; ΔT_b = 373.52 K – 373 K = 0.52 K.

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$M_2 = \frac{K_b \times W_2 \text{ in g}}{\Delta T_b \times W_1 \text{ in kg}} = \frac{0.52 \text{ K kg mol}^{-} \times 3 \text{ g}}{0.52 \text{ K} \times 0.02 \text{kg}}$$

$$\therefore \quad M_2 = 150 \text{ g mol}^{-}$$

EXAMPLE 52. *Calculate the boiling point of a solution containing 1.8 g of non - volatile solute dissolved in 90 g of benzene. The boiling point of pure benzene is 353.23 K, K_b = 2.53 K kg mol⁻. Molecular mass of solute is 58 g mol⁻.* **(AISB, 1994)**

SOLUTION. T_b = ? , wt. of solute, W_2 = 1.8 g ; wt. of solvent, W_1 = $\frac{90}{1000}$ kg = 0.09 kg ; ΔT_b = T_b – 353.23 K ; K_b = 2.53 K kg mol⁻ ; molar mass, M_2 = 58 g mol⁻. We know that :

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$T_b - 353.23 \text{ K} = \frac{2.53 \text{ K kg mol}^{-} \times 1.8 \text{ g}}{58 \text{ g mol}^{-} \times 0.09 \text{ kg}}$$

or T_b – 353.23 K = 0.872 K.

So, T_b = 0.872 K + 353. 23 = **354.102 K Ans**

EXAMPLE 53. *A solution of sucrose (molar mass, 342 g mol⁻) is prepared by dissolving 68.4 g in 1000 g of water. Find (i) the b.pt. and freezing point of solution (ii) vapour pressure at 293 K. Given : V.P. of H_2O at 293 K is 0.023 atm ; K_b = 0.52 K/m ; K_f = 1.86 K/m.*

SOLUTION. Mol. mass of sucrose, $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 × 16) = 342 g mol⁻ ; wt. of sucrose = 68.4 g ; wt. of solvent, H_2O = 1000 g, so volume of H_2O = mass/density = 1000/1 = 1000 mL = 1L. B.pt. = ? f.pt. = ? , vapour pressure, V.P. = ? , π = ? , T = 293 K, K_b = 0.5 K/m, K_f = 1.86 K/m: V.P. of H_2O = 0.023 atm.

(*i*) *To calculate V.P.* We know $p° - p_s/p° = x_B$ ... (*i*) no. of moles of solvent, water (H_2O), n_A = wt./ mol. wt. of H_2O = 1000/18 = 55.5. no. of moles of solute, n_B = wt./mol. wt. = 68.4/342 = 0.2. Mole fraction (x_B) of solute = $n_B/(n_A + n_B)$ = 0.2/55.5 + 0.2 = 0.2/55.7 = 3.6×10^{-3}. Substituting the values of x_B and $p°$ in (*i*), we get, $(0.023 - p_s)/\ 0.023 = 3.6 \times 10^{-3}$; **Or** $0.023 - p_s = 3.6 \times 10^{-3} \times 0.023$ **Or** $p_s = 0.023 - 3.6 \times 10^{-3} \times 0.023 = 0.023 - 8.28 \times 10^{-5} = 0.0229$ atm = 0.0229 × 760 mm = **17.417 mm Ans.**

(*ii*)
$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$
$$= \frac{0.52 \text{ K kg mol}^- \times 68.4 \text{ g}}{342 \text{ g mol}^- \times 1 \text{ kg}} = 0.104 \text{ K}$$
$$\left[\because \text{wt. of solvent, } w_1 = 1000 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1 \text{ kg}\right]$$

$\therefore$ Boiling point = 373 + 0.104 = **373.104 K** **Ans.**

(*iii*)
$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$
$$= \frac{1.86 \text{ K kg mol}^- \times 68.4 \text{ g}}{342 \text{ g mol}^- \times 1 \text{ kg}}$$
$$= 0.372 \text{ K}$$
$$[\because K_f = 1.86 \text{ K/m} = 1.86 \text{ K kg mol}^-]$$

$\therefore$ *F.pt.* = (273 – 0.372) K = **272.628 K** **Ans.**

18.10 COTTRELL'S METHOD

In this method, a known weight of the solvent is heated in a special tube. The solvent vapours act on the bulb of thermometer. Let $T°$ is the temperature when the temperature shown by the thermometer becomes constant.

A known weight of the solute is now added to the solvent through a side tube and boiling point of the solution is again determined as before. Let it be T_1. So, $\Delta T_b = T_1 - T°$. The molecular weight of the solute can be determined by the use of following relation.

$$\Delta T_b = \frac{1000\, K_b\, w}{W\, M}$$

or
$$M = \frac{1000\, K_b\, w}{W\, \Delta T_b}$$

$\because \Delta T_b$ = molality, $m \times K_b$ and $m = \dfrac{w}{M} \times \dfrac{1000}{W}$
w = wt. of solute
W = wt. of solvent; M = mol. wt. of solute
K_b = Molal elevation constant.

Note. Numericals are similar to "elevation in boiling point"

18.11 LANDSBERGER'S METHOD

In this technique, the liquid is heated by passing the vapours of the pure boiling solvent into it. Some of the vapours condense and as a result, latent heat is liberated which heats the liquid to its boiling point without any danger of super heating.

First of all, the boiling point ($T°$) of the pure solvent is noted from the constant temperature of thermometer. Now a known weight of the solute is added to the solvent and boiling point (T_1) of the solution is noted as before. Then elevation in b.pt., $\Delta T_b = T_1 - T_0$. Now by using the following relation, the molecular weight of the solute can be determined.

$$\Delta T_b = \frac{1000\, K_b\, w}{W\, M}$$

or
$$M = \frac{1000\, K_b\, w}{W\ \Delta T_b}$$

$\because \Delta T_b$ = molality, $m \times K_b$ and $m = \dfrac{w \times 1000}{M\, W}$
w = wt. of solute
W = wt. of solvent; M = mol. wt. of solute
K_b = Molal elevation constant.

Note. Numericals are similar to "elevation in boiling point"

18.12 DEPRESSION IN FREEZING POINT (ΔT_f)

The freezing point of a liquid is the temperature at which the vapour pressure of the liquid phase becomes equal to the vapour pressure of its solid phase. The freezing point of the solution is lower than that of the pure solvent. *The difference between the freezing point of pure solvent (T_f^o) and that of the solution (T_f) is called the* **depression in freezing point (ΔT_f).**

Thus : $\Delta T_f = T_f^o - T_f$
= F.pt. of solvent – F.pt. of solution.

It depends upon the amount (or concentration) and nature of the solvent. It is independent of the nature of solute added.

Molal depression constant (or cryoscopic constant) K_f may be defined as the depression in freezing point produced by dissolving 1 g. mol of any solute (non - electrolyte, non - volatile) in 1000 g (or 1 kg) of the solvent.

Mathematically : (*a*) $\Delta T_f = K_f \times m$ where m = molality of the solution.

Molality,
$$m = \frac{\text{wt. of solute, } W_2 \text{ (in g)}}{\text{mol. wt. of solute, } M_2 \text{ in g. mol}^-} \times \frac{1000}{\text{wt. of the solvent,} W_1 \text{ (in g)}}$$
$$= \text{no. of mol of solute} \times \frac{1}{\dfrac{\text{wt. of solvent, } W_1 \text{ (in g) kg}}{1000}}$$

$$\therefore \textbf{unit of molality} = \frac{\text{mol}}{\text{kg}} \text{ or mol kg}^{-}$$

$$\textbf{Unit of } K_f = \frac{°C}{m} \text{ or } \frac{K}{m} = \frac{°C}{\text{mol/kg}} \text{ or } \frac{K}{\text{mol/kg}}$$

$$= \frac{°C\text{ kg}}{\text{mol}} \text{ or } \frac{K.\text{kg}}{\text{mol}}$$

$$= °C \text{ kg mol}^{-} \text{ or } K.\text{ kg mol}^{-}$$

$$\textbf{unit of } \Delta T_f = °C \text{ or K}$$

$$\textbf{Unit of wt. of solvent} = \text{kg} \left(\begin{array}{l} e.g., W_1 g \times \dfrac{10^{-3}\text{kg}}{1\text{ g}} = \\ 10^{-3}\, W_1 \text{kg} = \dfrac{W_1}{1000}\text{kg} \end{array} \right)$$

Unit of wt. of solute = g

Unit of mol. wt. of molar mass = g mol^{-}

(*b*)
$$\Delta T_f = K_f \times m$$

$$= K_f \times \frac{\text{wt. of solute, } W_2 \text{ (in g)}}{\text{mol. wt. of solute, } M_2 \text{ in g. mol}^{-}} \times \frac{1000}{\text{wt. of solvent, } W_1 \text{ in g.}}$$

$$\Delta T_f = \frac{K_f\, W_2 \times 1000}{M_2 \times W_1}$$

$$\Delta T_f = \frac{K_f \text{ (in °C kg mol}^{-}) \times W_2 \text{ (in g)}}{M_2 \text{ (in g mol}^{-}) \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

or
$$\Delta T_f (\text{in } K) = \frac{K_f \text{ (in K. kg mol}^{-}) \times W_2 \text{ (in g)}}{M_2 \text{ (in g mol}^{-}) \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

(*c*) The value of Δf is same in °C and K units.

(*d*) The value of f.pt. is not same in °C and K units.

(*e*) If Δf is in °C (say, 2°C), then f.pt. = 0 – 2 = – 2°C

(*f*) If Δf is in K (say, $2K$), then f.pt. = 273 – 2 = 271 K

18.13 MOLECULAR DEPRESSION CONSTANT (K_f)

It is defined as the depression in freezing point of a solvent produced by the dissolution of 1 g mol of any solute (non - volatile, non - electrolyte) in 100 g of the solvent.

Example 54. *Calculate the freezing point of a 10% (by weight) solution of ethyl alcohol (C_2H_5OH) in water. (K_f for water = 1.86°C/m ; at. wt. C = 12, H = 1, O = 16).*

Solution. Wt. of C_2H_5OH, W_2 = 10 g ; wt. of water solvent, W_1 = 100 – 10 = 90 g. Mol. wt. of C_2H_5OH = (2 × 12) + (5 × 1) + 16 + 1 = 46.0 g mol^{-}, K_f = 1.86 °C/m = 1.86 °C kg mol^{-}. We know that :

$$\Delta T_f = \frac{K_f \text{ (in °C kg mol}^{-}) \times W_2 \text{ (in g)}}{M_2 \text{ (in g mol}^{-}) \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

$$= \frac{1.86 \text{ °C kg mol}^{-} \times 10 \text{ g}}{46 \text{ g mol}^{-} \times \dfrac{90}{1000} \text{kg}}$$

$$= 4.49 \text{ °C}$$

∴ Freezing point = **– 4.49°C Ans.**

Example 55. *0.534 g of solute is dissolved in 15 g of water, then freezing point temperature changes from 0°C to – 1.57°C. Molal depression constant of water, K_f = 1.85 K kg mol^{-1}. Find out (i) Molal concentration (ii) Molecular weight of solute.*

(AIPMT, 2009)

Solution. Given: K_f = 1.85 K kg mol^{-}; ΔT_f = 0 – (–1.57) = 1.57°C

(*i*) Molal concentration or molality,

$$m = \frac{\Delta T_f}{K_f} = \frac{1.57}{1.85} = 0.848 \text{ m.}$$

(*ii*) Mol. wt. of solute

$$= \frac{W_2 \text{ in g} \times K_f}{\Delta T_f \times W_1 \text{ in kg}}$$

$$= \frac{0.534 \text{ g} \times 1.85 \text{ K kg mol}^{-} \times 1000}{1.57 \text{ K} \times 15 \text{ kg}}$$

$$= \mathbf{41.95 \text{ g mol}^{-}} \qquad \textbf{Ans.}$$

Example 56. *Calculate the amount of methanol (CH_3OH) that should be added to 1.0 litre water so that the solution will not freeze at – 4°F. (K_f = 1.86 °C/m ; at. wt. of C = 12, H = 1, O = 16).*

Solution. $K_f = \dfrac{1.86°C}{m}$ = 1.86°C kg mol^{-}. Mol. wt. of CH_3OH = 12 + (3 × 1) + 16 + 1 = 32 g mol^{-}. We know that:

$$\frac{C}{5} = \frac{F - 32}{9}$$

$$C = \frac{5\,(F - 32)}{9} = \frac{5\,(-4 - 32)}{9}$$

$$= \mathbf{-20°C} = \Delta T_f$$

wt. of CH_3OH, W_2 = ? , wt. of solvent, W_1 = Volume × density = 1 L × 1 g (mL)$^{-}$ = 1000 mL × 1 g (mL)$^{-}$ = 1000 g. We know that :

$$\Delta T_f = \frac{K_f \text{ (in °C kg mol}^{-}) \times W_2 \text{ (in g)}}{M_2 \text{ in g mol}^{-} \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

$$\therefore \quad 20 \text{ °C} = \frac{1.86°C \text{ kg mol}^{-} \times W_2}{32 \text{ g mol}^{-} \times \dfrac{1000}{1000} \text{kg}};$$

$$W_2 = \frac{20°C \times 32 \text{ g mol}^{-} \times 1 \text{kg}}{1.86 \text{ °C kg mol}^{-}}$$

or
$$W_2 = \mathbf{344.09 \text{ g}} \qquad \textbf{Ans.}$$

EXAMPLE 57. *Suppose the radiator of an automobile contains 11.0 L water. How much will the freezing point be lowered by the addition of 4.6 kg of prestone [glycol, $C_2H_4(OH)_2$] ? Also calculate the amount of zerone [methyl alcohol, CH_3OH], that would be needed to produce the same result. Assume 100% purity of compounds added (K_f = 1.86 °C/m).*

SOLUTION. Mol. wt. of glycol $C_2H_4(OH)_2$ = (2 × 12) + (4 × 1) + 2 (16 + 1) = 62 g mol^{-}. Mol. wt. of methyl alcohol, CH_3OH = 12 + (3 × 1) + 16 + 1 = 32 g mol^{-}; wt. of glycol, W_2 = 4.6 kg ; wt. of solvent, W_1 = Volume × density = 11.0 L × 1 g $(\text{mL})^{-}$ = 11 × 1000 mL × 1 g $(\text{mL})^{-}$ = 11000 g; $K_f = \dfrac{1.86°\text{C}}{m}$ = 1.86°C kg mol^{-}; ΔT_f = ? we know that :

$$\Delta T_f = \frac{K_f\ (\text{in °C kg mol}^{-}) \times W_2\ (\text{in g})}{M_2 \text{ in g mol}^{-} \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

$$= \frac{1.86\ \text{°C kg mol}^{-} \times 4.6 \times 1000\ \text{g}}{62\ \text{g mol}^{-} \times \dfrac{11000}{1000}\ \text{kg}}$$

$$\Delta T_f = 12.5\ \text{°C}.$$

Hence freezing point = – 12.5 °C

In order to get the same freezing point depression with CH_3OH, we require same number of mol as of glycol. But:

no. of mol of glycol

$$= \frac{\text{wt. of glycol (in g)}}{\text{mol. wt. of glycol in g mol}^{-}}$$

$$= \frac{4.6 \times 1000\ \text{g}}{62\ \text{g mol}^{-}} = 74.19\ \text{mol}$$

∴no. of mol of CH_3OH = 74.19 mol

$$\therefore \text{ wt. of } CH_3OH = 74.19\ \text{mol} \times \frac{32\ \text{g}}{1\ \text{mol}} \times \frac{1\ \text{kg}}{1000\ \text{g}}$$

= **2.37 kg Ans.**

EXAMPLE 58. *An aqueous solution boils at 100.5°C. What will be the freezing point of the solution ? (K_f= 1.86 °C/m ; K_b = 0.512 °C/m)* **(ISC, 2012)**

SOLUTION. Boiling point of solution = 100.5°C ; boiling point of solvent, water = 100°C. So, ΔT_b = 100.5 °C – 100 °C = 0.5 °C. $K_f = \dfrac{1.86\ \text{°C}}{m}$ = 1.86 °C kg mol^{-} ; $K_b = \dfrac{0.512\ \text{°C}}{m}$ = 0.512 °C kg mol^{-}. Let wt. of solute = W_1 , wt. of solvent = W_2 , mol. wt. of solute = M_2 g mol^{-}. We know that :

$$(i) \qquad \Delta T_b = \frac{K_b\ (\text{in °C kg mol}^{-}) \times W_2}{M_2 \times W_1};$$

$$0.5 = \frac{0.512\ \text{°C kg mol}^{-} \times W_2}{M_2 \times W_1}$$

$$\therefore \qquad M_2 = \frac{0.512\ \text{°C kg mol}^{-} \times W_2}{0.5 \times W_1} \qquad ...(1)$$

$$(ii) \qquad \Delta T_f = \frac{K_f\ (\text{in °C kg mol}^{-}) \times W_2}{M_2 \times W_1} \qquad ...(2)$$

Substituting the value of M_2 from (1) in (2) we get :

$$\Delta T_f = \frac{1.86\ \text{°C kg mol}^{-} \times W_2 \times 0.5 \times W_1}{0.512\ \text{°C kg mol}^{-} \times W_2 \times W_1}$$

= 1.86°C

Freezing point of water = 0°C.

∴ Freezing point of solution

= 0 °C – 1.82 °C = **– 1.82 °C** **Ans.**

EXAMPLE 59. *What will be the molar mass of a substance that forms 6 % by mass solution in water which freezes at – 0.85 °C ? (K_f= 1.86 °C/m).*

SOLUTION. Wt. of solute, W_2 = 6 g ; wt. of solvent, H_2O, W_1 = 100 g, molar mass, M_2 = ? , $K_f = \dfrac{1.86\ \text{°C}}{m}$ = 1.86°C kg mol^{-}, ΔT_f = – 0.85°C. We know that :

$$\Delta T_f = \frac{K_f\ (\text{in °C kg mol}^{-}) \times W_2\ (\text{in g})}{M_2 \text{ in g mol}^{-} \times \left(\dfrac{W_1 \text{ in g}}{1000}\right) \text{kg}}$$

$$0.85\text{°C} = \frac{1.86\ \text{°C kg mol}^{-} \times 6\ \text{g}}{M_2 \times \dfrac{100}{1000}\ \text{kg}};$$

$$M_2 = \frac{1.86\ \text{°C kg mol}^{-} \times 6\ \text{g}}{0.85 \times 0.1\ \text{kg}}$$

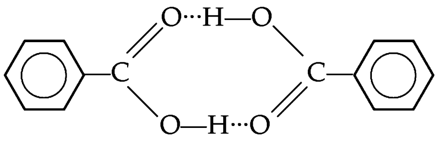
= **131.3 g mol^{-} Ans.**

EXAMPLE 60. *Normal boiling point of benzene is 82.6 °C. While the freezing point of certain solution of benzoic acid in benzene is 3.1 °C. Explain these observations and suggest the structure for benzoic acid at both the temperatures. (K_f for benzene = 5.12 °C/m, freezing point of benzene = 5.5 °C, K_b for benzene = 2.53 °C/m, boiling point of benzene = 80.1°C).*

SOLUTION. ΔT_f = 5.5 – 3.1 = 2.4 °C ; K_f = 5.12 °C/m. But $\Delta T_f = K_f m$

∴ ***m*** = $\Delta T_f/K_f$ = 2.4 °C/(5.12 °C/m) = **0.47 m.** Also, *m* = $\Delta T_b/K_b$ = (82.6 – 80.1) °C/(2.53 °C/m) = **0.99 m.**

From the values of *m* = 0.47 m and 0.99 m, it is clear that the number of moles of solute particles at the boiling point is about twice (0.99/0.47 ≃ 2) that at the freezing point of the solution. So benzoic acid dimerises (*i.e.*, forms double molecules) through hydrogen bonding at the lower temperature but the dimer breaks down at the higher temperature. Thus the structure of benzoic acid at lower temperature is :



Example 61. *Pure benzene freezes at 5.5 °C. A solution containing 7.24 g of $C_2H_2Cl_4$ in benzene (115.5 g) freezes at 3.55 °C. Calculate the cryoscopic constant of benzene (At. wt. C = 12, H = 1, Cl = 35.5)*

Solution. $\Delta T_f = 5.5\ °C - 3.55\ °C = 1.95\ °C$; wt. of solute, $W_2 = 7.24$ g ; wt. of solvent benzene, $W_1 = 115.3$ g ; $K_f = ?$; mol. wt. of $C_2H_4Cl_2 = (2 \times 12) + (4 \times 1) + (2 \times 35.5) = 168$ g mol$^-$. We know that :

$$\Delta T_f = \frac{K_f \times W_2\ (\text{in g})}{M_2\ \text{in g mol}^- \times \left(\frac{W_1\ \text{in g}}{1000}\right)\text{kg}}$$

$$\therefore \quad K_f = \frac{\Delta T_f \times M_2 \times \left(\frac{W_1\ \text{in g}}{1000}\right)\text{kg}}{W_2\ \text{in g}}$$

$$= \frac{1.95\ °\text{C} \times 168\ \text{g mol}^-}{7.24\ \text{g}} \times \frac{115.3}{1000}\text{kg}$$

$$K_f = \mathbf{5.21\ °C\ kg\ mol^-} \qquad \textbf{Ans.}$$

Example 62. *If the boiling point of an aqueous solution of non - volatile solute is 100.17 °C, calculate the temperature at which the solution will freeze. (K_f for H_2O = 1.86 °C /m : K_b for H_2O = 0.512 °C/m).*

Solution. Boiling point of water = 100 °C ; ΔT_b = 100.17 °C – 100 °C = 0.17 °C ; Freezing point of water = 0.0 °C ; $K_f = \frac{1.86\ °C}{m}$ = 1.86 °C kg mol$^-$; $K_b = \frac{0.512\ °C}{m}$ = 0.512 °C kg mol$^-$; wt. of solute = W_2 ; wt. of solvent = W_1. We know that :

$$\Delta T_b = \frac{K_b\ (\text{in °C kg mol}^-) \times W_2\ (\text{in g})}{M_2 \times W_1\ \text{in kg}};$$

$$0.17\ °\text{C} = \frac{0.512\ °\text{C kg mol}^- \times W_2\ \text{g}}{M_2\ \text{in g mol}^- \times W_1\ \text{kg}}$$

$$\therefore \quad M_2 = \frac{0.512\ °\text{C kg mol}^- \times W_2\ \text{g}}{0.17\ °\text{C} \times W_1\ \text{kg}} \qquad ...(1)$$

$$\text{Also,} \quad \Delta T_f = \frac{K_f\ (\text{in °C kg mol}^-) \times W_2\ (\text{in g})}{M_2 \times W_1\ \text{kg}} \qquad ...\ (2)$$

Substituting the value of M_2 in (2), we get :

$$\Delta T_f = \frac{1.86\ °\text{C kg mol}^- \times W_2\ \text{g}}{0.512\ °\text{C kg mol}^- \times W_2\ \text{g}} \times \frac{0.17\ °\text{C} \times W_1\ \text{kg}}{W_1\ \text{kg}}$$

$$= 0.62\ °\text{C}$$

∴ Freezing point = 0.00 – 0.62 = **– 0.62 °C** **Ans.**

Example 63. *An alloy of copper and zinc (80 % copper) melts at 1268 K. What is the molal freezing constant for copper if pure copper melts at 1357 K (Atomic mass of zinc is 65 g mol$^-$).*

Solution. ΔT_f = 1357 K – 1268 K = 89 K ; K_f = ? ; wt. of solute, Zn, W_2 = 100 – 80 = 20 g ; wt. of solvent, Cu, W_2 = 80 g ; at. wt. of Zn = 65 g mol$^-$. We know :

$$\Delta T_f = \frac{K_f \times W_2\ \text{g}}{\text{At. wt. in g mol}^- \times \left(\frac{W_1\ \text{g}}{1000}\right)\text{kg}};$$

$$K_f = \frac{\Delta T_f \times \text{at. wt. in g mol}^-}{W_2\ \text{g}} \times \frac{W_1\ \text{g}}{1000}\text{kg}$$

$$\text{or} \quad K_f = \frac{89\ \text{K} \times 65\ \text{g mol}^-}{20\ \text{g}} \times \frac{80}{1000}\text{kg}$$

$$= \mathbf{23.14\ K\ kg\ mol^-} \qquad \textbf{Ans.}$$

Example 64. *A solution containing 7.5 g of urea (Mol. wt. 60) in one kg of water freezes at the same temperature as another solution containing 15 g of solute S in the same amount of water. Calculate molecular mass of S.*

Solution. Wt. of solute, W_2 (urea) = 7.5 g ; mol. wt. of solute = 60 g mol$^-$. wt. of solvent water, W_1 = 1 kg ; wt. of second solute, W_2 = 15 g ; wt. of second solvent water, W_1 = 1 kg

First solution :

$$\Delta T_f = \frac{K_f \times W_2\ \text{g}}{M_2\ \text{g mol}^- \times W_1\ \text{kg}}$$

$$= \frac{K_f \times 7.5\ \text{g}}{60\ \text{g mol}^- \times 1\ \text{kg}} \qquad ...(1)$$

Second solution of solute S :

$$\Delta T_f = \frac{K_f \times W_2\ \text{g}}{M_2 \times W_1\ \text{kg}} = \frac{K_f \times 15\ \text{g}}{M_2 \times 1\ \text{kg}} \qquad ...(2)$$

Equating (1) and (2), we get :

$$\frac{K_f \times 7.5\ \text{g}}{60\ \text{g mol}^- \times 1\ \text{kg}} = \frac{K_f \times 15\ \text{g}}{M_2 \times 1\ \text{kg}};$$

$$M_2 = \frac{K_f \times 15\ \text{g} \times 60\ \text{g mol}^- \times 1\ \text{kg}}{K_f \times 7.5\ \text{g} \times 1\ \text{kg}}$$

$$\text{or} \quad M_2 = \mathbf{120\ g\ mol^-} \qquad \textbf{Ans.}$$

Example 65. *Calculate the amount of KCl which must be added to 1 kg of water so that its freezing point is depressed by 2 K. (k_f for water = 1.86 K kg mol$^-$; at. mass K = 39, Cl = 35.5).* **(CBSE, 2008)**

Solution. Wt. of KCl, W_B = ?, mol. wt. of KCl, M_B = 39 + 35.5 = 74.5 g mol$^-$; wt. of water, W_A = 1 kg; ΔT_f = 2 K. We know that :

$$\Delta T_f = \frac{K_f \times W_B \text{ in g}}{M_B \times W_A \text{ is kg}};$$

$$W_B = \frac{\Delta T_f \times M_B \times W_A \text{ in kg}}{K_f}$$

$$W_B = \frac{2\text{K} \times 74.5\,\text{g mol}^{-} \times 1\,\text{kg}}{1.86\,\text{K kg mol}^{-}} = \mathbf{80.1\ g}$$

Example 66. *A solution of urea in water has a boiling point 100.128 °C. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 °C and 0.512 °C respectively.* **(PSEB, 2006)**

Solution. ΔT_b = 100.128 °C – 100 °C = 0.128 °C ; K_b = 0.512 °C ; K_f = 1.86 °C.

$$\Delta T_b = K_b \times m \text{ (molality of solution)};$$

$$\therefore \quad m = \frac{\Delta T_b}{K_b} = \frac{0.128}{0.512}$$

$$\text{But} \quad \Delta T_f = K_f \times m;$$

$$\Delta T_f = 1.86 \times \frac{0.128}{0.512} = 0.465\ °\text{C}$$

∴ Freezing point of solution

$$= T_o - \Delta T_f = 0 - 0.465 = -0.465°\text{C}$$

$$= 273 - 0.465 = \mathbf{272.535\ K} \qquad \textbf{Ans.}$$

Example 67. *Calculate the freezing point of a solution that contains 30 g urea in 200 g water. Urea is a non-volatile, non-electrolyte solid. K_f for H_2O = 1.86°C/m*

(*a*) 4.65° C (*b*) –4.65° C

(*c*) –0.744° C (*d*) +0.744° C/m

(Orissa JEE, 2009, PSEB, 2012 type)

Solution. g. mol. wt. of urea, NH_2CONH_2 = 14 + (2 × 1) + 12 + 16 + 14 + (2 × 1) = 60 g mol⁻.

$$\text{Molality,} \quad m = \frac{\text{wt. of urea}}{\text{g. mol. wt. of urea}} \times \frac{1000}{\text{weight of solvent, } H_2O}$$

$$= \frac{30}{60} \times \frac{1000}{200} = 2.5\ \text{m}$$

$$\therefore \quad \Delta T_f = K_f \times m;$$

$$\Delta T_f = \frac{1.86°\,\text{C}}{m} \times 2.5\ \text{m}$$

$$= 4.65°\text{C}$$

∴ F.pt. of solution = 0.00 – 4.65°C = – 4.65°C

So, the correct answer is (*b*)

Type.

$$\Delta T_f = \frac{K_f \times \Delta p}{p° \times \text{mol. wt. of solvent say, } H_2O = \left(\frac{18}{1000}\ \text{kg mol}^{-}\right)}$$

Δp = Lowering of vapour pressure *i.e.*,

$p° - ps$

$p°$ = Vapour pressure of pure solvent, say water

Example 68. *An aqueous solution freezes at –0.2°C. What is the molality of the solution ? Determine also (i) elevation in the boiling point (ii) lowering of vapour pressure at 25°C, given that K_f = 1.86 °C kg mol⁻; K_b = 0.512°C kg mol⁻ and vapour pressure of water at 25°C is 23.756 mm.*

Solution. (*i*) ΔT_f = – 0.2 °C ; K_f = 1.86 °C kg mol⁻. But

$$\Delta T_f = K_f \times \text{molality}.$$

$$\text{Hence, molality} = \frac{\Delta T_f}{K_f} = \frac{0.2\ °\text{C}}{1.86\ °\text{C kg mol}^{-}}$$

or molality = **0.1075 kg⁻ mol** **Ans.**

(*ii*) ΔT_b = ?

But $\Delta T_b = K_b \times m$

$$= 0.512\ °\text{C kg mol}^{-} \times 0.1075\ \text{kg}^{-}\ \text{mol}$$

$$\therefore \quad \Delta T_b = \mathbf{0.055\ °C} \qquad \textbf{Ans.}$$

$$(iii)\ \Delta T_f = \frac{K_f \times \Delta p}{p° \times \text{mol. wt. of solvent, } H_2O = \frac{18}{1000}\ \text{kg mol}^{-}}$$

Substituting the values, we get

$$0.2\ °\text{C} = \frac{1.86\ °\text{C kg mol}^{-} \times \Delta p}{23.756\ mm \times \frac{18}{1000}\ \text{kg mol}^{-}}$$

$$\therefore \quad \Delta p = \frac{0.2\ °\text{C} \times 23.756\ \text{mm} \times 18\ \text{kg mol}^{-}}{1.86\ °\text{C kg mol}^{-} \times 1000}$$

$$= \mathbf{0.046\ mm} \qquad \textbf{Ans.}$$

Example 69. *Water is used in car radiators. In winter season, ethylene glycol is added to water so that water may not freeze. Assuming ethylene glycol to be non-volatile, calculate minimum amount of ethylene glycol that must be added to 6.0 kg of water to prevent it from freezing at – 0.3 °C. The molal depression constant of water is 1.86 °C/m.*

Solution. ΔT_f = 0.3 °C, K_f = 1.86 °C kg mol⁻, mol. wt. of ethylene glycol, $(CH_2OH)_2$ = 2 [12 + (2 × 1) + 16 + 1] = 62 g mol⁻ ; wt. of solute, W_2 = ? , wt. of solvent, W_1 = 6 kg, But :

$$\Delta T_f = \frac{K_f\ (\text{in °C kg mol}^{-}) \times W_2\ \text{g}}{M_2 \text{ in g mol}^{-} \times W_1 \text{ in kg}};$$

$$0.3\ °\text{C} = \frac{1.86\ °\text{C kg mol}^{-} \times W_2}{62\ \text{g mol}^{-} \times 6\ \text{kg}}$$

$$\therefore \quad W_2 = \frac{0.3\ °\text{C} \times 62\ \text{g mol}^{-} \times 6\ \text{kg}}{1.86\ °\text{C kg mol}^{-}}$$

$$= \mathbf{60\ g} \qquad \textbf{Ans.}$$

Example 70. *Addition of 0.643 g of a compound to 50 mL of benzene (density, 0.87 g/mL) lowers the freezing point from*

5.51°C to 5.03°C. If k_f for benzene is 5.12, calculate the molecular weight of the compound. **(HP Board, 2012)**

Solution. ΔT_f = 5.51°C – 5.03°C = 0.48°C = 0.48 K;

wt. of compound = 0.643 g; volume of solvent = 50 mL; density = 0.87 g $(\text{mL})^{-}$; K_f = 5.12 k kg mol^{-}.

(*i*) wt. of solvent = volume × density

= 50 mL × 0.87 g (mL) = 43.5 g

(*ii*) Molality,

$$m = \frac{\text{wt.}}{\text{mol. wt.}} \times \frac{1000\text{ g kg}^{-}}{\text{wt. of solvent}}$$

$$= \frac{0.643\text{g}}{\text{mol. wt.}} \times \frac{1000\text{ g kg}^{-}}{43.5\text{ g}}$$

But $\quad \Delta T_f = K_f \times m = 5.12\text{ K kg mol}^{-} \times \frac{0.643}{\text{mol. wt.}} \times \frac{1000\text{ g kg}^{-}}{43.5}$

or $\quad 0.48\text{ K} = \frac{75.68\text{ g K mol}^{-}}{\text{mol. wt.}}$

$\therefore \quad \text{mol. wt.} = \frac{75.68\text{ g K mol}^{-}}{0.48\text{ K}}$

$= \mathbf{157.67\text{ g mol}^{-}}$ **Ans.**

Example 71. *Find the elevation in boiling point and (ii) depression in freezing point of a solution containing 0.520 g glucose ($C_6H_{12}O_6$) dissolved in 80.2 g of water. For water k_f = 1.86 K/m. K_b = 0.52 K/m.*

Solution. ΔT_b = ?, ΔT_f = ? ; wt. of solute, W_2 = 0.52 g ; mol. wt. of solute ($C_6H_{12}O_6$), M_2 = (6 × 12) + (12 × 1) + (6 × 16) = 180 g mol^{-} ; $K_b = \frac{0.52\text{ K}}{m}$ = 0.52 K kg mol^{-}; K_f = 1.86 K/m = 1.86 K kg mol^{-} ; wt. of solvent, W_1 = 80.2 g

(*i*)

$$\Delta T_b = \frac{K_b \times W_2}{M_2 \times \left(\frac{W_1\text{ g}}{1000}\right)\text{kg}}$$

$$= \frac{0.52\text{ K kg mol}^{-} \times 0.52\text{ g}}{180\text{ g mol}^{-} \times \frac{80.2}{1000}\text{ kg}}$$

$$= \frac{0.52 \times 0.52 \times 1000}{180 \times 80.2}\text{ K}$$

or $\quad \Delta T_b = \mathbf{0.019\text{ K}}$ **Ans.**

(*ii*)

$$\Delta T_f = \frac{K_f \times W_2}{M_2 \times \frac{W_1}{1000}\text{ kg}}$$

$$= \frac{1.86\text{ K kg mol}^{-} \times 0.52\text{ g}}{180\text{ g mol}^{-} \times \frac{80.2}{1000}\text{ kg}}$$

$$= \frac{1.86 \times 0.52 \times 1000}{180 \times 80.2}\text{ K}$$

$\Delta T_f = \mathbf{0.067\text{ K}}$ **Ans.**

Example 72. *Find the depression in f.pt. of the solution which has 0.1. mol of sugar dissolved in 250 g water. (k_f for water is 1.86 °C kg mol^{-}).*

Solution. Mol. wt. of sugar, $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 + 16) = 342 g mol^{-}.

ΔT_f = ? , wt. of solute sugar, W_2 = 0.1 mol × 342 g mol^{-} = 34.2 g ; wt. of solvent, W_2 = 250 g. We know that :

$$\Delta T_f = \frac{K_f \times W_2}{M_2 \times \left(\frac{W_1\text{ in g}}{1000}\right)\text{kg}}$$

$$= \frac{1.86\text{ °C kg mol}^{-} \times 34.2\text{ g}}{342\text{ g mol}^{-} \times \frac{250}{1000}\text{ kg}}$$

$$= \frac{1.86 \times 34.2 \times 1000}{342 \times 250}\text{ °C}$$

or $\quad \Delta T_f = \mathbf{0.744\text{ °C}}$ **Ans.**

Example 73. *A solution of 1.25 g of a certain non - electrolyte in 20.0 gram of water freezes at 271.94 K. Calculate the molecular mass of the solute (k_f = 1.86 K/m).*

(DSSC, 1981, AISC, 1983, HP Board, 2007)

Solution. Wt. of solute, W_2 = 1.25 g ; wt. of solvent, W_2 = 20.0 g, Molecular mass, M_2 = ? K_f = 1.86 K/m = 1.86 K kg mol^{-}; ΔT_f = Freezing point of water – f.pt. of solution = 273 K – 271.94 K = 1.06 K. We know that :

$$\Delta T_f = \frac{K_f \times W_2}{M_2 \times W_1\text{ in kg}};$$

$$1.06\text{ K} = \frac{1.86\text{ K kg mol}^{-} \times 1.25\text{ g}}{M_2 \times \frac{20}{1000}\text{ kg}}$$

$$\therefore \quad M_2 = \frac{1.86\text{ K kg mol}^{-} \times 1.25\text{ g} \times 1000}{1.06\text{ K} \times 20\text{ kg}}$$

$= \mathbf{109.67\text{ g mol}^{-}}$ **Ans.**

Example 74. *45 g of ethylene glycol, $C_2H_6O_2$ is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) freezing point of the solution. K_f for water is 1.86 K kg mol^{-}.*

Solution. Wt. of solute $C_2H_6O_2$, W_2 = 45 g ; wt. of solvent water, W_2 = 600 g ; K_f = 1.86 K kg mol^{-} ; mol. wt. of $C_2H_6O_2$ = (2 × 12) + (6 × 1) + (2 × 16) = 62 g mol^{-}. We know that:

$$\Delta T_f = \frac{K_f \times W_2}{M_2 \times W_1\text{ in kg}}$$

$$= \frac{1.86\text{ K kg mol}^{-} \times 45\text{ g}}{62\text{ g mol}^{-} \times \frac{600}{1000}\text{ kg}}$$

$$= \frac{1.86\text{ K} \times 45 \times 1000}{62 \times 600} = 2.25\text{ K}$$

$\therefore$ Freezing point of solution = 273.15 K (*i.e.*, f.pt. of water) – 2.25 K = **270.9 K** **Ans.**

EXAMPLE 75. *An aqueous solution contains 5 % by weight of urea and 10 % by weight of glucose. What will be its freezing point ? (K_f for water = 1.86 K kg mol^{-})*

SOLUTION. Wt. of urea, NH_2CONH_2 = 5 g ; wt. of glucose, $C_6H_{12}O_6$ = 10 g. ; wt. of water, W_1 = 100 – (5 + 10) = 85 g ; K_f = 1.86 K kg mol^{-}. Freezing point = ? Mol. wt. of NH_2CONH_2 = 14 + (2 × 1) + 12 + 16 + 14 + (2 × 1) = 60 g mol^{-}

$$(i)\quad \Delta T_f \text{ for urea} = \frac{K_f \times \text{Wt. of urea}}{\text{Mol. wt. of urea} \times \left(\dfrac{W_1\text{ g}}{1000}\right)\text{kg}}$$

$$= \frac{1.86\text{ K kg mol}^{-} \times 5\text{ g}}{60\text{ g mol}^{-} \times \dfrac{85}{1000}\text{ kg}}$$

$$\Delta T_f(\text{urea}) = \frac{1.86\text{ K} \times 5 \times 1000}{60 \times 85} = 1.824\text{ K}$$

(*ii*) Mol. wt. of glucose $C_6H_{12}O_6$ = (6 × 12) + (12 × 1) + (6 × 16) = 180 g mol^{-}

$$\Delta T_f(\text{glucose}) = \frac{K_f \times \text{wt. of glucose}}{\text{Mol. wt. of glucose} \times \left(\dfrac{\text{wt. of solvent (in g)}}{1000}\right)\text{kg}}$$

$$= \frac{1.86\text{ K kg mol}^{-} \times 10\text{ g}}{180\text{ g mol}^{-} \times \dfrac{85}{1000}\text{ kg}}$$

$$= \frac{1.86\text{ K} \times 10 \times 1000}{180 \times 85} = 1.216\text{ K}$$

∴ Total ΔT_f = 1.824 K + 1.216 K = 3.04 K

∴Freezing point = **– 3.04 K.** **Ans.**

EXAMPLE 76. *The constant for the depression of f.pt. of water is 1.86 K kg mol^{-}. An aqueous solution of cane sugar froze at – 0.135 K. What is the molality of the solution ?*

SOLUTION. ΔT_f = – 0.135 K ; K_f = 1.86 K kg mol^{-}. We know that :

$$\Delta T_f = K_f \times \text{molality.}$$

$$\text{So, molality} = \frac{\Delta T_f}{K_f} = \frac{0.135\text{ K}}{1.86\text{ K kg mol}^{-}}$$

$$= \mathbf{0.072\ mol\ kg^{-}}$$ **Ans.**

Type. When K_f value for 100 g solvent is given, then convert this value to °C (or K) kg mol^{-} by multiplying K_f value by $\dfrac{100\text{ g}}{1000}$ because division by 1000 gives value in kg.

EXAMPLE 77. *The freezing point of a solution of 0.321 g of a solute in 11.2 g of benzene is 278.155 K. The freezing point of pure benzene is 278.40 K and molecular depression of freezing point per 100 g of solvent is 51.2 K. (100 g mol^{-}). Calculate the molecular mass of solute.*

SOLUTION. K_f = 51.2 K (100 g mol^{-}) = 51.2 K $\left(\dfrac{100}{1000}\text{ kg mol}^{-}\right) = 51.2 \times \dfrac{1}{10}$ K kg mol^{-} = 5.12 K kg mol^{-} ;

ΔT_f = 278.40 – 278.155 = 0.245 K, wt. of solute, W_2 = 0.321 g ; wt. of solvent, W_1 = 11.2 g = $\dfrac{11.2}{1000}$ kg. Molecular mass, M_2 = ?

We know that :

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$M_2 = \frac{K_f \times W_2 \text{ in g}}{\Delta T_f \times W_1 \text{ in kg}}$$

$$\text{or}\quad M_2 = \frac{5.12\text{ K kg mol}^{-} \times 0.321\text{ g}}{0.245\text{ K} \times \dfrac{11.2}{1000}\text{ kg}}$$

$$= \frac{5.12\text{ mol}^{-} \times 0.321\text{ g} \times 1000}{0.245 \times 11.2}$$

or M_2 = **598.95 g mol^{-}** **Ans.**

$$\text{or}\quad \Delta T_f = \frac{100 \times K_b \text{ in K. g mol}^{-} \times W_2 \text{ in g}}{M_2 \text{ in g mol}^{-} \times W_1 \text{ in g}};$$

$$0.245\text{ K} = \frac{100 \times 51.2\text{ K. g mol}^{-} \times 0.321\text{ g}}{M_2 \times 11.2\text{ g}}$$

∴ M_2 = 598.95 g mol^{-} **Ans.**

Type. (*i*) Molecular depression constant, $K_f = R\,\dfrac{\left(T_f^o\right)^2}{100\,L_f}$

where T_f^o = Freezing point of solvent in kelvin; K_f in K. g mol^{-}; Wt. of solute and solvent are in g.

L_f = Latent heat of fusion of solvent in cal g^{-}

R = Gas constant = 2 cal K^{-} mol^{-}

$$(ii)\quad \Delta T_f = \frac{K_f \text{ in °C (or K) kg mol}^{-} \times W_2 \text{ in g}}{M_2 \times W_1 \text{ kg}}$$

When K_f value for 100 g solvent is given, then convert this value to °C (or K) kg mol^{-} by multiplying K_f value by 100g/1000 because division by 1000 gives value in kg. ; W_1 = wt. of solvent in kg, W_2 = wt. of solute in g.

EXAMPLE 78. *A solution containing 2.423 g sulphur in 100 g naphthalene (m.p. 80.1°C) gave a lowering in freezing point of 0.641°C. The latent heat of fusion of naphthalene is 35.7 cal g^{-}. Calculate the molecular formula of sulphur in naphthalene (at. wt., S = 32)*

SOLUTION. T_f = 273 + 80.1 = 353.1 K, L_f = 35.7 cal g^{-}

But

$$K_f(\text{molecular}) = \frac{R\left(T_f^o\right)^2}{100\,L_f}$$

$$= \frac{2\ \text{cal K}^{-}\ \text{mol}^{-} \times (353.1\ \text{K})^2}{100 \times 35.7\ \text{cal g}^{-}}$$

$$= 69.85\ \text{K. g mol}^{-}\ \text{for 100 g solvent}$$

$\therefore K_f$ (molal) for 1000 g solvent

$$= 69.85 \times \frac{100}{1000} = 6.985\ \text{K kg mol}^{-}$$

Also,
$$\Delta T_f = \frac{K_f \times W_2}{M_2 \times \left(\dfrac{W_1\ \text{in g}}{1000}\right)\text{kg}};$$

$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1\ \text{kg}}$$

$$= \frac{6.985\ \text{K kg mol}^{-} \times 2.423\ \text{g} \times 1000}{0.641\ \text{K} \times 100\ \text{kg}}$$

$$= 264\ \text{g mol}^{-}$$

Atomic weight of sulphur = 32 g mol^{-}

$$\therefore\ \text{Atomicity of sulphur} = \frac{\text{Mol. wt.}}{\text{At. wt.}} \simeq \frac{264}{32} = 8$$

$\therefore$ Molecular formula of sulphur = S_8.

Example 79. *An aqueous solution containing 1.70 g of cane sugar in 100 mL water begins to freeze at –0.093°C. The cryoscopic constant (molal depression constant) of water is 1.86 K kg mol¯. Calculate the molecular weight of cane sugar.*

(ISC, 2007, 2011)

Solution. $\Delta T_f = -0.093°\text{C} = -0.093$ K; $K_f = 1.86$ K Kg mol^{-}

Mol. wt. ?; Molality, m = ?;

Wt. of 100 mL solvent water = 100 g. We know that

(*i*) $\Delta T_f = K_f \times m;$

$$m = \frac{\Delta T_f}{K_f} = \frac{0.093\ \text{K}}{1.86\ \text{K kg mol}^{-}} = 0.05$$

(*ii*)
$$\text{Molality} = \frac{\text{Wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Wt. of solvent}}$$

$$0.05 = \frac{1.7 \times 1000}{\text{Mol. wt.} \times 100};$$

$$\text{Mol. wt.} = \frac{1.7 \times 1000}{0.05 \times 100} = \mathbf{340\ g\ mol^{-}}$$ **Ans.**

Type. To find molal depression constant, K_f (and not molecular depression constant) when latent heat of fusion (L_f) is given, following relation is used.

$$K_f = \frac{MR\,(T_f^o)^2}{\Delta_{fus} H \times 1000} = \frac{R\,(T_f^o)^2}{\dfrac{\Delta_{fus} H}{M} \times 1000} = \frac{R\,(T_f^o)^2}{L_f \times 1000}$$

Where M = Molar mass of solvent

R = a gas constant = 2 cal K^{-} mol^{-}

$\Delta_{fus} H$ = Molar enthalpy of fusion of solvent

T_f^o = Freezing point of solvent

L_f = Latent heat of fusion of solvent in cal g^{-}; 1000 means 1000 g kg^{-}

When L_v is in Jg^{-}, R is equal to 8.314 J K^{-} mol^{-}

Example 80. *The latent heat of fusion of benzene is 30. 25 cal g¯. 0.0802 g of a substance when dissolved in 13.03 g of benzene lowers the freezing point by 0.49°C. If pure benzene freezes at 5.4 °C, then calculate the molecular weight of the substance.*

Solution. L_f = 30.25 cal g^{-} ; R = 2 cal K^{-} mol^{-}; wt. of solute, W_2 = 0.0802 g ; wt. of solvent, W_1 = 13.03 g = $\frac{13.03}{1000}$ kg ; ΔT_f = 0.49 °C ; M_2 = ? T_f^o = 273 + 5.4 = 278.4 K.

We know that :

(*i*)
$$K_f = \frac{R\left(T_f^o\right)^2}{1000 \times L_f}$$

$$= \frac{2\ \text{cal K}^{-}\text{mol}^{-} \times (278.4\ \text{K})^2}{1000\ \text{g kg}^{-} \times 30.25\ \text{cal g}^{-}}$$

$$= 5.12\ \text{K. kg mol}^{-}$$

(*ii*)
$$\Delta T_f = \frac{K_f\, W_2}{M_2\, W_1};$$

$$M_2 = \frac{K_f\, W_2}{\Delta T_f \times W_1}$$

$$= \frac{1000 \times 5.12\ \text{K. kg mol}^{-} \times 0.0802\ \text{g}}{0.49\ \text{K} \times 13.03\ \text{kg}}$$

Or $\mathbf{M_2 = 64.31\ g\ mol^{-}}$ **Ans.**

Example 81. *A 0.1589 molal aqueous solution of cane sugar (molar mass = 342 g mol⁻¹) has a freezing point of 271 K while the freezing point of pure water is 273.15 K. What will be the freezing point of an aqueous solution containing 5 g of glucose (mol. mass = 180 g mol¯) per 100 g solution.* **(CBSE, 2007)**

Solution. (*i*) For cane sugar; molality, m = 0.1589; ΔT_f = 273.15 – 273 = 2.15 K.

But $\Delta T_f = K_f \times m.$

So,
$$K_f = \frac{\Delta T_f}{m} = \frac{2.15}{0.1589} = 13.53\ \text{K kg mol}^{-}$$

(*ii*) For glucose. $f.pt$ = ?; Wt. of glucose, solute = 5.0 g Wt. of solution = 100 g; Wt. of solvent = 100 – 5 = 95 g Mol. mass of glucose = 180 g mol^{-}

$$\therefore \quad \text{Molality}, m = \frac{\text{Wt.}}{\text{Mol. mass}} \times \frac{1000}{\text{Wt. of solvent}}$$

$$= \frac{5\text{ g} \times 1000\text{ g kg}^{-}}{180\text{ g mol}^{-} \times 95\text{ g}} = 0.292\text{ mol kg}^{-}$$

But $\Delta T_f = K_f \times m = 13.53\text{ K kg mol}^{-} \times 0.292\text{ mol kg}^{-}$

$= 3.95\text{ K}$

$\therefore$ $f.pt$ = 273.15 – 3.95 = **269.2 K** **Ans.**

Example 82. *Two elements A and B form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of C_6H_6, 1.0 g of AB_2 lowers the freezing point by 2.3 K where as 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol⁻. Calculate atomic masses of A and B.* **(CBSE, 2004)**

Solution. Wt. of solute, W_2 in each case = 1 g ; wt. of solvent benzene, W_1 = 20 g. Let at. wt. of $A = a$: at. wt. of $B = b$.

Hence **mol. wt. of $AB_2 = a + 2b$;**

mol. wt. of $AB_4 = a + 4b$

(*i*) 20 g benzene contain

$AB_2 = 1\text{ g}$

1000 g benzene contain

$$AB_2 = \frac{1}{20} \times 1000 = 50\text{ g}$$

(*ii*) 20 g benzene contain

$AB_4 = 1\text{ g}$

1000 g benzene contain

$$AB_4 = \frac{1}{20} \times 1000 = 50\text{ g}$$

$$\therefore \quad \text{Molality of } AB_2 = \frac{50}{a + 2b};$$

$$\text{molality of } AB_4 = \frac{50}{a + 4b}$$

(*iii*) **For AB_2.**

$$\Delta T_f = K_f \times m;$$

$$2.3 = 5.1 \times \frac{50}{a + 2b}$$

$$\therefore \quad a + 2b = \frac{5.1 \times 50}{2.3}; a + 2b = 110.87 \qquad ...(1)$$

(*iv*) **For AB_4.**

$$\Delta T_f = K_f \times m;$$

$$1.3 = 5.1 \times \frac{50}{a + 4b}$$

$$\therefore \quad a + 4b = \frac{5.1 \times 50}{1.3};$$

$$a + 4b = 196.15 \qquad ...(2)$$

Subtracting (1) and (2), we get :

$a + 4b = 196.15$

Subtract: $\underline{a + 2b = 110.87}$

$$2b = 85.28 ; \boldsymbol{b} = \frac{85.28}{2} = 42.64\text{ s}$$

Substituting the value of b in (1) ; we get :

$a + 2\,(42.64) = 110.87$;

$\boldsymbol{a}$ = 110.87 – 85.28 = **25.59** **Ans.**

Example 83. *Calculate the freezing point of an aqueous solution having mole fraction of water, 0.8. Latent heat of fusion of ice is 80 cal g⁻. (R = 2 cal K⁻ mol⁻).*

Solution. T_f^o = f.pt. of ice = 0 + 273 = 273 K ; L_f = 80 cal g⁻. Mole fraction of solute, x_{solute} + mole fraction of solvent water, x_{H_2O} = 1; x_{H_2O} = 0.8 ; x_{solute} = 1 – 0.8 = 02

$$K_f = \frac{R\left(T_f^o\right)^2}{1000\,L_f} = \frac{2\text{ cal K}^{-}\text{ mol}^{-} \times 273\text{ K} \times 273\text{ K}}{1000\text{ g. kg}^{-} \times 80\text{ cal g}^{-}}$$

$$= 1.86\text{ K kg mol}^{-}$$

$$x_{H_2O} = \frac{n_1}{n_1 + n_2} \qquad ...(1)$$

$$x_{\text{solute}} = \frac{n_2}{n_1 + n_2} \qquad ...(2)$$

Dividing equation (2) by (1), we get

$$\left(\frac{n_2}{n_1 + n_2}\right) \Big/ \frac{n_1}{n_1 + n_2} = \frac{0.2}{0.8}; \frac{n_2}{n_1} = \frac{1}{4}; n_2 = \frac{n_1}{4} \qquad ...(3)$$

But no. of mol of H_2O,

$$n_1 = \frac{\text{wt. of } H_2O}{\text{mol. wt. of } H_2O} = \frac{1000\text{ g}}{18\text{ g mol}^{-}}$$

$$= 55.5\text{ mol}^{-}$$

$$\therefore \quad n_2 = \frac{55.5\text{ mol}}{4}$$

and hence molality,

$$m = \frac{55.5\text{ mol}}{4 \times \text{kg}}$$

But $\Delta T_f = K_f \times m$;

$$\Delta T_f = 1.86\text{ K kg mol}^{-} \times \frac{55.5\text{ mol}}{4 \times \text{kg}} = 25.8\text{ K}$$

$\therefore$ f.pt. of solution = 273 K – 25.8 K = **247.2 K** **Ans.**

Example 84. *The freezing point of a solution containing 50 cm³ of ethylene glycol in 50 g of water is found to be – 34 °C. Assuming ideal behaviour, calculate the density of ethylene glycol. (K_f for water is 1.86 K kg mol⁻¹)* **[Roorkee, 1999]**

Solution. K_f for water = 1.86 K kg mol^{-1}

Volume of ethylene glycol = 50 cm³. Wt. of ethylene glycol = 50 × d ; Mol. mass of glycol (CH_2 OH. CH_2 OH) = [12 + (2 × 1) + 16 + 1 + 12 + (2 × 1) + 16 + 1] = 62 g mol⁻; d = density of glycol.

$$\text{Wt. of water} = 50\text{ g} = \frac{50}{1000} = 0.05\text{ kg}$$

$$\Delta T_f = 34°\text{C} = 34\text{ K}$$

we know that :

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$34\text{ K} = \frac{1.86\text{ K kg mol}^{-} \times 50\text{ cm}^3 \times d}{62\text{ g mol}^{-} \times 0.05\text{ kg}}$$

$$\therefore \quad \boldsymbol{d} = \frac{34\text{ K} \times 62\text{ g mol}^{-} \times 0.05\text{ kg}}{1.86\text{ K kg mol}^{-} \times 50\text{ cm}^3}$$

$$= \mathbf{1.133\ g\ cm^{-3}} \qquad \textbf{Ans.}$$

EXAMPLE 85. *1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solid (A) dissolved in 100 g of benzene gave a solution which froze at 277.60 K. Calculate the molecular weight of (A).* **[Roorkee, 2000]**

SOLUTION. (*i*) Calculation of K_f of benzene. Weight of acetone, $W_2 = 1.4$ g ; Weight of benzene $W_1 = 100\text{ g} = \frac{100}{1000}$ *i.e.*, 0.1 kg ; $\Delta T_f = 278.4\text{ K} - 277.12\text{ K} = 1.28\text{ K}$; $K_f = ?$; mol. wt. of acetone, $CH_3COCH_3 = [12 + (3 \times 1) + 12 + 16 + 12 + (3 \times 1)] = 58\text{ g mol}^{-}$.

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$1.28\text{ K} = \frac{K_f \times 1.4\text{ g}}{58\text{ g mol}^{-} \times 0.1\text{ kg}}$$

$$\therefore \quad K_f = \frac{1.28\text{ K} \times 58\text{ g mol}^{-} \times 0.1\text{ kg}}{1.4\text{ g}}$$

$$= 5.3\text{ K kg mol}^{-}$$

(*ii*) Wt. of solute, $W_2 = 2.8$ g ; wt. of solvent, $W_1 = 100$ g $\frac{100}{1000}$ or 0.1 kg.

$\Delta T_f = 278.4\text{ K} - 277.60\text{ K} = 0.80\text{ K}$; $K_f = 5.3$ K kg mol^{-} ; mol. wt. of $A, M_2 = ?$.

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}};$$

$$0.8\text{ K} = \frac{5.3\text{ K kg mol}^{-} \times 2.8\text{ g}}{M_2 \times 0.1\text{ kg}}$$

$$\therefore \quad M_2 = \frac{5.3\text{ K kg mol}^{-} \times 2.8\text{ g}}{0.8\text{ K} \times 0.1\text{ kg}}$$

$$= \mathbf{185.5\ g\ mol^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 86. *To 500 cm^3 of water, 3.0 × 10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point ? K_f and density of water are 1.6 K kg mol^{-1} and 0.997 g cm^{-3} respectively.* **(IIT, 2000)**

SOLUTION. Volume of $H_2O = 500\text{ cm}^3$, density of water $= 1\text{ g cm}^{-3}$.

$\therefore$ wt. of solvent water, W_1 = volume × density = 500 cm^3 × 0.997 g cm^{-3} = 498.5 g = $\frac{498.5}{1000} = 0.4985$ kg ; wt. of solute acetic acid, $W_2 = 3.0 \times 10^{-3}$ kg $= 3.0 \times 10^{-3}$ kg $\times \frac{1000\text{ g}}{1\text{ kg}} = 3$ g ;

mol. wt. of $CH_3COOH = 12 + (3 \times 1) + 12 + 16 + 16 + 1 = 60\text{ g mol}^{-}$

$$\Delta T_f = \frac{i \times K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$\Delta T_f = \frac{i \times 1.86\text{ K kg mol}^{-} \times 3\text{ g}}{60\text{ mol}^{-} \times 0.4985\text{ kg}}$$

$$= 0.186\, i\text{ K}.$$

But $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$1-\alpha \qquad \alpha \qquad \alpha$ (α = degree of dissociation)

Total number of particles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$\therefore \quad i = \frac{1+\alpha}{1} = \frac{1 + 23/100}{1} = 1.23$$

$$\therefore \quad \Delta T_f = 0.186 \times 1.23\text{ K} = \mathbf{0.229\ K} \qquad \textbf{Ans.}$$

Note. '*i*' is van't Hoff factor. For details see section 18.21.

EXAMPLE 87. *When a solution containing benzene (0.9 mol) and naphthalene (0.1 mol) was cooled, some of the benzene separated out. The solution after removing solid benzene was heated to 353 K and vapour pressure of 670 torr was obtained. Calculate the temperature to which the solution was cooled and also calculate the weight of benzene that froze. Considering the solution to be ideal, K_f for benzene = 5 kg mol^{-} K, freezing point of benzene is 278.5 K and normal boiling point of benzene is 353 K.*

SOLUTION. In order to get molality (*m*) of the resulting solution (*i.e.*, a solution left behind after solid benzene is separated out), the following relation of Raoult's law is used.

$$m = \frac{x_{\text{naph}} \times 1000}{x_{\text{benz}} \times \text{mol. mass of benzene, } C_6H_6\ (=78)}$$

$$= \frac{\left(\frac{760 - 670}{760}\right)}{0.88 \times 78\text{ g mol}^{-}} \times 1000\text{ g kg}^{-} = 1.72\text{ mol kg}^{-}$$

$$\left[\begin{aligned} \because x_{\text{naph}} &= \frac{p^{\circ} - p}{p^{\circ}} \\ &= \frac{760 - 670}{760} \\ &= 0.118 \\ \because x_{\text{benz}} &= 1 - 0.118 = 0.88 \end{aligned}\right.$$

$\therefore$ wt. of benzene in the resulting solution $= \frac{1000\text{ g kg}^{-} \times 0.1\text{ mol}}{1.72\text{ mol kg}^{-}} = 58.1$ g.

[$\because$ 1 kg = 1000 g]

∴ wt. of benzene that changed into solid on cooling $= (0.9 \times 78) - 58.1 = 12.1$ g

But $\Delta T_f = k_f \times m = 5 \times 1.72 = 8.6$ K

Thus, the **temperature to which the solution was cooled** = 278.5 – 8.6 = **269.9 K** **Ans.**

18.14 BECKMANN'S METHOD

This method is based on the principle that the freezing point of a solvent is lowered when a solute is dissolved in it. This lowering or depression in freezing point (ΔT_f) is proportional to the molecular concentration of the solute. The depression in freezing point produced by **one g. mol** of a substance in 1000 g of a solvent is called **molal** depression constant. [However, the depression in freezing point (ΔT_f) produced by one gram **molecule** of a substance in 100 g of a solvent is called the **molecular** depression constant].

If w g of a solute (mol. wt., M) is dissolved in W g of the solvent, the depression in freezing point is calculated from the relation :

$$\Delta T_f = \frac{1000\, K_f\, w}{W\, M}$$

Or

$$M = \frac{1000\, K_f\, w}{W\ \Delta T_f}$$

$\because \Delta T_f = \text{molality}, m \times k_f$ and $m = \frac{w}{M} \times \frac{1000}{W}$

w = wt. of solute ; W = wt. solvent ;

M = mol. wt. of solute

K_f = molal depression constant

Note. Numericals are similar to "depression in freezing point"

18.15 DEPRESSION IN FREEZING POINT METHODS–RAST'S CAMPHOR METHOD

It includes the following method.

Rast's camphor method. In this method, a known weight of solid (whose mol. wt. is to be determined) is mixed with excess of camphor (acts as solvent) and melting point of this mixture is noted. The melting point of camphor is also determined separately. The difference in the melting points of mixture and camphor gives the depression in melting point. To know the molal depression of camphor, the molecular weight of the solid is calculated with the help of following relationship.

$$\Delta T_f = \frac{1000\, K_f\, w}{W\, M}$$

or

$$M = \frac{1000\, K_f\, w}{W\, M}$$

$\because \Delta T_f = \text{molality}, m \times K_f$ where

$m = \frac{w \times 1000}{M\, W}$; w = wt. of solute

W = wt. of solvent; M = mol. wt. of solute ;

K_f = molal depression constant.

Note. Numericals are similar to "depression in freezing point".

18.16 OSMOTIC PRESSURE AND OSMOSIS

Osmosis. It may be defined as a process in which the molecules of a solvent diffuse through semipermeable membrane from pure solvent (or from less concentrated solution) towards a more concentrated solution.

Osmotic pressure (π). It is defined as the excess pressure that is applied on the solution side to stop osmosis when both the solvent (or less concentrated solution) and the solution (more concentrated solution) are separated by a semipermeable membrane.

Law of osmotic pressure. According to Van't Hoff, the osmotic pressure (π) of dilute solutions is given by the following Van't Hoff equation :

$$\pi = nCRT = \frac{n}{V} RT \left(\because C = \frac{1}{V}\right)$$

or

$$\pi = \frac{\text{Wt. of solute, } w_2}{\text{Mol. wt. of solute, } M_2} \times \frac{RT}{V}$$

$$\left(\because n = \text{no. of mol} = \frac{\text{wt. of solute, } w_2}{\text{mol. wt. of solute, } M_2}\right)$$

∴

$$\pi = \frac{w_2\, RT}{M_2\, V}$$

Where $R = 0.0821$ L atm (degree)$^{-}$ mol^{-}

$= 0.0821$ L atm K^{-} mol^{-}.

Isotonic solution. These are such a pair of solutions which have the same osmotic pressure and do not involve any flow of molecules of solvent through semipermeable membrane.

18.17 SOME KEY POINTS

Table showing units in c.g.s. and S.I system for some quantities.

Quantity	*Units in c.g.s. system*	*Units in S.I. system*	*litre - atm.*
π	dyne cm^{-2}	Pascal or N m^{-2}	atm
C	mol (mL)$^{-}$	mol m^{-3}	mol L^{-}
R	8.314×10^{7} erg K^{-} mol^{-}	8.314 ***J*** K^{-} mol^{-}	0.0821 L atm. K^{-} mol^{-}
T	K	K	K
V	cc. or mL	m^{3}	L
M	g. mol^{-}	Kg mol^{-}	g. mol^{-}

18.18 OSMOTIC PRESSURE FOR NON - ELECTROLYTES

EXAMPLE 88. *A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr. at 25°C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass.* **(ICS, 2008, 2010)**

Solution. We know that osmotic pressure (π) is given as :

$$\pi = \frac{\text{wt. of solute (in g)}}{\text{Molar mass of solute (M)}} \times \frac{RT}{V} \qquad ...(1)$$

Given : $\pi = \frac{0.335}{760}$ atm,

wt. of solute = (8.95/1000) g,

R = 0.0821 L atm K^{-} mol^{-},

T = 25 + 273 = 298 K, V = (35/1000) L.

Substituting these values in equation (1), we get :

$$\frac{0.335}{760}\text{ atm} = \frac{8.95}{1000}\text{g} \times \frac{1}{M} \times 0.0821\text{ L atm }K^{-}\text{mol}^{-} \times 298\text{ K} \times \frac{1000}{35}\text{ L}^{-}$$

$$\therefore \quad M = \frac{8.95\text{ g}}{1000} \times \frac{760}{0.335} \times 0.0821\text{ mol}^{-} \times 298 \times \frac{1000}{35} = 14193\text{ g mol}^{-}$$

Example 89. *Compute the molar mass (M) of a solute if the osmotic pressure of a solution containing 10.0 g L⁻ of this solute at 27°C is 10.0 torr. (R = 0.0821 L atm/K mol)*

Solution. Wt. of solute = 10.0 g ;

molar mass of solute = M ;

T = (27 + 273) K = 300 K :

R = 0.0821 L atm/K. mol ; volume (V) = 1.0 L and osmotic pressure, $\pi = \left(\frac{10.0}{760}\right)$ atm. But :

$$\pi = \frac{\text{wt. of solute (in g)}}{\text{molar mass of solute (M)}} \times \frac{RT}{V};$$

$$\therefore \frac{10.0}{760}\text{atm} = \frac{(10.0\text{ g})(0.0821\text{ L atm/K mol})(300\text{ K})}{M \times 1.0\text{ L}}$$

$$\textbf{Or } M = \frac{(10.0\text{ g})(0.0821\text{ L atm / K. mol})(300\text{ K}) \times 760}{10.0\text{ atm} \times 1.0\text{L}}$$

$$= 18718.8\text{ g mol}^{-}$$

Example 90. *A solution of 0.75 g of pigmented protein (from crabs) was prepared in 125 mL of an aqueous medium. A rise of osmotic pressure of 2.6 mm of the solution was observed at 277 K. If the density of solution is 1.0 g (mL)⁻, compute the molecular weight of the protein (R = 0.0821 L atm /K. mol).*

(AIMPT, 2011)

Solution. Osmotic pressure,

$$\pi = \frac{2.6\text{ mm}}{(13.6 \times 760\text{ mm})/\text{atm}};$$

$$V = \frac{125}{1000}\text{L}; \; T = 277\text{ K};$$

$$R = 0.0821\text{ L atm/K. mol.}$$

We know $\pi = \frac{nRT}{V}$; $n = \frac{\pi V}{RT}$

$$= \frac{2.6\text{ mm}}{(13.6 \times 760\text{ mm})/\text{atm}} \times \frac{125}{1000} \times \text{L} \times \frac{1}{(0.0821\text{ L atm/K. mol}) \times 277\text{ K}}$$

or $\mathbf{n = 1.38 \times 10^{-6} mol.}$

But mol. wt. = [(wt of solute (in g)]/(no. of moles of solute)

= (0.75 g) / 1.38 × 10^{-6} mol

= $\mathbf{5.4 \times 10^{5}}$ **g/mol.** **Ans**

Example 91. *A 200 cm³ water solution containing 40.0 g of sucrose, $C_{12}H_{22}O_{11}$ at 27°C is separated from pure water with the help of semipermeable membrane. What pressure must be applied over the solution to stop osmosis ? (At. wt. of C = 12, H = 1, O = 16,) R = 0.0821 L atm/K. mol.*

Solution. Mol. wt. of $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 × 16) = 342 g mol⁻. V = 200 cm³ ; wt. of $C_{12}H_{22}O_{11}$ = 40.0 g ; number of moles of $C_{12}H_{22}O_{11}$ (***n***) = (40.0 g)/342 g mol⁻ = **0.117 mol** ; T = (27 + 273) K = 300 K.

We know that

Osmotic pressure

$$(\pi) = \frac{nRT}{V}$$

$$\pi = \frac{(0.117\text{ mol})(0.0821\text{ L atm/K. mol})(300\text{ K})}{(200/1000)\text{ L.}}$$

= **14.4 atm.** **Ans**

Example 92. *A solution containing 20.0 g per dm³ of glucose (mol. wt. 180) was found to be isotonic with a 8% solution of an organic non-volatile substance. Calculate the molar mass of the latter.*

Solution. Volume, V = 1 dm³ ; wt. of glucose (w) = 20.0 g ; g. mol. wt. of glucose, $C_6H_{12}O_6$ = 180 g mol⁻ ; molar mass of organic substance = M = ? ; wt. of organic substance = 8 g and volume of solution = 100 cm³ = (100/1000) dm³ = 0.1 dm³. Since solutions are isotonic, osmotic pressure of both solutions will be same.

(*a*) For glucose solution,

$$\pi = \frac{WRT}{MV} = \frac{20\,RT}{180\text{ g mol}^{-} \times 1\text{ dm}^3} \qquad ...(1)$$

(*b*) For organic substance solution,

$$\pi = \frac{WRT}{MV} = \frac{8\,RT}{M \times 0.1\text{ dm}^3} \qquad ...(2)$$

From relations (1) and (2), we have :

$$\frac{20\,RT}{180\text{ g mol}^{-} \times 1\text{ dm}^3} = \frac{8\,RT}{M \times 0.1\text{ dm}^3}$$

$$\therefore \quad \mathbf{M} = \frac{8\,RT}{0.1\,\text{dm}^3} \times \frac{180\text{ g mol}^{-} \times 1\,\text{dm}^3}{20\,RT}$$

$$= \mathbf{720\text{ g mol}^{-}}$$ **Ans.**

EXAMPLE 93. *Calculate the osmotic pressure of a solution obtained by mixing 150 cm^3 of 2% solution of glucose (mol. wt., 180) and 100 cm^3 of 2.5 % urea (mol. wt., 60) at 27°C. (R = 0.0821 L atm K^{-} mol^{-})*

SOLUTION. Total volume of both solutions

= 150 + 100 = 250 cm^3.

(*a*) For glucose solution, concentration,

$$C_1 = \frac{2 \times 1000}{250}\text{ g (dm)}^{-3} = 8\text{ g (dm)}^{-3}$$

$$= \frac{8\text{ g dm}^{-3}}{180\text{ g mol}^{-}} = 0.044\text{ mol L}^{-}$$

(*b*) For urea solution, concentration,

$$C_2 = \frac{2.5\text{ g (dm)}^{-3} \times 1000}{250} = 10\text{ g (dm)}^{-3}$$

$$= \frac{10\text{ g (dm)}^{-3}}{60\text{ g mol}^{-}} = 0.167\text{ mol dm}^{-3}$$

$$= 0.167\text{ mol L}^{-}$$

$\therefore$ Osmotic pressure due to glucose, $\pi_1 = C_1RT$

$$= 0.044\text{ mol L}^{-} \times 0.0821\text{ L atm K}^{-}\text{mol}^{-} \times (27 + 273)\text{ K}$$

$$= \mathbf{1.08\text{ atm}}$$

Osmotic pressure due to urea, $\pi_2 = C_2RT$

$$= 0.167\text{ mol L}^{-} \times 0.0821\text{ L atm. K}^{-}\text{mol}^{-} \times (27 + 273)\text{ K} = 4.1\text{ atm.}$$

$\therefore$ **Total osmotic pressure**

$$= (1.08 + 4.1)\text{ atm} = \mathbf{5.18\text{ atm.}}$$ **Ans.**

18.19 DETERMINATION OF OSMOTIC PRESSURE FROM LOWERING OF VAPOUR PRESSURE

$$\boxed{\pi \propto p° - ps}$$

i.e., Osmotic pressure (π) of a solution is directly proportional to the lowering of vapour pressure ($p° - ps$).

EXAMPLE 94. *Calculate the osmotic pressure of a solution having density 0.8149 g (mL)$^{-}$ and vapour pressure 742.60 mm. The vapour pressure of pure solvent (mol. wt. 78 g mol^{-}) is 751.86 mm at 80°C. (R = 0.0821 L atm. K^{-} mol^{-}).*

SOLUTION. We know that osmotic pressure (π) of a solution when density of solution is given as follows.

$$\pi = \frac{p° - ps}{p°}\left(\frac{dRT}{M_1}\right)$$

where M_1 = mol. wt. of solvent

$$d = 0.8149\text{ g (mL)}^{-} \times \frac{1000\text{ m L}}{1\text{ L}}$$

$$= 814.9\text{ g L}^{-}$$

Substituting the values, we get :

$$\pi = \frac{\frac{751.86}{760}\text{ atm} - \frac{742.60}{760}\text{ atm}}{\frac{751.86}{760}\text{ atm}}$$

$$\left[\frac{814.9\text{ g L}^{-} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times (80 + 273)\text{ K}}{78\text{ g mol}^{-}}\right]$$

$$= \frac{9.26}{751.89}\left[\frac{814.9\text{ g L}^{-} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 353\text{ K}}{78\text{ g mol}^{-}}\right]$$

Or $\pi = \mathbf{3.279\text{ atm.}}$ **Ans.**

EXAMPLE 95. *Calculate the molecular weight of the solute as well as the osmotic pressure of a dilute solution (density 0.9982 g/mL at 20°C) prepared by dissolving 36 g of solute in 1000 g of solvent (mol. wt., 18 g mol^{-}) (R = 0.0821 L atm K^{-} mol^{-}, vapour pressure of pure solvent is 17.5391 atm. and lowering of vapour pressure is 0.0614 atm.)*

SOLUTION. (*i*) Mol. wt. of solute = ? ; Osmotic presure = ? ; $T = 20 + 273 = 293$ K

$d = 0.9982\text{ g (mL)}^{-} = 0.9982 \times 1000\text{ g L}^{-}$; wt. of solute, $W_2 = 36$ g ; wt. of solvent, $W_1 = 1000$ g; mol. wt. of solvent water, $M_1 = 18\text{ g mol}^{-}$; $R = 0.0821\text{ L atm K}^{-}\text{ mol}^{-}$. $p° = 17.5391$ atm ; $p° - ps = 0.0614$ atm. We know that :

$$\frac{p° - ps}{p°} = \frac{W_2\,M_1}{W_1\,M_2}\,;\; M_2 = \frac{W_2\,M_1\,p°}{(p° - ps) \times W_1}$$

$$\therefore \quad M_2 = \frac{36\text{ g} \times 18\text{ g mol}^{-} \times 17.5391\text{ atm}}{0.0614\text{ atm} \times 1000\text{ g}}$$

$$= \mathbf{185.1\text{ g mol}^{-}}$$ **Ans.**

(*ii*) $$\pi = \frac{p° - ps}{p°}\left[\frac{dRT}{M_1}\right]$$

$$= \frac{0.0614\text{ atm}}{17.5391\text{ atm}} \times \left[\frac{0.9982 \times 1000\,g\text{ L}^{-} \times 0.0821\text{ L atm K}^{-}\text{ mol} \times 293\text{ K}}{18\,g\text{ mol}^{-}}\right]$$

$$= \mathbf{4.67\text{ atm}}$$ **Ans.**

EXAMPLE 96. *The depression in freezing point of a sample of abnormal blood was found to be 0.402 °C. Calculate its osmotic pressure at 37°C (K_f = 1.86°C kg mol^{-}; R = 0.08205 L atm K^{-} mol^{-}).*

SOLUTION. $\Delta T_f = 0.402$ °C. ($K_f = 1.86$ °C kg mol^{-} ; $T = 37 + 273 = 310$ K, $R = 0.08205$ L atm K^{-}mol^{-}. We know that

$$\Delta T_f = K_f \times \text{molality}\;;$$

$$\text{Molality} = \frac{\Delta T_f}{K_f} = \frac{0.402\text{ °C}}{1.86\text{ °C kg mol}^{-}}$$

But molality = concentration, C

But osmotic pressure,

$$\pi = CRT$$

$$\therefore \quad \pi = \frac{0.402°C}{1.86°C \text{ kg mol}^{-}} \times 0.08205 \text{ L atm K}^{-}\text{mol}^{-} \times 310\text{K}$$

$$= \mathbf{5.497 \text{ atm.}}$$ **Ans.**

Example 97. *At 10 °C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25 °C when the osmotic pressure is found to be 105.3 mm. Determine the extent of dilution.*

Solution (*i*) For initial solution :

$$\pi = 500 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} = \frac{50}{76} \text{ atm} ;$$

$$T = 10 + 273 = 283 \text{ K}$$

$$\pi = \frac{n}{V} RT ; \frac{50}{76} \text{ atm} = \frac{nR}{V} \times 283 \text{ K} \quad ...(1)$$

(*ii*) For diluted solution :

$$\pi = 105.3 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} = \frac{105.3}{760} \text{ atm}$$

$$T = 25 + 273 = 298 \text{ K.}$$

Let volume = V_1

$$\therefore \quad \pi = \frac{n}{V_1} \times RT = \frac{n}{V_1} \times R \times 298 \text{ K}$$

Thus

$$\frac{105.3}{760} \text{ atm} = \frac{nR}{V_1} \times 298 \text{ K} \quad ...(2)$$

Equating equations (1) and (2), we get :

$$= \frac{50 \text{ atm}/76}{105.3 \text{ atm}/760} = \frac{nR \times 283 \text{ K}}{V} \times \frac{V_1}{nR \times 298 \text{ K}}$$

$$\frac{50 \text{ atm} \times 760}{105.3 \text{ atm} \times 76} = \frac{283 \text{ V}_1}{298 \text{ V}}$$

$$50 \times 760 \times 298 \text{ V} = 283 \times 105.3 \times 76 \text{ V}_1$$

$$V_1 = \frac{50 \times 760 \times 298}{283 \times 105.3 \times 76} \text{V} = 5\text{V}$$

Thus the solution is diluted to five (= 5) times. **Ans.**

Type. $R = 8.314 \, J\,K^{-}\text{mol}^{-}$; osmotic pressure is in Nm^{2-}, use 1 Nm = 1 J; 1 L = $10^{-3}\, m^3$

Example 98. *The osmotic pressure of a solution of an organic substance containing 18 g in one litre of solution at 293 K is $2.414 \times 10^5 \, N\, m^{-2}$. Find molar mass of substance if R = 8.314 $J\,K^{-} mol^{-}$.*

Solution. $\pi = 2.414 \times 10^5 \, Nm^{-2}$; $R = 8.314 \, J \text{ K}^{-} \text{mol}^{-}$: wt. of solute, W_2 = 18 g ; volume (V) of solution = 1 L = 1 × 10^{-3} m^3. Mol. wt. of solute, M_2 = ? We know that :

$$\pi = \frac{W_2}{M_2 V} \times RT ;$$

$$M_2 = \frac{W_2}{\pi V} \times RT$$

$$= \frac{18 \text{ g} \times 8.314 \, J \text{ K}^{-} \text{ mol}^{-} \times 293 \text{ K}}{2.414 \times 10^5 \text{ N m}^{-2} \times 10^{-3} \text{ m}^3}$$

$$M_2 = \frac{181.64 \text{ g.} J\text{.mol}^{-}}{N\,m} = \frac{181.64 \text{ g.} J\text{.mol}^{-}}{1 J}$$

[∵ 1J = 1 Nm]

$$\therefore \quad M_2 = \mathbf{181.64 \text{ g mol}^{-}}$$ **Ans.**

Example 99. *A 0.45% (wt/vol) solution of cellulose acetate in acetone has specific gravity value 0.9. If the solution shows an osmotic pressure of 2.2 cm against pure acetone at 300 K, calculate the molar mass of the solute.*

Solution. Given weight of cellulose acetate = 0.45 g in 100 mL solution

Osmotic pressure,

$$\pi = 2.2 \text{ cm of pure acetone}$$

$$= \frac{2.2 \times 0.9}{13.6} \text{ cm of Hg}$$

$$= 0.1456 \text{ cm of Hg}$$

$$= \frac{0.1456}{76} = 1.9 \times 10^{-3} \text{ atm.}$$

Or $\quad \pi = \mathbf{1.9 \times 10^{-3}}$ **atm**

We know $\quad \pi = \frac{nRT}{V} = \frac{W}{M} \times \frac{RT}{V} \quad ...(1)$

Substituting the values of $\pi = 1.9 \times 10^{-3}$ atm, W = 0.45 g , m = ?, R = 0.082 L atm mol^{-}K^{-}, T = 300 K and V = 100 mL = (100/1000) = 0.1 L in relation (1), we get

$$1.9 \times 10^{-3} \text{ atm} = \frac{0.45 \text{ g}}{M} \times \frac{0.082 \text{ L atm mol}^{-} \text{ K}^{-} \times 300 \text{ K}}{0.1 \text{ L}}$$

Or $\quad M = \mathbf{58263 \text{ g mol}^{-}}$**.** **Ans.**

Example 100. *The given aqueous solution of a protein contains 1.26 g of the protein in 200 cm^3 solution. The osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.*

Solution. Wt. of protein = 1.26 g ; volume of solution $= 200 \text{ cm}^3 \times \frac{1\text{L}}{1000 \text{cm}^3} = 0.2$ L ; R = 0.0821 L atm K^{-} mol^{-} ; T = 200 K ; $\pi = 2.57 \times 10^{-3}$ bar = 2.57×10^{-3} atm. We know that :

$$\pi = \frac{W_2 RT}{M_2 V} ; \; M_2 = \frac{W_2 RT}{\pi V}$$

$$= \frac{1.26 \text{ g} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ atm} \times 0.2 \text{L}}$$

$$\therefore \quad M_2 = \mathbf{60377 \text{ mol}^{-}}$$

18.20 ISOTONIC SOLUTIONS

Type. Isotonic solutions are those whose osmotic pressures are same. The osmotic pressure, $\pi = \frac{CRT}{V} = \frac{W_2}{M_2 V} \times RT$,

$R = 0.0821$ L atm K^- mol^-, wt. of solute in g ; M_2 = mol. wt. of solute in g mol^-, volume of solution in litre ; T = absolute temperature.

Example 101. *A 5.13 % solution of sucrose ($C_{12}H_{22}O_{11}$) is isotonic with a 0.9 % solution of an unknown solute. Calculate the molar mass of the solute.* **(PSEB, 2001)**

Solution (*i*) For sucrose, π_1 = ? ; Mol. wt. of $C_{12}H_{22}O_{11}$; $M_2 = (12 \times 12) + (22 \times 1) + (11 \times 16) = 342$ g mol^- ; wt. of solute, $W_2 = 5.13$ g; concentration $C_1 = \frac{W_2}{M_2}$;

volume of solution, $V = 100\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ m L}} = 0.1\text{ L}$

$$\therefore \qquad \pi_1 = \frac{W_2}{M_2V}RT = \frac{5.13\text{ g } RT}{342\text{ g mol}^- \times 0.1\text{ L}} \quad ...(1)$$

(*ii*) For unknown solute, π_2 = ? ; mol. wt. of solute, M_2 = ? ; wt. of solute, $W_2 = 0.9$ g ;

volume $= 100\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ mL}} = 0.1$ L. We know that :

$$\pi_2 = \frac{W_2}{M_2V} \times RT = \frac{0.9\text{ g}}{M_2 \times 0.1\text{ L}} \times RT \quad ...(2)$$

Since the solutions are isotonic, their osmotic pressures are equal. So. $\pi_1 = \pi_2$. Hence from equations (1) and (2), we have :

$$\frac{5.13\text{ g} \times RT}{342\text{ g mol}^- \times 0.1\text{ L}} = \frac{0.9\text{ g} \times RT}{M_2 \times 0.1\text{ L}} ;$$

$$M_2 = \frac{0.9\text{ g} \times RT \times 342\text{ g mol}^- \times 0.1\text{ L}}{0.1\text{ L} \times 5.13\text{ g} \times RT}$$

$\therefore$ $\qquad$ $\mathbf{M_2 = 60\text{ g mol}^-}$ $\qquad$ **Ans.**

Example 102. *What is the molar concentration of solute particles in the human blood if the osmotic pressure is 7.2 atm. at the body temperature of 37 °C.* **(DSB, 1999 S)**

Solution. Molar concentration, $\frac{W_2}{M_2V}$ = ? ; $\pi = 7.2$ atm; $T = 37 + 273 = 310$ K ; $R = 0.0821$ L atm K^- mol^-. We know that :

$$\pi = \frac{W_2}{M_2V}RT$$

$$\frac{W_2}{M_2V} = \frac{\pi}{RT} = \frac{7.2\text{ atm}}{0.0821\text{ L atm K}^-\text{ mol}^- \times 310\text{ K}}$$

$= \mathbf{0.28\text{ mol L}^-}$ $\qquad$ **Ans.**

[$\because$ $\pi = \text{CRT} = \dfrac{nRT}{V} = \dfrac{W_2}{M_2V} \times RT$; W_2 = wt. of solute ; M_2 = mol. wt. of solute]

Example 103. *The osmotic pressure of a solution containing 9.2 gram of substance (molecular mass = 176) in 300 mL solution was found to be 4.1 atmosphere at 288.5 K. Calculate the value of solution constant.*

Solution. $\pi = 4.1$ atm ; $T = 288.5$ K ; R = solution constant = ? ; wt. of substance, $W_2 = 9.2$ g ; $M_2 = 176$ g mol^- ;

$$V = 300\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = 0.3\text{L}$$

We know that

$$\pi = \frac{W_2}{M_2V} \times RT ;$$

$$R = \frac{\pi M_2V}{W_2T}$$

$$= \frac{4.1\text{ atm} \times 176\text{ g mol}^- \times 0.3\text{ L}}{9.2\text{ g} \times 288.5\text{ K}}$$

$\therefore$ $\qquad$ $R = \mathbf{0.082\text{ L atm K}^-\text{ mol}^-}$ $\qquad$ **Ans.**

Example 104. *A solution of non-volatile solute with molecular mass 342 is obtained by dissolving 17.1 g of it in 500 g of water. Find out osmotic pressure of the solution at 27 °C. R = (0.082 atm L K^{-1} mol^{-1})*

Solution. Mol. wt., $M_2 = 342$ g mol^- ; wt. of solute, $W_2 = 17.1$ g ; density of water = 1 g $(mL)^-$; Wt. of water = 500 g. Hence volume of water $= V = \dfrac{\text{wt. of water}}{\text{density}} =$

$$\frac{500\text{ g}}{1\text{ g (mL)}^-} = 500\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = 0.5\text{ L} ;$$

$T = 27 + 273 = 300$ K ;

$R = 0.082$ L atm K^- mol^-. We know that osmotic pressure *i.e.*,

$$\pi = \frac{W_2}{M_2V} \times RT = \frac{17.1\text{ g} \times 0.0821\text{ L atm K}^-\text{ mol}^- \times 300\text{ K}}{342\text{ g mol}^- \times 0.5\text{ L}}$$

$= \mathbf{2.463\text{ atm}}$ $\qquad$ **Ans.**

Example 105. *The osmotic pressure of blood is 8.21 atmosphere at 37 °C. How much glucose per litre should be added for an intravenous injection i.e., at the same osmotic pressure as blood ?*

Solution. Wt. of glucose $C_6H_{12}O_6$, W_2 = ? ; mol. wt. of $C_6H_{12}O_6 = (6 \times 12) + (12 \times 1) + (6 \times 16) = 180$ g mol^- ; $\pi = 8.21$ atm ; $T = 37 + 273 = 310$ K ; volume = 1 L

We know that :

$$\pi = \frac{W_2}{M_2V} \times RT ;$$

$$W_2 = \frac{\pi M_2V}{RT}$$

$$\therefore \qquad W_2 = \frac{8.21\text{ atm} \times 180\text{ g mol}^- \times 1\text{ L}}{0.0821\text{ L atm K}^-\text{ mol}^- \times 310\text{ K}}$$

$= \mathbf{58.6\text{ g}}$ $\qquad$ **Ans.**

Example 106. *A solution of a polymer containing 5 g dm^{-3} was found to give an osmotic pressure of 4.5 mm Hg at 15 °C. Calculate the molecular mass of the polymer.*

Solution. Molar mass of polymer = M_2 = ? ; volume V = dm^3 = 1 L ; wt. of polymer, $W_2 = 5$ g ; $R = 0.0821$ L atm K^- mol^- ; $T = 15 + 273 = 288$ K.

$$\pi = 4.5\text{ mm} \times \frac{1\text{ atm}}{760\text{ mm}} = \frac{4.5}{760}\text{ atm}$$

Osmotic pressure,

$$\pi = \frac{W_2\ RT}{M_2 V}\ ;\ M_2 = \frac{W_2\ RT}{\pi\ V}$$

$$= \frac{5\text{ g} \times 0.0821\text{ L atm K}^{-}\text{mol}^{-} \times 288\text{ K} \times 760}{4.5\text{ atm} \times 1\text{ L}}$$

or M_2 = **19967 g mol^{-}** **Ans.**

EXAMPLE 107. *A 6% solution of urea is isotonic with :*

(*a*) *0.05 M solution of glucose*

(*b*) *6% solution of glucose*

(*c*) *25% solution of glucose*

(*d*) *1 M solution of glucose* **(Karnataka CET, 2009)**

SOLUTION. Mass of urea, W_u = 6 g; mass of glucose, $C_6H_{12}O_6$ (= w_g) = x g; molecular mass of glucose = 180 g mol^{-} (= m_g) ; molecular mas of urea, NH_2CONH_2 (= m_u) = 60 g mol^{-}. For isotonic solution of glucose and urea, their osmotic pressures will be same *i.e.*, $\pi_{\text{glucose}} = \pi_{\text{urea}}$; $C_{\text{glucose}} = C_{\text{urea}}$.

$$\text{So} : \frac{w_g \times 1000}{m_g \times 100} = \frac{m_u \times 1000}{m_u \times 100};\ \frac{x \times 1000}{180 \times 100} = \frac{6 \times 1000}{60 \times 100};\ x = 18\text{ g.}$$

i.e., 18 g of glucose are present in 100 mL of solution. In other words, 1 M solution of glucose (18 g in 100 mL) or 180 g in 1000 mL) is isotonic with 6% solution of urea. So, the correct answer is (*d*).

EXAMPLE 108. *Calculate the osmotic pressure of an aqueous solution containing 1 g each of sucrose and glucose per dm^3 at 300 K. If this pressure was measured and it were not known that the solute was a mixture, what molecular weight would be expected ?*

SOLUTION. Wt. of glucose, $C_6H_{12}O_6$ = 1 g ; mol. wt. of $C_6H_{12}O_6$ = (6 × 12) + (12 × 1) + (6 × 16) = 180 g mol^{-}, wt. of sucrose, $C_{12}H_{22}O_{11}$ = 1 g ; mol. wt. of $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 × 16) = 342 g mol^{-}.

(*i*) no. of mol of glucose

$$= \frac{1\text{ g}}{180\text{ g mol}^{-}} = 0.00556\text{ mol}$$

(*ii*) no. of mol of sucrose

$$= \frac{1\text{ g}}{342\text{ g mol}^{-}} = 0.00292\text{ mol.}$$

Hence total no. of mol,

$$n = 0.00556 + 0.00292 = 0.00848\text{ mol.}$$

We know that :

$$\pi = \frac{n\ RT}{V}$$

$$= \frac{0.00848\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 300\text{ K}}{1\text{ L}}$$

$$= 0.209\text{ atm.}$$

(*iii*) Total weight (W_2) of glucose and sucrose = 1 g + 1 g = 2 g ; Mol. wt. = M_2 = ? π = 0.209 atm. We know that :

$$\pi = \frac{W_2\ RT}{M_2\ V}\ ;\ M_2 = \frac{W_2\ RT}{\pi\ V}$$

$$= \frac{2\text{ g} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 300\text{ K}}{0.209\text{ atm} \times 1\text{ L}}$$

or M_2 = **235.69 g mol^{-}** **Ans.**

18.21 VAN'T HOFF FACTOR, *i*

In order to know the extent of dissociation or association of ionic solutes in a solution, van't Hoff introduced a factor '*i*' called van't Hoff factor. Mathematically:

$$i = \frac{\text{Theoretical (or normal) molar mass}}{\text{Experimental (or observed) molar mass}}$$

$$= \frac{\text{Experimental (or observed) colligative property}}{\text{Theoretical (or normal) colligative property}}$$

$$\left[\because\ \text{Molar mass} \propto \frac{1}{\text{Colligative property}}\right]$$

(*i*) $i < 1$ in case of dissociation

(*ii*) $i > 1$ in case of association

(*iii*) $i = 1$ when experimental mass = theoretical mass.

Based on above factor '*i*' the colligative properties of ionic solutes can be modified as :

Depression in f.pt, $\Delta T_f = i\ K_f\ m$

Elevation in b.pt, $\Delta T_b = i\ K_b\ m$

Osmotic pressure,

$$\pi = i\ CRT = \frac{i\ n\ RT}{V} = i\ \frac{W_2\ RT}{M_2\ V}$$

Where W_2 = wt. of solute per unit volume V and M_2 = mol. wt. of solute.

Degree of dissociation, $\alpha = \dfrac{i-1}{n-1}$ where n = number of effective particles (ions) after dissociation.

$$\text{e.g., in } CdSO_4 \rightleftharpoons \underset{1\text{ mol}}{Cd^{2+}} + \underset{1\text{ mol}\ ;\ n = 1 + 1 = 2\text{ mol.}}{SO_4^{2-}}$$

Degree of assoication,

$$\alpha = \frac{\mathbf{1} - \boldsymbol{i}}{\mathbf{1} - \dfrac{\mathbf{1}}{\boldsymbol{n}}}$$

where n = number of solute molecules which combine to form associated molecules.

van't Hoff factor,

$$\boldsymbol{i} = \frac{\text{no. of mol after association}}{\text{Total no. of mol before association}}$$

$$= \frac{\text{no. of mol after dissociation}}{\text{Total no. of mol before dissociation}}$$

EXAMPLE 109. *A solution containing 0.2965 g of benzoic acid (C_6H_5COOH) in 20.27 g of benzene froze at a temperature 0.317 °C below the freezing point of the solvent. The freezing point of benzene is 5.5 °C and its latent heat of fusion is 30.1 cal (g)$^{-}$. Calculate (i) the apparent molecular mass of benzoic acid (ii) the degree of association assuming that in solution, it forms double molecule (At. wt. C = 12, O = 16, H = 1)*

Solution. Wt. of solute (benzoic acid), $W_2 = 0.2965$ g ; wt. of solvent (W_1) benzene = $20.27\text{g} \times \frac{1\text{kg}}{1000\text{ g}} = 0.02027$ kg; $\Delta T_f = 0.317$ °C = 0.317 K ; Freezing point of solvent benzene, $T_f^o = 5.5 + 273 = 278.5$ K ; latent heat of fusion, $L_f = 30.1$ cal g^{-}, $R = 2$ cal K^{-} mol^{-}

$$K_f = \frac{R\left(T_f^o\right)^2}{L_f \times 1000}$$

$$= \frac{2 \text{ cal K}^{-} \text{ mol}^{-} \times 278.5 \text{ K} \times 278.5 \text{ K}}{\frac{30.1 \text{ cal}}{\text{g}} \times \frac{1000 \text{ g}}{1 \text{ kg}}}$$

$$= 5.15 \text{ K kg mol}^{-}$$

But $\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$; $M_2 = \frac{K_f \times W_2 \text{ in g}}{\Delta T_f \times W_1 \text{ in kg}}$

or $M_2 = \frac{5.15 \text{ K kg mol}^{-} \times 0.2965 \text{ g}}{0.317 \text{ K} \times 0.02027 \text{ kg}}$

$= 237.64 \text{ g mol}^{-}$

Theoretical molar mass of $C_6H_5COOH = (6 \times 12) + (5 \times 1) + 12 + 2\,(16) + 1 = 122 \text{ g mol}^{-}$

For	C_6H_5COOH	$\rightleftharpoons$	$\frac{1}{2}\,(C_6H_5COOH)_2$
Initial conc.	1		0
At equilibrium	$1 - \alpha$		$\alpha/2$

[α = degree of association]

$\therefore \quad i = 1 - \alpha + \alpha/2 = 1 - \alpha/2$ ... (1)

But $i = \frac{M_{Th}}{M_{obs}} = \frac{122}{237.64}$ ... (2)

Substituting the value of i from (2) in (1), we get

$$\frac{122 \text{ g mol}^{-}}{237.64 \text{ g mol}^{-}} = 1 - (\alpha/2);$$

$$0.513 = 1 - (\alpha/2);$$

$$\frac{\alpha}{2} = 1 - 0.513$$

$\therefore \quad \frac{\alpha}{2} = 0.487$ or $\alpha = 2 \times 0.487 = 0.947$

or $\alpha = 0.947 \times 100 =$ **94.7 % associated**

Ans.

Example 110. *The freezing point of a solution of 4.0 g CdI_2 in 95 g of water was – 0.25 °C. Calculate the degree of dissociation of salt. (K_f for 100 g of water = 18.5° ; (At. wt. Cd = 112 ; I = 127).*

Solution. Wt. of solute, $W_2 = 4.0$ g ; wt. of solvent, $W_1 = 95 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.095$ kg; $\Delta T_f = 0.25$ °C ; K_f for 100 g. water = 18.5°. Hence K_f for 1000 g water = 1.85 °C kg mol^{-}.

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}; \; M_2 = \frac{K_f \times W_2 \text{ in g}}{\Delta T_f \times W_1 \text{ in g}}$$

$$M_2 = \frac{1.85 \text{ °C kg mol}^{-} \times 4 \text{ g}}{0.25 \text{ °C} \times 0.095 \text{ kg}}$$

$$= 311.6 \text{ g mol}^{-}$$

Theoretical molar mass (M_{Th}) of $CdI_2 = 112 + (2 \times 127) = 366 \text{ g mol}^{-}$

For	CdI_2	$\rightleftharpoons$	Cd^{2+}	$+ 2\,I^{-}$
Initial conc.	1		0	0
At equilibrium	$1 - \alpha$		α	$2\,\alpha$

$\therefore \quad i = 1 - \alpha + \alpha + 2\,\alpha = 1 + 2\,\alpha$ ...(1)

But $i = \frac{M_{Th}}{M_{obs}} = \frac{366 \text{ g mol}^{-}}{311.6 \text{ g mol}^{-}}$ ...(2)

Substituting the value of i from (2) in (1), we get

$$\frac{366}{311.6} = 1 + 2\,\alpha \quad \text{or} \quad \alpha = \frac{1}{2}\left(\frac{366}{311.6} - 1\right)$$

Or $\alpha = 0.087$

or $0.087 \times 100 =$ **8.7 % dissociated**

Example 111. *The vapour pressure of a solution containing 6.69 g of $Ca(NO_3)_2$ in 100 g of water is 746.9 torr. at 100 °C. What is the degree of dissociation of the salt ? (At. wt. of Ca = 40, N = 14, O = 16)*

Solution. Vapour pressure of solution, $ps = 746.9$ torr. ; vapour pressure of pure solvent, H_2O ($p°$) = 760 torr. ; Weight of Ca $(NO_3)_2$ solute (W_2) = 6.69 g ; weight of solvent water (W_1) = 100.0 g ; mol. wt. of $H_2O = (2 \times 1) + 16 = 18$ g mol^{-} ; Observed mol. wt. of $Ca(NO_3)_2 = M_2 = ?$; Theoretical mol. wt. of $Ca(NO_3)_2 = 40 + 2\,[14 + (3 \times 16)] = 164$ g mol^{-}. We know that :

$$\frac{p° - ps}{p°} = \frac{W_2\,M_1}{W_1\,M_2};$$

$$\therefore \quad \frac{(760 - 746.9) \text{ torr}}{760 \text{ torr}} = \frac{6.69 \text{ g} \times 18 \text{ g mol}^{-}}{100 \text{ g} \times M_2}$$

$$\therefore \quad M_2 = \frac{6.69 \text{ g} \times 18 \text{ g mol}^{-} \times 760 \text{ torr}}{100 \text{ g} \times 3.1 \text{ torr}}$$

$$= \mathbf{69.86 \text{ g mol}^{-}}.$$

We know that :	$Ca(NO_3)_2$	$\rightleftharpoons$	Ca^{2+}	$+ 2\,NO_3^-$
Initial conc.	1		0	0
Conc, at equilibrium	$1 - \alpha$		α	$2\,\alpha$

[$\because$ α = degree of dissociation]

Total no. of moles at equilibrium

$= 1 - \alpha + \alpha + 2\,\alpha = 1 + 2\,\alpha.$

But $\frac{\text{Observed mol. wt}}{\text{Theoretical mol. wt}} = \frac{1}{1 + 2\,\alpha};$

$$\therefore \quad \frac{69.86}{164} = \frac{1}{1 + 2\,\alpha}$$

Or $1 + 2\,\alpha = \frac{164}{69.86} = 2.34;$

$\therefore \quad \alpha = 0.67$

Or $\alpha = 0.67 \times 100 =$ **67 % Ans.**

18.22 OSMOTIC PRESSURE FOR ELECTROLYTES; $\pi = \frac{\mathbf{i\,n\,RT}}{\mathbf{V}}$

Example 112. *A solution contains 7.45 g KCl per litre of solution. It has an osmotic pressure of 4.68 atm. at 300 K. Calculate the degree of dissociation for KCl in this solution (R = 0.082 L atm. K^- mol^-; atomic masses : K = 39.0, Cl = 35.5).*

(DSB, 2000 S)

Solution. Wt. of K Cl = 7.45 g ; mol. wt. of KCl = 39.0 + 35.5 = 74.5 g mol^-; number of moles of KCl, '*n*' = $\frac{7.45\text{ g}}{74.5\text{ g mol}^-}$ = 0.1 mol.; *V* = 1 L.

We know that for electrolytes :

$$\pi = \frac{i\,n\,RT}{V} \quad \textbf{Or} \quad i = \frac{\pi\,V}{n\,RT}$$

$$= \frac{(4.68\text{ atm})\,(1\text{ L})}{(0.1\text{ mol})\,(0.082\text{ L atm K}^-\text{ mol}^-)\,(300\text{ K})}$$

$$= \mathbf{1.9}$$

KCl ionises as :

$$\begin{array}{lccc} & KCl & \rightleftharpoons\ K^+ & +\ Cl^- \\ \text{Initial conc.} & 1 & 0 & 0 \\ \text{Conc. at equilibrium} & 1-\alpha & \alpha & \alpha \end{array}$$

[∵ α = degree of dissociation]

∴ Number of effective particles after dissociation

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

∴ **van't Hoff factor,**

$$\boldsymbol{i} = \frac{\text{no. of moles after dissociation}}{\text{no. of moles before dissociation}}$$

$$= \frac{1+\alpha}{1}$$

Or $i = 1 + \alpha\,;\ 1.9 = 1 + \alpha\,;\ \alpha = 1.9 - 1 = 0.9$

Or $\alpha = 0.9 \times 100$ *i.e.*, α = **90 %** **Ans.**

Example 113. *Calculate the amount of sodium chloride (electrolyte) which must be added to one kilogram of water so that the freezing point is depressed by 3 K (given K_f for water = 1.86 K kg /mol)* **(PbPMT, 1992)**

Solution. NaCl ionises as :

$$\underset{}{NaCl} \rightleftharpoons \underset{1\text{ mol}}{Na^+} + \underset{1\text{ mol}}{Cl^-}$$

∴ **van't Hoff factor,**

$$\boldsymbol{i} = 1 + 1 = 2$$

$$\Delta T_f = i\,K_f\,m \text{ (for electrolytes) ;}$$

Or $$m = \frac{\Delta T_f}{i\,K_f} = \frac{3\text{ K}}{2 \times 1.86\text{ K kg mol}^-}$$

$$= 0.806\text{ mol/kg}$$

But $$\text{Mol. wt.} = \frac{\text{wt. of solute (in g)}}{\text{molality} \times \text{wt. of solvent in kg}}$$

or **Wt. of solute (in g)**

= Mol. wt. × molality × Wt. of solvent in kg

$$= 58.5\text{ g mol}^- \times 0.806\text{ mol (kg)}^- \times 1\text{ kg}$$

$$= \mathbf{47.15\text{ g}}$$ **Ans.**

Example 114. *Calculate the freezing point of one molal barium nitrate solution assuming barium nitrate to be 100 % dissociated in water (K_f for water = 1.86 °C/m)]*

Solution. Barium nitrate $Ba(NO_3)_2$ ionises as :

$$Ba\,(NO_3)_2 \rightleftharpoons \underset{1\text{ mol}}{Ba^{2+}} + \underset{2\text{ mol}}{2NO_3^-}$$

Total number of ions = 1 + 2 = 3. Since Ba $(NO_3)_2$ gives three ions in solution, the depression in freezing point will be tripled *i.e.*, 3 × 1.86 = 5.58. So, the freezing point of solution will be – **5.58 °C** because freezing point of water is 0.0 °C.

Example 115. *A 0.104 M aqueous solution of organic acid A H causes a depression in freezing point of 0.2 °C. If the acid ionises as A $H_{(aq)} \rightleftharpoons A^+_{(aq)} + H^+_{(aq)}$, calculate the equilibrium constant of the organic acid (K_f for H_2O = 1.86 Kg mol^- K.)*

Solution. Given reaction is :

$$\begin{array}{lccc} & AH\,(aq) & \rightleftharpoons\ A^+\,(aq) & +\ H^+\,(aq) \\ \text{Initial concentration} & C & 0 & 0 \\ \text{Moles at equilibrium} & C\,(1-\alpha) & C\,\alpha & C\,\alpha \end{array}$$

Where α = degree of dissociation.

$$\therefore \quad i = \frac{C\,(1-\alpha) + C\,\alpha + C\,\alpha}{C} = 1 + \alpha$$

But $\Delta\,T_f = i\,k_f \times m$

[Here molality, *m* = molarity, M because solution is very dilute]

Substituting the values, we get

$$0.2 = 1.86\text{ kg mol}^-\text{ K} \times (1 + \alpha) \times 0.104$$

Or $$1 + \alpha = \frac{0.2}{1.86 \times 0.104} = 1.0341$$

Or $$\alpha = 1.034 - 1 = \mathbf{0.034}$$

$$\therefore \quad (AH) = C\,(1-\alpha) = C\,(1-0.034) = 0.966\text{ C}$$

$$(H^+) = C\,\alpha = C \times 0.034 = 0.034\text{ C}$$

$$(A^-) = C\,\alpha = 0.034\text{ C}$$

∴ Equilibrium constant,

$$K_a = \frac{(A^-)\,(H^+)}{(AH)} = \frac{0.034\text{ C} \times 0.034\text{ C}}{0.966\text{ C}}$$

$$= 1.19 \times 10^{-3}\text{ C mol L}^-$$

$$= 1.19 \times 10^{-3} \times 0.104$$

$$= 1.23 \times 10^{-4} \text{ or } K_a = \mathbf{1.23 \times 10^{-4}}$$

Ans.

Example 116. *Calculate the b.pt. of one molar aqueous solution (density = 1.04 g mL^-) of potassium chloride. (K_b for water = 0.52 K kg mol^-) (atomic masses, K = 39, Cl = 35.5)*

(CBSE, 1995)

Solution. We know that :

$$\Delta\,T_b = i.\,K_b.\,m \qquad \text{... (1)}$$

But $\Delta\,T_b$ = ? ; Boiling point = 373 + $\Delta\,T_b$ = ?

d = density of solution = 1.04 g mL^{-}

V = volume of solution = 1000 mL

$\therefore$ Mass of solution

$= V \times d = 1000\ (\text{mL}) \times 1.04\ \text{g}\ (\text{mL}^{-})$

$= 1040\ \text{g}$

KCl is a strong electrolyte. So, it ionises almost completely.

$$\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$$

$\therefore$ its van't Hoff factor

$(i) = 1 + 1 = 2$

($\because$ one mol K^+ ion + one mol Cl^- ion)

Molecular mass of

KCl = 39 + 35.5 = 74.5 g mol^-

$\therefore$ Mass of water

= 1040 – 74.5

= 965.5 g

$\therefore$ m = molality of solution

$$= \frac{\text{moles of solute}}{\text{wt. of H}_2\text{O in kg}} = \frac{1\ \text{mole}}{965.5/1000\ \text{kg}}$$

= 1.03 mol kg^-

Substituting the above values in relation (1), we get

$\Delta T_b = 2 \times 0.52\ \text{K kg mol}^- \times 1.03\ \text{kg}^-\ \text{mol}$

$= 1.07\ \text{K}$

$\therefore$ Boiling point = 373 + ΔT_b = 373 + 1.07 = **374.07 K.**

Example 117. *3.100 g of $BaCl_2$ in 250 g of water boils at 100.083 °C. Calculate the value of van't Hoff factor and molality of $BaCl_2$ in this solution. (K_f for water = 0.52 K m^-, molar mass of $BaCl_2$ = 208.3 g mol^-.)* **(CBSE, 2001)**

Solution. (*i*) Wt. of solute, W_2 = 3.1 g ; wt. of solvent water = 250 g = $250\ \text{g} \times \dfrac{1\ \text{kg}}{1000\ \text{g}}$ = 0.25 kg ; mol. wt. of BaCl_2 = 208.3 g mol^-

$$\therefore \text{Molality,}\quad m = \frac{W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$= \frac{3.1\ \text{g}}{208.3\ \text{g mol}^- \times 0.25\ \text{kg}}$$

= 0.05953 mol kg$^-$ **Ans.**

(*ii*) **To find van't Hoff factor, *i*.**

T_b = 100 °C, T_b = 100.083 °C ;

ΔT_b = 100.083 – 100 = 0.083 °C = 0.083 K;

$K_f = 0.52\ \text{K}\ m^- = 0.52\ \text{K kg mol}^-$. Also :

ΔT_b(normal) = $K_b \times m$ = 0.52 K kg mol^- × 0.05953 mol kg^-

= 0.03096 K

$$\therefore \quad i = \frac{\text{Observed } \Delta T_b}{\text{Normal } \Delta T_b} = \frac{0.083\ \text{K}}{0.03096\ \text{K}}$$

= 2.68 **Ans.**

Type. $\alpha = \dfrac{1-i}{1-\dfrac{1}{n}}$ for **solutes undergoing association**

Example 118. *Phenol associates in benzene to a certain extent to form dimer. A solution containing 2.0×10^{-2} kg of phenol in 1.0 kg of benzene has its freezing point decreased by 0.69 K. Calculate the degree of association of phenol (K_f for benzene = 5.12 K kg mol^-)* **(PSEB 2002, 2004)**

Solution. Wt. of solute phenol ($\text{C}_6\text{H}_5\text{OH}$), $W_2 = 2.0 \times 10^{-2}\ \text{Kg} \times \dfrac{1000\ \text{g}}{1\ \text{kg}}$ = 20 g ; mol. wt. of $\text{C}_6\text{H}_5\text{OH}$, M_2 = (6 × 12) + (5 × 1) + 16 + 1 = 94 g mol^-. K_f = 5.12 K kg mol^-; wt. of solvent benzene , W_1 = 1 kg. We know that :

$$\Delta T_f = i K_f m;$$

$$\Delta T_f = \frac{i K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$\therefore \quad i = \frac{T_f \times M_2 \times W_1 \text{ in kg}}{K_f \times W_2 \text{ in g}}$$

$$= \frac{0.69\ \text{K} \times 94\ \text{g mol}^- \times 1\ \text{kg}}{5.12\ \text{K kg mol}^- \times 20\ \text{g}}$$

= 0.633

Since phenol associates in benzene to form a dimer, so, n = 2. We know that degree of association, α *i.e.*,

$$\alpha = \frac{1-i}{1-\dfrac{1}{n}} = \frac{1-0.633}{1-\dfrac{1}{2}} = \frac{0.367}{\dfrac{1}{2}} = 0.734$$

Or α = 0.734 × 100 = **73.4 %** **Ans.**

Type. $\alpha = \dfrac{i-1}{n-1}$ for solutes which under go **dissociation.**

Example 119. *0.01 m aqueous solution of $K_3[Fe(CN)_6]$ freezes at – 0.062 °C. What is the apparent percentage of dissociation ? (K_f for water = 1.86 K kg mol^-.)* **(PSEB, 2002)**

Solution. (*i*) $\underset{}{\text{K}_3[\text{Fe(CN)}_6]} \rightleftharpoons \underset{3\ \text{mol}}{3\text{K}^+} + \underset{1\ \text{mol}}{[\text{Fe(CN)}_6]^{3-}}$

$\therefore$ $n = 3 + 1 = 4$

Molality, m = 0.01 mol kg^-,

ΔT_f = 0.062 °C = 0.062 K ;

K_f = 1.86 K kg mol^-.

We know that :

$$\Delta T_f = i\, k_f m.$$

$$\text{Hence :}\quad i = \frac{\Delta T_f}{K_f\, m}$$

$$= \frac{0.062\ \text{K}}{1.86\ \text{K kg mol}^- \times 0.01\ \text{mol/kg}}$$

= 3.33

For dissociation,

$$\alpha = \frac{i-1}{n-1} = \frac{3.33-1}{4-1} = \frac{2.33}{3} = 0.7766$$

or $\alpha = 0.7766 \times 100 = \mathbf{77.66\ \%}$

Example 120. *Calculate the van't Hoff factor and degree of dissociation of $CdSO_4$ (Mol. wt. 208.4) if the dissociation of 5.21 g of $CdSO_4$ in half litre water gives a depression in freezing point of 0.168 °C. (K_f of water is 1.86 K kg mol^{-}).* **(PSEB, 1996)**

Solution. $\Delta T_f = 0.168\ °C = 0.168\ K$

$k_f = 1.86\ K\ kg\ mol^{-}$;

density of water = 1 g cm^{-3}

$$\frac{1}{2}\ L\ water = 1000\ cm^3 \times \frac{1}{2} = 500\ cm^3$$

$$= \frac{500\ g \times 1\ kg}{1000\ g} = 0.5\ kg = W_2$$

Wt. of $CdSO_4$ solute,

$$W_2 = 5.21\ g$$

$$\Delta T_f = 0.168\ °C = 0.168\ K;$$

$$K_f = 1.86\ K\ kg\ mol^{-}.$$

$$\Delta T_f = \frac{i K_f \times W_2\ in\ g}{M_2 \times W_1\ in\ kg}$$

$$i = \frac{\Delta T_f \times M_2 \times W_1\ in\ kg}{K_f \times W_2\ in\ g}$$

$$= \frac{0.168\ K \times 208.4\ g\ mol^{-} \times 0.5\ kg}{1.86\ K\ kg\ mol^{-} \times 5.21\ g}$$

$$i = 1.81$$

For degree of dissociation (α) of

$$\underset{}{CdSO_4} \rightleftharpoons \underset{1\ mol}{Cd^{2+}} + \underset{1\ mol}{SO_4^{2-}} \text{ we have}$$

$\therefore$ $n = 1 + 1 = 2;$

$$\alpha = \frac{i-1}{n-1} = \frac{1.81-1}{2-1} = 0.81$$

or $\alpha = 0.81 \times 100 = \mathbf{81}\ \%.$

Type. $\pi = i\,CRT$ where C is the concentration *e.g.*, for 0.1 M solution, $C = 0.1$ M

Example 121. *Find the osmotic pressure of potassium ferrocyanide solution whose 0.1 M aqueous solution dissociates to 45 % at 298 K. (R = 0.0821 L atm K^{-} mol^{-})*

Solution. Osmotic pressure, π = ?,

$$\alpha = \text{degree of dissociation} = \frac{45}{100};$$

$$\text{concentration, } C = \frac{0.1\ mol}{L};$$

$R = 0.0821\ L\ atm\ K^{-}\ mol^{-}$;

$T = 298\ K$

	$K_4Fe(CN)_6$ $\rightleftharpoons$	$4K^+$ +	$[Fe(CN)_6]^{4-}$
Initial conc. (mol)	1	0	0
At equilibrium, conc. (mol)	$1-\alpha$	4α	1α

$\therefore$ Total no. of particles at equilibrium

$$= 1 - \alpha + 4\alpha + 1\alpha = 1 + 4\alpha$$

$$\therefore \quad i = \frac{\text{Total no. of particles at equilibrium}}{\text{Initial no. of mol}}$$

$$= \frac{1+4\alpha}{1}$$

$$= \frac{1+\left(4 \times \frac{45}{100}\right)}{1} = \frac{1+1.8}{1} = 2.8$$

But $\pi = iCRT$; $\pi = 2.8 \times \frac{0.1\ mol}{L} \times 0.0821$ L atm K^{-} mol^{-} × 298 K

$\therefore$ $\pi = \mathbf{6.85\ atm.}$ **Ans.**

Example 122. *A 5% solution of $CaCl_2$ at 0 °C developed 15 atmospheric pressure. Calculate the degree of dissociation (mol. wt. of $CaCl_2$ = 111 a.m.u., R = 0.0821 L atm K^{-} mol^{-})*

Solution. π = 15 atm ; degree of dissociation, α = ? , mol. wt. M_2 = 111 g mol^{-}, R = 0.0821 L atm K^{-} mol^{-} ; T = 0 + 273 = 273 K

	$CaCl_2$ $\rightleftharpoons$	Ca^{2+} +	$2Cl^{-}$
Initial conc. (mol)	1	0	0
Conc (mol) at equilibrium	$1-\alpha$	α	2α

Total no. of mol at equilibrium

$$= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$$

$$\therefore \quad i = \frac{\text{Total no. of mol at equilibrium}}{\text{Initial no. of mol}}$$

$$= \frac{1+2\alpha}{1} = 1 + 2\alpha.$$

Wt. of $CaCl_2$, W_2 = 5 g ;
volume (V) of solution

$$= 100\ mL \times \frac{1\ L}{1000\ mL} = 0.1\ L$$

$$\pi = i\frac{W_2\,RT}{M_2 V};$$

$$i = \frac{\pi M_2 V}{W_2\,RT}$$

$$= \frac{15\ atm \times 111\ g\ mol^{-} \times 0.1\ L}{5\ g \times 0.0821\ L\ atm\ K^{-}\ mol^{-} \times 273\ K}$$

$\therefore$ $i = 1.486.$

Thus $1 + 2\alpha = 1.486$;

$$\alpha = \frac{1.486-1}{2} = 0.243$$

$\therefore$ $\alpha = 0.243 \times 100 = \mathbf{24.3\ \%}$ **Ans.**

Example 123. *The freezing point of a solution containing 0.2 g acetic acid in 20 g of benzene is lowered by 0.45 °C. Calculate the degree of association of acetic acid in benzene. (K_f for benzene = 5.12 °C Kg mol^{-})*

Solution. Wt. of acetic acid, $W_2 = 0.2$ g ; wt. of solvent benzene, $W_1 = 20\text{ g} \times \dfrac{1\text{ kg}}{1000\text{ g}} = 0.02\text{ kg}$; $\Delta T_f = 0.45\ ^\circ\text{C}$; α = degree of association = ?

$$\Delta T_f = k_f m = \frac{k_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}} ;$$

$$0.45^\circ\text{C} = \frac{5.12\ ^\circ\text{C kg mol}^{-} \times 0.2\text{ g}}{M_2 \times 0.02\text{ kg}}$$

$$\therefore \quad M_2 = \frac{5.12\ ^\circ\text{C Kg mol}^{-} \times 0.2\text{ g}}{0.45\ ^\circ\text{C} \times 0.02\text{ kg}}$$

$$= 11378\text{ g mol}^{-}$$

[= experimental mol. wt.]

Calculated mol. wt. of CH_3COOH = 12 + (3 × 1) + 12 + 16 + 16 + 1 = 60 g mol^{-}

$$\therefore \quad i = \frac{\text{Calculated mol. wt. of } CH_3COOH}{\text{Experimental mol. wt. of } CH_3COOH}$$

$$= \frac{60\text{ g mol}^{-}}{113.78\text{ g mol}^{-}} = 0.527$$

$$CH_3COOH \rightleftharpoons 1/2\,(CH_3COOH)_2$$

Initial conc. (mol) $\quad 1 \quad\quad 0$

Conc. (mol) at equilibrium $\quad 1 - \alpha \quad\quad \dfrac{\alpha}{2}$

Total no. of mol at equilibrium $= 1 - \alpha + \dfrac{\alpha}{2} = 1 - \dfrac{\alpha}{2}$

$$\therefore \quad i = \frac{\text{Total no. of mol at equilibrium}}{\text{Initial no. of mol}}$$

$$= \frac{1 - \frac{\alpha}{2}}{1} = 1 - \frac{\alpha}{2}$$

$$\therefore \quad 1 - \frac{\alpha}{2} = 0.527 ; 1 - 0.527 = \frac{\alpha}{2} ;$$

$$\alpha = 2\,(1 - 0.527) = 2 \times 0.473$$

$$\therefore \quad \alpha = 0.946$$

or $\quad \alpha = 0.946 \times 100 = 94.6\ \%$ **Ans.**

Example 124. *Calculate the freezing point of one molal NaCl solution assuming NaCl to be 100 % dissociated in water. (K_f for water = 1.86 °C kg mol⁻)*

Solution. $\underset{1\text{ mol}}{NaCl} \rightleftharpoons \underset{1\text{ mol}}{Na^+} + \underset{}{Cl^-}$ (100 % dissociated)

∴ Total no. of ions after dissociation = 1 mol + 1 mol = 2 mol

Since the number of ions formed is two, the depression in freezing point will be doubled *i.e.,*

$$\Delta T_f = i\,k_f m$$

$$= 2 \times 1.86\ ^\circ\text{C kg mol}^{-} \times \frac{1\text{ mol}}{\text{kg}}$$

$$= 3.72\ ^\circ\text{C}$$

∴ **Freezing point**

$= 273 - 3.72 =$ **269.28 °C** **Ans.**

Example 125. *1% solution of KCl is dissociated to the extent of 80 %. What would be its osmotic pressure at 27 °C. (R = 0.0821 L atm K⁻ mol⁻)*

Solution. Wt. of solute, $W_2 = 1$ g (∵ 1 % solution) ; T = 27 + 273 = 300 K ; R = 0.0821 L atm K^{-} mol^{-} ; α = 80% = 80/100 = 0.8 ; volume = 100 mL (∵ 1 % solution) = $100\text{ mL} \times \dfrac{1\text{ L}}{1000\text{ mL}} = 0.1\text{ L}$; Mol. wt. of KCl = M_2 = 39 + 35.5 = 74.5 g mol^{-}. We know that:

Osmotic pressure,

$$\pi = i\,CRT = i\,\frac{W_2}{M_2\,V} \times RT$$

For $\quad \underset{1\text{ mol}}{KCl} \rightleftharpoons \underset{1\text{ mol}}{K^+} + Cl^-$

$n = 1 + 1 = 2$

(for one K^+ and one Cl^-, $n = 1 + 1 = 2$)

For dissociation,

$$\alpha = \frac{i-1}{n-1} ; \; 0.8 = \frac{i-1}{2-1} = \frac{i-1}{1} = i - 1 ;$$

or $\quad i = 1 + 0.8 = 1.8$

But $\quad \pi = \dfrac{i\,W_2\,RT}{M_2\,V}.$

So, $\quad \pi = \dfrac{1.8 \times 1\text{ g} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 300\text{ K}}{74.5\text{ g mol}^{-} \times 0.1\text{ L}}$

∴ $\quad \pi =$ **5.95 atm** **Ans.**

Example 126. *Calculate the b.pt. of 1 molar aqueous solution of KBr. Given that the density of solution is 1.06 g (m L)⁻, K_b for water is 0.52 K kg mol⁻ (atomic mass of K = 39, Br = 80).*

(DSB, 1995)

Solution. B.pt. = ? . Molarity = 1 M. So, volume of K Br solution = 1000 mL. But density = 1.06 g (mL)$^{-}$. So, wt. of K Br, solution = Volume × density = 1000 mL × 1.06 (mL)$^{-}$ = 1060 g ; mol. wt. (M_2) of K Br = 39 + 80 = 119 g mol^{-}

∴ Wt. of solute, W_2 = 119 g as solution is 1 M.

∴ Wt. of solvent, W_1 = 1060 g − 119 g = 941g

$$= 941\text{ g} \times \frac{1\text{ kg}}{1000\text{ g}} = 0.941\text{ kg}$$

$$\underset{}{KBr} \rightleftharpoons \underset{1\text{ mol}}{K^+} + \underset{1\text{ mol}}{Br^-}$$

∴ $\quad i = 1 + 1 = 2$

But $\quad \Delta T_b = \dfrac{i\,K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$

$$= \frac{2 \times 0.52\text{ K kg mol}^{-} \times 119\text{ g}}{119\text{ g mol}^{-} \times 0.941\text{ kg}}$$

$$= 1.105\text{ K}$$

∴ $\quad$ B.pt. = 373 + 1.105 = **374.105 K** **Ans.**

Example 127. *Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of CS_2 assuming 84 % dimerisation of the acid. The boiling point and K_b of CS_2 are 46.2 °C and 2.3 K kg mol^{-1} respectively.* **(Roorkee, 1997)**

Solution.
$$\alpha = \frac{1-i}{1-1/n} \quad \text{or} \quad 0.84 = \frac{1-i}{1-1/2}$$

(n = 2 in case of dimerisation)

$$1 - i = 0.84 \times 0.5 = 0.42 \; ; \; i = 1 - 0.42 = 0.58$$

(*ii*)
$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}}$$

Normal mol. mass of benzoic acid (C_6H_5COOH)

$$= 12 \times 6 + 1 \times 5 + 12 + 2 \times 16 + 1$$
$$= 122 \text{ g mol}^{-}$$

∴
$$0.58 = \frac{122}{\text{Observed mol. mass}}$$

Observed molecular mass

$$= \frac{122}{0.58} \text{ g mol}^{-} = 210 \text{ g mol}^{-}$$

(*iii*) Calculation of elevation in boiling point

Wt. of solute, W_2 = 0.61 g ; wt. of solvent (CS_2), W_1 = 50 g ; *b.pt.* of solution T_b = ? ;
b.pt. of solvent,

$$T^0_b = 46.2 \text{ °C} ;$$

Mol. wt.,

$$M_2 = 210 \text{ g mol}^{-}$$

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$= \frac{2.3 \text{ K kg mol}^{-} \times 0.61 \text{ g}}{210 \text{ g mol}^{-} \times \dfrac{50}{1000} \text{ kg}}$$

$$= \frac{2.3 \text{ K kg mol}^{-} \times 0.61 \text{ g} \times 1000}{210 \text{ g mol}^{-} \times 50 \text{ kg}}$$

$$= 0.1336 \, K$$

∴ B.pt. of solution = B.pt. of solvent + ΔT_b = 46.2 °C + 0.1336 °C = 46.3336 °C

or (46.2 + 273 + 0.1336)

$$K = 319.3336 \, K$$

Example 128. *Freezing point of ether was lowered by 0.6 °C on dissolving 2.0 g of phenol (C_6H_5OH, mol. wt. 94) in 100 g of ether. The molal depression constant for ether is 5.12°. Calculate the molecular mass of phenol in solution and comment on your result.*

Solution. ΔT_f = 0.6 °C ; wt. of solute phenol, C_6H_5OH = 2.0 g ; mol. wt. of C_6H_5OH, M_2 = 94 g mol^{-};

$$\text{wt. of ether, } w_1 = 100 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.1 \text{ kg}$$

$$K_f = 5.12\text{°C kg mol}^{-};$$

Molar mass of phenol in ether = ?

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}} ; M_2 = \frac{K_f \times W_2 \text{ in g}}{\Delta T_f \times W_1 \text{ in kg}}$$

$$= \frac{5.12 \text{ °C kg mol}^{-} \times 2 \text{ g}}{0.6 \text{ °C} \times 0.1 \text{ kg}}$$

or M_2 = 170.67 g mol^{-} = observed mol. wt.

Normal mol. wt. = 94 g mol^{-} (given)

∴ Van't Hoff factor,

$$i = \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}}$$

$$= \frac{94 \text{ g mol}^{-}}{170.67 \text{ g mol}^{-}} \simeq 1/2$$

Hence observed molecular weight of phenol in ether is two times the normal molecular weight of phenol.

Example 129. *The dissolution of 1.6 g of acetic acid in 100 g of benzene raised its boiling point by 0.35 °C. Calculate the van't Hoff factor and degree of association of acetic acid if acetic acid (CH_3COOH) forms a dimer in benzene (Molal elevation constant of benzene is 2.57).*

Solution. Normal molar mass of CH_3COOH = 12 + (3 × 1) + 12 + 16 + 16 + 1 = 60 g mol^{-})

Observed molar mass,

$$M = \frac{K_b \times W_2 \times 1000}{W_1 \text{ (in g)} \times \Delta T}$$

$$= \frac{2.57 \times 1.6 \times 1000}{100 \times 0.35} = 117.5 \text{ g mol}^{-}$$

∴ **van't Hoff factor,**

$$\boldsymbol{i} = \frac{\text{normal molar mass}}{\text{Observed molar mass}}$$

$$= \frac{60 \text{ g mol}^{-}}{117.5 \text{ g mol}^{-}} = \mathbf{0.51} \qquad \textbf{Ans.}$$

For association :

$$i = 1 - \alpha\left(1 - \frac{1}{n}\right)$$

or
$$0.51 = 1 - \alpha\left(1 - \frac{1}{2}\right) = 1 - \frac{\alpha}{2}$$

$$\frac{\alpha}{2} = 1 - 0.51 = 0.49.$$

Hence $\alpha = 2 \times 0.49 = 0.98$

∴ CH_3COOH is 98 % (0.98 × 100 = 98) associated in benzene.

18.23 DEGREE OF DISSOCIATION AND VAN'T HOFF FACTOR, *i* RELATED AS: *i* = 1 + (*n* – 1)α

***i* = 1 + (*n* – 1)** α. Where n = number of ions formed on the dissociation of one mole of electrolyte. For example, for

KCl; [KCl $\rightleftharpoons$ K^+ (1 mol) + Cl^- (1 mol), $n = 1 + 1 = 2$, for K_3 Fe $(CN)_6$; $K_3Fe\ (CN)_6 \rightleftharpoons 3\ K^+$ (3 mol) + $[Fe\ (CN)_6]^{3-}$ (1 mol)], $n = 3 + 1 = 4$ etc.

EXAMPLE 130. *An aqueous solution of potassium chloride containing 0.6 g of it in 100 mL water freezes at 0.24 °C. Calculate the van't Hoff factor and degree of dissociation of the given compound at the given concentration. (K_f for H_2O = 1.86).*

SOLUTION. Depression in freezing point and Van't Hoff factor, i are related as,

$$\Delta T_f = \frac{i \times K_f \times w \times 1000}{W \times M}$$

[M = molar mass of KCl = 39 + 35.5 = 74.5]

$$\therefore \quad 0.24 = \frac{i \times 1.86 \times 0.6 \times 1000}{100 \times 74.5}$$

$$\text{or} \quad i = \frac{0.24 \times 100 \times 74.5}{1.86 \times 0.6 \times 1000} = \mathbf{1.602} \quad \textbf{Ans.}$$

But $\quad i = 1 + (n - 1)\,\alpha$

where $\quad \alpha$ = degree of dissociation.

$\therefore \quad 1.602 = 1 + (2 - 1)\,\alpha$

[$\because$ For KCl $\rightleftharpoons$ K^+ (one mol) + Cl^- (one mol), $n = 1 + 1 = 2$]

or $\quad \alpha = 1.602 - 1 = 0.602 = 0.602 \times 100$

$= \mathbf{60.2\ \%}$ **Ans.**

EXAMPLE 131. *Calculate the weight of NaCl that must be used to prepare 1 dm^3 of its aqueous solution so that its osmotic pressure becomes same as that of 5.0 % solution of fructose at 290 K. The degree of ionisation of NaCl (molar mass 58.5 g mol^-) at 290 K is 0.82.*

SOLUTION. NaCl ionises in aqueous solution as :

	NaCl (aq) $\rightleftharpoons$	Na^+ (aq) +	Cl^-(aq).
Initial concentration	1	0	0
At equilibrium	1 - α	α	α

where α is the degree of ionisation. We know that :

$$i = \frac{(1-\alpha) + \alpha + \alpha}{1} = 1 + \alpha$$

$\therefore \quad i = 1 + 0.82 = 1.82 \quad (\because \alpha = 0.82$, given)

For 5.0 % solution of fructose, weight of fructose

$$= \frac{5}{100} \times 1000 = 50 \text{ g L}^-$$

Volume, V of solution

$= 1\ dm^3 = 1$ L

Molar mass of fructose,

$C_6H_{12}O_6 = (6 \times 12) + (12 \times 1) + (6 \times 16) = 180.$

$$\therefore \quad \pi_{\text{fructose}} = \frac{n\,RT}{V} = \frac{WRT}{M\,V} = \frac{50 \times RT}{180} \quad \text{... (i)}$$

$$\text{Similarly, } \pi_{\text{NaCl}} = i \times \frac{n\,RT}{V} = 1.82 \times \frac{W_1\,RT}{M_1\,V}$$

$$\pi_{\text{NaCl}} = \frac{1.82 \times W_1 \times RT}{58.5 \times 1} \quad \text{... (ii)}$$

Since both solutions are isotonic, $\pi_{\text{fructose}} = \pi_{\text{NaCl}}$

$$\therefore \quad \frac{1.82\,W_1\,RT}{58.5} = \frac{50\,RT}{180}$$

$$\text{or} \quad W_1 = \frac{50 \times 58.5}{180 \times 1.82} = \mathbf{8.93\ g.} \quad \textbf{Ans.}$$

EXAMPLE 132. *A 0.1 m aqueous solution of transition metal (M) complex MCl_3. xNH_3 shows ΔT_f equal to 0.56 °C. The complex assumes 100 % ionisation and coordination number of M is 6. Find the molecular formula of the complex if $K_f (H_2O)$ is 1.86 kg mol^- K*

SOLUTION. Molality of solution, $m = 0.1$; $K_f(H_2O) = 1.86$ kg mol^- K.

ΔT_f = depression in **f.pt.** = 0.56 °C.

We know that :

$\Delta T_f = i\,K_f \times m$ (i = Van't Hoff factor)

Or $\quad 0.56 = i \times 1.86 \times 0.1.$

$$\text{Thus} \quad i = \frac{0.56}{1.86 \times 0.1} = 3$$

The value of $i = 3$ shows that the complex on ionisation liberates three ions. Since, coordination number of M is 6, the value of x will be equal to 5.

$$MCl_3.\ 5\ NH_3 \rightleftharpoons \underset{\text{one cation}}{[M(NH_3)_5\ Cl]^{2+}} + \underset{\text{Two anions}}{2\ Cl^-}$$

Hence, the molecular formula of the complex is, $[M(NH_3)_5\ Cl]\ Cl_2$.

EXAMPLE 133. *A non-volatile organic compound (weight 286 g) having stoichiometric composition $C_x\ H_{2x}\ O_x$ was dissolved in 100 g of water. If the solution boils at 101.11 °C at one atmospheric pressure, calculate the molecular formula of the compound. [T_b (H_2O) = 100 °C, K_b (H_2O) = 0.512 Kg mol^- K].*

SOLUTION. Wt. of organic compound, W_2 = 286 g ; wt.of solvent, W_1 = 100 g ; elevation in b.pt. (ΔT_b) = 101.11 - 100 = 1.11 °C .

Since the compound is non - volatile organic compound and does not ionise, van't Hoff factor, $\boldsymbol{i = 1}$.

$$\Delta T_b = i\,K_b \times m = i \times k_b \times \frac{W_2}{M} \times \frac{1000}{W_1}$$

$$\textbf{Or} \quad M = \frac{1 \times 0.512 \text{ K kg mol}^- \times 286 \text{ g} \times 1000}{1.11 \text{ K} \times 100 \text{ kg}}$$

$= 1319.2$ g mol^-

= molar mass of solute.

Thus, molar mass of

$C_x\ H_{2x}\ O_x = 1319.2$

Or $(x \times 12) + (2x \times 1) + (x \times 16) = 1319.2; 30\,x = 1319.2$

$$\text{or} \quad x = \frac{1319.2}{30} = 44$$

$\therefore$ Molecular formula of compound = $\mathbf{C_{44}H_{88}O_{44}}$ **Ans.**

EXAMPLE 134. *A 2.8 g L^- solution of $Hg(CN)_2$ has an osmotic pressure of 0.31×10^5 Nm^{-2} at 298 K. Calculate the apparent molar mass and degree of dissociation of $Hg(CN)_2$ (Hg = 200.61, C = 12, N = 14).*

SOLUTION. Osmotic pressure, $\pi = \frac{n\,RT}{V} = \frac{WRT}{MV}$. Substituting the values of $W = 2.8 \times 10^{-3}$ kg, R = 8.314, etc, we get :

$$0.31 \times 10^5 = \frac{2.8 \times 10^{-3} \times 8.314 \times 298}{M \times 10^{-3}}$$

Or
$$M = \frac{2.8 \times 10^{-3} \times 8.314 \times 298}{0.31 \times 10^5 \times 10^{-3}}$$

$= 223.8 \times 10^{-3}$ kg = observed mol. wt.

$$Hg(CN)_2 \rightleftharpoons Hg^{2+} + 2\,CN^-\text{(ionisation)}$$

Initial conc. 1 0 0

At. equilibrium $1 - \alpha$ α $2\,\alpha$

No. of particles after dissociation

$= 1 - \alpha + \alpha + 2\,\alpha = 1 + 2\,\alpha$

Normal mol. wt. of

$Hg(CN)_2 = 200.61 + 2\,(12 + 14)$

$= 252.61 \times 10^{-3}$ kg

We know :

$$\frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{no. of particles after dissociation}}{\text{no. of particles before dissociation}}$$

$$\therefore \frac{252.61 \times 10^{-3}}{223.8 \times 10^{-3}} = \frac{1 + 2\,\alpha}{1} \quad \text{or} \quad 2\,\alpha = \frac{252.61 \times 10^{-3}}{223.8 \times 10^{-3}} - 1$$

$\therefore$ $\alpha = 0.06436 = 0.06436 \times 100\%$

$= \mathbf{6.436\ \%}$ **Ans.**

EXAMPLE 135. *A decinormal solution of sodium chloride exerts an osmotic pressure of 4.82 atmosphere at 27°C. Calculate the degree of dissociation of sodium chloride.* **(ISC, 2007)**

SOLUTION. Osmotic pressure, $\pi = 4.82$ atm.; $T = 27 + 273 = 300$ K; $V = 1$L; $n = 1/10 = 0.1$; $R = 0.0821$ L atm K^- mol^-; $i = ?$

For an electrolyte

$$\pi\,V = inRT$$

$$\therefore \quad i = \frac{\pi V}{nRT};$$

$$i = \frac{4.82 \text{ atm} \times 1 \text{ L}}{0.1 \text{ mol} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$= 1.956$

Let α = degree of dissociation of NaCl

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

	NaCl	Na^+	Cl^-
(Before dissociation)	1	0	0
(After dissociation)	$1 - \alpha$	α	α

Total no. of mol. after dissociation

$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$i = \frac{\text{No. of mol. after dissociation}}{\text{No. of mol before dissociation}}$$

$$= \frac{1 + \alpha}{1} = 1.956$$

$\therefore$ $\alpha = 1.956 - 1 = 0.956 = 0.956 \times 100$

$= \mathbf{95.6\%}$ **Ans.**

EXAMPLE 136. *Mercuric cyanide reacts with KCN to form a complex as follows :*

$Hg(CN)_2 + n\,KCN \rightleftharpoons K_n[Hg(CN)_{n+2}]$. Calculate the formula of this complex from the following data. The freezing point of KCN (aq) containing 0.191 mol kg^- of solvent is – 0.702 °C. The freezing point of the solution after the addition of 0.091mol of $Hg(CN)_2$ is – 0.501°C. $K_f(H_2O) = 1.86$ K kg mol^-.

SOLUTION. We know that

$$K_n[Hg(CN)_{n+2}] \rightleftharpoons nK^+ + [Hg(CN)_{n+2}]^-$$

Initial conc. 1 0 0

At equilibrium, conc. $1 - \alpha$ $n\,\alpha$ α

(α = degree of dissociation)

Or $i = 1 - \alpha + n\,\alpha + \alpha$ **or** $i = 1 + n\alpha$ ... (1)

Also, $\Delta T_f = i\ k_f\ m$. Substituting the values, we get :

$0.501 = i \times 1.86 \times 0.091$

or
$$i = \frac{0.501}{1.86 \times 0.091} \approx 3$$

Since KCN is 100 % dissociated, $\alpha = 1$. Substituting the value of $\alpha = 1$ and $i = 3$ in equation (1), we get :

$3 = 1 + n$ or $n = 3 - 1 = 2$

$\therefore$ Chemical formula of complex $K_n[Hg(CN)_{n+2}] = K_2[Hg(CN)_4]$ **Ans.**

18.24 DEGREE OF ASSOCIATION

EXAMPLE 137. *75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of $k_f = 14$. If the depression in freezing point is 7 K, then find the % age of phenol that dimerises.* **(IIT-JEE, 2006)**

SOLUTION. Wt. of phenol = 75.2 g ; mol. wt. of $C_6H_5OH = (6 \times 12) + (5 \times 1) + 16 + 1 = 92$ g mol^-; C = concentration in mol.

$$\therefore \text{ C of phenol} = \frac{\text{Wt.}}{\text{Mol. wt.}} = \frac{75.2}{92} = 0.817 \simeq 0.82$$

Reaction.	C_6H_5OH	$\rightleftharpoons$	$1/2\,(C_6H_5OH)_2$
Initial conc	C		0
conc at equilibrium	$C - C\,\alpha$		$\frac{C\,\alpha}{2}$

[α = degree of association]

$$\text{Total number of mol} = C - C\,\alpha + \frac{C\,\alpha}{2} = C - \frac{C\,\alpha}{2}$$

$$= C\left[1 - \frac{\alpha}{2}\right] = 0.82\left(1 - \frac{\alpha}{2}\right)$$

or molality, $m = 0.82\left(1-\frac{\alpha}{2}\right)$

But $\Delta T_f = k_f \times m;$

$$7 = 14\times 0.82\left(1-\frac{\alpha}{2}\right);$$

$$1-\frac{\alpha}{2} = \frac{7}{14\times 0.82};$$

$$\frac{\alpha}{2} = 1-\frac{7}{14\times 0.82} = 1-0.61 = 0.39$$

Hence $\alpha = 2 \times 0.39 = 0.78$

∴ % age of phenol = 0.78 × 100 = **78 %** **Ans.**

Example 138. *Assuming that the first ionisation of 0.1 m tartaric acid (aq) is important, calculate its ionisation constant (K_a). Given f.p. of acid = – 0.205 °C, $k_f(H_2O)$ = 1.86 K kg mol^{-}, 0.1 m = 0.1 M.*

Solution. Since first ionisation of the acid is important, the acid is considered as monobasic (AH). Thus.

	$AH \rightleftharpoons$	$A^- +$	H^+
Initial conc.	C	0	0
At equilibrium, conc.	C – C α	C α	C α

(α = degree of dissociation).

$$\therefore \quad i = \frac{C - C\alpha + C\alpha + C\alpha}{C}$$

$$= \frac{C(1-\alpha+\alpha+\alpha)}{C} = \mathbf{1+\alpha}$$

We know $\Delta T_f = i\, k_f\, m$. Substituting the values, we get :

$$0.205 = (1+\alpha)\times 1.86 \times 0.1$$

$$\therefore \quad 1+\alpha = \frac{0.205}{1.86\times 0.1} = 1.1$$

$$\therefore \quad \alpha = 1.1 - 1 = 0.1 \qquad ..(1)$$

For the reaction, $AH \rightleftharpoons A^- + H^+$

$$K_a = \frac{[A^-][H^+]}{[AH]} = \frac{C\alpha \times C\alpha}{C - C\alpha}$$

$$= \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Or $$K_a = \frac{0.1\times(0.1)^2}{1-0.1} = \mathbf{1.11\times 10^{-3}}$$ **Ans.**

Example 139. *Acetic acid (CH_3COOH) exists as partly as a dimer in benzene ($2A \rightleftharpoons A_2$). The f.p. of CH_3COOH (mole fraction, 0.019) in benzene is 277.4 K. K_f (benzene) = 5, f.p. of benzene = 278.4 K. Calculate the equilibrium constant for dimerisation.*

Solution. Let *A* and *B* represent acetic acid and benzene respectively. Suppose α part of acetic acid forms dimers in benzene. Thus :

	$2A \rightleftharpoons$	A_2
Initial conc.	1	0
After dimer formation	1 – α	α/2

$$\therefore \quad i = \frac{1-\alpha+\alpha/2}{1} = 1-\alpha/2. \qquad ...(1)$$

$$x_A = 0.019\,(\text{given});\ x_B = 1-0.019 = 0.981.$$

$$\therefore \text{ Molality of } A \text{ in } B = \frac{x_A\times 1000}{m_B\times x_B} = \frac{0.019\times 1000\text{ g kg}^{-}}{78\text{ g mol}^{-}\times 0.981}$$

$$= 0.248\text{ mol kg}^{-}$$

[∵ mol. wt. of $C_6H_6 = (6\times 12) + (6\times 1) = 78$]

$$\Delta T_f = 278.4 - 277.4 = 1.0$$

But $\Delta T_f = i\, k_f m$ **Or** $1.0 = i\times 5\times 0.248$

Or $$i = \frac{1}{5\times 0.248} = 0.8064.$$

Substituting this value in (1), we get:

$$0.8064 = 1-\frac{\alpha}{2} \text{ or } \frac{\alpha}{2} = 1-0.8064 = 0.1936$$

$$\therefore \quad \alpha = \mathbf{0.39}$$

Thus molality of *A* after dimer is formed = (1 – α) × initial molality

$$= (1-0.39)\times 0.248 = 0.151$$

Also molality of A_2 after dimer is formed

$$= \frac{\alpha}{2}\times \text{molality}$$

$$= \frac{0.39}{2}\times 0.248$$

$$= 0.04836$$

For the given reaction, $2A \rightleftharpoons A_2$

$$K_{eq} = \frac{[A_2]}{[A]^2} = \frac{0.04836}{(0.151)^2}$$

$$= \mathbf{2.12\text{ kg mol}^{-}}$$ **Ans.**

Example 140. *A one kg aqueous solution of sugar (molality, 0.8) was cooled and maintained at – 4 °C. Calculate the amount of ice that would separate from it. $K_f(H_2O)$ = 1.86 K kg mol^{-}.*

Solution. Molar mass of sugar ($C_{12}H_{22}O_{11}$) = (12 × 12) + (22 × 1) + (11 × 16) = 342. Molality, m = 0.8 m = 0.8 mol Kg^{-} solvent = 0.8 × 342 = 273.6 g sugar per kg solvent

∴ wt. of 1 m solution

$$= 1000 + 273.6 = 1273.6\text{ g.}$$

(∵ 1 kg = 1000 g)

∴ wt. of sugar present in 1 kg solution

$$= \frac{273.6}{1273.6}\times 1000 = 214.82\text{ g}$$

∴ wt. of solvent (H_2O) in 1 kg solution

$$= 1000 - 214.82 = 785.18\text{ g}$$

ΔT_f = 4 °C. We know that :

$$\Delta T_f = i\,k_f\,m = i\,K_f\,\frac{w}{m}\times\frac{1000}{W}$$

$$\therefore \quad 4 = \frac{1\times 1.86\times 214.82\times 1000}{342\times W}$$

(m = mol. wt. of sugar; w = wt. of solute)

Or $$W = \frac{1.86\times 214.82\times 1000}{4\times 342}$$

= 292.1 g = wt. of solvent required to maintain this solution at – 4°C .

The remaining weight of water will change into ice.

∴ Wt. of ice formed

= 785.18 – 292.1 = **493.08 g.** **Ans.**

EXAMPLE 141. *A sample of water contains 23.4 % NaCl and 11.1 % $CaCl_2$ by weight of solution. Assuming 95% ionisation of NaCl and 60 % ionisation of $CaCl_2$, calculate the normal boiling point of the solution. (K_b for H_2O = 0.52 K kg mol^-).*

SOLUTION. Molar mass of

NaCl = 23 + 35.5 = 58.5

Molar mass of

$CaCl_2$ = 40 + (2 × 35.5) = 111

$$\begin{array}{lccc} & NaCl & \rightleftharpoons Na^+ & + \; Cl^- \\ \text{Initial conc} & 1 & 0 & 0 \\ \text{At equilibrium, conc} & 1-\alpha & \alpha & \alpha \end{array}$$

(α = degree of dissociation)

$$\therefore \quad i = 1-\alpha+\alpha+\alpha = 1+\alpha = 1+\frac{95}{100}$$

$$= \mathbf{1.95} = i_{NaCl}$$

$$\begin{array}{lccc} & CaCl_2 & \rightleftharpoons Ca^{2+} & + \; 2Cl^- \\ \text{Initial conc} & 1 & 0 & 0 \\ \text{At equilibrium, conc} & 1-\alpha & \alpha & 2\alpha \end{array}$$

$$\therefore \quad i = 1-\alpha+\alpha+2\alpha = 1+2\alpha$$

$$\alpha = 1+2\times\frac{60}{100} = \mathbf{2.2} = i_{CaCl_2}$$

no. of moles of NaCl, $n_{NaCl} = \dfrac{23.4}{58.5} = 0.4$

no. of moles of

$CaCl_2$, $n_{CaCl_2} = \dfrac{11.1}{111} = 0.1$

wt. of solvent = 100 – [23.4 + 11.1] = 65.5 g.

$$\therefore \Delta T_b = \frac{\left[\left(i_{NaCl}\times n_{NaCl}\right)+\left(i_{CaCl_2}\times n_{CaCl_2}\right)\right]\times K_b\times 1000}{\text{Wt. of solvent}}$$

$$= \frac{(1.95\times 0.4)+(2.2\times 0.1)\times 0.52\times 1000}{65.5}$$

$$= \frac{(0.78+0.22)\times 0.52\times 1000}{65.5} = 7.94\ °C$$

∴ Boiling point of solution

= 100 + 7.94 = **107.94 °C.**

18.25 AIEEE PATTERN EXAMPLES

EXAMPLE 142. *In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to :*

(*a*) + 0.480 °C (*b*) – 0.481 °C

(*c*) – 0.360 °C (*d*) – 0.260 °C. **(AIEEE, 2003)**

SOLUTION. Given :

$$\begin{array}{lccc} & HX & \rightleftharpoons H^+ & + \; X^- \\ \text{Initial conc} & 1 & 0 & 0 \\ \text{Conc (mol) at equilibrium} & 1-0.3 & & \\ & =0.7 & 0.3 & 0.3 \end{array}$$

Total number of moles after dissociation

= 0.7 + 0.3 + 0.3 = 1.3

We know that;

$$\frac{K_f \text{ observed}}{K_f \text{ experimental}} = \frac{\text{no. of moles after dissociation}}{\text{no. of moles before dissociation}}$$

Or $$\frac{K_f \text{ observed}}{1.85} = \frac{1.3}{1}$$

∴ K_f observed = 1.3 × 1.85 = 2.405.

But $\Delta T_f = k_f \times$ molality.

Thus ΔT_f = 2.405 × 0.2 = 0.4810

∴ Freezing point of solution

= 0 – 0.4810

= – 0.481 °C.

So, the correct answer is (*b*)

EXAMPLE 143. *Freezing point of an aqueous solution is – 0.186 °C. Elevation in boiling point of the same solution is K_b = 0.512 °C, k_f = 1.86 °C, find the increase in boiling point.*

(*a*) 0.2372 °C (*b*) 0.092°C

(*c*) 0.0512°C (*d*) 0.186 °C. **(AIEEE, 2002)**

SOLUTION. K_f = 1.86 °C, K_b = 0.512 °C ;

ΔT_f = – 0.186 °C ;

ΔT_b = ? ; W_B = wt. of solute,

W_A = wt. of solvent

We know that :

$$\Delta T_b = \frac{K_b\,W_B}{M_B\,W_A}\times 1000 \qquad \text{...(1)}$$

$$\Delta T_f = \frac{K_f W_B}{M_B\,W_A}\times 1000 \qquad \text{... (2)}$$

Dividing (1) and (2), we get :

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}.$$

Substituting the values, we get :

$$\frac{\Delta T_b}{-0.186} = \frac{0.512}{1.86}$$

or $$\Delta T_b = \frac{0.512\times -0.186}{1.86} = -0.0512\ °C$$

Thus, elevation in

b.pt. = 0.0512 °C .

Hence the correct answer is (*c*).

EXAMPLE 144. *The elevation in boiling point for 13.44 g of $CuCl_2$ dissolved in 1 kg of water as solvent will be :*

(K_b = 0.52 K kg mol⁻; molar mass of $CuCl_2$ = 134.4 g/mol)

(*a*) *0.05* (*b*) *0.10*

(*c*) *0.16* (*d*) *0.20*

[IIT – JEE (Screening), 2005]

SOLUTION. Reaction :	$CuCl_2 \rightleftharpoons$	Cu^{2+} +	$2Cl^-$
Initial conc (mol)	1	0	0
Conc. after dissociation	$1-\alpha$	α	2α

($\because$ α = degree of dissociation)

$\therefore$ vant Hoff factor,

$$i = 1-\alpha+\alpha+2\alpha = 1+2\alpha$$

Assuming 100 % ionisation,

i = 1 (*i.e.*, one mol Cu^{2+}) + 2 (*i.e.*, two mol Cl^-) = 3

But elevation in *b.pt.*,

$$\Delta T_b = \frac{i \times 1000 \times K_b \times \text{wt. of solute}}{\text{mol. wt. of solute} \times \text{wt. of solvent}}$$

Wt. of solvent = 1 kg = 1 × 1000 g = 1000 g.

$$\therefore \qquad \Delta T_b = \frac{3 \times 1000 \times 0.52 \times 13.44}{134.4 \times 1000} = 0.156 \simeq 0.16$$

So, the correct answer is (*c*).

EXAMPLE 145. *A solution of urea (mol mass 56 g mol⁻) boils at 100.18 °C at the atmospheric pressure. If K_f and K_b for water are 1.86 and 0.512 K kg mol⁻ respectively, the above solution will freeze at:*

(*a*) *0.654 °C* (*b*) *– 0.654 °C*

(*c*) *6.54 °C* (*d*) *– 6.54 °C*

[(CBSE – PMT Prelims), 2005]

SOLUTION. $\Delta T_f = K_f m$ ...(1)

$\Delta T_b = K_b m$ ...(2)

From (1) and (2), we get :

$$\frac{\Delta T_f}{\Delta T_b} = \frac{K_f}{K_b} \qquad \text{... (3)}$$

K_f = 1.86 K kg mol⁻; K_b = 0.512 K kg mol⁻; *b.p.* of water = 100 °C ; freezing point of water = 0 °C ; *b.p.* of urea = 100.18 °C . f.pt. of urea in water = – T °C ; $\Delta T_f = T$

Substituting the values in equation (3), we get :

$$\frac{T}{0.18} = \frac{1.86}{0.512};$$

$$T = \frac{1.86}{0.512} \times 0.18$$

$$= 0.6539 \simeq 0.654\,^\circ C$$

So, the correct answer is (*a*).

EXAMPLE 146. *The vapour pressure of two liquids P and Q are 80 and 60 torr, respectively. The total vapour pressure of solution obtained by mixing 3 mol of P and 2 mol of Q are :*

(*a*) *72 torr* (*b*) *140 torr*

(*c*) *68 torr* (*d*) *20 torr*

[(CBSE - PMT Prelims), 2005]

SOLUTION. P_p^o = 80 torr, P_Q^o = 60 torr;

$$\text{mol fraction } x_P = \frac{3}{2+3} = \frac{3}{5};$$

$$\text{mol fraction } x_Q = \frac{2}{2+3} = \frac{2}{5}.$$

According to Raoult's law

$$P_T = P_p^o x_p + P_Q^o x_Q;$$

$$P_T = \left(80 \times \frac{3}{5}\right) + \left(60 \times \frac{2}{5}\right) = 48 + 24$$

P_T = 72 torr. So, the correct answer is (*a*).

EXAMPLE 147. *Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6°C will be: (k_f for water = 1.86 K kg mol⁻ and molar mass of ethylene glycol = 62 g mol⁻)*

(*a*) *804.32 g* (*b*) *204.30 g*

(*c*) *400.00 g* (*d*) *304.60 g* **[AIEEE, 2011]**

SOLUTION. Wt. of solute, w_2 = ?, wt. of solvent, w_1 in kg = 4, mol. wt. of solute, m_2 = 62g mol⁻, ΔT_f = 0 – (–6) = 6 °C = 6 K

But $$\Delta T_f = \frac{K_f (\text{in } K \text{ kg mol}^-) \times w_2\,(g)}{M_2 \text{ in g mol}^- \times w_1 \text{ in kg}}$$

$$6\,K = \frac{1.86 \text{ K kg mol}^- \times w_2 \text{ g}}{62 \text{ g mol}^- \times 4.0 \text{ kg}};$$

$$w_2 = \frac{6 \times 62 \times 4}{1.86} = 800 \text{ g}$$

So, the correct answer is (*a*).

EXAMPLE 148. *A solution has a 1 : 4 mole ratio of pentane to hexane. The vapour pressures of the pure hydrocarbons at 20 °C are 440 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*

[CBSE – PMT (Prelims), 2005]

SOLUTION. Ratio of pentane, C_5H_{12} and hexane, C_6H_{14}

i.e., $\dfrac{n_{C_5H_{12}}}{n_{C_6H_{14}}} = \dfrac{1}{4}$. Hence, mole fraction $x_{C_5H_{12}} = \dfrac{1}{1+4} = \dfrac{1}{5}$;

$$\text{mole fraction } x_{C_6H_{14}} = \frac{4}{1+4} = \frac{4}{5};$$

$P^o_{C_5H_{12}}$ = 440 mm ; $P^o_{C_6H_{14}}$ = 120 mm.

According to Raoult's law :

$$P_T = P^o_{C_5H_{12}} x_{C_5H_{12}} + P^o_{C_6H_{14}} x_{C_6H_{14}}$$

$$= \left(440 \times \frac{1}{5}\right) + \left(120 \times \frac{4}{5}\right)$$

$$= 88 + 96 = 184 \text{ mm.}$$

Also, $P_{C_5H_{12}} = P^o_{C_5H_{12}} x_{C_5H_{12}}$ ... (1)

Here $x_{C_5H_{12}}$ = mole fraction of C_5H_{12} in solution.
By Dalton's law :

$$P_{C_5H_{12}} = P \times x'_{C_5H_{12}} \qquad \text{... (2)}$$

Where $x_{C_5H_{12}}$ is the mole fraction of pentane above the solution. From (1) and (2), we have :

$$P^o_{C_5H_{12}} x_{C_5H_{12}} = P \times x'_{C_5H_{12}}$$

$$\therefore \qquad x'_{C_5H_{12}} = \frac{P^o_{C_5H_{12}}\, x_{C_5H_{12}}}{P} = \frac{440}{184} \times \frac{1}{5} = 0.478.$$

So, the correct answer is (*d*).

EXAMPLE 149. *The mole fraction of the solute in one molal aqueous solution is :*

(*a*) *0.009* (*b*) *0.018*
(*c*) *0.027* (*d*) *0.036*

[CBSE - PMT (Prelims), 2005]

SOLUTION. Mole fraction of solute, x_{solute} = ?

Mole of solute = 1 ; since the solution is one molal, the wt. of solvent water = 1 kg = 1000 g. Also, g. mol. wt. of $H_2O = (2 \times 1) + 16 = 18$ g. So, no. of mol of $H_2O = \frac{1000}{18} = 55.5$

$$\text{Hence} \quad x_{\text{solute}} = \frac{\text{mol of solute}}{\text{mol of solute + mol of } H_2O}$$

$$= \frac{1}{1 + 55.5} = \frac{1}{56.5} = 0.0177 \simeq \mathbf{0.018}.$$

So, the correct answer is (*b*).

EXAMPLE 150. *The boiling point of one molar aqueous solution [density = 1.04 g (mL)$^{-}$] of potassium chloride (at. wt., K = 39, Cl = 35.5 ; K_b for water = 0.52 K kg mol^{-}) will be :*

(*a*) *1.07 K* (*b*) *101. 07 K*
(*c*) *374.08 K* (*d*) *400 K*

SOLUTION. B.pt. = ? , molarity = 1 M. So, volume of KCl solution = 1000 mL. But density = 1.04 g (mL)$^{-}$. So, wt. of KCl solution = Volume × density = 1000 mL × 1.04 g (mL)$^{-}$ = 1040 g; mol. wt. of KCl = 39 + 35.5 = 74.5 g mol^{-}. Thus, wt. of solute, W_2 = 74.5 g as solution is 1 M.

Wt. of solvent = Wt. of solution – wt. of solute

$$= 1040 \text{ g} - 74.5 \text{ g} = 965.5 \text{ g} = 965.5 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.9655 \text{ kg}$$

$$KCl \rightleftharpoons \underset{1\text{ mol}}{K^+} + \underset{1\text{ mol}}{Cl^-}$$

$$\therefore \qquad i = 1 + 1 = 2$$

$$\text{But} \qquad \Delta T_b = \frac{i K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$= \frac{2 \times 0.52 \text{ K kg mol}^{-} \times 74.5 \text{ g}}{74.5 \text{ g mol}^{-} \times 0.9655 \text{ kg}}$$

$$= 1.08\, K$$

$$\therefore \qquad \text{B.pt.} = (373 + 1.08)\, K = 374.08\, K.$$

So, the correct answer is (*c*).

EXAMPLE 151. *A solution is prepared by dissolving 17.1 g of sucrose to make 1000 mL of solution in water. The osmotic pressure of the solution at 20 °C is :*

(*a*) *1.203 atm* (*b*) *1.203 mm*
(*c*) *1.203 cm* (*d*) *20 atm.*

SOLUTION. Wt. of solute, sucrose $C_{12}H_{22}O_{11} = W_2$ = 17.1 g ; volume of solution = $1000 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1 \text{ L}$; R = 0.0821 L atm K^{-} mol^{-} ; T = 20 + 273 = 293 K ; mol. wt. of $C_{12}H_{22}O_{11}$ = (12 × 12) + (22 × 1) + (11 × 16) = 342 g mol^{-}.

Osmotic pressure,

$$\pi = \frac{W_2}{M_2 V} \times RT$$

$$= \frac{17.1 \text{ g} \times 0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 293 \text{ K}}{342 \text{ g mol}^{-} \times 1 \text{ L}}$$

$$\therefore \qquad \pi = 1.203 \text{ atm}.$$

So, the correct answer is (*a*).

EXAMPLE 152. *A 0.0020 m aqueous solution of an ionic compound [Co (NH$_3$)$_5$ (NO)] Cl freezes at – 0.00732 °C. Number of moles of ions which one mole of ionic compound produces on being dissolved in water will be :*

(*a*) *3* (*b*) *4*
(*c*) *1* (*d*) *2; K_f = –1.86°C/m*

(CBSE-PMT, 2009)

SOLUTION. Number of moles of ions produced by 1 mol of ionic compound = *i*.

But :

$$\Delta T_f = i \times K_f \times m$$

$$\text{or} \qquad 0.00732 = i \times 1.86 \times 0.002\,;$$

$$i = \frac{0.00732}{1.86 \times 0.002} = 1.96 \simeq 2.$$

So, the correct answer is (*d*).

EXAMPLE 153. *1.02% solution of glycerine and 2% solution of glucose are isotonic. If molecular weight of glucose is 180, then find the molecular weight of glycerine.*

(AIPMT, 2009, Kerala PET, 2011)

SOLUTION. Since solutions are isotonic, their osmotic pressure, π and concentration, *C* will be same. Hence :

$$\pi_{\text{glycerine}} = \pi_{\text{glucose}}\,;$$

volume, *V* of solution

$$= 100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.1 \text{ L}.$$

Thus

$$\pi_{\text{glycerine}} = \frac{W_2}{M_2 V} RT = \frac{1.02 \text{ g}}{M_2 \times 0.1 \text{ L}} \times RT \qquad \text{...(1)}$$

$$\pi_{\text{glucose}} = \frac{W_2}{M_2 V} \times RT$$

$$= \frac{2 \text{ g}}{180 \text{ g mol}^{-} \times 0.1 \text{ L}} \times RT \qquad \text{...(2)}$$

For isotonic solution, equation (1) = equation (2). Thus

$$\frac{1.02\, g}{M_2 \times 0.1\, L} \times RT = \frac{2g \times RT}{180\, g \text{ mol}^{-} \times 0.1\, L}\,;$$

$$M_2 = \frac{1.02\, g \times 180\, g \text{ mol}^{-}}{2\, g} = 91.8\, g \text{ mol}^{-}$$

EXAMPLE 154. *The number of equivalents in 250 mL of* $\frac{N}{20}$ H_2SO_4 *are*

(*a*) *1.25* (*b*) *0.125* (*c*) *12.5* (*d*) *0.0125*

SOLUTION.

$$\text{Volume} = 250 \text{ mL} = \frac{250}{1000} = 0.25 \text{ L} ;$$

$$\text{Normality} = \frac{1}{20}$$

No. of equivalents

$$= \text{Normality} \times \text{Volume in litre}$$

$$= \frac{1}{20} \times 0.25 = 0.0125.$$

So, the correct answer is (*d*).

EXAMPLE 155. *The number of equivalents in 125 milliequivalents of* HNO_3 *are :*

(*a*) *125* (*b*) *12.5*
(*c*) 1.25 (*d*) *0.125*

SOLUTION. The number of equivalents

$$= \frac{\text{no. of milliequivalents}}{1000}$$

$$= \frac{125}{1000} = 0.125.$$

So, the correct answer is (*d*).

EXAMPLE 156. *Number of millilitre of 0.25 M* H_2SO_4 *required to dissolve 2.1 g magnesium carbonate (at. wt., Mg = 24, C = 12, O = 16) is :*

(*a*) *200 mL* (*b*) *100 mL*
(*c*) *50 mL* (*d*) *20.0 mL*

SOLUTION. 1000 mL of 1 M H_2SO_4 react with Mg CO_3 = g. mol. wt. of Mg CO_3 = 84 g

∴ *x* mL of 0.25 M H_2SO_4 react with

$$\text{Mg CO}_3 = \frac{84}{1000} \times x \times 0.25 \text{ g Mg CO}_3$$

$$\text{So : } \frac{84 \times x \times 0.25}{1000} = 2.1 \text{ g Mg CO}_3 \text{ (given).}$$

Or $x = 100$ mL.

So, the correct answer is (*b*).

EXAMPLE 157. *A corked soda-water bottle contains* CO_2 *gas at 3.8 atm pressure at 273 K. The bottle was opened and the air entered the bottle. The air and* CO_2 *at equilibrium had the pressure of* 3.5×10^{-4} *atm at 298 K. The concentration of* CO_2 *in corked bottle as well as in the open bottle at equilibrium are in mol* L^{-}*;*

(*a*) *0.1, 0.2* (*b*) *0.2, 0.3*
(*c*) *0.3, 0.4* (*d*) *0.2926,* 1.12×10^{-5}

The Henry's constants for aqueous solution of CO_2 *are :*

At 273 K = 7.7×10^{-2} *mol* L^{-} *atm*$^{-}$*; at 298 K =* 3.2×10^{-2} *mol* L^{-} *atm*$^{-}$.

SOLUTION. According to Henry's law, $C = kp$ where C is the concentration of gas in solution. k is Henry's constant and p is partial pressure of gas.

(*i*) For corked bottle,

$$C = kp; C = 7.7 \times 10^{-2} \text{ mol L}^{-} \text{atm}^{-} \times 3.8 \text{ atm}$$

∴ $C =$ **0.2926 mol L⁻** **Ans.**

(*ii*) For opened bottle,

$$C = kp; C = 3.2 \times 10^{-2} \text{ mol L}^{-} \text{atm}^{-} \times 3.5 \times 10^{-4} \text{ atm}$$

∴ $C = \mathbf{1.12 \times 10^{-5} \text{ mol L}^{-}}$ **Ans.**

So, the correct answer is (*d*).

EXAMPLE 158. *A solution is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9. Given vapour pressure of pure water and vapour pressure of pure ethanol are 32.8 mm Hg and 40 mm Hg respectively. The vapour pressure of solution M is :*

(*a*) *39.3 mm Hg* (*b*) *36.0 mm Hg*
(*c*) *29.5 mm Hg* (*d*) *28.8 mm Hg*

Vapour pressure of pure ethanol is 40 mm Hg.

(IIT–JEE, 2008)

SOLUTION. Let

$P =$ total vapour pressure.

Thus : $P = P_A^0 x_A = 40 \text{ mm} \times 0.9 = 36.0 \text{ mm Hg}$

Here, solute is non-volatile and vapour pressure of pure ethanol is 40 mm of Hg.

So, the correct answer is (*b*).

EXAMPLE 159. *The boiling point of an aqueous solution containing 10 g of urea (molar mass = 60) in 250 g of water* (L_v *= 539 cal g*$^{-}$*), will be :*

(*a*) *373.34 K* (*b*) *350.17 °C*
(*c*) *273 °C* (*d*) *274 K*

SOLUTION. We know $K_b = \frac{R\left(T_b^o\right)^2}{1000 \, L_v}$; $R = 2$ cal K^{-} mol^{-} ;

$T_b^o = 100 + 273 = 373$ *K*; wt. of solute, $W_2 = 10$ g ; wt. of solvent, $W_1 = 250/1000$ or 0.25 kg ; $\Delta T_b = ?$; $1000 \, L_v = 1000 \times 539$ cal kg^{-}. Thus :

$$K_b = \frac{2 \text{ cal K}^{-} \text{ mol}^{-} \times 373 \text{ K} \times 373 \text{ K}}{1000 \text{ g kg}^{-} \times 539 \text{ cal g}^{-}}$$

$$= 0.516 \, K \text{ kg mol}^{-}.$$

Also ; $$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$= \frac{0.516 \text{ K kg mol}^{-} \times 10 \text{ g}}{60 \text{ g mol}^{-} \times 0.25 \text{ kg}} = 0.34 \, K$$

∴ *B.pt.* = 373 + 0.34 *K* = **373.34 *K*.**

So the correct answer is (*a*).

EXAMPLE 160. *18 g of glucose $C_6H_{12}O_6$ (molar mass 180 g mol^-) is dissolved in 1 kg of water in a sauce pan. The temperature at which water will boil (1.013 bar pressure). (K_b for water = 0.52 K kg mol^-), will be :*

(*a*) *200.202 K* (*b*) *373.052 K*
(*c*) *373.202 K* (*d*) *100°C*

SOLUTION. Wt. of solute, W_2 = 18 g ; wt. of solvent, W_1 = 1 kg ; mol. wt. = 180 g mol^-; K_b = 0.52 K kg mol^-. We know that :

$$\Delta T_b = \frac{K_b \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}$$

$$= \frac{0.52 \text{ K kg mol}^- \times 18 \text{ g}}{180 \text{ g mol}^- \times 1 \text{ kg}} = 0.052\,K$$

$\therefore$ B.pt. = 373 K + 0.052 K = **373.052 *K*.**

So, the correct answer is (*b*).

EXAMPLE 161. *The boiling point of pure water is 373 K. Calculate the b.pt. of an aqueous solution containing 18 g of glucose (Mol. wt. = 180) in 100 g of water. Molal elevation constant of water is 0.52 K kg/mole.* **(ISC, 2009)**

SOLUTION. Mass of the solvent, W_A = 100 g ; mass of solute, W_B = 18 g. Molar mass of solute,

M_B = 180. Hence :

$$\text{Molality,} \quad m = \frac{W_B \times 1000}{M_B \times W_A} = \frac{18 \times 1000}{180 \times 100} = 1$$

$\Delta T_b = K_b \times m$; $\Delta T_b = 0.52 \times 1 = 0.52$ K.

B.pt. of solution = 373 + 0.52 = 373.52 K **Ans.**

EXAMPLE 162. *10 g of glucose are dissolved in 150 g of water. The mass percentage of glucose is :*

(*a*) *2.25 %* (*b*) *6.25 %*
(*c*) *7.50 %* (*d*) *2.22 %*

SOLUTION. Mass of glucose = 10 g ;

Mass of water = 150 g

$\therefore$ Total mass of glucose solution

= 10 + 150 = 160 g.

$$\text{Mass percent} = \frac{\text{Mass of glucose}}{\text{Mass of glucose solution}} \times 100$$

$$= \frac{10}{160} = 6.25\ \%$$

So, the correct answer is (*b*).

EXAMPLE 163. *The number of moles of H_2SO_4 in which mole fraction of water is 0.85 are:*

(*a*) *8.9* (*b*) *9.8*
(*c*) *8* (*d*) 9

SOLUTION. Mole fraction, x_1 of H_2O = 0.85

Mole fraction, x_2 of H_2SO_4 = 1 – 0.85 = 0.15

no. of moles of H_2O,

$$n_1 = \frac{1000}{\text{g. mol. wt. of } H_2O} = \frac{1000}{18}$$

= 55.55 mol.

no. of moles of

H_2SO_4, n_2 = ?

$$\text{But} \quad x_2 = \frac{n_2}{n_1 + n_2}.$$

Substituting the values, we get :

$$0.15 = \frac{n_2}{55.55 + n_2}.$$

$0.15\,(55.55 + n_2) = n_2$

$8.3325 + 0.15\,n_2 = n_2$ **Or** $n_2 - 0.15\,n_2 = 8.3325$

$0.85\,n_2 = 8.3325;$

$$\therefore \quad n_2 = \frac{8.3325}{0.85} = 9.8$$

So, the correct answer is (*b*).

EXAMPLE 164. *Ethylene chloride (V.P. = 236 mm) and benzene (V.P. = 268 mm) form ideal solution. The total pressure created by dissolving 3 mol of ethylene chloride and 2 mol of benzene will be :*

(*a*) *250 mm* (*b*) *249.8 mm*
(*c*) *361 mm* (*d*) *248.8 mm*

SOLUTION. V.P. of ethylene chloride = 236 mm ; no. of moles of ethylene chloride = 3 ; V.P. of benzene = 268 mm ; no. of mol of benzene = 2.

Total no. of mol of ethylene chloride and benzene

= 3 + 2 = 5

Pressure created by ethylene chloride

$$= \frac{3}{5} \times 236 = 141.6 \text{ mm}$$

Pressure created by benzene

$$= \frac{2}{5} \times 268 = 107.2 \text{ mm}$$

$\therefore$ Total pressure = 141.6 mm + 107.2 mm = **248.8 mm.**

So, the correct answer is (*d*).

EXAMPLE 165. *Which has minimum osmotic pressure ?*

(*a*) *200 mL of 2 M NaCl solution*
(*b*) *200 mL of 1 M glucose solution*
(*c*) *200 mL of 2 M Urea solution*
(*d*) *All have same* **(DCE, 2005)**

SOLUTION. Osmotic pressure is a colligative property. So, it depends upon the number of particles.

(*a*) $NaCl \rightleftharpoons Na^+ + Cl^-$ is an ionic compound and gives two particles. So, its osmotic pressure will be high.

(*b*) Concentration of particles is less in non - ionisable glucose than that in 2 M urea solution. So, 1 M glucose solution has minimum osmotic pressure. Hence the correct answer is (*b*).

EXAMPLE 166. *Solution A contains 7 g /L of $MgCl_2$ and solution B contains 7 g/L of NaCl. At room temperature, the osmotic pressure of*

(*a*) *Solution A is greater than B*
(*b*) *Both have same osmotic pressure*
(*c*) *Solution B is greater than A*
(*d*) *Cannot determine.* **(DCE, 2005)**

SOLUTION. $MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$ *i.e.,* $1 + 2 = 3$ particles

$NaCl \rightleftharpoons Na^+ + Cl^-$ *i.e.,* $1 + 1 = 2$ particles.

Osmotic pressure is a colligative property which depends upon the number of particles. The number of particles in $MgCl_2$ being more than that in NaCl, $MgCl_2$ solution will have higher osmotic pressure.

So, the correct answer is (*a*).

EXAMPLE 167. *The van't Hoff factor for $BaCl_2$ at 0.01 M concentration is 1.98. The percentage of dissociation of $BaCl_2$ at this concentration is :*

(*a*) 49 (*b*) 69 (*c*) 89 (*d*) 98 (*e*) 100 **(Kerala PET, 2005)**

SOLUTION.	$BaCl_2$	$\rightleftharpoons$	Ba^{2+}	$+ 2\,Cl^-$
Initial conc.	1		0	0
Conc. after dissociation	$1 - \alpha$		α	$2\,\alpha$

Total no. of mol $= 1 - \alpha + \alpha + 2\alpha = 1 + 2\alpha$

Hence van't Hoff factor

$$i = 1 + 2\,\alpha \quad \text{or} \quad \alpha = \frac{i-1}{2}$$

$$\therefore \quad \alpha = \frac{1.98 - 1}{2} = \frac{0.98}{2} = 0.49$$

$\therefore$ % age dissociation at 0.01 M concentration $= \dfrac{0.49}{0.01}$ $=$ **49**. So, the correct answer is (*a*).

EXAMPLE 168. *Two solutions of a substance (non - electrolyte) are mixed in the following manner. 480 mL of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final solution ?*

(*a*) *1.20 M* (*b*) *1.50 M*
(*c*) *1.344 M* (*d*) *2.70 M* **(AIEEE, 2005)**

SOLUTION. Total milli mol of non - electrolyte solute

$$= M_1 V_1 + M_2 V_2 \quad i.e., \quad (1.5 \times 480) + (1.2 \times 520) = 720 + 624 = 1344$$

Total volume = 480 mL + 520 mL = 1000 mL

$\therefore$ Molarity of final solution

$$= \frac{\text{Milli mol of solute}}{\text{Total volume in mL}}$$

$$= \frac{1344}{1000} = \mathbf{1.344\ M.}$$

So, the correct answer is (*c*).

EXAMPLE 169. *If α is the degree of dissociation of Na_2SO_4, the van't Hoff's factor (i) used for calculating the molecular mass is :*

(*a*) $1 + \alpha$ (*b*) $1 - \alpha$
(*c*) $1 + 2\,\alpha$ (*d*) $1 - 2\,\alpha$. **(AIEEE, 2005)**

SOLUTION.	Na_2SO_4	$\rightleftharpoons$	$2\,Na^+$	$+ SO_4^{2-}$
Initial mol	1		0	0
Mol after dissociation	$1 - \alpha$		2α	α

van't Hoff's factor,

$$i = \frac{\text{Total no. of mol after dissociation}}{\text{Total no. of mol before dissociation}}$$

$$= \frac{1 - \alpha + 2\alpha + \alpha}{1} = 1 + 2\,\alpha.$$

So, the correct answer is (*c*).

EXAMPLE 170. *The degree of dissociation (α) of a weak electrolyte $A_x B_y$ is related to van't Hoff factor (i) by the expression*

(*a*) $\alpha = \dfrac{i-1}{x+y-1}$ (*b*) $\alpha = \dfrac{i-1}{x+y+1}$

(*c*) $\alpha = \dfrac{x+y-1}{i-1}$ (*d*) $\alpha = \dfrac{x+y+1}{i-1}$

(AIEEE, 2011)

SOLUTION. $A_x B_y$ compound ionises as:

$$\begin{array}{ccc} A_x B_y & \rightleftharpoons & xA^{y+} + yB^{x-} \\ 1-\alpha & & x\alpha \quad\quad y\alpha \end{array}$$

(α = degree of dissociation)

$$\therefore \quad i = 1 - \alpha + x\,\alpha + y\,\alpha = 1 + \alpha(x + y - 1)$$

$$\therefore \quad \alpha = \frac{i-1}{x+y-1}.$$

So, the correct answer is (*a*).

EXAMPLE 171. *Benzene and toluene form nearly ideal solutions. At 20 °C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20 °C for a solution containing 78 g of benzene and 46 g of toluene in torr is :*

(*a*) *50* (*b*) *25*
(*c*) *37.5* (*d*) *53.5* **(AIEEE, 2005)**

SOLUTION. Mol. wt. of benzene,

$$C_6H_6 = (6 \times 12) + (6 \times 1) = 78$$

Mol. wt. of toluene,

$$C_6H_5CH_3 = (6 \times 12) + (5 \times 1) + (12 \times 1) + (3 \times 1) = 92$$

V.P. of benzene, P_B in solution = V.P. of pure benzene (P_B^o) × mol fraction of benzene (x_B)

$$= 75 \times \frac{\text{no. of mol of benzene}}{\text{no. of mol of benzene + no. of mol of toluene}}$$

$$= 75 \times \frac{\dfrac{\text{wt. of benzene}}{\text{mol. wt. of benzene}}}{\dfrac{\text{wt. of benzene}}{\text{mol. wt. of benzene}} + \dfrac{\text{wt. of toluene}}{\text{mol. wt. of toluene}}}$$

$$= 75 \times \frac{\dfrac{78}{78}}{\dfrac{78}{78} + \dfrac{46}{92}} = 75 \times \frac{1}{1 + \dfrac{1}{2}} = 75 \times \frac{2}{3} = \mathbf{50\ torr.}$$

$$\therefore \quad P_B = 50 \text{ torr.}$$

So, the correct answer is (*a*).

EXAMPLE 172. *Calculate the freezing point depression expected for 0.0711 m aqueous solution of Na_2SO_4. If this solution* *actually freezes at –0.320 °C, what would be the value of van't Hoff factor ? (k_f for water is 1.86°C mol^-).* **(CBSE, 2009)**

SOLUTION. Given, $m = 0.0711$, $\Delta T_f = 0.320°C$, $k_f = 1.86°C\ mol^-$; van't Hoff factor, i = ? We know that :

$$\Delta T_f = i\, k_f \times m\ ;$$

So, $$i = \frac{\Delta T_f}{k_f m} = \frac{0.320}{1.86 \times 0.0711} = 2.4 \quad \textbf{Ans.}$$

EXAMPLE 173. *One atom of an element weighs 3.819×10^{-23} g. The number of gram atoms in 46 kg of it will be :*

(*a*) *500 g atom* (*b*) *1000 g atom*

(*c*) *2000 g atom* (*d*) *3000 g atom*

SOLUTION. Wt. of 1 atom of element

$$= 3.819 \times 10^{-23}\ g$$

∴ Wt. of Avogadro's number of atoms ($= 6.023 \times 10^{23}$)

$$= 3.819 \times 10^{-23} g \times 6.023 \times 10^{23} = 23\ g$$

$$\therefore \quad 23\ g = \text{wt. of one gram atom.}$$

$$\textbf{Or} \quad 46 \times 1000\ g = \frac{1}{23} \times 46 \times 1000\ g$$

$$= \textbf{2000 g atom}\ [\because 46\ kg = 46 \times 1000\ g]$$

So, true answer is (*c*).

EXAMPLE 174. *The millilitre of 0.4M H_2SO_4 used to dissolve 1.2 g of $CuCO_3$ will be :*

(*a*) *2.01* (*b*) *4.001*

(*c*) *28.1* (*d*) *24.3*

SOLUTION. Reaction : $CuCO_3 + H_2SO_4$

$$= CuSO_4 + CO_2 + H_2O$$

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-};\ n = 2$$

In $CuCO_3$, '*n*' factor is 2 as $CuCO_3 \equiv H_2SO_4$

$$\text{Eq. of}\quad H_2SO_4 = \frac{\text{Vol. in mL} \times \text{molarity} \times n}{1000}$$

$$= \frac{V \times 0.4 \times 2}{1000}$$

$$\text{Eq. of}\quad CuCO_3 = \frac{\text{Wt.}}{\text{Eq. wt}} = \frac{1.2 \times 2}{123.5}$$

$$\left[\begin{aligned} \because \text{Eq. wt. of } CuCO_3 &= \frac{\text{Mol. wt.}}{2} \\ = \frac{63.5 + 12 + (3 \times 16)}{2} &= \frac{123.5}{2} \end{aligned}\right]$$

Since Eq. of

$$H_2SO_4 = \text{Eq. of } CuCO_3\text{, we have :}$$

$$\frac{V \times 0.4 \times 2}{1000} = \frac{1.2 \times 2}{123.5}\ ;$$

$$\therefore \quad V = \frac{1.2 \times 2}{123.5} \times \frac{1000}{0.4 \times 2} = \textbf{24.3}$$

So, the true answer is (*d*).

EXAMPLE 175. *Equal volumes of 1 M each of $K_2Cr_2O_7$ and $KMnO_4$ are used to oxidise Fe^{2+} ions of Mohr's salt solution in dil. H_2SO_4 medium. The amount of Fe^{2+} oxidised will be :*

(*a*) *Less with $K_2Cr_2O_7$* (*b*) *More with $K_2Cr_2O_7$*

(*c*) *More with $KMnO_4$* (*d*) *Not possible to estimate.*

SOLUTION. Reduction of $K_2Cr_2O_7$ and $KMnO_4$ involves the following electron changes represented by the factor, *n*.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ;\ n = 5$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O\ ;\ n = 6$$

Since $n = 6$ is greater than $n = 5$, so $K_2Cr_2O_7$ will have greater oxidising power than $KMnO_4$.

So, the true answer is (*b*).

EXAMPLE 176. *The number of oxalic acid molecules in 250 cm^3 of 0.02 N oxalic acid will be :*

(*a*) *2.5×10^{22}* (*b*) *3.0×10^{23}*

(*c*) *2.1×10^{20}* (*d*) *1.5×10^{21}*

SOLUTION. Oxalic acid $H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-}$, the valence factor *i.e.*, basicity of acid is 2.

Mol. wt. of

$$H_2C_2O_4 = (2 \times 1) + (2 \times 12) + (4 \times 16)$$

$$= 2 + 24 + 64 = 90$$

$$\text{But}\quad \text{molarity} = \frac{\text{Normality}}{\text{Valence factor}} = \frac{0.02}{2} = 0.01$$

∴ No. of millimoles

$$= \text{molarity} \times \text{Vol in } cm^3$$

$$= 0.01 \times 250 = 2.5$$

$$\text{No. of moles} = \frac{2.5}{1000} = \textbf{0.0025}$$

∴ No. of oxalic acid molecules

$$= 0.0025 \times 6.023 \times 10^{23}$$

$$[\because 1\ \text{mol} = 6.023 \times 10^{23}]$$

$$= 1.5 \times 10^{21}$$

So, the true answer is (*d*).

EXAMPLE 177. *An eight grams of a mixture of potassium nitrate and calcium nitrate solution was treated with Na_2CO_3 solution. Calcium carbonate got precipitated. These precipitate on heating yielded 1.5 g of CaO. The percent by mass of calcium nitrate in the original mixture will be :*

(*a*) *371.7* (*b*) *37.16*

(*c*) *5.491* (*d*) 54.91

(At. wt. Ca = 40, O = 16, N = 14)

SOLUTION. Mol. wt. of CaO = 40 + 16 = 56 ; mol. wt. of $Ca(NO_3)_2 = 40 + 2[14 + (3 \times 16)] = 40 + 124 = 164$; wt. of mixture = 8.0 g

$$\underset{1\ \text{mol}}{Ca(NO_3)_2} + Na_2CO_3 \longrightarrow \underset{1\ \text{mol}}{CaCO_3} + 2NaNO_3$$

$$\underset{1\ \text{mol}}{CaCO_3} \xrightarrow{\Delta} \underset{1\ \text{mol}}{CaO} + CO_2$$

(*a*) Moles of

$$CaO = \frac{\text{Wt. of CaO}}{\text{Mol. wt. of CaO}} = \frac{1.5}{56}$$

Moles of

$$Ca(NO_3)_2 = \text{Moles of CaO} = \frac{1.5}{56}$$

∴ Mass of

$$Ca(NO_3)_2 = \text{no. of moles} \times \text{Mol. wt.}$$

$$= \frac{1.5}{56} \times 164$$

(*b*) % age by mass of

$$Ca(NO_3)_2 = \frac{\text{Wt.}}{\text{Total wt. of mixture}} \times 100$$

$$= \frac{1.5 \times 164 \times 100}{56 \times 8}$$

$$= \mathbf{54.91}$$

So, the true answer is (*d*).

Example 178. *When 0.3 moles of $(NH_4)_3\,PO_4$ are mixed with 0.65 mol of $Ba(NO_3)_2$ and treated with water, the precipitate of $Ba_3\,(PO_4)_2$ formed will be :*

(*a*) *1 mol* (*b*) *2.1 mol*

(*c*) *0.15 mol* (*d*) *15 mol*

Solution. Reaction.

$$3\,Ba\,(NO_3)_2 + 2\,(NH_4)_3\,PO_4 \longrightarrow Ba_3\,(PO_4)_2\downarrow + 6\,NH_4\,NO_3$$

3 mol 2 mol 1 mol

Given. Moles of $(NH_4)_3\,PO_4 = 2$; moles of $Ba\,(NO_3)_2 = 3$

(*a*) 2 mol $(NH_4)_3\,PO_4 \equiv$ 3 moles $Ba\,(NO_3)_2$

$$0.3 \text{ mol } (NH_4)_3\,PO_4 \equiv \frac{3}{2} \times 0.3 = \frac{0.9}{2} = 0.45$$

Since the number of moles of $(NH_4)_3\,PO_4$ (= 0.45) is less than that of $Ba\,(NO_3)_2$ (= 0.65), so, $(NH_4)_3\,PO_4$ is a limiting reagent.

(*b*) 2 mol $(NH_4)\,PO_4$ form

$$Ba_3\,(PO_4)_2 = 1 \text{ mol}$$

0.3 mol $(NH_4)_3\,PO_4$ form

$$Ba_3\,(PO_4)_2 = \frac{1}{2} \times 0.3 = \mathbf{0.15\ mol}$$

So, the correct answer is (*c*).

Example 179. *25 mL of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a titre value of 35 mL. The molarity of $Ba(OH)_2$ solution was :*

(*a*) *0.35* (*b*) *0.07*

(*c*) *0.14* (*d*) *0.28* **(AIEEE, 2003)**

Solution. $Ba(OH)_2$ ionises as :

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2\,OH^-$$

$$HCl \rightleftharpoons H^+ + Cl^-] \times 2$$

$$Ba(OH)_2 + 2HCl \longrightarrow BaCl_2 + 2H_2O \quad ...(1)$$

Volume (V_2) of $Ba(OH)_2$ = 25 mL ; Molarity (M_2) of $Ba(OH)_2$ = ?

Volume (V_1) of HCl = 35 mL ; molarity (M_1) of HCl = 0.1 M

From relation (1), we know that

$$\frac{M_1\,V_1\,(HCl)}{M_2\,V_2\,[Ba\,(OH)_2]} = \frac{2}{1};\ \frac{M_1\,V_1\,(HCl)}{\text{no. of mol of HCl}}$$

$$= \frac{M_2\,V_2\,[Ba\,(OH)_2]}{\text{no. of mol of }Ba\,(OH)_2}$$

Substituting the values, we get :

$$\frac{0.1 \times 35}{2} = \frac{M_2 \times 25}{1}$$

Or $$M_2 = \frac{0.1 \times 35}{2 \times 25} \quad \therefore M_2 = \mathbf{0.07}$$

So, the correct answer is (*b*).

Example 180. *200 mL of an aqueous solution of a protein contains its 1.26 g. The osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. The molar mass of protein will be: (R = 0.083 L bar mol^{-} K^{-})*

(*a*) *51022 g mol^{-}* (*b*) *122044 g mol^{-}*

(*c*) *31011 g mol^{-}* (*d*) *61038 g mol^{-}* **(AIMPT, 2011)**

Solution. Osmotic pressure (π) of a solution is given as :

$$\pi V = n\,RT$$

where $$n = \text{wt}\,(w)/\text{mol. wt. (M)}.$$

So, $$\pi V = \frac{wRT}{M}$$

$$\therefore \quad M = \frac{wRT}{\pi V} = \frac{1.26 \times 0.083 \times 300}{2.57 \times 10^{-3} \times 200/1000}$$

$$= 61038 \text{ g mol}^{-}$$

so, the correct answer is (*d*).

Example 181. *A 0.01 molar solution of KI is found to be isotonic with 0.019 molar solution of urea. The apparent degree of ionisation of KI will be :*

(*a*) *70 %* (*b*) *80 %*

(*c*) *90 %* (*d*) *45 %*

Solution. (*i*) Theoretical osmotic pressure (π_{Th}) of 0.01 M KI solution = CRT = 0.01 RT

Let

α = degree of ionisation of K I (electrolyte).

	$KI \rightleftharpoons$	K^+	$+ I^-$
Initial conc. (mol)	1	0	0
Conc. after ionisation	$1-\alpha$	α	α

Total no. of

$$\text{mol} = 1 - \alpha + \alpha + \alpha = 1 + \alpha.$$

∴ Observed osmotic pressure

$$(\pi_{obs}) = \pi_{Th} \times (1 + \alpha) = 0.01\ RT\,(1 + \alpha) \quad ... (1)$$

Osmotic pressure of urea (non – electrolyte)

$$= CRT = 0.019\ RT \quad ... (2)$$

Since two solutions are isotonic, hence from (1) and (2), we get :

$$0.01\ RT\,(1 + \alpha) = 0.019\ RT$$

$$\therefore \qquad 1 + \alpha = \frac{0.019}{0.01} = 1.9\ ;$$

$$\alpha = 1.9 - 1 = 0.9 \text{ or } 0.9 \times 100 = 90\ \%$$

So, the correct answer is (*c*).

EXAMPLE 182. *A solution of mercuric cyanide containing 3 g L⁻ has an osmotic pressure of 232 mm at 25°C. The apparent molar mass and the degree of dissociation of mercuric cyanide is :*

(*a*) *120, 1.5 %* (*b*) *239.98, 2.63 %*

(*c*) *339.98, 26.3 %* (*d*) *147, 47 %*

(at. wt., Hg = 200.6, C = 12, N = 14)

SOLUTION. Wt. of $Hg(CN)_2 = 3\ g\ L^-$.

Mol. wt. of

$$\begin{aligned} Hg(CN)_2 &= 200.6 + 2\,(12 + 14) \\ &= 200.6 + 24 + 28 \\ &= 252.6\ g\ mol^- \\ T &= 25 + 273 = 298\ K\ ; \\ \pi_{obs} &= 232\ mm \times \frac{1\ atm}{760\ mm} = \frac{232}{760}\ atm. \end{aligned}$$

Theoretical osmotic pressure,

$$\begin{aligned} \pi_{Th} &= \frac{WRT}{M} \\ &= \frac{3\ g\ L^- \times 0.0821\ L\ atm\ K^-\ mol^- \times 298\ K}{252.6\ g\ mol^-} \\ &= 0.29\ atm. \end{aligned}$$

We know :	$Hg(CN)_2 \rightleftharpoons$	Hg^{2+}	$+2\,CN^-$
Initial conc. (mol)	1	0	0
Conc. after dissociation	$1 - \alpha$	α	2α

($\because$ α = degree of dissociation)

Total number of

$$\text{mol} = 1 - \alpha + \alpha + 2\alpha = 1 + 2\,\alpha$$

But Van't Hoff factor,

$$i = \frac{\pi_{obs}}{\pi_{Th}} = (1 + 2\,\alpha)$$

$$\text{or} \qquad 1 + 2\,\alpha = \frac{232}{760}\,atm \times \frac{1}{0.29\ atm} = 1.0526$$

$$\therefore \qquad 2\,\alpha = 1.0526 - 1 = 0.0526;$$

$$\alpha = \frac{0.0526}{2} = 0.0263$$

(*i*) $\therefore$ Degree of dissociation

$$= 0.0263 \ \textbf{ Or } \ 0.0263 \times 100 = 2.63\%.$$

(*ii*) Observed molar mass

$$= \frac{\text{Theoretical molar mass}}{1 + 2\,\alpha}$$

$$= \frac{252.6}{1 + (2 \times 0.0263)} = \frac{252.6}{1.0526} = \mathbf{239.98}$$

So, the correct answer is (*b*).

EXAMPLE 183. *0.1 molar solution of phenol in water exhibits an osmotic pressure of 1.88 atm. at 27 °C. The degree of association of phenol in water, if it is assumed that phenol forms a double molecule in water is :*

(*a*) *23.67%* (*b*) *11.84 %*

(*c*) *47.34 %* (*d*) *94.68%*

SOLUTION. Concentration, $C = 0.1\ g\ L^-$, $R = 0.0821\ L\ atm\ K^-\ mol^-$, $T = 27 + 273 = 300\ K$. $\pi_{obs} = 1.88\ atm.$; α = degree of association :

	$C_6H_5OH \rightleftharpoons$	$\frac{1}{2}(C_6H_5OH)_2$
Initial conc. (mol)	1	0
Conc. after association	$1 - \alpha$	$\frac{\alpha}{2}$

$$\text{Total no. of mol} = 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

Theoretical osmotic pressure,

$$\begin{aligned} \pi_{Th} &= CRT \\ &= 0.1\ mol\ L^- \times 0.0821\ L\ atm\ K^-\ mol^- \times 300\ K \\ &= 2.463\ atm. \end{aligned}$$

But van't Hoff factor,

$$i = \frac{\pi_{obs}}{\pi_{Th}} = 1 - \frac{\alpha}{2}$$

$$\therefore \qquad 1 - \frac{\alpha}{2} = \frac{1.88\ atm}{2.463\ atm} = 0.7633\ ;$$

$$\frac{\alpha}{2} = 1 - 0.7633 = 0.2367$$

$$\therefore \qquad \alpha = 2 \times 0.2367 = 0.4734$$

$$\text{or} \quad 0.4734 \times 100 = 47.34\ \%$$

So, the correct answer is (*c*).

EXAMPLE 184. *A 0.1 molal aqueous solution of a weak acid is 30 % ionised. If K_f for water is 1.86 °C/m, the freezing point of the solution will be :*

(*a*) *–0.180°C* (*b*) *–0.54°C*

(*c*) *–0.36°C* (*d*) *–0.24°C* **(AIPMT, 2011)**

SOLUTION. Molality, $m = 0.1$; vant Hoff's factor, i for a weak acid = $1 + \alpha$ where α = degree of dissociation = 30 % = 30/100 = 0.3. But $i = 1 + \alpha$. So, $i = 1 + 0.3 = 1.3$. Thus :

$$\Delta T_f = i\,K_f \times m = 1.3 \times 1.86 \times 0.1 = 0.24°C.$$

$\therefore$ Freezing point = 0 – 0.24°C = – 0.24°C. Hence, the correct answer is (*d*).

EXAMPLE 185. *2.0 g of benzoic acid in 25 g of benzene shows a freezing point depression of 1.62 °C. Molar depression constant of benzene = 4.9 °C kg mol⁻. The information derived about the molecular state of the acid in solution is :*

(*a*) *Dimer* (*b*) *Trimer*

(*c*) *Tetramer* (*d*) *None of these*

SOLUTION. $K_f = 4.9\ °C\ kg\ mol^-$,

wt. of solute, $W_2 = 2.0g$;

wt. of solvent,

$$W_1 = 25\text{ g} = \frac{25}{1000}\text{ kg}\ ;\ \Delta T = 1.62\ °\text{C}$$

Theoretical mol. wt. of benzoic acid,

$$C_6H_5COOH = (6 \times 12) + (5 \times 1) + 12 + 16 + 16 + 1$$

$$= 122\text{ g mol}^{-}$$

Observed mol. wt. of benzoic acid, M_{obs}

$$= \frac{K_f \times W_2}{W_1 \text{ in kg} \times \Delta T}$$

$$= \frac{1000 \times 4.9\ °\text{C kg mol}^{-} \times 2.0\text{ g}}{25\text{ kg} \times 1.62\ °\text{C}}$$

$$= 241.97\text{ g mol}^{-}$$

∴ Van't Hoff factor,

$$i = \frac{M_{Th}}{M_{obs}} = \frac{122}{241.97}$$

$$\simeq \frac{\mathbf{1}}{2}\ \ \textit{i.e.,}\ \mathbf{M_{obs} = 2 \times M_{Th}}.$$

So, the acid exists as dimer.

So, the correct answer is (*a*).

Example 186. *100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25°C, what is the molar mass of the protein ? (R = 0.0821 L atm mol⁻ K⁻ and 760 mm Hg = 1 atm.)*

(CBSE, 2009)

Solution. Wt., w = 100 mg = 100/1000 = 0.1 g; volume, V = 10.0 mL = 10/1000 L = 0.01 L, osmotic pressure, π = 13.3 mm Hg = 13.3/760 atm.

$$T = 25 + 273 = 298\text{ K},$$

$$R = 0.0821\text{ L atm K}^{-}\text{ mol}^{-}\ ;$$

Mol. wt., M = ?

We know that, molar mass,

$$M = wRT/\pi V.$$

Hence

$$M = \frac{0.1\text{ g} \times 0.0821\text{ L atm } K^{-}\text{ mol}^{-} \times 298\text{ K} \times 760}{13.3\text{ atm} \times 0.01\text{ L}}$$

$$= 13980.4\text{ g mol}^{-}.$$

Example 187. *Normality of sulphuric acid containing 50 g of the acid in 500 mL of solution is (at. masses, H = 1, S = 32, O = 16 a.m.u.)*

(*a*) *2.04 N* (*b*) *0.49 N*

(*c*) *0.98 N* (*d*) *0.35 N* **(BET, 2003)**

Solution.

Normality = ? , Volume of solution = 500 mL ;

g. eq. wt. of

$$H_2SO_4 = \frac{\text{g. mol. wt. of } H_2SO_4}{\text{Basicity of } H_2SO_4\ (= 2)}$$

$$= \frac{(2 \times 1) + 32 + (4 \times 16)}{2}$$

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

$$\text{Wt. of } H_2SO_4 = 50\text{ g}$$

We know :

$$\text{Normality} = \frac{\text{Wt. of } H_2SO_4}{\text{g. eq. wt. of } H_2SO_4} \times \frac{1000\text{ mL L}^{-}}{\text{volume of solution in mL}}$$

$$= \frac{50\text{ g}}{49\text{ g eq}^{-}} \times \frac{1000\text{ mL L}^{-}}{500\text{ mL}} = \frac{100}{49}$$

$$= \mathbf{2.04\ N\ or\ 2.04\ eq.\ L^{-}}$$

So, the correct answer is (*a*).

Example 188. *The osmotic pressure of 1 M sodium chloride solution at 27 °C is :*

(*a*) *12.3 atm* (*b*) *24.6 atm*

(*c*) *39.8 atm* (*d*) *49.2 atm.* **(BET, 2003)**

Solution.

$$\underset{1\text{ M}}{NaCl} \rightleftharpoons \underset{1\text{ M}}{Na^+} + \underset{1\text{ M}}{Cl^-}$$

We know $\pi V = n RT\ ;\ \pi = \dfrac{n RT}{V}$ ... (1)

∴ Osmotic pressure,

$$\pi = \frac{1\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 300\text{ K}}{1\text{ L}}$$

$$\simeq \mathbf{24.6\ atm.}$$

So, the correct answer is (*b*).

Example 189. *The concentration of glucose solution in molality which boils at 100.01 °C (K_b for water is 0.5 °C kg mol⁻) is :*

(*a*) *0.01* (*b*) *0.02*

(*c*) *0.03* (*d*) *0.04* **(SCRA, 2000)**

Solution. We know that

$$\Delta T_b = K_b \times m\ (\text{molality of solution})$$

Here, $\Delta T_b = 100.01 - 100 = 0.01\ °\text{C}\ ;$

$$K_b = 0.5\ °\text{C kg mol}^{-}$$

∴ $0.01\ °\text{C} = 0.5\ °\text{C kg mol}^{-} \times m\ ;$

$$m = \frac{0.01}{0.05} = \mathbf{0.02\ mol\ kg^{-}}$$

So, the correct answer is (*b*).

Example 190. *A solution containing 10 g per dm^3 of urea (molecular mass = 60 g mol⁻) is isotonic with a 5 % solution of a non - volatile solute whose molar mass is :*

(*a*) *200 g mol⁻* (*b*) *250 g mol⁻*

(*c*) *300 g mol⁻* (*d*) *350 g mol⁻*

(CBSE – PMT, 2006)

Solution. For isotonic solution :

Osmotic pressure of urea

= Osmotic pressure of non-volatile solute (*i*) For urea,

$$M = 60 \text{ g mol}^{-},$$
$$W = 10 \text{ g},$$
$$V = 1 \text{ dm}^3$$
$$\therefore \qquad \pi_1 = \frac{W\,RT}{M\,V} = \frac{10\,RT}{60 \times 1} \qquad \text{... (1)}$$

(*ii*) For non - volatile solute,

$$M = ?, \text{W} = 5 \text{ g};$$
$$V = \frac{100}{1000}\text{dm}^3 = 0.1 \text{ dm}^3$$
$$\therefore \qquad \pi_2 = \frac{W\,RT}{M\,V} = \frac{5\,RT}{M \times 0.1} \qquad \text{... (2)}$$

Equating (1) and (2), we get :

$$\frac{10\,RT}{60} = \frac{5\,RT}{0.1\,M};$$
$$M = \frac{5\,RT \times 60}{10\,RT \times 0.1} = \mathbf{300 \text{ g mol}^{-}}.$$

So, the correct answer is (*c*).

EXAMPLE 191. *1.0 g of a non - electrolyte solute (molar mass 250 g mol⁻) was dissolved in 51.2 g of benzene. If the freezing point depression constant, K_f of benzene is 5.12 K kg mol⁻, the freezing point of benzene will be lowered by :*

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

(CBSE – PMT, 2006, Orissa JEE, 2009)

SOLUTION. Wt. of solute, w = 10 g, molar mass, $M = 250 \text{ g mol}^{-}$, $K_f = 5.12\ K \text{ kg mol}^{-}$, $\Delta T_f = ?$, W = wt. of solvent = $51.2 \text{ g} = \frac{51.2}{1000}$ kg

$$\Delta T_f = K_f \times m = K_f\,\frac{W}{M} \times \frac{1}{W \text{ in kg}}$$
$$= \frac{5.12 \text{ K kg mol}^{-} \times 1.0 \text{ g} \times 1000}{250 \text{ g mol}^{-} \times 51.2 \text{ kg}} = \mathbf{0.4K.}$$

So, the correct answer is (*b*).

EXAMPLE 192. *Vapour pressure of pure A is 70 mm of Hg at 25°C. It forms an ideal solution with B in which mole fraction of A is 0.8. If the vapour pressure of the solution is 84 mm of Hg at 25°C, the vapour pressure of pure B at 25°C is :*

(*a*) *56 mm* (*b*) *70 mm*
(*c*) *140 mm* (*d*) *28 mm* **(Karnataka CET, 2009)**

SOLUTION. Given $x_A = 0.8$. So, $x_B = 1.0 - 0.8 = 0.2$; $P_A^o = 70$ mm and P = 84 mm. According to Raoult's law :

$$P = P_A^o x_A + P_B^o x_B;$$
$$84 = (0.8 \times 70) + (0.2 \times P_B^o)$$
$$84 = 56 + 0.2\,P_B^o;$$
$$P_B^o = (84 - 56)/0.2$$

= 140 mm. So, the correct answer is (*c*).

EXAMPLE 193. *The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25 °C. A sample containing 0.2 g of solute / 100 cm³ of solution developed a rise of 2.4 mm at osmotic equilibrium. If density of solution is 0.88 g cm⁻³, the molecular weight of isobutylene is:*

(*a*) *2.7 × 10⁵ g mol⁻* (*b*) *235362.5 g mol⁻*
(*c*) *2.6 × 10⁴ g mol⁻* (*d*) *10⁶ g mol⁻*

SOLUTION.

$$\text{Density, } d = \frac{0.88 \text{ g}}{\text{cm}^3} = \frac{0.88 \text{ g}}{\text{cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{10^6 \text{ cm}^3}{1 \text{ m}^3}$$
$$= 0.88 \times 10^3 \text{ kg m}^{-3}$$
$$h = 2.4 \text{ mm} = 2.4 \text{ mm} \times \frac{m}{1000 \text{ mm}}$$
$$= 2.4 \times 10^{-3} \text{ m};$$
$$g = 9.81 \text{ m s}^{-2}$$

∴ Osmotic pressure,

$$\pi = h\,dg = 2.4 \times 10^{-3} \text{ m} \times 0.88 \times 10^3 \text{ kg } m^{-3} \times 9.81 \text{ m s}^{-2}$$
$$= 20.7 \text{ kg m}^{-} \text{ s}^{-2}$$
$$\text{We know that } R = 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-} \text{mol}^{-};$$
$$T = 25 + 273 = 293 \text{ K};$$
$$100 \text{ cm}^3 = 100 \text{ cm}^3 \times \frac{m^3}{10^6 \text{ cm}^3} = 10^{-4} \text{ m}^3$$
$$\text{But} \qquad \pi = \frac{n\,RT}{V} \quad \text{or} \quad \pi = \frac{W_2}{M_2\,V} \times RT;$$
$$\text{or } M_2 = \frac{0.2 \text{ g} \times 8.314 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-} \text{ mol}^{-} \times 293 \text{ K}}{20.7 \text{ kg m}^{-} \text{ s}^{-2} \times 10^{-4} \text{ m}^3}$$
$$= \mathbf{235362.5 \text{ g mol}^{-}}$$

So, the correct answer is (*b*).

EXAMPLE 194. *Equal weights of two substances X and Y are dissolved in equal volume of water. The osmotic pressure of the solution containing Y is five times the osmotic pressure of the solution containing X. What is the mol. wt. of X, if that of Y is 60 ?* **(ISC, 2009)**

SOLUTION. Given : $\pi_y = 5\pi_x$;

$$\text{Also,} \qquad \frac{\pi_x}{\pi_y} = \frac{M_y}{M_x} \text{ where } M \text{ is mol. wt.}$$
$$\therefore \qquad \frac{\pi_x}{5\pi_x} = \frac{60}{M_x}; M_x = 300 \text{ g mol}^{-}. \textbf{ Ans.}$$

EXAMPLE 195. *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⁻* (*b*) *3.28 mol kg⁻*
(*c*) *2.28 mol kg⁻* (*d*) *0.44 mol kg⁻* **(AIEEE, 2006)**

SOLUTION. If M = molarity, m = molality, M_1 = Mol. wt, d = density, then m and M are related as

$$\text{Molality,} \qquad m = \frac{1000\,M}{1000\,d - M\,M_1}.$$

So : $$m = \frac{1000 \times 2.05}{1000 \times 1.02 - 2.05 \times 60}$$

[$\because$ Mol wt. of $CH_3COOH = 12 + (3 \times 1) + 12 + (2 \times 16) + 1 = 60\ g\ mol^{-}$]

$$= \frac{1000 \times 2.05}{1020 - 123} = \frac{2050}{897} = \mathbf{2.28\ mol\ (Kg)^{-}}$$

So, the correct answer is (*c*).

EXAMPLE 196. *Match the following if the molecular weights of X, Y and Z are same. K_b values for X, Y and Z are respectively.*

(*a*) *0.68, 1.0, 2.0* (*b*) *0.2, 0.3, 0.4*

(*c*) 0.68, 0.53, 0.98 (*d*) *0.53, 3.0, 2.1*

SOLUTION. At the boiling point, the liquid (less random) changes to vapours (more random). So, in the change liquid to vapours, randomness *i.e.*, **entropy** increases. Since the difference in the randomness between a liquid and vapour is extremely high, the extent of randomness change is almost same for all liquids.

Boiling point		K_b
X	100	0.68
Y	27	0.53
Z	253	0.98

Thus, $K_b \propto T_b$.

Thus, $K_b(X) = 0.68$;

$K_b(Y) = 0.53$ and $K_b(Z) = 0.98$.

So, the correct answer is (*c*).

EXAMPLE 197. *18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of this water for this aqueous solution at 100 °C is :*

(*a*) *759.00 torr* (*b*) *7.60 torr*

(*c*) *76.00 torr* (*d*) *752.3 torr.* **(AIEEE, 2006)**

SOLUTION. Mol. wt. of

$$C_6H_{12}O_6 = (6 \times 12) + (12 \times 1) + (6 \times 16) = 180\ g\ mol^{-}$$

wt. of glucose = 18 g

$\therefore$ no. of mol of glucose,

$$n = \frac{18\ g}{180\ g\ mol^{-}} = 0.1\ mol$$

Mol. wt. of $H_2O = (2 \times 1) + 16 = 18\ g\ mol^{-}$;

wt. of H_2O = 178.2 g

$\therefore$ no. of mol of

$$H_2O, N = \frac{178.2\ g}{18\ g\ mol^{-}} = 9.9\ mol\ ; P^\circ = 760\ torr.$$

We know that

$$\frac{P^\circ - ps}{p^\circ} = \frac{n}{N}\ ; \frac{760 - ps}{760} = \frac{0.1}{9.9}$$

$760\ (9.9) - 9.9\ ps = 0.1 \times 760$ *i.e.*,

$7524 - 76 = 9.9\ ps$;

$7448/9.9 = ps$

$\therefore$ $ps = 7448/9.9 = \mathbf{752.3\ torr.}$

So, the correct answers is (*d*).

EXAMPLE 198. *72.5 g phenol is dissolved in 1 kg of a solvent ($K_f = 14$) which leads to dimerisation of phenol and freezing point is lowered by 7 kelvin. The percent of total phenol that is present in dimeric form is :*

(*a*) *20%* (*b*) *25%*

(*c*) *35%* (*d*) *45%*

(IITJEE modified, 2006)

SOLUTION. $$\underset{\text{Phenol}}{C_6H_5OH} \rightleftharpoons \frac{1}{2}(C_6H_5OH)_2$$

no. of mol at $t = 0$ 1 0

After association $1 - \alpha$ $\alpha/2$

Total no. of mol

$$= 1 - \alpha + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}$$

M = mol. wt. of $C_6H_5OH = (6 \times 12) + (5 \times 1) + 16 + 1 = 94\ g\ mol^{-}$

wt. of phenol, W = 72.5 g, wt. of solvent = 1 kg

$$\therefore \quad \text{Molality}, m = \frac{W}{M \times \text{wt. of solvent in kg}} = \frac{72.5}{94 \times 1}$$

But $$\Delta T_f = i\,K_f \times m\ ; 7 = i \times 14 \times \frac{72.5}{94}$$

$$\therefore \quad i = \frac{7 \times 94}{14 \times 72.5} = 0.6483$$

Also, $$1 - \frac{\alpha}{2} = 0.6483\ ; \frac{\alpha}{2} = 1 - 0.6483$$

or $$\frac{\alpha}{2} = (1 - 0.6483) = 0.3517 \simeq 0.35$$

$$= 0.35 \times 100 = \mathbf{35\ \%}$$

So, 35 % phenol is present in dimeric form. So, the correct answer is (*c*).

EXAMPLE 199. *At some temperature, which pair of the following solutions are isotonic solutions ?*

(*a*) *0.2 M $BaCl_2$ and 0.2 M urea*

(*b*) *0.1 M urea and 0.1 M NaCl*

(*c*) *0.1 M NaCl and 0.1 M K_2SO_4*

(*d*) *0.1 M $Ba(NO_3)_2$ and 0.1 M Na_2SO_4*

(Gujarat CET, 2006, UPCMPT, 2011)

SOLUTION. Isotonic solutions are those which have same osmotic pressure and hence same molar concentration. We know that osmotic pressure, $\pi = i$ CRT where i = total no. of ions in electrolyte solution.

(*i*) $$\underset{1\ \text{ion}}{BaCl_2} \rightleftharpoons \underset{2\ \text{ion}}{Ba^{2+} + 2\,Cl^{-}} \quad \therefore \quad i = 1 + 2 = 3$$

$$\therefore \quad \pi = 3 \times 0.2\,RT = 0.6\,RT$$

Urea (0.2 M) does not ionise. So, $\pi = CRT = 0.2\,RT$

Since 0.6 RT and 0.2 RT differ, these are not isotonic solutions.

(*ii*) 0.1 M urea. Urea does not ionise . So, $\pi = CRT = 0.1\,RT$

$$0.1\text{ M NaCl.}\quad \text{NaCl} \rightleftharpoons \underset{1\text{ ion}}{\text{Na}^+} + \underset{1\text{ ion}}{\text{Cl}^-} \qquad i = 1 + 1 = 2$$

$$\therefore \qquad \pi = i\,CRT = 2 \times 0.1\,RT = 0.2\,RT$$

Since 0.1 RT and 0.2 RT differ, these are not isotonic solutions.

(*iii*) 0.1 M NaCl. $\pi = 0.2\,RT$ [see (*ii*) above]

$$0.1\text{ M } K_2SO_4.\quad K_2SO_4 \rightleftharpoons \underset{2\text{ ion}}{2K^+} + \underset{1\text{ ion}}{SO_4^{2-}};\ i = 2 + 1 = 3$$

$$\therefore \qquad \pi = i\,CRT = 3 \times 0.1\,RT = 0.3\,RT$$

Since 0.2 RT and 0.3 RT differ, These are not isotonic solutions

(*iv*) $0.1\text{ M Ba(NO}_3)_2.\ \text{Ba(NO}_3)_2 \rightleftharpoons \underset{1\text{ ion}}{\text{Ba}^{2+}} + \underset{2\text{ ions}}{2\text{NO}_3^-}$

$$i = 1 + 2 = 3$$

$$\therefore \qquad \pi = i\,CRT = 3 \times 0.1\,RT = 0.3\,RT$$

$$0.1\text{ M Na}_2\text{SO}_4.\ \text{Na}_2\text{SO}_4 \rightleftharpoons \underset{2\text{ ions}}{2\text{ Na}^+} + \underset{1\text{ ion}}{\text{SO}_4^{2-}}$$

$$i = 2 + 1 = 3$$

$$\therefore \qquad \pi = i\,CRT = 3 \times 0.1\,RT = 0.3\,RT$$

Since 0.3 RT value = 0.3 RT value, these solutions are isotonic. So the correct answer is (*d*).

EXAMPLE 200. *When 20 g of naphthoic acid ($C_{11}H_8O_2$) is dissolved in 50 g of benzene (K_f = 1.72 K kg mol¯), a freezing point depression of 2 K is observed. The Van't Hoff factor (i) is:*

(*a*) 0.5 (*b*) 1

(*c*) 2 (*d*) 3 **(IIT–JEE, 2007, 2011)**

SOLUTION. $i = ?;\ K_f = 1.72\,K\text{ kg mol}^{-};\ \Delta T_f = 2\,K$

$$M_2 = \text{Mol. wt. of } C_{11}H_8O_2$$
$$= (11 \times 12) + (8 \times 1) + (2 \times 16)$$
$$= 172\text{ g mol}^{-}$$

$$W_2 = 20\text{ g};\ W_1 = 50\text{ g} \times \frac{1\text{ kg}}{1000\text{ g}} = 0.05\text{ kg}$$

$$\text{Molality,}\qquad m = \frac{W_2\text{ in g}}{M_2\text{ in g mol}^{-} \times W_1\text{ in kg}}$$

$$= \frac{20\text{ g}}{172\text{ g mol}^{-} \times 0.05\text{ kg}}$$

$$\text{But}\qquad \Delta T_f = i\,K_f m;\quad i = \frac{\Delta T_f}{K_f\,m}$$

$$i = \frac{2\text{ K} \times 172\text{ g mol}^{-} \times 0.05\text{ kg}}{1.72\text{ K kg mol}^{-} \times 20\text{ g}} = 0.5$$

So, the correct answer is (*a*).

EXAMPLE 201. *Calculate the freezing point of an aqueous solution containing 10.50 g of $MgBr_2$ in 200 g of water. (Molar mass of $MgBr_2$ = 184 g) ; K_f for water = 1.86 K kg mol¯.*

(CBSE, 2011)

SOLUTION. $\Delta T_f = ?\ ; K_f = 1.86$ K kg mol¯ ; Mol. wt. (M_2) of $MgBr_2$ = 184 g mol¯ ; wt. of solvent (W_1) in kg = 200 g/1000 = 0.2 kg ; wt. of solute (W_2) in g = 10.50 g. But

$$\Delta T_f = \frac{K_f\ (\text{in } K\text{ kg mol}^{-}) \times W_2\text{ g}}{M_2\text{ in g mol}^{-} \times W_1\text{ in kg}}$$

$$= \frac{1.86\text{ K kg mol}^{-} \times 10.5\text{ g}}{184\text{ g mol}^{-} \times 0.2\text{ kg}} = 0.53\,K$$

∴ Freezing point = 273.15 K – 0.53 K = 272.62 K **Ans.**

EXAMPLE 202. *A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9. Given K_f(water) = 1.86 K kg mol¯; K_f(ethanol) = 2.0 K kg mol¯; K_b (water) = 0.52 K kg mol¯; K_b (ethanol) = 1.2 K Kg mol¯. Standard freezing point and boiling point of ethanol are 155.7 K and 351.5 K respectively. Molecular weights of water and ethanol are 18 g mol¯ and 46 g mol¯ respectively.*

1. *The freezing point of the solution M is :*

(*a*) 268.7 K (*b*) 268.5 K

(*c*) 234.2 K (*d*) 150.9 K

2. *Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is :*

(*a*) 380.4 K (*b*) 376.2 K

(*c*) 375.5 K (*d*) 354.7 K **(IIT-JEE, 2008)**

SOLUTION. (1) $\Delta T_f = K_f \times m = \dfrac{2\text{K kg mol}^{-} \times 0.1 \times 1000}{0.9 \times 46}$

$$\text{kg}^{-}\text{ mol} = 4.83\,K$$

∴ Freezing point of solution,

$$M, T_f' = T_f^0 - \Delta T_f = 155.7\,K - 4.83\,K$$
$$= 150.9\,K$$

(2) $$\Delta\,T_b = K_b \times m = \frac{0.52\text{ K kg mol}^{-} \times 0.1 \times 1000}{0.9 \times 18}$$

$$\text{kg}^{-}\text{ mol} = 3.2\,K$$

∴ Boiling point of solution,

$$T_b = T_b^{\,0} + \Delta\,T_b = 373 + 3.2 = 376.2\,K.$$

So, the correct answer is (*b*).

EXAMPLE 203. *The correct order of boiling points of the following aqueous solutions, 0.0001 M NaCl (I), 0.0001 M Urea (II), 0.001 M $MgCl_2$ (III), 0.01 M NaCl is:*

(*a*) *I < II < III < IV* (*b*) *IV < III < II < I*

(*c*) *II < I < III < IV* (*d*) *III < II < IV < I*

(AMU. Engg., 2012)

SOLUTION. Greater the value of ΔT_b, greater will be the boiling point. Since, $\Delta T_b = i \times K_b \times m$, we have:

(*i*) $\Delta T_b = 2 \times 0.0001$ M = 0.0002 M

[∵ $NaCl \rightleftharpoons Na^+$ (1 mol) + Cl^- (1 mol)]

(*ii*) $\Delta T_b = 1 \times 0.0001$ M = 0.0001 M [∵ Urea → Urea]

(*iii*) $\Delta T_b = 3 \times 0.001$ M = 0.003 M

[∵ $MgCl_2 \rightleftharpoons Mg^{2+}$ (1 mol) + 2 Cl^- (2 mol)]

(*iv*) $\Delta T_b = 2 \times 0.01$ M = 0.02 M.

Since 0.02 M (IV) > 0.003 M (III) > 0.0002 M (I) > 0.0001 M (II), so, II < I < III < IV. So, the correct answer is (*c*).

EXAMPLE 204. *15.0 g of an unknown material was dissolved in 450 g of water. The resulting compound was found to freeze at – 0.34°C.*

What is the molar mass of the material?

(K_f for water = 1.86 K kg mol^-). **(CBSE, 2012)**

SOLUTION. $W_A = 450$ g; $W_B = 15.0$ g; $\Delta T_f = 0 - (-0.34°C)$ = + 0.34°C or + 0.34 K;

M = Molar mass = ? We know that:

$$M = K_f \times \frac{W_B \times 1000}{W_A \times \Delta T_f} = \frac{1.86 \text{ K kg mol}^- \times 15.0\ g \times 1000}{450.0\ kg \times 0.34 \text{ K}}$$

∴ *M* = 182.4 g mol^- **Ans.**

EXAMPLE 205. *K_f for water is 1.86 K kg mol^-. If your automobile holds 1.0 kg of water, how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to – 2.8°C.*

(*a*) *93 g* (*b*) *39 g*

(*c*) *27 g* (*d*) *72 g* **(AIEEE, 2012)**

SOLUTION. $\Delta T_f = 0 - (-2.8) = 2.8°C.$; Mol. wt. ($M_2$) of $C_2H_6O_2 = (2 \times 12) + (6 \times 1) + (2 \times 16) = 24 + 6 + 32 = 62$ g mol^-; wt. of solute = W_2. We know that:

$$\Delta T_f = \frac{K_f \times W_2 \text{ in g}}{M_2 \times W_1 \text{ in kg}}; W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f} = \frac{2.8 \times 62 \times 1}{1.86}$$

= 93 g

So, the correct answer is (*a*).

EXAMPLE 206. *A solution of lactone containing 8.45g of water has a vapour pressure of 4.559 mm of Hg at 0°C. If the vapour pressure of pure water is 4.579 mm of Hg, calculate the molecular weight of lactone:* **(ISC, 2012)**

SOLUTION. V.P. of solvent, P_0 = 4.579 mm; V.P. of solution, P_s = 4.559 mm; Mol. wt. of lactone, M = ?; x_B = mole fraction of lactone where $x_B = n_A/(n_A + n_B)$ where

n_A = no. of moles of solvent, H_2O = (wt./Mol. wt) = $\frac{100}{18}$

n_B = no. of moles of solute, lactone = (wt./Mol. wt) = $\frac{8.45}{M}$

We know that: $x_B = \frac{P_0 - P_s}{P_0}$. Thus:

$$\frac{n_B}{n_A + n_B} = \frac{4.579 - 4.559}{4.579}; \frac{\frac{8.45}{M}}{(100/18) + (8.45/M)} = \frac{0.02}{4.579}$$

$$\text{Or } \frac{8.45/M}{[100\,M + (18 \times 8.45)]/18\,M} = \frac{0.02}{4.579};$$

$$\frac{8.45 \times 18}{100\,M + 152.1} = \frac{0.02}{4.579}$$

100 *M* × 0.02 + 152.1 × 0.02 = 152.1 × 4.579

∴ 2 *M* + 3.042 = 696.46; ***M* = 346.7 g mol¯** **Ans.**

EXAMPLE 207. *Which of the following aqueous solutions has the highest boiling point?*

(*a*) *0.1 M KNO_3* (*b*) *0.1 M Na_3PO_4*

(*c*) *0.1 M Ba Cl_2* (*d*) *0.1 M K_2SO_4*

(AFMC, 2012)

SOLUTION. (*a*) no. of particles in 0.1 M ($KNO_3 \rightleftharpoons K^+ + NO_3^-$) = 2

(*b*) no. of particles in 0.1 M ($Na_3PO_4 \rightleftharpoons 3Na^+ + PO_4^{3-}$) = 4 (*c*) no. of particles in 0.1 M ($BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$) = 3 and (*d*) no. of particles in 0.1 M ($K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$) = 3. For the same molar solutions, greater the number of particles i.e., value of vant Hoff factor, *i* in $\Delta T_f = i\,K_b m$, greater will be the boiling point. So, the correct answer is (*b*).

EXAMPLE 208. *The mass of a non-volatile solute of molar mass 40 g mol^- that should be dissolved in 114 g of octane to lower its vapour pressure by 20% is:*

(*a*) *10 g* (*b*) *11.4 g*

(*c*) *9.8 g* (*d*) *12.8 g*

(Karnataka, CET, 2012)

SOLUTION. Here $p°$ = V.P. of pure solvent, octane (C_8H_{18}) = 100

Lowering of V.P. = $p° - p = 20$; mol. wt. of C_8H_{18} = (8 × 12) + (18 × 1) = 114.

Mole fraction of solute, $x_B = p° - p/p^0; = \frac{20}{100} = \frac{1}{5}$

$$\text{But } x_B = \frac{w_B/M_B}{(W_B/M_B) + (W_A/M_A)} = \frac{20}{100}$$

$$\text{Or } \frac{W_B/40}{(W_B/40) + (114/114)} = \frac{1}{5}; \frac{W_B/40}{(W_B/40) + 1} = \frac{1}{5}$$

$$\therefore\ \frac{5W_B}{40} = \frac{W_B}{40} + 1; \frac{5W_B}{40} - \frac{W_B}{40} = 1;\ 4W_B = 40.$$

So, $W_B = 10$ g.

So, the correct answer is (*a*).

EXAMPLE 209. *Freezing point of an aqueous solution is –0.186°C. If the values of K_b and K_f of water are respectively 0.52 K kg mol^{-} and 1.86 K kg mol^{-}, then the elevation of boiling point of the solution in K is:*

(*a*) *0.52*	(*b*) *1.04*
(*c*) *1.34*	(*d*) *0.134*
(*e*) *0.052*	**(Kerala PET, 2012)**

SOLUTION. $\Delta T_f = 0 - (-0.186) = 0.186°C$.

Also, $\Delta T_f = i\,K_f.m$ and $\Delta T_b = i\,K_b.m$. Thus:

$\frac{\Delta T_f}{\Delta T_b} = \frac{i\,K_f m}{i\,K_b m} = \frac{K_f}{K_b}$. Substituting the values, we get:

$$\frac{0.186}{\Delta T_b} = \frac{1.86}{0.52};\ \Delta T_b = \frac{0.186 \times 0.52}{1.86} = 0.052K.$$

So, the correct answer is (*e*).

EXAMPLE 210. *Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 25°C are 200 mm Hg and 41.5 mm respectively. Vapour pressure of solution obtained by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at the same temperature will be (molecular mass of $CHCl_3$ = 119.5 u and molecular mass of CH_2Cl_2 = 85 U):*

(*a*) *173.9 mm Hg*	(*b*) *615.0 mm Hg*
(*c*) *347.9 mm Hg*	(*d*) *285.5 mm Hg*

(AIPMT, Mains, 2012)

SOLUTION. Moles of $CHCl_3$ = (wt./Mol. wt.)

$$= \frac{25.5}{119.5} = 0.213$$

Moles of CH_2Cl_2 = 40/85 = 0.470; p^0CHCl_3 = 200 mm Hg; $p^0CH_2Cl_2$ = 41.5 mm Hg

Mole fraction, $^{x}CHCl_3$

$$= \frac{0.213}{0.213 + 0.470} = 0.31;\ x_{CH_2Cl_2} = 1 - 0.31 = 0.69$$

$$p_{\text{Total}} = p^0_{CHCl_3} \times x_{CHCl_3} + p^0_{CH_2Cl_2} \times x_{CH_2Cl_2}$$

$= 2.00 \times 0.31 + 41.5 \times 0.69 = 62 + 28.63 = 90.63$.

So, no answer is correct.

EXAMPLE 211. *58.5 g NaCl and 180 g of glucose were separately dissolved in 1000 mL of water. Indentify the correct statement regarding the elevation of b.pt. of the resulting solutions.*

(*a*) *NaCl solution will show higher elevation of b.pt.*

(*b*) *Glucose solution will show higher elevation of b.pt.*

(*c*) *Both solutions will show equal elevation of b.pt.*

(*d*) *The b.pt. of elevation will be shown neither of the solution* **(W.B.JEE, 2012)**

SOLUTION. vant Hoff (*i*) for NaCl [Na^+ (1 mol) + Cl^- (1 mol)] = 1 + 1 = 2.

vant Hoff factor for glucose (non-electrolyte) = 1, wt. of solvent H_2O

1000 mL = 1000 g; Mol. wt. of glucose, $C_6H_{12}O_6$ = (6 × 12) + (12 × 1) + (6 × 16) = 180 g mol^{-}.

∴ Molality, *m* of NaCl

$$= \frac{wt.}{\text{Mol.}\,wt.} \times \frac{1000}{wt.\text{ of solvent}} = \frac{58.5}{58.5} \times \frac{1000}{1000} = 1m.$$

ΔT_f for NaCl = $i\,k_b \times m = 2 \times k_b \times 1 = 2K_b$

Molality, *m* of glucose

$$= \frac{wt.}{\text{Mol.}\,wt.} \times \frac{1000}{1000} = \frac{180}{180} \times \frac{1000}{1000} = 1m.$$

$\therefore\ \Delta T_b = i\,K_b \times m = 1 \times K_b \times 1 = K_b$

∴ ΔT_b for NaCl > ΔT_b for glucose. So, the correct answer is (*a*).

EXAMPLE 212. *For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solution in 100g of water, the elevation in boiling point at one atmospheric pressure is much lower than the concentration of solvent. The vapour pressure (mm of Hg) of the solution is (take K_b = 0.76 K kg mol^{-}):*

(*a*) *724*	(*b*) *740*
(*c*) *736*	(*d*) *718* **(IIT-JEE, 2012)**

SOLUTION. The molality, *m* of a solution is given as:

$$m = \frac{wt.}{\text{Mol.}\,wt.} \times \frac{1000}{\text{weight of solvent}} = \frac{2.5}{\text{Mol.}\,wt.} \times \frac{1000}{100}$$

$$= \frac{25}{\text{Mol.}\,wt.} \quad ...(1)$$

Also, $\Delta T_b = K_b \times m$ or $m = \frac{\Delta T_b}{K_b} = \frac{2}{0.76}$ ...(2)

From equations (1) and (2), we get:

$$\frac{25}{\text{Mol.}\,wt.} = \frac{2}{0.76};\ \text{Mol.}\,wt. = \frac{25 \times 0.76}{2} = 9.5$$

Given P^0_{solvent} = 1 atm. = 760 mm Hg

We know that: $\frac{P^0_{\text{solvent}} - P_{\text{solute}}}{P^0_{\text{solvent}}} = x_{\text{solute}}$

(mole fraction of solute)

$$\frac{760 - P_{\text{solute}}}{760} = \frac{(wt./\text{Mol.}\,wt)\text{ of solute}}{(wt./\,Mol.\,wt)\text{ of solvent}} = \frac{2.5/9.5}{100/18}$$

$$760 - P_{\text{solute}} = \frac{760 \times 2.5 \times 18}{9.5 \times 100} = 36$$

∴ P_{solute} = 760 – 36 = **724 mm Hg.**

So, the correct answer is (*a*).

EXAMPLE 213. *1.00 molal aqueous solution of trichloroacetic acid ($CCl_3.COOH$) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid (K_b for water = 0.512 K kg mol^{-})*

(CBSE, 2012)

SOLUTION. $K_b = 0.512$ K kg mol^{-}; $m = 1.00$; ΔT_b (obs.) = 100.18 – 100 = 0.18°C = 0.18 K. But; van't Hoff factor

$$i = \frac{\Delta T_b\,(\text{observed})}{\Delta T_b\,(\text{calculated})} = \frac{0.18}{0.512} = \mathbf{0.35} \qquad \textbf{Ans.}$$

EXAMPLE 214. *A solution X is prepared by dissolving three moles of glucose in one litre of water and a solution Y is prepared by dissolving 1.5 moles of sodium chloride in one litre of water. Will the osmotic pressure of X be higher, lower or equal to that of Y? Give a reason for your answer.* **(ISC 2012)**

SOLUTION. (*a*) For solution *X*, let osmotic pressure, $\pi = \pi_1$

No. of moles of glucose, $n = 3$; volume, $V = 1$ L.

$$\therefore\ \pi_1 = \frac{n}{V}.RT;\ \pi_1 = \frac{3\text{ mol}}{1\text{L}} \times RT \qquad ...(1)$$

(*b*) For solution *Y*, let osmotic pressure, $\pi = \pi_2$

No. of moles of NaCl, $n = 1.5$; Volume, $V = 1$L; vant's Hoff factor, *i* of NaCl (electroyte) = 2

[$\because$ NaCl (1 mol) $\rightleftharpoons$ Na^+ (1 mol) + Cl^- (1 mol)]

so, $i = 1 + 1 = 2$. But

$$\pi_2 = i\frac{n}{V}.RT;\ \pi_2 = 2 \times \frac{1.5\text{ mol}}{1\text{L}}.RT \qquad ...(2)$$

Dividing relations (1) and (2), we have:

$$\frac{\pi_1}{\pi_2} = \frac{3\text{ mol}}{1\text{ L}}.RT \times \frac{1\,L}{2 \times 1.5\text{ mol} \times RT} = 1$$

$\therefore\ \pi_1 = \pi_2$. Hence the osmotic pressure of both solutions is same. Note that glucose being non-electroyte, it does not ionise.

EXAMPLE 215. *1.5 g of a non-volatile, non-electrolyte is dissolved in 50 g benzene (K_b = 2.5 K kg mol^{-}). The elevention of the boiling point of the solution is 0.75 K. The molecular weight of the solute in g mol^{-} is:*

(*a*) 200 (*b*) 50

(*c*) 75 (*d*) 100

(*e*) 150 **(Kerala PMT, 2012)**

SOLUTION. We know that:

$$\Delta T_b = \frac{K_b \times W_2\text{ in g}}{M_2 \times W_1\text{ in kg}};\ \mathbf{0.75\ K} = \frac{2.5\text{ K kg mol}^{-} \times 1.5\text{ g}}{M_2 \times (50/1000)\text{ kg}}$$

$$\therefore\ M_2 = \frac{2.5 \times 1.5 \times 1000}{50 \times 0.75} = 100\text{ g mol}^{-}.$$

So, the correct answer is (*d*).

Note: Molality = $\dfrac{x_{\text{solute}}}{x_{\text{solvent}}} \times \dfrac{1000}{\text{Mol. wt. of solvent}}$

EXAMPLE 216. *Calculate the molality of iodine in $CHCl_3$ if the mole fraction of iodine in $CHCl_3$ is 0.25.*

(*a*) 1.5 (*b*) 1.59

(*c*) 2.79 (*d*) 3.79

(Haryana Board, 2012 modified)

SOLUTION. Mol. wt. of $CHCl_3$ = 12 + 1 + (3 × 35.5) = 119.5 g mol^{-}

Mole fraction of $I_2 = \dfrac{n}{n+N}$ = 0.25; so, mole fraction of solvent $CHCl_3 = \dfrac{N}{n+N}$ = 1 – 0.25 = 0.75. Dividing we get:

$$\frac{n}{N} = \frac{0.25}{0.75} = \frac{1}{3}$$

$$\text{Or } \frac{{}^{n}I_2}{W_{CHCl_3}} \times M_{CHCl_3} = \frac{1}{3} \qquad (1);$$

$$\frac{{}^{n}I_2}{W_{CHCl_3}} = \frac{1}{3} \div M_{CHCl_3}(=119.5) \qquad (2)$$

$$\text{So, Molality} = \frac{{}^{n}I_2}{W_{CHCl_3}} \times 1000 \qquad (3)$$

Substituting the value of (${}^{n}I_2/W_{CHCl_3}$) from (2) in (3), we get:

$$\text{Molality} = \frac{1}{3} \times \frac{1}{119.5} \times 1000 = 2.79$$

So, the correct answer is (*c*).

EXAMPLE 217. *Find the weight of NaCl that should be dissolved in 50 g water to give 15% solution by weight.*

(*a*) 14.0 g (*b*) 14.12 g

(*c*) 11.52 g (*d*) 10.59 g

(H.P. Board, 2012 modified)

SOLUTION. Let *w* = wt. of NaCl. So, we have:

$$\%\text{ age by wt.} = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

$$15 = \frac{w}{w+60} \times 100.\ \text{Thus, } w = 10.59\text{ g}$$

So, the correct answer is (*d*).

EXAMPLE 218. *A sample of sea water contains 47 ppm of NO_2^- ions. If the density of solution is 1.01 g (mL)$^{-}$, the approximate molarity of sea water is:*

(*a*) 1 mol (*b*) 0.1 mol

(*c*) 0.01 mol (*d*) 0.001 mol

(PSEB, 2012 modified)

SOLUTION. Mol. wt. of NO_2^- = 14 + (2 × 16) + 1

= 47 g mol^{-}

10^6 g sea water contains NO_2^- ions = 47 g = $\frac{47}{47}$ = 1 mol

$\therefore$ 1000 g sea water contains NO_2^- ions

$$= \frac{1 \times 1000}{10^6} = 0.001 \text{ mol}$$

$$= 0.001 \text{ M}$$

[$\because$ wt. of solution = wt. of H_2O = 1000 g;

Volume of solution = $\frac{1000}{\text{density } 1.01} \simeq 1000$ mL.]

EXAMPLE 219. *Calcium oxide formed, by burning 2.0 g of calcium in excess oxygen, was dissolved in water and the solution was made up to 500 mL. The normality and molarity of the solution respectively are:*

(*a*) 0.1, 0.1	(*b*) 0.2, 0.2
(*c*) 0.3, 0.1	(*d*) 0.4, 0.1

(ISC, 2012 modified)

SOLUTION. $2Ca + O_2 \equiv 2CaO$

Equivalent of Ca = Equivalent of CaO;

$$\text{Volume} = \frac{500}{1000} = 0.5 \text{ L}$$

$$\text{Equivalent of Ca} = \frac{\text{wt.}}{\text{Eq. wt. of Ca}} = \frac{2.0}{20} = \frac{1}{10} = 0.1$$

$$\because \text{Eq. wt. of Ca} = \frac{\text{At. wt. of } Ca}{\text{Valency } (= 2) \text{ of } Ca} = \frac{40}{2} = 20$$

$\therefore$ Normarity of CaO

$$= \frac{\text{Equivalent of } Ca}{\text{Vol. in litre}} = \frac{1}{10 \times 0.5} = \frac{1}{5} = 0.2$$

$$\text{Molarity of CaO} = \frac{0.2}{2} = 0.1$$

[$\because$ Molarity = Normality × Eq. wt./Mol. wt.]

So, the correct answer is (*a*).

EXAMPLE 220. *The mole fraction of the solute in one molal aqueous solution is:*

(*a*) 0.02	(*b*) 0.08
(*c*) 0.018	(*d*) 0.1

(D.B. 2012 modified)

SOLUTION. Molality = 1, mole fraction of solute = ?

Mol. wt. of solute, $H_2O = (2 \times 1) + 16 = 18$ g mol^{-}. But:

Mole fraction of solute

$$= \frac{\text{Molality}}{\text{Molality} + 1000/\text{Mol. wt. of solvent}}$$

$$\therefore \text{ Mole fraction of solute} = \frac{1}{1 + \frac{1000}{18}} = \frac{18}{1018} = 0.018.$$

So, the correct answer is (*c*).

Type. *x* molal (or *x m*) solution of a gas *A* = *x* mol

EXAMPLE 221. *If the solubility of gas A in water at NTP and at 0.95 bar pressure is 0.15 m, then calculate, Henry's law constant.* **(CBSE(D), 2012)**

SOLUTION. $^{n}H_2O = \frac{\text{wt. of } H_2O}{\text{g . mol. wt. of } H_2O} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-}}$

$$= 55.5 \text{ mol}$$

$$^{n}A = 0.15 \text{ mol (given)}$$

$$\therefore x_A = \frac{0.15}{0.15 + 55.5} = 2.69 \times 10^{-3}.$$

But $p_A = K_H \times x_A$

$\therefore$ $0.95 = K_H \times 2.69 \times 10^{-3}$.

Hence, K_H = **353.2 bar.**

EXAMPLE 222. *Find the amount of CO_2 gas in 250 mL of soda water when packed under 3.0 atm CO_2 at 25°C (K_H for CO_2 in water = 1.67×10^8 Pa)* **(CBSE (F), 2012)**

SOLUTION. Mass of water = volume × density.

$$= 250 \times 1 = 250 \text{ g}.$$

$$^{n}H_2O = \frac{250 \text{ g}}{18 \text{ g mol}^{-}} = 13.89 \text{ mol}$$

$$^{x}CO_2 = \frac{3.0 \times 10^5 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.8 \times 10^{-3} \quad [\because 1 \text{ atm} = 10^5 \text{ Pa}]$$

$$\text{But } ^{x}CO_2 = \frac{^{n}CO_2}{^{n}CO_2 + {}^{n}H_2O} \simeq \frac{^{n}CO_2}{^{n}H_2O}$$

$\therefore$ $^{n}CO_2 = {}^{n}CO_2 \times {}^{n}H_2O = 1.8 \times 10^{-3} \times 13.89 = 0.025$ mol

$\therefore$ Amount of $CO_2 = {}^{x}CO_2 \times$ molar mass of CO_2

$= 0.025 \times 44 =$ **1.1 g.**

PROBLEMS FOR PRACTICE

1. What is the freezing point of a 10% (by weight) solution of CH_3OH in water ?

Hint. wt. of solute = 10 g ; wt. of solvent = 100 – 10 = 90 g. **[Ans. – 6.45°C]**

2. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g water to – 9.3°C. (K_f for water = 1.86 K mol^{-} kg.) **[Roorkee, 1995] [Ans. 38.71g]**

Hint:

$$\Delta T_f = \frac{k_f \times w_2 \times 1000}{M \times w_1};\ 9.3 = \frac{1.86 \times 50 \times 1000}{62 \times w_1};\ w_1 = 161.29\text{ g}$$

$\therefore$ wt. of ice = 200 – 161.29 = 38.71 g **Ans.**

3. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f) when 0.01 mole of sodium sulphate is dissolved in 1 kg of water is (K_f = 1.86 K kg mol^{-})

(*a*) 0.0186 *K* (*b*) 0.0372 *K*
(*c*) 0.0558 *K* (*d*) 0.0744 *K*

(AIEEE, 2010). Ans. (*c*)

4. The vapour pressure of pure solvent is 0.8 mm of Hg at a particular temperature. On addition of a non-volatile solute, A, the vapour pressure of solution becomes 0.6 mm. The mole fraction of component, *A* is :

(*a*) 0.25 (*b*) 2.56
(*c*) 15.6 (*d*) 82.4

(Orissa JEE, 2010) Ans (*a*).

5. What is the osmotic pressure of a 0.002 mol dm^{-3} sucrose ($C_{12}H_{22}O_{11}$) solution at 20°C. (Molar gas constant, *R* = 8.314 J K^{-} mol^{-}, 1 dm^3 = 0.001 m^3)

(*a*) 4870 Pa (*b*) 4.87 Pa
(*c*) 0.00487 Pa (*d*) 0.33 Pa

(DUMET, 2010). Ans (*a*)

6. 1 g of a non-volatile, non-electrolyte solute of molar mass 250 g/mol was dissolved in 51.2 g of benzene. If the freezing point depression constant, K_f of benzene is 5.12 kg K mol^{-}, the freezing point of benzene is lowered by :

(*a*) 0.3 K (*b*) 0.5 K
(*c*) 0.2 K (*d*) 0.6 K
(*e*) 0.4 K **(Kerala PMT, 2010) Ans. (*e*)**

7. Four solutions of K_2SO_4 with the following concentrations 0.1 m, 0.01 m, 0.001m and 0.0001 m are available. The maximum value of van't Hoff factor '*i*' corresponds to :

(*a*) 0.0001 m solution (*b*) 0.001 m solution
(*c*) 0.01 m solution (*d*) 0.1 m solution

(AMU, 2010) Ans. (*a*).

8. The amount of solution (molar mass, 60 g mol^{-}) that must be added to 180 g water so that the vapour pressure of water is lowered by 10 % is :

(*a*) 30 g (*b*) 60 g
(*c*) 120 g (*d*) 12 g
(*e*) 24 g. **(Kerala PET, 2010) Ans. (*b*)**

9. A solution of protein (extracted from crabs) was prepared by dissolving 0.75 g in 125 cm^3 of an aqueous solution. At 4°C, the osmotic pressure rise of 2.6 mm of the solution was observed. Then molecular weight of protein is (assume density of solution is 1.0 g cm^{-3})

(*a*) 9.4×10^5 (*b*) 5.4×10^5
(*c*) 5.4×10^{10} (*d*) 9.4×10^{10}

(UP CPMT, 2010) Ans. (*b*)

10. At same temperature, which pair of the following solutions are isotonic ?

(*a*) 0.2 M $BaCl_2$ and 0.2 M urea
(*b*) 0.1 M urea and 0.1 M NaCl
(*c*) 0.1 M NaCl and 0.1 M K_2SO_4
(*d*) 0.1 M $Ba(NO_3)_2$ and 0.1 M Na_2SO_4

(UP CPMT, 2010) Ans (*d*).

11. 0.01 molar solution of NaI is found to be isotonic with 0.016 solution of glucose. The apparent degree of ionisation of NaI is :

(*a*) 85 % (*b*) 90 %
(*c*) 95 % (*d*) 60 % **[Ans. (*d*)]**

12. Calculate the boiling point of a solution containing 20 g of an organic compound (molar mass, 78 g mol^{-}) and 400 g water, when the barometer shows the boiling point of water at 99.834°C (K_b = 0.513°C kg mol^{-}) **[Ans 100.163°C]**

13. 0.561 M solution of an unknown electrolyte depresses the freezing point of water by 2.93°C. What is the vant's Hoff factor for this electrolyte. K_f for water is 1.86°C kg mol^{-}. **[CBSE (F), 2012]**

Hints: $\Delta T_f = k_f \times m = 1.86 \times 0.561 = 1.04$°C; ΔT_f observed = 2.93°C (given)

$\therefore$ $i = \Delta T_f\text{(observed)}/\Delta T_f\text{(calculated)} = 2.93/1.04$

= **2.82 Ans.**

14. If the solubility of a gas, A in water at N.T.P. and 0.95 bar is 0.15 m, calculate the Henry law constant. **[CBSE (D), 2012]**

Hint. ${}^{n}H_2O = 1000/18 = 55.5; {}^{n}A = 0.15;$

${}^{x}A = 0.15/(0.15 + 55.5) = 2.69 \times 10^{-3}$

But $p_A = k_H \times x_A$; ∴ $0.95 = K_H \times 2.69 \times 10^{-3}$;

$K_H = 353.2$ bar

15. Find the amount of CO_2 gas in 250 mL of soda water when packed under 3.0 atm CO_2 at 25°C (K_H for CO_2 in $H_2O = 1.67 \times 10^8$ Pa) **[CBSE (F), 2012]**

Hint. Mass of $H_2O = V \times d = 250 \times 1 = 250$ g ; ${}^{n}H_2O = 250/18 = 13.89$

$${}^{x}CO_2 = \frac{3.0 \times 10^5\ Pa}{1.67 \times 10^8\ Pa} = 1.8 \times 10^{-3};$$

$${}^{x}CO_2 = \frac{{}^{n}CO_2}{{}^{n}H_2O + {}^{n}CO_2} \simeq \frac{{}^{n}CO_2}{{}^{n}H_2O}$$

∴ ${}^{n}CO_2 = {}^{x}CO_2 \times {}^{n}H_2O = 1.8 \times 10^{-3} \times 13.89 = 0.025$ mol

∴ Amount of $CO_2 = {}^{n}CO_2 \times$ molar mass of CO_2 $= 0.025 \times 44 =$ **1.1 g** Ans.

16. Air contains about 20% O_2 and 79% N_2 by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. at 298 K. If Henry's law constant. K_H for O_2 is 3.3×10^7 mm and for N_2 is 6.51×10^7 mm, then calculate the composition of these gases in water at the same temperature.

Hint: $p_{O_2} = 10 \times \frac{20}{100} \times 760 = 1520\ mm;$

$$p_{N_2} = 10 \times \frac{79}{100} \times 760 = 6004\ mm;$$

But ${}^{x}O_2 = p_{O_2}/K_H = (1520/3.3 \times 10^7) = 4.61 \times 10^{-5}$;

${}^{x}N_2 = p_{N_2}/K_H = (6004/6.51 \times 10^7) = 9.22 \times 10^{-5}$. **Ans.**

19
CHAPTER

Electrochemistry

19.1 SOME IMPORTANT TERMS

Ohm's law. This law relates current (I) in amperes to the potential difference (E) in volts applied across the conductor and the electric resistance (R) of the conductor.

Mathematically : $I = \frac{E}{R}$.

Resistance. Resistance (R) is that which measures the obstruction to the flow of current. Mathematically :

$$R = \frac{\rho \times l}{a}$$

where ρ = **specific resistance** or **resistivity,** l = length of the conductor (in cm) and a = area of cross-section of the conductor (in cm^2).

Unit of resistance = ohm or Ω

Specific resistance or resistivity (ρ). We know that

$$R = \frac{\rho \times l}{a}$$

when, l = 1 cm, a = 1 cm^2, then $R = \rho$. Thus :

Specific resistance may be defined as the resistance of a conductor having length 1 cm and area of cross-section equal to 1 cm^2.

Units. C.G.S. units = ohm cm ; SI units = ohm metre or Ω m which is the resistance of a 1 m^3 of a conductor (or a conductor having length 1 metre and area of cross-section equal to 1 metre^2)

Conductance (C). It is the ease with which the electricity flows through the conductor. Mathematically :

$$C = \frac{1}{R}$$

Units. C.G.S. units = Ohm^{-} or mho ; **S.I. Units** = Siemens (S) and is expressed as Ω^{-}.

Specific conductance (**or conductivity** as recommended in IUPAC system), ***K***. It is the reciprocal of resistivity (ρ). Mathematically.

$$K = \frac{1}{\rho} = \frac{1}{R} \cdot \frac{l}{a}$$

= conductance × cell constant.

The cell constant $\frac{l}{a}$ depends upon the dimensions of the cell. It is denoted by C^*.

Since K = Conductance × $\frac{l}{a}$. So, when l = 1 cm, a = 1 cm^2, then ***K* = conductance**.

Hence specific conductance or conductivity (K) is equal to the conductance of a conductor having length 1 cm and area of cross - section equal to 1 cm^2.

Units. C.G.S. units = $\text{ohm}^{-}\,\text{cm}^{-}$ or S cm^{-} ; S.I. units = S m^{-} or $\Omega^{-}\,m^{-}$

In S.I. units, conductivity of a material (in $S\,m^{-}$) is the conductance of a material having length 1 m and area of cross - section 1 m^2.

$$1\,S\,cm^{-} = 100\,S\,m^{-}$$

Molar conductivity, $\wedge$ **(*lambda*) or** $\wedge_m$. It is defined as the molar conductance of all the ions produced by dissolving 1 g mol of an electrolyte in solution. **Mathematically:**

Molar Conductivity,

$$\wedge_m = \frac{K}{\text{Concentration}, C} = \frac{\text{Conductivity } (S\,\text{m}^{-})}{\text{Concentration (mol m}^{-3})}$$

Unit. $\text{Sm}^2\,\text{mol}^{-} = 10^4\,\text{S cm}^2\,\text{mol}^{-}$

$$\text{Or}\wedge_m\,(\text{S cm}^2\,\text{mol}^{-}) = \frac{K\,(S\,\text{cm}^{-}) \times 1000\,\frac{\text{cm}^3}{L}}{\text{Molarity}\left(\frac{\text{mol}}{L}\right)}$$

Also : $1\,S\,\text{m}^2\,\text{mol}^{-} = 10^4\,S\,\text{cm}^2\,\text{mol}^{-}$

or $1\,S\,\text{cm}^2\,\text{mol}^{-} = 10^{-4}\,S\,\text{m}^2\,\text{mol}^{-}$

Equivalent conductance, $\wedge$. It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte. Mathematically :

Equivalent conductance, $\wedge$ = **Specific conductance** (K) × Volume (cc). **Or** $\wedge = K \times V$ where V is the volume of the solution in c.c. which contains 1 g. equivalent of the electrolyte.

$$\text{Also :} \qquad \wedge = \frac{K\,(\text{in ohm}^{-}\,\text{cm}^{-}) \times 1000\,\text{cm}^3\,\text{L}^{-}}{\text{Normality}\,(\text{in g. eq. L}^{-})}$$

Units. C.G.S. units = $S\ cm^2\ (g.\ eq)^-$; S.I. units = $ohm^-\ m^2\ (g.\ eq)^-$ [∵ $S = ohm^-$]

Relation between $\wedge_m$ (molar conductance) and $\wedge$ (equivalent conductance).

$$\wedge_m = \wedge \times Z$$

Where Z = Total positive or negative charge per formula unit of electrolyte. *e.g.*, in case of

$Mg^{2+}\ (SO_4)^{2-}$, Z = 2.

Cell constant, $\frac{l}{a}$

$$= \frac{\text{Specific conductance or conductivity } (K) \text{ of } {}^{N}\!/_{50} \text{ KCl solution at 298 K}}{\text{Conductance of } {}^{N}\!/_{50} \text{ KCl from experiment}}$$

or Cell constant, $\frac{l}{a} = \frac{0.002765}{x}$;

Unit of cell constant

$$= \frac{\text{Length (cm)}}{\text{area}\left(cm^2\right)} = cm^-.$$

Ionic mobility $= \frac{\text{Ionic conductance of ion}}{96500}$ where ionic conductance = Transport number of ion.

19.2 SPECIFIC RESISTANCE

$$\text{Specific resistance} = \frac{1}{\text{Specific conductance}}$$

Example 1. *Two electrolytic solutions of substances A and B have 0.1 M concentration and respective specific conductances, 4.7×10^{-4} and 3.5×10^{-2} $ohm^-\ cm^-$. Which of these offers more resistance for the flow of current and which one is a stronger electrolyte ?*

Solution. We know that :

$$\text{Specific resistance, } \rho = \frac{1}{\text{Specific conductance } (K)}$$

For substance A : $\rho = \frac{1}{K}$

$$= \frac{1}{4.7 \times 10^{-4}\ ohm^- cm^-}$$

$$= 2127.66 \text{ ohm cm}$$

For substance, B : $\rho = \frac{1}{K}$

$$= \frac{1}{3.5 \times 10^{-2}\ ohm^- cm^-}$$

$$= 28.57 \text{ ohm cm}$$

Since the substance A offers more resistance (2127.66 ohm cm) than B, it is a weaker electrolyte and has less conductance. So, B is a stronger electrolyte.

19.3 SPECIFIC CONDUCTANCE AND MOLAR CONDUCTANCE

Type. (*i*) **Specific conductance** (K) = Conductance (C) × Cell constant $\left(\frac{l}{a}\right)$.

(*ii*) **Molar conductance,**

$$\wedge_m = \frac{K\left(ohm^-\ cm^-\right) \times \frac{1000\ cm^3}{L}}{\text{Molarity}\ (mol/L)}$$

Example 2. *The measured resistance of a conductance cell containing 7.5×10^{-3} M solution of KCl at 25 °C was 1005 ohm. Calculate (a) specific conductance (b) molar conductance of the solution. Cell constant = 1.25 cm^-* **(CBSE, 2002)**

Solution. R = 1005 ohm ; Molarity = 7.5×10^{-3} mol L^-; cell constant = 1.25 cm^-. We know that:

(*a*) Conductance, $C = \frac{1}{R} = \frac{1}{1005\ ohm}$;

Cell constant = 1.25 cm^-

∴ Specific conductance, K = Conductance × Cell constant

$$= \frac{1}{1005\ ohm} \times 1.25\ cm^-$$

$$= \mathbf{1.24 \times 10^{-3}\ ohm^-\ cm^-}$$

Ans.

(*b*) Molar conductance,

$$\wedge_m = \frac{K \times \frac{1000\ cm^3}{L}}{7.5 \times 10^{-3}\ mol/L}$$

$$= \frac{1.24 \times 10^{-3}\ ohm^-\ cm^- \times 1000\ cm^3}{7.5 \times 10^{-3}\ mol}$$

$$= \mathbf{165.3\ ohm^-\ cm^2\ mol^-}$$

Ans.

Example 3. *The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol$^-$. Calculate the conductivity of the solution.* **(ISC, 2011)**

Solution. $\wedge_m$ = 138.9 S cm^2 mol$^-$;

Conductivity, K = ?,

Molarity of solution = 1.5 mol L^-.

We know:

$$\wedge_m = \frac{K \times 100\ cm^3/L}{\text{Molarity}\ (mol\ L^-)};$$

$$138.9\ S\ cm^2\ mol^- = \frac{K \times 1000\ cm^3}{1.5\ mol\ L^- \times L}$$

$$\therefore \quad K = \frac{138.9\ S\ cm^2\ mol^- \times 1.5\ mol}{1000\ cm^3}$$

$$= 0.2084\ S\ cm^-$$

Ans.

19.4 EQUIVALENT CONDUCTANCE

Type. Equivalent conductance,

$$\wedge = \frac{\text{Specific conductance } (K) \times 1000\ cm^3}{\text{Normality}}$$

Example 4. *Calculate the equivalent conductivity of 1 M H_2SO_4 solution, if its conductivity is 26×10^{-2} $ohm^-\ cm^-$ (at. wt. of sulphur = 32)* **(CBSE, 1991)**

Solution. Molarity of

$$H_2SO_4 = 1\text{ M};$$

mol. wt. of $H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98\text{ g mol}^{-}$;

Eq. wt. of

$$H_2SO_4 = \frac{\text{Mol. wt.}}{2} = \frac{98}{2} = 49\text{ g. equiv}^{-}.$$

But Normality × Eq. Wt.

= Molarity × mol. wt.

∴ Normality of

$$H_2SO_4 = \frac{\text{Molarity} \times \text{mol. wt.}}{\text{Eq. wt.}}$$

$$= \frac{1\text{ mol L}^{-} \times 98\text{ g mol}^{-}}{49\text{ g. equiv}^{-}}$$

$$= 2\text{ eq. L}^{-}$$

∴ Equivalent conductivity,

$$\wedge = \frac{K \times \dfrac{1000\text{ cm}^3}{L}}{\text{Normality}}$$

$$= \frac{26 \times 10^{-2}\text{ ohm}^{-}\text{ cm}^{-} \times 1000\text{ cm}^3\text{ L}^{-}}{2\text{ g. equiv L}^{-}}$$

$$= \mathbf{130\ ohm^{-}\ cm^{2}\ (g.\ equiv)^{-}} \qquad \textbf{Ans.}$$

Example 5. *0.05 M NaOH solution offered a resistance of 31.6 ohm in a conductivity cell at 298 K. If the cell constant of the cell is 0.367 cm⁻, calculate the molar conductivity of the sodium hydroxide solution.* **(DSB, 1994)**

Solution. Specific conductance (K)= Conductance × Cell constant ... (1)

$$\text{Conductance} = \frac{1}{R} = \frac{1}{31.6\text{ ohm}};$$

$$\text{Cell constant} = 0.367\text{ cm}^{-}$$

Substituting the values in equation (1), we get :

$$K = \frac{1}{31.6\text{ ohm}} \times 0.367\text{ cm}^{-} \qquad \text{... (2)}$$

Also, molar conductivity,

$$\wedge_m = \frac{K \times 1000\text{ cm}^3\text{ L}^{-}}{\text{Molarity (mol/}L\text{)}}$$

$$= \frac{1}{31.6\text{ ohm}} \times \frac{0.367\text{cm}^{-} \times 1000\text{ cm}^3\text{/L}}{0.05\text{ mol/L}}$$

$$= \mathbf{232.3\ ohm^{-}\ cm^{2}\ mol^{-}} \qquad \textbf{Ans.}$$

Example 6. *The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10⁻³ S cm⁻ ?* **(CBSE, 2007)**

Solution. We know that conductivity,

$$K = \frac{1}{\text{Resistance, }R} \times \text{Cell constant}\left(\frac{l}{a}\right)$$

$$R = 1500\ \Omega = 1500\text{ ohm};$$

$$K = 0.146 \times 10^{-3}\text{ S cm}^{-}$$

$$= 0.146 \times 10^{-3}\text{ ohm}^{-}\text{ cm}^{-}$$

$$\therefore \quad \text{Cell constant} = K \times R = 0.146 \times 10^{-3}\text{ ohm}^{-}\text{ cm}^{-} \times 1500\text{ ohm}$$

$$= \mathbf{0.219\ cm^{-}} \qquad \textbf{Ans.}$$

19.5 SOME TYPICAL EXAMPLES

Example 7. *A resistance of 0.01 N NaCl solution at 25° is 200 Ω. Cell constant of the conductivity cell is unity. Calculate the equivalent conductance of the solution.* **(CBSE, 1992)**

Solution. Normality = 0.01 N ; resistance, R = 200 Ω ; Cell constant = 1 ; equivalent conductance ($\wedge_{eq}$) = ? . Specific conductance, K = Cell constant/Resistance = 1 cm⁻/200 Ω = 0.005 cm⁻ Ω⁻. We know $\wedge_{eq}$ = (K × 1000 cm³)/ normality = (0.005 cm⁻ Ω⁻ × 1000 cm³)/0.01 = **500 cm² Ω⁻** **Ans.**

Example 8. *The conductivity of 0.2 M solution of KCl at 298 K is 0.0248 S cm⁻. Calculate its molar conductivity in this solution.* **(CBSE, 2008)**

Solution. Molarity of solution, M = 0.2 M; Conductivity, K = 0.0248.5 cm⁻ = 0.0248 ohm⁻ cm⁻. But

$$\text{Molar conductivity, } \mu \text{ or} \wedge_m = \frac{K \times 1000}{M}\text{ohm}^{-}\text{ cm}^{2}\text{ mol}^{-}$$

$$= \frac{0.0248 \times 1000}{0.2}$$

$$= 124.05\text{ ohm}^{-}\text{ cm}^{2}\text{ mol}^{-} \qquad \textbf{Ans.}$$

Example 9. *Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 Ω and conductivity of 0.1 M KCl is 0.0129 S cm⁻. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 M KCl solution. (Conductivity of 0.1 M KCl = 1.29 S m⁻).*

Solution. (*i*) We know, cell constant = conductivity × resistance; or cell constant = 1.29 S m⁻ × 100 Ω = 129 m⁻. Thus, conductivity of 0.02 M KCl = cell constant/resistance = 129 m⁻/ 520 Ω = **0.248 S m⁻** **Ans.**

(*ii*) Given concentration = 0.02 mol L⁻ = 1000 × 0.02 mol m⁻³ = 20 mol m⁻³. But molar conductivity = conductivity/concentration. Thus molar conductivity = 0.248 *S m*⁻/20 mol *m*⁻³ = 124 × 10⁻⁴ *S m*² mol⁻

Example 10. *0.5 N solution of a salt placed between two Pt electrodes 2.0 cm apart and having area of cross-section 2.5 cm² has resistance of 25 ohms. Calculate the conductance and cell constant.*

Solution. (*i*) Resistance, R = 25 ohms. Hence conductance = 1/R = 1/25 ohm = 0.04 ohm⁻ **Ans.**

(*ii*) Cell constant = length/ (area of cross-section of electrode) = 2 cm/2.5 cm² = 0.8 cm⁻ **Ans.**

Example 11. *Conductivity of a solution containing one gram of anhydrous BaCl₂ in 200 ml of the solution has been found to be 0.00585 ohm⁻ cm⁻. Calculate the equivalent as well as molar conductance.*

Solution. Conductivity (K) = 0.00585 ohm⁻ cm⁻., wt. of $BaCl_2$ = 1 g ; Volume of solution = 200 mL ; g. mol. wt. of $BaCl_2$ = 137 + (2 × 35.5) = 208 g. So, molarity of $BaCl_2$ solution = (wt × 1000)/(g. mol. wt × vol. of solution in mL).

= (1 × 1000)/(208 × 200) = (5/208) M. We know molar conductance, $\wedge_m$ = (K × 1000 cm³) /Molarity. Substituting the values, we get. $\Lambda_m = (0.00585\ \text{ohm}^{-}\ \text{cm}^{-} \times 1000\ \text{cm}^3)\ (5/208) = 243.36\ \text{ohm}^{-}\ \text{cm}^2\ \text{mol}^{-}$. **Ans.** Also, Λ_m = equivalent conductance (Λ) × Z where Z = total positive or negative charge per formula unit of electrolyte $Ba^{2+}\ (Cl^{-})_2 = 2$. Substituting the values, we get, $243.36\ \text{ohm}^{-}\ \text{cm}^2\ \text{mol}^{-} = \Lambda \times 2$. Thus . $\Lambda = 243.36\ \text{ohm}^{-}\ \text{cm}^2/2 = 121.68\ \text{ohm}^{-}\ \text{cm}^2\ (\text{equiv})^{-}$.

EXAMPLE 12. *Calculate the resistivity, conductivity and molar conductivity of a 0.05 M NaOH solution if the resistance of its column having diameter 1 cm and length 50 cm is 5.55×10^3 ohm.*

SOLUTION. Radius, r = diameter/2 = 1 cm/2 = 0.5 cm ; resistance, $R = 5.55 \times 10^3$ ohm; length, l = 50 cm. We know, Area, $A = \pi r^2 = 3.14 \times (0.5\ \text{cm})^2 = 0.785\ \text{cm}^2$

(*i*) Resistivity, $\rho = RA/\rho = 5.55 \times 10^3\ \text{ohm} \times 0.785\ \text{cm}^2/50\ \text{cm}$ = **87.135 ohm cm** **Ans.**

(*ii*) Conductivity, $K = 1/\rho = 1/87.135\ \text{ohm cm} = 0.01148\ \text{ohm}^{-}\ \text{cm}^{-}$.

(*iii*) Molar conductivity, $\Lambda_m = K \times 1000\ \text{cm}^3$ / molarity $= 0.01148\ \text{ohm}^{-}\ \text{cm}^{-} \times 1000\ \text{cm}^3/0.05 = 229.6\ \text{ohm}^{-}\ \text{mol}^{-}\ \text{cm}^2$ **Ans.**

EXAMPLE 13. *Molar conductance of 1.5 M solution of electrolyte is found to be 138.9 S cm^2. What would be the specific conductance for this solution ?* **(DSB, 2001)**

SOLUTION. Molar conductance, $\Lambda_m = 138.9\ \text{S cm}^2$; molarity = 1.5 mol L^{-}. Specific conductance, K = ?

We know that: $\Lambda_m = \dfrac{K \times 1000\ \text{cm}^3/L}{\text{Molarity (mol}/L)}$.

$$\text{Thus } K = \frac{\Lambda_m \times \text{molarity}}{1000\ \text{cm}^3}$$

$$\text{or} \qquad K = \frac{138.9\ \text{S cm}^2\ \text{mol}^{-} \times 1.5\ \text{mol L}^{-}}{1000\ \text{cm}^3/L}$$

$$= \mathbf{0.208\ S\ cm^{-}} \qquad \textbf{Ans.}$$

19.6 KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

According to Kohlrausch's law, at infinite dilution, the molar conductance of an ion is independent of the nature of the other ion with which it is associated in the electrolyte and the limiting conductance (λ_m^{∞}) of an electrolyte is the sum of limiting molar conductances of its cation and anion.

Mathematically :

Λ_m^{∞} **(for electrolyte)** = $\lambda_+^{\infty} + \lambda_-^{\infty}$.

Similarly : $\Lambda_m^{\infty} = v_+ \lambda_+^{\infty} + v_- \lambda_-^{\infty}$ where

v_+ and v_- are the number of cations and anions per formula unit of electrolyte and λ_+^{∞} and λ_-^{∞} are the ionic conductances of cation and anion respectively.

Applications of Kohlrausch's law.

(*i*) It helps to calculate molar conductances of weak electrolytes at infinite dilution. e.g.,

$$\Lambda_m^{\infty}(CH_3COOH) = \lambda^{\infty}(CH_3COONa) + \lambda^{\infty}(HCl) - (\lambda^{\infty}NaCl)$$

$$= \lambda^{\infty}{}_{CH3COO^-} + \lambda^{\infty}_{Na^+} + \lambda^{\infty}_{H^+} + \lambda^{\infty}{}_{Cl^-} - \lambda^{\infty}{}_{Na^+} - \lambda^{\infty}{}_{Cl^-}$$

Since λ^{∞} for strong electrolytes such as CH_3COO^- Na, HCl and NaCl are known, λ^{∞} of weak electrolytes like CH_3COOH can be calculated.

(*ii*) It helps to calculate degree of dissociation (α) of weak electrolytes. Also, if α is known, the dissociation constant Kc of weak electrolytes like NH_4OH, CH_3COOH, etc., can be calculated from the following relation:

$$(i)\ \ \alpha_c = \frac{\Lambda_m^c}{\Lambda_m^{\infty}} \quad \text{and} \qquad (ii)\ \ K_c = \frac{C\alpha^2}{1-\alpha}$$

where Λ_m^c = molar conductivity of the electrolyte at concentration, C and

α_c = Degree of dissociation at concentration, C.

EXAMPLE 14. *The molar conductivity of NH_4Cl at infinite dilution is 149.7 ohm^{-1} cm^2 mol^{-1} and ionic conductances of hydroxyl ions and chloride ions are 198 and 76.3 respectively. Calculate the molar conductivity of NH_4OH at infinite dilution.*

SOLUTION. Molar conductance at infinite dilution of NH_4Cl *i.e.,*

$$\Lambda°NH_4Cl = 149.7\ \text{ohm}^{-}\ \text{cm}^2\ \text{mol}^{-}\ ;$$
$$\lambda°\ OH^- = 198\ ;$$
$$\lambda°\ Cl^- = 76.3\ ;\ \Lambda°NH_4OH\ ?$$

We know that $\Lambda°\ NH_4OH$

$$= \{\Lambda\ °NH_4Cl - \lambda\ °Cl^- + \lambda\ °OH^-\}.$$

Substituting the values, we get :

$$\Lambda°NH_4OH = 149.7 - 76.3 + 198$$
$$= \mathbf{271.4\ ohm^{-}\ cm^2\ mol^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 15. *Calculate $\Lambda°$ for $CaCl_2$ and $Mg\ SO_4$ from the following data :*

$$\lambda°\ Ca^{2+} = 119.0\ S\ cm^2\ mol^{-};$$
$$\lambda°\ Mg^{2+} = 106.5\ cm^2\ mol^{-}$$
$$\lambda°\ Cl^{-} = 76.3\ S\ cm^2\ mol^{-}\ ;$$
$$\lambda°\ SO_4^{2-} = 160.0\ S\ cm^2\ mol^{-}$$

SOLUTION. (*i*) According to Kohlrausch's law,

$$\Lambda°CaCl_2 = \lambda\ °Ca^{2+} + 2\ \lambda\ °Cl^-.$$

Substituting the values, we get,

$$\Lambda°CaCl_2 = 119.0 + 2\ (76.3)\ \text{S cm}^2\ \text{mol}^{-}$$
$$= 119 + 152.6$$
$$= 271.6\ \text{S cm}^2\ \text{mol}^{-} \qquad \textbf{Ans.}$$

$$(ii) \qquad \Lambda°\ Mg\ SO_4 = \lambda\ °\ Mg^{2+} + \lambda°\ SO_4^{2-} = 106 + 160$$
$$= \mathbf{266\ S\ cm^2\ mol^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 16. *Calculate the value of equivalent conductivity of $MgCl_2$, at infinite dilution if $\lambda^{\infty}(Mg^{2+}) = 106.12$ ohm^{-} cm^2 mol^{-}, $\lambda^{\infty}(Cl^{-}) = 76.34$ ohm^{-} cm^2 mol^{-}.*

SOLUTION. (*i*) According to Kohlrausch's law,

$$\Lambda_m^{\infty}(MgCl_2) = \lambda^{\infty}(Mg^{2+}) + 2\lambda^{\infty}\ Cl^-.$$

Substituting the values, we get :

$$\Lambda_m^{\infty} = 106.12 + 2\ (76.34)\ \text{ohm}^{-}\ \text{cm}^2\ \text{mol}^{-}$$
$$= 106.12 + 152.68$$
$$= 258.80\ \text{ohm}^{-}\ \text{cm}^2\ \text{mol}^{-}.$$

(*ii*) But $\Lambda^{\infty}_{eq} = \Lambda^{\infty}_{m}/Z$
where Z = number of positive or negative charges per formula unit.
Z for $MgCl_2 \longrightarrow Mg^{2+} + 2\,Cl^-$ is 2.
Hence, $\Lambda^{\infty}\,eq = 258.8/2 =$ **129.4 ohm⁻ cm² mol⁻** **Ans.**

Example 17. *The conductivity of 0.001028 M acetic acid is* 4.95×10^{-5} *S cm⁻. Calculate its dissociation constant if* $\Lambda°$ *for acetic acid is 390.5 S cm² mol⁻.*

Solution. Hint.

We know that
$$\Lambda_m = \frac{K \times 1000\ \text{cm}^3/L}{\text{Molarity (mol}/L)}$$
$$= \frac{4.95 \times 10^{-5}\ \text{S cm}^- \times 1000\ \text{cm}^3}{0.001028\ \text{mol}}$$
$$= 48.15\ S\ \text{cm}^2\ \text{mol}^-$$

But
$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{48.15\ \text{S cm}^2\ \text{mol}^-}{390.5\ \text{S cm}^2\ \text{mol}^-} = 0.123$$

Also, dissociation constant,
$$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.001028 \times (0.123)^2}{1 - 0.123 = 0.877}$$
$$= \mathbf{1.77 \times 10^{-5}}$$ **Ans.**

Example 18. *At 18°C, the equivalent conductivities at infinite dilution of* NH_4Cl*, NaOH and NaCl are 129.8, 217.4 and 108.9* Ω^{-1} *cm²(g. eq)⁻¹. If the equivalent conductance of a centinormal solution of* NH_4OH *is 9.33* Ω^- *cm² (g. eq)⁻¹, what is the percentage dissociation of* NH_4OH *at this dilution ?*

Solution. Equivalent conductance at infinite dilution, in Ω^- cm² (*g. eq*)⁻, for $\Lambda°\ NH_4Cl = 129.8$; $\Lambda°$ NaOH = 217.4 ; $\Lambda°$ NaCl= 108.9. Equivalent conductance of 0.1 N solution of NH_4OH *i.e.* Λ for $NH_4OH = 9.3\ \Omega^-$ cm² (*g. eq*)⁻. We know that $\Lambda°\ NH_4OH = \Lambda°\ NH_4Cl - \Lambda°\ NaCl + \Lambda°\ NaOH$. Substituting the values, we get : $\Lambda°\ NH_4OH = 129.8 - 108.9 + 217.4 = 283.3\ \Omega^-$ cm² (*g.* eq)⁻. Percentage dissociation of NH_4OH = [$\Lambda\ NH_4OH/\ \Lambda°\ NH_4OH$] × 100 = (9.33 × 100)/ 283.3 = **3.92 %** **Ans.**

Example 19. *The resistance of 0.01 M* CH_3COOH *solution was found to be 2220 ohm in a conductivity cell having cell constant 0.366 cm⁻¹. Calculate : (i) molar conductivity* (Λ_m) *of 0.01 M* CH_3COOH *(ii)* Λ^{∞}_m *(iii) degree of dissociation, α and (iv) dissociation constant of the acid.* $\lambda°\ (H^+) = 340.1$ *ohm⁻¹ cm² mol⁻¹,* $\lambda°\ (CH_3COO^-) = 40.9$ *ohm⁻ cm² mol⁻.*

Solution. (*i*) Molar conductance, Λ_m = cell constant × 1000 cm³/(molarity × resistance). Given, cell constant = 0.366 cm⁻ ; R = 2220 ohm ; molarity = 0.01 *M*. Substituting the values, we get : Λ_m = (0.366 cm⁻ × 1000 cm³)/0.01 × 2220 ohm. = 16.48 ohm⁻ cm² mol⁻. **Ans.** (*ii*) Molar conductance at infinite dilution, $\Lambda^{\infty}_m = \lambda^{\infty}\ CH_3COO^- + \lambda^{\infty}\ H^+$ = 40.9 ohm⁻ cm² mol⁻ + 349.1 ohm⁻ cm² mol⁻ = 390 ohm⁻ cm² mol⁻. **Ans.** (*iii*) Degree of dissociation, $\alpha = \Lambda_m/\Lambda^{\infty}$ = 16.48 ohm⁻ cm² mol⁻/ 390 ohm⁻ cm² mol⁻ = 0.0422 **Ans.** (*iv*) Dissociation constant, $K = C\,\alpha^2 / (1 - \alpha)$. Substituting the values, we get : $K = 0.01 \times (0.0422)^2/(1 - 0.0422)$ = **1.86 × 10⁻⁵ mol L⁻** **Ans.**

Example 20. *At infinite dilution, the molar conductances of* Na^+ *and* SO_4^{2-} *ions are 50 S cm² mol⁻ and 60 S cm² mol⁻ respectively. What will be the molar conductance of sodium sulphate at infinite dilution.* **(CBSE, 2000 S)**

Solution. $Na_2SO_4 \rightleftharpoons 2\,Na^+ + SO_4^{2-}$
$$\therefore\ \Lambda_m^{\circ}\,(Na_2\,SO_4) = 2\,\lambda°\,Na^+ + \lambda°\,SO_4^{2-}$$
$$= (2 \times 50) + 160$$
$$= \mathbf{260\ S\ cm^2\ mol^-}$$ **Ans.**

Example 21. *The conductivity of NaCl at 25°C has been found at different concentrations as given below :*

Concentration/M	*0.1*	*0.01*	*0.02*
10² × K/S m⁻	*106.74*	*11.85*	*23.15*

Calculate the value of Λ *for all concentrations.*

Solution. (*i*) $\Lambda_{m_1}\ (m_1 = 0.1\,M)$
$$= \frac{K\,(S\ \text{m}^-)}{\text{molarity}\left(\text{mol L}^-\right) \times 1000\ \text{L m}^{-3}}$$
$$= \frac{106.74 \times 10^{-2}}{0.1 \times 1000}$$
$$= 106.7 \times 10^{-4}\,S\ \text{m}^2\ \text{mol}^-$$

(*ii*) $\Lambda_{m_2}\ (m_2 = 0.01\,M)$
$$= \frac{11.85 \times 10^{-2}}{0.01 \times 1000}$$
$$= 11.85 \times 10^{-3}\ \text{S m}^2\ \text{mol}^-$$

(*iii*) $\Lambda_{m_3}\ (m_3 = 0.02\,M)$
$$= \frac{23.15 \times 10^{-2}}{0.02 \times 1000}$$
$$= \mathbf{115.7 \times 10^{-4}\ S\ m^2\ mol^-}$$ **Ans.**

19.7 SOME IMPORTANT TERMS REGARDING ELECTROCHEMICAL CELLS

Electrode. A metal rod dipped in the solution of its own ions is called an electrode and constitutes half-reaction.

Electrochemical cell. A cell or a device in which the energy liberated during a redox reaction is obtained in the form of electric current is called an **electrochemical cell** or **Galvanic cell** or **Voltaic cell**.

Anode. It is an electrode at which oxidation takes place *i.e.*, at which loss of electrons takes place. It is given negative sign in an electrochemical cell.

Cathode. It is an electrode at which reduction takes place *i.e.*, at which gain of electrons takes place. It is given a positive sign in an electrochemical cell.

Oxidation half-reaction. It is the half-reaction at which oxidation takes place.

Reduction half-cell. It is the half-cell at which reduction takes place.

Cell reaction. The reaction obtained by the addition of oxidation half-cell and reduction half-cell is called the cell reaction.

Electrode potential. The tendency of an electrode to lose or gain electrons is called electrode potential.

Oxidation potential. The tendency of an electrode to lose electrons or get oxidised is called oxidation potential *e.g.*, $Mg\ (s) \rightleftharpoons Mg^{2+} + 2\ e^-$; $E°$ oxidation = 2.37 V

Reduction potential. *The tendency* of an electrode to gain *electrons* or get reduced is called reduction potential. *e.g.*, $Mg^{2+} + 2\ e^- \rightleftharpoons Mg$; $E°$ reduction = – 2.37 V

Thus oxidation potential with sign changed gives the value of reduction potential, of an electrode. *e.g.*, Oxidation potential of Zn/Zn^{2+} (1.0 M) = 0.76 V at 25 °C. Hence : Reduction potential of Zn^{2+} (1.0M)/Zn = – 0.76 V at 25 °C.

Reduction potential of an electrode α concentration of ion.

Oxidation potential of an electrode α $\dfrac{1}{\text{Concentration of ion}}$. The electrode potential of standard hydrogen electrode is taken as zero.

Cell potential, $E_{cell} = E_{cathode} - E_{anode}$
Electrode potential is the reduction potential value of an electrode when dipped in its electrolyte in a half-cell.

E.M.F or **emf.** *It is the potential* difference between *two electrodes of the cell when the cell is not sending any current through the circuit.* It is the maximum voltage obtained from the cell and is responsible for the flow of steady current in the cell.

Potential difference. *It is the potential difference between two electrodes of the cell when the cell is sending current* through the circuit. It is less than emf of the cell and is not responsible for the flow of steady current in the cell.

Standard cell potential, $E°_{cell} = E°_{cathode} - E°_{anode}$

Calculation of emf (or E_{cell}) of a cell

$$\begin{aligned}\text{e.m.f or } E_{cell} &= [\text{Oxidation potential of anode + Reduction potential of cathode}]\\ &= E_{\text{anode (oxid.)}} + E_{\text{cathode (Reduction)}}\\ &= -\ E_{\text{anode (Reduction)}} + E_{\text{cathode (Reduction)}}\\ &= E_{\text{cathode (reduction)}} - E_{\text{anode (reduction)}}\\ &= E_{\text{(Right)}} - E_{\text{left}} \text{ where } E \text{ represents potential}\end{aligned}$$

Note. In order to calculate the cell potential :

(*i*) Write first of all half-cell reaction with higher value of reduction potential value (*i.e.*, $E°_{cathode}$). Now write the half-cell reaction with lower value of reduction potential value (*i.e.*, $E°_{anode}$). Now subtract the second half-cell from first half-cell and get E_{cell} or $E°_{cell}$ which will be always positive. **A cell reaction is feasible if E_{cell} or $E°_{cell}$ (standard) value is positive. (– 1) > (– 2) but (+ 2) > (– 1)**

(*ii*) While balancing electrons in both the half-cells, never multiply the $E°$ reduction potential value of an electrode with any integer.

(*iii*) **$E°_{cell} = E°_{cathode}$ (reduction) – $E°_{anode}$ (reduction).** In order to know which electrode is anode and which one is cathode, inspect as follows :

Consider the following cell.

Zn/Zn^{2+} (1 M) || Cu^{2+} (1 M)/Cu

Here $Zn \rightleftharpoons Zn^{2+} + 2e^-$ (oxidation). So, Zn/Zn^{2+} (1 M) is anode

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ (reduction). So, Cu^{2+} (1 M)/Cu is cathode.

It is better to use reduction potential values for solving numericals. So, if oxidation potential value of a half-cell is given, it should be converted to reduction potential value by changing the sign of its oxidation potential value. In the above cell :

Zn/Zn^{2+} (1 M) ; $E°$ oxidation = + 0.76 V
$\therefore$ Zn^{2+} (1 M)/Zn ; $E°$ reduction = – 0.76 V

So, the half-reaction should be written as :

$Zn^{2+} + 2\ e^- \rightleftharpoons Zn$ $\quad E°_{reduction} = -\ 0.76\ V$

19.8 TO CALCULATE EMF OF CELLS ETC

Type. $$E°_{cell} = \begin{bmatrix}\text{Half-cell (reduction)}\\ \text{with higher reduction}\\ \text{potential value}\end{bmatrix} - \begin{bmatrix}\text{Half-cell (reduction)}\\ \text{with lower reduction}\\ \text{potential value}\end{bmatrix}$$

Example 22. *Write the reduction half-cell reactions of the following cell.*

Cu(s) | Cu^{2+} (1 M)|| Ag^+ (1M) | Ag (s).

Solution. (*i*) $Cu^{2+}\ (1\ M) + 2e^- \rightleftharpoons Cu$

(*ii*) $Ag^+\ (1\ M) + e^- \rightleftharpoons Ag.$

Example 23. *Find the value of e.m.f. of the following cell.*

Zn | Zn^{2+} (1 M) || Ag^+ (1 M) | Ag

$E°\ Zn/Zn^{2+} = +\ 0.76\ V$; $E°\ Ag^+/Ag = +\ 0.79\ V$

Solution. Writing half-cell (reduction) reactions of the given cell, we have :

$$\begin{aligned}Zn^{2+} + 2\,e^- &\rightleftharpoons Zn; & E° &= -0.76\ V\\ Ag^+ + e^- &\rightleftharpoons Ag; & E° &= +\ 0.79\end{aligned}$$

Since the $E°$ value + 0.7 9 V > – 0.76 V, so by writing the half-cell reaction with higher reduction potential value first, we have :

$$\begin{array}{lcll} & Ag^+ + e^- \rightleftharpoons & Ag] \times 2\ ; & E° = +\ 0.79\ V\\ & Zn^{2+} + 2\,e^- \rightleftharpoons & Zn; & E° = -\ 0.76\ V\\ \textbf{Subtract :} & -\quad - & - & \qquad + \\ \hline & Zn + 2\ Ag^+ \rightleftharpoons & Zn^{2+} + 2\ Ag\ ; & E° = \mathbf{+\ 1.55\ V}\end{array}$$

Ans.

Example 24. *A voltaic cell is set up at 25°C with the following half-cells. Al^{3+} (0.001 M) and Ni^{2+} (0.50 M). Write an equation for the reaction that occurs when the cell generates* *an electric current and determine the cell potential. (Given* $E^\circ_{Ni^{2+}/Ni} = -0.25\ V$; $E^\circ_{Al^{3+}/Al} = -1.66\ V$). **(ISC, 2010)**

Solution. Given $E^\circ_{Ni^{2+}/Ni} = -0.25\ V$; $E^\circ_{Al^{3+}/Al} = -1.66 V$. Since, $-0.25\ V > -1.66\ V$, so, the half-cell reactions can be written as:

$$\begin{array}{lrcl} & Ni^{2+} + 2e^- & \longrightarrow & Ni] \times 3;\ E^\circ = -0.25\ V \\ & Al^{3+} + 3e^- & \longrightarrow & Al] \times 2;\ E^\circ = -1.66\ V \\ \textbf{Subtracting:} & - \quad - & & - \qquad\qquad + \\ \hline & 3Ni^{2+} - 2Al^{3+} & \longrightarrow & 3Ni - 2\,Al;\ E^\circ = 1.41 V \\ \text{Or} & 3Ni^{2+} + 2Al & \longrightarrow & 3Ni + 2Al^{3+};\ E^\circ = +1.41 V \end{array}$$

Example 25. *Predict the anode and cathode in the following cell on the basis of their reduction potential value.*

$$Zn\,|\,Zn^{2+}\,(1\,M)\ \|\ Cu^{2+}\,(1\,M)\,|\,Cu$$

$$E^\circ_{Zn/Zn^{2+}} = +0.76\ V \text{ and}$$
$$E^\circ_{Cu^{2+}/Cu} = +0.34\ V.$$

Solution.
$$\begin{array}{lrcll} & Zn & \rightleftharpoons & Zn^{2+} + 2e^- & ;\ E^\circ_{(oxidation)} = +0.76\ V \\ \therefore & Zn^{2+} + 2e^- & \rightleftharpoons & Zn & ;\ E^\circ_{(reduction)} = -0.76\ V \\ & Cu^{2+} + 2e^- & \rightleftharpoons & Cu & ;\ E^\circ_{(reduction)} = +0.34\ V \end{array}$$

Since $E^\circ_{(reduction)}$ value of Zn^{2+}/Zn electrode is less ($= -0.76\ V$) than Cu^{2+}/Cu ($= +0.34\ V$), zinc electrode is anode while copper electrode is cathode.

Example 26. *Given* $E^\circ_{Zn^{2+}/Zn} = -0.76 V$; $E^\circ_{Ni^{2+}/Ni} = -0.25\ V$. *Calculate the EMF of the cell where the following reaction is taking place.*

$$Zn(s) + Ni^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Ni(s).$$

(a) 0.51V *(b)* 1.01V

(c) –0.51V *(d)* 0.25V

(DSB, 1987; Orissa JEE, 2009)

Solution. A cell reaction is possible, if E_{cell} is positive.

Since $-0.25V > -0.76\ V$, So:

$$\begin{aligned} E_{cell} &= E^\circ_{red} \text{ of Ni} - E^\circ_{red} \text{ of Zn} \\ &= -0.25V - (-0.76\ V) = +0.51V \end{aligned}$$

So, the correct answer is (*a*).

Example 27. *Using standard electrode potentials predict the reaction if any, that occurs between* $Fe^{3+}(aq)$ *and* $I^-(aq)$?

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V ; $E^\circ_{I_2/2I^-} = 0.54$ V **(PSEB, 1996)**

Solution. Required reaction :

$$Fe^{3+} + 2I^- \rightleftharpoons Fe^{2+} + I_2 \qquad ...(1)$$

$$\begin{array}{lrcll} \text{But} & [Fe^{3+} + e^- & \rightleftharpoons & Fe^{2+}] \times 2; & E^\circ_{(reduction)} = 0.77\ V \\ & I_2 + 2e^- & \rightleftharpoons & 2I^-; & E^\circ_{(reduction)} = 0.54\ V \end{array}$$

Since anode has lower reduction potential value than cathode, so we have:

$$\begin{array}{rcll} Fe^{3+} + e^- & \rightleftharpoons & Fe^{2+}] \times 2; & E^\circ_{(reduction)} = 0.77\ V \text{ (cathode)} \\ I_2 + 2e^- & \rightleftharpoons & 2I^-; & E^\circ_{(reduction)} = 0.54\ V \text{ (anode)} \end{array}$$

Subtract:

$$\begin{array}{rcll} - \quad - & & - & \\ \hline Fe^{3+} + 2I^- & \rightleftharpoons & Fe^{2+} + I_2; & E^\circ = 0.23\ V \end{array}$$

It is the same equation as equation (1). Since E° is positive, the reaction is feasible. So, reaction between $Fe^{3+}(aq)$ and $I^-(aq)$ will take place.

Type. A metal will dissolve in an acid, if the reaction between the metal and acid (H^+) is feasible *i.e.*, e.m.f. of the reaction is positive.

Example 28. *Using standard electrode potentials, predict whether copper(s) will dissolve in 1 M HCl ?*

$E^\circ_{Cu^{2+}/Cu} = 0.34\ V$; $E^\circ_{2H^+/H_2} = 0.0\ V$.

Solution. $HCl \rightleftharpoons H^+ + Cl^-$

The reaction will be :

$$Cu(s) + 2H^+ \rightleftharpoons Cu^{2+} + H_2 \qquad ...(1)$$

This reaction will be possible if E°_{cell} is positive.

$$\begin{array}{lrcll} \text{But} & Cu^{2+} + 2e^- & \rightleftharpoons & Cu; & E^\circ_{(reduction)} = 0.34\ V \\ & 2H^+ + 2e^- & \rightleftharpoons & H_2; & E^\circ_{(reduction)} = 0.00\ V \end{array}$$

Since anode has lower reduction potential value than cathode, so we have :

$$\begin{array}{lrcll} & Cu^{2+} + 2e^- & \rightleftharpoons & Cu\ ; & E^\circ = 0.34\ V \\ & 2H^+ + 2e^- & \rightleftharpoons & H_2\ ; & E^\circ = 0.00\ V \\ \textbf{Subtract :} & - \quad - & & - & - \\ \hline & Cu^{2+} + H_2 & \rightleftharpoons & Cu + 2H^+\ ; & E^\circ = +0.34\ V ...(2) \end{array}$$

In order to get reaction (1), reaction (2) has to be reversed. Thus :

$$Cu + 2H^+ \rightleftharpoons Cu^{2+} + H_2; \qquad E^\circ = -0.34\ V$$

Since e.m.f. of the cell is negative, reaction (1) is not possible. Hence Cu(*s*) will not dissolve in 1 M HCl.

Example 29. *Can silver nitrate solution be stored in a copper vessel ? Given :*

$$E^\circ_{Cu^{2+}/Cu} = +0.34\ V : E^\circ_{Ag^+/Ag} = +0.79\ V.$$

Solution. Reaction :

$$\begin{array}{lrcll} & AgNO_3 & \rightleftharpoons & Ag^+ + NO_3^- & \\ & Cu + 2Ag^+ & \rightleftharpoons & Cu^{2+} + 2Ag & ...(1) \\ \text{But} & Cu^{2+} + 2e^- & \rightleftharpoons & Cu; & E^\circ_{(reduction)} = 0.34\ V \\ & Ag^+ + e^- & \rightleftharpoons & Ag; & E^\circ_{(reduction)} = 0.79\ V \end{array}$$

Since anode has lower reduction potential value than cathode, so, we have :

$$\begin{array}{lrcll} & [Ag^+ + e^- & \rightleftharpoons & Ag] \times 2; & E^\circ = 0.79\ V \\ & Cu^{2+} + 2e^- & \rightleftharpoons & Cu; & E^\circ = 0.34\ V \\ \textbf{Subtract :} & - \quad - & & - & - \\ \hline & 2Ag^+ + Cu & \rightleftharpoons & 2Ag + Cu^{2+}\ ; & E^\circ = +0.45\ V \\ & & & & ...(2) \end{array}$$

The equation (2) is same as equation (1). Since e.m.f. of the reaction is positive, so reaction (1) will take place *i.e.*, $AgNO_3$ solution will dissolve copper vessel. Hence $AgNO_3$ solution cannot be stored in copper vessel.

Example 30. *Can zinc sulphate solution be stored in a copper vessel ? Given :*

$$E^\circ_{Zn^{2+}/Zn} = -0.76\ V \quad ;\ E^\circ_{Cu^{2+}/Cu} = 0.34\ V.$$

Solution. $Zn\,SO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-}$

Reaction : $Cu + Zn\,SO_4 \rightleftharpoons CuSO_4 + Zn$ ...(1)

Since anode has lower reduction potential value than the cathode, so we have :

$$\begin{array}{lll} Cu^{2+} + 2e^- \rightleftharpoons Cu; & E° = +0.34\ V\ \text{(cathode)} \\ Zn^{2+} + 2e^- \rightleftharpoons Zn; & E° = -0.76\ V\ \text{(anode)} \\ \textbf{Subtract :}\ - \quad - \quad - \quad - & \\ \hline Cu^{2+} + Zn \rightleftharpoons Zn^{2+} + Cu; & E° = +1.10\ V \text{...(2)} \end{array}$$

In order to get equation (1), the equation (2) has to be reversed. So, we have :

$$Cu + Zn^{2+} \rightleftharpoons Cu^{2+} + Zn; \qquad E° = -1.10\ V$$

Since $E°$ value of the proposed reaction (1) is negative, the cell reaction will not take place. In other words, $ZnSO_4$ solution can be stored in a copper vessel.

19.9 TO PREDICT OXIDISING AND REDUCING AGENTS

Note: An electrode with lesser value of $E°$(reduction) is better reducing agent and that with higher value of $E°$(oxidation) is better oxidant.

Example 31. *Which element out of silver and magnesium is better reducing agent ? Given :*

$$E°_{Ag^+/Ag} = +0.79\ V; \qquad E°_{Mg^{2+}/Mg} = -2.37\ V.$$

Solution. $Ag^+ + e^- \rightleftharpoons Ag; \quad E°_{(reduction)} = +0.79\ V$

$$Mg^{2+} + 2e^- \rightleftharpoons Mg; \quad E°_{(reduction)} = -2.37\ V.$$

E°(reduction) value of Ag (= + 0.79 V) is higher than that of Mg (= – 2.37 V). So, Ag is weaker reducing agent than Mg. In other words, Mg is better reducing agent than silver.

Example 32. *Which element out of F_2 and Zn is better oxidant ? Given :*

$$E°_{F_2/2F^-} = +2.87\ V\ ; \qquad E°_{Zn^{2+}/Zn} = -0.76\ V.$$

Solution. $E°$(reduction) value of F_2(= + 2.87 V) is higher than that of Zn (= – 0.76 V), so F_2 is better oxidant than Zn.

Example 33. *The standard reduction potential at 298 K for different metal ions having + 2 charge is :*

(*a*) $E° = -0.76\ V$ (*b*) $E° = -0.74\ V$

(*c*) $E° = -0.00\ V$ (*d*) $E° = +0.77\ V$

Which of these is the strongest reducing agent ?

(HP Board, 2007)

Solution. The strongest reducing agent is that which has least value of standard reduction potential. Out of the given data, (*a*) is the correct answer because $E° = -0.76\ V$ is the least value.

19.10 TO PREDICT ANODE AND CATHODE

Example 34. *In the Zn–Cu cell, standard reduction potential of Zn = – 0.763 volt. Standard reduction potential of Cu = 0.335 volt. Name the cathode and anode in this electro-chemical cell.*

Solution. An anode is an electrode whose standard reduction potential value is less while cathode is an electrode whose standard reduction potential value is more than the other electrode. Hence, anode = Zn ($E° = -0.763\ V$) and cathode = Cu ($E° = +0.34\ V$).

Example 35. *Calculate the voltage of following electrochemical cell under standard conditions. Name anode and cathode in each cell.*

(i) Zn – Ag (ii) Co – Ni. The standard reduction potentials of various half cells are :

$$\begin{aligned} Zn^{2+}/Zn &= -0.76\ V : Ag^+/Ag = +0.80\ V\ ; \\ Co^{2+}/Co &= -0.28\ V : Ni^{2+}/Ni = -0.25\ V \\ Zn/Zn^{+2} &= \text{anode} : Ag/Ag^+ = \text{cathode}\ ; \\ Co/Co^{2+} &= \text{anode} : Ni/Ni^{2+} = \text{cathode} \end{aligned}$$

Solution. Anode is an electrode at which oxidation takes place and whose reduction potential value is less than the other. So, out of Zn and Ag, zinc electrode ($E° = -0.76V$) is anode and Ag electrode ($E° = +0.80\ V$) is cathode. **Cathode** is an electrode at which reduction takes place and whose reduction potential value is more than the other electrode. So, out of cobalt and nickel, Co electrode ($E° = -0.28\ V$) is anode and Ni electrode ($E° = -0.25\ V$) is cathode.

$$\begin{array}{llll} (i) & 2Ag^+ + 2e^- \longrightarrow 2Ag;\ ; & & E° = +0.8\ V \\ & Zn^{2+} + 2e^- \longrightarrow Zn;\ ; & & E° = -0.76\ V \\ \textbf{Subtracting :} & - \quad - \quad - & & + \\ \hline & Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}; & & E° = 1.56\ V\ \textbf{Ans.} \\ (ii) & Ni^{2+} + 2e^- \longrightarrow Ni\ ; & & E° = -0.25\ V \\ & Co^{2+} + 2e^- \longrightarrow Co\ ; & & E° = -0.28\ V \\ \textbf{Subtracting :} & - \quad - \quad - & & + \\ \hline & Co + Ni^{2+} \longrightarrow Ni + Co^{2+}; & & E° = 0.03V\ \textbf{Ans.} \end{array}$$

Example 36. *Arrange the following metals in the order in which they displace each other from the solution of their salts: Al, Cu, Fe, Mg, Zn ($E°$ for, $Al^{3+}/Al = -1.66\ V$; $Cu^{2+}/Cu = 0.34\ V$; $Fe^{2+}/Fe = -0.44\ V$; $Mg^{2+}/Mg = -2.73\ V$; $Zn^{2+}/Zn = -0.76\ V$).*

Solution. A metal with lesser value of $E°$ (reduction) will displace another metal from its solution. So, the order in which above metals would displace each other from the solution of their salts is :

$$Mg > Al > Zn > Fe > Cu.$$

Example 37. *Given the standard electrode potentials; $K^+/K = -2.93V$; $Ag^+/Ag = 0.80\ V$; $Hg^{2+}/Hg = 0.79\ V$; $Mg^{2+}/Mg = -2.37\ V$; $Cr^{3+}/Cr = -0.74\ V$. Arrange these metals in their increasing order of reducing power.*

Solution. Lesser the value of standard electrode reduction potential of an electrode, stronger the reducing agent, it will be. Hence, the increasing order of reducing power from the given data is Ag < Hg < Cr < Hg < K.

19.11 TO PREDICT FEASIBILITY OF A REACTION

Type. If $E°$ is positive, the cell reaction is feasible.

Example 38. *An iron wire is immersed in a solution containing $ZnSO_4$ and $NiSO_4$. When the concentration of each salt is 1 M, predict giving reactions which of the following reactions is likely to proceed : (i) Iron reduces Zn^{2+} ions (ii) Iron reduces Ni^{2+} ions.*

Given E° = – .076V for Zn^{2+}/Zn ; E° = –0.44 V for Fe^{2+}/Fe; E° = – 0.25 V for Ni^{2+}/Ni

Solution. (*i*) $Zn^{2+} + 2e^- \longrightarrow Zn;\quad E° = -0.76\ V$

$Fe^{2+} + 2e^- \longrightarrow Fe;\quad E° = -0.44\ V$

Subtract : – – – +

$Fe + Zn^{2+} \longrightarrow Zn + Fe^{2+};\ E° = -0.32\ V$

Since *E*° is negative, the reaction is not possible.

(*ii*) $Ni^{2+} + 2e^- \longrightarrow Ni;\quad E° = -0.25\ V$

$Fe^{2+} + 2e^- \longrightarrow Fe;\quad E° = -0.44\ V$

Subtract: – – – +

$Fe + Ni^{2+} \longrightarrow Ni + Fe^{2+};\ E° = +0.19\ V$

Since *E*° is positive, reaction is feasible. Hence iron reduces Ni^{2+} ions.

Example 39. *On the basis of standard electrode potential values stated for acid solution, predict whether Ti^{4+} species may be used to oxidise Fe^{II} to Fe^{III}.*

Reaction	*E°/V*
$Ti^{IV} + e^- \longrightarrow Ti^{3+}$	0.01 V
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+ 0.77 V

(CBSE, 2007)

Solution. Given :

$Fe^{3+} + e^- \longrightarrow Fe^{2+};\ E° = +0.77\ V$ (higher value)

$Ti^{4+} + e^- \longrightarrow Ti^{3+};\ E° = +0.01\ V$ (lower value)

Subtract: – – – –

$Fe^{3+} + Ti^{3+} \longrightarrow Fe^{2+} + Ti^{4+};\ E° = +0.76\ V$

For the oxidation of Fe^{2+} to Fe^{3+} by Ti^{4+}, the required equation is :

$Fe^{2+} + Ti^{4+} \longrightarrow Fe^{3+} + Ti^{3+};\ E° = -0.76\ V$

Since *E*° value is negative, Ti^{4+} cannot oxidise Fe^{2+} to Fe^{3+}.

Example 40. *Can chlorine gas be stored in copper cylinder? Given that E° $(Cu^{2+})/Cu$ = 0.34 V and E° $(Cl_2)/Cl^-$ = 1.36 V*

(PSEB, 2006)

Solution. $Cl_2 + 2e^- \longrightarrow 2Cl^-;\quad E° = 1.36\ V$

$Cu^{2+} + 2e^- \longrightarrow Cu;\quad E° = +0.34\ V$

Subtract: – – – –

$Cu + Cl_2 \longrightarrow Cu^{2+} + 2Cl^-;\quad E° = 1.02\ V$ ...(A)

Since *E*° is positive, the reaction (*A*) is feasible. So, Cl_2 cannot be stored in copper cylinder.

Example 41. *Two half-cell reactions of an electrochemical cell are given below.*

$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O(l);\quad E° = 1.51V$

$Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-;\quad E° = 0.15V$

Construct the redox equation from the two half-cell reactions and predict if this reaction favours the formation of reactants or products shown in the reaction **(DBS, 2009)**

Solution. A reaction is feasible if emf of cell is positive. Since 1.51 *V* > 0.51 *V*, so we have:

$[MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow Mn^{2+}_{(aq)} + 4H_2O(l)] \times 2;\quad E° = 1.51V$

$Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-] \times 5;\quad E° = 0.15\ V$

Subtract: – – – –

$2MnO^-_4 + 5\,Sn^{4+}_{(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Sn^{2+}_{(aq)};\quad E° = 1.36V$

Ans.

Since E° is ive, the reaction favours the formation of product.

Example 42. *The standard electrode potential for the half-cell reactions are:*

$Zn^{2+} + 2e^- \longrightarrow Zn;\quad E° = -0.76\ V$

$Fe^{++} + 2e^- \longrightarrow Fe;\quad E° = -0.44\ V$

The e.m.f. of the cell reaction, $Fe^{2+} + Zn \longrightarrow Zn^{++} + Fe$ is:

(*a*) –1.20V (*b*) + 1.20 V

(*c*) + 0.32 V (*d*) –0.32 V

(Karnataka CET, 2009)

Solution. In the cell reaction, $Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$, Zn is oxidised to Zn^{2+} and Fe^{2+} is reduced to Fe. So, the cell can be represented as:

$Zn/Zn^{2+}\ ||\ Fe^{2+}/Fe$

$$\therefore\quad E_{cell} = E_{right} - E_{left} = E_{Fe^{2+}/Fe} - E_{Zn^{2+}/Zn}$$

$$= (-0.44\ V) - (-0.76V)$$

$$= 0.76\ V - 0.44\ V = 0.32\ V$$

So, the correct answer is (*c*).

Example 43. *Why does blue colour of copper sulphate solution get discharged when iron rod is dipped into it? Given $E^\circ_{Cu^{2+}/Cu} = 0.34\ V$; $E^\circ_{Fe^{2+}/Fe} = -0.44\ V$.* **(HP Board, 2007)**

Solution. The reaction between iron rod (Fe) and copper sulphate solution is :

$Fe + \underset{\text{Blue colour}}{CuSO_4} \longrightarrow \underset{\text{Colourless}}{FeSO_4} + Cu\downarrow$

Or $Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu$ ...(1)

Given : $Cu^{2+} + 2e^- \longrightarrow Cu;\quad E° = +0.34\ V$

$Fe^{2+} + 2e^- \longrightarrow Fe;\quad E° = -0.44\ V$

Subtract: – – – +

$Fe + Cu^{2+} \longrightarrow Fe^{2+} + Cu;\ E° = +0.78\ V$ ...(2)

Since E° is positive, the above reaction is feasible. It means, iron rod will displace blue coloured Cu^{2+} ions and Cu will be precipitated. So, blue colour of $CuSO_4$ solution is discharged. It is what required by equation (1) also.

Example 44. *Standard oxidation potentials of some electrodes are given below :*

Electrode	*Standard oxidation Potential (Volts)*
Cd/Cd^{2+}	+ 0.40
Ni/Ni^{2+}	+ 0.25
H_2/H^+	0.0
Cu/Cu^{2+}	– 0.34
Ag/Ag^+	– 0.79

Out of the metals given above which will liberate hydrogen when treated with HCl at 25°C. **(Pb PMT, 1982)**

Solution. A metal will liberate hydrogen gas on treatment with HCl if the reaction given below is feasible.

$$M + 2H^+ \longrightarrow M^{2+} + H_2$$

The above reaction is feasible if the metal has higher tendency to lose electrons as compared to hydrogen. Thus, a metal with higher oxidation potential will liberate hydrogen on treatment with HCl. Hence, Cd, Ni which have higher oxidation potential values than hydrogen will liberate H_2 on treatment with HCl.

Example 45. *Iodine and bromine are added to a solution containing iodide and bromide ions. What reaction would occur if concentration of each species is 1 M ?*

$$2I^- \longrightarrow I_2 + 2e^-; \qquad E° = -0.54\ V$$

$$2\ Br^- \longrightarrow Br_2 + 2e^-; \qquad E° = -1.06\ V$$

Solution. As oxidation is the reverse of reduction, therefore,

$$I_2 + 2e^- \longrightarrow 2I^-; \qquad E° = 0.54\ V$$

$$Br_2 + 2e^- \longrightarrow 2Br^-; \qquad E° = 1.06\ V$$

On adding Br_2 and I_2 to the mixture solution of Br^- and I^- ions, either of the following reactions can take place :

(*i*) $2I^- + Br_2 \longrightarrow I_2 + 2Br^-$

(*ii*) $2Br^- + I_2 \longrightarrow Br_2 + 2I^-$

E.m.f. for reaction (*i*)

$$E°\ Br_2/Br^- - E° I_2/I^- = 1.06 - (0.54) = 0.52\ V$$

As e.m.f. is positive, therefore, reaction is feasible.; e.m. f. for cell reaction (*ii*)

$$= E° I_2/I^- - E°\ Br_2/Br- = 0.54 - 1.06 = -0.52\ V$$

As e.m.f. is negative, therefore, reaction (*ii*) is not feasible. Hence on adding Br_2 and I_2 to a mixture solution of Br^- and I^- ions, iodide ions are oxidised to I_2 while Br_2 is reduced to Br^{1-}.

Example 46. *Some standard electrode (or reduction) potentials in acidic solutions are as follows:*

$$Cu^{2+}/Cu = 0.34\ V,\quad Ag^+/Ag = 0.80\ V$$

Predict whether the following reactions occur :

(i) Will copper(s) reduce Ag^+ ion in aq. sol. ?

(ii) Will copper(s) dissolve in 1M HCl ? **(Pb PMT, 1984)**

Solution. A reaction is feasible if e.m.f. for the cell reaction is positive.

e.m.f. = Reduction potential of the electrode at which reduction takes place–Reduction potential of the electrode at which oxidation takes place.

(*i*) For the reaction.

$$Cu(s) + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

$$\text{e.m.f.} = 0.80\ V - 0.34\ V = \mathbf{0.46\ V}$$

As the e.m.f. for the reaction is positive, therefore, Cu(*s*) will reduce Ag^+ ion in aqueous solution.

(*ii*) For the reaction :

$$Cu(s) + 2HCl \longrightarrow CuCl_2 + H_2 \quad \text{or}$$

$$Cu(s) + 2H^+ \longrightarrow Cu^{2+} + H_2$$

$$\text{e.m.f.} = 0.0\ V - 0.34\ V = \mathbf{-0.34\ V}$$

As the e.m.f. is negative for the reaction, therefore, Cu(*s*) will not dissolve in 1M HCl.

Example 47. *A cell which has the overall chemical reaction*

$$Cu + 2H^+ \longrightarrow Cu^{2+} + H_2(g)$$

is represented schematically as

$$Cu/Cu^{2+}(1M)\ \|\ H^+(IM)/H_2(1\ atm),\ Pt$$

If electrons flow from Pt to Cu in a cell, write the anode and cathode reactions. What can be said about the relative ability of Cu and H_2 to be oxidized.

Solution. Anode reaction :

$$H_2 \longrightarrow 2H^+ + 2e^-$$

Cathode reaction :

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

If the above reactions take place at the anode and cathode, H_2 will have higher tendency to get oxidised as compared to Cu.

Example 48. *In a cell consisting of Zn/Zn^{2+} and H_2/H^+ half cells, e.m.f. is 0.76 volt. If the reduction potentials of the electrodes are measured with respect to Cu^{2+}/Cu as zero, what will be the e.m.f. of the cell ?*

Solution. E.M.F. of the cell in first case = 0.76 *V*

Now when reduction potential of Cu^{2+}/Cu electrode is zero, the reduction potential of $2H^+/H_2$ electrode will be – 0.34 *V* and that of Zn^{2+}/Zn electrode = – 0.76 – 0.34 = –1.10 *V*

$$\therefore \text{E.M.F. of the cell} = E°_{cathode} - E°_{anode}$$

$$= (-0.34) - (-1.10) = 0.76\ V$$

Thus E.M.F. of the cell will remain unaffected.

19.12 NERNST EQUATION

For the galvanic cells having different molar concentrations than 1*M* and operating at temperatures other than 298 *K*, the actual value of reduction potential of electrode and e.m.f. of the cell can be calculated. For a cell in which the net cell reaction involves '*n*' electrons, the following Nernst equation for a general reaction.

$$aA + bB \longrightarrow cC + dD \text{ is used.}$$

The Nernst equation is written as :

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303\ RT}{nF} \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

where $E^{\circ}_{cell} = E^{\circ}_{cathode}$ (reduction) $- E^{\circ}_{anode}$ (reduction)

$R = 8.314\ J\ K^- mol^-$;

T = Temperature in *K* ;

F = Faraday

= 96500 coulomb. Thus at 298 *K*

$$E_{cell} = E^{\circ}_{cell} - \frac{2.303 \times 8.314\ J\ K^-\ mol^- \times 298\ K}{n \times 96500\ \text{coulomb mol}^-} \times \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

(*i*) or $$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\textbf{Products}]}{[\textbf{Reactants}]}$$

or $$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Reactants}]}{[\text{Products}]}$$

Note :	[solid] = 1 e.g., [Zn(*s*)] = 1, [Cu(*s*)] = 1
(*ii*)	1 Joule = 1 coulomb volt or 1 CV

Details. The tendency of a cation (or an anion) to get reduced (or oxidised) depends upon their reduction potential value. We must know that E° tells us only whether products at a concentration of 1 M each will be formed from their reactants at a concentration of 1 M each or not. For example, the reaction, $Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$ having $E°$ value + 0.03 volt tells that this reaction takes place only if their concentration is 1 *M*. Experimental data tells that this reaction becomes reversed if the concentration of $Ni^{2+}(aq)$ is 0.01 *M* and that of $Co^{2+}(aq)$ equal to 1 *M*. From this we conclude that the *direction of spontaneous reaction depends upon the concentration of ions taking part in a reaction*. The dependence of the voltage of a galvanic cell is on concentration.

EXAMPLE 49. *If E° for copper electrode is + 0.34 V, how will you calculate its e.m.f. value when the solution in contact with it is 0.1 M in copper ions ? How does e.m.f. for copper electrode change when concentration of Cu^{2+} ions in the solution is decreased ?* **(CBSE, 2000)**

SOLUTION. Reaction :

$$Cu^{2+} + 2e^- \rightleftharpoons Cu;\ E^{\circ}_{\text{reduction}} = 0.34\ V$$

Using Nernst equation, we have :

$$E_{Cu^{2+}/Cu} = E^{\circ}_{Cu^{2+}/Cu} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= 0.34\ \text{V} - \frac{0.0591}{2} \log \frac{[Cu(s)]}{[Cu^{2+}]}$$

$$= 0.34\ \text{V} - \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$= 0.34 - \frac{0.0591}{2} \log 10$$

$$= 0.34\ \text{V} - 0.02955 \times 1 = \mathbf{0.3105\ V} \quad \textbf{Ans.}$$

But reduction potential of an electrode α conc. of ions. So, on decreasing the concentration of Cu^{2+} ions, the reduction potential of the electrode would decrease.

EXAMPLE 50. *Calculate the e.m.f. of the cell at 298 K. Cr/Cr^{3+} (0.1 M) || Fe^{2+} (0.01 M)/Fe. Given : $E^{\circ}_{(Cr^{3+}/Cr)} = -0.75\ V$; $E^{\circ}_{(Fe^{2+}/Fe)} = -0.45\ V$.*

(PSEB, 2005, HP Board, 2007, ISC, 2009, CBSE, 2009)

SOLUTION.

Since $E°$ value, – 0.45 *V* > – 0.75 *V*, so we have :

$$Fe^{2+} + 2e^- \rightleftharpoons Fe] \times 3; \qquad E^{\circ} = -0.45\ V$$

$$Cr^{3+} + 3e^- \rightleftharpoons Cr] \times 2; \qquad E^{\circ} = -0.75\ V$$

Subtract: – – – +

$$3Fe^{2+} + 2Cr \rightleftharpoons 3\,Fe + 2Cr^{3+}\ ;\ E^{\circ} = +0.30\ V$$

$$n = 6\ [\because 2e^- \times 3 = 6e^-; 3e^- \times 2 = 6e^-]$$

Using Nernst equation, we have :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= 0.30\ \text{V} - \frac{0.0591}{6} \log \frac{[Fe]^3 [Cr^{3+}]^2}{[Fe^{2+}]^3 [Cr]^2}$$

$$= 0.30\ \text{V} - \frac{0.0591}{6} \log \frac{1 \times (0.1)^2}{(0.01)^3 \times 1}$$

$$\begin{bmatrix} \log (0.1)^2 = 2 \log 0.1 = 2 \times -1 = -2 \\ \log (0.01)^3 = 3 \log 0.01 = 3 \times -2 = -6 \end{bmatrix}$$

$$= 0.3\ \text{V} - \frac{0.0591}{6} \times [-2 - (-6) = 4]$$

$$= 0.3\ V - 0.0394 = \mathbf{0.2606\ V} \qquad \textbf{Ans.}$$

EXAMPLE 51. *Calculate the potential for half-cell containing 0.1M $K_2Cr_2O_7$ (aq), 0.20 M Cr^{3+}(aq) and 1.0 × 10^{-4} M H^+(aq). The half-cell reaction is $Cr_2O_7^{2-}$ (aq) + $14H^+$(aq) + $6e^- \longrightarrow$ 2 Cr^{3+}(aq) + $7H_2O$(l) and the standard electrode potential is given as E° = 1.33 V* **(CBSE, 2007, HP Board, 2007, ISC, 2010)**

SOLUTION. To find potential of the half-cell, we use the Nernst equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= 1.33 - \frac{0.0591}{6} \log \frac{[Cr^{3+}]^2 [H_2O]^7}{[Cr_2O_7^{2-}]^1 [H^+]^{14}}$$

$$E_{\text{cell}} = 1.33 - \frac{0.0591}{6} \log \frac{[0.2]^2}{(0.1) \times (10^{-4})^{14}}$$

$$E_{\text{cell}} = 1.33 - \frac{0.059}{6} \log \left[\frac{4}{10^2 \times 10^{-1} \times 10^{-5}} = 4 \times 10^{55} \right]$$

$$= 1.33 - \frac{0.0591}{6}\ [\log 4 + 55 \log 10) = 0.6020 + 55 = 55.6020]$$

$$= 1.33 - \frac{0.0591}{6} \times 55.6020$$

$$= 1.33 - 0.5477 = \mathbf{0.78232}\ V \qquad \textbf{Ans.}$$

EXAMPLE 52. *A copper silver cell is set up. The copper ion concentration in it is 0.10 M. The concentration of silver ion is not known. The cell potential measured is 0.422 V. Determine the concentration of silver ion in the cell. Given, $E^{\circ}_{Ag^+/Ag}$ = + 0.80 V; $E^{\circ}_{Cu^{2+}/Cu}$ = + 0.34 V.* **(DB, 2009, CBSE, 2013)**

SOLUTION. A cell is feasible, if emf of the cell is positive.

Since + 0.80 *V* > + 0.34 *V*, So:

$$Ag^+ + e^- \longrightarrow Ag] \times 2; \quad E^{\circ} = +0.80\ V; n = 2$$

$$Cu^{2+} + 2e^- \longrightarrow Cu; \quad E^{\circ} = +0.34\ V; n = 2$$

Subtracting: – – – –

$$2Ag^+ + Cu \longrightarrow 2Ag + Cu^{2+}; \quad E^{\circ} = +0.46\ V$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$0.422 = 0.46 - \frac{0.059}{2}\log\frac{1}{[Ag^+]^2};$$

$$-\frac{0.059}{2}\ \log (Ag^+)^{-2} = 0.46 - 0.422$$

or $-2 \times -\frac{0.059}{2}\ \log [Ag^+] = 0.038\ V; 0.059 \log [Ag^+] = 0.038$

Taking antilog of both sides, we get:

$[Ag^+]$ = antilog 0.038/0.059 = **0.644 M**

Ans.

19.13 TO FIND PARTIAL PRESSURE OF A GAS

Type. To find partial pressure of a gas in a cell reaction, use Nernst equation.

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[Products]}{[Reactants]}$$

Example 53. *In the cell reaction, $4Cr^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3}(aq) + 2H_2O(l)$, the concentrations are : $[Cr^{2+}] = 0.1\,M$, $[Cr^{3+}] = 0.082\,M$, $[H^+] = 0.01M$. Find the partial pressure* of O_2 *gas at equilibrium at 25°C. E° Cr^{3+}/Cr^{2+} = – 0.41 V. E° O_2/H_2O = 1.23 V].*

Solution. (*i*) At equilibrium, $E_{cell} = 0.0$ V

(*ii*) $E°\ Cr^{3+}/Cr^{2+} = -0.42\ V$:

$E°O_2/H_2O = 1.23\ V$;

$[Cr^{2+}] = 0.1\ M$; $[Cr^{3+}] = 0.082\ M$;

$[H^+] = 0.01\ M$

(*iii*) $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O;\qquad E° = +1.23\ V$

$Cr^{3+} + e^- \longrightarrow Cr^{2+}] \times 4;\qquad E° = -0.41\ V$

Subtract: – – – +

$4Cr^{2+} + O_2 + 4H^+ \longrightarrow 4Cr^{3+} + 2H_2O;\qquad E° = 1.64\ V$

So, $n = 4$ from (*iii*) above and $E°_{cell} = 1.64$ V. Applying Nernst equation to given reaction, $4Cr^{2+}(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Cr^{3+}(aq) + 2H_2O(l)$, we have :

$E_{cell} = E°_{cell} - (0.0591/n)$ [log [Products]/(Reactants]. Substituting the values, we get : 0 = 1.64 – (0.0591/4) [log $(Cr^{3+}]^4 [H_2O]^2/[Cr^{2+}]^4 [pO_2] [H^+]^4$ = 1.64 – (0.0591/4) [log $[0.082]^4$ [constant]/$(0.1)]^4[pO_2][0.01]^4]$ = 1.64 – (0.0591/4) [4 log 0.082 + 0 – 4 log 0.1 – logpO_2 – 4 log 0.01] = 1.64 – (0.0591/4)[(4 × –1.0861) – (4 × – 1) – log pO_2 – (4 × – 2)] = 1.64 – (0.0591/4) [– 4.3444 + 4 – logpO_2 + 8] = 1.64 – (0.0591/4) [7.6556 – logpO_2]. **Or** – 1.64 = – 0.1131 + (0.0591/4) logpO_2. **Or** – 1.5269 = (0.0591/4) logpO_2 **Or** (–1.569 × 4/0.0591) = logpO_2. Hence log pO_2 = – 103.3435. **Or** pO_2 = antilog – 103.3434 *i.e.*, $\overline{104}.6566$ = 4.53×10^{-104} atm

Ans.

19.14 TO FIND pH OF A SOLUTION

Type. The pH of an acidic solution in a given cell can be found by firstly using the relation :

$$E = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Products]}{[Reactants]}$$

and then :

$$pH = -\log [H^+]$$

Example 54. *Derive a relation to measure the pH of a solution with the help of standard hydrogen electrode.*

Solution. The cell diagram is

Pt | H_2 (1 bar) | $H^+(aq)$, unknown || $H^+(aq)$ (1M) | H_2 (1 bar) | Pt

Reactions.

$H_2(g) + 2H^+(1M) \longrightarrow 2H^+(aq, unknown) + H_2(g)$

$\tfrac{1}{2} H_2(g) + H^+(1M) \longrightarrow H^+(aq, unknown) + \tfrac{1}{2} H_2(g)$ ...(1)

Here, $n = 1$ because $\tfrac{1}{2} H_2 \longrightarrow H^+ + 1e^-$

Using Nernst equation, for equation (1), we have :

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Products]}{[Reactants]}$$

$$= 0.0V - \frac{0.0591}{1}\ \log \frac{\left[H^+ (aq, unknown)\right]\left[pH_2\right]^{1/2}}{\left[pH_2\right]^{1/2}\left[H^+\right]}$$

$$= 0.0V - \frac{0.0591 \log \left[H^+ (aq, unknown)\right][1.0]^{1/2}}{1 \times 1}$$

$$= -0.0591 \log [H^+, (aq, unknown)]$$

$\therefore E_{cell}$ = **0.0591 pH** $[\because -\log (H^+) = pH]$

Example 55. *Find the pH of the following acid solution; Pt (H_2 (1 bar) | H^+ (aq, acid) || H^+ (1M) | H_2 (g, 1 bar) | Pt. The measured e.m.f. of the cell* = 0.182 *V.*

Solution. For finding the pH of an unknown acid, using the above cell connected with standard hydrogen electrode, we use the relation :

$$E_{cell} = 0.0591\ pH$$

$$\therefore \qquad pH = \frac{E_{cell}}{0.0591} = \frac{0.182\ V}{0.0591\ V} = \mathbf{3.079}\ \ \textbf{Ans.}$$

Example 56. *The e.m.f. of the following cell Pt | H_2(1atm) | $H^+(aq)$ || $Ag^+(1M)$ | Ag(s) at 25°C is 0.87 V. Calculate the pH of the acid solution.*

E° Ag^+/Ag = 0.80 V ; E° $2H^+/H_2$ = 0.0V

Solution. Reaction :

$2Ag^+ + 2e^- \rightleftharpoons 2Ag(s);\qquad E° = 0.8\ V$

$2H^+ + 2e^- \rightleftharpoons H_2;\qquad E° = 0.0\ V$

Subtract: – – – +

$2Ag^+ + H_2 \rightleftharpoons 2Ag(s) + 2H^+;\qquad E° = 0.8\ V$

Using Nernst equation, we have :

$$E_{cell} = E°_{cell} - \frac{0.0591}{2}\log$$

$$\left[\frac{[Ag(s)]^2\left[H^+\right]^2}{\left[Ag^+\right]^2[pH_2]} = \frac{1 \times (H^+)^2}{(1)^2 \times 1} = \left[H^+\right]^2\right]$$

$$0.87\ V = 0.80\ \text{V} - \frac{0.0591}{2} \times 2\log\left[\text{H}^+\right]$$

$$= 0.80\ V - 0.0591 \log \text{H}^+$$

$$0.87\ V - 0.80\ V = -\log[\text{H}^+] \times 0.0591\ ;$$

$$0.07\ V = \text{pH} \times 0.0591\ V$$

$$\therefore \quad \text{pH} = \frac{0.07\ \text{V}}{0.0591\ \text{V}} = \mathbf{1.184} \qquad \textbf{Ans.}$$

Example 57. *Calculate the equilibrium constant K for the following reaction at 298 K* **(CBSE, 2009, 2013)**

$$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Cu}(s).$$

Given : $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76\ \text{V}\ ;\ E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34\ V$

Solution. Since the E° (reduction) value $+ 0.34V > - 0.76\ V$

So, we have :

$$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}(s);\ E^\circ = +0.34\ V\ \text{(cathode)}$$

$$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}(s)\ ;\ E^\circ = -0.76\ V\ \text{(anode)}$$

Subtract: − − − +

$$\text{Cu}^{2+} + \text{Zn}(s) \rightleftharpoons \text{Cu}(s) + \text{Zn}^{2+}\ ; \qquad E^\circ = 1.10\ V$$

Using Nernst equation, we have :

$$\text{We know} \quad \log K_c = \frac{n\,\text{E}^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 1.1}{0.0591} = 37.22$$

$$\therefore \quad K_c = \text{antilog } 37.22$$

$$= \mathbf{1.66 \times 10^{37}} \qquad \textbf{Ans.}$$

19.15 USE OF ΔG° (OR MAXIMUM WORK OR ELECTRICAL ENERGY)= – nFE°$_{\text{cell}}$ AND ΔG° = – 2.303 RT LOG K$_c$

Example 58. The *equilibrium constant at 25°C for the process*

$$\text{Co}^{3+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}(aq)$$

is 2.0×10^7. *Calculate the value of* ΔG° *at* 25°C ($R = 8.314\ J\ K^- mol^-$). *In which direction is the reaction spontaneous when the reactants and products are under standard conditions ?* **(DSB, 1999 S)**

Solution. $K_c = 2.0 \times 10^7\ ;\ R = 8.314\ J\ K^-\ \text{mol}^-\ ;$

$$T = 25 + 273 = 298\ K$$

We know that : $\Delta G^\circ = -2.303\ RT \log K_c$

$$= -2.303 \times 8.314\ JK^-\ \text{mol}^- \times 298\ K \log 2.0 \times 10^7$$

$$= -2.303 \times 8.314\ JK^-\text{mol}^- \times 298\ K$$

$$[\log 2 + \log 10^7 = 0.3010 + 7 = 7.301]$$

$$= -2.303 \times 8.314\ JK^-\ \text{mol}^- \times 298\ K \times 7.301$$

$$= -41658\ J\ \text{mol}^-$$

$$\Delta G^\circ = \mathbf{-41.658\ KJ\ mol^-} \qquad \textbf{Ans.}$$

Since ΔG° is negative, the reaction is feasible in the forward direction.

Example 59. *Calculate equilibrium constant for the reaction at* 298 *K* :

$$4\,Br^- + O_2 + 4H^+ \rightleftharpoons 2Br_2 + 2H_2O$$

Given : $E^\circ_{cell} = 0.16\ V$ **(PSEB, 2001)**

Solution. For the given reaction, we have :

$$4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\ ; \qquad 2\text{Br}_2 + 4e^- \rightleftharpoons 4\text{Br}^-$$

These are four electron change reactions.

So, $n = 4.$

We know that : $E^\circ_{cell} = \dfrac{0.0591}{n} \log K.$

Substituting the values, we get :

$$0.16 = \frac{0.0591}{4} \log K$$

$$\therefore \quad \log K = \frac{0.16 \times 4}{0.0591} = 10.83$$

$$\text{or} \quad K = \text{antilog } 10.83 = \mathbf{6.76 \times 10^{10}}\ \textbf{Ans.}$$

Example 60. *Determine the values of equilibruim constant* (K_c) *and* ΔG° *for the following reaction:*

$$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}_{(aq)} + 2\,Ag(s); \quad E^\circ = 1.05\ V$$

(1F = 96500 C mol$^-$) **(CBSE Board, 2011)**

Solution. Given $E^\circ = 1.05$ V. At equilibrium, $E_{\text{cell}} = 0$. The given reaction can be written as:

$$\text{Ni}(s) \longrightarrow \text{Ni}^{2+} + 2e^-$$

$$2\text{Ag}^+_{(aq)} + 2e^- \longrightarrow 2\text{Ag}(s)$$

Here, $n = 2$ *i.e;* no. of electrons. Adding:

$$\text{Ni}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Ni}^{2+} + 2\text{Ag}(s); \qquad E^\circ = 1.05\ V$$

$$\text{But} \quad E_{\text{cell}} = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$= E^\circ - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$0 = 1.05 - (0.059/2) \log K_c$$

$$[\because \text{at equilibrium, } \log [\text{Ni}^{2+}]/[\text{Ag}^+]^2 = K_c]$$

$$\therefore \quad \log K_c = (2 \times 1.05)/0.0591$$

$$= 35.53;$$

$$K_c = \text{antilog } 35.53$$

$$\text{or} \quad K_c = 3.38 \times 10^{35}.$$

Also:

$$\Delta G^\circ = -n\text{F}E^\circ = -2 \times 96500 \times 1.05$$

$$= \mathbf{-202650\ J} \qquad \textbf{Ans.}$$

Note: We can also use, $\log K_c = \Delta G^\circ/-2.303\ RT$ to find K_c; $R = 8.314\ \text{JK}^-\ \text{mol}^-$, $T = 298\ K$.

Example 61. *Calculate* ΔG° *for the reaction :*

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Fe^{2+}(aq) + Cu(s).$$

$$[E^\circ_{Cu^{2+}/Cu} = 0.34\ V;\ E^\circ_{Fe^{2+}/Fe} = -0.44\ V).$$

(DSB, 1999S)

Solution.

Since $E^\circ_{\text{(reduction)}}$ value $+ 0.34\ V > - 0.44\ V$, so we have :

$$\text{Cathode } [\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}; \qquad E^\circ = +0.34\ V$$

$$\text{Anode } [\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}; \qquad E^\circ = -0.44\ V$$

Subtract: − − − + −

$$Cu^{2+} + \text{Fe} \rightleftharpoons \text{Cu} + \text{Fe}^{2+}\ ;\ E^\circ = +0.78\ V$$

[Here $n = 2$ as the reaction is of 2 electron change.]

$$\therefore \quad \Delta G^\circ = -nF\,E^\circ_{cell} = -2 \times 96500\ C\ mol^- \times 0.78\ V$$

$$= -150{,}540\ C\ V\ mol^- = -150{,}540\ J\ mol^- \qquad [\because J = CV]$$

$$= -150{,}540\ J\ mol^- \times \frac{1k\,J}{1000\,J}$$

$$= \mathbf{-150.54\ k\ J\ mol^-} \qquad \textbf{Ans.}$$

EXAMPLE 62. *Calculate the maximum electrical work that can be obtained from the following cell under the standard conditions at* 25° *C.* Zn/Zn^{2+} *(aq)* || Fe^{2+} *(aq)*/Fe. *Given that* $E^\circ\ Zn^2(aq)/\ Zn = -0.76\ V$; $E^\circ\ Fe^{2+}\ (aq)/Fe = -0.44\ V$ *and* $F = 96500\ C\ mol^-$. **(CBSE, 1995)**

SOLUTION. Maximum work, $(-\Delta G^\circ) = ?$

Since $E^\circ_{(reduction)}$ value -0.44 V > -0.76 V, so we have:

$$Fe^{2+} + 2e^- \rightleftharpoons Fe; \qquad E^\circ = -0.44\ V\ \text{(cathode)}$$

$$Zn^{2+} + 2e^- \rightleftharpoons Zn; \qquad E^\circ = -0.76\ V\ \text{(anode)}$$

Subtract: – – – +

$$Fe^{2+} + Zn \rightleftharpoons Fe + Zn^{2+}; \qquad E^\circ = 0.32\ V$$

But ΔG° (= maximum work) $= -nF\,E^\circ$cell

$$= -\ 2 \times 96500\ C\ mol^- \times 0.32\ V$$

$$= -61760\ C\ V\ mol^-$$

$$= -61760\ J\ mol^- \qquad [\because CV = J]$$

$$= -61760\,J\,mol^- \times \frac{1k\ J}{1000\ J}$$

$$= \mathbf{-61.76\ k\ J\ mol^-}\ \textbf{Ans.}$$

EXAMPLE 63. *Calculate the value of* ΔG *and* E_{cell} *at* 298 *K for the following cell.* Al/Al^{3+} (0.01M) || Fe^{2+} (0.02)/Fe. *Given that* $E^\circ Al^{3+}/Al = -1.66\ V$ *and* $E^\circ\ Fe^{2+}/Fe = -0.44\ V$ **(CBSE, 2001, 2007)**

SOLUTION. $\Delta G = ?$; $E_{cell} = ?$

The half cell reactions are :

$$Al^{3+} + 3e^- \longrightarrow Al] \times 2$$

$$Fe^{2+} + 2e^- \longrightarrow Fe] \times 3$$

Subtract: – – –

$$2\,Al^{3+} + 3Fe \longrightarrow 2Al + 3Fe^{2+}$$

So, no. of electrons = 6 Or $n = 6$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ Fe^{2+}/Fe - E^\circ\ Zn^{2+}/Zn$$

$$= -0.44 - (-1.66) = 1.22\ V.$$

According to Nernst equation,

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\ [Fe^{2+}]^3/[Al^{3+}]^2.$$

Or

$$E_{cell} = 1.22 - (0.0591/6)\log\ (0.02)^3/(0.01)^2$$

$$= 1.22 - (0.0591/6)\log 0.08$$

$$= 1.22 - (0.0591/6) \times -1.097$$

$$= 1.22 + 0.0108 = \mathbf{1.2308\ V} \qquad \textbf{Ans.}$$

Also, $\Delta G = -nF\,E_{cell}$

Substituting the values, we get :

$$\Delta G = -6 \times 96500\ C \times 1.2308\ V$$

$$= 712{,}633\ J = \mathbf{712.633\ k\ J}$$

$$[\because \mathbf{1CV = 1J}]\ \textbf{Ans.}$$

EXAMPLE 64. *Determine the equilibrium constant of the reaction at 298 K ;* $2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$. *From the obtained value of equilibrium constant, predict whether* Sn^{2+} *ions can reduce* Fe^{3+} *to* Fe^{2+} *quantitatively or not ? Given :* $E^\circ\ Fe^{3+}, Fe^{2+}/Pt = 0.771\ V$; $E^\circ\ Sn^{4+}/Sn^{2+}/Pt = 0.150\ V$. $[R = 8.314\ J\ K^-\ mol^-.]$ **(DSB, 1993S)**

SOLUTION. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$= E^\circ\ Fe^{3+}, Fe^{2+}/Pt - E^\circ\ Sn^{4+}/Sn^{2+}/Pt$$

$$= 0.771\ V - 0.150\ V$$

$$= 0.621\ V.$$

We know, for $Fe^{2+} + 2e^- \rightarrow Fe$ and $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$,

$$n = 2.$$

Also, $\quad -nF\,E^\circ_{cell} = -2.303\,RT\log K_c.$

Or $\quad \log K_c = (-nF\,E^\circ_{cell})/-2.303\,RT$

$$\therefore \quad \log K_c = (-2 \times 96500\ C\ mol^- \times 0.621\ V)/(-2.303 \times 8.314\ J\ K^-\ mol^- \times 298\ K$$

$$= 21.0053. \qquad [\because CV = J]$$

$$\therefore \quad K_c = \text{antilog}\ 21.0053 = \mathbf{1.01 \times 10^{21}}\ \textbf{Ans.}$$

Since the value of K_c is extremely high, the Sn^{2+} ions will reduce Fe^{3+} to Fe^{2+} completely.

EXAMPLE 65. *The standard reduction potential of* Cu^{2+}/Cu *and* Ag^+/Ag *electrodes are* 0.337 *and* 0.799 *volt respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of* Ag^+ *will the e.m.f. of the cell at* 25°C *be zero if the concentration of* Cu^{2+} *is* 0.01 *M* ? **(IIT, 1990; CBSE, 2009)**

SOLUTION.

Since $E^\circ_{Ag^+/Ag} > E^\circ_{Cu^{2+}/Cu}$, the half cell Ag^+/Ag will constitute the cathode of the galvanic cell. Hence, the required cell is :

$$Cu/Cu^{2+}\ ||\ Ag^+/Ag$$

Its standard e.m.f. is $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu}$

$$= 0.799\ V - 0.337\ V = 0.462\ V$$

The cell reaction in

Right half cell : $2Ag^+ + 2e^- \longrightarrow 2Ag$

Left half cell : $Cu \longrightarrow Cu^{2+} + 2e^-$

Net cell reaction is : $2Ag^+ + Cu \longrightarrow 2Ag + Cu^{2+}$

According to Nernst equation

$$E_{cell} = E^o_{cell} - \frac{RT}{2F}\,\text{In}\,\frac{\left[Cu^{2+}\right]}{\left[Ag^+\right]^2}$$

Substituting the given data, we get

$$0 = 0.462\ V - \frac{0.0591\ V}{2}\log\frac{0.01}{\left[Ag^+\right]^2}$$

$$\text{or} \quad \log\frac{0.01}{\left[Ag^+\right]^2} = \frac{2 \times 0.462\ V}{0.0591} = 15.6345$$

or $\log 0.01 - 2\log[Ag^+] = 15.6345$

or $-2 - 15.6345 = 2\log[Ag^+]$

or $\log[Ag^+] = \frac{-2-15.6345}{2} = -8.8173$

$\therefore$ $[Ag^+] = \text{antilog } \bar{9}.1827 = \mathbf{1.523 \times 10^{-9}\ M}$

EXAMPLE 66. *The standard reduction potential for the half-cell.*

$NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(aq) + H_2O(l)$ *is* 0.78 *V*

(*a*) *Calculate the reduction potential in* 8M H^+

(*b*) *What will be the reduction potential of the half-cell in a neutral solution ? Assume all the other species to be at unit concentration.* **(IIT, 1993)**

SOLUTION. For the half-cell reaction,

$NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(aq) + H_2O(l)$

The Nernst equation is

$$E = E^\circ - \frac{RT}{nF}\ln\frac{PNO_2}{[NO_3^-][H^+]^2}$$

(*a*) In 8M H^+, we have

$$E = 0.78\ V - (0.059\ V)\log\frac{1}{(8)^2}$$

[Here, $n = 1$]

$$= 0.78\ V + (0.059\ V)\log 8^2$$
$$= 0.78\ V + (0.059\ V)(1.806)$$
$$= 0.886\ V$$

(*b*) For a neutral solution at 25°C, $[H^+] = 10^{-7}$ M

Hence $$E = 0.78\ V - (0.059\ V)\log\frac{1}{(10^{-7})^2}$$
$$= 0.78\ V - (0.059V)(14) = \mathbf{0.076\ V.}$$

EXAMPLE 67. *The standard reduction potential of the* Ag^+/Ag *electrode at* 298 *K is* 0.799 *V. Given that for AgI,* $K_{sp} = 8.7 \times 10^{-17}$*, evaluate the potential of the* Ag^+/Ag *electrode in a standard solution of AgI. Also calculate the standard reduction potential of the* $I^-/AgI/Ag$ *electrode.* **(IIT, 1994)**

SOLUTION. For $Ag^+ \mid Ag$, half cell involving standard solution of AgI, the cell reaction is:

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

Nernst equation is :

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} - \frac{RT}{nF}\ln\frac{1}{[Ag^+]}$$

The concentration of Ag^+ in the solution can be calculated from the solubility product constant of AgI.

$$AgI(s) \rightleftharpoons |Ag^+(aq)| + |I^-(aq)|$$

Solubility s s

Hence $K_{sp} = [Ag^+][I^-]$

$8.7 \times 10^{-17}\ M^2 = (s)(s)$

or $s = \sqrt{8.7 \times 10^{-17}\ M^2} = 9.33 \times 10^{-9}$ M

Now, from the Nernst equation, we get

$$E_{Ag^+/Ag} = 0.799\ V$$
$$-(0.059\ V)\log\left(\frac{1}{9.33\times10^{-9}}\right)$$
$$= 0.799\ V - (0.059)(8.030)$$
$$= (0.799\ V - 0.475)\ V = 0.324\ V$$

Standard Reduction potential of $I^- \mid AgI \mid Ag$. Consider Ag/AgI electrode dipped in a standard solution of AgI. Its potential may be computed from either of the following two methods:

(*a*) Considering $Ag^+ \mid Ag$ half-cell, we have cell reaction : $Ag^+_{(aq)} + e^- \rightarrow Ag(s)$

Electrode potential :

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} - \frac{RT}{F}\ln\frac{1}{[Ag^+]} \quad \ldots(i)$$

(*b*) Considering $I^- \mid AgI \mid Ag$ half-cell

Cell reaction :

$$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-(aq)$$

Electrode potential :

$$E_{I^-}\,|AgI|\,Ag = E^\circ_{I}-|AgI|Ag - \frac{RT}{F}\ln[I^-] \ldots(ii)$$

Thus, $Ag^+/Ag = E_{I^-} \mid AgI/Ag$

Equating equation (*i*) and (*ii*), we get

$$E^\circ\ Ag^+|Ag - \frac{RT}{F}\ln\frac{1}{[Ag^+]}$$
$$= E^\circ_{I^-}/AgI/Ag - \frac{RT}{F}\ln[I^-]$$

or $$E^\circ_{I^-} \mid AgI/Ag = E^\circ_{Ag^+/Ag} + \frac{RT}{F}\ln[Ag^+][I^-]$$
$$= E^\circ\ Ag^+/Ag + \frac{RT}{F}\ln Ksp\,(AgI)$$
$$= 0.799\ V + (0.0591V)\log(8.7 \times 10^{-17})$$
$$= 0.799\ V - (0.0591 \times 16.060)\ V$$
$$= (0.799\ V - 0.950\ V) = \mathbf{-0.151\ V}$$

EXAMPLE 68. *An excess of liquid mercury is added to an acidified solution of* 1.0×10^{-3} *M* Fe^{3+}*. It is found that* 5% Fe^{3+} *remains at equilibrium at* 25°C*. Calculate* $E^\circ\ Hg^{2+}/Hg$*, assuming that the only reaction that occurs is* $2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$ *(Given* $E^\circ Fe^{3+}/Fe^{2+} = 0.77V$*)* **(IIT, 1995)**

SOLUTION. The reaction involved is

$$2Hg \quad + \quad 2Fe^{3+} \rightleftharpoons Hg_2^{2+} \quad + \quad 2Fe^{2+}$$

Initial conc. 1.0×10^{-3} M

Equb. conc 0.05×10^{-3} $\quad \frac{0.95\times10^{-3}}{2}$ $\quad 0.95 \times 10^{-3}$

$= 0.475 \times 10^{-3}$

According to Nernst equation,

$$E = \left(E^\circ_{Fe^{3+}/Fe^{2+}}\right) - E^\circ_{(Hg_2^{2+}/Hg)}$$
$$- \frac{0.059}{n}\log\frac{[Fe^{2+}]^2[Hg_2^{2+}]}{[Fe^{3+}]^2}$$

At equilibrium, $E = 0$

$$0 = 0.77 - E^\circ_{Hg_2^{2+}/Hg} - \frac{0.059}{2}\log$$

$$\frac{\left(0.95\times10^{-3}\right)^2\left(0.475\times10^{-3}\right)}{\left(0.05\times10^{-3}\right)^2}$$

or $$E^\circ_{Hg_2^{2+}/Hg} = 0.77 - \frac{0.059}{2}\log\frac{0.4287\times10^{-9}}{2.5\times10^{-9}}$$

$$= 0.77 + 0.022 = \mathbf{0.792\ V}$$

EXAMPLE 69. *A cell Ag | Ag^+ || Cu^{2+} | Cu, initially contains 1 M Ag^+ and 1M Cu^{2+} ions. Calculate the change in cell potential after the passage of* 9.65 *A of current for* 1 *h*.**(IIT, 1999)**

SOLUTION. Quantity of electricity passed is

$$Q = At = (9.65\ \text{A})\ (60\times60\text{s})$$
$$= 34740\ \text{C}$$

Amount of electrons = $\frac{34740}{96500}$ moles = 0.36 mol.

The half cell reactions are :

Left half cell : $Ag\,(s) \longrightarrow Ag^+\,(aq) + e^-$

Right half cell : $\frac{1}{2}Cu^{2+}\,(aq) + e^- \longrightarrow \frac{1}{2}Cu(s)$

Net reaction : $Ag(s) + \frac{1}{2}Cu^{2+} \longrightarrow Ag(s) + \frac{1}{2}Cu^{2+}$

According to the given data :

$$Ag(s) + \frac{1}{2}Cu^{2+}\,(aq) \longrightarrow Ag^+(aq) + \frac{1}{2}Cu\,(s)$$

$t = 0$ 1M 1M

After passing the current [1 – (0.36/2) M = 0.82 (1 + 0.36) M

According to the Nernst equation,

$$E = E^\circ - \frac{RT}{nF}\ln\frac{\left[Ag^+\right]}{\left[Cu^{2+}\right]^{1/2}}$$

Substituting the given data,

$$E_1 = E^\circ - (0.059\ \text{V})\log\frac{1\,\text{M}}{(1\,\text{M})^{1/2}}\ E^\circ$$

$$\left[\because n = 1 \text{ for one electron change}\right]$$

$$E_2 = E^\circ - (0.059\ \text{V})\log\frac{1.36}{(0.82)^{1/2}}$$
$$= E^\circ - 0.010\ \text{V}$$
$$\Delta E = E_2 - E_1 = \mathbf{-\,0.010\ V}$$

EXAMPLE 70. *A silver electrode is immersed in a saturated $Ag_2SO_4(aq)$ solution. The potential difference between silver and the standard hydrogen electrode is found to be* 0.711 *V. Determine K_{sp} (Ag_2SO_4). [Given E° (Ag^+ /Ag) = 0.799 V].*

(Roorkee, 2000)

SOLUTION. According to the given values of electrode potentials, Ag^+ | Ag electrode acts as a cathode and the reactions occurring are :

$2Ag^+\,(aq) + 2e^- \longrightarrow 2Ag_{(s)}$ $E^\circ = 0.799\ V$ (Reduction)

$H_{2(g)} \longrightarrow 2H^+ + 2e^-$ $E^\circ = 0.0V$ (Oxidation)

Net cell reaction is :

$$2\,Ag^+\,(aq) + H_2(g) \longrightarrow 2Ag(s) + 2H^+$$
$$E^\circ_{cell} = E^\circ_{(Ag^+\,|Ag)} - E^\circ_{(2H^+\,|\,H_2)}$$
$$= 0.799 - 0.0 = 0.799\ V$$

According to Nernst equation :

$$E = E^\circ - \frac{0.0591}{n}\log.\frac{\left[H^+\right]^2}{\left[Ag^+\right]^2\times pH_2}$$

$$E_{cell} = 0.711\ \text{V}\ ; pH_2 = 1\ \text{atm}\ ;$$
$$[H^+] = 1\ ; n = 2$$

$$\therefore\quad 0.711 = 0.799 - \frac{0.591}{2}\log\frac{1}{\left[Ag^+\right]^2}$$

$$(0.799 - 0.711) = \frac{0.0591}{2}\log\frac{1}{\left[Ag^+\right]^2}$$

or $$\log\frac{1}{\left[Ag^+\right]^2} = \frac{0.088\times2}{0.0591} = 2.978$$

Taking antilogs,

$$\frac{1}{\left[Ag^+\right]^2} = 950.6$$

or $[Ag^+] = 3.24\times10^{-2}$

For Ag_2SO_4, $Ag_2SO_4(s) \rightleftharpoons 2Ag^+ + SO_4^{2-}$

Since $[Ag^+] = 3.24\times10^{-2}$

$$[SO_4^{2-}\ ] = \frac{1}{2}\left[Ag^+\right] = 1.62\times10^{-2}$$

$$\therefore\quad K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$$
$$= (3.24\times10^{-2})^2\,(1.64\times10^{-2})$$
$$= \mathbf{1.72\times10^{-5}}$$

EXAMPLE 71. *A solution containing* 4.5 *mM of $Cr_2O_7^{2-}$ and* 15 *mM of Cr^{3+} shows a pH of* 2.0. *Calculate the potential of half reaction (standard potential of the reaction* **(Roorkee, 2001)** *$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ is* 1.33 *V).*

SOLUTION. The half reaction may be represented as :

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$pH = 2\ ; [H^+] = 10^{-2}\ \text{M};$$
$$[Cr_2O_7^{2-}] = 4.5\times10^{-3}\ \text{M}\ ;$$
$$[Cr^{3+}] = 15\times10^{-3}\ \text{M}$$

According to Nernst equation,

$$E = E^\circ - \frac{0.0591}{n}\log\frac{\left[Cr^{3+}\right]^2}{\left[Cr_2O_7^{2-}\right]\left[H^+\right]^{14}}$$

$$= 1.33 - \frac{0.0591}{6}\log\frac{\left(15\times10^{-3}\right)^2}{\left(4.5\times10^{-3}\right)\left(10^{-2}\right)^{14}}$$

$$= 1.33 - \frac{0.0591}{6}\log 5\times10^{26}$$

$$= 1.33 - \frac{0.0591}{6}\left[26 + 0.599\right]$$

$$= 1.33 - 0.263 = \mathbf{1.067\ V}$$

EXAMPLE 72. *The zinc/silver oxide cell is used in hearing aids and electrical watches*

$Zn \rightleftharpoons Zn^{2+} + 2e^-; \qquad E° = 0.76\ V$

$Ag_2O + H_2O + 2e^- \rightleftharpoons 2Ag + 2OH^-; \qquad E° = 0.344\ V$

(a) What is oxidised and reduced

(b) Find E° of the cell and ΔG° in joules.

(HSB,1996 ; PSEB, 1999, CBSE, 2008)

SOLUTION. Since the E°(reduction) value + 0.344 V > – 0.76 V, so we have :

$Ag_2O + H_2O + 2e^- \rightleftharpoons 2Ag + 2OH^-;$

$E° = +\,0.344\ V$ (cathode)

$Zn^{2+} + 2e^- \rightleftharpoons Zn; \qquad E° = -\,0.76 V$ (anode)

Subtract: $- \quad - \qquad - \qquad +$

$Ag_2O + H_2O + Zn \rightleftharpoons 2Ag + 2OH^- + Zn^{2+}$;

$E° = 1.104\ V$ ...(1)

Here, no. of electrons involved = 2. So, $n = 2$. We know that :

$$\Delta_r G° = -nF\,E°_{cell}$$

$= -\,2 \times 96500$ coulomb mol$^-$ $\times\ 1.104\ V$

= 213,072 coulomb volt mol$^-$

= 213,072 J [∵ 1 coulomb volt = 1 Joule]

= 213.072 k J mol$^-$ **Ans.**

EXAMPLE 73. *The E° values at 298 K corresponding to the following two reduction electrode processes are* :

(*i*) $Cu^+/Cu = 0.52\ V$ (*ii*) $Cu^{2+}/Cu^+ = 0.16\ V$

Formulate the galvanic cell for their combination. What will be the cell potential ? Calculate the $\Delta_r G°$ for the cell reaction (F = 96500 C mol$^-$) **(CBSE, 2005)**

SOLUTION. Since anode electrode has less value of E°(reduction), so the galvanic cell obtained by the combination of anode and cathode will be :

Cu^+ (1M)/Cu^{2+} || Cu^+ (1M) /Cu(s)

Since $E°_{(reduction)}$ value, + 0.52 V > + 0.16 V, so we have:

$Cu^+ + 1e^- \rightleftharpoons Cu; \quad E° = +\,0.52\ V$ (cathode)

$Cu^{2+} + e^- \rightleftharpoons Cu^+; \quad E° = +\,0.16\ V$ (anode)

Subtract: $- \quad - \qquad - \qquad -$

$2Cu^+ \rightleftharpoons Cu + Cu^{2+}; \qquad E° = +\,0.36\ V$

Since, the reaction is a one electron change, $n = 1$.

But : $\Delta_r G° = -nF\,E°_{cell}$

$= -\,1 \times 96500\ C \times 0.36\ V$

= 34740 C V = 34740 J[1 C V = 1 J]

$= 34740\ J \times \frac{1\ kJ}{1000\ J} =$ **34.74 k J Ans.**

EXAMPLE 74. *Find the equilibrium constant of the following reaction,*

$Cu^{2+}(aq) + Sn^{2+}(aq) \longrightarrow Cu(s) + Sn^{4+}(aq)$, *at 25°C,*

$E°Cu^{2+}/Cu = 0.34V;\ E°\ Sn^{4+}/Sn^{2+} = 0.155V.$

SOLUTION. $E°_{cell} = E°_{cathode} - E°_{anode}$

$= E°Cu^{2+}/Cu - E°$

$Sn^{4+}/Sn^{2+} = 0.34 - 0.155 = 0.185V$

But $\log k = (n \times E°_{cell})/0.0591.$

Also, $Cu^{2+} + 2e^- \longrightarrow Cu$; So, $n = 2$.

Hence : $\log k = (2 \times 0.185)/0.0591$

$= 6.26.$

Hence k = antilog 6.26.

Or $k = 1.819 \times 10^6$ **Ans.**

EXAMPLE 75. *Calculate the equilibrium constant for the following cell reaction :*

$1/2\ Cl_2(g) + Br^- \longrightarrow 1/2Br_2(l) + Cl^-;\ E° = 0.30\ V$

SOLUTION. $E°_{cell} = 0.30\ V.$

We know, $\log k = (n \times E°_{cell})/0.0591.$

Also, $Br^- \longrightarrow Br + e^-$, so, $n = 1$

Hence, $\log k = (1 \times 0.30)/0.059 = 5$

∴ k = antilog 5 = **10^5**. **Ans.**

EXAMPLE 76. *The Edison storage cell is represented as Fe(s) | FeO(s) | KOH (aq) | Ni_2O_3(s) | Ni(s)*

The half-cell reactions are

$Ni_2O_3(s) + H_2O\ (l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-;$

$E° = +\,0.40\ V$

$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-;$

$E° = -\,0.87\ V$

(*a*) *What is the cell reaction ?*

(*b*) *What is the cell e.m.f. ? How does it depend on the concentration of KOH ?*

(*c*) *What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?* **(IIT, 1994)**

SOLUTION. (*a*) The cell reaction is obtained by subtracting reduction reaction of left half cell from that of right half cell. Reduction half reactions are :

Right half-cell :

$Ni_2O_3(s) + H_2O_{(l)} + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$

Left half-cell :

$FeO(s) + H_2O_{(l)} + 2e^- \rightleftharpoons Fe(s) + 2OH^-$

∴ Cell reaction is

$Fe(s) + Ni_2O_3(s) \rightleftharpoons FeO\ (s) + 2NiO(s)$

(After subtraction)

(*b*) The cell e.m.f. $= E°_R - E°_L = 0.40 - (-\,0.87)$

$= 1.27\ V$

The cell e.m.f. is independent of concentration of KOH as no OH^- appears in the cell reaction.

(*c*) Electrical energy produced = $nF\,E_{cell}$

$= 2 \times 96500\ C\ mol^{-1} \times 1.27\ V$

$= 2.4511 \times 10^5$ J

= 245.11 k J mol^{-1}

EXAMPLE 77. *The following electrochemical cell is set up at 25°C.*

$$Zn \mid Zn^{2+} (a = 1) \parallel Cd^{2+} (a = 1) \mid Cd$$

(*a*) *Write the cell reaction.*

(*b*) *Calculate e.m.f. of the cell*

$(E°\ Zn^{2+}/Zn = -0.763\ V,\ E°\ Cd^{2+}/Cd = -0.403\ V)$

(*c*) *Calculate the value of* $\Delta G°$ *for the cell reaction at 25°C. (Given that F = 96500 C).*

(*d*) *Is the reaction spontaneous ? Discuss.* **(BCEE, 2002)**

SOLUTION. (*a*) The cell reaction involved is

$$Zn + 2Cd^{2+} \longrightarrow Zn^{2+} + Cd$$

(*b*) $E°_{cell} = E°_{cathode} - E°_{anode} \qquad [\because a_{Zn}{}^{2+} = a_{Cd}{}^{+2} = 1]$

$$= -0.0403 - [-0.763] = \mathbf{0.36\ V}$$

(*c*) $\Delta G° = -nF\,E° = -2 \times 96500 \times 0.36$

$$= \mathbf{-69480\ volt\ coulomb}$$

or $\Delta G° = \mathbf{-69480\ J}$

(*d*) As $E°_{cell}$ is positive and ΔG is negative, the cell reaction is spontaneous.

EXAMPLE 78. *Find the equilibrium constant for the reaction*

$$Cu^{2+}{}_{(aq)} + In^{2+}{}_{(aq)} \rightleftharpoons Cu^{+}_{(aq)} + In^{3+}_{(aq)}$$

Given that $E°_{Cu^+/Cu} = 0.15\ V;\ E°_{In^{2+}/In^+} = -0.4\ V;$

$E°_{In^{3+}/In^+} = -0.42\ V$ **[IIT, 2004]**

SOLUTION. $Cu^{2+}_{(aq)} + In^{2+}{}_{(aq)} \rightleftharpoons Cu^{+}_{(aq)} + In^{3+}{}_{(aq)}$;

$$E°_{cell} = E°_{Cu^{2+}/Cu^+} - E°_{In^{3+}/In^{2+}}$$

$$E°_{cell} = 0.15 - E°_{In^{3+}/In^{2+}}$$

Now for In^{3+}/In^{2+}

$In^{3+} + 2e^- \longrightarrow In^+; \qquad E° = -0.42\ V$

Add : $In^+ \longrightarrow In^{2+} + e; \qquad E° = 0.40\ V$

$In^{3+} + e^- \longrightarrow In^{2+}; \qquad E° = ?$

Applying $\Delta G° = \Delta G°_1 + \Delta G°_2$

or $-nF\,E° = -2F(-0.42) - 1F(0.40)$

or $-E° = 0.84 - 0.40;\ E°_{In^{3+}/In^{2+}} = -0.44\ V$

$\therefore$ $E°_{cell} = 0.15 + 0.44 = 0.59\ V$

Now $E°_{cell} = \dfrac{2.303\ RT}{nF} \log K_c$

$\therefore$ $0.59 = \dfrac{0.059}{1} \log K_c$

or $\log K_c = 10.\ \ \mathbf{K_c = Antilog\ 10 = 10^{10}}$

EXAMPLE 79. *Calculate the value of equilibrium constant and Gibb's free energy change in the reaction given below :* **[CBSE PMT (Final) 2004]**

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow Cr^{3+} + 3I_2 + 7H_2O$$

Given that :

(*a*) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^3 + 7H_2O;$

$$E° = 1.33\ V$$

(*b*) $2I^- \longrightarrow I_2 + 2e^-;$

$$E° = -0.54\ V$$

SOLUTION. Half reactions taking place are :

Oxidation : $2I^- \longrightarrow I_2 + 2e^-; \quad E°_{oxi} = -0.54\ V$

Reduction :

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O; E°_{red} = 1.33V$$

Overall Reaction :

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O;$$

$$E° = E°_{oxi} + E°_{red} = -0.54 + 1.33$$

$$= 0.79\ V$$

Now $E°_{cell} = \dfrac{2.303RT}{nF} \log K_c$ (Here $n = 6$)

$\therefore$ $\log K_c = \dfrac{n\,E°}{0.059} = \dfrac{6 \times 0.79}{0.059} = 80.338$

$$K_c = \text{Antilog } 80.338 = \mathbf{2.178 \times 10^{80}}$$

$$\Delta G° = -nFE° = -6 \times 96500\ C \times 0.79\ V$$

$$= 457410\ J = \mathbf{457.41\ k\,J}$$

EXAMPLE 80. *The standard potential of the following cell is 0.23 V at 15°C and 0.21 V at 35° C.*

$$Pt \mid H_2(g) \mid HCl(aq) \parallel AgCl/Ag(s)$$

(*a*) *Write the cell reaction.*

(*b*) *Calculate* $\Delta H°$ *and* $\Delta S°$ *for the cell reaction by assuming that these quantities remain unchanged in the range of 15°C to 35°C.*

(*c*) *Calculate the solubility of AgCl in water at 25°C. Given: The standard reduction potential of* $Ag^+(aq) \mid Ag(s)$ *couple is 0.80 V at 25°C.* **(IIT, 2001)**

SOLUTION. (*a*) The two half cell reactions are :

$$\frac{1}{2}H_2(g) \longrightarrow H^+ + e^- \text{(Oxidation)}$$

$$AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^- \text{(Reduction)}$$

Net cell reaction is :

$$\frac{1}{2}H_{2(g)} + AgCl_{(s)} \longrightarrow HCl_{(aq)} + Ag_{(s)}$$

(*b*) $E_{cell} = 0.23\ V$ (at 15°C)

$$-\Delta G° = nF\,E° = 1 \times 96500\ C \times 0.23\ V$$

$$= 22195\ J \text{ (at 15°C)}$$

$$-\Delta G° = 1 \times 96500\ C \times 0.21\ V$$

$$= 20265\ J \text{ (at 35°C)}$$

Also, $\Delta G° = \Delta H° - T\,\Delta S°$

$\therefore$ $-22195 = \Delta H° - 288 \times \Delta S°$

$$-20265 = \Delta H° - 308 \times \Delta S°$$

Subtracting, $-1930 = 20\ \Delta S°$

or $\Delta S° = \mathbf{-96.50\ J\ K^{-1}\ mol^{-1}}$

Now $-22195 = \Delta H° - 288(-96.50)$

or $\Delta H° = -22195 - 27792 = -49987\ J$

$$= \mathbf{-49.987\ k\,J}$$

(*c*) $E°$ at the average temperature of 298 K

$$= \frac{0.23 + 0.21}{2} = 0.22\ V$$

$$E°_{cell} = 0.22 - 0.80 = -0.58\ V$$

$$E° = 0.059 \log K_{sp} = -0.58$$

On usual calculations,

$$K_{sp} = \mathbf{1.48 \times 10^{-10}\ mol^2\ L^{-2}}$$

19.16 FARADAY'S FIRST AND SECOND LAW OF ELECTROLYSIS

Faraday's first law of electrolysis. According to this law, the weight or mass (*w*) liberated or *deposited at* any electrode as a result of electrolysis is directly proportional to the quantity of electricity (Q) passed through the electrolyte.

Mathematically : $W \propto Q$ or $W = ZQ$ ...(1)

where $Q = It$.

Thus $\mathbf{W = Z\,I\,t}$ ...(2)

where I is the current in amperes, *t* is the time in seconds and Z is **the electrochemical equivalent.**

when I = 1 ampere, *t* = 1 second, then $W = Z$. Thus :

Electrochemical equivalent (Z) is equal to the weight of the substance liberated when one ampere current is passed for 1 second.

Note that : (*i*) 1 coulomb of electricity = 1 ampere current × 1 second time.

(*ii*) When 96500 coulomb (or one Faraday) of electricity is passed through an electrolyte then 1 gram equivalent weight of the substance is liberated.

∴ 1 Faraday = 96500 coulomb and wt. of substance liberated when 96500 coulomb electricity is passed = 1 g. equivalent. e.g., when 96500 coulomb of electricity is passed through aluminium chloride solution then wt. of Al (eq.wt. = At. wt/valency = 27/3 = 9) liberated = 9 g.

Thus : Gram equivalent weight = Z × 96500 coulomb

Or $$Z = \frac{\text{Gram eq. wt.}}{96500 \text{ coulomb}}$$

Also : $$Z = \frac{\text{Wt. of substance (W)}}{\text{Quantity of electricity (Q)}}$$

[from relation (1) above]

Unit of $Z = gC^{-}$ where *C* represents coulomb

Faraday's second law of electrolysis. *According* to this law, *when same* quantity of electricity is passed through *different electrolyte* solutions connected in series, the weights of different substances liberated at the electrodes are proportional to their equivlent weights. For example, consider three electrolytic cells containing solutions of $AgNO_3$, $CuSO_4$ and dil. H_2SO_4 which are connected in series and same amount of current is passed for the same time, then:

$$\frac{\text{Wt. of Ag}}{\text{Eq. Wt. of Ag}} = \frac{\text{Wt. of Cu}}{\text{Eq. Wt. of Cu}} = \frac{\text{Wt. of } H_2}{\text{Eq. Wt. of } H_2}$$

To understand the law, consider the following reactions :

(*i*) $H^+ + e^- \longrightarrow H \,;\, H + H \longrightarrow H_2$

(*ii*) $Cu^{2+} + 2e^- \longrightarrow Cu$;

(*iii*) $Al^{3+} + 3e^- \longrightarrow Al$

Suppose that these three reactions take place in three separate electrolytic cells connected in series. When *'a' moles of electrons* are passed through these three cells, the mass of H_2, Cu and Al liberated/deposited are 1a g, 31.75a g and 9a g respectively. Here, 1, 31.75 and 9 are the chemical equivalent weights (*E*) of H, Cu and Al respectively. Thus:

$$W = \textbf{moles of electrons } (a) \times E$$

The charge possessed by one mole (= 6.022×10^{23}) of **electrons** = $1.6 \times 10^{-19} \times 6.022 \times 10^{23}$ = **96500** C. This charge (96500 C) is called one **Faraday**.

This means that by passing one mol of electrons and by passing one Faraday of charge, one gram equivalent weight of the substance will be liberated or deposited

$$\therefore \quad W = \frac{\textbf{Q (in coulomb)}}{\textbf{96500 coulomb}} \times \textbf{Eq. wt.}$$

19.17 FARADAY'S FIRST LAW OF ELECTROLYSIS

Example 81. *Find the weight of chlorine gas produced when one ampere current is passed for 15 minutes through molten sodium chloride. (Atomic mass of chlorine* = 35.5*).* **(PSEB, 1995S)**

Solution. Time (*t*) = 15 minutes = 15 × 60 = 900 seconds; current = 1 ampere. Reaction : $Cl^- - 1\,e^- \longrightarrow 1/2\,Cl_2$. Eq. wt. of Cl_2 = At. wt. of Cl/1 = 35.5/1 = 35.5. Electrochemical equivalent, Z = g.eq.wt. of Cl/96500 C = 35.5/96500. We know, wt = Z × current in amperes × time in seconds = (35.5 × 1 × 15 × 60)/96500) = **0.331 g** **Ans.**

Example 82. *For how long a current of 1.5 amperes has to be passed through the electrolyte in order to deposit 1.5 g of Al when the electrode reaction is*

$$Al^{3+} + 3e^- \longrightarrow Al \quad (\textit{Atomic mass of Al} = 27)$$

Solution. Reaction : $\underset{1\text{ mol}}{Al^{3+}} + \underset{3\text{ mol}}{3e^-} \longrightarrow \underset{1\text{mol } (=27\text{g})}{Al}$

Charge on 3 mol of electrons = 3 × 96500 coulombs :

(*a*) Total charge to deposit 27 g Al = 3 × 96500 C

∴ Charge to deposit 1.5 g Al = (3 × 96500 × 1.5)/27 = 16083.3 C ...(1)

(*b*) **To Calculate time (t).** Current = 1.5 ampere; time (*t*) = ?.

No. of coulombs = ampere × time (in seconds) = 1.5 × *t*. C. ...(2)

Equating (1) and (2), we get : 1.5 *t* = 16083.3

Or *t* = (16083.3)/1.5 sec. **Or** (16083.3)/(1.5 × 60 × 60) = 2.978 hours **Ans.**

Example 83. *A galvanic cell is set up from a zinc bar weighing 100 g and one litre of 1 M $CuSO_4$ solution. Assuming that the cell delivers a steady current of 1.0 ampere, how long the cell would work ?* (at. wt., Zn = 65.38g mol⁻)

Solution. Wt. of Zn = 100 g ;

At wt. of Zn = 65.38 g mol⁻.

So, no. of mol of Zn = $\dfrac{100\text{ g}}{65.38\text{ g mol}^-}$ = 1.58 mol

1 M CuSO = 1 mol $CuSO_4$ per litre.

But $CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$

$\therefore$ $Cu^{2+} + 2e^- \longrightarrow Cu$

$\therefore$ One mol of $CuSO_4$ can produce electricity,

Q = 2 × 96500 coulomb

But Q = Current in amperes × time in seconds

$\therefore$ 2 × 96500 coulomb = 1 ampere × time in seconds

$$\therefore \text{Time in seconds} = \frac{2 \times 96500 \text{ ampere second}}{1 \text{ ampere}}$$

($\because$ C = ampere × second)

= 193000 s

$$= 193000\text{s} \times \frac{1\text{min}}{60\text{s}} \times \frac{1\text{hr}}{60\text{min}}$$

= **53.6 hr** **Ans.**

EXAMPLE 84. *How much charge is required for the following reduction of :*

(*a*) 1 *mol of* Al^{3+} *to Al* (*b*) 1 *mol of* Cu^{2+} *to Cu.*

SOLUTION. (*a*) The required reduction is,

$Al^{3+} + 3e^- \longrightarrow Al$ *i.e.*, 1 mole of Al = 3 Faradays as it is a 3 electron change

(*b*) The required reduction is, $Cu^{2+} + 2e^- \rightarrow Cu$ *i.e.*, 1 mole of Cu = 2 Faradays as it is a 2 electron change.

EXAMPLE 85. *Calculate the number of coulombs required to deposit* 5.4 *g of Al when the electrode reaction is :*

$Al^{3+} + 3e^- \longrightarrow Al$:

(*atomic mass of Al* = 27 *g mol*$^-$; *F* = 96500 *mol*$^-$)

(DSB,1994)

SOLUTION. From the reaction, $Al^{3+} + 3e^- \longrightarrow Al$, eq. wt. of Al = At. wt. of Al/3 = 27/3 = 9. Hence electrochemical equivalent, Z = g.eq. wt. of Al/96500 = 9/96500. We know, wt = Z × (current in ampere × time in sec) = Z × no. of coulombs. Substituting the values, we get :

5.4 = (9/96500) × no. of coulombs.

Hence, no. of coulombs = (5.4 × 96500)/9

= **57900 coulombs**. **Ans.**

EXAMPLE 86. *Write anode and cathode reactions for the electrolysis of water. How much charge will be transported for the decomposition of* 3.6 *g of* H_2O ? **(CBSE, 2000S)**

SOLUTION. For the electrolysis of water, the reactions taking place at different electrodes are :

At anode. $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (Oxidation)

2 × 18 = 36 g 4 × 96500 coulombs ...(1)

At cathode. $2H^+ + 2e^- \longrightarrow H_2$ (Reduction) ...(2)

wt. of H_2O = 3.6g.

From reaction (1), we have:

36 g H_2O require for electrolysis

= 4 × 96500 coulombs.

$\therefore$ 3.6 g H_2O require for electrolysis

= (4 × 96500 × 3.6)/36

= **38600 coulombs.** **Ans.**

EXAMPLE 87. *Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0 × 10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminum is produced? (Assume 100% current efficiency, at. mass of Al = 27g mol$^-$)*

(*a*) *8.1 × 10^4g* (*b*) *2.4 × 10^5g*

(*c*) *1.3 × 10^4 g* (*d*) *9.0 × 10^3 g*

(PSEB, 2007, CBSE-PMT, 2009)

SOLUTION. Eq. wt. of

Al = At. wt of Al/Valency = 27/3 = 9.

Z = Electrochemical equivalent

= g. eq. wt/96500 coulomb

$\therefore$ *g*. eq. wt. of Al = *Z* × 96500 *C*; 9g = *Z* × 96500 *C*

$$\therefore \quad Z = \frac{9g}{96500C}.$$

We know

Mass of Al = *Z* × *I* × *t*;

$$\text{mass of Al} = \frac{9g}{96500C} \times 4 \times 10^4 \text{ amp.} \times 6 \times 60 \times 60 \text{ s}$$

$$= 8.1 \times 10^4 \text{ g.} \frac{\text{amp.s}}{\text{C}} = 8.1 \times 10^4 \text{ g.}$$

So, the correct answer is (*a*).

EXAMPLE 88. *How many coulombs are required for the following reduction ?*

(*a*) 1 *mol of* $C_6H_5NO_2$ to $C_6H_5NH_2$

(*b*) 1 *mol of* MnO_4^- *to* Mn^{2+} **(PSEB, 1999S)**

SOLUTION. (*a*)

$C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

1mol 6mol

6*F*

So, 6*F* = 6 × 96500 C

= **579000 coulombs** **Ans.**

(*b*) $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

1 mol 5 mol

5*F*

So, 5*F* = 5 × 96500 Coulombs

= **482500 Coulombs** **Ans.**

EXAMPLE 89. *How many moles of mercury will be produced by electrolysing 1.0 M Hg(NO$_3$)$_2$ solution with a current of 2.0 A for 3 hours? (Hg = 200.6g mol$^-$).* **(ISC, 2010)**

SOLUTION.

$Hg(NO_3)_2$ (1M) $\rightleftharpoons Hg^{2+}$ (1M) + $2NO_3^-$ (2M)

$Hg^{2+} + 2e^- \longrightarrow Hg$

Charge = current in A × time in second

= 2.0 × 3 × 60 × 60 = 21600 s

At. wt. of Hg = 200.6g mol$^-$. Since at. wt. of Hg is 200.6g mol$^-$, so we require

2F or 2 × 96500 C to deposit

Hg = 200.6 g mol$^-$ = 1 mol

$\therefore$ 21600 C are required to deposit

$$\text{Hg} = \frac{1}{2 \times 96500} \times 21600 = 0.112 \text{ mol.}$$

EXAMPLE 90. *How many coulombs are required for the following oxidation ?*

(*a*) 1 *mol of* H_2O *to* O_2

(*b*) 1 *mol of FeO to* Fe_2O_3. **(PSEB, 1999S)**

SOLUTION. (*a*)

$$\begin{array}{llll} 2H_2O & \longrightarrow 4H^+ + & O_2(g) & + 4e^- \\ 2\text{ mol} & & 1\text{ mol} & 4\text{mol} \\ 1\text{ mol} & & \frac{1}{2}\text{mol} & \frac{4}{2} = 2\text{ mol} = 2 \times 96500 \text{ coulombs} \end{array}$$

(*a*) 1 mol H_2O require charge

$= 2 \times 96500$ coulombs

$=$ **193000 coulombs** **Ans.**

$$\begin{array}{llll} (b) & Fe^{2+} \longrightarrow & Fe^{3+} & + 1e^- \\ & 1\text{ mol} & 1\text{ mol} & 1\text{ F} = 1 \times 96500 \text{ coulombs} \end{array}$$

$\therefore$ 1 mol of FeO require 1 mol electrons *i.e.*, **1 × 96500 coulombs.** **Ans.**

EXAMPLE 91. *A current of* 8.0 *amperes is used to prepare* MnO_2 *by the electrolysis of* $MnSO_4$ *that uses* 85% *of the current passing through the cell. Calculate the time in which* 60 *g of* MnO_2 *can be prepared.*

SOLUTION. The reaction involved is :

$$Mn^{2+}(aq) + 2H_2O(l) \longrightarrow Mn^{4+}O_2(s) + 2H^+(aq) + H_2(g).$$

[At. mass, Mn = 55, O = 16]

Wt. of MnO_2 = 60 g ; eq. wt. of

$$MnO_2 = \frac{55 + (2 \times 16)}{2} = 43.5$$

[$\because Mn^{2+} + 2H_2O \to MnO_2 + 4H^+ + 2e^-$ is a 2 electron change].

Current (I), in amperes

$= 85\%$ of 8 amperes

$$= \frac{8 \times 85}{100} = 6.8 \text{ amperes}$$

But $W = Z\,I\,t.$

So, $t = \dfrac{W}{ZI}$

$$= \frac{60 \times 96500}{43.5 \times 6.8} \text{sec}.$$

$$\left[\because Z = \frac{\text{g. eq. wt. of } MnO_2}{96500} = \frac{43.5}{96500}\right]$$

$$= 19374 \text{ sec} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{1 \text{ hr}}{60 \text{ min}}$$

$=$ **5.437 hours** **Ans.**

EXAMPLE 92. *If the charge on an electron is* 1.6×10^{-19} *coulomb, calculate the value of Avogadro's number.*

(1*F* = 96500 *coulomb*)

SOLUTION. 1 F or 96500 coulomb is charge on electrons = 1 mol

Hence 1.6×10^{-19} coulomb × Avogadro's no.

= 96500 coulomb

$$\therefore \text{ Avogadro's no.} = \frac{96500 \text{ coulomb}}{1.6 \times 10^{-19} \text{ coulomb}}$$

$=$ **6.03 × 10²³** **Ans.**

19.18 FARADAY'S SECOND LAW OF ELECTROLYSIS.

EXAMPLE 93. *An electric current is passed through three cells in series, respectively containing solutions of copper sulphate, silver nitrate and potassium iodide. What weights of silver and iodine will be liberated while* 1.25 *g of copper are being deposited? (at. wt. of Ag* = 108, *I* = 127, *Cu* = 63.5*)*

SOLUTION. Eq. wt. of

$$\text{Ag} = \frac{\text{At. wt. of Ag}}{\text{Valency of Ag}} = \frac{108}{1} = 108\,;$$

$$\text{Eq. wt. of I} = \frac{\text{At. wt. of I}}{\text{Valency of I}} = \frac{127}{1} = 127\,;$$

$$\text{Eq. wt. of Cu} = \frac{\text{At. wt. of Cu}}{\text{Valency of Cu}} = \frac{63.5}{2} = 31.75$$

According to Faraday's second law of electrolysis :

$$\frac{\text{Wt. of Cu}}{\text{Eq. wt. of Cu}} = \frac{\text{Wt. of iodine}}{\text{Eq. wt. of iodine}} = \frac{\text{Wt. of Ag}}{\text{Eq. wt. of Ag}}$$

$$\frac{1.25 \text{ g}}{31.75} = \frac{\text{Wt. of iodine}}{127} = \frac{\text{Wt. of Ag}}{108}$$

$$\therefore \quad \text{Wt. of iodine} = \frac{1.25 \text{ g}}{31.75} \times 127 = \mathbf{5.0 \text{ g}}$$

$$\text{Also,} \quad \text{Wt. of Ag} = \frac{1.25 \text{ g}}{31.75} \times 108 = \mathbf{4.25 \text{ g}}$$

EXAMPLE 94. *When an aqueous solution of sodium chloride was electrolysed, 0.1 g of chlorine was liberated. Calculate the volume of hydrogen measured at 15° C and 745 mm pressure which will be liberated at the same time. (at. wt., Cl = 35.5 : H = 1).*

SOLUTION. Eq. wt. of

$$\text{H} = \frac{\text{At. wt. of H}}{\text{Valency of H}} = \frac{1}{1} = 1$$

$$\text{Eq. wt. of Cl} = \frac{\text{At. wt. of Cl}}{\text{Valency of Cl}} = \frac{35.5}{1} = 35.5$$

According to Faraday's second law of electrolysis :

$$\frac{\text{Wt. of H}}{\text{Eq. wt. of H}} = \frac{\text{Wt. of Cl}}{\text{Eq. wt. of Cl}}\,;\ \frac{\text{Wt. of H}}{1} = \frac{0.1}{35.5}$$

$$\therefore \text{ Wt. of H} = \frac{1}{355} \text{ g}.$$

We know that :

2g (*i.e.*, 1 g. equivalent) of H_2 occupies volume at N.T.P. = 22400 mL

$\frac{1}{355}$ g of H_2 occupies volume at N.T.P.

$$= \frac{22400 \text{ mL}}{2\text{g}} \times \frac{1}{355} \text{g} = \mathbf{31.55 \text{ mL}}$$

Now ; $P_1 = 745$ mm, $V_1 = ?$,

$T_1 = 15 + 273$

$= 288\ K$;

At N.T.P., $P_2 = 760$ mm;

$V_2 = 31.55$ mL, $T_2 = 273\ K$

Using gas equation, we have :

$$\frac{P_1V_1}{T_2} = \frac{P_2\,V_2}{T_2}\,;\; V_1 = \frac{P_2\,V_2}{T_2}\times\frac{T_1}{P_1}$$

$$= \frac{760\text{ mm}\times 31.55\text{ mL}\times 288\text{ K}}{273\text{ K}\times 745\text{ mm}}$$

$\therefore \quad V_1 = \mathbf{33.95\ mL.}$ **Ans.**

Example 95. *A current of electricity was passed through a series of cells containing $AgNO_3$, $CuSO_4$ and H_2SO_4 solutions for a period of 25 minutes. If the silver deposited was 0.5394 g, what would be (a) the weight of copper and (b) the volume of H_2 at N.T.P. liberated by the current ? What was the strength of current assuming that it remained constant ? (at. wt., Ag = 108 ; Cu = 63.57 ; 1 Faraday = 96500 C).*

Solution. (*a*) To find wt. of Cu and volume of H_2 at N.T.P.

According to Faraday's second law of electroysis :

$$\frac{\text{Wt. of Cu}}{\text{Eq. wt. of Cu}} = \frac{\text{Wt. of H}}{\text{Eq. wt. of H}} = \frac{\text{Wt. of Ag}}{\text{Eq. wt. of Ag}}$$

$$\frac{\text{Wt. of Cu}}{63.5/2} = \frac{\text{Wt. of H}}{1} = \frac{0.5394\text{g}}{108}$$

$$\therefore \quad \text{Wt. of Cu} = \frac{63.5}{2}\times\frac{0.5394\text{g}}{108} = \mathbf{0.1586\ Ans.}$$

$$\text{Wt. of H} = 1\times\frac{0.5394\text{g}}{108} = 0.00499\text{ g}$$

$$\left[\begin{array}{l} \text{Eq. wt. of Cu} = \dfrac{\text{At. wt.}}{\text{Valency}} = 63.5/2 \\ \text{Eq.wt. of H} = \dfrac{\text{At. wt.}}{\text{Valency}} = \dfrac{1}{1} = 1 \\ \text{Eq. wt. of Ag} = \dfrac{\text{At. wt.}}{\text{Valency}} = \dfrac{108}{1} \end{array}\right]$$

But 2g (= g. mol. wt of H_2) of H_2 at N.T.P. occupies volume = 22400 mL

0.00499g H_2 occupies volume at N.T.P.

$$= \frac{22400\text{ mL}}{2\text{g}}\times 0.00499\text{ g}$$

$$= \mathbf{55.89\ mL} \qquad \textbf{Ans.}$$

(*b*) 108 g (= 1 g. equivalent of Ag) of Ag is liberated by = 96500 C

0.5394 g of Ag is liberated by

$$= \frac{96500\text{ C}}{108\text{ g}}\times 0.5394\text{g} = \text{Q}$$

But Q = Current in ampere × time in seconds :

$$25\text{ min} = 25\text{ min}\times\frac{60\text{ sec}}{1\text{min}} = 1500\text{s}$$

$$\therefore \quad \text{Current} = \frac{\text{Q}}{\text{time}} = \frac{96500\text{ C}\times 0.5394\text{ g}}{108\text{ g}\times 1500\text{ s}}$$

$$= \mathbf{0.3213\ ampere} \qquad \textbf{Ans.}$$

$$\left[\because \frac{\text{C}}{\text{s}} = \text{ampere}\right]$$

Type. (*a*) When one Faraday (= 96500 coulomb) of electricity is passed then one gram atom (= 6.023 × 10^{23} atoms) of Ag^+ ions (say) are liberated.

(*b*) 1 Coulomb = 3 × 10^9 e.s.u.

Example 96. *Calculate the electrostatic charge on Ag^+ ions when one Faraday of electricity is passed through the solution containing these ions.*

Solution. Electrostatic charge on Ag^+ ions

$$= \frac{96500\text{ coulomb}}{6.023\times 10^{23}}$$

($\because$ 1 Faraday = 96500 coulombs)

But 1 coulomb = 3 × 10^9 e.s.u. *i.e.*, electrostatic unit.

$$\therefore \quad \frac{96500\text{ C}}{6.023\times 10^{23}} = \frac{96500\times 3\times 10^9}{6.023\times 10^{23}}\text{ e.s.u.}$$

$$= \mathbf{4.81\times 10^{-10}\ e.s.u.} \qquad \textbf{Ans.}$$

Example 97. *A steady current of 1.8 amperes was passed through three electrolytic cells A, B, and C (connected in series) containing $CuSO_4$, $ZnSO_4$ and $AgNO_3$ solutions respectively till 2.16 g of silver was deposited at the cathode. Calculate the time for which the current was passed Also calculate the weight of copper and zinc deposited.*

Solution. (*i*) Wt. of Ag deposited = 1.7 g, current passed = 1.8 amperes ; quantity of electricity passed, Q = ? ; t = ?

$$\text{Reaction : } \underset{1\text{mol}}{Ag^+} + \underset{\substack{1\text{ mol} \\ = 96{,}500\text{ C}}}{e^-} \longrightarrow \underset{1\text{mol} = 108\text{g}}{Ag}$$

[$\because$ at. wt. of Ag = 108]

108 g Ag is deposited by charge = 96500 coulombs

2.16 g of Ag is deposited by charge

$$= \frac{96500}{108}\times 2.16 = 1930\text{ coulomb}$$

We know Q = current in amperes × time in seconds

$$\therefore \quad t = \frac{\text{Q}}{\text{C}} = \frac{1930\text{ coulombs}}{1.8\text{ amperes}}$$

$$= \mathbf{1072\ seconds} \qquad \textbf{Ans.}$$

(*ii*) $\text{Eq. wt. of Cu} = \dfrac{\text{At. wt.}}{\text{Valency}} = \dfrac{63.5}{2} = 31.75$

Let wt. of Cu deposited = *x* g

$$\text{But} \quad \frac{\text{Wt. of Cu}}{\text{Wt. of Ag}} = \frac{\text{Eq. Wt. of Cu}}{\text{Eq. Wt. of Ag}};$$

$$\frac{x}{2.16} = \frac{31.75}{108}$$

$$\left[\text{Eq. wt. of Ag} = \frac{\text{At. Wt. of Ag}}{\text{Valency}} = \frac{108}{1}\right]$$

$$\therefore \quad x = \mathbf{0.635\ g} \qquad \textbf{Ans.}$$

(*iii*) $\text{Eq. wt. of Zn} = \dfrac{\text{At. wt.}}{\text{Valency}} = \dfrac{65}{2} = 32.5$

Let wt. of Zn = *x* g

$$\text{But} \quad \frac{\text{Wt. of Zn}}{\text{Wt. of Ag}} = \frac{\text{Eq. wt.of Zn}}{\text{Eq. wt. of Ag}};$$

$$\frac{x}{2.16} = \frac{32.5}{108};\; x = \mathbf{0.65\ g} \qquad \textbf{Ans.}$$

EXAMPLE 98. *The amount of electricity which releases 2.6267 g of gold from a gold salt is same as that which dissolves 1.26 g of copper from copper anode during the electrolysis of copper sulphate solution. What is the oxidation number of gold in the gold state ? (At. wts. of Cu = 63.5, Au = 197).* **(W.B.J.E.E., 2003)**

SOLUTION. According to Faraday's second law of electrolysis,

$$\frac{\text{Weight of copper dissolved}}{\text{Weight of gold deposited}} = \frac{\text{Eq. wt. of copper}}{\text{Eq. wt. of gold}} \qquad ...(1)$$

Equivalent weight of an element

$$= \frac{\text{Atomic weight}}{\text{Valency}}$$

$$\text{Eq. wt. of copper} = \frac{63.5}{2} = 31.75\,;$$

$$\text{Eq. wt. of gold} = \frac{197}{x}$$

where x is the oxidation number (or valency) of gold

Substituting the values in equation (1), we get :

$$\frac{1.26}{2.6267} = \frac{31.75x}{197}$$

$$x = \frac{1.26 \times 197}{2.6267 \times 31.75} \simeq \mathbf{3} \qquad \textbf{Ans.}$$

EXAMPLE 99. *A 100 W, 110 V incandescent lamp is connected in series with an electrolytic cell containing $CdSO_4$ solution. What mass of cadmium will be deposited at the cathode after 4 hours of electrolysis ? Calculate gram equivalent of acid that will be formed ? [Cd = 112.2]* **[WBJEE, 2004]**

SOLUTION. 100 W, 110 V bulb sends current

$$= \frac{100}{110} \text{ amp. per second}$$

Electricity passed through the solution in 4 hours

$$= \frac{100}{110} \times 4 \times 60 \times 60 \text{ C}$$

$$= 13091 \text{ C} = 0.1356 \text{ F}$$

$$[\because 1\text{F} = 96500 \text{ C}]$$

Reactions taking place during electrolysis are :

$$CdSO_4 \rightleftharpoons Cd^{2+} + SO_4^{2-}$$

At cathode : $Cd^{2+} + 2e^- \longrightarrow Cd$

At anode : $SO_4^{2-} + H_2O \longrightarrow H_2SO_4 + 1/2\,O_2 + 2e^-$

$\therefore$ 2 × 96500 C produce Cd = 112.2 g

$$13091 \text{ C produce Cd} = \frac{112.2}{2 \times 96500} \times 13091 \text{ g} = 7.61 \text{ g}$$

According to equation,

2F give 1 mol or 2 gram equivalent of acid; or 1F gives 1gram equivalent of acid

$\therefore$ 0.1356 F give acid = 0.1356 g equivalent

EXAMPLE 100. *The density of copper is 8.94 g/c. c. Find out the number of coulombs of electricity needed to plate an area of 10 cm × 10 cm to a thickness of 10^{-2} cm using copper sulphate solution as an electrolyte (Cu = 63.5).*

SOLUTION. Density,

$$d = 8.94 \text{g/c.c.;} \text{ Volume to be plated}$$

$$= 10 \times 10 \times 10^{-2} = 1 \text{c.c.}$$

$$\text{Mass} = d \times V = 8.94 \times 1 = 8.94 \text{ g}$$

$$\underset{\substack{2\text{mol}\\2 \times 96500 \text{ C}}}{Cu^{2+} + 2e^-} \longrightarrow \underset{\substack{1\text{mol}\\63.5 \text{ g}}}{Cu}$$

Number of coulombs required to deposit 63.5 g Cu = 2 × 96500 C

Number of coulombs required to deposit 8.94 g

$$\text{Cu} = \frac{2 \times 96500}{63.5} \times 8.94 = \mathbf{27172\ C\ Ans.}$$

EXAMPLE 101. *A current of 5A is passing through copper wire. Calculate the number of electrons passing through a point per second. ($e = 1.6 \times 10^{-19}$ C).* **(WBJEE, 2003)**

SOLUTION. Current passed = 5A

Coulombs of electricity which pass through the copper wire in one sec = I × t = 5 × 1= 5C

Charge on an electron = 1.6×10^{-19} C

1.6×10^{-19} C of charge is carried by electrons = 1

5C charge is carried by electrons

$$= \frac{1}{1.6 \times 10^{-19}} \times 5$$

$$= \mathbf{3.125 \times 10^{19}\ electrons} \qquad \textbf{Ans.}$$

EXAMPLE 102. *Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 minutes. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.* **(IIT, 2001)**

SOLUTION. Quantity of electricity passed is

$$Q = At = 2 \times 10^{-3} \text{ A} \times (16 \times 60\text{s}) = 1.92$$

Amount of electrons passed

$$= \frac{1.92}{96500} \text{ mol} = 1.98 \times 10^{-5} \text{ mol}$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

$\therefore$ No. of moles of Cu^{2+} ions discharged

$$= \frac{1.98}{2} \times 10^{-5} \text{ mol} = 9.9 \times 10^{-6} \text{mol.}$$

Hence initial concentration

$$= 9.9 \times 10^{-6} \times 2 \text{ mol per 250 mL}$$

$$= \frac{9.9 \times 10^{-6} \times 2 \times 1000}{250} \text{M}$$

$$= \mathbf{7.92 \times 10^{-5}\ M} \qquad \textbf{Ans.}$$

EXAMPLE 103. *The following electrochemical cell has been set up :*

$$Pt\,(1) \mid Fe^{3+}, Fe^{2+}{}_{(a\,=\,1)} : Ce^{4+}, Ce^{3+}{}_{(a\,=\,1)} \mid Pt\,(2)$$

$$E°\,(Fe^{3+} \mid Fe^{2+}) = 0.77\ V,\ E°\,(Ce^{4+} \mid Ce^{3+}) = 1.61\ V$$

If an ammeter is connected between two platinum electrodes, predict the direction of flow of current. Will the current increase or decrease with time ? **(IIT, 2000)**

Solution. From the given values of reduction potentials, for the e.m.f. to be positve, the following reaction should occur :

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

∴ $Ce^{4+} | Ce^{3+}$ electrode will act as cathode and $Fe^{3+} | Fe^{2+}$ electrode will act as anode

$$E°_{cell} = E°_{cathode} - E°_{anode} = E°(Ce^{4+} | Ce^{3+}) - E°\,(Fe^{3+} | Fe^{2+})$$

$$= \mathbf{1.61 - 0.77 = 0.84\ V}$$

E.M.F. is positive and therefore, reaction is spontaneous.

∴ *Current will flow from Ce electrode to iron electrode and will decrease with time.* (Electrons will flow from iron electrode to Ce electrode)

19.19 MISCELLANEOUS EXAMPLES

Example 104. *Calculate the current required to be passed in the reaction*

$2NH_4HSO_4 \longrightarrow (NH_4)_2S_2O_8 + H_2$ *(electrolytic reaction) to form enough*

$(NH_4)_2S_2O_8 + 2H_2O \longrightarrow H_2O_2 + 2NH_4HSO_4$ *(Steam distilation) intermediate* $(NH_4)_2S_2O_8$, *to yield 50 g of pure hydrogen peroxide per hour. Assume 75% current efficiency in the process.*

Solution. (*a*) Molar mass of

$$H_2O_2 = (2 \times 1) + (2 \times 16) = 34.$$

In NH_4HSO_4, all the oxygen atoms have –2 oxidation state. In $(NH_4)_2S_2O_8$, two oxygen atoms are linked to each other through peroxide linkage. So, these oxygen atoms have –1 oxidation state. It means, two oxygen atoms have got oxidised from –2 to –1state. Thus when two moles of NH_4HSO_4 (given) react, 2 moles of electrons are formed.

Also, 50 g of pure H_2O_2 will be 50/34 moles of H_2O_2. Moles of $(NH_4)_2S_2O_8$ that would have reacted = moles of $(NH_4)_2S_2O_8$ that need to be formed from $NH_4HSO_4 = \frac{50}{34}$.

∴ Moles of NH_4HSO_4 that need to react $= \frac{50}{34} \times 2 = \frac{50}{17}$.

or Moles of electrons given by $\frac{50}{17}$ moles of

$$NH_4HSO_4 = \frac{50}{17}$$

Hence, $\text{charge} = \frac{50}{17} \times 96500$

$$= \mathbf{283823.5\ coulombs.} \qquad \textbf{Ans.}$$

(*b*) **Current with 75% efficiency.**

$$= \frac{283823.5\ C}{60 \times 60\,s} \times \frac{100}{75}$$

$= 105.12$ A *i.e.*, ampere[∵ 1A = Cs^{-}]
∵ 1 hour = 60 × 60 seconds]

Example 105. *During electrolysis of a solution, 125 ampere current was passed for 500 seconds. If one of the electrodes is that of impure copper (containing only Ag , Au and Fe), the mass of the cathode increased by 20.02 g and that of the anode decreased by 20.5 g. Calculate the percentage of copper and iron originally present in the sample.*

Solution. In order to solve this problem, we have to make certain assumptions:

(*a*) *The cathode* should either be an *inert electrode or a pure copper electrode:* It means, anode should be of impure copper. In this situation, metals in impure copper will get oxidised when electric current is passed. This assumption is necessary because, we are to find the percentage of Cu and Fe in the anode. This fact can be related to mass increase of cathode only if the metal from the anode gets deposited on the cathode. Based on their reduction potential values, Fe will be oxidised first and then copper. When Cu is competely oxidised, Ag and Au fall into the electrolyte as anode mud below anode.

(*b*) *Type of electrolyte used.* The electrolyte used should not contain Cu^{2+} ions. The reason is that mass increase of the cathode during the oxidation of Fe to Fe^{2+}, would be due to copper and the mass increase of the cathode, during the oxidation of copper would also be due to copper. Hence percentage of Cu and Fe cannot be determined in the anode. To overcome this difficulty, the electrolyte used should be an acid with an anion having a low standard oxidation potential. It means, H^+ of solution will get reduced to H_2 gas and Fe gets oxidised to Fe^{2+}. Since H_2 is a gas, the mass of cathode does not increase. After Fe, Cu gets oxidised to Cu^{2+} and at this time, it is Cu^{2+} that would be reduced to Cu and mass of the cathode starts increasing.

∴ Decrease in mass of anode = mass of Cu, Ag, Au, Fe = 20.5 g. Increase in mass of cathode = mass of Cu in the anode = 20.02 g.

% age of Cu in impure sample (anode)

$$= \frac{20.02}{20.5} \times 100$$

$$= \mathbf{97.66\ \%} \qquad \textbf{Ans.}$$

Moles of electrons passed

$$= \frac{500 s \times 125\ A}{96500 C} = 0.648$$

Moles of electrons used for

$$Cu = \frac{20.02}{63.5} \times 2 = 0.631$$

[∵ At. wt. of Cu = 63.5 : $Cu^{2+} + 2e^- \rightarrow Cu$]

Moles of electrons used for

$$Fe = 0.648 - 0.631 = 0.017$$

$$\text{Moles of Fe} = \frac{0.017}{2} = 0.0085$$

[∵ $Fe^{2+} + 2e^- \rightarrow Fe$; At. wt. of Fe = 56]

% age of Fe in the anode

$$= \frac{0.0085 \times 56}{20.5} \times 100 = \mathbf{2.32\%} \quad \textbf{Ans.}$$

EXAMPLE 106. *A person is interested to coat a metal surface of 60 cm^2 area with 0.004 mm thick layer of silver. Calculate the time for which he must pass a current of four amperes through a silver nitrate solution ? Atomic weight of Ag is 107.9 g mol$^-$ and density of Ag is 10.5 g cm^{-3}.*

SOLUTION. Let us assume that the Ag–coating has to be done on one side of the metal surface.

Volume of Ag needed for coating

$$= 60\ \text{cm}^2 \times \left(\frac{0.004}{10}\ \text{cm}\right) = 0.024\,\text{cm}^3$$

$$\text{Mass of Ag} = \text{Volume} \times \text{density}$$

$$= 0.024\ \text{cm}^3 \times 10.5\ \text{g cm}^{-3} = 0.252\ \text{g}$$

$$\text{Moles of Ag} = \text{mass/At.wt.} = 0.252/107.9$$

$$= 2.34 \times 10^{-3}$$

$$\text{Moles of electrons} = (2.34 \times 10^{-3}) \times 1$$

$$[\because Ag^+ + 1e^- \rightarrow Ag \text{ is a one electron change}]$$

$$\text{Hence, charge passed} = 2.34 \times 10^{-3} \times 96500$$

$$= \mathbf{225.81\ coulomb's.}$$

$$\therefore \quad \text{Time} = \text{charge passed in coulombs/}$$

$$\text{current in amperes} = \frac{225.81}{4}$$

$$= \mathbf{56.4525\ seconds.\ Ans.}$$

EXAMPLE 107. *When a metal (at. wt., a) salt solution was electrolysed for 100 minutes with 0.2 A of current, 0.696 g of the metal was deposited. Calculate the value of 'a'. Given that specific heat of metal = 0.0566 cal (g)$^-$ °C. Also, according to Dulong and Petit's law, approximate atomic weight = 6.4/specific heat.*

SOLUTION. From the given data :

$$\text{Approximate at. wt.} = \frac{6.4}{\text{sp. heat}} = \frac{6.4}{0.0566} = 113.07$$

To get exact atomic weight, exact equivalent weight must be known. So, we have :

$$\text{Charge passed} = 0.2\ \text{A} \times 100 \times 60\text{s} = 1200\ \text{coulombs}$$

Mass of metal deposited

$$= 0.696\ \text{g}$$

$$\text{Mole of electrons} = \frac{1200\ \text{coulombs}}{96500\ \text{coulombs}} = 0.0124$$

$$\therefore \text{Equivalent weight} = \frac{0.696}{0.0124} = 56.13$$

Approximate valency

$$= \frac{\text{Approximate at. wt.}}{\text{Eq. wt.}}$$

$$= \frac{113.07}{56.13} = 2.014 \approx 2$$

$$\therefore \quad \text{Exact at. wt., } a = \text{Eq. wt.} \times \text{valency}$$

$$= 56.13 \times 2 = \mathbf{112.26} \qquad \textbf{Ans.}$$

EXAMPLE 108. *Given:*

(i) $Cu^{2+} + 2e^- \longrightarrow Cu;\ E° = 0.337\ V$

(ii) $Cu^{2+} + e^- \longrightarrow Cu^+;\ E° = 0.153\ V$

Electrode potential for the reaction, $Cu^+ + e^- \longrightarrow Cu$ will be:

(a) 0.90 V *(b)* 0.30 V

(c) 0.38 V *(d)* 0.52 V

(CBSE-PMT, 2009)

SOLUTION. Given:

(*i*) $Cu^{2+} + 2e^- \longrightarrow Cu;\ E° = 0.337\ V$

(*ii*) $Cu^{2+} + e^- \longrightarrow Cu^+;\ E° = 0.153\ V$

(*iii*) $Cu^+ + e^- \longrightarrow Cu;\ E° = ?$

In order to get equation (*iii*), we have equation (*i*) – equation (*ii*). Thus, we have

(*i*) $Cu^{2+} + 2e^- \longrightarrow Cu;\ E_1^\circ = 0.337\ V;\ n = 2$ due to $2e^-$ s

(*ii*) $Cu^{2+} + e^- \longrightarrow Cu^+;\ E_2^\circ = 0.153\ V;\ n = 1$

$\quad - \quad - \quad\quad -$

---

or (*iii*) $Cu^+ + e^- \longrightarrow Cu;\ E_3^\circ = ?;\ n_3 = 1$

Since the required equation involves an electron; so:

$$n_3E_3^\circ = n_1E_1^\circ - n_2E_2^\circ;$$

$$E_3^\circ = \frac{n_1E_1^\circ - n_2E_2^\circ}{n_3}$$

$$\therefore \quad E_3^\circ = \frac{(2 \times 0.337) - (1 \times 0.153)}{1}$$

$$= (0.674 - 0.153)\text{V}$$

$$= \mathbf{0.521V \approx 0.52\ V.}$$

So, the correct answer is (*d*).

EXAMPLE 109. *An experimental data indicates a linear graph between E_{cell} and log $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ with intercept on E_{cell} axis 1.1 volt. Calculate the E_{cell} for Zn/Zn^{2+} (0.01 M) || Cu^{2+} (0.1 M)/Cu.*

SOLUTION. For the cell reaction $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$, the value of $n = 2$ [$\because Zn \rightarrow Zn^{2+} + 2e^-;\ Cu^{2+} + 2e^- \rightarrow Cu$].

$$\therefore \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

...(1) (Nernst equation)

Comparing equation (1) with $Y = mx + C$ we have :

$$C = E^\circ_{\text{cell}} = 1.1\ \text{V}.$$

Substituting the values in equation (1),

$$\text{we get :} \quad E_{\text{cell}} = 1.1 - \frac{0.0591}{2}\log\frac{0.01}{0.1}$$

$$= 1.1 - \frac{0.0591}{2}(-\log 10)$$

$$= 1.1 + 0.0295 = \mathbf{1.1295}\ \boldsymbol{V} \qquad \textbf{Ans.}$$

EXAMPLE 110. *Calculate the reduction potential at p_{OH} = 14 for the couple $E°_{Cu^{2+}/Cu}$ = 0.34 V. Given that (K_{sp}) $Cu(OH)_2$ = 1.0 × 10^{-19}.*

SOLUTION. Since pOH = 14,

$$\text{pOH} = -\log OH^- = 1\ \text{M}$$

$$\text{or} \quad [OH^-] = 1\ \text{M}.$$

$$\text{But} \quad [Cu^{2+}][OH^-]^2 = K_{sp}.$$

$$\text{Thus} \quad [Cu^{2+}][1]^2 = 1.0 \times 10^{-19}$$

$$\textbf{Or} \quad [Cu^{2+}] = 10^{-19}\text{M}$$

$$\text{Also,} \quad Cu^{2+} + 2e^- \longrightarrow Cu$$

So, using Nernst equation, we have :

$$E_{Cu^{2+}/Cu} = E°_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{[OH^-]^2}{[Cu^{2+}]}$$

$$= 0.34 - 0.0295\log\frac{(1)^2}{10^{-19}}$$

$$= 0.34 - 0.0295 \times 19 \log 10$$
$$= 0.34 - 0.0295 \times 19$$
$$0.34 - 0.56 = -\mathbf{0.22\ volt} \qquad \textbf{Ans.}$$

EXAMPLE 111. (*i*) *Write the cell reaction for the Edison storage cell which is represented as :*

Fe(s) | FeO (s) | KOH(aq) | $Ni_2O_3(s)$ | Ni(s) ; E° Ni_2O_3/ NiO = 0.40 *V* ; E° *FeO/Fe* = – 0.87 *V*

(*ii*) *Calculate its e.m.f. How does it depend upon the concentration of KOH ?*

(*iii*) *Calculate the maximum amount of electrical energy available from one mole of nickel trioxide.*

SOLUTION. For the given cell, Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3(s) | Ni(s), the half-cell reactions are :

(*i*) $Ni_2O_3(s) + H_2O\,(l) + 2e^- \longrightarrow 2\,NiO(s) + 2OH^-(aq)$ ...(*i*)

$$E° = 0.4\ V$$

$$FeO(s) + H_2O\,(l) + 2e^- \longrightarrow Fe(s) + 2OH^- \quad ...(ii)$$
$$E° = -0.87\ V.$$

Subtracting half-reaction (2) from (1) we get :

$$Ni_2O_3(s) + Fe(s) \longrightarrow FeO(s) + 2NiO(s);$$
$$E°_{cell} = +1.27\ V \qquad \textbf{Ans.}$$

It is the required cell reaction.

(*ii*) Cell e.m.f. = + 1.27 V as shown above. Since the net cell reaction does not involve any OH^- ions, the cell e.m.f. does not depend upon the concentration of KOH solution.

(*iii*) Maximum amount of electrical energy,

$$\Delta G° = -nF\,E°\text{cell}.$$

Substituting the values, we get :

$$\Delta G° = -2 \times 96500\ C \times 1.27\ V$$
$$= 245110\ J\ mol^-$$
$$= \frac{245110}{10^3}\ k\ J\ mol^-$$
$$= \mathbf{245.11\ k\ J\ mol^-} \qquad \textbf{Ans.}$$

EXAMPLE 112. *By mistake, the H^+ ion concentration of a MnO_4^-/Mn^{2+} couple was decreased by a student, from 1 M to 10^{-2} M at 25°C. By how much will the oxidising power of the MnO_4^-/Mn^{2+} couple be decreased. Assume that the concentration of other species does not alter.*

SOLUTION. The reduction reaction of MnO_4^- in acidic medium is represented as :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ;\ (n = 5)$$

Using Nernst equation,

$$E = E° - \frac{0.0591}{n} \log \frac{[Mn^{2+}][H_2O]^4}{[MnO_4^-][H^+]^8};$$

we have : $E - E° = -\dfrac{0.0591}{5} \log \dfrac{1}{(10^{-2})^8}$

$$= -0.0118 \log 10^{16}$$
$$= -0.0118 \times 16 \log 10$$
$$= -0.0118 \times 16$$
$$= -0.19\ V.$$

Hence, MnO_4^- /Mn^{2+} couple will move to position of less oxidising power by 0.19 V.

EXAMPLE 113. *Calculate K_a of HSO_3^- i.e., for the equilibrium, $HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$ with the help of following data:*

$E°_{Zn^{2+}/Zn}$ = – 0.76 *V ; e.m.f. of the cell.*

Pt, H_2 (1 atm) | HSO_3^- (0.4 M), SO_3^{2-} (6.4 × 10^{-3} M) || Zn^{2+} (0.3 M) /Zn is –0.46 V.

SOLUTION. The half-cell reactions for the given cell as :

(*a*) $H_2 \longrightarrow 2H^+ + 2e^-;$ $\quad E° = 0.0\ V$

(*b*) $Zn^{2+} + 2e^- \longrightarrow Zn;$ $\quad E° = -0.76\ V$

Adding equations (*a*) and (*b*), we get

$$H_2 + Zn^{2+} \longrightarrow 2H^+ + Zn;\ E° = -0.76\ V ...(1)$$

Applying Nernst equation, we have :

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{[H^+]^2}{[Zn^{2+}][pH_2]}$$

$$-0.46 = -0.76 - \frac{0.0591}{2} \log \frac{[H^+]^2}{(0.3)\times(1)}$$

Or $\quad 0.76 - 0.46 = -0.02955 \log \dfrac{[H^+]^2}{0.3}$

Or $\quad 0.3 = -0.02955 \log \dfrac{[H^+]^2}{0.3}$

∴ $\quad \log \dfrac{[H^+]^2}{0.3} = -10.1523$

Or $\quad \dfrac{[H^+]^2}{0.3} = \text{antilog} - 10.1523$

∴ $\quad \dfrac{[H^+]^2}{0.3} = 7.04 \times 10^{-11}$

Or $\quad (H^+) = (0.3 \times 7.04 \times 10^{-11})^{½}$

$$= 4.6 \times 10^{-6}\ M$$

The given reaction is :

$$\underset{0.4\ M}{HSO_3^-} \rightleftharpoons \underset{4.6 \times 10^{-6}\ M}{H^+} + \underset{6.4 \times 10^{-3}\ M}{SO_3^{2-}}$$

∴ $\quad K_a = \dfrac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$

$$= \frac{(4.6 \times 10^{-6}) \times (6.4 \times 10^{-3})}{0.4}$$
$$= \mathbf{7.36 \times 10^{-8}} \qquad \textbf{Ans.}$$

EXAMPLE 114. *From the following given data, calculate the solubility product of $CdSO_4$.*

$E°_{Cd^{2+}/Cd}$ = – 0.403 V ; e.m.f. of the cell, Cd/$CdSO_4$ | H_2SO_4 (0.01M) | H_2 (1 atm) | Pt = + 0.362 V.

SOLUTION. The half-cell reactions are :

(*a*) $Cd \longrightarrow Cd^{2+} + 2e^-$ (oxidation) ;

$$E° = +0.403\ V$$

(*b*) $2H^+(aq) + 2e^- \longrightarrow H_2$ (reduction) ;

$$E° = 0\ V$$

Adding equations, (*a*) and (*b*) we get :

$$Cd + 2\,H^+(aq) \longrightarrow Cd^{2+} + H_2;$$
$$E° = +0.403\ V.$$

Applyig Nernst equation we have :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[Cd^{2+}][pH_2]}{[Cd][H^+]^2}$$

$$+0.362 = +0.403 - \frac{0.0591}{2}\log\frac{[Cd^{2+}]\times 1}{1\times(0.01\times 2)^2}$$

$$[\because H_2SO_4 \rightleftharpoons \underset{2\times 0.01}{2H^+} + SO_4^{2-}]$$

$$-0.041 = -0.02955\log\frac{[Cd^{2+}]}{4\times 10^{-4}}$$

Or $\log\frac{[Cd^{2+}]}{4\times 10^{-4}} = 1.3875 \quad \therefore \quad \frac{[Cd^{2+}]}{4\times 10^{-4}} = 24.41$

Or $[Cd^{2+}] = 24.41 \times 4 \times 10^{-4}$

$= 97.64 \times 10^{-4}$ M

We know

$$\underset{97.64\times 10^{-4}M}{CdSO_4 \rightleftharpoons Cd^{2+}} + SO_4^{2-}; \qquad H_2SO_4 \rightleftharpoons 2H^+ + \underset{0.01\ M}{SO_4^{2-}}$$

But K_{sp} for $CdSO_4 = [Cd^{2+}][SO_4^{2-}]$

$= (97.64 \times 10^{-4}) \times (0.01)$

$= \mathbf{9.764 \times 10^{-5}}$ **Ans.**

EXAMPLE 115. *When an electric current of 50 microamperes is passed through a solution containing Ag⁺ ions for half an hour using Pt electrodes, a uniform single atom thick layer of Ag is deposited on the cathode surface. If 40% cathode surface is covered by Ag atoms, calculate the total surface of the cathode. Given that 5.4×10^{-16} cm² surface is covered by each Ag–atom. (At. wt. Ag. = 108).*

SOLUTION. Current passed = 50μ A = 50×10^{-6} A ; time = 30 min = 30 × 60 = 1800 seconds. Also, $Ag^+ + 1e^- \rightarrow Ag$. Thus :

(*a*) Total charge passed = 50×10^{-6} A × 1800 s = 0.09 coulomb or C.

(*b*) Total mass of Ag deposited at cathode $= \frac{108\times 0.09}{96500}$ g $= 1.01 \times 10^{-4}$ g

(*c*) Total number of Ag–atoms deposited $= \frac{1.01\times 10^{-4}}{108} \times 6.022 \times 10^{23} = 5.6 \times 10^{17}$

Hence, surface area of cathode covered by Ag–atoms

$= 5.6 \times 10^{17} \times 5.4 \times 10^{-16} = 302.4$ cm².

Thus, total surface area of cathode

$= \frac{302.4\times 100}{40} = \mathbf{756\ cm^2}$ **Ans.**

EXAMPLE 116. *Find the magnitude of equilibrium constant for the reaction, $2H_2O \rightarrow OH^- + H_3O^+$ at 298K. Given that the standard reduction potential at 298 K for the reaction, $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ is – 0.8277 Volt.*

SOLUTION. Given : (*a*) $2H_2O + 2e^- \rightarrow 2OH^- + H_2$; E° = – 0.8277 V. For hydrogen electrode, (*b*) $2H^+ + 2e^- \rightarrow H_2$; E° = 0.0 V

Subtracting reaction (*a*) from (*b*), we get positive value of E°.

Thus : net cell reaction is :

$$2H^+ + 2OH^- \longrightarrow 2H_2O\ ;\ E^\circ = +0.8277\ V$$

Using Nernst equation, we have :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{(H_2O)^2}{[H^+]^2[OH^-]^2}$$

$$= 0.8277 - \frac{0.0591}{2}\log\frac{(1)^2}{(K_w)^2}$$

$$= 0.8277 - 2\times\frac{0.0591}{2}\log\frac{1}{K_w}$$

At equilibrium, $E_{\text{cell}} = 0$.

Hence : $0 = 0.8277 - 0.0591\log\frac{1}{K_w}$

or $\log\frac{1}{K_w} = \frac{-0.8277}{-0.0591} = 14.0051$

$\therefore \quad \log K_w = -14.0051$

$\therefore \quad K_w = \text{Antilog} - 14.0051 = \mathbf{9.88 \times 10^{-15}}$

For $2H_2O \rightleftharpoons H_3O^+ + OH^-$, $\quad K_w = [H_3O^+][OH^-]$

$\therefore \quad K_w = \mathbf{9.88 \times 10^{-15}}$ **Ans.**

EXAMPLE 117. *On electrolysis of 9.5 gram of fused stannous chloride using inert electrodes, 0.0595 g of tin was deposited. Calculate the ratio of weights of stannous chloride and stannic chloride after electrolysis. At. Wt. of Sn = 119. Also, no species was given out during electrolysis.*

SOLUTION. $SnCl_2$ ionises as :

$$SnCl_2 \rightleftharpoons Sn^{2+} + 2Cl^-$$

During electrolysis : $2Cl^- \longrightarrow Cl_2 + 2e^-$ (oxidation)

$Sn^{2+} + 2e^- \longrightarrow Sn$ (reduction)

Since no species was given out, Cl_2 will react with $SnCl_2$ to form $SnCl_4$.

$$SnCl_2 + Cl_2 \longrightarrow SnCl_4$$

Thus, g. equivalent of $SnCl_2$ converted to $SnCl_4$ during electrolysis = g. equivalent of Cl_2 formed = g. equivalent of Sn formed.

Hence : g. equivalent of Cl_2 formed $= \frac{0.0595}{(119/2)} = 10^{-3}$

∴ g. equivalent of $SnCl_4$ formed = g. equivalent of $SnCl_2$ lost = 10^{-3}. It means, *total loss of g. equivalent* of $SnCl_2$ lost + g. equivalent of $SnCl_2$ reacted with $Cl_2 = 10^{-3} + 10^{-3} = 2 \times 10^{-3}$

Initial g. equivalent of $SnCl_2 = \frac{\text{Wt. of } SnCl_2}{\text{g. eq. wt. of } SnCl_2}$

$$= \frac{9.5}{(190/2)} = 0.1$$

∴ g. equivalent of $SnCl_2$ left in solution

$= 0.1 - (2 \times 10^{-3})$

$= 0.1 - 0.002 = 0.098$

From above, we find that, g. equivalent of $SnCl_4$ formed

$= 10^{-3}$

Hence, $\dfrac{\text{Wt. of SnCl}_2\text{ left behind}}{\text{Wt. of SnCl}_4\text{ formed}}$

$$= \frac{0.098 \times (190/2)}{10^{-3} \times (261/2)}$$

$$\left[\begin{array}{l}\because \text{g. eq. wt. of SnCl}_4 \\ = \{119 + (4 \times 35.5)\}/2 = 261/2\end{array}\right]$$

$$= \frac{9.31}{0.1305} = \mathbf{71.34\ Ans.}$$

EXAMPLE 118. *Calculate potential of the Ag^+/Ag electrode in a saturated solution and also calculate the standard reduction potential of $I^-/AgI/Ag$ electrode from the following data.*

$E^\circ_{Ag^+/Ag}$ *at 298 K = 0.799 V : Ksp (AgI) = 8.7×10^{-17}*

SOLUTION. (*a*) K_{sp} for AgI(s) $\rightleftharpoons$ $Ag^+(aq) + I^-(aq)$ is given as :

$$K_{sp} = [Ag^+][I^-] = [Ag^+]^2\ [\because (Ag^+) = (I^-)]$$

$$\therefore \quad [Ag^+] = [K_{sp}]^{1/2} = (8.7 \times 10^{-17})^{1/2} = 9.33 \times 10^{-9}$$

For Ag^+/Ag electrode, the reaction is :

$$Ag^+ + e^- \longrightarrow Ag$$

Using Nernst equation, we have :

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} - \frac{0.0591}{n}\log\frac{1}{[Ag^+]}$$

$$= 0.799 - \frac{0.0591}{1}\log\frac{1}{9.33 \times 10^{-9}}$$

$$= 0.799 - 0.0591 \log 107181136$$

$$= 0.799 - (0.0591 \times 8.0301)$$

$$= 0.799 - 0.475 = \mathbf{0.324} \qquad \textbf{Ans.}$$

(*b*) We know, $Ag \longrightarrow Ag^+ + 1e^-$ (oxidation)

$AgI + e^- \longrightarrow Ag + I^-$ (reduction)

On adding, we get, $AgI \longrightarrow Ag^+ + I^-$

$$\therefore \quad E^\circ_{cell} = \frac{0.0591}{n}\log[Ag^+][I^-]$$

$$= \frac{0.0591}{1}\log K_{sp}$$

$$E^\circ_{Ag/Ag^+} + E^\circ_{I^-/AgI/Ag} = 0.0591 \log 8.7 \times 10^{-17}$$

$$= 0.0591\,[\log 8.7 + \log 10^{-17}]$$

$$-0.799 + E^\circ_{I^-/AgI/Ag} = 0.0591\,[0.9395 - 17]$$

$$= 0.0591\,(-16.0605)$$

$$E^\circ_{I^-/AgI/Ag} = +0.799 - 0.949 = \mathbf{-0.150\ V} \quad \textbf{Ans.}$$

EXAMPLE 119. 2.5 *ampere current was passed for 1.5 hours through one litre of 0.1 M Fe^{3+} solution. Assuming that only Fe^{3+} ions are reduced to Fe ($Fe^{3+} + 3e^- \rightarrow Fe$), calculate the number of moles of Fe, those will be produced.*

SOLUTION. Current passed = 2.5 A, time = 1.5 hr = $1.5 \times 60 \times 60 = 5400$ s. Hence total charge passed = $2.5\text{ A} \times 5400\text{ s} = 13500$ coulombs = $\dfrac{13500}{96500}$ Faraday = 0.140 F.

The reduction of Fe^{3+} to Fe takes place through following steps.

(*i*) $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (*ii*) $Fe^{2+} + 2e^- \longrightarrow Fe$

The charge used to reduce Fe^{3+} to Fe^{2+} = 0.1 F

[∵ solution is 0.1 M]

∴ Charge left behind which is used to reduce Fe^{2+} to Fe = 0.140 – 0.1 = 0.04 F

Hence the number of moles of Fe those are produced

$$= \frac{1 \times 0.04}{2} = \mathbf{0.02} \qquad \textbf{Ans.}$$

EXAMPLE 120. *Cu^+ disproportionates as, $2Cu^+ \rightleftharpoons Cu^{2+} + Cu(s)$. Calculate standard reduction potential $E^\circ_{Cu^{2+}/Cu}$ if (i) standard reduction potential for $Cu^{2+}/Cu^+ = +0.15$ V and (ii) at equilibrium, the magnitude of $Cu^{2+}/(Cu^+)^2 = 1.8 \times 10^6$.*

SOLUTION. At equilibrium e.m.f. = Zero. Since $E^\circ_{Cu^{2+}/Cu^+} = +0.15$ V, $E^\circ_{Cu^+/Cu^{2+}} = -0.15$ V. The given disproportionate reaction is :

$$2Cu^+ \rightleftharpoons Cu^{2+} + Cu$$

$$E^\circ_{Cu^{2+}/Cu^+} = +0.15\text{ V};\ Cu^{2+}/[Cu^+]^2 = 1.8 \times 10^6$$

$$\text{We know : } \quad E^\circ_{cell} = \frac{0.0591}{n}\log\frac{Cu^{2+}}{[Cu^+]^2}$$

$$\therefore E^\circ_{Cu^+/Cu^{2+}} + E^\circ_{Cu^+/Cu} = \frac{0.0591}{1}\log\frac{[1.8 \times 10^6]}{1}$$

$$[\because Cu^+ + 1e^- \longrightarrow Cu,\ n = 1]$$

$$-0.15\text{ V} + E^\circ_{Cu^+/Cu} = 0.0591\,[\log 1.8 + \log 10^6]$$

$$= 0.0591\,[0.2553 + 6]$$

$$= 0.0591 \times 6.2553 = 0.3697$$

$$\text{Hence,} \quad E^\circ_{Cu^+/Cu} = 0.3697 + 0.15 = \mathbf{0.5197\ V} \qquad \textbf{Ans.}$$

EXAMPLE 121. *The charging and discharging reactions in a lead storage battery are :*

(*a*) *$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$ (charging) (b) $PbO_2 + 4H^+ + 2e^- + SO_4^{2-} \longrightarrow PbSO_4 + 2H_2O$ (discharging). H_2SO_4 of density 1.139 g $(mL)^-$ is 20% H_2SO_4 by weight while H_2SO_4 of density 1.294 g $(mL)^-$ is 39% H_2SO_4 by weight. The density of H_2SO_4 during discharge falls from 1.294 to 1.139 g $(mL)^-$. Calculate the number of ampere hours for which the battery has been used if battery holds 3.5 L of acid and volume remains practically constant during the discharge.*

SOLUTION. Given :

(*a*) $\underset{1\text{ mol}}{Pb + SO_4^{2-}} \longrightarrow \underset{1\text{ mol}}{PbSO_4} + 2e^-$ (Charging)

(*b*) $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$ (discharging)

Adding reactions (*a*) and (*b*), the net reaction is :

(*c*) $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2\,PbSO_4 + 2H_2O$

We see from reaction (*a*) that one mole of Pb gets oxidised to one mole of Pb^{2+} (in $PbSO_4$). Also, 2 moles of H_2SO_4 are consumed with the consumption of 2 moles of electrons. Hence, number of moles of H_2SO_4 = number of Faradays consumed. Density = 1.294 g (mL^-) = 1.294×10^3 g L^-. Similarly, density 1.139 g mL^- = 1.139×10^3 g L^-.

Before discharge. Mass of sample in 3.5 L of acid

= Volume × density

= $3.5\text{ L} \times 1.294 \times 10^3\text{ g L}^- = 4529$ g.

$$\text{Mass of 39\% } H_2SO_4 = 4529 \times \frac{39}{100} = 1766.31\text{ g}$$

$$\text{Moles of } H_2SO_4 = \frac{\text{Mass}}{\text{Mol. mass}} = \frac{1766.31}{98} = \mathbf{18.02}$$

After discharge. Mass of sample in 3.5 L of acid

$$= \text{Volume} \times \text{density}$$

$$= 3.5\text{ L} \times 1.139 \times 10^3 \text{ g L}^{-} = 3986.5 \text{ g}$$

$$\text{Mass of 20\% } H_2SO_4 = 3986.5 \times \frac{20}{100} = 797.3 \text{ g}$$

$$\text{Moles of } H_2SO_4 = \frac{797.3}{98} = \mathbf{8.136}$$

Number of moles of H_2SO_4 consumed

$$= 18.02 - 8.136 = 9.884$$

∴ Number of Faradays consumed = 9.884 F

Hence total charge = 9.884 × 96500 = 953806 C

But one ampere hour = charge passed by one ampere current in one hour = 1 × 60 × 60 = 3600 C

[∵ 1 hr = 60 × 60 = 3600 seconds]

Hence required number of ampere hours

$$= \frac{953806 \text{ C}}{3600 \text{ C}} = \mathbf{264.95} \qquad \textbf{Ans.}$$

Example 122. *Using K_a value of CH_3COOH (= 1.8×10^{-5}) and K_b value of NH_4OH (= 1.8×10^{-5}), calculate the e.m.f. of the following cell.*

Pt, H_2 (1 atm) | CH_3COOH (0.01 M) | NH_4OH (0.001) | H_2, Pt

Solution. We know that :

$$\frac{1}{2} H_2 \longrightarrow H_a^+ + e^- \text{ (at anode, oxidation)}$$

$$H^+_c + e^- \longrightarrow \frac{1}{2} H_2 \text{ (at cathode, reduction)}$$

$$\therefore \text{ Net reaction is : } H_c^+ \longrightarrow H_a^+$$

Using Nernst equation, we have :

$$E = E° - \frac{0.0591}{n} \log [H_a^+]/[H_c^+] \quad ...(1)$$

At anode :

$$\begin{array}{lcl} CH_3COOH & \rightleftharpoons & CH_3COO^- + H_a^+ \text{ (ionisation)} \\ C - C\alpha & & C\alpha \qquad\quad C\alpha \end{array}$$

(α = degree of ionisation)

$$\therefore \quad (H_a^+) = C\alpha$$

$$= C\sqrt{\frac{K_a}{C}} = \sqrt{K_a C}$$

Or

$$[H_a^+] = (K_a \times [CH_3COOH]))^{1/2}$$

$$= (1.8 \times 10^{-5} \times 0.01)^{1/2}$$

$$= (0.18 \times 10^{-6})^{1/2} = \mathbf{0.424 \times 10^{-3} \ M}$$

At cathode :

$$\begin{array}{lcl} NH_4OH & \rightleftharpoons & NH_4^+ + OH^- \text{ (ionisation)} \\ C - C\alpha & & C\alpha \qquad C\alpha \end{array}$$

(α = degree of ionisation)

$$\therefore \quad [OH^-] = C\alpha = C\left[\frac{K_b}{C}\right]^{1/2} = [K_b C]^{1/2}$$

$$\therefore \quad [H_c^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{[K_b C]^{1/2}}$$

$$= \frac{K_w}{\{K_b \times [NH_4OH]\}^{1/2}}$$

[∵ K_w = [H⁺] [OH⁻]]

$$= \frac{10^{-14}}{(1.8 \times 10^{-5} \times 0.001)^{1/2}}$$

$$= \frac{10^{-14}}{0.01342 \times 10^{-3}} = 7.452 \times 10^{-11} \text{ M}$$

Using Nernst equation, we have :

$$E = E° - \frac{0.0591}{n} \log \frac{[H_a^+]}{[H_c^+]}$$

$$= 0 - \frac{0.0591}{1} \log \frac{0.424 \times 10^{-3}}{7.452 \times 10^{-11}}$$

$$= -0.0591 \log 5689748$$

$$= -0.0591 \times 6.7551 = \mathbf{-0.3992 V} \ \textbf{Ans.}$$

Example 123. *The electrolytic oxidation of sulphuric acid gives the following products, along with O_2, $2H_2SO_4 \rightarrow 2H^+ + 2e^- + H_2S_2O_8$ (perdisulphuric acid). (= 2.56 g) and H_2 (= 0.64 g) as by product at N.T.P. Calculate the weight of $H_2S_2O_8$ formed and also the quantity of current passed for electrolysis.*

Solution. Reactions. At anode :

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^- \qquad \text{(oxidation)}$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad \text{(oxidation)}$$

At cathode. $2H^+ + 2e^- \longrightarrow H_2$ (reduction).

From above reactions, it is clear that first of all H_2SO_4 oxidises to give $H_2S_2O_8$ and then H_2O to give O_2. At the same time, H_2 is liberated which continues during electrolysis. Thus :

(*a*) Total charge needed to form 2.56 g O_2

$$= \frac{4 (= e^- \text{-charge}) \times 96500 \times 2.56}{32} \text{ C}$$

[∵ Mol. wt. of O_2 = 32]

$$= \mathbf{30880 \ C}$$

(*b*) Total charge needed to form 0.64 g H_2

$$= \frac{2 (= e^- \text{ charge}) \times 96500 \times 0.64}{2} \text{ C}$$

[∵ Mol. wt. of H_2 = 2]

$$= 61760 \text{ C.}$$

∴ Total charge used to get

$$H_2S_2O_8 = 61760 - 30880 = 30880 \text{ C.}$$

$$\text{Hence, weight of } H_2S_2O_8 \text{ generated} = \frac{194 \times 30880}{2 \times 96500}$$

[∵ Mol. wt. of $H_2S_2O_8$ = 194]

$$= \mathbf{31.04 \ g}$$

Example 124. *A given 0.1 M MnO_4^- and 0.8 M H^+ solution when treated with 80% of Fe^{2+}, reduces the whole MnO_4^- to Mn^{2+}. ($MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$; E° = + 1.51 V). Calculate the potential of an indicator electrode versus the standard hydrogen electrode.*

Solution. Consider a Galvanic cell involving MnO_4^- and Mn^{2+}. H_2 (1 atm), Pt | H^+ (1M) || MnO^-_4 (H^+) | Mn^{2+}, Pt.

Reaction at anode :

H_2 (1atm) $\longrightarrow$ $2H^+ + 2e^-$ (oxidation)

At cathode : $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

$$\begin{array}{llll} \text{Initial conc.} & 0.1M & 0.8M & 0.1M \\ \text{After complete oxidation of } Fe^{2+} & \left[\begin{array}{l} 0.1-\dfrac{0.1\times 80}{100} \\ = 0.1-0.08 \\ = 0.02 \end{array}\right] & \left[\begin{array}{l} 0.8-\dfrac{0.1\times 80\times 8}{100} \\ = 0.8-0.64 \\ = 0.16 \end{array}\right] & \left[\begin{array}{l} \dfrac{0.1\times 80}{100} \\ = 0.08 \end{array}\right] \end{array}$$

The electrode potential of indicator electrode is given by the relation :

$$E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} - \frac{0.0591}{n} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= +1.51 - \frac{0.0591}{5} \log \frac{0.08}{0.02 \times (0.16)^8}$$

$$= 1.51 - 0.01182 \log \frac{0.08}{8 \times 10^{-9}}$$

$$= 1.51 - 0.01182 \log 10^7$$

$$= 1.51 - 0.01182 \times 7.0$$

$1.51 - 0.0827 = \mathbf{1.427}\ V$ **Ans.**

Example 125. *In order to plate nickel in $NiSO_4$ bath, a student passed a current of 20 amperes. He found that both Ni and H_2 were formed at the cathode (a) What volume of H_2 gas at N.T.P. is formed per hour? Density of Ni is 8.9 g (mL)$^-$ (b) If current efficiency with respect to the formation of nickel is 50%, how many grams of Ni will be plated out in one hour. (c) Also calculate the thickness of the plating of the cathode consisting of a rectangular sheet of metal of length 5cm and breadth 4 cm which is coated on both faces. (At. wt. of Ni = 58.69).*

Solution. Current passed = 20 amperes :

time = 1 hour = 1 × 60 × 60 = 3600 seconds

Hence : Total charge passed in 3600 seconds

= 20 amperes × 3600s

= 72000 coulombs

Since, the current efficiency with respect to Ni is 50%, so :

charge used to deposit Ni

$$= \frac{72{,}000 \times 50}{100} = 36{,}000\ C$$

It means, the rest of charge is used to evolve H_2 gas.

Hence : charge used to evolve

H_2 gas = 72,000 – 36,000 = 36,000 C

But $Ni^{2+} + 2e^- \longrightarrow Ni$

So :Weight of Ni (plated)

$$= \frac{58.69 \times 36000}{2 \times 96500} = 10.95\ g$$

Volume of rectangular Ni sheet required to be coated on both faces = Mass/density

$$= \frac{10.95\ g}{8.9\ g\ (mL)^-} = 1.23\ mL\ (\text{or } cm^3)$$

So, volume of rectangular Ni sheet required to be coated on one face $= \frac{1.23}{2} = 0.615\ cm^3$

But

Volume = Length × breadth × thickeness of plate

∴ $0.615\ cm^3$ = 5 cm × 4 cm × thickness of plate

∴ Thickness of plate

$$= \frac{0.615\ cm^3}{5\ cm \times 4\ cm} = 0.03075\ cm$$

We know $2H^+ + 2e^- \longrightarrow H_2$

Thus, volume of H_2 gas liberated at N.T.P.

$$= \frac{22.4L \times 36000\ C}{2 \times 96500\ C} = \mathbf{4.178\ L}\ \textbf{Ans.}$$

Example 126. *When a cadmium chloride solution was electrolysed in presence of mercury cathode, cadmium amalgam was formed. Calculate the time in minutes for which the electrolysis be done to prepare 10% (by weight) of cadmium amalgam using 4 amperes current and 45 g of mercury. (At. wt. of Cd = 112)*

Solution. 10% by wt. of cadmium amalgam means 10 g Cd and 90 g (100 – 10 = 90) mercury. Thus :

Wt. of Cd in 90 g Hg = 10 g;

Wt. of Cd in 45g

$$\text{Hg} = \frac{10}{90} \times 45 = 5g$$

$$\text{g. eq. wt. of Cd} = \frac{\text{g. At. wt.}}{\text{Valency}} = \frac{112}{2} = 56\ g$$

Charge required to deposit 56 g Cd = 96500 coulombs

Charge required to deposit 5 g Cd

$$= \frac{96500}{56} \times 5 = 8616.07\ C$$

Time in seconds required for electrolysis

$$= \frac{\text{Charge in coulombs}}{\text{Current in amperes}} = \frac{8616.07}{4}$$

$$= 2154.02 \text{ seconds} = \frac{2154.02}{60}$$

= **35.9 min** **Ans.**

Example 127. *Find the value of equilibrium constant for the reaction :*

$$Fe^{2+} + Ag^+ \longrightarrow Fe^{3+} + Ag$$

Given that : $Ag^+ + e^- \longrightarrow Ag;$ $E^\circ = 0.799V;$

$Fe^{3+} + e^- \longrightarrow Fe^{2+};$ $E^\circ = 0.771$ V;

Solution. The given reaction at equilibrium is given as:

$$Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$$

For reaction at equilibrium, $E_{cell} = 0$.

But $$E^\circ_{cell} = \frac{0.0591}{n} \log K$$

Hence

$$E^\circ_{Fe^{2+}/Fe^{3+}} + E^\circ_{Ag^+/Ag} = \frac{0.0591}{n} \log K$$

$$\left[\begin{aligned}\text{Since } E^\circ_{Fe^{3+}/Fe^{2+}} &= 0.771\,V,\\ E^\circ_{Fe^{2+}/Fe^{3+}} &= -0.771\,V\end{aligned}\right]$$

$$-0.771 + 0.779 = \frac{0.0591}{1}\log K$$

Or $\quad 0.008 = 0.0591 \log K$

∴ $\quad \log K = \dfrac{0.008}{0.0591} = 0.1354$

Or $\quad K = \text{antilog } 0.1354 = \mathbf{1.366}$

EXAMPLE 128. *For the reaction*

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

Given.

Species	ΔG°*(KJ/mol)*
$Ag^+(aq)$	+ 77
$Cl^-(aq)$	− 129
$AgCl(s)$	− 109

(*i*) *Write the cell representation of the above reaction and*

(*ii*) *Calculate E° at 298 K.*

(*iii*) *Calculate the* $\log_{10} K_{sp}$ *(AgCl) at 298 K.*

(*iv*) *If* 6.539×10^{-2} *g of metallic zinc is added to 100 mL saturated solution of AgCl, find the value of* $\log_{10}\dfrac{[Zn^{2+}]}{[Ag^+]^2}$.

(*v*) *How many moles of Ag will be precipitated in the above reaction? Given that :*

$$Ag^+ + e^- \longrightarrow Ag\,; \qquad E^\circ = -0.80\ V.$$
$$Zn^{2+} + 2e^- \longrightarrow Zn\,; \qquad E^\circ = -0.76\ V.$$

(*at. wt., Zn = 65.39*) **[IIT–JEE (mains), 2005]**

SOLUTION. (*i*) For the given reaction, the cell can be represented as :

Ag(s) | AgCl(s) | Cl^-(aq) || Ag^+(aq) | Ag(s)

(*ii*) ΔG° (reaction) for

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$,

we have :

$$\begin{aligned}\Delta G^\circ \text{ (reaction)} &\longrightarrow \Delta G^\circ_{AgCl} - (\Delta G^\circ_{Ag^+} + \Delta G^\circ_{Cl^-})\\ &= -109 - (77 - 129)\\ &= -109 - 77 + 129 = -57 \text{ k J}\end{aligned}$$

$$\therefore \quad E^\circ_{cell} = \frac{\Delta G^\circ\text{ (reaction)}}{nF} = \frac{57 \times 10^3 \text{ J } (= \text{CV})}{1 \times 96500 \text{ C}} = \mathbf{0.59\ V\ \ Ans.}$$

(*iii*) For cell reaction, $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$, we have :

$$\begin{aligned}\Delta G^\circ \text{ (reaction)} &= 2.303\, RT \log K_{sp} \text{ (AgCl)}\\ -57 \times 10^3 \text{ J} &= 2.303 \times 8.314 \text{ J K}^- \times 298 \text{ K} \log K_{sp} \text{ (AgCl)}\end{aligned}$$

$$\therefore \quad \log K_{sp}\text{ (AgCl)} = -\frac{57 \times 10^3 \text{J}}{2.303 \times 8.314 \text{J K}^- \times 298 \text{ K}} \approx -10$$

$$\therefore \quad K_{sp}\text{ (AgCl)} = \text{antilog } (-10) = 10^{-10}\ M^2$$

$$[Ag^+] = [K_{sp}\text{(AgCl)}]^{1/2} = [10^{-10} M^2]^{1/2} = 10^{-5}\ M$$

$$\text{Mol of } Zn^{2+} = \frac{\text{Wt. of } Zn^{2+}}{\text{At. wt. of } Zn^{2+}} = \frac{6.539 \times 10^{-2}\text{ g}}{65.39} = 10^{-3}$$

For the following reaction, applying Nernst equation we have :

$$2\,Ag^+(aq) + Zn^{2+}(aq) \rightleftharpoons 2\,Ag(s) + Zn^{2+}(aq)$$

$$E = E^\circ - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$

At equilibrium, $E = 0$, E° cell $= 1.56V$

$$0 = 1.56 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2};$$

$$\frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ag^+]^2} = 1.56$$

$$\therefore \quad \log\frac{[Zn^{2+}]}{[Ag^+]^2} = \frac{1.56 \times 2}{0.059} = 52.88;\ \log Kc = 52.88$$

$$\therefore \quad K_c = \text{antilog } 52.88 = 10^{52.88}$$

Since the value of K_c is very high, the reaction will almost go to completion. Hence mol of Ag precipitated is 10^{-5} (already found).

EXAMPLE 129. *Two students use same stock solution of* $ZnSO_4$ *and a solution of* $CuSO_4$. *The e.m.f. of one cell is 0.03 V higher than the other. The conc. of* $CuSO_4$ *in the cell with higher e.m.f. value is 0.5 M. Find out the concentration of* $CuSO_4$ *in the other cell. (2.302 RT/F = 0.06)* **(IIT, 2003)**

SOLUTION. From the given data, we see that there are two Daniell cells *i.e.*, Zn | Zn^{2+} || Cu^{2+} | Cu. Hence :

(*i*) Zn | $Zn^{2+}(C_1)$ || Cu^{2+}(C = ?) | Cu ; $E_{cell} = E_1$

(*ii*) Zn | $Zn^{2+}(C_2)$ || Cu^{2+}(C = 0.5) | Cu ; $E_{cell} = E_2$ where $E_2 > E_1$

Also, $\quad E_2 - E_1 = 0.03\ V$; $C_1 = C_2$. The cell reaction will be

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

while $\quad Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

We know that $E_{cell} = E^\circ_{cell} - \dfrac{0.06}{n}\log Q \quad$ or $\quad \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

Or $\quad E_1 = E_{cell} = E^\circ_{cell} - \dfrac{0.06}{2}\log\dfrac{C_1}{C}$

[∵ for $Zn \rightleftharpoons Zn^{2+} + 2e^-$, $n = 2$]

$$E_2 = E_{cell} = E^\circ_{cell} - \frac{0.06}{2}\log\frac{C_2}{0.5}$$

$$\therefore \quad E_2 - E_1 = -\frac{0.06}{2}\log\frac{C_2}{0.5} - \left(-\frac{0.06}{2}\log\frac{C_1}{C}\right)$$

$$= \frac{0.06}{2}\log\frac{C_1}{C} - \frac{0.06}{2}\log\frac{C_2}{0.5}$$

$$\therefore \quad 0.03 = \frac{0.06}{2}\left[\log\frac{C_1}{C} - \log\frac{C_2}{0.5}\right]$$

$$= 0.03\left[\frac{\log\frac{C_1}{C}}{\log\frac{C_2}{0.5}} \quad \text{Or} \quad \log\frac{C_1}{C}\times\frac{0.5}{C_2}\right]$$

$$0.03 = 0.03\left[\log\frac{0.5}{C}\right] \qquad [\because C_1 = C_2]$$

$$\text{or} \qquad \log\frac{0.5}{C} = 1$$

Taking antilog of both sides, we get :

$$\frac{0.5}{C} = \text{antilog } 1 = 10;$$

$$C = \frac{0.5}{10} = \mathbf{0.05} \qquad \textbf{Ans.}$$

Example 130. *A current of 10 A is passed for 80 min. and 27 seconds through a cell containing dilute sulphuric acid.*

(1) *How many moles of oxygen gas will be liberated at the anode ?*

(2) *Calculate the amount of zinc deposited at the cathode when another cell containing $ZnSO_4$ solution is connected in series (Zn = 65).* **(ISC, 2007)**

Solution. $H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

and $2H_2O \rightleftharpoons H_3O^+ + OH^-$

(1) Current, $C = 10$ A; time, $t = 80$ min. and 27 seconds

$= (80 \times 60 \text{ s}) + 27\text{s} = 4827$ s.

Reaction at anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

∴ Eq. wt. of oxygen

$$= \frac{\text{Mol. wt. of } O_2}{\text{no. of } e^{-}\text{s involved}} = \frac{2\times 16}{4} = 8$$

$$\text{But Wt. of oxygen} = \frac{\text{Eq. wt.} \times C \times t}{96500} = \frac{8\times 10\times 4827}{96500}$$

$$= 4 \text{ g}$$

$$\text{no. of mol. of } O_2 = \frac{\text{Wt.}}{\text{Mol. wt.}} = \frac{4}{32} = \mathbf{0.125} \qquad \textbf{Ans.}$$

$$(2) \quad \text{Eq. wt. of Zn} = \frac{\text{At. wt.}}{\text{Valency}} = \frac{65}{2} = 32.5;$$

eq. wt. of oxygen = 8

Wt. of oxygen = 4 g

We know that by second law of electrolysis :

$$\frac{\text{Wt. of Zn}}{\text{Wt. of oxygen}} = \frac{\text{Eq. wt. of Zn}}{\text{Eq. wt. of oxygen}};$$

$$\frac{\text{Wt. of Zn}}{4} = \frac{32.5}{8}$$

$$\therefore \quad \text{Wt. of Zn} = \frac{32.5\times 4}{8} = \mathbf{16.25\ g} \qquad \textbf{Ans.}$$

19.20 AIEEE PATTERN EXAMPLES

Example 131. *If the conductance and specific conductance of a solution is same, then its cell constant is equal to :*

(*a*) *zero* (*b*) *1*

(*c*) *2* (*d*) *3*

Solution. We know that :

Specific conductance = Observed conductance × Cell constant

$$\therefore \quad \text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

When specific conductance

= Observed conductance, then :

Cell constant = 1.

So, the correct answer is, (*b*).

Example 132. *The specific conductance of a salt of 0.01 concentration is 1.061×10^{-4}. Molar conductance will be*

(*a*) *1.061×10^{-4}* (*b*) *1.061*

(*c*) *10.61* (*d*) *106.1*

(Pb PMT, 1993)

Solution. Molar conductance,

$$\Lambda_m = \frac{\text{specific conductance} \times 1000}{\text{concentration}}$$

$$= 1.061 \times 10^{-4} \times \frac{1000}{0.01}$$

$$= \mathbf{10.61}$$

So, the correct answer is (*c*).

Example 133. *Equivalent conductance of NaCl, HCl and C_2H_5COONa at infinite dilution are 126.45, 426.16 and 91 ohm⁻ cm² respectively. The equivalent conductance of C_2H_5COOH* is:

(*a*) *201.28 ohm⁻ cm²* (*b*) *390.71 ohm⁻cm²*

(*c*) *698.28 ohm⁻ cm²* (*d*) *540.48 ohm⁻cm²*

(CBSE, 1997)

Solution. We know that ;

$$\Lambda^\circ_{C_2H_5COOH} = \Lambda^\circ_{C_2H_5COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$$

$$= (91 + 426.16 - 126.45)\ \text{Ohm}^{-}\ \text{cm}^2$$

$$= 390.71\ \text{ohm}^{-}\text{cm}^2$$

So, the correct answer is (*b*).

Example 134. *The resistance of a cell (cell constant = 1.1 cm^{-1}) containing $\frac{N}{50}$ KCl was found to be 400 ohms. The equivalent conductivity of KCl at this dilution is :*

(*a*) *68.75 ohm⁻* (*b*) *437.5 ohm⁻*

(*c*) *200 cm⁻* (*d*) *137.5 ohm⁻ cm² (g. equiv)⁻*

Solution. Cell constant = 1.1 cm⁻ ;

R = 400 ohms ; Λ = ? ,

$$\text{normality} = \frac{N}{50}.$$

$$\text{Specific conductance, } K = \frac{1}{R} \times \text{cell consstant}$$

$$= \frac{1}{400 \text{ ohm}} \times 1.1 \text{ cm}^{-}$$

But equivalent conductance,

$$\Lambda = \frac{K \times 1000 \text{ cm}^3}{\text{Normality}}$$

$$= \frac{1}{400 \text{ ohm}} \times \frac{1.1 \text{ cm}^{-} \times 1000 \text{ cm}^3}{(1/50)\text{ g. equiv}}$$

$$= \mathbf{137.5\ ohm^{-}\ cm^{2}\ (g.\ equiv)^{-}}$$

So, the correct answer is (*d*).

EXAMPLE 135. *The specific conductivity of 0.01 N KCl is 0.0014106 ohm*$^{-}$ *cm*$^{-}$ *at 298 K. When a conductivity cell was filled up with the same solution, it offered a resistance of 484 ohm at 298 K. The same cell was then filled with 0.001 N solution of NaCl at the same temperature which gave a resistance of 5496 ohms. The value of equivalent conductivity of 0.001 N NaCl solution is :*

(*a*) *124.2 ohm* (*b*) *124.2 ohm*$^{-}$*cm*^{2}*(g. equiv)*$^{-}$

(*c*) *62.1 cm*$^{-}$ (*d*) *6.21 cm*$^{-}$

SOLUTION. (*a*) Cell constant

$$= K \times \frac{1}{\text{conductance } (=1/R)} = K \times R$$

$$= 0.0014106\ \text{ohm}^{-}\ \text{cm}^{-} \times 484\ \text{ohm}$$

∴ *K* for 0.001 N NaCl

$$= \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{0.0014106\ \text{ohm}^{-}\ \text{cm}^{-} \times 484\ \text{ohm}}{5496\ \text{ohm}}$$

But
$$\Lambda = \frac{\text{K} \times 1000\ \text{cm}^3}{\text{Normality in (g equiv)}}$$

$$= \frac{0.0014106\ \text{cm}^{-} \times 484}{5496\ \text{ohm}} \times \frac{1000\ \text{cm}^3}{0.001\ \text{g. equiv}}$$

$$= \mathbf{124.2\ ohm^{-}cm^{2}\ (g.\ equiv)^{-}}$$

So, the correct answer is (*b*).

EXAMPLE 136. *Specific conductances of two electrolytic solutions of the 0.1. M concentration of the substances A and B are 8.5 × 10*$^{-3}$ *and 4.5 × 10*$^{-4}$ *ohm*$^{-}$ *cm*$^{-}$ *respectively. The one which offers less resistance for the flow of current and the one which is a stronger electrolyte are :*

(*a*) *A, A* (*b*) *A, B*

(*c*) *B, A* (*d*) *B, B*

SOLUTION. Specfic conductances (*K*) of solution,

$$\text{A} = 8.5 \times 10^{-3}\ \text{ohm}^{-}\ \text{cm}^{-}.$$

∴ Specific resistance offered by solution,

$$\text{A} = 1/(8.5 \times 10^{-3}\ \text{ohm}^{-}\ \text{cm}^{-})$$

$$= 117.65\ \text{ohm cm}.$$

Specific conductance (*K*) of solution,

$$\text{B} = 4.5 \times 10^{-4}\ \text{ohm}^{-}\ \text{cm}^{-}$$

∴ Specific resistance of solution, B = 1/(4.5 × 10^{-4} ohm^{-} cm^{-}) = 2222.2 ohm cm. Since solution A offers less resistance (= 117.65 ohm cm) than B (= 2222.2 ohm cm), A is stronger electerolyte. So, the correct answer is (*a*).

EXAMPLE 137. *For a cell given below Ni/Ni*$^{2+}$ *(0.1 M) ‖ Au*$^{3+}$ *(1M) |Au,* $E°_{\text{Ni/Ni}^{2+}} = +0.25\ V$; $E°_{\text{Au/Au}^{+3}} = +1.5\ V$. *The e.m.f. of the cell will be :*

(*a*) *0.1679 V* (*b*) *– 1.1786 V*

(*c*) *+ 1.779 V* (*d*) *– 1.77955 V*

SOLUTION. Cell reaction is written as :

$$\text{Ni} \longrightarrow \text{Ni}^{2+} + 2e^-] \times 3;\ E° = +0.25\ V$$

$$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}] \times 2; \qquad E° = +1.5\ V$$

Adding : $3\text{Ni} + 2\text{Au}^{3+} \longrightarrow 3\text{Ni}^{2+} + 2\text{Au};$

$$E° = 0.25 + 1.5 = 1.75\ V$$

Using Nernst equation, we have :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]^3}{[\text{Au}^{3+}]^2}$$

$$= 1.75 - \frac{0.0591}{6} \log \frac{(0.1)^3}{(1)^2}$$

$$= 1.75 - \frac{0.0591}{6} \log 10^{-3}$$

$$= 1.75 - \frac{0.0591}{6} \times -3$$

$$= 1.75 + 0.02955 = \mathbf{+\,1.779\ V.}$$

So, the corect answer is (*c*).

EXAMPLE 138. *Which represents disproportionation.*

(*a*) $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

(*b*) $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

(*c*) $3I_2 \longrightarrow 5I^- + I^{5+}$

(*d*) $2Cu^+ \longrightarrow Cu + Cu^{2+}$

SOLUTION. In a disproportionation reaction, one substance is oxidised as well as reduced. I_2 is oxidised to I^{5+} as well as reduced to I^-. Also, Cu^+ is oxidised to Cu^{2+} as well as reduced to Cu. So, the answers are, (*c*) and (*d*).

EXAMPLE 139. *When an electric current is passed through a solution containing* $AgNO_3$, $Hg_2(NO_3)_2$, $Ba(NO_3)_2$ *and* $Cu(NO_3)_2$ *using inert electrode, their cations got liberated at the cathode. With increasing voltage, the sequence of deposition of metals on the electrodes will be :*

(*a*) *Ba, Hg, Cu, Ag* (*b*) *Mg, Ag, Cu, Hg*

(*c*) *Hg, Ag, Cu, Ba* (*d*) *Ag, Hg, Cu.*

$E^{\circ}_{Ba^{2+}/Ba} = -2.90\ V;\ E°_{Hg_2^{2+}/2Hg} = +0.79\ V : E^{\circ}_{Cu^{2+}/Cu} = +0.34\ V$ *and* $E°_{Ag^+/Ag} = +0.779\ V$

SOLUTION. We know that greater the standard reduction potential value, greater is its tendency to undergo reduction. Barium will not be deposited because its standard reduction potential value is negative. The increasing order of standard reduction potential value of Ag, Cu, Hg is Cu < Hg <Ag. So, the sequence of deposition of metals on the electrodes is, Ag, Hg, Cu. Hence, the answer is (*d*).

EXAMPLE 140. *When an electric current is passed through dil.* H_2SO_4, *the gases liberated at anode and cathode are :*

(*a*) H_2 *and* O_2 *respectively*

(*b*) O_2 *and* H_2 *respectively*

(*c*) SO_2 *and* O_2 *respectively*

(*d*) SO_2 *and* H_2 respectively

SOLUTION. The reactions that take place are :

At anode. $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

At cathode. $2H^+ + 2e^- \longrightarrow H_2$

Since O_2 is liberated at anode and H_2 at cathode, the answer is (*b*).

EXAMPLE 141. *The standard redox potentials for the reactions, $Mn^{2+} + 2e^- \longrightarrow Mn$ and $Mn^{3+} + e^- \longrightarrow Mn^{2+}$ are –1.18 V and 1.51 V respectively. What is the redox potential for the reaction, $Mn^{3+} + 3e^- \longrightarrow Mn$?*

(*a*) *0.33 V* (*b*) *1.69 V*

(*c*) *–0.28 V* (*d*) *–0.85 V*

(*e*) *0.85 V* **(Kerala PET, 2011)**

SOLUTION. $Mn^{2+} + 2e^- \longrightarrow Mn$ ...(1);

$$\Delta G^\circ = -nFE^\circ = -2F \times -1.18 = 2.36\ F$$

$$Mn^{3+} + e^- \longrightarrow Mn^{2+} \quad ...(2);$$

$$\Delta G^\circ = -nFE^\circ = -1.51\ F$$

By adding equations (1) and (2), we get:

$Mn^{3+} + 3e^- \longrightarrow Mn$; $\Delta G^\circ = 2.36\ F + (-1.51\ F) = 0.85\ F$

$\Delta G^\circ = -nFE^\circ$; $0.85F = -3 \times F \times E^\circ$; $E^\circ = -0.28$ V

So, the correct answer is (*c*).

EXAMPLE 142. *Being unstable, Cu^+ undergoes disproportionation. E° for Cu^+ disproportionation is :*

(*a*) *– 0.367 V* (*b*) *+ 0.377 V*

(*c*) *– 0.726 V* (*d*) *+ 0.666V*

$E^\circ_{Cu^{2+}/Cu^+} = +\ 0.153\ V$; $E^\circ_{Cu^+/Cu} = 0.53\ V.$

SOLUTION. The reaction for disproportionation of Cu^+ is :

$$2Cu^+ \longrightarrow Cu + Cu^{2+}$$

$$E^\circ_{cell} = E^\circ_{Cu^+/Cu^{2+}} + E^\circ_{Cu^+/Cu}$$

Substituting the values, we get :

$$E^\circ_{cell} = -0.153 + 0.53 = \mathbf{+0.377}\ V$$

Hence, the answer is (*b*).

EXAMPLE 143. *Following are given two half-cell reactions along with their standard reduction potential values at 25°C.*

$$Mg^{2+} + 2e^- \longrightarrow Mg \ ; \ E^\circ = -2.37\ V$$

$$Zn^{2+} + 2e^- \longrightarrow Zn \ ; \ E^\circ = -0.76\ V$$

Some zinc dust is now added to $MgCl_2$ solution. Predict :

(*a*) *Zinc dissolves in solution*

(*b*) *$ZnCl_2$ is formed*

(*c*) *No reaction takes place*

(*d*) *Mg gets precipitated.*

SOLUTION. Reaction. $Zn + Mg\ Cl_2 \longrightarrow ZnCl_2 + Mg$

But $E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$$= E^\circ_{Zn/Zn^{2+}} + E^\circ_{Mg^{2+}/Mg} = +0.76 - 2.37$$

$$= \mathbf{-1.61\ V}$$

Since E°_{cell} is negative , reaction will not take place.

Hence, the answer is (*c*)

EXAMPLE 144. *Stronger the oxidant, greater will be the :*

(*a*) *Ionic character*

(*b*) *Standard reduction potential value*

(*c*) *Standard oxidation potential value*

(*d*) *None of these*

SOLUTION. We know that species having higher value of standard reduction potential are stronger oxidants. Hence, the answer is (*b*).

EXAMPLE 145. *The reductant H_2 will reduce :*

(*a*) *Heated aluminium oxide*

(*b*) *Heated lead (II) oxide*

(*c*) *Heated ferric oxide*

(*d*) *Heated cupric oxide.*

$E^\circ_{2H^+/H_2} = 0.0V$; $E^\circ_{Fe^{3+}/Fe^{2+}} = +\ 0.771\ V$;

$E^\circ_{Al^{3+}/Al} = -\ 1.66\ V$

$E^\circ_{Cu^{2+}/Cu} = +\ 0.34\ V$; $E^\circ_{Pb^{2+}/Pb} = -\ 0.126\ V$.

SOLUTION. An element with lower reduction potential value can reduce element with higher reduction potential value. Since the reduction potential value of Cu and Fe is greater than that of H_2, the latter will reduce their oxides.

$$Fe_2O_3 + H_2 \longrightarrow 2FeO + H_2O\ ;$$

$$CuO + H_2 \longrightarrow Cu + H_2O$$

Hence, the answers are (*c*) and (*d*)

EXAMPLE 146. *During the discharge of lead storage battery, which one of the following is true?*

(*a*) *Lead is formed* (*b*) *$PbSO_4$ is consumed*

(*c*) *H_2SO_4 is consumed* (*d*) *SO_2 is liberated*

SOLUTION. Following reactions take place in lead storage battery.

At anode :

$$Pb + H_2SO_4 \longrightarrow PbSO_4 + 2H^+ + 2e^- \quad \text{(oxidation)}$$

At cathode :

$$PbO_2 + H_2SO_4 + 2H^+ + 2e^- \longrightarrow PbSO_4 + H_2O \quad \text{(reduction)}$$

Net reaction.

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

From the net discharge reaction, we see that only H_2SO_4 is consumed during discharging. So, (*c*) is true.

EXAMPLE 147. *Three electrolytic cells containing Ag^+, Cu^{2+} and Al^{3+} ions are connected to-gether in series. Now a current of three Faraday was passed. The molar ratio in which the above three metal ions are liberated at the electrodes is :*

(*a*) *2 : 3 : 6* (*b*) *6 : 3 : 2*

(*c*) *1 : 2 : 3* (*d*) *2 : 3 : 6*

SOLUTION. According to second law of electrolysis :

$$\frac{\text{Wt. of element}}{\text{Eq. wt. of element}} = \text{Constant}$$

Thus : g. Eq. wt. of Ag^+

= g. Eq. wt. of Cu^{2+}

= g. eq. wt. of Al^{3+} = *a* (suppose)

(*a*) Mole of Ag^+ = *a* [$\because Ag^+ + e^- \rightarrow Ag$]

(*b*) Mole of $Cu^{2+} = \frac{a}{2}$ [$\because Cu^{2+} + 2e^- \rightarrow Cu$]

(*c*) Mole of $Al^{3+} = \frac{a}{3}$ [$\because Al^{3+} + 3e^- \rightarrow Al$]

Hence, molar ratio of Ag^+, Cu^{2+}, Al^{3+}

$$= \frac{a}{1} : \frac{a}{2} : \frac{a}{3}$$

$$= \frac{6:3:2}{6\,(=\text{LCM})} \quad \textit{i.e.,} \quad 6:3:2$$

Hence, true answer is (*b*).

EXAMPLE 148. *Standard reduction electrode potentials of three metals A, B and C are respectively +0.5V, – 3.0 V and – 1.2 V. The reducing powers of these metals are :*

(*a*) $A > C > B$ (*b*) $B > C > A$

(*c*) $A > B > C$ (*d*) $C > B > A$

(AIEEE, 2003)

SOLUTION. We know that as the value of standard reduction electrode potential decreases, the power of these elements to act as reducing agent increases. Since – 3.0 V < – 1.2 V < + 0.5V, the reducing power of these metals decreases as : B > C > A. So, the correct answer is (*b*).

EXAMPLE 149. *For a cell reaction involving a two electron change, the standard e.m.f. of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be :*

(*a*) 1×10^{10} (*b*) 1×10^{-10}

(*c*) 29.5×10^{-2} (*d*) 10 **(AIEEE, 2003)**

SOLUTION. Given, $n = 2$ because reaction is of two electron change.

$$E^\circ_{\text{cell}} = 0.0295 \text{ V}; \; \log K = ?$$

We know that : $E^\circ_{\text{cell}} = \dfrac{0.0591}{n} \log \text{K}$

$$\therefore \qquad \log K = \frac{n \times E^\circ_{\text{cell}}}{0.059} = \frac{2 \times 0.295}{0.059} = \mathbf{10}$$

So, the correct answer is (*d*).

EXAMPLE 150. *A solution contains Fe^{2+}, Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C. E° for Fe^{3+}/Fe^{2+} is + 0.77 V and E° for $I_2/2I^-$ = 0.536 V. The favourable redox reaction is:*

(*a*) *I_2 will be reduced to I^-.*

(*b*) *There will be no redox reaction*

(*c*) *I^- will be oxidised to I_2*

(*d*) *Fe^{2+} will be oxidised to Fe^{3+}*

(AIPMT, 2011)

SOLUTION. Greater the value of reduction potential, greater will be its tendency to get reduced. Since the reduction potential value of Fe^{3+}/Fe^{2+} (= + 0.77 V) is greater than that of $I_2/2I^-$ (= 0.536 V), Fe^{3+} will be reduced to Fe^{2+} and I^- will be oxidised to I_2. So, the correct answer is (*c*).

EXAMPLE 151. *Conductance (unit siemen's S) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel, then the unit of constant of proportionality is :*

(*a*) *$Sm\,mol^-$* (*b*) *$S^2m^2\,mol^{-2}$*

(*c*) *$Sm^{-2}\,mol^-$* (*d*) *$S^{-2}\,m^2\,mol.$*

(AIEEE, 2002)

SOLUTION. Given : Conductance, $C \;\alpha\; a \times \text{concentration} \times \dfrac{1}{l}$

or $\qquad C = K \times a \times \text{conc.} \times \dfrac{1}{l}$

where $\qquad K$ = Constant called conductivity

$$\therefore \qquad K = \frac{Cl}{a \times \text{Conc}} = \frac{\text{S} \times m \times \text{m}^{-3}}{\text{m}^2 \times \text{mol}}$$

$$= \mathbf{Sm^{-2}\,mol^{-}}$$

So, the correct answer is (*c*).

EXAMPLE 152. *The equivalent conductances at infinite dilutions ($\wedge_o$) for electrolytes BA and CA are 140 and 120 S cm² eq⁻. The equivalent conductance at infinite dilution for BX is 198 S cm² eq⁻. The $\wedge_o$ (in S cm² eq⁻) of CX is :*

(*a*) *218* (*b*) *198*

(*c*) *178* (*d*) *130*

SOLUTION. We know

$$\wedge^\circ_{CX} = \wedge^\circ_{C} + \wedge^\circ_{X} = \wedge^\circ_{CA} - \wedge^\circ_{BA} + \wedge^\circ_{BX}$$

$$= 120 - 140 + 198 = \mathbf{178\ S\ cm^2\ eq^-}$$

So, the correct answer is (*c*).

Note : $\wedge^\circ_{CA} = \wedge^\circ_{C} + \wedge^\circ_{A}\,;\; \wedge^\circ_{BA} = \wedge^\circ_{B} + \wedge^\circ_{A}\,;\; \wedge^\circ_{BX} = \wedge^\circ_{B} + \wedge^\circ_{X}$

EXAMPLE 153. *The equilibrium constant (K) for the reaction $Cu\,(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}\,(aq) + 2Ag(s)$ will be :*

(*a*) *K_c = Antilog 4.5*

(*b*) *K_c = Antilog 42.2*

(*c*) *K_c = Antilog 9.5*

(*d*) *K_c = Antilog 15.6; (E°_{cell} = 0.46 V)*

SOLUTION. We know,

$$E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_c \qquad \text{...(1)}$$

In the given reactions,

$$\text{Cu(s)} \rightleftharpoons \text{Cu}^{2+} + 2e^-$$

$$2\text{Ag}^+ + 2e^- \rightleftharpoons 2\text{Ag},$$

there is two electron change.

So, $\qquad n = 2$

Substituting the values, in (1) we get :

$$0.46 = \frac{0.0591}{2} \log K_c$$

or $\qquad \log K_c = \dfrac{2 \times 0.46}{0.059} = 15.6$

or $\qquad K_c$ = **Antilog 15.6**

So, the correct answer is (*d*).

EXAMPLE 154. *The equilvalent conductance at infinite dilution of the salt AB is 160.84 ohm⁻ cm² (eq)⁻. If the transport number of A^+ is 0.40, the ionic mobility of B^- in cm²s⁻ V⁻ is :*

(*a*) *8.9×10^{-5}* (*b*) *4.5×10^{-3}*

(*c*) *1.0×10^{-3}* (*d*) *6.9×10^{-4}*

SOLUTION. We know that, *ionic conductance of an ion*

= Transport number of that ion.

$\therefore$ B $\wedge^\circ_{\text{eq}}$ of strong electrolyte containing that ion

$$= (1 - 0.40) \times 160.84$$

$$= 0.6 \times 160.84 = 96.504$$

$$\therefore \quad \text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

$$= \frac{96.504}{96500} = \mathbf{1.0 \times 10^{-3}}$$

So, the correct answer is (*c*).

Example 155. *Given standard electrode potentials :*

$Fe^{3+} + 3e^- \longrightarrow Fe\ ;\ E° = -0.036\ V;$

$Fe^{2+} + 2e^- \longrightarrow Fe\ ;\ E° = -0.440\ V$

The standard electrode potential,

$E°$ for $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ is :

(*a*) *0.02 V* (*b*) *0.0277 V*

(*c*) *0.772 V* (*d*) *– 0.772 V*

(AIEEE, 2009)

Solution. Given :

$$Fe^{3+} + 3e^- \longrightarrow Fe\ ;\ E° = -0.036\ V \quad ...(1)$$

$$Fe^{2+} + 2e^- \longrightarrow Fe\ ;\ E° = -0.440\ V \quad ...(2)$$

For reaction (1), $\Delta G = -nF\,E°_{cell} = -3F\,(-0.036)$

$$= 0.108\ F \quad ...(3)$$

For reaction (2), $\Delta G = -nF\,E°_{cell} = -2F\,(-0.440)$

$$= 0.88\ F \quad ...(4)$$

Subtracting reaction (2) from (1) and their ΔG values, we have :

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}\ ;$$

$$\Delta G = 0.108\ F - 0.88\ F = -0.772\ F$$

$$\therefore E° \text{ of the reaction} = -\frac{\Delta G}{nF} = -\frac{(-0.772F)}{1F} = \mathbf{+0.772\ V}$$

So, the correct answer is (*c*).

Example 156. *How many coulombs of electricity are consumed when a 100 mA current is passed through a solution of $AgNO_3$ for half an hour during an electrolysis experiment ?*

(*a*) *80 C* (*b*) *180 C*

(*c*) *360 C* (*d*) *3600C*

Solution. $1mA = 10^{-3}$ ampere

$\therefore \quad 100mA = 100 \times 10^{-3} A$

Time = ½ hr = ½ × 60 × 60 = 1800 second

∴ Quantity of electricity to be passed

= Current in amperes × time in seconds

$= 100 \times 10^{-3}\ A \times 1800\ s = 180 As$

= 180 C

So, the correct answer is (*b*).

Example 157. *Three Faradays of electricity are passed through molten Al_2O_3, aqueous solution of $CuSO_4$ and molten NaCl taken in three different electrolytic cells. Then the mole ratio of Al, Cu and Na deposited on cathode will be:*

(*a*) *3 : 4 : 6* (*b*) *2 : 1 : 6*

(*c*) *3 : 2 : 1* (*d*) *2 : 3 : 6*

(J and K-CET, 2011)

Solution. The required reduction reactions are:

(*i*) $Al^{3+} + 3e^- \longrightarrow Al$

(*ii*) $Cu^{2+} + 2e^- \longrightarrow Cu$

(iii) $Na^+ + e^- \longrightarrow Na$

Since 3 Faradays of electricity is passed, so, the amount of Al, Cu and Na deposit in mole will be:

$$\text{Al: Cu : Na or } \frac{3}{3} : \frac{3}{2} : \frac{3}{1} \text{ or } 1 : 1.5 : 3 \text{ i.e.,}$$

$$1 : \frac{3}{2} : 3 \text{ or } (1 \times 2) : \left(\frac{3}{2} \times 2\right) : 3 \times 2 = 2 : 3 : 6.$$

So, the correct answer is (*d*).

Example 158. *A current of 9.65 ampere flowing for 10 minutes deposits 3.0 g of the metal which is monovalent. The atomic mass of the metal is :*

(*a*) *150* (*b*) *100*

(*c*) *50* (*d*) *5.0*

Solution. Wt. of metal deposited = 3.0 g ;

quantity of electricity passed,

Q = Current in amperes × time in seconds

= 9.65 A × (10 × 60s)

= 9.65 A × 600s

= 5790 As = 5790 C.

$$\text{But Eq. wt. of metal} = \frac{\text{Wt. of metal}}{Q} \times 96500$$

$$= \frac{3.0}{5790} \times 96500 = 50$$

Valency of metal = 1 (given)

∴ Atomic weight = Eq. wt. × Valency

or At. wt. = 50 × 1 = **50**

So, the correct answer is (*c*).

Example 159. *The standard e.m.f. of a galvanic cell involving two moles of electrons in its redox reaction is 0.59 V. The equilibrium constant for a redox reaction of the cell is:*

(*a*) 10^{20} (*b*) 10^5

(*c*) *10* (*d*) 10^{10}

(Karnataka CET, 2011)

Solution. Galvanic cell is represented as:

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

$$[Zn \rightleftharpoons Zn^{2+} + 2e^-;\ n = 2.]$$

At equilibrium, $E_{cell} = 0$. But equilibrium constant K_C is found from the relation:

$$E°_{cell} = \frac{0.059}{n} \log K_C$$

$$0.59 = \frac{0.059}{2} \log K_C;$$

$$\log K_C = \frac{2 \times 0.59}{0.059} = 20;$$

$$\therefore \quad K_C = \text{antilog } 20 = 10^{20}.$$

So, the correct answer is (*a*).

EXAMPLE 160. *The volume of H_2 gas at N.T.P. obtained by passing 4 amperes through acidified H_2O for 30 minutes is :*

(*a*) *0.0836 L*	(*b*) *0.0432L*
(*c*) *0.1672 L*	(*d*) *0.836 L*

(DCE, 2005)

SOLUTION. Time, *t* in seconds

$$= 30 \text{ min} \times \frac{60 \text{ sec}}{1 \text{ min}} = 1800s$$

$$\text{Current, C} = 4 \text{ amperes}$$

$$\therefore \quad Q = 4 \text{ amperes} \times 1800 \text{ s}$$

$$= 7200 \text{ amperes} = 7200 \text{ Coulomb}$$

$$= 7200 \text{ C}$$

Reaction. $H_2O \longrightarrow H_2 + 1/2\, O_2$;

$$\underset{2 \times 96500 \text{ C}}{2H^+ + 2e^-} \longrightarrow \underset{1 \text{ mol } i.e., 22400 \text{ mL at N.T.P.}}{H_2}$$

$$2 \times 96500 \text{ C will give } H_2 = 22400 \text{ mL}$$

$$\therefore \quad 7200 \text{ C will give } H_2 = \frac{22400 \text{ mL} \times 7200 \text{ C}}{2 \times 96500 \text{ C}}$$

$$= 835.64 \text{ mL} = \mathbf{0.836\ L}$$

So, the correct answer is (*d*).

EXAMPLE 161. *The standard electrode potential of Ag^+ / Ag is +0.08 V and Cu^{2+} / Cu = 0.34 V. These electrodes are connected through a salt bridge and if*

(*a*) *Copper electrode acts as a cathode, then $E°_{cell}$ is +0.46V*
(*b*) *Silver electrode acts as anode, then $E°_{cell}$ is –0.34 V*
(*c*) *Copper electrode acts as anode, then $E°_{cell}$ is +0.46 V*
(*d*) *Silver electrode acts as a cathode then $E°_{cell}$ is –0.34 V*
(*e*) *Silver electrode acts as anode and $E°_{cell}$ is +1.14 V*

(Kerala PET, 2005)

SOLUTION. The cell reaction is

$$Cu(s) + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$$

The two half-cell reactions are :

$$Cu(s) \rightleftharpoons Cu^{2+} + 2e^- \text{ (oxidation, anode)}$$

$$Ag^+ + e^- \rightleftharpoons Ag \quad \text{(Reduction, cathode)}$$

$$\therefore \quad E°_{\text{cell}} = E_{\text{ox}} + E_{\text{red}} = -\,0.34 + 0.80$$

$$= +\,0.46\ V.$$

Since *E*° is positive, the reaction is feasible. So, the correct answer is (*c*).

EXAMPLE 162. *Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (at. mass = 27 amu; 1 Faraday = 96,500 coulombs). The cathode reaction is $Al^{3+} + 3e^- \to Al°$. To prepare 5.12 kg of aluminium metal by this method would require.*

(*a*) *5.49×10^7 C of electricity*
(*b*) *1.83×10^7C of electricity*
(*c*) *5.49×10^4 C of electricity*
(*d*) *5.49×10^1 C of electricity.*

(AIEEE, 2005)

SOLUTION. Reaction.

$$\underset{3 \times 96500 \text{ C}}{Al^{3+} + 3e^-} \longrightarrow \underset{27 \text{ g}}{Al}$$

$$\text{wt. of Al} = 5.12 \text{ kg} = 5.12 \times 1000 = 5120 \text{ g}$$

27 g Al require electricity = 3 × 96500 C

5120g Al require electricity

$$= \frac{3 \times 96500}{27} \times 5120 = \approx \mathbf{5.49 \times 10^7 C}$$

So, the correct answer is (*a*).

EXAMPLE 163.

Electrolyte	*KCl,*	*KNO_3,*	*HCl,*	*NaOAC,*	*NaCl*
$\wedge^\infty$(S cm^2 mol$^-$)	*149.4*	*145*	*426.2*	*91.0*	*126.5*

Calculate $\wedge^\infty_{\text{HOAC}}$ using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C.

(*a*) 517.2	(*b*) 552.7
(*c*) 390.7	(*d*) 217.5

SOLUTION. $\wedge^\infty_{\text{HOAC}} = \wedge^\infty_{\text{NaOAC}} + \wedge^\infty_{\text{HCl}} - \wedge^\infty\text{NaCl}$

$$= 91 + 426.2 - 126.5$$

$$= \mathbf{390.7\ S\ cm^2\ mol^-}$$

So, the correct answer is (*c*).

EXAMPLE 164. *9.65 coulombs of electric current is passed through fused anhydrous $MgCl_2$. The Mg metal thus obtained is completely converted into a Grignard reagent. The number of moles of Grignard reagent obtained is:*

(*a*) *5×10^{-4}*	(*b*) *1×10^{-4}*
(*c*) *5×10^{-5}*	(*d*) *1×10^{-5}*

(Karnataka CET, 2011)

SOLUTION. Eq. wt. of Mg = At. wt./valency = 24/2 = 12g mol$^-$.

We know that:

96500 coulombs of electric current deposits Mg = 12g

9.65 coulombs of electric current deposit Mg.

$$= \frac{12}{96500} \times 9.65 = 1.2 \times 10^{-3} \text{ g of Mg.}$$

$$\text{But } MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$$

$$Mg^{2+} + 2e^- \longrightarrow Mg$$

∴ Number of moles of Grignard reagent obtained

$$= \frac{1.2 \times 10^{-3}}{24} = 5 \times 10^{-5} \text{ mol.}$$

So, the correct answer is (*c*).

EXAMPLE 165. *The two Pt electrodes fitted in a conductance cell are 1.5 cm apart while the crossectional area of each electrode is 0.75 cm^2. What is the cell constant ?*

(*a*) *1.125*	(*b*) *0.5 cm*
(*c*) *2.0 cm$^-$*	(*d*) *0.2 cm$^-$*

(PUCET, 1989)

SOLUTION. Cell constant

$$= \frac{\text{length}}{\text{area}} = \frac{1.5 \text{ cm}}{0.75 \text{ cm}^2} = \mathbf{2.0\ cm^-}$$

So, the correct answer is (*c*).

EXAMPLE 166. *How much silver will be displaced by that quantity of current which displaces 5.6 L of H_2 :*

(*a*) *13.5 g* (*b*) *20 g*
(*c*) *54 g* (*d*) *168 g*

(Pb PMT, 1993)

SOLUTION. 22.4 L volume is occupied by H_2 = 1 mol

5.6 L volume is occupied by H_2

$$= \frac{1}{22.4} \times 5.6 = 0.25 \text{ mol}$$

$$= 0.25 \text{ mol} \times \frac{2 \text{ g. equivalent}}{1 \text{ mol}}$$

$$= 0.5 \text{ g equivalent}$$

∴ Wt. of silver displaced = 0.5 × 108 g = 54g

[∵ eq. wt. of Ag = 108)

So, the correct answer is (*c*).

EXAMPLE 167. *What is the number of coulombs required for the conversion of one mol of* MnO_4^- *to one mol of* Mn^{2+} *?*

(*a*) *96500* (*b*) *96500 × 3*
(*c*) *96500 × 5* (*d*) *96500 × 7*

(Orissa, MBBS, 1993)

SOLUTION.

Reaction : $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

The reaction involves 5 electrons :

∴ Coulombs required = 5 × 96500 coulombs.

So, the correct answer is (*c*).

EXAMPLE 168. *A 0.05 M NaOH solution offered a resistance of 31.6 ohm in a conductivity cell. If the cell constant of a conductivity cell is 0.378 cm⁻, determine the molar conductivity of sodium hydroxide solution at this temperature.* **(ISC, 2008)**

SOLUTION. Resistance,

$$R = 316 \text{ ohm};$$

$$\text{Molarity} = 0.05 \text{ M};$$

$$\text{cell constant} = 0.378 \text{ cm}^-;$$

$$\text{conductance} = \frac{1}{R} = \frac{1}{31.6} \text{ohm}^-.$$

Specific conductance (K) = Conductance × cell constant

$$= \frac{1}{31.6} \text{ ohm}^- \times 0.378 \text{ cm}^-$$

$$= 0.0119 \text{ ohm}^- \text{ cm}^-$$

$$\therefore \text{ Molar conductance} = \frac{\text{K} \times 1000 \text{ cm}^3}{\text{Molarity}}$$

$$= \frac{0.0119 \text{ ohm}^- \text{ cm}^- \times 1000 \text{ cm}^3}{0.05 \text{ mol}}$$

$$= \mathbf{238 \text{ ohm}^- \text{ cm}^2 \text{ mol}^-}.$$

EXAMPLE 169. *When electricity is passed through aqueous solution of aluminium chloride, 13.5 g of Al are deposited. The number of Faradays of electricity passed must be :*

(*a*) *2.0* (*b*) *1.5*
(*c*) *1.0* (*d*) *0.5*

(Pb CET, 1994)

SOLUTION. $AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$;

$$Al^{3+} + 3e^- \rightleftharpoons Al$$

3F 27 g

(∵ At. wt. of Al = 27)

27g Al is deposited from faradays = 3

$$13.5 \text{ g Al is deposited from faradays} = \frac{3}{27} \times 13.5 = \mathbf{1.5}$$

So, the correct answer is (*b*).

EXAMPLE 170. *2.5 Faradays of electricity is passed through a solution of* $CuSO_4$*. The number of gram equivalents of copper deposited at cathode are :*

(*a*) *1* (*b*) *2*
(*c*) *2.5* (*d*) *1.25*

(CPMT, 1996)

SOLUTION. $CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$;

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

2F 1g. eq.

2F electricity deposits Cu = 1 g. equivalent

$$2.5 \text{ F electricity deposits Cu} = \frac{1\text{g. equivalent} \times 2.5}{2}$$

$$= \mathbf{1.25 \text{ g equivalent}}$$

So, the correct answer is (*d*).

EXAMPLE 171. *An electrolytic cell contains a solution of* Ag_2SO_4 *and has Pt electrodes. A current is passed till 1.6g* O_2 *has been liberated at anode. The amount of silver deposited at cathode will be.*

(*a*) *107.88 g* (*b*) *1.6 g*
(*c*) *0.8 g* (*d*) *21.60 g*

(CPMT, 1996)

SOLUTION. wt. of O_2 = 1.6 g ; wt. of Ag deposited = ? ;

eq. wt. of oxygen = 8, eq. wt. of Ag = 108

We know :

$$\frac{\text{Wt. of Ag}}{\text{Wt. of } O_2} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of } O_2}$$

$$\text{Hence } \frac{\text{Wt. of Ag}}{1.6 \text{ g}} = \frac{108}{8} \text{ Or}$$

$$\text{Wt. of Ag deposited} = \frac{108 \times 1.6}{8} = \mathbf{21.60 \text{ g}}$$

So, the correct answer is (*d*).

EXAMPLE 172. *In a solution of* $CuSO_4$*, how much time will be required to precipitate 2 g copper by 0.5 ampere current ?*

(*a*) *12157.48 sec* (*b*) *102 sec*
(*c*) *510 sec* (*d*) *642 sec.*

(BIT Ranchi, 1996)

SOLUTION. Wt. of Cu = 2g ;

Current, I = 0.5 ampere ; t = time is sec = ?;

Z (= electrochemical equivalent)

$$= \frac{\text{g. eq. wt. of Cu}}{96500}$$

$$\text{or} \quad Z = \frac{63.5}{2 \times 96500}$$

According to Faraday's first law of electrolysis :

$$W = ZIt\ ;\ t = \frac{W}{ZI}$$

$$t = \frac{2\text{ g} \times 2 \times 96500\text{ C}}{63.5\text{ g} \times 0.5\text{ ampere}}$$

$$= \mathbf{12157.48\ sec.}$$

So, the correct answer is (*a*).

EXAMPLE 173. *What would be the weight of deposited silver on passing 965 coulombs of electricity in a solution of silver nitrate ?*

(*a*) *1.08 g* (*b*) *2.16 g*

(*c*) *0.54 g* (*d*) *0.27 g*

(MP CET, 1998)

SOLUTION. Reaction

$$Ag^+ + \underset{96500C}{1e^-} \longrightarrow \underset{108\text{ g}}{Ag}$$

96500 C electricity deposits

$$Ag = \text{g. eq. wt. of Ag} = 108\text{ g}$$

$$965\text{ C electricity deposits Ag} = \frac{108}{96500} \times 965 = 1.08\text{ g}$$

So, the correct answer is (*a*).

EXAMPLE 174. *What is the amount of chlorine evolved when 2 amperes of current is passed for 30 minutes in an aqueous solution of NaCl ?*

(*a*) *66 g* (*b*) *1.32 g*

(*c*) *33 g* (*d*) *99 g* **(BHU 1998)**

SOLUTION. Charge (Q) passed = Current (I) in amperes × time (t) in seconds

$$= 2\text{ amperes} \times 30\text{ min} \times \frac{60\text{ sec}}{1\text{ min}}$$

$$= 3600\text{ coulombs}$$

($\because$ Ampere × sec = Coulomb).

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Cl^- \rightleftharpoons \underset{\substack{1/2 \times (2 \times 35.5) \\ = 35.5\text{ g}}}{1/2Cl_2} + \underset{96500C}{1e^-}$$

96500 C produce chlorine

= 35.5 g (= g. equivalent of chlorine)

3600 C produce chlorine

$$= \frac{35.5\text{ g}}{96500\text{ C}} \times 3600\text{C} = \mathbf{1.32\ g}$$

So, the correct answer is (*b*).

EXAMPLE 175. *When $CuCl_2$ solution was electrolysed, the mass of the cathode increased by 3.175 g. What occurred at the copper anode ?*

(*a*) *0.01 mol of Cu^{2+} passed into solution*

(*b*) *0.05 mol of Cu^{2+} passed into solution*

(*c*) *1.1L Cl_2 was produced*

(*d*) *1.1 L O_2 was produced*

SOLUTION. $CuCl_2 \rightleftharpoons Cu^{2+} + 2\,Cl^-$

The mass of cathode increased by 3.175 g. It is due to the deposition of Cu^{2+} ions at cathode. As a result, the Cl^- ions would dissolve same amount of Cu from anode *i.e.*, 3.175 g of copper. Thus :

63.5 g Cu that passed into solution = 1 mol

$$3.175\text{ g Cu that passed into solution} = \frac{3.175\text{ g}}{63.5}$$

$$= \mathbf{0.05\ mol}$$

So, the correct answer is (*b*).

EXAMPLE 176. *A galvanic cell was set up from zinc rod (= 100 g) and 1L of 1 M $CuSO_4$ solution. If the cell delivers a steady current of one ampere, the time for whch the cell would work is:*

(*a*) *5.36 hr* (*b*) *2.68 hr*

(*c*) *26.8 hr* (*d*) *53.6 hr.*

SOLUTION. No. of mol of Zn

$$= \frac{\text{Wt. of Zn}}{\text{at. wt. of Zn}} = \frac{100}{65} = 1.54\text{ mol}$$

Also, 1L of 1M $CuSO_4$ = 1 mol $CuSO_4$

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}\ ;$$

$$\underset{1\text{ mol}}{Cu^{2+}} + \underset{2 \times 96500\text{ C}}{2e^-} \longrightarrow Cu$$

$\therefore$ 1 mol of $CuSO_4$ produces electricity,

$$Q = 2 \times 96500\text{ C}$$

But Q = Current in amperes × time in seconds

$\therefore$ 2 × 96500 C = 1 ampere × time in seconds

[$\because$ 1 ampere sec = 1C]

$$\therefore \text{Time in seconds} = \frac{2 \times 96500\text{ ampere sec}}{1\text{ ampere}}$$

$$= 2 \times 96500\text{ seconds}$$

$$= 2 \times 96500\text{ sec} \times \frac{1\text{ min}}{60\text{ sec}} \times \frac{1\text{ hr}}{60\text{ min}}$$

$$= \mathbf{53.6\ hr}$$

So, the correct answer is (*d*).

EXAMPLE 177. *Calculate the weight of copper that would be deposited at the cathode in the electrolysis of 0.2 M solution of copper sulphate when a quantity of electricity equal to that required to liberate 2.24 L of hydrogen from 0.1 M equeous sulphuric acid, is passed. Atomic mass of Cu = 63.5.*

(*a*) *1.59 g* (*b*) *3.18g*

(*c*) *6.35 g* (*d*) *12.7 g*

(ISM Dhanbad, 1994)

SOLUTION. Eq.wt. of $H_2 = \dfrac{\text{Mol. wt. of } H_2}{2}$

We know : 22.4 L H_2 = 1 mol H_2 at N.T.P.

$$\therefore\ \frac{22.4}{2}\text{ L } H_2 = 1\text{ g. equivalent of } H_2 \text{ at N.T.P.}$$

$$= 96500\text{ C}$$

$$2.24\text{ L } H_2 = 2.24 \times \frac{2}{22.4}$$

$$= 0.2\text{ g equivalent of } H_2$$

$$= 0.2 \times 96500\text{ C}$$

Also, $$\underset{2 \times 96500\ C}{Cu^{2+} + 2e^-} \longrightarrow \underset{63.5\ g}{Cu}$$

$$\therefore \quad 0.2 \times 96500\ C = \frac{63.5}{2 \times 96500} \times 0.2 \times 96500$$
$$= 6.35\ g\ Cu$$

So, the correct answer is (*c*).

EXAMPLE 178. *How many grams of copper will be deposited from a solution of $CuSO_4$ by passing 0.5 F of electric current ?*

(*a*) *31.75* (*b*) *63.5*
(*c*) *15.875* (*d*) *127*

(EAM, CET, 1994)

SOLUTION. $$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

Hence : $$\underset{\substack{2 \times 96500\ C \\ = 2F}}{Cu^{2+} + 2e^-} \longrightarrow \underset{63.5\ g}{Cu}$$

$$\text{2F electric current produces Cu} = 63.5\ g$$
$$\therefore \quad \text{0.5 F electric current produces Cu} = \frac{63.5}{2} \times 0.5$$
$$= 15.875\ g$$

So, the correct answer is (*c*).

EXAMPLE 179. *How many electrons are in one coulomb ?*

(*a*) *6.023×10^{23}* (*b*) *1.64×10^{-24}*
(*c*) *6.24×10^{18}* (*d*) *6.24×10^{-24}*

(Bihar, CEE, 1995)

SOLUTION. 1 mol of electrons = 6.02×10^{23} electrons = 96500 C

Hence : 96500 C contain electrons = 6.02×10^{23}
1 C contain electrons

$$= \frac{6.02 \times 10^{23}}{96500} = 6.24 \times 10^{18}$$

So, the correct answer is (*c*).

EXAMPLE 180. *Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 milli-ampere current. The time required to liberate 0.01 mol of H_2 gas at the cathode is (1 Faraday = 96500 C mol$^-$)*

(*a*) *9.65×10^4 sec* (*b*) *19.3×10^4 sec*
(*c*) *28.95×10^4 sec* (*d*) *38.6×10^4 sec*

(IIT-JEE, 2008)

SOLUTION. We know $Q = It$. I = 10 milliampere = 10×10^{-3} ampere

So, $Q = 10 \times 10^{-3}$ ampere $\times\ t$ (is seconds). ...(1)

Reaction : $$\underset{2 \times 0.01F = 0.02F}{2H_2O + 2e^-} \longrightarrow H_2 + 2OH^-$$

0.1 mol H_2 is liberated by charge (= 0.02 Faraday),
Q = 0.02 × 96500 C ...(2)

From (1) and (2), we have; $10 \times 10^{-3}\ t = 0.02 \times 96500$ C

$$\therefore \quad t = \frac{0.02 \times 96500\ C}{10 \times 10^{-3} C s^-} = 19.3 \times 10^4\ s$$

(ampere = C s^-)

So, the correct answer is (*b*).

EXAMPLE 181. *If $\lambda°_{H^+} = 349.8$ ohm$^-$ cm^2, $\lambda°_{OH^-} = 198.5$ ohm$^-$ cm^2 and specific conductance (K) of water at 298 K is 5.54×10^{-8} ohm$^-$ cm$^-$, then ionic product (kw) of water is :*

(*a*) *10^{-13}* (*b*) *10^{-10}*
(*c*) *10^{-9}* (*d*) *1.02×10^{-14}*

SOLUTION. We know that

$$\Lambda°_m = \frac{K(\text{in ohm}^- \text{cm}^-) \times 1000\ \text{cm}^3\ \text{L}^-}{\text{Molarity}(\text{in mol L}^-)}$$

So, molarity *i.e.*, $[H^+][OH^-]$

$$= \frac{K(\text{in ohm}^- \text{cm}^-) \times 1000\ \text{cm}^3\ \text{L}^-}{\Lambda°_m(= \lambda°_{H^+} + \lambda°_{OH^-})}$$

$$\therefore \quad \text{Molarity} = \frac{5.54 \times 10^{-8}\ \text{ohm}^- \text{cm}^- \times 1000\ \text{cm}^3\ \text{L}^-}{349.8 + 198.5 = 548.3\ \text{ohm}^- \text{cm}^2}$$
$$= 1.01 \times 10^{-7}\ \text{g ion L}^-$$

$$\therefore \quad K_w = [H^+][OH^-]$$
$$= (1.01 \times 10^{-7}) \times (1.01 \times 10^{-7})$$
$$= 1.02 \times 10^{-14}$$

So, the correct answer is (*d*).

EXAMPLE 182. *Calculate the standard free energy change for the reaction $2Ag + 2H^+ \rightarrow H_2 + 2Ag^+$, given that E° for $Ag^+ + e^- \rightarrow Ag$ is 0.8 V.*

(*a*) *+ 154.4 k J* (*b*) *+ 308.8 k J*
(*c*) *– 154.4 k J* (*d*) *– 308.8 k J*

(ISM Dhanbad, 1994)

SOLUTION. Since E°Ag^+/Ag = + 0.8 V, the value of E°Ag/Ag^+ of the given reaction is –0.8V. But for $2Ag^+ + 2e^- \rightarrow 2Ag$, n = 2. So :

$$\Delta G° = -n E°F,$$
So, $$\Delta G° = -2 \times -0.8\ V \times 96500\ C$$
or $$\Delta G° = 154{,}400\ VC = 154{,}400\ J \quad (\because C\ V = J)$$
$$= 154{,}400\ J \times \frac{k\ J}{1000\ J} = \mathbf{154.4\ k\ J}$$

Hence, the correct answer is (*a*).

EXAMPLE 183. *The emf of a cell involving the following reaction, $2Ag^+ + H_2 \longrightarrow 2\ Ag + 2H^+$ is 0.80 volt. The standard oxidation potential of silver electrode is:*

(*a*) *–0.80 volt* (*b*) *0.80 volt*
(*c*) *0.40 volt* (*d*) *– 0.40 volt*

[AMU (engg, 2011)]

SOLUTION. For the cell reaction, $H_2 \mid 2H^+ \mid\mid 2Ag^+/2Ag$.

$$H_2 \longrightarrow 2H^+ + 2e^- \text{ and}$$
$$Ag^+ + e^- \longrightarrow \text{A. Given, emf.} = 0.8V.$$

Since $E°_{\text{reduction}}$ for Ag^+/Ag is + 0.80 V, the oxidation potential will be –0.80 V. So, the correct answer is (*a*).

EXAMPLE 184. *The e.m.f. of a particular cell is 1.1 volts. If the value of Faraday is 96500 coulombs per mole, the change in free energy in k J. is :*

(*a*) *212.30* (*b*) *–212.30*
(*c*) *106.5* (*d*) *–106.50 (n = 2)*

(Pb CET, 1995)

SOLUTION. n = 2 ; F = 96500 C, E = 1.1 V

We know that : $\Delta G = -n\ F\ E = -2 \times 96500\ C \times 1.1\ V$
$= 212{,}300\ CV = 212{,}300$ J

$$[\because 1\,\text{CV} = 1\,\text{J}]$$

or $\quad \Delta G = (212,300/1000)\ \text{kJ} = \mathbf{212.3\ kJ}$

So, the correct answer is (*a*).

Example 185. *The standard e.m.f. for the cell reaction, $Zn + Cu^{2+} \rightleftharpoons Cu + Zn^{2+}$ is 1.10 V at 25°C. The e.m.f. for the cell reaction, when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used at 25°C is:*

(*a*) 1.10 V (*b*) 0.110V

(*c*) –1.10 V (*d*) – 0.110 V

(MLNR, 1994)

Solution. E° for $Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$ is 1.10 *V*.

The Nernst equation for this reaction is :

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

Since $\quad Zn \rightleftharpoons Zn^{2+} + 2e^-$ is 2 electron change, $n = 2$

$$\therefore \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[Zn^{2+}][Cu(s)]}{[Zn(s)][Cu^{2+}]} \text{ or } \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= 1.10\,V - \frac{0.0591}{2} \log \frac{0.1}{0.1}$$

$$= 1.10\,V - \frac{0.0591}{2} \log 1$$

$$= 1.10\,V - \frac{0.0591}{2} \times 0 = \mathbf{1.10\ V}$$

So, the correct answer is (*a*).

Example 186. *The value of potential of a hydrogen electrode, pH = 10 is :*

(*a*) 0.4 V (*b*) –0.4 V

(*c*) – 0.3V (*d*) – 0.591 V

Solution. $\quad pH = -\log [H^+]\,;\ [H^+] = 10^{-pH} = 10^{-10}$

Since, $\quad H^+ + 1e^- \longrightarrow \frac{1}{2} H_2, \qquad n = 1.$

Using Nernst equation, we have :

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{products}]}{[\text{reactants}]}$$

$$= 0 - \frac{0.0591}{1} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$= -0.0591 \log \frac{1}{[H^+]}$$

$$= -0.0591 \log \frac{1}{10^{-10}}$$

$$= -0.0591 \times [\log 1 - \log 10^{-10}]$$

$$= -0.0591[0 - (-10)]$$

$$= \mathbf{-0.591\ V}$$

So, the correct answer is (*d*).

Example 187. *The E° value at 298 K of $Cl_2(g) + 2\,Br^-(aq) \longrightarrow 2\,Cl^-(aq) + Br_2$ is 0.29 V. The e.m.f. of the cell when $[Cl^-] = [Br_2] = [Br^-] = 0.015$ M and $Cl_2(g)$ is at 1 atmospheric pressure will be:*

(*a*) 0.172 V (*b*) 0.172 V

(*c*) 0.344 V (*d*) – 0.344 V

Solution. For the reaction, $Cl_2\,(g) + 2Br^-\,(aq) \rightarrow 2\,Cl^-\,(aq) + Br_2$, the Nernst equation, will be :

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Cl^-(aq)]^2\,[Br_2]}{[Cl_2(g)]\,[Br^-(aq)]^2}$$

$$\left[\begin{array}{l} Cl_2\,(g) + 2e^- \rightleftharpoons 2\,Cl^-\,(aq) \\ \therefore\ n = 2 \end{array}\right]$$

$$E = 0.29 - \frac{0.0591}{2} \log \frac{(0.015)^2 \times (0.015)}{1 \times (0.015)^2}$$

$$= 0.29 - \frac{0.0591}{2} \log 0.015$$

$$= 0.29 - \frac{0.0591}{2} \times -1.824$$

$$= 0.29 + 0.054 = \mathbf{0.344V}$$

So, the correct answer is (*c*).

Example 188. *The potential of the cell containing two hydrogen electrodes as represented below*

$$Pt\,;\ \tfrac{1}{2}\,H_2(g)\,|\,H^+\,(10^{-8}\,M)\,|\,|\,H^+\,(0.001\,M)\,|\ \tfrac{1}{2}\,H_2(g);\,Pt,$$

is:

(*a*) 0.296 V (*b*) – 0.295 V

(*c*) 0.13 V (*d*) – 0.13 V

Solution. At anode :

$$\frac{1}{2}\,H_2 \longrightarrow H^+\,(10^{-8}\,M) + e^-\,;$$

(n = 1, since electron change = 1)

At Cathode : $\quad H^+\,(0.001\,M) + e^- \longrightarrow \frac{1}{2}\,H_2\,(g)$

Cell reaction : $\quad H^+\,(0.001\,M) \longrightarrow H^+\,(10^{-8}\,M)$

Applying Nernst equation, we have :

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

$$= 0 - \frac{0.0591}{1} \log \frac{10^{-8}}{0.001 \text{ or } 10^{-3}}$$

$$= -0.0591 \log 10^{-8+3}$$

or $\quad E = -0.0591[-5 \log 10 = -5];$

$$E = \mathbf{0.296\ V}$$

So, the correct answer is (*a*).

Example 189. *Consider the following cell reaction $2Fe(s) + O_2(g) + 4\,H^+_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + 2H_2O(l)$; E° = 1.67 V. If $(Fe^{2+}) = 10^{-3}$M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is:*

(*a*) 1.47 V (*b*) 1.77 V

(*c*) 1.87 V (*d*) 1.57 V

(IIT-JEE, 2011)

Solution. (*i*) $Fe(s) \longrightarrow Fe^{2+} + 2e^-] \times 2$ $\quad$ At anode

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $\quad$ At cathode

no. of e^-s involved, $n = 4$

Adding: $2Fe(s) + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2H_2O$

$$\therefore \quad Q = \frac{[Fe^{2+}]^2}{[H^+]^4 \times P_{O_2}} = \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1} = 10^7$$

$$\text{(ii)} \quad E_{cell} = E^\circ - \frac{0.0591}{n} \log Q$$

$$= 1.67 - \frac{0.0591}{4} \log 10^7$$

$$= 1.67 - \frac{0.0591}{4} \times [7 \log 10 = 7]$$

$$= 1.57 \text{ V}$$

So, the correct answer is (*d*).

Example 190. *When 9.65 coulombs of electricity is passed through a solution of silver nitrate (at. mass of Ag = 108 amu), the amount of silver deposited is :*

(*a*) *10.8 mg*	(*b*) *5.4 mg*
(*c*) *16.2 mg*	(*d*) *21.2 mg*

(Karnataka, CET, 2000, BET, 2003)

Solution. 96500 coulomb electricity deposit Ag

= g. eq. wt. of Ag = 108 g

∴ 9.65 coulomb of electricity deposit Ag

$$= \frac{108 \text{ g}}{96500} \times 9.65 = 0.0108 \text{ g}$$

$$= 0.0108 \times 1000 = \mathbf{10.8\ mg}$$

So, the correct answer is (*a*).

Example 191. *1A current is supplied for 30 minutes through NaCl. How much chlorine will be liberated ?*

(*a*) *0.66 gm*	(*b*) *0.66 mol*
(*c*) *0.33 g*	(*d*) *0.33 mol*

(IMS – BHU, 2003)

Solution. Total charge suppplied

= current in ampere × time in seconds

= 1 A × 30 × 60s

= 1800 As = 1800 coulombs

$$NaCl \rightleftharpoons Na^+ + \underset{35.5\text{ g}}{Cl^-}$$

96500 coulombs liberate

Cl_2 = Eq. wt. of Cl_2 = 35.5 g

∴ 1800 coulombs liberate

$$Cl_2 = \frac{35.5 \times 1800}{96500} = \mathbf{0.66\ g}$$

∴ The correct answer is (*a*).

Example 192. *4.5 g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at S.T.P. from H^+ ions in solution by the same quantity of electric charge will be :*

(*a*) *44.8 L*	(*b*) *22.4 L*
(*c*) *11.2 L*	(*d*) *5.6 L*

(CBSE - PMT (Prelims) – 2005)

Solution. Eq. wt. of Al (Valency = 3)

$$= \frac{\text{at. wt.}}{\text{Valency}} = \frac{27}{3} = 9$$

According to Faraday's first law :

1 Faraday charge liberates Al = Eq. wt. of Al = 9

$$\therefore \quad \text{No. of Equilvalent of Al} = \frac{\text{wt. of Al}}{\text{eq. wt. of Al}}$$

$$= \frac{4.5}{9} = 0.5$$

∴ No. of equivalent of H_2 produced = 0.5

But volume occupied by 1 equivalent of

$$H_2 = \frac{22.4 \text{ L}}{2} = 11.2 \text{ L}$$

∴ Volume occupied by 0.5 equivalent of

$$H_2 = (11.2 \times 0.5) \text{ L}$$
$$= 5.6 \text{ L. at STP.}$$

So, the correct answer is (*d*).

Example 193. *100 mL of a neutral solution containing 0.2 g copper was electrolysed till the whole of copper was deposited. The current strength was maintained at 1.2 amperes and the volume of solution was maintained at 100 mL. Assuming 100% current efficiency, the time it would take to deposit copper will be :*

(*a*) *253 sec*	(*b*) *506 sec*
(*c*) *1012 sec*	(*d*) *2024 sec*

(at. wt. of Cu = 63.5)

Solution. Eq.wt. of

$$Cu = \frac{\text{at. wt.}}{\text{Valency}} = \frac{63.5}{2} = 31.75$$

$$Z \text{ for Cu} = \frac{\text{g. eq. wt.}}{96500 \text{ C}} = \frac{31.75 \text{ g}}{96500 \text{ C}}$$

But, $\quad$ wt., $w = Z \times I \times t$

or $\quad t = \dfrac{w}{Z \times I}$

$$= \frac{0.2 \text{ g} \times 96500 \text{ C}}{31.75 \text{ g} \times 1.2 \text{ amp}}; \ \mathbf{506\ seconds}$$

[∵ C = amp. × sec

So, the correct answer is (*b*).

Example 194. *The current strength in amperes that is required to liberate 10 g of iodine from KI solution in 1 hour will be :*

(*a*) *1.05*	(*b*) *2.1*
(*c*) *13.9*	(*d*) *1.12*

(at. wt. of I = 127)

Solution. Eq. wt. of

$$I = \frac{\text{At. wt. of I}}{\text{Valency of I}} = \frac{127}{1} = 127$$

127 g (= 1 g. equivalent of I) of iodine is liberated by

= 96500 C

∴ 10g of iodine is liberated by

$$= \frac{96500 \text{ C}}{127 \text{ g}} \times 10 \ g = Q$$

But Q in coulomb = Current in ampere × time in seconds

where $$t = 1\text{ hr} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ sec}}{1\text{ min}} = 3600\text{ s}$$

$$\therefore \quad \text{Current} = \frac{Q}{\text{time}} = \frac{96500 \times 10}{127}\text{ C} \times \frac{1}{3600\text{s}}$$
$$= \mathbf{2.1\ amp} \qquad [\because \text{C} = \text{amp.} \times \text{sec}]$$

So, the correct answer is (*b*).

EXAMPLE 195. *Tollen's reagent is used for the detection of aldehyde. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed.*

$$2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$$
$$Ag^+ + e^- \longrightarrow Ag\ ;\ E^\circ_{red} = 0.8\ V\ ;$$
$$C_6H_{12}O_6 + H_2O \longrightarrow \text{gluconic acid} + 2H^+ + 2e^-\ ;$$
$$E^\circ_{red} = -0.05\ V$$

Find ln K of this reaction.

(*a*) *66. 13* (*b*) *58.45*
(*c*) *28.30* (*d*) *46.29*

(IIT - JEE, 2006)

SOLUTION. $$\text{Ag}^+ + e^- \longrightarrow \text{Ag(s)}] \times 2\ ;\ E^\circ_{red} = 0.8\ V$$
$$\text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow \text{gluconic acid} + 2\text{H}^+ + 2e^-;$$
$$E^\circ_{red} = -0.05\ V$$

Add :

$$2\ \text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2\text{O} \longrightarrow 2\text{Ag(s)} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+;$$
$$E^\circ = 0.8 - 0.05 = 0.75\ V$$

Here, number of electrons = 2. So, $n = 2$

Using $2.303\dfrac{RT}{F} = 0.0591$, we have $\dfrac{RT}{F} = \dfrac{0.0591}{2.303}$

But $$E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K\ ;\ 0.75 = \frac{0.0591}{2 \times 2.303}\ln K$$

$$\therefore \quad \ln K = \frac{0.75 \times 2 \times 2.303}{0.0591} = \mathbf{58.45}$$

So, the correct answer is (*b*).

EXAMPLE 196. *When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much ?*

(*a*) E°_{oxd} *wil increase by a factor of 0.65 from* E°_{oxd}
(*b*) E°_{oxd} *will decrease by a factor of 0.65 from* E°_{oxd}
(*c*) E°_{red} *wil increase by a factor of 0.65 from* E°_{red}
(*d*) E°_{red} *will decrease by a factor of 0.65 from* E°_{red}

[IIT, JEE 2006]

SOLUTION. Since on the addition of NH_3 to the solution, the pH, 11 is reached, it means the concentration of H^+ should decrease.

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0591}{n}\log(\text{H}^+)$$
$$= 0 - \frac{0.0591}{1}\log 10^{-11}$$
$$= -0.0591 \times -11\log 10$$
$$= -0.0591 \times -11 \times 1 = \mathbf{+0.65}$$

So, the correct answer is (*c*).

EXAMPLE 197. *The reduction potential of hydrogen half cell will be negative if*

(*a*) *$p(H_2)$ = 1 atm and $[H^+]$ = 2.0 M*
(*b*) *$p(H_2)$ = 1 atm and $[H^+]$ = 1.0 M*
(*c*) *$p(H_2)$ = 2 atm and $[H^+]$ = 1.0 M*
(*d*) *$p(H_2)$ = 2 atm and $[H^+]$ = 2.0 M*

(AIEEE, 2010)

SOLUTION. $2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$

$$E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0591}{n}\log\frac{\text{pH}_2}{[\text{H}^+]^2}$$

where n = no. of electrons involved

$$E_{\text{red}} = 0 - \frac{0.0591}{2}\log\frac{2}{(1)^2} \qquad \ldots(1)$$

From equation (1), it is clear that E_{red} will be negative only if $\text{pH}_2 > [\text{H}^+]$. So, the correct answer is (*c*).

EXAMPLE 198. *The equivalent conductance at infinite dilution of HCl and NaCl are 426.15 and 126.15 mho cm^2 g eq^- respectively. It can be said that the mobility of*

(*a*) *H^+ ions is much more than that of Cl^- ions.*
(*b*) *Cl^- ions is much more than that of H^+ ions.*
(*c*) *H^+ ions is much more than that of Na^+ ions.*
(*d*) *Na^+ ions is much more than that of H^+ ions.*

(Gujrat CET, 2006)

SOLUTION. We know that ionic conductances (λ) are proportional to the ionic mobilities (μ) of the ions. At infinite dilution:

$$\lambda c = k\,\mu c\ ;\ \lambda a = k\,\mu a$$

where λc and λa are the ionic conductances of cations and anions respectively. Value of k = 1 Faraday. μc and μa are the ionic mobilities of cations and anions respectively. Thus higher the value of λ, higher will be the value of μ. So, the correct answer is (*c*).

EXAMPLE 199. *The molar conductivities Λ°_{NaOAC} and Λ°_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 S cm^2/mol respectively. To calculate Λ°_{HOAC}, the additional value required is :*

(*a*) $\Lambda^\circ_{H_2O}$ (*b*) Λ°_{KCl}
(*c*) Λ°_{NaOH} (*d*) Λ°_{NaCl}

(AIEEE, 2006)

SOLUTION. $\text{CH}_3\text{COONa} + \text{HCl} \longrightarrow \text{NaCl} + \text{CH}_3\text{COOH}$

From this reaction, we find that :

$$\Lambda^\circ_{\text{CH}_3\text{COONa}} + \Lambda^\circ_{\text{HCl}} \longrightarrow \Lambda^\circ_{\text{NaCl}} + \Lambda^\circ_{\text{CH}_3\text{COOH}} \text{ or } \Lambda^\circ_{\text{HOAC}}$$

So, to calculate $\Lambda^\circ_{\text{HOAC}}$, we need $\Lambda^\circ_{\text{NaCl}}$ because $\Lambda^\circ_{\text{CH}_3\text{COONa}}$ and $\Lambda^\circ_{\text{HCl}}$ are given. So, the correct answer is (*d*).

EXAMPLE 200. *The limiting molar conductivities of HCl, CH_3COONa and NaCl are respectively 425, 90 and 125 mho cm^2 mol^- at 25°C. The molar conductivity of 0.1M CH_3COOH solution is 7.8 mho cm^2 mol^- at the same temperature. The degree of dissociation of 0.1 M acetic acid solution at the same temperature is:*

(*a*) 0.10 (*b*) 0.02

(*c*) 0.15 (*d*) 0.03

(*e*) 0.20 **(Kerala PET, 2011)**

Solution. We know that:

$$\Lambda^\circ_{(CH_3COOH)} = \lambda^\circ_{Na^+} + \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-}$$
$$= \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+} \cdots\cdots\cdots \quad (1)$$

Substituting the values in equation (1), we get:

$$\Lambda^\circ_{(CH_3COOH)} = 90 + 425 - 125$$
$$= 390 \text{ mho cm}^2 \text{ mol}^-$$

∴ Degree of dissociation,

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{7.8}{390} = 0.02$$

So, the correct answer is (*b*).

Example 201. *Given the data at 25°C*

$$Ag + I^- \longrightarrow AgI + e^- \ ; \quad E^\circ = 0.152 \text{ V}$$
$$Ag \longrightarrow Ag^+ + e^- \ ; \quad E^\circ = -0.800 \text{ V}$$

What is the value of $\log K_{sp}$ *for* AgI? $\left[2.303\frac{RT}{F} = 0.059V\right]$

(*a*) − 8.12 (*b*) + 8.612

(*c*) − 37.83 (*d*) − 16.11

(AIEEE, 2006)

Solution. $AgI(s) + e^- \longrightarrow Ag(s) + I^-\ ;\ E^\circ = -0.152 \text{ V}$

$$Ag(s) \longrightarrow Ag^+ + e^-\ ;\ E^\circ = -0.8 \text{ V}$$

Add : $AgI(s) \longrightarrow Ag^+ + I^-\ ;\ E^\circ = -0.952 \text{ V}$

But $E^\circ_{cell} = \frac{0.0591}{n}\log K_{sp}$

So, $-0.952 = \frac{0.0591}{1}\log K_{sp}$

∴ $\log K_{sp} = -\frac{0.952}{0.0591} = \mathbf{-16.11}$

So, the correct answer is (*d*).

Example 202. *Resistivity of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m⁻. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of the electrolyte will be:*

(*a*) 124×10^{-2} S m² mol⁻ (*b*) 1240×10^{-4} S m² mol⁻

(*c*) 1.24×10^{-4} S m² mol⁻ (*d*) 12.4×10^{-4} S m² mol

(AIEEE, 2006)

Solution. Conductivity,

$$K = \frac{1}{R}\left(\frac{l}{a}\right);$$
$$1.29 = \frac{1}{100}\left(\frac{l}{a}\right)$$

∴ $\frac{l}{a} = 1.29 \times 100 = 129 \text{ m}^-$

Also, $K = \frac{1}{R}\left(\frac{l}{a}\right) = \frac{1}{520} \times 129$

$R = 520\Omega$ for 0.2 M, C = 0.02 M

∴ $\Lambda_m = K \times \frac{1000}{\text{Molarity}}$

$$= \frac{1 \times 129}{520} \times \frac{1000}{0.02} \times 10^{-6} \text{ m}^3$$
$$= \mathbf{124 \times 10^{-2} \text{ S m}^2 \text{ mol}^-}.$$

So, the correct answer is (*a*).

EXAMPLE 203. *The molar conductivities at infinite dilution (*Λ°_m*) for* $Ba(OH)_2$ *= 457.6 Ω⁻cm² mol⁻;* $BaCl_2$ *= 240.6 Ω⁻ cm² mol⁻ and* NH_4Cl *= 129.8 Ω⁻cm² mol⁻. The* Λ°_m *value for* NH_4OH *is Ω⁻cm² mol⁻ will be :*

(*a*) 828 (*b*) 417

(*c*) 238.3 (*d*) 303.2

Solution. $\Lambda^\circ_m\ Ba(OH)_2 = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ(OH^-);$

457.6 Ω⁻ cm² mol⁻ ...(*i*)

$\Lambda^\circ_m\ BaCl_2 = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ\ Cl^-;$

240.6 Ω⁻ cm² mol⁻ ...(*ii*)

$\Lambda^\circ_m\ NH_4Cl = \lambda^\circ_{NH_4^+} + \lambda^\circ\ Cl^-;$

129.8 Ω⁻ cm² mol⁻ ...(*iii*)

$\Lambda^\circ_m\ NH_4OH = \lambda^\circ_{NH_4^+} + \lambda^\circ\ (OH^-)$ ...(*iv*)

In order to get equation (*iv*), we have :

$$\Lambda^\circ_m\ NH_4OH = \left[\frac{1}{2}\times\text{equation } (i)\right] - \frac{1}{2}$$

[equation (*ii*)] + Equation (*iii*)

$$= \left[\frac{1}{2}\overset{\circ}{\lambda}_{Ba^{2+}} + \frac{1}{2}\times 2\,\overset{\circ}{\lambda}_{OH^-}\ ;\ \frac{1}{2}\times 457.6\ \Omega^-\text{cm}^2\text{ mol}^-\right]$$
$$-\frac{1}{2}\overset{\circ}{\lambda}_{Ba^{2+}} - \frac{1}{2}\times 2\overset{\circ}{\lambda}_{Cl^-}\ ;\ -\frac{1}{2}\times 240.6\ \Omega^-\text{cm}^2\text{ mol}^-\Big]$$
$$+\left[\overset{\circ}{\lambda}_{NH_4^+} + \overset{\circ}{\lambda}_{Cl^-}\ ;\ +129.8\ \Omega^-\text{cm}^2\text{ mol}^-\right]$$
$$= \overset{\circ}{\lambda}_{NH_4^+} + \overset{\circ}{\lambda}_{OH^-}\ ;$$

(228.8 – 120.3 + 129.8 = 238.3 Ω⁻ cm² mol⁻)

∴ $\overset{\circ}{\Lambda}_m(NH_4OH) = 238.3\ \Omega^-\text{ cm}^2\text{ mol}^-$

So, the correct answer is (*c*).

Example 204. *The conductivity of a saturated solution of AgCl at 288 K is found to be* 1.382×10^{-6} *ohm⁻ cm⁻. If ionic conductances of* Ag^+ *and* Cl^- *ions at infinite dilution are 61.9 ohm⁻ cm² mol⁻ and 76.3 ohm⁻ cm² mol⁻ respectively, then its solubility in g L⁻ will be :*

(*a*) 0.7×10^{-3} (*b*) 1.435×10^{-3}

(*c*) $0.7 \times 10^{+3}$ (*d*) 2.87×10^{-6}

(molar mass of AgCl = 143.5 g mol⁻)

Solution.

$$\Lambda^\circ_m(AgCl) = \lambda^\circ_{Ag^+} + \lambda^\circ_{Cl^-} = 61.9 + 76.3$$
$$= 138.2 \text{ ohm}^- \text{ cm}^2 \text{ mol}^-$$

$$\text{Solubility} = \frac{K(\text{in ohm}^-\text{cm}^-) \times 1000 \text{ cm}^3 \text{ L}^-}{\overset{\circ}{\Lambda}_m(\text{in ohm}^-\text{cm}^2\text{mol L}^-)}$$

$$= \frac{1.382 \times 10^{-6}\text{ohm}^-\text{cm}^- \times 1000 \text{ cm}^3 \text{ L}^-}{138.2 \text{ ohm}^-\text{cm}^2\text{mol}^-.\text{ mol L}^-}$$

$= 10^{-5}\ \text{mol}^-$

$= 10^{-5} \times 143.5\ \text{g}\ L^- = 1.435 \times 10^{-3}\text{g}\ L^-$

So, the correct answer is (*b*).

Example 205. *Out of Na^+, K^+, H^+ and Li^+ cations, the one with highest ionic mobility and another with lowest ionic mobility respectively are :*

(*a*) H^+, K^+
(*b*) H^+, Li^+
(*c*) Li^+, Na^+
(*d*) H^+, K^+

Solution. According to Grothus mechanism, H^+ cation has the maximum ionic mobility. On the other hand, Li^+ has the maximum charge density. So, it is most hydrated ion among all the given cations. So, Li^+ cation has the least ionic mobility. So, the true answer is (*b*)

Example 206. *Specific conductance has the unit*

(*a*) *Ohm⁻ cm*
(*b*) *Ohm⁻cm²*
(*c*) *Ohm⁻ cm⁻*
(*d*) *Ohm cm.*

Solution. Specific conductance

$$= \text{Observed conductance} \times \frac{l}{a}$$

$$= \text{Ohm}^- \times \frac{\text{cm}}{\text{cm}^2} = \mathbf{Ohm^-\ cm^-}$$

So, the correct answer is (*c*).

Example 207. *Specific conductance of 0.01 M NaCl solution is p ohm⁻ cm⁻. When conductivity cell is filled with the above solution, the observed conductance is q ohm⁻. When the same cell is filled with 0.01 M H_2SO_4, the observed conductance was r ohm⁻ cm⁻. So, the specific conductance of 0.01 M H_2SO_4 is :*

(*a*) pq
(*b*) qr
(*c*) $\frac{r}{pq}$
(*d*) $\frac{pr}{q}$

Solution. Specific conductance of 0.01 MH_2SO_4

$$= \text{Observed conductance} \times \text{cell constant} \qquad \text{... (1)}$$

$$\text{But Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

$$= \frac{p}{q}\ \text{cm}^- \qquad \text{...(2)}$$

Substituting the value of cell constant from (2) in (1), we get ;

Specific conductance of 0.01 MH_2SO_4

$$= r\ \text{ohm}^- \times \frac{p}{q}\ \text{cm}^- = \frac{rp}{q}\ \text{ohm}^-\ \text{cm}^-$$

Hence, the true answer is (*d*).

Example 208. *The value of equivalent conductance of 1M CH_3COOH is 12 ohm⁻ cm² (equiv)⁻ and that at infinite dilution is 240 ohm⁻ cm² (equiv)⁻. The percent ionisation of CH_3COOH will be :*

(*a*) 2
(*b*) 3
(*c*) 4
(*d*) 5.

Solution. We know that : Percent ionisation,

$$\mu = \frac{\Lambda_c}{\Lambda_\infty} \times 100 = \frac{12}{240} \times 100 = \mathbf{5}$$

So, the true answer is (*d*).

Example 209. *Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values.*

$I_2 + 2e^- \longrightarrow 2I^-, E° = 0.54;\ Cl_2 + 2e^- \longrightarrow 2Cl^-, E° = 1.36;$
$Mn^{3+} + e^- \longrightarrow Mn^{2+}, E° = 1.50;\ Fe^{3+} + e^- \longrightarrow Fe^{2+}, E° = 0.77;$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O, E° = 1.23V$$

Using above data, among the following, identify the correct statement.

(*a*) *Chloride ion is oxidised by O_2*
(*b*) *Fe^{2+} is oxidised by iodine*
(*c*) *Iodide ion is oxidised by chlorine*
(*d*) *Mn^{2+} is oxidised by chlorine.* **(IIT-JEE, 2007)**

Solution.

$$\begin{array}{lrcll}
(a) & O_2 + 4H^+ + 4e^- & \longrightarrow & 2H_2O; & E° = 1.23\ V \\
\textbf{Add:} & 2Cl^- & \longrightarrow & Cl_2 + 2e^-] \times 2; & E° = -1.36\ V \\
\hline
 & O_2 + 4Cl^- + 4H^+ & \longrightarrow & 2H_2O + 2Cl_2; & E° = -0.13\ V
\end{array}$$

Since E° is negative, reaction is not feasible.

$$\begin{array}{lrcll}
(b) & Fe^{2+} & \longrightarrow & Fe^{3+} + 1e^-] \times 2; & E° = -0.77\ V \\
\textbf{Add:} & I_2 + 2e^- & \longrightarrow & 2I^-; & E° = +0.54\ V \\
\hline
 & 2Fe^{2+} + I_2 & \longrightarrow & 2Fe^{3+} + 2I^-; & E° = -0.23\ V
\end{array}$$

Since E° is negative, reaction is not feasible.

$$\begin{array}{lrcll}
(c) & Cl_2 + 2e^- & \longrightarrow & 2Cl^-; & E° = 1.36\ V \\
 & I_2 + 2e^- & \longrightarrow & 2I^-; & E° = 0.54\ V \\
\textbf{Subtract:} & - \quad - & & - & - \\
\hline
 & Cl_2 + 2I^- & \longrightarrow & 2Cl^- + I_2; & E° = +0.82\ V
\end{array}$$

Since E° is positive, reaction is feasible.

$$\begin{array}{lrcll}
(d) & Mn^{2+} & \longrightarrow & Mn^{3+} + 1e^-] \times 2; & E° = -1.50\ V \\
\textbf{Add:} & Cl_2 + 2e^- & \longrightarrow & 2Cl^-; & E° = +1.36\ V \\
\hline
 & 2Mn^{2+} + 2Cl_2 & \longrightarrow & 2Mn^{3+} + 2Cl^-; & E° = -0.14\ V
\end{array}$$

Since E° is negative, the reaction is not feasible.

Hence, the correct answer is (*c*).

Example 210. *Using E° data given in example 209, while Fe^{3+} is stable, Mn^{3+} is not stable in acidic solution because*

(*a*) *O_2 oxidises Mn^{2+} to Mn^{3+}*
(*b*) *O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}*
(*c*) *Fe^{3+} oxidises H_2O to O_2*
(*d*) *Mn^{3+} oxidises H_2O to O_2.* **(IIT-JEE, 2007)**

Solution.

$$\begin{array}{lrcll}
(a) & O_2 + 4H^+ + 4e^- & \longrightarrow & 2H_2O; & E° = 1.23\ V \\
\textbf{Add:} & Mn^{2+} & \longrightarrow & Mn^{3+} + e^-] \times 4; & E° = -1.50\ V \\
\hline
 & O_2 + 4Mn^{2+} + 4H^+ & \longrightarrow & 2H_2O + 4Mn^{3+}; & E° = -0.27\ V
\end{array}$$

Since E° is negative, the reaction is not feasible.

$$\begin{array}{lrcll}
(b) & O_2 + 4H^+ + 4e^- & \longrightarrow & 2H_2O; & E° = 1.23\ V \\
\textbf{Add:} & Fe^{2+} & \longrightarrow & Fe^{3+} + 1e^-] \times 4; & E° = -0.77\ V \\
\hline
 & O_2 + 4Fe^{2+} + 4H^+ & \longrightarrow & 2H_2O + 4Fe^{3+}; & E° = +0.46\ V
\end{array}$$

Since E° is positive, this reaction is feasible. But O_2 does not oxidise Mn^{2+} to Mn^{3+} [See (*a*) above].

$$\begin{array}{lrcll}
(c) & Fe^{3+} + 1e^- & \longrightarrow & Fe^{2+}] \times 4; & E° = +0.77\ V
\end{array}$$

$$\begin{array}{lrl} \textbf{Add:} & 2H_2O & \longrightarrow O_2 + 4H^+ + 4e^-; E^\circ = -1.23\ V \\ \hline & 4Fe^{3+} + 2H_2O & \longrightarrow 4Fe^{2+} + O_2 + 4H^+; \\ & & \qquad E^\circ = -0.46\ V \end{array}$$

Since E° is negative, the reaction is not feasible.

$$\begin{array}{lrl} (d) & Mn^{3+} + e^- & \longrightarrow Mn^{2+}] \times 4; \quad E^\circ = 1.50\ V \\ \textbf{Add:} & 2H_2O & \longrightarrow O_2 + 4H^+ + 4e^-; E^\circ = -1.23\ V \\ \hline & 4Mn^{3+} + 2H_2O & \longrightarrow 4Mn^{2+} + O_2 + 4H^+; \\ & & \qquad E^\circ = +\ 0.27\ V \end{array}$$

Since E° is positive, the reaction is feasible. Hence, the correct answer is (*d*).

EXAMPLE 211. *A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes (at. mass : Na = 23; Hg = 200; 1 Faraday = 96500 coulombs)*

(*i*) *The total number of moles of chlorine gas evolved is :*

(*a*) *0.5* (*b*) *1.0*

(*c*) *2.0* (*d*) *3.0*

(*ii*) *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*

(*iii*) *The total charge (coulombs) required for complete electrolysis is :*

(*a*) *24125* (*b*) *48250*

(*c*) *96500* (*d*) *193000*

(IIT-JEE, 2007)

SOLUTION. (*i*) NaCl = 4 mol. L⁻. Thus : 1000 mL solution contain NaCl = 4 mol

$$\therefore \text{ 500 mL solution contain NaCl} = \frac{4}{1000} \times 500 = 2 \text{ mol}$$

$$\begin{array}{lccc} & NaCl & \rightleftharpoons Na^+ & + Cl^- \\ \text{No. of mol} & 2 & 2 & 2 \end{array}$$

$$\therefore \text{no. of mol of } Cl_2 \text{ gas formed} = 1 \left[\begin{array}{lcr} \because 2NaCl & \equiv & Cl_2 \\ 2\text{ mol} & & 1\text{ mol} \end{array}\right]$$

So, the correct answer is (*b*).

(*ii*) From (*i*) above, we see that, no. of mol of Na⁺ = 2.

$$\begin{array}{lccc} \text{Also} & 2NaCl \equiv 2\,Na & & \\ \text{and} & Na\ +\ Hg & \rightleftharpoons & Na/Hg\ (\text{amalgam}) \\ \text{no. of mol} & 2 \qquad 2 & & 2 \\ \text{Maximum wt.} & 2\times23 \quad 2\times200 & & (2\times23) + (2\times200) \\ \text{of Na/Hg} & = 46\text{ g} \quad = 400\text{ g} & & = 446\text{ g} \end{array}$$

∴ The correct answer is (*d*).

$$\begin{array}{lccc} (iii) & Na^+ + e^- & \rightleftharpoons & Na \\ \text{no. of mol} & 2 \qquad 2 & & 2 \end{array}$$

[See part (*i*) above]

∴ Total charge required = 2 Faraday

[∵ no. of electrons required = 2 mol]

= 2 × 96500 coulomb

= 193000 coulomb.

∴ The correct answer is (*d*).

EXAMPLE 212. *The current is passed through two cells connected in series. The first cell contains $X(NO_3)_3 .X(aq)$ and the second cell contains $Y(NO_3)_2$ (aq). The relative atomic masses of X and Y are in the ratio 1 : 2. What is the ratio of the liberated mass of X to that of Y?*

(a) 3 : 2 *(b) 1 : 2* *(c) 1 : 3* *(d) 3 : 1*

(e) 2 : 1 **(Kerala PMT, 2011)**

SOLUTION. In $X(NO_3)_3$ (aq), oxidation state of X = + 3. In Y $(NO_3)_2$ (*aq*), the oxidation state of Y = + 2. The ratio of given atomic masses is 1 : 2. Hence, the ratio of equivalent masses is $\frac{1}{3} : \frac{2}{2}$ or $\frac{1}{3}$: 1 or 1 : 3. So, the correct answer is (*c*).

EXAMPLE 213. *Consider two half-cells based on the reaction, $Ag^+_{(aq)} + e^- \longrightarrow Ag(s)$*

The left half-cell contain Ag⁺ ions at unit concentration, and the right half-cell initially had the same concentration of Ag⁺ ions, but just enough NaCl(aq) had been added to completely precipitate the Ag⁺(aq) as AgCl. If the emf of the cell is 0.29 V, then $\log_{10} K_p$ would have been:

(*a*) *9.804* (*b*) *–9.804*

(*c*) *–4.907* (*d*) *10.004*

(AMU (medical), 2012)

SOLUTION. We know that:

Electrode potential is :

$$E_{Cl^-/AgCl/Ag} = E^\circ_{Cl^-/AgCl/Ag} + \frac{0.0591}{1}\log\frac{1}{[Cl^-]}$$

$$E_{Cl^-/AgCl/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.0591}{1}\log K_{sp}/AgCl;$$

$$0.29 = 0 + \frac{0.0591}{1}\log K_{sp/AgCl}$$

$$\therefore \log K_{sp}\,(AgCl) = \frac{-0.29}{0.0591} = -\,4.907.$$

So, the correct answer is (*c*).

EXAMPLE 214. *Consider the cell,*

$Pt/H_2(g, 1\ atm) \mid H^+_{(aq)}, 1\ M) \mid\mid Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \mid Pt_{(s)}$

Given that $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771V$, the ratio of concentration of $Fe^{2+}_{(aq)}$ to $Fe^{3+}_{(aq)}$ is, when the cell potential is 0.830 V.

(*a*) *0.101* (*b*) *0.924*

(*c*) *0.120* (*d*) *none of these*

(AMU (medical), 2012)

SOLUTION. We know that for oxidation-reduction in half-cell:

Pt/Fe²⁺, Fe³⁺, the half-cell is, $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$

$$\therefore\ E_{Fe^{3+}/Fe^{2+}} = E^\circ_{Fe^{3+}/Fe^{2+}} - \frac{0.0591}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$0.83 = 0.771 - \frac{0.0591}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]};$$

$$-\frac{0.0591}{0.0591} = \log\frac{[Fe^{2+}]}{[Fe^{3+}]}; -1 = \log\frac{[Fe^{2+}]}{[Fe^{3+}]}; \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= \text{antilog} - 1 = 0.1$$

So, the correct answer is (*a*).

EXAMPLE 215. *In the button cell, widely used in watches, the following reaction takes place.*

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}.$$

Determine E° and ΔG° for the reaction.

(Given $E^\circ_{Ag^+/Ag} = +0.80\ V; E^\circ_{Zn^{2+}/Zn} = -0.76V$ *)*

(CBSE, 2012)

SOLUTION. Given: $E^\circ_{Ag^+/Ag} = +0.80$ V;

$E^\circ_{Zn^{2+}/Zn} = -0.76$V.

But $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.80 - (-0.76) = 1.56\ V$

Also, $\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.56$

$[\because Zn^{2+} + 2e^- \longrightarrow Zn$; For $2e^-$ s, $n = 2]$

$= -301080$ J mol$^-$

$= -301.08$ kJ mol$^-$ **Ans.**

EXAMPLE 216. *The conductance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146 × 10*$^{-3}$*S cm*$^-$ *?* **(CBSE, 2012)**

SOLUTION. Given conductivity, $K = 0.146 \times 10^{-3}$ S cm$^-$

Resistance, $R = 1500$ ohm. But:

$$\text{Cell constant} = \frac{\text{Conductivity }(K)}{\text{Conductance }(G)}$$

= Conductivity (K) × Resistance, R

$\therefore$ Cell constant $= 0.146 \times 10^{-3}$ S cm$^-$ × 1500 ohm

$= 0.219$ cm$^-$ **Ans.** $(\because S = \text{ohm}^-)$

EXAMPLE 217. *A weak electrolyte having the limiting equivalent conductance of 400 S cm*^{2} *g. equivalent at 298 K is 2% ionised in its 0.1 N solution. The resistance of this solution (in ohms) in an electrolytic cell of cell constant 0.4 cm*$^{-1}$ *at this temperature is:*

(a) *200* *(b)* *300*

(c) *400* *(d)* *500*

(e) *600* **(Kerala PET, 2012)**

SOLUTION. Degree of ionisation,

$\alpha = \frac{2}{100}$; $\Lambda_\infty = 400\ S\ \text{cm}^2 g\ eq^-$

But $\alpha = \frac{\Lambda_m}{\Lambda_\infty}$. So, $\Lambda_m = \alpha \times \Lambda_\infty = \frac{2}{100} \times 400 = 8$

$$\text{Also, } \Lambda_m = \frac{K \times 1000}{\text{Normality}} = \frac{1}{R} \times \frac{\text{Cell constant} \times 1000}{\text{Normality}}$$

$$\left[\because K = \frac{1}{R} \times \text{cell constant}\right]$$

$$\therefore R = \frac{\text{cell constant} \times 1000}{\Lambda_m \times \text{normality}} = \frac{0.4 \times 1000}{8 \times 0.1} = 500 \text{ ohm.}$$

So, the correct answer is (*d*).

EXAMPLE 218. *The solubility product (*K_{sp}*; mol*^{3} *dm*$^{-9}$*) of* MX_2 *at 298K based on the information available for the given concentration cell (*$[M^{2+}] = 0.001$*) is : (take 2.303 × R × 198/F = 0.059 V)*

(a) 1×10^{-15} *(b)* 4×10^{-15}

(c) 1×10^{-12} *(d)* 4×10^{-12}

(IIT-JEE, 2012)

SOLUTION. $MX_2 - 2e^- \rightleftharpoons M^{2+} + 2X^-; C_1 = ?, C_2 = 0.001$
0.001 M

$$\text{But } E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1}; 0.059 = \frac{0.0591}{2}\log\frac{0.001}{C_1}$$

$\therefore \log\frac{0.001}{C_1} = \frac{2 \times 0.059}{0.0591} = 2.$ Taking antilog of both sides,

we get:

$$\frac{0.001}{C_1} = \text{antilog } 2 = 100; \therefore C_1 = \frac{0.001}{100} = 10^{-5}$$

$$\underset{\text{Solubility}}{MX_2} \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$$

$\therefore K_{sp} = [M^{2+}][X^-]^2 = S \times (2S)^2 = 4S^3 = 4 \times (10^{-5})^3$

$= 4 \times 10^{-15}$ mol^3 dm^{-9}

So, the correct answer is (*b*).

EXAMPLE 219. *The conductivity of 0.2 M KCl solution is 3 × 10*$^{-2}$ *ohm*$^-$ *cm*$^-$*. Calculate the molar conductance.*

(ISC, 2012)

SOLUTION. Conductivity, $K = 3 \times 10^{-2}$ ohm$^-$ cm$^-$

Molarity = 0.2 mol L$^-$

Λ_m = Molar conductance = ?

$$\text{We know } \Lambda_m = \frac{K \times \frac{1000\text{ cm}^3}{L}}{\text{Molarity}}$$

$$= \frac{3 \times 10^{-2}\text{ ohm}^-\text{cm}^- \times 1000\text{ cm}^3}{0.2\text{ mol L}^- \times \text{L}} = 150\text{ ohm}^-\text{cm}^-\text{mol}^-$$

Ans.

EXAMPLE 220. *The value of ΔG (kJ mol*$^-$*) for the given cell is (take 1F = 96500 C mol*$^-$*,* $M - 2e^- \rightarrow M^{2+}$*)*

(a) *– 5.7* *(b)* *5.7*

(c) *11.4* *(d)* *–11.4*

(IIT-JEE, 2012)

SOLUTION. In $M - 2e^- \longrightarrow M^{2+}$, $n = 2$ due to 2 electron change.

But $\Delta G = -nFE$. Substituting the value, we get:

$\Delta G = -2 \times 96500 \times 0.059 = -11387$ J mol$^-$ = –11.387 kJ mol$^-$

≃ – 11.4 kJ mol$^-$. So the correct answer is (*d*).

EXAMPLE 221. *On passing C amperes of current for time, t sec through one litre of 2 M* $CuSO_4$ *solution (at. wt of Cu = 63.5), the amount (m) of Cu (in g) deposited on cathode will be:*

(a) $m = \frac{Ct}{63.5 \times 96500}$ *(b)* $m = \frac{Ct}{31.25 \times 96500}$

(c) $m = \frac{Ct}{31.25 \times t}$ *(d)* $m = \frac{31.75 \times C \times t}{96500}$

(W.B. JEE, 2012)

Solution. We know, $m = ZCt$ (Faraday's law) ...(1)

Where Z = Eq. wt. of metal/96500.

Eq. wt. of Cu = At. wt./Valency = 63.5/2 = 31.75

$\therefore Z = \dfrac{31.75}{96500}$. Substituting the value in equation (1),

We get:

$m = \dfrac{31.75}{96500} \times C \times t$. So, the correct answer is (*d*).

Example 222. *Given that the standard reduction potential for M⁺/M and N⁺/N electrodes at 298 K are 0.52 V and 0.25 V respectively. Which of the following is correct in respect of the following electrochemical cell?*

$M/M^+ \,||\, N^+/N$

(*a*) *The overall cell reaction is a spontaneous reaction*

(*b*) *The standard emf of the cell is – 0.27 V*

(*c*) *The standard emf of the cell is + 0.77V*

(*d*) *The standard emf of the cell is – 0.77 V*

(*e*) *The standard emf of the cell is + 0.27 V*

(Kerala PET, 2012)

Solution. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

$= E^\circ_{\text{Right}} - E^\circ_{\text{Left}}$

$= 0.25 - 0.52 = -0.27\ V$. So, the correct answer is (*b*).

Example 223. *The quantity of electricity required to deposit 1.15g of sodium from molten NaCl (Na = 23, Cl = 35.5) is:*

(*a*)	*1F*	(*b*)	*0.5F*
(*c*)	*0.05F*	(*d*)	*1.5F*

(ISC, 2012)

Solution. NaCl (molten) $\rightleftharpoons Na^+ + Cl^-$

At cathode: $\underset{1F}{Na^+ + e^-} \longrightarrow \underset{23g}{Na}$

To deposit 23 g Na, quantity of electricity needed = 1 F

To deposit 1.15 g Na, quantity of electricity needed $= \dfrac{1F}{23\,g} \times 1.15\,g = 0.05\,F$

So, the correct answer is (*c*).

Example 224. *In a plot of log K vs 1/T, the slope is:*

(*a*)	$-E_a/2.303$	(*b*)	$E_a/2.303R$
(*c*)	$E_a/2.303$	(*d*)	$-E_a/2.303R$

(ISC, 2012)

Solution. According to Arrhenius law:

$\log k = \log A - \dfrac{E_a}{2.303\,R} \times \dfrac{1}{T}$

So, the correct answer is (*d*).

Example 225. *From the following data at 25°C,*

(i) $Cr^{3+}_{(aq)} + e^- \longrightarrow Cr^{2+}_{(aq)}\,;\ E^\circ = -0.424V$

(ii) $Cr^{2+}_{(aq)} + 2e^- \longrightarrow Cr\ (s)\ ;\ E^\circ = -0.90\ V$

Find E° at 25°C for the reaction, $Cr^{3+} + 3e^- \longrightarrow Cr(s)$ ...(1)

(*a*)	*– 0.741V*	(*b*)	*–1.324V*
(*c*)	*–0.476V*	(*d*)	*+ 0.741V*

(AMU. Engg., 2012)

Solution. $Cr^{3+}_{(aq)} + e^- \longrightarrow Cr^{2+}_{(aq)}\ ;\ -1 \times F \times -0.424 = +0.424\ F$ ...(*i*)

$Cr^{2+}_{(aq)} + 2e^- \longrightarrow Cr(s)\ ;\ -2 \times F \times -0.90 = +1.8\ F$ ...(*ii*)

Adding equations (*i*) and (*ii*), we get:

$$Cr^{3+} + 3e^- \longrightarrow Cr(s); E^\circ = -\left[\frac{0.424\,F + 1.84F}{(1+2)F}\right] = 0.741\,V$$

So, the correct answer is (*a*).

Example 226. *The approximate time duration in hours to electroplate 30 g of calcium from molten calcium chloride using a current of 5 amp. is:*

(*a*)	*8*	(*b*)	*80*
(*c*)	*10*	(*d*)	*16*

(Karnataka, CET 2012)

Solution. We know: $W = ZCt$ ...(1)

Where W = wt. of Ca deposited = 30 g; Z = Electrochemical equivalent, C = current in amperes and t = time in seconds. Here:

Z = Eq. wt. of Ca/96500 coulomb = 20/96500. Substituting the values in equation (1), we get:

$$30 = \frac{40}{96500} \times 5 \times t;\ t = \frac{30 \times 96500}{40 \times 5}\ \text{seconds}$$

$$= \frac{30 \times 96500}{20 \times 5 \times 60 \times 60}\ \text{hr.}$$

Or $t = 8.04 \simeq 8$ hours. So, the correct answer is (*a*).

Example 227. *Molar conductivities* (Λ°_m) *at infinite dilution of NaCl, HCl and* CH_3COONa *are 126.4, 425.9 and 91.0 Scm² mol⁻ respectively.* (Λ°_m) *for* CH_3COOH *will be:*

(*a*)	*425.5 S cm² mol⁻*	(*b*)	*180.5 S cm² mol⁻*
(*c*)	*290.8 S cm² mol⁻*	(*d*)	*390.5 S cm² mol⁻*

(AIPMT, Mains, 2012)

Solution. Given : $\Lambda^\circ_{NaCl} = 126.4\ S\ cm^2\ mol^-$; $\Lambda^\circ_{HCl} = 425.9\ S\ cm^2\ mol^-$; $\Lambda^\circ_{CH_3COONa} = 91.0\ S\ cm^2\ mol^-$. Thus:

$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{HCl} + \Lambda^\circ_{CH_3COONa} - \Lambda^\circ_{NaCl}$

$= 425.9 + 91.0 - 126.4 = 390.5\ S\ cm^2\ mol^-$.

So, the correct answer is (*d*).

Example 228. *A current strength of 3.86 amp. was passed through molten calcium oxide for 41 minutes and 40 seconds. The mass of calcium in grams deposited at the cathode is (atomic mass of Ca is 40g/mol, 1F = 96500 C).*

(*a*)	*4*	(*b*)	*2*
(*c*)	*6*	(*d*)	*8*
(*e*)	*1*		

(Kerala, PMT, 2012)

Solution. Current, $I = 3.86$ amp; $t = 41$ min. 40 sec. = (41 × 60) + 40 = 2500 seconds, eq. wt. of Ca = At. wt./valency = 40/2 = 20

$\therefore$ Z = Eq. wt./96500 = 20/96500. But:

Mass deposited = ZIt = $\frac{20}{96500} \times 3.86 \times 2500 = 2g$.

So, the correct answer is (*b*).

Example 229. *The electrode potential ($E_{Zn^{2+}/Zn}$) of a zinc electrode at 25°C with an aquoes solution of 0.1 M $ZnSO_4$ is ($E_{Zn^{2+}/Zn} = -0.76V$. Assuming $\frac{2.303\ RT}{F} = 0.06$ at 298K)*

(*a*) + 0.73 (*b*) – 0.79

(*c*) – 0.82 (*d*) – 0.70

(*e*) + 0.79

(**Kerala PMT, 2012**)

Solution. For $Zn^{2+} + 2e^- \longrightarrow Zn$, $n = 2$. But

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{2.303\ RT}{nF} \log \frac{[Zn]}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.06}{2} \log \frac{1}{0.1 \text{ or } 10^{-1}} = -0.76 - 0.03 \log 10$$

= – 0.76 – 0.03 × 1 = – 0.79 V. So, the correct answer is (*b*).

Example 230. *The E° values of the following reduction reactions are given:*

$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$; $E^\circ = 0.771V$; $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$; $E^\circ = -0.447V$.

What will be the free energy change for the reaction?

$Fe^{3+}_{(aq)} + 3e^- \longrightarrow Fe_{(s)}$; 1F = 96485 C mol$^-$

(*a*) + 18.51 kJ mol$^-$ (*b*) + 11.87 kJ mol$^-$

(*c*) – 8.10 kJ mol$^-$ (*d*) – 10.41 kJ mol$^-$

(**AMU (medical), 2012**)

Solution. We know that $\Delta G^\circ = -nFE^\circ_{cell}$

(*i*) $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$; $\Delta G^\circ_1 = -F \times 0.771$

(*ii*) $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$; $\Delta G^\circ_2 = -2 \times F \times -0.447 = +0.894\ F$

(*iii*) $Fe^{3+} + 3e^- \longrightarrow Fe_{(s)}$; $\Delta G^\circ_3 = ?$

But $\Delta G^\circ_3 = \Delta G^\circ_1 + \Delta G^\circ_2$; $\Delta G^\circ_3 = -0.771\ F + 0.894\ F$

= + 0.123 *F* = 0.123 × 96485 = 11867.6 ≃ 11.87 kJ mol$^-$.

So, the correct answer is (*b*).

Example 231. *A current of 10.0 A is passed through 1.0 L of 1.0 M HCl solution for 965 seconds. The pH at the end of the experiment is:*

(*a*) 0 (*b*) 0.2

(*c*) 0.8 (*d*) none of these

(**AMC (medical), 2012**)

Solution. 1 L of 1.0 M HCl solution contain HCl = 1mol

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

$\therefore$ 1 Faraday produce $H_2 = \frac{1}{2} \times 1 = 0.5$ mol

$$\frac{965 \times 10}{96500} \text{ Faraday produce } H_2 = \frac{0.5 \times 965 \times 10}{96500} = 0.05 \text{ mol } H_2$$

$\therefore$ 0.05 mol H_2 contain H^+ = 0.1 mol

So, H^+ ions left in solution = 1 – 0.1 = 0.9 mol.

$\therefore$ pH = – log (H^+) = – log 0.9 = (–) × – 0.0457 = + 0.0475.

So, the correct answer is (*d*).

Example 232. *Calculate the maximum work that can be obtained from the given electrochemical cell constructed with two metals, M and N. ($E^\circ_{M^{2+}/M} = -0.76V$; $E^\circ_{N^{2+}/N} = +0.34$ V). The cell reaction is, $M + N^{2+} \longrightarrow M^{2+} + N$.*

(**ISC, 2012**)

Solution.

$$\begin{array}{ll} & N^{2+} + 2e^- \longrightarrow N\ ;\ E^\circ = +0.34\text{ V} \\ & M^{2+} + 2e^- \longrightarrow M\ ;\ E^\circ = -0.76\text{ V} \\ \text{Subtract} & -\quad -\quad\quad -\quad\quad + \\ \hline & M + N^{2+} \longrightarrow M^{2+} + N\ ;\ E^\circ = 1.10\text{ V} \end{array}$$

But the maximum work = – *nFE*°. ...(1)

Since the reduction process involves two electrons change, so, *n* = 2; F = 96500 coulombs; *E*° = 1.10 V. Substituting the values in equation (1), we get:

Maximum work = – 2 × 96500 C × 1.10 V

= – 221300 CV = – 221300 J

[∵ 1 CV = I J]

= – 221.3 kJ **Ans.**

Example 233. *The standard reduction potential for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are – 0.76, – 0.23 and – 0.44V respectively. The reaction, $X + Y^{2+} \longrightarrow X^{2+} + Y$ will be spontaneous when:*

(*a*) X = Ni, Y = Zn (*b*) X = Fe, Y = Zn

(*c*) X = Zn, Y = Ni (*d*) X = Ni, Y = Fe

(**AIEEE, 2012**)

Solution. A reaction is spontaneous, if E° of the reaction is positive. But $E^\circ = E^\circ_{reduction}$ (higher value) – $E^\circ_{reduction}$ (lower value). Since – 0.23 V > – 0.44 > – 0.76 V, we see that in order to get + ve value, *X* must be Zn (∵ Zn^{2+}/Zn = – 0.76). So, using data of (*c*), we have:

E° = – 0.23 – (– 0.76) = +0.53 V.

So, the correct answer is (*c*).

Example 234. *Standard electrode potential of half-cell reactions are given below:*

$Cu^{2+} + 2e^- \longrightarrow Cu$; $E^\circ = 0.34$ V

$Zn^{2+} + 2e^- \longrightarrow Zn$; $E^\circ = -0.76$ V

What is the emf of the cell ?

(*a*) *+ 1.10 V* (*b*) *– 1.10 V*

(*c*) *– 0.42 V* (*d*) *+ 0.42 V*

(J&K– CET, 2012)

SOLUTION. Subtracting reduction reaction with less E° value from reduction reaction with more E° value, we have:

$$Cu^{2+} + 2e^- \longrightarrow Cu\ ;\ E° = +0.34\ \text{V}$$
$$Zn^{2+} + 2e^- \longrightarrow Zn\ ;\ E° = -0.76\ \text{V}$$
$$-\quad -\qquad -\qquad +$$
$$\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn} + \text{Cu}\ ;\ E° = +1.10\ \text{V}$$

So, the correct answer is (*a*).

EXAMPLE 235. *The equilibrium constant for the reaction* $A_{(s)} + 2B^+_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + 2B_{(s)};\ E°_{cell} = 0.0295V$ *is:* $\left[\dfrac{2.303\,RT}{F} = 0.059\right]$*:*

(*a*) *10* (*b*) 2×10^2

(*c*) 3×10^2 (*d*) 2×10^5

(Karnataka, CET, 2012)

SOLUTION. In the reaction, $\text{A}_{(s)} + 2\text{B}^+_{(aq)} \rightleftharpoons \text{A}^{2+}_{(aq)} + 2\text{B}_{(s)}$ the $\text{A}_{(s)} \rightleftharpoons \text{A}^{2+}_{(aq)} + 2e^-$ has $n = 2$ ($\because$ of $2e^-$ change)

But $\log K_c = \dfrac{n \times E^\circ_{\text{cell}}}{0.059}$; $\log K_c = \dfrac{2 \times 0.0295}{0.059} = 1$

$\therefore K_c = \text{antilog } 1 = 10.$

So, the correct answer is (*a*).

PROBLEMS FOR PRACTICE

1. A cell with parallel electrodes (area = 1.88 cm^2) has a solution of specific conductance 1.51×10^{-2} ohm^{-} cm^{-}. If resistance of solution is 170.5 ohms, find the distance between the electrodes and cell constant.

[Hint and Ans. Distance, $l = k\,R\,a = 1.5 \times 10^{-2}\ \text{ohm}^{-}\ \text{cm}^{-} \times 170.5\ \text{ohm} \times 1.88\ \text{cm}^2 = 4.81\ \text{cm}$; cell constant $= l/a = k\,R = 1.5 \times 10^{-2}\ \text{ohm}^{-}\ \text{cm}^{-} \times 170.5\ \text{ohm}$ = **2.558 cm^{-}** **Ans.]**

2. The resistance of a cell containing N/10 AgNO_3 solution and N/10 KCl solution was 362.62 ohms and 337.62 ohms respectively. The specific conductance of N/10 KCl is 0.01286 S cm^{-}. Calculate the equivalent conductance of N/10 AgNO_3 and the cell constant.

[Hint and Ans. Cell constant = 0.01286 × 337.62 = 4.342 cm^{-} ; Λ_{eq} of N/10 AgNO_3 = (observed conductivity × cell constant × 1000)/Normality

$$= \frac{1}{362.65} \times \frac{4.342 \times 1000}{1/10}$$

= **119.73 ohm^{-} cm^2 (g. equiv)$^{-}$Ans.]**

3. The equivalent conductivity of centinormal solution of HCl, NaCl, CH_3COO Na and CH_3COOH are 369.3, 101.7, 71.7 and 14.3 respectively. Calculate the degree of dissociation and H^+ ion concentration of centinormal acid assuming that other electrolytes are completely ionised. Also, calculate the dissociation constant of the acid.

[Hint and Ans. $\Lambda_{\text{CH}_3\text{COOH}} = (\lambda_{\text{H+}} + \lambda\text{Cl}^-) + (\lambda_{\text{CH}_3\text{COO}^-} + \lambda\ \text{Na}^+) - (\lambda\ \text{Na}^+ + \lambda\ \text{Cl}^-) = 369.3 + 71.7 - 101.7 = 339.3$ mhos ; Degree of dissociation, $\alpha = \lambda_c/\lambda° = 14.3/339.3$ **= 0.042 or 4.2 %** **Ans.]**

$$[\text{H}^+] = \text{C}\,\alpha = \frac{1}{100} \times 0.042$$

= 0.00042 g ion L^{-} **Ans.**

$$K_c = \frac{C\,\alpha^2}{1-\alpha} \simeq C\,\alpha^2 = 0.01 \times (0.042)^2$$

= 1.764 ×10^{-5} mol L^{-} **Ans.**

4. Equivalent conductivities at infinite dilution of KCl, HCl and CH_3COOK are 0.01301, 0.03794 and 0.00956 Ω^{-} m^2 (g.eq)$^{-}$ respectively at 291 K. If specific conductivity of 0.001 N CH_3COOH at 291 K is 4.09×10^{-3} Ω^{-} m^{-}, find its degree of dissociation.

[Hint and Ans.

(*i*)
$$\Lambda_{eq} = \frac{K}{C\,(\text{g. eq}/\text{m}^3)}$$
$$= \frac{4.09 \times 10^{-3}\ \Omega^{-}\ \text{m}^{-}}{0.001 \times 10^3\ \text{g. eq m}^{-3}}$$
$$= 4.09 \times 10^{-3}\ \Omega^{-}\ \text{m}^2\ (\text{g. eq.})^{-}$$

(*ii*) $\Lambda°\ (\text{CH}_3\text{COOH}) = \Lambda°\ (\text{CH}_3\text{COOK}) + \Lambda°\ (\text{HCl}) - \Lambda°\ (\text{KCl})$

$= (0.00956 + 0.03794 - 0.01301)$

$= 0.03449\ \Omega^{-}\ \text{m}^2\ (\text{g. eq})^{-}$.

Hence, degree of dissociation

$$\alpha = \frac{4.09 \times 10^{-3}\ \Omega^{-}\ \text{m}^2\ (\text{g. eq.})^{-}}{0.03449\ \Omega^{-}\ \text{m}^2\ (\text{g. eq.})^{-}}$$

= 0.1186 **Ans.]**

5. Calculate the molar conductivity of 0.00241 M CH_3COOH if its conductivity is 7.896×10^{-5} ohm^{-} cm^{-}. If $\Lambda°$ (CH_3COOH) is 390.5 ohm^{-} cm^2 mol^{-}, find its dissociation constant.

[Hint and Ans. $\Lambda = (7.896 \times 10^{-5} \times 1000)/0.00241 = 32.76\ \text{ohm}^{-}\ \text{cm}^2\ \text{mol}^{-}$; $\alpha = 32.76/390.5 = 0.084$; $K = C\,\alpha^2/1 - \alpha = 0.00241 \times (0{,}084)^2/1 - 0.084$ **= 1.85 × 10^{-5}** **Ans.]**

6. In a Co – Zn cell, $E°_{\text{Zn}^{2+}/\text{Zn}} = -0.76\ V$ and $E°_{\text{Co}^{2+}/\text{Co}} = -0.28\ V$. Name the anode and cathode.

[Ans. Zn is anode : Co is cathode]

7. Find the pH of the following acid solution Pt | H_2(1bar) | H^+(*aq.* acid) || $H^+(g)$ 1 bar| Pt. The measured e.m.f. of the cell is 0.178 V.

[Hint and Ans. pH = $\dfrac{E_{cell}}{0.0591} = \dfrac{0.178}{0.159}$ = **3.012 Ans.]**

8. Calculate the maximum work that can be obtained from the following cell Zn/Zn^{2+} (*aq*) || Ag^+(*aq*)/Ag. Given that $E°$ Zn^{2+}/Zn = – 0.76 *V* and $E°$ Ag^+/Ag = 0.80 *V* **(PSEB, 1999)**

[Hint: Maximum work = – $nE°F$ = – 2 × 1.56 = 96500 = 301.08] **Ans. 301.08 kJ]**

9. How many hours does it take to reduce 3 mol of Fe^{3+} to Fe^{2+} with 2 ampere current? **(DSB, 1997)**

[Hint and Ans. $Fe^{3+} + 1e^- \rightarrow Fe^{2+}$. To reduce 3 mol Fe^{3+}, quantity of electricity required = 3 F = 3 × 96500 C; time in hour = ?. But Q = current in amp × time in seconds. So, time in seconds = (3 × 96500)/2 = 144750 sec = 144750 sec × $\dfrac{1\text{ hr}}{3600\text{ sec}}$ = **40.2 hr Ans.]**

10. How many coulombs are required to produce (*a*) 20.0g of calcuim from molten $CaCl_2$? (*b*) 40.0g of aluminium from molten Al_2O_3 ? **(HSB, 1998)**

[Hint and Ans.

$$\begin{array}{cccc} Ca^{2+} & + \ 2e^- & \longrightarrow & Ca \\ 1\text{ mol} & 2\text{mol} & & 1\text{mol} \\ 1\text{mol} & 2F & & 40g \\ \frac{1}{2}\text{mol} & \frac{2}{2} = 1\text{ F} & & \frac{40}{2} = 20\text{ g} \end{array}$$

∴ To produce 20g Ca, charge required

= 1 F = **1 × 96500 coulombs Ans.**

(*b*)

$$\begin{array}{cccc} Al^{3+} & + \ 3e^- & \longrightarrow & Al \\ 1\text{ mol} & 3\text{ mol} & & 1\text{mol} \\ 1\text{mol} & 3\text{ F} & & 27\text{ g} \end{array}$$

27 g Al is formed from charge = 3 F = 3 × 96500 coulombs

40 g Al is formed from charge

$$= \frac{3 \times 96500}{27} \times 40$$

= **428, 888.9 Coulombs Ans.]**

11. A current of 0.67 ampere when passed through a solution of $CuSO_4$ ($Cu^{2+} + 2e^- \rightarrow Cu$) for 5 hours, 7.9 g Cu was deposited. (*a*) How many coulombs will be used to deposit 1 mol of Cu and (*b*) how many moles of Cu are deposited ?

[Hint and Ans.

$$\begin{array}{ccc} Cu^{2+} & + \ 2e^- \longrightarrow & Cu \\ 1\text{mol} & 2\text{mol} = 2F & 1\text{mol} \end{array}$$

From the reaction, it is clear that :

(*i*) One mol of copper is deposited from coulombs = 2 × 96500 = **193000 Ans.]**

(*ii*) Coulombs of electricity passed = Current in amperes × (time in seconds)

$$= 0.67\text{amp} \times 5\text{hr} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ sec}}{1\text{ min}}$$

= 12060 Coulombs

But 2 × 96500 coulomb deposit

Cu = 1 mol

12060 coulomb deposit

$$Cu = \frac{1}{2 \times 96500} \times 12060$$

= **0.06249 mol Ans.]**

12. On passing electric current through acidulated water and solution of copper sulphate, 0.571 g of copper and 203 mL of H_2 at N.T.P. are liberated. Calculate the equivalent weight of copper .

[Hint and Ans. wt. of 203 mL H_2 at N.T.P. = 0.00009 g × 203 = 0.01827 g

∵ 1mL H_2 at N.T.P. weighs = 0.00009g.

But $\dfrac{\text{Wt. of Cu}}{\text{Wt. of }H_2} = \dfrac{\text{Eq. wt. of Cu}}{\text{Eq. wt. of }H_2}; \dfrac{0.571}{0.01827} = \dfrac{E}{1.008};$

***E* = 31.5 Ans.]**

13. A graph between E_{cell} and log $\dfrac{[Cu^{2+}]}{[Ag^+]^2}$ was linear with intercept on E_{cell} axis 0.46 V. Calculate E_{cell} for Cu/Cu^{2+} (0.1 M) || Ag^+(0.01M)/Ag. **Ans. 0.383 V**

14. Calculate the reduction potential at p_{OH} = 14 for the couple

$E°_{Zn^{2+}/Zn} = -0.76$ V.

Given that

$(K_{sp})_{Zn(OH)_2} = 1.0 \times 10^{-15}$ **Ans. – 1.2025 Volt**

15. In the electrolysis of acidulated water, it is desired to obtain 1.12 cc. of hydrogen per second under S.T.P. condition. The current to be passed is:

(*a*) 9.65 A (*b*) 19.3 A

(*c*) 0.965 A (*d*) 1.93 A

(Karnataka CET, 2009)

SOLUTION. Number of moles of

$$H_2 = \frac{\text{Volume of } H_2}{22400\text{ cc.}} = \frac{1.12}{22400}$$

∴ Number of equivalents of

$$H_2 = \frac{1.12}{22400} \times 2 = 10^{-4}$$

Hence no. of Faradays needed = 10^{-4}

∴ Current to be passed in 1 sec = 96500 × 10^{-4} = 9.65 A. So, the correct answer is (*a*).

16. Which represents disproportionation.

(*a*) $3HNO_2 \longrightarrow 2NO + HNO_3 + H_2O$

(*b*) $Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$

(*c*) $3Ni + 2\,Au^{3+} \longrightarrow 3\,Ni^{2+} + 2Au$

(*d*) None. **Ans. (*a*)**

17. Given $E°_{Cr^{3+}/Cr} = -0.74$ V; $E°_{MnO_4^-/Mn^{2+}} = 1.51$ V; $E°_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V; $E°_{Cl/Cl^-} = 1.36$ V. Based on the data given above, strongest oxidising agent will be:

1. Cr^{3+} 2. Mn^{2+}
3. MnO_4^- 4. Cl^-

(JEE Main, 2013)

Solution: A stronger oxidising agent is that whose reduction potential value is more. Out of the given data, the reduction potential, E° is maximum for $E°_{MnO_4^-/Mn^{2+}}$ = 1.55 V. So, the correct answer is (3).

18. The same current was passed through two electrolytic cells (connected in series) containing $AgNO_3$ and $ZnSO_4$ solution respectively. The concentration of two solutions is in the ratio 1 : 2. The ratio of weights of Ag and Zn deposited on Pt electrode is :

(*a*) 107.9 : 65 (*b*) 65 : 107.9
(*c*) 107.9 : 32.5
(*d*) 32.5 : 107.9; At. wt. Ag = 107.9 ; Zn = 65. **Ans.** (*c*)

Hint: Consult example, 93.

19. The equivalent conductance of monobasic acid at infinite dilution is 438 $ohm^- cm^2 eq^{-1}$. If the resistivity of the solution containing 15 g of acid (mol. wt. = 49) in 1L is 18.5 ohm cm, what is the degree of dissociation of acid?

(*a*) 12.2% (*b*) 20.2%
(*c*) 30.2% (*d*) 40.3% **Ans.** (*d*)

20. When 0.1 milli Faraday of electricity was passed through molten Al_2O_3, the weight of Al deposited at the cathode was:

(*a*) 1.23 mg (*b*) 19.3 mg
(*c*) 24.7 mg (*d*) 0.9 mg

Ans. (*d*)

21. If the 0.05 molar solution of M^+ is replaced by a 0.0025 M molar M^+ solution, then the magnitude of cell potential would be: ($E_{cell\ (1)}$ = 70 mV)

(*a*) 35 mV (*b*) 70 mV
(*c*) 140 mV (*d*) 700 mV

(IIT-JEE, 2010) Ans. (*c*)

22. A certain current liberates 0.504 g of hydrogen in 2 hours. How many grams of oxygen can be liberated by the same current in same time?

(*a*) 2.0 g (*b*) 0.4 g
(*c*) 4.0 g (*d*) 8.0 g

(J and K CET, 2010) Ans. (*c*)

23. The number of Faradays required to deposit 1 mol of Cu from a solution of $CuSO_4$ will be:

(*a*) 0.1 (*b*) 0.2
(*c*) 1 (*d*) 2

(Bihar CECE, 2009) Ans. (*d*)

24. At 18°C, the conductance of H^+ and CH_3COO^- at infinite dilution are 315 and 35 mho cm^2 eq^- respectively. The equivalent conductivity of CH_3COOH at infinite dilution is ...... mho cm^2 eq^-:

(*a*) 350 (*b*) 280
(*c*) 30 (*d*) 315

(AFMC, 2010) Ans. (*a*)

25. One Faraday of electricity is passed through Al_2O_3, aqueous solution of $CuSO_4$ and molten NaCl taken in three different electrolytic cells connected in series. The mole ratio of Al, Cu and Na deposited at the respective cathode is:

(*a*) 2 : 3 : 6 (*b*) 6 : 2 : 3
(*c*) 6 : 3 : 2 (*d*) 1 : 2 : 3
(*e*) 3 : 6 : 2 **(Kerala PET, 2010) Ans. (*a***

26. The value of equivalent conductance of 1.1 M CH_3COOH is 14 ohm^- cm^2 $(equiv)^-$ and that at infinite dilution is 238 ohm^- cm^2 eq^-. The percent ionisation of CH_3COOH will be:

(*a*) 5.9 (*b*) 10
(*c*) 1.2 (*d*) 15

Ans. (*a*)

27. For how long a current of 2.5 ampere has to be passed through the electrolyte in order to deposit 2.0 g of copper when electrode reaction is $Cu^{2+} + 2e^- \longrightarrow Cu$. **Ans. 0.844 hrs**

28. Calculate the electrostatic charge on Na^+ ions when one Faraday of electricity is passed through the solution containing these ions.

Ans. 4.8×10^{-10} e s u.

29. Silver is electrodeposited on a metallic vessel of total surface 500 cm^2 by a current of 0.5 ampere for two hours. Calculate the thickness of silver deposited (density of silver = 10.5 g cm^{-3}, at. wt. of Ag = 108 amu, *F* = 96500 C mol^-) **(CBSE (AI), 2006)**

Hint: $W = ZIt = \frac{108}{96500} \times 0.5 \times 2 \times 60 \times 60 = 4.029$ g;

Volume, *V* = mass/density = 4.029 g/10.5 g cm^{-3} = 0.3837 cm^3. But volume = Area × thickness. So, Thickness = (Volume/area) = (0.3837/500) = 7.67×10^{-4} cm.

20
CHAPTER

Chemical Kinetics

20.1 RATE OF REACTION

It is defined as the quantity of a reactant species consumed or the quantity of a product species formed in unit time. It is also defined as the '*rate of change of concentration of the reactants with time*'.

Mathematically :

$$\text{Rate of reaction} = \frac{\text{Amount of substances transformed}}{\text{Time taken in transformation}}$$

(*i*) For a reaction, A → B

$$\text{Rate of reaction} = -\frac{\Delta[\text{A}]}{\Delta t} \quad \textbf{or}$$

$$\text{Rate of reaction} = +\frac{\Delta[\text{B}]}{\Delta t}$$

$$\text{In general, rate of reaction} = -\frac{dx}{dt} \ or \ +\frac{dx}{dt}$$

(*ii*) For a general reaction : $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$$\text{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}.$$

For the **formation of a compound,** rate of reaction is given a **positive sign** while for the **disappearance of a compound,** the rate of reaction is given a **negative** sign.

20.2 RATE OF DISAPPEARANCE OF A COMPOUND

Type : Rate of disappearance of a compound, is given a negative sign while rate of formation of a compound is given a positive sign. For $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$.

$$\text{Rate of reaction,} \quad r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}.$$

EXAMPLE 1. *Nitrogen dioxide (NO_2) reacts with fluorine (F_2) to yield nitryl fluoride (NO_2F)*

$$2\,NO_2(g) + F_2(g) \rightarrow 2\,NO_2F(g).$$

Write the rate of reaction in terms of (i) rate of formation of NO_2F, (ii) rate of disappearance of NO_2 (iii) rate of disappearance of F_2.

SOLUTION. Given : $2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\,\text{NO}_2\text{F}(g)$. (*i*) For the formation of a compound, rate of reaction is given a positive sign while for the disappearance of a substance, there is decrease in concentration and rate is given a negative sign. Hence :

(*i*) Rate of formation of

$$\text{NO}_2\text{F} = +\frac{1}{2}\frac{\Delta[\text{NO}_2\text{F}]}{\Delta T}$$

(*ii*) Rate of disappearance of

$$\text{NO}_2 = -\frac{1}{2}\frac{\Delta[\text{NO}_2]}{\Delta T}$$

(*iii*) Rate of disappearance of

$$\text{F}_2 = -\frac{\Delta[\text{F}_2]}{\Delta T}.$$

EXAMPLE 2. *Consider the following reaction which proceeds in a closed vessel. 3X → 2Y + Z. The rate of disappearance of X, $-\frac{\Delta[X]}{\Delta t}$ is found to be 0.075 mol^{-} L^{-} s^{-}. Calculate $\frac{\Delta[Y]}{\Delta t}$ and $\frac{\Delta[Z]}{\Delta t}$.*

SOLUTION. The reaction 3X → 2Y + Z can be written as: $\text{X} \rightarrow \frac{2}{3}Y + \frac{1}{3}Z$. Since $-\frac{\Delta[X]}{\Delta t}$ = 0.075 mol^{-} L^{-} s^{-}, we have,

$$(i) \qquad \frac{\Delta[Y]}{\Delta t} = \frac{2}{3} \times 0.075 = 0.05 \text{ mol L}^{-}\text{ s}^{-} \qquad \textbf{Ans.}$$

$$(ii) \qquad \frac{\Delta[Z]}{\Delta t} = \frac{1}{3} \times 0.075 = 0.025 \text{ mol L}^{-}\text{ s}^{-} \qquad \textbf{Ans.}$$

EXAMPLE 3. *For the straight reaction, $X_2(g) + 2Y_2(g) \rightarrow 2XY_2(g)$, write the rate equation in terms of disappearance of Y_2.* **(AISB, 1992, PSEB 1999 S, HSB, 1996)**

SOLUTION. The equation in terms of disappearance of Y_2 in the rate equation.

$X_2(g) + 2Y_2(g) \longrightarrow 2XY_2(g)$ is : rate $= -\frac{1}{2}\frac{d[Y_2]}{dt}$ **Ans.**

Example 4. *How will you express the rate of following reactions : (i) $N_2 + 3H_2 \rightarrow 2NH_3$ in terms of disappearance of H_2 (ii) $H_2 + I_2 \rightleftharpoons 2HI$.* **(CBSE, 2007)**

Solution. (*i*) For $N_2 + 3H_2 \rightleftharpoons 2NH_3$, rate in terms of disappearance of $H_2 = -\frac{1}{3}\frac{d[H_2]}{dt}$

(*ii*) For $H_2 + I_2 \rightleftharpoons 2HI$;

$$\text{rate} = \frac{-d[H_2]}{dt} = \frac{-d[I_2]}{dt} = +\frac{1}{2}\frac{d[HI]}{dt}$$

20.3 AVERAGE RATE OF REACTION

Type : Average rate of reaction = $\frac{-[R_2 - R_1]}{t_2 - t_1}$ *i.e.*, rate $= -\frac{\Delta[R]}{\Delta t}$ where R_1 = rate of reaction at time t_1 and R_2 is the rate of reaction at t_2; $t_2 > t_1$; $R_1 > R_2$.

Example 5. *The concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction during units of time both in minutes and seconds.*

Solution. For the reaction, R $\rightarrow$ products

$R_1 = 0.03$ M; $R_2 = 0.02$ M; $t_1 = 0$ min; $t_2 = 25$ min.

But average rate of reaction

$$= -\frac{(R_2 - R_1)}{t_2 - t_1} = -\frac{(0.02 - 0.03)\,\text{mol L}^{-}}{(25 - 0)\,\text{min}}$$

$$= \frac{0.01\,\text{mol L}^{-}}{25\,\text{min}} = 4 \times 10^{-4} \text{ or}$$

0.4×10^{-3} mol L^{-} min^{-} **Ans.**

$$= \frac{0.01\text{ mol L}^{-}}{25 \times 60s} = 6.67 \times 10^{-6}\text{ s}$$ **Ans.**

Example 6. *The decomposition of N_2O_5 in CCl_4 solution at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially, the concentration of N_2O_5 is 2.33 M and after 184 minutes, it is reduced to 2.08 M. The reaction takes place according to the equation :*

$$2N_2O_5 \rightarrow 4NO_2 + O_2$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period ?

Solution. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$;

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta T}$$

$$= \frac{-1}{2}\frac{[2.08 - 2.33]\,\text{mol L}^{-}}{(184 - 0)\,\text{min}} = \frac{-1}{2}\left(\frac{-0.25}{184}\right)$$

$$= \frac{6.8 \times 10^{-4}\,\text{mol L}^{-}}{\text{min}}$$

$$= 6.8 \times 10^{-4}\,\frac{\text{mol L}^{-}}{\text{min}} \times \frac{60\text{ min}}{1\text{h}}$$

$$= \frac{4.08 \times 10^{-2}\text{ mol L}^{-}}{\text{hr}}$$ **Ans.**

Also, $$\text{Rate} = \frac{6.08 \times 10^{-4}\text{mol L}^{-}}{\text{min} \times 1\text{ min}/60\text{sec}}$$

$$= \frac{1.13 \times 10^{-5}\text{ mol L}^{-}}{\text{s}}$$ **Ans.**

Also, $$\text{Rate} = \frac{1}{4}\frac{d[NO_2]}{dt}.$$

Or $$\frac{6.8 \times 10^{-4}\text{mol L}^{-}}{\text{min}} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

Hence, $$\frac{d[NO_2]}{dt} = \frac{4 \times 6.8 \times 10^{-4}\text{mol L}^{-}}{\text{min}}$$

$$= \frac{2.72 \times 10^{-3}\text{ mol L}^{-}}{\text{min}}$$ **Ans.**

Example 7. *From the concentration of reactant A at different times given below, calculate the average rate of reaction $A \rightarrow B$ during different intervals of time.*

t/s	0	5	10	20	30
[A] × 10^3 mol L^{-}	160	80	40	10	2.5

Solution. (*i*) For time $t_1 = 0$ and $t_2 = 5$, the rate $R_1 = 160 \times 10^3$ and $R_2 = 80 \times 10^3$.

$$\text{So, average rate} = \frac{[-(R_2 - R_1) \times 10^3]}{t_2 - t_1}$$

$$= \frac{(-80 + 160) \times 10^3}{5 - 0} = 16 \times 10^3.$$

(*ii*) For time $t_1 = 5$, $t_2 = 10$, the rate $R_1 = 80 \times 10^3$ and $R_2 = 40 \times 10^3$.

$$\text{So, average rate} = \frac{[-(R_2 - R_1) \times 10^3]}{t_2 - t_1}$$

$$= -\frac{(40 - 80) \times 10^3}{10 - 5} = 8 \times 10^3$$ **Ans.**

(*iii*) For time $t_1 = 10$, $t_2 = 20$, the rate $R_1 = 40 \times 10^3$, $R_2 = 10 \times 10^3$.

$$\text{So, average rate} = \frac{-(R_2 - R_1) \times 10^3}{t_2 - t_1}$$

$$= \frac{[-(10 - 40) \times 10^3}{20 - 10} = 3 \times 10^3$$ **Ans.**

(*iv*) Try your self. **Ans.** 0.75×10^3.

Example 8. *8 mol L^{-} of $BaCO_3$ are heated. After 4 seconds, the concentration of $BaCO_3$ left is 4 mol L^{-}. Calculate the rate of reaction.*

Solution. Time = 4 seconds; no. of moles of $BaCO_3$ consumed = 8 – 4 = 4 mol L^{-}. But rate of reaction = no. of moles per litre of reactant consumed / Time taken = 4 mol/ 4 seconds = 1 mol s^{-} **Ans.**

Example 9. *When 50 mL of 2 M solution of N_2O_5 was heated, 0.28 L of O_2 at NTP was formed after 30 minutes. Calculate the concentration of unreacted N_2O_5 at that time and also find the average rate of reaction.*

Solution. N_2O_5 decomposes as

$$\underset{1\,\text{mol}=(2\times14+5\times16=108\,\text{g})}{N_2O_5} \longrightarrow N_2O_4 + \underset{\frac{1}{2}\text{mol}=\frac{1}{2}\times32=16\,\text{g}}{1/2O_2} \quad ...(i)$$

(*i*) To find wt. of O_2 formed. 22.4 L O_2 weighs = 32 g.

0.28 L O_2 weighs

$$= \frac{(32\times0.28)}{22.4} = 0.4\,g.$$

From relation (*i*), we have;

16 g O_2 is formed from N_2O_5 = 108 g

∴ 0.4 g O_2 is formed from N_2O_5

$$= \frac{(108\times0.4)}{16} = 2.7\text{ g}$$

= wt, of N_2O_5 decomposed.

(*ii*) To find total wt. of N_2O_5 present in 50 mL of 2M N_2O_5;

$$\text{Molarity} = \frac{(\text{wt. of }N_2O_5\times1000)}{\text{g. Mol. wt. of }N_2O_5\times\text{Vol. of }N_2O_5\text{ in mL}}$$

$$\text{or} \qquad 2 = \frac{\text{wt. of }N_2O_5\times1000}{108\times50}$$

or Wt. of N_2O_5 = 10.8 g

Hence, wt. of N_2O_5 left unreacted

= 10.8 – 2.7 = 8.1. g.

Hence, molarity or concentration of N_2O_5 unreacted

$$= \frac{(\text{wt.}\times1000)}{\text{g.mol.wt.of }N_2O_5\times\text{Vol.of }N_2O_5}$$

$$\text{or} \qquad \text{Molarity} = \frac{(8.1\times1000)}{(108\times50)} = \mathbf{1.5\,M} \qquad \textbf{Ans.}$$

(*iii*) Average rate of reaction.

$$\frac{(2\text{M} - 1.5\text{M})}{(\text{Time in seconds})}$$

$$= \frac{0.5\text{ M}}{(30\times60\text{ seconds}) - 0\text{ second}}$$

$$= \frac{0.5\text{ M}}{1800\text{ second}} = 0.000278\text{ Ms}^- \quad \textbf{Ans.}$$

Example 10. *For the reaction $2X + Y + Z \rightarrow X_2YZ$, the rate equation is, Rate = $k[X][Y]^2$ with $k = 3.0 \times 10^{-6}$ mol^{-2} L^2s^-. If [X] = 0.1 mol L^-, [Y] = 0.2 mol L^- and [Z] = 0.7 mol L^-, determine (i) the initial rate of reaction and also (ii) the rate after 0.02 mol of X has been reacted.*

Solution. The given rate equation is rate, = $k[X]\,[Y]^2$ and $k = 3.0 \times 10^{-6}$ mol^{-2} L^2s^-

[X] = 0.1 mol L^-; [Y] = 0.2 mol L^- and

[Z] = 0.7 mol L^-

∴ Initial rate = $(3.0 \times 10^{-6}\text{ mol}^{-2}\text{ L}^2\text{ s}^-)\ (0.1\text{ mol L}^-)\ (0.2\text{ mol L}^-)^2$

= $\mathbf{12 \times 10^{-9}\ mol\ L^-\ s^-}$

Concentration of X after 0.02 mole has been reacted

[X] = 0.1 – 0.02 = 0.08 mol L^-

From the given reaction it is clear that when 2 moles of X are consumed then one mole of Y gets consumed.

∴ moles of Y consumed when 0.02 moles of X have been consumed

$$= 0.02\times\frac{1}{2} = 0.01\text{ mole}$$

∴ [Y] = 0.2 – 0.01 = 0.19 mol L^-

Rate = $(3.0 \times 10^{-6}\text{ mol}^{-2}\text{L}^2\text{s}^{-2})\ (0.08\text{ mol L}^-)\ (0.19\text{ mol L}^{-1})^2$

= $\mathbf{8.66 \times 10^{-9}\ mol\ L^-\ s^-}$.

Type : Calculation of rate of reaction when concentration is given. Rate = *k* × conc. of reactants.

Example 11. *The rate of 1st order reaction when conc. of reactants is 10^{-2} mol L^- is 3×10^{-4} mol L^-s^-. What will be the rate of reaction when conc. of the reactant is 10^{-4} mol L^-?*

Solution. (*i*) $r = k\,[A]$

$$\therefore \qquad k = \frac{r}{[A]} = \frac{3\times10^{-4}}{10^{-2}} = 3\times10^{-2}s^-$$

(*ii*) $r = k[A] = 3 \times 10^{-2} \times 10^{-4}$

$= 3 \times 10^{-6}$ mol L^-s^-.

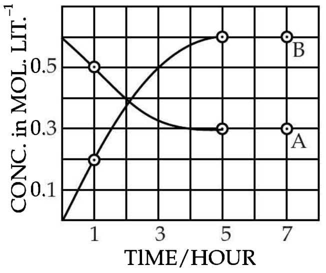
Example 12. *The progress of the reaction $A \rightleftharpoons nB$, with time is presented in the figure. Determine*

(*i*) *the value of n,*

(*ii*) *the equilibrium constant, K, and*

(*iii*) *the initial rate of conversion of A.* **(IIT,1994)**

Solution. (*i*) According to Fig. below, the concentration of reactant and products becomes constant after 5 hours indicating the establishment of equilibrium. In the time span of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3 M (0.5 – 0.3 = 0.2) and that of B increases from 0.2 M to 0.6 M (0.6 – 0.2 = 0.4). Thus increase in concentration of B in a given time is twice $\left(\frac{0.4}{0.2} = 2\right)$ the decrease in concentration of A. Hence $n = 2$.



(*ii*) Equilibrium reaction can be represented as :

$$A \rightleftharpoons 2B$$

$$\therefore \qquad K = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = 1.2M$$

(*iii*) In the time interval 0 to 1 hour, the plot of [A] and [B] are almost linear. Hence the initial rate of conversion of A may be evaluated over this time interval.

$$\text{Initial rate} = -\frac{d[A]}{dt} = \frac{(0.6-0.5)\,M}{1\,\text{hour}} = \mathbf{0.1\ mol\ L^{-1}s^{-1}}$$

Example 13. *The gases X and Y are enclosed in a cubical container. Write down the effect of following changes on the reaction rate between the gases :*

(i) the pressure is doubled

(ii) the temperature is lowered at constant volume

(iii) the number of molecules of gas Y are doubled.

Solution. (*i*) When the pressure is increased, the volume would decrease. Hence concentration will increase and the rate of reaction would become doubled.

(*ii*) When the temperature is lowered, the kinetic energy of the molecules would decrease and the reaction will slow down.

(*iii*) On increasing the number of molecules of Y, the rate of reaction will increase.

Example 14. *The decomposition of N_2O_5 in CCl_4 was studied by measuring the oxygen gas evolved from it. In one hour, 24 ml of the gas was evolved while 35 ml of the gas were evolved when no more oxygen was coming out. Calculate the fraction of N_2O_5 that decomposed in one hour.*

Solution. Here concentration of oxygen gas increases with time. Since 35 mol is the total volume of the gas evolved and 24 mol gas was evolved in one hour, so :

Fraction of N_2O_5 that decomposed in one hour

$$= \frac{24}{35} = \mathbf{0.686.}$$

Example 15. *An experiment was performed on the study of decomposition of H_2O_2 by titration with $KMnO_4$ solution. At the initial stage, 5 ml of the reaction mixture required 46.0 ml of $KMnO_4$ solution. After 5 minutes, the same volume of the reaction mixture needed 37.0 ml of $KMnO_4$ solution. Calculate the fraction of H_2O_2 that decomposed in five minutes.*

Solution. Here concentration of H_2O_2 decreases with time.

Let, initial concentration of H_2O_2 = 1 mol L^-

Fraction of concentration of H_2O_2 at 5 minutes

$$= \frac{37}{46} = 0.804$$

$\therefore$Fraction of H_2O_2 that decomposed in 5 minutes

$$= 1 - 0.804 = \mathbf{0.196.}$$

Example 16. *$PCl_{5(g)}$ (initial pressure 150 mm, Hg) was heated to get $PCl_{3(g)}$ and $Cl_2(g)$ and the final pressure recorded was 350 mm Hg. Calculate the fraction of $PCl_{5(g)}$ that remained unchanged when the pressure was 200 mm Hg.*

Solution. (*i*) For complete change of PCl_5 to PCl_3 and Cl_2 :

Change of pressure = 350 – 150 = 200 mm Hg.

(*ii*) For fractional change, change of pressure = 200 – 150 = 50 mm Hg

$$\therefore \qquad \text{Fraction changed} = \frac{50}{200} = 0.25$$

Hence fraction unchanged = 1 – 0.25 = **0.75 Ans.**

Example 17. *A reactant R was allowed to decompose. After 20 minutes, it was found that its concentration changed from 0.05 M to 0.025 M. Calculate the average rate of the reaction during these 20 minutes.*

Solution. We know that :

$$\text{rate} = -\frac{\Delta[R]}{\Delta t} = -\frac{(0.05-0.025)}{20\ \text{min mol L}^-}$$

$$= -\frac{0.025}{20}$$

$$= \mathbf{-1.25 \times 10^{-3}\ mol\ L^-\ min^-}$$

Example 18. *Consider the following reaction*

$$2\,NO_{(g)} + 2H_2 \longrightarrow N_{2(g)} + 2H_2O$$

Following rate law has been observed for it experimentally

$$R = k\,[NO]^2\,[H_2]^1$$

Predict the reaction rate change, if the following changes are made in the concentration of the reactants.

(i) [NO] is doubled but the concentration of other reactant is kept constant.

(ii) $[H^+]$ is doubled but the concentration of other reactant (NO) is kept constant.

(iii) [NO] is halved but $[H^+]$ is kept constant.

(iv) The concentration of NO as well as H_2 are doubled.

Solution. (*i*) The rate of reaction would become four times because it is proportional to power two of the molar concentration of $NO_{(g)}$.

(*ii*) The reaction rate would become double because it is proportional to single power of the molar concentration of H_2.

(*iii*) The reaction rate would be reduced to one fourth as it is proportional to power two of the molar concentration of $NO_{(g)}$.

(*iv*) The reaction rate would become six times, four times for $NO_{(g)}$ and two times for $H_{2(g)}$.

Example 19. *The following reaction was carried out in H_2O*

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$

The initial concentration of I^- was 0.25 mol L^- and concentration after 10 min. is 0.23 mol L^-. Calculate rate of disappearance of I^- and appearance of I_2.

Solution.

$$-\frac{1}{2}\frac{\Delta[I^-]}{\Delta t} = +\frac{\Delta[I_2]}{\Delta t}$$

$$\Delta[I^-] = [I^-]_{\text{final}} - [I^-]_{\text{initial}}$$

$$= 0.23 - 0.25$$

$$= -0.02\ \text{mol L}^-$$

$$\Delta t = 10 - 0 = 10\ \text{min}$$

$$\therefore \text{Rate of disappearance of } I^- = -\frac{1}{2}\frac{\Delta[I^-]}{\Delta t} = -\frac{1}{2}\frac{-0.02}{10}$$

$$= 0.001\ \text{mol L}^-\ \text{min}^-$$

$$\text{Also, rate of appearance of } I_2 = \frac{\Delta[I_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[I^-]}{\Delta t}$$

$$= 0.001 \text{ mol L}^- \text{ min}$$

20.4 ORDER OF REACTION-FIRST ORDER EQUATION

It is defined as the sum of the *exponents (powers)* to which the molar concentration are *raised in the* rate law or rate equation.

For a general reaction, $lA + mB \rightarrow$ Products,

$$\text{Rate,} \quad r = \frac{-dx}{dt} = k[A]^a[B]^b$$

where $a = l$ or $a \neq l$;

$b = m$ or $b \neq m$.

∴ order of reaction $= a + b$.

First order reaction : *These are* the reactions in which the rate of reaction is determined by the variation of one concentration term only. For a reaction; A → Products :

$$r = -\frac{dx}{dt} = \frac{-d[A]}{dt} = k[A]$$

or

$$\frac{dx}{dt} = k(a - x)$$

On solving, we get: $k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$

or $k = \dfrac{2.303}{t}\log\dfrac{No}{N}$ First order equation

when, $x = \dfrac{a}{2}$;

$$k = \frac{2.303}{t} \times \log \frac{a}{a - a/2 \, (= a/2)}$$

$$= \frac{2.303}{t_{0.5} \text{ or } t_{1/2}} \log 2$$

$$\therefore \quad k = \frac{2.303 \times 0.310}{t_{0.5}}$$

$$k = \frac{0.693}{t_{0.5}}$$

where $t_{0.5}$ or $t_{1/2}$ = half-change time. a or No = Initial concentration; $a - x$ or N = concentration after time, t.

∴ ***For first order reaction.*** $k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$;

$$t_{0.5} = \frac{0.693}{k}$$

Second order reaction. These are the reactions in which the rate of reaction is determined by the variation of two concentration terms only.

For second order reaction, $k = \dfrac{1}{t} \times \dfrac{x}{a(a-x)}$ when initial concentration of reactants are equal. When initial concentration of reactants are not equal, then :

$$k = \frac{2.303}{t(a-b)}\log\frac{b(a-x)}{a(b-x)}$$

Third order reaction. These are the reactions in which the rate of reaction is determined by the variation of three concentration terms only.

$$\text{For third order reaction, } k = \frac{1}{t} \times \frac{x(2a-x)}{2a^2(a-x)^2}$$

20.5 UNITS OF RATE CONSTANT

The unit of a rate constant is different for different order of reactions (n). For

$$nA \longrightarrow \text{Products}$$

$$\text{Rate} = k[A]^n; \; k = \frac{\text{Rate}}{[A]^n}$$

(*i*) ***For non-gaseous substances,***

$$k = \frac{\text{Concentration}}{\text{time}} \times \frac{1}{[A]^n}$$

or

$$k = \frac{(\text{mol L}^-)^1}{\text{time}} \times \frac{1}{(\text{mol L}^-)^n}$$

$$= \mathbf{(mol\ L^-)^{1-n}\ time^-}.$$

Since **L$^-$ = dm^{-3}, unit of *k* =** (mol dm^{-3})$^{1-n}$ time$^-$.

(*ii*) ***For gaseous substances,***

$$k = \frac{\text{Concentration}}{\text{time}} \times \frac{1}{[A]^n}$$

or

$$k = \frac{(\text{atm})^1}{\text{time}} \times \frac{1}{(\text{atm})^n}$$

$$= (\text{atm})^{1-n} \text{ time}^-$$

∴ For zero order reaction ($n = 0$), k = (mol L$^-$)$^{1-0}$ time$^-$ = mol L$^-$ time$^-$. When time is in seconds, k = **mol L$^-$s$^-$.**

Also, k = (atm)$^{1-0}$ time$^-$ = atm time$^-$. When time is in seconds, ***k* = *atm s*$^-$**. Similarly

order of reaction	*Unit of rate constant*
0	mol L$^-$ time$^-$ or atm time$^-$
1	time$^-$
2	L mol$^-$ time$^-$ or atm$^-$ time$^-$
3	L^2 mol^{-2} time$^-$ or atm^{-2} time$^-$

Type : To know the order of a reaction from the units of rate constant. For this purpose, use the following relation.

k = (mol L$^-$)$^{1-n}$s$^-$ (*i.e.*, time$^-$)

or k = (mol dm^{-3})$^{1-n}$s$^-$ (*i.e.*, time$^-$)

k = (atm)$^{1-n}$s$^-$ *i.e.*, time$^-$

EXAMPLE 20. *Identify the order of a reaction if the units of its rate constant are* (*i*) L$^-$ mol s$^-$ (*ii*) L mol$^-$ s$^-$

(ISC, 2010, CBSE 2012)

SOLUTION. k = (mol L$^-$)$^{1-n}$s$^-$ where n is the order of reaction.

(*a*) Put $n = 0$; k = (mol L$^-$)$^{1-0}$s$^-$ = mol L$^-$s$^-$

So, the reaction

(*i*) is of zero order

(*b*) Put $n = 1$; $k = (\text{mol L}^{-})^{1-1}\text{s}^{-} = \text{s}^{-}$.

So, order of reaction in not 1.

(*c*) Put $n = 2$; $k = (\text{mol L}^{-})^{1-2}\text{s}^{-} = \text{L mol}^{-}\text{s}^{-}$.

So, order of reaction for the units given in (*ii*) is two.

EXAMPLE 21. *Find the order of a reaction if the units of its rate constant is* $L^2\ mol^{-2}\ sec^{-}$.

SOLUTION. We know that, $k = (\text{mol L}^{-})^{1-n}\text{s}^{-}$ where n is the order of reaction.

(*i*) Put $n = 0, k = \text{mol L}^{-}\ \text{s}^{-}$

(*ii*) Put $n = 1, k = (\text{mol L}^{-})^0\text{s}^{-} = \text{s}^{-}$

(*iii*) Put $n = 2, k = (\text{mol L}^{-})^{1-n}\text{s}^{-}$

$= (\text{mol L}^{-})^{1-2}\text{s}^{-} = (\text{mol L}^{-})^{-1}\text{s}^{-}$

$= \text{mol}^{-}\text{L s}^{-}$

(*iv*) Put $n = 3, k = (\text{mol L}^{-})^{1-n}\text{s}^{-}$

$= (\text{mol L}^{-})^{1-3}\ \text{s}^{-} = (\text{mol L}^{-})^{-2}\text{s}^{-}$

$= \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-}$.

$\therefore$ order of reaction $= 3$.

EXAMPLE 22. *The time for half-life of a certain reaction A → products is 1 hour. When the initial concentration of the reactant, A is 2.0 mol L*$^{-}$*, how much time does it take for its concentration to come from* 0.50 *to 0.25 mol L*$^{-}$*, if it is a zero order reaction.*

(*a*) 1 hr (*b*) 4 hr (*c*) 0.5 hr (*d*) 0.25 hr

(AIEEE, 2010)

SOLUTION. For zero order reaction, $t_{1/2} = [A_0]/2k$; $k = [A_0]/2\,t_{1/2} = 2\text{mol}/2 \times 1\text{ hr} = 1\text{ mol L}^{-}\text{hr}^{-}$. The integrated rate law for zero order reaction is:

$[A] = -kt + [A_0]$. So, $0.25 = -1 \times t + 0.5$.

Hence, $t = 0.25$ hr.

So, the correct answer is (*d*)

EXAMPLE 23. *The unit of rate constant for a zero order reaction is:*

(*a*) $\text{mol L}^{-}\ \text{s}^{-}$ (*b*) $\text{L mol}^{-}\ \text{s}^{-}$ (*c*) $\text{L}^2\ \text{mol}^{2-}\ \text{s}^{-}$ (*d*) s^{-}

(AIPMT, 2011)

SOLUTION. Unit of rate constant, $k = (\text{mol L}^{-})^{1-n}$ time^{-}. For zero order reaction, $n = 0$. Thus, the unit of k is : $k = (\text{mol L}^{-})^{1-0}\ \text{s}^{-} = (\text{mol L}^{-})^1\ \text{s}^{-} = \text{mol L}^{-}\ \text{s}^{-}$.

So, the correct answer is (*a*).

EXAMPLE 24. *Find the units of rate constant for second order oreation if :*

(*i*) *reactants and products are in aqueous state*

(*ii*) *reactants and products are in gaseous state*

SOLUTION. (*i*) For aqueous state, units of

$k = (\text{mol L}^{-})^{1-n}\text{s}^{-}$

Since order of reaction, $n = 2$

$\therefore$ $k = (\text{mol L}^{-})^{1-2}\text{s}^{-}$

$= (\text{mol L}^{-})^{-1}\text{s}^{-} = \text{L mol}^{-}\text{s}^{-}$

(*ii*) For gaseous state, unit of

$k = (\text{atm})^{1-n}\text{s}^{-}$

Since order of reaction, $n = 2$

$\therefore$ $k = (\text{atm})^{1-2}\text{s}^{-} = \text{atm}^{-}\text{s}^{-}$.

EXAMPLE 25. *Find the order of a reaction if the units of its rate constant is atm*$^{-}$ *sec*$^{-}$.

SOLUTION. We know, unit of $k = (\text{atm})^{1-n}\text{s}^{-}$

(*i*) Put $n = 0$, $k = (\text{atm})^{1-0}\ \text{s}^{-} = \text{atm . s}^{-}$

(*ii*) Put $n = 1$, $k = (\text{atm})^{1-1}\ \text{s}^{-} = (\text{atm})^0\text{s}^{-} = \text{s}^{-}$

(*iii*) Put $n = 2$, $k = (\text{atm})^{1-2}\ \text{s}^{-} = (\text{atm})^{-1}\text{s}^{-} = \text{atm}^{-}\text{s}^{-}$

$\therefore$ Order of reaction = 2

Type : *To find order of reaction* from the various steps given for a complete reaction or to find order of reaction from rate equation.

(*a*) The slowest step in the rate determining step.

(*b*) Sum of exponents in a rate equation or rate law is the order of reaction.

EXAMPLE 26. *For the reaction*

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

the following mechanism is suggested.

(*i*) $NO_2 + F_2 \longrightarrow NO_2F + F$ (*slow*)

(*ii*) $NO_2 + F \longrightarrow NO_2F$ (*fast*)

What is the predicted rate law ? **(PSEB, 2007)**

SOLUTION. We know that slow step is the rate determining step. So, the rate law for the slow reaction (*i*) is :

Rate = $[NO_2]\,[F_2]$ Ans.

EXAMPLE 27. *What is the rate of reaction and the order of the reaction if the mechanism of reaction is :*

$2NO + H_2 \longrightarrow N_2 + H_2O_2$ (*slow*)

followed by $2H_2O_2 \longrightarrow 2H_2O + O_2$ (*fast*)

SOLUTION. Rate equation is, rate $= k\,[\text{NO}]^2\,[\text{H}_2]^1$ (for slow reaction only)

$\therefore$ order of reaction $= 2 + 1 = 3$

EXAMPLE 28. *Decomposition of* N_2O_5 *is expressed by the equation :*

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

If during a certain time interval, the rate of decomposition of N_2O_5 *is* 1.8×10^{-3} *mol L*$^{-}$ *min*$^{-}$*, what will be the rate of formation of* NO_2 *and* O_2 *during the same interval.*

SOLUTION. Rate expression for decomposition of N_2O_5:

$$-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{NO}_2]}{\Delta t} = 2\frac{\Delta[\text{O}_2]}{\Delta t}$$

$\therefore$ Rate of formation of NO_2 is :

$$\frac{1}{2}\frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

$$\therefore \quad \frac{\Delta[\text{NO}_2]}{\Delta t} = 2 \times -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

$$= 2 \times 1.8 \times 10^{-3}\ \text{mol L}^{-}\ \text{min}^{-}$$

and

$$\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \times \frac{1}{2}$$

$$= 1.8 \times 10^{-3} \times \frac{1}{2}\ \text{mol L}^{-}\text{min}^{-}$$

20.6 HALF-LIFE PERIOD

Relation between half-life period (or half-change time), $t_{1/2}$ and initial concentration (a) of a reaction. $t_{1/2}$ and a are related as :

(*i*) $\mathbf{t_{1/2} = 1/a^{n-1}}$ where n = order of reaction.

∴ For zero order, first order, second order and third order reactions :

$$t_{1/2} = \frac{1}{a^{-1}}, \frac{1}{a^{0}} \text{ or } \frac{1}{1} \text{ or } 1, \frac{1}{a} \text{ and } \frac{1}{a^{2}} \text{ respectively.}$$

(*ii*) Number of half-life periods

$$= \frac{\text{Total time}}{\text{Time of half-life period}}$$

(*iii*) Quantity of reactant life after '*n*' half-life period

$$= \left(\frac{1}{2}\right)^{n} \times \text{Initial amount of reactant.}$$

(*iv*) $t_{1/2}$ or $t_{0.5} = \dfrac{0.693}{k}$

EXAMPLE 29. *The half-life period of first order reaction $A \longrightarrow B$ is 600 sec. What percent of A remains after 30 minutes? Also, find its rate constant.* **(PSEB, 1999, ISC, 2013)**

SOLUTION. Half-life period = 600 sec = 10 min.

[∵ 1 min = 60s]

Let a = initial amount of reactant.

Number of half-lives in 30 min.

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

Amount of A left after three half-lives

$$= \frac{a}{2^3} = \frac{a}{8} = \frac{a}{8} \times 100$$

$$= \mathbf{12.5 \text{ of } a \ \%.}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600\,s} = 1.16 \times 10^{-3} s$$

EXAMPLE 30. *The half-life of a substance in certain enzyme catalyzed reaction is 138* s. *The time required for the concentration of the substance to fall from 1.28 mg L^{-} to 0.04 mg L^{-} is:*

(*a*) 414 s (*b*) 552 s (*c*) 690 s (*d*) 276 s

(AIPMT, 2011)

SOLUTION. n = no. of half-life periods is given as:

$$\frac{0.04 \text{ mg L}^{-}}{1.28 \text{ mg L}^{-}} = \frac{1}{32}; \left(\frac{1}{2}\right)^{n} = \left(\frac{1}{2}\right)^{5} \quad \text{or} \quad n = 5$$

∴ Time required = $n \times t_{1/2} = 5 \times 138$ s = 690 s.

So, the correct answer is (*c*)

EXAMPLE 31. *Identify the reaction order from each of the following rate constants.*

(*i*) $k = 5 \times 10^{-5}\ s^{-}$, (*ii*) $k = 9 \times 10^{-4}\ mol^{-}litre\ s^{-}$,

(*iii*) $k = 6 \times 10^{-2}$ *litre* $mol^{-}s^{-}$.

SOLUTION. The unit of rate constant, k is given as : $k = (\text{mol L}^{-})^{1-n}\text{s}^{-}$ where n is the order of the reaction. Using this relation, the unit of rate constant is found and compared with the units of k given. Thus, order of reaction can be decided.

For example :

(*a*) When $n = 0, k = (\text{mol L}^{-})^{1-n}s^{-}$

$= (\text{mol L}^{-})^{1-0}s^{-} = \text{mol L}^{-}s^{-}$.

(*b*) When $n = 1, k = (\text{mol L}^{-})^{1-n} . s^{-} = (\text{mol L}^{-})^{1-1}s^{-}$

$= (\text{mol L}^{-})^{0}s^{-} = s^{-}$

So, reaction (*i*) is of first order.

(*c*) When $n = 2, k = (\text{mol L}^{-})^{1-n} . s^{-} = (\text{mol L}^{-})^{1-2}s^{-}$

$= (\text{mol L}^{-})^{-}s^{-} = \text{mol}^{-} \text{Ls}^{-}$.

So, reactions (*ii*) and (*iii*) are of second order ($n = 2$).

EXAMPLE 32. *The rate equation for a reaction, $A \rightarrow B$ is $r = k\ (A)^0$. If the initial concentration of the reactant is a mol dm^{-3}, the half-period of the reaction is:*

(*a*) $k/2$ (*b*) a/k (*c*) $2a/k$ (*d*) $a/2k$

(Karnataka CET, 2009)

SOLUTION. Given: rate = $k[\text{A}]^0$. So order of reaction is zero. For a zero order reaction, $t_{1/2} \propto a$

∴ $t_{1/2} = \dfrac{a}{2k}$. So, the correct answer is (*d*).

EXAMPLE 33. *Carbonyl chloride gas decomposes to give carbon monoxide gas and chlorine gas.*

$$COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$$

It follows the rate law : rate = k $[COCl_2]^{3/2}$. Calculate the units of its rate constant.

SOLUTION. Given : Rate = $k\ [\text{COCl}_2]^{3/2}$. Hence order of reaction, $n = \dfrac{3}{2}\cdot$ To find units of rate constant, k, we have: $k = (\text{mol L}^{-})^{1-n}. \text{s}^{-}$. Substituting the value of $n = \dfrac{3}{2}$, we get $k = (\text{mol L}^{-})^{1-3/2} . \text{s}^{-} = (\text{mol L}^{-})^{1/2}\text{s}^{-}$. So, unit of k = $(\text{mol L}^{-})^{-1/2}.\text{s}^{-}$. **Ans.**

Type : Order of a reaction in which rate = $k\ [\text{A}]^a[\text{B}]^b$ (slowest step reaction) = Sum of exponents = $a + b$; k = rate constant or specific reaction rate.

EXAMPLE 34. *Cyclopropane rearranges to form propene*

$$\longrightarrow \text{CH}_3 - \text{CH} = \text{CH}_2$$

This follows first order kinetics. The rate constant is 2.714 × 10^{-3} sec^{-}. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec?

(*a*) 0.035 *M* (*b*) 0.22 *M* (*c*) 0.145 *M* (*d*) 0.0018 *M*

(Orissa JEE, 2009)

SOLUTION. Rate constant, $k = 2.714 \times 10^{-3}$ sec^{-}, initial concentration $a = 0.29\ M$; concentration left after 100 sec, $(a - x)$ = ? We know that: rate constant,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}.$$

Thus 2.714×10^{-3} sec

$$= \frac{2.303}{100 \text{ sec}} \log \frac{0.29}{a-x};$$

$$\frac{0.27}{2.303} = \log \frac{0.29}{a-x}; 0.117 = \log \frac{0.29}{a-x}.$$

Taking antilog, we get

$$\text{Anti log } 0.117 = \frac{0.29}{a-x}; a-x = \frac{0.29}{1.3091} = 0.22\,M.$$

So, the correct answer is (*b*).

EXAMPLE 35. *Consider the following first order reaction*

$$2H_2O_2(aq) \xrightarrow{I^-(aq)} 2H_2O(l) + O_2(g)$$

If the rate constant of the reaction is 1.01×10^{-2} *min*$^{-}$ *(i) what concentration of* H_2O_2 *would give rate of* 1.12×10^{-2} *mol L*$^{-}$ *min*$^{-}$*? (ii) Calculate rate of reaction when* $[H_2O_2] = 0.5$ *mol L*$^{-}$*.*

SOLUTION. (*i*) For first order reaction, rate = $k[H_2O_2]$. Substituting the values, we get,

$$1.12 \times 10^{-2} \text{ mol L}^{-} \text{ min}^{-} = 1.01 \times 10^{-2} \text{ min}^{-} [H_2O_2].$$

Hence,
$$[H_2O_2] = \frac{1.12 \times 10^{-2} \text{ mol L}^{-} \text{ min}^{-}}{1.01 \times 10^{-2} \text{ min}^{-}}$$
$$= 1.11 \text{ mol L}^{-}$$

(*ii*) rate = $k[H_2O_2]$.

Substituting the values, we get;

$$\text{rate} = 1.01 \times 10^{-2} \text{ min}^{-} \times 0.5 \text{ mol L}^{-}$$
$$= 5.05 \times 10^{-3} \text{ mol L}^{-} \text{ min}^{-}$$ **Ans.**

EXAMPLE 36. *The decomposoition of*

$$N_2O_{5(g)} \longrightarrow NO_2(g) + NO_{3(g)}$$

proceeds as a first order reaction with a half-life period of 30 seconds at a certain temperature. If the initial concentration $[N_2O_5] = 0.4$ *M, what is the rate constant of the reaction?*

(*a*) 0.00924 sec (*b*) 0.0231 sec (*c*) 75 sec (*d*) 12 sec

(Orissa JEE, 2009)

SOLUTION. Given $t_{1/2} = 30$ sec. For a first order reaction: rate constant, $k = 0.693/t_{1/2}$. Thus, $k = 0.693/30$ sec = 0.0231 sec. So, the correct answer is (*b*).

Type : To find rate law, rate constant, order of reaction and half-life period from *k*.

(*i*) $$\text{Rate} = -\frac{\Delta x}{\Delta t} = k\,[\text{reactant}]$$

∴ $$\text{Numerical value of } k = \frac{\Delta x}{\Delta t[\text{Reactant}]}$$

(*ii*) $$\text{Half-life period, } t_{1/2} = \frac{0.693}{k}$$

(*iii*) If a reaction is *y*% complete in time, *t*, then:

$a = 100; a - x = 100 - y$

(*iv*) If it takes time, *t* for *y* % of a reactant (initial concentration = *a*) to be decomposed, Then, $a - x = a - (a \times y/100)$

EXAMPLE 37. *The experimental data for the decomposition of* N_2O_5 *in gaseous phase at 318 K is as follows :*

$$2\,N_2O_5 \longrightarrow 4\,NO_2(g) + O_2(g)$$

Time (seconds)	*[N$_2$O$_5$] mol L^{-}*	*Time (sec)*	*[N$_2$O$_5$] mol L^{-}*
0	1.36×10^{-2}		
400	1.36×10^{-2}	1600	0.78×10^{-2}
800	1.14×10^{-2}	2000	0.64×10^{-2}
1200	0.95×10^{-2}	2400	0.53×10^{-2}

Calculate rate law, rate constant, order of reaction and half life period.

SOLUTION. Rate law :

$$\text{rate} = -\frac{\Delta x}{\Delta t} = k[N_2O_5] \therefore\ k = \frac{\Delta x}{\Delta t[N_2O_5]}$$

(*i*) $$k = \frac{(1.63 - 1.36) \times 10^{-2}}{(400 - 0) \times 1.36 \times 10^{-2}}$$
$$= 4.9632 \times 10^{-4} \text{ s}^{-}$$

(*ii*) $$k = \frac{(1.36 - 1.14) \times 10^{-2}}{(800 - 400) \times 1.14 \times 10^{-2}}$$
$$= 4.8246 \times 10^{-4} \text{s}^{-}$$

(*iii*) $$k = \frac{(1.14 - 0.95) \times 10^{-2}}{(1200 - 800) \times 0.95 \times 10^{-2}}$$
$$= 5.0 \times 10^{-4} \text{s}^{-}$$

(*a*) Since the value of *k* is constant, rate = $k\,[N_2O_5]^1$.

(*b*) Mean value of rate constant,

$$k = \frac{(4.9632 \times 10^{-4} + 4.8246 \times 10^{-4} + 5.0 \times 10^{-4})\text{s}^{-}}{3}$$
$$= 4.9293 \times 10^{-4} \text{ s}^{-}.$$

(*c*) Order of reaction = 1.

(*d*) Half life period,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.9293 \times 10^{-4} \text{s}^{-}}$$
$$\simeq \mathbf{1406\ s}$$ **Ans.**

EXAMPLE 38. *Decomposition of a gas is of first order. It takes 80 minutes for 80% of the gas to be decomposed when its initial concentration is* 8×10^{-3} *mole/litre. Calculate the specific reaction rate.*

SOLUTION. We know, $$t = \left(\frac{2.303}{k}\right)\log\frac{a}{a - x}$$

where,
$$a = 8 \times 10^{-3} \text{mol L}^{-},$$
$$x = 8 \times 10^{-3} \times \left(\frac{80}{100}\right);$$
$$= 6.4 \times 10^{-3};$$
$$t = 80 \text{ minutes.}$$

Substituting the values, we get :

$$80 = \left(\frac{2.303}{k}\right)\log\frac{(8 \times 10^{-3})}{(8 \times 10^{-3} - 6.4 \times 10^{-3})}$$
$$= \left(\frac{2.303}{k}\right)\log\frac{(8 \times 10^{-3})}{1.6 \times 10^{-3}}$$
$$= \left(\frac{2.303}{k}\right)\log 5$$
$$= 2.303 \times 0.6989$$

or
$$k = \frac{(2.303 \times 0.6989)}{80 \text{ min.}}$$
$$= 0.02012 \text{ min}^{-}$$ **Ans.**

EXAMPLE 39. *The rate constant of a first order reaction is* 4.5×10^{-2} *sec*$^{-}$*. What will be the time required for the initial* *concentration of 0.4 m of the reactant to be reduced to 0.2 m.* **(ISC, 2008)**

SOLUTION. $k = 4.5 \times 10^{-2}\ s^{-}$. Since the initial concentration (0.4 m) is to be reduced to one half (= 0.2 m), the time required will be equal to half-life period, $t_{0.5}$. For a first order reaction:

$$t_{0.5} = \frac{0.693}{k} = \frac{0.693}{4.5 \times 10^{-2} s^{-}}$$

$$= \mathbf{15.4s}$$ **Ans.**

EXAMPLE 40. *A first order reaction is 20% complete in 10 min. Calculate (i) the time taken for the reaction to go to 75% completion (ii) specific reaction rate.* **(IIT, 1983)**

SOLUTION. (*i*) Here, $k = \frac{2.303}{t_{20\%}} \log \frac{a}{a-x}$

$$= \frac{2.303}{10} \log \frac{100}{100-20}$$

$$= 0.022\ \text{min}^{-}.$$

(*ii*) $$k = \frac{2.303}{t_{75\%}} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t_{75\%}} \log \frac{100}{100-75=25} \text{ or } \log 4.$$

$$\therefore \quad 0.022\ \text{min}^{-} = \frac{2.303}{t_{75\%}} \log 4;$$

$$\therefore t_{75\%} = \frac{2.303}{0.022} \log 4 \text{ or } 0.6021 = 63 \text{ min.}$$

EXAMPLE 41. *A reaction is of second order with respect to a reactant. How will rate of reaction be affected if the concentration of this reactant is (i) doubled (ii) reduced half.* **(CBSE, 2009).**

SOLUTION. We know that for a second order reaction, rate = $k[A]^2$. Let [A] = a. So, rate = ka^2

(*i*) If [A] = $2a$, rate = $k(2a)^2 = 4k\,a^2$ = 4 times

(*ii*) If [A] = $a/2$, rate = $k(a/2)^2 = 1/4\ k\,a^2$ = 1/4 th.

EXAMPLE 42. *The thermal decomposition of HCO_2H is a first order reaction with a rate constant of $2.4 \times 10^{-3} s^{-}$ at a certain temperature. Calculate how long will it take for three fourths of initial quantity of HCO_2H to decompose (log 0.25 = – 0.6021)* **(CBSE, 2007; ISC, 2010)**

SOLUTION. 3/4 = 0.75; $k = 2.4 \times 10^{-3} s^{-}$. We know that:

$$t_f = \frac{2{\cdot}303}{k} \log \frac{1}{1-f}$$

where f is fraction of reactant that is left behind after a given time.

$$\therefore \quad t_{0.75} = \frac{2{\cdot}303}{2{\cdot}4 \times 10^{-3} s^{-}} \log \frac{1}{1-0{\cdot}75\,(=0.25)}$$

$$= \frac{2{\cdot}303}{2{\cdot}4 \times 10^{-3} s^{-}} [\log 1 - \log 0.25]$$

$$= \frac{2{\cdot}303}{2{\cdot}4 \times 10^{-3} s^{-}} [0 - (-0.6021) = +0.6021]$$

$$= \mathbf{577.8s}$$ **Ans.**

EXAMPLE 43. *What will be the initial rate of a first order reaction with initial concentration, 0.2 mol dm^{-3}, if its rate constant is 10^{-3} min^{-1} and how much of the reactant will be converted into the products in 200 minutes ?* **(Roorkee, 1992)**

SOLUTION. Rate constant, $k = 10^{-3}$ min^{-1}

∴ Reaction is a first order reaction

$$\text{Initial rate} = k[A] = 10^{-3}\ \text{min}^{-1} \times 0.2\ \text{mol dm}^{-3}$$
$$= 2.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{min}^{-1}$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

$$\text{or} \quad \log \frac{a}{(a-x)} = \frac{kt}{2.303} = \frac{10^{-3} \times 200}{2.303} = 8.684 \times 10^{-2}$$

Taking antilog we have,

$$\frac{a}{(a-x)} = \text{antilog } 8.684 \times 10^{-2}$$

$$\text{or} \quad \frac{a}{(a-x)} = 1.221$$

$$\therefore \quad a = 1.221\,a - 1.221\,x;\ 1.221\,x = 0.221\,a$$

$$x = \frac{0.221}{1.221} a = 0.181a$$

∴ Percentage conversion

$$= \frac{0.181a}{a} \times 100 = \mathbf{18.1\%}.$$

EXAMPLE 44. *The decomposition of N_2O_5 according to the equation.*

$$2\,N_2O_5(g) \rightleftharpoons 4\,NO_2(g) + O_2(g)$$

is a first order reaction. After 30 min. from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

SOLUTION. Dissociation of N_2O_5 is represented as :

$$2\,N_2O_5(g) \rightleftharpoons 4\,NO_2(g) + O_2(g)$$

From the equation, we find that two moles of N_2O_5 on decomposition give a total of five moles of gaseous species (4 mol NO_2 and 1 mol O_2).

$$\text{Hence, initial pressure of } N_2O_5 = \frac{584.5 \times 2}{5} = 233.8 \text{ mm Hg}$$

Let x be the amount of N_2O_5 decomposed after 30 minutes.

∴ After 30 min.

$$\text{Pressure due to } N_2O_5 = 233.8 - x$$
$$\text{Pressure due to } NO_2 = 2x$$
$$\text{Pressure due to } O_2 = \frac{x}{2}$$

Total pressure after 30 minutes = 284.5 mm Hg

$$\therefore \quad (233.8 - x) + 2x + \frac{x}{2} = 284.5$$

$$\therefore \quad x = \frac{284.5 - 233.8}{1.5}$$

$$= 33.8 \text{ mm Hg}$$

Hence pressure of N_2O_5 after 30 minutes

$$= 233.8 - 33.8$$

$$= 200 \text{ mm Hg}$$

$$\therefore \quad k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$= \frac{2.303}{30}\log\frac{233.8}{200}$$

$$= \frac{2.303}{30} \times 0.0678$$

$$= 5.20 \times 10^{-3} \text{ min}^{-1}.$$

Example 45. *The reaction, $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ is a first order reaction. What percentage of SO_2Cl_2 is decomposed on heating it for 90 minutes ($k = 2.2 \times 10^{-5}\ s^{-}$ at 595 K).*

Solution. Let initial concentration (a) of SO_2Cl_2

$$= 100 \text{ mol L}^{-}$$

Degree of dissociation of $SO_2Cl_2 = x$ mol L^{-} (say)

Using the first order equation

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

We have,

$$90 \times 60 = \frac{2.303}{2.2 \times 10^{-5}}\log\frac{100}{100-x}$$

$$[\because 90 \text{ min} = 60 \times 90\text{s} = 5400 \text{ s}]$$

$$5400 = \frac{2.303}{2.2 \times 10^{-5}}\log\frac{100}{100-x}$$

$$\log\frac{100}{100-x} = \frac{5400 \times 2.2 \times 10^{-5}}{2.303}$$

$$= 0.0516$$

Taking antilogs of both sides, we get

$$\frac{100}{100-x} = \text{antilog } 0.0516 = 1.126$$

$$\therefore \quad \mathbf{x = 11.19.}$$

Example 46. *Show that the time required for the completion of 75% of a reaction of first order is twice the time required for the completion of 50% of the reaction.* **(ISC, 2010)**

Solution. (*i*) $t_{1/2} = \dfrac{2\cdot303}{k}\log\dfrac{1}{1-0.5}$

$$[\because 50\% = 50/100 = 0.5 = 1/2\,]$$

or

$$t_{1/2} = \frac{2\cdot303}{k}\log\frac{1}{0\cdot5} = \frac{2\cdot303}{k}\log 2$$

(*ii*)

$$t_{0.75} = \frac{2\cdot303}{k}\log\frac{1}{1-0\cdot75}$$

$$= \frac{2\cdot303}{k}\log\frac{1}{0.25} = \frac{2\cdot303}{k}\log 4$$

Dividing (*i*) and (*ii*), we get $\dfrac{t_{0.75}}{t_{0.5}} = \dfrac{\log 4}{\log 2}$

$$= \frac{0\cdot6020}{0\cdot3010} = \mathbf{2}$$

Ans.

Example 47. *The half change time for the thermal decomposition of N_2O_5 at 303 K is 4.2 hours. Using this date, calculate the following :*

(i) how much of N_2O_5 will be left behind after 16 hours if initial concentration of N_2O_5 is 100 g.

(ii) If the number of molecules of N_2O_5 present initially are 5×10^{20}, after what time, the number of molecules left behind would be 10^{18} ?

Solution. Hint. Find $(a - x) = 0.9822$ g; $t = 21.5$ hrs.

Example 48. *Show that for a unimolecular reaction, the time needed for 99.9% of the reaction to take place is ten times as needed for half of the reaction.*

Solution. Let initial concentration of reactant = 1 mol L^{-}.

Using first order equation, we have :

(*i*) For 99.9% of the reaction to take place, we have.

$$t_{99.9\%} = \frac{2.303}{k}\left[\log\frac{1}{1-\dfrac{99.9}{100}} \textit{ or } \frac{100}{0.1} = \log 1000 = \log 10^3 = 3\right]$$

$$t_{99.9\%} = \frac{2.303}{k} \times 3 \qquad ...(i)$$

For half *i.e.*, 50% of the reaction to take place, we have :

$$t_{50\%} = \frac{2.303}{k}\left[\log\frac{1}{1-\dfrac{50}{100}} \text{ or } \frac{100}{50} = \log 2 = 0.301\right]$$

$$= \frac{2.303}{k} \times 0.301 \qquad ...(ii)$$

Dividing equation (*i*) by (*ii*), we get :

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{2.303}{k} \times 3 \times \frac{k}{2.303 \times 0.301} \simeq 10$$

$\therefore$ Time taken for 99.9% is 10 times the time taken for half of the reaction.

Type : (*i*) Half life $t_{1/2}$ or $t_{0.5} = \dfrac{0.693}{k}$.

Example 49. *The first order reaction is found to have a rate constant $k = 7.39 \times 10^{-5}$ sec^{-}. Find the half life of this reaction.*

(CBSE, 1981, 2013, DSB., 1973, AISB, 1987, HSB and PSEB 1989)

Solution. Given: half-life $t_{1/2} = 7.39 \times 10^{-5}$ sec^{-}

We know, rate constant,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{7.39 \times 10^{-5} s^{-}}$$

$$= 9377.54 s^{-}$$

$$= \left(\frac{9377.54}{60 \times 60}\right) \text{ hours}$$

$$= 2.6 \text{ hours}$$

Ans.

Example 50. *For which order reaction, unit of rate is equal to unit of rate constant?* **(AIPMT, 2009)**

Solution. We know that rate constant, $k = (\text{mol L}^{-})^{1-n}$ time^{-} where n is the order of reaction.

Put $n = 0$ (i.e; zero order reaction) in $k = (\text{mol L}^{-})^{1-n}$ time^{-}, we get:

$k = (\text{mol L}^{-})^{1-0}$ time^{-} = **mol L^{-} time^{-}**.

Also for zero order reaction, rate = $\frac{dx}{dt} = k[\text{A}]^0 = k$ *i.e.,* rate constant.

Hence, unit of rate = unit of rate constant = mol L^{-} time^{-}.

Example 51. *If half life of a 1st order reaction in A is 2 min (a) How long will it take [A] to reach 25% of its initial concentration, or 1/4 of the reactant to be left behind. (b) 10% of its initial conc.* **(PSEB, 2013)**

Solution. $t_{1/2} = \frac{0.693}{k} \quad \therefore \quad k = \frac{0.693}{t_{1/2}}$ or

$$k = \frac{0.693}{2} = 0.3465\,\text{min}^{-}$$

(*a*) Let initial conc.,

$$a = 100 \text{ mol L}^{-}. \quad \therefore \quad a - x = 25 \text{ mol L}^{-}.$$

But $\quad k = \frac{2.303}{t}\log\frac{a}{a-x}$ or

$$0.3465 = \frac{2.303}{t}\log\frac{100}{25}$$

$$t = \frac{2.303}{0.3465}\log 4 = \frac{2.303}{0.3465} \times 0.6020$$

$$= 4 \text{ min}$$

(*b*) Let initial conc., $a = 100$ mol L^{-}. $\therefore$ $a - x = 10$ mol L^{-}

But, $\quad k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$\therefore \quad 0.3465 = \frac{2.303}{t}\log\frac{100}{10} \text{ or } 10$$

$$\therefore \quad t = \frac{2.303}{0.3465} \times 1 = 6.65\,\text{min}.$$

Example 52. *Benzene diazonium chloride decomposes as* $C_6H_5N_2Cl \rightarrow C_6H_5Cl + N_2$. *The volume of* N_2 *evolved at different intervals was measured and following results were obtained.*

Time (min)	*0*	*20*	*70*	*∞*
Vol. of N2 (mL)	*0*	*10*	*32*	*162*

Show that reaction is of first order.

Solution. Here $a \propto V_\infty$ and $x \propto V_t \quad \therefore a - x \propto V_\infty - V_t$

At 20 min, $\quad k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$= \frac{2.303}{20}\log\frac{162}{162-10} = 3.186 \times 10^{-3}$$

At 70 min $\quad k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$= \frac{2.303}{70}\log\frac{162}{162-32} = 3.144 \times 10^{-3}$$

Example 53. *A reaction that is of 1st order w.r.t. reactant A has a rate constant 6 min*$^{-}$. *If we start with [A] = 5 mol L*$^{-}$, *when would [A] reach the value of 0.05 mol L*$^{-}$ *?*

Solution. $\quad t = \frac{2.303}{k}\log\frac{a}{a-x}$

$$\therefore \quad t = \frac{2.303}{6}\log\frac{5}{0.05} \quad \therefore \quad t = 0.768 \text{ min.}$$

Example 54. *The rate of a first-order reaction is 0.04 mol L*$^{-}$ *s*$^{-1}$ *at 10 minutes and 0.03 mol L*$^{-}$*s*$^{-1}$ *at 20 minutes after initiation. Find the half-life of the reaction.* **(IIT, 2001)**

Solution. For a first order reaction, A $\longrightarrow$ Products.

$$\text{rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}]$$

or $\quad -\frac{d[\text{A}]}{[\text{A}]} = k\,dt$

$$\text{Integrating} \; -\int_{[\text{A}]_1}^{[\text{A}]_2}\frac{d[\text{A}]}{\text{A}} = k\int_{t_1}^{t_2} dt$$

i.e., $\quad \ln\frac{[\text{A}]_1}{[\text{A}]_2} = k(t_2 - t_1)$

Hence, $\quad \ln\frac{(\text{rate})_1}{(\text{rate})_2} = k(t_2 - t_1)$

or $\quad k = \frac{\ln[(\text{rate})_1/(\text{rate})_2]}{(t_2 - t_1)}$

$$= \frac{\ln(0.04/0.03)}{(20-10)\,\text{min}}$$

$$= 2.88 \times 10^{-2}\,\text{min}^{-1}$$

For a first order reaction, $t_{0.5} = \frac{0.693}{k}$

$$= \frac{0.693}{2.88 \times 10^{-2}\,\text{min}^{-}}$$

$$= \mathbf{24.06\ min.}$$

Example 55. *In an experiment when the initial concentrations of A and B are 0.1 M each, the initial rate is 1.0 × 10*$^{-4}$ *M per minute. In the second experiment when the initial concentrations of A and B are 0.1 M and 0.30 M respectively, the initial rate is 9.0 × 10*$^{-4}$ *M per minute. In the third experiment when the initial concentrations of both A and B are 0.30 M, the initial rate is 2.7 × 10*$^{-3}$ *M per minute.*

(a) Write the rate law for this reaction.

(b) Calculate the value of specific rate constant for this reaction. **(Roorkee, 1987)**

Solution. Let the order of the reaction with respect to A and B be a and b respectively.

Now according to rate law, $\frac{dx}{dt} = k[\text{A}]^a[\text{B}]^b$

According to the given data

(*i*) $1.0 \times 10^{-4}\,\text{M min}^{-1} = k\,[0.1\,\text{M}]^a\,[0.1\,\text{M}]^b$

(*ii*) $9.0 \times 10^{-4}\,\text{M min}^{-1} = k\,[0.1\,\text{M}]^a\,[0.3\,\text{M}]^b$

(*iii*) $2.7 \times 10^{-3}\,\text{M min}^{-1} = k\,[0.3\,\text{M}]^a\,[0.3\,\text{M}]^b$

For calculating the value of b, divide (ii) by (i)

$$\frac{9.0\times10^{-4}}{1.0\times10^{-4}} = \frac{[0.3M]^b}{[0.1M]^b}$$

or $$9 = (3)^b \text{ or } (3)^2 = (3)^b \therefore b = 2$$

Similarly, for calculating 'a' divide (iii) by (ii)

$$\frac{2.7\times10^{-3}}{9\times10^{-4}} = \frac{[0.3\text{M}]^a}{[0.1\text{M}]^a} \text{ or } (3)^1 = (3)^a$$

$$\therefore \qquad a = 1$$

Thus the required rate law is $\frac{dx}{dt} = k[A][B]^2$

(b The value of k can be obtained by substituting the values of a and b in either of the three equations.

For example,

$$1.0\times10^{-4}\text{ M min}^{-1} = k\,[0.10\text{ M}]\,[0.10\text{ M}]^2$$

$$\therefore \qquad k = \frac{1.0\times10^{-4}\text{M min}^{-1}}{[0.10\text{M}]^3}$$

$$= 1.0\times10^{-1}\text{ M}^{-2}\text{ min}^{-1}$$

$$= \mathbf{0.10\ M^{-2}\ min^{-1}}$$

$$= \mathbf{0.10\ L^2\ mol^{-2}\ min^{-}}.$$

EXAMPLE 56. *The experimental data for the reaction :*

$$2A + B_2 \longrightarrow 2AB \text{ is :}$$

Experiment No.	*[A]*	*[B]*	*rate (mol^{-1} s^{-})*
1.	*0.50*	*0.50*	*1.6×10^{-4}*
2.	*0.50*	*1.00*	*3.2×10^{-4}*
3.	*1.00*	*1.00*	*3.2×10^{-4}*

Write the most probable rate equation for the reaction giving reasons for your answer. **(Roorkee, 1991)**

SOLUTION. (i) According to the given data, rate of reaction gets doubled when concentration of B_2 is doubled keeping that of A constant.

$$\therefore \qquad \text{rate} \propto [B_2]^2$$

(ii) Rate of reaction does not change if the conc. of A is doubled keeping that of B constant.

$$\therefore \qquad \text{rate} \propto [A]^0$$

$$\therefore \qquad \text{Rate law is : } \frac{dx}{dt} = k[B_2]^1.$$

Type : When amount or percentage of the reactant that will be left after a given time t is to be found then use :

(i) $t_{1/2} = \frac{0.693}{k}$ and

(ii) $t_f = \frac{2.303}{k}\log\frac{1}{1-f}$ where f is the fraction of the reactant that is left behind after a given time.

(iii) When time is to be found out for y% of the reactant to be decomposed, then $f = \frac{y}{100}$

EXAMPLE 57. *The half-life of a first order reaction is 30 min. (i) Calculate the specific rate constant of the reaction. (ii) What fraction of the reactant remains after 70 min ? (iii) How long would be required for 25% of the reactant to be decomposed ?*

SOLUTION. We know, half life, $t_{1/2} = \frac{0.693}{k}$; $t_{1/2} = 30$ min. Substituting the values,

we get : $$30\text{ min} = \frac{0.693}{k}$$

or $$k = \frac{0.693}{30\text{ min}}$$

$$= 0.0231\text{ min}^{-} \qquad \textbf{Ans.}$$

(ii) $$t = 70\text{ min},$$

$$k = 0.0231\text{ min}^{-}.$$

We know, $$t = \left(\frac{2.303}{k}\right)\log\left(\frac{a}{af}\text{ or }\frac{1}{f}\right)$$

$$= \left(\frac{2.303}{k}\right)\log(-f).$$

Substituting the values, we get :

$$70\text{ min.} = \frac{2.303\log - f}{0.0231\text{min}^{-}}$$

or $$\log(-f) = \frac{(70\text{min}\times0.0231\text{min}^{-})}{2.303}$$

$$= 0.7021$$

Taking antilog of both sides, we get :

or $$f = \text{antilog}\,(-0.7021)$$

$$= -1 - 0.7021 + 1$$

$$= \bar{1}.2979 = 0.1985.$$

Hence fraction of the reactant left after 70 minutes = 0.1985 or 0.1985 × 100 = **19.85%.**

(iii) We know, $$t_{25\%} = \frac{2.303}{k}\log\frac{1}{1-f}$$

$$= \left(\frac{2.303}{k}\right)\log\frac{1}{1-0.25}$$

or $$\frac{1}{0.75}\text{or } 1.333$$

Substituting the values, we get :

$$t_{25\%} = \left(\frac{2.303}{0.0231}\right)\log 1.333$$

or $$t_{25\%} = \left(\frac{2.303}{0.0231}\right)\times 0.1248$$

$$= 12.44\text{ min} \qquad \textbf{Ans.}$$

EXAMPLE 58. *A first order reaction (A $\longrightarrow$ Products) has a specific reaction rate of 2.1×10^{-3} sec^{-}. How much time will it take for 99% of A to be consumed ?* **(PSEB, 1988 S)**

Solution. We know that, $t_f = \frac{2.303}{k}\log\frac{1}{1-f}$

For f = 99% or 0.99,

$$t_{0.99} = \frac{2.303}{2.1\times10^{-3}\ \text{sec}^{-}}$$

$$\log\frac{1}{1-0.09} = \frac{2.303}{2.1\times10^{-3}\ \text{sec}^{-}}$$

log 1/0.01 or 10^2)

$$= \frac{2.303}{2.1\times10^{-3}\ \text{sec}^{-}}\times 2$$

= 2.19 × 10^3 sec **Ans.**

Example 59. *For the decomposition of a compound AB at 600 K, the following data were obtained.*

	[AB] mol dm^{-3}	*Rate of decomposition of AB in mol dm^{-3}s^{-}*
(*i*)	0.20	2.75 × 10^{-8}
(*ii*)	0.40	11.0 × 10^{-8}
(*iii*)	0.60	24.75 × 10^{-8}

The order for the decomposition of AB is:

(a) 0 *(b) 1* *(c) 2* *(d) 1.5*

(Karnataka CET, 2009)

Solution. We know that, rate = $k[AB]^n$ (rate equation)

For

Case (*i*), $2.75\times10^{-8} = k[0.2]^n$

Case (*ii*), $11.0\times10^{-8} = k[0.4]^n$

Case (*iii*), $24.75\times10^{-8} = k[0.6]^n$

Dividing (*ii*) by (*i*), we get,

$$\frac{11\cdot0\times10^{-8}}{2\cdot75\times10^{-8}} = \frac{k[0.4]^n}{k[0.2]^n}$$

or $4 = 2^n;\ 2^2 = 2^n$ or $n = 2$.

Similarly, n = 2 when case (*iii*) is divided by case (*i*). So, order of reaction is 2 and the correct answer is (*c*).

Example 60. *For a first order reaction, calculate the ratio between the time taken for the completion of three fourth of the reaction and the time taken for the completion of half the reaction.*

Solution.(*i*) $t_{0.5} = \frac{2.303}{k}\log\frac{1}{1-0.5}$

$$= \frac{2.303}{k}\log 2$$

(*ii*) $t_{0.75} = \frac{2.303}{k}\log\frac{1}{1-0.75}$

$$= \frac{2.303}{k}\log 4 \quad \left[\because \frac{3}{4} = 0.75\right]$$

$$\therefore \quad \frac{t_{0.75}}{t_{0.5}} = \frac{\log 4}{\log 2} = \frac{0.6020}{0.3010} = \frac{2}{1}.$$

Example 61. *A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion.* **(IIT, 1979 modified, CBSE, 1999)**

Solution. $t_{20\%} = \frac{2.303}{k}\log\frac{100}{100-20}$

$$\therefore \quad 20 = \frac{2.303}{k}\log\frac{5}{4}$$

$$\therefore \quad k = \frac{2.303}{20}\log\frac{5}{4}$$

$$t_{80\%} = \frac{2.303}{k}\log\frac{100}{100-80}$$

i.e., $5 = 5 = \frac{20\log 5}{\log 5/4} = \frac{20\times0.6990}{\log 5-\log 4}$

$$= \frac{20\times0.6990}{0.6990-0.6021}$$

= 144.27 minutes.

Example 62. *(a) Derive a general expression for the time taken for the reactant to reduce to nth fraction (b) The rate constant of first order reaction is 60 s^{-}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?* **(NCERT)**

Solution. (*a*) $t = \frac{2.303}{k}\log\frac{a}{a-x}$.

Put $a - x = \frac{a}{n}$ and we have :

$$t = \frac{2.303}{k}\log\frac{a}{a/n} \quad \text{or}$$

$$t = \frac{2.303}{k}\log n.$$

(*b*) $t = \frac{2.303}{k}\log\frac{a}{a-x}$

(first order equation); $a - x = \frac{a}{16}$

Substituting the values of k and $a - x$ in above equation, we get :

$$t = \frac{2.303}{60\,s^{-}}\log\frac{a}{a/16}$$

$$= \frac{2.303}{60\,s^{-}}\log 16 = \frac{2.303}{60\,s^{-}}\times 1.2041$$

t = **4.62 × 10^{-2} s** **Ans.**

Example 63. *A first order reaction undergoes 25% completion in 20 minutes. How much percent will it complete in one hour 40 minutes ?*

Solution. Using first order equation :

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

We have, $t_{25\%} = \frac{2.303}{k}\log\frac{100}{100-25} = \frac{2.303}{k}\log\frac{100}{75}$

$$= \frac{2.303}{k}[\log 100 - \log 75]$$

$$= \frac{2.303}{k} \times 0.1249 \qquad ...(i)$$

$$100 = \frac{2.303}{k}\log\frac{100}{100-x} \qquad ...(ii)$$

[x = percent completed; 1 hr. 40 min = 100 min.]

Dividing (*ii*) by (*i*), we get

$$\frac{100}{t_{25\%}} = \frac{\frac{2.303}{k}\log\frac{100}{100-x}}{\frac{2.303}{k}\times 0.1249}$$

$$0.1249 \times \frac{100}{20} = \log\frac{100}{100-x}$$

$$= \log 100 - \log(100 - x)$$

$$= 2 - \log(100 - x)$$

$$0.6245 = 2 - \log 100 - x$$

$$\log 100 - x = 2 - 0.6245 = 1.3755$$

Taking antilog of both sides, we get

$$\therefore \quad 100 - x = \text{antilog } 1.3755 = 23.74$$

$$\therefore \quad x = 100 - 23.74$$

$$= \mathbf{76.26\%}$$

EXAMPLE 64. *Using the following data prove that the decomposition of H_2O_2 in aqueous solution is a first order reaction.*

't' (minuts)	*0*	*10*	*20*
'n' (ml)	*22.8*	*13.8*	*8.2*

Where n represents the number of ml of $KMnO_4$ required to decompose a definite volume of H_2O_2.

SOLUTION. (*i*) $t = 0$, the initial concentration (a) of H_2O_2 is proportional to 22.8 ml of $KMnO_4$.

(*ii*) At $t = 10$ minutes, the concentration $(a - x)$ of H_2O_2 is proportional to 13.8 ml of $KMnO_4$.

(*iii*) At $t = 20$ minutes, the concentration $(a - x)$ of H_2O_2 is proportional to 8.2 ml of $KMnO_4$.

Using first order equation

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

We have, (1)

$$10 \times 60\, s = \frac{2.303}{k}\log\frac{22.8}{13.8}$$

[$\therefore$ 10 minutes = 10 × 60 seconds]

$$\therefore \quad k = \frac{2.303}{600\,s}[\log 22.8 - \log 13.8]$$

$$= \frac{2.303}{600\,s}[1.358 - 1.140]$$

$$= = \frac{2.303}{600} \times 0.218 = \mathbf{8.37 \times 10^{-4} s^{-}}$$

(2)

$$20 \times 60\, s = \frac{2.303}{k}\log\frac{22.8}{8.2}$$

[$\therefore$ 20 minutes = 20 × 60 seconds]

$$\therefore \quad k = \frac{2.303}{1200\,s}[\log 22.8 - \log 8.2]$$

$$= \frac{2.303}{1200\,s}[1.358 - 0.914]$$

$$= \frac{2.303}{1200} \times 0.444 = \mathbf{8.52 \times 10^{-4}\ s^{-}}$$

$$\text{Average value of } k = \frac{8.37 \times 10^{-4} + 8.52 \times 10^{-4}}{2}$$

$$= \mathbf{8.45 \times 10^{-4} s^{-}}$$

Since the value of k is almost same in all the experiments, the reaction is of first order.

EXAMPLE 65. *The half-life for first order reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 10 minutes. In what period of time would the concentration of PCl_5 be reduced to 10% of the original concentration?*

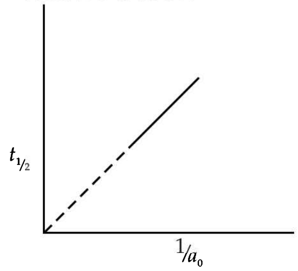
SOLUTION. (*i*) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\,\text{min}} = 0.0693\,\text{min}^{-}$

(*ii*) $t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{0.0693\,\text{min}^{-}}$

$$\left[\log\frac{100}{10} = \log 10 = 1\right]$$

$$t = \frac{2.303}{0.0693\,\text{min}^{-}} = 33.23\,\text{min} \quad \textbf{Ans.}$$

EXAMPLE 66. *The following graph shows how $t_{1/2}$ (half life) of a reactant, R changes with the initial reactant concentration, a_0. The order of the reaction will be:*



(*a*) 0 (*b*) 1 (*c*) 2 (*d*) 3 **(West Bangal JEE, 2009)**

SOLUTION. We know that half-life period $t_{1/2} \propto \frac{1}{a_0^{n-1}}$ or $a_0^{n-1} = a_0^1$ (given) where a_0 = initial reactant concentration.

$\therefore \quad n - 1 = 1$. Hence, $n = 1 + 1 = 2$,

where n is the order of reaction. So, the correct answer is (*c*).

EXAMPLE 67. *For the reaction, $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$, if we write $K_p = K_c(RT)^x$, then x becomes:*

(*a*) –1 (*b*) $-\frac{1}{2}$ (*c*) $\frac{1}{2}$ (*d*) 1 **(West Bengal, JEE, 2009)**

SOLUTION. Given:

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

$$1\text{mol} \qquad \frac{1}{2}\text{mol} \qquad 1\text{mol};\ \Delta n_g = 1 - \left(1 + \frac{1}{2}\right) = \frac{-1}{2}$$

Since $K_p = K_c\,(RT)^x$, we have $x = \Delta n_g = \frac{-1}{2}$ explained above. So, the correct answer is (*b*).

Example 68. *The half life period of a first order reaction is 60 minutes. What percentage of the reactant will be left after 120 minutes ?*

Solution. $t_{0.5} = 60$ min. Total time = 120 min.

$\therefore \quad n =$ no. of half lives $= \frac{120 \text{ min}}{60 \text{ min}} = 2$

$\therefore$ Amount of substance left after n (= 2) half lives

$$= \frac{A_0}{2^n} = \frac{A_0}{2^2} = \frac{A_0}{4} \times 100 = 25\ \%\ \text{of}\ A_0$$

(= initial amount).

Example 69. *The following rate data were obtained at 300 K for the reaction 2A + B → C + D.*

Experiment No.	*[A] mol L$^-$*	*[B] mol L$^-$*	*Rate of formation of D mol L$^-$ min$^-$*
1	0.1	0.1	5.0×10^{-3}
2	0.3	0.2	6.0×10^{-2}
3	0.3	0.4	2.4×10^{-1}
4	0.4	0.1	2.0×10^{-2}

Calculate (1), the order with respect to A and B for the reaction (2) Rate constant for the reaction and (3) the rate of formation of D when : [A] = 0.5 mol L$^-$ and [B] = 0.2 mol L$^-$.

(CBSE, 1996; ISC, 2011)

Solution. Rate of reaction is given as : Rate = $k\,[A]^x[B]^y$.

(*i*) For experiment 1, $\quad 5.0 \times 10^{-3} = k(0.1)^x(0.1)^y$

(*ii*) For experiment 2, $\quad 6.0 \times 10^{-2} = k(0.3)^x\,(0.2)^y$

(*iii*) For experiment 3, $\quad 2.4 \times 10^{-1} = k(0.3)^x\,(0.4)^y$

(*iv*) For experiment 4, $\quad 2.0 \times 10^{-2} = k(0.4)^x\,(0.1)^y$

Determination of *x*. Dividing equation (*i*) and (*iv*), we get :

$$\frac{5.0\times10^{-3}}{2.0\times10^{-2}} = \frac{k\ (0.1)^x(0.1)^y}{k\ (0.4)^x(0.1)^y} \quad \text{or} \quad \left(\frac{1}{4}\right)^1 = \left(\frac{1}{4}\right)^x.$$

Hence, **x = 1.**

Determination of *y*. Dividing equation (*ii*) by (*iii*), we get :

$$\frac{6\times10^{-2}}{2.4\times10^{-}} = \frac{k}{k}\,\frac{(0.3)^x\,(0.2)^y}{(03)^x\,(0.4)^y}$$

$$\text{or} \quad \frac{1}{4} = \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^y.$$

Hence, $\quad$ **y = 2**

From experiment (*i*), we see that

$$5 \times 10^{-3} = k(0.1)^{x\,=\,1}\,(0.1)^{y\,=\,2}$$

$$\text{Thus,} \quad k = \frac{5\times10^{-3}}{0.1\times0.1\times0.1} = 5$$

$$\text{Hence,} \quad \text{rate} = k(\text{A})^x\,(\text{B})^y = 5 \times (0.5)^1(0.2)^2$$

$$= 0.1\ \text{mol L}^-\ \text{min}^-.$$

Example 70. *Nitrogen pentoxide decomposes according to the equation,*

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g).$$

This first order reaction was allowed to proceed at 40°C and the data below were collected.

[N_2O_5]M	*Time (min)*
0.400	*0.00*
0.289	*20.0*
0.209	*40.0*
0.151	*60.0*
0.109	*80.0*

(*a*) *Calculate the rate constant. Include units with your answer.*

(*b*) *What will be the concentration of N_2O_5 after 100 minutes?*

(*c*) *Calculate the initial rate of reaction.* **(CBSE, 2011)**

Solution. (*a*) a = Initial concentration of N_2O_5, [N_2O_5] = 0.400 M; [N_2O_5] after 20 minutes (t) = 0.289 M (= $a - x$). But rate constant (k) is:

$$k = \frac{l}{t}\ln\frac{a}{a-x} = \frac{1}{20\,\text{min}}\log\frac{0\cdot400}{0\cdot289}\times 2\cdot303$$

$$= \frac{1}{20}\ [\log 400 - \log 289] \times 2\cdot303$$

$$= \frac{1}{20}\ [(2.6020 - 2.4609) \times 2.303]$$

$$= 0.0162\ \text{min}^-$$

$\therefore$ Rate constant,

$k = 0.0162\ \text{min}^-$ **Ans.**

(*b*) When t = 100 minutes, let concentration after 100 min = $a - x'$

$$\text{Thus:} \quad k = \frac{1}{t}\ln\frac{a}{a-x},$$

$$0.0162 = \frac{1}{100}\times 2.303\log\frac{0.400}{a-x'}$$

$$\text{or} \quad \frac{0.0162\times100}{2.303} = \log 0.400 - \log\,(a-x');$$

$$0.7034 = -\,0.3979 - \log\,(a - x')$$

$$\therefore \quad \log\,(a - x') = -\,1.1013;$$

$$a - x' = \text{antilog}\,(-1.1013) = \mathbf{0.07919\ M}$$

$\therefore$ Concentration of N_2O_5 after 100 minutes = 0.07919 M.

(*c*) We know,

Initial rate = rate constant, (k) × initial concentration of N_2O_5.

Here: Initial rate = 0.0162 × 0.400

$$= \mathbf{6.48 \times 10^{-3}\ mol\ dm^{-3}\ min^{-1}}$$ **Ans.**

Example 71. *Rate of reaction A + B ⟶ products is given below as a function of different initial concentrations of A and B.*

[A] (mol/L)	*[B] (mol/L)*	*Initial rate (mol $L^{-}min^{-}$)*
0.01	0.01	0.005
0.02	0.02	0.010
0.01	0.02	0.005

Determine the order of the reaction with respect to A and with respect to B. What is the half life of A in the reactions ?

(IIT, 1982)

Solution. Let the rate r of a reaction between A and B be given by $r = k\,[A]^a[B]^b$.

According to the given data, initial rate becomes twice when the concentration of A is increased to double its value. Hence, the order of reaction with respect to A *i.e.,* a is equal to 1. However, the rate remains constant when the concentration of B is doubled. Thus, the order of reaction with respect to B *i.e., b* is equal to zero.

Total order = 1 + 0 = 1.

As the initial rate is equal to 0.005 mol L^{-} when concentration of A and B is equal to 0.01 mol L^{-}.

$$\therefore \qquad 0.005 = k[0.01]^1\,[0.01]^0$$

$$\text{or} \qquad k = \frac{0.005}{0.01} = \mathbf{0.5\ min^{-1}}$$

$$\therefore \qquad \text{Half life of A} = \frac{0.693}{0.5} = \mathbf{1.386\ min.}$$

Example 72. *For the reaction A + B → Products, it is observed that:*

(i) On doubling the initial concentration of A only, the rate of reaction is also doubled.

(ii) On doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction. The rate of reaction is given by:

(*a*) rate = $k[A][B]^2$ (*b*) rate = $k\,[A]^2[B]^2$

(*c*) rate = $k[A][B]$ (*d*) rate = $k[A]^2[B]$

(CBSE-PMT, 2009)

Solution. We know that, rate,

$$R = k\,[A]^m[B]^n \qquad ...(i)$$

$$\text{But} \qquad 2R = k[2A]^m[B]^n \qquad ...(ii)$$

$$\text{and} \qquad 8R = k[2A]^m\,[2B]^n \qquad ...(iii)$$

Dividing equation (*i*) by (*ii*), we get:

$$\frac{R}{2R} = \frac{k \times [A]^m \times [B]^n}{k \times 2^m \times [A]^m \times [B]^n};$$

$$\frac{1}{2^1} = \frac{1}{2^m}.\ \text{So, } m = 1$$

Dividing equation (*ii*) by (*iii*), we get

$$\frac{2R}{8R} = \frac{k \times 2^m \times [A]^m \times [B]^n}{k \times 2^m \times [A]^m \times 2^n \times [B]^n};$$

$$\frac{1}{4} = \frac{1}{2^n};\ \frac{1}{2^2} = \frac{1}{2^n};\ \boldsymbol{n = 2}$$

Thus, rate = $k\,[A][B]^2$. So the correct answer is (*a*).

Example 73. *The kinetics of hydrolysis of methyl acetate in excess of hydrochloric acid solution at 298 K were followed by withdrawing 2 mL of the reaction mixture at intervals of time (t), adding 50 mL of water and titrating against baryta-water. The following results were obtained :*

t (min)	*0*	*10*	*28*	*58*	*115*	*∞*
Titre (mL)	*18.5*	*19.1*	*20.1*	*21.65*	*24.6*	*34.8*

Determine the velocity constant of the hydrolysis.

Solution. Initial concentration, a = 34.8 – 18.5 = 16.3. At time 10 min, $a - x$ = 34.8 – 19.1 = 15.7; at time 28 min., $a - x$ = 34.8 – 20.1 = 14.7; at time 58 min., $a - x$ = 34.8 – 21.6 = 13.2 and at time 115 min., $a - x$ = 34.8 – 24.6 = 10.2. We know,

$$k = \left(\frac{2.303}{10}\right)\log\frac{a}{a-x} \qquad ...(i)$$

(*a*) At time, 10 min.

$$k = \left(\frac{2.303}{10}\right)\log\frac{16.3}{15.7}$$

$$= 0.2303 \log 1.0382 = 0.2303 \times 0.01628$$

$$= 3.749 \times 10^{-3}$$

(*b*) At time, 28 min.,

$$k = \left(\frac{2.303}{28}\right)\log\frac{16.3}{14.7}$$

$$= \frac{2.303}{28}\log 1.1088$$

$$= \left(\frac{2.303}{28}\right) \times 0.04485 = 3.689 \times 10^{-3}$$

(*c*) At time, 58 min.

$$k = \frac{2.303}{58}\log\frac{16.3}{13.2} = \left(\frac{2.303}{58}\right)\log 1.2348$$

$$= \left(\frac{2.303}{58}\right) \times 0.0916 = 3.637 \times 10^{-3}$$

(*d*) At time 115 min,

$$k = \frac{2.303}{115}\log\frac{16.3}{10.2}$$

$$= \left(\frac{2.303}{115}\right)\log 1.5980 = \left(\frac{2.303}{115}\right)$$

$$= 0.2035 = 4.07 \times 10^{-3}$$

Average value of

$$k = (3.749 \times 10^{-3} + 3.689 \times 10^{-3} + 3.637 \times 10^{-3} + 4.07 \times 10^{-3})/4$$

$$= 0.003786$$

Ans.

Type : (*i*) In rate = $k[A]^a[B]^b$, order, $n = a + b$

Example 74. *The rate of reaction,* $2NO + Cl_2 \longrightarrow 2NOCl$ *is doubled when concentration of* Cl_2 *is doubled and it becomes 8 times when concentration of both NO and* Cl_2 *are doubled. Deduce the order of this reaction.* **(CBSE, 2000S)**

Solution. The rate of reaction is given as :

$$\text{Rate} = k[NO]^x[Cl_2]^y. \qquad ...(A)$$

Given :

Experiment No.	*[NO]*	*[Cl_2]*	*Rate*
1	0.1	0.1	1 (say)
2	0.1	0.2	2 (given)
3	0.2	0.2	8 (given)

(*i*) For experiment 1, $1 = k(0.1)^x(0.1)^y$

(*ii*) For experiment 2, $2 = k(0.1)^x(0.2)^y$

(*iii*) For experiment 3, $8 = k(0.2)^x(0.2)^y$

Determination of y. Dividing equations (*i*) and (*ii*), we get :

$$\frac{1}{2}=\frac{k(0.1)^x(0.1)^y}{k(0.1)^x(0.2)^y} \text{ or } \left(\frac{1}{2}\right)^1=\left(\frac{1}{2}\right)^y. \text{ Hence, } y=1$$

Determination of x. Dividing equations (*ii*) and (*iii*), we get :

$$\frac{2}{8}=\frac{k(0.1)^x(0.2)^y}{k(0.2)^x(0.2)^y} \text{ or } \left(\frac{1}{2}\right)^2=\left(\frac{1}{2}\right)^x. \text{ Hence, } x=2.$$

Substituting the values of x and y in equation (A), we get, Rate = $k[NO]^2[Cl_2]^1$. Hence order of reaction = 2 + 1 = 3

Ans.

EXAMPLE 75. *Three experimental runs were carried out for the reaction between Cl_2 and NO.*

$$Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$$

The following rate data were obtained

Run	*· Initial concentration*		*Initial Rate (mol L^-s^-)*
	[Cl_2](mol L^-)	*[NO](mol L^-)*	
1	0.020	0.01	2.40×10^{-4}
2	0.020	0.030	2.16×10^{-3}
3	0.040	0.030	4.32×10^{-3}

Determine (i) the order w.r.t. Cl_2 and NO (ii) the rate law and (iii) the rate constant.

SOLUTION. Rate of reaction is given as :

Rate = $k[Cl_2]^x[NO]^y$ ...(A)

(*i*) For experiment 1, $2.40 \times 10^{-4} = k(0.02)^x(0.01)^y$

(*ii*) For experiment 2, $2.16 \times 10^{-3} = k(0.02)^x(0.03)^y$

(*iii*) For experiment 3, $4.32 \times 10^{-3} = k(0.04)^x(0.03)^y$

Determination of x. Dividing equation (*ii*) by (*iii*), we get :

$$\frac{2.16\times10^{-3}}{4.32\times10^{-3}} = =\frac{k(0.02)^x(0.03)^y}{k(0.04)^x(0.03)^y} \text{ or}$$

$$\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x. \text{ Hence, } x=1$$

Determination of y. Dividing equation (*i*) by (*ii*), we get :

$$\frac{2.40\times10^{-4}}{2.16\times10^{-3}} = \frac{k(0.02)^x(0.01)^y}{k(0.02)^x(0.03)^y} \text{ or}$$

$$\frac{1}{9} = \left(\frac{1}{3}\right)^y \text{ or } \left(\frac{1}{3}\right)^2=\left(\frac{1}{3}\right)^y. \text{ or } y=2.$$

Substituting the value of x and y in equation (A), the rate equation is : rate = $k[Cl_2][NO]^2$; order of reaction w.r.t. Cl_2 = 1, w.r.t. NO = 2.

Determination of k. From experiment 1, we see that

$$2.40 \times 10^{-4} = k(0.02)^x(0.01)^y = k(0.02)\,(0.01)^2$$

$$\textbf{or} \quad k = \frac{(2.40\times10^{-4})}{(0.02\times0.01\times0.01)} = 120 \quad \text{or}$$

$$1.2 \times 10^2 \text{ mol}^{-2}\text{L}^2\text{s}^-$$ **Ans.**

EXAMPLE 76. *The following results were obtained for the decomposition of nitrous acid in contact with gold surface at 900C.*

t (minutes)	*15*	*30*	*45*	*65*	*80*
% decomposed	*17*	*32*	*44.5*	*57*	*65*

Show that order of reaction is unity.

SOLUTION. Initial concentration, a = 100 (say). x = 17, 32, 44.5, 57 and 65. So, $a - x$ = 100 – 17 = 83; 100 – 32 = 68; 100 – 44.5 = 55.5; 100 – 57 = 43; 100 – 65 = 35. We know that

$$k = \left(\frac{2.303}{t}\right)\log\frac{a}{a-x}.$$

(a) At time 15 min.,

$$k = \frac{2.303}{15}\log\frac{100}{83} = \left(\frac{2.303}{15}\right)\log 1.2048 = \left(\frac{2.303}{15}\right)\times 0.0809 = 0.0124$$

(b) At time 30 min.,

$$k = \frac{2.303}{30}\log\frac{100}{68} = \left(\frac{2.303}{30}\right)\log 1.4705 = \left(\frac{2.303}{30}\right)\times 0.1674 = 0.01285$$

(c) At time 45 min.,

$$k = \left(\frac{2.303}{45}\right)\log\frac{100}{55.5} = \left(\frac{2.303}{45}\right)\log 1.8018 = \left(\frac{2.303}{45}\right)\times 0.2557 = 0.01308$$

(d) At time 65 min.,

$$k = \left(\frac{2.303}{65}\right)\log\frac{100}{43} = \left(\frac{2.303}{65}\right)\log 2.3255 = \left(\frac{2.303}{65}\right)\times 0.3665 = 0.01298$$

(e) At time 80 min.,

$$k = \left(\frac{2.303}{80}\right)\log\frac{100}{35} = \left(\frac{2.303}{80}\right)\log 2.8571 = \frac{2.303}{80}\times 0.4559 = 0.01312$$

Since the value of k is almost same in all experiments, considering first order equation, the order of reaction is unity.

EXAMPLE 77. *In the following second order reaction, $2NO_2 \longrightarrow 2NO + O_2$ the rate of decomposition of NO_2 having 0.5 M concentration was found to be 1.4×10^{-3} mol L^- min^-. Find the rate of decomposition of NO_2 when the concentration of NO_2 is 0.75 M.*

SOLUTION. (*i*) Rate = 1.4×10^{-3} mol L^- min^-; $[NO_2] = 0.5$ M. For second order reaction, rate = $k[NO_2]^2$.

So $k = \text{rate}/[NO_2]^2$. Substituting the values, we get :

$$k = \frac{(1.4 \times 10^{-3})}{(0.5)^2} = 5.6 \times 10^{-3}$$

(*ii*) Also, rate = $k[NO_2]^2$

Substituting the values, we get :

$$\text{rate} = 5.6 \times 10^{-3} \times 0.75 \times 0.75$$
$$= 3.15 \times 10^{-3} \text{ mol L}^- \text{ min}^-$$ **Ans.**

EXAMPLE 78. *Calculate the order of the reaction with respect to the reactant A, and also the rate constant from the following data.*

$[A_0]_1 = 2 \times 10^{-3}$ M; $[r_0]_1 = 2.40 \times 10^{-4}$ Ms^-};

$[A_0)]_2 = 1 \times 10^{-3}$ M; $[r_0]_2 = 0.60 \times 10^{-4}$ Ms^-.

SOLUTION. We know,

$$r_0 = k[A_0]^a. \text{ Thus, } \frac{[r_0]_1}{[r_0]_2} = \left\{\frac{[A_0]_1}{[A_0]_2}\right\}^a$$

Taking logs, we get

$$\log\left\{\frac{[r_0]_1}{[r_0]_2}\right\} = \log\left\{\frac{[A_0]_1}{[A_0]_2}\right\}^a$$

or
$$a = \frac{\log\left[\frac{(r_0)_1}{(r_0)_2}\right]}{\log[(A_0)_1/[A_0)_2]}$$

$$= \frac{\left[\log\left(\frac{2.4 \times 10^{-4}}{(0.6 \times 10^{-4})}\right)\right]}{\left[\log\frac{(2 \times 10^{-3})}{(1 \times 10^{-3})}\right]}$$

$$= \left[\frac{\log 2.4 + \log 10^{-4} - \log 0.6 - \log 10^{-4}}{\log 2 + \log 10^{-3} - \log 1 - \log 10^{-3}}\right]$$

$$= 0.3802 - 4 - (-0.2218)$$
$$+ 4/0.3010 - 3 - 0 + 3 = \frac{0.602}{0.301} = 2.$$

So, the reaction is of second order.

But : rate constant, $k = \dfrac{\text{rate}}{[A]^2}$ or $k = \dfrac{2.4{\times}10^{-4}\text{mol L}^{-}\text{s}^-}{(2{\times}10^{-4}\text{mol L}^-)^2}$

$$= 6 \times 10^3 \text{ or } 0.6 \times 10^4 \text{ mol}^- \text{ Ls}^-$$ **Ans.**

EXAMPLE 79. *The initial rate of reaction, $A + 5B + 6C \longrightarrow 3D + 3E$ has been determined by measuring the rate of disappearance of A under the following conditions*

Experiment	*Initial concentration (mol L^-)*			*Initial rate*
	A	*B*	*C*	
I	0.02	0.02	0.02	2.08×10^{-3}
II	0.01	0.02	0.02	1.04×10^{-3}
III	0.02	0.04	0.02	4.16×10^{-3}
IV	0.02	0.02	0.04	8.32×10^{-3}

(i) Determine the order of reaction with respect to each reactant and overall order of the reaction (ii) What is the rate constant (iii) Calculate the initial rate of the reaction when concentration of all the reactants is 0.01 M (iv) Calculate the initial rate of change in concentration of B and D.

SOLUTION. The general rate expression is,

$$r = k[A_0]^a[B_0]^b[C_0]^c$$

(*i*) In experiment I and II,

$$[A_0] = [B_0] = [C_0] = 0.02 = k_0[A_0]^a.$$

Hence : $$\frac{(r_0)_1}{(r_0)_2} = \frac{2.08 \times 10^{-3}}{1.04 \times 10^{-3}}$$

$$= \frac{[A_0]_1^a}{[A_0]_2^a} = \frac{(0.02)^a}{(0.01)^a} \quad \text{or} \quad (2)^a = (2)^1$$

or $a = 1$ *i.e*,

order with respect to A = 1.

Similarly, $$\frac{(r_0)_3}{(r_0)_1} = \frac{4.16 \times 10^{-3}}{2.08 \times 10^{-3}} = \frac{(B_0)_3^b}{(B_0)_1^b} = \frac{(0.04)^b}{(0.02)^b}$$

or $(2)^b = (2)^1$ or $b = 1$ *i.e.*,

order with respect to B = 1.

Similarly, $$\frac{(r_0)_4}{(r_0)_1} = \frac{8.32 \times 10^{-3}}{2.08 \times 10^{-3}} = \frac{(C_0)_4^c}{(C_0)_1^c} = \frac{(0.04)^c}{(0.02)^c}$$

or $(2)^c = (2)^2$ or $c = 2$ *i.e*,

order with respect to $c = 2$. Hence overall order of reaction = 1 + 1 + 2 = **4** **Ans.**

We know, $$k = \frac{r}{[A_0]^a[B_0]^b[C_0]^c} = \frac{r}{[A_0][B_0][C_0]^2}$$

Using the data of set I, we have

$$k = \frac{2.08{\times}10^{-3}\text{ M min}^-}{16{\times}10^{-8}\text{M}^4}$$

$$= 1.3 \times 10^4 \text{ M}^{-3} \text{ min}^-$$ **Ans.**

Rate of reaction when $[A_0] = [B_0] = [C_0] = 0.01$ M, $r = k\,[A_0][B_0][C_0]^2 = 1.3 \times 10^4\ M^{-2}\ min^-$ (0.01 M) (0.01 M) $(0.01 \text{ M})^2 = 1.3 \times 10^{-4}$ M min^- **Ans.**

But $$r = \frac{-d[B]}{5dt} = \frac{1}{3} \cdot \frac{d[D]}{dt} = 1.3 \times 10^{-4} \text{ Mmin}^-$$

thus, $$\frac{d[B]}{dt} = -5 \times 1.3 \times 10^{-4} \text{ M min}^-$$

$$= -6.5 \times 10^{-4} \text{ M min}^-$$

Similarly, $$\frac{d[D]}{dt} = 3 \times 1.3 \times 10^{-4} \text{ M min}^-$$

$$= 3.9 \times 10^{-4} \text{ M min}^-$$ **Ans.**

Example 80. *In presence of an acid, N-chloroacetanilide changes slowly into p-chloroacetanilide. The former substance liberates I_2 from KI and not the latter and hence the progress of reaction can be measured by titrating the iodine liberated with $Na_2S_2O_3$ solution. The results obtained are :*

t(hours)	*0*	*1*	*2*	*4*	*6*	*8*
(a – x) i.e., Volume of hypo in mL ($Na_2S_2O_3$)	*45*	*32*	*22.5*	*11.3*	*5.7*	*2.3*

Show that the reaction is of first order and find out the fraction of N-chloroacetanilide decomposed after three hours.

Solution. $a = 45$, at time 1 hr, $a - x = 32$; at 2 hr, $a - x = 22.5$; at 4 hrs. $a - x = 11.3$; at 6 hrs. $a - x = 5.7$; at 8 hrs, $a - x = 2.3$. Using the relation, $k = \left(\frac{2.303}{t}\right)\log\frac{a}{a-x}$, we have :

(*a*) At time 1 hr,

$$k = \left(\frac{2.303}{1}\right)\log\frac{45}{32} = 2.303\log 1.4062$$

$$= 2.303 \times 0.1480 = 0.3408.$$

(*b*) At time 2 hr,

$$k = \left(\frac{2.303}{2}\right)\log\frac{45}{22.5} = 1.1515\log 2$$

$$= 1.1515 \times 0.3010 = 0.3466.$$

(*c*) At time 4 hrs,

$$k = \left(\frac{2.303}{4}\right)\log\frac{45}{11.3} = \left(\frac{2.303}{4}\right)\log 3.9823$$

$$= \left(\frac{2.303}{4}\right) \times 0.6001 = 0.3455$$

(*d*) At time 6 hrs,

$$k = \frac{2.303}{6}\log\frac{45}{5.7} = \left(\frac{2.303}{6}\right)\log 7.8947$$

$$= \left(\frac{2.303}{6}\right) \times 0.8973 = 0.3973 = 0.3444$$

(*e*) At time 8 hrs,

$$k = \left(\frac{2.303}{8}\right)\log\frac{45}{2.3} = \left(\frac{2.303}{8}\right)\log 19.5652$$

$$= \left(\frac{2.303}{8}\right) \times 1.2914 = 0.3717$$

Average value of

$$k = \frac{(0.3408 + 0.3466 + 0.3455 + 0.3444 + 0.3717)}{5}$$

$$= 0.3498$$

Let x = fraction of N-chloroacetanilide decomposed after 3 hours. Hence we have :

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \quad \textbf{or}$$

$$0.3498 = \left(\frac{2.303}{3}\right)\log\frac{45}{45-x}$$

or $\frac{(0.3498 \times 3)}{2.303} = \log 45 - \log(45 - x)$

or $0.4556 = 1.6532 - \log(45 - x)$

or $\log(45 - x)$

$= 1.6532 - 0.4556 = 1.1976$

or $45 - x = \text{antilog } 1.1976 = 15.7615$

or $x = 45 - 15.7615 = 29.24$ **Ans.**

Type : $t_{1/2} \propto a$ *i.e.,* initial concentration.

Example 81. *The half-life period of a substance is 50 minutes at a certain concentration. When the concentration is reduced to one half of the initial concentration, the half-life period is 25 minutes. Calculate the order of the reaction.*

Solution. On reducing the concentration to one half, the value of half-life ($t_{0.5}$) becomes one half the original value Or $t_{0.5}$ is directly proportional to the initial concentration. Hence the reaction is a zero order reaction.

Type : (*i*) $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{P_2}{P_1}\right)^{n-1}$ where n = order of reaction and P_1 and P_2 are the pressures at half-lives $(t_{1/2})_1$ and $(t_{1/2})_2$ respectively.

(*ii*) For y% hydrolysis in a given time t, $k = \frac{2.303}{t}\log\frac{a}{a-x}$ where $a = 100$, $a - x = y$.

(*iii*) If $t_{1/2}$ values are almost same irrespective of the initial pressure or concentration, reaction is of first order *i.e.,* $n = 1$.

Example 82. *At a certain temperature, the half-life period for the decomposition for the substance A is as follows :*

P(mm)	*500*	*700*	*900*
Half-life period	*18*	*17.9*	*18*

What is the order of reaction ?

Solution. Since the half-life periods are almost same irrespective of the initial concentration *i.e.,* pressure, the reaction is of **first order**.

Example 83. *Following data were obtained for the catalytic decomposition of ammonia.*

Initial pressure (mm)	*50*	*100*	*200*
Half-life (hrs)	*3.52*	*1.92*	*1.00*

Find the order of reaction.

Solution. We know, $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{P_2}{P_1}\right)^{n-1}$

Substituting the values for the given data we have :

(*i*) $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{P_2}{P_1}\right)^{n-1}$

$$\text{or} \qquad \left(\frac{3.52}{1.92}\right) = \left(\frac{100}{50}\right)^{n-1}$$

Taking logs, we get,

$$\log 3.52 - \log 1.92 = (n-1)\log 2$$

$$\text{or} \qquad 0.5440 - 0.2833 = (n-1) \times 0.301$$

$$\text{or} \qquad 0.2607 = 0.301\,(n-1)$$

$$\text{Thus,} \qquad n-1 = \frac{0.2607}{0.301} = 0.866.$$

$$\text{Hence,} \qquad n = 1 + 0.866 = 1.866 \approx 2.$$

$$(ii) \qquad \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{P_2}{P_1}\right)^{n-1}$$

$$\text{or} \qquad \left(\frac{1.92}{1}\right) = \left(\frac{200}{100}\right)^{n-1}$$

Taking logs, we get, $\log 1.92 = \log (2)^{n-1}$;

$$\log 1.92 = (n-1)\log 2$$

$$0.2833 = 0.301\,(n-1);$$

$$n-1 = \frac{0.2833}{0.301} = 0.941.$$

$$\text{Hence,} \qquad n = 1 + 0.941 = 1.941 \approx 2.$$

The order, n in both cases is 2.

EXAMPLE 84. *It was found that a solution of canesugar was hydrolysed to the extent of 25% in one hour. Calculate the time that would be taken for the sugar to be 50% hydrolysed assuming that the reaction is of first order.*

SOLUTION. Let initial concentration, $a = 100$; $x = 25$; $t = 1$ hour $= 60$ minutes. For first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

Substituting the values, we get :

$$k = \left(\frac{2.303}{60}\right)\log\frac{100}{100-25}$$

$$= \frac{92.303}{60}\log\frac{100}{75}$$

$$= \left(\frac{2.303}{60}\right)\log 1.3333$$

$$= \left(\frac{2.303}{60}\right) \times 0.1249 = 0.00479$$

Let t = time to hydrolyse sugar;

$a = 100$; $x = 50$.

$$\text{We know,} \qquad k = \left(\frac{2.303}{t}\right)\log\frac{a}{a-x}$$

Substituting the values, we get,

$$0.00479 = \left(\frac{2.303}{t}\right)\log\frac{100}{100-50} = \left(\frac{2.303}{t}\right)\log 2$$

$$= (2.3031 \times 0.3010)/t$$

$$\text{or} \qquad t = \frac{(2.303 \times 0.3010)}{0.00479} = 144.7\,\text{min}. \quad \textbf{Ans.}$$

EXAMPLE 85. *Pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below :*

t/s	*0*	*100*	*200*	*300*
p/Pa	*4.0 × 10^3*	*3.50 × 10^3*	*3.00 × 10^3*	*2.5 × 10^3*

Determine the order of reaction, its rate constant and half-life period.

SOLUTION. (*i*) For time interval 0 to 100*s*,

$$\text{rate} = \frac{-(3.5-4.0)10^3\text{Pa}}{(100-0)\,\text{s}}$$

$$= \frac{0.5{\times}10^3\text{Pa}}{100} = 5\text{Pas}^-$$

(*ii*) For time interval 100s to 200*s*,

$$\text{rate} = \frac{-(3.0-3.5)10^3\text{Pa}}{(200-100)\text{s}}$$

$$= \frac{0.5{\times}10^3}{100} = 5\text{Pas}^-$$

(*iii*) For time interval 200*s* to 300*s*, rate

$$= \frac{-(2.5-3.0)10^3\text{Pa}}{(300-200)\text{s}} = 5\ \text{Pas}^-.$$

Since the rate remains constant, the reaction is of zero order because for the units Pas$^-$ of rate constant, the order is zero.

(*iv*) Since k = rate = 5 Pas$^-$,

$$t_{0.5} = \frac{\text{(Initial concentration or pressure)}}{2k}$$

$$\text{Thus,} \qquad t_{0.5} = \frac{4.0{\times}10^3\text{Pa}}{2{\times}5\text{Pas}^-} = 400\text{s} \qquad \textbf{Ans.}$$

EXAMPLE 86. *The gas phase decomposition of dimethyl ether follows first order kinetics :*

$$CH_3 - O - CH_3(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes ? Assume ideal gas behaviour. **(IIT,1993)**

SOLUTION. $CH_3 - O - CH_3 \longrightarrow CH_4(g) + H_2 + CO$

Initial state	p_0	0	0	0	*Total pressure,* p_0
After 12 min.	$p_o - p$	p	p	p	$p_0 + 2p$

For a first order reaction

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} = 4.78 \times 10^{-2}\,\text{min}^{-1}$$

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

In the present case $a \propto p_0$ and $(a - x) \propto p_0 - p$

$$\therefore \qquad k = \frac{2.303}{t}\log\frac{p_0}{(p_0 - p)}$$

$$\text{or} \quad \log\frac{p_0}{(p_0 - p)} = \frac{kt}{2.303}$$

$$\text{or} \quad \log\frac{p_0 - p}{p_0} = -\frac{kt}{2.303} = -\frac{4.78 \times 10^{-2} \times 12}{2.303}$$

$$= -0.249$$

$$\text{or} \quad \frac{p_0 - p}{p_0} = \text{Antilog}\ (-0.249) = 0.564$$

$$\text{or} \quad p = p_0 - 0.564\, p_0 = p_0\,(1 - 0.564)$$

$$= (0.40\ \text{atm})\ (0.436) = 0.1744\ \text{atm}$$

Hence, total pressure of the system is

$$p_0 + 2p = (0.40 + 2 \times 0.1744)\ \text{atm}$$

$$= \mathbf{0.7488\ atm.}$$

Example 87. *Some $PH_3(g)$ is introduced into flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of reaction and calculate the rate constant.*

Time	*0*	*60*	*120*	*∞*
P(mm)	*262.40*	*272.90*	*275.51*	*276.40*

(Roorkee, 2001)

Solution. Total increase in pressure due to complete decomposition of $PH_3 \propto$ Initial conc. of PH_3 *i.e.,* $a \propto P_\infty - P_0$ or $a \propto (276.40 - 262.40)$ or $a \propto 14.0$

Increase in pressure at any time $\propto$ amount of PH_3 decomposed at that time.

i.e., $\quad P_t - P_0 \propto x$

∴ $\quad (a - x) \propto (P_\infty - P_0) - (P_t - P_0)$

i.e., $\quad (a - x) \propto (P_\infty - P_t)$

If the reaction follows first order rate law,

$$k = \frac{2.303}{t}\log\frac{a}{(a - x)}$$

$$= \frac{2.303}{t}\log\frac{P_\infty - P_0}{P_\infty - P_t}$$

$$\text{At } t = 60s, \quad k_t = \frac{2.303}{650}\log\frac{(276.4 - 262.4)}{(276.4 - 272.90)}$$

$$= \frac{2.303}{60}\log\frac{14}{3.5} = 2.31 \times 10^{-2}\, s$$

$$\text{At } t = 120s, \quad k_2 = \frac{2.303}{120}\log\frac{276.4 - 262.4}{276.4 - 275.51}$$

$$= \frac{2.303}{120}\log\frac{14}{0.89} = 1.967 \times 10^{-2} s^{-}$$

Since k comes out to be nearly constant, reaction is a first order reaction.

$$k = \frac{k_1 + k_2}{2} = \frac{2.31 + 1.967}{2} \times 10^{-2} s^{-}$$

$$= 2.138 \times 10^{-2} s^{-}$$ **Ans.**

Example 88. *While studying the decomposition of gaseous N_2O_5, it is observed that a plot of logarithm of its partial pressure versus time is linear. What kinetic parametres can be obtained from this observation ?* **(IIT, 1985)**

Solution. As the graph of logarithm of partial pressure versus time is linear, the reaction is of first order. Thus :

$$k = \frac{2.303}{t}\log\frac{p_0}{p}$$

$$\text{or} \qquad \log\frac{p_0}{p} = \frac{kt}{2.303};\ \log p_0 - \log p = \frac{kt}{2.303}$$

$$\text{or} \qquad \log p = \log p_0 - \frac{kt}{2.303}$$

Therefore, the slope of the line obtained by plotting $\log p$ against time, t will be $\frac{-k}{2.303}\cdot$ Thus, the value of rate constant k can be calculated from the slope. Hence the kinetic parameters that can be obtained from the graph are: (*i*) specific reaction rate (*ii*) order of reaction.

Example 89. *The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask, 10 mol of A is mixed with 12 mol of B. However as soon as B is added, A starts polymerising into a completely insoluble solid. This polymerisation follows first order kinetics. After 100 minutes, 0.525 mol of a solute is dissolved which arrests the polymerisation completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerisation reaction. Assume negligible volume change on mixing and polymerisation and ideal behaviour for the final solution.* **(IIT, 2001)**

Solution. Let the number of moles of A left after 100 min be Z.

∴ Total number of moles after 100 min

$$= Z + 12 + 0.525 = Z + 12.525$$

$$\text{Mole fraction of } A,\ x_A = \frac{Z}{Z + 12.525}$$

$$\text{Mole fraction of } B,\ x_B = \frac{12}{Z + 12.525}$$

$P°_A$ = Vapour pressure of pure A = 300 mm

$P°_B$ = Vapour pressure of pure B = 500 mm

According to Raoult's law.

$$P_{\text{mix}} = x_A \times P°_A + x_B \times P°_B$$

$$= \left(\frac{Z}{Z + 12.525} \times 300\right) + \left(\frac{12}{Z + 12.525} \times 500\right)$$

$$\therefore \qquad 400 = \frac{300\,Z}{(Z + 12.525)} + \frac{12 \times 500}{(Z + 12.525)}$$

$$= \frac{6000 + 300Z}{Z + 12.525}$$

This on solving gives, Z = 9.9 mol

According to first order rate law, $k = \dfrac{2.303}{t}\log\dfrac{[A_0]}{A}$

where $[A]_0 = 10$ mol., $[A] = 9.9$ mol and $t = 100$ min.

$$\therefore \quad k = \frac{2.303}{100\,\text{min}}\log\frac{10}{9.9}$$

$$= \mathbf{1.005 \times 10^{-4} min^{-1}}.$$

Example 90. *The rate constant for an isomerisation reaction, $A \to B$ is 4.5×10^{-3} min^{-1}. If the initial concentration of A is 1M, calculate the rate of reaction after one hour.* **(IIT, 1999; CBSE, 2009)**

Solution. From the units of rate constant (min^{-1}), it is clear that the given reaction is a first order reaction. Thus,

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$k = 4.5 \times 10^{-3}\ \text{min}^{-1}, a = 1\text{M}, (a-x) = ?$$

$$t = 1\text{hr} = 60\ \text{min}.$$

$$\therefore \quad 4.5 \times 10^{-3} = \frac{2.303}{60}\log\frac{1}{a-x}$$

$$\log\frac{1}{(a-x)} = \frac{4.5 \times 10^{-3} \times 60}{2.303} = 0.1172$$

$$\frac{1}{a-x} = \text{antilog}\ 0.1172$$

$$\text{or} \quad \frac{1}{(a-x)} = 1.310$$

$$\text{or} \quad (a-x) = 0.7634\ M$$

$\therefore$ Rate of reaction after 1 hr

$$= k[A] = 4.5 \times 10^{-3} \times 0.7634$$

$$= \mathbf{3.44 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}.$$

Example 91. *1.0 cm^3 of ethyl acetate was added to 25 cm^3 of 0.5 NHCl. 2.0 cm^3 of the mixture were withdrawn from time to time during the progress of the hydrolysis of ester and titrated against standard NaOH solution. The amount of NaOH required for titration at various intervals is given below.*

Time (min)	*0*	*20*	*75*	*119*	*∞*
NaOH added (cm^3)	*20.24*	*21.73*	*25.20*	*27.60*	*43.95*

The value of ∞ time was obtained by completing the hydrolysis on boiling. Show that it is a reaction of first order.

Solution. For pseudo first order reaction *e.g.*, hydrolysis of esters, $k = \dfrac{2.303}{k}\log\dfrac{V_\infty - V_0}{V_\infty - V_t}$.

Amount of NaOH used at $t = 0$ ($=V_0$) $\propto$ HCl present

Amount of NaOH used at any time, t (V_t) $\propto$ [HCl present + CH_3COOH formed]

$\therefore$ CH_3COOH formed at any time $\propto$ ethyl acetate reacted; $V_t - V_0 \propto x$.

Amount of NaOH used at time, $t = \infty$ ($= V_\infty$) $\propto$ [HCl present + maximum acetic acid formed]

But maximum CH_3COOH formed $\propto$ initial conc. of ethyl acetate *i.e.*, $V_\infty - V_0 \propto a$. For first order reaction :

$$k = \frac{2.303}{t}\log\frac{a}{a-x}; k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

t(min) 0	V_t 20.24	$V_\infty - V_t$ 43.95 – 20.24 = 23.71	$k = \dfrac{2.303}{t}\log$ $\dfrac{V_\infty - V_0}{V_\infty - Vt}$
20	21.73	43.95 – 21.73 = 22.22	$\therefore k = \dfrac{2.303}{20}\log\dfrac{23.71}{22.22}$ $= \dfrac{2.303}{20}$ log 23.71 – log 22.22 $= \dfrac{2.303}{20}$ (1.3749 – 1.3467 = 0.02816) = 0.00324 min^{-}
75	25.20	43.95 – 25.20 = 18.75	$k = \dfrac{2.303}{75}\log\dfrac{23.71}{18.75}$ = 0.000313 min^{-}
119	27.60	43.95 – 27.60 = 16.35	$k = \dfrac{2.303}{119}\log\dfrac{23.71}{16.35}$ = 0.00312 min^{-}

Since the value of k is almost constant, the reaction is of first order.

20.7 ZERO ORDER REACTIONS

Example 92. (*i*) *During the decomposition of a gas on the surface of a solid catalyst, the pressure of the gas at different times was observed to be as follows :*

t/s	*0*	*100*	*200*	*300*
p/Pa	*5.0 × 10^3*	*4.2 × 10^3*	*3.4 × 10^3*	*2.6 × 10^3*

Calculate the order of the reaction.

(*ii*) *The decomposition on platinum surface,*

$$2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$$

is a zero order reaction with k = 2.5 × 10^{-4} ms^{-}. What are the rate of production of N_2 and H_2? **(CBSE, 2007)**

Solution. (*i*) In order to get the order of reaction, let us first of all calculate the rate of reaction during different intervals of time.

Interval	**Rate of reaction**
0 to 100 s	$-\dfrac{(4.2-5)\times 10^3\,\text{Pa}}{100\ -\ 0} = \dfrac{0.8\times 10^3\,\text{Pa}}{100\ \text{s}} = 8\ \text{Pa s}^{-}$
100 to 200 s	$-\dfrac{(3.4-4.20)\times 10^3\,\text{Pa}}{200\ -\ 100} = \dfrac{0.8\times 10^3\,\text{Pa}}{100\ \text{s}} = 8\ \text{Pa s}^{-}$

$$200 \text{ to } 300 \text{ s} - \frac{(2.6-3.4)\times 10^3 \text{ Pa}}{300\ -\ 200} = \frac{0.8\times 10^3 \text{ Pa}}{100 \text{ s}} = 8 \text{ Pa s}^{-}$$

From above it is found that, as the rate of reaction remains constant through out, so the order of reaction is **zero.**

(*ii*) Reaction: $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

$$\text{Rate} = -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt}$$
$$= \frac{1}{3}\frac{d[H_2]}{dt}$$

For a zero order reaction, rate does not depend upon the concentration of reactants. Hence :

$$r = k[NH_3]^{\circ} = k \times 1 = k$$

Thus : (*i*)
$$\frac{d[N_2]}{dt} = \frac{1}{2}\times\frac{d[NH_3]}{dt}$$
$$= \frac{1}{2}\times k = \frac{1}{2}\times 2.5\times 10^{-4} \text{ms}^{-}$$
$$= 1.25 \times 10^{-4} \text{ ms}^{-}$$ **Ans.**

(*ii*)
$$\frac{d[H_2]}{dt} = \frac{3}{2}\times\frac{d[NH_3]}{dt}$$
$$= \frac{3}{2}\times k = \frac{3}{2}\times 2.5\times 10^{-4} \text{ms}^{-}$$
$$= 3.75 \times 10^{-4}$$ **Ans.**

Note. For zero order reaction, $t_{\frac{1}{2}} = \frac{a}{2k}$ while for first order reaction $t_{\frac{1}{2}} = 0.693/k$ where a is initial concentration and k is rate constant **(AIPMT, 2009)**

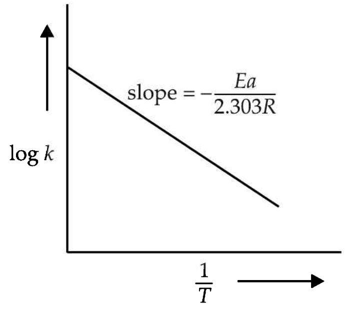
20.8 ARRHENIUS LAW

Effect of temperature on rate constant – Arrhenius equation. According to Arrhenius equation :

$$k = Ae^{-Ea/RT} \qquad ...(i)$$

where A = constant called frequency factor, Ea = energy of activation, R is gas constant and T is absolute temperature.

Calculation of *Ea*. *First method.* Taking logs of equation (*i*), we get,



$$\ln k = \ln A + \ln e^{-Ea/RT}; \ln k = \ln A - \frac{Ea}{RT}$$

$$2.303 \log k = 2.303 \log A - \frac{Ea}{RT}$$

$$\therefore \quad \log k = \log A - \frac{Ea}{2.303R}\times\frac{1}{T}$$

When a graph is drawn between log k and $\frac{1}{T}$, we get a straight line having slope = $-\frac{Ea}{2.303R}$.

Hence, **Ea = – 2.303 R × slope.**

Second method. Let k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively. Hence by using Arrhenius equation, we have :

$$\log k_1 = \log A - \frac{Ea}{2.303RT_1} \qquad ...(i)$$

$$\log k_2 = \log A - \frac{Ea}{2.303RT_2} \qquad ...(ii)$$

Subtracting equation (*i*) from (*ii*), we get :

$$\log k_2 - \log k_1 = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or
$$\log\frac{k_2}{k_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$
$$= \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\therefore \quad E_a = \left(\log\frac{k_2}{k_1}\right)\times\frac{2.303R(T_1T_2)}{T_2 - T_1}$$

Activation energy of forward reaction (E_a^f) and activation energy of backward reaction (E_a^r) are related to enthalpy of reaction ($\Delta_r H^0$) by the equation :

$$\Delta_r H^0 = E_a^f - E_a^r$$

Example 93. *For a chemical reaction, A → B, the rate of the reaction is* 2×10^{-3} *mol dm*$^{-3}$*s*$^{-}$*, when the initial concentration is 0.25 mol dm*$^{-3}$*. The rate of the same reaction is* 1.6×10^{-2} *mol dm*$^{-3}$*s*$^{-}$ *when the initial concentration is* 0.1 *mol dm*$^{-3}$*. The order of the reaction is:*

(*a*) 0 (*b*) 3 (*c*) 1 (*d*)2. **(Karnataka, CET, 2009)**

Solution. We know that, rate = $k[A]^n$ where R is rate constant, n is order of reaction and [A] is concentration of reactant.

Given: $\text{Rate}_I = 2 \times 10^{-3} \text{ mol dm}^{-3}\text{s}^{-}; [A_0] = 0.05 \text{ mol dm}^{-3}$
$\text{Rate}_{II} = 1.6 \times 10^{-2} \text{ mol dm}^{-3}\text{s}^{-}; [A_0] = 0.1 \text{ mol dm}^{-3}$
$\therefore \quad 2 \times 10^{-3} = k[0.05]^n$ —(1); $1.6 \times 10^{-2} = k[0.1]^n$ ...(2)

Dividing (1) by (2), we get; $\frac{2\times 10^{-3}}{1.6\times 10^{-2}} = \left(\frac{0.05}{0.10}\right)^n$

or $\frac{(0.05)^n}{(0.05)^n \times 2^n}$ or $\frac{1}{2^n} = \frac{1}{8}$ or $\frac{1}{2^3}$. Hence, n = 3.

So, the correct answer is (*b*).

Example 94. *For a first order reaction, A → P, the temperature (T) dependent rate constant (k) was found to follow the equation, log k* = –(2000) $\frac{1}{T}$ + *6.0. The pre-exponential factor, A and the activation energy, Ea respectively are:*

(*a*) $1.0 \times 10^6 s^{-}$ and 9.2 J mol^{-} (*b*) $6.0 s^{-}$ and 16.6 J mol^{-}

(*c*) $1.0 \times 10^6 s^{-}$ and 16.6 kJ mol^{-} (*d*) $1.0 \times 10^6 s^{-}$ and 38.3k J mol^{-} **(IIT-JEE, 2009)**

Solution. Given $\log k = -(2000)\dfrac{1}{T} + 6.0$ ...(*i*)

But $\log k = \log A - \dfrac{Ea}{2.303RT}$ ...(*ii*) (Arrhenius equation)

Comparing equations (*i*) and (*ii*), we get:

$\log A = 6$; $A = 1 \times 10^6 s^{-}$ and

$$\frac{-E_a}{2.303RT} = -\frac{2000}{T};\ E_a = 2000 \times 2.303 \times 8.314\ \text{J}$$

$(\because R = 8.314\ \text{J})$

or $E_a = 38294\ \text{J} \simeq 38.3\ k\text{J mol}^{-}$. So, the correct answer is (*d*).

Example 95. *The bacterial growth follows the rate low, $\dfrac{dN}{dt} = kN$, where k is a constant and N is the number of bacterial cell at anytime. If the population of bacteria (no. cells) is doubled in 5 minutes, find the time by which the population will be eight times of the initial one* **(WB-JEE, 2011)**

Solution. Given $dN/dt = kN$; $N = N_0\, e^{kt}$. Also: in 5 minutes, $N_0 = 2N_0$. So, $k = \dfrac{2.303}{t} \log N/N_0$

$$= (2.303/5)\log\frac{2N_0}{N_0} = \frac{2.303}{5}\log 2 = \frac{2.303}{5} \times 0.3010 = 0.138$$

$$\text{For } 8\,N_0,\ t = \frac{2.303}{0.138}\log\frac{8N_0}{N_0} = \frac{2.303}{0.138}\log 8$$

$$= \frac{2.303}{0.138} \times 0.9030$$

$\simeq$ 15 minutes. **Ans**

Example 96. *The value of rate constant for a second order reaction is 6.7×10^{-5} mol^{-} Ls^{-} at 298 K and 1.64×10^{-4} mol^{-}Ls^{-} at 313 K. Find the Arrhenius frequency factor A and activation energy of the reaction.*

Solution. Given : Rate constant, $k_1 = 6.7 \times 10^{-5}$ mol^{-} Ls^{-}; $T_1 = 298\ K$; $k_2 = 1.64 \times 10^{-4}$ mol^{-} $L\ s^{-}$; $T_2 = 313\ K$; Arrhenius frequency, A = ?; activation energy, E_a = ?; $R = 8.314$ JK^{-} mol^{-}. We know that (*a*),

$$E_a = \left(\frac{2.303RT_1T_2}{T_2 - T_1}\right)\log\frac{k_2}{k_1}$$

Substituting the values we get :

$$E_a = \frac{(2.303 \times 8.314 \times 313}{(313 - 298)}\log\frac{(1.64 \times 10^{-4})}{(6.7 \times 10^{-5})}$$

$= 119{,}062.03 \times \log 2.4477$

$= 119{,}062.03 \times 0.3887$

$= 46{,}279.4$ J = 46.2794 kJ **Ans.**

(*b*) $\log k_1 = \log A - E_a/(2.303\ RT_1)$; $\log 6.7 \times 10^{-5} = \log A - 46279.4/8.314 \times 298)$; $\log 6.7 + \log 10^{-5} = \log A - 18.679$; $0.826 - 5 = \log A - 18.679$; $\log A = 0.826 - 5 + 18.679 = 14.505$. Hence, A = antilog of $14.505 = 3.19 \times 10^{14}$ at 298 K **Ans.**

Example 97. *The rate constant for a reaction is 1.6×10^{-5} and $6.36 \times 10^{-3} s^{-}$ at 600 K and 700 K respectively. Calculate the activation energy for the reaction.* **(PSEB, 1995, HSB, 2002)**

Solution. Rate constant, $k_1 = 1.6 \times 10^{-5}$; $k_2 = 6.36 \times 10^{-3} s^{-}$; $T_1 = 600\ K$; $T_2 = 700\ K$; activation energy, E_a = ? $R = 8.314$ J K^{-} mol^{-}. We know that,

$$E_a = \left(\frac{2.303RT_1T_2}{T_2 - T_1}\right)\log\frac{k_2}{k_1}$$

Substituting the values, we get :

$$E_a = \left[\frac{2.303 \times 8.314 \times 600 \times 700}{700 - 600}\right]\log\frac{(6.36 \times 10^{-3})}{(1.6 \times 10^{-5})}$$

$= 80418 \times \log 397.5$

$= 80418 \times 2.5993 = 209030$ J

$= 209.03\ k$J **Ans.**

Example 98. *Calculate the activation energy of a reaction whose reaction rate at 27°C get doubled for 10°C rise in temperature. (R = 8.314 JK^{-} mol^{-}, log 2 = 0.301)* **(JEE Main, 2013)**

Solution. Activation energy, E_a = ?; $T_1 = 27 + 273 = 300\ K$; $T_2 = 300 + 10 = 310\ K$; $\dfrac{k_2}{k_1} = 2$

We know that : $E_a = \left(\dfrac{2.303RT_1T_2}{T_2 - T_1}\right)\log\dfrac{k_2}{k_1}$

Substituting the values, we get :

$$E_a = \left[\frac{2.303 \times 8.314 \times 300 \times 310}{(310 - 300)}\right]\log 2$$

$= 178068.4 \times 0.3010 = 53599$ J

$= 53.599\ k$J mol^{-} **Ans.**

Example 99. *If a first order reaction has activation energy of 25000 cal and a frequency factor of 5×10^{12} sec^{-1}, at what temperature will the reaction rate have a half life of 1 minute ?*

Solution. Activation energy, E_a = 25000 cal = 25000 × 4.1846 J (*i*) $t_{1/2}$ = 1 minute = 60 seconds; A = $5 \times 10^{12} s^{-}$; temperature, T = ?; (*ii*) $t_{1/2}$ = 80 days = 80 × 24 × 60 × 60 seconds = 6912000 seconds. We know that rate constant,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 0.01155.$$

But, $\log k = \log A - \left[\dfrac{E_a}{2.303RT}\right]$

where, $R = 8.314$ JK^{-} mol^{-}

Substituting the values, we get :

$$\log 0.01155 = \log 5 \times 10^{12} - \left[\frac{25000 \times 4.1846}{2.303 \times 8.314 \times T}\right]$$

$$-1.9374 = \log 5 + \log 10^{12} - \left[\frac{5463.7}{T}\right]$$

$$-1.9374 = 0.6989 + 12 - \left(\frac{5463.7}{T}\right)$$

$$-1.9374-0.6989-12=\left[\frac{-5463.7}{T}\right]$$

$$-14.6363=\frac{-5463.7}{T} \quad \text{or} \quad T=\frac{-5463.7}{-14.6363}$$

$$=373.2K \qquad \textbf{Ans.}$$

EXAMPLE 100. *Rate constant k of a reaction varies with temperature according to equation : log k = constant – E_a/2.303 RT. What is the activation energy for the reaction ? When a graph is plotted for log k versus 1/T, a straight line with a slope – 6670 K is obtained. Calculate energy of activation for this reaction. (R = 8.314 JK^{-} mol^{-}).*

SOLUTION. Activation energy, E_a = ? ; R = 8.314 JK^{-} mol^{-}; slope = –6670 K. We know, E_a = – 2.303 R × slope. Substituting the values, we get :

$$E_a=-2.303\times 8.314\times -6670$$

$$=127711\text{ J}=127.711\text{ kJ} \qquad \textbf{Ans.}$$

EXAMPLE 101. *The following values for the first order rate constant were obtained for a certain reaction.*

Temperature (K)	*k(sec)$^{-}$*
298	*3.46×10^{-5}*
308	*13.50×10^{-5}*

Calculate the activation energy. R = 8.314 J K^{-} mol^{-}.

(AISB, 1990 comptt., 1991 Comptt.)

SOLUTION. T_1 = 298 K; T_2 = 308 K; $k_1=3.46\times 10^{-5}s^{-}$; $k_2=13.50\times 10^{-5}s^{-}$. Activation energy, E_a = ? ; R = 8.314 JK^{-} mol^{-}. We know that,

$$E_a=\left(\frac{2.303RT_1T_2}{T_2-T_1}\right)\log\frac{k_2}{k_1}$$

Substituting the values, we get :

$$E_a=\left[\frac{2.303\times 8.314\times 298\times 308}{308-298}\right]\log\left(\frac{13.50\times 10^{-5}}{3.46\times 10^{-5}}\right)$$

$$=175740.1\log 3.9=175740.1\times 0.591$$

$$=103862.4\text{ J}=103.8624\,k\text{J} \qquad \textbf{Ans.}$$

EXAMPLE 102. *The no. of flashes of a fire fly changes with temperature as follows :*

t°C	*No. of flashes per minute*
25	*7*
28	*10*

Calculate the energy of activation for the chemical reaction that leads to the flash.

SOLUTION. $k_1=7\text{ min}^{-}$; $k_2=10\text{ min}^{-}$; $T_1=273+25=298$K; $T_2=273+28=301$ K; R = 8.314 JK^{-} mol^{-}.

$$\therefore \quad \log\frac{10}{7}=\frac{E_a}{2.303\times 8.314}\left[\frac{301-298}{301\times 298}\right]$$

$$\therefore \quad E_a=88.678\text{ kJ mol}^{-}.$$

EXAMPLE 103. *The slope of the line in the graph of log k (k = rate constant) Vs $\frac{1}{T}$ for a reaction is – 5841 K. Calculate the energy of activation for this reaction (R = 8.314 JK^{-} mol^{-}].*

SOLUTION. Slope = $\dfrac{-E_a}{2.303R}$

$$\therefore \quad -5841\,K=\frac{-E_a}{2.303\times 8.314\,\text{JK}^{-}\text{mol}^{-}}$$

$$\therefore \quad E_a=\mathbf{111838\ kJ\ mol^{-}}.$$

EXAMPLE 104. *The experimental data for the decomposition of nitrogen pentoxide in the gaseous phase at 300 K is as follows :*

E_a = 100 kJ mol^{-}, A (frequency constant) = $10^{10}s^{-}$. What is the half life period of the reaction at 300 K ?

SOLUTION. (1)

$$\log k=\log A-\frac{E_a}{2.303RT}$$

$$=\log 10^{10}-\frac{100000}{2.303\times 8.314\times 300}$$

$$=-7.409$$

$$=-1+1-7.409=\bar{8}.591$$

Antilog of .591 is 3.899.

$$\therefore \quad k=\text{antilog }\bar{8}.591=3.899\times 10^{-8}s^{-}$$

$$(2) \quad t_{0.5}=\frac{0.693}{3.899\times 10^{-8}s^{-}}=1.8\times 10^{7}s$$

EXAMPLE 105. *The specific rate constant for a reaction increases by a factor 4 if the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction.*

(IIT, Advance entrance, 1980, CBSE, 1991, PSEB, 1999)

SOLUTION. 27°C = 27 + 273 = 300 K

47°C = 47 + 273 = 320 K

Using Arrhenius equation (relating rate constant and activation energy),

$$\text{We have : }\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

$$\log\frac{4k_1}{k_1}=\frac{E_a}{2.303\times 1.98}\left(\frac{320-300}{300\times 320}\right)$$

[∵ R = 1.98 cal.]

$$\log 4=\frac{E_a}{2.303\times 1.98}\left(\frac{20}{96000}\right)$$

$$0.6021=\frac{E_a\times 20}{2.303\times 1.98\times 96000}$$

$$\therefore \quad E_a=\frac{0.6021\times 2.303\times 1.98\times 96000}{20}$$

$$=13179\text{ cal}=\mathbf{13.179\ k\ cal.}$$

EXAMPLE 106. *The following data were obtained during the first order decomposition of $2A_{(g)}\rightarrow B_{(g)}+C_{(s)}$ at a constant volume and at a particular temperature. The rate constant in min^{-1} is:*

(*a*) 0.0693 (*b*) 69.3 (*c*) 6.93 (*d*) 6.93×10^{-4}

(Karnataka CET, 2011)

S. No.	*Time*	*Total pressure in pascal*
1	*At the end of 10 minutes*	*300*
2	*After completion*	*200*

SOLUTION. $2A_{(g)} \rightarrow B_{(g)} + C_{(s)}$

At the end of 10 min.$2(1-x)$ $\quad x$

$2-2x$

Total number of moles $= 2 - 2x + x = 2 - x$

At the end of reaction, 1 mol of gas present has pressure $= 200$ pascal

$\therefore$ 2 mol of gas has pressure

$= 200 \times 2 = 400$ pascal

$\therefore \quad 400 - x = 300; x = 400 - 300 = 100$

Pressure due to $2 - 2x$ mol of

$A = 400 - 200 = 200$ pascal

$\therefore$ Rate constant,

$$k = \frac{2.303}{10}\log\frac{a}{a-x} = \frac{2.303}{10}\log\frac{400}{200}$$

or
$$k = \frac{2.303}{10}\log 2$$

$$= \frac{2.303}{10} \times 0.3010 = 0.0693 \text{ min}^{-}.$$

So, the correct answer is (*a*)

EXAMPLE 107. *A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol^{-1}.* **(I.I.T., 2000)**

SOLUTION. According to the Arrhenius equation,

$$K = Ae^{-Ea/RT}.$$

Let E_a of the reaction in absence of catalyst $= x$ kJ mol^{-1}.

$\therefore \quad E_a$ in presence of catalyst $= x - 20$ kJ mol^{-1}

Therefore, the Arrhenius equation in the two conditions is :

$$K = Ae^{-\frac{x}{R\times 500}} \qquad ...(i)$$

$$K = Ae^{-\frac{x-20}{R\times 400}} \qquad ...(ii)$$

Dividing equation (*i*) by (*ii*), we get :

$$e^{-\frac{x}{500R}} = e^{-\frac{x-20}{400R}}$$

or
$$\frac{x}{500} = \frac{x-20}{400}$$

$\therefore \quad x = 100$ kJ mol^{-1}

EXAMPLE 108. *At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C.*

SOLUTION. $T_1 = 380 + 273 = 653$ K;

$T_2 = 450 + 273 = 723$ K

$t_{1/2}$ at 653 K $= 360$ min

$$k_{653} = \frac{0.693}{t_{1/2}} = \frac{0.693}{360} = 1.925 \times 10^{-3}\text{ min}^{-1}$$

Calculation of k_{723}

$$E_a = 200 \text{ kJ mol}^{-1} = 200 \times 10^3 \text{ J mol}^{-1}$$

According to Arrhenius law

$$\log\frac{k_{723}}{k_{635}} = \frac{E_a}{2.303R}\frac{[T_2 - T_1]}{T_1T_2}$$

or
$$\log\frac{k_{723}}{1.925\times10^{-3}\text{ min}^{-1}} = \frac{200\times10^3}{2.303\times8.314}\frac{[723-653]}{723\times653}$$

$$\log\frac{k_{723}}{1.925\times10^{-3}\text{ min}^{-1}} = 1.5487$$

or
$$\frac{k_{723}}{1.925\times10^{-3}} = \text{Antilog } 1.5487 = 35.376$$

or
$$k_{723} = 35.376 \times 1.925 \times 10^{-3}$$

$$= \mathbf{6.81 \times 10^{-2}\ min^{-1}}$$

Calculation of time required for 75% completion. For a first order reaction,

$$t = \frac{2.303}{k}\log\frac{a}{(a-x)}$$

$$= \frac{2.303}{6.81\times10^{-2}}\log\frac{100}{(100-75)}$$

$$= \frac{2.303}{6.81\times10^{-2}}\log 4 = 33.817 \times 06020$$

$$= \mathbf{20.35\ min.}$$

EXAMPLE 109. *A first order reaction, $A \longrightarrow B$ requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 25 minutes, 25% decomposition took place. What will be the percentage decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.* **(IIT, 1993)**

SOLUTION. Calculation of rate constant at 25°C (298 K), k_1

Here, $a = 100$, $(a - x) = 100 - 25 = 75$, $t = 20$ min.

$$\therefore \quad k_1 = \frac{2.303}{20}\log\frac{100}{75} = 0.014386\text{ min}^{-1}$$

Calculation of rate constant at 40°C (313 K), k_2. According to Arrhenius equation :

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\therefore \log\frac{k_2}{0.014386} = \frac{70\times10^3}{2.303\times8.314}\times\left[\frac{1}{298} - \frac{1}{313}\right]$$

$$= \frac{70\times10^3\times15}{2.303\times8.314\times298\times313} = 0.587$$

$$\frac{k_2}{0.014386} = \text{Antilog } 0.587$$

$$= 3.8636;$$

$$k_2 = 0.014386 \times 3.8636$$

$$= 0.05558$$

Calculation of percentage decomposition at 40°C. Let the % decomposition in this case = x.

Thus here $a = 100$, $(a - x) = 100 - x$.

$$t = 20 \text{ min}; k_2 = 0.05558.$$

Substituting the values in the first order rate equation

$$k_2 (= 0.05558) = \frac{2.303}{20} \log \frac{100}{100 - x}$$

$$= \frac{0.0558 \times 20}{2.303} = \log \frac{100}{(100 - x)}$$

$$\log \frac{100}{(100 - x)} = 0.48458 \quad \frac{100}{(100 - x)}$$

$$= \text{Antilog } 0.48458 = 3.052$$

$$100 - x \times 3.052 = 100 ; 305.2 - 3.052x = 100$$

$$\text{or} \quad 3.052x = 305.2 - 100 = 205.2;$$

$$x = 67.2346 = 67.23\%.$$

EXAMPLE 110. *Two reactions (i) A $\longrightarrow$ Products (ii) B $\longrightarrow$ Products follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K.*

(IIT, 1992)

SOLUTION. $T_1 = 300$ K. Let k_1 and k_2 be the rate constants for reaction (*i*) at temperature T_1 and T_2 respectively.

According to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \quad E_a = \log \frac{k_2}{k_1} \times \frac{2.303R(T_1 T_2)}{T_2 - T_1}$$

$$= \log 2 \times \frac{2.303 \times 300 \times 310 \times R}{(310 - 300)}$$

$$= \frac{0.301 \times 2.303 \times 8.314 \times 300 \times 310}{10} \text{ J}$$

$$= 53598.593 \text{ J}$$

$$E_a = \mathbf{53.598 \text{ kJ}}$$

Activation energy for second reaction,

$$E_a = \frac{53.598}{2} = \mathbf{26.799 \text{ kJ}}$$

$t_{1/2}$ for first reaction at 310 K = 30 min.

Rate constant for first reaction at 310 K (k_2)

$$= \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{min}^{-1}$$

Rate constant for second reaction at 310 K (k_2)

$$= 0.0231 \times 2 = 0.0462 \text{ min}^{-1}$$

Now according to Arrhenius equation,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \frac{[T_2 - T_1]}{T_1 T_2}$$

$$= \frac{26799}{2.303 \times 8.314} \times \frac{(310 - 300)}{310 \times 300}$$

$$\log \frac{k_2}{k_1} = 0.1504$$

$$\text{or} \quad \log 0.0462 - \log k_1$$

$$= 0.1504$$

$$\log k_1 = \log 0.0462 - 0.1504$$

$$= \bar{2}.6646 - 0.1504$$

$$\log k_1 = \bar{2}.5142$$

$$\therefore \quad k_1 = \text{antilog } \bar{2}.5142 = 0.03267.$$

EXAMPLE 111. *The activation energy of a reaction is 75.2 kJ mol^{-} in the absence of a catalyst and 50.14 kJ mol^{-} with a catalyst. How many times will the rate of reaction grow in the presence of the catalyst if the reaction proceeds at 25°C ? (R = 8.314 JK^{-} mol^{-}).* **(CBSE,2005)**

SOLUTION. Let k_1 and k_2 are the rate constants. Let E_1 = activation energy in the absence of a catalyst. E_2 = activation energy in the presence of a catalyst. T = 25 + 273 = 298 K.

$$\ln k_1 = \ln A - \frac{E_1}{RT} \quad \text{...(1)}$$

$$\ln k_2 = \ln A - \frac{E_2}{RT} \quad \text{...(2)}$$

Subtracting equation (1) from (2), we get :

$$\ln k_2 - \ln k_1 = \frac{E_1}{RT} - \frac{E_2}{RT} ; \ln \frac{k_2}{k_1} = \frac{1}{RT}[E_1 - E_2]$$

$$\textbf{or} \quad \log \frac{k_2}{k_1} = \frac{1}{2.303RT}[E_1 - E_2]$$

$$= \frac{(75.2 - 50.14) \times 1000 \text{ J mol}^{-}}{2.303 \times 8.314 \text{ JK}^{-}\text{mol}^{-} \times 298 \text{ K}}$$

$$= \frac{25.06 \times 1000}{2.303 \times 8.314 \times 298} = 4.392$$

$$\therefore \quad \frac{k_2}{k_1} = \text{antilog } 4.392 = 24660$$

Hence, the rate of reaction increases by 24660 times.

Ans.

EXAMPLE 112. *$N_2O_5(g)$ decomposes at 473 K as $N_2O_5(g) \longrightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$. If the initial pressure is 114 mm and after 25 minute of reaction, total pressure of gaseous* *mixture is 133 mm, calculate the average rate of reaction in (a) atm min^{-} (b) mol L^{-}.*

SOLUTION. (*a*) Let p = decrease in pressure of N_2O_5 in 25 minutes, then

$$N_2O_5\,(g) \longrightarrow N_2O_4\,(g) + \frac{1}{2}O_2(g)$$

Initial pressure	114 mm	0	0
Pressure after 25 min.	$114 - p$	p	$\frac{1}{2}p$

$$\text{Total pressure} = 114 - p + p + \frac{1}{2}p = 114 + \frac{p}{2}.$$

So, $\quad 114 + p/2 = 133$ mm (given)

$\therefore \quad p = 2 \times (133 - 114 = 19\text{ mm})$

$= 38$ mm or $(38/760)$ atm.

$$\therefore \text{ Average rate of reaction} = \frac{(38/76)\text{ atm}}{25\text{ min}}$$

$= \mathbf{0.002\ atm\ min^{-}}$ **Ans.**

(*b*) Applying $pV = nRT$ *i.e.*, $\frac{n}{V} = \frac{p}{RT}$;

decrease in molar concentration

$$= \frac{(38/760)\text{ atm}}{0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 473\text{ K}}$$

$= \mathbf{0.0012875\ mol\ L^{-}}$ **Ans.**

EXAMPLE 113. *The rate constants of a reaction at 700 K and 760 K are 0.011 M^{-}s^{-} or L mol^{-}s^{-} and 0.105 M^{-} s^{-} or L mol^{-} s^{-} respectively. Calculate the values of E_a and frequency factor, A.* **(DB 2009)**

SOLUTION. $k_1 = 0.011$ M^{-}s^{-}; $k_2 = 0.105$ M^{-}s^{-}; $T_1 = 700$ K; $T_2 = 760$ K; E_a = ?

We know that :

(*i*) $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$\log 0.105 - \log 0.011$

$$= \frac{E_a}{2.303 \times 8.314\text{ JK}^{-}\text{mol}^{-}}\left[\frac{760 - 700}{760 \times 700}\right]\text{K}^{-}$$

$[-0.9788 - (-1.9586)]$ *i.e.*, 0.9798

$$= \frac{E_a}{2.303 \times 8.314\text{ J mol}^{-}}\left[\frac{60}{760 \times 700}\right]$$

$$\therefore \quad E_a = \frac{0.9798 \times 2.303 \times 8.314\text{ J mol}^{-} \times 760 \times 700}{60}$$

$= 166342$ J mol^{-}

(*ii*) $$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

$$\log 0.011 = \log A - \frac{166342\text{ J mol}^{-}}{2.303 \times 8.314\text{ J K}^{-}\text{mol}^{-}} \times \frac{1}{700\text{ K}}$$

$-1.9586 = \log A - 12.41;$

$\log A = 12.41 - 1.9586 = 10.4514$

$\therefore \quad A = \text{antilog } 10.4514 = 2.82 \times 10^{10}$ **Ans.**

EXAMPLE 114. *In a pseudo first order hydrolysis of ester in water, the following results are obtained.*

t in second	*0*	*30*	*60*	*90*
(Ester)M	*0.55*	*0.31*	*0.17*	*0.085*

Calculate the average rate of reaction between the time interval 30 to 60 seconds. **(ISC, 2011)**

SOLUTION. For first order reaction, rate constant

$$k = \frac{2.303}{t}\log\frac{a}{a - x} \qquad \ldots(1)$$

When $t = 0, a = 0.55$; $t = 30, a - x = 0.31$; $t = 60$, $a - x = 0.17$; $t = 90, a - x = 0.085$. Substituting these values is equation (1), one by one, we get:

(*i*) $$k = \frac{2.303}{30}\log\frac{0.55}{0.31} = \frac{2.303}{30}$$

$[\log 55 - \log 31 = 1.7404 - 1.4914 = 0.249]$

$$= \frac{2.303}{30} \times 0.249 = 0.0191$$

(*ii*) $$k = \frac{2.303}{60}\log\frac{0.55}{0.17} = \frac{2.303}{60}$$

$[\log 55 - \log 17 = 1.7404 - 1.2304 = 0.51]$

$$= \frac{2.303}{60} \times 0.51 = 0.0191$$

(*iii*) $$k = \frac{2.303}{90}\log\frac{0.550}{0.085}$$

$= \frac{2.303}{90}$ $[\log 550 - \log 85 = 2.7404 - 1.9294 = 0.811]$

$$= \frac{2.303}{90} \times 0.811 = 0.02$$

$\therefore$ Average rate of reaction

$= (0.0191 + 0.0191 + 0.02)/3 = 0.0194$

EXAMPLE 115. *At 310 K, in presence of a catalyst, the activation energy of a reaction is lowered by 2 k cal. Calculate how much rate of reaction will increase. ($R = 2 \times 10^{-3}$ k cal mol^{-} K^{-})*

SOLUTION. $$\log k = \log A - \frac{E_a}{2.303\,RT} \qquad \ldots(i)$$

In presence of catalyst, let rate constant = k' ;

$E_a = E_a - 2$

$$\therefore \quad \log k' = \log A - \frac{E_a - 2}{2.303\,RT} + \frac{2k\text{ cal mol}^{-}}{2.303\,RT} \qquad \ldots(ii)$$

Subtracting equation (*i*) from equation (*ii*), we get :

$$\log k' - \log k = \frac{2k\text{ cal mol}^{-}}{2.303\,RT}$$

$$\log\frac{k'}{k} = \frac{2k \text{ cal mol}^{-}}{2.303\times 2\times 10^{-3}\, k \text{ cal mol}^{-}\ \text{K}^{-}\times 300\ \text{K}}$$

$$\log\frac{k'}{k} = 1.4474;\ \frac{k'}{k} = \text{antilog } 1.4474 = 28;$$

$k' = 28\,k$. *i.e.*, rate of reaction will increase 28 times.

EXAMPLE 116. *At constant temperature and volume, X decomposes as :*

$$2X(g) \longrightarrow 3Y(g) + 2Z(g)$$

Px is the partial pressure of X :

Observation No.	*Time (in minute)*	*Px (in mm of Hg)*
1	*0*	*800*
2	*100*	*400*
3	*200*	*200*

What is the order of reaction with respect to X ?

(i) Find the rate constant.

(ii) Find the time for 75% completion of the reaction.

(iii) Find the total pressure when pressure of X is 700 mm of Hg. **(IIT-JEE(mains), 2005)**

SOLUTION. For first order reaction, $k = \frac{2.303}{t}\log\frac{P_0}{P_t}$

Or
$$k_1 = \frac{2.303}{100}\log\frac{800}{400}$$
$$= \frac{2.303}{100}\log 2 = \frac{2.303}{100}\times 0.301$$
$$= 6.932\times 10^{-3}\ \text{min}^{-}$$

Similarly,
$$k_2 = \frac{2.303}{t}\log\frac{P_0}{P_1} = \frac{2.303}{200}\log\frac{800}{200}$$
$$= \frac{2.303}{200}\log 4$$
$$= \frac{2.303}{200}\times 0.602 = 6.932\times 10^{-3}\ \text{min}^{-}.$$

From above we see that the value of k_1 = value of k_2. So, the reaction is of first order and hence :

Order of reaction with respect to X = 1 **Ans.**

(*i*) Rate constant, $k = 6.932\times 10^{-3}$ min^{-} (found above) **Ans.**

(*ii*) To find time for 75% completion of reaction; $a = 100$, $a - x = 100 - 75 = 25$.

$$\therefore\ 6.932\times 10^{-3} = \frac{2.303}{t}\log\frac{100}{25} = \frac{2.303}{t}\log 4$$

$$6.932\times 10^{-3} = \frac{2.303}{t}\times 0.602$$

$$\therefore\quad t = \frac{2.303\times 0.602}{6.932\times 10^{-3}} = \mathbf{200\ min.}$$ **Ans.**

(*iii*) For reaction :	$2X(g)$	$\longrightarrow$	$3Y(g)$	+	$2Z(g)$
Initial pressure	800		0		0
After time, t	800 – 2P		3P		2P

When pressure of X is 700 mm of Hg, then :

$$800 - 2P = 700;\ 2P = 100;$$
$$P = \frac{100}{2} = 50 \text{ mm of Hg.}$$

$$\text{Total pressure} = 800 - 2P + 3P + 2P$$
$$= 800 + 3P \textit{ i.e.}, 800 + (3\times 50)$$
$$= \mathbf{950\ mm\ of\ Hg}$$ **Ans.**

EXAMPLE 117. *The value of rate constant of a reaction increases by 9% when its temperature is raised from 27°C to 28°C while the equilibrium constant increases by 4%. Calculate the activation energy of the forward and backward reaction.*

SOLUTION. (*a*) $T_1 = 27 + 273 = 300$ K; $T_2 = 28 + 273 = 301$ K.

Let rate constant at 300 K = k; k_1 = rate constant at 301 K.

$$= k + \frac{k\times 9}{100} = k + 0.09k = 1.09k = k_2$$

Using Arrhenius equation, we have :

$$\log\frac{k_2}{k_1} = \frac{E_a^f}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right];$$

$$\log\frac{1.09}{1} = \frac{E_a}{2.303\times 8.314}\left[\frac{301-300}{300\times 301}\right]$$

$$0.0374 = \frac{E_a^f}{2.303\times 8.314}\left[\frac{1}{300\times 301}\right]$$

$$E_a^f = 0.0374\times 2.303\times 8.314\times 300\times 301$$

[$\because$ R = 8.314 JK^{-} mol^{-}]

$$\therefore\quad E_a^f = 64664 \text{ J mol}^{-} = 64.664 \text{ kJ mol}^{-}.$$

(*b*) At 300 K, equilibrium constant, k_1 = K

At 301 K, equilibrium constant, $k_2 = \text{K} + \frac{4\text{K}}{100} = 1.04\,\text{K}$

Using Arrhenius equation, we have :

$$\log\frac{k_2}{k_1} = \frac{\Delta_r\text{H}^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right];$$

$$\log\frac{1.04}{1} = \frac{\Delta_r\text{H}^\circ}{2.303\times 8.314}\left[\frac{301-300}{300\times 301}\right]$$

$$0.017 = \frac{\Delta_r\text{H}^\circ}{2.303\times 8.314}\left[\frac{1}{300\times 301}\right]$$

$$\therefore\quad \Delta_r\text{H}^\circ = 0.017\times 2.303\times 8.314\times 300\times 301$$
$$= 29393 \text{ J mol}^{-} = 29.393 \text{ kJ mol.}$$

But, $\Delta_r\text{H}^\circ = E_a^f - E_a^r$.

Hence
$$E_a^r = E_a^f - \Delta_r\text{H}^\circ$$
$$= 64.664 \text{ kJ mol}^{-} - 29.393 \text{ kJ mol}^{-}$$
$$= 35.271 \text{ kJ mol}^{-}.$$

For endothermic reaction, $\Delta_r\text{H}^\circ > 0$. Hence $E_a^r < E_a^f$.

For exothermic reaction $\Delta_r\text{H}^\circ < 0$. Hence $E_a^r > E_a^f$.

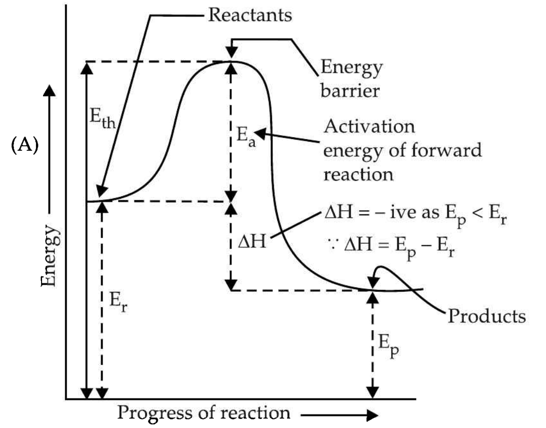
20.9 THRESHOLD ENERGY, ACTIVATION ENERGY ETC.

Type : Calculation of threshold energy, activation energy, energy of reactants and products, enthalpy change (ΔH) from exothermic and endothermic reactions.

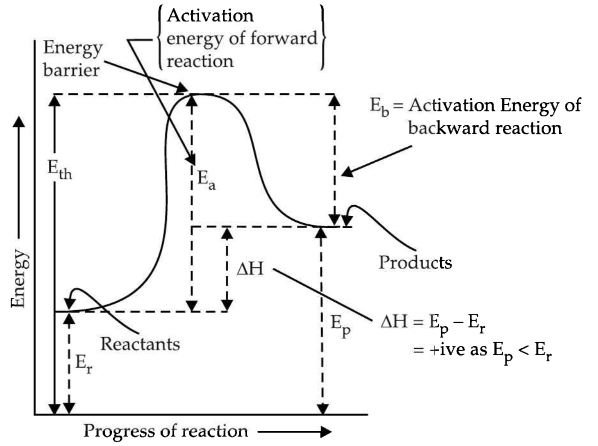
(*i*) $\left.\begin{array}{l}\text{Threshold energy for}\\ \text{forward reaction } (E_{th})\end{array}\right] = \text{Energy of reactants } (E_R) + \text{Activation energy } (E_a)$

(*ii*) $\left.\begin{array}{l}\text{Threshold energy for}\\ \text{backward reaction } (E_{th})\end{array}\right] = \text{Energy of products } (E_P) + \text{Activation energy of backward reaction } (E_b)$

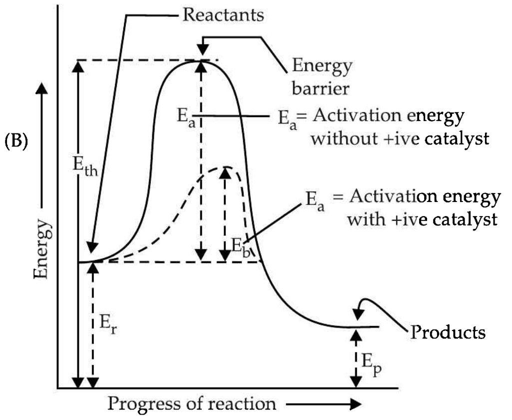
(*iii*) Energy level diagram for endothermic, exothermic, catalysed and uncatalysed reactions.

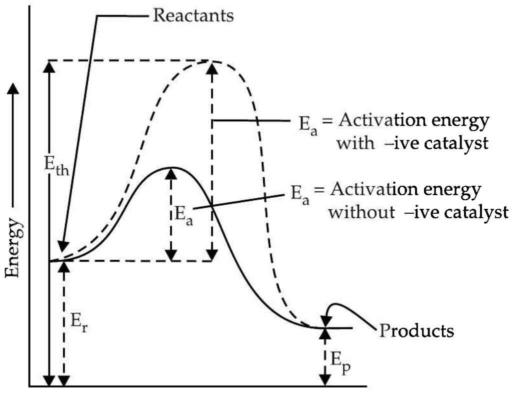


(Exothermic reaction, ΔH = –ive)



(Endothermic reaction, ΔH = +ive)





Example 118. *For a hypothetical reaction, the mean potential energies of reactants and products are 40 and 25 k cal mol⁻. Calculate the activation energies of the forward and reverse reactions if the threshold energy is 65 k cal. Also, calculate the heat of reaction.*

Solution. (*i*) Activation energy of the forward reaction,

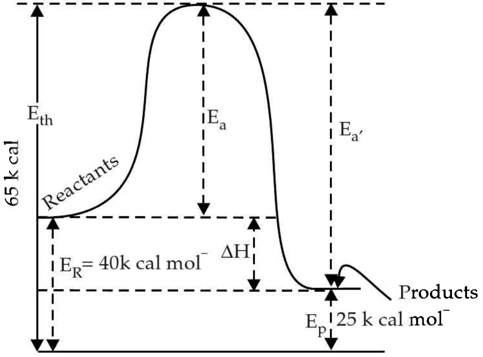
$$E_a = E_{th} - E_R = 65 - 40 = 25\ k\ \text{cal.} \qquad \textbf{Ans.}$$

(*ii*) Activation energy of the backward reaction,

$$E_{a'} = E_{th} - E_P = 65 - 25 = 40\ k\ \text{cal.} \qquad \textbf{Ans.}$$

(*iii*) $\Delta H = E_P - E_R = 25 - 40 = -15\ k$ cal.

Ans. (see figure)



Example 119. *From the data of the reaction $A \to B$, $\Delta H = +\ 20\ k$ cal mol⁻, $E_{act} = 30\ k$ cal mol⁻. Find the value of ΔH and E_{act} of the reverse reaction, $B \to A$.*

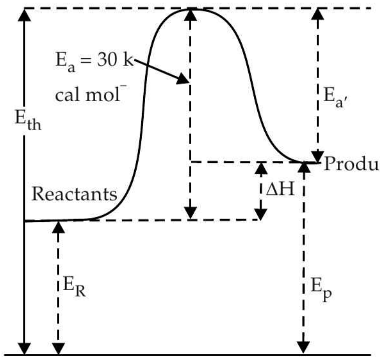
Solution. (*i*) $\Delta H = E_P - E_R$; $20 = E_P - E_R$.

ΔH for the reverse reaction, $E_P - E_R = -20\ k$ cal mol⁻.

(*ii*) Activation energy of the reverse reaction,

$$E'_a = E_a - \Delta H = 30 - (+\ 20) = 10\ k\ \text{cal.}$$

Ans. (see figure).

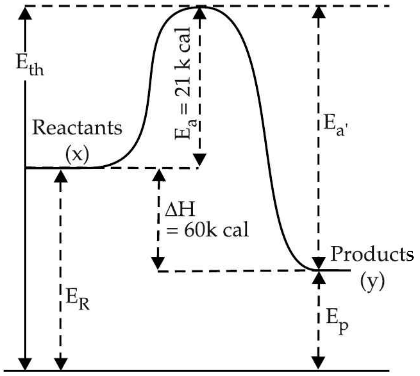


Example 120. *An exothermic reaction, $x \rightarrow y$ has an activation energy of 21.0 k cal mol^{-} of x and heat of reaction is 60 k cal. Find the activation energy of the reaction, $y \rightarrow x$.*

Solution. Activation energy of the backward reaction,

$$E'_a = E_a + \Delta H = 21 + 60$$

$$= 81\ k\ \text{cal.}$$ **Ans.**



Example 121. *The reaction, $A + B \rightarrow C + D + 40$ kJ has an activation energy of 18 kJ. Then the activation energy for the reaction, $C + D \rightarrow A + B$ is:*

(*a*) 58 kJ (*b*) –40 kJ (*c*) –18 kJ (*d*) 22 kJ

(J and K-ECT, 2011)

Solution. Activation energy of products

= ΔH + Activation energy of reactants

= 40 + 18 = 58 kJ

So, the correct answer is (*a*).

Example 122. *The activation energy of a reaction at a given temperature is found to be 2.303 RTJ mol^{-}. The ratio of rate constant to the Arrhenius factor is:*

(*a*) 0.01 (*b*) 0.1 (*c*) 0.02 (*d*) 0.001

(Karnataka CET, 2011)

Solution. Let E_a = activation energy, *k* is rate constant and *A* is Arrhenius factor. We know that:

$$\log\frac{k}{A} = \frac{-E_a}{2.303\,RT};\ \log\frac{k}{A} = -\frac{2.300\,RT}{2.303\,RT} = -1;$$

$$\frac{k}{A} = \text{antilog}(-1) \text{ or } \frac{k}{A} = 0.1.$$

So, the correct answer is (*b*).

20.10 AIEEE PATTERN EXAMPLES

Example 123. *The rate law for a reaction between the substance A and B is given by, Rate = $k[A]^n[B]^m$. On doubling the concentration of A and halving that of B, the ratio of the new rate to the earlier rate of reaction will be as :*

(*a*) $2^{(n-m)}$; (*b*) $\frac{1}{2^{(m+n)}}$; (*c*) $(m + n)$; (*d*) $(n - m)$.

(AIEEE, 2003)

Solution. Given : $R = k[A]^n[B]^m$ ....(1)

New concentration of A = $(2A)^n$;

New concentration of B = $\left(\frac{B}{2}\right)^m$

$$\therefore \quad \text{New rate, } R_1 = k[2A]^n\left[\frac{B}{2}\right]^m \quad ...(2)$$

Dividing relation (2) by (1), we get :

$$\frac{R_1}{R} = \frac{k\,2^n[A]^n[B]^m}{k[A]^n[B]^m 2^m}$$

$$= 2^n \times 2^{-m} = 2^{(n-m)}.$$

Hence, the answer is (*a*).

Example 124. *For the gaseous reaction $2A + B \rightarrow C + D$, the rate is given by K [A] (B]. The volume of the container containing the reaction mixture is suddenly reduced to one fourth of its original volume. With respect to the original rate, now the rate would be :*

(*a*) $\frac{1}{16}$ *times* ; (*b*) *12 times;*

(*c*) *4 times;* (*d*) $\frac{1}{4}$ *times.*

Solution. Since the volume of the container is reduced to one fourth of its original volume, the concentration and hence rate would become four times. So, the correct answer is (*c*).

Example 125. *Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reactions is:*

(*a*) *0.5 mol^{-} dm^3* (*b*) *1.0 mol dm^{-3}*

(*c*) *1.5 mol dm^{-3}* (*d*) *2.0 mol^{-} dm^{-3}* **(IIT–JEE, 2008)**

Solution. (*i*) For zero order reaction,

$$t_{1/2} = \frac{A_0}{2k_0}$$

$$\therefore \quad k_0 = \frac{A_0}{2 \times t_{1/2}} = \frac{1.386\,\text{mol dm}^{-3}}{2 \times 20\,s} \quad ...(1)$$

(*ii*) For first order reaction,

$$k_1 = \frac{2.303}{t_{1/2}}\log\frac{a}{0.5a}$$

$$= \frac{2.303}{t_{1/2}}\log 2 = \frac{2.303}{t_{1/2}} \times 0.301 = \frac{0.693}{t_{1/2}}$$

$$\therefore \quad k_1 = \frac{0.693}{40\,s} \quad ...(2)$$

From equations (1) and (2), we have

$$\frac{k_1}{k_0} = \frac{0.693}{40s} \times \frac{2 \times 20s}{1.386\ \text{mol dm}^{-3}} = 0.5\ \text{mol}^{-}\,\text{dm}^3$$

So, the correct answer is (*a*).

Example 126. *The rate law for the reaction, $xA + yB \rightarrow mP + nQ$ is rate = $k[A]^c[B]^d$. What is the total order of reaction?*

(*a*) $x + y$ (*b*) $m + n$ (*c*) $c + d$ (*d*) x/y (*e*) two

(Kerala PMT, 2011)

Solution. Rate = $k[A]^c[B]^d$. So, order of reaction = sum of exponents = $c + d$.

So, the correct answer is (*c*).

EXAMPLE 127. *The rate of reaction,* $2N_2O_5 \rightarrow 4NO_2 + O_2$ *can be written is three ways:*

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5];\ \frac{d[NO_2]}{dt}$$

$$= k'[N_2O_5];\ \frac{d(O_2)}{dt} = k''[N_2O_5].$$

The relationship between k and k' and between k and k'' are

(*a*) $k' = 2k,\ k'' = k$; (*b*) $k' = 2k;\ k'' = k/2$;

(*c*) $k' = 2k;\ k = 2k$; (*d*) $k' = k;\ k'' = k$

(AMU, 2010; AIPMT, 2011)

SOLUTION. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$:

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

Rate constant: k k' k''

∴ $1/2\,k = 1/4\,k' = k''$. Hence, $k' = 2k$; $k'' = 1/2k$. So, the correct answers is (*b*).

EXAMPLE 128. *The rate of reaction, A + B → products is given by the equation, r = k [A] [B]. If B is taken in large excess, the order of reaction would be :*

(a) 1.5; *(b) 2.5;*

(c) 1; *(d) unpredictable.*

SOLUTION. It is given that concentration of B is in large excess. So, the reaction will follow first order kinetics because in such a case, the rate will not depend upon the concentration of B. So, order of reaction = 1. Thus, the correct answer is (*c*).

EXAMPLE 129. *In a reaction,* $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, *the rate of appearance of ammonia is* 2.5×10^{-4} *mol* $L^{-}s^{-}$, *the rate of disappearance of* H_2 $\frac{-d[H_2]}{dt}$ *will be:* **(CBSE-PMT, 2009)**

(a) Cannot be predicted; *(b)* 375×10^{-9};

(c) 2.1×10^{-9}; *(d)* 3.00×10^{-4}.

SOLUTION. Given reaction : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. For one mol of NH_3, we have :

$$\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g) \quad \text{[After dividing by 2]}$$

∴ Rate of disappearance of H_2

$$= \frac{3}{2} \times \text{Rate of appearance of } NH_3$$

$$= \frac{3}{2} \times 2.5 \times 10^{-4}$$

$$= 3.75 \times 10^{-4}\ \text{mol}\ L^{-}s^{-}$$

So, the correct answer is, (*d*).

EXAMPLE 130. *For a first order reaction A → B, the reaction rate at reactant concentration of 0.01 M is found to be* 2.0×10^{-5} *mol* $L^{-}s^{-}$. *The half-life period of the reaction is :*

(a) 30s; *(b) 220s;* *(c) 300s;* *(d) 347s.*

[CBSE–PMT (Prelims), 2005]

SOLUTION. In A → B reaction, rate of reaction = 2×10^{-5} mol $L^{-}s^{-}$. Order of reaction, $n = 1$ (given). But rate = $k\,[A]^n$.

Where k = rate (or velocity) constant ; [A] = 0.01 M.

$$\therefore \quad \text{Rate} = k\,[A]^1$$

$$\text{or} \quad k = \frac{\text{rate}}{[A]} = \frac{2\times10^{-5}\ \text{mol}\,L^{-}s^{-}}{0.01\,\text{mol}\,L^{-}}$$

$$\text{or} \quad k = 2 \times 10^{-3}s^{-}$$

$$\text{But, half-life } t_{0.5} = \frac{0.693}{k}$$

$$\therefore \quad t_{0.5} = \frac{0.693}{2\times10^{-3}s^{-}} \approx 347\,s$$

So, the correct answer is (*d*).

EXAMPLE 131. *The time required for 100% completion of a zero order reaction is:*

(*a*) *a k* (*b*) *a*/2 *k* (*c*) *a*/*k* (*d*) 2*k*/*a*

[Karnataka CET, 2011]

SOLUTION. Time needed for 100% completion of reaction is the time at which the concentration of A i.e.; [A] = 0

$$\therefore \quad t_{\text{completion}} = \frac{[A]_0}{k} = \frac{a}{k}.$$

So, the correct answer is (*c*).

EXAMPLE 132. *For reaction,* $2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$, K_C *at 427°C is* 3×10^{-6} *L mol*$^{-}$. *The value of* K_p *is nearly :*

(a) 7.5×10^{-5}; *(b)* 2.5×10^{-5};

(c) 2.5×10^{-4}; *(d)* 1.72×10^{-4}. **(AIIMS – 2005)**

SOLUTION. $K_C = 3 \times 10^{-6}$ L mol^{-}; $T = 427 + 273 = 700$ K, $R = 0.0821$ L atm K^{-} mol^{-}.

For the reaction :

$$\underset{2\,\text{mol}}{2NOCl(g)} \rightarrow \underset{2\,\text{mol}}{2NO(g)} + \underset{1\,\text{mol}}{Cl_2(g)}$$

$$\Delta n = n_p - n_R = (2 + 1) - 2 = 1\ \text{mol}$$

We know that ;

$$K_p = K_c\,(RT)^{\Delta n} = 3.0 \times 10^{-6}\ L\ \text{mol}^{-} \times (0.0821\ L\ \text{atm}\ \text{mol}^{-}\ K^{-} \times 700\ K)^1$$

$$\therefore \quad k_p = 1.72 \times 10^{-4}\ L^2\ \text{mol}^{-2}\ \text{atm}.$$

So, the correct answer is (*d*).

EXAMPLE 133. *The rate of reaction between two reactants A and B decreases by a factor of 4 if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is:*

(a) 2; *(b) –2;* *(c) 1;* *(d) –1*

[CBSE – PMT (Prelims), 2005]

SOLUTION. Let a = order of reaction with respect to A

b = order of reaction with respect to B

But rate of reaction = $k\,[A]^a[B]^b$; [B] = [2B].

$$\text{So,} \quad \frac{r_1}{r_2} = \frac{k[A_0]^a[B]^b}{k[A_0]^a[2B]^b}$$

$$4 = \left(\frac{1}{2}\right)^b$$

Taking logs of both sides, we get :

$$\log 4 = b \log\left(\frac{1}{2}\right)$$

$$0.602 = b \times -0.301;\ b = \frac{0.602}{-0.301} = -2$$

So, the correct answer is (*b*).

Example 134. *The rate of a chemical reaction doubles for every 10°C rise in temperature. If the temperature is raised by 50°C, the rate of reaction increases by about:*

(a) 10 times (b) 24 times; (c) 32 times (d) 64 times

[AIEEE, 2011]

Solution. Since rate of a reaction becomes 2 times for every 10°C, we have;

Rate of reaction at 50°C $= 2^{50/10} = 2^5 = 32$ times.

So, the correct answer is (*c*).

Example 135. *The rate constant k_1 and k_2 for two different reactions are $10^{16}.e^{-2000/T}$ and $10^{15}.\ e^{-1000/T}$ respectively. The temperature at which $k_1 = k_2$ is :*

(a) 2000 K (b) $\frac{1000}{2.303}K$ (c) 1000 K (d) $\frac{2000}{2.303}K$

(CBSE–PMT, 2008 Prelims)

Solution. Given : $k_1 = 10^{16}.\ e^{-2000/T};\ k_2 = 10^{15}.\ e^{-1000/T}$

The temperature at which $k_1 = k_2$ will be :

$$10^{16}.\ e^{-2000/T} = 10^{15}.\ e^{-1000/T};\ \text{or}\ \frac{10^{15}}{10^{16}} = \frac{e^{-2000/T}}{e^{-1000/T}}$$

$$\text{or} \qquad 10^{-1} = e^{-1000/T}$$

$$\log_e e^{-1000/T} = \log_e 10^{-1};$$

$$2.303 \log_{10} e^{-1000/T} = 2.303 \log_{10} 10^{-1}$$

$$\text{or} \quad -\frac{1000}{T}\log_{10} e = -1.\ \text{So,}\ T = \frac{1000}{2.303}K.$$

Hence the correct answer is (*b*).

Example 136. *For the reaction : $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ if the concentration of NO_2 increases by 5.2×10^{-3} M in 100 seconds, then the rate of reaction is :*

(a) $1.3 \times 10^{-5}\ Ms^{-}$; (b) $5 \times 10^{-4} Ms^{-}$

(c) $7.6 \times 10^{-4} Ms^{-}$; (d) $2 \times 10^{3}\ Ms^{-}$; (e) $2.5 \times 10^{-5}\ Ms^{-}$.

(Kerala PET, 2005)

Solution. $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

∴ Rate of reaction with respect to NO_2 will be :

$$\text{rate} = \frac{1}{4}\frac{d(NO_2)}{dt} = \frac{1}{4} \times \frac{5.2 \times 10^{-3} M}{100 s}$$

$$= \mathbf{1.3 \times 10^{-5}\ Ms^{-}}.$$

So, the correct answer is (*a*).

Example 137. *$t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its initial value. If the rate constant for the first order reaction is k, the $t_{1/4}$ can be written as :*

(a) $\frac{0.10}{k}$; (b) $\frac{0.29}{k}$; (c) $\frac{0.69}{k}$; (d) $\frac{0.75}{k}$.

(AIEEE, 2005)

Solution. We know that for first order reaction :

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

Substituting the values, we get :

$$t_{1/4} = \frac{2.303}{k}\log\left(\frac{1}{3/4}\ \text{or}\ \frac{4}{3}\right)$$

$$= \frac{2.303}{k}[\log 4 - \log 3]$$

$$= \frac{2.303}{k}[0.602 - 0.477]$$

$$= \frac{2.303 \times 0.125}{k} = \frac{0.29}{k}.$$

So, the correct answer is (*b*).

Example 138. *For a first order reaction, the time taken to reduce the initial concentration by a factor of 1/4 is 20 minutes. The time required to reduce initial concentration by a factor of 1/16 is*

(a) 20 min (b) 10 min (c) 80 min (d) 40 min

(e) 5 min

(Kerala PMT, 2011)

Solution. The various steps to reduce the initial concentration are

$$\xrightarrow[\text{half-life}]{\text{first}} \frac{1}{2} \xrightarrow[\text{half-life}]{\text{Second}} \frac{1}{4} \xrightarrow[\text{half-life}]{\text{Third}} \frac{1}{8}$$

$\xrightarrow[\text{half-life}]{\text{Fourth}} \frac{1}{16}$. So 1/16 is four half-lives. Also, 1/4 is 2 half-lives. Since time taken for 2 half-lives is 20 minutes, the time taken for four half-lives will be 40 minutes. So, the correct answer is (*d*).

Example 139. *Consider an endothermic reaction $X \longrightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions respectively. In general,*

(a) $E_b < E_f$; (b) $E_b > E_f$; (c) $E_b = E_f$;

(d) There is no definite relation between E_b and E_f.

(AIEEE, 2005)

Solution. For an endothermic reaction, ΔH = positive.

∴ $\Delta H = E_f - E_b$ or $E_b + \Delta H = E_f$ *i.e.*, $E_b < E_f$.

So, the correct answer is (1).

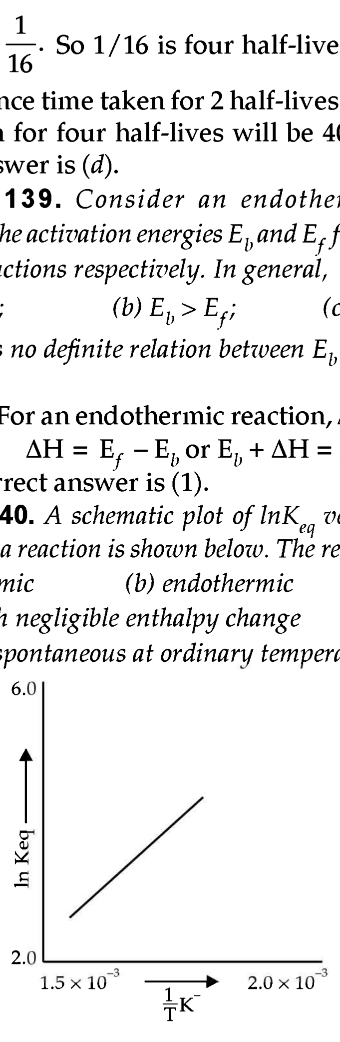
Example 140. *A schematic plot of $\ln K_{eq}$ versus inverse of temperature for a reaction is shown below. The reaction must be :*

(a) exothermic (b) endothermic

(c) one with negligible enthalpy change

(d) highly spontaneous at ordinary temperature.

(AIEEE, 2005)



Solution. From the diagram, it is clear that, $k_1 = 2.0$ and $k_2 = 6$; $\frac{1}{T_1} = 1.5 \times 10^{-3}$, $\frac{1}{T_2} = 2.0 \times 10^{-3}$.

But, $$\ln\frac{k_2}{k_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\frac{2.303\log k_2}{2.303\log k_1} = \frac{\Delta H}{R}[1.5\times10^{-3}-2.0\times10^{-3}]$$

$$\log\frac{6}{2} = \frac{\Delta H}{R}(-0.5\times10^{-3})$$

$$\therefore \qquad \Delta H = \frac{(-\log 3)\times R}{0.5\times10^{-3}} = -\text{ive}$$

Since the value of ΔH is negative, the reaction is exothermic. So, the correct answer is (*a*).

Example 141. *For a spontaneous reaction, the ΔG, equilibrium constant (K) and $E°_{cell}$ will be respectively.*

(*a*) –*ive*, >1, +*ive*, (*b*) +*ive*, >1, –*ive*,

(*c*) –*ive*, < 1, –*ive*, (*d*) –*ive*, > 1, –*ive*.

(AIEEE, 2005)

Solution. The conditions for a spontaneous reaction are, ΔG = – ve, K > 1 and $E°_{cell}$ = +ive. So, the correct answer is (*a*).

Example 142. *For the reaction, A ⟶ B, the rate of reaction is quadrupled when the concentration of A is doubled. The rate expression of the reaction is $r = k[A]^n$ when the value of n is :*

(*a*) 1 (*b*) zero (*c*) 3 (*d*) 2

(P.U., PET 1983 CPMT, 1988)

Solution. The rate expression for the reaction which becomes 4 times on doubling the concentration can be written as :

(*i*) $r = k[A]^n$; (*ii*) $4r = k\,[2A]^n$]

Dividing (*ii*) by (*i*), we get,

$$\frac{4r}{r} = \frac{k[2A]^n}{k[A]^n} \text{ or } 4 = (2)^n \textbf{ or } (2)^2 = (2)^n.$$

Hence, $n = 2$. Hence rate = $k\,[A]^2$. So, the correct answer is (*d*).

Example 143. *For a first order reaction, we have k = 100 sec⁻. The time for completion of 50% (or half life time for completion) reaction is:*

(*a*) 1m sec; (*b*) 4 m sec; (*c*) 7m sec; (*d*) 10m sec.

(U.P.S.E., 1991, CBSE-PMT, 2009)

Solution. Time for completion of 50% reaction, $t_{1/2} = \frac{0.693}{k}$ for a first order reaction.

or $t_{1/2} = \frac{0.693}{100\,\text{sec}^-} \approx \frac{0.7}{100} = 7\times10^{-3}$ seconds = 7 milliseconds **or** 7 m sec. So, the correct answer is (*c*).

Example 144. *The half-life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301)*

(*a*) 230.3 minutes (*b*) 23.03 minutes

(*c*) 46.06 minutes (*d*) 460.6 minutes

(AIEEE, 2009)

Solution. $t_{1/2}$ = 6.93 minutes. For first order reaction:

$$\lambda = \frac{0.693}{t_{1/2}};\ \lambda = \frac{0.693}{6.93}$$

For a first order kinetic reaction, $t = \frac{2.303}{\lambda}\log\frac{[A_0]}{[A]}$

Where $[A_0]$ and [A] are initial concentration and concentration at time, *t* respectively. For 99% reaction complete, $\frac{[A_0]}{A} = \frac{100}{1}$. Hence, $t = \frac{2.303}{0.693}\times 6.93\times\log 100$

∴ $t = 23.03 \times 2 = 46.06$ minutes.

So, the correct answer is (*c*)

Example 145. *The rate of reaction between reactants A and B is expressed as Rate = k [A] [B]². On doubling the concentrations of both the reactants A and B, the rate is increased by a factor of :*

(*a*) 4; (*b*) 3; (*c*) 8; (*d*) 6.

(SCRA, 2000)

Solution. Given : $\text{Rate}_1 = k\,[A]\,[B]^2$. New concentrations of A and B are 2A and 2B respectively. Hence,

$\text{Rate}_2 = k\,[2A]\,[2B]^2 = k \times 2 \times 2^2\,[A]\,[B]^2 = 8k\,[A]\,[B]^2$.

∴ $\text{Rate}_2 = 8 \times \text{Rate}_1$. So, the correct answer is (*c*).

Example 146. *If a plot of $\log_{10}(t_{1/2})$ Vs $\log_{10}a$ gives a straight line with a slope of –1, the order of reaction would be :*

(*a*) 0; (*b*) 1; (*c*) 2; (*d*) 3

(SCRA, 2000)

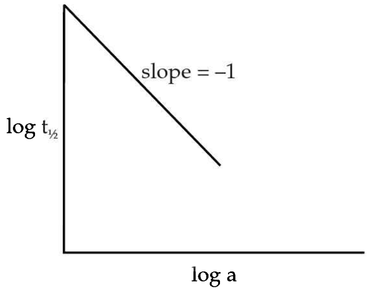
Solution. We know that for a second order reaction $t_{1/2} = K\cdot\frac{1}{a}$ where *a* = initial concentration of the reactants.

$$\therefore \qquad t_{1/2} = K\,.\,a^{-1}.$$

Taking logs of both sides, we get,

$$\log t_{1/2} = \log K + \log a^{-1}$$
$$\log t_{1/2} = \log K - \log a.$$

So, from the following graph we find the slope = – 1. So, the correct answer is (*c*).



Example 147. *Plot of log C (concentration) as a function of time gives a straight line for a first order reaction. The slope of this line gives :*

(*A*) *k*; (*B*) 1/*k*; (*c*) –*k*; (*d*) –1/*k*.

(BET, 2003)

SOLUTION. For a reaction, A $\longrightarrow$ Products.

$$\text{Rate} = -\frac{\Delta A}{\Delta t} = kt \,;\ \ln[A] = -kt + \ln[A_0]$$

or $$kt = \ln[A_0] - \ln[A]$$
$$= 2.303 \log[A_0] - 2.303 \log[A]$$

or $2.303 \log[A] = -kt + 2.303 \log[A_0]$ ...(1)

But $Y = mx + C$ is an equation of a straight line. So comparing this equation with (1), we can say that : a plot of Y (= log A) versus X (= t) is a straight line with slope, m (= $-k$) and intercept, C (= log A_0). So, for first order reaction, slope = $-k$ and the correct answer is, (*c*).

EXAMPLE 148. *A plot of ln k against 1/T (abscissa) is expected to be a straight line with intercept on the ordinate axis :*

(a) $\Delta S°/2.303\ R$ *(b) $\Delta S°/R$*

(c) $-\Delta S°/R$ *(d) $R \times \Delta S°$* **(WB-JEE, 2011)**

SOLUTION. We know: $\Delta G° = -RT \ln k$

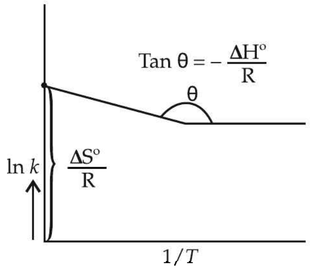
or $\Delta H° - T\Delta S° = -RT \ln k$

$$\therefore \quad \ln k = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \quad \text{...(1)}$$

But $y = mx + C$ ...(2) (equation of a straight line)

Comparing (1) and (2), we get:

Intercept, $y = \Delta S°/R$. So, the correct answer is (*b*)



EXAMPLE 149. *A reaction following zero order kinetics is 50% complete in 10 minutes. If the initial concentration of the reactants is 1×10^3 mol dm^{-3}, the rate constant of the reaction is :*

(a) 5 mol dm^{-3}min^{-}; *(b) 50 mol dm^{-3} min^{-};*

(c) 250 mol dm^{-3} min^{-}; *(d) 500 mol dm^{-3}min^{-}.*

(BET, 2003)

SOLUTION. For zero order reaction, $[A] = -kt + [A_0]$ ...(1)

But [A] = 50% *i.e.*, $= [A_0] \times \frac{50}{100} = \frac{[A_0]}{2}$; t = 10 min.

Substituting the values in (1), we get:

$$\frac{[A_0]}{2} = -kt + [A_0];$$

$$kt = [A_0] - \frac{[A_0]}{2} = \frac{[A_0]}{2}; k = \frac{[A_0]}{2t}$$

$$\therefore \quad k = \frac{1 \times 10^3 \text{mol dm}^{-3}}{2 \times 10 \text{min}}$$

$$= 50 \text{ mol dm}^{-3} \text{ min}^{-}$$

So, the correct answer is (*b*).

EXAMPLE 150. *$r = k\,[NO]^2[O_2]$. Rate constant can be increased by :*

(1) Increasing concentration of NO; (2) Increasing concentration of O_2; (3) Increasing temperature; (4) Decreasing temperature. **(IMS–BHU, 2003)**

SOLUTION. Since rate constant (r) depends upon temperature, it can be increased by increasing the temperature. So, the correct answer is (3).

EXAMPLE 151. *A reaction that is of first order with respect to reactant A has rate constant 6 min^{-}. If we start with [A] = 0.5 mol L^{-}, when would [A] reach the value 0.05 mol L^{-} ?*

(a) 0.15 min; *(b) 0.384 min;*

(c) 3.84 min; *(d) 3 min.* **(Karnataka – CET, 2000)**

SOLUTION. k = 6 min^{-}, initial concentration, N_0 = 0.5 mol L^{-}. Final concentration of A, N = 0.05 mol L^{-}. We know that :

$$t = \frac{2.303}{k} \log \frac{N_0}{N};$$

$$t = \frac{2.303}{6 \text{ min}^{-}} \log \frac{0.5}{0.05} = \frac{2.303}{6 \text{min}^{-}} \log 10$$

or $$t = \frac{2.303}{6 \text{ min}^{-}} \times 1 = 0.384 \text{min}.$$

So, the correct answer is (*b*).

EXAMPLE 152. *A reaction was found to be of second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled with everything else kept the same, the rate of reaction will :*

(a) remain unchanged; *(b) be tripled;*

(c) increase by a factor of 4; *(d) be doubled.*

(AIEEE, 2006)

SOLUTION. Since the reaction is of second order, we have :

$$\text{Rate} = \frac{dx}{dt} = k[CO]^2.$$

Hence, according to rate law expression, doubling the concentration of CO increases the rate by a factor of 4. So, the correct answer is (*c*).

EXAMPLE 153. *The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr.*

$$NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$$
$$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$$

If the second step is the rate determining step, the order of the reaction with respect to NO(g) is :

(a) 1; *(b) 0;*

(c) 3; *(d) 2.* **(AIEEE, 2006)**

SOLUTION. Given : $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$ ...(*i*)

$NOBr_2(g) + NO(g) \rightleftharpoons 2NOBr(g)$ ...(*ii*)

Since second step is the rate determining step, we have,

Rate of reaction, $r = K\,[NO]\,[NOBr_2]$

But, $$K_C = \frac{[NOBr_2]}{[NO][Br_2]} \text{ (from first step)}$$

$$\therefore \quad [NOBr_2] = K_C\,[NO]\,[Br_2]$$

$$\therefore \quad r = K[NO] \times K_C\,[NO]\,[Br_2]$$

$$= KK_C\,[NO]^2[Br_2]$$

So, the order of reaction with respect to NO = 2. So, the correct answer is (*d*).

Example 154. *For the reaction $N_2O_5 \longrightarrow 2NO_2 + 1/2\ O_2$*

$$\frac{d\,[N_2O_5]}{dt} = k_1\,[N_2O_5]; \frac{d[NO_2]}{dt} = k_2\,[N_2O_5]; \frac{d[O_2]}{dt} = k_3[N_2O_5]$$

the relation between k_1, k_2, and k_3 is:

(a) $2k_1 = k_2 = 4k_3$ *(b) $k_1 = k_2 = k_3$*
(c) $2k_1 = 4k_2 = k_3$ *(d) none of these.*

(AMU (engg), 2011)

Solution. For the given equation, $N_2O_5 \rightarrow 2NO_2 + 1/2\ O_2$; $\dfrac{-d[N_2O_5]}{dt} = \dfrac{1}{2}\dfrac{d[NO_2]}{dt} = \dfrac{2d[O_2]}{dt}$. Hence, after comparing with given data in question, $k_1 : k_2 : k_3$ ratio is $1 : \frac{1}{2} : 2$ or $(2 \times 1) : (2 \times \frac{1}{2}) : (2 \times 2)$ or $2 : 1 : 4$ *i.e.*, $2k_1 = k_2 = 4k_3$. So, the correct answer is (*a*).

Example 155. *The inversion of cane sugar was studied in IN HCl at 298 K. The following polarimeter readings were obtained at different intervals of time.*

Time (min)	*0*	*7.18*	*18.0*	*27.05*	*∞*
Reading (degree)	*+ 24.09*	*+ 21.41*	*+ 17.74*	*+ 15.00*	*– 10.74*

The reaction of inversion of cane sugar is :

(a) Unimolecular *(b) bimolecular*
(c) trimolecular *(d) tetramolecular*

Solution. For inversion of sugar, $k = \dfrac{2.303}{t} \log \dfrac{r_0 - r_\infty}{r_t - r_\infty}$

where r_0, r_t and r_∞ are readings of polarimeter at zero time, any time, *t* and at infinite time respectively.

time (min)	r_t	$r_t - r_\infty$	$k = \dfrac{2.303}{t} \log \dfrac{r_0 - r_\infty}{r_t - r_\infty}$
7.18	+ 21.41	21.41 – (– 10.74) = 32.15	$k = \dfrac{2.303}{7.18} \times \log \dfrac{24.09 - (-10.74) = 34.83}{32.15}$ $= \dfrac{2.303}{7.18\text{ min}} \times [\log 34.83 - \log 32.15]$ $= \dfrac{2.303}{7.18\text{ min}} \times [1.5419 - 1.5072 = 0.0347]$ $= 0.01113$
18.0	+ 17.74	17.74 – (– 10.74) = 28.48	$k = \dfrac{2.303}{18} \log \dfrac{34.83}{28.48} = 0.01118$
27.05	+ 15.0	15.0 – (– 10.74) = 25.74	$k = \dfrac{2.303}{27.05} \log \dfrac{34.83}{25.74} = 0.01118$

Since the value of *k* is almost same, the reaction is of first order. So, the correct answer is (*a*).

Example 156. *Consider a reaction a G + b H → Products. When concentration of both the reactants G and H is doubled, the rate increases eight times. However, when concentration of G is doubled, keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is:*

(a) 0 *(b) 1* *(c) 2* *(d) 3*

(IIT-JEE, 2007)

Solution. Reaction: $a\,\text{G} + b\,\text{H} \longrightarrow \text{Products}$

$$\therefore \quad \text{Rate, } r = k[\text{G}]^x\,[\text{H}]^y \qquad ...(i)$$

Given

Expt. no.	*[G] mol L^{-}*	*[H] mol L^{-}*	*Rate, r in mol L^{-} time^{-}*
1	*a*	*b*	*r*
2	2*a*	2*b*	8*r*
3	2*a*	*b*	2*r*

But $\quad 8\,r = k[2\text{G}]^x\,[2\text{H}]^y \qquad$ (expt. no. 2)

$$8\,r = k \cdot 2^x \times 2^y \cdot [\text{G}]^x\,[\text{H}]^y \qquad ...(ii)$$

Substituting the value of *r* from equation (*i*) in equation (*ii*), we get

$$8\,k[\text{G}]^x\,[\text{H}]^y = k \times 2^x \times 2^y \cdot [\text{G}]^x\,[\text{H}]^y$$

$$\therefore \quad 2^{x+y} = 8; \quad 2^{x+y} = (2)^3.$$

Hence $x + y = 3$. So, the order of reaction is 3. Hence the correct answer is (*d*).

Example 157. *The rate of a reaction A → products, at the initial concentration of 3.24×10^{-2} M, is nine times its rate at another initial concentration of 1.2×10^{-3} M. The order of the reaction is:*

(a) 1/2 *(b) 3/4* *(c) 3/2*
(d) 2/3 *(e) 1/3* **(Kerala PET, 2011)**

Solution. Let α = order of reaction and *r* is the rate of reaction

(*i*) For initial rate (*r*) of reaction, $r = k(1.2 \times 10^{-3})^\alpha$ ...(1)

(*ii*) For initial rate (9*r*) of reaction, $9r = k\,(3.24 \times 10^{-2})^\alpha$ ...(2)

Dividing equations (1) and (2) we get:

$$\frac{9r}{r} = \frac{k(3.24 \times 10^{-2})}{k(1.2 \times 10^{-3})^\alpha};$$

$$9 = (27)^\alpha; 3^2 = 3^{3\alpha}; 3\,\alpha = 2 \text{ or } \alpha = \frac{2}{3}$$

So, the correct result is (*d*).

Example 158. *The initial rates of reaction, 3A + 2B + C products at different initial concentrations are given below.*

Initial rate, Ms^{-}	$[A]_0$M	$[B]_0$M	$[C]_0$ M	
5.0×10^{-3}	0.010	0.005	0.010	...(*i*)
5.0×10^{-3}	0.010	0.005	0.015	...(*ii*)
1.0×10^{-2}	0.010	0.010	0.010	...(*iii*)
1.25×10^{-3}	0.005	0.005	0.010	...(*iv*)

The order with respect to the reactants, A, B and C are respectively.

(*a*) 3, 2, 0 (*b*) 3, 2, 1
(*c*) 2, 2, 0 (*d*) 2, 2, 1
(*e*) 2, 1, 0 **(Kerala PMT, 2011)**

SOLUTION. (1) Consider first and second sets of data. Both have same rate with change in the concentration of C. So, **order** with respect to C = **zero**.

(2) Consider first and third sets of data. Divide equation (*i*) by (*iii*).

$$\frac{5.0\times10^{-3}}{1.0\times10^{-2}} = \left(\frac{0.005}{0.010}\right)^x;$$
$$(0.5)^1 = (0.5)^x; x = 1.$$

So, **order** with respect to *B* is **1**

(3) Consider first and fourth sets of data. Divide equation (*iv*) by (*i*).

$$\frac{1.25\times10^{-3}}{5.0\times10^{-3}} = \left(\frac{0.005}{0.010}\right)^y \text{ or}$$
$$0.25 = (0.5)^y; (0.5)^2 = (0.5)^y; y = 2.$$

So, order with respect to A is **2**. Thus the order with respect to *A*, *B* and *C* is 2, 1 and 0. Hence the correct answer is (*e*).

EXAMPLE 159. *For the reaction,* $2NH_3 \longrightarrow N_2 + 3H_2$

$$\frac{-d[NH_3]}{dt} = k_1\,[NH_3];$$
$$\frac{d[N_2]}{dt} = k_2[NH_3]; \frac{d[H_2]}{dt} = k_3[NH_3].$$

Then, the relation between k_1, k_2, and k_3 is:

(*a*) $k_1 = 4\,k_2 = 5k_3$ (*b*) $1.5\,k_1 = 3\,k_2 = k_3$
(*c*) $10\,k_1 = k_2 = 0.3\,k_3$ (*d*) $k_1 = 2k_2 = 3k_3$.

SOLUTION. For $2NH_3 \longrightarrow N_2 + 3H_2$,

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = +1\,\frac{d[N_2]}{dt} = \frac{+1}{3}\frac{d[H_2]}{dt} \qquad ...(1)$$

Comparing (1) with given data in question, we have:

$$k_1 : k_2 : k_3 = \frac{1}{2} : 1 : \frac{1}{3} = 3 : 6 : 2$$

or $$k_1 : k_2 : k_3 = \frac{3}{2} : \frac{6}{2} : \frac{2}{2}$$
$$= 1.5 : 3 : 1$$

Hence $1.5\,k_1 : 3k_2 : k_3$.

So, correct answer is (*b*)

EXAMPLE 160. *In the following reaction,* $aA \longrightarrow bB$

$$\log\frac{-d[A]}{dt} = \log\frac{d[B]}{dt} + 0.3$$ *where negative sign indicates rate of disappearance of the reactant.*

Thus; a : b is:

(*a*) 2 : 1 (*b*) 3 : 1
(*c*) 3 : 10 (*d*) 1 : 2

SOLUTION. $$\log\frac{d[A]}{dt} - \log\frac{d[B]}{dt} = 0.3 \qquad ...(1)$$

For $$aA = bB, \frac{1}{a}\frac{[-dA]}{dt} = \frac{1}{b}\frac{[dB]}{dt}.$$

Taking logs of both sides: $$\log\frac{1}{a} + \log\frac{[-dA]}{dt}$$
$$= \log\frac{1}{b} + \log\frac{dB}{dt} \qquad ...(2)$$

$$\therefore \log\frac{[-dA]}{dt} - \log\frac{[dB]}{dt} = \log\frac{1}{b} - \log\frac{1}{a} \qquad ...(2)$$

Comparing equations (1) and (2), we get,

$$\frac{\log\frac{1}{b}}{\log 1/a} = 0.3$$

or $$\frac{1/b}{1/a} = \frac{0.3}{1} = \frac{3}{10} \text{ or } a : b = 3 : 10.$$

So, correct answer is (*c*)

EXAMPLE 161. *A study of chemical kinetics of the reaction A + B ⟶ Products gave the following data at 25°C.*

Experiment	*[A]*	*[B]*	$\frac{d\,[Products]}{dt}$
1	*1.0*	*0.15*	4.20×10^{-6}
2	*2.0*	*0.15*	8.40×10^{-6}
3	*1.0*	*0.20*	5.60×10^{-6}

Find:

(1) The order of reaction with respect to A
(2) The order of reaction with respect to B
(c) The rate law **(ISC, 2012)**

SOLUTION. Rate law = $k\,[A]^x\,[B]^y$

$4.2\times10^{-6} = k\,[1]^x\,[0.15]^y$ ...(1)
$8.4\times10^{-6} = k\,[2]^x\,[0.15]^y$ ...(2)
$5.6\times10^{-6} = k\,[1]^x\,[0.2]^y$ ...(3)

(*a*) Dividing equation (1) by (2), we get:

$$\frac{4.2\times10^{-6}}{8.4\times10^{-6}} = \frac{k\,[1]^x\,[0.15]^y}{k\,[2]^x\,[0.15]^y}; \left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x; \text{ so, } x = 1$$

(*b*) Dividing equation (1) by (3), we get:

$$\frac{4.2\times10^{-6}}{5.6\times10^{-6}} = \frac{k\,[1]^x\,[0.15]^y}{k\,[1]^x\,[0.2]^y}; \left(\frac{3}{4}\right)^1 = \left(\frac{3}{4}\right)^y; \text{ so, } y = 1$$

∴ Order with respect to *A* = 1

Order with respect to *B* = 1

Rate law = $k\,[A]^1\,[B]^1 = k\,[A]\,[B]$. **Ans.**

EXAMPLE 162. *A first order reaction is 60% complete in 20 minutes. How long will the reaction take to be 84% complete?*

(a) 54 mins. *(b) 68 mins.*

(c) 40 mins. *(d) 76 mins.*

(Karnataka, CET, 2012)

Solution. For first order reaction:

$$k=\frac{2.303}{t}\log\frac{a}{a-x} \qquad ...(1)$$

Since the reaction is 60% complete, it means, $a = 100$; $a - x = 100 - 60 = 40$; $t = 20$ mins. Substituting the values in equation (1), we get:

$$k=\frac{2.303}{20}\log\frac{100}{40}(=2.5).\text{ Thus}:$$

$$k=\frac{2.303}{20}\times 0.3979=0.0458$$

Also, $a = 100$; $a - x = 100 - 84 = 16$; $t = ?$ Substituting these values in equation (1), we get:

$$0.0458=\frac{2.303}{t}\log\frac{100}{16}(=6.25)$$

$$\therefore\ t=\frac{2.303}{0.0458}\times 0.7959=40.02\simeq 40,\text{ mins.}$$

So, the correct answer is (*c*).

Note: y % complete reaction means, $a = 100$; $a - x = 100 - y$

Example 163. *A given sample of milk turns sour at room temperature (27°C) in 5 hours. In a refrigerator at –3°C, it can be stored 10 times longer. The energy of activation of souring of milk is:*

(a) 2.303 × 10R kJ mol^{-} *(b) 2.303 × 5R kJ mol*$^{-}$

(c) 2.303 × 3R kJ mol^{-} *(d) 2.303 × 2.7R kJ mol*$^{-}$

(Karnataka, CET, 2012)

Solution. $T_1 = 273 + 27 = 300\ K$; $T_2 = 273 - 3 = 270\ K$; Let rate constant at 27°C is k_1 and at – 3°C is k_2.

$$(i)\ \text{At } 27°\text{C}, k_1=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{5}\log\frac{a}{a-x} \qquad ...(1)$$

$$(ii)\ \text{At } -3°\text{C}, k_2=\frac{2.303}{5\times10}\log\frac{a}{a-x}=\frac{2.303}{50}\log\frac{a}{a-x} \qquad ...(2)$$

$$\text{Thus: } \frac{k_2}{k_1}=\left[\frac{2.303}{50}\log\frac{a}{a-x}\right]\times\frac{5}{2.303\log a/a-x}=10^{-1}$$

$$\text{But } \log\frac{k_2}{k_1}=\frac{E_a}{2.303\,R}\times\left[\frac{T_2-T_1}{T_1T_2}\right]=\frac{E_a}{2.303R}\times\left[\frac{270-300}{270\times300}\left(=-\frac{1}{2700}\right)\right]$$

$$\therefore\ \log 10^{-1}=\frac{E_a}{2.303\,R}\times-\frac{1}{2700};\ -1=\frac{E_a}{2.303\,R}\times\frac{-1}{2700};$$

$E_a = 2.303R \times 2700$ J mol^{-}

Or $Ea = 2.303\ R \times 2.7$ kJ mol^{-}. So, the correct answer is (*d*).

Example 164. *In the following reaction, the initial concentrations of the reactant and initial rate at 298 K are given:*

$$2A \longrightarrow C + D$$

$[A]_0$ mol^{-}	*Initial rate in mol L^{-} s^{-}*
0.01	*5.00×10^{-5}*
0.02	*2.0×10^{-4}*

The value of rate constant of this reaction at 298 K is:

(a) 0.01s^{-} *(b) 5×10^{-3} mol L^{-} s^{-}*

(c) 2.0×10^{-2} mol^{-} L s^{-} *(d) 5×10^{-1} mol^{-} L s^{-}*

(e) 5.0×10^{-1} mol L^{-} s^{-} **(Kerala PET, 2012)**

Solution. Let a = order of reaction with respect to A

Rate = $k\,[A]^a$

$5.0\times10^{-5}=k\,[0.01]^a$ ...(*i*)

Also: $2.0\times10^{-4}=k\,[0.02]^a$ ...(*ii*)

Dividing (*ii*) by (*i*), we get:

$$\frac{2\times10^{-4}}{5\times10^{-5}}=\frac{k\,[0.02]^a}{k\,[0.01]^a};\ 4=(2)^a;\ (2)^2=(2)^a;\ a=2$$

Substituting $a = 2$ in equation (*i*) we get:

5.0×10^{-5} mol L^{-} s^{-} = k [0.01 mol L^{-}]^2

$$\therefore\ k=\frac{5.0\times10^{-5}\text{ mol }L^{-}s^{-}}{0.01\text{ mol }L^{-}\times0.01\text{ mol }L^{-}}=5\times10^{-1}\text{ mol}^{-}\ L\,s^{-}$$

So, the correct answer is (*d*).

Example 165. *In a first order reaction, the concentration of the reactant is reduced to 1/8 of the initial concentration in 75 minutes at 298 K. What is the half-life period of the reaction in minutes?*

(a) 50 *(b) 15*

(c) 45 *(d) 25*

(e) 30 **(Kerala PMT, 2012)**

Solution. Here initial concentration, $a = 1$, $a - x = 1/8$, $t = 75$ minutes. For first order reaction:

$$k=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{75}\log\frac{1}{1/8}$$

$$=\frac{2.303}{75}\log 8=\frac{2.303\times0.903}{75}\text{ min}^{-}$$

For first order reaction:

$$\text{Half life, } t_{1/2}=\frac{0.693}{k}=\frac{0.693\times75}{2.303\times0.903}=24.99\simeq 25\text{ min.}$$

So, the correct answer is (*d*).

Example 166. *In the Arrhenius plot of ln k vs 1/T, a linear plot is obtained with a slope of – 2×10^4 K. The energy of activation of the reaction (in kJ mol*$^{-}$*) is (R value is 8.3 J K*$^{-}$ *mol*$^{-}$*)*

(a) 83 *(b) 166*

(c) 249 *(d) 332*

(e) 830 **(Kerala PMT, 2012)**

Solution. Arrhenius equation is: $k = A\, e^{-E_a/RT}$ Or

$\ln k = \log A - \frac{E_a}{RT}$. For $\ln k$ *vs* $1/T$.

Intercept = $\ln A$; slope = $\frac{-E_a}{R} = -2\times 10^4 K$

$\therefore\ E_a = (-)\,(-)\,2\times 10^4\, K \times R = 2\times 10^4\, K \times 8.3\ \text{J K}^{-}\text{mol}^{-}$

$= 16.6\times 10^4\ \text{J mol}^{-}$ or $16.6\times 10^4 \times 10^{-3}\ \text{kJ mol}^{-}$

$= 166\ \text{kJ mol}^{-}$

So, the correct answer is (*b*).

Example 167. *For the reaction*

$$2\,NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

the following data were collected. All the measurements were taken at 263 K.

Experiment no.	*Initial [NO] (M)*	*Initial [Cl_2] (M)*	*Initial rate of disapperance of Cl_2 (M/Min)*
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

(c) What is the initial rate of disappearance of Cl_2 in exp. 4?

(CBSE, 2012)

Solution. (*a*) Suppose, rate law = $k\,[\text{NO}]^x\,[\text{Cl}_2]^y$

From expt. 1; $0.60 = k\,[0.15]^x\,[0.15]^y$ ...(1)

From expt. 2; $1.20 = k\,[0.15]^x\,[0.30]^y$ ...(2)

From expt. 3; $2.40 = k\,[0.30]^x\,[0.15]^y$ ...(3)

Dividing equation (2) and (1), we get:

$$2 = \frac{k\,[0.15]^x\,[0.30]^y}{k\,[0.15]^x\,[0.15]^y} = (2)^y;\ (2)^1 = (2)^y,\ \text{so } y = 1$$

Dividing equation (3) by (1), we get:

$$4 = \frac{k\,[0.30]^x\,[0.15]^y}{k\,[0.15]^x\,[0.15]^y} = 2^x;\ (2)^2 = (2)^x;\ \text{so, } x = 2$$

(*b*) Using equation (1), we have:

$$0.60 = k\,[0.15]^2\,[0.15]^1;\ k = \frac{0.60}{0.15\times 0.15\times 0.15}$$

$= 177.77\ \text{mol}^{-2}\ \text{L}^2\ \text{min}^{-1}$

[$\because$ Unit of k for $n = 3$ is $(\text{mol } L^{-})^{1-n}\ \text{min}^{-}$

$= (\text{mol } L^{-})^{1-3=2}\ \text{min}^{-} = \text{mol}^{-2}\ L^2\ \text{min}^{-}$]

(*c*) Rate = $k\,[\text{NO}]^2\,[\text{Cl}_2]^1$

$= 177.77 \times (0.25)^2 \times 0.25 = 2.77\ \text{mol } L^{-}\ \text{min}^{-}$ **Ans.**

Example 168. *At 300K, a gaseous reaction, $A \to B + C$, was found to follow first order kinetics. Starting with pure A, the total pressure at the end of 20 minutes was 100 mm of Hg. The total pressure after the completion of the reaction is 180 mm of Hg. The partial pressure of A (in mm of Hg) is:*

(a) 100 *(b) 90*

(c) 180 *(d) 80*

(Karnataka, CET, 2012)

Solution. Given $A \longrightarrow B + C$ ...(1)

From equation (1), we find that 1 mol of A decomposes to give a total of 2 mol (1 mol of B + 1 mol of C) of gases.

$\therefore$ Initial pressure of $A = \frac{180\times 1}{2} = 90$ mm.

Let x = Amount of A decomposed after 20 minutes.

$\therefore$ Pressure due to $A = 90 - x$. Also, pressure due to $B = x$ and due to $C = x$.

Total pressure after 20 minutes = 100 m.m.

$\therefore\ 90 - x + x + x = 100;\ x = 10$ m.m.

$\therefore$ Pressure of A after 20 minutes = 90 – 10 = 80 m.m.

So, the correct answer is (*d*).

Example 169. *The initial rate, $-\frac{d\,[A]}{dt}$ at t = 0 was found to be 2.6×10^{-2} mol $L^{-}\,s^{-}$ for the reaction, $A + 2B \longrightarrow$ products. The initial rate, $-\frac{d\,[B]}{dt}$ at t = 0 is*

(a) 0.1 mol $L^{-}\,s^{-}$ *(b) 2.6×10^{-2} mol $L^{-}\,s^{-}$*

(c) 5.2×10^{-2} mol $L^{-}\,s^{-}$ *(d) 6.5×10^{-3} mol $L^{-}\,s^{-}$*

(AMU, Engg. 2012)

Solution. For $A + 2B \longrightarrow$ Products:

$$-\frac{d\,[A]}{dt} = -\frac{1}{2}\frac{d\,[B]}{dt}$$

$$2.6\times 10^{-2}\ \text{mol } L^{-}\,s^{-} = -\frac{1}{2}\frac{d\,[B]}{dt}$$

$$\therefore\ -\frac{d\,[B]}{dt} = 2\times 2.6\times 10^{-2} = 5.2\times 10^{-2}\ \text{mol } L^{-}\,s^{-}.$$

So, the correct answer is (*c*).

Example 170. *For the reaction $A + B \longrightarrow C + 2D$, experimental results were collected for three trials and the data obtained are given below:*

Trial	*[A], M*	*[B], M*	*Initial rate, M s^{-}*
1	0.40	0.20	5.5×10^{-4}
2	0.80	0.20	5.5×10^{-4}
3	0.40	0.40	2.2×10^{-3}

the correct rate law of the reaction is:

(a) rate = $k\,[A]^0\,[B]^2$ *(b) rate = $k\,[A]\,[B]^2$*

(c) rate = $k\,[A]\,[B]$ *(d) rate = $k\,[A]\,[B]^0$*

(d) rate = $k\,[A]^0\,[B]$

(Kerala PMT, 2012)

Solution. Let rate law = $k\,[A]^x\,[B]^y$. From experiments, we have:

$$5.5\times10^{-4}=k\,[0.4]^x\,[0.2]^y \qquad ...(i)$$

$$5.5\times10^{-4}=k\,[0.8]^x\,[0.2]^y \qquad ...(ii)$$

$$2.2\times10^{-3}=k\,[0.4]^x\,[0.4]^y \qquad ...(iii)$$

From equations (*i*) and (*ii*), we have:

$$\frac{5.5\times10^{-4}}{5.5\times10^{-4}}=\frac{k[0.4]^x\,[0.2]^y}{k[0.8]^x\,[0.2]^y};1=\left[\frac{0.4}{0.8}\right]^x=\left(\frac{1}{2}\right)^x;\left(\frac{1}{2}\right)^0=\left(\frac{1}{2}\right)^x.$$

So, $x = 0$.

From equation (*i*) and (*iii*), we have:

$$\frac{5.5\times10^{-4}}{2.2\times10^{-3}}=\frac{k\,[0.4]^x\,[0.2]^y}{k\,[0.4]^x\,[0.4]^y};\frac{1}{4}=\left(\frac{1}{2}\right)^y;\left(\frac{1}{2}\right)^2=\left(\frac{1}{2}\right)^y.$$

So, $y = 2$.

Substituting these values in rate law, we get:

rate law: $k\,[A]^0\,[B]^2$. So, the correct answer is (*a*).

Example 171. *If first order reaction is 60% completed in 60 minutes, then 50% reaction completes in:*

(a) 40 min *(b) 45 min*

(c) 60 min *(d) 50 min*

(AFMC, 2012)

Solution. For a given reaction, $a = 100; a - x = 100 - 60 = 40; t = 60$ min. For second reaction, $a = 100, a - x = 100 - 50 = 50$. We know that:

$$(i)\ k=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{60}\log\frac{100}{40}=\frac{2.303}{60}\log 2.5.$$

$$=\frac{2.303}{60}\times0.3979=0.0153$$

$$(ii)\ k=\frac{2.303}{t}\log\frac{a}{a-x};t=\frac{2.303}{0.0153}\log\frac{100}{50}=\frac{2.303}{0.0153}\log 2$$

$$=\frac{2.303}{0.0153}\times0.3010\ =45.31\text{ min}\simeq45\text{ min.}$$

So, the correct answer is (*b*).

Example 172. *For a reaction: A + B ⟶ Products, the rate of the reaction at various concentrations are given below:*

Experiment no.	*[A]*	*[B]*	*Rate (mol $dm^{-3}\,s^{-}$)*
1	0.2	0.2	2
2	0.2	0.4	4
3	0.2	0.4	36

The rate law for the above reaction is:

(a) $r = k\,[A]^2\,[B]$ *(b)* $r = k\,[A]\,[B]^2$

(c) $k\,[A]^3\,[B]$ *(d)* $k\,[A]^2\,[B]^2$

(Karnataka, CET, 2012)

Solution. (*i*) For experiment, 1; $2 = k\,[A]^x\,[B]^y = k\,[0.2]^x\,[0.2]^y$

(*ii*) For experiment, 2; $4 = k\,[0.2]^x\,[0.4]^y$

(*iii*) For experiment, 3; $36 = k\,[0.6]^x\,[0.4]^y$

Dividing (*i*) and (*ii*), we get: $\left(\frac{2}{4}\right)=\left(\frac{0.2}{0.4}\right)^y;\left(\frac{1}{2}\right)^1=\left(\frac{1}{2}\right)^y$

$y = 1$

Dividing (*ii*) and (*iii*), we get:

$$\frac{4}{36}=\left(\frac{2}{6}\right)^x;\left(\frac{1}{3}\right)^2=\left(\frac{1}{3}\right)^x;x=2$$

∴ $r = [A]^x\,[B]^y = [A]^2\,[B]^1$. So, the correct answer is (*a*).

Example 173. *The rate constant for a first order reactions is doubled when the temperature is increased from 20°C to 25°C. How many times the rate constant will increases if the temperature is raised from 20°C to 40°C ?*

(a) 4 *(b) 8*

(c) 16 *(d) 32*

(e) 64 **(Kerala, PET, 2012)**

Solution. (*i*) Increase in temperature = 25 – 20 = 5°C.

(*ii*) Increase in temperature = 40 – 20 = 20°C.

5°C increase causes increase in rate constant = 2 times

20°C increase will cause increase in rate constant = $(2)^{20/5} = 2^4 = 16$. So, the correct answer is (*c*).

Example 174. *For a first order reaction, A ⟶ products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is:*

(a) 3.47×10^{-4} *M/min* *(b)* 3.47×10^{-5} *M/min*

(c) 1.73×10^{-4} *M/min* *(d)* 1.73×10^{-5} *M/min.*

(AIEEE, 2012)

Solution. $a = 0.1\,M, a - x = 0.025\,M, t = 40$ minutes. For the first order reaction:

$$k=\frac{2.303}{t}\log\frac{a}{a-x}=\frac{2.303}{40}\log\frac{0.1}{0.025}$$

$$=\frac{2.303}{40}\log4=\frac{2.303}{40}\times0.602=0.0347\text{ min}^{-}$$

For the given reaction, rate = $k\,[A] = 0.0347\text{ min}^{-} \times 0.01$ M

∴ Rate = 3.47×10^{-4}. So, the correct answer is (*a*).

Example 175. *The decomposition of ammonia on tungstan surface at 500 K follows zero order kinectics. The half-life period of this reactions is 45 minutes, when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is:*

(a) 120 *(b) 60*

(c) 240 *(d) 180*

(e) 300

(Kerala PMT, 2012)

Solution. For zero order reaction, $t_{1/2} = a_0$ (initial concentration of pressure). So:

$$(t_{1/2}) = P_1 \,;\, (t_{1/2})_2 = P_2 \,;\, \frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1}.$$

$\therefore \ \frac{(t_{1/2})_2}{45} = \frac{16}{4}; (t_{1/2})_2 = 4 \times 45 = 180$ minutes. So, the correct answer is (*d*).

Example 176. *In a zero order reaction, for every 10°C rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become:*

(a) 256 times *(b) 512 times*
(c) 64 times *(d) 128 times.*

(AIPMT, Pre. 2012)

Solution. Since rate of reaction increases 2 times for every 10°C, so we have:

$$\frac{r_{100°C}}{r_{10°C}} = 2^{\left[\frac{100-10}{10}\right]} = 2^9 = 512 \text{ times.}$$

So, the correct answer is (*b*).

Example 177. *A reacts to form P. A plot of the reciprocal of the concentration of A vs time is a straight line. When the initial concentration of A is 1.0 × 10^{-2} M, its half-life is found to be 20 min. When initial concentration of A is 3.0 × 10^{-3} M, the half life will be:*

(a) 20 min *(b) 40 min*
(c) 56 min *(d) 67 min*

(AMC (medical) 2012)

Solution. Given $A \longrightarrow P$. A plot of $1/[A]$ *vs* time is a straight line. It indicates second order reaction. For second order, $t_{1/2} \propto 1/k[A]_0$.

$[A]_0$ = Initial concentration of *A*.

(*i*) When $[A]_0 = 1.0 \times 10^{-2}\,M$, $t_{1/2} = 20$ min;

$$20 = \frac{1}{k\,(10^{-2})}; k = \frac{1}{20} \times 10^{-2} \quad ...(1)$$

(*ii*) When $[A]_0 = 3.0 \times 10^{-3}\,M$, $t_{1/2} = \frac{1}{k\,(3 \times 10^{-3})}$ ...(2)

Substituting of *k* from (1) in (2), we get:

$$t_{1/2} = \frac{20 \times 10^{-2}}{3 \times 10^{-3}} = 6.66 \times 10 \simeq 67 \text{ min.}$$

So, the correct answer is (*d*).

Example 178. *A first order reaction has a rate constant, k = 3.01 × 10^{-3}/s. How long it will take to decompose half of the reaction?*

(a) 2.303 s *(b) 23.03 s*
(c) 230.3 s *(d) 2303 s*

(J&K, CET, 2012)

Solution. For first order reaction:

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \text{ Or } t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Given $x = a/2$ and $k = 3.01 \times 10^{-3}\,s^{-}$. Substituting the values we get:

$$t = \frac{2.303}{3.01 \times 10^{-3}\,s^{-}} \log\left[\frac{a}{a - a/2} = \frac{a}{a/2} = 2\right]$$

$$= \frac{2.303}{3.01 \times 10^{-3} s^{-}} \times 0.3010 = 230.3\,s$$

So, the correct answer is (*c*).

Example 179. *In a reaction, A + B ⟶ product, rate is doubled when the concentration of B is doubled, and rate increase by a factor of 8 when the concentration of both the reactants (A and B) are doubled. The rate law for the reaction can be written as:*

(a) rate = k [A] $[B]^2$ *(b) rate = k $[A]^2$ $[B]^2$*
(c) rate = k [A] [B] *(d) rate = k $[A]^2$ [B].*

(AIPMT, Pre. 2012)

Solution. For reactants *A*, *B* and rate, *R*, we have:

A	*B*	rate	
a	*b*	*R*	...(*i*)
a	2*b*	2*R*	...(*ii*)
2*a*	2*b*	8*R*	...(*iii*)

Let rate law is : rate = $k\,[A]^x\,[B]^y$

From (*i*) $(a)^x\,(b)^y = R$ ...(*iv*)

From (*ii*) $(a)^x\,(2b)^y = 2R$ ...(*v*)

From (*iii*) $(2a)^x\,(2b)^y = 8R$ ...(*vi*)

Dividing equation (*v*) by (*iv*), we get,

$$\frac{(a)^x\,(2b)^y}{(a)^x\,(b)^y} = \frac{2R}{R}; 2^y = 2^1$$

$\therefore y = 1$

Dividing (*vi*) by (*v*), we get,

$$\frac{(2a)^x\,(2b)^y}{(a)^x\,(2b)^y} = \frac{8R}{2R}; 2^x = 2^2; x = 2$$

Substituting $x = 2$ and $y = 1$ in rate = $k\,[A]^x\,[B]^y$, we get: rate: $k\,[A]^2\,[B]$. So, the correct answer is (*d*).

Example 180. *An organic compound undergoes first order decomposition. The time taken for decomposition to 1/8 and 1/10 its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10}^{2} = 0.3$)* **(IIT-JEE, 2012)**

Solution. Let a_0 = initial concentration, a = concentration after sometime, *t*. We know that:

$$k = \frac{2.303}{k} \log \frac{a_0}{a}; a = a_0/8 \text{ at } t_{1/8}$$

$$\therefore t_{1/8} = \frac{2.303}{k} \log \frac{a_0}{a_0/8} = \frac{2.303}{k} \log 8 \quad ...(i)$$

$$k = \frac{2.303}{t} \log \frac{a_0}{a}; a = a_0/10 \text{ at } t_{1/10}$$

$$\therefore t_{1/10} = \frac{2.303}{k} \log \frac{a_0}{a_0/10} = \frac{2.303}{k} \log 10 \quad ...(ii)$$

From equation (*i*) and (*ii*), we have

$$\frac{[t_{1/8}]}{[t_{1/10}]}\times 10 = \frac{2.303}{k}\log 8 \times \frac{k}{2.303\log 10}\times 10$$

$$= \frac{\log 2^3}{\log 10}\times 10 = \frac{3\log 2}{1}\times 10 = 3\times 0.3\times 10 = 9.$$

Example 181. *For the reaction given below:*

$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+ \longrightarrow 3Br_2(aq) + 3H_2O(l)$

the rate of formation of bromine is related to rate of consumption of Br^- *by the following relation.*

(*a*) $\frac{d[Br_2]}{dt} = \frac{-5}{3}\frac{d[Br^-]}{dt}$ (*b*) $\frac{d[Br_2]}{dt} = \frac{-d[Br^-]}{dt}$

(*c*) $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$ (*d*) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}.$

(AMU. Engg., 2012)

Solution. For the reaction:

$5Br^-(aq) + BrO_3^-(aq) + 6H^+ \longrightarrow 3Br_2(aq) + 3H_2O(l)$

We have:

$$\frac{1}{3}\frac{d[Br_2]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt} \text{ Or } \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}.$$

So, the correct answer is (*d*).

Type. Fraction of original amount of reactant that remains undecomposed after time, $t = \frac{a-x}{a}$.

Example 182. *Decomposition of phosphine* (PH_3) *at 120°C proceeds according to the equation:*

$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$

It is found that this reaction follows the following rate equation.

Rate = $k\,[PH_3]$

The half-life of PH_3 *is 37.9 s at 120°C.*

(a) How much time will be required for 3/4 of PH_3 *to decompose?*

(b) What fraction of original amount of PH_3 *will remain undecomposed after one minute?* **(CBSE (F), 2012)**

Solution. $t_{1/2} = 37.9\ s$; $k = 0.693/t_{1/2} = 0.693/37.9\ s^-$; $k = 0.01828\ s^-$

$$(i)\ t_{3/4} = \frac{2.303}{k}\log\frac{a}{a-x};\ t_{3/4} = \frac{2.303}{0.01828}\log\frac{1}{1-3/4} = 4$$

$$\therefore\ t_{3/4} = \frac{2.303}{0.01828}\times 0.602 = \mathbf{75.84}\ s \qquad \textbf{Ans.}$$

(*ii*) Fraction of original amount of PH_3 that will remain undecomposed = $\frac{a-x}{a}$. So:

$$k = \frac{2.303}{t}\log\frac{a}{a-x};\ 0.01828 = \frac{2.303}{1\times 60\ s}\log\frac{a}{a-x};$$

$$\log\frac{a}{a-x} = 0.4762$$

$$\therefore\ \log\frac{a-x}{a} = -0.4762;\ \frac{a-x}{a} = \text{antilog} - 0.4762 = \mathbf{0.334}$$

Ans.

Type. For $pA(g) \longrightarrow q\,B(g) + r\,C(g)$ reaction, when only pressure are given as concentrations, then in the first order reaction:

$$k = \frac{2.303}{t}\log\frac{a}{a-x}.\ \text{Use:}$$

(*i*) $a = Ci$ = Initial pressure at time, $t = 0$ (given). If $t = 0$ not given, then:

$a = Ci$ = [Total pressure after complete decomposition of A] × $\frac{p}{q+r}$

(*ii*) Ct = Pressure at time, t (given). So:

$a - x = Ci - p\left[\frac{Ct - Ci}{q+r-p}\right]$ where p, q and r are the number of moles of A, B and C in the given reaction.

Example 183. *The following data were obtained during the first order thermal decomposition of* $N_2O_5\,(g)$ *at constant volume.*

$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$

Calculate the rate constant.

S. No.	Time/s	Total pressure in atm.
1	0	0.5
2	100	0.512

Solution. Using formula given in above type, we have: $p = 2$ (of N_2O_5), $q = 2$ (of N_2O_4) and $r = 1$ (for O_2).

$a = Ci = 0.5$ atm; $a - x = Ci - p\left[\frac{Ct - Ci}{q+r-p}\right]$ where, C_t at 100 s = 0.512 atm.

$$\therefore\ a - x = 0.5 - 2\left[\frac{0.512 - 0.5}{2+1-2=1}\right] = 0.5 - 0.024 = 0.476$$

atm.

$$\therefore\ k = \frac{2.303}{t}\log\frac{a}{a-x};\ k = \frac{2.303}{100}\log\frac{0.5}{0.476} = 1.05042$$

$$\therefore\ k = \frac{2.303}{100}\times 0.02136 = 4.92\times 10^{-4} s$$

Example 184. *In hydrogenation reaction at 25°C, it is observed that hydrogen gas pressure falls from 2 atm. to 1.2 atm. in 50 minutes. Calculate the rate of reaction in molarity per second.* (*R* = *0.0 821 L atm degree*$^-$ *mol*$^-$)

(Haryana School board, 2013)

Solution. (*i*) Rate $= \frac{dp}{dt} = \frac{(2-1.2)\text{ atm}}{50\times 60\ s}$

$= 2.666\times 10^{-4}$ atm s^-.

$$(ii)\ PV = nRT;\ \frac{P}{\text{sec}} = \left(\frac{n}{V}\right)\frac{RT}{\text{sec}};\ \left(\frac{n}{V}\right)\times\frac{1}{\text{sec}} = \frac{p}{\text{sec}}\times\frac{1}{RT}$$

∴ Rate (molarity/sec)

$$= \frac{2.666\times 10^{-4}\text{ atm s}^-}{0.0821\text{ L atm deg}^-\text{ mol}^-\times 298\text{ degree}}$$

$= 1.09\times 10^{-5}$ mol L^- s^- **Ans.**

EXAMPLE 185. *A drop of a solution (volume 0.05 mL) contains 3×10^{-6} mol H^+ ions. If the rate of disappearance of H^+ ions is 1×10^{7} mol L^- sec^-, how long would it take for H^+ ions in the drop to disappear ?* **(H.P. Board, 2013)**

SOLUTION. Concentration of drop

$$= \frac{\text{mol}}{\text{volume in mL}} \times 1000\ (\text{mL})\text{L}^-$$

$$= \frac{3 \times 10^{-6}\ \text{mol}}{0.0\,5} \times 1000\ \text{L}^- = 0.06\ \text{mol}\ \ \text{L}^-$$

$$\therefore \text{ Rate of disappearance} = \frac{\text{Concentration change}}{\text{time}}$$

$$1 \times 10^{-7}\ \text{mol L}^- = \frac{0.06\ \text{mol L}^-}{\text{time}}\text{; time} = \frac{0.06}{1 \times 10^{-7}}$$

$$= 6 \times 10^{-9}\ \text{sec. } \textbf{Ans.}$$

EXAMPLE 186. *A compound A decomposes in acid solution to give B and C according to first order rate law, with $t_{1/2} = 3$ hours. What fraction of A remains after 6 hours.*

SOLUTION. $t_{1/2} = 3$ hours. $\therefore k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{3} = 0.231\ hr^-$

We know: $k = \dfrac{2.303}{t} \log \dfrac{a}{a-x}$. Since fraction of A **left behind** is to be found, it means, $\dfrac{a-x}{a}$ is to be found.

$$\therefore 0.231\ hr^- = \frac{2.303}{6} \log \frac{a}{a-x}; \log \frac{a}{a-x} = \frac{0.231 \times 6}{2.303}$$
$$= 0.6018$$

$$\therefore \frac{a}{a-x} = \text{antilog } 0.6018 = 3.9976.$$

Hence, $\dfrac{a-x}{a} = \dfrac{1}{3.9976} = 0.25$ **Ans.**

EXAMPLE 187. *For a reaction $A \rightarrow B$ with $k = 1.9 \times 10^{-2}$ s^-, find the concentration of A left behind after 90 s if the initial concentartion of A is 1.0 mol L^-.*

SOLUTION. Units of *k* shows the reaction as first order. So:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}; 1.9 \times 10^{-2} s^- = \frac{2.303}{90} \log \frac{1.0}{a-x}$$

or $\log a - x = -0.7425$; $\therefore a - x = \text{antilog} - 0.7425 = 0.1809$ mol L^- **Ans.**

EXAMPLE 188. *The following data was obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.*

$SO_2Cl_2\,(g) \longrightarrow SO_2\,(g) + Cl_2(g)$

Calculate the rate of reaction when total pressure is 0.65 atm.

Experiment	Time, in s^-	Total pressure in atm
1	0	0.5
2	100	0.6

SOLUTION. $\underset{1\ \text{mol}}{SO_2Cl_2(g)} \longrightarrow \underset{1\ \text{mol}}{SO_2(g)} + \underset{1\ \text{mol}}{Cl_2(g)}$

(*i*) $a = 0.5; a - x = 0.5 - 1\left[\dfrac{0.6-0.5}{1+1-1}\right] = 0.4; t = 100\ s$. So:

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{100\ s} \log \frac{0.5}{0.4} = 2.23 \times 10^{-3} s^- \textbf{ Ans.}$$

(*ii*) Rate $= k \times p_{SO_2Cl_2(g)}$

$= 2.23 \times 10^{-3}\ s^- \times 0.35$ atm

$= 7.805 \times 10^{-4}$ atm s^- **Ans.**

$$\left[\begin{array}{l} \because p_{SO_2Cl_2\,(g)} = C_t - [C_t - C_i] \\ \qquad\qquad = 0.65 - [0.65 - 0.5] \\ \qquad\qquad = 0.35\ \text{atm} \\ \because C_t = \text{Total pressure} \\ \quad C_i = \text{Initial pressure} \end{array}\right]$$

EXAMPLE 189. *For the reaction $2A + B \rightarrow A_2B$, rate = k [A] $[B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^-. Find the initial rate of the reaction when [A] = 0.1 mol L^- and [B] = 0.2 mol L^-. Also, find the rate of reaction after [A] is reduced to 0.06 mol L^-.*

SOLUTION. (*a*) Initial rate $= k\,[A]\,[B]^2 = 2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ s^- \times 0.1\ \text{mol L}^- \times (0.2\ \text{mol L}^-)^2$

$= 8 \times 10^{-9}$ mol L^- s^- **Ans.**

(*b*) $2A + B \rightarrow A_2B \quad \therefore \quad A + \dfrac{1}{2}B \rightarrow \dfrac{1}{2}A_2B$

As given that [*A*] is reduced to 0.06 mol L^-, so reactant *A* = 0.1 – 0.06 = 0.04. Since *B* reacts with *A*, therefore, reacted $B = \dfrac{1}{2} \times 0.04 = 0.02$ mol L^-.

$\therefore [B] = 0.2 - 0.02 = 0.18$ mol L^-

Hence, Rate $= k\,[A]\,[B]^2 = 2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ s^- \times 0.06\ \text{mol L}^- \times (0.18\ \text{mol L}^-)^2 = 3.89 \times 10^{-9}\ \text{mol L}^- s^-$.

EXAMPLE 190. *The energy of activation of a reaction is 150 kJ mol^-. Presence of a catalyst lowers the energy of activation by 60%. What will be the effect on rate of reaction at 25°C if all other things remain same?*

(*a*) $\dfrac{r_2}{r_1}$ *[r_1 = without catalyst; r_2 = with catalyst].*

(*b*) $\dfrac{r_2}{r_1} = 5.97 \times 10^{15}$

(*c*) $r_1 = r_2$

(*d*) $\dfrac{r_1}{r_2} = 6$ **(IIT-JEE, modified)**

SOLUTION. We know, $k = A\,e^{-Ea/RT}$.

Hence, $k_1 = Ae^{-150/RT}$ ...(1)

$k_2 = Ae^{-60/RT}$ ...(2)

From (1) and (2), we get $\dfrac{k_1}{k_2} = \dfrac{e^{-150/RT}}{e^{-60/RT}}$.

Taking logs of both sides, we get:

$$\log_e \frac{k_1}{k_2} = \frac{\log_e e^{-150/RT}}{\log_{\in} e^{-150/RT}} = -150 - (-60)/RT = -\frac{90}{RT}$$

$$\therefore \ \text{loge} \ \frac{k_1}{k_2} = \frac{90 \times 10^3 \text{ J mol}^-}{8.314\ J\ K^-\ \text{mol}^- \times 298\ K} = 36.325$$

$[\because T = 25 + 273 = 298\ K]$

Or $\frac{k_1}{k_2}$ = antilog 36.325 = 5.97×10^{15}.

For *n*th order reaction, *n* and [ ] *i.e.*, concentrations are same for both reactions. Thus:

$\frac{r_2}{r_1} = \frac{k_2}{k_1} = 5.97 \times 10^{15}$. So, the correct answer is (*b*).

Example 191. *The composition of a compound follows the equation* $k = (4.4 \times 10^{11}\ s^-)\ e^{-25000\ K/T}$. *Calculate* E_a.

Solution. According to Arrhenius equation,

$$k = Ae^{-E_a/RT}$$

$$\therefore \ -\frac{E_a}{RT} = \frac{-25000\ K}{T} \quad \text{or } E_a = 25000\ K \times R$$

$= 25000 \text{ K} \times 8.314 \text{ JK}^- \text{ mol}^- = 207850 \text{ JK}^- \text{ mol}^-$

$= 207.85 \text{ kJ mol}^-$.

PROBLEMS FOR PRACTICE

1. An exothermic reaction, $y \rightarrow z$ has an activation energy of 20 k cal mol$^-$ of *y*. The heat of reaction is 38 *k* cal. Calculate the activation energy of the reverse reaction. **Ans.** 58 k cal.

2. The threshold energy of a reaction A → B is 60 k cal. If the activation energy of the forward reaction is 25 k cal, find the energy of the reactants. **Ans.** 35 k cal.

3. If the activation energy for the forward reaction is 150 kJ mol$^-$ and that of the reverse reaction is 260 kJ mol$^-$, what is the enthalpy change for the reaction?

(*a*) 410 kJ mol$^-$ (*b*) –110 kJ mol$^-$

(*c*) 110 kJ mol$^-$ (*d*) –410 kJ mol$^-$

(*e*) 90 kJ mol$^-$

(Kerala PET, 2010)

Ans. (*b*)

4. The reaction, $2\ A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$ is begun with the concentration of A and B both at an initial value of 1.0 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by:

(*a*) $[(0.75)^3\ (0.25)] + [(1.0)^2\ (1.0)]$

(*b*) $[(0.75)^3\ (0.25)^2]/(0.5)^2\ (0.75)$

(*c*) $[(10.75)^2\ (0.25)] + [(0.5)^2\ (0.25)]$

(*d*) $[(0.75)^3\ (0.25)] + [(0.75)^2\ (0.25)]$

(CBSE, PMT, 2010)

Ans. (*b*)

5. The first order reaction is 50% complete in 69.3 minutes. The time required for 90% completion for this reaction is:

(*a*) 100 minutes (*b*) 230 minutes

(*c*) 2303 minutes (*d*) 125 minutes

(Orissa JEE, 2010)

Ans. (*b*)

6. For a reaction $A + 2(B) \longrightarrow C$, the amount of C formed by starting the reaction with 5 moles of A and 8 moles of B is

(*a*) 5 moles (*b*) 8 moles

(*c*) 16 mole (*d*) 4 moles

(*e*) 1 mole

(Kerala PMT, 2010)

Ans. (*d*)

7. For an isomerisation reaction $A \longrightarrow B$, the rate constant is 4.5×10^{-3} min$^-$. If the initial concentration of A is 1M, calculate the rate of reaction after 1 hour.

Ans. 3.4354×10^{-3}

8. The rate of a first order reaction is 0.08 mol L$^-$ at 15 minutes and 0.06 mol L$^-$ at 25 minutes from the start of reaction. Find the half-life of reaction.

Ans. 24.06 min.

9. If the rate constant for the decomposition of a reaction is given by log *k* (s$^-$) = 12.14 – (1.41 × 10^4/T), then (*i*) calculate the energy of activation and (*ii*) value of *k* at 800 K.

(**Ans.** (*i*) E_a = 269.97 kJ; (*ii*) $k = 3.27 \times 10^{-6}$)

10. The rate constant for a first order reaction, $X \longrightarrow Y$ is 0.03465 min$^-$. Find the rate (*i*) at the beginning and (*ii*) after 40 minutes if initial concentration of *X* is 2.0 M.

Ans. 0.017325

11. If the rate constant for the decomposition of a certain compound at 20°C is 3.0×10^{-3} mol$^-$ s$^-$ and at 45° C is 1.2×10^{-2} mol$^-$ s$^-$, then calculate the values of Arrhenius parameters of the reaction.

Ans. 3.5×10^{14}

12. A catalyst lowers the activation energy of a reaction from 30 *k*J mol$^-$ to 20 *k*J mol$^-$. The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at 25°C is:

(*a*) 500 K (*b*) 447 K

(*c*) 600 K (*d*) 700 K

Ans. (*b*)

13. The activation energy for the reaction,

$2HI(g) \rightarrow H_2(g) + I_2(g)$ is 209.5 kJ mol$^-$ at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy.

Hint. Fraction of molecules,

$$x = \frac{n}{N} = e^{-E_a/RT}; \log x = \frac{-E_a}{2.303\ RT}$$

$$\left[\because \log e^{-E_a/RT} = \frac{-E_a}{2.303\ RT}\right]$$

$$\therefore \log x = -\frac{209.5 \times 1000\ J\ \text{mol}^-}{2.303 \times 8.314\ J\ K^-\ \text{mol}^- \times 581\ K}$$

$= -18.8323 = -18 - 1 + 1 - 0.8323$

$= \overline{19}.1677; x = \text{antilog}\ \overline{19}.1677 = 1.471 \times 10^{-19}$ **Ans.**

14. Tha rate constant for the decomposition of a hydrocarbon is $2.418 \times 10^{-5}\ s^-$ at 546 K. If the energy of activation is 179.9 kJ mol$^-$, find the value of pre-exponential factor.

Hint. $k = 2.418 \times 10^{-5}\ s^-$, $E_a = 179.9$ kJ mol$^-$, $T = 546\ K$, $R = 8.314$ JK$^-$ mol$^-$.

Putting the value of k, E_a and T in, $\log k = \log A - \frac{E_a}{2.303\ RT}$ and solving, $A = 3.912 \times 10^{12}\ s^-$. **Ans.**

15. The half-life for a decay of a radioactive ^{14}C is 5730 years. An archaeological artefact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artefact. **(CBSE, D, 2012)**

Hint. $k = \frac{0.693}{5730\ yr} = 1.209 \times 10^{-4}\ yr^-; t = \frac{2.303}{1.209 \times 10^{-4}}$

$\log \frac{100}{80} = 1847.7$ Yrs. **Ans.**

2nd Method: $\left(\frac{1}{2}\right)^n = \frac{80}{100}$ or $\frac{8}{10}; \left(\frac{2}{1}\right)^n = \frac{10}{8};$

$\log 2^n = \log 10 - \log 8; n \log 2 = 1 - 0.9031;$

$n \times 0.301 = 0.0970; n = 0.0970/0.301; t = n \times t_{1/2}$

$= (0.0970/0.301) \times 5730$ yrs. $= 1846.5$ yrs.

21

CHAPTER

Nuclear Chemistry

21.1 NUCLEAR CHEMISTRY

A reaction in which nucleus of an atom undergoes a change is called a ***nuclear reaction*** and *the branch* of chemistry which deals with the study of nuclear *reactions* is called ***nuclear chemistry***.

Nucleons. The nuclei of atoms contain ***protons*** and ***neutrons*** which are collectively called ***nucleons***.

Some notations of particles

(*i*) Proton = $^{1}_{1}\text{H}$

(*ii*) Neutron = $^{1}_{0}n$

(*iii*) Electron or beta (β) particle = $^{0}_{-1}e$ or $^{0}_{-1}\beta$

(*iv*) Positron = $^{0}_{+1}e$

(*v*) Alpha particle, a = $^{4}_{2}\text{He}$

(*vi*) Gamma rays, $\gamma = {}^{0}_{0}\gamma$

21.2 BALANCING OF NUCLEAR EQUATIONS

In the notation of particles (say $^{4}_{2}\text{He}$), the superscript (*i.e.*, 4) represents *mass number* while the subscript (*i.e.*, 2) represents the atomic number or charge. The nuclear reactions are balanced by the addition or elimination of particles like, $^{4}_{2}\text{He}$, $^{o}_{-1}e$, $^{0}_{0}\gamma$, $^{1}_{0}n$, $^{0}_{1+}e$, $^{1}_{1}\text{H}$ (proton), $^{2}_{1}\text{D}$ or $^{2}_{1}\text{H}$ (deuterium), $^{3}_{1}\text{T}$ or $^{3}_{1}\text{H}$ (tritium) etc.

α – decay means, $-{}^{4}_{2}\text{He}$; β – decay means, $-{}^{0}_{-1}e$.

Type. To balance nuclear equations, the **sum of mass numbers** on the reactant side should be equal to that on product side. Similarly, ***sum of atomic numbers or charges*** on the reactant side should be equal to that on the product side. There is conservation of both atomic number and mass number in the equation of a nuclear reaction.

A balanced equation (say, $^{23}_{11}\text{Na} + {}^{1}_{1}\text{H} \rightarrow {}^{23}_{12}\text{Mg} + {}^{1}_{0}n$) can also be represented as, $^{23}_{11}\text{Na}({}^{1}_{1}\text{H}, {}^{1}_{0}n){}^{23}_{12}\text{Mg}$ or $^{23}_{11}\text{Na}$ $(p, n){}^{23}_{12}\text{Mg}$.

EXAMPLE 1. *Balance the following nuclear reaction.*

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{239}_{92}U + ?$$

SOLUTION. (*i*) $^{238}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} + ?$. Let unknown particle is $^{a}_{b}\text{A}$.

$\therefore$ $^{238}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} + {}^{a}_{b}\text{A}$. Thus equating mass numbers of both sides, we have :

$$238 + 1 = 239 + a; a = 238 + 1 - 239 = 0.$$

Equating the atomic numbers of both sides, we have

$92 + 0 = 92 + b$; $b = 92 + 0 - 92 = 0$.

So, the particle is $^{0}_{0}\text{A}$ *i.e.*, $^{0}_{0}\gamma$. So, the required balanced equation is :

$$^{238}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} + {}^{0}_{0}\gamma \qquad \textbf{Ans.}$$

EXAMPLE 2. *Balance the following nuclear reactions.*

$^{14}_{7}N(?, \gamma){}^{15}_{8}O$ **(MP PMT, 2000)**

SOLUTION. (*i*) $^{14}_{7}\text{N} + ? \rightarrow {}^{15}_{8}\text{O} + {}^{0}_{0}\gamma$. Let unknown particle is $^{a}_{b}\text{A}$.

$\therefore$ $^{14}_{7}\text{N} + {}^{a}_{b}\text{A} \rightarrow {}^{15}_{8}\text{O} + {}^{0}_{0}\gamma$. Equating the mass numbers of both sides, we have :

$$14 + a = 15 + 0; a = 1$$

Equating the atomic numbers of both sides, we have :

$$7 + b = 8 + 0; b = 8 - 7 = 1$$

So, the particle is $^{1}_{1}\text{A}$ *i.e.*, $^{1}_{1}\text{H}$. Hence :

$$^{14}_{7}\text{N} + {}^{1}_{1}\text{H} \rightarrow {}^{15}_{8}\text{O} + {}^{0}_{0}\gamma \qquad \textbf{Ans.}$$

EXAMPLE 3. *Complete and balance the following nuclear reactions.*

(*i*) $^{234}_{92}\text{U} \rightarrow \ldots\ldots + {}^{4}_{2}\text{H}$, (*ii*) $^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow \ldots\ldots + {}^{1}_{0}n$ + energy.

(BIT, Mesra; Ranchi 1989, Pb. PMT, 1990)

SOLUTION. (*i*) $^{234}_{92}\text{U} \rightarrow \ldots\ldots + {}^{4}_{2}\text{H}$. Let the missing element is $^{a}_{b}\text{A}$.

$$^{234}_{92}\text{U} \rightarrow {}^{a}_{b}\text{A} + {}^{4}_{2}\text{He}$$

Equating the mass numbers of both sides, we have : $234 = a + 4$; $a = 230$

Equating the atomic numbers of both sides, we have : $92 = b + 2$; $b = 90$

So, the missing element is $^{230}_{90}\text{A}$ *i.e.*, $^{230}_{90}\text{Th}$.

(*ii*) $^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow \ldots\ldots + {}^{1}_{0}n$. Let the missing element is $^{a}_{b}\text{A}$. So, we have :

$$^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{a}_{b}\text{A} + {}^{1}_{0}n + \text{energy}$$

Equating the mass numbers of both sides, we have : $2 + 3 = a + 1$; $a = 4$

Equating the atomic numbers of both sides, we have :

$$1 + 1 = b + 0; b = 2$$

∴ Missing element is ${}_{2}^{4}$A *i.e.*, ${}_{2}^{4}$He **Ans.**

Example 4. *${}_{98}^{246}Cf$ was emitted along with neutrons when an unknown radioactive substance was bombarded using ${}_{6}^{12}$C as projectile. Predict the unknown radioactive substance (at. wt. 238) and the type of nuclear reaction.*

(CBSE Sample Paper, 1991)

Solution. Let the unknown element is ${}_{Z}^{A}$X. So, we have : ${}_{Z}^{A}X + {}_{6}^{12}C \rightarrow {}_{98}^{246}Cf + x\,{}_{0}^{1}n$

Equating atomic numbers on both sides of the equation, we have :

$$Z + 6 = 98 + 0; Z = 92 \text{ or uranium element}$$

But at. wt. of unknown element is 238, so we have :

$$A + 12 = 246 + x; 238 + 12 = 246 + x; x = 4$$

∴ ${}_{92}^{238}U + {}_{6}^{12}C \rightarrow {}_{98}^{246}Cf + 4\,{}_{0}^{1}n$. Type of reaction is ${}_{6}^{12}$C, ${}_{0}^{1}n$.

Example 5. ${}_{92}^{234}X \xrightarrow[-6\beta]{-7\alpha} Y$. *Find the atomic number, mass number of Y and identify it.* **(I.I.T., 2004)**

Solution. Decrease in mass number by the loss of 7 α-particles = 7 × 4 = 28.

∴ Mass number of Y

$$= 234 - 28 = 206$$

Decrease in atomic number by the loss of 7α-particles

$$= 7 \times 2 = 14$$

Increase in atomic number by the loss of 6 β-particles

$$= 6 \times 1 = 6.$$

Net decrease in atomic number

$$= 14 - 6 = 8.$$

∴ Atomic number of

$$Y = 92 - 8 = \mathbf{84}$$

Thus Y is ${}_{84}^{206}$Po.

Type. To calculate the atomic number, mass number and electron configuration of daughter element.

(*i*) Write the balanced nuclear reaction and

(*ii*) Write the electron configuration of the new element or daughter element.

Example 6. *A radioactive element A, mass number 32 that emits a beta particle has electron configuration $1s^22s^22p^63s^23p^3$. What will be the atomic number, mass number and electron configuration of the daughter element.*

Solution. The element with given electron configuration, $1s^22s^22p^63s^23p^3$ has electrons = 2 + 2 + 6 + 2 + 3 = 15.

Since in a neutral atom, at. no. = no. of electrons.

So, at. no. = 15, *i.e.*, phosphorus atom.

Since mass number of element = 32.

∴ nucleide = ${}_{15}^{32}$P.

When ${}_{15}^{32}$P loses a beta particle (${}_{-1}^{0}e$), we have : ${}_{15}^{32}P \rightarrow {}_{16}^{32}S + {}_{-1}^{0}e$

For ${}_{16}^{32}$S, at. no. of S = 16 and mass no. = 32.

∴ Electron configuration of daughter element

$${}_{16}S = 1s^22s^22p^63s^23px^23py^13pz^1.$$

21.3 π-MESONS

These are nuclear particles which are responsible for the interconversion of nuclear particles into one another. Three types of π-mesons are, positive meson (π^+), negative meson (π^-) and neutral meson (π).

To solve problems regarding π-meson, proceed as follows :

(*i*) proton → neutron + π^+ ; neutron + π^+ → proton.

(*ii*) neutron → proton + π^- ; proton + π^- → neutron

(*iii*) neutron 1 → neutron′ 1 + π^0; neutron 2 + π^0 → neutron′ 2

Example 7. *Fill in the blanks. (i) proton → neutron + ?, (ii) proton + ? → neutron.*

Solution. (*i*) proton → neutron + ?

∴ proton → neutron + π^+

(*ii*) proton + ? → neutron

∴ proton + π^- → neutron.

Example 8. *Predict the missing particles.*

(i) neutron 1 → neutron′ 1 + ?, (ii) neutron 2 + ? → neutron′ 2.

Solution. (*i*) neutron 1 → neutron′ 1 + ? ∴ neutron 1 → neutron′ 1 + π^0.

(*ii*) neutron 2 + ? → neutron′ 2,

∴ neutron 2 + π^0 → neutron′ 2.

Type. To find fraction of the atom that is occupied by a nucleus, use the relation :

$$\text{Volume of nucleus} = \frac{4}{3}\pi r^3$$

$$\text{Atomic volume} = \frac{4}{3}\pi r^3$$

Example 9. *Nuclear radius is of the order of 10^{-13} cm while atomic radius is of the order of 10^{-8}cm. Assuming the nucleus and the atom to be spherical, what fraction of the atom is occupied by a nucleus.* **(DSB, 1979)**

Solution. Radius of nucleus,

$$r = 10^{-13} \text{ cm}$$

Volume of nucleus

$$= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \times \left(10^{-13}\text{cm}\right)^3$$

$$= \frac{4}{3}\pi \times 10^{-39}\text{cm}^3 \qquad \text{...(1)}$$

Radius of atom,

$$r = 10^{-8} \text{ cm}$$

Atomic volume

$$= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (10^{-8}\text{ cm})^3$$

$$= \frac{4}{3}\pi \times 10^{-24}\text{cm}^3 \qquad \text{...(2)}$$

Dividing (1) and (2), we get :

Volume occupied by nucleus as compared to that of the atom as a whole

$$= \frac{\frac{4}{3}\pi \times 10^{-39}\text{cm}^3}{\frac{4}{3}\pi \times 10^{-24}\text{cm}^3} = 10^{-39+24} = \mathbf{10^{-15}}$$

Ans.

21.4 RADIUS OF NUCLEUS

Type. To calculate the radius of the nucleus of an atom having mass number, A. For this purpose, use the relation : Radius = $R_0\,(A)^{1/3}$ where R_0 is a constant = 1.4×10^{-13}cm = 1.4×10^{-15} m.

Radius = $(A)^{1/3}$ (1.4×10^{-13} cm) = $(A)^{1/3}$ (1.4×10^{-15} m).

Where A = mass number of the given element.

Example 10. *Find the radius of the nucleus of $^{40}_{19}K$.*

Solution. A = mass number of K = 40.

∴ Radius of nucleus of 40

$$K = (40)^{1/3}\,(1.4 \times 10^{-13}\text{ cm})$$

To solve $(40)^{1/3}$, take logs.

$$\therefore \quad \log (40)^{1/3} = \frac{1}{3}\log 40 = \frac{1}{3} \times 1.602 = 0.534.$$

Taking antilog of 0.534, we have : antilog 0.534 = 3.4198.

∴ Radius of nucleus of ^{40}K = $3.4198 \times 1.4 \times 10^{-13}$ cm = 4.79×10^{-13} cm **Ans.**

Type. Calculation of radius of nucleus.

Use : Area (A) of circle = πr^2.

Example 11. *What will be the effective neutron capture radius of nucleus having a cross- section of 1.0 barn ?*

Solution.

$$1.0\text{ barn} = 1.0 \times 10^{-24}\text{ cm}^2$$

Area (A) of a circle = πr^2;

$$r = \left(\frac{A}{\pi}\right)^{1/2} = \left(\frac{10^{-24}\text{cm}^2 \times 7}{22}\right)^{1/2}$$

Taking logs of both sides, we get :

$$\begin{aligned}\log r &= \frac{1}{2}[\log 10^{-24} + \log 7 - \log 22]\\ &= \frac{1}{2}[-24\log 10 + 0.8451 - 1.3424]\\ &= \frac{1}{2}[-24 \times 1 + 0.8451 - 1.3424]\\ &= -12.2486\\ \therefore \quad r &= \text{antilog} - 12.2486\\ &= \text{antilog} - 12 - 1 + 1 - 0.2486\\ &\qquad (= \overline{13}.7514)\\ &= \mathbf{5.64 \times 10^{-13}\ cm}\end{aligned}$$

Ans.

Type. Calculation of coulombic repulsion energy (or coulombic barrier, V). Such energy between any two nuclei having atomic numbers Z_1 and Z_2 respectively can be calculated by using the relations :

(*i*) $r = R_0\,(A)^{1/3}$ where r = radius, R_0 is a constant = 1.4 × 10^{-13}cm. A = at. wt. of atom.

(*ii*) $V = \dfrac{Z_1Z_2(e)^2}{d}$ where e = protonic charge = 4.8 × 10^{-10} esu and d = distance between the two nuclei.

Example 12. *Calculate the coulombic repulsion energy between an α-particle and $^{232}_{90}Th$ assuming that the distance between them is equal to the sum of their radii. ($R_0 = 1.4 \times 10^{-13}$cm).*

Solution. For $^{232}_{90}$Th Z_1 = 90, A = 232; r_1 = radius, $R_0 = 1.4 \times 10^{-13}$, $r_1 = R_0\,(A)^{1/3} = 1.4 \times 10^{-13} \times (232)^{1/3} = 1.4 \times 10^{-13} \times 6.1446 = 8.6 \times 10^{-13}$. For α-particle, $^4_2$He, Z_2 = 2, A = 4, r_2 = radius, $R_0 = 1.4 \times 10^{-13}$, $r_2 = R_0\,(A)^{1/3} = 1.4 \times 10^{-13} \times (4)^{1/3} = 1.4 \times 10^{-13} \times 1.5874 = 2.22 \times 10^{-13}$.

$$\therefore r_1 + r_2 = 8.6 \times 10^{-13} + 2.22 \times 10^{-13} = 10.82 \times 10^{-13} = \boldsymbol{d}.$$

Coulombic repulsion energy

$$\begin{aligned}(V) &= \frac{Z_1Z_2(e)^2}{d} = \frac{90 \times 2 \times (4.8 \times 10^{-10})^2}{10.82 \times 10^{-13}}\\ &= 3.83 \times 10^{-5}\text{ erg} = 3.83 \times 10^{-5}\text{erg}\\ &\quad \times \frac{1eV}{1.602 \times 10^{-12}\text{erg}} \times \frac{1\text{MeV}}{10^6\,eV}\\ &= \mathbf{23.9\ MeV}\end{aligned}$$

Ans.

21.5 CALCULATION OF α AND β PARTICLES

Example 13. *$_{90}Th^{234}$ emits 7 alpha particles and 6 beta particles. What will be the atomic number and mass number of the resulting atom?* **(ISC, 2007)**

Solution.

Since $^{234}_{90}$Th loses 7α ($^4_2$He) and 6β ($^0_{-1}e$)particles, so the resulting atom (^d_cY, say)can be written as:

$$^{234}_{90}\text{Th} \longrightarrow 7\,^4_2\text{He} + 6\,^0_{-1}e + {}^d_c\text{Y}$$

(*i*) Mass no. of reactants = Mass no. of products

$$\therefore \quad 234 = (7 \times 4) + (6 \times 0) + d;$$

$$d = 234 - 28 = \mathbf{206 = mass\ no.}$$ **Ans.**

(*ii*) At. no. of reactants = At. no. of products

$$\therefore \quad 90 = (7 \times 2) + 6(-1) + c\,;$$

$$c = 90 - 14 + 6 = \mathbf{82 = at.\ no.}$$ **Ans.**

Example 14. *In a radioactive emission, actinium loses an α-particle and the product loses another α-particle followed by the product (the new radioactive element) losing one β-particle. Calculate (i) Mass number and (ii) Atomic number of the finally formed element (Atomic number of actinium = 89, mass number of actinium = 227).* **(CBSE, Sample Paper, 1997)**

Solution. Given $^{227}_{89}$Ac. (*a*) On loss of α-particle ($^4_2$He) we have $^{227}_{89}\text{AC} \rightarrow {}^4_2\text{He} + {}^{223}_{87}\text{A}$ (where A = new element); $^{223}_{87}\text{A} \rightarrow {}^4_2\text{He} + {}^{219}_{85}\text{B}$ (where B = new element); $^{219}_{85}\text{B} \rightarrow {}^{219}_{86}\text{C} + {}^0_{-1}\beta$. Hence (*i*) mass no. = 219 and (*ii*) at. no. of finally formed element = 86 [∵ 85 = 86 – 1] **Ans.**

Example 15. *A radioactive element $^{227}_{89}Ac$ undergoes a series of disintegrations and finally yields $^{207}_{82}Pb$. What is the minimum number of α and β-particles involved in this disintegration ?* **(WBJEE 2000)**

Solution. $^{227}_{89}\text{Ac} \rightarrow {}^{207}_{82}\text{Pb} + x.\,^4_2\text{He} + y\,^0_{-1}e.$

Equating mass numbers, we have:

$$227 = 207 + 4x + 0y\,;\, 4x = 20 \text{ or } x = \frac{20}{4} = 5.$$

$\therefore$ Number of α-particles emitted = 5.

Equating charge number or atomic number

$$89 = 82 + 2 \times 5 - y\,;\, 89 = 92 - y$$

or $\quad y = 92 - 89 = 3.$

$\therefore$ Number of β-particles emitted = 3.

EXAMPLE 16. *$^{238}_{92}$U is radioactive and it emits α and β-particles to form $^{206}_{90}$Pb. Calculate the number of α and β-particles emitted in the conversion. An ore of $^{238}_{92}$U is found to contain $^{238}_{92}$U and $^{206}_{82}$Pb in the mass ratio of 1 : 0.1. The half-life period of $^{238}_{92}$U is 4.5 × 10^9 years. Calculate the age of the ore.*

(IIT, 2000)

SOLUTION. The emission of an α-particle causes :

(*i*) Decrease in atomic number = 2.

(*ii*) Decrease in mass number = 4.

The emission of β-particle causes :

(*i*) Increase in atomic number = 1.

(*ii*) Decrease in mass number = zero.

Decrease in mass number when $^{238}_{92}$U changes to

$$^{206}_{82}\text{Pb} = 238 - 206 = 32.$$

Since the mass number changes only due to the emission of α-particles, the number of α-particles emitted = $\frac{32}{4} = 8$

The decrease in atomic number due to the loss of 8 α-particles = 2 × 8 = 16.

Actual decrease in atomic number = 92 – 82 = 10.

Increase in atomic number due to loss of β-particles = 16 – 10 = 6.

$\therefore$ Number of β-particles emitted = 6.

Half-life period = 4.5 × 10^9 years.

Disintegration constant.

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^{9}\text{year}}$$

$$= 1.54 \times 10^{-10}\ \text{year}^{-1}$$

See section 21.11.

Assuming atomic mass equal to mass number, we will have :

	U	:	Pb
Mass ratio	1	:	0.1
Mole ratio	$\frac{1}{238}$	:	$\frac{0.1}{206}$ *i.e.,*
	4.202 × 10^{-3}	;	4.854×10^{-4}

Original amount of

$$\text{U, [U]}_0 = \text{[U]} + \text{[Pb]}$$

$$= (4.202 \times 10^{-3} + 4.854 \times 10^{-4})\ \text{mol}$$

$$= 4.687 \times 10^{-3}\ \text{mol}$$

Present amount of

$$\text{U, [U]} = 4.202 \times 10^{-3}\ \text{mol}$$

Now, $$t = \frac{2.303}{\lambda}\log\frac{[\text{U}_0]}{[\text{U}]} = \frac{2.303}{1.54 \times 10^{-10}\text{year}}\log\frac{4.687 \times 10^{-3}}{4.202 \times 10^{-3}}$$

$$= \mathbf{7.09 \times 10^{8}\ year}$$

EXAMPLE 17. *Thorium $^{232}_{90}$Th emits one α-particle and two β-particles. What will be the daughter element ?*

SOLUTION. α-particles = 1; β-particles = 2. For the transformation of $^{b}_{a}\text{X} \rightarrow {}^{d}_{c}\text{Y}$, we have : For $^{232}_{90}$Th (*i*) no. of α-particles = $b - d/4$ **Or** $1 = (232 - d)/4$ or $4 = 232 - d$.

$\therefore d = 232 - 4 = 228$. (*ii*) no. of β-particles = $[c + (b - d/2) - a$. Thus $2 = [c + (232 - 228/2)] - 90$; $2 = c + 2 - 90$ or $c = 90$. Hence daughter element = $^{228}_{90}$Th.

21.6 SODDY-FAJAN-RUSSEL'S GROUP DISPLACEMENT LAW

According to this law :

(*i*) The emission of an α-particles ($^4_2$He) from a radioactive element decreases the mass number of the nucleide by four units and atomic number by two units resulting in the formation of a daughter element which lies two groups to the left in the periodic table. *e.g.,*

$$\underset{\text{group 16}}{^{215}_{84}\text{Po}} \rightarrow \underset{\text{group 14}}{^{211}_{82}\text{Pb}} + \underset{\alpha\text{-particle}}{^{4}_{2}\text{He}}$$

(*ii*) The emission of *a* β-particle ($^{0}_{-1}e$) does not change the mass number but increases the atomic number by one. The resulting nucleide lies one group to the right of the parent nucleide in the periodic table *e.g.,*

$$\underset{\text{group 14}}{^{211}_{82}\text{Pb}} \rightarrow \underset{\text{group 15}}{^{211}_{83}\text{Bi}} + \underset{\beta\text{-particle}}{^{0}_{-1}e}$$

Isotopes. *Different* atoms of the same element having same atomic number but different mass numbers are called isotopes of each other.

Isobars. *Atoms of different* elements having same mass number but different atomic numbers are called *isobars.*

α-decay or – ($^4_2$He). It is a process in which the daughter element has mass number less by 4 units and atomic number less by 2 units from the parent element *e.g.,*

$$^{a}_{b}\text{A} \xrightarrow[\text{or } -\alpha]{-(^{4}_{2}\text{He})} {}^{a-4}_{b-2}\text{B}$$

β-decay or – ($^{0}_{-1}\beta$ or $^{0}_{-1}e$). It is a process in which the daughter element has mass number same but atomic number more by one unit from that of parent element. *e.g.,*

$$^{a}_{b}\text{A} \xrightarrow[-(^{0}_{-1}\beta)]{-(^{0}_{-1}e)\text{or}} {}^{a}_{b+1}\text{A}$$

Type. To calculate atomic mass, atomic number and group number of daughter nucleus from parent nucleus $^{A}_{Z}$X by the emission of α and β particles respectively, use the relation:

$$\underset{\substack{\text{Group no. (say, N)}\\ \text{of periodic table}}}{^{A}_{Z}\text{X}} \xrightarrow[-(^{4}_{2}\text{He})]{-\alpha-\text{particle}} \underset{\substack{\text{N}-[\text{Z}-(\text{Z}-2)]\\ =\text{N}-2}}{^{A-4}_{Z-2}\text{X}_1} \xrightarrow[-(^{0}_{-1}e)]{-\beta-\text{particle}} \underset{\substack{=\text{Z}-1\\ \text{N}-[\text{Z}-(\text{Z}-1)]\\ =\text{N}-1}}{^{A-4}_{Z-2+1}\text{X}_2}$$

EXAMPLE 18. *A radioactive atom A, changes to B by emitting one alpha particle. B changes to C by losing one beta particle and further to D by emitting another beta particle. If the mass number of A is 214 and the atomic number of A is 84, what are the mass numbers of B, C and D ? If A belongs to a group VI of the periodic table, what are the groups to which B, C and D belong ?* **(ISC, 1987)**

SOLUTION. Mass no. of A = 214, at. no. of A = 84. So, A is ${}^{214}_{84}\text{A}$ Hence :

$$ {}^{214}_{84}\text{A} \xrightarrow[\text{or}-{}^{4}_{2}\text{He}]{-\alpha-\text{particle}} {}^{214-4}_{84-2}\text{B} \text{ or } {}^{210}_{82}\text{B} \xrightarrow[\text{or }-({}^{0}_{-1}e)]{-\beta-\text{particle}} {}^{210-0}_{82+1}\text{C} $$

$$ \text{or } {}^{210}_{83}\text{C} \xrightarrow[\text{or }-({}^{0}_{-1}e)]{-\beta-\text{particle}} {}^{210-0}_{83+1}\text{D} \text{ or } {}^{210}_{84}\text{D} $$

$$ \underset{\text{Group}}{\text{Or}} \quad \underset{\text{VI}}{{}^{214}_{84}\text{A}} \xrightarrow{-{}^{4}_{2}\text{He}} \underset{\text{VI}-(84-82)=\text{IV}}{{}^{210}_{82}\text{B}} \xrightarrow{-({}^{0}_{-1}e)} \underset{\text{VI}-(84-83)=\text{V}}{{}^{210}_{83}\text{C}} $$

$$ \xrightarrow{-({}^{0}_{-1}e)} \underset{\text{VI}-(84-84)=\text{VI}}{{}^{210}_{84}\text{D}} $$

EXAMPLE 19. *If a radioactive nucleide of group 15 undergoes β-particle emission, in which group will the daughter element be found ?* **(NCERT Textbook Problem)**

SOLUTION. Let group 15 nucleide is ${}^{a}_{b}\text{A}$. With the emission of β-particle $-({}^{0}_{-1}e)$ we have :

$$ \underset{\text{Group15}}{{}^{a}_{b}\text{A}} \rightarrow \underset{\text{Group16}}{{}^{a}_{b+1}\text{B}} + {}^{0}_{-1}e1 $$

Since the daughter element has at. no. more by one unit, the daughter element will belong to group 16.

EXAMPLE 20. *Write nuclear equation for the following reaction. ${}^{218}_{85}$At undergoesα-decay.* **(NCERT text book)**

SOLUTION. Since α (or ${}^{4}_{2}\text{He}$) decay involves loss of mass number by 4 units and loss of atomic number by 2 units, so the reaction will be :

$$ {}^{218}_{85}\text{Al} \longrightarrow {}^{218-4}_{85-2}\text{X} + {}^{4}_{2}\text{He} \text{ or } \left({}^{214}_{83}\text{X} + {}^{4}_{2}\text{He}\right) $$

EXAMPLE 21. ${}^{238}_{92}$U *undergoes one α, two β and one α-decays in succession. Choose the isotopes formed.*

SOLUTION.

$$ {}^{238}_{92}\text{U} \xrightarrow{-({}^{4}_{2}\text{He})} {}^{234}_{90}\text{A} \xrightarrow{-({}^{0}_{-1}e)} {}^{234}_{91}\text{B} \xrightarrow{-({}^{0}_{-1}e)} {}^{234}_{92}\text{C} $$

$$ \xrightarrow{-({}^{4}_{-2}\text{He})} {}^{230}_{90}\text{D} $$

Out of above elements formed.

(*i*) ${}^{234}_{90}\text{A}$ and ${}^{230}_{90}\text{D}$ are isotopes of each other.

(*ii*) ${}^{238}_{92}\text{U}$ and ${}^{234}_{92}\text{C}$ are isotopes of each other because both have same at. no. but different mass numbers.

EXAMPLE 22. ${}^{211}_{82}$*Pb undergoes one beta decay. Whether the daughter element will be isotope or isobar of the parent element?*

SOLUTION. *Reaction* : $\underset{\substack{\text{Parent}\\\text{element}}}{{}^{211}_{82}\text{Pb}} \longrightarrow {}^{0}_{-1}e + \underset{\substack{\text{Daughter}\\\text{element}}}{{}^{211}_{83}\text{X}}$

Since the parent element and daughter element have same mass number but different atomic numbers, both the elements are isobars of each other.

Type. *The emission* of a positron (β⁺) or ${}^{0}_{+1}e$ from the nucleus decreases the atomic number by one unit but does not change the mass number. The resulting nucleide is shifted one group to the left of the original position of the parent nucleide in the periodic table.

EXAMPLE 23. ${}^{23}_{12}$*Mg of group 2 undergoes emission of positron. To which group will the new element belong ?*

SOLUTION. *Reaction* : $\underset{\text{Group2}}{{}^{23}_{12}\text{Mg}} \longrightarrow \underset{\text{Positron}}{{}^{0}_{+1}e} + \underset{\text{Group}(2-1)=1}{{}^{23}_{11}\text{Na}}$

So, the daughter element belongs to group 1.

EXAMPLE 24. ${}^{210}_{82}$*Pb is a β-emitter and* ${}^{226}_{88}$*Ra is an alpha emitter radioactive element. What will be the atomic masses and atomic numbers of the daughter elements of these radioactive elements? Predict the position of daughter elements in the periodic table.* **(HSB, 1995)**

SOLUTION. (*a*) Let daughter element of ${}^{210}_{82}\text{Pb}$ = A. Thus, ${}^{210}_{82}\text{Pb} \rightarrow {}^{210}_{83}\text{A} + {}^{0}_{-1}\beta.1$ Hence at no. of A = 83, mass number = 210.

(*b*) Let daughter element of ${}^{226}_{88}\text{Ra}$ = B. Thus, ${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{B} + {}^{4}_{2}\text{He}$. Hence at. no. of B = 86, mass no. 222. Since group no. of ${}_{82}\text{Pb}$ $[(\text{Xe})^{54}4f^{14}5d^{10}6s^{2}6p^{2}$ (group no. = 2 of *s* + 10 of *d* + 2 of *p* = 14] is 14 that of A will be 15. Similarly, group no. of ${}_{88}\text{Ra}$ $[(\text{Rn})^{86}7s^{2}]$ being 2, then that of ${}_{86}\text{B}$ will be 0(*i.e.*, 2–2= 0) or 18.

EXAMPLE 25. ${}^{40}_{19}$*K (group 1) undergoes electron capture. To which group the daughter element will belong ?*

SOLUTION. *Reaction* : $\underset{\text{Group1}}{{}^{40}_{19}\text{K}} + {}^{0}_{-1}e \rightarrow \underset{\text{group zero}(i.e., 1-1=0)}{{}^{40}_{18}\text{Ar} + \text{X} - \text{rays}}$

So, the daughter element ${}^{40}_{18}\text{Ar}$ belongs to zero group or group 18 of the periodic table.

Type. Neutron absorption or emission changes the mass number of a nucleide by unity while the atomic number remains the same. Thus, the group number in the periodic table remains the same.

EXAMPLE 26. *Write the isotopes or isobars along with the group number of the daughter element in the periodic table.*

$$ \underset{\text{group3}}{{}^{238}_{92}\text{U}} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} $$

SOLUTION. (*i*) $\underset{\text{group3}}{{}^{238}_{92}\text{U}} + {}^{1}_{0}n \rightarrow \underset{\substack{\text{group3}\\(\text{Daughter element})}}{{}^{239}_{92}\text{U}}$

Since there is no change in atomic number of the ${}^{238}_{92}\text{U}$, the group number of daughter element will be the same *i.e.*, 3. Also, the atomic numbers of parent and daughter elements are same, so both are ***isotopes*** of each other.

21.7 CALCULATION OF PACKING FRACTION

Type. To calculate **packing fraction**, use the relation :

$$ \text{Packing fraction} = \frac{\text{Isotopic mass} - \text{mass no.}}{\text{mass no.}} \times 10^{4} $$

EXAMPLE 27. *Calculate the packing fraction, mass defect and energy released in the formation of ${}^{98}_{42}$Mo. Isotopic mass of molybdenum = 97.906, proton = 1.007825; neutron = 1.008665.*

Solution. (*i*) Mass no. = 98 a.m.u.; isotopic mass = 97.906 a.m.u.

$$\therefore \text{Packing fraction} = \frac{\text{Isotopic mass} - \text{mass no.}}{\text{mass no.}} \times 10^4$$

$$= \frac{97.906 - 98}{98} \times 10^4 = \frac{-0.094}{98}$$

$$= \mathbf{-9.5918} \qquad \textbf{Ans.}$$

(*ii*) In ${}^{98}_{42}\text{Mo}$, no. of protons = 42; no. of neutrons = 98 – 42 = 56.

Total mass of 42 protons + 56 neutrons = (42 × 1.007825 + 56 × 1.008665) a.m.u. = 42.32865 + 56.48524 = 98.81389 a.m.u.

Isotopic mass of

Mo = 97.906 a.m.u

∴ Mass defect,

$$\Delta m = 98.81389 - 97.906$$

$$= \mathbf{0.90789\ a.m.u.} \qquad \textbf{Ans.}$$

(*iii*) But 1 a.m.u. = 931 MeV. Hence :

Energy released = 0.90789 × 931 MeV

$$= 45.23559 \simeq 845.24\ \mathbf{MeV} \qquad \textbf{Ans.}$$

21.8 MASS DEFECT, Δm

Type. Energy released in a reaction = mC^2 *or* ΔmC^2 where Δm or m = mass consumed in a reaction.

= Sum of masses of reactant species – Sum of masses of product species.

C = Velocity of light = $3.0 \times 10^8\ ms^-$; m_u means a.m.u.

1 a.m.u. = 1.66×10^{-27} kg; J = kg m^2s^{-2}; 1 *e*V = 1.6×10^{-19} J; 1 MeV = 10^6 *e*V.

1 g = 2.15×10^{10} k cal.

Example 28. *Calculate the energy released (i) in Joules in the following nuclear reaction* ${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n$. *(ii) in MeV in the following nuclear reaction:* ${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$

Given masses in amu of ${}^{2}_{1}H = 2.0141, {}^{3}_{2}He = 3.0160, {}^{1}_{0}n = 1.0087, {}^{3}_{1}H = 3.0160, {}^{4}_{2}He = 4.0026.$

(MLNR, 1997, Kerala-PET, 2005)

Solution. (*i*) Mass of ${}^{2}_{1}\text{H}$ = 2.0141 a.m.u., ${}^{3}_{2}\text{He}$ = 3.016 a.m.u. and ${}^{1}_{0}n$ = 1.0087 a.m.u. *Reaction* : ${}^{2}_{1}\text{H} + {}^{2}_{1}\text{H} \rightarrow {}^{3}_{2}\text{He} + {}^{1}_{0}n.$

Energy released = ΔmC^2 ...(1)

where, Δm = [masses of $({}^{2}_{1}\text{H} + {}^{2}_{1}\text{H})$] – [masses of $({}^{3}_{2}\text{He} + {}^{1}_{0}n)$]

= (2.0141 + 2.0141) – (3.016 + 1.0087)

= 4.0282 – 4.0247 = 3.5×10^{-3} a.m.u.

= $3.5 \times 10^{-3} \times 1.66 \times 10^{-27}$ kg

C = $3.0 \times 10^8\ ms^-$

[∵ 1 a.m.u. = 1.66×10^{-27} kg]

∴ Energy released = $\Delta mC^2 = 3.5 \times 10^{-3} \times 1.66 \times 10^{-27}\text{kg} \times (3.0 \times 10^8\ ms^-)^2$

= 5.229×10^{-13} kg m^2s^{-2} ≃ 5.2×10^{-3}J

[∵ J = kg m^2s^{-2}]

(*ii*) *Reaction* : ${}^{2}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + {}^{1}_{0}n$.

Energy released = ΔmC^2 ; C = $3.0 \times 10^8\ ms^-$

Δm = [Masses of $[{}^{2}_{1}\text{H} + {}^{3}_{1}\text{He}]$

$- \left[\text{Masses of } \left({}^{4}_{2}\text{H} + {}^{1}_{0}n\right)\right]$

= (2.0141 + 3.0160) – (4.0026 + 1.0087)

= 5.0301 – 5.0113 = 0.0188 a.m.u.

= $0.0188 \times 1.66 \times 10^{-27}$kg

[∵ 1 a.m.u. = 1.66×10^{-27}kg]

∴ Energy released = $0.0188 \times 1.66 \times 10^{-27}\text{kg} \times (3.0 \times 10^8\ ms^-)^2$

= 2.81×10^{-12} kg m^2s^{-2} = 2.81×10^{-12} J

[∵ J = kg m^2s^{-2}]

$$= 2.81 \times 10^{-12}\text{J} \times \frac{1eV}{1.6 \times 10^{-19}\text{J}}$$

[∵ 1 *e*V = 1.6×10^{-19} J]

$$= 2.81 \times 10^{-12}\ \text{J} \times \frac{1eV}{1.6 \times 10^{-19}\text{J}} \times \frac{1\,\text{MeV}}{10^6 eV}$$

[∵ 1 MeV = 10^6 *e*V]

= 17.6 MeV.

Example 29. *Calculate the energy released in k.cal during the fission of one mol of* ${}^{239}_{94}Pu$ *as given below :*

$${}^{239}_{94}Pu + {}^{1}_{0}n \rightarrow {}^{146}_{58}Ce + {}^{90}_{38}Sr + 2\,{}^{0}_{-1}e + 4\,{}^{1}_{0}n.$$

Given. *Observed mass of different isotopes are* ${}^{239}_{94}\text{Pu}$ = *239.0006,* ${}^{146}_{58}\text{Ce}$ = *145.8865,* ${}^{90}_{38}\text{Sr}$ = *89.8864;* ${}^{0}_{-1}e$ = *0.000549,* ${}^{1}_{0}n$ = *1.00867.*

Solution. *Reaction* : ${}^{239}_{94}\text{Pu} + {}^{1}_{0}n \rightarrow {}^{146}_{58}\text{Ce} + {}^{90}_{38}\text{Sr} + 2\,{}^{0}_{-1}e + 4\,{}^{1}_{0}n.$

Energy released =

= ΔmC^2 ; C = $3.0 \times 10^8\text{ms}^-$

Δm = Masses of reactants – masses of products.

= (masses of ${}^{239}_{94}\text{Pu} + {}^{1}_{0}n$)

– (masses of ${}^{146}_{58}\text{Ce} + {}^{90}_{38}\text{Sr} + 2\,{}^{0}_{-1}e + 4\,{}^{1}_{0}n$)

= (239.0006 + 1.00867) – (145.8865 + 89.8864 + (2 × 0.000549 + 4 × 1.00867)

= 240.00927 – (145.8865 + 89.8864 + 0.001098 + 4.03468)

= 240.00927 – 239.80868 = 0.20059 g.

But 1g = 2.15×10^{10} k cal.

∴ Energy released = 0.20059 × 2.15×10^{10} = 4.31×10^9 k cal. **Ans.**

Example 30. *$^{235}_{92}$U on bombardment with neutrons liberated $^{98}_{42}$Mo and $^{136}_{54}$Xe. Write down the elementary particles released. Also, calculate the energy liberated in the reaction. Isotopic masses of ^{235}U, ^{98}Mo, ^{136}Xe, $^{0}_{-1}e$ and $^{1}_{0}n$ are 235.044, 97.906, 135.907, 0.005486 and 1.0086 a.m.u. respectively.*

Solution. *Reaction* :

$$\underbrace{^{235}_{92}\text{U}+^{1}_{0}n}_{\text{Reactants}} \rightarrow \underbrace{^{98}_{42}\text{Mo}+^{136}_{54}\text{Xe}+2\,^{1}_{0}n+4\,^{0}_{-1}e}_{\text{Products}}$$

∴ Elementary particles liberated are neutrons and electrons

Energy liberated = ($\Delta m \,.\, C^2$) **or** Δm a.m.u. *i.e.*, $\Delta m \times 931$ MeV (∵ 1 a.m.u. = 931 MeV).

$$\begin{aligned}\Delta m &= \text{(Mass of reactants)}\\ &- \text{(Mass of poducts) a.m.u.}\\ &= (235.044 + 1.0086) - [97.906 + 135.907\\ &\quad + 2\,(1.0086) + 4\,(0.005486)\text{ a.m.u.}\\ &= 236.0526 - (97.906 + 135.907 + 2.0172\\ &\quad + 0.021944)\\ &= 236.0526 - 235.852144\\ &= 0.200456 \text{ a.m.u.}\end{aligned}$$

Enegy released = Δm a.m.u. = 0.200456 × 931 MeV

[∵ 1 a.m.u. = 931 MeV]

= **186.62 MeV** **Ans.**

Example 31. *Calculate the nuclear binding energy of $^{4}_{2}$He. (Proton = 1.00813 a.m.u., neutron = 1.00898 a.m.u., atomic mass of He = 4.00387 a.mu., 1 a.m.u. = 931 MeV).*

(UP Board, 1989)

Solution. In $^{4}_{2}$He . (*i*) no. of protons = 2, (*ii*) no. of neutrons = 4 – 2 = 2.

∴ Mass of $^{4}_{2}$He = Mass of 2 protons + mass of 2 neutrons

= (2 × 1.00813) + (2 × 1.00898) a.m.u.

= 2.01626 + 2.01796 = 4.03422 a.m.u.

Atomic mass of

$^{4}_{2}$He = 4.00387 a.mu.

∴ Mass defect,

Δm = 4.03422 – 4.00387 = 0.03035 a.m.u.

∴ Binding energy

= 0.03035 × 931 MeV

(∵ 1 a.m.u. = 931 MeV)

= **28.26 MeV** **Ans.**

Example 32. *Calculate the energy released (in joules) in the fusion reaction per atom of helium formed ($^{2}_{1}H+^{3}_{1}H \rightarrow ^{4}_{2}He+^{1}_{0}n$) . Given $^{2}_{1}H$ = 2.014 a.m.u.; $^{3}_{1}H$ = 3.016 a.m.u; $^{4}_{2}He$ = 4.003 a.m.u; $^{1}_{0}n$ = 1.009 a.m.u.; 1 a.m.u. = 931.5 MeV ; 1 MeV = 1.622 × 10^{-13} J.* **(DSB, 2001, CBSE, 2003)**

Solution. *Reaction is* : $^{2}_{1}H+^{3}_{1}H \rightarrow ^{4}_{2}He+^{1}_{0}n.$

Mass of reactants = 2.014 + 3.016 = 5.030

Mass of products = 4.003 + 1.009 = 5.012.

Mass defect, Δm = 5.030 – 5.012 = 0.018 m_u

∴ Energy released = 931.5 Δm MeV

= 931.5 × 0.018 MeV.

But 1 MeV = 1.622 × 10^{-13}J. So, energy released = 931.5 × 0.018 × 1.622 × 10^{-13} = 2.72 × 10^{-12}J **Ans.**

Example 33. *Calculate the binding energy per nucleon for ^{12}C and ^{16}O and comment on their relative magnitudes. Masses of proton and neutron are 1.0078 and 1.0087 m_u (1m_u = 931 MeV).*

Solution. Mass of proton = 1.0078; mass of neutron = 1.0087.

(*i*) For $^{12}_{6}$C, protons = 6, neutrons = 12 – 6 = 6. So, mass of 6 protons = 6 × 1.0078 = 6.0468; mass of 6 neutrons = 6 × 1.0087 = 6.0522. Sum total of masses of 6 protons and 6 neutrons = 6.0468 + 6.0522 = 12.099. Hence mass defect, Δm = 12.099 – 12 = 0.099. Hence binding energy for 12 nucleons = 931 Δm MeV = 931 × 0.099 = 92.169. So, binding energy per nucleon = 92.169/12 = 7.68075 MeV **Ans.**

(*ii*) For $^{16}_{8}$O, protons = 8, neutrons = 16 – 8 = 8. So, mass of 8 protons = 8 × 1.0078 = 8.0624; mass of 8 neutrons = 8 × 1.0087 = 8.0696. Sum total of masses of 8 protons and 8 neutrons = 8.0624 + 8.0696 = 16.132. Hence mass defect, Δm = 16.132 – 16 = 0.132. Hence binding energy for 16 nucleons = 931 Δm MeV = 931 × 0.132 = 122.892. So, binding energy per nucleon = 122.892/16 = 7.68075 MeV **Ans.** Since binding energy per nucleon is the same, the relative stability of all the nucleides is also of same order.

Example 34. *Naturally occurring boron consists of two isotopes whose atomic weights are 10.01 and 11.01. The atomic weight of natural boron is 10.81. Calculate the percentage of each isotope in natural boron.* **(IIT, 1982, BIT, 1989, MLNR, 1994)**

Solution. Let %age of boron isotope with at.wt. 10.01 = x.

%age of boron isotope with at.wt. 11.01 = 100 – x

$$\text{But} \qquad \text{at. wt.} = \frac{(12.00\times x)+[13.00334\times(100-x)}{100}$$

∴ 10.81 × 100 = [10.01x + 1101 – 11.01x]; x = 20

∴%age of boron with

at.wt. 10.01 = 20% **Ans.**

%age of boron with

at.wt. 11.01 = 100 – 20 = 80% **Ans.**

21.9 K.E. AND VELOCITY OF PARTICLES

Type. To calculate the ***velocity of particles emitted***, firstly find kinetic energy of particles emitted by the relation :

K.E. of emitted particle = Disintegration energy – K.E. of product *i.e.*, K.E. retained by nucleus.

Now use, $\text{K.E.} = \frac{1}{2} m\text{V}^2$ or $\text{V} = \left(\frac{2\text{K.E}}{m}\right)^{1/2}$ where

$$m = \frac{\text{g. at. wt. of particle}}{6.023 \times 10^{23}}\text{g}$$

$$1\ \text{MeV} = 1.6 \times 10^{-6}\ \text{erg.}$$

Example 35. *The energy of alpha particle emitted by $^{218}_{84}Po$ (radio active isotope of Po) is 6.11 MeV. If the energy retained by the product nucleus is about 1.49% of the energy, what would be the velocity of the emitted alpha particle ?*

Solution. We know that :

K.E. of α-particle = Disintegration energy – K.E. of the product *i.e.,* K.E. retained by the nucleus.

$$= 6.11\ \text{MeV} - \left(\frac{6.11 \times 1.49}{100}\right)$$

$$\text{MeV} = 6.11\ \text{MeV} - 0.091\ \text{MeV} = 6.019\ \text{MeV}$$

$$= 6.019\,\text{MeV} \times \frac{1.6 \times 10^{-6}\text{erg}}{1\text{MeV}}$$

$$= 9.6 \times 10^{-6}\ \text{erg} = 9.6 \times 10^{-6}\ \text{g cm}^2 s^{-2}$$

$$(\because 1\ \text{erg} = \text{g cm}^2 s^{-2})$$

$$m = (\text{mass of } \alpha\text{-particle, } ^4_2\text{He})$$

$$= \frac{\text{at. wt. of He}}{\text{Avog. no.}} = \frac{4}{6.023 \times 10^{23}}$$

$$= 6.64\ 5\ 10^{-24}\ \text{g}$$

But $\text{K.E.} = \frac{1}{2} m\text{V}^2$

$$\therefore\ \text{V} = \left(\frac{2\text{K.E.}}{m}\right)^{1/2} = \left(\frac{2.96 \times 10^{-6}\text{g cm}^2\ \text{s}^{-2}}{6.64 \times 10^{-24}\text{g}}\right)^{1/2}$$

$$= (2.89 \times 10^{18}\ \text{cm}^2 s^{-2})^{1/2}$$

$$= 1.7 \times 10^9\ \text{cm}\ s^{-}\quad \textbf{Ans.}$$

Example 36. *With what velocity should an α-particle travel towards the nucleus of a copper atom so as to arrive at a distance of 10^{-13} metre from the nucleus of the copper atom ?* **(IIT, 1997)**

Solution. Mass of α-particle, $^4_2\text{He} = 4$ a.m.u. $= 4 \times 1.674 \times 10^{-27}$g. ($\because$ 1 a.m.u. $= 1.674 \times 10^{-27}$ g); charge on electron, $e = 1.6 \times 10^{-19}$ coulomb. Z for Cu = 29, $r = 10^{-13}$ metre; in $_2$He, e^-s = 2.

Kinetic energy of α-particle

$$= \frac{1}{2} m\text{V}^2 \qquad \text{...(1)}$$

Electrostatic energy

$$= \frac{\text{K(Ze)}(2e)}{r} \qquad \text{...(2)}$$

Equating (1) and (2), we get :

$$\frac{1}{2} m\text{V}^2 = \frac{\text{K(Ze)}(2e)}{r}; \text{V}^2 = \frac{2\text{K(Ze)}(2e)}{mr}$$

$$\therefore\quad V = \left[\frac{2\text{K(Ze)}(2e)}{mr}\right]^{1/2}$$

$$= \left[\frac{2 \times (9 \times 10^9)(29 \times 1.6 \times 10^{-19} \times 2 \times 1.6 \times 10^{-19}}{4 \times 1.674 \times 10^{-27} \times 10^{-13}}\right]^{1/2}$$

$$= \left(3.99 \times 10^{13}\right)^{1/2} = \left(3.99 \times 10^{13} \times \frac{10^{-1}}{10^{-1}}\right)^{1/2}$$

$$= (39.9 \times 1012)^{1/2}$$

$$= 6.32 \times 10^6\ \text{ms}^{-} \qquad \textbf{Ans.}$$

Example 37. *Helium has mass number 4 and atomic number 2. Calculate its binding energy and nuclear binding energy per nucleon. (neutron = 1.00893 a.m.u., proton = 1.00814 a.m.u., He = 4.0039 a.m.u., and mass of electron is negligible).*

(UP Board, 1981)

Solution. No. of protons = at. no. of He = 2; no. of neutrons = mass no. – no. of protons = 4 – 2 = 2; no. of electrons = no. of protons = 2. But mass of electrons is negligible.

∴ Total mass of 2 protons + 2 neutrons = (2 × 1.00814) + (2 × 1.00893) a.m.u.

$$= (2.01628 + 2.01786)\ \text{a.m.u.}$$

$$= 4.03414\ \text{a.m.u.}$$

Isotopic mass of

$$\text{He} = 4.0039\ \text{a.m.u.}$$

∴ Mass defect,

$$\Delta m = 4.03414 - 4.0039 = 0.03024\ \text{a.m.u.}$$

∴ Binding energy

$$= 0.03024 \times 931\ \text{MeV}$$

$$[\because 1\ \text{a.m.u.} = 931\ \text{MeV}]$$

$$\text{No. of nucleons} = \text{no. of protons} + \text{no. of neutrons}$$

$$= 2 + 2 = 4.$$

∴ Binding energy for nucleon

$$= \frac{\text{Binding energy}}{\text{no. of nucleons}}$$

$$= \frac{0.03024 \times 931\,\text{MeV}}{4}$$

$$= \mathbf{7.038\ MeV} \qquad \textbf{Ans.}$$

Example 38. *The spectrographic mass of isotope is 12.01112 a.m.u. If the mass of a proton = 1.00732 a.m.u. and that of neutron = 1.00865 a.m.u., what will be the binding energy per nucleon in MeV. How much energy will be released during the formation of one mol of $^{12}_{6}C$ atoms from protons and neutrons (1 MeV = 1.602 × 10^{-6} erg, 1 a.m.u. = 1.66 × 10^{-24}g).*

SOLUTION. No. of protons = 6, no. of neutrons = mass no. – no. of protons = 12 – 6= 6.

∴ Total mass of 6 protons + 6 neutrons

$$= (6 \times 1.00732) + (6 \times 1.00865)\ \text{a.m.u.}$$

$$= (6.04392 + 6.05190)\ \text{a.m.u.}$$

$$= 12.09582\ \text{a.m.u.}$$

Spectrographic mass of isotope

$$= 12.01112\ \text{a.m.u.}$$

∴ Mass defect,

$$\Delta m = 12.09582 - 12.01112 = 0.0847\ \text{a.m.u.}$$

$$= 0.0847 \times 1.66 \times 10^{-24}\ \text{g}$$

$$[\because 1 \text{ a.m.u.} = 1.66 \times 10^{-24}\text{g}]$$

$$\text{Binding energy} = \Delta m C^2 = 0.0847 \times 1.66 \times 10^{-24}\text{g} \times (3.0 \times 10^{10}\text{cms}^{-})^2$$

Total number of nucleons

$$= \text{no. of protons} + \text{no. of neutrons}$$

$$= 6 + 6 = 12.$$

∴ Binding energy per nucleon

$$= \frac{\text{Binding energy}}{\text{no. of nucleons}}$$

$$= \frac{0.0847 \times 1.66 \times 10^{-24}\text{g} \times 9 \times 10^{20}\text{cm}^2\text{s}^{-2}}{12}$$

$$= 1.05 \times 10^{-5} \text{ g cm}^2\text{s}^{-2} = 1.05 \times 10^{-5} \text{ erg}$$

$$[\because \text{erg} = \text{g cm}^2\text{s}^{-2}]$$

$$= \frac{1.05 \times 10^{-5}\text{erg}}{1.602 \times 10^{-6}\text{erg}}\text{MeV} = 6.55 \text{ MeV}$$

$$[\because 1 \text{ MeV} = 1.602 \times 10^{-6} \text{ erg}]$$

Now, energy released in the formation of per atom = mass no. of C × binding energy per nucleon. = 12 × 6.55 MeV = 78.60 MeV

Hence energy released in the formation of per mol

$$= 78.6 \times 6.023 \times 10^{23} \text{ MeV}$$

$$(\because 1 \text{ mol} = 6.023 \times 10^{23})$$

$$= \mathbf{4.73 \times 10^{25} \text{ MeV}}$$ **Ans.**

21.10 RADIOACTIVITY AND ITS UNITS

Radioactivity. The phenomenon of spontaneous emission of some invisible radiations by elements like uranium is called ***radioactivity***. The elements which emit such radiations are called ***radioactive elements***. It can be natural or artificial radioactivity.

Units of radioactivity :

(*i*) ***Becqueral (Bq).*** It is SI unit of radioactivity. It is defined as the quantity of any radioactive substance which gives one disintegration per second (*dps* or *ds*⁻).

(*ii*) ***Rutherford (rd).*** It is the quantity of any radioactive substance which gives ***10⁶ dps.***

i.e., ***Rutherford (rd). 1 rd = 10⁶ dps***

Millirutherford (mrd). 1 mrd = 10³ dps Micro-rutherford (μrd). 1 μrd = 1 dps.

(*iii*) ***Curie (C or Ci).*** It is the quantity of any radioactive substance which gives 3.7 × 10¹⁰dps or which gives the measure of the rate of disintegration of one gram of radium.

∴ ***Curie (C or Ci) : 1C or Ci***

$$= 3.7 \times 10^{10} \text{ dps} = 3.7 \times 10^4\text{rd}$$

$$[\because 1 \text{ rd} = 10^6 \text{ dps}]$$

$$= 2.22 \times 10^{12} \text{ dpm}$$

(*i.e.,* disintegration per minute)

Millicurie (mc)

$$\mathbf{1mc} = 3.7 \times 10^7 \text{ dps} = 2.22 \times 10^9 \text{ dpm}$$

Microcurie

$$(\mu c) = 1\ \mu\text{c} = \frac{3.7 \times 10^{10}\text{dps}}{10^6\text{dps}} = 3.7 \times 10^4\text{dps}$$

Specific activity. It may be given in terms of :

(*i*) Curies per gram (cg⁻).

(*ii*) millicuries per milligram [mc (mg)⁻]

(*iii*) millicuries per mol (mc mol⁻)

(*iv*) disintegration per minute per millimol [dp min (m.mol)⁻]

(*v*) counts per minute per micromol [cpm (μ.mol)⁻]

Radioactive equilibrium. For A → B → C.

At equilibrium, rate of formation of B = rate of decay of B

$$\therefore \quad \lambda_1 N_1 = \lambda_2 N_2 \text{ or } \lambda_A N_A = \lambda_B N_B$$

21.11 ACTIVITY OR RATE OF DISINTEGRATION – HALF-LIFE PERIOD

Activity or rate of disintegration at time t, is given as:

$$\frac{-dN}{dt} = \lambda N$$

and rate of radioactive decay (λ) is given as

$$\lambda = \frac{2.303}{t}\log\frac{No}{N}$$

or

$$\lambda = \frac{2.303}{t}\log\frac{a}{a-x}.$$

where ***No or a*** = the number of atoms of radioactive substance taken initially and

N or (a – x) = number of atoms at any time, *t*. λ = Disintegration (or decay) constant.

This equation indicates radioactive decay constant (λ) which always follows ***first order kinetics.***

Unit of disintegration constant, λ = (time)⁻ like sec⁻, min⁻, hour⁻, year⁻ etc.

Half-life period, $t_{1/2}$ or $t_{0.5}$. The *time* required for the disintegration of one half of the original amount of the *radioactive* substance is called the half-life period.

$$t_{1/2} = \frac{\mathbf{0.693}}{\boldsymbol{\lambda}} \quad \textbf{or} \quad \lambda = \frac{0.693}{t_{1/2}}$$

> **Note.** If initial amount of radioactive substance = No or *a*, then :

(*i*) Amount of substance left after one half-life period

$$= \text{No} \times \left(\frac{1}{2}\right)^1.$$

(*ii*) Amount of substance left after two half life periods

$$= \frac{\text{No}}{4} = \text{No} \times \left(\frac{1}{2}\right)^2.$$

(*iii*) Amount of substance left after three half-life periods

$$= \frac{\text{No}}{8} = \text{No} \times \left(\frac{1}{2}\right)^3$$

Where *n* = number of half-lives.

Also, total time *= n × $t_{1/2}$ and*

Total amount used in half-lives

$$= \text{No} - \frac{\text{No}}{2''} = \text{No}\left(1 - \frac{1}{2''}\right) = \text{No}\left(\frac{2''-1}{2''}\right)$$

Average life period, $\tau = \frac{1}{\lambda}$ or $\frac{1}{k}$ where λ or *k* is decay constant.

$$\therefore \qquad \tau = \frac{t_{1/2}}{0.693} = \mathbf{1.44 \times half\text{-}life\ period.}$$

Type. To calculate number of particles emitted per second (activity) when half-life period $t_{1/2}$ is given, proceed as follows ;

(*i*) Firstly find λ from,

$$\lambda = \frac{0.693}{t_{1/2}}.$$

(*ii*) Number of particles emitted per second,

$$\frac{dN}{dt} = \lambda \text{No}.$$

$$\text{where No} = \frac{\text{Avogadro's number} \times \text{weight of sample}}{\text{Mass number of sample}}.$$

EXAMPLE 39. *$^{232}_{90}Th$ is an α-particle emitter with a half-life of 1.41 × 10^{10} years. Given a 0.25g sample of this thorium. How many α-particles will it emit per second ? (Avogadro number, N_A = 6.02 × 10^{23} mol^{-}).*

SOLUTION. Since the α-particles emitted per second are required, so $t_{1/2}$ is changed to seconds.

$$\therefore \qquad t_{1/2} = 1.41 \times 10^{10}\text{years} \times \frac{365 \text{ days}}{1 \text{ year}} \times \frac{24 \text{ hours}}{1 \text{ day}} \times \frac{60 \text{ min}}{1 \text{ hour}} \times \frac{60 \text{ sec.}}{1 \text{min.}}$$

$$\text{But} \qquad \lambda = \frac{0.693}{t_{1/2}},$$

$$\text{so} \qquad \lambda = \frac{0.693}{1.41 \times 10^{10} \times 365 \times 24 \times 60 \times 60s}$$

∴ No. of particles emitted per second

$$= \lambda \times \frac{\text{Avogadro no.} \times \text{wt. of sample}}{\text{Mass no. of sample}}$$

$$= \frac{0.693}{1.41 \times 10^{10} \times 365 \times 24 \times 60 \times 60 s} \times \frac{6.02 \times 10^{23}\text{mol}^{-} \times 0.25\text{g}}{232\text{g mol}^{-}}$$

$$= \mathbf{1011\ s^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 40. *Calculate the number of disintegrations which 1 g of ^{226}Ra ($t_{1/2}$ = 1600 years) would undergo per second. What quantity of $^{24}_{11}Na$ (half-life = 15 hr) would undergo the same disintegrations per unit time ?*

SOLUTION. Mass number of radium = 226; no. of atoms in 226 g of Ra = 6.02 × 10^{23}. Hence (*i*) no. of atoms in 1 g Ra = (6.02 × 10^{23} × 1)/226. But λ = 0.693/$t_{1/2}$ = 0.693/1600 × 365 × 24 × 60 × 60 seconds. Hence no. of disintegrations per second = (0.693 × 6.02 × 10^{23} × 1/1600 × 365 × 24 × 60 × 60 = 3.658 × 10^{10} *dps* **Ans.**

(*ii*) no. of disintegrations per second (*dps*) = 3.658 × 10^{10} *dps*; no. of atoms present in 24g Na = 6.02 × 10^{23}. Hence no. of atoms (No) in *x* g of Na = 6.02 × 10^{23} × *x*)/24; λ = 0.693/$t_{1/2}$ = 0.693/15 hr = 0.693/15 × 60 × 60*s*. Hence no. of *dps* = λ × No **Or** 3.658 × 10^{10} = (0.693/15 × 60 × 60) × (6.02 × 10^{23} × *x*/24). Hence, *x* = (3.658 × 10^{10} × 24 × 15 × 60 × 60)/0.693 × 6.02 × 10^{23} = 1.136 × 10^{-7}g **Ans.**

EXAMPLE 41. *^{235}U gives 4770 dps mg^{-1}. Calculate its half life and disintegration constant (1 year = 3.15 × 10^7s).*

SOLUTION. Atoms disintegrating in unit time = λA = 4770/sec. ...(*i*)

$$\text{A = total number of atoms} = 1\text{mg} \times \frac{1\text{g}}{1000\,\text{mg}} \times \frac{1\text{mol}}{235\text{g}} \times \frac{6.02 \times 10^{23}\text{atoms}}{1\,\text{mol}} = 2.56 \times 10^{18}.$$

Substituting the value of A in (*i*), we get, λ = (4770/sec)/2.56 × 10^{18} = 1.86 × 10^{-15} sec^{-} = 1.86 × 10^{-15} sec^{-} × $\frac{60\,\text{sec}}{1\,\text{min}} \times \frac{60\,\text{min}}{1\,\text{hr}} \times \frac{24\,\text{hr}}{1\text{day}} \times \frac{365\,\text{day}}{1\text{year}}$ = 5.86 × 10^{-8} yr^{-} **Ans.** Also, half-life, $t_{1/2}$ = 0.693/λ. Substituting the value of λ, we get : $t_{1/2}$ = 0.693/(5.86 × 10^{-8} yr^{-}) = 11825938 yr ≈ 1.18 × 10^7 year.

EXAMPLE 42. *Half-life period of ^{90}Sr, a β-emitter, is 28 years. Find out the activity of a 1g sample of ^{90}Sr.* **(CBSE, 1999S)**

SOLUTION. Activity indicates no. of particles emitted per second or number of disintegrations per second (dps).

Since the disintegrations are required per second, so, $t_{1/2}$ is changed to seconds.

$$\therefore \qquad t_{1/2} = 28\,\text{years} \times \frac{365\,\text{days}}{1\text{year}} \times \frac{24\,\text{hr}}{1\text{day}} \times \frac{60\,\text{min}}{1\,\text{hr}} \times \frac{60\,\text{s}}{1\text{min}}$$

$$\text{But,} \qquad \lambda = \frac{0.693}{t_{1/2}}.$$

$$\text{So,} \qquad \lambda = \frac{0.693}{28 \times 365 \times 24 \times 60 \times 60s}$$

∴ Activity (or no. of disintegrations per second)

$$= \lambda \times \frac{\text{Avogadro no.} \times \text{wt. of sample}}{\text{Mass no. of sample}}$$

$$= \frac{0.693}{28 \times 365 \times 24 \times 60 \times 60s} \times \frac{6.02 \times 10^{23}\text{mol}^{-} \times 1\text{g}}{90\,\text{g mol}^{-}}$$

$$= \mathbf{5.25 \times 1012\ dps} \qquad \textbf{Ans.}$$

EXAMPLE 43. *The half-life of a radioactive isotope is 10 hours. How many atoms of this isotope will be left after 4 hours if initially 1 g mole of the radioactive isotope was taken?*

(ISC, 2007)

SOLUTION. (*a*) $t_{1/2} = 10$ hours; $a = 1$ g mol; $a - x = ?$

$$\text{We know} \quad t_{1/2} = \frac{0.693}{\lambda};\ \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\text{ hr}}$$

$$= 0.0693\text{ hr}^{-}$$

(*b*)
$$t = \frac{2.303}{\lambda}\log\frac{a}{a-x};$$

$$4\text{ hr} = \frac{2.303}{0.0693\text{ hr}^{-}}\log\frac{1}{a-x}$$

$$\therefore \quad \log\frac{1}{a-x} = \frac{4 \times 0.0693}{2.303}$$

$$\log 1 - \log(a-x) = 0.1204;\ 0 - \log(a-x) = 0.1204$$

$$\therefore \quad \log(a-x) = -0.1204 = -1 + 1 - 0.1204 = \bar{1}.8796$$

Taking antilog of both sides, we get :

$$a - x = \text{antilog } \bar{1}.8796 = 7.578 \times 10^{-1}$$

$$= 0.7578 \text{ mol}$$

We know that:

$$1 \text{ mol atoms} = 6.02 \times 10^{23} \text{ atoms}$$

$$\therefore \quad 0.7578 \text{ mol} = 6.02 \times 10^{23} \times 0.7578$$

$$= \mathbf{4.56 \times 10^{23}\ atoms} \qquad \textbf{Ans.}$$

Type. (*i*)
$$\lambda = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{t}\log\frac{No}{N}$$

(*ii*) %age activity left behind after time, $t = a - x\%$ when $a = 100$. (or = N % when No = 100).

EXAMPLE 44. *The half-life of cobalt is 5.26 years. Calculate its percentage activity remaining after 4 years.*

SOLUTION. $t_{1/2} = 5.26$ years. But

$$\lambda = \frac{0.693}{t_{1/2}} \cdot So,\ \lambda = \frac{0.693}{5.26\text{ years}}$$

We know that,

$$\lambda = \frac{2.303}{t}\log\frac{a}{a-x} \qquad ...(1)$$

Here $t = 4$ years; $a = 100$; $a - x = ?$ Substituting the value in equation (1), we get :

$$\frac{0.693}{5.26\text{ years}} = \frac{2.303}{4\text{ years}}\log\frac{100}{a-x};$$

$$\log\frac{100}{a-x} = \frac{0.693 \times 4}{5.26 \times 2.303} = 0.229.$$

Or $\log 100 - \log(a-x)$

$$= 0.229;\ 2 - \log(a-x) = 0.229$$

$$\therefore \quad \log(a-x) = 2 - 0.229 = 1.771$$

$$\therefore \quad a - x = \text{antilog } 1.771 = 59$$

∴ %age activity left behind after 4 years = **59%** **Ans.**

Type. When activitiy of a radioactive substance becomes or reduced to y% of its original value, then : $a = 100$; $a - x = y$.

EXAMPLE 45. *The half-life period of a radioactive element is 1.4×10^{10} years. Calculate the time in which the activity of the element is reduced to or becomes 90% of its original value.*

(PSEB, 2000)

SOLUTION. $t_{1/2} = 1.4 \times 10^{10}$ years;

$a = 100$, $a - x = 90$; $t = ?$

(*i*)
$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.4 \times 10^{10}\text{years}}$$

(*ii*)
$$t = \frac{2.303}{\lambda}\log\frac{a}{a-x}$$

$$= \frac{2.303 \times 1.4 \times 10^{10}\text{years}}{0.693}\log\frac{100}{90}$$

$$= \frac{2.303 \times 1.4 \times 10^{10}\text{years}}{0.693} \times 0.0458$$

$$\simeq \mathbf{2.13 \times 10^{9}\ years.}$$

$$\left[\because \log\frac{100}{90} = \log 100 - \log 90 = 2.0 - 1.9542 = 0.0458\right]$$

EXAMPLE 46 *The half-life period of a radioactive element is 27.96 days. Calculate the time taken by a given sample to reduce to 1/8th of its activity.* **(PSEB, 2000)**

SOLUTION. Hint. $a = 1$, $a - x = {}^{1}/_{8}$; 83.92 days **Ans.**

Type. When time is to be calculated for the activity of a known weight (w) to fall to y% then :

$$\text{No or} \qquad a = \text{wg; N or } a - x = \text{w} \times \frac{y}{100}\text{g.}$$

EXAMPLE 47. *Two microgram of phosphorus-32 was injected into a living system for a biological tracer studies. The half-life period of $^{32}_{15}P$ is 14.3 days. How long will it take the radioactivity to fall to 20%.*

SOLUTION. $t_{1/2} = 14.3$ days; $a = 2$ microgram; $a - x = 2$ microgram $\times \frac{20}{100} = 0.4$ microgram; $t = ?$

(*i*)
$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3\text{ days}}$$

(*ii*)
$$t = \frac{2.303}{\lambda}\log\frac{a}{a-x}$$

$$= \frac{2.303 \times 14.3\text{ days}}{0.693}\log\frac{2\text{ microgram}}{0.4\text{ microgram}}$$

$$t = \quad \text{or} \quad t = \mathbf{33.22\ days} \qquad \textbf{Ans.}$$

Type. Total time = $n \times t_{1/2}$ where n = number of half-lives *i.e.*, after n half-lives, the amount of substance left behind $= \text{No}\left(\frac{1}{2}\right)^{n}$ where No = initial amount of substance.

EXAMPLE 48. *Three quarters of Sr^{90}, a radioactive element, disappeared in 56 years. What is the half-life period of the radioactive decay ? What is the rate constant for the decay of strontium?*

(I.S.C., 1996)

SOLUTION.

Total time = 56 years; Three quarters of

$$Sr^{90} = \frac{3}{4} = 3 \times \left(\frac{1}{2}\right)^2 .$$

So, n = no. of half-lives, $t_{1/2} = 2$.

But, total time = $n \times t_{1/2}$; 56 years = $2 \times t_{1/2}$

$$\therefore \quad t_{1/2} = \frac{56}{2} = 28\,\text{years}$$

∴ Rate constant,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{28\ \text{years}}$$

$$= \mathbf{0.02475\ yr^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 49. *1.0 g of Sr – 90 was reduced to 0.953 g after two year. Calculate the half-life period of Sr – 90.*

(PSEB, 2006, ISC, 2009)

SOLUTION. Initial amount, a = 1.0 g ; Amount left after 2 years (= $a - x$) = 0.953 g. But :

$$\lambda = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$= \frac{2.303}{2} \log \frac{1.0}{0.953} = \frac{2.303}{2} \log 1.0493$$

$$= \frac{2.303}{2} \times 0.0209 = 0.02406\ \text{yr}^{-}$$

$$\therefore \text{Half-life,}\ t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.02406\ \text{yr}^{-}} = 28.80\ \text{years}$$

EXAMPLE 50. *The half-life of ${}_{53}I^{125}$ is 60 days. What percent of the original radioactivity would be present after 180 days ?*

(PSEB, 2006)

SOLUTION. Initial concentration,

$$a = 100; a - x \text{ or } 100 - x = ?\ t_{1/2} = 60\ \text{days.}$$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{60\ \text{days}} = 0.01155\ (\text{days})^{-}$$

$$t = \frac{2.303}{\lambda} \log \frac{a}{a - x};$$

$$180\ \text{days} = \frac{2.303}{0.01155\,(\text{days})^{-}} \log \frac{100}{100 - x}$$

$$\therefore \quad \log \frac{100}{100 - x} = \frac{180\,\text{days} \times 0.01155\,(\text{days})^{-}}{2.303}$$

$\log 100 - \log (100 - x)$

$= 0.9027$ **Or** $2.0 - \log (100 - x)$

$= 0.9027$

$\log (100 - x) = 2 - 0.9027 = 1.0973$

$\therefore \quad 100 - x$ = antilog 1.0973 = 12.5

∴ %age of original radioactivity present after 180 days = **12.5%** **Ans.**

Second Method : $t_{1/2}$ = 60 days. Total time = 180 days.

∴ no. of half-lives

$$= \frac{\text{Total time}}{t_{1/2}} = \frac{180}{60} = 3$$

∴ %age of radioactivity left after 3 half-lives

$$= \frac{\text{No}}{2^n} = \frac{100}{2^3} = \frac{100}{8} = \mathbf{12.5\%} \qquad \textbf{Ans.}$$

Type. (*i*) If initial amount (w) of a radioactive substance is given along with the amount (w_1) of this substance after decay, then

Initial amount, a = w; Amount after decay, $w_1 = a - x$.

(*ii*) If initial amount of a radioactive substnace is not given but amount of the same substance left behind equal to 'y' times its initial amount is given, then : Initial amount, $a = 1$; $a - x = y \times 1 = y$.

EXAMPLE 51. *A radioactive substance decays at such a rate that after 46 days, only 0.25 of its original amount is left behind. Calculate the disintegration constant and half-life period.*

(PSEB, 2002)

SOLUTION. t = 46 days; $a = 1$; $a - x = 0.25 \times 1 = 0.25$; λ =?

$$(i) \qquad \lambda = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{46\,\text{days}}$$

$$\log \frac{1}{0.25} = \frac{2.303}{46\,\text{days}} \log 4$$

$$\lambda = \frac{2.303}{46\,\text{days}} \times 0.6020 = \mathbf{0.03\ day^{-}} \quad \textbf{Ans.}$$

$$(ii) \qquad t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.03\,\text{day}^{-}} = \mathbf{23.1\ day}\ \textbf{Ans.}$$

EXAMPLE 52. *After an hour, the amount of a radioactive substance disintegrated was 15/16th of the original amount. What is the half-life of the radioactive substance ?*

(PSEB, 2002)

SOLUTION. Time, $t = 1\ \text{hr} = 1 \times 60 \times 60 = 3600s$; let initial concentration $a = 1$ and hence $x = 1 \times 15/16 = 15/16$. We know, $k = (2.303/t) \log a/a - x$. Substituting the values, we get $k = 2.303/3600) \log 1/1 - 15/16)$. Or $k = (2.303/3600) \times 1.2041 = 7.7029 \times 10^{-4}$. But half-life $t_{1/2} = 0.693/k$. Substituting the values, we get : $t_{1/2} = 0.693/(7.7029 \times 10^{-4}) = 899.7s$ $= 899.7/60 = 15$ min. **Ans.**

EXAMPLE 53. *A wood piece obtained from an archaeological source shows a ${}^{14}C$ activity which is 10% of the activity found in green wood. Calculate the age of the wood piece. ($t_{1/2}$ ${}^{14}C$ = 5770 years).*

SOLUTION. (*i*) $t_{1/2}$ = 5770 years. Thus $\lambda = \dfrac{0.693}{5770\,\text{yrs}}$ = 1.2× × 10^{-4} yr^{-}

$$(ii) \qquad t = \frac{2.303}{\lambda} \log \frac{a}{a - x} \qquad \ldots(1)$$

Here t = age of wood = ?; Initial activity, $a = a$ suppose.

$\therefore \quad a - x$ (= activity left behind)

$$= a \times \frac{10}{100} = 0.1a$$

Substituting the values in equation (1), we get:

$$t = \frac{2.303}{1.2 \times 10^{-4}\,\text{yr}^{-}} \log \frac{a}{0.1a}$$

$$= \frac{2.303}{1.2 \times 10^{-4}\,\text{yr}^{-}} \log 10$$

$$= \frac{2.303}{1.2 \times 10^{-4}\,\text{yr}^{-}} \times 1$$

t = **19191.7 years = age of wood** **Ans.**

Example 54. *A piece of charred bone found in the ruins of a village has the ^{14}C to ^{12}C ratio 0.72 times found in living organisms. Calculate the age of the bone piece. ($t_{1/2}$ for ^{14}C decay = 5.73×10^3 years).*

Solution. t = age of charred bone piece.

Initial concentration,

$$a = a \text{ (say)}$$

$\therefore$ $a - x = 0.72 \times a$; $t_{1/2} = 5.73 \times 10^3$ years

(*i*) $$\lambda = \frac{0.693}{t_{1/2}};\ \lambda = \frac{0.693}{5.73 \times 10^3\,\text{yrs}}$$

(*ii*) $$t = \frac{2.303}{\lambda} \log \frac{a}{a-x}$$

$$= \frac{2.303 \times 5.73 \times 10^3\,yrs}{0.693} \log \frac{a}{0.72a}$$

Or $$t = \frac{2.303 \times 5.73 \times 10^3\,\text{yrs} \times 0.1427}{0.693}$$

= **2717.3 years** **Ans.**

$$\because \left[\log \frac{a}{0.72a} = \log 1.3889 = 0.1427\right]$$

Example 55. *The bones of a prehistoric animal were found to have a $^{14}_{6}C$ activity of 1.53 dps (disintegrations per second) g^{-} carbon. How long ago did the animal live ? The current $^{14}_{6}C$ activity is 15.3 dps per gram of carbon. Half-life of $^{14}_{6}C$ is 5730 years.*

Solution. Initial activity, a = 15.3 dps g^{-}; $a - x$ = 1.53 dps g^{-}, $t_{1/2}$ = 5730 years.

(*i*) $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\,\text{years}}$$

(*ii*) $$t = \frac{2.303}{\lambda} \log \frac{a}{a-x} \quad \text{...(1)}$$

Substituting the values in (1), we get :

$$t = \frac{2.303 \times 5730\,\text{years}}{0.693} \log \frac{15.3\,\text{dps}\,g^{-}}{1.53\,\text{dps}\,g^{-}}$$

$$\because [\log \frac{15.3}{1.53} = \log 10 = 1]$$

$$\therefore \quad t = \frac{2.303 \times 5730\,\text{yrs}}{0.693} \times 1$$

= **1.9042×10^4 years** **Ans.**

Example 56. *One gram of carbon made from green wood gives 15.3 counts per minute whereas one gram of carbon derived from the wood of an Egyptian mummy case gives 9.4 counts per minute under the same conditions. How old is the wood of the mummy case ? ($t_{1/2}$ for ^{14}C = 5770 years).*

Solution. $t_{1/2}$ = 5770 years. We know, $k = 0.693/t_{1/2}$ = 0.693/5770 yr. = 1.2×10^{-4} yr. Also, $\log No/N_t = kt/2.303$. Substituting the values we get, $\log \frac{15.3}{9.4} = \frac{kt}{2.303}$

or $t = \frac{2.303}{k}\left(\log \frac{15.3}{9.4}\right)$. Substituting the values, we get :

$\therefore$ $t = [2.303\,(1.1846 - 0.9731]/1.2 \times 10^{-4}$

Or $t = (2.303 \times 0.2115)/1.2 \times 10^{-4}$

= 4059 yrs. **Ans.**

Example 57. *What should be the age of fossil for meaningful determination of its age ?*

(a) 6 years, (b) 6000 years, (c) 60,000 years, (d) it can be used to calculate any age. **(IIT-JEE, 2006)**

Solution. Radio carbon-dating method ceases to be accurate over periods longer than 30,000 years. So, the correct answer is (*b*).

Example 58. *A sample of a rock contains 0.02 g of Pb-206 for every gram of U-238 present in it. Calculate the age of the rock if half-life of U-238 is 4.5×10^9 years.*

Solution. Wt. of Pb-206 = 0.02 g for every 1g of U-238 present in it.

Let wt. of U-238 present originally = a

$\therefore$ a = [wt. of U-238 present now *i.e.*, at the time of analysis] + wt. of U-238 converted to Pb-206. = Pb-206. 1g + $\left(\frac{238}{206} \times 0.02\text{g}\right)$ = 1g + 0.023g = 1.023g

Also, $a - x$ = wt. of U-238 at the time of analysis = 1g;

$t_{1/2} = 4.5 \times 10^9$ years.

(*i*) $$\lambda = \frac{0.693}{t_{1/2}};\ \lambda = \frac{0.693}{4.5 \times 10^9\,\text{years}}$$

(*ii*) $$t = \frac{2.303}{\lambda} \log \frac{a}{a-x}$$

$$= \frac{2.303 \times 4.5 \times 10^9\,\text{yrs}}{0.693} \log \frac{1.023}{1}$$

$$t = \frac{2.303 \times 4.5 \times 10^9\,\text{yrs}}{0.693} \times 9.876 \times 10^{-3}$$

= **1.477×10^8 yrs** **Ans.**

Example 59. *A sample of uraninite was found on analysis to contain 0.214 g of lead for every gram of uranium. Assuming that all the lead resulted from the radio-active disintegration of* *the uranium since the geological formation of the uraninite and that all isotopes of uranium other than ^{238}U can be neglected, estimate the date when the mineral was formed in the earth's crust. The half life of ^{238}U is 4.5 × 10^9 years.*

Solution. Half-life, $t_{1/2} = 4.5 \times 10^9$ years; disintegration constant, $\lambda = 0.693/t_{1/2} = 0.693/4.5 \times 10^9$ years. Wt. of U-238 present at time of analysis = 1g; Wt. of U-238 present originally = wt. of U-238 present now + wt. of U-238 converted to Pb-206 = 1 + (238/206) × 0.214) = 1 + 0.2472 = 1.2472 g. Let time t is time in which 1.2472 g of U-238 reduced to 1g. Hence $t = (2.303/\lambda)$ [log $a/a - x$] = [2.303 × 4.5 × 10^9/0.693] [log 1.2472/1 = 0.09593].

$\therefore t = (2.303 \times 4.5 \times 10^9 \times 0.09593)/0.693 = 1434589545$ years ≈ 1.4 × 10^9 years **Ans.**

Example 60. *A sample of uranium contains 0.277 g of Pb-208 and 1.667 g of U-238. Calculate the age of sample assuming that all the lead had accumulated due to decay of uranium ($t_{1/2}$ for U-238 = 4.50 × 10^9 years).*

SOLUTION. Half-life, $t_{1/2} = 4.5 \times 10^9$ years; disintegration constant, $\lambda = 0.693/t_{1/2} = 0.693/4.5 \times 10^9$ yrs = 1.54×10^{-10} yr^{-}. Wt. of U-238 = $a - x$ = 1.667 g; wt. of U-238 (initially present) = wt. of U-238 present now + wt. of U-238 converted to Pb-208 = 1.667 + (238 × 0.277/208) = 1.667 + 0.3169 = 1.9839 g. We know that $t = (2.303/\lambda)$ log $a/a - x$. Substituting the values, we get $t = (2.303/1.54 \times 10^{-10}\ \text{yr}^{-})$ [log 1.9839/1.667 = log 1.9839 – log 1.667 = 0.2975 – 0.2219 = 0.0756] **Or** t = (2.303 × 0.0756)/1.54 × 10^{-10} yr^{-} = 1130563636 ≃ 1.13 × 10^9 years **Ans.**

21.12 AVERAGE LIFE

Type. *Average life,*

$$T = \frac{1}{\lambda} \text{ or } \frac{1}{k} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$$

Example 61. *The half life time of a radioactive element is 6930 days. Find its average life.*

Solution. Half-life $t_{1/2}$ = 6930 days. Let average life = T. We know, T = 1.44 × $t_{1/2}$ = 1.44 × 6930 = 9979.2 days **Ans.**

Type. When w g of a nucleide loses y% of its radioactivity, then :

$$a = wg;\ a - x = w - \left(w \times \frac{y}{100}\right) g$$

Example 62. *The average life of a radioactive nucleide is 100 hours. How long will it take 10 grams of the nucleide to lose 75% of its radioactivity.*

Solution. Average life, T = 100 hours. Time = t = ?; initial concentration a = 10g; $a - x$ = 10 – (75 × 10/100) = 2.5 g. We know, T = 1.44 × $t_{1/2}$. ∴ $t_{1/2}$ = 1.44/T = 1.44/100 hours = 1.44 × 10^{-2} hrs. But $k = 0.693/t_{1/2}$ = 0.693/1.44 × 10^{-2} = 48.125. But $k = (2.303/t)$ log $a/a - x$. **Or** 48.125 = $(2.303/t)$ (log 10/2.5 or log 4) = $(2.303/t)$ × 0.6020 **Or** t (2.303 × 0.6020)/48.125 = 0.0288 hr. **Ans.**

Type. When initial amount (w) or counts s^{-} (or min^{-}, hr^{-}) of a radioactive substance is given but the mass of substance left behind after given time, t, is to be found out, then :

(i) $a = w$ or count s^{-} or min^{-} or hr^{-} etc. (ii) $a - x$ = ?, (iii) λ *or* $k = \dfrac{2.303}{t} \log \dfrac{a}{a - x}$

Example 63. *The half life of strontium (90) is 28 years. If 2 micro grams of strontium (90) is absorbed by a newly born child, how much of it is left behind in the child (person) after (1) 28 years and (2) 84 years ?* **(IIT 1995 modified)**

Solution. Half-life, $t_{1/2}$ = 28 yrs; initial concentration, a = 2 μg; k = ? $a - x$ = ? Amount left behind after (i) 28 years = ? (ii) 84 years = ?. We know $k = 0.693/t_{1/2}$ = 0.693/28 = 0.02475 yr^{-}. We know, (i) $k = (2.303/t)$ log $a/a - x$. **Or** 0.02475 = (2.303/28) log 2/$a - x$ = (2.303/28) [log 2 – log ($a - x$)] **Or** (0.02457 × 28/2.303) = 0.3010 – log ($a - x$). 0.3009 – 0.3010 = – log ($a - x$) **Or** – 0.0001 = – log ($a - x$) **Or** $a - x$ = antilog of 0.0001 = 1μg = 1 × 10^{-6} g **Ans.** (ii) 0.02475 = (2.303/84) (log 2/$a - x$)] = (2.303/84) [0.3010 – log ($a - x$) or 0.9027 – 0.3010 = – log ($a - x$) **Or** 0.6017 = – log ($a - x$) **Or** log ($a - x$) = – 0.6017. Thus, $a - x$ = antilog – 0.6017 = 0.25 μ g = 0.25 × 10^{-6} g **Ans.**

Example 64. *β-particle emitter element (half-life period = 60.6 min) registers 2408 counts per second. Determine the counting rate after 1.5 hours ?*

Solution. Half-life, $t_{1/2}$ = 60.6 min. = 60.6 × 60 = 3636.0 seconds; time t = 1.5 hours = 1.5 × 60 × 60 = 5400 seconds. Number of counts per second = 2408. We know, k = 0.693/ $t_{1/2}$ = 0.693/3636. But 2.303 log $a/a - x = kt$ **Or** 2.303 log $\dfrac{2408}{a - x}$ = (0.693/3636) × 5400 or log 2408 – log ($a - x$) = 0.693/ (3636 × 2.303) × 5400 = 0.4469 **Or** 3.3816 – log ($a - x$) = 0.4469 – 3.3816 = – 2.9347 **Or** –log ($a - x$) = – 2.9347. Thus $a - x$ = antilog of 2.9347 = 860.3 counts **Ans.**

Example 65. *Starting with 1.0 g of the radioactive sample, 0.25 g of it left after 5 days. Calculate the amount left after one day.* **(CBSE, 1993)**

Solution. Initial concentration, a = 1.0g; $a - x$ = 0.25 g; time = 5 days. Wt. left after one day (time) = ? We know, $k = (2.303/t)$ log $a/a - x$ = (2.303/5) log 1/0.25 = (2.303/5) log 4 = (2.303/5) × 0.6020 = 0.2772. Using relation, $k = (2.303/t)$ log $a/a - x$, we have, 0.2772 = (2.303/1) log 1/$a - x$ **Or** 0.2772/2.303 = log 1 – log ($a - x$) **Or** 0.1203 = 0 – log ($a - x$) or log ($a - x$) = – 0.1203. Hence, $a - x$ = antilog – 0.1203 = 0.758 g **Ans.**

Example 66. *A radioactive substance has a half-life period of 30 days. Calculate (i) the radioactive disintegration constant (ii) the average life period (iii) the time taken by 3/4 of the original number of atoms to disintegrate and (iv) the time taken by 1/8 of the original number of atoms to remain unchanged.*

Solution. Half life $t_{1/2}$ = 30 days; radioactive disintegration constant, λ = ?; average life period, T = ?; time (t_1) taken by 3/4 of the original no. of atoms to disintegrate = ?; time (t_2) taken by 1/8 of the original no. of atoms to remain unchanged = ?. We know (i) $\lambda = 0.693/t_{1/2}$ = 0.693/30 days = 0.0231 day$^-$ **Ans.** (*ii*) T = 1.44 × $t_{1/2}$ = 1.44 × 30 days = 43.20 days. **Ans.** (*iii*) $\lambda = (2.303/t)$ [log 1/1-3/4 = log 4] **Or** 0.0231 = 2.303/t [0.6020]. ∴ t = (2.303 × 0.6020)/0.0231 = 60 days **Ans.** (*iv*) λ = 2.303/t [log 1/1/8 = log 8] **Or** 0.0231 = (2.303/t) [0.9030]. ∴ t = (2.303 × 0.9030)/0.0231 = 90 days **Ans.**

Type. When loss in weight (w_1) of a substance from a given weight (w) of that substance in a given time is given, then :

$$a = w\ ;\ a - x = w - w_1$$

EXAMPLE 67. *One gram of a radioactive substance loses 0.01 g in 50 seconds. Calculate its half-life and average life.*

SOLUTION. Initial amount, a = 1.0 g, $a - x$ = 1.0 – 0.01 = 0.99g; t = 50 sec. We know, $\lambda = (2.303/t)\log a/a - x$ = (2.303/50) [log 1/0.99 **Or** 100/99) = (2.303/50) [log 100 – log 99 = 2.0 – 1.9956 = 0.0044) = (2.303 × 0.0044)/50 = 2.026 × 10^{-4}. But $t_{1/2} = 0.693/\lambda$ = 0.693/2.026 × 10^{-4} = 3420 *s* **Ans.** But average life = 1.44 × $t_{1/2}$ = 1.44 × 3420 ≈ 4925*s* **Ans.**

Type. Activity $-\dfrac{dN}{dt} = \lambda N$; N = no. of atoms.

$\mu = 10^{-6}$; Ci = 3.7 × 10^{10} dps

Activity means no. of particles emitted per second or no. of disintegrations per second.

EXAMPLE 68. *The half-life of $^{100}_{43}Tc$, a β-emitter, is 16 seconds. How many atoms of $^{100}_{43}Tc$ are present in a sample with an activity of 0.200 μ Ci ? Also determine the mass of the sample.*

SOLUTION. Half-life $t_{1/2}$ = 16 sec; no. of atoms, N = ?; activity – dN/dt = 0.2 × 10^{-6} × 3.7 × 10^{10} *dps*. But $-dN/dt = \lambda N$. But $\lambda = 0.693/t_{1/2}$ = 0.693/16 = 0.04331. Substituting the values of $-dN/dt$ and λ, we get : 0.2 × 10^{-6} × 3.7 × 10^{10} = 0.04331 × N. Hence, N = (0.2 × 10^{-6} × 3.7 × 10^{10})/0.04331 = 1.71 × 10^5 atoms **Ans.** Also, 6.02 × 10^{23} atoms weigh = 100 g of $^{100}_{43}$Tc. So, 1.71 × 10^5 atoms would weigh = (100 × 1.71 × 10^5)/6.02 × 10^{23} = 2.8 × 10^{-17}g **Ans.**

EXAMPLE 69. *Na has a half-life period 14.8 hours. How much time will it take to lose 90% of its activity.* **(PSEB, 2000)**

SOLUTION. $t_{1/2}$ = 14.8 hr, a = 100;
$a - x$ = 100 – 90 = 10; t = ?

(*i*) $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.8\text{ hr}}$$

(*ii*) $$t = \frac{2.303}{\lambda}\log\frac{a}{a-x}$$

$$= \frac{2.303 \times 14.8\text{ hr}}{0.693}\log\frac{100}{10}$$

$$= \frac{2.303 \times 14.8\text{ hr}}{0.693} \times 1$$

$$\left[\because \log\frac{100}{10} = \log 10 = 1\right]$$

t = **49.18 hr** **Ans.**

EXAMPLE 70. *The amount of ^{14}C content in a piece of wood is found to be 1/16 of the original amount. Calculate the age of the wood. ($t_{1/2}$ = 5770 years).*

SOLUTION. Half-life $t_{1/2}$ = 5770 yrs; age (t) of wood = ?; initial amount a = 1, $a - x$ = (1/16) × 1 = 1/16. We know, $\lambda = 0.693/t_{1/2}$ = 0.693/5770 yrs. = 1.2 × 10^{-4} yr. But, $t = (2.303/\lambda)$ [log 1/1/16 = log 16] = 1.2041 **Or** t = (2.303/1.2 × 10^{-4}) × 1.2041 = 23108 yrs. **Ans.**

EXAMPLE 71. *What is the age of a vegetation beverage whose tritium content is only 15% of level in living plants ? ($t_{1/2}$ for tritium = 12.3 years).*

SOLUTION. Half-life $t_{1/2}$ = 12.3 yrs; λ = ? age *i.e.*, time, t = ? initial concentration, a = 100; $a - x$ = 15. We know that : $\lambda = 0.693/t_{1/2}$ = 0.693/12.3 yrs. = 0.05634 yr$^-$. Also, $t = (2.303/\lambda)\log a/a - x$ **Or** t = (2.303/0.05634) log 100/15 = (2.303/0.05634) [log 100 – log 15 = 2.0 – 1.1761 = 0.8239) = 33.68 years. **Ans.**

EXAMPLE 72. *A freshly cut sample of a plant gives 20.4 counts per minute per gram. If it is assumed that counts are due to the presence of radioactive carbon (At. wt. 14) only, how many counts would it give after 100 years, if the half life period of ^{14}C is 5760 years ?*

SOLUTION. Half-life, $t_{1/2}$ = 5760 years; decay constant, $\lambda = 0.693/t_{1/2}$ = (0.693/5760 × 365 × 24 × 60 min). = 2.289 × 10^{-10} min$^-$; time, t = 100 years = 100 × 365 × 24 × 60 min; initial concentration, a = ? $a - x$ = 20.4 counts min$^-$g$^-$. We know, $t = (2.303/\lambda)$ [log a/20.4 = log a – log 20.4 = log a – 1.3096]. Substituting the values, we get : 100 × 365 × 24 × 60 min = 2.303/2.289 × 10^{-10} min [log a – 1.3096] **Or** log a – 1.3096 = 100 × 365 × 24 × 60 min. × 2.289 × 10^{-10}min$^-$/2.303. **Or** log a – 1.3096 = 0.00522 **Or** log a = 1.3096 + 0.00522 = 1.3148. Hence a = antilog 1.3148 = 20.6 **Ans.**

EXAMPLE 73. *The ratio of C-14 in an old wooden piece is 13% that of the atmosphere. Calculate the age of the wooden article ($t_{1/2}$ of ^{14}C is 5580 years).*

SOLUTION. Half-life $t_{1/2}$ = 5580 years; decay constant, λ = $0.693/t_{1/2}$ = 0.693/5580 years = 1.2419 × 10^{-4} years$^-$. Age of article, t = ? We know, $t = 2.303/\lambda$ [log 100/13 = log 100 – log 13 = 2.000 – 1.1139 = 0.8861). **Or** t = [2.303/1.2419 × 10^{-4} yr$^-$] × 0.8861 = 16432 yrs **Ans.**

EXAMPLE 74. *Equal amounts of two samples of carbon are burnt and the radioactivities of CO_2 formed were measured. The activities were 2100 and 1400 counts per week respectively. Find the age difference of the samples. In showing radioactivity, how does ^{14}C nucleus change ? [$t_{1/2}$ for ^{14}C = 5600 years].* **(WBJEE, 2004)**

SOLUTION. According to decay rate,

$$-\frac{dN}{dt} = \lambda N$$

$$\therefore \qquad -\frac{dN_1}{dt} = \lambda N_1 = 2100\text{ counts} \qquad ...(i)$$

$$-\frac{dN_2}{dt} = \lambda N_2 = 1400\text{ counts} \qquad ...(ii)$$

Dividing equation (*i*) by equation (*ii*), we have

$$\frac{2100}{1400} = \frac{N_1}{N_2} = \frac{N_0.e^{-\lambda t_1}}{N_0.e^{-\lambda t_2}} = \frac{e^{-\lambda t_1}}{e^{-\lambda t_2}} = e^{-\lambda t_1} + e^{\lambda t_2}$$

or $$\frac{3}{2} = e^{\lambda(t_2 - t_1)} \text{ or } \ln\frac{3}{2} = \lambda(t_2 - t_1)$$

or $$2.303 \log\frac{3}{2} = \frac{0.693}{t_{1/2}}(t_2 - t_1) \qquad \left[\because \lambda = \frac{0.693}{t_{1/2}}\right]$$

or $$2.303 \times 0.1761 = \frac{0.693}{5600\,\text{yrs}}(t_2 - t_1)$$

or $$(t_2 - t_1) = \frac{2.303 \times 0.1761 \times 5600\,\text{yrs}}{0.693}$$

$$= 3277 \text{ years}$$

Thus, the age difference in the two samples is 3277 years.

${}^{14}_{6}C$ is a β-emitter and gets transformed into ${}^{14}_{7}N$ by losing a β-particle.

$${}^{14}_{7}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$

EXAMPLE 75. *The isotopes ^{238}U and ^{235}U occur in nature in the ratio 140 : 1. Assuming that at the time of earth formation, they were present in the equal ratio, make an estimation of the age of earth. The half-life period of ^{238}U and ^{235}U are 4.5 × 10^9 and 7.13 × 10^8 years respectively.* **(Roorkee, 1983)**

SOLUTION. In nature

$$\frac{N_U{}^{238}}{N_U{}^{235}} = \frac{140}{1} \text{ at } t = t$$

At the time of earth formation,

$$\frac{N_0{}^{238}}{N_0{}^{235}} = \frac{1}{1} \text{ at } t = 0$$

$$\therefore \quad \frac{N_0{}^{238}}{N_0{}^{235}} \times \frac{N_U{}^{235}}{N_U{}^{238}} = \frac{1}{140}$$

For $$U^{238}, \frac{N_0{}^{238}}{N_U{}^{238}} = e^{\lambda^{238}}$$

For $$U^{235}, \frac{N_0{}^{235}}{N_U{}^{235}} = e^{\lambda^{235}}$$

$$\therefore \quad \frac{N_0{}^{238}}{N_0{}^{235}} \times \frac{N_U{}^{235}}{N_U{}^{238}} = e^{(\lambda^{238} - \lambda^{235})t}$$

or $$= \frac{1}{140}\, e^{(\lambda^{238} - \lambda^{235})t}$$

or $$(\lambda^{238} - \lambda^{235})t = \log_e 1 - \log_e 140$$

or $$\left[\frac{0.693}{4.5 \times 10^9} - \frac{0.693}{7.13 \times 10^8}\right] \times t$$

$$= -\,2.303 \log_{10} 140 = -\,4.9425.$$

$$\therefore \quad t = 6.04 \times 10^9 \text{ years.}$$

EXAMPLE 76. *A sample of ^{238}U (half life = 4.5 × 10^9 years) ore is found to contain 23.8 g of ^{238}U and 20.6 g of ^{206}Pb. Calculate the age of the ore.* **(Roorkee, 1996)**

SOLUTION. ^{238}U decays according to the reaction :

$${}^{238}_{92}U \rightarrow {}^{206}_{82}Pb + 8\,{}^{4}_{2}He + 6\,{}^{0}_{-1}e$$

Thus one gram atoms of ^{238}U give one gram atoms of ^{206}Pb.

^{206}Pb present in the ore

$$= \frac{20.6}{206} = 0.1 \text{ gm atoms}$$

$$= {}^{238}U \text{ decayed.}$$

^{238}U present in the ore

$$= \frac{23.8}{238} = 0.1 \text{ g atom}$$

$$N = 0.1 \text{ g atom}$$

$$N_0 = \text{U present + U decayed}$$

$$= 0.1 + 0.1 = 0.2 \text{ g atom}$$

$$\lambda = \frac{0.693}{t_{0.5}} = \frac{0.693}{4.5 \times 10^9 \text{years}}$$

Now, $$t = \frac{2.303}{\lambda}\log\frac{N_0}{N}$$

$$= \frac{2.303 \times 4.5 \times 10^9}{0.693}\log\frac{0.2}{0.1}\text{years}$$

or $t = 4.5 \times 10^9$ years. **Ans.**

21.13 RADIOACTIVE DISINTEGRATION SERIES

The *spontaneous* series of changes, involving transformation of the parent radioactive element into non-radioactive end product is called radioactive disintegration series. For disintegration, series are summarised below :

				Value of n	
Series	*Name of series*	*Initial element*	*Last stable elements*	*Initial element*	*Final element*
4*n*	Thorium series	Thorium 232	Lead 208	58	52
4*n* + 1	Neptunium series	Plutonium 241	Bismuth 209	60	52
4*n* + 2	Uranium series	Uranium 238	Lead 206	59	51
4*n* + 3	Actinium series	Uranium 235	Lead 207	58	51

Location of disintegration series. Divide the mass number by 4 and find out the remainder. 4*n* + remainder gives the name of the series.

Type. To know the name of the disintegration series.

EXAMPLE 77. *Name the series to which (i) ^{226}Ra, (ii) ^{235}U, (iii) ^{209}Bi, (iv) ^{208}Pb belong.*

SOLUTION. (*i*) ^{226}Ra : $\frac{226}{4}$ = 56 + remainder, 2. So, it belongs to 4*n* + 2 series.

(*ii*) ^{235}U : $\frac{235}{4}$ = 58 + remainder, 3. So, it belongs to 4*n* + 3 series.

(*iii*) ^{209}Bi : $\frac{209}{4}$ = 52 + remainder, 1. So, it belongs to 4*n* + 1 series.

(*iv*) ^{208}Pb : $\frac{208}{4}$ = 52 + no remainder. So, it belongs to 4*n* series.

Type. Mass number of an element in a given disintegration series.

= 4 × *n* for element of 4*n* series.

= (4 × *n*) + 1 for element of (4*n* + 1) series.

= (4 × *n*) + 2 for element of (4*n* + 2) series.

= (4 × *n*) + 3 for element of (4*n* + 3) series.

EXAMPLE 78. *Find the mass number of an element in (i) 4n + 2 series having value of n equal to 59. (ii) 4n series having n = 52.*

SOLUTION. (*i*) 4*n* + 2 series, with *n* = 59.

∴ Mass number = 4*n* + 2 = 4 × 59 + 2 = 236 + 2 = 238 a.m.u. **Ans.**

(*ii*) 4*n* series, with

$n = 52$

∴Mass number = 4*n* = 4 × 52 = 208 a.m.u. **Ans.**

EXAMPLE 79. *A 2.4 × 10⁻⁵ g sample of radioactive,* $^{24}_{11}Na$ *disintegrates at the rate of 7.73 × 10¹² atoms per second. Calculate the half-life of* $^{24}_{11}Na$.

SOLUTION. Wt. of ^{24}Na = 2.4×10^{-5}g; at. wt. of ^{24}Na = 24.

∴ Atoms present in 2.4×10^{-5}g ^{24}Na

$$= \frac{2.4 \times 10^{-5}\ \text{g}}{\text{at. wt. of }^{24}\text{Na}} \times 6.02 \times 10^{23}$$

$$= \frac{2.4 \times 10^{-5}}{24} \times 6.02 \times 10^{23} = 6.02 \times 10^{17}$$

Atoms disintegrating per second

$= 7.73 \times 10^{12}$

∴ λ = Fraction of atoms which decay

$$= \frac{\text{Atoms disintegrating per second}}{\text{Atoms present}}$$

$$= \frac{7.73 \times 10^{12}}{6.02 \times 10^{17}}\ \text{s}^{-} = 1.28 \times 10^{-5}\text{s}^{-}$$

But $t_{1/2} = \frac{0.693}{\lambda}$;

$$t_{1/2} = \frac{0.693}{1.28 \times 10^{-5}} \simeq 5.4 \times 10^{4}\ \text{sec}.$$

$$= 5.4 \times 104\ \text{sec} \times \frac{1\,\text{min.}}{60\,\text{sec.}} \times \frac{1\,\text{hr}}{60\,\text{min.}}$$

$$\times \frac{1\,\text{day}}{24\,\text{hr}} \times \frac{1\,\text{yr}}{365\,\text{days}} = \mathbf{1.7 \times 10^{-3}\ year.}$$

EXAMPLE 80. *You have 0.1g atom of a radioactive isotope* $^{A}_{Z}X$ *(half-life = 5 days). How many number of atoms will decay during the eleventh day ?* **(Roorkee, 1988)**

SOLUTION. $t_{1/2}$ = 5 days. Hence,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5\ \text{days}} = 0.1$$

1g atom of isotope contain atoms

$= 6.023 \times 10^{23}$ atoms

∴ 0.1g atom of isotope contain atoms

$= 6.023 \times 10^{23} \times 0.1 = 6.023 \times 10^{22}$ atoms

Since $t_{1/2}$ = 5 days, so, the no. of atoms after 10 days

$$= \frac{6.023 \times 10^{22}}{2^{n} = 2^{2}} = 1.506 \times 10^{22}\ \text{atoms}$$

$$\left[\because\ n = \frac{10\ \text{days}}{5\ \text{days}} = 2 = \text{no. of half-lives}\right]$$

∴ No. of atoms (N) after 11 days

$= \text{No} \times e^{-\lambda t}$

Or $\frac{\text{No}}{\text{N}} = e^{\lambda t}$. Taking logs of both sides,

We get, $\log\frac{\text{No}}{\text{N}} = \frac{\lambda t}{2.303}$

∴ log No – log N

$$= \frac{\lambda t}{2.303}$$

log 6.023 × 10²² – log N

$$= \frac{0.1386\,\text{day}^{-} \times 11\,\text{days}}{2.303}$$

log 6.023 + log 10²² – log N

= 0.662

0.7798 + 22 – 0.662

= log N; log N = 22.1178

∴ N = antilog 22.1178 = 1.311×10^{22} atoms.

∴ No. of atoms that decay during eleventh day = (1.506×10^{22}) – (1.311×10^{22}) = 10^{22} (1.506 – 1.311) = **0.195×10^{22} atoms** **Ans.**

EXAMPLE 81. *During treatment in a hospital, a patient was injected with one microgram* $^{24}_{11}Na$. *Calculate the time in which* *its radioactivity would become 10% of the original atom ($t_{1/2}$ $^{24}_{11}$Na. = 14.8 hours).*

Solution. $t_{1/2}$ = 14.8 hours.

Hence, $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.8\,\text{hrs}}$$

But $$t_{10\%} = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}}$$

$$t_{10\%} = \frac{2.303}{0.693/14.8\,\text{hr}}\log\frac{\text{M}}{\text{M}/10}$$

$$= \frac{2.303}{0.693/14.8\,\text{hr}}\log 10$$

$$\left[\because \text{M}\times\frac{10}{100} = \frac{\text{M}}{10}\right]$$

Or $$t_{10\%} = \frac{2.303\times 14.8\times 1}{0.693} = \mathbf{49.18\ hours}$$ **Ans.**

Example 82. *Calculate the time in which 75% of $^{95}_{36}Kr$ ($t_{1/2}$ = 10.6 year) would disintegrate.*

Solution. $t_{1/2}$ = 10.6 years.

Hence $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.6\,\text{yrs}} = 0.06538\,\text{yr}^{-}$$

Here, No = 100. So, N = 100 – 75 = 25. We know that :

$$t = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}};$$

$$t = \frac{2.303}{0.06538\,\text{yr}^{-}}\log\frac{100}{25}\ i.e., 4$$

$$\therefore\quad t = \frac{2.303}{0.06538\,\text{yr}^{-}}\times 0.602$$

$$= \mathbf{212\ years}$$ **Ans.**

Example 83. *Calculate the number of curies of $^{239}_{93}Np$ ($t_{1/2}$ = 2.33 days) needed to produce 0.15 mg of $^{239}_{94}Pu$.*

Solution. $t_{1/2}$ = 2.33 days.

Hence $$\lambda = \frac{0.693}{2.33\,\text{days}}$$

$$= \frac{0.693}{2.33\,\text{days}}\times\frac{1\,\text{day}}{24\,\text{hr}}\times\frac{1\,\text{hr}}{60\,\text{min}}\times\frac{1\,\text{min}}{60\text{s}}$$

$$= 3.442\times 10^{-6}\,\text{s}^{-}$$

$$\text{wt. of }^{239}_{94}\text{Pu} = 0.15\text{ mg} = \frac{0.15}{1000}\text{g};$$

$$\text{g at.wt.of }^{239}_{94}\text{Pu} = 239\text{ g}$$

1 g atom of $^{239}_{94}$Pu (= 239 g) contain atoms

$$= 6.023\times 10^{23}.$$

$$\therefore\ \frac{0.15}{1000}\text{g of }^{239}_{94}\text{Pu contains atoms}$$

$$= \frac{6.023\times 10^{23}}{239}\times\frac{0.15}{1000} = 3.78\times 10^{17}\text{ atoms}$$

∴ In order to get 0.15 mg $^{239}_{94}$Pu, $^{239}_{93}$Np must disintegrate.

∴ Rate of disintegration

$$= \text{No. of atoms}\times\text{decay constant}$$

$$= 3.78\times 10^{17}\text{ atoms}\times 3.442\times 10^{-6}s^{-}$$

$$= 1.3\times 10^{12}\text{ atoms }s^{-}$$

One curie = 3.7×10^{10} disintegrations s^{-} (or *dps*)

∴ 3.7×10^{10} dps = 1 curie

$$1.3\times 10^{12}\text{ dps} = \frac{1.3\times 10^{12}}{3.7\times 10^{10}} = \mathbf{35.14\ curie}$$ **Ans.**

Type. To calculate the weight of a radioactive element left behind from a known weight and time when its half-life is given. Use the relation :

Number of half-lives '

$$n' = \frac{\text{Given time after which the sample left behind is required}}{\text{Half-life time}}$$

Wt. of sample left behind

$$= \text{Given weight (in g)}\times\left(\frac{1}{2}\right)^{n}$$

Example 84. *The half-life period of ^{60}Co is 5.2 years. Calculate the wt. of ^{60}Co left behind from a 8.0 g sample of it that will still be radioactive after 20.8 years.*

Solution. $t_{1/2}$ of ^{60}Co = 5.2 years. Wt. of sample = 8.0 g

Time after which ^{60}Co is to remain radioactive = 20.8 years.

∴Number of half-lives,

$$'n' = \frac{20.8}{5.2} = 4.$$

Wt. in gram of sample that will be left behind

$$= 8.0\times\left(\frac{1}{2}\right)^{4}$$

$$= 8\times 0.0625 = 0.5\text{ g}$$

Example 85. *The radioactivity of an element decreases to half its initial value in 5 hours; still how long it will take for the activity to become 1/8th of the initial activity ?* **(BIT, 1995)**

Solution. $t_{1/2}$ = 5 hours. Total time of disintegration =?

Let N = no. of nuclei of radioactive substance after time, *t*.

No = no. of nuclei of radioactive substance initially present

n = no. of half-lives

We know that :

$$N = No\left(\frac{1}{2}\right)^n ;$$

$$N = No \times \frac{1}{8} = \frac{No}{8} \text{ (Given).}$$

Hence, $\frac{No}{8} = No\left(\frac{1}{2}\right)^n ; \frac{1}{8} = \left(\frac{1}{2}\right)^n ; \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n .$

Hence, $n = 3$

∴ Total time of disintegration

$= n \times t_{1/2} = 3 \times 5 \text{ hr} = \mathbf{15\ hr.}$ **Ans.**

EXAMPLE 86. *A radioactive isotope has a half-life of 50 days. What fraction of the material will be left after 100 days?* **(ISC, 1988)**

SOLUTION. $t_{1/2} = 50$ days.

Time after which material is to be left behind = 100 days.

∴No. of half-lives

$$= \frac{100\,\text{days}}{50\,\text{days}} = 2$$

∴ Amount left after 2 half-lives

$$= 1\left(\frac{1}{2}\right)^2 = \frac{1}{4} = \frac{1}{4} \times 100 = \mathbf{25\%}$$ **Ans.**

EXAMPLE 87. *What amount of radioactivity is left behind when one millicurie of radioactive element of half-life 14 days is stored for 42 days ?* **(ISC, 1989)**

SOLUTION. $t_{1/2} = 14$ days.

Time for which the radioactive element was stored = 42 days.

∴ No. of half-lives

$$= \frac{42\,\text{days}}{14\,\text{days}} = 3$$

Hence amount of radioactivity left behind

$$= 1 \times \left(\frac{1}{2}\right)^3 \text{ millicurie} = \frac{1}{8} \textbf{ millicurie}$$

Ans.

EXAMPLE 88. *One gram of* $^{198}_{79}Au$ ($t_{1/2}$ = *65 hours) decays by β-emission to produce stable mercury.*

(i) Write the nuclear reaction for the process.

(ii) How much mercury will be present after 260 hrs ? **(Roorkee, 1984)**

SOLUTION. (*i*) *Reaction* : $^{198}_{79}\text{Au} \rightarrow {}^{198}_{80}\text{Hg} + {}^{0}_{-1}\beta.$

(*ii*) $t_{1/2} = 65$ hrs.

Time after which mercury will be present = 260 hrs.

∴no. of half-lives

$$= \frac{260\,\text{hrs}}{65\,\text{hrs}} = 4.$$

Hence amount of gold that will be left after 260 hrs.

$$= 1 \times \left(\frac{1}{2}\right)^4 = \frac{1}{16}\text{g}$$

∴ Amount of

$$\text{Hg} = 1 - \frac{1}{16} = \frac{15}{16}\text{g}$$ **Ans.**

EXAMPLE 89. *The activity of a radioactive substance reduces to* $\frac{1}{16}$*th of its original value in one and a half hour. Find the value of decay constant of this substance.*

SOLUTION. We know that,

$$\frac{N}{No} = \left(\frac{1}{2}\right)^n$$

∴ $\frac{1}{16} = \left(\frac{1}{2}\right)^4 .\text{Hence}, n = 4$

Also, time $= n \times t_{1/2}$.

So, $t_{1/2} = \frac{\text{time}}{\text{n}} = \frac{1.5\text{ hr}}{4} \times \frac{60\text{ min.}}{1\text{ hr}} = 22.5\text{min.}$

∴ $t_{1/2} = 22.5$ min. But decay constant,

$$\lambda = \frac{0.693}{t_{1/2}}$$

∴ $\lambda = \frac{0.693}{22.5\,\text{min.}} = 0.0308\ \text{min}^{-}$

$= 3.08 \times 10^{-2}\ \text{min}^{-}$ **Ans.**

EXAMPLE 90. *A radioactive isotope has a half-life of 25 days starting with 4g of the isotope. What will be the mass remaining after 75 days ?* **(ISC, 1993)**

SOLUTION. $t_{1/2} = 25$ days.

Time after which the mass left is to be calculated

= 75 days.

∴no. of half-lives

$$= \frac{75\,\text{days}}{25\,\text{days}} = 3$$

∴ Mass remaining after 75 days

$$= 4\text{g} \times \left(\frac{1}{2}\right)^3 = 4 \times \frac{1}{8} = \mathbf{0.5g.}$$

EXAMPLE 91. *A certain radioisotope* $^{A}_{Z}X$ *(half-life 10 days) decays to give* $^{A-4}_{Z-2}Y$. *If 1.0g atom of* $^{A}_{Z}X$ *is kept in a sealed vessel, how much helium would accumulate in 20 days. Express the results in cm³ at STP and in g.* **(Roorkee, 1987)**

SOLUTION. $t_{1/2} = 10$ days.

Time for which helium has to be accumulated

= 20 days.

∴ no. of half-lives

$$= \frac{20\,\text{days}}{10\,\text{days}} = 2$$

∴ Wt. of radioisotope left after 20 days

$$= 1.0\text{g} \times \left(\frac{1}{2}\right)^2 = \frac{1}{4}\text{g}$$

∴ Helium produced

$$= 1-\frac{1}{4}=\frac{3}{4}\text{g atom.}$$

$$= \frac{3}{4}\times 4 = 3g \quad [\because \text{at.wt.of He}=4]$$

1 g. atom of helium occupy volume at STP = 22400 cm^3

∴ $\frac{3}{4}$ g atom of helium occupy volume at STP = 22400 cm^3 × $\frac{3}{4}$

$$= 16800 \text{ cm}^3 = \mathbf{1.68 \times 10^4 cm^3} \qquad \textbf{Ans.}$$

EXAMPLE 92. *A radioactive isotope of polonium,* $^{210}_{84}Po$ *decays by emitting α-particles to ultimately give* $^{206}_{82}Pb$ *(*$t_{1/2}$ *= 138.4 days). If 1.0g of this isotope is placed in a sealed graduated tube, calculate the volume of helium gas that will be collected is 44.4 days. Express the result in cm³ at N.T.P.*

SOLUTION. (*i*) $t_{1/2}$ = 138.4 days. Hence,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{138.4\,\text{days}}$$

or $\lambda = 5.007 \times 10^{-3}$ day$^-$

wt. of Po^{210} = 1.0g

∴ No. of

$$\text{Po}^{210}\text{ atoms} = \frac{\text{wt. in g}}{\text{g at. wt. of Po}} \times 6.023 \times 10^{23}$$

$$= \frac{1.0\text{g} \times 6.023 \times 10^{23}}{210\text{g}}$$

$$= \mathbf{2.87 \times 10^{21}\ atoms\ g^- = No.}$$

No = 2.87 × 10^{21} atoms g$^-$;

N = ? t = 44.4 days

We know that :

$$\lambda = \frac{2.303}{t}\log\frac{\text{No}}{\text{N}};$$

$$5.007\times10^{-3}\,\text{day}^- = \frac{2.303}{44.4\,\text{days}}\log\frac{2.87\times10^{21}}{\text{N}}$$

$$\therefore \log\frac{2.87\times10^{21}}{\text{N}} = \frac{5.007\times10^{-3}\text{day}^-\times 44.4\,\text{days}}{2.303}$$

$$= 0.09653$$

Taking antilogs of both sides, we get :

$$\frac{2.87\times10^{21}}{\text{N}} = \text{antilog } 0.09563 = 1.2489$$

$$\therefore \quad \text{N} = \frac{2.87\times10^{21}}{1.2489} = \mathbf{2.29 \times 10^{21}\ atoms\ g^-}$$

Hence no. of atoms of helium formed = No – N = (2.87 × 10^{21}) – (2.29 × 10^{21}) = 0.58 ×10^{21} atoms g$^-$.

(*ii*) 6.023 × 10^{23} atoms of helium occupy volume = 22400 cm^3 at NTP.

∴ 0.58 × 10^{21} atoms of helium would occupy volume

$$= \frac{22400\,\text{cm}^3}{6.023\times10^{23}} \times 0.58 \times 10^{21}$$

$$= \mathbf{21.57\ cm^3} \qquad \textbf{Ans.}$$

Type. *To calculate value of Avogadro's constant when nuclear particles like α-particles are emitted from a radioactive substance.*

EXAMPLE 93. *A sample of the radioactive element, radium, disintegrated at an average rate of 2.24 × 10^{13} alpha particles per minute. Each alpha particle takes up 2 particles from the air and becomes a neutral He atom. After 420 days, the helium gas collected amounted to 0.5 mL measured at 27°C and 750 mm of mercury pressure. From the above data, calculate the value of Avogadro's constant.* **(ISC, 1991; MLNR, 1991)**

SOLUTION. (*i*) No. of α-particles emitted = 2.24 × 10^{13} min$^-$.

P$_1$ = 750 mm, V$_1$ = 0.5 mL, T$_1$ = 27 + 273 = 300 K. At NTP, P$_2$ = 760 mm, V$_2$ = ?, T$_2$ = 273K. Using gas equation, we have :

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

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2}$$

$$= \frac{750\,\text{mm}\times0.5\,\text{mL}\times273\,\text{k}}{300\,\text{K}\times760\,\text{mm}} = 0.449\,\text{mL}$$

(*ii*) 22400 mL He = 1 mol.

$$\therefore\ 0.449\text{ mL He} = \frac{0.449\,\text{mL}}{22400\,\text{mL}}\text{ mol} = 2.0045\times10^{-5}\text{ mol}$$

(*iii*) In 420 days × $\frac{24\,\text{hrs}}{1\,\text{day}}\times\frac{60\,\text{min}}{1\,\text{hr}}$ He gas collected

= 2.0045 × 10^{-5} mol

In 1 minute, He gas collected

$$= \frac{2.0045\times10^{-5}\text{mol}}{420\times24\times60} = 3.3143\times10^{-11}\text{mol.}$$

(*iv*) 3.3143 × 10^{-11} mol

= 2.24 × 10^{13} α-particles

$$\therefore \qquad 1\text{ mol} = \frac{2.24\times10^{13}}{3.3143\times10^{-11}} = \mathbf{6.76\times10^{23}} \qquad \textbf{Ans.}$$

EXAMPLE 94. *Calculate the total radioactivity resulting from radioactive* $^{40}_{19}K$ *decay in a 60kg human body. Half-life of* ^{40}*K = 1.3 × 10^9 years. The human body contains about 0.35% potassium by weight while* ^{40}*K constitutes 0.012% of potassium in nature.*

SOLUTION. (*i*) Wt. of human body

= 60 kg = 60 × 10^{3}g

$$\therefore \qquad \text{Total }^{40}\text{K} = \frac{0.012}{100}\times\frac{0.35}{100}\times60\times10^3\,\text{g} = 0.0252\,\text{g.}$$

(*ii*) No. of ^{40}K atoms,

$$\text{'N'} = \frac{\text{wt. in g}}{\text{g. at. wt. of }^{40}\text{K}} \times 6.02 \times 10^{23}\text{atoms}$$

$$= \frac{0.0252\text{g}}{40\text{g}} \times 6.02 \times 10^{23}\text{atoms}$$

$$= 3.79 \times 10^{20} \text{ atoms}$$

$$(iii)\ \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.3 \times 10^9\text{yr}} \times \frac{1\text{yr}}{365\text{days}} \times \frac{1\text{day}}{24\text{hr}} \times \frac{1\text{hr}}{60\text{min}} =$$

$$= 1.01 \times 10^{15} \text{ min.}$$

$$(iv) \qquad -\frac{dN}{dt} = N\lambda = 3.79 \times 10^{20} \text{ atoms} \times 1.01 \times 10^{-15} \text{ min}^-$$

$$= 3.82 \times 10^5 \text{ dpm.}$$

Example 95. $^{235}_{92}U$ *yields 4770 disintegrations per minute per mg. Calculate its decay constant (λ) and half-life period ($t_{0.5}$).*

Solution. g at. wt. of ^{235}U = 235 g mol$^-$, Avogadro's number = 6.023×10^{23} mol$^-$.

N [= No. of atoms (nuclei) of $^{235}_{92}$U]

$$= \frac{\text{wt. in g}}{\text{g at. wt. of }^{235}\text{U}} \times 6.023 \times 10^{23}\text{mol}^-$$

$$= \frac{10^{-3}\text{g} \times 6.023 \times 10^{23}\text{mol}^-}{235\,\text{g mol}^-}$$

$$= \frac{6.023 \times 10^{20}}{235}$$

Activity of sample = No. of disintegrations per second

$$= \frac{4770}{60\,\text{sec.}} \qquad [\because 1 \text{ min} = 60 \text{ sec.}]$$

Or $\quad -\frac{dN}{dt} = \frac{4770}{60}\text{s}^-$. But $-\frac{dN}{dt} = N\lambda$.

Hence, $\quad \lambda = -\frac{dN}{dt} \times \frac{1}{N}$

$$\therefore \qquad \lambda = \frac{4770}{60\,\text{s}} \times \frac{1}{N} = \frac{4770}{60\text{s}} \times \frac{60\text{s}}{1\,\text{min}}$$

$$\times \frac{60\,\text{min}}{1\,\text{hr}} \times \frac{24\,\text{hr}}{1\,\text{day}} \times \frac{365\,\text{days}}{1\,\text{year}} \times \frac{235}{6.023 \times 10^{20}}$$

$$= \mathbf{9.78 \times 10^{-10}\ yr^-} \qquad \textbf{Ans.}$$

Also, $\quad t_{1/2} = \frac{0.693}{\lambda};\ t_{1/2} = \frac{0.693}{9.78 \times 10^{-10}\text{yr}^-}$

$$= \mathbf{7.086 \times 10^8\ years} \qquad \textbf{Ans.}$$

Example 96. *Calculate the value of alpha activity in terms of disintegrations per minute of 10^{-4}g sample of ^{232}Th ($t_{1/2} = 1.39 \times 10^{10}$ years; 1 year = 3.15×10^7s).*

Solution. $\quad t_{1/2} = 1.39 \times 10^{10}$ year.

But $\quad \lambda = \frac{0.693}{t_{1/2}};\ \lambda = \frac{0.693}{1.39 \times 10^{10}\text{year}}$

Since 1 year = $3.15 \times 10^7 s$, so 1 year = $3.15 \times 10^7 s \times \frac{1\text{min}}{60 s}$

$$\therefore \qquad \lambda = \frac{0.693}{1.39 \times 10^{10}\text{yr}} \times \frac{1\text{yr}}{3.15 \times 10^7\text{s}} \times \frac{60\,\text{s}}{1\,\text{min}}$$

Also, N (= no. of atoms or nuclei in a given sample).

$$= \frac{\text{wt. in g}}{\text{g. at. wt. of }^{232}\text{Th}} \times 6.023 \times 10^{23}$$

×

$$= \frac{10^{-4}\text{g}}{232\,\text{g mol}^-} \times 6.023 \times 10^{23}\text{mol}^-$$

$$= \frac{6.023 \times 10^{19}}{232}$$

∴ Activity,

$$-\frac{dN}{dt} = \lambda N = \frac{0.693 \times 60\,\text{min}^-}{1.39 \times 10^{10} \times 3.15 \times 10^7} \times \frac{6.023 \times 10^{19}}{232}$$

$$= 24.65 \text{ disintegrations per minute}$$

Ans.

Example 97. *Find the value of mass (in g) and specific activity (Ci g$^-$) of radioactive isotope $^{40}_{19}K$ ($t_{1/2} = 1.3 \times 10^9$ years).*

Solution. $\quad t_{1/2} = 1.3 \times 10^9$ yr. We know that,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.3 \times 10^9\text{yr}}$$

Or

$$\lambda = \frac{0.693}{1.3 \times 10^9\text{yr}} \times \frac{1\text{yr}}{365\text{days}} \times \frac{1\text{day}}{24\,\text{hr}}$$

$$\times \frac{1\text{hr}}{60\,\text{min}} \times \frac{1\text{min}}{60\,\text{s}} = 1.69 \times 10^{-17} s^-$$

But $\quad 1 \text{ Ci} = 3.7 \times 10^{10}$ dps

$$= -\frac{dN}{dt} \cdot \text{ We know that,}$$

$$-\frac{dN}{dt} = \lambda N;$$

$$N = -\frac{dN}{dt} \times \frac{1}{\lambda} = 3.7 \times 10^{10} \text{ dps} \times \frac{1}{1.69 \times 10^{-17} s^-}$$

$$= \mathbf{2.19 \times 10^{27}\ disintegrations.}$$

Mass no. of K = 40; Avogadro no. = 6.023×10^{23}.

∴ Mass of Ci *i.e.*, curie of

$$^{40}_{19}\text{K} = \frac{N \times \text{mass no.}}{\text{Avogadro no.}}$$

$$= \frac{2.19 \times 10^{27} \times 40}{6.023 \times 10^{23}} \simeq \mathbf{145,442\ g} \qquad \textbf{Ans.}$$

Hence specific activity

$$= \frac{1}{\text{mass of Ci of } {}^{40}_{19}\text{K}} = \frac{1}{145,442\text{g}}\text{Ci}$$

$$= \mathbf{6.87 \times 10^{-6}\ Ci\ g^{-}}$$ **Ans.**

Example 98. *Find the value of mass (in g) of 1 curie and one rd of ${}^{214}_{82}Pb$ (half-life =26.8 min).*

Solution. (*i*) Let wt. of ${}^{214}_{82}\text{Pb} = xg$; mass no. of Pb = 214.

∴ Total no. of atoms (N) in

$$xg \text{ of } {}^{214}_{82}\text{Pb} = \frac{\text{wt. in g}}{\text{g at. wt.}} \times 6.023 \times 10^{23}\text{atoms}$$

$$= \frac{x \times 6.023 \times 10^{23}}{214}\text{atoms}$$

(*ii*) $t_{1/2}$ = 26.8 min. Hence,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{26.8\,\text{min}} \times \frac{1\,\text{min}}{60\,\text{s}}$$

Or $\lambda = 4.31 \times 10^{-4}s^{-}$. Here time is converted to seconds because according to definition of curie, 1 curie = 3.7×10^{10} disintegrations s^{-} (or dps). We know that,

$$-\frac{dN}{dt} = \lambda N;$$

$$-\frac{dN}{dt} = 4.31 \times 10^{-4}\text{s}^{-} \times \frac{x \times 6.023 \times 10^{23}}{214}$$

Or $$-\frac{dN}{dt} = 1.21 \times 10^{18}x \text{ dps.}$$

∴ 1 curie or 3.7×10^{10} dps

$$= 1.21 \times 10^{18}\ x \text{ dps.}$$

Or $$x = \frac{3.7 \times 10^{10}}{1.21 \times 10^{18}} = 3.06 \times 10^{-8}\text{ g}$$ **Ans.**

(*iii*) But 1 rd *i.e.*, rutherford = 10^6 dsp. Hence, 10^6dps = $1.21 \times 10^{18}x$ dps

∴ $$x = \frac{10^6}{1.21 \times 10^{18}}\text{g} = \mathbf{8.26 \times 10^{-23}\ g}$$ **Ans.**

Type. Concentration of radioactive substance in a solution

$$= \frac{\text{One m mol. in a given solution}}{\text{specific activity in mc (mol)}^{-} \times \text{Volume of solution in mL}}$$

$$= x \text{ m. mol (mL)}^{-} = x\text{M.}$$

Example 99. *A solution of ${}^{14}C$ (uniformally labelled) amino acid contains 1mc of this acid in 3.0 mL of solution. If specific activity of the above acid is 225 mc/m mol, calculate (i) concentration of labelled amino acid in the solution and*

(ii) activity of the solution in terms of CPM/mL at the counting efficiency of 75%.

Solution. (*a*) Given : 1 m. mol = 225 mc

$$\therefore \text{ no. of m. mol that correspond to 1 mc} = \frac{1\text{m.mol}}{225\,\text{mc}}$$

But 1 mc is dissolved in 3.0 mL. Hence :

$$\text{Concentration} = \frac{1\text{m.mol}}{225} \times \frac{1}{3\,\text{mL}}$$

$$= 1.48 \times 10^{-3}\text{m mol (mL)}^{-}$$

$$= 1.48 \times 10^{-3}\text{ M}$$ **Ans.**

(*b*) We know that,

$$1 \text{ mc} = 2.22 \times 10^9 \text{ DPM}$$

∴Total activity in

$$3 \text{ mL} = 2.22 \times 10^9 \text{ DPM} \times \frac{75}{100}$$

∴Total activity in

$$\text{one mL} = 2.22 \times 10^9 \text{ DPM} \times \frac{75}{100} \times \frac{1}{3\,\text{mL}}$$

$$= 5.55 \times 10^8$$

DPM (or CPM)/mL. **Ans.**

Example 100. *Consider an α-particle just in contact with a ${}^{238}_{92}U$ nucleus. Calculate the coulombic repulsion energy (i.e., the height of coulombic repulsion energy between ${}^{238}U$ and α-particle) assuming that the distance between them is equal to the sum of their radii.* **(MLNR, 1996)**

Solution. Radius of Nucleus = $1.3 \times 10^{-13} \times (A)^{1/3}$ where A is mass number

$$\text{Radius of U}^{238} = 1.3 \times 10^{-13}\,(238)^{1/3} = 8.06 \times 10^{-13}\text{ cm}$$

$$\text{Radius of He}^4 = 1.3 \times 10^{-13}\,(4)^{1/3} = 2.06 \times 10^{-13}\text{ cm}$$

∴ Total distance in between ^{238}U and α-nuclei

$$= 8.06 \times 10^{-13} + 2.06 \times 10^{-13}$$

$$= 10.12 \times 10^{-13}\text{ cm}$$

Coulombic repulsion energy

$$= \frac{q_1q_2}{r^2} = \frac{92 \times 4.8 \times 10^{-10} \times 2 \times 4.8 \times 10^{-10}}{(10.12 \times 10^{-13})^2}\text{erg}$$

$$= \frac{4239.36 \times 10^{-20}}{102.41 \times 10^{-26}}\text{erg} = 41.396 \times 10^6\text{erg}$$

$$= 41.396 \times 10^6 \times 6.242 \times 10^{11}\text{ eV}$$

$$= 41.396 \times 6.242 \times 10^{11}\text{ MeV}$$

$$= \mathbf{2.584 \times 10^{13}\ MeV}$$ **Ans.**

Type. To calculate average life T, use the relation,

$$T = \frac{1}{\lambda}\text{or}\frac{1}{k}\text{ where}$$

$$\lambda \text{ or } k = \frac{2.303}{t}\log\frac{a}{a-x} \text{ or } \frac{N}{No}$$

Also, average life,

$$T = 1.44 \times \text{half-life period.}$$

Example 101. *The disintegration concentration of 6.0 mol of radioactive substance was found to be 4.0 mol after 930 hours. Calculate its average life.*

Solution. We know that :

$$\lambda = \frac{2.303}{t}\log\frac{a}{a-x} \qquad \text{... (1).}$$

Where $a = 6.0$ mol; $x = 4.0$ mol; $a - x = 6.0 - 4.0 = 2.0$ mol; $t = 930$ hr. Thus, from relation (1), we have : $\lambda = \frac{2.303}{930\,\text{hr}}\log\frac{6}{2}$ *i.e.*, 3; $\lambda = \frac{2.303}{930\,\text{hr}} \times 0.4771$.

∴ Average life,

$$T = \frac{1}{\lambda} = \frac{1}{2.303 \times 0.4771} \times 930\text{ hr}$$

= 846.4 hr. **Ans.**

Example 102. *The half life of radioactive element is 6930 days. What is the average life of the element ?* **(ISC, 1983)**

Solution. Average life, T = 1.44 × half-life time = 1.44 × 6930 days = **9979.2 days** **Ans.**

Example 103. *The activity of a sample of* $^{35}_{16}S$ *falls to 25% of its initial value after 174.2 days. Calculate the average life as well as half-life of the given isotope of sulphur.*

Solution. (*i*) $a = 100, a - x = 25, t = 174.2$ days. We know that :

$$\lambda = \frac{2.303}{t}\log\frac{a}{a-x}$$

$$= \frac{2.303}{174.2\,\text{days}}\log\frac{100}{25}\ \textit{i.e.},\ 4$$

$$\lambda = \frac{2.303 \times 0.602}{174.2\,\text{days}} = 7.96 \times 10^{-3}\,(\text{days})$$

(*ii*) $$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{7.96 \times 10^{-3}(\text{days})^{-}}$$

$$= 87.06 \text{ dyas}$$

(*iii*) Average life,

$$T = \frac{1}{\lambda} = \frac{1}{7.96 \times 10^{-3}(\text{days})^{-}}$$

= 125.63 days **Ans.**

Example 104. *A radioactive sample on analysis gave the following results :*

(*i*) *In the beginning, its counting state is 23.7 alpha particles per minute.*

(*ii*) *After 5 minutes, its counting state is 13.5 α-particles per minute.*

Calculate the half-life as well as average life of the sample.

Solution. (*i*) $t = 5$ min., No = 23.7, N = 13.5. We know that :

$$\lambda = \frac{2.303}{t}\log\frac{\text{No}}{\text{N}};\ \lambda = \frac{2.303}{5\,\text{min}}\log\frac{23.7}{13.5}$$

$$\lambda = \frac{2.303}{5\,\text{min}}[\log 23.7 - \log 13.5]$$

$$= \frac{2.303}{5\,\text{min}}[1.3747 - 1.1303]$$

$$\lambda = \frac{2.303}{5\,\text{min}} \times 0.2444 = 0.1126\,\text{min}^{-}$$

(*ii*) Half-life, $t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.1126\,\text{min}^{-}}$

= 6.15 min. **Ans.**

(*iii*) Average life,

$$T = \frac{1}{\lambda};\ T = \frac{1}{0.1126\,\text{min}^{-}}$$

= 8.88 min. **Ans.**

(Or T = 1.44 $t_{1/2}$ = 1.44 × 6.15 min = 8.86 min).

Example 105. *If half-life of 10 g of a radioactive isotope is 30 days, what would be the half-life of 1g of the sample ?* **(UP Board, 1989)**

Solution. We know that half-life period is independent of initial concentration of the radioactive substance for radioactive disintegration (first order reaction). So, the half-life of 1g sample = half-life of 10g sample = **30 days** **Ans.**

Example 106. *Radioactivity is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant (in* year^{-}*) for the decay ? What fraction would remain after 11540 years ?* **(IIT, 1984)**

Solution. $t_{1/2}$ = 5770 years. We know that :

$$\text{Rate constant, } \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770\,\text{yr}}$$

$= \mathbf{1.2 \times 10^{-4}\ yr^{-}}$ **Ans.**

No = 1 (say), N = ? t = 11540 yrs.

But, $$\lambda = \frac{2.303}{t}\log\frac{\text{No}}{\text{N}};$$

$$1.2 \times 10^{-4}\,\text{yr}^{-} = \frac{2.303}{11540\,\text{yr}}\log\frac{1}{\text{N}}$$

∴ $$\log\frac{1}{\text{N}} = \frac{1.2 \times 10^{-4}\,\text{yr}^{-} \times 11540\,\text{yr}}{2.303} = 0.6013$$

Taking antilog of both sides, we get : $\frac{1}{\text{N}}$ = antilog 0.6013; $\frac{1}{\text{N}} = 3.993$; $\text{N} = \frac{1}{3.993} = 0.25$

Hence, N = 0.25 × 100 = **25%**. So, the fraction that would remain after 11540 years = **25%** **Ans.**

Example 107. *Calculate the age of dead sea scrolls, the sample of carbon of which is decaying at the rate of 11.5 disintegrations* $\text{min}^{-}\text{g}^{-}$. *(*$t_{1/2}$ *for* ^{14}C *= 5760 yrs). The carbon obtained from living plants disintegrate at the rate of 15.3 disintegrations* $\text{min}^{-}\text{g}^{-}$.

Solution. $t_{1/2}$ = 5760 yrs; No = 15.3 disintegrations $\text{min}^{-}\text{g}^{-}$; N = 11.5 disintegrations $\text{min}^{-}\text{g}^{-}$. We know that :

$$\lambda = \frac{0.693}{t_{1/2}};\ \lambda = \frac{0.693}{5760\,\text{yrs}}$$

Also, $$t = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}};$$

$$t = \frac{2.303 \times 5760\,\text{yrs}}{0.693} \log \frac{15.3}{11.5}$$

$$\therefore \quad t = \frac{2.303 \times 5760\,\text{yrs}}{0.693} [\log 15.3 - \log 11.5]$$

$$= \frac{2.303 \times 5760\text{ yrs}}{0.693} [1.1847 - 1.0607]$$

$$= \frac{2.303 \times 5760\,\text{yrs} \times 0.124}{0.693}$$

$= 2373.58$ years **Ans.**

EXAMPLE 108. *$_{92}U^{238}$ by successive radioactive decay changes to $_{82}Pb^{206}$. A sample of uranium ore was analysed and found to contain 1.0g of U^{238} and 0.1g of Pb^{206}. Assuming that all the Pb^{206} had accumulated due to decay of U^{238}, find out the age of the ore (half-life of U^{238} = 4.5 × 10^9 years).* **(Roorkee, 1990)**

SOLUTION. (*i*) $t_{1/2} = 4.5 \times 10^9$ yrs. Hence

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \text{yrs}}$$

Or $\lambda = 1.54 \times 10^{-10} \text{yr}^{-}$

(*ii*) $206\text{g Pb}^{206} \equiv 238\text{g U}^{238}$.

$$0.1\text{g Pb}^{206} \equiv \frac{238}{206} \times 0.1\text{g U}^{238} \equiv 0.1155\text{g U}^{238}$$

Given weight of

$U^{238} = 1.0$ g.

∴ Total weight of

$U^{238} = 1.0 + 0.1155 =$ **1.1155 g**

∴ No = 1.1155g; N = 1 (say). Hence :

$$t = \frac{2.303}{\lambda} \log \frac{\text{No}}{\text{N}};$$

$$t = \frac{2.303}{1.54 \times 10^{-10} \text{yr}^{-}} \log \frac{1.1155}{1}$$

Or
$$t = \frac{2.303}{1.54 \times 10^{-10} \text{yr}^{-}} \times 0.04747$$

≃ 7.099 × 10 years = age of ore. Ans.

EXAMPLE 109. *Calculate the total energy emitted per second in watts by 15 mg of a β-emitter $^{141}_{58}Ce$ ($t_{1/2}$ = 31.11 days). The average energy of β-particles emitted by $^{141}_{58}Ce$ is 0.442 MeV.*

SOLUTION. We know that :

Rate of disintegration s^{-} = no. of β-particles emitted s^{-} = Decay constant (λ) × No. of atoms ...(1).

$$(i)\ \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{31.11\text{day}} \times \frac{1\text{day}}{24\,\text{hr}} \times \frac{1\,\text{hr}}{60\,\text{min}} \times \frac{1\,\text{min}}{60\,s}$$

$= 2.58 \times 10^{-7}\, s^{-}$

(*ii*) wt. of sample

$$= 15\text{ mg} = \frac{15}{1000}\text{g} = 0.015\text{g}$$

∴No. of atoms in

$$0.015\text{ g } ^{141}_{58}\text{Ce} = \frac{\text{wt. in g}}{\text{g. at. wt.}} \times 6.023 \times 10^{23}$$

$$= \frac{0.015}{141\text{g}\,(\text{atom})^{-}} \times 6.023 \times 10^{23}$$

$= 6.4 \times 10^{19}$ atoms

Substituting the values of λ and no. of atoms in (1), we get : no. of β-particles = $2.58 \times 10^{-7} s^{-} \times 6.4 \times 10^{19}$ atoms $= 1.65 \times 10^{13}$. Hence total energy = 0.442 MeV × 1.65×10^{13} $= 7.293 \times 10^{12}$ MeV.

$$= 7.293 \times 10^{12}\text{MeV} \times \frac{1.6 \times 10^{-6}\text{erg}\, s^{-}}{1\,\text{MeV}}$$

$$\times \frac{1\,\text{watt}}{10^7\,\text{erg}\, s^{-}} \simeq \textbf{1.167 watt Ans.}$$

[∵ 1 MeV = 1.6×10^{-6} erg s^{-}; 1 Watt = 10^7 erg s^{-}].

EXAMPLE 110. *The half of ^{238}U decomposes to ^{206}Pb in 4.5 × 10^8 years. What will be the age of rock that contain equal masses of both ?* **(BIT, 1986)**

SOLUTION. Let *t* = age of earth; final wt. of U = w g.

(*i*) 206g Pb is obtained from

U = 238g

∴ w g Pb is obtained from

$$\text{U} = \frac{238}{206}\text{w}$$

∴ Initial wt. of U in the rock,

$$a = \text{w} + \frac{238\text{w}}{206} = \text{w}\left(1 + \frac{238}{206}\right) = \frac{444}{206}\text{w}$$

Hence, final wt. of

U, $(a - x) = \text{w}$

$(ii)\ \lambda = \dfrac{0.693}{t_{1/2}}$, $(iii)\ \lambda = \dfrac{2.303}{t} \log \dfrac{a}{a - x}\cdot$ From (*i*), (*ii*) and (*iii*), we have :

$$\frac{0.693}{4.5 \times 10^8 \text{yr}} = \frac{2.303}{t} \log \frac{\frac{444\,\text{w}}{206}}{\text{w}} \quad i.e., \ \frac{444}{206}$$

$$\therefore \quad t = \frac{2.303 \times 4.5 \times 10^8 \text{yr}}{0.693} [\log 444 - \log 206]$$

$$= \frac{2.303 \times 4.5 \times 10^8 \text{yr}}{0.693} [2.6474 - 2.3139]$$

$$= \frac{2.303 \times 4.5 \times 10^8 \times 0.3335\,\text{yr}}{0.693}$$

$= 4.98 \times 10^8$ yrs

∴ Age of rock = **4.98 × 10^8 years** **Ans.**

EXAMPLE 111. *The relative abundance of two isotopes of uranium $^{235}_{92}U$ and $^{238}_{92}U$ is 0.8% and 99.2% respectively. Calculate the age of the earth if their half-lives are respectively 7.1 × 10^8 years and 4.5 × 10^9 years.*

SOLUTION. For ^{235}U, decay constant,

$$\lambda_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{7.1\times10^{8}\text{yr}}$$

$$= 9.76 \times 10^{-10}\ \text{yr}^{-}$$

For ^{238}U, decay constant,

$$\lambda_2 = \frac{0.693}{4.5\times10^{9}\text{yr}} = 1.54\times10^{-10}\text{yr}^{-}$$

We know that :

$$(i)\quad \frac{N(^{238}U)}{N(^{235}U)} = \frac{99.2\%}{0.8\%}$$

$$(ii)\quad N(^{235}U) = No(^{235}U) \times e^{-\lambda_1 t};$$

$$N(^{238}U) = No(^{238}U) \times e^{-\lambda_2 t};$$

$$\therefore\quad \frac{N(^{238}U)}{N(^{235}U)} = \frac{No(^{238}U)\times e^{-\lambda_2 t}}{No(^{238}U)\times e^{-\lambda_1 t}};\ 124 = \frac{e^{-\lambda_2 t}}{e^{-\lambda_1 t}}$$

Taking logs of both sides, we get :

$$\log_e 124 = -\lambda_2 t - (-\lambda_1 t)\ i.e.,$$

$$\lambda_1 t = \lambda_2 t = t(\lambda_1 - \lambda_2).$$

$$\textbf{Or}\ 2.303 \log 124 = t\,(9.76 \times 10^{-10}) - (1.54 \times 10^{-10})t$$

$$= 10^{-10}t\,(8.22)$$

$$\textbf{Or}\ \frac{2.303\times2.0934}{8.22\times10^{-10}} = t\ ;\ t \simeq 5.86 \times 10^{9}\ \text{years}$$

$\therefore$ Age of earth = 5.86×10^9 years

EXAMPLE 112. *Half life of $^{238}U = 4.5 \times 10^9$ years. If ratio by weight of ^{206}Pb and ^{238}U in a uranium mineral is 0.32 : 1, what will be the age of the mineral ?*

SOLUTION. Given : $^{206}Pb : ^{238}U = 0.32 : 1$.

$$\therefore\ \text{Ratio by mol} = \frac{0.32}{206} : \frac{1}{238}\ \ i.e.,\ 1.55\times10^{-3} : 4.2\times10^{-3}$$

$$= \frac{1.55}{4.2} : \frac{4.2}{4.2}\ i.e.,\ 0.369 : 1$$

$\therefore$ No = g. atoms of ^{238}U originally present = 1 + 0.369 = 1.369; N = 1

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5\times10^{9}\text{yr}} = 1.54\times10^{-10}\text{yr}^{-}$$

$$\text{But}\qquad t = \frac{2.303}{\lambda}\log\frac{No}{N};$$

$$t = \frac{2.303}{1.54\times10^{-10}\text{yr}^{-}}\log\frac{1.369}{1}$$

$$\therefore\qquad t = \frac{2.303}{1.54\times10^{-10}\text{yr}^{-}} \times 0.1364$$

$$\simeq 2.04 \times 10^{9}\ \text{yers}$$

EXAMPLE 113. *An old table of wood shows $^{14}_{6}C$ activity which is 80% of the activity found to-day. Find the age of the table. Half-life period of $^{14}_{6}C$ is 5770 years.*

(PSEB, 2007, CBSE, 2008, CBSE (D), 2012)

SOLUTION. $t_{1/2}$ = 5770 yr

$$\therefore\qquad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770\ \text{yr}} = 1.2\times10^{-4}\ \text{yr}^{-}$$

Let amount of ^{14}C present in wood to-day = *a*

$$\text{Amount of } ^{14}C \text{ present in old wood} = \frac{a\times80}{100} = 0.8\,a.$$

Let *t* = age of wood piece

$$\text{Then}\qquad t = \frac{2.303}{\lambda}\log\frac{a}{a-x}$$

$$= \frac{2.303}{1.2\times10^{-4}\text{yr}^{-}}\log\frac{a}{0.8\,a};$$

$$t = \frac{2.303}{1.2\times10^{-4}\text{yr}^{-}}\log\frac{10}{8}$$

$$t = \frac{2.303}{1.2\times10^{-4}\text{yr}^{-}}[\log 10 - \log 8];$$

$$t = \frac{2.303}{1.2\times10^{-4}\text{yr}^{-}}(1 - 0.903)$$

$$\text{or}\qquad t = \frac{2.303}{1.2\times10^{-4}\text{yr}^{-}} \times 0.097$$

= **1861.59 years** **Ans.**

EXAMPLE 114. *10 gram atoms of an α-active radio-isotope are disintegrating in a sealed container. In one hour, the helium gas collected at STP is 11.2 cm^3. Calculate the half-life of radio-isotope.* **(Roorkee, 1989)**

SOLUTION. 1 g atom of isotope contain atoms

$$= 6.023 \times 10^{23}$$

10 g atoms of isotope contain atoms

$$= 6.023 \times 10^{23} \times 10 = 6.023 \times 10^{24}$$

$\therefore$ No. of atoms,

$$N = 6.023 \times 10^{24} \qquad ...(1)$$

Also,22400 mL volume contain atoms

$$= 6.023 \times 10^{23}$$

11.2 mL volume contain atoms

$$= \frac{6.023\times10^{23}}{22400}\times11.2$$

$$= 3.01 \times 10^{20}\ \text{hr}^{-}$$

$$\therefore\qquad -\frac{dN}{dt}(= \text{no. of atoms}) = 3.01 \times 10^{20}\ \text{hr}^{-} \qquad ...(2)$$

$$\text{But}\qquad -\frac{dN}{dt} = \lambda N;\ 3.01 \times 10^{20} = \lambda \times 6.023 \times 10^{24}$$

$$\therefore\qquad \lambda = \frac{3.01\times10^{20}\text{hr}^{-}}{6.023\times10^{24}} = 4.998\times10^{-5}\text{hr}^{-}$$

$$\text{But}\qquad t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{4.998\times10^{-5}\ \text{hr}^{-}}$$

$$= 13865.55\ \text{hr.}$$

$$\therefore \quad t_{1/2} = 13865.55 \text{ hr} \times \frac{1\text{day}}{24\text{hr}} \times \frac{1\text{hr}}{365\text{days}}$$

$\simeq$ **1.582825 years** **Ans.**

EXAMPLE 115. *Radon is an α-particle emitter. Calculate the amount of heat liberated by a curie of this element in (i) 45 minutes and (ii) its mean life. (Kinetic energy of one α-particle = 6.11 MeV and decay constant for radon = 2 × $10^{-6}s^{-}$).*

SOLUTION. (*i*) 1 curie = 3.7×10^{10} ds^{-}. Reaction : ${}_{86}Rn \rightarrow {}_{84}Po + {}_{2}He$; $\lambda = 2 \times 10^{-6}s^{-}$.

Rate of disintegration = λ No ;

$$\text{No} = \frac{\text{Rate of disintegration}}{\lambda}$$

$$\therefore \quad \text{No} = \frac{3.7 \times 10^{10}\text{ds}^{-}}{2 \times 10^{-6}\text{s}^{-}} = 1.85 \times 10^{16}$$

Let, N = Amount of Rn left after time,

t = 45 min.

$$\therefore \quad t = 45 \text{ min} \times \frac{60\text{s}}{1\text{min}} = 2700\text{ s}$$

But $$t = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}};$$

$$2700\text{s} = \frac{2.303}{2 \times 10^{-6}\text{s}^{-}}\log\frac{1.85 \times 10^{16}}{\text{N}}$$

$$\therefore \log\frac{1.85 \times 10^{16}}{\text{N}} = \frac{2700\text{s} \times 2 \times 10^{-6}\text{s}^{-}}{2.303}$$

$= 2.345 \times 10^{-3} = 0.002345$

log 1.85 + log 10^{16} – log N

= 0.002345; 0.2672 + 16 – log N = 0.002345

∴ log N = 16.2672 – 0.002345 = 16.2648

∴ **N** = antilog 16.2648 = 1.84×10^{16}

Hence number of α-particles formed (= no. of Rn atoms decay)

$= 1.85 \times 10^{16} - 1.84 \times 10^{16} = 0.01 \times 10^{16}$.

K.E. of one α-particle

= 6.11 MeV

∴K.E. of 0.01×10^{16} α-particles

$= 6.11 \text{ MeV} \times 0.01 \times 10^{16}$

$$\times \frac{10^{6}\text{eV}}{1\text{MeV}} \times \frac{1.602 \times 10^{-19}}{1\text{eV}}\text{J}$$

= 97.88 J **Ans.**

(*ii*) Mean life or average life period,

$$t = \frac{1}{\lambda}$$

Let, N = no. of Rn-atoms left after mean time, t.

But, $$t = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}};$$

$$\frac{1}{\lambda} = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}};$$

$$\log\frac{\text{No}}{\text{N}} = \frac{1}{2.303} = 0.4342$$

Or $\log\frac{1.85 \times 10^{16}}{\text{N}}$ = 0.4342; log 1.85 + log 1016 – log N

= 0.4342

0.2672 + 16 – log N

= 0.4342; log N

= 16.2672 – 0.4342 = 15.833

∴ N = antilog 15.833 = 6.81×10^{15}

$= 0.681 \times 10^{16}$

Hence no. of α-particles (= no. of Rn-atoms decay)

$= 1.85 \times 10^{16} - 0.68 \times 10^{16} = 1.169 \times 10^{16}$.

K.E. of one α-particle

= 6.11 MeV

∴K.E. of 1.169×10^{16} α-particles

$= 1.169 \times 10^{16} \times 6.11$ MeV

$$\times \frac{10^{6}\text{eV}}{1\text{MeV}} \times \frac{1.602 \times 10^{-19}\text{J}}{1\text{eV}}$$

= **11442.43 J** **Ans.**

EXAMPLE 116. *An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of ${}^{99}_{42}Mo$, which is a beta emitter is 66.6 hours. Find the minimum of ${}^{99}_{42}Mo$ required to carry out the experiment in 6.909 hours.* **(IIT, 1989)**

SOLUTION. Minimum Number of β-particles required = 346 min^{-1}.

Number of β-particles required to carry out the experiment in 6.909 hours or 6.909 × 60 min.

= 346 × 6.909 × 60

= 143430.84 = 143431 particles

∴ No. of moles of β-particles required

$$= \frac{143431}{6.023 \times 10^{23}} = 2.3814 \times 10^{-19}\text{mol}$$

$t_{1/2}$ = 66.6 hours

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{66.6} = 0.0104054\text{ hr}^{-1}$$

Also, $$\lambda = \frac{2.303}{t}\log\frac{a}{(a-x)}$$

$$\log\frac{a}{(a-x)} = \frac{\lambda t}{2.303} = \frac{0.0104054 \times 6.909}{2.303}$$

or $$\log\frac{a}{(a-x)} = 0.0312162$$

or $$\frac{a}{(a-x)} = 1.07452$$

[∵ antilog 0.0312162 = 1.07452]

Substituting, $x = 2.3814 \times 10^{-19}$

$$\frac{a}{(a - 2.3814 \times 10^{-19})} = 1.07452$$

$$a = 1.07452\,a - 1.07452 \times 2.3814 \times 10^{-19}$$

or $$0.07452\,a = 1.07452 \times 2.3814 \times 10^{-19}$$

$$a = \frac{1.07452 \times 2.3814 \times 10^{-19}}{0.07452}$$

$$= 3.4338 \times 10^{-18} \text{ mol}$$

Example 117. *Calculate the weight of* ^{14}C *(*$t_{1/2} = 5720$ *years) atoms which give* 3.70×10^7 *disintegrations per second.* **(Roorkee, 1986)**

Solution. $t_{1/2} = 5720$ years

$$= 5720 \times 365 \times 24 \times 60 \times 60\text{s}$$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5720 \times 365 \times 24 \times 60 \times 60\text{s}}$$

$$= 3.84 \times 10^{-12}\text{s}^{-}$$

Now, $$-\frac{dN}{dt} = \lambda N$$

If w is the weight of ^{14}C then

$$N = \frac{w}{14} \times 6.023 \times 10^{23} \text{ atoms}$$

∴ $$-\frac{dN}{dt} = \lambda . \frac{w}{14} \times 6.023 \times 10^{23}$$

or $$3.70 \times 10^7 = \frac{3.84 \times 10^{-12} \times w \times 6.023 \times 10^{23}}{14}$$

or $$w = \frac{3.70 \times 10^7 \times 14}{3.84 \times 6.023 \times 10^{11}} = 2.24 \times 10^{-4}\text{g}$$

Example 118. ^{64}Cu *(half-life = 12.8 h) decays by* β^- *emission (38%),* β^+ *emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.* **(IIT, 2002)**

Solution. The nuclear reactions are as follows :

β^- emission : ${}^{64}_{29}Cu \rightarrow {}^{64}_{30}Zn + {}^{0}_{-1}\beta$

β^+ emission : ${}^{64}_{29}Cu \rightarrow {}^{64}_{28}Ni + {}^{0}_{1}\beta$

Electron capture : ${}^{64}_{29}Cu + {}^{0}_{-1}e \rightarrow {}^{64}_{28}Ni$

Overall disintegration constant,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8\,\text{h}} = 5.414 \times 10^{-2}\text{hr}^{-1}$$

If r_1, r_2 and r_3 are the respective rates of decay of Cu and r is the overall rate of decay of Cu, then $r = r_1 + r_2 + r_3$.

Or $$\lambda\,[Cu] = \lambda_1\,[Cu] + \lambda_2\,[Cu] + \lambda_3\,[Cu]$$

or $$\lambda = \lambda_1 + \lambda_2 + \lambda_3 \qquad ...(1)$$

Now it is given that

$$\frac{\lambda_1}{\lambda_3} = \frac{38}{43} = 0.884 \text{ and } \frac{\lambda_2}{\lambda_3} = \frac{19}{43} = 0.442$$

or $$\lambda_1 = 0.884\,\lambda_3 \text{ and } \lambda_2 = 0.442\,\lambda_3$$

Substituting these values in eq. (1), we have :

$$\lambda = 0.884\lambda_3 + 0.442\,\lambda_3 + \lambda_3 = 2.326\,\lambda_3$$

Hence, $$\lambda_3 = \frac{\lambda}{2.326} = \frac{5.414 \times 10^{-2}}{2.326}\text{hr}^{-1}$$

$$= 2.328 \times 10^{-2}\text{ hr}^{-1}$$

$$(t_{1/2})_3 = \frac{0.693}{\lambda_3} = \frac{0.693}{2.328 \times 10^{-2}}\text{hr} = 29.77 \text{ hour}$$

$$\lambda_1 = 0.884\,\lambda_3 = 0.884 \times 2.328 \times 10^{-2}\text{ hr}^{-1}$$

$$= 2.058 \times 10^{-2}\text{ hr}^{-1}$$

$$(t_{1/2})_1 = \frac{0.693}{\lambda_1} = \frac{0.693}{2.058 \times 10^{-2}\text{hr}^{-1}}$$

$$= 33.67 \text{ hour}$$

$$\lambda_2 = 0.442\,\lambda_3 = 0.442 \times 2.328 \times 10^{-2}\text{ hr}^{-1}$$

$$= 1.029 \times 10^{-2}\text{ hr}^{-1}$$

$$(t_{1/2})_2 = \frac{0.693}{\lambda_2} = \frac{0.693}{1.029 \times 10^{-2}\text{hr}^{-1}} = 67.35\,\text{hr}$$

Example 119. *An element X has a half-life of 30 days. Calculate the amount of element left after 90 days if you start with an amount of 0.25 g.* **(BCECE, 2000)**

Solution. The number of half-lives elapsed

$$(n) = \frac{T}{t_{1/2}} = \frac{90}{30} = 3$$

Now, $$N_t = N_0\left(\frac{1}{2}\right)^n = 0.25 \times \left(\frac{1}{2}\right)^3 = 0.031\text{g}$$

Hence, 0.031 g of element will be left after 90 days.

Example 120. *The nuclidic ratio* ${}^{3}_{1}H$ *to* ${}^{1}_{1}H$ *in a sample of water is* $8.0 \times 10^{-18} : 1$*. Tritium undergoes decay with a half-life period of 12.3 years. How many tritium atoms would 10.0 g of such a sample contain 40 years after the original sample is collected ?* **(IIT, 1992)**

Solution. Molecular mass of water = 18.

∴ 18 g of water contains 6.023×10^{23} molecules = $2 \times 6.023 \times 10^{23}$ atoms of hydrogen

10 g of water contains hydrogen atoms

$$= \frac{2 \times 6.023 \times 10^{23} \times 10}{18}\text{atoms}$$

$$= 6.692 \times 10^{23} \text{ atoms}$$

$${}^{1}_{1}H : {}^{3}_{1}H = 1 : 8 \times 10^{-18}$$

∴ Number of ${}^{3}_{1}H$ atoms in 10g of water

$$= 6.692 \times 10^{23} \times 8 \times 10^{-18} = 5.3537 \times 10^{6}$$

Half life of ${}^{3}_{1}H$ = 12.3 years

Time of decay = 40 years; $N = N_0\left(\frac{1}{2}\right)^n$

Where n is the number of half-lives elapsed

$$n = \frac{40}{12.3}$$

$$\begin{aligned} N &= (5.3537 \times 10^6)\,(0.5)^{40/12.3} \\ &= (5.3537 \times 10^6)\,(0.5)^{3.252} \\ \log N &= (\log 5.3537 + 6 \log 10 + 3.252 \log 0.5) \\ &= 0.7287 + 6.0 + 3.252\,(\overline{1}.6990) \\ &= 6.7287 - 3.252 \times 0.3010 \\ &\qquad [\because 1 - 0.6990 = 0.3010] \\ &= 6.7287 - 0.9788 = 5.7499 \\ N &= \text{Antilog}\,(5.7499) = \mathbf{5.622 \times 10^5}. \end{aligned}$$

Example 121. *In nature, a decay chain series starts with* $^{232}_{90}Th$ *and finally terminates at* $^{208}_{82}Pb$. *A thorium ore sample was found to contain* 8×10^{-5} *ml of helium at STP and* 5×10^{-7} *g of* ^{232}Th. *Find the age of the ore sample assuming the source of helium to be only due to the decay of* ^{232}Th. *Also assume complete retention of helium with the ore. (Half life of* $^{232}_{90}Th$ $= 1.39 \times 10^{10}$*y).* **(Roorkee, 1992)**

Solution. $\left[{}^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Pb} + {}^{4}_{2}\text{He}\right]$

$$\begin{aligned} \text{Decrease in mass} &= 232 - 208 = 24 \\ \text{He gas obtained} &= 8 \times 10^{-5}\text{ ml;} \\ 22400 \text{ ml of He at STP} &= 1 \text{ mol} \\ 8 \times 10^{-5}\text{ ml of He at STP} &= \frac{1}{22400} \times 8 \times 10^{-5}\text{ mol} \\ &= 3.57 \times 10^{-9}\text{ mol} \end{aligned}$$

Since 1 mol of thorium gives 6 moles of helium, no. of thorium disintegrated

$$\begin{aligned} &= \frac{1}{22400} \times 10^{-9}\text{ mol} \\ &= 0.59 \times 10^{-9}\text{ mol} \end{aligned}$$

$\therefore$ Number of α-particles emitted by an atom of thorium $= \frac{24}{4} = 6.$

Number of moles of thorium present in the ore

$$\begin{aligned} &= \frac{5 \times 10^{-7}}{232}\text{ mol} \\ &= 2.155 \times 10^{-9}\text{ mol} \end{aligned}$$

Number of moles of thorium present initially = (2.155 + 0.59) × 10^{-9} = 2.745×10^{-9} mol

Half-life period for

$$\begin{aligned} {}^{232}_{90}\text{Th} &= 1.39 \times 10^{10}\text{ year} \\ \therefore \qquad \lambda &= \frac{0.693}{t_{1/2}} = \frac{0.693}{1.39 \times 10^{10}} \\ &= 0.4985 \times 10^{-10}\text{ year}^{-} \\ t &= \frac{2.303}{\lambda} \log \frac{a}{a - x} \\ \therefore \qquad t &= \frac{2.303}{0.4985 \times 10^{-10}\text{year}^{-1}} \log \frac{2.745 \times 10^{-9}}{2.155 \times 10^{-9}} \\ t &= \frac{2.303}{0.4985 \times 10^{-10}\text{year}^{-1}} \times 0.1051 \\ &= \mathbf{4.885 \times 10^9 \text{ year}} \end{aligned}$$

$\therefore$ Age of the ore is 4.885×10^9 years.

21.14 RADIOACTIVE EQUILIBRIUM

If two members *i.e.*, elements A and B are in equilibrium, then :

$$\frac{N_A}{N_B} = \frac{k_B}{k_A} = \frac{t_A}{t_B} \text{ where}$$

N_A and N_B are the number of atoms of elements A and B respectively; k_A and k_B are their respective disintegration constants while t_A and t_B are their respective half-lives.

Example 122. *At radioactive equilibrium, the ratio between the atoms of two radioactive elements A and B is* $1 : 3.1 \times 10^9$. *If the half-life period of element A is 6.45 years, calculate the half-life of B and decay constant of B.*

Solution. No. of atoms of A, $N_A = 1$, that of B = 3.1×10^9. $t_{1/2}$ of t_A is 6.45 yrs. $t_{1/2}$ of B, t_B = ?

(*i*) At radioactive equilibrium,

$$\frac{N_A}{N_B} = \frac{t_A}{t_B} \quad \therefore \quad \frac{1}{3.1 \times 10^9} = \frac{6.45\,\text{yrs}}{t_B}$$

$$\begin{aligned} t_B &= 6.45\text{ yrs} \times 3.1 \times 10^9\text{ yrs} \\ &= \mathbf{2 \times 10^{10}\text{ yrs.}} \end{aligned}$$ **Ans.**

(*ii*) $t = 2 \times 10^{10}$ yrs; λ_B = ?

Since $\lambda_B = \frac{0.693}{t_B}$, we have :

λ_B (= decay constant of B)

$$= \frac{0.693}{2 \times 10^{10}\text{yrs}} = 3.465 \times 10^{-11}\text{yr}^{-}$$ **Ans.**

Example 123. ^{227}Ac *has a half life of 21.8 years with respect to radioactive decay. The decay follows two parallel paths, one leading to* ^{227}Th *and one leading to* ^{223}Fr. *The percentage yield of these two daughter nuclides are 1.2% and 98.8% respectively. What is the rate constant, in year*$^{-1}$*, for each of the separate paths.* **(IIT, 1996)**

Solution. $\lambda_{Ac} = \frac{0.693}{t_{1/2}} = \frac{0.693}{21.8\,\text{year}}$

$$= 3.18 \times 10^{-2}\text{ year}^{-1}$$

Now, the overall rate constant for a set of parallel first order reactions is equal to the sum of the separate rate constants *i.e.*, $\lambda_{Ac} = \lambda_{Th} + \lambda_{Fr}$

Also the fraction yield of either process is equal to the ratio of the rate constant for that process to the overall rate constant *i.e.*,

9 $\qquad \frac{\lambda_{Th}}{\lambda_{Ac}}$ = fractional yield of Th

or $$\lambda_{Th} = 0.012 \times 3.18 \times 10^{-2}\ \text{year}^{-1} \quad \left[\because 1.2\% = \frac{1.2}{100} = 0.012\right]$$

$$= \mathbf{3.8 \times 10^{-4}\ year^{-1}}$$

and $$\frac{\lambda_{Fr}}{\lambda_{Ac}} = \text{fractional yield of Fr}$$

or $$\lambda_{Fr} = 0.988 \times 3.18 \times 10^{-2}\ \text{year}^{-1} \quad \left[\because 98.8\% = \frac{98.8}{100} = 0.988\right]$$

$$= \mathbf{3.14 \times 10^{-2}\ year^{-1}}.$$

21.15 AIEEE PATTERN EXAMPLES

EXAMPLE 124. *An element E has a half-life of 10 years. The time taken to reduce its activity to about 1/8 of its original value will be :*

(a) 80 years *(b) 1.25 years*
(c) 10 years *(d) 30 years.*

SOLUTION. $t_{1/2}$ = 10 years. We know that :

$$\frac{1}{8} = \left(\frac{1}{2}\right)^n;$$

$$\left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n$$

So, $n = 3$

∴ No. of half-lives gone through = 3

Hence time taken = 3 × 10 = 30 years. So, the correct answer is (*d*).

EXAMPLE 125. *Which one of the following is not a nuclear isomer or isomeric nuclei.*

(a) ^{80}Br *(*$t_{1/2}$ *= 4.4 hr) and* ^{80}Br *(*$t_{1/2}$ *= 18 min)*
(b) ^{69}Zn *(*$t_{1/2}$ *= 13.8 hr) and* ^{69}Zn *(*$t_{1/2}$ *= 57 min)*
(c) P^{3-} *and* S^{2-}
(d) ^{60}Co *(*$t_{1/2}$ *= x yrs) and* ^{60}Co *(*$t_{1/2}$ *= y yrs).*

SOLUTION. Nuclear isomers are the atoms with the same atomic number and same mass number but with different radioactive properties. Since isomers shown in (*a*), (*b*) and (*d*) have same atomic number among themselves and have different half-life period, so these are nuclear isomers between each other. P^{3-} and S^{2-} do not have the properties of nuclear isomers, so these are not nuclear isomers. Hence correct answer is (*c*).

EXAMPLE 126. *The isotopes of hydrogen are :*

(a) $^{35}_{17}Cl, ^{2}_{1}H$ *(b)* $^{3}_{1}H, ^{19}_{9}F$
(c) $^{2}_{1}H, ^{1}_{1}H$ *(d) none of these*

SOLUTION. ***Isotopes.*** Atoms of the same element having same atomic number but different mass number are called isotopes of that element. Here $^{2}_{1}H$ and $^{1}_{1}H$ have same atomic number (= 1) but different mass numbers, 2 and 1 respectively. So, the correct answer is (*c*).

EXAMPLE 127. *The isobars among the following are :*

(a) $^{35}_{17}Cl, ^{37}_{17}Cl$ *(b)* $^{65}_{30}Zn, ^{69}_{30}Zn$
(c) $^{3}_{1}H, ^{4}_{2}He$ *(d)* $^{40}_{19}K, ^{40}_{20}Ca$

SOLUTION. Atoms of different elements having same mass number but different atomic number are called isobars of each other. So, $^{40}_{19}K$ and $^{40}_{20}Ca$ are isobars because these have same mass number (= 40) but different atomic numbers 19 and 20 respectively. So, the correct answer is (*d*).

EXAMPLE 128. *The isotones among the following are :*

(a) $^{3}_{1}H, ^{7}_{3}Li$ *(b)* $^{30}_{14}Si, ^{32}_{16}S$
(c) $^{35}_{17}Cl, ^{80}_{35}Br$ *(d)* $^{4}_{2}He, ^{1}_{1}H$

SOLUTION. Atoms of different elements with the same number of neutrons but different mass numbers are called isotones.

$^{3}_{1}H$: no. of neutrons = 3 – 1 = 2; $^{7}_{3}Li$: no. of neutrons = 7 – 3 = 4.

$^{30}_{14}Si$: no. of neutrons = 30 – 14 = 16; $^{32}_{16}S$: no. of neutrons = 32 – 16 = 16

$^{35}_{17}Cl$: no. of neutrons = 35 – 17 = 18; $^{80}_{35}Br$: no. of neutrons = 80 – 35 = 45

$^{4}_{2}He$; no. of neutrons = 4 – 2 = 2; $^{1}_{1}H$: no. of neutrons = 1 – 1 = 0.

So, the correct answer is (*b*).

EXAMPLE 129. *Which of the following is not isodiapher ?*

(a) $^{39}_{19}K$ and $^{19}_{9}F$ *(b)* $^{65}_{29}Cu$ and $^{55}_{24}Cr$
(c) $^{235}_{92}U$ and $^{231}_{90}Th$ *(d)* $^{1}_{1}H$ and $^{4}_{2}He$

SOLUTION. Atoms having same isotopic number are called *isodiaphers. Isotopic number* (isotopic excess) = N – Z or A – 2Z where A, N and Z are the mass number, neutrons and atomic number respectively.

$^{39}_{19}K$: N = 39 – 19 = 20; Z = 19. So, N – Z = 20 – 19 = 1

$^{19}_{9}F$: N = 19 – 9 = 10; Z = 9. So, N – Z = 10 – 9 = 1

$^{65}_{29}Cu$: N = 65 – 29 = 36; Z = 29. so, N – Z = 36 – 29 = 7

$^{55}_{24}Cr$: N = 55 – 24 = 31; Z = 24. So, N – Z = 31 – 24 = 7.

$$\left.\begin{array}{l} ^{235}_{92}U: N = 235 - 92 = 143; Z = 92. \text{ So, } N - Z = 143 - 92 = 51 \\ ^{231}_{90}Th: N = 231 - 90 = 114; Z = 90. \text{ So, } N - Z = 141 - 90 = 51 \end{array}\right]$$

Isodiaphers

$$\left.\begin{array}{l} ^{1}_{1}H: N = 1 - 1 = 0; Z = 1. \text{ So, } N - Z = 0 - 1 = -1 \\ ^{4}_{2}He: N = 4 - 2 = 2; Z = 2. \text{ So, } N - Z = 2 - 2 = 0 \end{array}\right]$$

Not Isodiaphers

So, the correct answer is (*d*).

EXAMPLE 130. *Which of the following species is not an isoster?*

(a) N_2 *and CO* *(b)* CO_2 *and* H_2O

Solution. Molecules which have same number of atoms and also same number of electrons are called isosters.

(*a*) N_2 has no. of atoms = 2; CO has one C and one O atoms. So, total no. of atoms = 1 + 1 = 2.

2_7N : no. of electrons

$$= 2\,(Z \text{ of } N) = 2 \times 7 = 14$$

In CO : no. of electrons in

$_6C$ = Z of C = 6; no. of electrons in O_8 = Z of O = 8.

So, total no. of electrons in CO = 6 + 8 = 14. So, N_2 and CO are isosters.

(*b*) CO_2 has no. of atoms

$$= 1 \text{ of } C + 2 \text{ of } O = 3$$

$_6C$: no. of electrons

$$= Z = 6;$$

2_8O : no. of electrons

$$= 2\,(Z \text{ of } O) = 2 \times 8 = 16$$

Hence total no. of electrons in

CO_2 = 6 + 16 = 22.

H_2O : no. of atoms

$$= 2 \text{ of } H + 1 \text{ of } O = 3$$

2_1H : no. of electrons

$$= 2\,(Z \text{ of } H) = 2 \times 1 = 2$$

$_8O$: no. of electrons

$$= Z \text{ of } O = 8$$

∴ Total no. of electrons in H_2O = 2 + 8 = 10

Since CO_2 and H_2O do not obey the conditions of isosters, so, the correct answer is (*b*).

Example 131. *An alpha particle is given out by $_{92}X^{238}$. The new species Y should be :*

(*a*) $^{234}_{90}Y$ (*b*) $^{238}_{90}Y$

(*c*) $^{234}_{92}Y$ (*d*) $^{234}_{94}Y$ **(BET, 2003)**

Solution. $_{92}X^{238} \xrightarrow[-{}^4_2He]{-\alpha \text{ or}} \underset{92-2}{X^{238-4}}$ or $_{90}X^{234}$. So, the correct answer is (*a*).

Example 132. *An element has half-time period of 6.5 hours. Initial number of atoms is 48×10^{19}. Then after 26 hours, the number of atoms will be :*

(*a*) 1.6×10^{19} (*b*) 3×10^{19}

(*c*) 2.4×10^{19} (*d*) 5×10^{19} **(IMS-BHU, 2003)**

Solution. No. of half-time,

$$n = \frac{\text{Total time}}{t_{1/2}}$$

Or $$n = \frac{26\,\text{hr}}{6.5\,\text{hr}} = 4.$$

But $$N = No\left(\frac{1}{2}\right)^n ; No = 48 \times 10^9$$

∴ $$N = 48 \times 10^{19} \times \left(\frac{1}{2}\right)^4$$

$$= 48 \times 10^{19} \times \frac{1}{16} = 3.0 \times 10^{19}.$$

So, the correct answer is (*b*).

Example 133. *A substance has half-life period of 4 sec. After t = 20 sec., how much percentage of substance is destroyed ?*

(*a*) 96.87 (*b*) 3

(*c*) 40 (*d*) 50 **(IMS-BHU, 2003)**

Solution. No. of half-lives

$$= \frac{\text{Total time}}{t_{1/2}} = \frac{20\,\text{sec}}{4\,\text{sec}} = 5$$

Hence, $$\frac{N}{No} = \left(\frac{1}{2}\right)^5 = \frac{1}{32};\ N = \frac{No}{32}$$

Hence, $$\Delta N = No - \frac{No}{32} = No\left[1 - \frac{1}{32}\right]$$

Or $$\Delta N = \frac{31}{32}No.$$

Hence, $$\frac{\Delta N}{No}\% = \left(\frac{\Delta N}{No}\right) \times 100 = \frac{31}{32} \times 100 = 96.87\%$$

So, the correct answer is (*a*).

Example 134. *One gram atom of a radioactive isotope ($t_{1/2}$ = 10 hours) that emits alpha particles was placed in a sealed container. The time taken for 0.875g atom of helium to accumulate in the container is :*

(*a*) 10 hours (*b*) 20 hours

(*c*) 30 hours (*d*) 40 hours

(J and K-CET, 2011)

Solution. $t_{1/2}$ = 10 hours means that 1 g atom of radioactive isotope will change to half by emitting one α-particle. So, the amount of helium emitted in :

10 hours = 0.5 g atom ; 2 × 10 i.e., 20 hours

= 0.5/2 = 0.25 g atom ; 3 × 10

i.e., 30 hours = 0.25/2 = 0.125 g atom. But (0.5 + 0.25 + 0.125) g.

atom = 0.875 g. So total time taken = 30 hours. So,. the correct answer is (*c*).

Example 135. *A radioactive isotope having a half-life of 3 days was received after 12 days. It was found that there were 3g of the isotope in the container. The initial weight of the isotope when packed was :*

(*a*) 48g (*b*) 36g

(*c*) 24g (*d*) 12g

(Karnataka CET, 2000)

Solution. Given N_t = 3g; No = ?; $t_{1/2}$ = 3 days.

$$\text{No. of half-lives} = \frac{\text{Total time}}{t_{1/2}} = \frac{12\,\text{days}}{3\,\text{days}} = 4$$

We know that : $$N_t = No\left(\frac{1}{2}\right)^n ; 3g = No\left(\frac{1}{2}\right)^4 = \frac{No}{16}$$

∴ No = 16 × 3g = 48g. So, the correct answer is (*a*).

EXAMPLE 136. *A sample of radioactive element undergoes 80% decomposition in 325 minutes. Its $t_{1/2}$ in minutes is :*

(a) $\frac{ln 2}{ln 4}$ (b) $\frac{ln 4}{ln 2}$

(c) $\frac{ln 2}{ln 5}$ (d) none of these.

SOLUTION.
$$t_{0.8} = \frac{1}{k}\ln\frac{100}{100-80} = \frac{1}{k}\ln 5$$

$$t_{0.5} \text{ or } t_{1/2} = \frac{1}{k}\ln\frac{100}{100-50} = \frac{1}{k}\ln 2$$

$$\therefore \quad \frac{t_{1/2}}{t_{0.8}} = \frac{1}{k}\ln 2 \times \frac{k}{\ln 5} = \frac{\ln 2}{\ln 5}$$

So, the correct answer is (*c*).

EXAMPLE 137. *If the mass of Co – 59 = 58.9332, the value of its packing fraction will be :*

(a) +11.322 (b) –11.322

(c) +5.661 (d) –5.661

SOLUTION. We know that,

$$\text{Packing fraction} = \frac{\text{Actual mass } - \text{ Mass number}}{\text{Mass number}} \times 10^4$$

$$= \frac{58.9332-59}{59} \times 10^{-4}$$

$$= \frac{-0.0668 \times 10^4}{59} = -11.322$$

So, the correct answer is (*b*).

EXAMPLE 138. *The mass number of a nucleide is 64. What is its nuclear radius in Fermi ?*

(a) 2.8 Fermi (b) 1.4 Fermi

(c) 5.6 Fermi (d) 11.2 Fermi

SOLUTION. Mass number, A = 64; Ro = 1.4×10^{-13} cm.

We know that nuclear radius,

$$R = Ro\,(A)^{1/3}. \text{ Thus :}$$
$$R = 1.4 \times 10^{-13} \text{ cm} \times (64)^{1/3}$$
$$= 1.4 \times 10^{-13} \text{ cm} \times (4 \times 4 \times 4)^{1/3}$$
$$= 1.4 \times 10^{-13} \text{ cm} \times 4$$
$$= 5.6 \times 10^{-13} \text{ cm} = 5.6 \text{ Fermi}$$

[∵ 1 Fermi = 10^{-13}cm]

So, the correct answer is (*c*).

EXAMPLE 139. *The fission of a single $^{235}_{92}U$ nucleus releases energy equal to 200 MeV. The number of fissions that occur per second to produce a power of one kW is :*

(a) $3.125 \times 10^{13}s^{-}$ (b) $3.2 \times 10^{-8}s^{-}$

(c) $3.2 \times 10^{14}s^{-}$ (d) $1.6 \times 10^{14}s^{-}$

SOLUTION. 1 MeV = 10^6 eV; 1 eV = 1.6×10^{-19}J. Thus, 1 MeV = $1.6 \times 10^{-19} \times 10^6$J.

Thus, **200 MeV** = $200 \times 1.6 \times 10^{-19} \times 10^6$ J

$$= \mathbf{3.2 \times 10^{-11}\ J}$$

Required energy

$$= 1 \text{ kW} = 1 \times 10^3 \text{ W} = 1 \times 10^3 \text{ Js}^{-}$$

[∵ 1 Watt = 1 Js^{-}]

Required number of fissions

$$= \frac{\text{Required energy}}{\text{Energy released per fission}}$$

$$= \frac{10^3 \text{Js}^{-}}{3.2 \times 10^{-11}\text{J}}$$

$$= 3.125 \times 10^{13}\text{s}^{-}$$

So, the correct answer is (*a*).

EXAMPLE 140. *Chlorine-35 (34.96885 a.m.u.) is formed when sulphur-35 (34.96903 a.m.u.) emits β-particle but no gamma particle. The maximum energy emitted in the process is:*

(a) 167.67 MeV (b) 16.767 MeV

(c) 1.6767 MeV (d) 0.16767 MeV

SOLUTION. Mass defect,

$$\Delta m = 34.96903 \text{ a.m.u.} - 34.96903 \text{ a.m.u.}$$
$$= 1.8 \times 10^{-4} \text{ a.m.u.}$$

Since energy emitted by

1 a.m.u. = 931.5 MeV, so :

Energy emitted by 1.8×10^{-4}

a.m.u. = $1.8 \times 10^{-4} \times 931.5$

MeV = 0.16767 MeV

So, the correct answer is (*d*).

EXAMPLE 141. *The number of α-particles emitted per second by 2g of thorium ($t_{1/2}$ ^{232}Th = 1.39×10^{10} yrs) will be :*

(a) 8.20×10^3 (b) 4.104×10^3

(c) 2.052×10^4 (d) 2.052×10^{23}

(Avogadro's no. = 6.023×10^{23})

SOLUTION.

Wt. of ^{232}Th = 2g

No. of ^{232}Th atoms,

$$N = \frac{\text{wt. in g}}{\text{g. at. wt. of } ^{232}\text{Th}} \times 6.023 \times 10^{23} \text{atoms}$$

$$= \frac{2}{232} \times 6.023 \times 10^{23} \text{ atoms}$$

$$= 5.19 \times 10^{21} \text{ atoms}$$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.39 \times 10^{10}\text{yr}} \times \frac{1\text{yr}}{365\text{d}}$$

$$\times \frac{1\text{d}}{24\text{hr}} \times \frac{1\text{hr}}{60\text{min}} \times \frac{1\text{min}}{60\text{sec}} = 1.58 \times 10^{-18}\text{s}^{-}$$

No. of α-particles emitted per second

$$= -\frac{dN}{dt} = N\lambda$$

$$= 5.19 \times 10^{21} \text{ atoms} \times 1.58 \times 10^{-18}\text{s}^{-}$$

$$= 8.2 \times 10^3 \text{ atoms}$$

So, the correct answer is (*a*).

EXAMPLE 142. *The loss in mass accompanying combustion of one mol of fuel to release 900 kJ heat energy is :*

(a) 2×10^{9} *kg*	*(b)* 2×10^{11} *kg*
(c) 3×10^{11} *kg*	*(d)* 10^{11}*kg*

SOLUTION. Loss in mass = Δm, ΔE = Energy released, C = velocity of light (= $3 \times 10^{8}\ ms^{-}$). We know that : $\Delta E = \Delta m C^2$. Hence :

$$\Delta m = \frac{\Delta E}{C^2} = \frac{900\,kJ}{(3 \times 10^{8} ms^{-})^2} = \frac{900 \times 1000\,J}{(3 \times 10^{8} ms^{-})^2}$$

$$= \frac{900 \times 1000\,kg\,m^2s^{-2}}{9 \times 10^{16} m^2 s^{-2}}$$

$[\because J = kg\ m^2s^{-2}]$

$$= \mathbf{1.0 \times 10^{-11}\ kg.}$$

So, the correct answer is (*d*).

EXAMPLE 143. *A sample of ordinary neon gas was found to contain* ${}^{20}_{10}Ne$, ${}^{21}_{10}Ne$ *and* ${}^{22}_{10}Ne$ *isotopes in the percentage 90.92%, 0.26% and 8.82% respectively. The actual atomic mass of neon is:*

(a) *30.2*	*(b)* *20.18*
(c) *25.17*	*(d)* *10.09*

SOLUTION. Actual atomic mass of neon

$$= \frac{(20 \times 90.92) + (21 \times 0.26) + (22 \times 8.82)}{90.92 + 0.26 + 8.82}$$

$$= \frac{1818.4 + 5.46 + 194.04}{100}$$

$$= \frac{2017.9}{100} \simeq \mathbf{20.18}$$

So, the correct answer is (*b*).

EXAMPLE 144. *The half-life of a radioactive element is 4.8 min. The time taken by a given sample of the element to reduce to 1/4th of its initial activity will be :*

(a) *4.8 min*	*(b)* *9.6 min*
(c) *19.2 min*	*(d)* *1 hour*

SOLUTION. (*i*) $t_{1/2} = 4.8$ min; $\lambda = \frac{0.693}{t_{1/2}}$; $\lambda = \frac{0.693}{4.8\,min}$

(*ii*) $t = ?$ But $t = \frac{2.303}{\lambda}\log\frac{No}{N}$; $t = \frac{2.303 \times 4.8\,min}{0.693}\log\frac{1}{1/4}$

$$\therefore\ t = \frac{2.303 \times 4.8\,min}{0.693}\log 4 = \frac{2.303 \times 4.8\,min \times 0.602}{0.693}$$

or $t = 9.6$ min.

So, the correct answer is (*b*).

EXAMPLE 145. *A radioactive substance decays at such a rate that after 35 minutes, only a quarter of the original substance is left behind. The disintegration constant and half-life of the radioisotope are :*

(a) *0.0396* min^{-}, *17.5 min*	*(b)* *1.2* min^{-}, *10 min*
(c) *2.4* min^{-}, *20 min*	*(d)* *0.003* min^{-}, *1 min*

SOLUTION. (*i*) $t = 35$ min, No = 1, $N = \frac{1}{4}$; λ = disintegration constant. We know that:

$$\lambda = \frac{2.303}{t}\log\frac{No}{N};$$

$$\lambda = \frac{2.303}{35\,min}\log\frac{1}{1/4} = \frac{2.303}{35\,min}\log 4$$

$$\therefore\qquad \lambda = \frac{2.303}{35\,min} \times 0.602 = 0.0396\,min^{-}$$

(*ii*) $$t_{1/2} = \frac{0.693}{\lambda} = \frac{0.693}{0.0396} = 17.5\,min$$

So, the correct answer is (*a*).

EXAMPLE 146. *The half-life of a radioactive isotope is three hours. If the initial mass of the isotope was 256 g, the mass of it remaining undecayed after 18 hours would be :*

(a) *16.0 g*	*(b)* *4.0 g*
(c) *8.0g*	*(d)* *12.0 g* **(AIEEE, 2003)**

SOLUTION. Half-life $t_{1/2}$ = 3 hours; Total hours = 18 hours.

$\therefore$ Number of half-lives,

$$n = \frac{18}{3} = 6$$

But amount of substance left

$$= \frac{\text{Initial mass}}{2^n} = \frac{256}{2^6} = \frac{256}{64} = 4.0\,g$$

So, the correct answer is, (*b*).

EXAMPLE 147. *The radionucleide* ${}^{234}_{90}Th$ *undergoes two successive* β*-decays followed by one* α*-decay. The atomic number and the mass number respectively of the resulting nucleides are:*

(a) *92 and 230*	*(b)* *92 and 234*
(c) *94 and 230*	*(d)* *90 and 230* **(AIEEE, 2003)**

SOLUTION. The decay products can be represented as :

${}^{234}_{90}Th \xrightarrow{-({}^{0}_{-1}\beta)} {}^{234}_{91}X \xrightarrow{-({}^{0}_{-1}\beta)} {}^{234}_{92}Y \xrightarrow{-({}^{4}_{2}\alpha)} {}^{230}_{90}Th$. Since atomic number is 90 and mass number is 230, the correct answer is, (*d*).

EXAMPLE 148. *If No and N are the number of radioactive particles at t = 0 and at time t, then:*

(a) $\lambda = \frac{2.303}{t}\log NoN$	*(b)* $\lambda = \frac{2.303}{t}\log\frac{N}{No}$
(c) $\lambda = \frac{2.303}{t}\log\frac{No}{N}$	*(d)* $\lambda = \frac{1}{t}\log\frac{No}{N}$

SOLUTION. At $t = 0$ and at time t, No and N are related to λ as $\lambda = \frac{2.303}{t}\log\frac{No}{N}\cdot$ So, the correct answer is (*c*).

EXAMPLE 149. *In the first order reaction, the concentration of the reactants is reduced to 25% in one hour. The half-life period of the reaction is :*

(a) *30 seconds*	*(b)* *30 minutes*
(c) *1.5 hr*	*(d)* *.5 hr*

SOLUTION. The concentration has reduced to 25%. It means 75% (100 – 25 = 75) has reacted *i.e.*, $\frac{75}{100} = \frac{3}{4}$. Thus $2 \times t_{1/2}$ (half-life) $= t_{3/4}$ or $t_{1/2} = \frac{1}{2} \times t_{3/4} = \frac{1}{2} \times 1\,\text{hr} = \frac{1}{2}\,\text{hr} = \frac{1}{2} \times 60$ min = 30 min. So, correct answer is, (*b*).

Example 150. *The half-life of a first order reaction is 60 sec. The percentage of reactant left after 3 minutes is :*

(a) 2.5 *(b) 25*

(c) 12.5 *(d) 1.25*

Solution. 3 minutes = 3 × 60 = 180 seconds. Number of half lives, $n = \frac{180\,\text{sec}}{60\,\text{sec}} = 3$.

$\therefore$ Concentration (C) after *n* half-lives

$$= \frac{\text{Co}}{2^n} = \frac{\text{Co}}{2^3} = \frac{\text{Co}}{8}$$

Where Co is original concentration.

$\therefore$ Percentage left

$$= \frac{\text{Co}}{8} \times 100 = \frac{1}{8} \times 100 = \mathbf{12.5}$$

So, the correct answer is (*c*).

Example 151. *Complete the following statements for nuclear reactions.*

(i) $^{239}_{94}Pu\,(\alpha, \beta^-)\,........$

(ii) $........(\alpha, 2n)^{211}_{85}At$

(iii) $^{246}_{96}Cm + {}^{12}_{6}C \longrightarrow .... + 4\,^{1}_{0}n$

(iv) $^{27}_{13}Al(\alpha, n)$

You may use 'X' as symbol if the correct symbol in a reaction is not known.

(CBSE, 2007, HP Board, 2008)

Solution. (*i*) $^{239}_{94}\text{Pu}\,(\alpha, \beta^-)\,........$ is written as

$$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{0}_{-1}e + {}^{243}_{97}\text{Bk} \quad \left(\because \beta^- = {}^{0}_{-1}e\right)$$

or $^{239}_{94}\text{Pu}\,(\alpha, \beta^-)^{243}_{97}\text{Bk}$ or $^{243}_{97}\text{X}$

(*ii*) $^{209}_{83}\text{Bi} + {}^{4}_{2}\text{He} + 2\,^{1}_{0}\text{n} + {}^{211}_{85}\text{At}$; **Or** $^{209}_{83}\text{Bi}\,(\alpha, 2n)^{211}_{85}\text{At}$

or $^{209}_{83}\text{X}\,(\alpha, 2n)^{211}_{83}\text{At}$

(*iii*) $^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4\,^{1}_{0}\text{n}$

or $^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{X} + 4\,^{1}_{0}\text{n}$

(*iv*) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \longrightarrow {}^{1}_{0}\text{n} + {}^{30}_{15}\text{P}$

Note. In all above cases (*i*) sum of mass no. of reactants = sum of mass no. of products. (*ii*) Sum of at. no. of reactants = sum of at. no. of products.

EXAMPLE 152. *The half-life period of polonium is 140 days. If one starts with 1g of polonium, 75% of it would have undergone disintegration in :*

(a) 28 days *(b) 280 days*

(c) 560 days *(d) 1 year*

Solution. $t_{1/2}$ = 140 days. But decay constant, $\lambda = \frac{0.693}{t_{1/2}}; \therefore \lambda = \frac{0.693}{140\,days} = 4.95 \times 10^{-3}$ (days)⁻. We know that :

$$t = \frac{2.303}{\lambda} \log \frac{a}{a - \left(\frac{75}{100}a\right)}$$

$$= \frac{2.303}{4.95 \times 10^{-3}} \log \frac{1}{1 - 0.75}$$

$$= \frac{2.303}{4.95 \times 10^{-3}} \log 4$$

$$\left[\because \frac{1}{1 - 3/4} = \frac{1}{1/4} = 4\right]$$

$$= \frac{2.303}{4.95 \times 10^{-3}} \times 0.6020 = 280\,\text{days}$$

So, the correct answer is, (*b*).

Example 153. *A certain nucleide has half-life period of 30 min. If a sample containing 6 × 10¹⁰ atoms is allowed to decay for 90 min., how many atoms will remain :*

(a) 2.9×10^9 atoms *(b) 7.0×10^9 atoms*

(c) 9.9×10^9 atoms *(d) 7.5×10^9 atoms.*

Solution. $t_{1/2}$ = 30 minutes. Total time = 90 minutes.

$\therefore$ No. of half-lives,

$$n = \frac{90}{30} = 3.$$

Total number of atoms,

$$\text{N} = 6 \times 10^{10}$$

But, $\quad \text{No} = \dfrac{\text{N}}{\left(\frac{1}{2}\right)^n}$

$$\therefore \quad \text{N} = \text{No} \times \left(\frac{1}{2}\right)^n$$

$$= 6.0 \times 10^{10} \times \left(\frac{1}{2}\right)^3 = \frac{6 \times 10^{10}}{8}$$

$$= 0.75 \times 10^{10} = 7.5 \times 10^9$$

So, the correct answer is, (*d*).

Example 154. *The $t_{0.5}$ of radioactive element is related to its average life by the expression :*

(a) $2.1\,t_{0.5}$ *(b) $2.88\,t_{0.5}$*

(c) $1.44\,t_{0.5}$ *(d) $4.32\,t_{0.5}$*

Solution. We know,

$$\text{Average life, T} = \frac{1}{\lambda\,(\text{decay constant})}$$

$$= \frac{1}{0.693 / t_{0.5}} = \frac{t_{0.5}}{0.693} = 1.44\,t_{0.5}$$

So, the correct answer is (*c*).

Example 155. *In a certain old wooden chair, the ratio of* $^{14}_{6}C$ *to* $^{12}_{6}C$ *is 13% that of the atmosphere. If half-life of* $^{14}_{6}C$ *is 5770 years, the age of the wood is :*

(a) 16.991 yrs *(b) 1512 yrs*
(c) 84955 yrs *(d) 16991 yrs*

Solution. (*i*) $t_{1/2}$ = 5770 years.

Hence, $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770\text{ years}}$$

(*ii*) *t* (= age of wood) = ?, No = 100, N = 13. We know:

$$t = \frac{2.303}{\lambda}\log\frac{\text{No}}{\text{N}};$$

$$t = \frac{2.303 \times 5770\text{ years}}{0.693}\log\frac{100}{13}$$

$$= \frac{2.303 \times 5770\text{ yrs}}{0.693}[\log 100 - \log 13]$$

$$= \frac{2.303 \times 5770\text{ yrs}}{0.693}[2.0 - 1.1139]$$

$$t = \frac{2.303 \times 5770\text{ yrs} \times 0.8861}{0.693}$$

$$= 16991\text{ yrs.}$$

So, the correct answer is (*d*).

Example 156. *An experiment on radioactivity revealed that a radioactive element lost its half activity in 2 days and 12 hours. The decay constant as well as average life of the element are :*

(a) 0.01155 hr⁻, 86.58 hr *(b) 0.1155 hr⁻, 8hr*
(c) 1.2 hr⁻, 7hr *(d) 0.0057 hr⁻, 3hr*

Solution. (*i*) $t_{1/2}$ = 2 days + 12 hrs

$$= \left(2\text{days} \times \frac{24\text{ hr}}{1\text{day}}\right) + 12\text{ hrs} = 60\text{ hrs.}$$

∴ Decay constant,

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{60\text{ hr}} = 0.01155\text{ hr}^{-}$$

(*ii*) Average life,

$$\text{T} = \frac{1}{\lambda} = \frac{1}{0.01155\text{ hr}^{-}} = 86.58\text{ hr}$$

So, the correct answer is (*a*).

Example 157. *If the amount of radioactive substance is increased three times, the number of atoms disintegrated per unit time would*

(a) be doubled *(b) be tripled*
(c) remain one-third *(d) not change*

(MPPMT, 1994)

Solution. Since the rate of disintegration is directly proportional to the number of radioactive atoms, the number of atoms disintegrated per unit time would be tripled. So, the correct answer is (*b*).

Example 158. *The half-life of a radioactive element is 30 minutes. One sixteenth of the original quantity of the element will remain unchanged after*

(a) One hour *(b) 16 hours*
(c) 4 hours *(d) 2 hours* **(MPPMT, 1994)**

Solution. We know,

$$\frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^n;\ \frac{1}{16} = \frac{1}{16}$$

Hence, $n = 4$

∴ Time = 4 half-lives = 4 × 30 min = 120 min

$$= 120\text{ min} \times \frac{1\text{hr}}{60\text{ min}} = 2\text{hr.}$$

So, the correct answer is (*d*).

Example 159 *After the emission of one α-particle followed by one β-particle from the atom of* $^{238}_{22}X$, *the number of neutrons in the atoms will be*

(a) 142 *(b) 146*
(c) 144 *(d) 143* **(CBSE, 1995)**

Solution. $^{238}_{22}X \xrightarrow{-\alpha\text{ or }^{4}_{-2}\text{He}} {}^{238-4}_{92-2}Y \xrightarrow{-\beta\text{ or }^{0}_{-1}e} {}^{238-4-0}_{92-2+1}Z$ or $^{234}_{91}Z$

∴ No. of neutrons in Z = 234 – 91 = 143. So, the correct answer is (*d*).

Example 160. *Half-life for radioactive* ^{14}C *is 5760 years. In how many years 200 mg of* ^{14}C *sample will be reduced to 25 mg?*

(a) 11520 yrs *(b) 23040 yrs*
(c) 5760 yrs *(d) 17280 yrs* **(CBSE, 1995)**

Solution. We know that :

$$\text{N} = \text{No}\left(\frac{1}{2}\right)^n;\ \frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^n;\ \frac{25}{200}$$

or $$\frac{1}{8} = \left(\frac{1}{2}\right)^3;\ n = 3$$

∴ $t = n \times t_{1/2}$ = 3 × 5760 years = 17280 years. So, the correct answer is (*d*).

Example 161. *The average life period of a radioactive element is the reciprocal of its*

(a) half-life period
(b) disintegration constant
(c) number of atoms present at any time
(d) number of neutrons **(MPPET, 1995)**

Solution. Average life period,

$$\text{T} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}\,.$$

So, the correct answer is (*b*).

Example 162. *An isotope* $^{X}_{Y}A$ *undergoes a series of m alpha and n beta disintegrations to form a stable isotope* $^{X-32}_{Y-10}B$. *The values of m and n are, respectively,*

(a) 6 and 8 *(b) 8 and 10*
(c) 5 and 8 *(d) 8 and 6*

(MPPET, 1995)

Solution. Loss in mass = 32. Hence no. of α (*i.e.*, ^{4}He) particles = $\frac{32}{4} = 8$. Decrease in at. no. = 10.

∴ Decrease in at. no. due to the emission of 8 α-particles ($_2$He) = 8 × 2 = 16.

∴ No. of β-particles ($_{-1}^{0}e$) emitted = 16 – 10 = 6. So, the correct answer is (*d*).

Example 163. *In the nuclear reaction:* $^{14}_{7}N + ^{4}_{2}He \rightarrow ^{a}_{b}X + ^{1}_{1}H$, *the nucleus X is :*

(*a*) *Nitrogen of mass 16* (*b*) *Nitrogen of mass 17*
(*c*) *Oxygen of mass 16* (*d*) *Oxygen of mass 17*

(MLNR, 1995)

Solution. To balance a nuclear reaction :

(*i*) Sum of mass no. of reactants = Sum of mass no. of products

$$14 + 4 = a + 1; a = 18 - 1 = 17$$

(*ii*) Sum of at. no. of reactants =Sum of at. no. of products

$$7 + 2 = b + 1; b = 9 - 1 = 8$$

∴ Nucleus, X = $^{17}_{8}$X. Since atomic no. 8 is that of oxygen, so, X is = $^{17}_{8}$O. So, the correct answer is (*d*).

Example 164. *The radioactive decay of* $^{88}_{35}$X *by a beta emission produces an unstable nucleus which spontaneously emits a neutron. The final product is*

(*a*) $^{88}_{37}X$ (*b*) $^{89}_{35}Y$
(*c*) $^{88}_{34}Z$ (*d*) $^{87}_{36}W$ **(MLNR, 1995)**

Solution. $^{88}_{35}\text{X} \xrightarrow[-(^{0}_{-1}e)]{-\beta\text{or}} {}^{88-0}_{35+1}\text{Y} \text{ or } {}^{88}_{36}\text{Y} \longrightarrow {}^{87}_{36}\text{Z} + {}^{1}_{0}n.$

So, the correct answer is (*d*).

Example 165. *A radioactive sample has half-life of 1500 years. A sealed tube containing 1g of the sample will contain after 3000 years :*

(*a*) *1g of the sample* (*b*) *0.5 g of the sample*
(*c*) *0.25 g of the sample* (*d*) *0.00 g of the sample.*

(M.L.N.R., 1994)

Solution. No. of half-lives

$$= \frac{3000\,\text{yrs}}{1500\,\text{yrs}} = 2.$$

So, $n = 2$. But N = No × $\left(\frac{1}{2}\right)^n$;

$$\text{N} = 1\text{g} \times \left(\frac{1}{2}\right)^2 = \frac{1}{4} = 0.25\text{g}.$$

So, the correct answer is (*c*).

Example 166. *Complete the following nuclear reactions* $^{55}_{25}Mn(n, \gamma)$

(*a*) $^{55}_{25}Mn$ (*b*) $^{56}_{25}Mn$
(*c*) $^{56}_{24}Cr$ (*d*) $^{54}_{24}Cr$ **(ISM Dhanbad, 1994)**

Solution. $^{55}_{25}\text{Mn} + ^{1}_{0}n \rightarrow ^{55+1}_{25+0}\text{Mn}$ or $^{56}_{25}\text{Mn} + ^{0}_{0}\gamma$. So, the correct answer is (*b*).

Example 167. $^{232}_{90}Th$ *is the starting material of a decay chain series. This series by successive decays terminates at* $^{208}_{82}Pb$. *The number of α and β-particles emitted in this process are*

(*a*) *6α and 4β* (*b*) *4α and 6β*
(*c*) *10α and 6β* (*d*) *6α and 10β*

(Punjab CET, 1996)

Solution. For $^{232}_{90}\text{Th} \rightarrow ^{208}_{82}\text{Pb}$, (*i*) no. of α-particles = $\frac{232 - 208}{4} = 6$

Decrease in charge = 90 – 82 =8

∴ No. of β-particles = no. of α-particles × 2 – decrease in charge = (6 × 2) – 8 = 4.

So, the correct answer is (*a*).

Example 168. *The half-life of a radionucleide 'X' is 24 hours. The time required for 12.5% of the original X to remain is*

(*a*) *1 day* (*b*) *2 days*
(*c*) *3 days* (*d*) *4 days* **(Pb CET 1996)**

Solution. $\text{N} = \text{No}\left(\frac{1}{2}\right)^n ; 12.5 = 100\left(\frac{1}{2}\right)^n ;$

$$\frac{12.5}{100} = \left(\frac{1}{2}\right)^n ; \frac{1}{8} = \left(\frac{1}{2}\right)^n \text{ or } \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n.$$

Hence $n = 3$.

∴ t = 3 days. So, the correct answer is (*c*).

Example 169. *1.0g of radioactive isotope was found to reduce to 125 mg after 24 hours. The half-life of the isotope is*

(*a*) *8 hrs* (*b*) *24 hrs*
(*c*) *6 hrs* (*d*) *4 hrs*

(MPCET, 1996. J and K CET, 2010)

Solution. $1.\text{g} = 1000\text{ mg}. \frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^n ; \frac{125}{1000} = \left(\frac{1}{2}\right)^n ;$

$$\frac{1}{8} = \left(\frac{1}{2}\right)^n ; \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n.$$

∴ $n = 3$. But $t = t_{1/2} \times n$;

$$t_{1/2} = \frac{t}{n} = \frac{24\,\text{hrs}}{3} = 8\,\text{hrs}.$$

So, the correct answer is (*a*).

Example 170. *The half-life period of a radioactive element is 140 days. In 560 days, a sample of this element would be reduced to ...... of its initial mass :*

(*a*) $\frac{1}{2}$ (*b*) $\frac{1}{4}$
(*c*) $\frac{1}{8}$ (*d*) $\frac{1}{16}$ **(MPCET, 1998)**

Solution. $\frac{\text{Total time}}{t_{1/2}} = \frac{560\,\text{days}}{140\,\text{days}} = 4$

$$\therefore \qquad \frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}.$$

So, the correct answer is (*d*).

EXAMPLE 171. *2 g of a radioactive sample having a half-life of 15 days was synthesised on 1st Jan 2009. The amount of the sample left behind on first March, 2009 (including both days) :*

(*a*) 0.125 g (*b*) 1 g
(*c*) 0.5 g (*d*) 0 g

(AIEEE, 2004, Karnataka CET, 2009)

SOLUTION. No. of days of Jan (31) + Feb (28) + March (31) = 60 days. $t_{1/2}$ = 15 days (given). Thus, no. of half-lives, n = ?

Total time, $T = n \times t_{1/2}$; $n = \frac{60}{15} = 4$

Initial amount, No = 2g. So, sample present after 4 half-lives, $\text{N} = \left(\frac{1}{2}\right)^n \text{No} = \left(\frac{1}{2}\right)^4 \times 2 = \frac{2}{16} = 0.125$ g. So, the correct answer is (*a*)

EXAMPLE 172. *The half-life of a radioactive isotope is three hours. If the initial mass of isotope was 300g, the mass that remained undecayed in 18 hours would be :*

(*a*) 2.34 g (*b*) 1.17 g
(*c*) 9.36g (*d*) 4.68 g **(CBSE, 2000)**

SOLUTION. $$n = \frac{\text{Total time}}{t_{1/2}} = \frac{18\,\text{hrs}}{3\,\text{hrs}} = 6.$$

Also, $$\text{N} = \text{No} \times \left(\frac{1}{2}\right)^n = 300\text{g} \times \left(\frac{1}{2}\right)^6$$

or $$\text{N} = 300\text{ g} \times \frac{1}{64} = 4.68\text{g}.$$

So, the correct answer is (*d*).

EXAMPLE 173. *A human body required 0.01M activity of a radioactive substance after 24 hours. Half-life of the radioactive substance is 6 hours. The injection of maximum activity of the radioactive substance that can be injected is :*

(*a*) 0.08 (*b*) 0.04
(*c*) 0.16 (*d*) 0.32 **(CBSE, 2001)**

SOLUTION. $$n = \frac{\text{Total time}}{t_{1/2}} = \frac{18}{3} = 6.$$

Also, $$\text{N} = \text{No} \times \left(\frac{1}{2}\right)^n ; 0.01\text{M} = \text{No} \times \left(\frac{1}{2}\right)^4 ;$$

$$0.01\text{M} = \text{No} \times \frac{1}{16}$$

Hence, $\text{No} = 16 \times 0.01\text{ M} = 0.16\text{ M}.$

So, the correct answer is (*c*).

EXAMPLE 174. *The radioisotope tritium (^3_1H) has a half-life of 12.3 years. If the initial amount of tritium is 32 mg, how many milligrams of it would remain after 49.2 years ?*

(*a*) 1 mg (*b*) 2 mg
(*c*) 4 mg (*d*) 8 mg **(CBSE, 2003)**

SOLUTION. $$n = \frac{\text{Total time}}{t_{1/2}} = \frac{49.2\,\text{years}}{12.3\,\text{years}} = 4;$$

$$\text{N} = \text{No} \times \left(\frac{1}{2}\right)^n = 32\,\text{mg} \times \left(\frac{1}{2}\right)^4$$

$$\therefore \qquad \text{N} = 32\text{ mg} \times \frac{1}{16} = 2\text{mg}$$

So, the correct answer is (*b*).

EXAMPLE 175. *A radioactive isotope decays at such a rate that after 192 minutes only 1/16 of the original amount remains. The half-life of the radioactive isotope is*

(*a*) 32 min (*b*) 48 min
(*c*) 12 min (*d*) 24 min

(Karnatka CET, 2004)

SOLUTION. $$\frac{\text{N}}{\text{No}} = \frac{1}{16};$$

Hence, $$\frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^4 ; \frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^n$$

So, n = 4. Also,

$$t_{1/2} = \frac{\text{Total time}}{n} = \frac{192\,\text{min}}{4} = 48\,\text{min}.$$

So, the correct answer is (*b*).

EXAMPLE 176. *If radioactive substance after 48 days remains 25% of initial value, then find disintegration constant.*

(*a*) $2.89 \times 10^{-2}\ T^{-1}$ (*b*) $3.89 \times 10^{-3}T^{-1}$
(*c*) $4.89 \times 10^{-2}T^{-1}$ (*d*) *none of these* **(BCECE, 2004)**

SOLUTION. $$\frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^n ; \frac{\text{N}}{\text{No}} = \frac{25}{100} = \frac{1}{4} \text{ or } \left(\frac{1}{2}\right)^2.$$

Hence n = 2.

But $$t_{1/2} = \frac{\text{Total time}}{n} = \frac{48\,\text{days}}{2} = 24\,\text{days}$$

$$\therefore \qquad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{24}\text{T}^{-1} = 2.89 \times 10^{-2}\text{T}^{-}.$$

So, the correct answer is (*a*).

EXAMPLE 177. *What is the half-life of a radioactive substance if 87.5% of any given amount of the substance disintegrates in 40 minutes ?*

(*a*) 0 min (*b*) 20 min
(*c*) 160 min (*d*) 13 min 20 sec.

(Manipal, UGET, 2004)

SOLUTION. Amount of substance left

$$= 100 - 87.5 = 12.5\text{ g}.$$

$$\frac{\text{N}}{\text{No}} = \left(\frac{1}{2}\right)^n . \text{But} \frac{\text{N}}{\text{No}} = \frac{12.5}{100} \textit{ i.e., } \frac{1}{8}.$$

So, $$\frac{1}{8} = \left(\frac{1}{2}\right)^n ; \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n. \text{ Hence } n = 3.$$

But $$t_{1/2} = \frac{\text{Total time}}{n} ; t_{1/2} = \frac{40}{3} = 13\,\text{min}\ 20\,\text{sec}.$$

So, the correct answer is (*d*).

EXAMPLE 178. *A radioactive element has $t_{1/2}$ of 60 minutes. The amount remaining after 3 hrs is*

(a) 17.5% *(b)* 12.5%
(c) 25% *(d)* 50% **(BHU, 1997)**

SOLUTION. $t_{1/2} = 60$ min.

$$\text{Total time} = 3\text{ hrs} \times \frac{60\text{ min}}{1\text{ hr}} = 180\text{ min}.$$

$$\therefore \quad n = \frac{\text{Total time}}{t_{1/2}} = \frac{180\text{ min}}{60\text{ min}} = 3.$$

Hence, $\quad \mathrm{N} = \mathrm{No} \times \left(\frac{1}{2}\right)^3 ; \mathrm{N} = 100 \times \left(\frac{1}{2}\right)^3$

Or $\quad \mathrm{N} = 100 \times \frac{1}{8} = 12.5\%.$

So, the correct answer is (*b*).

EXAMPLE 179. *The half-life of an isotope is 10 hrs. How much will be left after 4 hrs in one gram mole sample ?*

(a) 45.6×10^{23} atoms *(b)* 4.56×10^{23} atoms
(c) 4.56×10^{21} atoms *(d)* 4.56×10^{20} atoms

(BHU 1997)

SOLUTION. $t_{1/2} = 10$ hrs;

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\text{ hrs}} = 0.0693\text{ hr}^{-}.$$

But : $\quad t = \frac{2.303}{\lambda}\log\frac{a}{a-x}$

So, $\quad 4 = \frac{2.303}{0.0693}\log\frac{1}{1-x};$

$$\log\frac{1}{1-x} = \frac{4 \times 0.0693}{2.303} = 0.1204.$$

Taking antilogs of both sides, we get :

$$\frac{1}{1-x} = \text{antilog } 0.1204 = 1.3195.$$

Hence, $\quad 1 - x = \frac{1}{1.3195} = 0.7579\text{ g mole}$

But $\quad$ 1g mol = 6.02×10^{23} atoms

$\therefore$ 0.7579g mol = $6.02 \times 10^{23} \times 0.7579$ atoms

$= 4.56 \times 10^{23}$ atoms

So, the correct answer is (*b*).

EXAMPLE 180. *A radioactive element X emits 3α, 1β and 1γ -particles and forms $^{225}_{76}Y$. Element X is :*

(a) $^{237}_{81}X$ *(b)* $^{237}_{80}X$

(c) $^{236}_{81}X$ *(d)* $^{236}_{80}X$ **(CMEET, Bihar, 1997)**

SOLUTION. (*i*) Decrease in mass due to emission of 3α *i.e.,* 3 ^{4}He particles = 3 × 4 = 12.

$\therefore$ Mass of X = 225 + 12 = 237

Decrease in at. no. due to emission of 3α *i.e.,* 3 $_2$He particles = 3 × 2 = 6

(*ii*) Increase in at. no. due to emission of β (= $^{0}_{-1}e$) particles = 1

(*iii*) Change in mass no. and at. no. due to $^{0}_{0}\gamma$ -radiations = zero.

$\therefore$ Net decrease in at. no.

= 6 – 1 = 5

$\therefore$ At. no. of X = 76 + 5 = 81. Hence, X is $^{237}_{81}X$. So, the correct answer is (*a*).

EXAMPLE 181. *Which does not take place by α-disintegration?*

(a) $_{92}U^{238} \rightarrow {}_{90}Th^{234}$ *(b)* $_{90}Th^{232} \rightarrow {}_{88}Ra^{228}$
(c) $_{88}Ra^{226} \rightarrow {}_{86}Rn^{222}$ *(d)* $_{83}Bi^{213} \rightarrow {}_{84}Po^{213}$

(MPPMT, 1997)

SOLUTION. (*a*) $_{92}\mathrm{U}^{238} \rightarrow {}_{90}\mathrm{Th}^{234} + {}_{2}\mathrm{He}^{4}$ (possible).

(*b*) $_{90}\mathrm{Th}^{232} \rightarrow {}_{88}\mathrm{Ra}^{228} + {}_{2}\mathrm{He}^{4}$ (possible)

(*c*) $_{88}\mathrm{Ra}^{226} \rightarrow {}_{86}\mathrm{Rn}^{222} + {}_{2}\mathrm{He}^{4}$ (possible)

(*d*) $_{83}\mathrm{Bi}^{213} \rightarrow {}_{84}\mathrm{Po}^{213} + {}_{2}\mathrm{He}^{4}$ (not possible because mass no. of reactants (= 213) is not equal to that of products (= 213 + 4 = 217). So, the correct answer is (*d*). In fact (*d*) should be $_{83}\mathrm{Bi}^{213} \rightarrow {}_{84}\mathrm{Po}^{213} + {}^{0}_{-1}e$ β-particle.

EXAMPLE 182. *Which one of the following notations shows the product incorrectly.*

(a) $^{242}_{96}Cm(\alpha, 2n)\,^{242}_{97}Bk$ *(b)* $^{10}_{5}B(\alpha, n)\,^{13}_{7}N$

(c) $^{14}_{7}N(n, p)\,^{14}_{6}C$ *(d)* $^{28}_{14}Si(d, n)\,^{29}_{15}P$

(MPPET, 1998)

SOLUTION. (*a*) $^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{242}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}n$ (not balanced).

(*b*) $^{10}_{5}\mathrm{B} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{13}_{7}\mathrm{N} + {}^{1}_{0}n$ (balanced)

(*c*) $^{14}_{7}\mathrm{N} + {}^{1}_{0}n \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{H}$ (balanced)

(*d*) $^{28}_{14}\mathrm{Si} + {}^{2}_{1}\mathrm{D} \rightarrow {}^{29}_{15}\mathrm{P} + {}^{1}_{0}n$ (balanced). So, the correct answer is (*a*).

EXAMPLE 183. *Number of neutrons in a parent nucleus X, which gives $^{14}_{7}N$ after two successive β-emissions would be*

(a) 6 *(b)* 7
(c) 8 *(d)* 9 **(CBSE, 1998)**

SOLUTION.

$$^{14}_{5}\mathrm{X} \xrightarrow[-({}^{0}_{-1}e)]{-\beta\text{ or}} {}^{14}_{5+1}\mathrm{C} \textit{ i.e., } {}^{14}_{6}\mathrm{C} \xrightarrow[-({}^{0}_{-1}e)]{-\beta\text{ or}} {}^{14}_{6+1}\mathrm{N} \text{ or } {}^{14}_{7}\mathrm{N}$$

$\therefore$ No. of neutrons in $^{14}_{5}\mathrm{X} = 14 - 5 = 9$. So, the correct answer is (*d*).

EXAMPLE 184. *The activity of a radioactive nucleide X^{100} is 6.023 curie. If the disintegration constant is 3.7×10^{4} sec^{-}, the mass of X is :*

(a) 110^{-23}g *(b)* 10^{-15}g
(c) 10^{-16}g *(d)* 10^{-14}g **(EAMCET, 1998)**

SOLUTION. 1 curie = 3.7×10^{10} ds^{-}; $-\frac{d\mathrm{N}}{dt} = \mathrm{lN}$; 6.023 × 3.7×10^{10} d s^{-} = 3.7×10^{4} sec^{-} × N

$$\therefore \qquad N = \frac{6.023 \times 3.7 \times 10^{10}}{3.7 \times 10^{4}} = 6.023 \times 10^{6}$$

= no. of radioactive atoms.

$$\therefore \quad \text{Mass of X} = \frac{6.023 \times 10^{6}}{6.023 \times 10^{23}} \times 100 = 10^{-15}\text{g}.$$

So, the correct answer is (*b*).

EXAMPLE 185. *If $_{90}Th^{228}$ disintegrates to $_{83}Bi^{212}$, then the number of α and β-particles emitted is :*

(*a*) 4 and 7	(*b*) 4 and 1
(*c*) 4 only	(*d*) 7 only **(AFMC, 1998)**

SOLUTION. *Reaction* : $_{90}\text{Th}^{228} \rightarrow {}_{83}\text{Bi}^{212}$.

(*i*) no. of α-particles (^4_2He) emitted = $\dfrac{228-212}{4} = \mathbf{4}.$

(*ii*) Decrease in at. no. due to the emission of four α-particles = 2 × 4 = 8.

Actual decrease in at. no. = 90 – 83 = 7. Hence β-particles emitted = 8 – 7 = **1**.

So, the correct answer is (*b*).

EXAMPLE 186. *Loss of a β-particle from neutron is equivalent to*

(*a*) *Increase of one proton only*

(*b*) *Decrease of one neutron only*

(*c*) *Both (a) and (b)*	(*d*) *None of these* **(IIT, 1998)**

SOLUTION. Reaction is : $^1_0n \rightarrow {}^1_1p + {}^{\;\,0}_{-1}e$ *i.e.*, β-particle. So, the correct answer is (*c*).

EXAMPLE 187. *The number of neutrons accompanying the formation of $^{139}_{54}Xe$ and $^{94}_{38}Sr$ by the absorption of slow neutron by $^{235}_{92}U$ followed by nuclear fission is :*

(*a*) 0	(*b*) 2
(*c*) 1	(*d*) 3 **(IIT, 1999)**

SOLUTION. *Reaction is* : $^{235}_{92}\text{U} + {}^1_0n \rightarrow {}^{139}_{54}\text{Xe} + {}^{94}_{38}\text{Sr} + 3\,{}^1_0n$

∴ no. of neutrons = 3. So, the correct answer is (*d*).

EXAMPLE 188. *If it a assumed that $^{235}_{92}U$ decays only by emitting α and β-particles, the possible product of the decay is :*

(*a*) $^{225}_{89}Ac$	(*b*) $^{227}_{89}Ac$
(*c*) $^{230}_{89}Ac$	(*d*) $^{231}_{89}Ac$

(West Bengal, JEE, 2009)

SOLUTION. We know that the number of α and β-particles, emitted should be a whole number. So:

(*a*) $^{235}_{92}\text{U} = {}^{225}_{89}\text{Ac} + x\,{}^4_2\text{He} + y\,{}^{\;\,0}_{-1}e$

∴ 235 = 225 + 4*x* + 0; 4*x* = 10/4 = 2.5.

It is not a whole number.

(*b*) $^{235}_{92}\text{U} = {}^{227}_{89}\text{Ac} + x\,{}^4_2\text{He} + y\,{}^{\;\,0}_{-1}e$

∴ 235 = 227 + 4*x* + 0; 4*x* = 8/4 = 2.

It is a whole number and is possible.

Also, 92 = 89 + 2*x* – *y*; 92 = 89 + (2 × 2) – *y*;

y = 93 – 92 = 1.

It is a whole number and the number of β-particles is possible. So, the correct answer is (*b*).

> **Note.** Number of α-particles (n_α) and β-particles (n_β) can be calculated by using the relations, n_α= (change in mass no.)/4 and n_β = (change in at. no.) - 2n_α

EXAMPLE 189. *Which of the following has maximum N/p ratio ?*

(*a*) ^{16}Ne	(*b*) ^{16}O
(*c*) ^{16}F	(*d*) ^{16}N **(DPMT, 2000)**

SOLUTION. Writing at. no. (or protons) of each species, we have :

$^{16}_{10}\text{Ne}, {}^{16}_{8}\text{O}, {}^{16}_{9}\text{F}$ and $^{16}_{7}\text{N}$. Thus, no. of neutrons in :

(*i*) $^{16}_{10}\text{N} = 16 - 10 = 6$, (*ii*) $^{16}_{8}\text{O} = 16 - 8 = 8$,

(*iii*) $^{16}_{9}\text{F} = 16 - 9 = 7$, (*iv*) $^{16}_{7}\text{N} = 16 - 7 = 9$.

Hence, N/p ratio in (*i*) $^{16}_{10}\text{N} = \dfrac{6}{10} = 0.6$, (*ii*) $^{16}_{8}\text{O} = \dfrac{8}{8} = 1$, (*iii*) $^{16}_{9}\text{F} = \dfrac{7}{9} = 0.77$ and (*iv*) $^{16}_{7}\text{N} = \dfrac{9}{7} = 1.28$. So, the correct answer is (*d*).

EXAMPLE 190. *Decay of $^{235}_{92}U$ is .... order reaction*

(*a*) *zero*	(*b*) *first*
(*c*) *second*	(*d*) *hird* **(OJEE, 2004)**

SOLUTION. All radioactive decay reactions are first order reactions. So, the correct answer is (*b*).

EXAMPLE 191. *An artificial radioactive isotope gave $^{14}_{7}N$ after two successive β-particle emissions. The number of neutrons in the present nucleus must be*

(*a*) 9	(*b*) 14
(*c*) 5	(*d*) 7 **(Karnataka CET, 2004)**

SOLUTION. Increase in at. no. by the emission of 2β ($^{\;\,0}_{-1}e$) particles = 2 × 1 = 2.

Hence, the at. no. of artificial radioactive isotope = 7 – 2 = 5.

So, the nucleide will be $^{14}_{5}\text{B}$. Hence no. of neutrons = 14 – 5 = 9. So, the correct answer is (*a*).

EXAMPLE 192. *A radioactive atom ^x_yM emits two alpha particles successively. The number of neutrons in the nuclous of the product will be :*

(*a*) *x* – 4 – *y*	(*b*) *x* – *y* – 5
(*c*) *x* – *y* – 3	(*d*) *x* – *y* – 6 **(WB-JEE, 2011)**

SOLUTION. Using group displacement law, we have :

$$^{x}_{y}\text{M} \xrightarrow{-\,^4_2\text{He}} {}^{x-4}_{y-2}\,\text{N} \xrightarrow{-\,^4_2\text{He}} {}^{x-4-4}_{y-2-2}\;\text{O} \xrightarrow{^{\;\,0}_{-1}e} {}_{y-2-2+1\,=\,y-3}{}^{x-8}\ \text{P}$$

∴ At. no. of Product = *y* – 3;

mass no. of product = *x* – 8

∴ No. of neutrons = Mass no. – At. no.

= (*x* – 8) – (*y* – 3) = *x* – *y* – 5.

So, the correct answer is (*b*)

EXAMPLE 193. *If the mass defect of ${}^{9}_{4}X$ is 0.09 a.m.u., then binding energy per nucleon is (1 a.m.u. = 931.5 MeV) :*

(a) 9.315 MeV *(b) 931.5 MeV*

(c) 83.0 MeV *(d) 8.38 MeV* **(JKCET, 2004)**

SOLUTION. We know that : Binding energy per nucleon

$$= \frac{\text{Mass defect}}{\text{mass no.}} = \frac{0.09\,\text{a.m.u.}}{9}$$

$$= \frac{0.09 \times 931.5\,\text{MeV}}{9}$$

$$= 9.315\text{ MeV}$$

So, the correct answer is (*a*).

EXAMPLE 194. *Consider the following nuclear reactions :*

$${}^{238}_{92}M \rightarrow {}^{x}_{y}N + 2\,{}^{4}_{2}He\,;\; {}^{x}_{y}N \rightarrow {}^{A}_{B}L + 2\beta^{+}$$

The number of neutrons in the element L is :

(a) 142 *(b) 144*

(c) 140 *(d) 146* **(AIEEE, 2004)**

SOLUTION. ${}^{238}_{92}\text{M} \rightarrow {}^{\text{x}}_{\text{y}}\text{N} + 2\,{}^{4}_{2}\text{He}$.

(*i*) Sum of mass no. of reactants = Sum of mass no. of products

$$238 = X + (2 \times 4)\;;\; X = 230$$

(*ii*) Sum of at. no. of reactants =Sum of at. no. of products

$$92 = y + (2 \times 2);\, y = 92 - 4 = 88.$$

Hence, ${}^{\text{x}}_{\text{y}}\text{N}$ is ${}^{230}_{88}\text{N}$.

Given : ${}^{230}_{88}\text{N} \rightarrow {}^{\text{A}}_{\text{B}}\text{L} + 2\,{}^{0}_{+1}\text{e}$ *i.e.*, β^{+}

$\therefore$ 230 = A + (2 × 0) ; A = 230.

88 = B + (2 × +1); B = 88 – 2 = 86.

So, ${}^{\text{A}}_{\text{B}}\text{L} = {}^{230}_{86}\text{L}$.

It contains neutrons

= 230 – 86 = 144.

So, the correct answer is (*b*).

EXAMPLE 195. *If n_t number of radioatoms are present at time, t, the following expression will be constant.*

(a) n_t/t *(b) $\ln n_t/t$*

(c) $d\ln n_t/dt$ *(b) $t.\, n_t$.* **(West Bengal JEE, 2009)**

SOLUTION. Since $-\dfrac{dn_t}{dt} = \lambda n_t$, so $\lambda = -\dfrac{1}{n_t}\cdot\dfrac{dn_t}{dt}$

or $\dfrac{d}{dt}(\ln n_t) = -\lambda$, a constant. So, the correct answer is (*c*).

EXAMPLE 196. *A first order reaction is 10% complete in 20 minutes. The time taken for 19% completion is :*

(a) 30 min *(b) 40 min*

(c) 50 min *(d) 38 min*

(e) 45 min **(Kerala, PET, 2005)**

SOLUTION. For first order reaction,

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

(*i*) ***First case.*** t = 20 min.

$$\therefore \quad k = \frac{2.303}{20}\log\frac{90}{100} \qquad [\because 100 - 10 = 90]$$

(*ii*) ***Second case.*** t = ?

$$\therefore \quad k = \frac{2.303}{t}\log\frac{81}{100} \qquad [\because 100 - 19 = 81]$$

$$\therefore \frac{2.303}{20}\log\frac{90}{100} = \frac{2.303}{t}\log\frac{81}{100}$$

$$\text{or} \quad t = \frac{\dfrac{2.303 \times 20}{2.303}\left(\log\dfrac{81}{100}\right)}{\log\dfrac{90}{100}}$$

$$= \frac{20[\log 81 - \log 100]}{\log 90 - \log 100}$$

$$= \frac{20(1.908 - 2)}{1.954 - 2} = \frac{20(-0.092)}{-0.046} = \mathbf{40\ min.}$$

So, the correct answer is (*b*).

EXAMPLE 197. *The atomic radius and nuclear radii are of the order of 10^{-8} cm and 10^{-13} cm respectively. The fraction of atomic volume occupied by the nucleus, assuming that atom as well as nucleus are spherical in nature is :*

(a) 10^{-12} *(b) 10^{15}*

(c) 10^{-15} *(d) 10^{-13}*

SOLUTION. Let r = radius of sphere. So, volume of sphere $= \dfrac{4}{3}\pi r^3$

(*i*) Volume of atom

$$= \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10^{-8}\text{cm})^3$$

$$= 4.19 \times 10^{-24}\text{ cm}^3.$$

(*ii*) Volume of nucleus

$$= \frac{4}{3}\pi\, r^3 = \frac{4}{3} \times \frac{22}{7} \times (10^{-13}\text{cm})^3$$

$$= 4.19 \times 10^{-39}\text{ cm}^3.$$

(*iii*) Fraction of volume occupied by nucleus

$$= \frac{4.19 \times 10^{-39}\text{cm}^3}{4.19 \times 10^{-24}\text{cm}^3} = \mathbf{10^{-15}} \qquad \textbf{Ans.}$$

So the correct answer is (*c*).

EXAMPLE 198. *A photon of hard gamma radiation knocks a proton out of ${}^{24}_{12}Mg$ nucleus to form :*

(a) the isotope of parent nucleus

(b) the isobar of parent nucleus

(c) the nucleide ${}^{23}_{11}Na$ *(d) the isobar of ${}^{23}_{11}Na$*

(AIEEE, 2005)

SOLUTION. *Reaction :* ${}^{24}_{12}\text{Mg} + {}^{0}_{0}\gamma \rightarrow {}^{1}_{1}p + {}^{23}_{11}\text{Na}$. Since ${}^{24}_{12}\text{Mg}$ and ${}^{23}_{11}\text{Na}$ do not have same at. no., these are not isotopes.

These also do not have same mass number. So, these are not isobars. Hence, $^{23}_{11}\text{Na}$ is nucleide. So, the correct answer is (*c*).

EXAMPLE 199. *The half life of a first order reaction having rate constant* $k = 1.7 \times 10^{-5}s^{-}$ *is :*

(*a*) 12.1 h (*b*) 9.7 h
(*c*) 11.3 h (*d*) 1.8 h

(CBSE, 1999, IMS-BHU, 2005)

SOLUTION. Rate constant $k = 1.7 \times 10^{-5}s^{-}$. Half life $t_{1/2}$ is given as :

$$t_{1/2} = \frac{0.693}{k}; t_{1/2} = \frac{0.693}{1.7\times10^{-5}\text{s}^{-}}\times\frac{1\text{hr}}{3600\text{s}} = \mathbf{11.3\,h}$$

So, the correct answer is (*c*).

EXAMPLE 200. *When* $^{27}_{13}Al$ *is bombarded with α-particle, a radioactive isotope of phosphorus* $^{30}_{15}P$ *is formed. Which particle is emitted along with* $^{30}_{15}P$*?*

(*a*) Deutron (*b*) Proton
(*c*) electron (*d*) neutron **(Gujrat, 2006)**

SOLUTION. $^{27}_{13}\text{Al} + \underset{(\alpha\text{-particle})}{^4_2\text{He}} \rightarrow {}^{30}_{15}\text{P} + \underset{\text{Neutron}}{^1_0 n}$

So, the correct answer is (*d*).

EXAMPLE 201. *In a transformation of* $^{238}_{92}U$ *to* $^{234}_{92}U$*, if one emission is an α-particle, what should be the other emission(s)?*

(*a*) two beta (*b*) two β and one β^+
(*c*) one β^- and one γ (*d*) one β^+ and one β^-

(AIEEE, 2006)

SOLUTION. $^{238}_{92}\text{U} \rightarrow {}^{234}_{92}\text{U} + {}^4_2\text{He}$

In the above reaction, though atomic weights are balanced but the sum of atomic numbers are not balance. So, we have

$^{238}_{92}\text{U} \rightarrow {}^{234}_{92}\text{U} + {}^4_2\text{He} + 2\,{}^0_{-1}\beta$. So, the correct answer is (*a*).

EXAMPLE 202. *The net nuclear reaction of a radioactive decay series is written as :*

$$^{238}_{92}U \longrightarrow {}^{206}_{82}Pb + 8\,{}^4_2He + 6\,{}^0_{-1}e$$

Write three points of information that you get from the above equation. **(CBSE, 2007)**

SOLUTION. The three points of information from $^{238}_{92}\text{U} \longrightarrow {}^{206}_{82}\text{Pb} + 8\,{}^4_2\text{He} + 6\,{}^0_{-1}e$ are :

(*i*) It is a uranium decay series.
(*ii*) The stable isotope formed is $^{206}_{82}\text{Pb}$.
(*iii*) In this decay reaction 8 alpha particles and 6 beta particles are liberated.

EXAMPLE 203. *A positron is emitted from* $^{23}_{11}Na$*. The ratio of the atomic mass and atomic number of the resulting nucleide is*

(*a*) $\frac{22}{10}$ (*b*) $\frac{22}{10}$
(*c*) $\frac{23}{10}$ (*d*) $\frac{23}{12}$ **(IIT-JEE, 2007)**

SOLUTION. Reaction: $^{23}_{11}\text{Na} \longrightarrow {}^0_{+1}\beta + {}^{23}_{10}\text{A}$

$$\therefore \quad \frac{\text{Atomic mass of A}}{\text{at. no. of A}} = \frac{23}{10}.$$

So, the correct answer is (*c*).

Type 1. To find number of half-lives (= *n*), use:

$$\left(\frac{1}{2}\right)^n = \frac{\%\text{ age of substance left behind}}{100}$$

or $\left(\frac{1}{2}\right)^n$ = Activity of substance left behind

or $\left(\frac{1}{2}\right)^n$ = Amount of substance left behind after the decay or disintegration

2. Time of disintegration = $t_{1/2}$ × number of half-lives (= *n*)

3. Decay constant, $\lambda = 0.693/t_{1/2}$

EXAMPLE 204. *It is observed that only 6.25% of a given radioactive sample is left undecayed after a period of 16 days. What is the decay constant of this sample in day*$^{-}$*?*

SOLUTION. (*i*) % age of sample left behind = 6.25. We know that:

$$\left(\frac{1}{2}\right)^n = \frac{\%\text{ age of sample left behind}}{100} = \frac{6.25}{100} = \frac{1}{16} = \left(\frac{1}{2}\right)^4$$

∴ number of half-lives (= *n*) = 4

(*ii*) Half-life, $t_{1/2}$

$$= \frac{\text{Time of disintegration}}{\text{number of half-lives}} = \frac{16\text{ days}}{4} = 4\text{ days.}$$ **Ans.**

(*iii*) Decay constant, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{4\text{ days}} = 0.173\text{ day}$

EXAMPLE 205. *The half-life of a radioactive substance is 20 s. Calculate the time taken for the sample to decay 7/8 of the initial value.*

SOLUTION. $t_{1/2}$ = 20 *s*; since the sample has decayed by 7/8, so:

the amount of sample left behind = 1 – 7/8 = 1/8

$$\therefore \left(\frac{1}{2}\right)^n = \text{Amount of sample left behind} = \frac{1}{8} = \left(\frac{1}{2}\right)^3$$

∴ *n* = 3

Hence, time taken to decay = $t_{1/2}$ × number of half-lives = 20 s × 3 = 60 s. **Ans.**

EXAMPLE 206. *Find the half-life of a radioactive material if its activity drops to 1/16th of its original value in 30 years.*

SOLUTION. $t_{1/2}$ = ? ; Activity left behind = 1/16

Time of disintegration = 30 years. But :

$$\left(\frac{1}{2}\right)^n = \frac{1}{16} = \left(\frac{1}{2}\right)^4 \text{ ; so } n = 4$$

$$t_{1/2} = \frac{\text{Time of disintegration}}{\text{number of half-lives}} = \frac{50\text{ years}}{4} = 12.5\text{ years.}$$

PROBLEMS FOR PRACTICE

1. Fill in the blanks for the following reactions.

(*i*) $^{238}_{92}\mathbf{U} \rightarrow {}^{234}_{90}\mathbf{Th} + ?$, (*ii*) $^{234}_{90}\mathbf{Th} \rightarrow {}^{234}_{91}\mathbf{Pa} + ?$,

(*iii*) $^{27}_{13}\mathbf{Al}(\mathbf{D}, ?)^{25}_{12}\mathbf{Mg}$ **[Ans.** (*i*) $^{4}_{2}\mathbf{He}$, (*ii*) $^{0}_{-1}e$, (*iii*) $^{4}_{2}\mathbf{He}$

2. Fill in the blanks in the following : (*i*) neutron → proton + ?, (*ii*) neutron + ? → proton
(Ans. (*i*) π^-, (*ii*) π^+**)**

3. $^{133}_{56}\text{Ba}$ (group 2) undergoes K-capture. To which group the new element would belong ?
(Ans. Group 1**)**

4. Calculate the packing fraction, mass defect and energy released in the formation of $^{40}_{18}\text{Ar}$. Isotopic mass of proton = 1.007825, neutron = 1.008665 and Ar = 39.962384 amu.

(Ans. Packing fraction = – 9.4025; Mass defect = 0.369096 amu, Energy released = 343.81 MeV**)**

5. The amount of C-14 isotope in a piece of wood is found to be one sixth of its amount present in a fresh piece of wood. Calculate the age of wood. Half-life period of ^{14}C is 5770 years. **(Ans.** 14922 years**)**

6. A piece of wood was found to have C^{14}/C^{12} ratio 0.7 times that in a living plant. How long ago the plant was cut ? (Half-life of ^{14}C = 5770 years).
(Ans. 2970 years**)**

7. A piece of wood shows a ^{14}C activity which is 70% of the activity found in a fresh wood today. Calculate the age of the wood. ($t_{1/2}$ for $^{14}_{6}\text{C}$ is 5770 years).
(PSEB, 2000) (Ans. 2972 yrs**)**

8. Calculate the mass number of an element of 4*n* + 3 series having *n* = 58. **(Ans.** 235 a.m.u.**)**

9. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant (in year^{-1}) for the decay ? What fraction would remain after 11540 years ? **(I.I.T., 1984) (Ans.** 25%**)**

10. It is known that 1g of ^{226}Ra emits 11.6×10^{17} α-particles per year. Given the half-life of ^{226}Ra be 1600 years. Compute the value of Avogadro's number.
(M.L.N.R., 1983) (Ans. 6.052×10^{23}**)**

11. The activity of a radio isotope falls to 12.5% in 90 days. Compute the half-life and the decay constant of the radio-isotope. **(M.L.N.R., 1986)**
(Ans. 30 days**)**

12. Number of β-particles emitted during the transformation of $^{x}_{y}\text{A}$ to $^{m}_{n}\text{B}$

(*a*) $x - m/4$ (*b*) $n + (x - m/2) + y$

(*c*) $n + (x + m/2) - y$ (*d*) $2y - n + x - m$

(AMU, MEd, 2010). Ans (*c*)

13. The number of neutrons emitted when $^{235}_{92}\text{U}$ undergoes controlled nuclear fission to $^{142}_{54}\text{Xe}$ and $^{90}_{38}\text{Sr}$ is : **(Ans. 3) (IIT-JEE, 2010)**

14. Calculate the rate of decay of 1g radium (at. mass = 226) having $t_{1/2}$ = 1600 years in rutherford.
(Ans; 3.7 × 10^4 rutherford).

15. To which radioactive series, $^{227}_{89}\text{Ac}$ appears during disintegration? **(Ans; 4*n* + 3 series).**

16. A positron is emitted from $^{39}_{19}\text{K}$. The ratio of the atomic mass and atomic number of resulting nucleide is :

(*a*) 4 (*b*) 3.1

(*c*) 2.16 (*d*) 1.12 **[Ans. (c)].**

17. What is the half-life of a radioactive substance if 93.75% of any given amount of the substance disintegrates in 30 minutes.

(*a*) 7 min. 30 second (*b*) 6 min

(*c*) 12 min (*d*) 15 min **[Ans. (*a*)].**

18. The radius of nucleus of Ar-40 is :

(*a*) 2×10^{9} m (*b*) 5.1×10^{-15} m

(*c*) 4.4×10^{-9} (*d*) 3.5×10^{-10} **[Ans. (b)].**

19. If the packing mass of S-35 is 34.96903, the value of packing fraction will be :

(*a*) –1.1 (*b*) –2.3

(*c*) –7.234 (*d*) –8.848 **[Ans. (d)].**

20. If half-life of 15g of a radioactive isotope is 25 days, calculate the half-life of 1g sample. **(Ans. 25 days)**

21. Calculate the amount of radioactivity that is left behind when two millicurie of radioactive element of half-life 6 days is stored for 18 days.
(Ans. 1/4 millicurie).

22
CHAPTER

Volumetric Analysis

22.1 VOLUMETRIC ANALYSIS

The analysis which involves the exact measurement of volumes is called volumetric analysis.

Standard Solution. It is a solution of known strength. The concentration of a substance in a given volume of its solution is called its strength.

Standard substances (**Primary standards**). All such substances which are available in pure state and whose standard solution can be prepared by direct weighing are called primary standards. For example, anhydrous sodium carbonate, oxalic acid, potassium dichromate, ferrous ammonium sulphate (Mohr's salt) etc. Such substances are highly pure, stable in air, have high mol. wt. and are readily soluble in water.

Secondary standards. All such substances which do not satisfy the conditions of primary standard and whose standard solutions cannot be prepared by direct weighing are called secondary standards. For example, potassium permanganate, HCl, H_2SO_4, sodium thiosulphate, iodine, sodium hydroxide etc.

Strength of a Solution. It is expressed in gL^-, normality (*i.e.*, gram equivalent per litre) or molarity (*i.e.*, gram mol L^-).

A normal solution (1N) of a substance is that whose 1L solution contains gram equivalent of that substance. A molar solution (1M) of a substance is that whose 1L solution contains gram molecular weight of a substance.

Strength in gL^- = Normality × Eq. wt.

22.2 NORMALITY EQUATION OR LAW OF NORMALITIES

This law is based on the law of equivalents. **According to this law :**

"*Equal volumes of equinormal solutions will completely react with each other*". The substances react in the ratio of their equivalent weights. Thus according to this law, 50 mL of 1N Na_2CO_3 solution will be equivalent to 50 mL of 1N HCl solution. Similarly 50 mL of 1N Na_2CO_3 solution will be equivalent to 100 mL of N/2 HCl solution. It can also be expressed in terms of the following **normality equation** :

$$N_1V_1\text{(one substance)} = N_2V_2\text{ (another substance)}$$

In case of acid-base titration :

$$\mathbf{N_1V_1\text{ (acid)} = N_2V_2\text{ (base)}}$$

This equation is based on the fact that the number of g-equivalents of a given substance contained in a given volume of the given solution is equal to the same number of g. equivalents of the same or different substances contained in the corresponding volume of that solution. Knowing any three of these factors (*i.e.*, N_1, V_1, N_2, V_2) in the normality equation, the fourth factor can be calculated. Here N_1 and V_1 represent the normality and volume of one substance while N_2 and V_2 represent the normality and volume of another substance.

22.3 MOLARITY EQUATION.

A molar solution (1M) of a substance is that which contains one gram molecular weight (or one g. mol) of it per litre of the solution.

For calculations in terms of molarity. Consider the following :

1. **Redox (or oxidation-reduction) reactions.** Consider the following redox reaction between $KMnO_4$ (oxidant) and $H_2C_2O_4$ (reductant)

$$\underset{\text{2 mol}}{2KMnO_4} + 3H_2SO_4 + \underset{\text{5 mol}}{5H_2C_2O_4} \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

According to balanced chemical equation, 2 mol of $KMnO_4$ react with 5 mol of $H_2C_2O_4$ (oxalic acid)

Hence :

$$\frac{(M_1V_1)/1000}{(M_2V_2)/1000} = \frac{2}{5} \text{ or } \frac{M_1V_1}{2} = \frac{M_2V_2}{5}$$

In general. $$\frac{(M_1V_1)\text{ solution A}}{(M_2V_2)\text{ solution B}} = \frac{\text{no. of mol of A in balanced equation}}{\text{no. of mol of B in balanced equation}}$$

Strength = Molarity of solution × mol. wt. (or molar mass) of solute.

Note: Normality = Molarity × (Valence factor)

2. **Acid - Base reactions.** Consider the following reaction

$$\underset{2\text{ mol}}{2NaOH} + \underset{1\text{ mol}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O.$$

$$\text{Here, } \frac{M_1V_1(\text{NaOH})}{M_2V_2(H_2SO_4)} = \frac{\text{no. of mol of NaOH in the balanced equation}}{\text{no. of mol of } H_2SO_4 \text{ in the balanced equation}}$$

$$i.e., \quad \frac{M_1V_1(\text{NaOH})}{M_2V_2(H_2SO_4)} = \frac{2}{1}$$

22.4 ACID-BASE TITRATIONS-VISUAL METHOD (SINGLE TITRATION)

Visual method. In this method, different indicators are used to locate the titration end point. The indicators are organic compounds which have different colours at different pH ranges as shown in the following table 22.1.

Table 22.1

Indicator	*pH range and colours*	*Solution of indicator*
Methyl orange	3.0 (Red) – 4.4 (yellow)	0.1% in water
Methyl red	4.4 (red) – 6.2 (yellow)	0.2% in 60% alcohol
Litmus	5.0 (red) – 8.0 (blue)	2.5% in water, filtered on standing and made acidic with 1–2 drops of dil. HNO_3
Phenolphthalein	8.2 (colourless) - 10.0 (red)	0.1% in 50% alcohol

Note. Use methyl orange indicator in Na_2CO_3 or $NaHCO_3$ titrations and phenolphthalein indicator in titrations involving NaOH or KOH alkalies.

Following examples will help to know the use of above indicators in acid-base titrations.

1. **Single titrations.**

EXAMPLE 1. *Prepare exact 100 ml of N/10 HCl solution from the given concentrated acid. Provided N/10 Na_2CO_3 solution.*

SOLUTION. HCl is not a primary standard acid. Thus, following procedure is used to prepare exact N/10 HCl.

(1) *To prepare dilute HCl solution.* Take about 3 ml of concentrated HCl acid in a 250 ml measuring flask with the help of burette. Add distilled water, till exact 250 ml solution is obtained. Shake well.

(2) *To find the normality of above dilute HCl.* Take 20 ml of N/10 Na_2CO_3 solution in a titration flask, add 2-3 drops of methyl orange indicator. Titrate with dilute acid prepared above till yellow to pink colour is obtained. This is the end point. Let normality of dilute acid is N_1.

(3) To prepare, exact 100 ml of N/10 HCl. Using following normality equation we have

Dilute acid prepared *N/10 HCl to be prepared*

$$N_3V_3 = N_4V_4\,;$$

$$N_3 \times V_3 = \frac{1}{10} \times 100\,; \qquad \therefore \quad V_3 = \frac{10}{N_3} \text{ ml} = x \text{ ml (say)}$$

Take x ml of dilute acid prepared in 100 ml measuring flask, add more distilled water and make up the solution to exact 100 ml. It is exact N/10 HCl.

Note. For diluting conc. H_2SO_4, add conc. H_2SO_4 to excess water and not water to conc. H_2SO_4 because of the exothermic nature of the reaction.

EXAMPLE 2. *Prepare exact 100 mL of N/10 NaOH solution. Provided N/10 oxalic acid.*

SOLUTION. NaOH is not a primary standard substance. Thus, following procedure is used to prepare exact N/10 NaOH solution.

(1) **To prepare approximately N/10 NaOH SOLUTION. Eq. wt. of NaOH is 40.** In order to prepare approximately, N/10 NaOH solution, weigh $\frac{40 \times 250}{10 \times 1{,}000}$ *i.e.,* one gram of NaOH, dissolve in distilled water taken in a 250 ml flask, add more water to get 250 ml solution. Take 20 ml of this solution in a titration flask, add 1-2 drops of phenolphthalein as indicator and titrate with $N/10$ oxalic acid till pink to colourless solution is obtained which is the end point. Using normality equation ($N_1V_1 = N_2V_2$), find the normality (N_1) of NaOH.

(2) **To prepare exact 100 ml of N/10 NaOH SOLUTION.** Using normality equation, we have:

N/10 NaOH to be prepared NaOH of N_1 normality

$$N_3V_3 = N_1V_4\,;$$

$$\frac{1}{10} \times 100 = N_1 \times V_4\,;$$

$$\therefore \qquad V_4 = \frac{10}{N_1} \text{ml} = \boldsymbol{x} \textbf{ ml} \text{ (say)}$$

Take x ml of NaOH of N_1 normality in a 100 ml measuring flask, add distilled water and make up the solution to exact 100 ml. It is exact N/10 NaOH solution.

EXAMPLE 3. *Find the percentage purity of sodium carbonate in soda-ash, 2 g of which have been dissolved per 250 mL of the given solution. Provided N/10 H_2SO_4.*

SOLUTION.

250 ml solution contain soda-ash = 2 g

$$1{,}000 \text{ ml solution contain soda-ash} = \frac{2}{250} \times 1{,}000 = \mathbf{8\ g}$$

$$\therefore \qquad \text{Strength of } Na_2CO_3 = 8\ (gL^{-})$$

(2) Strength of pure Na_2CO_3 = Normality × Eq. wt. of $Na_2CO_3 = N_1 \times 53\ (gL^{-})$

(3) % age purity of Na_2CO_3

$$= \frac{53\ N_1}{8} \times 100 = x \text{ (say)}$$

EXAMPLE 4. *Determine the number of molecules (x) of crystallisation in $Na_2CO_3 . xH_2O$, 8 gram of which have been dissolved per litre of the given solution. Provided $N/10\ H_2SO_4$.*

SOLUTION. (1) Calculate normality (N_1) of Na_2CO_3 solution with the help of normality equation ($N_1V_1 = N_2V_2$)

(2) Eq. wt. of $Na_2CO_3xH_2O = 8/N_1 = a$ (say)

(3) Mol. wt. of $Na_2CO_3xH_2O$ = Eq. wt. × acidity of $Na_2CO_3xH_2O = a \times 2 = 2a$

(4) Mol. wt. of anhydrous $Na_2CO_3 = (2 \times 23) + 12 + (3 \times 16) = 106$

(5) Number of water molecules

$$(x) = \frac{\begin{array}{c}\text{Mol. wt. of}\\ Na_2CO_3 . xH_2O\end{array} (-) \begin{array}{c}\text{Mol. wt. of}\\ Na_2CO_3\end{array}}{18}$$

$$= \frac{2a - 106}{18} = \boldsymbol{b}\ \textbf{(say)}$$

EXAMPLE 5. *You are provided with a solution of sodium carbonate and potassium carbonate, 6.0 g of which have been dissolved per litre of the given solution. Calculate their percentage composition. Provided N/10 HCl.*

SOLUTION. (1) Using normality equation, ($N_1V_1 = N_2V_2$), let total normality of mixture is N_1.

(2) To find weight of Na_2CO_3 and K_2CO_3. Let Strength of $Na_2CO_3 = x$ (gL^-).

∴ Strength of $K_2CO_3 = 6 - x$ (gL^-)

Eq. wt. of $Na_2CO_3 = 53$; Eq. wt. of $K_2CO_3 = 69$

$$\therefore \text{Normality of } Na_2CO_3 = \frac{\text{Strength}}{\text{Eq. Wt.}} = \frac{x}{53}; \text{Normality of } K_2CO_3 = \frac{6-x}{69}$$

$$\therefore \quad \frac{x}{53} + \frac{6-x}{69} = N_1 \text{ (already calculated). From}$$

this equation, find x.

(3) Percentage composition of

$$Na_2CO_3 = \frac{x \times 100}{6} = a \text{ (say) ; Percentage}$$

composition of $K_2CO_3 = 100 - a = b$ (say).

EXAMPLE 6. *5.3 g of carbonate of a monovalent metal are dissolved per litre of a given solution. Determine volumetrically the atomic weight of the metal. Given $N/10\ H_2SO_4$.*

SOLUTION. *Reaction :*

$$M_2CO_3 + H_2SO_4 \longrightarrow M_2SO_4 + CO_2 + H_2O$$

Using normality equation ($N_1V_1 = N_2V_2$), find the normality (N_1) of the carbonate solution.

Eq. wt. of metal carbonate
= Strength/Normality ;
= $5.3/N_1 = x$ (say)

∴ Mol. wt. of M_2CO_3
= Eq. wt. × acidity of
M_2CO_3 ; $= x \times 2 = 2x$

If a = at. wt. of M, then

$a + 12 + (3 \times 16) = 2x$;

$$\therefore \quad a = \frac{2x - 60}{2}$$

22.5 DOUBLE TITRATIONS IN ACID-BASE REACTIONS

Such titrations are based on the selective use of indicators. The indicator phenolphthalein is affected by CO_2 while methyl orange is not. So, in order to determine the percentage composition of a mixture of NaOH and Na_2CO_3 or mixture of Na_2CO_3 and $NaHCO_3$, *firstly methyl orange is used as indicator.* This leads to the complete neutralisation of NaOH + Na_2CO_3 or Na_2CO_3 + $NaHCO_3$ respectively with standard acids.

$$NaOH + HCl \rightarrow NaCl + H_2O \ ; \ Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

In the second titration, phenolphthalein indicator is used which leads to the complete neutralisation of NaOH and half neutralisation of Na_2CO_3 with standard acid.

$$NaOH + HCl \longrightarrow NaCl + H_2O \ ; \ Na_2CO_3 + HCl \longrightarrow NaHCO_3 + HCl.$$

A similar method is used to analyse a mixture of (*i*) NaOH + K_2CO_3 (*ii*) KOH + Na_2CO_3 (*iii*) KOH + K_2CO_3 (*iv*) $KHCO_3$ + Na_2CO_3. (*v*) $KHCO_3$ + K_2CO_3 (*iv*) K_2CO_3 + $NaHCO_3$

EXAMPLE 7. *Determine the percentage composition of a mixture of sodium hydroxide and sodium carbonate in a solution. Provided 0.1 N HCl. Also 20 mL of given solution require 18.10 mL of acid (methyl orange indicator) and 11.80 mL of acid (phenolphthalein indicator used) for neutralisation.*

SOLUTION. First titration (methyl orange indicator). 20 mL of mixture solution ≡ 18.10 mL of 0.1 N HCl used to neutralise total NaOH and Na_2CO_3.

Second titration (phenolphthalein indicator). 20 mL of mixture solution ≡ 11.80 mL of 0.1 N HCl used to neutralise total NaOH and half of Na_2CO_3.

∴ Vol. of 0.1 N HCl used to neutralise Na_2CO_3 only = 2 (18.10 – 11.80) = 12.60 mL

Vol. of 0.1 N HCl used to neutralise NaOH = 18.10 – 12.60 = 5.5 mL

(*a*) To find strength of Na_2CO_3 (eq. wt. 53)

(*b*) To find strength of NaOH (eq. wt. 40)

Na_2CO_3 HCl	NaOH HCl
$N_1V_1 = N_2V_2$	$N_3V_3 = N_4V_4$
$N_1 \times 20.0 = 0.1 \times 12.6$,	$N_3 \times 20 = 0.1 \times 5.5$;
$\therefore N_1 = (0.1 \times 12.6)/20 = \frac{126}{2000}$	$\therefore N_3 = 55/2000$
Strength of $Na_2CO_3 = N_1 \times$ Eq. wt. = $(126 \times 53)/2000 = 3.339\ gL^-$	Strength of NaOH = $N_3 \times$ Eq. wt. = $(55 \times 40)/2000 = 1.1\ gL^-$
Total amount of Na_2CO_3 and NaOH = 3.339 + 1.1 = 4.439 g.	

∴ % age of Na_2CO_3 = (3.339 × 100)/4.439 = **75.22%**; % age of NaOH = 100 – 75.22 = **24.78%**

EXAMPLE 8. *Determine the percentage composition of sodium carbonate and sodium bicarbonate in a solution. Provided 0.095 N HCl. Also, 20 mL of the given solution require 21.30 mL of acid (methyl orange indicator) and 7.5 mL of acid (phenolphthalein indicator)* for *neutralisation.*

SOLUTION. *First titration (methyl orange indicator).* 20 mL of mixture solution ≡ 21.30 mL of 0.095 N HCl used to neutralise total Na_2CO_3 and $NaHCO_3$.

Second titration (phenolphthalein indicator). 20 mL of mixture solution ≡ 7.5 mL of 0.095 N HCl to neutralise half of Na_2CO_3

∴ Volume of 0.095 N HCl used for complete neutralisation of $Na_2CO_3 = 2 \times 7.5 = 15.0$ mL

Volume of 0.095 N HCl used to neutralise $NaHCO_3$ = 21.30 – 15.0 = 6.30 mL

(*a*) To find strength of Na_2CO_3 (eq. wt. 53)

Na_2CO_3 HCl

$N_1 V_1 = N_2 V_2$

$N_1 \times 20 = 0.095 \times 15$;

$\therefore N_1 = (15 \times 0.095)/20$

Strength of Na_2CO_3 $= N_1 \times$ Eq. wt. (= 53)

= (15 × 0.095) × 53/20

= 3.78 *g*

(*b*) To find strength of $NaHCO_3$ (eq. wt. 84)

$NaHCO_3$ HCl

$N_3 V_3 = N_4 V_4$; $N_3 \times 20 = 0.095 \times 6.3$

$N_3 = (0.095 \times 6.3)/20 = 0.0299$

Strength of $NaHCO_3$ $= N_3 \times$ Eq. wt. = 0.0299 × 84 = 2.51 gL^-

Total strength of Na_2CO_3 and $NaHCO_3$ = 3.78 + 2.51 = 6.29 gL^-

% age of Na_2CO_3 = (3.78 × 100)/6.29 = 60.1% ; % age of $NaHCO_3$ = 100 – 60.1 = 39.9%

EXAMPLE 9. *5g of a mixture of NaOH and KOH is dissolved in water and the solution made up to one litre. 20 mL of this solution required 22.0 mL of 0.095 N NHCl for complete neutralisation. Calculate the percentage composition of the mixture.*

SOLUTION. $NaOH + HCl \longrightarrow NaCl + H_2O$;

$KOH + HCl \longrightarrow KCl + H_2O$.

Let wt. of NaOH = *x* g ;

wt. of KOH = (5 – *x*) g.;

Eq. wt. of NaOH = 40 ;

∴ normality of NaOH = *x*/40; Eq. wt. of KOH = 56;

∴ Normality of KOH = (5 – *x*)/56

∴ Total normality = *x*/40 + (5 – *x*)/56

To find total normality of NaOH + KOH solution mixture.

Mixture alkali HCl

$N_1 V_1 = N_2 V_2$; $N_1 \times 20 = 0.095 \times 22$;

$N_1 = (0.095 \times 22)/20 = 0.1045$ (*ii*)

From (*i*) and (*ii*) we get, *x*/40 + (5 – *x*)/56 = 0.1045 or 56*x* + 200 – 40*x* = 234.08

or *x* = 2.13 g = wt. of NaOH ; wt. of KOH = 5 – 2.13 = 2.87 g

∴ % age of NaOH = (2.13 × 100)/5 = **42.6%** ; % age of KOH = 100 – 42.6 = 57.4%

EXAMPLE 10. *2.76g of a mixture of $CaCO_3$ and $MgCO_3$ was treated with 75 mL of 0.97 N HCl solution. The excess of acid required 12.75 mL of 1N NaOH for neutralisation. Calculate the percentage composition of the mixture.*

SOLUTION. Let wt. of $CaCO_3$ = *x* g ; wt. of $MgCO_3$ = 2.76 – *x* g.

Total acid taken = 75 mL of 0.97 N HCl = 75 × 0.97 = 72.75 mL of 1N HCl.

Acid left unreacted = 12.75 mL of 1N NaOH = 12.75 mL of 1N HCl.

∴ Vol. of 1N acid used = 72.75 – 12.75 = 60.0 mL.

(*a*) $\underset{100\text{ g}}{CaCO_3} + \underset{\substack{2\times1000\text{ mL}\\ \text{of 1 N acid}}}{2HCl} \longrightarrow CaCl_2 + CO_2 + H_2O$;

$\underset{84\text{ g}}{MgCO_3} + \underset{\substack{2\times1000\text{ mL}\\ \text{of 1 N acid}}}{2HCl} \longrightarrow MgCl_2 + CO_2 + H_2O$

100 g $CaCO_3$ require 1 N HCl = 2000 mL

x g $CaCO_3$ require 1 N HCl = (2000 *x*)/100 mL = 20 *x*

84 g $MgCO_3$ require 1N HCl = 2000 mL

(2.76 – *x*) g $MgCO_3$ require 1 N HCl = 2000 × (20.76 – x)/84

∴ Total 1N HCl acid used = [20 *x* + 2000 (2.76 – *x*)]/84 ;

∴ [20 *x* + 2000 (2.76 – *x*)/84] = 60

∴ *x* = 1.5 g = wt. of $CaCO_3$; wt. of $MgCO_3$ = 2.76 – 1.5 = 1.26 g.

% age of $CaCO_3$ = (1.5 × 100)/2.76 = **54.36%** ; % age of $MgCO_3$ = 100 – 54.36 = **45.64%**

EXAMPLE 11. *What volume of 12N H_2SO_4 be mixed with 3N H_2SO_4 to give one litre of 6N H_2SO_4 ?*

SOLUTION. Let *x* mL of 12N H_2SO_4 is mixed with *y* mL of 3N H_2SO_4. So, *x* × 12 + *y* × 3 = (*x* + *y*) × 6 or 12*x* + 3*y* = 6*x* + 6*y* or 2*x* = *y*.

But *x* + *y* = 1000 mL ; (∵ 2*x* = *y*)

∴ *x* + 2*x* = 100 ml; *x* = 1000 mL/3

or *x* = 333.33 mL and

y = 1000 – 333.33 = 666.67 mL.

Hence volume of 12N H_2SO_4 = 333.33 mL and that of 3N H_2SO_4 (= 666.67 mL) should be mixed to get 1L of 6N H_2SO_4.

EXAMPLE 12. *Calculate the strength of the resulting solution obtained by mixing 20 mL of N/2 HCl with 19.6 mL of 2N HNO_3 and 12.4 mL of N/10 H_2SO_4.*

SOLUTION. 20 mL of *N*/2 HCl = 10 mL of 1N HCl;

19.6 mL of 2N HNO_3 = 39.2 mL of 1N HNO_3 ;

12.4 mL of $N/10$ H_2SO_4 = 1.24 mL of 1N H_2SO_4.

Thus, total volume of given resulting solution

= 20 + 19.6 + 12.4

= 52.0 mL

Let N_1 = strength of resulting solution.

52 mL of resulting solution of

N_1 strength = 10 + 39.2 + 1.24

= 50.44 mL of 1 N acid

∴ $N_1 = (50.44 \times 1)/52 =$ **0.97.**

Example 13. *0.5 g of carbonate of a metal was dissolved in 12.5 mL of 1N HCl. The resulting solution required 25 mL of N/10 NaOH for complete neutralisation. Calculate the equivalent weight of the metal carbonate and the metal.*

Solution. 25 mL of $N/10$ NaOH = 25 × 1/10 = 2.5 mL of 1N NaOH

Volume of unreacted 1N HCl = 2.5 mL of 1N NaOH = 2.5 mL of 1N HCl

∴ Vol. of 1N HCl that reacted with 0.5 g metal carbonate = 12.5 – 2.5 = 10 mL

10 mL of 1N HCl reacted with metal carbonate = 0.5 g

1000 mL of 1N HCl that will react with 0.5 g metal carbonate = (0.5 × 1000)/10 = **50 g**

∴ Eq. wt. of metal carbonate = **50**

Eq. wt. of metal = Eq. wt. of metal carbonate – Eq. wt. of CO_3^{2-} = 50 – 30 = **20**

Example 14. *12.5 mL of a solution of N/10 H_2SO_4 exactly neutralised 10 mL of a base containing 2.4 g per 500 mL of the solution. Calculate the equivalent weight of the base.*

Solution. Since 12.5 mL of N/10 HCl ≡ 10 mL of N_1 base. So the normality (N_1) of the base = 12.5/ (10 × 10) = 0.125. Hence

$$\text{Eq. wt. of base} = gL^{-}/N_1 = \frac{(1000/500 \times 2.4)}{0.125} = \mathbf{38.4}$$

Example 15. *1.5 g of an acid having mol. wt. 90 required 33.2 mL of 1N NaOH for complete neutralisation. Calculate the basicity of the acid.*

Solution. 33.2 mL of 1N NaOH ≡ 1.5 g of acid

1000 mL of 1N NaOH ≡ (1.5 × 1000)/33.2 = 45 g of acid = g. Eq. wt. of acid

∴ Basicity of acid = Mol. wt/Eq. wt. = 90/45 = **2.**

Example 16. *1.03 g of a given sample of chalk ($CaCO_3$) was dissolved in 50 mL of 1N HCl and solution was made up to 250 mL. 20 mL of given 0.11N NaOH neutralised 18.5 mL of diluted residual acid. Calculate the percentage purity of chalk (at. wt. of Ca = 40, C = 12, O = 16).*

Solution. Wt. of chalk ($CaCO_3$) = 1.03 g ; Eq. wt. of $CaCO_3$ = [40 + 12 + (3 × 16)]/2 = 50

(*a*) *To find normality of diluted acid.*	(*b*) *To find volume of acid left unused.*
Diluted acid NaOH	Original HCl Diluted HCl
$N_1 V_1 = N_2 V_2$;	$N_3 V_3 = N_4 V_4$
$N_1 \times 18.5 = 0.11 \times 20$;	$1 \times V_3 = 0.1189 \times 250$;
∴ $N_1 = (0.11 \times 20)/18.5 =$ 0.1189	∴ $V_3 = 29.72$ mL
	∴ Vol of 1N HCl used to decompose $CaCO_3$ = 50 – 29.72 = 20.28 mL

(*c*) Wt. of pure $CaCO_3$ in 1.03 g chalk = (20.28 × 50)/1000 = 1.014 g.

(*d*) Percentage purity of chalk = (1.014 × 100)/1.03 = **98.45%**

Example 17. *5 mL of 8N nitric acid, 4.8 mL of 5N HCl and a certain volume of 17 M H_2SO_4 are mixed together and made up to 2 litre. 30 mL of this mixture exactly neutralised 42.9 mL of sodium carbonate solution containing 1g of Na_2CO_3. $10H_2O$ in 100 mL of water. Calculate the amount in grams of the sulphate ions in the solution.*

Solution. Molarity of H_2SO_4 = 17 M;

∴ Normality of H_2SO_4 = 2 × 17 = 34 N

Let volume of 34 N H_2SO_4 = V mL ; Na_2CO_3 per litre

= (1 × 1000)/100 = 10 g

∴ Total number of *m* gm equivalent of acid mixture

= (8 × 5) + (5 × 4.8) + 34

V = 64 + 34V

Normality of mixture solution = (64 + 34 V)/2000

[∵ 2L = 2 × 1000 = 2000 mL]

Number of *m*gm equivalent in 30 mL mixture solution

= (64 + 34 V) × 30/2000

Also, normality of $Na_2CO_3.10H_2O$ solution

= gL^{-}/Eq. wt. of $Na_2CO_3.10H_2O$

= 10/143 ...(*i*)

∴ Number of *m*gm equivalent of $Na_2CO_3.10H_2O$

= (10 × 42.9)/143 ...(*ii*)

Form (*i*) and (*ii*), we get, (64 + 34 V)/2000

= (10 × 42.9)/143

Thus 64 + 34 V = 200 or 34V = 136 or V = 4 mL

∴ mgm. equivalent of 34N H_2SO_4 = 34 × 4 = 136

Number of equivalents of H_2SO_4 = 136/1000 = 0.136

Number of equivalents of SO_4^{2-} = 0.136

Hence wt. of SO_4^{2-} in solution = 0.136 × Eq. wt. of SO_4^{2-} = 0.136 × 48 = **6.53g**

Example 18. *1.1g of impure sodium carbonate is dissolved in water and the solution is made up to 250 mL. To 50 mL of this made up solution, 50 mL of 0.1 NHCl is added and the mixture after shaking well required 10 mL of 0.16N NaOH solution for complete neutralisation. Calculate the percentage purity of the sample of sodium carbonate.*

Solution. No. of *m*gm equivalents of HCl added to 50 mL Na_2CO_3 solution = 50 × 0.1 = 5

mgm. equivalents of HCl left after reaction with 50 mL of Na_2CO_3 solution = *m*gm. equivalent of NaOH used = 10 × 0.16 = 1.6

$\therefore$ No. of *m*gm eq. of HCl used for 50 mL Na_2CO_3 solution = 5 – 1.6 = 3.4

$\therefore$ No of the *m*gm. eq. of Na_2CO_3 in 250 mL solution = (3.4 × 250)/50 = 17

$\therefore$ Amount of Na_2CO_3 in 17 *m*gm. eq. = (17 × 53)/1000 = 0.901g

[$\because$ Eq. wt. of Na_2CO_3 = 53]

Hence % age purity of Na_2CO_3 = (0.901 × 100)/1.1 = **81.9%**

Example 19. *A solution contains $NaHCO_3$ and Na_2CO_3. 20 mL of this solution required 4 mL of 1N HCl for titration with phenolphthalein as indicator. The titration was repeated with the same volume of the solution but with methyl orange as indicator. 10.5 mL of 1N HCl was required this time. Calculate the amount of $NaHCO_3$ and Na_2CO_3 in the solution.*

Solution. *Experiment 1*, when phenolphthalein is the indicator.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

[Here eq. wt. of Na_2CO_3 = 106]

Experiment 2, when methyl orange is indicator

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + HCl\,;$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O.$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O$$

(originally present).

(*i*) With phenolphthalein, no. of *m*gm. eq. of

Na_2CO_3 = 4 mL of 1N HCl = 1.0 × 4 = 4

$\therefore$ g. eq. of Na_2CO_3 = 4/1000 = 0.004;

$\therefore$ wt. of Na_2CO_3 = 0.004 × 106 = 0.424 g.

(*ii*) With methyl orange, no. of mgm. equivalent of Na_2CO_3 + mgm. eq. of $NaHCO_3$ (produced) + mgm. eq. of $NaHCO_3$ (originally present) = mgm eq. of 10.5 mL of 1.0N HCl

Or 4 + 4 + mgm. eq. of

$NaHCO_3$ = 1 N × 10.5 = 10.5;

8 + mgm. eq. of $NaHCO_3$ = 10.5

$\therefore$ mgm. eq. of $NaHCO_3$ = 10.5 – 8 = 2.5 ;

$\therefore$ wt. of $NaHCO_3$ = (2.5 × 84)/1000

= **0.21 g.**

22.6 TITRATIONS INVOLVING CALCULATIONS IN TERMS OF MOLARITY

In such titrations in which molarity of a reaction is involved, molarity of unknown solution can be calculated by the use of following general relation.

$$\frac{(\text{Molarity, }M_1 \times \text{Volume, }V_1)\text{ of acid}}{(\text{Molarity, }M_2 \times \text{Volume, }V_2)\text{ of alkali or base}}$$

$$= \frac{\text{no. of moles of acid used in acid – base reaction}}{\text{no. of moles of base used in acid – base reaction}}$$

For example, in sodium hydroxide and oxalic acid ($H_2C_2O_4$) titration, the balanced equation is :

$$\underset{\text{2 mole}}{2NaOH} + \underset{\text{1 mole}}{H_2C_2O_4} \longrightarrow Na_2C_2O_4 + 2H_2O$$

In this reaction, 2 mole of NaOH react completely with 1 mole of oxalic acid to form the products. So, if 20 mL of *M*/20 NaOH is neutralised by 20.1 mL of $H_2C_2O_4$ having unknown molarity, M_1 then M_1 can be calculated by using the relation :

$$\frac{(\text{Molarity, }M_1 \times \text{Volume, 20.1 mL})\text{ of }H_2C_2O_4}{(\text{Molarity, }1/20 \times \text{Volume, 20 mL})\text{ of NaOH}}$$

$$= \frac{\text{no. of moles of }H_2C_2O_4(=1)}{\text{no. of moles of NaOH}(=2)}$$

$$\therefore \quad \frac{M_1 \times 20.1}{1/20 \times 20} = \frac{1}{2}\,;$$

$$M_1 = \frac{1}{2} \times \frac{1}{20} \times \frac{20}{20.1} = \frac{1}{40.2}$$

Method to find strength in gL⁻. The strength of an acid or base can be determined by using the relation :

Strength = (Molarity × Molecular weight) of acid or base in gram per litre.

Following example is given for better understanding.

Example 20. *Calculate the atomic weight of the metal in the given solution of metal carbonate (M_2CO_3), 5.3 g of which are dissolved in one litre solution. 20 mL of carbonate solution is completely neutralised by 20.1 mL of the given M/10 HCl.*

Solution. $\underset{\text{1 mole}}{M_2CO_3} + \underset{\text{2 mole}}{2HCl} \longrightarrow 2MCl + CO_2 + H_2O$

(*i*) *To find molarity of M_2CO_3.* Applying molarity equation, we have

$$\frac{(\text{Molarity, }M_1 \times \text{Volume, }V_1)\text{ of HCl}}{(\text{Molarity, }M_2 \times \text{Volume, }V_2)\text{ of }M_2CO_3} = \frac{2}{1}$$

Substituting the values, we get

$$\frac{1/10 \times 20.1}{M_2 \times 20} = \frac{2}{1} \text{ or } M_2 = \frac{1}{10} \times \frac{20.1}{2 \times 20} = \frac{201}{4000}$$

(*ii*) *To find atomic weight of metal, M*

Wt. of M_2CO_3 = 5.3 gL⁻. Volume of M_2CO_3 taken for each titration, V_1 = 20 mL; Molarity of HCl,

M_2 = 1/10 Volume of HCl used

= 20.1 mL Molarity of M_2CO_3.

M_1 = ? Let atomic weight of metal,

M = *a*; Mol. wt. of M_2CO_3

= 2*a* + 12 + 48 = 2*a* + 60

Strength of M_2CO_3 = Molarity × mol. wt.

$$5.3 = \frac{201}{4000} \times (2a + 60)$$

$$\therefore \quad a = \frac{1}{2}\left[\frac{5.3 \times 4000}{201} - 60\right]$$

or *a* = 22.73 i.e., atomic weight of metal, M.

22.7 REDOX OR OXIDATION-REDUCTION TITRATIONS-$KMnO_4$, $K_2Cr_2O_7$, I_2 etc.

Equivalent weights of oxidising and reducing agents.

(*i*) In a redox reaction, **the equivalent weight of an oxidising agent** (oxidant) *is the weight that accepts one mole of electrons.*

(*ii*) In a redox reaction, **the equivalent weight of a reducing agent** (reductant) *is the weight that loses one mole of electrons.*

Thus equivalent weight of an oxidant or reductant is equal to its molecular weight divided by the number of electrons gained or lost in its ion-electron equation respectively.

Table 22.2

Substance	*Ion-electron equation*	*Eq. wt = mol wt. / No. of electrons lost or gained*
1. Potassium Permanganate ($KMnO_4$)	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	$\frac{158}{5} = 31.6$
2. Hydrated ferrous sulphate ($FeSO_4.7H_2O$)	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	$\frac{278}{1} = 278$
3. Anhydrous ferrous sulphate ($FeSO_4$)	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	$\frac{152}{1} = 152$
4. Hydrated oxalic acid ($H_2C_2O_4.2H_2O$)	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$\frac{126}{2} = 63$
5. Anhydrous oxalic acid ($H_2C_2O_4$)	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	$\frac{90}{2} = 45$
6. Mohr's salt (Ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4.6H_2O$)	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$	$\frac{392}{1} = 392$
7. Ferrous oxalate $FeC_2O_4.2H_2O$	$Fe^{+2} \longrightarrow Fe^{3+} + e^-$ $C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $Fe^{2+} + C_2O_4^{2-} \longrightarrow Fe^{3+} + 2CO_2 + 3e^-$	$\frac{180}{3} = 60$
8. Sodium oxalate, $Na_2C_2O_4$	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$\frac{134}{2} = 67$
9. Ammonium oxalate $(NH_4)_2C_2O_4$,	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$	$\frac{142}{2} = 71$
10. Sulphur dioxide (SO_2)	$SO_2 + 2H_2O \longrightarrow HOSO_3^- + 3H^+ + 2e^-$	$\frac{64}{2} = 32$
11. Potassium dichromate ($K_2Cr_2O_7$)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	$\frac{294}{6} = 49$
12. Iodine (I_2)	$2I + 2e^- \longrightarrow 2I^-$	$\frac{254}{2} = 127$
13. Copper sulphate (hydrated) ($CuSO_4.5H_2O$)	$Cu^{2+} + e^- \longrightarrow Cu^+$	$\frac{249.5}{1} = 249.5$
14. Anhydrous copper sulphate, $CuSO_4$	$Cu^{2+} + e^- \longrightarrow Cu^+$	$\frac{159.5}{1} = 159.5$
15. Sodium thiosulphate ($Na_2S_2O_3.5H_2O$)	$S_2O_3^{2-} \longrightarrow \frac{1}{2}S_4O_6^{2-} + e^-$	$\frac{248}{1} = 248$
16. Sodium thiosulphate (anhydrous)	$S_2O_3^{2-} \longrightarrow \frac{1}{2}S_4O_6^{2-} + e^-$	$\frac{158}{1} = 158$
17. Stannous chloride ($SnCl_2.2H_2O$)	$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$	$\frac{225.6}{2} = 112.8$
18. Arsenous oxide (As_2O_3)	$2As^{3+} \longrightarrow 2As^{5+} + 4e^-$	$\frac{198}{4} = 49.5$
19. Arsenic (As)	$As^{3+} \longrightarrow As^{5+} + 2e^-$	$\frac{75}{2} = 37.5$
20. Sodium arsenite (Na_3AsO_3)	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$	$\frac{192}{2} = 96$
21. Tartaremtic CH(OH)COOK | $CHOHCOO(OSb)\frac{1}{2}H_2O$	$Sb^{3+} \longrightarrow Sb^{5+} + 2e^-$	$\frac{334}{2} = 167$
22. Antimonous oxide (Sb_2O_3)	$2Sb^{3+} \longrightarrow 2Sb^{5+} + 4e^-$	$\frac{292}{4} = 73$
23. Antimony (Sb)	$Sb^{3+} \longrightarrow Sb^{5+} + 2e^-$	$\frac{122}{2} = 61$

Another definition of equivalent weight. *The equivalent weight of a substance is that weight of it which gives rise to or react with 127 parts by weight of iodine and 8 parts by weight of oxygen.* The equivalent weight of some oxidants and reductants are found as follows by using this definition.

(*i*) **To find equivalent weight of $KMnO_4$** from the equation

$$\underset{\substack{3(39+55+64)\\=316\text{ g}}}{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + \underset{\substack{5\times16\\=80\text{g}}}{5O}$$

we have, 80 g oxygen ≡ 316 g $KMnO_4$;

$$\therefore \quad 8 \text{ g oxygen} \equiv \frac{316}{80} \times 8 = 31.6 \text{ g } KMnO_4$$

$\therefore$ Eq. wt. of $KMnO_4$ = **31.6.**

(*ii*) **To find equivalent weight of $FeSO_4$** from the reaction.

$$\underset{\substack{2(56+32+64)\\=304\text{ g}}}{2FeSO_4} + H_2SO_4 + \underset{\substack{1\times16\\=16\text{ g}}}{O} \longrightarrow Fe_2(SO_4)_3 + H_2O$$

we have,

$$16 \text{ g oxygen} = 304 \text{ g } FeSO_4;$$

$$\therefore \quad 8 \text{ g Oxygen} = \frac{304}{16} \times 8 = 152 \text{ g } FeSO_4.$$

$$\therefore \quad \text{Eq. wt. of } FeSO_4 = 152.$$

22.8 POTASSIUM PERMANGANATE TITRATIONS

$KMnO_4$ (potassium permanganate) is a powerful oxidising agent. It acts as an oxidant in acidic, basic as well as neutral medium. But in basic and neutral medium, it does not change exclusively into Mn^{2+} ions. So, **$KMnO_4$ titrations** to estimate reducing agents like *ferrous sulphate, ferrous ammonium sulphate* (*Mohr's salt*), *oxalic acid, oxalates* and *hydrogen peroxide* are done in **acidic medium.** The titrations in acidic medium involve the following key equation.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O;$$

Or $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (Ionic equation)

The electrons required in the above reaction are provided by reducing agents such as :

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \,;\, C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$$

Use of H_2SO_4 in titration. Out of the mineral acids (H_2SO_4, HCl, HNO_3) available, only H_2SO_4 is used in the redox titrations because it has no action on reductants in $KMnO_4$ solution. HNO_3 is not suitable because it is itself an oxidant and may oxidise some reducing agents like Fe^{2+} ions. HCl cannot be used because it reacts with $KMnO_4$ particularly in presence of Fe^{2+} ions to produce *chlorine* (an oxidant).

Visual method. $KMnO_4$ solution has dark purple colour. During redox titration (say $KMnO_4$ *vs.* Fe^{2+} in acidic medium), $KMnO_4$ (oxidant) solution is taken in the burette and Fe^{2+} (*i.e.* $FeSO_4$) solution is taken in the titration flask. When a drop of $KMnO_4$ is added to Fe^{2+} ion solution, the pink colour disappears because of the formation of Mn^{2+} ions (colourless). As soon as, the reducing agent (say Fe^{2+}) is used up, a single drop of $KMnO_4$ imparts faint pink colour, which is the end point. So, $KMnO_4$ acts as a **self-indicator.**

Following examples will help to know the method of titration and applications of $KMnO_4$ as **self-indicator.**

EXAMPLE 21. *How can you prepare one litre of 0.02 M solution of $KMnO_4$? (at. wt. K = 39, Mn = 55).*

SOLUTION. $KMnO_4$ is not a primary standard. So, its standard solution (0.02M) can be prepared by titrating it with a primary standard reducing agent such as Mohr's salt *i.e.* $FeSO_4.(NH_4)_2SO_4.6H_2O$, sodium oxalate etc.

Procedure. g. mol. wt. of $KMnO_4 = 39 + 55 + (4 \times 16) = 158$ g

$\therefore$ 1M $KMnO_4 \equiv 158$ gL⁻ $KMnO_4$; 0.02 M $KMnO_4 \equiv 158 \times 0.02$ or 3.16 g L⁻ $KMnO_4$. Take a pyrex beaker of 1500 mL capacity, add about 3.2g $KMnO_4$ in it, add 1L water, cover the beaker with a clock glass, boil gently for 15 to 30 minutes, filter the solution through a funnel containing a plug of purified glass wool, store this $KMnO_4$ solution in a clean glass stoppered dark brown glass bottle. This solution is approximately 0.02 M.

Prepare a standard solution of 0.1 M Mohr's salt (primary standard) and titrate it with $KMnO_4$ solution prepared above. Let 19.8 mL of $KMnO_4$ is needed to oxidise 20 mL of Mohr's salt solution in dil H_2SO_4 medium (end point = appearance of pink colour). Now use the following equation to find the molarity of $KMnO_4$.

$$\underset{2\text{ mole}}{2KMnO_4} + 8H_2SO_4 + \underset{10\text{ mole}}{10FeSO_4} \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

(*i*) *To find molarity, M_1 of $KMnO_4$ prepared.*

$$\frac{(\text{Molarity, } M_1 \times \text{Volume, } V_1) \text{ of } KMnO_4}{(\text{Molarity, } M_2 \times \text{Volume, } V_2) \text{ of Mohr's salt}} = \frac{2}{10};$$

$$\frac{M_1 \times 19.8}{0.1 \times 20} = \frac{2}{10}$$

$$\therefore \quad M_1 = \frac{2 \times 0.1 \times 20}{10 \times 19.8} = \frac{0.4}{19.8}$$

(*ii*) *To prepare exact 0.02 M $KMnO_4$.* Applying molarity equation, we have :

$KMnO_4$ solution to be prepared *$KMnO_4$ solution already prepared*

$$M_3 V_3 = M_4 V_4$$

$$0.02 \times 1000 = \frac{0.4}{19.8} \times V_4$$

$$\therefore \quad V_4 = [(0.02 \times 1000) \times 19.8]/0.4 = 990 \text{ mL}$$

Thus take 990 mL $KMnO_4$ solution prepared above in a 1L flask, add water and make the solution exact one litre. This solution is exact 0.02 M.

EXAMPLE 22. *How one litre of 0.1 N $KMnO_4$ solution is prepared ? (At. wt. of K = 39, Mn = 55, O = 16)*

SOLUTION. Eq. wt. of

$KMnO_4$ = 31.6 (See table 22.2)

Procedure. Prepare $KMnO_4$ solution as shown in example 21 by weighing 3.2 g $KMnO_4$; this solution is approximately 0.1 N.

Now prepare a standard solution of 0.1N Mohr's salt (primary standard) and titrate it with $KMnO_4$ solution prepared above. Let 19.0 mL of $KMnO_4$ is needed to oxidise 20 mL of Mohr's salt solution in dil. H_2SO_4 medium (end point = appearance of pink colour). Now use the following equation to find the normality (N_1) of $KMnO_4$ solution prepared.

(*i*) $KMnO_4$ solution Mohr's salt solution prepared

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 19.0 = 0.1 \times 20$$

$$\therefore \quad N_1 = (0.1 \times 20)/19 = 2/19$$

(*ii*) To prepare exact 0.1N $KMnO_4$

Required $KMnO_4$ Solution (say, 1000 mL) Prepared $KMnO_4$ solution

$$N_3 V_3 = N_4 V_4$$

$$0.1 \times 1000 = 2/19 \times V_2$$

$$\therefore \quad V_2 = (0.1 \times 1000 \times 19)/2 = 950 \text{ mL}$$

(*iii*) Thus take 950 mL of the $KMnO_4$ solution in one litre flask, add distilled water and make up the solution to exact one litre. This solution will be exact 0.1N.

EXAMPLE 23. *How will you prepare 250 mL of N/20 oxalic acid solution ?*

SOLUTION. Eq. wt. oxalic acid ($H_2C_2O_4.2H_2O$) = 63 (from table 22.2)

$$\begin{aligned} \therefore \quad \text{1 N oxalic acid} &\equiv \text{1 g equivalent of} \\ \text{oxalic acid/1,000 ml} &= \text{63 g/1,000 ml.} \\ \text{N/20 oxalic acid} &= \frac{63}{20}\ \text{g/1,000 ml or} \\ \text{3.15 g/litre} &= \frac{63 \times 250}{20 \times 1,000}\ \text{g/250 ml} \\ &= \text{0.7875 g/250 ml.} \end{aligned}$$

Weigh exactly 0.7875 g oxalic acid on a watch glass, transfer to 250 ml measuring flask, shake to dissolve, add more distilled water and make up the solution to exact 250 ml. It is N/20 oxalic acid.

EXAMPLE 24. *Determine the percentage purity of a given sample of $KMnO_4$, 0.8 g of which have been dissolved per 250 ml of the given solution. Provided N/10 $FeSO_4$ solution.*

SOLUTION. (*1*) *To find strength of $KMnO_4$.* Take 20 mL of $FeSO_4$ solution, add 20 ml dil H_2SO_4 and titrate with $KMnO_4$ solution till light pink colour (end point). From the volume of $KMnO_4$ used and using normality equation ($N_1V_1 = N_2V_2$), find the normality (N_1) of $KMnO_4$.

$$\begin{aligned} \text{Strength of } KMnO_4 &= \text{Normality} \times \text{Eq. wt. of } KMnO_4 \\ &= N_1 \times 31.6\ (gL^-) = a\ \text{(say)} \end{aligned}$$

(2) *% age purity of $KMnO_4$:*

$$\begin{aligned} \text{250 ml solution contains } KMnO_4 &= 0.8\ \text{g} \\ \text{1,000 ml solution contains } KMnO_4 &= \frac{0.8 \times 1,000}{250} \\ &= 3.2\ \text{g} \\ \therefore \quad \text{\% age purity of } KMnO_4 &= \frac{a}{3.2} \times 100 \end{aligned}$$

EXAMPLE 25. *Determine the number of molecules of water of crystallisation in oxalic acid, $H_2C_2O_4.xH_2O$, 6.3 g of which have been dissolved per litre of the given solution. Provided N/10 $KMnO_4$.*

SOLUTION. (1) *To find normality of oxalic acid.* Take 20 ml of oxalic acid, 20 mL dil. H_2SO_4, heat to 60° and titrate with N/10 $KMnO_4$ till just pink colour (end point). Let volume of $KMnO_4$ used is V_1. Using normality equation ($N_1V_1 = N_2V_2$), calculate the normality (N_2) of oxalic acid.

(2) Eq. wt. of oxalic acid = Strength/normality

$$= 6.3/N_2 = a\ \text{(say)}$$

Mol. wt. of (hydrated) oxalic acid = Eq. wt. × basicity of acid = a × 2 or **2*a*.**

(3) *To find the value of x.*

Mol. wt. of anhydrous oxalic acid,

$$H_2C_2O_4 = (2 \times 1) + (2 \times 12) + (4 \times 16) = 90$$

Mol. wt. of hydrated oxalic acid ($H_2C_2O_4.xH_2O$) (–)

Mol. wt. of anhydrous oxalic acid,

$$H_2C_2O_4 = 18x\ ;\ 2a - 90 = 18x$$

$$x = \mathbf{2a - 90/18.}$$

EXAMPLE 26. *You are provided with a solution of mixture of potassium permanganate and potassium sulphate, 4 g of which have been dissolved per litre of the given solution. Find the percentage composition of $KMnO_4$ and K_2SO_4. Provided N/10 $FeSO_4$ solution.*

SOLUTION. K_2SO_4 does not react with $KMnO_4$ but $FeSO_4$ reacts (see reaction page 581)

(1) *To find normality of $KMnO_4$ solution.* Take 20 ml of $FeSO_4$ solution in a titration flask, add 20 ml dil. H_2SO_4 and titrate with N/10 $KMnO_4$ till just pink colour (end point). Let the volume of $KMnO_4$ used is V_1 ml. Using normality equation ($N_1V_1 = N_2V_2$), the normality (N_1) of $KMnO_4$ is found out.

$$\begin{aligned} \text{(2) Strength of } KMnO_4 &= \text{Normality} \times \text{Eq. wt. of } KMnO_4 \\ &= N_1 \times 31.6 = a\ (gL^-)\ \text{(say)} \\ \text{(3) \% age of } KMnO_4 &= a \times 100/4 = \mathbf{25a}\ ; \\ \text{\% age of } K_2SO_4 &= \mathbf{100 - 25\,a.} \end{aligned}$$

EXAMPLE 27. *You are provided with a solution of a mixture of $FeSO_4$ and Mohr's salt, 35 g of which have been dissolved per litre of the given solution. Find the percentage composition of the mixture. Provided N/10 $KMnO_4$ solution.*

SOLUTION. (1) *To find total normality of mixture.* Take 20 ml of mixture solution, add 20 ml dil. H_2SO_4 and titrate with *N*/10 $KMnO_4$ solution till just pink colour (end point) is obtained. Let volume of *N*/10 $KMnO_4$ used is V_2. Using normality equation ($N_1V_1 = N_2V_2$), the normality (N_2) of mixture is found.

$$\begin{aligned} \text{(2) Let weight of } FeSO_4 &= x\ \text{g and thus wt. of} \\ \text{Mohr's salt} &= (35 - x)\ \text{g} \\ \text{Eq. wt. of } FeSO_4 &= 278\ ;\ \text{Eq. wt. of Mohr's salt} = 392 \end{aligned}$$

$$\therefore \text{ Normality of } FeSO_4 = \text{Strength/Eq. wt.} = \frac{35}{278}$$

$$\text{Normality of Mohr's salt} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{35 - x}{392}$$

$$\therefore\ N_2\ \text{(found experimentally)} = \frac{35}{278} + \frac{35 - x}{392}$$

From this equation, value of 'x' is calculated.

$$\begin{aligned} \text{(3) \quad \% age of } FeSO_4 &= x \times 100/35 = a\ \text{(say)} \\ \text{\% age of Mohr's salt} &= \mathbf{100 - a.} \end{aligned}$$

22.9 BACK TITRATIONS

EXAMPLE 28. *Calculate the percentage purity of a given sample of lead acetate $Pb(CH_3COO)_2 3H_2O$, 1.1g of which was boiled with 50 mL of N/3 oxalic acid and about 5 mL of acetic acid, filtered and filtrate was made to exact 250 mL. 20 mL of* *diluted residual oxalic acid was completely oxidised by 18.50 mL of N/20 KMnO$_4$ (at. wt. of Pb = 207, C = 12, O = 16)*

Solution. The given 100 mL solution of lead acetate is boiled with 50 mL of N/3 oxalic acid, filtered and filtrate made up to exact 250 mL solution.

$$Pb(CH_3COO)_2 + H_2C_2O_4 \longrightarrow PbC_2O_4\downarrow + 2CH_3COOH$$

(*i*) *To find normality of diluted residual oxalic acid*

Residual diluted KMnO$_4$ Oxalic acid

$N_1 V_1 = N_2 V_2$

Or $N_1 \times 20 = 1/20 \times 18.5$;

$\therefore$ $N_1 = 185/4000 = 0.04625$

(*ii*) *To find volume of N/3 oxalic acid used.*

Diluted oxalic acid Original oxalic acid.

$N_3 V_3 = N_4 V_4$

$0.04625 \times 250 = 1/3 \times V_4$

$\therefore$ $V_4 = 0.04625 \times 250 \times 3$

$= 34.89$ mL

(*iii*) *Eq. wt. of hydrated lead acetate is as :*

$Pb(CH_3COO)_2.3H_2O \equiv H_2C_2O_4 \equiv O$

379 g 16 g

379/2 **8 g**

$\therefore$ Eq. wt. of hydrated lead acetate

$= 379/2 =$ **189.5**

(*iv*) Wt. of lead acetate = 1.10 g

(*v*) % age purity of sample

$= (0.967 \times 100)/1.1$

$= 87.9\%$ **Ans.**

$\therefore$ Volume of N/3 oxalic acid used

$= 50 - 34.69 = 15.31$ mL

Thus 15.31 mL of N/3 oxalic acid

$\equiv$ 0.967 g lead acetate

$\therefore$ Wt. of pure lead acetate

= (Eq. wt. × Vol. ×

normality)/1000 = $(189.5 \times 15.31)/3 \times 1000$

$= 0.967$ g

Example 29. *Calculate the percentage of MnO$_2$ and available oxygen in pyrolusite, 1.1 g of which was boiled with 50 mL of 1N oxalic acid and 50 mL dil. H$_2$SO$_4$, filtered and filtrate was made to exact 250 mL. 20 mL of this residual oxalic acid required 23.5 mL of 0.1N KMnO$_4$ for complete oxidation. Also calculate the available oxygen in the pyrolusite. (at. wt. of Mn = 55, O = 16).*

Solution. Wt. of pyrolusite = 1.1 g ;

volume of residual oxalic acid = 250 mL

(*i*) *To find volume of 1N oxalic acid consumed.*

(*a*) Residual oxalic acid KMnO$_4$

$N_1V_1 = N_2 V_2$

$N_1 \times 20 = 0.1 \times 23.5$;

$\therefore N_1 = (0.1 \times 23.5)/20 = 0.1175$

(*b*) Residual oxalic acid Original oxalic acid

$N_3V_3 = N_4V_4$

$0.1175 \times 250 = 1 \times V_4$;

$\therefore$ $V_4 = 29.375$ mL

(*c*) Vol. of 1N oxalic acid used

$= 50 - 29.375 = 20.625$ mL

(*d*) Eq. wt. MnO$_2$ = Mol. wt./2 = 87/2 = 43.5

$[\therefore\ MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + \underset{\text{Available oxygen}}{O}]$

$H_2C_2O_4 + O \longrightarrow 2CO_2 + H_2O$

$\therefore$ $MnO_2 \equiv O$; 16g 16g O ≡ 87 g MnO$_2$

55 + (2 × 16)g ; = 87g 8g O ≡ (87 × 8)/16 = 43.5]

$\therefore$ Wt. of pure MnO$_2$ in 1.1g pyrolusite

$= (20.625 \times 43.5)/1000 = 0.897$ g

(*e*) $\therefore$ % age of MnO$_2$ = $(0.897 \times 100)/1.1 = 81.54\%$

(*f*) *To find available oxygen.* (eq. wt. of O = 8)

Wt. of available 'O' in 1.1g pyrolusite

$= (20.625 \times 8)/1000 = 0.165$ g

$\therefore$ % age of available oxygen = $(0.165 \times 100)/1.1 = 15\%$

22.10 DOUBLE TITRATIONS

Example 30. *Calculate volumetrically the amount of each of oxalic acid (H$_2$C$_2$O$_4$) and sulphuric acid (H$_2$SO$_4$) per litre of the given solution if 18.7 mL of acid solution neutralises 20 mL of 0.1N NaOH and 20 mL of the mixture is oxidised completely by 21.2 mL of 0.05 N KMnO$_4$.*

Solution. *First titration*

Mixed acid solution NaOH solution

$N_1V_1 = N_2V_2$

$N_1 \times 18.7 = 1/10 \times 20$;

$\therefore$ $N_1 = 20/18.7 = 0.017$

Or Total normality of H$_2$SO$_4$, and oxalic acid = 0.107

$\therefore$ Normality of H$_2$SO$_4$ = 0.107– 0.053 = 0.054

Second titration. Only oxalic acid will react with KMnO$_4$

Oxalic acid solution KMnO$_4$ solution

$N_3V_3 = N_4V_4\ N_3 \times 20$

$= 0.05 \times 21.2$;

$\therefore$ $N_3 = (0.05 \times 21.2)/20 = 0.053$

= normality of oxalic acid

$\therefore$ Strength of H$_2$SO$_4$ = 0.054 × 49 = 2.64 gL$^-$

($\because$ Eq. wt. of H$_2$SO$_4$ = 49)

Also, strength of oxalic acid = 0.053 × 45 = 2.835 gL$^-$

($\because$ Eq. wt. of oxalic acid = 45)

Example 31. *Calculate volumetrically the amount of each of KOH and sodium oxalate Na$_2$C$_2$O$_4$ per litre of the given solution if 17.5 mL of the 0.1 N HCl neutralises 20 mL of the given solution and 20 mL of the given solution oxidises completely 22.6 mL of 0.1N KMnO$_4$.*

Solution. (*a*) *Titration I.* Mixture Vs HCl

$$N_1V_1 = N_2V_2\ ;\ N_1 \times 20 = 0.1 \times 17.5$$

$$\therefore \quad V_1 = (0.1 \times 17.5)/20 = 0.0875\ ;$$

Eq. wt. KOH = 56

∴ Wt. of KOH = 0.0875 × 56 = 4.9 gL^-

(*b*) *Titration II.* Mixture Vs $KMnO_4$

$$N_3V_3 = N_4V_4$$

$$N_3 \times 20 = 0.1 \times 22.6\ ;$$

$$N_3 = (0.1 \times 22.6)/20 = 0.113\ ;$$

Eq. wt. of $Na_2C_2O_4$ = Mol. wt./2 = 134/2 = 67

∴ Wt. of $Na_2C_2O_4$ = 0.113 × 67 = 7.571 g L^-

(*c*) Total wt. of KOH and $Na_2C_2O_4$

= 4.9 + 7.571 = 12.471 g

% age of KOH = (4.9 × 100)/12.471

= **39.29%**

% age of $Na_2C_2O_4$ = 100 – 39.29 = **60.71%**

22.11 $KMnO_4$ TITRATIONS IN TERMS OF MOLARITY OF A GIVEN SOLUTION

Following relation is used for this purpose.

$$\frac{(\text{Molarity, } M_1 \times \text{Volume, } V_1) \text{ of } KMnO_4 \text{ (oxidant)}}{(\text{Molarity, } M_2 \times \text{Volume, } V_2) \text{ of reductant (e.g., } FeSO_4)}$$

$$= \frac{\text{no. of moles of } KMnO_4 \text{ used in redox reaction}}{\text{no. of moles of reductant (e.g., } FeSO_4) \text{ used in redox reaction.}}$$

Method to find strength in gL^-. The strength of an oxidant ($KMnO_4$) or reductant (*e.g.*, $FeSO_4$) can be determined by using the relation :

Strength = (Molarity × Molecular weight) of oxidant, $KMnO_4$ or reductant (*e.g.* $FeSO_4$) respectively.

Following example is given for clarity.

Example 32. *Determine the molarity and strength in* gL^- *of a given solution of* $KMnO_4$ *if 20 mL of M/50 oxalic acid need 20.5 mL of* $KMnO_4$ *for its complete oxidation.*

Solution.

$$\underset{2\text{ mole}}{2KMnO_4} + 3H_2SO_4 + \underset{5\text{ mole}}{5H_2C_2O_4} \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

From above relation, we find that 2 moles of $KMnO_4$ oxidise 5 moles of oxalic acid. Volume of $KMnO_4$ used, V_1 = 20.5 mL

$$\therefore \frac{(\text{Molarity} \times \text{Volume}) \text{ of } KMnO_4}{(\text{Molarity} \times \text{Volume}) \text{ of oxalic acid}} = \frac{2}{5} \qquad ...(i)$$

Molarity of $KMnO_4$, M_1 = ?

Substituting the values in equation (*i*),

Volume of oxalic acid, V_2 = 20 mL
Molarity of oxalic acid, M_2 = 1/50

$$\text{we get :} \quad \frac{M_1 \times 20.5}{1/50 \times 20} = \frac{2}{5}\ ;$$

$$M_1 = \frac{2}{5} \times \frac{1}{50} \times \frac{20}{20.5}$$

$$= \mathbf{7.8 \times 10^{-3}} \qquad \textbf{Ans.}$$

Example 33. *Determine the number of molecules of water of crystallisation in a given sample of Mohr's salt,* $FeSO_4.(NH_4)_2SO_4.xH_2O$, *9.8 g of which have been dissolved per 250 mL of the given solution. Experiment indicates that 19.8 mL of M/50* $KMnO_4$ *completely oxidised 20 mL of Mohr's salt solution.*

Solution. The required reaction is :

$$\underset{(2\text{ mole})}{2KMnO_4} + 8H_2SO_4 + \underset{(10\text{ mole})}{10FeSO_4.(NH_4)_2SO_4.xH_2O} \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + (10x + 8)H_2O$$

From above relation, we find that 2 moles of $KMnO_4$ oxidise 10 moles of Mohr's salt.

(*i*) *To find molarity of Mohr's salt.*

$$\frac{(\text{Molarity} \times \text{Volume}) \text{ of } KMnO_4}{(\text{Molarity} \times \text{Volume}) \text{ of Mohr's salt}} = \frac{2}{10} \qquad ...(1)$$

Substituting the values in equation (1), we get :

$$\frac{1/50 \times 19.8}{M_2 \times 20} = \frac{2}{10}\ ;\ M_2 = 0.099\ ;$$

Molarity of Mohr's salt = 0.099.

(*ii*) *To find the value of x.*

Volume of $KMnO_4$ used, V_1 = 19.8 mL
Volume of oxalic acid, V_2 = 20 mL
Molarity of $KMnO_4$, M_1 = 1/50
Molarity of Mohr's salt, M_2 = ?
Mol. wt. of Mohr's salt = 248 + 18*x*
Wt. of Mohr's salt = (9.8 × 1000)/250
= 39.2 g

Strength of Mohr's salt = Molarity × Mol. wt. of Mohr's salt

$$39.2 = 0.099 \times (284 + 18x)$$

$$\therefore \quad x = \frac{1}{18}\left[\left(\frac{39.2}{0.099}\right) - 284\right]$$

$$= \mathbf{6.2 \simeq 6} \qquad \textbf{Ans.}$$

22.12 POTASSIUM DICHROMATE ($K_2Cr_2O_7$) TITRATIONS

For such titrations, one must know the equivalent weights and molecular weights of oxidants and reductants taking part in their redox titrations. *e.g.*,

(*i*) To find equivalent weight of $K_2Cr_2O_7$ from the ionic reactions in acidic medium.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 6H_2O \text{ (reduction)}$$

$$\therefore \text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt. of } K_2Cr_2O_7}{\text{no. of electrons gained}}$$

$$= \frac{(2 \times 39) + (2 \times 52) + (7 \times 16)}{6} = 49$$

(*ii*) To find equivalent weight of reductants like $FeSO_4.7H_2O$, Mohr's salt, oxalic acid, sodium oxalate, SO_2 etc, see table 22.2.

Example 34. *You are provided with a solution of Mohr's salt,* $FeSO_4.(NH_4)_2SO_4.xH_2O$, *20 g of which have been dissolved* *per litre. Determine volumetrically, the value of x. Given N/20 $K_2Cr_2O_7$ solution.*

Solution. (1) *To find the normality of Mohr's salt.* Take 20 ml of the Mohr's salt solution, add 100 ml of 2 N H_2SO_4, about 8 drops of N-phenylanthranilic acid as indicator and titrate with N/20 $K_2Cr_2O_7$ solution till green to violet red colour (end point). From the volume (V_2) of $K_2Cr_2O_7$ used, calculate the *normality* (N_1) of Mohr's salt solution using normality equation ($N_1V_1 = N_2V_2$).

(2) *To find the value of 'x'*

Eq. wt. of hydrated Mohr's salt = Strength/normality = $20/N_1 = a$ (say) = Mol. wt. of hydrated salt

Eq. wt. of anhydrous Mohr's salt, $FeSO_4.(NH_4)_2SO_4$ = 284.

Mol. wt. of hydrated salt (–) Mol. wt. of anhydrous salt = $18x$; $a - 284 = 18x$

$$\boldsymbol{x = a - 284/18.}$$

Example 35. *The given solution has been prepared by dissolving ferric alum, $Fe_2(SO_4)_3.(NH_4)_2SO_4.\ 24H_2O$ in very dilute sulphuric acid. Determine volumetrically, the following:*

(*i*)*Fe^{3+} ions in gram molecules* (*ii*) *Ferric alum in gram equivalents. Provided N/10 Mohr's salt solution.*

Solution. A known volume of ferric alum is reduced with stannous chloride method and titrated with $K_2Cr_2O_7$ to get different strengths of ions etc.

Reactions

(*i*) $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O \longrightarrow Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 24H_2O$

(*ii*) $Fe_2(SO_4)_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2SO_4$;

$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(*iii*) $\underset{\text{(excess)}}{SnCl_2} + 2HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2\downarrow$;

$$2FeCl_2 + 2HCl + \underbrace{[O]}_{\text{From } K_2Cr_2O_7/H_2SO_4} \longrightarrow 2FeCl_3 + H_2O$$

Eq. wt. of ferric alum. From above equations, we have

$$\underset{\text{964 parts}}{Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O} \equiv Fe_2(SO_4)_3 \equiv 2FeCl_3 \equiv 2FeCl_2 \equiv \underset{\text{16 parts}}{O}$$

16 parts by weight of oxygen ≡ 964 parts by weight of ferric alum

8 parts by weight of oxygen ≡ $\frac{964}{16} \times 8$ parts by weight of ferric alum ≡ 482

(*i*) *To find ferric alum in g.equivalents.* Let normality of $K_2Cr_2O_7$ is N_1 and V_1 mL of it is used for oxidation of Fe^{2+} ions.

$N_1V_1(K_2Cr_2O_7) = N_2$ (Fe^{2+} obtained after reducing ferric alum) × V_2; $N_2 = \frac{N_1V_1}{V_2}$

(*ii*) *To find Fe^{3+} ions in g. molecules L^- or molarity.* N_2 × Eq. wt. = Molarity × mol. wt.

∴ Molarity = (N_2 × 482)/964 (found above) = $N_2/2$ **Ans.**

Example 36. *A solution 'B' contains 17 g of partially dehydrated sample of Mohr's salt dissolved per litre. Determine volumetrically, the percentage of dehydration of the given sample. Provided N/20 $K_2Cr_2O_7$ solution.*

Solution. (1) *To find normality of Mohr's solution.* Take 20 ml of Mohr's solution, add 100 ml of 2 N H_2SO_4, about 8 drops of N-phenylanthranilic acid indicator and titrate with N/20 $K_2Cr_2O_7$ solution till green to violet red colour (end point). Let volume of $K_2Cr_2O_7$ solution used is V_2 ml. From this find the **normality (N_1) of** Mohr's solution using normality equation ($N_1V_1 = N_2V_2$).

(2)*To find percentage dehydration of the given sample.*

Eq. wt. of hydrated Mohr's salt [$FeSO_4.(NH_4)_2SO_4.6H_2O$] = 392

Strength of hydrated Mohr's salt = Normality × Eq. wt. = $N_1 \times 392 = a$ (gL^-) say.

But strength of partially hydrated sample = 17 gL^-

∴ Loss in weight due to dehydration of Mohr's salt = $a - 17 = b$ g (say)

Thus, % age dehydration of the sample = $\boldsymbol{b \times 100/a}$.

(*b*) **$K_2Cr_2O_7$ titrations in terms of molarity of a solution.** For calculations see section 22.3.

Example 37. *You are provided with a solution af alkali metal dichromate ($M_2Cr_2O_7$), 2.2 g of which have been dissolved per 250 mL of the given solution. Find volumetrically, the atomic weight of the metal if 19.8 mL of 0.1 M oxalic acid reduces completely 20 mL of the given dichromate solution.*

Solution. The required equation is :

$$\underset{\text{(1 mole)}}{K_2Cr_2O_7} + 4H_2SO_4 + \underset{\text{3 mole}}{3H_2C_2O_4} \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6CO_2$$

From above equation we see that

$$\frac{(\text{Molarity } M_1 \times \text{Volume, } V_1) \text{ of } M_2Cr_2O_7}{(\text{Molarity, } M_2 \times \text{Volume, } V_2) \text{ of } H_2C_2O_4} = \frac{1}{3}$$

$$\frac{M_1 \times 20}{0.1 \times 19.8} = \frac{1}{3} \ \therefore\ M_1 = \frac{0.1 \times 19.8}{20 \times 3} = 0.033$$

But strength of $M_2Cr_2O_7$

= Molarity × mol. wt. of $M_2Cr_2O_7$

8.8 = 0.033 × ($2a$ + 216)

∴ a = (266.7)– 216)/2 = **25.35.**

∴ Atomic weight of metal,

M = **25.35 a.m.u.**

250 mL solution contain

$M_2Cr_2O_7$ = 2.2g; 1000 mL solution contain

$M_2Cr_2O_7 = \frac{2.2 \times 1000}{250} = 8.8\ gL^-$; Volume of

$M_2Cr_2O_7$ used = 20 mL; Volume of

$H_2C_2O_4$ used = 19.8 mL

Mol. wt. of $M_2Cr_2O_7$ = 2 × at. wt. of M + 2 × 52 + 7 × 16

= $2a$ + 216 **where at. wt. of metal,**

M = a

22.13 IODINE TITRATIONS-IODIMETRY

Iodine is insoluble in water. Its solution is prepared in KI solution because of the formation of soluble KI_3. This **iodine solution acts as an oxidant.** Strong reducing agents like sodium thiosulphate and stannous chloride can react completely with iodine even in the acidic medium. However, weak reducing agents like arsenous oxide, sodium arsenite, trivalent antimony (*e.g.* tartaremetic, Sb_2O_3 etc.) react completely with iodine in **neutral medium.** The reactions of iodine with some reducing agents are :

(*i*) $I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$.
(*ii*) $I_2 + SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2HI$.
(*iii*) $I_2 + Na_3AsO_3 + H_2O \longrightarrow Na_3AsO_4 + 2HI$.
(*iv*) $2I_2 + Sb_2O_3 + 2H_2O \longrightarrow Sb_2O_5 + 4HI$.

From the above reactions, the equivalent weight of reducing agents ($Na_2S_2O_3$, $SnCl_2$, As_2O_3, Na_3AsO_3, Sb_2O_3 and tartaremetic) can be calculated by the use of following relations. The equivalent weight of the reducing agent will be equal to the number of parts of the substance that combine with 127 parts of iodine, I. (at. wt. of I = 127, Na = 23, S = 32, O = 16, Sn = 118.6, As = 75, Sb = 122)

$$I_2 \equiv 2Na_2S_2O_3.5H_2O \equiv$$
$$\frac{1}{2}As_2O_3 \equiv Na_3AsO_3 \equiv \frac{1}{2}Sb_2O_3 \equiv \text{Tartaremtic}$$

or
$$I \equiv Na_2S_2O_3.5H_2O \equiv \frac{1}{4}As_2O_3 \equiv$$
$$\frac{1}{2}Na_3AsO_3 \equiv \frac{1}{4}Sb_2O_3 \equiv \frac{1}{2}\text{ Tartaremtic} \quad ...(1)$$

No. of parts for equation (1) i.e., for I, $Na_2S_2O_3.5H_2O$...
(= eq. wt.) 127 248 1/4 × 198 1/2 × 192 1/4 × 292 1/2 × 334
= 49.5 = 96 = 73 = 167

For equivalent weights also see table 22.2.

EXAMPLE 38. *How will you prepare 1 litre of 0.1N and 0.1M sodium thiosulphate solution?*

SOLUTION. Sodium thiosulphate is a secondary standard substance. It reacts with iodine quantitatively as follows.

$$\underset{\text{2 mole}}{2Na_2S_2O_3} + \underset{\text{1 mole}}{I_2} \longrightarrow 2NaI + Na_2S_4O_6$$

Dissolve 24.8 g $Na_2S_2O_3$ in boiled out distilled water and make up the solution to one litre. Add 0.1 g Na_2CO_3 or a few drops of chloroform to make it stable for a few days.

(*I*) *To find exact molarity of $Na_2S_2O_3$ solution.* Let 19.6 mL of $Na_2S_2O_3$ solution reduce 20 mL of already standardised I_2 solution (0.05 M) completely. Thus we have,

1 mole $Na_2S_2O_3.5H_2O$
= [46 + 64 + 48 + 5(48)] = 248 g
1 mole I_2 = 2 × 127 = 254 g
∴ 1M $Na_2S_2O_3$ ≡ 248 g
0.1 M $Na_2S_2O_3$ ≡ 24.8 gL^-
Also 1M I_2 ≡ 254 gL^-
0.1 M I_2 ≡ 25.4 gL^-
Eq. wt. of
$Na_2S_2O_3.5H_2O$ = 248
Eq. wt. of I_2 = 127.

$$\frac{(\text{Molarity, } M_1 \times \text{Volume, } V_1) \text{ of } I_2}{(\text{Molarity, } M_2 \times \text{Volume, } V_2) \text{ of } Na_2S_2O_3} = \frac{1}{2}; \textbf{ Or } \frac{0.05 \times 20}{M_2 \times 19.6} = \frac{1}{2}$$

$$\therefore \quad M_2 = \frac{2 \times 0.05 \times 20}{19.6} = \frac{2}{19.6}$$

(*ii*) *To prepare exact 1000 mL of 0.1 M $Na_2S_2O_3$ solution.*

$Na_2S_2O_3$ solution to be prepared vs Orignal $Na_2S_2O_3$ solution.

$$M_3V_3 = M_4V_4;$$

Or 0.1 × 1000 mL = 2/19.6 × V_4 ; V_4 = 980 mL. Take 980 mL of $Na_2S_2O_3$ solution in a 1L flask and add water to get exact 1L solution. It will be exact 0.1 M $Na_2S_2O_3$. Or Take 1/2 × 980 *i.e.* 440 mL of $Na_2S_2O_3$ solution in a 500 mL measuring flask, add water to get exact 500 mL solution. It will be exact **0.1 M $Na_2S_2O_3$ SOLUTION.**

(*II*) (*i*) *To find exact normality of $Na_2S_2O_3$ solution.* Let 19.6 mL of $Na_2S_2O_3$ solution reduce 20 mL of already standardised I_2 solution (0.1N) completely. Thus, we have :

$Na_2S_2O_3$ solution vs I_2 solution

$$N_1V_1 = N_2V_2; N_1 \times 19.6 = 0.1 \times 20;$$
$$\therefore N_1 = \frac{2}{19.6}$$

(*ii*) *To prepare exact 1000 mL of 0.1N $Na_2S_2O_3$ solution.*

Required $Na_2S_2O_3$ Original $Na_2S_2O_3$ solution

$$N_3V_3 = N_4V_4;$$
$$0.1 \times 1000 \text{ mL} = 2/19.6 \times V_4; \therefore V_4 = 980 \text{ mL}$$

Take 980 mL of $Na_2S_2O_3$ solution in a 1L flask, add water to get exact 1 litre. This solution will be exact 0.1N $Na_2S_2O_3$ solution.

EXAMPLE 39. *How will you prepare 1L of 0.05 N iodine solution?*

SOLUTION. Iodine is a secondary standard substance. In order to prepare its standard solution, its approximate 0.05 N solution is prepared and its exact normality is found experimentally by the primary standard reductant (0.05 N As_2O_3 solution). From the redox reaction.

$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4HI$$

Equivalent weight of As_2O_3 = 49.5

∴ 1N As_2O_3 ≡ 49.5 gL^- As_2O_3
0.05 N As_2O_3 ≡ 49.5 × 0.05
= 2.475 gL^- As_2O_3
Similarly, 1N I_2 ≡ 127 g L^- I_2
0.05 N I_2 ≡ 127 × 0.05 = 6.35 gL^-

$$\begin{aligned} 2I_2 \text{ or } 4I &\equiv As_2O_3 \\ 4 \times 127 \text{ gI} &\equiv (2 \times 75) + (23 \times 16) \equiv 198 \text{ g} \\ \therefore \quad 127 \text{ gI} &\equiv 198/4 = 49.5 \text{ g} \\ \therefore \text{Eq wt. of } As_2O_3 &= 49.5; \text{Eq. wt. of } I_2 = 127 \end{aligned}$$

Weigh about 6.35 g I_2, add in 1L measuring flask, dissolve it in concentrated KI solution, add more water and make up the solution to exact one litre with distilled water. Stopper the measuring flask and keep in a cool, dark place.

(*i*) *To find exact normality of I_2 solution.* Suppose 19.70 mL of I_2 solution completely oxidise 20 mL of 0.05 N As_2O_3 (reductant) solution. Using normality equation, we have :

$$\begin{array}{lcl} I_2 \text{ solution} & \text{vs} & As_2O_3 \text{ solution} \\ N_1V_1 & = & N_2V_2\,; \\ N_1 \times 19.7 & = & 0.05 \times 20;\ \therefore N_1 = 20 \times 0.05/19.7 \end{array}$$

(*ii*) *To prepare exact 1000 mL of 0.05 N I_2 solution.*

I_2 solution to be prepared vs Original I_2 solution

$$\begin{aligned} N_1V_1 &= N_2V_2\,; 0.05 \times 1000 \text{ mL} \\ &= (20 \times 0.05)/19.7 \times V_2 \\ \therefore \quad V_2 &= \frac{0.05 \times 1000 \times 19.7}{20 \times 0.05} \\ &= 985 \text{ mL} \end{aligned}$$

Take 985 mL of original I_2 solution in a 1L measuring flask, add distilled water and make up the solution to exact one litre. This solution will be exact 0.05N I_2 solution.

Example 40. *How will you prepare 1 litre of 0.05 M iodine solution?*

Solution. Iodine is a secondary standard substance. In order to prepare its standard solution, its approximate 0.05 M solution is prepared and then its exact molarity is found experimentally by a primary standard reductant (*e.g.*, 0.025M arsenic (III) oxide solution). Mol. wt. of I_2 is 254 (*i.e.* 2 × 127 = 254). So, 1M $I_2 \equiv 254 \text{ gL}^- I_2$; 0.05 M $I_2 \equiv 0.05 \times 254 = 12.7 \text{ gL}^- I_2$.

Weigh about 12.7 g I_2 and prepare its solution as shown in example 39

(*i*) *To find exact molarity of iodine solution.* Suppose 19.8 mL of I_2 solution completely oxidise 20 mL of 0.025 M As_2O_3 (reductant) solution according to following equation

$$As_2O_3 + 2I_2 + 2H_2O \rightleftarrows As_2O_5 + 4HI$$

1 mole 2 mole

$$\text{We know that: } \frac{(\text{Molarity, } M_1 \times \text{Volume, } V_1) \text{ of } I_2}{(\text{Molarity, } M_2 \times \text{Volume, } V_2) \text{ of } As_2O_3}$$

$$= \frac{2}{1}\,; \frac{M_1 \times 19.8}{0.025 \times 20} = \frac{2}{1}$$

$$M_1 = \frac{0.025 \times 20 \times 2}{19.8} = 0.0505$$

(*ii*) *To prepare exact 1 litre of 0.05 M I_2 solution.*

I_2 solution to be prepared Original I_2 solution.

$$\begin{aligned} M_1V_1 &= M_2V_2 \\ 0.05 \times 1000 \text{ mL} &= 0.505 \times V_2 \\ V_2 &= (0.05 \times 1000)/0.0505 \\ &= 990.1 \text{ mL} \end{aligned}$$

Take 990.1 mL of original iodine solution in 1L measuring flask, add distilled water and make exact 1000 mL. This solution will be 0.05 M I_2 solution.

Example 41. *12.4 g of $Na_2S_2O_3.xH_2O$ are dissolved per litre. Find the value of x. Given N/20 iodine solution. Use 20 mL of $Na_2S_2O_3.xH_2O$ solution for titration.*

Solution. 20 ml of $Na_2S_2O_3xH_2O$ solution is mixed with 2-3 drops of freshly prepared starch solution **(indicator)** and titrated with N/20 iodine solution till end point (colourless to blue) is reached.

Let V_2 ml of iodine solution is used to get end point. The normality (N_1) of $Na_2S_2O_3xH_2O$ is calculated as follows:

$$\begin{array}{ll} Na_2S_2O_3xH_2O & I_2 \text{ solution} \end{array}$$

$$N_1V_1 = N_2V_2$$

$$N_1 \times 20 = \frac{1}{20} \times V_2\,; \quad \therefore \quad N_1 = \frac{V_2}{400}$$

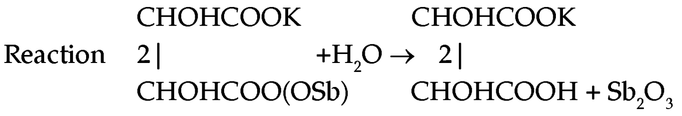
To calculate value of '*x*'

$$\begin{aligned} \text{Eq. wt. of } Na_2S_2O_3xH_2O &= \frac{\text{Strength}}{\text{Normality}} \\ &= \frac{12.4}{N_1 \textit{ i.e.}, V_2/400} = a \text{ (say)} \\ &= \text{Mol. wt. of } Na_2S_2O_3 \cdot xH_2O \\ \text{Mol. wt. of } Na_2S_2O_3 &= 2 \times 23 + 2 \times 32 + 3 \times 16 \\ &= 158 \end{aligned}$$

$$\begin{aligned} \text{Mol. wt. of } Na_2S_2O_3xH_2O \ (-) \text{ Mol. wt. of} & \\ Na_2S_2O_3 &= 18x\,; a - 158 = 18x \\ \boldsymbol{x} &= \boldsymbol{a - 158/18} \end{aligned}$$

Example 42. *Calculate the percentage of antimony in potassium antimony tartrate (tartaremtic), 2 g of which are dissolved per 250 mL of the given solution. Provided N/20 I_2* solution.

Solution.



$$\text{Reaction} \quad 2\begin{array}{l} CHOHCOOK \\ | \\ CHOHCOO(OSb) \end{array} + H_2O \rightarrow 2\begin{array}{l} CHOHCOOK \\ | \\ CHOHCOOH \end{array} + Sb_2O_3$$

$$Sb_2O_3 + 2I_2 + 2H_2O \rightleftarrows Sb_2O_5 + 4HI$$

Let V_1 ml of tartaremtic solution is used to get end point.

(*i*) The normality (N_1) of tartaremtic is calculated as follows :

$$\begin{array}{lcl} \text{Tartaremtic} & & I_2 \text{ solution} \\ N_1V_1 & = & N_2V_2 \end{array}$$

$$N_1 \times V_1 = \frac{1}{20} \times 20\,; \; N_1 = \frac{1}{V_1}$$

(*ii*) **To calculate strength of tartaremtic and antimony.**

250 ml solution contains tartaremtic = 2 g

1,000 ml solution contains tartaremtic

$$= \frac{2}{250} \times 1{,}000 = \mathbf{8\ gL^-}$$

Eq. wt. of antimony = 61

Strength of antimony = Normality × Eq. wt.

$$= N_1 \times 61 = x\ \text{gL}^-$$

To calculate percentage of antimony (Sb). Strength of tartaremtic $= 8\ \text{gL}^-$

$$\%\ \text{age of Sb} = \frac{x\ \text{gL}^-}{8\ \text{gL}^-} \times 100 = \frac{\mathbf{25}x}{\mathbf{2}}.$$

Example 43. *0.3 g of a sample of arsenous oxide (As_2O_3) was dissolved in NaOH solution, neutralised by HCl and volume made up to 100 ml. Determine volumetrically, the percentage purity of the sample. Given $\frac{N}{20}$ iodine solution.*

Solution. *Reaction* :

$$As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O\ ;$$

$$Na_3AsO_3 + I_2 + H_2O \rightleftharpoons Na_3AsO_4 + 2HI$$

The above reaction is reversible. To check the backward reaction due to HI formed, sodium bicarbonate is added which neutralises HI and the reaction becomes irreversible.

$$NaHCO_3 + HI \longrightarrow NaI + CO_2 + H_2O$$

20 ml of N/20 iodine solution is mixed with 2-3 drops of freshly prepared starch solution (*indicator*) and titrated with sodium arsenite solution till end point (blue to colourless) is obtained.

Let V_1 ml of arsenite solution is used to get end point.

(*i*)The normality (N_1) of arsenite solution is calculated as follows :

Arsenite solution I$_2$-solution

$$N_1V_1 = N_2V_2$$

$$N_1 \times V_1 = \frac{1}{20} \times 20\ ;\ N_1 = \frac{1}{V_1}$$

(*ii*) **To calculate strength of arsenous oxide.**

100 ml solution contains As_2O_3 = 0.3 g

$$1{,}000 \text{ ml solution contains } As_2O_3 = \frac{0.3}{100} \times 1{,}000 = 3.0\ \text{g}$$

$$\text{Eq. wt. of } As_2O_3 = \frac{198}{4} = 49.5$$

Strength of As_2O_3 = Normality × Eq. wt.

$$= N_1 \times 49.5\ \text{gL}^- = x \text{ (say)}$$

(*iii*) **To calculate the percentage purity of arsenous oxide.**

Wt. of impure sample = 3.0 gL$^-$; Wt. of pure sample $= x\ \text{gL}^-$

$$\therefore \text{Percentage purity} = \frac{\mathbf{x}}{\mathbf{3}} \times \mathbf{100}.$$

22.14 IODOMETRIC TITRATIONS

In such titrations, the oxidants like $K_2Cr_2O_7$, $KMnO_4$, $CuSO_4.5H_2O$ etc. are treated with KI solution in acidic medium. The iodine so produced is titrated with standard sodium-thiosuphate solution, using freshly prepared starch solution as indicator. Disappearance of blue colour is the end point.

The equivalent weight of oxidants and reductants in such titration are given in table 22.2.

Example 44. *You are provided with a mixture of ferrous sulphate ($FeSO_4.7H_2O$) and sodium sulphate (Na_2SO_4), 20 g of which have been dissolved per litre of the given solution. Determine volumetrically, the percentage composition of the mixture. Provided 0.05 N hypo (sodium thiosuphate) solution and approximately 0.05N $K_2Cr_2O_7$ solution.*

Solution. (1) Let the normality of $K_2Cr_2O_7$ solution is N_1.

(2) Let the normality of $FeSO_4$ (because Na_2SO_4 does not react with $K_2Cr_2O_7$) solution is N_2.

(3) *Strength of $FeSO_4.7H_2O$* = Normality × Eq. wt. of $FeSO_4.7H_2O = N_2 \times 278 = x$ (gL$^-$)

(4) *Percentage of $FeSO_4.7H_2O$* $= \frac{x \times 100}{20} = 5x$

Example 45. *Determine the percentage purity and available oxygen in the given commercial sample of potassium permanganate, 2 g of which have been dissolved per litre of the given solution. Provided N/20 hypo solution.*

Solution. (1) *Let the normality of $KMnO_4$ is N_1.*

(2) Strength of $KMnO_4$ = Normality × Eq. wt. of $KMnO_4 = N_1 \times 31.6 = x$ (gL$^-$)

(3) Percentage purity of $KMnO_4 = \frac{x \times 100}{2} = 50x$

(4) Eq. wt. of oxygen = 8

Strength of available oxygen = Normality × Eq. wt. $= N_1 \times 8 = y$ (gL$^-$)

$$\therefore \text{Percentage of available oxygen} = \frac{y \times 100}{2} = 50y$$

Example 46. *Write the procedure for finding the nomality of a given solution of $CuSO_4$ iodometrically if 20 mL of the given solution require 19.9 mL of 0.1N $Na_2S_2O_3$ solution.*

(1) *To find normality of $CuSO_4$ solution.* Take 20 ml of given $CuSO_4$ solution, add a pinch of Na_2CO_3 to get turbidity, and 1 : 1 acetic acid till turbidity dissolves, add 10 ml of 10% KI solution, wait for one minute to liberate I_2, dilute with water and titrate with hypo solution. Add freshly prepared starch solution near the end point when solution is pale yellow. Blue to white precipitate of cuprous iodide (Cu_2I_2) is the end point. (*i*) *To find normality of $CuSO_4$ solution.*

$CuSO_4$ solution. vs $Na_2S_2O_3$ solution

$$N_1V_1 = N_2V_2\ ;\ N_1 \times 20 = 0.1 \times 19.9\ ;$$

$$\therefore \quad N_1 = 199/2000 = \mathbf{0.0995}$$

22.15 IODINE (I_2) TITRATIONS IN TERMS OF MOLARITY
(For Calculations see section 22.3)

Example 47. *Calculate the atomic weight (m) of a metal, M in $M_2S_2O_3.5H_2O$, 2.48 g of which have been dissolved per 100 mL of the given solution. 19.9 mL of the given solution reduced 20 mL of 0.05 M I_2.*

Solution. The required reaction is :

$$\underset{2 \text{ mole}}{2Na_2S_2O_3} + \underset{1 \text{ mole}}{I_2} \longrightarrow 2NaI + Na_2S_4O_6$$

We know

$$\frac{(\text{Molarity, } M_1 \times \text{Volume, } V_1) \text{ of } I_2}{(\text{Molarity, } M_2 \times \text{Volume, } V_2) \text{ of } M_2S_2O_3.5H_2O} = \frac{1}{2}$$

$$\frac{0.05 \times 20}{M_2 \times 19.9} = \frac{1}{2}; \therefore M_2 = \frac{2 \times 0.05 \times 20}{19.9} = 0.1005$$

$\therefore$ Strength of $M_2S_2O_3.5H_2O$

$= \text{Molarity} \times \text{Mol. wt. of } M_2S_2O_3.5H_2O$

$24.8 = 0.1005 \times (2m + 202)$

$$\therefore \quad m = \frac{1}{2}\left[\frac{24.8}{0.1005} - 202\right] = \mathbf{22.4}$$

$\therefore$ At. wt. of metal, M = **22.4 a.m.u.**

100 mL solution contain

$M_2S_2O_3.5H_2O = 1.24$ g

1000 mL solution contain

$M_2S_2O_3.5H_2O = (2.48 \times 1000)/100$

$= 24.8\ gL^{-}$

Molarity of I_2 = 0.05M

Volume of I_2 = 20 mL Molarity of

$M_2S_2O_3.5H_2O = M_2$ = ? Volume of

$M_2S_2O_3.5H_2O$ = 19.9 mL

Let at. wt. of M = m

Mol. wt. of $M_2S_2O_3.5H_2O$

$= 2m + (2 \times 32) + (3 \times 16) + 5(18)$

$= 2m + 202$

Notes: (*i*) *For $K_2Cr_2O_7$ titrations in presence of KI and dil. H_2SO_4.*

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + H_2O + I_2;$$

$$I_2 + \text{Starch} \rightarrow I_2\text{-starch [complex (blue)]}$$

(*ii*) *For $KMnO_4$ titrations in presence of KI and dil. H_2SO_4.*

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$2KI + H_2SO_4 + O \longrightarrow K_2SO_4 + H_2O + I_2;$$

$$I_2 + \text{Starch} \longrightarrow I_2 - \text{starch complex (blue)}$$

(*iii*) *For $CuSO_4.5H_2O$ titrations in presence of KI, Na_2CO_3 and acetic acid.*

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4;$$

$$I_2 + \text{Starch} \longrightarrow I_2 - \text{starch complex (blue).}$$

In all the above three cases, I_2 produced is titrated with sodium thiosulphate solution (hypo). The quantitative reaction that takes place is given below.

$$\underset{\text{Sodium thiosulphate}}{2Na_2S_2O_3} + I_2 \longrightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$$

Example 48. *$Na_2S_2O_3.5H_2O$ was partially dehydrated and 20.2 g of the latter were dissolved per litre of the given solution. 20 mL of 0.1 N $K_2Cr_2O_7$ solution was treated with dil. H_2SO_4 and excess of KI. I_2 liberated required 18.5 mL of given thiosulphate solution. Calculate the precentage loss of weight due to dehydration of salt.*

Soluton. *To find normality of $Na_2S_2O_3$ solution.*

$Na_2S_2O_3$ vs $K_2Cr_2O_7$

$N_1V_1 = N_2V_2$; $N_1 \times 18.5 = 0.1 \times 20$;

$$N_1 = \frac{20}{185}$$

(*i*) Eq. wt. of $Na_2S_2O_3.5H_2O$ = 248

(*ii*) Wt. of partially dehydrated thiosulphate = 20.2 g.

$\therefore$ Wt. of $Na_2S_2O_3.5H_2O$ = (20/185) × 248 = 26.81 g

Loss of weight due to dehydration = 26.81 – 20.2 = 6.61 g

% loss of weight due to partial dehydration = (6.61 × 100)/26.81 = 24.65%

Example 49. *Calculate the value of x in $CuSO_4xH_2O$, 6.575 g of which have been dissolved per 250 mL of the given solution. 20 mL of this solution on treatment with dil. H_2SO_4 and KI liberated I_2 which was reduced by 21.1 mL of 0.1N $Na_2S_2O_3$ solution (At. wt. of Cu = 63.5, S = 16, O = 16, H = 1).*

Solution. (*i*) To find normality (N_1) of $CuSO_4$ solution.

$CuSO_4$ $K_2Cr_2O_7$

$N_1V_1 = N_2V_2$

$N_1 \times 20 = 0.1 \times 21.1$;

$\therefore N_1 = 211/2000 = 0.1055$

$\therefore$ Eq. wt. of $CuSO_4.xH_2O$ = Strength/N_1 = 26.3/0.1055 = 249.23

Now 159.5 + 18x = 249.23 ; x = (249.23 – 159.5)/18

$x = 4.985 \simeq 5$

(*i*) 250 mL $CuSO_4$ solution ≡ 6.575 g $CuSO_4xH_2O$
1000 mL $CuSO_4$ solution ≡ (6.575 × 1000)/250 = 26.3 gL^{-}

(*ii*) Eq. wt. of $CuSO_4$ = 63.5 + 32 + (4 × 16) = 159.5

Example 50. *Calculate volumetrically, the atomic weight (m) of an alkali metal, 6.0 g of the arsenite of which has been dissolved per 250 mL of the given solution. 20 mL of the arsenite solution require 19.9 mL of 0.1N I_2 solution.*

Solution. Let alkali metal arsenite = M_3AsO_3

(*i*) *To find normality of M_3AsO_3 solution.*

M_3AsO_3 solution $\qquad$ I_2 solution

$$N_1V_1 = N_2V_2$$

$$\therefore \quad N_1 \times 20 = 0.1 \times 19.9\,;$$

$$N_1 = 199/2000 = 0.0995$$

Let at. wt. of M $= m$;

250 mL solution contain $M_3AsO_3 = 6.0$ g

1000 mL solution contain

$$M_3AsO_3 = (1 \times 1000)/250 = 24 \text{ g}$$

∴ Eq. wt. or Mol. wt. of

$$M_3\,AsO_3 = 24.0/0.0995 = 241.2 \text{ g}$$

∴ Eq. wt. or mol. wt. of

$$M_3AsO_3 = 3\,m + 75 + (3 \times 16) = 3m + 123$$

$$\therefore \quad 3m + 123 = 241.2\,;\ m = (241.2 - 123)/3 = \mathbf{39}$$

EXAMPLE 51. *You are provided with a solution of 7.5 g of arsenous oxide (As_2O_3) and sodium arsenite (Na_3AsO_3) per litre. If 20 mL of this solution consumed 20.30 mL of 0.1 NI_2 solution for reducing I_2, calculate the percentage composition of the mixture (at. wt. of As = 75, O = 16, Na = 23).*

SOLUTION. Let wt. of

$$As_2O_3 = x \text{ g};$$

$$\text{wt. of } Na_3AsO_3 = 7.5 - x \text{ g}.$$

$$\text{Eq. wt. of } As_2O_3 = 49.5\,;$$

Eq. wt. of Na_3AsO_3= 96 (from table 22.2)

(*i*) To find total normality of solution

Mixed solution vs I_2 solution

$$N_1V_1 = N_2V_2$$

$$N_1 \times 20 = 0.1 \times 20.3\,;$$

$$\therefore \quad N_1 = \frac{203}{2000} = \mathbf{0.1015}$$

(*ii*) $$\text{Normality of } As_2O_3 = \frac{x}{49.5}\,;$$

$$\text{normality of } Na_3AsO_3 = (7.5 - x)/96$$

(*iii*) From (*i*) and (*ii*) $$\frac{x}{49.5} + \frac{7.5 - x}{96} = 0.1015$$

$$96x + 371.25 - 49.5x = 482.33$$

$$\therefore \quad 46.5x = 111.08\,;\ x = 2.39 \text{ g}$$

$$\therefore \quad \%\text{ age of } As_2O_3 = (2.39 \times 100)/7.5 = \mathbf{31.87\%}$$

$$\%\text{ age of } Na_3AsO_3 = 100 - 31.87 = \mathbf{68.13\%}$$

EXAMPLE 52. *8.82 g of potassium antimony tartrate. $C_4H_4O_6K(SbO)\frac{1}{2}H_2O$ salt were dissolved in water and the solution made up to one litre. Calculate the atomic weight of antimony if 20 mL of this solution reduced 21.55 mL of 0.049 N I_2 solution completely (at. wt. of K = 39, C = 12, H = 1, O = 16)*

SOLUTION. (*i*) *To find mol. wt. of potassium antimony tartrate* (*ii*) *Let at. wt. of Sb = x*

Given solution $\qquad$ I_2 solution

$$N_1V_1 = N_2V_2\,;\ 20 \times N_1 = 0.049 \times 21.55$$

$$\therefore \quad N_1 = (0.049 \times 21.55)/20 = 0.0428$$

$$\text{Wt. of given salt} = 8.82 \text{ gL}^{-}\,;\ \text{eq. wt.}$$

$$\text{of salt} = 8.82/0.0528 = 167.$$

(*iii*) Mol. wt. of $C_4H_4O_6.K(SbO).\ \frac{1}{2}H_2O$

$$= (4 \times 12) + (4 \times 1) + (6 \times 16) + 39 + x + 16 + 9 = \mathbf{212 + x.}$$

Equating mol. wts we have,

$$212 + x = 334\,; \qquad \therefore\ x = 334 - 212 = \mathbf{122}$$

Or $\qquad$ Mol. wt. $= 2 \times 167 = 334$

($\because$ Eq. wt. of salt = 167 (see table 22.2)

22.16 NORMALITY = MOLARITY × CHANGE IN OXIDATION STATE

EXAMPLE 53. *In a volumetric experiment, it was found that a solution of $KMnO_4$ is reduced to $MnSO_4$. If the normality of a solution is 1.0 N, then molarity of the solution will be:*

(*a*) 0.5 M $\qquad$ (*b*) 0.2 M

(*c*) 1.0 M $\qquad$ (*d*) 0.4 M

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SOLUTION. Normality = Molarity × change in oxidation state. ...(1)

Given $K\overset{7+}{Mn}O_4 \longrightarrow \overset{2+}{Mn}SO_4$. So, change in oxidation state = 7 – 2 = 5. Substituting in equation (1), we have: 1 = Molarity × 5. So, molarity = 1/5 = 0.2. So, the correct answer is (*b*)

22.17 MISCELLANEOUS EXAMPLES

EXAMPLE 53. *Calculate the normality of NaOH solution whose 25 mL are exactly neutralised by 20 mL of N/20 H_2SO_4.*

SOLUTION. Normality of NaOH = N_1, Volume = 25 mL; Normality of $H_2SO_4 = \frac{1}{20}$, Volume = 20 mL. Using normality equation, we have :

$$N_1V_1\,(NaOH) = N_2V_2\,(H_2SO_4)$$

$$N_1 \times 25 = \frac{1}{20} \times 20\,;$$

$$N_1 = \frac{20 \times 1}{20 \times 25} = \frac{1}{25} = \mathbf{0.04\ N} \qquad \textbf{Ans.}$$

EXAMPLE 54. *Calculate the molarity of NaOH solution whose 25 mL are exactly neutralised by 20 mL of M/20 H_2SO_4.*

SOLUTION. *Reaction* :

$$\underset{2\text{ mol}}{2NaOH} + \underset{1\text{ mol}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$$

$$\frac{M_1V_1(NaOH)}{M_2V_2(H_2SO_4)} = \frac{\text{no. of mol of NaOH in balanced equation}}{\text{no. of mol of } H_2SO_4 \text{ in balanced equation}}$$

$$\frac{M_1 \times 25}{\frac{1}{20} \times 20} = \frac{2}{1} \quad M_1, = 2 \times \frac{1}{20} \times \frac{20}{25}$$

$$= \mathbf{0.08\ M} \qquad \textbf{Ans.}$$

EXAMPLE 55. *Calculate the molarity of $KMnO_4$ solution whose 25 mL exactly oxidise 20 mL of M/20 oxalic acid solution.*

SOLUTION. Reaction.

$$\underset{2\text{ mol}}{2KMnO_4} + \underset{5\text{ mol}}{5H_2C_2O_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$$\frac{M_1V_1\,(\text{K MnO}_4)}{M_2V_2\,(\text{H}_2\text{C}_2\text{O}_4)} = \frac{\begin{array}{l}\text{no. of mol of KMnO}_4\\ \text{in a balanced equation}\end{array}}{\begin{array}{l}\text{no. of mol of H}_2\text{C}_2\text{O}_4\\ \text{in a balanced equation}\end{array}}$$

$$\frac{\text{M}_1\times 25}{\frac{1}{20}\times 20} = \frac{2}{5}\,;\; M_1 = \frac{2}{5}\times\frac{1}{20}\times\frac{20}{25}$$

$$= \mathbf{0.016\ M} \qquad \textbf{Ans.}$$

EXAMPLE 56. *Determine the number of molecules of water of crystallisation in Mohr's salt [$FeSO_4.(NH_4)_2SO_4.xH_2O$] whose 9.8 g have been dissolved per 250 mL of the solution. 20 mL of this solution required 20 mL of M/50 $KMnO_4$ for complete oxidation. (at. wt., Fe = 56, S = 32, O = 16, N = 14, H = 1)*

SOLUTION. Mol. wt. of $\text{FeSO}_4.(\text{NH}_4)_2\text{SO}_4.x\text{H}_2\text{O}$ = 56 + 32 + (4 × 16) + 2[14 + (4 × 1)] + 32 + (4 × 16) + x[(2 × 1) + 16] = 248 + 18x

Reaction. $\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

1 mol 5 mol

$$\frac{M_1V_1\,(\text{K MnO}_4)}{M_2V_2\,(\text{Mohr's salt})} = \frac{\begin{array}{l}\text{no. of mol of K MnO}_4\\ \text{in the balanced equation}\end{array}}{\begin{array}{l}\text{no. of mol of Fe}^{2+}\\ \text{in the balanced equation}\end{array}}$$

$$\frac{\frac{1}{50}\times 20}{M_2\times 20} = \frac{1}{5}\,;\; M_2 = \frac{1}{50}\times\frac{20}{20}\times 5 = \frac{1}{10}\,M$$

(*i*) ∴ Strength of Mohr's salt = Molariy × mol. wt.

$$= \frac{1}{10}\times(284+18x)$$

(*ii*) 250 mL solution contain Mohr's salt = 9.8 g

1000 mL solution contain Mohr's salt

$$= \frac{9.8}{250}\times 1000 = 39.2\ \text{g}$$

From (*i*) and (*ii*), we have

$$\frac{284+18\,x}{10} = 39.2\,;\; 18x = (39.2\times 10) - 284$$

$$= 108\,;\; x = \frac{108}{18} = 6$$

∴ no. of molecules of water of crystallisation = **6** **Ans.**

> **Note.** For more numericals, see chapter 17 "Solution-Concentration"

DIFFERENT METHODS TO EXPRESS CONCENTRATION OF SOLUTION.

Methods to express concentration of solutions include **normality** (N), **molarity** (M), **molality** (*m*), **Strength of solution** (S) in **terms of percentage, mole fraction** (*x*)., **Formality** (F) and **ionic strength** (μ)

1. **Normality (N).** The number of equivalents of a solute present in one litre of solution gives the normality of solution.

(*a*) **Equivalent (Eq.) of solute** = Normality (N) × Volume in litre (L) = $\dfrac{\text{wt. of solute}}{\text{Eq. wt. of solute}}$

Or $\quad$ **Eq.** $= \boldsymbol{N\times V}$ **in L** $= \dfrac{\mathbf{W}}{\mathbf{E}}$

Where : **Normality (*N*)**

$$= \frac{\text{Equivalent of solute}}{\text{Volume of solution in litre (L)}}\,;$$

$$= \frac{\text{wt. of solute (= w)}}{\text{Eq. wt. of solute (E)}\times\text{Volume of solution in litre (L)}}$$

Or $\quad N = \dfrac{W}{E\times V\text{ in }L}\ \text{g. eq L}^{-}.$

Since 1L = 1000 mL = 1000 cm^3

$$\therefore\quad N = \frac{W}{E}\times\frac{1000}{V\text{ in mL (or cm}^3)}$$

Also,no. of equivalent of an acid

$$= \frac{\text{wt.}}{\text{Formula wt.}}\times\text{basicity}$$

no. of equivalents of a base

$$= \frac{\text{wt.}}{\text{Formula wt.}}\times\text{Acidity}$$

(*b*) **Milliequivalent** (M.eq) of solute = Normality (*N*) × Volume in mL (or cm^3)

$$= \frac{\text{wt. of solute}}{\text{Eq. wt. of solute}}\times 1000$$

Or $\quad \text{M.eq} = \dfrac{W}{E}\times 1000$

> **Note1.** Normality of a solution depends upon temperature because it involves volumes which changes with temperature. It changes with dilution.
> **2.** Equivalent and milliequivalent of reactants react in equal number to give same number of equivalent or milliequivalent of products. Also, eq. and M.eq do not change with dilution.
> **3.** While solving numericals based on equivalent or milliequivalent, there is no need to balance the chemical reaction. In such cases :
> **4.** No. of M.eq = Normality × Volume in mL
> **5.** Normality = m.eq (mL)$^-$ *i.e.*, no. of milliequivalent per millilitre of solution.

EXAMPLE 57. *Calculate the number of milliequivalent in 25 mL of 0.1 N $CaCl_2$ solution.*

SOLUTION. $\text{CaCl}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{Cl}^-$

∴ No. of M.eq = Normality × Volume in mL

= 0.1 × 25 = **2.5** **Ans.**

EXAMPLE 58. *1.98 L of ammonia at 303 K and 0.2 atm pressure neutralised completely 130 mL of sulphuric acid. Find the normality of sulphuric acid.*

SOLUTION. P = 0.2 atm, V = 1.98 L, n = no. of mol of NH_3, R = 0.0821 L atm K$^-$ mol$^-$, T = 303 K. We know that :

$$PV = nRT\,;$$

$$n = \frac{PV}{RT} = \frac{0.2\ \text{atm}\times 1.98\ \text{L}}{0.0821\ \text{L atm K}^{-}\text{mol}^{-}\times 303\ \text{K}}$$

Or $n = 0.01592$

But no. of mol of

NH_3 = no. of equivalent of NH_3

no. of equivalent of

$H_2SO_4 = 0.01592$ ∴ M.eq of NH_3

= No. of equivalent of $NH_3 \times 1000$

$= 0.01592 \times 1000 = 15.92$

But no. of M.eq of

H_2SO_4 = no. of M.eq of NH_3

Or Normality × Volume in mL of

$H_2SO_4 = 15.92$

$N \times 130 = 15.92$;

$$N = \frac{15.92}{130} = \mathbf{0.1225} \qquad \textbf{Ans.}$$

EXAMPLE 59. *The formula weight of an acid is 82.0. 100 cm³ of a solution of this solution containing 39.0 g of the acid per litre were completely neutralised by 95.0 cm³ of aqueous NaOH containing 40.0 g of NaOH per litre. What is the basicity of the acid?* **(UPSEAT, 2000)**

SOLUTION. (*i*) wt. of acid = 39.0 g ;

Formula weight of acid = 82.0g. Basicity of acid $= n$;

$$\text{Eq. wt. of acid} = \frac{\text{Formula wt.}}{\text{Basicity}} = \frac{82}{n}$$

$$\therefore \quad \text{Normality of acid} = \frac{\text{wt.}}{\text{eq. wt.} \times \text{volume in litre}}$$

$$= \frac{39}{\frac{82}{n} \times 1} = \frac{39\,n}{82}$$

(*ii*) wt. of alkali = 40 g ; eq. wt. of

$$\text{NaOH} = \frac{23+16+1}{1} = 40,$$

Volume = 1L

$$\therefore \text{ Normality of NaOH} = \frac{\text{wt.}}{\text{eq. wt.} \times \text{volume in litre}}$$

$$= \frac{40}{40 \times 1} = 1.$$

Using normality equation, we have :

N_1V_1 (acid) $= N_2V_2$ (alkali)

$$\frac{39n}{82} \times 100 = 1 \times 95 ;$$

$$n = \frac{95 \times 82}{39 \times 100} = 1.99 \simeq 2$$

∴ Basicity of acid = **2** **Ans.**

EXAMPLE 60. *Find the normality of the resulting solution obtained by mixing 4 drops (0.2 mL) of 0.1N H_2SO_4 in one litre of distilled water.*

SOLUTION. Note that the milliequivalents of a solute do not change on dilution

∴ M.eq. of dil H_2SO_4 = M.eq. of conc. H_2SO_4

$N_1V_1 = N_2V_2$

[∵ M.eq = Normality × Volume in mL}

$N_1 \times 1000 = 0.1 \times 0.2$;

$$N_1 = \frac{0.1 \times 0.2}{1000} = \mathbf{2 \times 10^{-5}N} \quad \textbf{Ans.}$$

Type. No. of equivalents $= \dfrac{\text{wt.}}{\text{Eq. wt.}}$;

$$\text{Normality} = \frac{\text{no. of equivalents}}{\text{Volume in litre}}$$

EXAMPLE 61. *2 g of calcium was burnt in excess of oxygen to get CaO. CaO so formed was dissolved in water and the solution was made up to 500 mL. Calculate the normality of the alkaline solution. (at. wt. Ca = 40, O = 16)*

SOLUTION. $\underset{\substack{40\text{ g}\\20\text{ g}}}{Ca} + \underset{\substack{16\text{ g}\\8\text{ g}}}{1/2\,O_2} \longrightarrow \underset{\substack{40+16=56\text{ g}\\28\text{ g}}}{CaO}$ ...(*i*)

wt. of Ca = 2 g ; Eq. wt. of

$$\text{Ca} = \frac{\text{At. wt.}}{\text{Valency}} = \frac{40}{2} = 20.$$

$$\text{Eq. wt. of CaO} = \frac{\text{Mol. wt. of CaO}}{\text{Total} + \text{ve charge}} = \frac{40+16}{2} = 28$$

From equation (*i*) : 20 g Ca form

CaO = 28 g; 2 g Ca form

$$\text{CaO} = \frac{28}{20} \times 2 = 2.8\text{ g}$$

(*ii*) Normality of

$$\text{CaO} = \frac{\text{wt. of CaO}}{\text{Eq. wt. of CaO}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{2.8}{28} \times \frac{1000}{500} = 0.2 \qquad \textbf{Ans.}$$

Type. *To find specific gravity of acid or base*

EXAMPLE 62. *25 cm³ of a H_3PO_4 solution, whose 1 cm³ was diluted to 250 cm³, needed 35.15 cm³ of 0.101 N NaOH solution for neutralisation when phenolphthalein was used as an indicator. Calculate the specific gravity of H_3PO_4 (at. wt ; H = 1 P = 31, O = 16)*

SOLUTION. Mol. wt. of

H_3PO_4 ($H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-}$)

$= (3 \times 1) + 31 + (4 \times 16) = 98.$

$$\text{So,Eq. wt of } H_3PO_4 = \frac{\text{Mol. wt.}}{\text{Total charge on cation or anion}}$$

$$= \frac{98}{3} = 32.67$$

(*i*) *To find normality of original H_3PO_4.*

H_3PO_4 NaOH

$N_1V_1 = N_2V_2$

$N_1 \times 1 = 0.101 \times 35.15$

∴ $N_1 = 0.101 \times 35.15 = 3.55$

(*ii*) *To find normality of diluted H_3PO_4.*

Original H_3PO_4 Diluted H_3PO_4

$N_3V_3 = N_4V_4$; $(0.101 \times 35.15) \times 250$

$= N_4 \times 25$

$$\therefore \quad N_4 = \frac{0.101 \times 35.15 \times 250}{25} = 35.5$$

$$\text{But} \quad \text{Normality} = \frac{\text{wt. of } H_3PO_4}{\text{Eq. wt. of } H_3PO_4} \times \frac{1000}{\text{Volume in cm}^3}$$

$$\therefore \quad \text{wt. of } H_3PO_4$$

$$= \frac{\text{normality} \times \text{Eq. wt. of } H_3PO_4 \times \text{Volume in cm}^3}{1000}$$

$$= \frac{35.5 \times 32.67 \times 1}{1000} = 1.597 \simeq 1.16 \text{ g}$$

$\therefore$ Specific gravity of H_3PO_4 = **1.16 gL$^-$ Ans.**

Double titration

In such titrations, different indicators are used. For example, consider the titration of a solution containing NaOH, Na_2CO_3 and inert impurities, with HCl. In this titration, two indicators are used. One is phenolphthalien while the other is methyl orange.

(*a*) **Use of phenolphthalein indicator.** When phenolphthalein indicator is used, NaOH is completely neutralised while Na_2CO_3 gets neutralised to half of its amount present. The reactions are :

(*i*) $NaOH + HCl \longrightarrow NaCl + H_2O$
$(n = 1)$

(*ii*) $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$
$(n = 2)$

$$\text{Here, eq. of } \underset{(n=1)}{NaOH} = \frac{1}{2} \text{ eq. of } \underset{(n=2)}{Na_2CO_3} = \text{eq. of HCl} \quad ...(1)$$

For $NaOH \rightleftharpoons Na^+ + OH^-$
1 mol
oxidation state = + 1
$\therefore n = 1 \times 1 = 1$
For $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$
2 mol
oxidation state = +1
$\therefore n = 2 \times 1 = 2$

Phenolphthalein indicates end point when Na_2CO_3 is converted to $NaHCO_3$.

(*b*) Use of methyl orange indicator. When methyl orange indicator is used, NaOH as well as Na_2CO_3 get completely neutralised by HCl. The reactions are :

(*i*) $NaOH + HCl \longrightarrow NaCl + H_2O$

(*ii*) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

Here, eq. of NaOH = eq. of Na_2CO_3 = eq. of HCl.
$n = 2$

Note. Titration of a mixture of solutions of NaOH, Na_2CO_3 and inert impurities can be done by two methods :

(*i*) Firstly use phenolphthalein indicator and titrate with acid (say, HCl) till pink to colourless end point is obtained. Now, use methyl orange indicator in the same solution till light yellow to pink end point is obtained.

(*ii*) Firstly use phenolphthalein indicator and titrate solution with acid (say, HCl) till pink to colourless end point is obtained. Volume of HCl used gives the neutralisation of total NaOH and half of Na_2CO_3. Now again take known volume of mixture, add methyl orange indicator and titrate with acid (HCl) till light yellow to pink end point is obtained. Volume of HCl used gives the neutralisation of total NaOH and total Na_2CO_3. Using law of equivalents ($N_1V_1 = N_2V_2$), the percentage composition of mixture can be calculated.

EXAMPLE 63. *1.98 g sample of a mixture of potassium sulphate, sodium carbonate and sodium bicarbonate was heated till CO_2 gas stopped coming out. The volume of CO_2 gas liberated at 298 K and 740 mm pressure was 125 mL. A 1.48 g of the sample required 145 mL of 0.1 M HCl for complete neutralisation. Calculate the % age composition of the given mixture.*

SOLUTION. Out of K_2SO_4, Na_2CO_3 and $NaHCO_3$, K_2SO_4 and Na_2CO_3 do not liberate CO_2 gas on heating. $NaHCO_3$ decomposes as :

$$\underset{(2\text{ mol})}{2NaHCO_3} \longrightarrow Na_2CO_3 + \underset{(1\text{ mol})}{CO_2} + H_2O \quad ...(1)$$

$$P = \frac{740}{760} \text{ atm} ; V = \frac{125}{1000} \text{L} ;$$

R = 0.082 L atm K$^-$ mol$^-$;

T = 298 K ; number of moles of

CO_2, n = ? We know :

$$PV = nRT \quad \textbf{Or} \quad n = \frac{PV}{RT}$$

$$\textbf{Or} \quad n = \frac{740}{760} \text{ atm} \times \frac{125}{1000} \text{ L} \times \frac{1}{0.82 \text{ L atm K}^- \text{mol}^-} \times \frac{1}{298 \text{ K}}$$

$= 4.98 \times 10^{-3}$ mol

$\therefore$ Number of moles of $NaHCO_3$ from reaction (1)

$$= 4.98 \times 10^{-3} \times 2 \left[\begin{matrix} 2NaHCO_3 & \equiv CO_2 \\ 2 \text{ mol} & 1 \text{ mol} \end{matrix} \right.$$

$= 9.96 \times 10^{-3}$

Equivalents of HCl used

$$= \text{vol in L} \times \text{normality} = \frac{145}{1000} \times 0.1$$

$= 0.0145$

$$\underset{1\text{ mol}}{NaHCO_3} + \underset{1\text{ mol}}{HCl} \longrightarrow NaCl + CO_2 + H_2O \quad ...(2)$$

Equivalents of $NaHCO_3$ in 1.98 g sample = 9.96×10^{-3}

Equivalents of $NaHCO_3$ in 1.48 g sample

$$= \frac{9.96 \times 10^{-3}}{1.98} \times 1.48 = 7.4 \times 10^{-3}$$

$\therefore$ Equivalents of $Na_2CO_3 = 0.0145 - (7.4 \times 10^{-3}) = 0.0145 - 0.0074 = 7.1 \times 10^{-3}$

$$\underset{1\text{ mol}}{Na_2CO_3} + \underset{2\text{ mol}}{2HCl} \longrightarrow 2NaCl + CO_2 + H_2O \qquad ...(3)$$

Since no atom in reaction (3) undergoes oxidation number change, so 'n' factor of $Na_2CO_3 = 2$

$$\left[\therefore\ Na_2CO_3 \rightleftharpoons \underset{2\times +1 = 2}{2Na^+} + CO_3^{2-}\right]$$

$$\therefore \text{Moles of } Na_2CO_3 = \frac{7.1\times 10^{-3}}{n(=2)} = 3.55\times 10^{-3}$$

(*a*) Mass of $NaHCO_3$ in 1.48 g = Equivalents of $NaHCO_3$ × Eq. wt. of $NaHCO_3 = 7.4 \times 10^{-3} \times 84 = 0.6216$ g.

$$\left[\because \text{Eq.wt. of } NaHCO_3 = \frac{\text{Mol. wt.}}{2} = \frac{23+1+12+3\times 16}{1} = 84\right]$$

$$\therefore \text{ \% age of } NaHCO_3 = \frac{\text{wt. of } NaHCO_3}{\text{Total wt.}} \times 100$$

$$= \frac{0.6216}{1.48} \times 100 = \mathbf{42} \quad \textbf{Ans.}$$

(*b*) Mass of Na_2CO_3 in 1.48 g sample = Equivalents of Na_2CO_3 × Eq. wt. of $Na_2CO_3 = 7.1 \times 10^{-3} \times 53 = 0.3763$

$$\left[\begin{aligned}&\because \text{Eq. wt. of } Na_2CO_3 = \frac{\text{Mol. wt.}}{2}\\ &= \frac{(2\times 23)+12+(3\times 16)}{2} = 53\end{aligned}\right]$$

$$\text{\% age of } Na_2CO_3 = \frac{\text{wt. of } Na_2CO_3}{\text{Total wt.}} \times 100$$

$$= \frac{0.3763}{1.48} \times 100 = \mathbf{25.43} \qquad \textbf{Ans.}$$

(*c*) Mass of K_2SO_4 = Total mass – (mass of $NaHCO_3$ + mass of Na_2CO_3) = 1.48 – (0.6216 + 0.3763) = 1.48 – 0.9979 = 0.4821

$$\text{\% age of } K_2SO_4 = \frac{\text{wt. of } K_2SO_4}{\text{Total wt.}} \times 100$$

$$= \frac{0.4821\times 100}{1.48} = \mathbf{32.57} \qquad \textbf{Ans.}$$

EXAMPLE 64. *20 mL of a solution containing NaOH and Na_2CO_3 was titrated with 0.96 N HCl using phenolphthalein indicator. As a result, 16 mL of acid was used up to the end point. With methyl orange indicator, 20 mL of the mixture solution required 22 mL of the same acid up to the end point. Calculate the amount of each substance in the mixture in grams per litre.*

SOLUTION. (*a*) *Use of phenolphthalein indicator.*

$$\begin{aligned}\text{M.eq. of HCl acid} &= \text{Volume in mL}\\ \times \text{ normality} &= 20 \times 0.96 = 19.20\end{aligned}$$

$$\text{But M.eq. of acid} = \text{M.eq. of NaOH} + \frac{1}{2} \text{ M.eq. of } Na_2CO_3 \qquad ...(1)$$

$$19.20 = \text{M.eq. of NaOH} + \frac{1}{2} \text{ M.eq. of } Na_2CO_3 \qquad ...(2)$$

(*b*) *Use of methyl orange indicator.*

$$\begin{aligned}\text{M.eq. of HCl acid} &= \text{Volume in mL}\\ \times \text{ Normality} &= 22 \times 0.96 = 21.12\end{aligned}$$

$$\text{But M.eq. of acid} = \text{M.eq. of NaOH} + \text{M.eq. of } Na_2CO_3$$

$$21.12 = \text{M.eq. of NaOH} + \text{M.eq. of } Na_2CO_3 \qquad ...(3)$$

Subtracting equation (1) from (2), we get :

$$\begin{aligned}21.12 &= \text{M.eq. of NaOH} + \text{M.eq. of } Na_2CO_3\\ 19.20 &= \text{M.eq. of NaOH} + \frac{1}{2}\text{ M.eq. of } Na_2CO_3\\ - \quad & \quad - \qquad\qquad\qquad -\\ \hline 1.92 &= \frac{1}{2}\text{ M.eq. of } Na_2CO_3.\end{aligned}$$

$\therefore$ M.eq. of $Na_2CO_3 = 2 \times 1.92 = 3.84$ ...(4)

Substituting the value of M.eq. of Na_2CO_3 from equation (4) in equation (3), we get :

$$21.12 = \text{M.eq. of NaOH} + 3.84$$

$$\therefore \text{ M.eq. of NaOH} = 21.12 - 3.84 = 17.28 \qquad ...(5)$$

(*c*) M.eq. of

$$Na_2CO_3 = \frac{\text{wt. of } Na_2CO_3}{\text{Eq. wt. of } Na_2CO_3} \times 1000$$

$$3.84 = \frac{\text{wt. of } Na_2CO_3}{53} \times 1000$$

$$\left[\begin{aligned}&\because \text{Eq. wt. of } Na_2CO_3 = \frac{\text{Mol. wt.}}{2}\\ &= \frac{(2\times 23)+12+(3\times 16)}{2} = 53\end{aligned}\right]$$

$$\therefore \quad \text{wt. of } Na_2CO_3 = \frac{53\times 3.84}{1000}$$

Wt. of Na_2CO_3 in one litre

$$= \frac{53\times 3.84}{1000} \times \text{Eq. wt. of } Na_2CO_3$$

$$= \frac{53\times 3.84\times 53}{1000} = \mathbf{10.79\ g} \qquad \textbf{Ans.}$$

$$(d)\ \text{M.eq. of NaOH} = \frac{\text{wt. of NaOH}}{\text{Eq. wt. of NaOH}} \times 1000$$

$$17.28 = \frac{\text{wt. of NaOH}}{40} \times 1000$$

$$\left[\because \text{ Eq. wt. of NaOH} = \frac{\text{Mol. wt.}}{1} = \frac{23+16+1}{1} = \frac{40}{1} = 40\right]$$

$$\therefore \quad \text{Wt. of NaOH} = \frac{17.28\times 40}{1000}$$

$$\text{Wt. of NaOH in one litre} = \frac{17.28\times 40}{1000} \times \text{Eq, wt. of NaOH}$$

$$= \frac{17.28\times 40\times 40}{1000} = \mathbf{27.65\ g} \qquad \textbf{Ans.}$$

EXAMPLE 65. *50 mL of a solution containing one gram of each of NaOH, $NaHCO_3$ and Na_2CO_3 was titrated with 1N HCl. What will be the titre reading if :*

(*a*) *Only methyl orange is used as indicator from the very beginning.*

(*b*) *Only phenolphthalein is used as an indicator.*

(*c*) *Methyl orange is added after the first end point with phenolphthalein.*

(*at. wt. Na = 23, O = 16, H = 1, C = 12*)

Solution. Mixture solution contains NaOH, $NaHCO_3$ and Na_2CO_3.

$$\text{Eq. wt. of NaOH} = \frac{\text{Mol. wt.}}{1} = \frac{23+16+1}{1} = 40.$$

$$\text{Eq. wt. of } Na_2CO_3 = \frac{\text{Mol. wt.}}{2}$$

$$= \frac{(2\times 23)+12+(3\times 16)}{2} = \frac{106}{2} = 53$$

$$\text{Eq. wt. of } NaHCO_3 = \frac{\text{Mol. wt.}}{1}$$

$$= \frac{23+12+12+(3\times 16)}{1} = 84.$$

Wt. of NaOH = 1 g ; Na_2CO_3 = 1 g ; $NaHCO_3$ = 1 g.

$$\text{M.eq. of NaOH} = \frac{\text{wt.}}{\text{Eq. wt.}}\times 1000 = \frac{1}{40}\times 1000 = 25$$

$$\text{M.eq. of } Na_2CO_3 = \frac{\text{wt.}}{\text{Eq. wt.}}\times 1000 = \frac{1}{53}\times 1000 = \frac{1000}{53}$$

$$\text{M.eq. of } NaHCO_3 = \frac{\text{wt.}}{\text{Eq. wt.}}\times 1000 = \frac{1}{84}\times 1000 = \frac{1000}{84}$$

(*a*) When methyl orange is used as an indicator, whole of NaOH, Na_2CO_3 and $NaHCO_3$ get neutralised by HCl

$$NaOH + HCl \longrightarrow NaCl + H_2O\ ;$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2 + H_2O.$$

Let Volume of 1N HCl used = V_1 mL

M.eq. of NaOH + M.eq. of $NaHCO_3$ + M.eq. of

$$Na_2CO_3 = \text{Volume}\times\text{normality}$$

$$= V_1\times 1 = V_1$$

$$25+\frac{1000}{84}+\frac{1000}{53} = V_1$$

Or $$\frac{25\times 84\times 53+1000\times 53+1000\times 84}{84\times 53} = V_1$$

Or $$V_1 = \frac{111300+53000+84000}{4452}$$

$$= \mathbf{55.8\ mL}$$ **Ans.**

(*b*) When only phenolphthalein is used as an indicator, whole of NaOH and 1/2 of Na_2CO_3 reacts with HCl to form $NaHCO_3$.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

Let volume of 1N HCl used = V_2 mL

M.eq. of NaOH + $\frac{1}{2}$ M.eq. of

$$Na_2CO_3 = \text{Volume}\times\text{normality}$$

$$= V_2\times 1 = V_2$$

$$25+\frac{1}{2}\times\frac{1000}{53} = V_2$$

Or $$V_2 = \frac{25}{1}+\frac{500}{53} = \frac{25\times 53+500}{53}$$

$$= \frac{1325+500}{53},$$

Or $$V_2 = \frac{1825}{53} = \mathbf{34.4\ mL}$$ **Ans.**

(*c*) When methyl orange is added after the first end point with phenolphthalein, let the volume of HCl used is V_3 mL

V_3 = Volume of HCl used when methyl orange in used as indicator – Volume of HCl used when phenolphthallein is used as indicator

$$V_3 = 55.8 - 34.4 = \mathbf{21.4\ mL}$$ **Ans.**

Example 66. *A mixture of Na_2CO_3 and $NaHCO_3$ has a mass of 22.0 g. Treatment with excess HCl solution liberates 6.00 litre CO_2 at 25°C and 0.947 atm. Determine the percentage of Na_2CO_3 in the mixture.* **(IIT 1993)**

Solution. Let there be *x* g of Na_2CO_3 in the mixture

Weight of $NaHCO_3$ in the mixture = (22.0 – *x*) g

Let the volume of CO_2 collected at NTP be V litre

∴ According to gas equation, $(P_1V_1/T_1) = P_2V_2/T_2$

$$\frac{1\times V}{273} = \frac{0.947\times 6}{273+25}$$

or $$V = \frac{0.947\times 6\times 273}{298} = 5.2 \text{ litre}$$

Reactions involved are :

$$\underset{\substack{2\,\times\,23\,+\,12\,+\,3\,\times\,16\\=\,106\text{ g}}}{Na_2CO_3} + 2HCl \longrightarrow 2NaCl + H_2O + \underset{22.4\text{ L at NTP}}{CO_2}$$

$$\underset{\substack{23\,+\,1\,+\,12\,+\,3\,\times\,16\\=\,84\text{ g}}}{NaHCO_3} + HCl \longrightarrow NaCl + H_2O + \underset{22.4\text{ L at NTP}}{CO_2}$$

According to the balanced chemical equation,

106 g of Na_2CO_3 liberates CO_2 = 22.4 L at NTP

$$x \text{ g of } Na_2CO_3 \text{ liberates } CO_2 = \left(\frac{22.4}{106}\times x\right)\text{L at NTP}$$

$$= 0.2113x \text{ L at NTP}$$

Again 84 g of $NaHCO_3$ liberates

CO_2 = 22.4 L at NTP

∴ (22 – *x*) g of $NaHCO_3$ liberates

$$CO_2 = \frac{22.4}{84}\times(22-x)$$

L et NTP =0.267(22 – *x*) L at NTP

Thus, $0.2113x + 0.267\,(22-x) = 5.2$

or $5.874 + 0.2113x - 0.267x = 5.2$

or $5.874 - 5.2 = 0.267x - 0.2113x$

or $0.674 = 0.0557x$

∴ $$x = \frac{0.674}{0.0557} = \mathbf{12.1.}$$

Hence weight of Na_2CO_3 in the mixture = 12.1 g

Weight of $NaHCO_3$ in the mixture = 22 – 12.1 = 9.9 g
Hence percentage of Na_2CO_3 in the mixture

$$= \frac{12.1}{22} \times 100 = \mathbf{55\%}$$

Percentage of $NaHCO_3$ in the mixture

$$= \frac{9.9}{22} \times 100 = \mathbf{45\%}$$

Example 67. *A mixture of potassium carbonate and lithium carbonate weighing 0.5 g needed 25 mL of 0.3 N HCl for complete neutralisation. Calculate the percentage of lithium carbonate in the mixture. (at. wt ; Li = 7, K = 39, C = 12, O = 16,)*

(Roorkee, 1989)

Solution. Let wt. of $K_2CO_3 = x$ g ; wt. of $Li_2CO_3 = (0.5 - x)$g

Reactions. (A)

$$\underset{\substack{(2\times 39)+12+(3\times 16)\\ = 138\text{ g}}}{K_2CO_3} + \underset{\substack{2(1+35.5)\\ = 73\text{ g}}}{2HCl} \longrightarrow 2KCl + CO_2 + H_2O$$

138 g K_2CO_3 require HCl = 73 g

$$x \text{ g } K_2CO_3 \text{ require HCl} = \frac{73\,x}{138} \text{ g} \qquad ...(i)$$

$$\text{(B) } \underset{\substack{(2\times 7)+12+(3\times 16)\\ = 74\text{ g}}}{Li_2CO_3} + \underset{\substack{2(1+35.5)\\ = 73\text{ g}}}{2HCl} \longrightarrow 2LiCl + CO_2 + H_2O$$

74 g Li_2CO_3 need HCl = 73 g

$$(0.5 - x) \text{ g } Li_2CO_3 \text{ need HCl} = \frac{73}{74} \times (0.5 - x) \text{ g} \qquad ...(ii)$$

From (*i*) and (*ii*), total wt. of HCl used

$$= \left[\frac{73\,x}{138} + \frac{73}{74}(0.5 - x)\right] \text{g} \qquad ...(iii)$$

(*c*) Eq. wt. of HCl = 1 + 35.5 = 36.5. Also :

$$\text{Normality of HCl} = \frac{\text{wt. of HCl}}{\text{Eq. wt. of HCl}} \times \frac{1000}{\text{Volume of HCl used in mL.}}$$

$\therefore$ wt. of HCl

$$= \frac{\text{Normality} \times \text{Eq. wt. of HCl} \times \text{Volume of HCl used}}{1000}$$

$$= \frac{0.3 \times 36.5 \times 25}{1000} = 0.2737 \text{ g} \qquad ...(iv)$$

Equating equations (*iii*) and (*iv*), we have :

$$\frac{73\,x}{138} + \frac{73}{74}(0.5 - x) = 0.2737\ (73x \times 74) + (138 \times 73)$$

$$(0.5 - x) = 138 \times 74 \times 0.2737\ 5402x + 5037$$

$$-\ 10{,}074x = 2795.02\ ;\ 4672x = 2241.98$$

$$\therefore \quad x = 0.4798 \text{ g} = \text{wt. of } K_2CO_3$$

$$\therefore \quad \text{wt. of } Li_2CO_3 = 0.5 - 0.4798 = 0.0202 \text{ g}$$

$$\%\text{ age of } Li_2CO_3 = \frac{0.0202}{0.5} \times 100 = \mathbf{4.04\%} \qquad \textbf{Ans.}$$

Example 68. *12 mL of 1.25 M H_2SO_4, 20 mL of 5M HCl and 20 mL of HNO_3 of unknown normality were mixed and made up to one litre. 25mL of this solution required 30 mL of $Ba(OH)_2$ solution prepared by dissolving 4.8 g of $Ba(OH)_2.8H_2O$ in water and making up the solution to 250 mL. Calculate the normality of HNO_3 solution. (at. wt., Ba = 137, O = 16, H = 1).*

Solution. (*i*) Eq. wt. of $Ba(OH)_2.\ 8H_2O$

$$[Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-]$$

$$= \frac{137 + 2(16+1) + 8[(2\times 1) + 16]}{(\text{Total + ve or} - \text{ve charge}) = 2}$$

$$= \frac{315}{2} = 157.5.$$

$$(ii) \qquad \text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{4.8 \times 1000}{157.5 \times 250} = 0.122 \qquad ...(A)$$

(*iii*) Normality of acid mixture

$$= \frac{N_1V_1 + N_2V_2 + N_3V_3}{1000}$$

$$= \frac{(12 \times 1.25 \times 2) + (20 \times 5) + (20 \times x)}{1000}$$

where x = normality of HNO_3 ;
mol. wt. of H_2SO_4 = (2 × 1) + 32 + (4 × 16) = 98 ;
Eq. wt. of H_2SO_4 ($H_2SO_4 \rightleftharpoons 2H^+ + H_2SO_4$)

$$= \frac{\text{Mol. wt.}}{2} = \frac{98}{2}$$

= 49 and for H_2SO_4 :

Normality × Eq. wt. = Molarity × Mol wt

Normality × 49 = 1.25 × 98

$$\therefore \qquad \text{Normality} = \frac{1.25 \times 98}{49} = 1.25 \times 2 \text{ N.}$$

$\therefore$ Normality of acid mixture

$$= \frac{30 + 100 + 20\,x}{1000} = \frac{130 + 20\,x}{1000} \qquad ...(B)$$

(*iv*) To find normality of HNO_3 in mixture solution.

Acid mixture $\quad Ba(OH)_2.8H_2O$

$$N_1V_1 = N_2V_2$$

$$\frac{130 + 20x}{1000} \times 25 = 0.122 \times 30$$

$$\frac{0.122 \times 30 \times 1000}{25} = 130 + 20x\ ;\ 146.4 - 130 = 20x\ ;$$

$$x = \mathbf{0.82\ N} \qquad \textbf{Ans.}$$

Example 69. *Excess of carbon dioxide is passed through 50 mL of 0.5 M calcium hydroxide solution: After the completion of reaction, the solution was evaporated to dryness. The solid calcium carbonate was completely neutralised by 0.1 N hydrochloric acid. The volume of hydrochloric acid required is (at. mass of calcium = 40)*

(*a*) 200 cm^3 (*b*) 500 cm^3
(*c*) 400 cm^3 (*d*) 300 cm^3

(Karnataka CET, 2009)

SOLUTION. Reaction:

$$\underset{\substack{74\\(=1\text{ mol})}}{Ca(OH)_2} + \underset{\substack{44\\(=1\text{ mol})}}{CO_2} \longrightarrow \underset{\substack{100\\(=1\text{ mol})}}{CaCO_3} + \underset{\substack{18\\(=1\text{ mol})}}{H_2O}$$

Mol. wt.

Eq. wt. of $CaCO_3$ = Mol. wt./2 = 100/2 = 50; normality of $CaCO_3$ = ? We know: N_{CaCO_3} × Eq. wt. of $CaCO_3$ = Molarity of $CaCO_3$ × Mol. wt. of $CaCO_3$

$$N_{CaCO_3} \times 50 = 0.5 \times 100; N_{CaCO_3} = \frac{0.5 \times 100}{50} = 1N$$

Volume of C_{CaCO_3} = 50 mL (given). But

$$N_{HCl} \times V_{HCl} = N_{CaCO_3} \times V_{CaCO_3}$$
$$0.1 \times V_{HCl} = 1 \times 50;$$
$$V_{HCl} = \frac{1 \times 50}{0.1} = \frac{50 \times 10}{1} = 500 \text{ mL.}$$

So, the correct answer is (*b*)

Type. Eq. wt. of an acid

$$= \frac{\text{Mol. wt. of acid}}{\text{no. of replacable H}^+ \text{ ions}}$$

EXAMPLE 70. *Calculate the equivalent weight of* H_3PO_4 *in the following reaction.*

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

$CaHPO_4$ formation shows that number of replaceable H^+ ions in H_3PO_4 = 2.

$$\therefore \text{Eq. wt. of } H_3PO_4 = \frac{\text{Mol. wt.}}{2}$$
$$= \frac{(3 \times 1) + 31 + (4 \times 16)}{2} = \frac{98}{2} = \mathbf{49}$$

Ans.

Type. Eq. wt. of a base

$$= \frac{\text{Mol. wt. of base}}{\text{no. of replaceable OH}^- \text{ ions}}$$

EXAMPLE 71. *Calculate the equivalent weight of* $Ca(OH)_2$ *in the following reaction.*

$$Ca(OH)_2 + HCl \longrightarrow Ca(OH)Cl + H_2O.$$

The Ca(OH)Cl formation shows that number of replaceable OH^- ions in $Ca(OH)_2$ = 1

$$\therefore \text{Eq. wt. of } Ca(OH)_2 = \frac{\text{Mol. wt. of } Ca(OH)_2}{\text{no. of replaceable OH}^- \text{ ions}}$$
$$= \frac{40 + 2(16+1)}{1} = \mathbf{74} \qquad \textbf{Ans.}$$

EXAMPLE 72. *A partially hydrated sodium carbonate* $Na_2CO_3.H_2O$ *weighing 0.31 g is added to 100 mL of 0.05 N* H_2SO_4 *solution. Will the resulting solution be neutral, acidic or basic?*

SOLUTION. Eq. wt. of

$$H_2SO_4 = \frac{(2 \times 1) + 32 + (4 \times 16)}{2} = \frac{98}{2} = 49.$$

$$\text{Normality of } H_2SO_4 = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$\therefore \quad \text{Wt. of } H_2SO_4 = \frac{\text{Normality} \times \text{Eq. wt.} \times \text{Volume in mL}}{1000}$$
$$= \frac{0.05 \times 49 \times 100}{1000} = 0.245 \text{ g}$$

Reaction.

$$Na_2CO_3.H_2O + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + 2H_2O$$

(2 × 23) + 12 + (3 × 16) + [(2 × 1) + 16] = 124 g (2 × 1) + 32 + (4 × 16) = 98 g

98 g H_2SO_4 need $Na_2CO_3.H_2O$ = 124 g

$$0.245 \text{ g } H_2SO_4 \text{ need } Na_2CO_3.H_2O = \frac{124}{98} \times 0.245$$
$$= \mathbf{0.31\ g.}$$

Since the wt. of given $Na_2CO_3.H_2O$ (= 0.31 g) is the same as the wt. of $Na_2CO_3.H_2O$ neutralised, no quantity of $Na_2CO_3.H_2O$ is left behind. So, the resulting solution is neutral.

EXAMPLE 73. *Two acids X and Y were separately titrated each time with 20 mL of 1N NaOH solution and needed 8.0 mL and 32 mL respectively for complete neutralisation. What volume of acids X and Y would be needed to mix to produce 1L of 1N acid?*

SOLUTION. (*i*) Acid, *X*.

$$N_1V_1 \text{ (acid)} = N_2V_2 \text{ (NaOH)}$$
$$N_1 \times 8 = 1 \times 20 ; N_1 = \frac{20 \times 1}{8} = 2.5$$

(*ii*)Acid, *Y*. N_3V_3 (acid) = N_4V_4 (NaOH)

$$N_3 \times 32 = 1 \times 20 ; N_3 = \frac{20}{32} = 0.625$$

According to the law of normalities, the acids should be mixed in the inverse ratio of their normalities to form equinormal solutions. At the same time, their normalities will be one each. So, the ratio of volumes of *X* and *Y* is : 0.625 : 2.5 *i.e.,* $\frac{0.625}{0.625} : \frac{2.5}{0.625}$ *i.e.,* 1 : 4. Hence to get 1L *i.e.,* 1000 mL solution of 1N : Volume of $X = \frac{1 \times 1000}{1+4} = 200$ mL ; volume of $Y = \frac{4 \times 1000}{1+4} = 800$ mL.

EXAMPLE 74. *4.8 mL of 6N HCl, 5.0 mL of 5N* HNO_3 *and a certain volume of 17 M* H_2SO_4 *were mixed togather and the volume was made up to 1.5 litre. 25 mL of this acid mixture exactly neutralised 35 mL of sodium carbonate solution containing 1.0 g of* $Na_2CO_3.10H_2O$ *in 100 mL of water. Find the amount in gram of* SO_4^{2-} *ions in the solutions.*

SOLUTION. Volume of solution = 1.5 L = 1.5 × 1000 mL = 1500 mL.

(*i*) *Resultant normality of HCl* $= \frac{4.8\times 6}{1000} = \frac{28.8}{1000} = 0.0288$

(*ii*) *Resultant normality of* $HNO_3 = \frac{5\times 5}{1000} = \frac{25}{1000} = 0.025$

Let normality of H_2SO_4 in the acid mixture = N.

$$\text{Eq. wt. of } Na_2CO_3.10H_2O = \frac{\text{Mol. wt.}}{2}$$

$$= \frac{(2\times 23)+12+(3\times 16)+10[(2\times 1)+16]}{2} = \frac{286}{2} = 143$$

(*iii*) *To find normality of* Na_2CO_3*. 10* H_2O *solution.*

$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt}}\times\frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{1}{143}\times\frac{1000}{100} = \frac{10}{143}$$

(*iv*) *To find normality of acid mixture.*

Acid mixture $Na_2CO_3 10H_2O$ solution

$$N_1V_1 = N_2V_2$$

$$N_1 \times 25 = \frac{10}{143}\times 35 \;;\; N_1 = \frac{10\times 35}{143\times 25} = 0.0979$$

(*v*) *To find normality of* H_2SO_4*.*

0.0288 HCl + 0.025 HNO_3 + $NH_2SO_4 = 0.0979$

∴ $NH_2SO_4 = 0.0979 - 0.0288 - 0.025 = 0.0441$

Ionic weight of SO_4^{2-} ion = 32 + (4 × 16) = 96

$$\therefore \text{ionic eq. wt. of } SO_4^{2-} \text{ ion} = \frac{\text{Ionic wt.}}{\text{Total valency of ion } (= 2)}$$

$$= \frac{96}{2} = 48$$

$$\text{But normality} = \frac{\text{wt.}}{\text{Eq. wt.}}\times\frac{1000}{\text{Volume of solution in mL}}$$

$$\therefore \text{wt. of } SO_4^{2-} \text{ ions} = \frac{\text{normality}\times\text{Eq. wt.}\times\text{Volume in mL}}{1000}$$

$$= \frac{0.0441\times 48\times 1500}{1000} = 3.1752 \text{ g}$$

EXAMPLE 75. *1.0 g of a fuming sulphuric acid (or oleum) was diluted with water. The resulting solution needed 26.5 mL of 0.8 N NaOH for complete neutralisation. Calculate the percentage of* SO_3 *is the fuming sulphuric acid.*

SOLUTION. (*i*) *To find weight of NaOH for complete neutralisation.*

$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}}\times\frac{1000}{\text{Vol of solution in mL}}$$

$$\therefore \quad \text{wt. of NaOH} = \frac{\text{Normality}\times\text{Eq. wt.}\times\text{Volume in mL}}{1000}$$

$$= \frac{0.8\times 40\times 26.5}{1000} = 0.848 \text{ g.} \quad \ldots(A)$$

Fuming sulphuric acid = $H_2SO_4 + SO_3$.

Reactions

$$(i) \quad \underset{\substack{2(23+16+1)\\ = 80\text{ g}}}{2NaOH} + \underset{\substack{(2\times 1)+32\\ +(4\times 16) = 98\text{ g}}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$$

Let wt. of H_2SO_4 = x g ; wt. of SO_3 = $(1 - x)$g.

(*i*) 98 g H_2SO_4 need NaOH = 80 g

x g H_2SO_4 need NaOH = $\frac{80}{98}\times x$ g .

$$(ii) \quad \underset{\substack{2(23+16+1)\\ = 80\text{ g}}}{2NaOH} + \underset{\substack{32+(3\times 16)\\ = 80\text{ g}}}{SO_3} \longrightarrow Na_2SO_4 + H_2O$$

80 g SO_3 need NaOH = 80 g

$(1 - x)$ g SO_3 need NaOH = $\frac{80}{80}\times 1 - x = (1 - x)$ g

$$\text{Total NaOH needed} = \left(\frac{80x}{98} + 1 - x\right)\text{g} \quad \ldots(B)$$

Equating equations (*A*) and (*B*), we get :

$$0.848 = \frac{80x}{98} + 1 - x$$

$$98 \times 0.848 = 80x + 98 - 98x \;;\; 83.1 - 98 = -18x$$

$$\therefore \quad x = \frac{14.9}{18} = 0.828 \text{ g} = \text{wt. of } H_2SO_4$$

$$\therefore \quad \text{wt. of } SO_3 = 1 - 0.828 = 0.172 \text{ g}$$

$$\%\text{ age of } SO_3 = \frac{0.172}{1}\times 100 = \mathbf{17.2\%} \quad \textbf{Ans.}$$

EXAMPLE 76. *A mixture of oxalic acid,* $(COOH)_2$ *and formic acid HCOOH was heated with conc.* H_2SO_4*. The resulting gas was passed through KOH solution. The volume of gas reduced by 1/6 th. Find the molar ratio of two acids in original mixture of acids.*

SOLUTION. Let amount of HCOOH = x mol ; amount of $(COOH)_2$ = y mol.

Reactons.

$$(i) \quad \underset{x\text{ mol}}{HCOOH} \xrightarrow{H_2SO_4} H_2O + \underset{x\text{ mol}}{CO\uparrow}$$

$$(ii) \quad \underset{y\text{ mol}}{(COOH)_2} \xrightarrow{H_2SO_4} \underset{y\text{ mol}}{CO\uparrow} + \underset{y\text{ mol}}{CO_2\uparrow} + H_2O$$

It may be noted that only CO_2 is absorbed by KOH.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O.$$

Total mol of CO and CO_2 = $x + 2y$

$$\therefore \quad \text{Mole fraction of } CO_2 = \frac{y}{x+2y}$$

$$\text{Hence} \quad \frac{y}{x+2y} = \frac{1}{6} \;;\; 6y = x + 2y \;;$$

$$6y - 2y = x \;;\; 4y = x$$

or $x : y$ = 4 : 1. Thus ; the ratio of

HCOOH : $(COOH)_2$ = **4 : 1** **Ans.**

EXAMPLE 77. *An alkaline solution contains 4.0 g caustic soda and 2.65 g* Na_2CO_3 *per 500 mL. 20 mL of this mixture was titrated with decinormal HCl. Calculate the reading if* (*i*) *phenolphthalein is used as indicator in the beginning and if* (*ii*) *methyl orange in used as indicator in the beginning.*

SOLUTION. (*i*) 500 mL NaOH solution contain

NaOH = 4.0 g

∴ 1000 mL (= 1L) NaOH solution contain

$$\text{NaOH} = \frac{4}{500}\times 1000 = 8\text{ g}$$

$$\therefore\ \text{Normality of NaOH} = \frac{\text{wt. L}^-}{\text{Eq. wt.}} = \frac{8}{40} = 0.2$$

(*ii*)
$$\text{Eq. wt. of Na}_2\text{CO}_3 = \frac{\text{Mol. wt.}}{\text{Total + ive charge on Na}^+}$$
$$= \frac{(2\times 23)+12+(3\times 16)}{2}$$
$$= \frac{106}{2} = 53$$

500 mL Na_2CO_3 solution contain Na_2CO_3 = 2.65 g CO_3
1000 mL (= 1L) Na_2 solution contain Na_2CO_3
$$= \frac{2.65}{500}\times 1000 = 5.3\text{ g}$$

$$\text{Normality of Na}_2\text{CO}_3 = \frac{\text{wt. L}^-}{\text{Eq. wt.}} = \frac{5.3}{53} = 0.1$$

(*iii*) When methyl orange is used as an indicator, whole of the NaOH as well as Na_2CO_3 get titrated.

(*iv*) When phenolphthalein is used as an indicator, whole of NaOH and half the amount of Na_2CO_3 get titrated.

(*v*) *To find volume of HCl used by NaOH*

NaOH HCl
$$N_1V_1 = N_2V_2$$
$$0.2 \times 20 = 0.1 \times V_2\ ;\ V_2 = \frac{0.2\times 20}{0.1} = 40\text{ mL}$$

(*vi*) *To find volume of HCl used by Na_2CO_3*

Na_2CO_3 HCl
$$N_3V_3 = N_4V_4$$
$$0.1 \times 20 = 0.1 \times V_4\ ;\ V_4 = \frac{0.1\times 20}{0.1} = 20\text{ mL}$$

∴ Volume of HCl used when methyl orange is used as indicator = 40 mL + 20 mL = 60 mL

[See (*iii*) above]

Volume of HCl used when phenolphthalein is used as indicator
$$= 40+\left(\frac{1}{2}\times 20\right) = 40 + 10$$
= 50 mL **Ans** [see (*iv*) above]

EXAMPLE 78. *20 mL of a mixture of sodium bicarbonate and sodium carbonate needed 8.0 mL of 0.05 N H_2SO_4 when titrated in presence of phenolphthalein indicator. Also, 20 mL of the same mixture when titrated separately in presence of methyl orange indicator needed 20 mL of 0.05 N H_2SO_4. Find the respective amounts of both compounds in gL^-.*

SOLUTION. (*i*) When methyl orange is used as an indicator, total Na_2CO_3 and total $NaHCO_3$ solution get titrated.

(*ii*) When phenolphthalein is used as an indicator, half the amount of Na_2CO_3 only gets titrated.

∴ For $\frac{1}{2}$ amount of Na_2CO_3 titration, 0.5

N H_2SO_4 used = 8.0 mL

For full amount of Na_2CO_3 titration, 0.5N

H_2SO_4 used = 8 × 2 = 16 mL

(*iii*) When methyl orange is used as an indicator, full amount of Na_2CO_3 and full amount of $NaHCO_3$ is titrated.

Volume of 0.5 N H_2SO_4 used to titrate total Na_2CO_3 and total $NaHCO_3$ = 20 mL (given)

∴ Volume of 0.5 N H_2SO_4 used to titrate total

$NaHCO_3$ = 20 – 16 = 4 mL

(*iv*) Eq. wt. of
$$\text{Na}_2\text{CO}_3 = \frac{\text{Mol. wt.}}{\text{Total + ve charge on Na}^+}$$
$$= \frac{(2\times 23)+12+(3\times 16)}{2} = \frac{106}{2} = 53$$
$$\text{Eq. wt. of NaHCO}_3 = \frac{\text{Mol. wt.}}{\text{Total + ve charge on Na}^+}$$
$$= \frac{23+1+12+(3\times 16)}{1} = 84$$

(*v*) *To find normality of Na_2CO_3.*

Na_2CO_3 H_2SO_4
$$N_1V_1 = N_2V_2$$
$$N_1 \times 20 = 0.05 \times 16\ ;\ N_1 = \frac{0.05\times 16}{20}$$
$$\therefore\ \text{Strength of Na}_2\text{CO}_3 = N_1 \times \text{Eq. wt}$$
$$= \frac{0.05\times 16}{20}\times 53 = \mathbf{2.12\ gL^-}$$ **Ans.**

(*vi*) *To find normality of $NaHCO_3$.*

$NaHCO_3$ H_2SO_4
$$N_3V_3 = N_4V_4$$
$$N_3 \times 20 = 0.05 \times 4\ ;\ N_3 = \frac{0.05\times 4}{20}$$
$$\therefore\ \text{Strength of NaHCO}_3 = N_3 \times \text{Eq. wt.}$$
$$= \frac{0.05\times 4}{20}\times 84 = \mathbf{0.84\ gL^-}$$ **Ans.**

EXAMPLE 79. *One gram of a sample containing chalk ($CaCO_3$) and $CaSO_4$ was dissolved in 200 mL of decinormal HCl. 35 mL of N/9.6 NaOH is needed to neutralise the excess acid. Calculate the percentage of chalk and $CaSO_4$ in the mixture.*

SOLUTION. Let wt. of chalk ($CaCO_3$) = x g ; $CaSO_4$ does not react with HCl, wt of $CaSO_4$ = 1 – x.

(*i*) *To find volume of unused HCl.*
$$N_1V_1\ (\text{HCl}) = N_2V_2\ (\text{NaOH})$$
$$\frac{1}{10}\times V_1 = \frac{1}{9.6}\times 35\ ;$$
$$V_1 = \frac{1}{9.6}\times 35\times 10 = 36.45\text{ mL}$$

∴ Volume of used HCl = 200 – 36.45 = 163.55

(*ii*) Eq. wt. of HCl = 1 + 35.5 = 36.5
$$\text{Normality of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of HCl used in mL}}$$
$$\therefore\ \text{wt. of HCl} = \frac{\text{Normality}\times\text{Eq. wt.}\times\text{Volume of HCl in mL}}{1000}$$

$$= \frac{1}{10} \times \frac{36.5 \times 163.55}{1000} = 0.5969 \text{ g} \quad ...(A)$$

Reaction. $CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$

$40 + 12 + (3 \times 16) = 100 \text{ g}$ $\quad 2(1 + 35.5) = 73 \text{ g}$

100 g $CaCO_3$ react with HCl = 73 g

$$x \text{ g } CaCO_3 \text{ react with HCl} = \frac{73\,x}{100} \quad ...(B)$$

Equating equations (*A*) and (*B*), we have :

$$0.5969 = \frac{73\,x}{100}\,; x = \frac{100 \times 0.5969}{73}$$

$$= 0.8177 \text{ g} = \text{wt of } CaCO_3$$

$$\therefore \quad \%\text{ age of } CaCO_3 = \frac{0.8177}{1} \times 100$$

$$= \mathbf{81.77\%} \quad \textbf{Ans.}$$

$$\%\text{ age of } CaSO_4 = 100 - 81.77$$

$$= \mathbf{18.23\%} \quad \textbf{Ans.}$$

EXAMPLE 80. *2L of NH_3 neutralised 125 mL of H_2SO_4 at 27°C and 0.95 atmospheric pressure. Calculate the normality of H_2SO_4.*

SOLUTION. (*i*) *To find wt.* (*W*) *of NH_3.* Mol. wt. of NH_3 = 14 + (3 × 1) = 17 g mol^-; P = 0.95 atm; V = 2L ; wt. = ? ; R = 0.0821 L atm K^- mol^- ; T = 27 + 273 = 300 K

$$\text{But} \quad PV = \frac{W}{M} \times RT\ ; W = \frac{MPV}{RT}$$

$$= \frac{17 \text{ g mol}^- \times 0.95 \text{ atm} \times 2\text{L}}{0.0821 \text{ L atm K}^-\text{mol}^- \times 300 \text{ K}}$$

$$= 1.31 \text{ g}$$

(*ii*) *Reaction.* $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$2[14 + (3 \times 1)] = 34 \text{ g}$ $\quad (2 \times 1) + 32 + (4 \times 16) = 98 \text{ g}$

34 g NH_3 need H_2SO_4 = 98 g

$$1.31 \text{ g } NH_3 \text{ need } H_2SO_4 = \frac{98}{34} \times 1.31 = 3.7759 \text{ g}$$

(*iii*) *To find normality of H_2SO_4.*

$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of acid in mL}}$$

$$= \frac{3.7759 \times 1000}{49 \times 125} = \mathbf{0.616} \quad \textbf{Ans.}$$

EXAMPLE 81. *0.6238 g of oxalic acid $H_2C_2O_4.xH_2O$ are dissolved in water and volume made up to 100 mL. 20 mL of this acid required 19.8 mL of N/10 NaOH for complete neutralisation. Calculate the value of x.*

SOLUTION. (*i*) $N_1V_1 \text{ (acid)} = N_2V_2 \text{ (NaOH)}$

$$N_1 \times 20 = \frac{1}{10} \times 19.8\,;$$

$$N_1 = \frac{19.8}{10 \times 20} = \frac{198}{2000}$$

(*iii*) To find eq. wt. of acid.

$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of acid in mL}}$$

$$\therefore \quad \text{Eq. wt.} = \frac{\text{wt.} \times 1000}{\text{Normality} \times \text{Volume of acid in mL}}$$

$$= \frac{0.6238 \times 1000 \times 2000}{198 \times 100} = 63$$

Since the acid is dibasic ; Eq. wt. of

$$H_2C_2O_4.xH_2O = \frac{\text{Mol. wt. of } H_2C_2O_4.xH_2O}{2}$$

$$63 = \frac{(2 \times 1) + (2 \times 12) + (4 \times 16) + x[(2 \times 1) + 16]}{2}$$

$$= \frac{90 + 18\,x}{2}\ \frac{(2 \times 63) - 90}{18}$$

$$= x\,;\ x = \frac{36}{18} = \mathbf{2} \quad \textbf{Ans.}$$

Type. Estimation of mixture of acids.

EXAMPLE 82. *20 mL of $\frac{N}{10}$ NaOH was needed to neutralise 12 mL of a solution containing HCl and H_2SO_4. When excess of $BaCl_2$ solution was added to 20 mL of acid solution, 0.296 g of $BaSO_4$ was obtained. Calculate the amount of HCl per litre of the solution. (at. wt., Ba = 137, S = 32, O = 16, H = 1)*

SOLUTION. (*i*) Only H_2SO_4 reacts with $BaCl_2$ solution.

$$\therefore \quad BaCl_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HCl$$

$(2 \times 1) + 32 + (4 \times 16) = 98 \text{ g}$ $\quad 137 + 32 + (4 \times 16) = 233 \text{ g}$

233 g $BaSO_4$ is obtained from

H_2SO_4 = 98 g

0.296 g $BaSO_4$ is obtained from H_2SO_4

$$= \frac{98}{233} \times 0.296 = 0.1245 \text{ g}$$

(*ii*) 20 mL solution contain

H_2SO_4 = 0.1245 g

1000 mL solution contain

$$H_2SO_4 = \frac{0.1245}{20} \times 1000 = 6.225 \text{ gL}^-$$

$= \text{Strength of } H_2SO_4$

$$\text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt.}}{2} = \frac{(2 \times 1) + 32 + (4 \times 16)}{2}$$

$= 49 \qquad \therefore$ Normality of

$$H_2SO_4 = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{6.225}{49} = 0.127$$

(*iii*) N_1V_1 (acid mixture)

$= N_2V_2$ (NaOH)

$$N_1 \times 12 = \frac{1}{10} \times 20\,; N_1 = \frac{20}{10 \times 12} = 0.167$$

$\therefore$ Normality of HCl = 0.167 – 0.127 = 0.04

$$(iv) \text{ Eq. wt. of HCl} = \frac{1 + 35.5}{1} = 36.5$$

$\therefore$ Strength of HCl = Normality × Eq. wt

$= 0.04 \times 36.5 = \mathbf{1.46\ gL^-}$ **Ans.**

Type. Solutions whose sp. gravity or density is given.

EXAMPLE 83. *A 20 mL solution of Na_2CO_3 (sp. gravity, 1.35) needed 26.3 mL of HCl solution containing 87.5 g of acid per litre for complete neutralisation. Find the volume of 0.75N H_2SO_4 that would be required to completely neutralise 106 g of Na_2CO_3 solution.*

SOLUTION. (*i*) Eq. wt. of

$$\text{HCl} = 1 + 35.5 = 36.5$$

$$\therefore \text{ Normality of HCl} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{87.5 \text{ g L}^{-}}{36.5} = 2.4$$

(*ii*) $N_1V_1\,(Na_2CO_3) = N_2V_2\,(HCl)$

$$N_1 \times 20 = 2.4 \times 26.3\,;\, N_1 = \frac{2.4 \times 26.3}{20} = 3.156$$

(*iii*) Volume of 106 g Na_2CO_3 solution

$$= \frac{\text{wt.}}{\text{sp. gr.}} = \frac{106}{1.35} = 78.5 \text{ mL}$$

(*iv*) $N_1V_1\,(Na_2CO_3) = N_2V_2\,(H_2SO_4)$

$$3.156 \times 78.5 = 0.75 \times V_2\,;$$

$$V_2 = \frac{3.156 \times 78.5}{0.75} = 330.3 \text{ mL}$$

$\therefore$ 330.3 mL H_2SO_4 will be used to neutralise 106 g Na_2CO_3.

EXAMPLE 84. *A mixture of anhydrous Na_2CO_3 and K_2CO_3 weighing 1.0 g was dissolved in 250 mL measuring flask. 17.4 mL of this solution was neutralised by 18 mL of HCl. The resulting solution required 15.0 mL of N/10 $AgNO_3$ solution for precipitation. Calculate the strength of HCl and percentage composition of the sample.*

SOLUTION. (*i*) N_1V_1 (HCl)

$$= N_2V_2\,(AgNO_3)$$

$$N_1 \times 18 = \frac{1}{10} \times 15\,;\, N_1 = \frac{15}{180}$$

(*ii*) wt. of HCl used by mixture (250 mL) is calculated as follows.

$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of acid in mL}}$$

$$\text{Eq. wt. of HCl} = 1 + 35.5 = 36.5$$

$$\therefore \quad \text{wt.} = \frac{\text{Normality} \times \text{Eq. wt.} \times \text{Volume in mL}}{1000}$$

$$= \frac{15}{180} \times \frac{36.5 \times 18}{1000}$$

17.4 mL solution contain $Na_2CO_3 + K_2CO_3$

$$= \frac{15 \times 36.5 \times 18}{180 \times 1000} \text{ g}$$

$\therefore$ 250 mL solution contain $Na_2CO_3 + K_2CO_3$

$$= \frac{15 \times 36.5 \times 18}{180 \times 1000} \times \frac{250}{17.4} = 0.7866 \text{ g}$$

(*iii*) Let wt. of Na_2CO_3 = x g ; wt. of K_2CO_3 = $(1 - x)$ g

$$\underset{\substack{(2 \times 23) + 12 + (3 \times 16) \\ = 106 \text{ g}}}{Na_2CO_3} + \underset{\substack{2[1 + 35.5] \\ = 73 \text{ g}}}{2HCl} \longrightarrow 2NaCl + CO_2 + H_2O$$

106 g Na_2CO_3 need

$$\text{HCl} = 73 \text{ g}$$

$$x \text{ g } Na_2CO_3 \text{ need HCl} = \frac{73\,x}{106} \text{ g}$$

$$\underset{\substack{(2 \times 39) + 12 \\ + (3 \times 16) = 138 \text{ g}}}{K_2CO_3} + \underset{\substack{2[1 + 35.5] \\ = 73 \text{ g}}}{2HCl} \longrightarrow 2KCl + CO_2 + H_2O$$

138 g K_2CO_3 need

$$\text{HCl} = 73 \text{ g}$$

$$(1 - x) \text{ g } K_2CO_3 \text{ need HCl} = \frac{73}{138}(1 - x)\text{g}$$

$$\therefore \quad \frac{73\,x}{106} + \frac{73(1-x)}{138} = 0.7866$$

$$73 \times 138x + 106 \times 73 - 106 \times 73x = 0.7866 \times 106 \times 138\ 10{,}074 + 7738$$

$$- 7738x = 11506.4\,;\, 7738x = 6305.6$$

$$\therefore \quad x = \frac{6305.6}{7738} = 0.8149 \text{ g.}$$

$\therefore$ wt. of Na_2CO_3 = 0.8149 g

$$\% \text{ age of } Na_2CO_3 = \frac{0.8149}{1} \times 100 = \mathbf{81.49\%} \qquad \textbf{Ans.}$$

$$\% \text{ age of } K_2CO_3 = 100 - 81.49 = \mathbf{18.51\%} \qquad \textbf{Ans.}$$

EXAMPLE 85. *25 mL of a solution of HCl neutralises 27.0 mL of 4% solution of Na_2CO_3. How much water should be added to get 250 mL of N/10 HCl.*

SOLUTION. wt. of Na_2CO_3 = 4.0 g ; Volume = 100 mL because of 4% Na_2CO_3 solution. Eq. wt. of Na_2CO_3 = Mol. wt/2 = [(2 × 23) + 12 + (3 × 16)]/2 = 53 ; wt. of Na_2CO_3 per 1000 mL (= 1L) = $\frac{4 \times 1000}{100}$ = 40 g L^{-}.

$\therefore$ Normality of

$$Na_2CO_3 = \frac{\text{Strength in g L}^{-}}{\text{Eq. wt.}} = \frac{40}{53} = 0.7547$$

(*ii*) $N_1V_1\,(Na_2CO_3) = N_2V_2\,(HCl)$

$$0.7547 \times 27 = N_2 \times 25\,;\, N_2 = \frac{0.7547 \times 27}{25} = 0.815$$

(*iii*) To find volume of water to be added to get 250 mL of $\frac{N}{10}$ HCl.

$$N_1V_1 \text{ (given HCl)} = N_2V_2 \text{ (acid to be prepared)}$$

$$0.815 \times V_1 = \frac{1}{10} \times 250\,;$$

$$V_1 = \frac{250}{10} \times \frac{1}{0.815} = 30.7 \text{ mL}$$

$\therefore$ In order to prepare 250 mL of N/10 HCl, take exact 30.7 mL of given acid in 250 mL measuring flask, add water to get exact 250 mL.

$\therefore$ Volume of water to be added to 30.7 mL given acid

$$= 250 - 30.7 = \mathbf{219.3 \text{ mL}} \qquad \textbf{Ans.}$$

EXAMPLE 86. *48 cm^3 of a solution containing a mixture of $NaHCO_3$ and Na_2CO_3 were titrated with N HCl. First of* *all phenolphthalein was used as indicator and the end point was obtained with 28 cm^3 of N HCl. After this, methyl orange indicator was added to this resulting solution and end point was obtained with further addition of 48 cm^3 of N HCl. Calculate the strength of both $NaHCO_3$ and Na_2CO_3 in gL$^-$.*

(IIT 1979, Orissa JEE, 2009)

Solution. (*i*) *Phenolphthalein indicator.* Only half Na_2CO_3 is neutralised.

$\therefore$ 1N HCl used to titrate $\frac{1}{2}$ Na_2CO_3 = 28 cm^3

(*ii*) *Methyl orange indicator.* Here $\frac{1}{2}Na_2CO_3$ and full $NaHCO_3$ is neutralised.

$\therefore$ 1N HCl used to titrate $\frac{1}{2}Na_2CO_3$ + full

$NaHCO_3$ = 48 cm^3.

$\therefore$ 1N HCl used to titrate full

$NaHCO_3$ = 48 – 28 = 20 cm^3.

Also, 1N HCl used to neutralise full

Na_2CO_3 = 2 × 28 = 56 cm^3.

(*iii*) Eq. wt. of

$$Na_2CO_3 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times23)+12+(3\times16)}{2} = \frac{106}{2} = 53$$

$$N_1V_1\,(Na_2CO_3) = N_2V_2\,(HCl)$$

$$N_1 \times 48 = 1 \times 56\,;\; N_1 = \frac{56}{48}$$

$$\text{Normality} = \frac{\text{wt. of } Na_2CO_3}{\text{Eq. wt. of } Na_2CO_3} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$\therefore \quad \text{wt. of } Na_2CO_3 = \frac{\text{Normality}\times\text{Eq. wt.}\times\text{Volume}}{1000}$$

$$= \frac{56}{48}\times53\times\frac{1000}{1000} = \mathbf{61.83\ gL^-}\ \textbf{Ans.}$$

(*iv*) $N_1V_1\,(NaHCO_3) = N_2V_2\,(HCl)$

$$N_1 \times 48 = 1 \times 20\,;\; N_1 = \frac{20}{48}$$

$$\text{Eq. wt. of } NaHCO_3 = 23 + 1 + 12 + (3 \times 16) = 84$$

$$\text{Normality of } NaHCO_3 = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$\therefore \quad \text{wt.} = \frac{\text{Normality}\times\text{Eq. wt.}\times\text{Volume of solution in mL}}{1000}$$

$$= \frac{20}{48}\times\frac{84\times1000}{1000} = \mathbf{35\ gL^-}\quad \textbf{Ans.}$$

Example 87. *48 mL of a solution containing NaOH and Na_2CO_3 were neutralised by 40 mL of 1N H_2SO_4, using methyl orange indicator from the very beginning. Na_2CO_3 was precipitated by adding $CaCl_2$ solution and solution filtered. The resulting solution containing NaOH required 19.0 mL of 1N H_2SO_4 for complete neutralisation using phenolphthalein as indicator. Calculate the weight of Na_2CO_3 and NaOH in gL$^-$ in the mixture.*

Solution. (*i*) *Phenolphthalein indicator.*

$$N_1V_1\,(NaOH) = N_2V_2\,(H_2SO_4)$$

$$N_1 \times 48 = 1 \times 19\,;\; N_1 = \frac{19}{48}$$

$$\text{But wt. of NaOH} = \frac{\text{Normality}\times\text{Eq. wt.}\times\text{Volume of solution in mL}}{1000}$$

$$= \frac{19}{48}\times\frac{40\times1000}{1000} = \mathbf{15.83\ gL^-}\ \textbf{Ans.}$$

(*ii*) **Methyl orange indicator**. Here, full NaOH and full Na_2CO_3 will be neutralised by H_2SO_4.

$\therefore$ Volume of 1N H_2SO_4 used = 40 – 19 = 21 mL

$$N_1V_1\,(Na_2CO_3) = N_2V_2\,(H_2SO_4)$$

$$N_1 \times 48 = 1 \times 21\,;\; N_1 = \frac{21}{48}$$

$$\therefore \quad \text{wt. of } Na_2CO_3 = \frac{\text{Normality}\times\text{Eq. wt.}\times\text{Volume of solution in mL}}{1000}$$

$$= \frac{21}{48}\times\frac{53\times1000}{1000} \simeq \mathbf{23.19\ gL^-}\ \textbf{Ans.}$$

Example 88. *0.68 g sample containing washing soda, caustic soda and inert substance was dissolved in water and titrated with 0.48 N H_2SO_4 using phenolphthalein indicator. 19.8 mL of this acid was used to get end point. 4.8 mL of more acid was added to get end point of red colour using methyl orange as indicator. Calculate the percentage composition of the given sample.*

(Orissa JEE, 2009)

Solution. (*i*) Phenolphthalein indicator. Total NaOH and $\frac{1}{2}$ Na_2CO_3 gets neutralised with the given acid.

$\therefore$ Volume of 0.48 N H_2SO_4 used to neutralise total NaOH + $\frac{1}{2}$ Na_2CO_3 = 19.8 mL

(*ii*) Methyl orange indicator. $\frac{1}{2}$ Na_2CO_3 is neutralised by 0.48 N H_2SO_4

$\therefore$ Volume of 0.48 N H_2SO_4 used to neutralise total

Na_2CO_3 = 2 × 4.8 = 9.6 mL

$\therefore$ Volume of 0.5 N H_2SO_4 used to neutralise

NaOH = 19.8 – 4.8 = 15 mL

(*iii*) 9.6 mL of 0.48 N H_2SO_4

$\equiv$ 9.6 mL 0.48 N Na_2CO_3

$\therefore$ 1000 mL of 1N

Na_2CO_3 = g. eq. wt. of Na_2CO_3 = 53 g

$$9.6\text{ mL of }0.48\text{ N } Na_2CO_3 = \frac{53}{1000}\times9.6\times0.48 = 0.244\text{ g}$$

$\therefore$ % age of $Na_2CO_3 = \dfrac{0.244}{0.68} \times 100$ = **35.88%** **Ans.**

(*iv*) 15mL of 0.48 N

$H_2SO_4 \equiv$ 15 mL of 0.48 N NaOH

$\therefore$ 1000 mL of 1N NaOH

$\equiv$ g. eq. wt. of NaOH = 40 g

$\therefore$ 15 mL of 0.48 N NaOH

$= \dfrac{40}{1000} \times 15 \times 0.48 = 0.288$ g

$\therefore$ % age of NaOH $= \dfrac{0.288}{0.68} \times 100$ = **42.35%** **Ans.**

(*v*) % age of inert substance

= 100 − 35.88 − 42.35 = **21.77%** **Ans.**

Example 89. *2.1 g of a sample containing NaOH and Na_2CO_3 was dissolved in water and solution was made up to exact 250 mL. A 20 mL of this solution required 40 mL of N/10 H_2SO_4 for complete neutralisation. Calculate the percentage by weight of NaOH and Na_2CO_3.*

Solution. Let wt. of

$Na_2CO_3 = x$ g ; wt. of NaOH = (2.1 − x) g

(*i*) $Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

$(2 \times 23) + 12 + (3 \times 16) = 106$ g $\quad (2 \times 1) + 32 + (4 \times 16) = 98$ g

106 g Na_2CO_3 react with H_2SO_4 = 98 g

x g Na_2CO_3 react with $H_2SO_4 = \dfrac{98\,x}{106}$ g

(*ii*) $2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

2[23 + 16 + 1] = 80 g $\quad (2 \times 1) + 32 + (4 \times 16) = 98$ g

80 g NaOH react with H_2SO_4 = 98 g

(2.1 − x) g NaOH react with $H_2SO_4 = \dfrac{98}{80} \times (2.1 - x)$g

$\therefore$ Total H_2SO_4 required $= \dfrac{98x}{106} + \dfrac{98(2.1-x)}{80}$ ...(*A*)

(*iii*) 20 mL solution require N/10

H_2SO_4 = 40 mL; 250 mL solution require

N/10 $H_2SO_4 = \dfrac{40}{20} \times 250$ = 500 mL.

$\therefore$ Wt. of $H_2SO_4 = \dfrac{\text{Normality} \times \text{Eq. wt.} \times \text{Volume in mL}}{1000}$

$= \dfrac{1}{10} \times 49 \times \dfrac{500}{1000} = 2.45$ g ...(*B*)

Equating equations (*A*) and (*B*), we get :

$$\frac{98\,x}{106} + \frac{98(2.1-x)}{80} = 2.45$$

98 × 80x + (98 × 106 × 2.1) − (106 × 98x)

= 2.45 × 106 × 80

7840x + 21814.8 − 10388x

= 20776 ; 2548x = 1038.8 ;

x = 0.4077 g = wt. of Na_2CO_3

% age of $Na_2CO_3 = \dfrac{0.4077}{2.1} \times 100$ = **19.4%** **Ans.**

% age of NaOH = 100 − 19.4 = **80.6%** **Ans.**

Example 90. *Firstly 24 cm^3 of formaldehyde were added to 48 cm^3 of 1N NaOH and then oxidised with hydrogen peroxide. The resulting solution needed 25 mL of 0.85 N HCl for complete neutralisation. Calculate the concentration of the formaldehyde solution.*

Solution. Reaction.

(*i*) $HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$.

Formaldehyde $\quad$ Formic acid

$HCOOH + NaOH \longrightarrow HCOONa + H_2O$.

(*ii*) N_1V_1 (NaOH) = N_2V_2 (HCl); 1 × V_1 = 0.85 × 25 ;

V_1 = 0.85 × 25 = 21.25 cm^3.

It is the volume of unused NaOH

$\therefore$ Volume of used NaOH = 48 − 21.25 = 26.75 cm^3.

(*iii*) Eq. wt. of

HCHO = 1 + 12 + 1 + 16 = 30 26.75 cm^3 of

1N NaOH ≡ 26.75 cm^3 of 1N HCHO.

Also, 1000 cm^3 of 1N HCHO contain

HCHO = g. eq. wt. of

HCHO = 30 g

26.75 cm^3 of 1N HCHO contain HCHO $= \dfrac{30}{1000} \times 26.75 \times 1$

= 0.8025 g

(*iv*) 24 cm^3 solution contain

HCHO = 0.8025 g

1000 cm^3 solution contain HCHO

$= \dfrac{0.8025}{24} \times 1000$ = **33.44 gL^{-}** **Ans.**

Example 91. *1.1 g of a mixture of Na_2CO_3 and K_2CO_3 was dissolved in water and solution was made up to 100 mL. 19.5 mL of this solution required 39.5 mL of decinormal HCl for complete neutralisation. Find the amount of Na_2CO_3 in the mixture if another solution of 19.5 mL of solution is treated with excess of $BaCl_2$. Find the weight of precipitate formed. (at. wt. of Ba = 137).* **(IIT 1976)**

Solution. Let wt. of

$Na_2CO_3 = x$ g ; wt. of K_2CO_3 = (1.1 − x) g

(*i*) $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$

$(2 \times 23) + 12 + (3 \times 16) = 106$ g $\quad 2[1 + 35.5] = 73$ g

106 g Na_2CO_3 react with

HCl = 73 g

x g Na_2CO_3 react with HCl $= \dfrac{73}{106} \times x = \dfrac{73\,x}{106}$ g

(*ii*) $K_2CO_3 + 2HCl \longrightarrow 2KCl + CO_2 + H_2O$

$(2 \times 39) + 12 + (3 \times 16) = 138$ g $\quad 2(1 + 35.5) = 73$ g

138 g K_2CO_3 react with

$$\text{HCl} = 73 \text{ g}$$

$$(1.1 - x) \text{ g } K_2CO_3 \text{ react with HCl} = \frac{73}{138} \times (1.1 - x)$$

$$\therefore \text{ Total HCl used} = \frac{73\,x}{106} + \frac{73\,(1.1 - x)}{138} \quad ...(A)$$

(*iii*) 19.5 mL solution = 39.5 mL of 0.1N HCl 100 mL

$$\text{solution} = \frac{39.5}{19.5} \times 100 \text{ mL of 0.1N HCl}$$

$$= 202.55 \text{ mL of 0.1N HCl.}$$

$$\text{Eq. wt. of HCl} = 1 + 35.5 = 36.5$$

$$\text{Normality of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$\therefore \quad \text{wt. of HCl} = \frac{\text{Normality} \times \text{Eq. wt.} \times \text{Volume in mL}}{1000}$$

$$= \frac{1}{10} \times \frac{36.5 \times 202.55}{1000} = 0.7393 \text{ g} \; ...(B)$$

Equating equations (*A*) and (*B*), we get.

$$\frac{73\,x}{106} + \frac{73\,(1.1 - x)}{138} = 0.7393$$

$$(73 \times 138x) + (106 \times 73 \times 1.1) - (106 \times 73x) = 0.7393 \times 106 \times 138 \;\; 10074x + 8511.8$$

$$- 7738x = 10814.48 \; ; \; 2336x = 2302.68$$

$$\therefore \quad x = \frac{2302.68}{2336} = \mathbf{0.9857 \text{ g}}$$

$$= \textbf{wt. of } \mathbf{Na_2CO_3}$$

$$\textbf{wt. of } \mathbf{K_2CO_3} = 1.1 - 0.9857 = \mathbf{0.1143 \text{ g}}$$

(*iv*) $\underset{\substack{(2 \times 23) + 12 + (3 \times 16) \\ = 106 \text{ g}}}{Na_2CO_3} + BaCl_2 \longrightarrow \underset{\substack{137 + 12 + (3 \times 16) \\ = 197 \text{ g}}}{BaCO_3} + 2NaCl$

$\underset{\substack{(2 \times 39) + 12 + (3 \times 16) \\ = 138 \text{ g}}}{K_2CO_3} + BaCl_2 \longrightarrow \underset{\substack{137 + 12 + (3 \times 16) \\ = 197 \text{ g}}}{BaCO_3\downarrow} + 2KCl$

To find the weight of $BaCO_3$ ppt. in 20 mL of given mixture.

wt. of Na_2CO_3 in 20 mL mixture solution = 0.9857 g

wt. of K_2CO_3 in 20 mL mixture solution = 0.1143 g

(*a*) 106 g Na_2CO_3 form $BaCO_3$ ppt. = 197 g

0.9857 g Na_2CO_3 form $BaCO_3$ ppt.

$$= \frac{197}{106} \times 0.9857 = 1.8319 \text{ g}$$

(*b*) 138 g K_2CO_3 form $BaCO_3$ ppt.

$$= 197 \text{ g}$$

$$0.1143 \text{ g } K_2CO_3 \text{ form } BaCO_3 \text{ ppt.} = \frac{197}{138} \times 0.1143$$

$$= 0.1632 \text{ g}$$

∴ Total wt. of $BaCO_3$ ppt.

$$= 1.8319 + 0.1632 = \mathbf{1.9951 \text{ g}} \quad \textbf{Ans.}$$

EXAMPLE 92. *A commercial sample (3.0 g) containing $CaCO_3$ and SiO_2 was treated with 98 mL of 1N HCl. After filtration, the solution was made up to 200 mL. 20 mL of this solution required 24.5 mL of 0.2 N NaOH for neutralisation. Find the weight of $CaCO_3$ in the given sample.*

SOLUTION. Let. wt. of $CaCO_3$ = *x* g ; wt. of SiO_2 = (3.0 – *x*) g. Only $CaCO_3$ will react with HCl.

(*i*) $\underset{\substack{40 + 12 + (3 \times 16) \\ = 100 \text{ g}}}{CaCO_3} + \underset{\substack{2(1 + 35.5) \\ = 73 \text{ g}}}{2HCl} \longrightarrow CaCl_2 + CO_2 + H_2O$

100 g $CaCO_3$ react with

$$\text{HCl} = 73 \text{ g}$$

$$x \text{ g } CaCO_3 \text{ react with HCl} = \frac{73\,x}{100} \text{ g}. \quad ...(A)$$

(*ii*) To find volume of unused HCl :

$$N_1V_1 \text{ (HCl)} = N_2V_2 \text{ (NaOH)}$$

$$1 \times V_1 = 0.2 \times 24.5 \; ;$$

$$V_1 = 0.2 \times 24.5 = 4.9 \text{ mL}$$

$$= \text{Volume of unused HCl}$$

∴ Volume of used

$$\text{HCl} = 98 - 4.9 = 93.1 \text{ mL}$$

(*iii*) Eq. wt. of HCl = 1 + 35.5 = 36.5

$$\text{Normality of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of acid in mL}}$$

$$\therefore \quad \text{wt. of HCl} = \frac{\text{Normality} \times \text{Eq. wt.} \times \text{Volume of acid in mL}}{1000}$$

$$= \frac{1}{10} \times \frac{36.5 \times 93.1}{1000} = 0.3398 \text{ g} \quad ...(B)$$

From equations (*A*) and (*B*), we have :

$$\frac{73\,x}{100} = 0.3398 \; ; \; x = \frac{0.3398 \times 100}{73}$$

$$= \mathbf{0.4655 \text{ g}} = \text{wt. of } CaCO_3 \quad \textbf{Ans.}$$

EXAMPLE 93. *In a volumetric method, a few gram of $CaCO_3$ completely neutralised 550 mL of N/10 HCl and no acid was left behind. The $CaCl_2$ so formed was completely converted to plaster of Paris. Find the weight of Plaster of Paris so formed.*

(Dhanbad 1991)

SOLUTION.

(*i*) To find weight of HCl.

$$\text{wt. of HCl} = \frac{\text{Normality} \times \text{Eq.wt.} \times \text{Volume in mL}}{1000}$$

$$= \frac{1}{10} \times \frac{36.5 \times 550}{1000} = 2.0 \text{ g}$$

(*ii*) $\underset{\substack{40 + 12 + (3 \times 16) \\ = 100 \text{ g}}}{CaCO_3} + \underset{\substack{2(1 + 35.5) \\ = 73 \text{ g}}}{2HCl} \longrightarrow CaCl_2 + CO_2 + H_2O$

73 g HCl react with

$$CaCO_3 = 100 \text{ g}$$

$$2 \text{ g HCl react with } CaCO_3 = \frac{100}{73} \times 2 = \mathbf{2.7397 \text{ g}}$$

1 mol $CaCO_3$ ≡ 1 mol plaster of Paris *i.e.*, $CaSO_4 \cdot \frac{1}{2} H_2O$.

$$40 + 12 + (3 \times 16) \qquad 40 + 32 + (4 \times 16) + \frac{1}{2}[(2 \times 1) + 16]$$

$$= 100 \text{ g} \qquad\qquad = 145 \text{ g}$$

100 g $CaCO_3$ form plaster of Paris

$$= 145 \text{ g}$$

$$2.7397 \text{ g } CaCO_3 \text{ form plaster of Paris} = \frac{145}{100} \times 2.7397$$

$$= \mathbf{3.9726 \text{ g}} \qquad \textbf{Ans.}$$

Type. To fnd number of molecules of water of crystallisation.

Example 94. *1.5 g of hydrated sodium carbonate were dissolved in 100 cm^3 of water. 20 cm^3 of the solution required 10.4 cm^3 of N/5 H_2SO_4 for complete neutralisation. Calculate the number of molecules of water of crystalisation of hydrated sodium carbonate.*

Solution. Let hydrated sodium carbonate

$$= Na_2CO_3.xH_2O$$

Eq. wt. of $Na_2CO_3\ xH_2O$

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

$$= \frac{(2 \times 23) + 12 + (3 \times 16) + x[(2 \times 1) + 16]}{2} = 53 + 9x.$$

(*i*) $N_1V_1\ (Na_2CO_3) = N_2V_2\ (H_2SO_4)$

$$N_1 \times 20 = \frac{1}{5} \times 10.4\ ; N_1 = \frac{1}{5} \times \frac{10.4}{20} = 0.104$$

Strength of $Na_2CO_3.xH_2O$ = Normality × eq. wt.

$$= 0.104 \times (53 + 9x) \text{ gL}^- \qquad ...(A)$$

(*ii*) 100 cm^3 solution contain $Na_2CO_3.xH_2O$ = 1.5 g
1000 cm^3 (= 1L) solution contain

$$Na_2CO_3.xH_2O = \frac{1.5}{100} \times 1000 = 15 \text{ g} \qquad ...(B)$$

Equating equations (*A*) and (*B*) we get :

$$0.104(53 + 9x) = 15\ ; (0.104 \times 53) + (0.104 \times 9x)$$

$$= 15\ 5.512 + 0.936x = 15\ ; 0.936x$$

$$= 15 - 5.512 = 9.488$$

$$\therefore \qquad x = \frac{9.488}{0.936} \simeq 10.$$

So, number of molecules of water of crystallisation of

$$Na_2CO_3.xH_2O = \mathbf{10} \qquad \textbf{Ans.}$$

Example 95. *20 cm^3 of a solution containing 6.1 gL$^-$ of compound $K_xH_y(C_2O_4)_z.nH_2O$ required for titration, 28.8 cm^3 of N/20 NaOH and 38.55 cm^3 of N/20 $K_2Cr_2O_7$ for complete oxidation. Calculate the value of x, y, z and n. (At. wt., K = 39, H = 1, C = 12, O = 16)*

Solution. The compound oxalate $K_xH_y(C_2O_4)_z.nH_2O$ can act both as an acid and reductant.

(*i*) **As acid.**N_1V_1 (acid)

$$= N_2V_2 \text{ (NaOH)}$$

$$N_1 \times 20 = \frac{1}{20} \times 28.8\ ; N_1 = \frac{28.8}{20 \times 20} = 0.072$$

$$\text{Eq. wt. of acid} = \frac{\text{Strength}}{\text{normality}} = \frac{6.1}{0.072} = 84.72$$

$$\text{Also,eq. wt. of acid} = \frac{\text{Mol. wt.}}{\text{Basicity (= no. of replaceable } H^+ \text{ ions)}}$$

$$84.72 = \frac{\text{Mol. wt.}}{y} \qquad ...(i)$$

(*ii*) *As reductant.*N_1V_1 (reductant)

$$= N_2V_2\ (K_2Cr_2O_7)$$

$$N_1 \times 20 = \frac{1}{20} \times 38.55\ ; N_1 = \frac{38.55}{20 \times 20} = 0.096.$$

$$\therefore \text{ Eq. wt. of reductant} = \frac{\text{Strength}}{\text{normality}} = \frac{6.1}{0.096} = 63.54$$

Also,Eq. wt. of reductant

$$= \frac{\text{Mol. wt.}}{2z} \left[\because C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-\right]$$

$$63.54 = \frac{\text{Mol. wt.}}{2z} \qquad ...(ii)$$

Dividing equations (*i*) by (*ii*), we get

$$\frac{84.72}{63.54} = \frac{2z}{y}\ ; y = \frac{2 \times 63.54}{84.72} z\ ;$$

$$y = 1.5z \qquad ...(iii)$$

(*iii*) In $K_xH_y(C_2O_4)_z.nH_2O$, total positive charge = total negative charge.

$$\therefore x \times (+1) + y \times (+1) = 2 \times z\ ; x + y = 2z$$

$$\text{or} \qquad x + 1.5z = 2z\ ; \mathbf{x = 0.5z}$$

$$\therefore \qquad x : y : z = 0.5z : 1.5z : z\ ;\ x : y : \underline{z}$$

$$= \frac{36}{18}\ i.e\ ; 1 : 3 : 2$$

$$\therefore \qquad \mathbf{x = 1, y = 3, z = 2} \qquad \textbf{Ans.}$$

(*iv*) Mol. wt. = 84.72 y [from equation, (*i*)]

$$= 84.72 \times 3$$

$$= 254.16 \text{ g mol}^- \simeq 254 \text{ g mol}^-$$

∴ Mol. wt. of

$$K_xH_y(C_2O_4)_z.nH_2O = 254\ (x \times 39) + (y \times 1) + z[(2 \times 12) + (4 \times 16)] + n[(2 \times 1) + 16]$$

$$= 254\ 39x + y + 88z + 18n$$

$$= 254\ (39 \times 1) + 3 + (88 \times 2)$$

$$+ 18n = 254\ ; 39 + 3 + 176 + 18n = 254$$

$$\therefore \qquad n = \frac{36}{18} = 2$$

$$\therefore \qquad \mathbf{x = 1, y = 3\ z = 2, n = 2} \qquad \textbf{Ans.}$$

Example 96. *A 10 cm^3 solution of ammonium sulphate was boiled with excess NaOH solution. The evolved ammonia gas was absorbed in 40 cm^3 of 0.1N HCl. 25 cm^3 of 0.1N NaOH was required to neutralise the unreacted HCl. Calculate the strength of ammonium sulphate in the solution.*

Solution. Reactions

(*i*) $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$

(*ii*) $NH_3 + HCl \longrightarrow NH_4Cl$

(*iii*) $NaOH + HCl \longrightarrow NaCl + H_2O$

$$\text{Eq. wt. of HCl} = 1 + 35.5 = 36.5$$

(*iv*) N_1V_1 (excess HCl) = N_2V_2 (NaOH)

$$0.1 \times V_1 = 0.1 \times 25 \; ; \; V_1 = 25 \text{ cm}^3$$

∴ Volume of HCl used by NH_3

$$= 40 - 25 = 15 \text{ cm}^3$$

$$\therefore \quad \text{wt. of HCl} = \frac{\text{Normality} \times \text{eq. wt.} \times \text{Volume in mL}}{1000}$$

$$= \frac{0.1 \times 36.5 \times 15}{1000} = 0.05475 \text{ g}$$

(*v*)

$$\underset{\substack{14 + (3 \times 1) \\ = 17 \text{ g}}}{NH_3} + \underset{\substack{1 + 35.5 \\ = 36.5 \text{ g}}}{HCl} \longrightarrow NH_4Cl$$

36.5 g HCl react with

$$NH_3 = 17 \text{ g}$$

0.05475 g HCl react with

$$NH_3 = \frac{17}{36.5} \times 0.05475 = 0.0255 \text{ g}$$

(*vi*)

$$\underset{\substack{2[14 + (4 \times 1)] + 32 \\ + (4 \times 16) = 132 \text{ g}}}{(NH_4)_2SO_4} + 2NaOH \longrightarrow Na_2SO_4 + \underset{\substack{2[14 + (3 \times 1)] \\ = 34 \text{ g}}}{2NH_3} + 2H_2O$$

34 g NH_3 is produced from

$$(NH_4)_2SO_4 = 132 \text{ g}$$

0.0255 g NH_3 is produced from

$$(NH_4)_2SO_4 = \frac{132}{34} \times 0.0255 = 0.099 \text{ g}$$

(*vii*) 10 cm³ solution contain $(NH_4)_2SO_4$ = 0.099 g

∴ 1000 cm³ (= 1L) solution contain

$$(NH_4)_2SO_4 = \frac{0.099}{10} \times 1000 = \mathbf{9.9 \ gL^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 97. *A sample of carbon weighing 10.9 g reacts completely with 21.1 L oxygen at 291 K and 750 mm pressure. The liberated gases were cooled and passed through 1.9 L of 2.4 N NaOH solution. Calculate the amount of NaOH remaining in solution which is not converted to sodium carbonate. Also calculate the mole fraction of CO in the gases also. Note that under the above conditions, CO does not react with NaOH solution. (At. wt., C = 12)*

SOLUTION. (*i*) At. wt. (or mol. wt.) of

carbon = 12 g mol⁻. Wt. of carbon = 10.9 g

$$\therefore \text{Moles of carbon} = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{10.9}{12} = 0.9083$$

(*ii*)

$$P = 750 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}} = \frac{75}{76} \text{ atm} \; ;$$

$$V = 21.1\text{L}, n = ? \; ;$$

$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-} \; ;$$

$$T = 291 \text{ K. We know; } PV = nRT \; ;$$

$$n = \frac{PV}{RT} = \frac{75}{76} \text{ atm} \times \frac{21.1 \text{ L}}{0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 219 \text{ K}}$$

or n = 0.8716 mol = no. of mol of O_2

(*iii*) Let mol of CO_2 formed = x ; mol of CO formed = y

$$\underset{x \text{ mol}}{C} + \underset{x \text{ mol}}{O_2} \longrightarrow \underset{x \text{ mol}}{CO_2} \quad ; \quad \underset{y \text{ mol}}{C} + \underset{\frac{1}{2} y \text{ mol}}{\frac{1}{2} O_2} \longrightarrow \underset{y \text{ mol}}{CO}$$

$$\therefore \text{ No. of mol of carbon} = x + y$$

$$0.9083 = x + y \qquad \ldots(A)$$

$$\text{No. of mol of } O_2 = x + \frac{1}{2}y$$

$$0.8716 = x + \frac{1}{2}y \qquad \ldots(B)$$

Subtracting equation (*B*) from equation (*A*), we get

$$x + y - x - \frac{1}{2}y = 0.9083 - 0.8716 \; ;$$

$$\frac{1}{2}y = 0.0367$$

$$\therefore \quad y = 2 \times 0.0367 = \mathbf{0.0734 \ mol}$$

$$= \text{mol of CO}$$

Using equation (*A*), we have ; 0.9083 = x + 0.0734

$$\therefore \quad x = 0.9083 - 0.0734$$

$$= \mathbf{0.8349 \ mol} = \text{mol of } CO_2$$

(*iv*) Mole fraction of CO =

$$\frac{y}{x + y} = \frac{0.0734}{0.0734 + 0.8349} = \frac{0.0734}{0.9083} = \mathbf{0.08081}$$

(*v*) Eq. wt. of NaOH = 23 + 16 + 1 = 40;

Volume = 1.9 × 1000 = 1900 mL

$$\text{Normality of NaOH} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume of NaOH in mL}}$$

$$\therefore \quad \text{wt. of NaOH} = \frac{\text{Normality} \times \text{Eq. wt.} \times \text{Volume of NaOH in mL}}{1000}$$

$$= \frac{2.4 \times 40 \times 1900}{1000} = 182.4 \text{ g}$$

$$\therefore \text{ no. of mol of NaOH} = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{182.4}{40} = 4.56$$

Strength of remaining NaOH

$$= \frac{\text{no. of mol}}{\text{Volume in litre}} = \frac{4.56}{1.9}$$

$$= \mathbf{2.4} \qquad \textbf{Ans.}$$

EXAMPLE 98. *What volume at NTP of ammonia gas will be required to be passed into 30 mL 1N H_2SO_4 to bring down the acid normality to 0.2 N.* **(UPSEAT, 1991)**

SOLUTION. No. of milliequivalent (Meq) = Normality × Volume in mL

(*i*) No. of Meq of H_2SO_4 given = 1 × 30 = 30

(*ii*) No. of Meq of H_2SO_4 required = 0.2 × 30 = 6

∴ No. of Meq. of H_2SO_4 consumed = 30 – 6 = 24

∴ Meq of NH_3 passed

= Meq. of H_2SO_4 consumed = 24

∴ Meq. of NH_3 passed

$$= \frac{\text{wt. of } NH_3}{\text{Eq. wt. of } NH_3} \times 1000\,;$$

$$24 = \frac{\text{wt. of } NH_3}{17} \times 1000$$

$$\therefore \quad \text{wt. of } NH_3 = \frac{17 \times 24}{1000} = 0.408 \text{ g.}$$

(*iii*) 22400 mL NH_3 weighs

$$= \text{g. eq. wt. of } NH_3 = 17 \text{ g}$$

Or 17 g NH_3 occupy volume

$$= 22400 \text{ mL}$$

0.408 g NH_3 occupy volume

$$= \frac{22400}{17} \times 0.408 = \mathbf{537.6\ mL} \qquad \textbf{Ans.}$$

EXAMPLE 99. *What volume of a solution of hydrochloric acid containing 73 g of acid per litre would suffice for the exact neutralisation of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water?* **(UPSEAT, 1997)**

SOLUTION. Reactions

$$Na + H_2O \longrightarrow NaOH + \frac{1}{2} H_2 \qquad \ldots(A)$$

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad \ldots(B)$$

(*i*) wt. of HCl = 73 g ; eq. wt. of HCl

$$= \frac{\text{Mol. wt.}}{\text{Total + ve charge}} = \frac{1 + 35.5}{1}$$

= 36.5 ; Volume of HCl = ?

$$\text{Normality of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume in mL} (= 1000 \text{ mL})}$$

$$= \frac{73}{36.5} \times 1 = 2$$

(*ii*) From reactions (*A*) and (*B*), we see that :

Meq of Na = Meq. of NaOH = Meq of HCl

$$\therefore \quad \text{Meq. of Na} = \frac{\text{wt. of Na}}{\text{Eq. wt. of Na}} \times 1000$$

$$= \frac{0.46}{23} \times 1000$$

Meq. of HCl = Normality × Volume in mL

$$= 2 \times V = 2V$$

$$\text{Thus,} \quad 2V = \frac{0.46}{23} \times 1000\,;$$

$$V = \frac{0.46}{23} \times \frac{1000}{2} = \mathbf{10\ mL} \qquad \textbf{Ans.}$$

EXAMPLE 100. *Calculate the weight of $BaSO_4$ precipitate formed when 25 mL of 0.1 M $Ba(NO_3)_2$ solution is mixed with 20 mL of 0.25 M of $Al_2(SO_4)_3$ solution.* (*At. wt., Ba = 137, S = 32, O = 16*)

SOLUTON.

$$3Ba(NO_3)_2 + Al_2(SO_4)_3 \longrightarrow 3BaSO_4\downarrow + 2Al(NO_3)_3$$

(Balanced)

Or $Ba(NO_3)_2 + Al_2(SO_4)_3 \longrightarrow BaSO_4\downarrow + Al(NO_3)_3$ (unbalanced).

Total charge on Ba^{2+} = 2 ; total + ve charge on

$$2Al^{3+} = 2 \times 3 = 6$$

[∵ $Ba(NO_3)_2 \rightleftharpoons Ba^{2+} + 2NO_3^-$; $Al_2(SO_4)_3 \rightleftharpoons 2Al^{3+} + 3SO_4^{2-}$]

First method. Use of unbalanced equation.

∴ In	$Ba(NO_3)_2$ +	$Al_2(SO_4)_3$ ⟶	$BaSO_4\downarrow$ +	$Al(NO_3)_3$
Meq before reaction = *m* × *V* in mL × valency factor	0.1 × 25 × 2 = 5	0.25 × 20 × 6 = 30	0	0
Meq after reacton	5 – 5 = 0	30 – 5 = 25	5	5

[∵ Out of 5 and 30 Meq of reactants, 5 is less than 30, so 5 Meq of $Ba(NO_3)_2$ will react with 5 Meq of $Al_2(SO_4)_3$ to form 5 Meq of $BaSO_4$ and 5 Meq of $Al(NO_3)_3$. *i.e.*, Meq $Ba(NO_3)_2$ = Meq $Al_2(SO_4)_3$ = Meq $BaSO_4$ = Meq $Al(NO_3)_3$].

$$\text{Hence Meq of } BaSO_4 = 5; \ \frac{\text{wt. of } BaSO_4}{\text{Eq. wt. of } BaSO_4} \times 1000 = 5$$

$$\left[\text{Eq. wt. of } BaSO_4 = \frac{\text{Mol. wt.}}{\text{Total + ve charge}} \right.$$

$$\left. \frac{137 + 32 + (4 \times 16)}{2} = \frac{233}{2} = 116.5 \right]$$

$$\frac{\text{wt. of } BaSO_4}{116.5} \times 1000 = 5$$

$$\therefore \quad \text{wt. of } BaSO_4 = \frac{5 \times 116.5}{1000} = \mathbf{0.5825\ g} \qquad \textbf{Ans.}$$

Second method. Use of balanced equation.

	$3Ba(NO_3)_2$ +	$Al_2(SO_4)_3$ →	$3BaSO_4\downarrow$ +	$2Al(NO_3)_3$
	3 mol	1 mol	3 mol	2 mol
	1 mol	$\frac{1}{3}$ mol	$\frac{3}{3}$ or 1 mol	$\frac{2}{3}$ mol
m. mol before reaction = $M \times V$ in L	0.1×25 $= 2.5$	0.25×20 $= 5$	0	0
m mol after reaction	$2.5 - 2.5$ $= 0$	$5 - \left(2.5 \times \frac{1}{3}\right)$	2.5×1 $= 2.5$	$2.5 \times \frac{2}{3}$

$$\therefore \ m \text{ Mol of } BaSO_4 = 2.5; \ \frac{\text{wt.}}{\text{mol. wt.}} \times 1000 = 2.5$$

$$\therefore \quad \text{wt. of } BaSO_4 = \frac{2.5 \times \text{mol. wt. of } BaSO_4}{1000}$$

$$= \frac{2.5 \times 233}{1000}\,;$$

$$\text{wt. of } BaSO_4 = \mathbf{0.5825\ g} \qquad \textbf{Ans.}$$

Type. Mixing of same type of solutions.

EXAMPLE 101. *How will you prepare exactly 4.0 L of 0.5 M HCl by mixing portions of stock solutions of 2.5 M HCl and 0.4 M HCl?*

Solution. Required : $4.0\,L \times \frac{0.5 \text{ mol.}}{L} = 2.0$ mol;

Let x = number of L of 2.5 M HCl

∴ no. of mol = $2.5 \times x = 2.5x$;

$4 - x$ = number of L of 0.4 M HCl

∴ no. of mol = $0.4(4 - x)$

∴ $2.5x + 0.4(4 - x) = 2$; $2.5x + 1.6 - 0.4$

$x = 2$; $2.1\,x = 0.4$

∴ $x = \frac{0.4}{2.1} = 0.19$ L ;

$4 - x = 4 - 0.19 = 3.81$ L

Hence by mixing 0.19 L of 2.5 M HCl and 3.81 L of 0.4 M HCl, we get 4.0 L of 0.5 M HCl.

Example 102. *How will you prepare exactly 2.5 L of 2.0 M NaCl by mixing portions of stock solutions of 4.5 M NaCl and 0.2 M NaCl?*

Solution. Needed : $2.5\,L \times \frac{2.0 \text{ mol.}}{L} = 5.0$ mol;

Let x = no. of L of 4.5 M NaCl ;

∴ no. of mol = $4.5 \times x = 4.5x$; Total volume required = 2.5 L ;

∴ $2.5 - x$ = no. of L of 0.2 M NaCl

Hence, no. of mol of

HCl = $(2.5 - x)\,0.2 = 0.5 - 0.2\,x$

∴ $4.5x + 0.5 - 0.2x = 5.0$ mol ; $4.3x = 4.5$

Or $x = \frac{4.5}{4.3} = 1.05$;

$2.5 - x = 2.5 - 1.05 = 1.45$

∴ 2.5 L of 2 M NaCl solution can be prepared by mixing 1.05 L of 4.5 M NaCl and 1.45 L of 0.2 M NaCl.

Example 103. *How will you prepare 3.0 L of 1.0 M NaOH by mixing portions of stock solutions of 2.0 M NaOH and 0.35 M NaOH ?*

Solution. Required number of mol of

NaOH = Molarity × Volume in L

$= \frac{1.0 \text{ mol}}{L} \times 3.0\,L = 3.0$ mol

Let x = no. of L of 2.0 M NaOH ;

∴ no. of mol = $2.0 \times x = 2x$;

Total volume = 3.0 L

$3 - x$ = no. of L of 0.35 M NaOH ;

∴ no. of mol = $0.35(3 - x)$

$(x \times 2) + (3 - x) \times 0.35 = 3.0$ mol ; $2x + 1.05 - 0.35x = 3$

$1.65x = 1.95$; $x = \frac{1.95}{1.65} = 1.18$ L ;

$2 - x = 2 - 1.18 = 0.82$ L

∴ By mixing 1.18 L of 2.0 M NaOH with 0.82 L of 0.35 M NaOH, 3.0 L of 1.0 M NaOH solution is prepared.

TYPE. Mixing of different salt solutions.

Example 104. *Calculate the concentration of each type of ion which remains in solution when 75 mL of 0.5 M NaCl is mixed with 40 mL of 0.25 M KCl.*

Solution. (*a*) $NaCl \rightleftharpoons Na^+ + Cl^-$

1 mol 1 mol 1 mol

No. of m. mol of $Na^+ = 75 \times 0.5 = 37.5$

No. of m. mol of $Cl^- = 75 \times 0.5 = 37.5$

(*b*) $KCl \rightleftharpoons K^+ + Cl^-$

1 mol 1 mol 1 mol

No. of m. mol of $K^+ = 40 \times 0.25 = 10$

No. of m. mol of $Cl^- = 40 \times 0.25 = 10$

Total volume of NaCl solution and KCl solution = 75 + 40 = 115 mL

∴ $[Na^+] = \frac{37.5 \text{ m. mol of } Na^+}{\text{Total volume} = 115 \text{ mL}}$

= **0.33 M** **Ans.**

$[K^+] = \frac{10 \text{ m. mol of } K^+}{\text{Total volume} = 115 \text{ mL}}$

= **0.087 M** **Ans.**

Total m. mol of Cl^- = 37.5 + 10 = 47.5.

∴ $[Cl^-] = \frac{47.5 \text{ m. mol of } Cl^-}{\text{Total volume} = 115 \text{ mL}}$

= **0.41 M** **Ans.**

Example 105. *Calculate the concentration of each type of ion which remains in solution when 50 mL of 0.4 M KCl is mixed with 75 mL of 2.0 m. mol of KCl and 125 mL of water.*

Solution. $KCl \rightleftharpoons K^+ + Cl^-$

1 mol 1 mol 1 mol

No. of m. mol of K^+ = $(0.4 \times 50) + 2.0 = 22$

Total volume of solution = 50 + 75 + 125 = 250 mL

∴ $[K^+] = \frac{22 \text{ m. mol}}{250 \text{ mL}} = 0.088 = [Cl^-]$ **Ans.**

Example 106. *Calculate the concentration of each type of ion which remains in solution when 100 mL of 0.5 M KCl is mixed with 50 mL of 0.25 M $AgNO_3$.*

Solution.

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$; $KCl \rightleftharpoons K^+ + Cl^-$

1 mol 1 mol 1 mol 1 mol 1 mol 1 mol

$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$

(*a*) No. of m. mol of $K^+ = 0.5 \times 100 = 50$

No. of m. mol of $Cl^- = 0.5 \times 100 = 50$

(*b*) No. of m. mol of $Ag^+ = 50 \times 0.25 = 12.5$

= no. of m. mol of NO_3^-

Since 12.5 m. mol of Ag^+ react with 12.5 m. mol of Cl^- to form AgCl ppt, the no. of m. mol of Cl^- left behind = 50 − 12.5 = 37.5.

Total volume = 100 + 50 = 150 mL

∴ $[Cl^-] = \frac{37.5}{150}$ = **0.25 M** **Ans.**

$[K^+] = \frac{50}{150}$ = **0.33 M** **Ans.**

$$[NO_3^-] = \frac{12.5}{150} = \mathbf{0.083\ M} \qquad \textbf{Ans.}$$

EXAMPLE 107. *Calculate the volume of 96% H_2SO_4 density, 1.84 g/mL that is needed to prepare 1.5 L of 2.5 M H_2SO_4 solution. (At. wt., H = 1, S = 32, O = 16).*

SOLUTON. (*a*) No. of mol of

$$H_2SO_4 = \text{Molarity} \times \text{Volume in L}$$

$$= \frac{2.5\ \text{mol}}{\text{L}} \times 1.5\ \text{L} = .3.75\ 96\%$$

H_2SO_4 means that 96 g of H_2SO_4 is present in 100 g solution.

$$\text{g. mol. wt. of } H_2SO_4 = (2 \times 1) + 32 + (4 \times 16)$$

$$= \mathbf{98\ g = 1\ mol}\ H_2SO_4$$

$$1 \text{ mol } H_2SO_4 \text{ weighs} = 98 \text{ g}$$

$\therefore$ 3.75 mol H_2SO_4 weighs

$$= 98 \times 3.75 = 367.5 \text{ g}$$

(*b*) 96 g H_2SO_4 is present in solution = 100 g

$$367.5 \text{ g } H_2SO_4 \text{ is present in solution } = \frac{100}{96} \times 367.5 \text{ g}$$

(*c*) $\text{Density} = \frac{\text{mass}}{\text{Volume}}$; $\text{Volume} = \frac{\text{mass}}{\text{density}}$

$$= \frac{100 \times 367.5}{96 \times 1.84} = \mathbf{208\ mL} \qquad \textbf{Ans.}$$

EXAMPLE 108. *How many mL of 2.0 M of HCl should be added to react completely with 16.8 g $NaHCO_3$? (At. wt., Na = 23, H = 1, C = 12, O = 16)*

SOLUTION. Reaction :

$$\underset{\substack{1\ \text{mol} \\ 23+1+12+ \\ (3\times 16) = 84\ \text{g}}}{NaHCO_3} + \underset{1\ \text{mol}}{HCl} \longrightarrow NaCl + CO_2 + H_2O$$

$$\text{Molarity of } NaHCO_3 = \frac{\text{wt.}}{\text{g. mol. wt.}} = \frac{16.8}{84} = 0.2\ \text{molL}^-$$

Using molarity equation, we have :

$$\frac{M_1V_1(\text{HCl})}{M_2V_2(\text{NaHCO}_3)} = \frac{1 \text{ mol HCl}}{1 \text{ mol NaHCO}_3}$$

$$\frac{2 \times V_1}{0.2 \times 1 L} = \frac{1}{1}; V_1 = \frac{0.2}{2} = 0.1 \text{ L}$$

$$= 0.1 \times 1000 \text{ mL} = \mathbf{100\ mL} \qquad \textbf{Ans.}$$

EXAMPLE 109. *Calculate the volume in mL of 0.45 M $KMnO_4$ solution that will react completely with 18.0 g of $K_2C_2O_4.H_2O$ as follows :*

$$2MnO_4^- + 5C_2O_4^{2-} + 16\,H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(At. wt. K = 39, C = 12, O = 16, H = 1)

SOLUTION. Reaction :

$$\underset{2\ \text{mol}}{2MnO_4^-} + \underset{5\ \text{mol}}{5C_2O_4^{2-}} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Molarity (M_1) of $KMnO_4$ = 0.45 M ; Volume, V_1 = ?

wt. of $K_2C_2O_4.H_2O$ = 18.0 g ; g. mol. wt. of $K_2C_2O_4.H_2O$ = (2 × 39) + (2 × 12) + (4 × 16) + (2 × 1) + 16 = 184 g.

$\therefore$ Molarity (M_2) of

$$K_2C_2O_4.H_2O = \frac{18}{184} \text{ mol} = 0.098 \text{ M}$$

Volume of $K_2C_2O_4.H_2O$ = 1L = 1000 mL

$$\text{We know}: \frac{M_1V_1(\text{KMnO}_4)}{M_2V_2(\text{K}_2\text{C}_2\text{O}_4\text{H}_2\text{O})}$$

$$= \frac{\text{no. of mol of KMnO}_4}{\text{no. of mol of K}_2\text{C}_2\text{O}_4.\text{H}_2\text{O}}$$

$$\frac{0.45 \times V_1}{0.098 \times 1000} = \frac{2}{5};$$

$$V_1 = \frac{2 \times 0.098 \times 1000}{5 \times 0.45} = \mathbf{87\ mL.} \qquad \textbf{Ans.}$$

Type. To calculate mass of a substance when molarity and volume of substance from which it is formed, is given.

EXAMPLE 110. *Calculate the mass of calcium chlorate formed from 0.2 L of 1.5 M chloric acid solution plus excess of calcium hydroxide. (At. wt., Ca = 40, Cl = 35.5, O = 16)*

SOLUTION. Reaction :

$$Ca(OH)_2 + \underset{2\ \text{mol}}{2HClO_3} \longrightarrow \underset{\substack{1\ \text{mol} \\ 40 + 2[35.5 + (3 \times 16)] \\ = 207\ \text{g}}}{Ca(ClO_3)_2} + 2H_2O$$

(*a*) number of mol of $HClO_3$

$$= \text{Molarity} \times \text{Volume in litre}$$

$$= \frac{1.5 \text{ mol}}{\text{L}} \times 0.2 \text{ L} = 0.3 \text{ mol}$$

(*b*) 2 mol $HClO_3$ form $Ca(ClO_3)_2$ = 207 g

$$\therefore 0.3 \text{ mol } HClO_3 \text{ form } Ca(ClO_3)_2 = \frac{207}{2} \times 0.3$$

$$= \mathbf{31.05\ g} \qquad \textbf{Ans.}$$

EXAMPLE 111. *How many gram of $(NH_4)_2SO_4$ are required to prepare 250 mL of 0.1 M $(NH_4)_2SO_4$ solution? (At. wt., N = 14, H = 1, S = 32, O = 16)*

SOLUTION. g. mol. wt. of $(NH_4)_2SO_4$ = 2[14 + (4 × 1)] + 32 + (4 × 16) = 132 g

(*a*) Number of mol of $(NH_4)_2SO_4$

$$= \text{Molarity} \times \text{Volume in litre}$$

$$= \frac{0.1 \text{ mol}}{\text{L}} \times \frac{250}{1000} \text{ L} = 0.025 \text{ mol.}$$

1 mol of $(NH_4)_2SO_4$ weigh

$$= 132 \text{ g}$$

$\therefore$ 0.025 mol of $(NH_4)_2SO_4$ weigh

$$= 132 \times 0.025 = \mathbf{3.3\ g} \qquad \textbf{Ans.}$$

Type. To find weight of a substance from weight of atoms.

EXAMPLE 112. *Calculate the molarity of each ion in solution after mixing 2L of 1.5 M $MnCl_2$ with 1.5 L of 4.0 M $AgNO_3$ solution.*

SOLUTION. Reactions :

$$MnCl_2 + 2AgNO_3 \longrightarrow 2AgCl\downarrow + Mn(NO_3)_2$$

(*i*) No. of mol of $MnCl_2 = 2\text{ L}\times\frac{1.5\text{ mol}}{\text{L}} = 3.0\text{ mol}$

(*ii*) No. of mol of $AgNO_3 = 1.5\text{ L}\times\frac{4.0\text{ mol}}{\text{L}} = 6.0\text{ mol}$

(*a*) 3.0 mol $MnCl_2$ is 3.0 mol Mn^{2+} + 2 × 3.0 *i.e.*, ; 6.0 mol Cl^-

(*b*) 6.0 mol $AgNO_3$ is 6.0 mol NO_3^- + 6 mol Ag^+

Adding :

$$\frac{3.0\text{ mol Mn}^{2+}}{\text{Total Volume} = 2+1.5 = 3.5\text{ L}} = 0.86\text{ M Mn}^{2+}$$ **Ans.**

$$\frac{6.0\text{ mol NO}_3^-}{3.5\text{ L}};\ 6.0\text{ mol AgCl(s)} = 1.71\text{ M NO}_3^-$$ **Ans.**

Type. Number of m. mol = Molarity × Volume in mL.

EXAMPLE 113. *Calculate the concentration of each ion in solution after mixing 25 mL of 0.3 M HNO_3 with 50 mL of 0.5 M NH_3.*

SOLUTION. Reaction : $NH_3 + HNO_3 \longrightarrow NH_4^+ + NO_3^-$

(*a*) No. of m. mol of HNO_3

$= 0.3\text{ M} \times 25.0\text{ mL} = 7.5$ m. mol

(*b*) No. of m. mol of NH_3

$= 0.5\text{ M} \times 50\text{ mL} = 25$ m. mol

7.5 m. mol HNO_3 is 7.5 m. mol. H^+ + 7.5 m. mol NO_3^-

$$\underset{7.5\text{ m. mol}}{NH_3} + \underset{7.5\text{ m. mol}}{H^+} \longrightarrow \underset{7.5\text{ m. mol}}{NH_4^+}$$

The reaction yields 7.5 m. mol of NH_4^+. So, m. mol of NH_3 left unreacted = 25.0 – 7.5 = 17.5 m. mol. Total volume = 25 mL + 50 mL = 75 mL

∴ Concentration of different ions left unreacted are :

(*i*) $NH_3 = \frac{17.5\text{ m. mol}}{\text{Total Volume} = 75\text{ mL}}$

$= \mathbf{0.23\ M}$ **Ans.**

(*ii*) $NO_3^- = \frac{7.5\text{ m. mol}}{75\text{ mL}} = \mathbf{0.1M}$ **Ans.**

(*iii*) $NH_4^+ = \frac{7.5\text{ m. mol}}{75\text{ mL}} = \mathbf{0.1\ M}$ **Ans.**

EXAMPLE 114. *Calculate the volume of 4.2 M H_2SO_4 required to react exactly with 10.8 g aluminium. (At. wt., Al = 27, H = 1, S = 32, O = 16)*

SOLUTION. Reaction $\underset{\substack{2\times 27\\ = 54\text{ g}}}{2Al} + \underset{3\text{ mol}}{3H_2SO_4} \longrightarrow Al_2(SO_4)_3 + 3H_2$

54 g Al require

$H_2SO_4 = 3$ mol

10.8 g Al require

$H_2SO_4 = \frac{3}{54\text{ g}}\times 10.8 = 0.6$ mol.

We know :number of mol of

H_2SO_4 = Molarity of H_2SO_4 × Volume in litre

∴ 0.6 = 4.2 × Volume in litre ; Volume of

H_2SO_4 in litre $= \frac{0.6}{4.2} = .0143$ L

Or Volume of H_2SO_4 required

= 0.0143 × 1000 mL = **143 mL Ans.**

EXAMPLE 115. *What will be the molarity of each type of ion that remains in solution after mixing 40 mL of 2.5 M $Ba(OH)_2$, 20.0 mL of 6.5 M HNO_3 and 50.0 mL water?*

SOLUTION. (*i*) No. of m. mol of $Ba(OH)_2$

$= 40\text{ mL}\times\frac{2.5\text{ m. mol}}{\text{mL}} = 100$ m. mol

(*ii*) No. of m. mol of

$HNO_3 = 20.0\text{ mL}\times\frac{6.5\text{ m. mol}}{\text{mL}}$

= 130.0 m. mol

∴ 100 m. mol of $Ba(OH)_2$ yield, 100 m. mol of Ba^{2+} + 2 × 100 *i.e.*, 200 m. mol of OH^-

130 m. mol of HNO_3 yield, 130 m. mol of H^+ + 130 m. mol of NO_3^-

But $\underset{1\text{ m. mol}}{H^+} + \underset{1\text{ m. mol}}{OH^-} \longrightarrow H_2O$

∴ no. of m. mol of OH^- left behind = 200 – 130 = 70 m. mol. So, ions left behind are :

∴ $Ba^{2+} = \frac{100\text{ m. mol}}{\text{Total Volume}(= 40+20+50 = 110\text{ mL})}$

$= 0.91\text{ M Ba}^{2+}$;

$OH^- = \frac{70\text{ m. mol}}{110\text{ mL}} = 0.64\text{ M OH}^-$;

$NO_3^- = \frac{130\text{ m. mol}}{110\text{ mL}} = \mathbf{1.18\ M\ NO_3^-}$ **Ans.**

EXAMPLE 116. *When 100 mL of 2.5 M NaOH solution was added to 90.0 mL of H_2SO_4, it required 37.0 mL of 0.48 M HCl to neutralise the excess NaOH. Calculate the original concentration of H_2SO_4 used.*

SOLUTION. (*i*) No. of m. mol of NaOH

= Molarity × Volume in mL

$= \frac{2.5\text{ m. mol}}{\text{mL}}\times 100\text{ mL}$

= 250 m. mol

(*ii*) No. of m. mol of HCl $= \frac{0.48\text{ m. mol}}{\text{mL}}\times 37.0\text{ mL}$

= 17.8 m. mol

∴ m. mol of NaOH that reacted with

H_2SO_4 = 250 – 17.8 = 232.2

Reaction. $\underset{2\text{ m. mol}}{2NaOH} + \underset{1\text{ m. mol}}{H_2SO_4} \longrightarrow Na_2SO_4 + 2H_2O$

Thus :2 m. mol NaOH reacted with

H_2SO_4 = 1 m. mol

232.2 m. mol NaOH reacted with

$H_2SO_4 = \frac{1}{2}\times 232.2 = 116.1$ m. mol

∴ Original concentration of

H_2SO_4 used $= \frac{116.1\text{ m. mol}}{90.0\text{ mL}}$

$= \mathbf{1.29\ M\ H_2SO_4}$ **Ans.**

EXAMPLE 117. *While standardising silver nitrate solution, 45.7 mL of this solution precipitated all the Cl^- ions present in 35.0 mL of 0.5 M KCl solution. Find the weight in g of Ag that could be obtained from 90.0 mL of the silver nitrate solution. (At. wt., Ag = 108).*

SOLUTION. *Reaction.* $\underset{1\text{ mol}}{AgNO_3} + \underset{1\text{ mol}}{KCl} \longrightarrow AgCl\downarrow + KNO_3$

(*i*) Number of mol of KCl

$$= \text{Molarity} \times \text{Volume in litre}$$

$$= \frac{0.5\text{ mol}}{\text{L}} \times \frac{35.0}{1000}\text{ L} = 0.0175\text{ mol.}$$

$\therefore$ no. of mol of KCl = no. of mol of $AgNO_3$ = 0.0175 mol.

$$\underset{1\text{ mol}}{AgNO_3} \rightleftharpoons \underset{\substack{1\text{ mol}\\108\text{ g}}}{Ag^+} + NO_3^-$$

45.7 mL solution contain

$$AgNO_3 = 0.0175\text{ mol}$$

$\therefore$ 90.0 mL solution contain

$$AgNO_3 = \frac{0.0175}{47.5} \times 90 = 0.033\text{ mol}$$

(*ii*) 1 mol of $AgNO_3$ contain

$$Ag = 108\text{ g}$$

0.033 mol of $AgNO_3$ contain

$$Ag = 108 \times 0.033 \simeq \mathbf{3.6\ g}$$ **Ans.**

EXAMPLE 118. *During the titration of 50.0 mL HCl solution with 0.1 M NaOH, two drops of phenolphthalein indicator were added. When 40.0 mL of NaOH solution was added, pink colour appeared which disappeared on shaking. The addition of NaOH solution was continued till pink colour persisted with one drop of added NaOH solution. At this end point, 41.8 mL of NaOH solution was consumed. Calculate the concentration of HCl solution used.*

SOLUTION. *Reaction :* $\underset{1\text{ m. mol}}{NaOH} + \underset{1\text{ m. mol}}{HCl} \longrightarrow NaCl + H_2O$

$$\frac{M_1V_1\,(\text{NaOH})}{M_2V_2\,(\text{HCl})} = \frac{1\text{ m. mol of NaOH}}{1\text{ m. mol of HCl}}$$

[no. of m. mol = Molarity × Volume in mL]

$$\frac{\frac{0.1\text{ m. mol}}{\text{mL}} \times 41.8\text{ mL}}{M_2 \times 50\text{ mL}} = \frac{1}{1};$$

$$M_2 = \frac{0.1\text{ m. mol} \times 41.8}{50\text{ mL}} = 0.0836\text{ M}$$

$\therefore$ Concentration of HCl = **0.0836 M** **Ans.**

EXAMPLE 119. *How would you prepare 40.0 g of 8.0% $BaCl_2$ solution, starting with $BaCl_2.2H_2O$ and deionised water? (At. wt., Ba = 137, Cl = 35.5, H = 1, O = 16)*

SOLUTION. g. mol. wt. of $BaCl_2.2H_2O$

$$= 137 + (2 \times 35.5) + 2[(2 \times 1) + 16]$$

$$= 244\text{ g}$$

g. mol. wt. of $BaCl_2$ = 137 + (2 × 35.5) = 208 g

(*a*) 8% $BaCl_2$ solution means that 8 g of $BaCl_2$ is present in 100 g solution. So :

100 g solution contain

$$BaCl_2 = 8\text{ g}$$

$\therefore$ 40 g solution contain

$$BaCl_2 = \frac{8}{100} \times 40 = 3.2\text{ g}$$

$$\underset{\substack{1\text{ mol}\\244\text{ g}}}{BaCl_2.2H_2O} \longrightarrow \underset{\substack{1\text{ mol}\\208\text{ g}}}{BaCl_2} + 2H_2O$$

$\therefore$ 208 g $BaCl_2$ is present in $BaCl_2.2H_2O$

$$= 244\text{ g}$$

3.2 g $BaCl_2$ is present in

$$BaCl_2.2H_2O = \frac{244}{208} \times 3.2 = \mathbf{3.75\ g}$$ **Ans.**

EXAMPLE 120. *Calculate the molar concentration of each ion when 300 mL of 1.5 M KCl is diluted to 0.75 L.*

SOLUTION. Number of m. mol of

$$KCl = \text{Molarity} \times \text{Volume in mL}$$

$$= \frac{1.5\text{ m. mol}}{\text{mL}} \times 300\text{ mL}$$

$$= 450\text{ m. mol}$$

Total volume = 0.75 L = 0.75 × 1000 = 750 mL

$$\underset{\substack{1\text{ m. mol}\\450\text{ m. mol}}}{KCl} \rightleftharpoons \underset{\substack{1\text{ m. mol}\\450\text{ m. mol}}}{K^+} + \underset{\substack{1\text{ m. mol}\\450\text{ m. mol}}}{Cl^-}$$

$$\therefore \quad K^+ = \frac{450\text{ m. mol}}{750\text{ mL}} = 0.6\text{ M }K^+;$$

$$Cl^- = \frac{450\text{ m. mol}}{750\text{ mL}} = 0.6\text{ M }Cl^-$$ **Ans.**

EXAMPLE 121. *Calculate the molar concentration of each ion when 300 mL of 2.0 M $Al_2(SO_4)_3$ is added to 200 mL of 1.5 M $Al_2(SO_4)_3$ solution.*

SOLUTION. (*i*) No. of m. mol of

$$Al_2(SO_4)_3 = \text{Molarity} \times \text{Volume in mL}$$

$$= \frac{2\text{ m. mol}}{\text{mL}} \times 300\text{ mL} = 600\text{ m. mol}$$

(*ii*) No. of m. mol of

$$Al_2(SO_4)_3 = \frac{1.5\text{ m. mol}}{\text{mL}} \times 200\text{ mL}$$

$$= 300\text{ m. mol}$$

$\therefore$ Total m. mol of

$$Al_2(SO_4)_3 = 600 + 300 = 900\text{ m. mol}$$

$$\underset{\substack{1\text{ m. mol}\\900\text{ m. mol}}}{Al_2(SO_4)_3} \rightleftharpoons \underset{\substack{2\text{ m. mol}\\2 \times 900\\= 1800\text{ m. mol}}}{2Al^{3+}} + \underset{\substack{3\text{ m. mol}\\3 \times 900\\2700\text{ m. mol}}}{3SO_4^{2-}}$$

Total Volume = 300 mL + 200 mL = 500 mL

$$\therefore \quad Al^{3+} = \frac{1800\text{ m. mol}}{500\text{ mL}} = 3.6\text{ M }Al^{3+};$$

$$SO_4^{2-} = \frac{2700\text{ m. mol}}{500\text{ mL}} = \mathbf{5.4\ M\ SO_4^{2-}}$$ **Ans.**

EXAMPLE 122. *Calculate the molar concentration of each ion when 200 mL of 1.5 M KOH and 100 mL of 2.0 M HCl are mixed with 50 mL water and 150 mL of 4.0 M NaCl.*

SOLUTION. (*i*) no. of m. mol of

$$\text{KOH} = \frac{1.5 \text{ m. mol}}{\text{mL}} \times 200 \text{ mL}$$

$$= 300 \text{ m. mol}$$

$\therefore$ 300 m. mol KOH yield 300 m. mol K^+ and 300 m. mol OH^- $[\because KOH \rightleftharpoons K^+ + OH^-]$

(*ii*) no. of m. mol of

$$\text{HCl} = \frac{2.0 \text{ m. mol}}{\text{mL}} \times 100 \text{ mL}$$

$$= 200 \text{ m. mol}$$

$HCl \rightleftharpoons H^+ + Cl^-$. So, m. mol of H^+ = m. mol of Cl^- = 200 m. mol.

(*iii*) no. of m. mol of

$$\text{NaCl} = \frac{4.0 \text{ m. mol}}{\text{mL}} \times 150 \text{ mL}$$

$$= 600 \text{ m. mol.}$$

$NaCl \rightleftharpoons Na^+ + Cl^-$. So, m. mol. of

Na^+ = m. mol = Cl^- = 600 m. mol

But $H^+ + OH^- \longrightarrow H_2O$

$\therefore$ m. mol of OH^- left behind

= 300 – 200 = 100 m. mol

Total Volume = 200 + 100 + 50 + 150 = 500 mL

Total m. mol of Cl^- ions = 200 + 600 = 800

$$\therefore \quad OH^- = \frac{100 \text{ m. mol}}{\text{Total Volume} = 500 \text{ mL}}$$

$$= 0.2 \text{ M } OH^- ;$$

$$K^+ = \frac{300 \text{ m. mol}}{500 \text{ mL}} = 0.6 \text{ M } K^+ ;$$

$$Na^+ = \frac{600 \text{ m. mol}}{500 \text{ mL}} = 1.2 \text{ M } Na^+$$

$$Cl^- = \frac{800 \text{ m. mol}}{500 \text{ mL}} = 1.6 \text{ M } Cl^- \quad \textbf{Ans.}$$

EXAMPLE 123. *Calculate the concentration of each ion present in solution obtained by mixing 2.0 L of 3.5 M NH_4Cl and 3.5 L of 3.0 M $MnCl_2$ and diluted to 8 litre.*

SOLUTION. (*i*)no. of mol of

NH_4Cl = Molarity × Volume in litre

$$= \frac{3.5 \text{ mol}}{\text{L}} \times 2.0 \text{ L} = 7 \text{ mol}$$

$$\begin{array}{ccccc} NH_4Cl & \rightleftharpoons & NH_4^+ & + & Cl^- \\ 7 \text{ mol} & & 7 \text{ mol} & & 7 \text{ mol} \end{array}$$

(*ii*) no. of mol of

$MnCl_2$ = Molarity × Volume in litre

$$= \frac{3.0 \text{ mol}}{\text{L}} \times 3.5 \text{ L} = 10.5 \text{ mol}$$

$$\begin{array}{ccccc} MnCl_2 & \rightleftharpoons & Mn^{2+} & + & 2Cl^- \\ 1 \text{ mol} & & 1 \text{ mol} & & 2 \text{ mol} \\ 10.5 \text{ mol} & & 10.5 \text{ mol} & & 2 \times 10.5 = 21 \text{ mol} \end{array}$$

$\therefore$Concentrations of : (*i*)

$$Mn^{2+} = \frac{10.5 \text{ mol}}{\text{Total Volume} = 8 \text{ L}} = 1.31 \text{ M}$$

(*ii*)Total mol of Cl^- = 7 + 21 = 28 mol

$$\therefore \quad \text{Conc. of } Cl^- = \frac{28 \text{ mol}}{8 \text{ L}} = 3.5 \text{ M} ;$$

$$NH_4^+ = \frac{7 \text{ mol}}{8 \text{ L}} = \mathbf{0.875 \text{ M}} \quad \textbf{Ans.}$$

EXAMPLE 124. *200 mL of 4.5 M antifreeze were mixed with 400 mL of 4.0 M antifreeze and the solution was diluted to 4.0 litre with water. Calculate the final concentration of the solute.*

SOLUTION. (*i*) no. of mol of antifreeze

= Molarity × Volume in litre

$$= \frac{4.5 \text{ mol}}{\text{L}} \times \frac{200 \text{ L}}{1000} = 0.9 \text{ mol}$$

(*ii*) no. of mol of antifreeze

=Molarity × Volume in litre.

$$= \frac{4.0 \text{ mol}}{\text{L}} \times \frac{400}{1000} \text{ L} = 1.6 \text{ mol}$$

Total mol of antifreeze

= 0.9 + 1.6 = 2.5 mol

Total Volume = 4 L

$\therefore$ Molar concentration of antifreeze

$$= \frac{2.5 \text{ mol}}{4.0 \text{ L}} = \mathbf{0.625 \text{ M}} \quad \textbf{Ans.}$$

EXAMPLE 125. *One litre of a mixture of O_2 and O_3 at NTP was allowed to react with an excess of acidified solution of KI. The iodine liberated required 40 ml of M/10 sodium thiosulphate solution for titration. What is the weight per cent of ozone in the mixture? Assuming that one photon can decompose one ozone molecule, how many photons would have been required for the complete decomposition of ozone in the original mixture?*

(IIT, May 1997)

SOLUTION. The reactions involved are :

$$O_3 + 2I^- + 2H^+ \longrightarrow I_2 + O_2 + H_2O$$

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

$$\therefore \quad 2 \text{ mol } S_2O_3^{2-} \equiv 1 \text{ mol } I_2 \equiv 1 \text{ mol } O_3$$

Amount of $S_2O_3^{2-}$ consumed

$$= (40 \times 10^{-3} \text{ L})\left(\frac{1}{10} \text{mol L}^{-1}\right)$$

$$= 40 \times 10^{-4} \text{ mol} = 4 \times 10^{-3} \text{ mol}$$

$$\equiv 2 \times 10^{-3} \text{ mol } I_2 \equiv 2 \times 10^{-3}$$

$$= 0.2 \times 10^{-2} \text{ mol } O_3$$

Amount of O_3 present in 1L mixture

$$= 2 \times 10^{-3} \times 48 \text{ g} = \mathbf{9.6 \times 10^{-2} \text{ g}}$$

$[\because$ Mol. wt. of $O_3 = 3 \times 16 = 48$ g mol$^{-1}]$

Total amount of O_2 and O_3 present in one L mixture of O_2 and O_3 at STP is given by

$$n_{\text{total}} = \frac{PV}{RT}$$

$$= \frac{1 \text{ atm.} \times 1 \text{ L}}{(0.0821 \text{ L atm. K}^{-1}\text{mol}^{-1}) \times 273 \text{ K}}$$

$$= 4.462 \times 10^{-2} \text{ mol}$$

Amount of O_2 present in 1L of mixture

$$= (4.462 \times 10^{-2} - 0.2 \times 10^{-2}) \text{ mol}$$

$$= 4.262 \times 10^{-2} \text{ mol}$$

Mass of O_2 pesent in 1L of mixture

$$= 4.262 \times 10^{-2} \times 32 \text{ g}$$

$$[\because \text{Mol. wt. of } O_2 = 2 \times 16 = 32 \text{ g mol}^{-}]$$

$$= 1.364 \text{ g}$$

Mass percent of O_3 in the mixture

$$= \frac{9.6 \times 10^{-2}}{9.6 \times 10^{-2} + 1.364} \times 100 = 6.575$$

Amount of photons required to decompose O_3

$$= \text{Amount of } O_3 = 2 \times 10^{-3} \text{ mol}$$

Number of photons required

$$= 2 \times 10^{-3} \times 6.02 \times 10^{23} = \mathbf{1.204 \times 10^{21}}$$

Example 126. *0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. Iodine liberated required 100 cm³ of 0.15 N sodium thiosulphate solution for titration. Find the percent amount of each in the mixture.*

(Roorkee 1995)

Solution. The redox changes involved are :

$$\underset{(\text{in } MnO_4^-)}{Mn^{7+} + 5e^- \longrightarrow Mn^{2+}} \qquad \underset{(\text{in } Cr_2O_7^{2-})}{Cr_2^{6+} + 6e^- \longrightarrow 2Cr^{3+}}$$

$$2I^- \longrightarrow I_2 + 2e^-$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

Let the amounts of $K_2Cr_2O_7$ and $KMnO_4$ be a and b g respectively.

$$\therefore \qquad a + b = 0.5; \quad b = 0.5 - a$$

Further Meq. of $K_2Cr_2O_7$ + Meq. of $KMnO_4$

= Meq. of KI = Meq. of I_2 liberated

= Meq. of $Na_2S_2O_3$ used

$$\text{Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt.}}{6} = \frac{294}{6}$$

$$\text{Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt.}}{5} = \frac{158}{5}$$

$$\text{Meq. of } Na_2S_2O_3 = 0.15 \times 100 = 15$$

$$\therefore \frac{a}{\frac{294}{6}} \times 1000 + \frac{b}{\frac{158}{5}} \times 1000 = 15$$

$$\text{or } \frac{a}{49} \times 1000 + \frac{(0.5 - a)}{31.6} \times 100 = 15;$$

$$20.408a + (0.5 - a)31.64 = 15$$

$$(20.408 - 31.64)a + 15.82 = 15$$

$$\text{or} \qquad 11.23a = 0.82; \; a = \frac{0.82}{11.23} = 0.073 \text{ g}$$

$$b = 0.5 - 0.073 = 0.427 \text{ g}$$

$$\therefore \% \text{ age of } K_2Cr_2O_7 = \frac{0.073}{0.5} \times 100 = \mathbf{14.6\%}$$

$$\% \text{ of } KMnO_4 = \frac{0.427}{0.5} \times 100 = \mathbf{85.4\%}$$

Example 127. *The Mn_3O_4 formed on strong heating of a sample of $MnSO_4.4H_2O$ was dissolved in 100 cm³ of 0.1 N $FeSO_4$ containing H_2SO_4. The resulting solution reacted completely, with 50 cm³ of $KMnO_4$ solution, 25 cm³ of this $KMnO_4$ solution requires 30 cm³ of 0.1 N $FeSO_4$ solution for complete reaction. Calculate the amount of $MnSO_4.4H_2O$ in the sample.*

(Roorkee 2001)

Solution. From the given problem, we see that 25 cm³ of $KMnO_4$ solution = 30 cm³ of 0.1 N $FeSO_4$ solution

$$\therefore \text{ 50 cm}^3 \text{ of } KMnO_4 \text{ solution} \equiv \frac{30}{25} \times 50 = 60 \text{ cm}^3 \text{ of 0.1}$$

N $FeSO_4$ solution

It means that 0.1 N $FeSO_4$ left unreacted = 60 cm³

$\therefore$ 0.1 N $FeSO_4$ consumed = 100 – 60 = 40 cm³

Thus, Mn_3O_4 reacted ≡40 cm³ of 0.1N $FeSO_4$ ≡ 40 × 0.1 i.e., 4 milli eq.

$MnSO_4$. $4H_2O$ in sample = 4 milli eq.

$$MnSO_4.4H_2O \longrightarrow MnSO_4 + 4H_2O$$

$$3MnSO_4 \cdot 4H_2O + \frac{1}{2}O_2 \longrightarrow Mn_3O_4 + 3SO_3$$

$\therefore$ Equivalent weight of $MnSO_4.4H_2O$

$$= \frac{3 \times 223}{2} = 334.5$$

Hence 4 milli equivalents of $MnSO_4.4H_2O$

$$\frac{4}{1000} \times 334.5 = \mathbf{1.338 \text{ g}}$$

$$\left\{ \begin{array}{lcl} 3MnSO_4 \cdot 4H_2O & \equiv & \frac{1}{2}O_2 \\ 3(55 + 32 + 4 \times 16) & & \frac{1}{2} \times 2 \times 16 \\ + 4(2 \times 1 + 16) & = & 16 \text{ parts} \\ = 3 \times 223 \text{ parts} & & \frac{16}{2} = 8 \text{ parts} \end{array} \right.$$

$$= \frac{3 \times 223}{2} \text{ parts}$$

Example 128. *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 into Fe^{2+} along with liberation of iodine. The resulting solution is diluted to 100 ml. A 20 mL of the diluted 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 the oxidation of Fe^{2+}. Calculate the percentages of Fe_2O_3 and Fe_3O_4 in the original shape.* **(IIT 1996)**

Solution. We know that Fe_3O_4 is an equimolar mixture of FeO and Fe_2O_3. The reactions involved in the given problem are :

$$(i) \quad FeO + H_2SO_4 \longrightarrow FeSO_4 + H_2O$$

$$\text{Also} \quad Fe_2O_3 + 2H_2SO_4 \longrightarrow 2FeSO_4 + 2H_2O + O$$

$$2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI$$

$$\underline{2HI + O \longrightarrow H_2O + I_2}$$

$$(ii) \quad Fe_2O_3 + 3H_2SO_4 + 2KI \longrightarrow 2FeSO_4 + K_2SO_4 + 3H_2O + I_2$$

$$(iii) \quad 2Na_2SO_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

$$2FeSO_4 + H_2SO_4 + O \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$$

Add: $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + Fe_2(SO_4)_3 + 8H_2O$

1 mol   10/2 = 5 mol

In the problem, it is given that the resulting solution containing I_2 and Fe^{2+} after dilution = 100 mL

20 mL of diluted solution

$= 11$ mL of 0.5 M $Na_2S_2O_3$

$\therefore$ 100 ml of diluted solution $\dfrac{11}{20} \times 100$

$= 55$ ml of 0.5 M $Na_2S_2O_3$

$= \dfrac{55 \times 0.5}{1000}$

$= 0.0275$ moles of $Na_2S_2O_3$

Thus, $\dfrac{0.0275}{2} = 0.01375$ moles of

$I_2 = 0.01375$ moles of Fe_2O_3

(See chemical reactions above)

50 ml of diluted solution

$= 12.8$ mL of 0.25 M $KMnO_4$

$\therefore$ 100 ml of diluted solution $= \dfrac{12.8}{50} \times 100$

$= 25.6$ ml of 0.25 M $KMnO_4$

$= \dfrac{25.6 \times 0.25}{1000}$

$= 0.0064$ moles of $KMnO_4$

$= 5 \times 0.0064 = 0.032$ mole of $FeSO_4$

Clearly 0.032 moles of $FeSO_4$ is obtained from 0.01375 mole of Fe_2O_3 and the remaining from FeO

Since, 1 mole Fe_2O_3 = 2 mole $FeSO_4$

0.01375 mole $Fe_2O_3 = 2 \times 0.01375$ mole

$FeSO_4 = 0.0275$ mole of $FeSO_4$

$\therefore$ $FeSO_4$ formed from FeO

$= 0.032 - 0.0275 = 0.0045$ mole

But 1 mole $FeSO_4$ = 1 mole FeO

$\therefore$ 0.0045 mole $FeSO_4$ = 0.0045 mole FeO.

Also Fe_3O_4 contains equal moles of FeO and Fe_2O_3

$\therefore$ Fe_2O_3 present in Fe_3O_4

$= 0.0045$ mol

Thus, free Fe_2O_3 present in the mixture

$= 0.01375 - 0.0045 = 0.00925$ mole

Hence the amount of Fe_3O_4 in the mixture

$= 0.0045$ mole $= 0.0045 \times 232$

$= 1.044$ g

[$\because$ Mol. wt. of $Fe_3O_4 = (3 \times 56) + (4 \times 16) = 232\ \text{g mol}^{-}$]

Amount of Fe_2O_3 = 0.00925 mole

$= 0.00925 \times 160 = 1.48$ g

[$\because$ Mol. wt. of $Fe_2O_3 = (2 \times 56) + (3 \times 16) = 160\ \text{g mol}^{-}$]

$\therefore$ Precentage of Fe_3O_4 in the mixture

$= \dfrac{1.044}{3} \times 100 = \mathbf{34.8}$

Percentage of Fe_2O_3 in the mixture

$= \dfrac{1.48}{3} \times 100 = \mathbf{49.33}$

EXAMPLE 129. *An aqueous solution containing 0.1 g* KIO_3 *(formula weight = 214.0) was treated with an excess of KI solution. The solution was acidified with HCl. The liberated* I_2 *consumed 45.0 mL of thiosulphate solution to decolourise the blue starch-iodine complex. Calculate the molarity of the sodium thiosulphate solution.* **(IIT 1998)**

SOLUTION. The reactions involved are :

$KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3H_2O + 3I_2$

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

From the above equations, we can write

1 mole $KIO_3 \equiv 3$ mol I_2

1 mole $I_2 = 2$ mol $S_2O_3^{2-}$

Amount of $KIO_3 = \dfrac{0.1\ \text{g}}{214\ \text{g mol}^{-1}} = 4.6729 \times 10^{-4}$ mol

Amount of I_2 liberated

$= 3 \times 4.6729 \times 10^{-4}$ mol

Amount of $S_2O_3^{2-}$ consumed

$= 2 \times (3 \times 4.6729 \times 10^{-4})$ mol

Let *M* be the molarity of thiosulphate solution

$\therefore$ Amount of $S_2O_3^{2-}$ consumed

$= M \times V = M \times (45 \times 10^{-3}\ \text{L})$

or $M\,(45 \times 10^{-3}\ \text{L}) = 2(3 \times 4.6729 \times 10^{-4}\ \text{mol})$

$$M = \frac{2 \times 3 \times 4.6729 \times 10^{-4}\ \text{mol}}{45 \times 10^{-3}\ \text{L}}$$

$= \mathbf{0.0623\ molL^{-1}}$

EXAMPLE 130. *You are given 2.198 g sample containing a mixture of XO and* X_2O_3*. It requires 0.015 mol of* $K_2Cr_2O_7$ *to oxidise. The sample reacts to form* XO_4^- *and* Cr^{3+}*. If 0.0187 mol of* XO_4^- *is formed, what is the atomic mass of X?* **(Roorkee 2001)**

SOLUTION. For the given reaction, the chemical equation can be written as

(*i*) $XO + 3H_2O \longrightarrow XO_4^- + 6H^+ + 5e] \times 6$

$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O] \times 5$

$6XO + 5Cr_2O_7^{2-} + 34H^+ \longrightarrow 6XO_4^- + 17H_2O + 10Cr^{3+}$

(*ii*) Also$X_2O_3 + 5H_2O \longrightarrow 2XO_4^- + 10H^+ + 8e^-] \times 3$

$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O] \times 4$

$3X_2O_3 + 26H^+ + 4Cr_2O_7^{2-} \longrightarrow 6XO_4^- + 8Cr^{3+} + 13H_2O$

In a mixture, let the amount of

$XO = wg = \dfrac{\text{w mol}}{\text{M + 16}}$

(*M* is the at. wt. of *X*)

Amount of X_2O_3 in the mixture

$= (2.198 - w)\ \text{g} = \dfrac{(2.198 - w)\ \text{mol}}{2M + 48}$

1 mol $XO \equiv 1$ mol of XO_4^-

Also, 1 mol $X_2O_3 \equiv 2$ mol of XO_4^-

Thus, $\dfrac{w}{M+16} + \dfrac{2(2.198 - w)}{2M + 48}$

$= 0.0187$ ...(*iii*)

From the equation (*i*) 6 mol

$$XO \equiv 5 \text{ mol } Cr_2O_7^{2-}$$

From equation (*ii*) 3 mol of $X_2O_3 \equiv 4$ mol $Cr_2O_7^{2-}$

Thus, $$\frac{5w}{6(M+16)} + \frac{4}{3} \times \frac{(2.198 - w)}{2M + 48} = 0.015 \qquad \text{...}(iv)$$

Multiplying equation (*iii*) by $\frac{2}{3}$; we get

$$\frac{2w}{3(M+16)} + \frac{4}{3} \times \frac{(2.198 - w)}{2M + 48} = 0.0125 \qquad \text{...}(v)$$

Subtracting equation (*v*) from (*iv*), we get

$$\frac{1}{6} \cdot \frac{w}{M+16} = 0.0025 \quad \text{or}$$

$$w = 0.0150\text{M} + 0.24 \qquad \text{...}(vi)$$

Also multiplying equation (*iii*) by 5/6

$$\frac{5}{6} \times \frac{w}{(M+16)} + \frac{5}{3} \times \frac{(2.198 - w)}{(2M + 48)} = 0.0156 \qquad \text{...}(vii)$$

Subtracting (*iv*) from (*vii*) $\frac{1}{3}$.

$$\frac{(2.198 - w)}{2M + 48} = 0.0006\ 2.198 - w$$

$$= 0.0036\,M + 0.0864$$

or $$w = 2.1116 - 0.0036\,M \qquad \text{...}(viii)$$

From equations (*vi*) and (*viii*)

$$0.0150\,M + 0.24 = 2.1116 - 0.0036\,M$$

On solving,0.0186 M = 1.8716 or M = 100.6

Hence, the atomic weight of

$$M = 100.6$$

Example 131. *Calculate the molality of one litre solution of 93%* H_2SO_4 *by volume. The density of solution is 1.84 g mL⁻.*

(IIT, 2003)

Solution. Volume = 1L ; Volume of H_2SO_4 = 100 mL ; wt. of H_2SO_4 = 93 g ; density = 1.84 g (mL)⁻ ; mol. wt. of $H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98$ g mol⁻

$\therefore$ wt. of solution = Volume × density

$$= 100 \text{ mL} \times 1.84 \text{ g (mL)}^{-} = 184 \text{ g}$$

wt. of H_2O (solvent) = 184 – 93 = 91 g

$$= 91 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}} = \frac{91}{1000} \text{ kg}$$

$$\therefore \quad \text{Molality} = \frac{\text{wt.}}{\text{Mol. wt.} \times \text{wt. of solvent in kg}}$$

$$= \frac{93 \times 1000}{98 \times 91} = \mathbf{10.43} \qquad \textbf{Ans.}$$

Example 132. *A 100 mL solution of* Na_2CO_3 *is prepared by dissolving 8.653 g of the salt in water. The density of the solution is 1.0816 gram per milli litre. What are the molality and molarity of the solution? (At. wt., Na = 23, C = 12, O = 16).*

(MDU 1980)

Solution. (*i*) wt. of Na_2CO_3 = 8.653 g ; mol. wt. of $Na_2CO_3 = (2 \times 23) + 12 + (3 \times 16) = 106$ g mol⁻, Volume = 100 mL.

$$\text{Molarity of } Na_2CO_3 = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{8.653 \text{ g}}{106 \text{ g mol}^{-}} \times \frac{1000}{100}$$

$$= \mathbf{0.816\ M} \qquad \textbf{Ans.}$$

(*ii*) wt. of solution = Volume × density = 100 mL × 1.0816 g (mL)⁻ = 108.16 g

wt. of solute = 8.653 g. Hence wt. of solvent = 108.16 – 8.653 = 99.507 g

$\therefore$ Molality of Na_2CO_3

$$= \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{wt. of solvent}}$$

$$= \frac{8.653}{106} \times \frac{1000}{99.507}$$

$$= \mathbf{0.82\ m} \qquad \textbf{Ans.}$$

> **Note.** For more numericals, see chapter 17 of solution – concentration.

2. **Ionic strength (μ) of a Solution.** It is given by the relation :

$$\mu = \frac{1}{2} \sum C Z^2$$

where Z = valence of ion ;

C = concentration in mol L⁻.

Example 133. *Calculate the ionic strength of a solution that is 0.2 M in* $(NH_4)_3PO_4$, *0.5 M in* $AlCl_3$ *and 0.4 M in* $ZnSO_4$.

Solution. (*i*) $(NH_4)_3PO_4 \rightleftharpoons 3NH_4^+ + PO_4^{3-}$

For $3NH_4^{+1}$, $Z = 1$, $C = 3 \times 0.2 = 0.6$ mol L⁻.

For PO_4^{3-}, $Z = 3$, $C = 0.2$ mol L⁻

(*ii*) $AlCl_3 \rightleftharpoons Al^{3+} + 3Cl^-$

For Al^{3+}, $Z = 3$, $C = 0.5 \times 1 = 0.5$ mol L⁻.

For $3Cl^{-1}$, $Z = 1$, $C = 3 \times 0.5 = 1.5$ mol L⁻

(*iii*) $ZnSO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-}$

For Zn^{2+}, $Z = 2$, $C = 0.4$ mol L⁻. For SO_4^{2-}, $Z = 2$, $C = 0.4$ mol L⁻

We know that : $$\mu \text{ (Ionic strength)} = \frac{1}{2} \sum C Z^2 \qquad \text{...}(A)$$

C = concentration of ion in mol L⁻, Z = Valency of ion.

Substituting the values of Z and C in equation (A) for ions of $(NH_4)_3PO_4$, $AlCl_3$ and $ZnSO_4$, we have :

$$\mu = \frac{1}{2} [(0.6 \times 1^2 + 0.2 \times 3^2) + (0.5 \times 3^2 + 1.5 \times 1^2) + (0.4 \times 2^2 + 0.4 \times 2^2)] \text{ mol L}^{-}$$

$$= \frac{1}{2} [0.6 + 1.8 + 4.5 + 1.5 + 1.6 + 1.6] = \frac{1}{2} \times 11.6 = \mathbf{5.8} \qquad \textbf{Ans.}$$

Example 134. *How much amount of NaOH is needed to neutralise 20 meq. of HCl?*

Solution. *Reaction :*

$$\underset{20 \text{ meq.}}{NaOH} + \underset{20 \text{ meq.}}{HCl} \longrightarrow NaCl + H_2O.$$

From above reaction, we find that 20 meq.

NaOH = 20 meq. HCl.

But No. of meq. of a solute

$$= \frac{\text{wt. of solute (g)}}{\text{g. eq. wt. of solute}} \times 1000$$

$$\therefore \quad 20 = \frac{\text{wt. of solute (g)}}{40} \times 1000$$

Or wt. of solute $= \frac{20 \times 40}{1000} = \mathbf{0.8\ g}$ **ns.**

EXAMPLE 135. *Calculate the volume of 2.5 M H_2SO_4 required to neutralise a solution containing 2.0 g of sodium hydroxide.*

SOLUTION. NaOH = 2.0 g ; g. eq. wt. of NaOH = 23 + 16 + 1 = 40 g.

$$\text{Meq. of NaOH} = \frac{\text{wt. of NaOH}}{\text{g. eq. wt. of NaOH}} \times 1000$$

$$= \frac{2}{40} \times 1000 = 50$$

Now Meq. of H_2SO_4 = Meq. of NaOH.

H_2SO_4 ionises as : $\underset{2.5\text{ M}}{H_2SO_4} \rightleftharpoons \underset{2 \times 2.5\text{ M}}{2H^+} + SO_4^{2-}$

Let Volume of H_2SO_4 = V mL

$\therefore$ Meq. of H_2SO_4 = $V \times 2 \times 2.5 = 5V$

$\therefore$ $5V = 50$ or $V = 50/5 = \mathbf{10\ mL}$ **Ans.**

EXAMPLE 136. *Calculate the volume of 0.1 M NaOH needed for the neutralisation of 20 mL of 0.05 M oxalic acid.*

SOLUTION. Let volume of NaOH = V mL.

$$\underset{0.1\text{ M}}{NaOH} \rightleftharpoons Na^+ + \underset{0.1\text{ M}}{OH^-}$$

$\therefore$ Meq. of NaOH = $V \times 0.1$ ...(1)

Oxalic acid, $H_2C_2O_4$ ionises as :

$$\underset{0.05\text{ M}}{H_2C_2O_4} \rightleftharpoons \underset{2 \times 0.05\text{ M}}{2H^+} + C_2O_4^{2-}$$

$\therefore$ Meq. of $H_2C_2O_4$ = $20 \times 2 \times 0.05$ ...(2)

Since Meq. of NaOH = Meq. of $H_2C_2O_4$

$\therefore$ $V \times 0.1 = 20 \times 2 \times 0.05$

$\therefore$ $V = \frac{20 \times 2 \times 0.05}{0.1} = \mathbf{20\ mL}$ **Ans.**

EXAMPLE 137. *One kilogram of a sea water sample contains 6 mg of dissolved oxygen. The concentration of O_2 in the sample in ppm is :*

(*a*) 0.6
(*b*) 6.0
(*c*) 60.0
(*d*) 16.0
(*e*) 32.0

(Kerala PMT, 2010)

SOLUTION. ppm is parts per million. It is the quantity of the solute in grams persent in 10^6 grams of solution. 6 mg = 6×10^{-3} g. Thus : ppm = [Mass of solute/mass of solution] $\times 10^6$ = $(6 \times 10^{-3}\text{ g}/1000\text{g}) \times 10^6 = 6$ [$\because$ 1 kg = 1000g].

So, correct answer is (*b*).

EXAMPLE 138. *7.2 g of bleaching powder was suspended in 500 mL water. 20 mL of this solution when treated with KI solution in presence of HCl, liberated I_2. This I_2 required 18.9 mL of 0.1 N $Na_2S_2O_3$ for complete oxidation. Calculate the percentage of available chlorine from the bleaching powder.*

SOLUTION. Meq. of $Na_2S_2O_3$ = Meq. of I_2 = Meq. of Cl_2.

Meq. of $Na_2S_2O_3$ = Volume of $Na_2S_2O_3$ × normality of $Na_2S_2O_3$ = $18.9 \times 0.1 = \mathbf{1.89}$

Meq. of Cl_2 in 20 mL = 1.89

$$\text{Meq. of } Cl_2 \text{ in 500 mL} = \frac{1.89}{20} \times 500 = 47.25$$

But Meq. of Cl_2 = Meq. of bleaching powder = Meq. of available Cl_2 in bleaching powder

$$\text{Meq. of } Cl_2 = \frac{\text{wt. of } Cl_2}{\text{Eq. wt. of } Cl_2} \times 1000$$

$$\left[\text{Eq. wt. of } Cl_2 = \frac{\text{Mol. wt.}}{2} = \frac{2 \times 35.5}{2} = 35.5\right]$$

$$47.25 = \frac{\text{wt. of } Cl_2}{35.5} \times 1000$$

$$\text{or} \quad \text{wt. of } Cl_2 = \frac{47.25 \times 35.5}{1000} = 1.68$$

$$\therefore \quad \%\text{ age of } Cl_2 = \frac{\text{wt. of } Cl_2}{\text{wt. of bleaching powder}} \times 100$$

$$= \frac{1.68 \times 100}{7.2}$$

or % age of Cl_2 = **23.3** **Ans.**

EXAMPLE 139. *An excess of acidified KI solution was treated with 1000 cm^3 of a mixture of oxygen and ozone. I_2 so liberated required 41.3 cm^3 of 0.1 M $Na_2S_2O_3$ solution for quantitative titration. If U.V. radiations of wavelength 300 nm can decompose ozone and one photon can decompose one ozone molecule, calculate the number of photons required to decompose ozone completely in the original mixture. Also, calculate the mass percent of ozone in the mixture.*

SOLUTION. 1000 cm^3 = 1L

$\therefore$ Moles of O_2 and O_3 in the mixture

$$= \frac{1\text{ L}}{22.4\text{ L}} = 0.0446$$

Equivalents of

$$Na_2S_2O_3 = \text{vol.} \times \text{molarity} \times n$$

$$= \frac{41.3}{1000} \times \frac{1}{10} \times 1 = 4.13 \times 10^{-3}$$

Equivalent of I_2 = Equivalent of KI = Equivalent of O_3 = 4.13×10^{-3}

For the reaction :

$$S_2O_3^{2-} \rightarrow \frac{1}{2}\, S_4O_6^{2-} + 1e^-;\ n = 1$$

$$\underset{1\text{ mol}}{O_3} \rightarrow O_2 + O$$

$$KI + H_2O + \underset{1\text{ mol}}{O} \rightarrow 2KOH + I_2$$

$$2Na_2S_2O_3 + \underset{1\text{ mol}}{I_2} \rightarrow Na_2S_4O_6 + 2NaI$$

When O_3 reacts with KI, it converts to O^{2-} and O_2^0. So '*n*' factor = oxidation number change = 0 – (– 2) = 2.

$$\therefore \quad \text{Moles of } O_3 = \frac{4.13\times10^{-3}}{n} = \frac{4.13\times10^{-3}}{2}$$

$$= 2.065\times10^{-3} = 0.002065$$

$$\text{Moles of } O_2 = 0.0446 - 0.002065 = 0.042535$$

$$\text{Mass of } O_3 = \text{no. of moles} \times \text{mol. wt.}$$

$$= 0.002065 \times (3 \times 16) = 0.09912 \text{ g}$$

$$\text{Mass of } O_2 = \text{no. of moles} \times \text{mol. wt}$$

$$= 0.042535 \times (2 \times 16) = 1.36112$$

$$\%\text{ age of } O_3 = \frac{\text{wt. of } O_3}{\text{wt. of } O_3 + \text{wt. of } O_2} \times 100$$

$$= \frac{0.09912}{0.09912 + 1.36112} \times 100$$

$$= \frac{0.09912}{1.46024} \times 100 = \mathbf{6.79}$$ **Ans.**

Number of O_3 molecules

$$= \text{no. of moles} \times 6.023 \times 10^{23}$$

$$= 0.002065 \times 6.023 \times 10^{23}$$

$$= \mathbf{1.24 \times 10^{21}}$$ **Ans.**

Hence number of photons required

$$= \mathbf{1.24 \times 10^{21}}$$ **Ans.**

EXAMPLE 140. *During a titration of a solution of 0.2 g of a compound containing Cu^{2+} and $C_2O_4^{2-}$ ions, 22.6 mL of 0.02 M $KMnO_4$ oxidant was consumed. The resulting solution was neutralised with sodium carbonate solution and then acidified with dil. CH_3COOH and treated with excess KI. The liberated iodine required 11.3 mL of N/20 hypo solution for complete reduction. Calculate the mole ratio of Cu^{2+} to $C_2O_4^{2-}$ in the compound. Also write the redox reactions involved.*

SOLUTION. $KMnO_4$ and Cu^{2+} are oxidants while $C_2O_4^{2-}$ and I^- (of KI) are reductants. $KMnO_4$ is a stronger oxidant and would react with $C_2O_4^{2-}$ ions as follows.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Now I^- ions react with Cu^{2+} ions as follows :

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

Now I_2 reacts with hypo ($Na_2S_2O_3$) as follows :

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

Equivalents of $KMnO_4$ solution

$$= \frac{\text{Vol in mL} \times \text{molarity} \times n}{1000}$$

$$[MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O;\ n = 5]$$

$$= \frac{22.6 \times 0.02 \times 5}{1000} = 0.00226$$

$$\therefore \quad \text{Moles of } C_2O_4^{2-} = \frac{0.00226}{n} = \frac{0.00226}{2} = 0.00113$$

$$\left[\because\ C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-;\ n = 2\right]$$

Equivalents of $Na_2S_2O_3$ solution

$$= \frac{\text{Vol in mL} \times \text{normality}}{1000}$$

$$= \frac{11.3 \times 1}{20 \times 1000} = 5.65 \times 10^{-4}$$

$$\therefore \quad \frac{\text{Moles of } Cu^{2+} \text{ ions}}{n} = \text{Equivalents of } Na_2S_2O_3$$

Or $$\frac{\text{Moles of } Cu^{2+} \text{ ions}}{1} = 5.65 \times 10^{-4}$$

$$[\because\ Cu^{2+} + 1e^- \longrightarrow Cu^+]$$

But moles of $C_2O_4^{2-}$ = 0.00113 (found above)

∴ Ratio of moles of Cu^{2+} to $C_2O_4^{2-}$

$$= \frac{5.65 \times 10^{-4}}{0.00113} = \mathbf{0.5}$$ **Ans.**

EXAMPLE 141. *Calculate the mass of $KMnO_4$ that is required to produce from excess oxalic acid ($H_2C_2O_4$), 4.5 L of CO_2 at 71°C and 1.02 atmospheric pressure (At. wt. Mn = 55, K = 39, O = 16)*

SOLUTION. P = 1.02 atm. ; V = 4.5 L ; R = 0.0821 L atm K^- mol$^-$; T = 71 + 273 = 244 K. n = no. of moles of CO_2 required. We know :

$$PV = nRT \text{ Thus, } n = \frac{PV}{RT}$$

$$= \frac{1.02 \text{ atm} \times 4.5 \text{ L}}{0.0821 \text{ L atm K}^- \text{mol}^- \times 244 \text{ K}}$$

or $$n = 0.229 \text{ mol}$$

Reactions. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

2 mol 10 mol

1 mol 5 mol

5 mol of CO_2 is due to $KMnO_4$ = 1 mol

0.229 mol of CO_2 is due to $KMnO_4$

$$= \frac{1 \times 0.229}{5} = 0.0458 \text{ mol}$$

g. molar mass of

$$KMnO_4 = 39 + 55 + (4 \times 16)$$

$$= 39 + 55 + 64 = 158 \text{ g}$$

$$\therefore \text{ Mass of } KMnO_4 = \text{no. of moles} \times \text{Mol. wt}$$

$$= 0.0458 \times 158 = \mathbf{7.2364 \text{ g}}$$ **Ans.**

EXAMPLE 142. *3.32×10^{-3} mol of A^{n+} ions in a solution require 2.0×10^{-3} mol of MnO_4^- for the complete oxidation of A^{n+} into AO_3^- in acidic solution. Calculate the value of n.*

(IIT 1984)

SOLUTION. Reaction

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \text{...(1)}$$

$$n = 5$$

'*n*' factor in reaction (1) is 5.

∴ Equivalents of MnO_4^-

$$= \text{Moles of } KMnO_4 \times \text{'}n\text{' factor}$$
$$= 2.0 \times 10^{-3} \times 5 = 10.0 \times 10^{-3}$$

Equivalents of $A^{n+} = 10.0 \times 10^{-3}$

$\therefore$ n factor of $AO_3^- = 5 - n$

Thus $(5 - n) \times 3.32 \times 10^{-3} = 10.0 \times 10^{-3}$

Or $$5 - n = \frac{10.0 \times 10^{-3}}{3.32 \times 10^{-3}} = 3$$

Or $n = 5 - 3 = 2$ $\therefore$ $n = \mathbf{2}$ **Ans.**

EXAMPLE 143. *How much volume of HCl (sp. gr. 1.2 g mL^- and 5% nature by weight) and amount of MnO_2 are needed to liberate 1.5 L of Cl_2 gas at N.T.P. by the reaction.*

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + H_2O.$$

(At. wt. Mn = 55, O = 16)

SOLUTION. (*a*) Given reaction is :

$$\begin{array}{cccc} MnO_2 & + \; 4HCl & \longrightarrow MnCl_2 + Cl_2 + H_2O & \quad ...(1) \\ 1 \text{ mol} & 4 \text{ mol} & 22.4 \text{ L} & \\ = 55 + (2 \times 16) & = 4 \times 36.5 & = 1 \text{ mol} & \\ = 87 & = 146 & & \end{array}$$

$$\text{Moles of } Cl_2 = \frac{\text{Vol of } Cl_2 \text{ in L}}{22.4 \text{ L}}$$
$$= \frac{1.5 \text{ L}}{22.4 \text{ L}} = 0.067 \text{ mol}$$

But from reaction (1), Moles of

MnO_2 = Moles of Cl_2

$\therefore$ Moles of $MnO_2 = 0.067$

$\therefore$ Wt. of MnO_2 = no. of moles × g. mol. wt. of MnO_2

$= 0.067 \times 87$ g

Wt. of MnO_2 = **5.829 g** **Ans.**

[$\because$ Mol. wt. of $MnO_2 = 55 + (2 \times 16) = 87$]

(*b*) 87 g MnO_2 react with HCl

= 146 g [from reaction (1)]

$\therefore$ 5.829 g MnO_2 react with

$$HCl = \frac{146}{87} \times 5.829 = 9.782 \text{ g.}$$

$\therefore$ Mass of HCl = 9.782 g

$$\text{Volume} \times \text{density} = \text{Mass} \quad \textbf{Or} \quad \text{Volume} \times 1.2 \times \frac{5}{100} = \text{Mass.}$$

$$\text{Volume} \times 1.2 \times \frac{5}{100} = 9.782$$

Or $$\text{Volume} = \frac{9.782 \times 100}{1.2 \times 5} = \mathbf{163 \text{ ml}}$$ **Ans.**

EXAMPLE 144. *A mixture containing $NaHC_2O_4$ and $H_2C_2O_4$ was dissolved in water and the solution was made up to one litre. 10 cm^3 of this mixture solution required 3.0 cm^3 of N/10 NaOH solution for complete neutralisation. In second experiment, 10 cm^3 of the same mixture required 4 cm^3 of N/10 $KMnO_4$ in dil. H_2SO_4 medium for complete oxidation. Calculate the amounts of $NaHC_2O_4$ and $H_2C_2O_4$ in the mixture.*

SOLUTION. Let wt. of $H_2C_2O_4$ in the mixture = x gL^-

Wt. of $NaHC_2O_4$ in the mixture = y gL^-

$\therefore$ Wt. of $H_2C_2O_4$ in 10 cm^3

$$= \frac{x}{1000} \times 10 = \frac{x}{100} \text{ g}$$

($\because$ 1L = 1000 cm^3)

Wt. of $NaHC_2O_4$ is 10 cm^3

$$= \frac{y}{1000} \times 10 = \frac{y}{100} \text{ g}$$

(*a*) Equivalents of NaOH

$$= \frac{\text{Vol. in cm}^3 \times \text{normality}}{1000 \text{ cm}^3}$$
$$= \frac{3 \times 1}{10 \times 1000} = 0.0003$$

Both $H_2C_2O_4$ and $NaHC_2O_4$ are acids. So, these will react with NaOH

$$(H_2C_2O_4 \rightleftharpoons 2H^+ + C_2O_4^{2-};$$
$$\mathbf{n = 2}$$
$$NaHC_2O_4 \rightleftharpoons Na^+ + H^+ + C_2O_4^{2-})$$
$$\mathbf{n = 1}$$

Mol. wt. of $H_2C_2O_4 = (2 \times 1) + (2 \times 12) + (4 \times 16)$

$= 2 + 24 + 64 = 90$

Mol. wt. of $NaHC_2O_4 = 23 + 1 + (2 \times 12) + (4 \times 16)$

$= 23 + 1 + 24 + 64 = \mathbf{112}$

Equivalents of $H_2C_2O_4$ = no. of moles × n

$$= \frac{\text{wt.}}{\text{mol. wt.}} \times n = \frac{x}{100 \times 90} \times 2 = \frac{x}{4500}$$

Equivalents of $NaHC_2O_4$ = no. of moles × n

$$= \frac{\text{wt.}}{\text{mol. wt.}} \times n = \frac{y}{100 \times 112} \times 1$$
$$= \frac{y}{11200}$$

But, Equivalents of $H_2C_2O_4$ + Equivalents of $NaHC_2O_4$ = Equivalents of NaOH

Or $$\frac{x}{4500} + \frac{y}{11200} = 0.0003 \quad ...(1)$$

(*b*) Equivalents of $KMnO_4$

$$= \frac{\text{Vol. in mL} \times \text{normality}}{1000}$$
$$= \frac{4 \times 1}{10 \times 1000} = 0.0004$$

$KMnO_4$ oxidises $H_2C_2O_4$ (oxidation state of C = + 3) to CO_2 (oxidation state of C = +4), the oxidation no. change = + 4 – (+ 3) = + 1

For two C-atoms in both $H_2C_2O_4$ and NaH C_2O_4, the 'n' factor = + 1 × 2 = 2.

Hence, from equation (1), we have.

$$\frac{x \times 2}{90 \times 100} + \frac{y \times 2}{100 \times 112} = 0.0004$$

Or $$\frac{x}{4500} + \frac{y}{5600} = 0.0004 \quad ...(2)$$

Subtracting equation (1) from (2), we get.

$$\frac{y}{5600}-\frac{y}{11200} = 0.0004 - 0.0003$$

Or $$\frac{2y-y}{11200} = 0.0001$$

$y = 0.0001 \times 11200 = 1.12$ g

= wt. of $NaHC_2O_4$ **Ans.**

Substituting the value of

$y = 1.12$ in equation (2), we get :

$$\frac{x}{4500}+\frac{1.12}{5600} = 0.0004$$

Or $\frac{x}{4500}+0.0002 = 0.0004;\ \frac{x}{4500}$

$= 0.0004 - 0.0002 = 0.0002$

or $x = 0.0002 \times 4500 = 0.9$ g

∴ Wt. of $H_2C_2O_4$ = **0.9 g** **Ans.**

Back Titration.

EXAMPLE 145. *1.8 g of pyrolusite ore was warmed with 50 mL of 1N oxalic acid and some dil. H_2SO_4. The undecomposed oxalic acid solution was diluted to exact 250 mL. 25 mL of this solution on titration with 0.1 N $KMnO_4$ required 32 mL of the solution. Calculate the percentage of MnO_2 and available oxygen in pyrolusite. (At. wt. Mn = 55, O = 16).* **(Roorkee, 1996)**

SOLUTION. (*a*) wt. of pyrolusite, MnO_2 = 1.8 g.

Let normality of diluted oxalic acid

$= N_1$; Volume, V_1 = 250 mL

Meq. of excess dil. oxalic acid is 25 mL

= Meq. of $KMnO_4$

= Vol. of $KMnO_4$ × normality of

$KMnO_4 = 32 \times 0.1$

∴ Meq. of excess dil. oxalic acid in 250 mL

$$= \frac{32 \times 0.1}{25} \times 250 = 32$$

Meq. of oxalic acid added

= Vol of oxalic acid × normality

= 50 × 1 = 50

But Meq. of MnO_2 = Meq. of oxalic acid added – Meq. of excess oxalic acid. = 50 – 32 = **18**

Let weight of MnO_2 = w g.

But $$\text{Meq.} = \frac{\text{wt. of } MnO_2}{\text{Eq. wt. of } MnO_2} \times 1000$$

$$18 = \frac{\text{wt. of } MnO_2}{\frac{87}{2}} \times 1000$$

∴ $$\text{wt. of } MnO_2 = \frac{18 \times 87}{2} \times \frac{1}{1000} = 0.783 \text{ g.}$$

$$\text{\% age of } MnO_2 = \frac{\text{wt. of } MnO_2}{\text{wt. of pyrolusite}} \times 100$$

$$= \frac{0.783}{1.8} \times 100 = \mathbf{43.5}$$ **Ans.**

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

∴ n = 2 because of two e⁻s.

$$\therefore \text{Eq. wt. of } MnO_2 = \frac{\text{Mol. wt. of } MnO_2}{n}$$

$$= \frac{55+(2\times16)}{2} = \frac{87}{2}$$

(*b*) 1g. eq. of MnO_2 produces oxygen = 1 g eq ;

$$\text{Meq} = \frac{\text{wt. of } O_2}{\text{Eq. wt. of } O_2} \times 1000\ ;$$

$$18 = \frac{\text{wt. of } O_2}{8} \times 1000$$

∴ $$\text{wt. of } O_2 = \frac{18 \times 8}{1000} = 0.144 \text{ g}$$

∴ % age of available oxygen

$$= \frac{0.144}{1.8} \times 100 = \mathbf{6.33\%}$$ **Ans.**

EXAMPLE 146. *10 g of a sample of gas liquor (NH_4^+ salt) is boiled with NaOH and the resulting NH_3 is passed into 60 mL of 0.9 N H_2SO_4. Excess H_2SO_4 required 10 cm³ of 0.4 N NaOH. What is the percentage of NH_3 in gas liquor ?*

SOLUTION. Meq. of H_2SO_4 taken

= Vol of H_2SO_4 × Normality of

H_2SO_4 = 60 × 0.9 = **54**

Volume of NaOH = 10 cm³ or 10 mL

Meq. of excess H_2SO_4 left behind

= Meq. of NaOH

Meq. of NaOH = Vol of NaOH × normality of

NaOH = 10 × 0.4 = 4 = Meq of NH_3

∴ Meq. of excess H_2SO_4 = 4

∴ Meq. of H_2SO_4 used to form

NH_3 = 54 – 4 = 50.

Let wt. of NH_3 = wg ; Eq. wt. of

NH_3 = 14 + (3 × 1) = 17

But $$\text{Meq. of } NH_3 = \frac{\text{wt. of } NH_3}{\text{Eq. wt. of } NH_3} \times 1000$$

$$50 = \frac{\text{wt. of } NH_3}{17} \times 1000$$

∴ $$\text{Wt. of } NH_3 = \frac{17 \times 50}{1000} = 0.85 \text{ g}$$

$$\text{\% age of } NH_3 = \frac{\text{wt. of } NH_3}{\text{wt. of } NH_4^+ \text{ salt}} \times 100$$

$$= \frac{0.85 \times 100}{10} = \mathbf{8.5}$$ **Ans.**

EXAMPLE 147. *The formula weight of an acid is 82.0. In a titration, 100 cm³ of a solution of this acid containing 39.0 g of the acid per litre were completely neutralised by 95.0 cm³ of aqueous solution containing 40.0 g of NaOH per litre. What is the basicity of the acid.* **(Roorkee 2000)**

SOLUTION. Given that 40 g of NaOH is present in 1 litre solution.

It means that the normality of NaOH is 1N

[∵ Eq. wt. of NaOH = 23 + 16 + 1 = 40]

Let the normality of the acid

$$= N_1$$

Volume of the acid used = 100 cm^3

Applying normality equation

$$N_1V_1 = N_2V_2$$

$$N_1 \times 100 = 1\times 95 \therefore \text{Normality of the solution}$$

$$(N_1) = \frac{95}{100}$$

Given the strength of acid solution = 39 g litre^{-1}

∴ Equivalent weight of acid

$$= \frac{\text{Strength}}{\text{normality}} = \frac{39}{95/100}$$

$$= \frac{39\times 100}{95} = 41.105$$

Molecular mass of acid = 82.0 (given)

$$\therefore \text{ Basicity of acid } = \frac{\text{Mol. mass}}{\text{Eq. wt.}} = \frac{82}{41.05} = 2$$

Hence, the basicity of the acid = 2.

EXAMPLE 148. *Calculate the molarity and mass of sodium bromate of the solution required to prepare 86.5 mL of 0.55 N solution when the half cell reaction is* $2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$? (*At. wt. Na = 23, Br = 80, O = 16*)

SOLUTION. *Given reaction.*

$$2BrO_3^- + 12H^+ + 10e^- \longrightarrow Br_2 + 6H_2O.$$

For 1 mole of BrO_3^-, the reaction will be :

$$BrO_3^- + 6H^+ + 5e^- \longrightarrow \frac{1}{2} Br_2 + 3H_2O$$

$$n = 5$$

(*a*) Mol. wt. of $NaBrO_3$ (sodium bromate)

$$= 23 + 80 + (3 \times 16) = 151$$

$$\text{Eq. wt. of } NaBrO_3 = \frac{\text{Mol. wt.}}{n} = \frac{151}{5}$$

But Molarity × Mol. wt. = Normality × Eq. wt.

$$\therefore \quad \text{Molarity} = \frac{\text{Normality}\times\text{Eq. wt.}}{\text{Mol. wt.}}$$

$$= \frac{0.55}{151}\times\frac{151}{5} = \mathbf{0.11} \qquad \textbf{Ans.}$$

(*b*)To find mass of $NaBrO_3$. We know :

$$\text{Molarity} = \frac{\text{wt. of solute}}{\text{g. mol. wt. of solute}} \times \frac{1000}{\text{Volume of solution in mL}}$$

Substituting the values, we get :

$$0.11 = \frac{\text{wt. of solute}}{151}\times\frac{1000}{86.5}$$

Or $\text{wt. of solute} = \frac{0.11\times 151\times 86.5}{1000}$ ∴ wt. of solute

$$(NaBrO_3) = \mathbf{1.4368\ g}$$

EXAMPLE 149. *A 1.2 g sample of* Fe_2O_3 *solid of 46% purity was dissolved in an acid. The resulting solution was reduced by heating with zinc dust. This solution was then cooled and diluted to exact 100 cm³. 25 cm³ of this solution required 18.9 mL of 0.015 M solution of an oxidant for titration. Calculate the number of electrons taken up by the oxidant in the reaction of above titration.* (*At. wt. Fe = 56, O = 16*).

SOLUTION. Wt. of impure Fe_2O_3 = 1.2 g ;

% age purity = 46%

$$\therefore \text{ Wt. of pure } Fe_2O_3 = \frac{1.2\times 46}{100} = 0.552 \text{ g.}$$

$$\text{Mol. wt. of } Fe_2O_3 = (2 \times 56) + (3 \times 16)$$

$$= 112 + 48 = 160.$$

$$\therefore \text{ Moles of } Fe_2O_3 = \text{wt/Mol. wt}$$

$$= 0.552/160 = 3.45 \times 10^{-3}$$

Equivalent of oxidant

$$= \frac{n\times\text{Vol. of oxidant}\times\text{molarity of oxidant}}{1000}$$

[n = no. of electrons involved in oxidant reaction]

$$= \frac{n\times 18.9\times 0.015}{1000} = 2.84 \times 10^{-4}\, n$$

Zinc dust has reduced total Fe^{3+} ions of Fe_2O_3 to Fe^{2+} ions.

$$(\underset{1\text{ mol}}{Fe_2O_3} \longrightarrow \underset{2\text{ mol}}{2Fe^{2+}}\ ;\ n = 2)$$

∴ Moles of Fe^{2+} in 100 cm^3

$$= 2 \times 3.45 \times 10^{-3}$$

Moles of Fe^{2+} in 25 cm^3

$$= \frac{2\times 3.45\times 10^{-3}}{100}\times 25 = 1.725 \times 10^{-3}$$

According to law of equivalents :

Equivalents of oxidant = Equivalent of Fe^{2+}

$$2.84 \times 10^{-4}\, n = 1.725 \times 10^{-3}$$

$$\therefore \qquad n = \frac{1.725\times 10^{-3}}{2.84\times 10^{-4}} = 6.07 \simeq 6 \qquad \textbf{Ans.}$$

EXAMPLE 150. *A sample weighing 7.5 g contained* Fe_2O_3, Fe_3O_4 *and inert material. When treated with an excess of aqueous KI solution in acidic medium, reduced* Fe^{3+} *ions to* Fe^{2+} *ions. The resulting solution was diluted to 50 mL. Out of it, 10 mL was taken. The liberated* I_2 *in this solution required 7.4 mL of 1M* $Na_2S_2O_3$ *for reduction to iodide. Iodine from another 25 mL sample was extracted, after which the* Fe^{2+} *ions was titrated with 1M* $KMnO_4$ *in acidic medium. The volume of* $KMnO_4$ *solution used was found to be 4.15 mL. Calculate the mass percentages of* Fe_2O_3 *and* Fe_3O_4 *in the original mixture.*

SOLUTION. Wt. of Fe_2O_3 + wt. of

Fe_3O_4 = 7.5 g ; $Fe_3O_4 = Fe_2O_3 + FeO$.

Let moles of Fe_3O_4 = x g ; moles of Fe_2O_3 = y g

(*a*) *First titration.* Equivalents of

$$Na_2S_2O_3 = \frac{\text{Vol}\times\text{molarity}\times n}{1000}$$

$$\left[S_2O_3^{2-} \rightarrow \frac{1}{2}S_4O_6^{2-} + 1e^- ; n = 1\right]$$

$$= \frac{7.4\times 1\times 1}{1000} = 7.4 \times 10^{-3}$$

Since equivalent of $Na_2S_2O_3$ = equivalent of I_2

$= \text{Equivalent of } Fe_2O_3 + Fe_2O_3$ (from Fe_3O_4)

$\therefore$ Equivalent of 10 mL

$I_2 = 7.4 \times 10^{-3}$

Equivalent of 50 mL

$$I_2 = \frac{7.4\times10^{-3}}{10}\times 50 = 3.7 \times 10^{-2}$$

$\therefore$ Total equivalent of

$Fe_2O_3 = 3.7 \times 10^{-2}$

Fe_3O_4 consists of Fe_2O_3 + FeO. For Fe_2O_3 and Fe_2O_3 (from Fe_2O_3 + FeO), n factor is 2 because Fe_2O_3 on reduction gives Fe^{2+} *i.e.*, $Fe_2O_3 \rightarrow 2Fe^{2+}$). Thus :

$$2x + 2y = 3.7 \times 10^{-2} \qquad ...(1)$$

(*b*) **Second titration**. In acidic $KMnO_4$, we have :

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$n = 5$

$\therefore$ Equivalent of $KMnO_4$

$$= \frac{\text{Vol.}\times\text{molarity}\times n}{1000} = \frac{4.15\times1\times5}{1000} = 2.08 \times 10^{-2}$$

But Equivalent of $KMnO_4$ = Equivalent of Fe^{2+}

Equivalent of Fe^{2+} in 25 mL = 2.08×10^{-2}

$\therefore$ Equivalent of Fe^{2+} in 50 mL

$$= \frac{2.08\times10^{-2}\times50}{25} = 4.16 \times 10^{-2}$$

$\therefore$ Moles of $Fe^{2+} = 4.16 \times 10^{-2}$

For Fe_3O_4, n = 3 because $Fe_3O_4 \rightarrow 3Fe^{2+}$ and for Fe_2O_3, n = 2 because $Fe_2O_3 \rightarrow 2Fe^{2+}$.

Thus, $3x + 2y = 4.16 \times 10^{-2}$ ...(2)

Subtracting equation (1) from (2), we get :

$$3x + 2y - 2x - 2y = 4.16 \times 10^{-2} - 3.7 \times 10^{-2}$$
$$= 10^{-2}(4.16 - 3.7) = 0.46 \times 10^{-2}$$

Or $x = 4.6 \times 10^{-3}$.

Or moles of $Fe_3O_4 = 4.6 \times 10^{-3}$

(*c*) $\therefore$ Wt. of $Fe_3O_4 = 4.6 \times 10^{-3} \times 232 = 1.0672$ g

[$\because$ Mol. wt. of $Fe_3O_4 = (3 \times 56) + (4 \times 16) = 232$]

$\therefore$ % age of $Fe_3O_4 = \frac{1.0672}{7.5}\times 100 =$ **14.23%** **Ans.**

(*d*) *To find weight of* Fe_2O_3.

Substituting the value of $x = 4.6 \times 10^{-3}$ in equation (1), we get :

$2 \times 4.6 \times 10^{-3} + 2y = 3.7 \times 10^{-2}$

Or $9.2 \times 10^{-3} + 2y = 3.7 \times 10^{-2}$

Or $0.92 \times 10^{-2} + 2y = 3.7 \times 10^{-2}$

Or $2y = 3.7 \times 10^{-2} - 0.92 \times 10^{-2}$

$2y = 10^{-2}(3.7 - 0.92) = 10^{-2} \times 2.78$

or $y = (2.78 \times 10^{-2})/2 = 1.39 \times 10^{-2}$

$\therefore$ Moles of $Fe_2O_3 = 1.39 \times 10^{-2}$

Wt. of $Fe_2O_3 = 1.39 \times 10^{-2} \times 160 = 2.224$ g

[$\because$ Mol. wt. of $Fe_2O_3 = (2 \times 56) + (3 \times 16) = 160$]

$$\%\text{ age of } Fe_2O_3 = \frac{\text{wt. of } Fe_2O_3}{\text{Total wt.}}\times 100 = \frac{2.224}{7.5}\times 100$$

= **29.65%** **Ans.**

EXAMPLE 151. *18 g of a sample of* $Ba(OH)_2$ *is dissolved in 50 mL of 0.1 N HCl solution. The excess of HCl was titrated with 0.1 N NaOH solution. The volume of NaOH used was 18.9 mL. Calculate the percentage of* $Ba(OH)_2$ *in the sample (at. wt. Ba = 137, O = 16, H = 1)*

SOLUTION. $Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

$n = 2$

$$\text{Eq. wt. of } Ba(OH)_2 = \frac{171}{2}$$

$$\left[\because \text{Eq. wt.} = \frac{\text{Mol. wt.}}{n} = \frac{137+2(16+1)}{2} = \frac{171}{2}\right]$$

Initial milliequivalent of HCl

= Vol × normality = 50 × 0.1 = **5**

Milliequivalent of HCl in excess

= Vol × normality = 18.9 × 0.1 = **1.89**

$\therefore$ M.eq. of NaOH consumed = 1.89

Meq. of HCl consumed

= Meq. of $Ba(OH)_2$ = 5 – 1.89 = 3.11

Equivalents of $Ba(OH)_2$

$$= \frac{\text{Meq. of } Ba(OH)_2}{1000} = \frac{3.11}{1000}$$

$$\text{Wt. of } Ba(OH)_2 = \frac{3.11}{1000}\times\frac{171}{2} = 0.266 \text{ g}$$

$$\%\text{ age of } Ba(OH)_2 = \frac{\text{wt. of } Ba(OH)_2}{\text{Total wt.}}\times 100$$

$$= \frac{0.266 \text{ g}}{18}\times 100 = \mathbf{1.48}$$ **Ans.**

EXAMPLE 152. *Calculate the volume of 0.1 M* $KMnO_4$ *used to completely oxidise 20 mL of 0.05 M* $FeSO_4$ *under acidic conditions.*

SOLUTION. In acidic medium, $KMnO_4$ or MnO_4^- undergoes reduction as follows :

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$. Thus, $n = 5$

$\therefore$ Meq. of $KMnO_4$ = Vol. of solution in mL × molarity × n Let Volume of

$KMnO_4 = V$ mL

$\therefore$ Meq. of $KMnO_4 = V \times 0.1 \times 5$ ...(1)

$FeSO_4$ undergoes oxidation as :

$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$; Thus $n = 1$

$\therefore$ Meq. of $FeSO_4$ = Vol. of solution in mL × molarity × n

Meq. of $FeSO_4 = 20 \times 0.05 \times 1$ ...(2)

But Meq. of $KMnO_4$ = Meq. of $FeSO_4$. Hence from (1) and (2) we have:

$$V \times 0.1 \times 5 = 20 \times 0.05 \times 1$$

$$\therefore \quad V = \frac{20\times0.05}{0.1\times5} = \mathbf{2.0 \text{ mL}}$$ **Ans.**

EXAMPLE 153. *For the following half cell reaction*

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$$

calculate the weight of sodium bromate as well as molarity of solution to prepare 250 mL of 0.3N solution. (At. wt. Na = 23, Br = 80, O = 16)

SOLUTION. g. mol. wt. of sodium bromate, $NaBrO_3 = 23 + 80 + (3 \times 16) = 151$ g. Since the given reaction

$$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$$

involves six electron change, so :

$$\text{Eq. wt. of } NaBrO_3 = \frac{\text{Mol. wt.}}{6} = \frac{151}{6}$$

$$\text{Meq. of } NaBrO_3 = \text{Vol in mL} \times \text{normality}$$
$$= 250 \times 0.3 = 75$$

$$\text{But} \qquad \text{Meq} = \frac{\text{wt. of solute}}{\text{Eq. wt. of solute}} \times 1000$$

$$\therefore \qquad 75 = \frac{\text{wt. of solute}}{151/6} \times 1000$$

$$\text{Or} \quad \text{wt. of solute} = \frac{75 \times 151}{1000 \times 6} = 1.8875 \text{ g}$$

$$\text{Molarity} = \frac{\text{wt. of solute}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{Vol. of solution in mL}}$$

$$= \frac{1.8875}{151} \times \frac{1000}{250} = \mathbf{0.05\ M} \qquad \textbf{Ans.}$$

EXAMPLE 154. *0.2986 g of a sample of iron piece was dissolved in dil. H_2SO_4 and solution was made up to 150 mL. 30.0 mL of this solution required 25 mL of N/25 $K_2Cr_2O_7$ solution for oxidation. Calculate the percentage of pure iron in the given piece. (at. wt. Fe = 56).*

SOLUTION. $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \uparrow$

$$FeSO_4 \rightleftharpoons Fe^{2+} + SO_4^{2-};$$
$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$$

$$\therefore \quad \text{Eq. wt. of } Fe^{2+} = \frac{\text{at. wt. of Fe}}{1} = \frac{56}{1} = 56.$$

To find normality of Fe^{2+} solution.

$FeSO_4$ solution $\quad K_2Cr_2O_7$ solution

$$N_1V_1 = N_2V_2$$
$$N_1 \times 30 = 25 \times \frac{1}{25}; N_1 = \frac{1}{30}$$

We Know that :

1000 mL of 1N $FeSO_4$ solution contain

Fe = Eq. wt. of Fe = 56 g

150 mL of $\frac{N}{30}$ $FeSO_4$ solution contain

$$Fe = \frac{56}{1000} \times 150 \times \frac{1}{30} = 0.28 \text{ g}$$

$$\therefore \quad \%\text{ age of Fe} = \frac{\text{wt. of pure Fe}}{\text{wt. of Fe sample}} \times 100$$

$$= \frac{0.28}{0.2986} \times 100 = \mathbf{93.8\%} \qquad \textbf{Ans.}$$

EXAMPLE 155. *(a) $CuSO_4$ reacts quantitatively with KI in an acidic medium to liberate I_2. Write the balanced equation for this reaction.*

(b) Mercuric iodate $[Hg_5(IO_6)_2]$ reacts with a mixture of KI and HCl according to the following equation.

$$Hg_5(IO_6)_2 + 34KI + 24HCl \longrightarrow 5K_2HgI_4 + 8I_2 + 24KCl + 12H_2O$$

The liberated iodine is treated with $Na_2S_2O_3$ solution, one mL of which is equivalent to 0.0499 g of $CuSO_4.5H_2O$. What volume (in mL) of the $Na_2S_2O_3$ solution will be required to react with iodine liberated from 0.7245 g of $Hg_5(IO_6)_2$? (Hg = 200.5, Cu = 63.5, I = 127). **(IIT, 1970)**

SOLUTION. (*a*) *Reaction.*

$$2CuSO_4.5H_2O + 4KI \longrightarrow Cu_2I_2 \downarrow + I_2 + 2K_2SO_4 + 10H_2O$$

(*b*) $Hg_5(IO_6)_2 + 34KI + 24HCl \longrightarrow 5K_2HgI_4 + 8\,I_2 + 24KCl + 12H_2O$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

From reaction

(*a*) $\qquad I_2 \equiv 2CuSO_4 . 5H_2O$

$8I_2 \equiv 2 \times 8\ CuSO_4.5H_2O$

or $\ 16CuSO_4.5H_2O$

From reaction

(*b*) $\qquad Hg_5(IO_6)_2 \equiv 8I_2$

$\therefore \qquad Hg_5(IO_6)_2 \equiv 8I_2 \equiv 16CuSO_4.5H_2O$

$(5 \times 200.5) + 2[127 + (6 \times 16)] = 1002.5 + 446 = 1448.5$

$16[63.5 + 32 + (4 \times 16) + 5(2 \times 1 + 16)] = 16[63.5 + 32 + 64 + 90] = 3992$

(*i*) 1448.5 g $Hg_5(IO_6)_2$

$\equiv 3992$ g $CuSO_4.5H_2O$

$$0.7245 \text{ g } Hg_5(IO_6)_2 \equiv \frac{3992}{1448.5} \times 0.7245 \text{ g } CuSO_4 . 5H_2O$$

(*ii*) 0.0499 g $CuSO_4.5H_2O$

$\equiv 1$ mL of $Na_2S_2O_3$ solution

$$\frac{3992}{1448.5} \times 0.7245 \text{ g } CuSO_4 . 5H_2O$$

$$\equiv \frac{3992 \times 0.7245}{1448.5 \times 0.0499} = \mathbf{40\ mL} \qquad \textbf{Ans.}$$

EXAMPLE 156. *The reaction, $Zn + CuSO_4 \rightarrow Cu + ZnSO_4$ goes completely to right. In one experiment, 10.0 g of metallic zinc was added to 200 mL of copper sulphate solution. After, all the copper was precipitated, it was found that not all the zinc had dissolved. After filtration, the total solid at the end of reaction was 9.81 g. Calculate (i) the weight of copper deposited and (ii) molarity of copper sulphate in the original solution (Cu = 63.5, Zn = 65.4).* **(IIT 1971)**

SOLUTION. Volume of $CuSO_4$ solution = 200 mL. Let *m* = molarity of $CuSO_4$ solution.

But M (= Molarity of Cu^{2+})

$$= \frac{\text{wt. of Cu}}{\text{mol. wt. of Cu}} \times \frac{1000}{\text{Volume of solution in mL(= 200 mL)}}$$

= at wt. of Cu = (63.5)

$$\therefore \qquad \text{wt. of Cu} = \frac{M \times 63.5 \times 200}{1000} = 12.7 \text{ m g.}$$

In $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$, Zn and Cu react in equivalent proportion, so :

$$\text{wt. of Zn reacted} = 65.4\ \text{M} \times \frac{200}{1000}\ \text{g} = 13.08\ \text{mg}$$

[∵ at. wt. of Zn = 65.4]

wt. of unreacted zinc

$$= 10 - 13.08\ \text{M}$$

$$\therefore 12.7\ \text{M} + 10 - 13.08\ \text{M}$$

$$= 9.81\ \text{(given)}\ ; 0.38\ \text{M} = 0.19$$

$$\therefore \quad \text{M} = \frac{0.19}{0.38} = \mathbf{0.5\ M} \qquad \textbf{Ans.}$$

wt. of Cu deposited = 12.7 m = 12.7 × 0.5 = **6.35 g** **Ans.**

Example 157. *Find out the volume in mL of 0.1N hydrochloric acid required to react completely with 1g of a mixture of sodium carbonate and sodium bicarbonate containing equimolar amounts of the two compounds.* **(IIT 1971)**

Solution. wt. of a substance = no. of mol × mol. wt.

(*i*) Mol. wt. of

$$Na_2CO_3 = (2 \times 23) + 12 + (3 \times 16)$$

$$= 106\ \text{g mol}^{-}.$$

$$\text{Mol. wt. of } NaHCO_3 = 23 + 1 + 12 + (3 \times 16) = 84\ \text{g mol}^{-}$$

no. of mol of Na_2CO_3 = no. of mol of

$NaHCO_3$ = x suppose.

$$\therefore \quad \text{wt. of } Na_2CO_3 = \text{no. of mol} \times \text{Mol. wt.}$$

$$= x \times 106 = 106x\ \text{g}$$

$$\text{wt. of } NaHCO_3 = \text{no. of mol} \times \text{mol. wt.}$$

$$= x \times 84 = 84x\ \text{g}$$

$$\therefore \quad 106x + 84x = 1\ \text{g (given)}\ ; x = \frac{1}{190}$$

(*ii*)

$$\underset{\substack{1\ \text{mol} \\ 1/190\ \text{mol}}}{Na_2CO_3} + \underset{\substack{2\ \text{mol} \\ 2/190\ \text{mol}}}{2HCl} \longrightarrow NaCl + CO_2 + H_2O$$

(*iii*)

$$\underset{\substack{1\ \text{mol} \\ \frac{1}{190}\ \text{mol}}}{NaHCO_3} + \underset{\substack{1\ \text{mol} \\ \frac{1}{190}\ \text{mol}}}{HCl} \longrightarrow NaCl + CO_2 + H_2O$$

∴ Total amount of HCl required

$$= \frac{2}{190} + \frac{1}{190} = \frac{3}{190}\ \text{mol}$$

(*iv*)

$$1\ \text{mol of HCl} = 1\text{L of 1N HCl}$$

$$= 10\text{L of 0.1N HCl}$$

(∵ given HCl = 0.1N)

$$\frac{3}{190}\ \text{mol of HCl} = 10 \times \frac{3}{190}\ \text{L of 0.1N HCl} = \frac{3}{19}\ \text{L}$$

$$= \frac{3}{19}\text{L} \times \frac{1000\ \text{mL}}{1\ \text{L}} = \mathbf{157.9\ mL} \textbf{Ans.}$$

Example 158. *A piece of aluminium weighing 2.7 g is heated with 75.0 mL of sulphuric acid (sp. gr. 1.18 containing 24.7 percent H_2SO_4 by weight). After the metal is carefully dissolved, the solution is diluted to 400 mL. Calculate the molarity of free H_2SO_4 in the resulting solution. (at. wt., Al = 27, S = 32, O = 16, H = 1)* **(IIT 1972)**

Solution. (*i*) **Reaction.**

$$\underset{\substack{2 \times 27 \\ = 54\ \text{g}}}{2Al} + \underset{\substack{3[(2 \times 1) + 32 + \\ (4 \times 16)] = 294\ \text{g}}}{3H_2SO_4} \longrightarrow Al_2(SO_4)_3 + 3H_2$$

54 g Al react with H_2SO_4 = 294 g

2.7 g Al react with

$$H_2SO_4 = \frac{294}{54} \times 2.7 = 14.7\ \text{g}$$

(*ii*) wt. of H_2SO_4 in 75 mL

$$H_2SO_4 = \frac{\text{Volume} \times \text{sp. gr.} \times \text{percent}}{100}$$

$$= \frac{75 \times 1.18 \times 24.7}{100} = 21.86\ \text{g}$$

∴ wt. of unreacted H_2SO_4 diluted to 400 mL

$$= 21.86 - 14.7 = 7.16\ \text{g}$$

$$\therefore \text{Molarity of } H_2SO_4 = \frac{\text{wt.}}{\text{mol. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{7.16 \times 1000}{98 \times 400} = \mathbf{0.183} \qquad \textbf{Ans.}$$

Example 159. *Upon heating a litre of a N/2 HCl solution, 2.675 g of hydrogen chloride is lost and the volume of the solution shrinks to 750 mL. Calculate (i) the normality of the resulting solution and (ii) number of milliequivalents of HCl in 100 mL of the original solution.* **(IIT 1975)**

Solution. (*i*) 1000 mL of 1N HCl weighs = g. eq. wt. of

$$HCl = 1 + 35.5 = 36.5\ \text{g}$$

$$\text{One litre (= 1000 mL) of } \frac{N}{2}\ \text{HCl weighs}$$

$$= \frac{36.5}{1000} \times 1000 \times \frac{1}{2} = 18.25\ \text{g}$$

wt of HCl evaporated = 2.675 g

∴ wt. of HCl left behind

$$= 18.25 - 2.675 = 15.575\ \text{g}$$

$$\text{Normality} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{15.575}{36.5} \times \frac{1000}{750} = \mathbf{0.569} \qquad \textbf{Ans.}$$

(*ii*) No. of milliequivalent of original solution

$$= \begin{array}{c}\text{Normality of} \\ \text{original HCl}\end{array} \times \text{Volume in mL}$$

$$= \frac{1}{2} \times 100 = 50\ \text{milliequivalent} \quad \textbf{Ans.}$$

Example 160. *How many milli litre of conc. H_2SO_4 (sp. gr. 1.84 containing 98% H_2SO_4 by weight) are required to prepare 200 mL of 0.5 N solution?* **(IIT 1976)**

Solution. Volume of conc.

$$H_2SO_4 = ?\ \text{sp. gr.} = 1.84,\ \%\ \text{age} = 98$$

$$\text{Eq. wt. of } H_2SO_4 = \frac{(2 \times 1) + 32 + (4 \times 16)}{\text{Basicity of } H_2SO_4} = \frac{98}{2} = 49$$

(*i*) 1000 mL of 1N H_2SO_4 contain

$$H_2SO_4 = \text{g. eq. wt. of } H_2SO_4 = 49\ \text{g}$$

200 mL of 0.5N H_2SO_4 contain

$$H_2SO_4 = \frac{49}{1000}\times 200\times 0.5 = 4.9\text{ g}$$

(*ii*) $$\text{wt. of } H_2SO_4 = \frac{\text{Volume}\times\text{sp. gr.}\times\text{percent}}{100}$$

$$4.9\text{ g} = \frac{\text{Volume}\times 1.84\times 98}{100};$$

$$\text{Volume} = \frac{4.9\times 100}{1.84\times 98} = 2.72\text{ mL.}$$

∴ Volume of conc.

H_2SO_4 = **2.72 mL.** **Ans.**

EXAMPLE 161. *0.108 g of finely divided copper was treated with an excess of ferric sulphate solution until copper was completely dissolved. The solution after addition of excess dilute sulphuric acid required 33.7 mL of 0.1N $KMnO_4$ for complete oxidation. Find the equation which represents the reaction between metallic copper and ferric sulphate solution. (Cu = 63.5, Fe = 56)* **(IIT, 1971)**

SOLUTION. Cu powder reduces $Fe_2(SO_4)_3$ to $FeSO_4$ *i.e.,* Fe^{2+} ions

33.7 mL of 0.1N $KMnO_4$ ≡ 33.7 mL of 0.1N $FeSO_4$

But 1000 mL of 1N $FeSO_4$ or Fe^{2+}

≡ g. at. wt of Fe^{2+} = 56 g

33.7 mL of 0.1N $FeSO_4$ of

$$Fe^{2+} \equiv \frac{56}{1000}\times 33.7\times 0.1\text{ g}$$

(*i*) ∴ No. of g atoms of Fe^{2+} reacted

$$= \frac{56\times 33.7\times 0.1}{1000}\times\frac{1}{56}$$

[∵ g. at. wt. of Fe = 56]

= 0.00337

(*ii*) no. of g. atoms of

$$Cu = \frac{\text{wt.}}{\text{at. wt.}} = \frac{0.108}{63.5} = 0.0017$$

0.0017 g. atom of Cu produce

Fe^{2+} = 0.00337 g atom

1 g. atom of Cu produce

$$Fe^{2+} = \frac{0.00337}{0.0017} \simeq 2\text{ g atom or 2g. mol of}$$

$FeSO_4$

∴ *Reaction* $Cu + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2FeSO_4$.

1 g atom 2 g atom.

EXAMPLE 162. *1.0 g of a moist sample of a mixture of potassium chloride and potassium chlorate was dissolved in water and made up to 250 mL. 25 mL of this solution was treated with SO_2 to reduce the chlorate to chloride and excess SO_2 was removed by boiling. The total chloride was precipitated as silver chloride. The weight of the precipitate was 0.1435 g. In another experiment, 25 mL of the original solution was heated with 30 mL of 0.2N solution of ferrous sulphate and unreacted ferrous sulphate required 37.5 mL of 0.08N solution of an oxidising agent for complete oxidation. Calculate the molar ratio of the chlorate to the chloride in the given mixture. Fe^{2+} reacts with ClO_3^- according to the following reaction.*

$$ClO_3^- + 6Fe^{+2} + 6H^+ \longrightarrow Cl^- + 6Fe^{+3} + 3H_2O$$ **(IIT, 1972)**

SOLUTION. (*i*) N_1V_1 (oxidant) = N_2V_2 ($FeSO_4$)

$0.08 \times 37.5 = 0.2 \times V_2$;

$$V_2 = \frac{0.08\times 37.5}{0.2} = 15\text{ mL}$$

∴ Volume of 0.2N $FeSO_4$ used

= 30 mL (given) – 15 mL

= 15 mL. by $KClO_3$

(*ii*) 1000 mL of 1N

$FeSO_4$ = 1 g. eq. wt. of

$FeSO_4$ = 1 g mol of $FeSO_4$. 15 mL of 0.2N

$$FeSO_4 = \frac{1}{1000}\times 15\times 0.2$$

$= 3 \times 10^{-3}$ mol of $FeSO_4$.

From the reaction :

$$ClO_3^- + 6Fe^{2+} + 6H^+ \longrightarrow Cl^- + 6Fe^{+3} + 3H_2O$$

1 mol 6 mol

it is clear that 6 mol Fe^{2+} used

$KClO_3$ = 1 mol

3×10^{-3} mol Fe^{2+} uses

$$KClO_3 = \frac{1}{6}\times 3\times 10^{-3} = 0.5\times 10^{-3}\text{ mol } KClO_3$$

(*iii*) wt. of AgCl ppt. obtained from 25 mL solution

= 0.1435 g

Mol. wt. of AgCl = 108 + 35.5 = 143.5 g mol^-

∴ no. of mol of AgCl = no. of mol of

$$Cl^- = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{0.1435}{143.5} = \mathbf{1.0\times 10^{-3}}$$

But 1.0×10^{-3} mol Cl^- are obtained from Cl^- and ClO_3^-.

So: no. of mol of Cl^- + no. of mol of

$ClO_3^- = 1.0 \times 10^{-3}$

no. of mol of $ClO_3^- = 0.5 \times 10^{-3}$

∴ no. of mol of Cl^- = $(1.0 \times 10^{-3}) - (0.5 \times 10^{-3})$

= $\mathbf{0.5 \times 10^{-3}}$ **Ans.**

EXAMPLE 163. *A 0.5 g sample of an iron containing mineral mainly in the form of $CuFeS_2$ was reduced suitable to convert all the ferric iron into the ferrous form and was obtained as a solution. In the absence of any interferring matter, the solution required 42.0 mL of 0.01 M $K_2Cr_2O_7$ solution for titration. Calculate the percentage of $CuFeS_2$ in the mineral. (Cu = 63.5, Fe = 55.8, S = 32, O = 16).* **(I.I.T., 1976)**

SOLUTION. (*i*) *Reaction.*

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$\therefore \text{ Eq. wt. of } K_2Cr_2O_7 = \frac{\text{Mol. wt.}}{\text{no. of electrons gained}}$$

$$= \frac{(2\times 39)+(2\times 52)+(7\times 16)}{6}$$

$$= \frac{294}{6} = 49$$

Normality of 0.01M

$K_2Cr_2O_7$ = molarity × valency factor

= 0.01 × 6 = 0.06 N 1000 mL of 1N

$$K_2Cr_2O_7 = \text{g. eq. wt. of } K_2Cr_2O_7 = 49 \text{ g}$$

$$42 \text{ mL of } 0.06 \text{ N } K_2Cr_2O_7 = \frac{49 \text{ g}}{1000} \times 42 \times 0.06 = 0.1235 \text{ g}$$

(*ii*)
$$\begin{aligned}
K_2Cr_2O_7 + 4H_2SO_4 &\longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O \\
CuFeS_2 &\longrightarrow CuS + FeS] \times 6 \\
FeS + H_2SO_4 &\longrightarrow FeSO_4 + H_2S] \times 6 \\
2FeSO_4 + H_2SO_4 + O &\longrightarrow Fe_2(SO_4)_3 + H_2O\} \times 3 \\
\hline
K_2Cr_2O_7 + 13H_2SO_4 + 6CuFeS_2 &\longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6CuS + 6H_2S + 3Fe_2(SO_4)_3
\end{aligned}$$

$$\therefore \quad K_2Cr_2O_7 \equiv 6CuFeS_2$$

$(2 \times 39) + (2 \times 52) + (7 \times 16) = 294$ g $\qquad 6[63.5 + 56 + (2 \times 32)] = 6 \times 183.5$ g

$$294 \text{ g } K_2Cr_2O_7 \equiv 6 \times 183.5 \text{ g } CuFeS_2$$

$$0.1235 \text{ g } K_2Cr_2O_7 \equiv \frac{6 \times 183.5 \text{ g}}{294 \text{ g}} \times 0.1235 \text{ g} \equiv 0.462 \text{ g}$$

$$\therefore \ \% \text{ age of } CuFeS_2 = \frac{\text{wt. of } CuFeS_2}{\text{Total wt.}} \times 100$$

$$= \frac{0.462}{0.5} \times 100 = \mathbf{92.4\%}$$ **Ans.**

EXAMPLE 164. *1.0 g of a mixture, consisting of equal number of mol of carbonates of two alkali metals, required 44.4 mL of 0.5 N HCl for complete reaction. If atomic weight of one of the metals is 7.0, find the at. wt. of the other metal. What will be the amount of sulphate formed on quantitative conversion of 1.0 g of mixture into sulphates? (at. wt., Ca = 40, S = 32, O = 16)*

(IIT 1972)

SOLUTION. (*i*)1000 mL of

1N HCl ≡ 1 g. equivalent of HCl

$$44.4 \text{ mL of } 0.5\text{N HCl} = \frac{1}{1000} \times 44.4 \times 0.5$$

$$= 0.0222 \text{ g. eq. of HCl}$$

Reaction. $M_2CO_3 + 2HCl \longrightarrow 2MCl + CO_2 + H_2O$

1 g. eq $\qquad$ 2 g. eq

$\frac{0.0222}{2}$ $\qquad$ 0.0222 g. eq.

= 0.111 g mol

(*ii*) *One of the alkali metal.*

at. wt. = 7

∴ Mol. wt. of $M_2CO_3 = (2 \times 7) + 12 + (3 \times 16) = 74$ g mol$^-$

Second alkali metal. Let at. wt. of this metal = *a*

∴ Mol. wt. of $M_2CO_3 = 2a + 12 + (3 \times 16) = 2a + 60$

Since the mixture contains equal no. of moles of each carbonate, so :

wt. of one of the carbonates

$$= \frac{74 \times 0.0111}{2} = 0.4107$$

wt. of second carbonate

$$= \frac{(2x + 60) \times 0.0111}{2}$$

$$= (x + 30) \times 0.0111$$

Hence $0.4107 + (x + 30) \times 0.0111$

= 1.0 (given) ; $0.4107 + 0.0111x + 0.333$

$= 1 \ 0.0111x = 0.2563$. Hence, x

$= 0.2563/0.0111 = 23.1$

∴ at. wt. of second metal = 23.1 a.m.u.

(*iii*) *To find amount of sulphate formed*

Reaction $M_2CO_3 + H_2SO_4 \longrightarrow M_2SO_4 + H_2O + CO_2$

Mol. wt. of first carbonate = (2 × 7) + 12 + (3 × 16) = 74 g mol$^-$; Mol. wt. of M_2SO_4 = (2 × 7) + 32 + (4 × 16) = 142.2 g mol$^-$

Mol. wt. of second carbonate = (2 × 23.1) + 12 + (3 × 16) = 106.2 g mol$^-$; mol. wt. of M_2SO_4 = (2 × 23.1) + 32 + (4 × 16) = 110 g mol$^-$

∴wt. of M_2SO_4 formed from $\frac{0.0111}{2}$ mol of each carbonate will be :

no. of mol × mol. wt. of M_2SO_4 + no. of mol × mol. wt. of second M_2SO_4

$$= \frac{0.0111}{2} \times 110 + \frac{0.0111}{2} \times 142.2$$

$$= 0.6105 + 0.7892 \simeq \mathbf{1.4 \text{ g}}$$ **Ans.**

EXAMPLE 165. (*i*) *A solution of a mixture of potassium chloride and potassium hydroxide was neutralised with 120 mL of 0.12 N hydrochloric acid. Calculate the amount of potassium hydroxide in the mixture.*

(*ii*) *After titration, the resultant solution was made acidic with nitric acid. Then excess of silver nitrate solution was added to precipitate the silver chloride which weighed 3.7 g after drying. Calculate the percentage of potassium hydroxide in the original mixture.*

(IIT, 1973)

SOLUTION. (*i*) Only KOH will react with HCl.

So ; 1000 mL of 1N KOH weigh

= g. eq. wt. of KOH = 39 + 16 + 1

= 56 g

120 mL of 0.12 N

$$\text{KOH weigh} = \frac{56}{1000} \times 120 \times 0.12 = 0.8064 \text{ g}$$

Also,no. of g. equivalents of

$$\text{KOH} = \frac{\text{Volume in mL} \times \text{normality}}{1000}$$

$$= \frac{120 \times 0.12}{1000} = 0.0144.$$

(*ii*) In this process, AgCl is formed from KCl as well as from KOH from the following reaction

$$KOH + HCl \longrightarrow KCl + H_2O$$

∴ no. of g. equivalents of AgCl formed from KOH and

$$\text{KCl} = \frac{\text{wt. of AgCl}}{\text{eq. wt. of AgCl}}$$

$$= \frac{3.7}{108 + 35.5 = 143.5} = 0.0258$$

$\therefore$ no. of equivalents of KCl initially present

$$= 0.0258 - 0.0144 = 0.0114$$

$\therefore$ wt of KCl initially present

$$= \text{no. of g. eq} \times \text{mol. wt. of KCl}$$
$$= 0.0114 \times (39 + 35.5 = 74.5)$$
$$= 0.8493 \text{ g}$$

$$(iii)\ \%\text{ age of KOH} = \frac{0.8064}{0.8064 + 0.8493} \times 100$$
$$= \frac{0.8064}{1.6557} \times 100 = \mathbf{48.7\%} \qquad \textbf{Ans.}$$

EXAMPLE 166. (*i*) *In a quantitative determination of iron in an ore, an analyst converted 0.42 g of the ore into its ferrous form. This required 42.0 mL of 0.1N solution of* $KMnO_4$ *for titration.*

(*ii*) *How many milliequivalents of iron were present in the sample of the ore taken for analysis.*

(*iii*) *How many grams of iron were present in the sample ?*

(*iv*) *What is the percentage of iron in the ore?*

(*v*) *What is the molarity of* $KMnO_4$ *solution used?*

(*vi*) *How many moles of* $KMnO_4$ *were used for titration?*

(Fe = 56) **(IIT 1974)**

SOLUTION. (*i*) No. of milliequivalents of

$$KMnO_4 = \text{Normality} \times \text{Volume in mL}$$
$$= 0.1 \times 42$$
$$= \mathbf{4.2\ milliequivalent} \qquad \textbf{Ans.}$$

(*ii*) No. of milliequivalents of iron

$$= \text{no. of milliequivalents of } KMnO_4$$
$$= 4.2 \text{ milliequivalents}$$

[see (*i*) above]

$\therefore$ No. of equivalents of iron

$$= \frac{4.2}{1000} = \mathbf{0.0042\ equivalent.} \quad \textbf{Ans.}$$

(*iii*) Eq. wt. of Fe in $Fe^{2+} \rightarrow Fe^{+3} + 1e^-$

$$= \frac{\text{at. wt. of Fe}}{1} = \frac{56}{1} = 56$$

$$\therefore \quad \text{wt. of iron} = 0.0042 \times 56 = \mathbf{0.2352\ g} \qquad \textbf{Ans.}$$

$$(iv)\quad \%\text{ age of iron} = \frac{\text{wt. of iron}}{\text{Total wt.}} \times 100$$
$$= \frac{0.2352 \text{ g}}{0.42 \text{ g}} \times 100 = \mathbf{56\%} \qquad \textbf{Ans.}$$

(*v*) *Reaction* $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$

$\therefore$ Valency factor = 5 due to 5 electrons.

$$\text{Molarity} = \frac{\text{Normality}}{\text{Valency factor}} = \frac{0.1}{5}$$
$$= \mathbf{0.02\ M} \qquad \textbf{Ans.}$$

(*vi*) No. of mol of

$$KMnO_4 = \text{Molarity} \times \text{Volume in litre}$$
$$= 0.02 \times \frac{42}{1000} = \mathbf{8.4 \times 10^{-4}\ mol} \quad \textbf{Ans.}$$

EXAMPLE 167. *A commercial sample (2.013 g)* o*f NaOH containing* Na_2CO_3 *as an impurity was dissolved to give 250 mL of solution. A 10 mL portion of this solution required 20 mL of 0.1N* H_2SO_4 *for complete neutralisation. Calculate the percentage by weight of* Na_2CO_3 *in the sample.* **(IIT, 1977)**

SOLUTION. (*i*) N_1V_1 (NaOH)

$$= N_2V_2\ (H_2SO_4)$$
$$N_1 \times 10 = 0.1 \times 20\ ;\ N_1 = \frac{0.1 \times 20}{10} = \mathbf{0.2\ N.}$$

(*ii*) Letwt. of NaOH = x g ; wt. of

$$Na_2CO_3 = (2.013 - x) \text{ g.}$$
$$\text{Eq. wt. of NaOH} = \frac{23 + 16 + 1}{1} = 40\ ;$$
$$\text{eq. wt. of } Na_2CO_3 = \frac{(2 \times 23) + 12 + (3 \times 16)}{2} = 53$$

250 mL solution contain

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

1000 mL solution contain

$$\text{NaOH} = \frac{x}{250} \times 1000 = 4x \text{ g}$$

$$\therefore \textbf{ normality of NaOH} = \frac{\text{Strength}}{\text{eq. wt.}} = \frac{4x}{40}$$

250 mL solution contain

$$Na_2CO_3 = (2.013 - x) \text{ g}$$

1000 ml solution contain

$$Na_2CO_3 = \frac{2.013 - x}{250} \times 1000 = 8.052 - 4x$$

$$\therefore \text{Normality of } Na_2CO_3 = \frac{\text{Strength}}{\text{eq. wt.}} = \frac{8.052 - 4x}{53}$$

$$(iii)\quad \frac{4x}{40} + \frac{8.052 - 4x}{53} = 0.2\ ;\ 4x \times 53 + (40 \times 8.052) - 40(4x)$$
$$= 0.2 \times 40 \times 53$$
$$212x + 322.08 - 160x = 424\ ;\ 52x = 101.92\ ;$$
$$x = 1.96 \text{ g} = \text{wt. of NaOH}$$
$$\therefore \quad \text{wt. of } Na_2CO_3 = 2.013 - 1.96 = 0.053 \text{ g}$$
$$\%\text{ age of } Na_2CO_3 = \frac{0.053}{2.013} \times 100 = \mathbf{2.63\%} \qquad \textbf{Ans.}$$

EXAMPLE 168. A *sample of magnesium metal containing some magnesium oxide as impurity was dissolved in 125 mL of 0.1N* H_2SO_4*. The volume of hydrogen evolved at 27.3°C and 1 atm was 120.1 mL. The resulting solution was found to be 0.02 N with respect to sulphuric acid. Calculate (i) the weight of sample dissolved and (ii) the percentage by weight of magnesium in the sample. Neglect any change in the volume of the solution.* (*Mg = 24.3*). **(IIT 1977)**

SOLUTION. Given condition. P_1 = 1 atm; V_1 = 120.1 mL, T_1 = 27.3 + 273 = 300.3 K ; at NTP, P_2 = 1 atm, V_2 = ?, T_2 = 273 K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$
$$= \frac{1 \text{ atm} \times 120.1 \text{ mL} \times 273 \text{ K}}{300.3 \text{ K} \times 1 \text{ atm}}$$
$$= 109.2 \text{ mL}$$

$$\underset{24.3\text{ g}}{Mg} + H_2SO_4 \longrightarrow MgSO_4 + \underset{22400\text{ mL}}{H_2}$$

(*i*) 22400 mL H_2 is formed from

$$Mg = 24.3 \text{ g}$$

109.2 mL H_2 is formed from

$$Mg = \frac{24.3}{22400} \times 109.2 = 0.1185 \text{ g}$$

$\therefore$ wt. of Mg = 0.1185 g.

(*ii*) 1000 mL of 1N H_2SO_4 weigh

$$= \text{g. eq. wt. of } H_2SO_4$$

$$= \frac{(2\times1)+32+(4\times16)}{2} = 49 \text{ g}$$

125 mL of 0.1 N H_2SO_4 weigh

$$= \frac{49 \text{ g}}{1000 \text{ mL}} \times 125 \text{ mL} \times 0.1$$

$$= 0.6125 \text{ g} \qquad \therefore \text{ wt. of original}$$

$$H_2SO_4 = 0.6125 \text{ g } 1000 \text{ mL of } 1 \text{ N}$$

$$H_2SO_4 \text{ weigh} = \text{g eq. wt. of } H_2SO_4 = 49 \text{ g}$$

125 mL of 0.02 N H_2SO_4 weigh

$$= \frac{49 \text{ g}}{1000 \text{ mL}} \times 125 \text{ mL} \times 0.02$$

$$= 0.1225 \text{ g}$$

$\therefore$ wt. of unused H_2SO_4 = 0.1225 g

$\therefore$ wt. of used H_2SO_4 by Mg and

$$MgO = 0.6125 - 0.1225 = 0.49 \text{ g}$$

(*iii*)
$$\underset{24.3\text{ g}}{Mg} + \underset{(2\times1)+32+(4\times16)=98\text{ g}}{H_2SO_4} \longrightarrow MgSO_4 + H_2$$

24.3 g Mg uses H_2SO_4 = 98 g

$$0.1185 \text{ g Mg uses } H_2SO_4 = \frac{98}{24.3} \times 0.1185 = 0.4779 \text{ g}$$

$\therefore$ wt. of H_2SO_4 used by

$$MgO = 0.49 - 0.4779 = 0.0121 \text{ g}$$

(*iv*)
$$\underset{\substack{24.3+16\\=40.3\text{ g}}}{MgO} + \underset{\substack{(2\times1)+32\\+(4\times16)=98\text{ g}}}{H_2SO_4} \longrightarrow MgSO_4 + H_2O$$

98 g H_2SO_4 is used by

$$MgO = 40.3 \text{ g}$$

0.0121 g H_2SO_4 is used by

$$MgO = \frac{40.3}{98} \times 0.0121 = 0.00498 \text{ g}$$

$\therefore$ wt. of MgO = 0.00498 g Total wt. of

$$Mg + MgO = 0.1185 \text{ g} + 0.00498 \text{ g} = 0.1235 \text{ g}$$

$$\%\text{ age of Mg} = \frac{\text{wt. of Mg}}{\text{Total wt.}} \times 100 = \frac{0.1185 \text{ g}}{0.1235 \text{ g}} \times 100$$

$$= \mathbf{95.95\%}$$ **Ans.**

EXAMPLE 169. (*a*) *A zinc rod weighing 25 g was kept in 100 mL of 1 M $CuSO_4$ solution. After a certain time, the molarity of Cu^{++} in the solution was 0.8. What was the molarity of SO_4^{2-}? What was the weight of zinc rod after cleaning?* (*b*) *If the above experiment is done with copper rod of weight 25g and 50 mL of 2M $ZnSO_4$ solution, what would be the molarity of Zn^{++} at the end of the same interval?* (*Zn = 65.4, Cu = 63.5*).

SOLUTION. Wt. of Zn rod = 25 g

Reaction. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

Or $\underset{65.4\text{ g}}{Zn} + \underset{63.5\text{ g}}{Cu^{2+}} \longrightarrow Zn^{2+} + Cu$

$$ZnSO_4 \rightleftharpoons Zn^{2+} + SO_4^{2-}$$

Initial molarity of Cu SO_4 or

$$Cu^{2+} = 1M$$

Molarity of Cu^{2+} after sometime = 0.8 M

Decrease in molarity = 1.0 – 0.8 = 0.2 M

$\therefore$ wt. of Cu reacted = 0.2 × 63.5

$$= 12.70 \text{ g}$$

63.5 g Cu react with Zn = 65.4 g

$$12.7 \text{ g Cu react with Zn} = \frac{65.4}{63.5} \times 12.7 = \mathbf{13.08 \text{ g}}$$

$\therefore$ wt. of Zn rod after cleaning

$$= 25.0 \text{ g} - 13.08 \text{ g} = \mathbf{11.92 \text{ g}}$$ **Ans.**

There is no change in the concentration of SO_4^{2-} ions as it does not take part in the reaction. So, the concentration of SO_4^{2-} ion is the same as that of 1 M $CuSO_4$ *i.e.,* 1M.

(*b*) Oxidation potential of Zn (= + 0.76 V) is greater than that of Cu (= – 0.34 V), so Cu will not react with 2 M $ZnSO_4$ solution. Hence the molarity of Zn^{2+} will be the same as that of 2M $ZnSO_4$ *i.e.,* **2 M.**

EXAMPLE 170. *What is the molarity and molality of a 13% solution* (*by weight*) *of sulphuric acid? Its density is 1.090 g/mL. To what volume should 100 mL of this acid be diluted in order to prepare 1.5 N solution?*

(*b*) *Two litres of ammonia at 30°C and 0.2 atm pressure neutralised 134 mL of a solution of sulphuric acid. Calculate the normality of the acid.* **(IIT, 1978)**

SOLUTION. (*a*) wt. of H_2SO_4 = 13 g ; wt. of solution = 100 g

wt. of solvent = 100 – 13 = 87 g ; mol. wt. of

$$H_2SO_4 = (2\times1) + 32 + (4\times16) = 98 \text{ g mol}^{-}$$

$$\therefore \quad \text{Molality} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{wt. of solvent}}$$

$$= \frac{13}{98} \times \frac{1000}{87} = \mathbf{1.52 \text{ m}}$$ **Ans.**

$$\text{Volume of solution} = \frac{\text{wt. of solution}}{\text{density}} = \frac{100 \text{ g}}{1.09 \text{ g (mL)}^{-}}$$

$$\therefore \quad \text{Molarity} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{13}{98} \times 1000 \times \frac{1.09}{100}$$

$$= \mathbf{1.44 \text{ M}}$$ **Ans.**

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

2 = valency factor

$$\therefore \quad \text{Normality} = \text{Molarity} \times \text{Valency factor}$$

$$= 1.44 \times 2 = \mathbf{2.88 \text{ N}}$$ **Ans.**

$$N_1V_1 \text{ (original acid)} = N_2V_2 \text{ (dilute acid)}$$

$$2.88 \times 100 = 1.5 \times V_2$$

$$V_2 = \frac{2.88\times100}{1.5} = \mathbf{192\ mL} \qquad \textbf{Ans.}$$

(*b*) Given conditions. $P_1 = 0.2$ atm, $V_1 = 2\text{L} = 2 \times 1000 = 2000$ mL ; $T_1 = 30 + 273 = 303$ K; **At NTP.** $P_2 = 1$ atm, $V_2 = ?$, $T_2 = 273$ K.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ ;\ V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} \quad \text{(Gas law)}$$

$$\therefore \quad V_2 = \frac{0.2\ \text{atm}\times2000\ \text{mL}\times273\ \text{K}}{303\ \text{K}\times1\ \text{atm}}$$

$$= 360.4\ \text{mL.}$$

Reaction $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

2×22400 ml $\quad (2 \times 1) + 32 +$

$= 2[14 + (3 \times 1)] = 34$ g $\quad (4 \times 16) = 98$ g

(*i*) 2×22400 mL NH_3 weigh

$$= 34\ \text{g}$$

$$360.4\ \text{mL } NH_3 \text{ weigh} = \frac{34\ \text{g}}{2\times22400\ \text{mL}}\times360.4$$

(*ii*) 34 g NH_3 neutralise

$$H_2SO_4 = 98\ \text{g}$$

$$\frac{34\times360.4}{2\times22400}\ \text{g } NH_3 \text{ neutralise}$$

$$H_2SO_4 = \frac{98}{34}\times\frac{34\times360.4}{2\times22400} = 0.788\ \text{g}$$

∴ Normality of

$$H_2SO_4 = \frac{\text{wt.}}{\text{Eq. wt.}}\times\frac{1000}{\text{Volume in mL}}$$

$$= \frac{0.788}{49}\times\frac{1000}{134}$$

$$= \mathbf{0.12\ N} \qquad \textbf{Ans.}$$

EXAMPLE 171. *A polyvalent metal weighing 0.1 g and having atomic weight 51.0, reacted with dil. H_2SO_4 to give 43.9 mL of H_2 at NTP. This solution containing the metal in the lower oxidation state was found to require 58.8 mL of 0.1 N permanganate for complete oxidation. What are the valencies of the metal?* **(IIT, 1977)**

SOLUTION. Wt. of metal

= 0.1 g ; at. wt. of metal = 51.0

Volume of H_2 = 43.9 mL. But wt. of 1mL

H_2 = 0.00009 g

∴ Wt. of 43.9 mL $H_2 = 43.9 \times 0.00009\ \text{g} = 3.951 \times 10^{-3}$ g

$$\text{But} \quad \frac{\text{wt. of metal}}{\text{wt. of } H_2} = \frac{\text{Eq. wt. of metal}}{\text{Eq. wt. of } H_2}\ ;$$

$$\frac{0.1}{3.951\times10^{-3}} = \frac{E}{1.008}$$

$$\therefore \text{Eq. wt. of metal} = \frac{0.1\times1.008}{3.951\times10^{-3}} = 25.5$$

At. wt. of metal = 51.0 (given)

$$\therefore \text{Valency of metal} = \frac{\text{At. wt.}}{\text{Eq. wt.}} = \frac{51}{25.5} = 2 \qquad \textbf{Ans.}$$

(*b*) 58.8 mL of 0.1 N $KMnO_4$ is reduced by metal in its lower oxidation state = 0.1 g

∴ 1000 mL of 1N $KMnO_4$ is reduced by metal in its lower oxidation state

$$= \frac{0.1}{58.8\times0.1}\times1000\times1$$

= 17 g = eq. wt. of metal

At. wt. of metal = 51 ; eq. wt. of metal = 17

∴ Valency of metal in the lower oxidation state

$$= \frac{\text{at. wt.}}{\text{Eq. wt.}} = \frac{51}{17} = 3$$

∴ Valencies of the metal are 2 and 2 + 3 (= 5). **Ans.**

EXAMPLE 172. (*a*) (*i*) *A sample of $MnSO_4.4H_2O$ is strongly heated in air. The residue is Mn_3O_4. (ii) The residue is dissolved in 100 mL of 0.1N $FeSO_4$ solution containing dil. H_2SO_4. (iii) The solution reacts completely with 60 mL of $KMnO_4$ solution, (iv) 25 mL of the $KMnO_4$ solution used in step (ii) require 30 mL of 0.1 N $FeSO_4$ solution for complete reaction. Find the amount of $MnSO_4.4H_2O$ present in the sample.*

(*b*) *0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution is completely neutralised by 26.7 mL of 0.4 N NaOH. Find the percentage of free SO_3 in the sample of oleum.* **(IIT, 1980)**

SOLUTION. Reaction.

$$\begin{array}{rcl} Mn_3O_4 + 3H_2SO_4 & \longrightarrow & 3MnSO_4 + 3H_2O + O \\ 2FeSO_4 + H_2SO_4 + O & \longrightarrow & Fe_2(SO_4)_3 + H_2O \\ \hline Mn_3O_4 + 4H_2SO_4 + 2FeSO_4 & \longrightarrow & 3MnSO_4 + 4H_2O \\ & & + Fe_2(SO_4)_3 \end{array}$$

∴ $2FeSO_4 \equiv 3MnSO_4$ **Or** $2FeSO_4.7H_2O \equiv 3MnSO_4.4H_2O$

$2[56 + 32 + (4 \times 16)$ $\quad 3[55 + 32 + (4 \times 16)]$

$+ 7(2 \times 1) + 16] = 2 \times 278$ g $\quad = 3 \times 223$ g

(*i*) 60 mL of given $KMnO_4$ = 60 mL of 0.1 N $FeSO_4$

∴ Volume of $FeSO_4$ solution used by

Mn_3O_4 = 100 – 60 = 40

(*ii*) 1000 mL of 1N $FeSO_4$

= g eq. wt. of $FeSO_4.7H_2O$ = 278 g

$$40\ \text{mL of 0.1N } FeSO_4 = \frac{278\times40\times0.1}{1000}\ \text{g} = 1.112\ \text{g}$$

But 2×278 g $FeSO_4.7H_2O$

$\equiv 3 \times 223$ g $MnSO_4.4H_2O$

$$\therefore\ 1.112\ \text{g } FeSO_4.7H_2O \equiv \frac{3\times223}{2\times278}\times1.112 = \mathbf{1.338\ g} \qquad \textbf{Ans.}$$

(*b*) Oleum = $H_2SO_4 + SO_3$. Let wt. of $SO_3 = x$; wt. of $H_2SO_4 = (0.5 - x)$ g

Reactions. $SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$ ...(*A*)

$32 + (3 \times 16)$ $\quad 2(23 + 16 + 1)$

$= 80$ g $\quad = 80$ g

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$ ...(*B*)

$(2 \times 1) + 32$ $\quad 2[23 + 16 + 1]$

$+ (4 \times 16) = 98$ g $\quad = 80$ g

(*i*) 1000 mL of 1N NaOH = g. eq. wt. of

$$\text{NaOH} = 23 + 16 + 1 = 40 \text{ g}$$

$$26.7 \text{ mL of } 0.4 \text{ N NaOH} = \frac{40 \text{ g}}{1000} \times 26.7 \times 0.4 = 0.4272 \text{ g}$$

(*ii*) Let wt. of $SO_3 = x$ g : wt. of $H_2SO_4 = (0.5 - x)$ g

From reaction (*A*) :

80 g SO_3 react with NaOH = 80 g

∴ x g SO_3 react with

$$\text{NaOH} = \frac{80}{80} \times x = x \text{ g}$$

(*iii*) From equation (*B*) :

98 g H_2SO_4 react with

NaOH = 80 g

$(0.5 - x)$ g H_2SO_4 react with

$$\text{NaOH} = \frac{80}{98} \times (0.5 - x)\text{g} = \frac{40 - 80\,x}{98}$$

$$\therefore x \text{ g} + \frac{40 - 80\,x}{98} = 0.4272 \text{ g} ; 98x + 40 - 80x$$

$$= 98 \times 0.4272 \text{ g}$$

$$\therefore \quad 18x = 41.8656 \text{ g} - 40 = 1.8656 \text{ g} ;$$

$$x = 0.1036 \text{ g} = \text{wt. of } SO_3$$

$$\therefore \quad \% \text{ age of } SO_3 = \frac{\text{wt. of } SO_3}{\text{Total wt.}} \times 100 = \frac{0.1036}{0.5} \times 100$$

$$= \mathbf{20.72\%}$$ **Ans.**

EXAMPLE 173. *A given solution of sulphuric acid contains 45 g of the acid per litre [sp. gr = 1.049 g (mL)*$^{-}$*]. Find the strength of the solution in terms of normality, molality and milliequivalents.*

SOLUTION. Wt. of H_2SO_4 = 45 g ;

Volume = 1L = 1000 mL ;

$$\text{Eq. wt. of } H_2SO_4 = \frac{\text{Mol. wt.}}{\text{basicity}} = \frac{(2 \times 1) + 32 + (4 \times 16)}{2}$$

= 49 ; wt. of solution

= Volume × sp. gr.

= 1000 mL × 1.049 g $(\text{mL})^{-}$

= 1049 g

∴ wt. of solvent, H_2O = 1049 – 45 = 1004 g

(*i*) $$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{45}{49} \times \frac{1000}{1000} = \frac{45}{49} N$$ **Ans.**

(*ii*) $$\text{Molality} = \frac{\text{wt.}}{\text{mol. wt.}} \times \frac{1000}{\text{wt. of solvent}}$$

$$= \frac{45}{98} \times \frac{1000}{1004} = \mathbf{0.457 \ m}$$ **Ans.**

(*iii*) no. of milli equivalents per litre

$$= \left(\frac{\text{Wt.}}{\text{Eq. wt.}} \times 1000\right) = \frac{45}{49} \times 1000$$

Or no. of milliequivalents per mL

$$= \frac{45}{49} \times \frac{1000}{1000} = \mathbf{0.918}$$ **Ans.**

22.18 AIEEE PATTERN EXAMPLES

EXAMPLE 174. *Equal volumes of molar hydrochloric acid and sulphuric acid are neutralised by dilute NaOH solution and x k cal and y k cal of heat are liberated respectively. Which of the following is true?*

(*a*) $x = y$ (*b*) $x = y/2$

(*c*) $x = 2y$ (*d*) *none of the above*

(West Bengal JEE, 2009)

SOLUTION. $HCl \rightleftharpoons H^+ + Cl^-$;

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

∴ By equal volumes of molar HCl and H_2SO_4, the ratio of H^+ ions furnished = 1 : 2

∴ Ratio of heat liberated

$$= \frac{x}{y} = \frac{1}{2} ; x = y/2.$$

So, the correct answer is (*b*)

EXAMPLE 175. *An aqueous solution containing 6.5 g of NaCl of 90% purity was subjected to electrolysis. After the complete electrolysis, the solution was evaporated to get solid NaOH. The volume of 1M acetic acid required to neutralise NaOH obtained above is:*

(*a*) *2000 cm*^{3} (*b*) *100 cm*^{3}

(*c*) *200 cm*^{3} (*d*) *1000 cm*^{3}

(Karnataka CET, 2009)

SOLUTION. Wt. of pure NaCl

$$= 6.5 \text{ g} \times \frac{90}{100} = 5.85 \text{ g}$$

No. of equivalents of

$$\text{NaCl} = \frac{\text{wt. of NaCl}}{\text{Molar mass of NaCl}}$$

$$= \frac{5.85}{58.5} = 0.1$$

∴ $N_{NaOH} \times V_{NaOH} = N_{CH_3COOH} \times V_{CH_3COOH}$; 0.1 × 1000 = 1 × V_{CH_3COOH}; V_{CH_3COOH} = 100 cm^3.

So, the correct answer is(*b*)

EXAMPLE 176. *The strength of N/50 potassium bicarbonate in gram per litre is :*

(*a*) 2.0 (*b*) 3.0

(*c*) 4.0 (*d*) 1.5

(*At. wt., K = 39, H = 1, C = 12, O = 16*)

SOLUTION. Strength in gL$^-$ = Normality × eq. wt.

$$KHCO_3 \rightleftharpoons K^+ + HCO_3^-$$

$$\text{Eq. wt. of } KHCO_3 = \frac{\text{Mol. wt.}}{\text{Total + ve charge}}$$

$$= \frac{39 + 1 + 12 + (3 \times 16)}{1} = 100$$

$$\therefore \quad \text{Strength} = \text{Normality} \times \text{eq. wt.}$$

$$= \frac{1}{50} \times 100 = 2.0 \text{ gL}^-$$

So, the correct answer is (*a*).

EXAMPLE 177. *The strength of 1.5 N HNO_3 in gram equivalents per litre is :*

(*a*) *0.152* (*b*) *1.68*
(*c*) *6.1* (*d*) *1.5*

(*at. wt., H = 1 N = 14, O = 16*)

SOLUTION. Normality of HNO_3 = 1.5 N.

But : no. of gram equivalent per litre = Normality.

So : no. of gram equivalent of HNO_3 per litre = 1.5. So, the correct answer is (*d*).

EXAMPLE 178. *The number of gram mol of 2.0 L of 3 M H_2SO_4 are :*

(*a*) *2.0* (*b*) *3.0*
(*c*) *6.0* (*d*) *none of these*

SOLUTION. 3M H_2SO_4 means 3 g mol of H_2SO_4 per litre.

$\therefore$ 1L H_2SO_4 contain g. mol = 3

2.0 L H_2SO_4 contain g. mol = 3 × 2 = 6 g mol.

So, the correct answer is (*c*).

EXAMPLE 179. *The number of grams of $Ca(OH)_2$ in 1.5 litre of 0.25 M $Ca(OH)_2$ are :*

(*a*) 25.0 g (*b*) 27.75 g
(*c*) 1.5 g (*d*) 15 g

(*at. wt., Ca = 40, O = 16, H = 1*)

SOLUTION. No. of gram of substance

$$= \text{Molarity} \times \text{Volume in L} \times \text{mol. wt}$$
$$= 0.25 \times 1.5 \times 74 = 27.75 \text{ g}$$

So, the correct answer is (*b*).

EXAMPLE 180. *The molarity of sulphuric acid [sp. gr. 1.249 g $(mL)^{-}$] containing 98% by weight of sulphuric acid is :*

(*a*) *1.4 M* (*b*) *2.8 M*
(*c*) *6.245 M* (*d*) *12.49 M*

SOLUTION. wt. of H_2SO_4 = 98 g ; wt. of H_2SO_4 solution = 100 g (because of 98% H_2SO_4 by weight)

$\therefore$ Volume of H_2SO_4 solution

$$= \frac{\text{wt.}}{\text{sp. gr.}} = \frac{100 \text{ g}}{1.249 \text{ g (mL)}^{-}}$$
$$= 80.06 \text{ mL ;}$$

$$\text{mol. wt. of } H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98 \text{ g mol}^{-}$$

$$\therefore \quad \text{Molarity} = \frac{\text{wt.}}{\text{mol. wt.}} \times \frac{1000}{\text{Volume in mL}}$$
$$= \frac{98 \text{ g}}{98 \text{ g mol}^{-}} \times \frac{1000}{80.06}$$
$$= 12.49 \text{ M}$$

So, the correct answer is (*d*).

EXAMPLE 181. *The number of millimoles of $Cd(NO_3)_2 . 4H_2O$ present in 250 mL of 2.5 M $Cd(NO_3)_2$ solution are :*

(*a*) *2.5* (*b*) *250*
(*c*) *1.25* (*d*) *625*

SOLUTION. Molarity = 2.5 M, Volume = 250 mL.

$$\text{But : no. of millimol} = \text{Molarity} \times \text{Volume in mL}$$
$$= 2.5 \times 250 = 625 \text{ millimoles.}$$

So, the correct answer is (*d*).

Second method. 2.5 M solution contain 2.5 mol L^{-} of $Cd(NO_3)_2$. Thus :

1000 mL (= 1L) solution contain millimol

= 2.5 × 1000 millimoles

250 mL solution contain millimoles

$$= \frac{2.5 \times 1000 \text{ millimoles}}{1000 \text{ mL}} \times 250 \text{ mL}$$
$$= 625 \text{ millimoles.}$$

So, the correct answer is (*d*).

EXAMPLE 182. *A certain volume of H_2SO_4 (eq. wt. 49) containing 9.8 gL^{-} was diluted with equal amount of water. The volume of diluted acid required to make one litre of N/25 solution will be:*

(*a*) *1000 mL* (*b*) *100 mL*
(*c*) *400 mL* (*d*) *1 L*

SOLUTION. 1L of original solution contain H_2SO_4 = 9.8 g

But the solution is diluted with equal amount of water *i.e.*, 1L.

So : 2L diluted solution contain

$$H_2SO_4 = 9.8 \text{ g}$$

1L diluted solution contain

$$H_2SO_4 = \frac{9.8 \text{ g}}{2} = 4.9 \text{ g}$$

$\therefore$ Strength of diluted

$$H_2SO_4 = 4.9 \text{ gL}^{-}$$

(*i*)
$$\text{Normality} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume in mL}}$$
$$= \frac{4.9}{49} \times \frac{1000}{1000 \text{ mL}} = 0.1 \text{ N}$$

(*ii*) N_1V_1 (dilute solution) = N_2V_2 (required solution)

$$0.1 \times V_1 = \frac{1}{25} \times 1000 \text{ mL ;}$$
$$V_1 = \frac{1000}{25 \times 0.1} = 400 \text{ mL}$$

So, the correct answer is (*c*).

EXAMPLE 183. *The normality of a solution prepared by diluting 100 cm^3 of 0.25 N H_2SO_4 with 1000 cm^3 of water would be :*

(*a*) *0.0227 N* (*b*) *1.12 N*
(*c*) *0.09 N* (*d*) *none of these.*

SOLUTION. Original volume = 100 cm^3. Water added = 1000 cm.

$\therefore$ New volume = 100 + 1000 = 1100 cm^3

N_1V_1(original solution) = N_2V_2 (new solution)

$$0.25 \times 100 = N_2 \times 1100 \text{ ;}$$
$$N_2 = \frac{0.25 \times 100}{1100} = 0.0227$$

So, the correct answer is (*a*).

EXAMPLE 184. *10 mL of 1M NaOH solution will neutralise.*

(*a*) *2.5 mL* (*b*) *5 mL*
(*c*) *10 mL* (*d*) *20 ml. of 1 M H_2SO_4*

(IIT, 1975)

Solution. (*i*) $NaOH \rightleftharpoons Na^+ + OH^-$

one OH^- ; valency factor = 1

$$\text{Normality of NaOH} = \text{Molarity} \times \text{Valency factor} = 1 \times 1 = 1$$

$$\text{Volume} = 10 \text{ mL}$$

(*ii*) $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

Two H^+ ; valency factor = 2

$$\therefore \text{Normality of } H_2SO_4 = \text{Molarity} \times \text{Valency factor} = 1 \times 2 = 2$$

$$N_1V_1 \text{ (NaOH)} = N_2V_2 \text{ } (H_2SO_4)$$

$$1 \times 10 = 2 \times V_2 \text{ ; } V_2 = \frac{10}{2} = 5 \text{ mL.}$$

So, the correct answer is (*b*).

Example 185. *The equivalent weight of a metal carbonate, 0.84 g of which react exactly with 40 mL of N/2 sulphuric acid is :*

(*a*) *21* (*b*) *42*

(*c*) *84* (*d*) *8.4.* **(M.D.U. 1980)**

Solution. Given 40 mL of N/2 H_2SO_4 ; wt. of metal carbonate = 0.84 g

1000 mL of 1N H_2SO_4 weigh = g. eq. wt. of H_2SO_4

$$= \frac{(2\times1)+32+(4\times16)}{2} = \frac{98}{2} = 49 \text{ g}$$

40 mL of N/2 H_2SO_4 weigh

$$= \frac{49 \text{ g}}{1000} \times 40 \times \frac{1}{2} = 0.98 \text{ g}$$

$$\text{But } \frac{\text{wt. of metal carbonate}}{\text{wt. of } H_2SO_4} = \frac{\text{Eq. wt. of metal carbonate}}{\text{Eq. wt. of } H_2SO_4}$$

$$\therefore \quad \frac{0.84 \text{ g}}{0.98 \text{ g}} = \frac{\text{Eq. wt. of metal carbonate}}{49}$$

$\therefore$ Eq. wt. of metal carbonate

$$= \frac{0.84 \times 49}{0.98} = 42.$$

So, the correct answer is (*b*).

Example 186. *5.5 g of a mixture of $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.9H_2O$ require 5.4 mL of 0.1N $KMnO_4$ solution for complete oxidation. The number of g. moles of hydrated ferric sulphate in the mixture are :*

(*a*) *774 mol* (*b*) *0.774 mol*

(*c*) *0.00774* (*d*) *none of these.*

(IIT, 1979 modified)

Solution. wt. of $FeSO_4.7H_2O + Fe_2(SO_4)_3.9H_2O = 5.5$ g

Out of $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3.9H_2O$, only Fe^{2+} of $FeSO_4.7H_2O$ would be oxidised by 5.4 mL of 0.1 N $KMnO_4$.

(*i*) no. of milliequivalents of

$$KMnO_4 = \text{Normality} \times \text{Volume in mL} = 0.1 \times 5.4 = 0.54.$$

Since $FeSO_4.7H_2O$ solution is completely oxidised.

no. of m eq. of $KMnO_4$ = no. of m eq. of $FeSO_4.7H_2O$ = 0.54

But meq. of $FeSO_4.7H_2O$

$$= \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000 \text{ ;}$$

$$0.54 = \frac{\text{wt.}}{278} \times 1000$$

$$\therefore \text{ wt. of } FeSO_4.7H_2O = \frac{0.54 \times 278}{1000} = 0.15 \text{ g}$$

$\because$ $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$

$$\therefore \text{Eq. wt. of } FeSO_4.7H_2O = \frac{\text{Mol. wt.}}{1} = \frac{56+35+(4\times16)+7[(2\times1)+16]}{1} = \frac{278}{1} = 278$$

wt. of $Fe_2(SO_4)_3.9H_2O$

$$= 5.5 - 0.15 = 4.35 \text{ g}$$

Mol. wt. of

$$Fe_2(SO_4)_3.9H_2O = (2 \times 56) + 3[32 + (4 \times 16) + 9[(2 \times 1) + 16] = 112 + 288 + 162 = 562 \text{ g mol}^-$$

$\therefore$ no. of mol of $Fe_2(SO_4)_3.9H_2O$

$$= \frac{\text{wt.}}{\text{mol. wt.}} = \frac{4.35 \text{ g}}{562 \text{ g mol}^-} = 7.74 \times 10^{-3} \text{ mol} = 0.00774 \text{ mol.}$$

So, the correct answer is (*c*).

Example 187. *A 1.0 g sample of H_2O_2 solution containing x per cent H_2O_2 by weight requires x mL of a $KMnO_4$ solution for complete oxidation under acidic conditions. The normality of $KMnO_4$ solution is :*

(*a*) *0.588 N* (*b*) *1.16 N*

(*c*) *0.244 N* (*d*) *0.1 N*

(IIT, 1981 modified)

Solution. Reactions

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-] \times 5$$

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

or $2KMnO_4 \equiv 5H_2O_2$

$2[39 + 55 + (4 \times 16)]$ $5[(2 \times 1) + (2 \times 16)]$

$= 2 \times 158$ g $= 5 \times 34$ g

$$\text{wt. of } H_2O_2 = 1 \times \frac{x}{100} = \frac{x}{100} \text{ g ;}$$

Volume of $KMnO_4 = x$ mL

5×34 g H_2O_2 is oxidised by $KMnO_4$ = 2×158 g

$\frac{x}{100}$ g H_2O_2 is oxidised by $KMnO_4$

$$= \frac{2 \times 158 \times x}{5 \times 34 \times 100} \times \frac{1000}{31.6 \times x} \text{ } KMnO_4$$

We know that : Normality of

$$KMnO_4 = \frac{\text{wt.}}{\text{Eq. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{2 \times 158 \times x}{5 \times 34 \times 100} \times \frac{1000}{31.6 \times x} = 0.588 \text{ N.}$$

$$\left[\because \text{Eq. wt. of } KMnO_4 = \frac{\text{Mol. wt.}}{\text{no. of electrons gained}} = \frac{39+55+(4\times16)}{5} = 31.6\right.$$

So, the correct answer is (*a*).

EXAMPLE 188. *The volume of 0.5M H_2SO_4 required to produce 34.0 g H_2S by the reaction*

$$8NaI + 5H_2SO_4 \longrightarrow 4Na_2SO_4 + 4H_2O + 4I_2 + H_2S$$

will be :

(*a*) *2.5 L* (*b*) *5 L*

(*c*) *8 L* (*d*) *10 L*

SOLUTION. Reaction.

$$\underset{5\text{ mol}}{8NaI + 5H_2SO_4} \longrightarrow 4Na_2SO_4 + 4H_2O + 4I_2 + \underset{1\text{mol}}{H_2S}$$

wt. of H_2S = 34.0 g ; mol. wt. of

H_2S = (2 × 1) + 32 = 34g mol^{-}

$$\therefore \text{ no. of mol of } H_2S = \frac{\text{wt. of } H_2S}{\text{mol. wt. of } H_2S}$$

$$= \frac{34 \text{ g}}{34 \text{ g mol}^{-}} = 1 \text{ mol}$$

∴ 1 mol H_2S ≡ 5 mol H_2SO_4. It means :

$0.5 \times V(H_2SO_4) = 5$

∴ Volume of 0.5 M H_2SO_4 required

$$= \frac{5}{0.5} = 10 \text{ L}$$

So, the correct answer is (*d*).

EXAMPLE 189. *The amount of NaOH required to neutralise 25 Meq of the following*

(*i*) *CO_2* (*ii*) *HCl*

(*iii*) *$NaHSO_4$ is :*

(*a*) *0.5 g* (*b*) *1.0 g*

(*c*) *1.5 g* (*d*) *2.0 g*

SOLUTION. Since 25 Meq of each (*i*), (*ii*) and (*iii*) separately react with NaOH, so each time 25 Meq of NaOH are required. *i.e.*,

Meq of NaOH needed = 25

$$\text{But Meq of NaOH} = \frac{\text{wt. of NaOH}}{\text{Eq. wt. of NaOH}} \times 1000$$

$$25 = \frac{\text{wt. of NaOH}}{40} \times 1000$$

$$\left[\because \text{Eq. wt. of NaOH} = \frac{23+16+1}{1} = 40\right]$$

$$\therefore \quad \text{wt. of NaOH} = \frac{25 \times 40}{1000} = 1 \text{ g.}$$

So, the correct answer is (*b*).

EXAMPLE 190. *If density of water is 1000 kg m^{-3}, the molarity of water will be :*

(*a*) *18* (*b*) *5.6*

(*c*) *55.6* (*d*) *none of these*

SOLUTION. Let volume of water

= 1 L = 1000 mL = 10^{-3} m^3

∴ 1 m^3 H_2O weighs = 10^3 kg

$$10^{-3} \text{ m}^3 \text{ } H_2O \text{ weighs} = \frac{10^3 \text{ kg}}{1 \text{ m}^3} \times 10^{-3} \text{m}^3 = 1 \text{ kg} = 1000 \text{ g}$$

Mol. wt. of water (H_2O)

= (2 × 1) + 16 = 18 g mol^{-}

$$\text{Molarity} = \frac{\text{wt. of } H_2O}{\text{mol. wt. of } H_2O} \times \frac{1000}{\text{Volume in mL}} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-}} \times \frac{1000}{1000} = 55.6.$$

So, the correct answer is (*c*).

EXAMPLE 191. *An aqueous solution of KOH (6.9 M) contains 30% KOH by weight. The density of solution will be :*

(*a*) *0.6 g $(mL)^{-}$* (*b*) *2.4 g mL^{-}*

(*c*) *0.23 g $(mL)^{-}$* (*d*) *1.288 g $(mL)^{-}$*

SOLUTION. (*i*) 30% KOH by weight means :

Wt. of KOH = 30 g ; Wt. of solution = 100g.

Mol. wt. of KOH = 39 + 16 + 1 = 56 g mol^{-}

$$\therefore \text{ Volume of solution} = \frac{\text{Mass of solution}}{\text{density of solution}} = \frac{100 \text{ g}}{d}$$

(*ii*)
$$\text{Molarity} = \frac{\text{wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{30}{56} \times \frac{1000 \times d}{100}$$

$$6.9 = \frac{30}{56} \times \frac{1000\, d}{100} \text{ ;}$$

$$d = \frac{6.9 \times 56 \times 100}{30 \times 1000}$$

= 1.288 g (mL^{-}) **Ans.**

So, the correct answer is (*d*).

EXAMPLE 192. *A metal foil [d = 2.7 g (mL^{-}), thickness 10^{-4}m] was treated with one drop of 12 M HCl on its surface. The maximum area of the hole produced on the Al foil surface if one drop of acid occupies 0.04 mL volume will be*

(*a*) *0.1 cm^2* (*b*) *0.15 cm^2*

(*c*) *0.2 cm^2* (*d*) *0.16 cm^2*

SOLUTION. We know that : Meq of Al = Meq of HCl

But Meq of HCl = Molarity of HCl × Volume in mL × total + ve charge on H^+

= 12 × 0.04 × 1 = 0.48 = Meq of Al

$$\therefore \quad \text{Meq of Al} = \frac{\text{wt. of Al}}{\text{Eq. wt. of Al}} \times 1000$$

$$\left[\begin{array}{l}\because \text{ Valency of Al} = 3\text{, so :} \\ \text{eq. wt. of Al} = \dfrac{\text{at. wt. of Al}}{\text{Valency}} = \dfrac{27}{3} = 9\end{array}\right]$$

$$\therefore \quad \text{Wt. of Al} = \frac{\text{Meq of Al} \times \text{eq. wt. of Al}}{1000}$$

$$= \frac{0.48 \times 9}{1000}$$

$$\text{Volume of Al – foil} = \frac{\text{Mass}}{\text{density}} = \frac{0.48\text{ g} \times 9}{1000} \times \frac{\text{cm}^3}{2.7\text{ g}}$$

$$= 1.6 \times 10^{-3}\text{ cm}^3$$

$$\therefore \quad \text{Area} = \frac{\text{Volume}}{\text{thickness}} = \frac{1.6 \times 10^{-3}\text{cm}^3}{0.01\text{ cm}}$$

$$= 0.16\text{ cm}^2$$

$$\left[\because \text{ Thickness} = 10^{-4}\text{m} \times \frac{100\text{ cm}}{\text{m}} = 0.01\text{ cm}\right]$$

So, the correct answer is (*d*).

EXAMPLE 193. *Gastric juice contains 3.0 g of HCl per litre. If a person produces 2.5 litre of gastric juice per day, the number of anti-acid tablets each containing 400 mg of Al(OH)$_3$ needed to neutralise the acid produced in one day will be :*

(*a*) *14* (*b*) *12*

(*c*) *10* (*d*) *2*

(Dhanwad 1991, modified)

SOLUTION. Wt. of HCl = 3.0 g ; eq. wt. of HCl = 1 + 35.5 = 36.5 g

$$\therefore \quad \text{Volume} = 2.5\text{ L} = 2.5\text{ L} \times \frac{1000\text{ mL}}{1\text{ L}}$$

$$= 2500\text{ mL.}$$

$$\text{Normality of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} = \frac{3}{36.5}$$

(*i*) Milliequivalent *i.e*, Meq of

$$\text{HCl} = \text{Normality} \times \text{Volume}$$

$$= \frac{3}{36.5} \times 2500 = 205.48$$

(*ii*) wt. of $Al(OH)_3 = w$; $Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

$$\therefore \text{ Eq. wt. of } Al(OH)_3 = \frac{\text{Mol. wt.}}{3} = \frac{27 + 3(16+1)}{3}$$

$$= \frac{27+51}{3} = \frac{78}{3} = 26$$

$$\text{Meq. of } Al(OH)_3 = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000 = \frac{w}{26} \times 1000$$

But Meq of Al(OH)$_3$ required = Meq. of HCl

$$\therefore \quad \frac{w}{26} \times 1000 = 205.48\text{ ;}$$

$$w = \frac{205.48 \times 26}{1000} = 5.342\text{ g}$$

$$\text{or} \quad \frac{5.342\text{ g} \times 1000\text{ mg}}{1\text{ g}} = 5342\text{ mg.}$$

∴ No. of anti acid tablets

$$= \frac{5342\text{ mg}}{400\text{ mg}} \simeq 14.$$

So, the correct answer is (*a*).

EXAMPLE 194. *The volume of a solution of HCl containing 73 g of acid per litre that would suffice for the exact neutralisation of sodium hydroxide obtained by allowing 0.46 g of metallic sodium to act upon water is :*

(*a*) *2 mL* (*b*) *5 ml*

(*c*) *10.0 mL* (*d*) *15.0 mL*

(MLNR, 1997 modified)

SOLUTION. Reactions : $Na + H_2O \longrightarrow NaOH + \frac{1}{2} H_2$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

(*i*) wt. of Na = 0.46 g ; eq. wt. of Na = 23

$$\therefore \quad \text{Meq. of Na} = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000 = \frac{0.46}{23} \times 1000$$

(*ii*) wt. of HCl = 73 g,

eq. wt. of HCl = 1 + 35.5 = 36.5

$$\text{meq. of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \text{Volume} = \frac{73}{36.5} \times V$$

But Meq of Na = Meq of HCl

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

$$V = \frac{0.46}{23} \times \frac{1000 \times 36.5}{73} = 10\text{ mL.}$$

So, the correct answer is (*c*).

EXAMPLE 195. *25 mL of a solution of Na$_2$CO$_3$ having a specific gravity of 1.25 g (mL)$^-$ required 32.9 mL of a solution of HCl containing 109.5 gram of the acid per litre for complete neutralisation. The volume of 0.84 N H$_2$SO$_4$ that will be completely neutralised by 125 gram of the Na$_2$CO$_3$ solution is:*

(*a*) *117.5 mL* (*b*) *470 mL*

(*c* *3.25 cm^3* (*d*) *325 mL*

(MLNR, 1991, modified)

SOLUTION. (*i*) wt. of HCl = 109.5 g, eq. wt. of HCl = 1 + 35.5 = 36.5, Volume of HCl = 32.9 mL

$$\therefore \quad \text{Meq of HCl} = \frac{\text{wt.}}{\text{Eq. wt.}} \times \text{Volume} = \frac{109.5}{36.5} \times 32.9$$

$$= 98.7 = N_2V_2\text{ (HCl)}$$

$$\text{Also : } N_1V_1\ (Na_2CO_3) = N_2V_2\text{ (HCl)}$$

$$N_1 \times 25 = 98.7\text{ ;}$$

$$N_1 = \frac{98.7}{25} = \text{Normality of } Na_2CO_3$$

(*ii*) Volume of Na$_2$CO$_3$

$$= \frac{\text{wt. of } Na_2CO_3}{\text{Density or sp. gr. of } Na_2CO_3}$$

$$= \frac{125\text{ g}}{1.25\text{ g (mL)}^-} = 100\text{ mL}$$

$$\text{Also : } N_1V_1\ (H_2SO_4) = N_2V_2\ (Na_2CO_3)$$

$$0.84 \times V_1 = \frac{98.7}{25} \times 100\text{ ;}$$

$$V_1 = \frac{98.7 \times 100}{0.84 \times 25} = 470\text{ mL}$$

So, the correct answer is (*b*).

EXAMPLE 196. *4.0 g of a mixture of NaCl and Na_2CO_3 were dissolved in water and volume made up to 250 mL. 25 mL of this solution required 50 mL of N/10 HCl for complete neutralisation. The percentage of Na_2CO_3 will be :*

(*a*) *33.75%* (*b*) *66.25%*
(*c*) *16.8%* (*d*) *8.16%*

(Roorkee 1982, modified)

SOLUTION. Out of NaCl and Na_2CO_3, only Na_2CO_3 reacts with HCl. Eq. wt. of

$$Na_2CO_3 = \frac{\text{Mol. wt. of } Na_2CO_3}{2} = \frac{(2\times23)+12+(3\times16)}{2} = 53$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

$$N_1V_1\,(Na_2CO_3) = N_2V_2\,(HCl)$$

$$N_1 \times 25 = \frac{1}{10}\times 50\,;\ N_1 = \frac{1}{10}\times\frac{50}{25} = 0.2$$

∴ Strength of Na_2CO_3

$$= \text{Normality} \times \text{Eq. wt.}$$

$$= 0.2 \times 53 = 10.6\ g\ L^{-}$$

1000 mL Na_2CO_3 solution contain Na_2CO_3 = 10.6 g

250 mL Na_2CO_3 solution contain

$$Na_2CO_3 = \frac{10.6\ g}{1000\ mL}\times 250\ mL = 2.65\ g$$

$$\therefore \%\text{ age of } Na_2CO_3 = \frac{\text{wt. of } Na_2CO_3}{\text{Total wt. of } Na_2CO_3}\times 100 = \frac{2.65\ g}{4.0\ g}\times 100 = 66.25\%$$

So, the correct answer is (*b*).

EXAMPLE 197. *The equivalent weight of each of the following compounds (i) $Na_2SO_4.12H_2O$ (ii) $Na_3PO_4.12H_2O$ and (iii) $Ca_3(PO_4)_2$, assuming the formula weight of these compounds as X, Y and Z is :*

(*a*) *X/3, Y/2, Z/6* (*b*) *X/2, Y/3/, Z/6*
(*c*) *X/6, Y/3, Z/2* (*d*) *X/2, Y/6, Z/3*

(at. wt. Na = 23, P = 31, O = 16, H = 1, Ca = 40)

(MLNR, 1991, modified)

SOLUTION. Eq. wt. of a salt = $\dfrac{\text{Mol. wt. of salt.}}{\text{Total + ve or – ve charge}}$

(*i*) $Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$. Total + ve charge = 2

$$\therefore \quad \text{Eq. wt. of } Na_2SO_4 = \frac{X}{2}$$

(*ii*) $Na_3PO_4 \rightleftharpoons 3Na^+ + 2PO_4^{3-}$. Total + ve charge = 3

$$\therefore \text{ Eq. wt. of } Na_3PO_4.12H_2O = \frac{Y}{3}$$

(*iii*) $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$. Total + ve charge = 3 × 2 = 6

$$\therefore \quad \text{Eq. wt. of } Ca_3(PO_4)_2 = \frac{Z}{6}$$

So, the correct answer is (*b*).

EXAMPLE 198. *Equivalent weight of KIO_3 in the reaction*

$$IO_3^- \longrightarrow ICl \quad \text{is :}$$

(*a*) *214* (*b*) *107*
(*c*) *10.7* (*d*) *53.5*

(*at. wt. I = 127, O = 16, Cl = 35.5, K = 39*)

SOLUTION. (*i*) In IO_3^-, O.N. of I + 3 × O. N. of O = –1; O. N. of I + 3(–2) = – 1 ; O. N. of I = –1 + 6 = +5

(*ii*) In ICl, O. N. of I + O.N. of Cl = 0

O. N. of I+ (–1) = 0 ; O. N. of I = 0 + 1 = 1

$$I^{+5}O_3^- \longrightarrow I^+Cl$$

Change in O. N = +5 – (+1) = + 4

$$\therefore \text{ Eq. wt. of } KIO_3 = \frac{39+127+(3\times16)}{4} = \frac{214}{4} = 53.5. \qquad \textbf{Ans.}$$

So, the correct answer is (*d*).

EXAMPLE 199. A *sample of $Na_2CO_3.H_2O$ weighing 0.62 g is added to 100 mL of 0.1 N H_2SO_4. The resulting solution will be :*

(*a*) *Acidic* (*b*) *Basic*
(*c*) *neutral*

(IIT 1976 modified)

SOLUTION. Eq. wt. of

$$Na_2CO_3.H_2O = \frac{(2\times23)+12+(3\times16)+[(2\times1)+16]}{2} = \frac{124}{2} = 62$$

wt. of Na_2CO_3 = 0.62 g

$$\therefore \text{Meq. of } Na_2CO_3 = \frac{\text{wt.}}{\text{Eq. wt.}}\times 1000 = \frac{0.62\ g}{62}\times 1000 = 10$$

Meq. of H_2SO_4 = Normality × Volume in mL
= 0.1 × 100 = 10

Since Meq. of Na_2CO_3 (= 10) = Meq. of H_2SO_4 (= 10), so the solution is neutral.

So, the correct answer is (*c*).

EXAMPLE 200. *The formula weight of an acid is 82.0. In a titration, 100 cm^3 of a solution of this acid containing 39.0 g of the acid per litre were completely neutralised by 95 cm^3 of aqueous NaOH containing 40 g of NaOH per litre. The basicity of the acid is :*

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

(Roorkee, 2000 modified)

SOLUTION. (*i*) wt. of acid = 39 g ; Formula wt. of acid = 82. Basicity of acid = *x*.

But no. of equivalent of acid

$$= \frac{\text{wt.}}{\text{Formula wt.}}\times \text{basicity} = \frac{39\,x}{82} = \text{Normality}$$

(*ii*) wt. of NaOH = 40 g ; Formula wt. of NaOH = 23 + 16 + 1 = 40, acidity of NaOH = 1.

No. of equivalent of

$$\text{NaOH} = \frac{\text{wt.}}{\text{Formula wt.}} \times \text{acidity}$$

$$= \frac{40}{40} \times 1 = 1 = \text{Normality}$$

But N_1V_1 (acid) = N_2V_2 (acid)

$$\frac{39\,x}{82} \times 100 = 1 \times 95$$

$$\therefore \quad x = \frac{95 \times 82}{100 \times 39} \simeq 2.$$

So, the correct answer is (*b*).

Example 201. A *1.0 g sample of Fe_2O_3 solid of 55.2 percent purity is dissolved is acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made up to 100.0 mL. An aliquot of 25.0 mL requires 17.0 mL of 0.0167 M solution of an oxidant for titration. The number of electrons taken up by the oxidant in the reaction of the above titration is :*

(*a*) *1*	(*b*) *2*
(*c*) *4*	(*d*) *6*

(IIT 1991 modified)

Solution. wt. of pure $Fe_2O_3 = \frac{55.2}{100} \times 1.0 \text{ g} = 0.552 \text{ g}$

Mol. wt. of Fe_2O_3 = (2 × 56) + (3 × 16) = 112 + 48 = 160 g mol^-

$Fe_2O_3 \equiv 2Fe^{3+}$

$$\therefore \text{ no. of mol of } Fe_2O_3 = \frac{\text{wt.}}{\text{Mol. wt.}} = \frac{0.552 \text{ g}}{160 \text{ g mol}^-}$$

$= 3.45 \times 10^{-3}$ mol

no. of mol of $Fe^{3+} = 2 \times 3.45 \times 10^{-3} \text{ mol} = 6.9 \times 10^{-3}$ mol

$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$ (Reduction by $1e^-$)

(*i*) ∴ Amount of Fe^{2+} in 100 ml solution

$$= 6.9 \times 10^{-3} \text{mol} \times \frac{1 \text{ m. mol}}{10^{-3}\text{mol}}$$

= 6.9 m mol of reductant, Fe^{2+}.

= 6.9 m eq because Fe^{3+} to Fe^{2+} is one electron change. So, the mol. wt. = equivalent weight.

(*ii*) To find m mol of oxidant and number of electrons taken up by the oxidant.

25 mL reductant require oxidant = 17 mL

100 mL reductant require oxidant

$$= \frac{17 \text{ mL}}{25 \text{ mL}} \times 100 \text{ mL} = 68 \text{ mL}$$

∴ Amount of oxidant used for 100 mL

Fe^{2+} solution = 68 × 0.0167 m mol

$$\frac{\text{m mol (oxidant)}}{\text{m mol (reductant)}} = \frac{\text{no. of electrons lost by reductant}}{\text{no. of electrons gained by oxidant}}$$

$$\frac{68 \times 0.0167}{6.9} = \frac{1}{n} \; ; n = \frac{6.9}{68 \times 0.0167} = 6.$$

So, the correct answer is (*d*).

Example 202. *0.804 g sample of an iron ore was dissolved in acid. Iron was reduced to +2 state and it required 47.2 mL of 0.112 N $KMnO_4$ solution for titration. The percentage of Fe and Fe_3O_4 in the ore is :*

(*a*) *36.82, 60*	(*b*) *50.87, 36.82*
(*c*) *36.82, 50.87*	(*d*) *18.41, 25.44*

(*at. wt. Fe = 56, K = 39, Mn = 55, O = 16*)

(Roorkee 1988, modified)

Solution. (*i*) wt. of

Fe^{2+} = *w* g, $Fe^{2+} \longrightarrow Fe^{3+} + 1e^-$. So :

$$\text{Eq. wt. of } Fe^{2+} = \frac{\text{at. wt.}}{1} = \frac{56}{1} = 56$$

$$\therefore \quad \text{Meq. of } Fe^{2+} = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000 = \frac{w}{56} \times 1000 .$$

(*ii*) $Mn^{7+}O_4^- + 5e^- \longrightarrow Mn^{2+}$

Meq. of $KMnO_4$

= Normality × Volume is mL

= 0.112 × 47.2

But Meq. of Fe^{2+} = Meq of $KMnO_4$

$$\frac{w \times 1000}{56} = 0.112 \times 47.2 \; ;$$

$$w = \frac{0.112 \times 47.2 \times 56}{1000} = 0.296$$

$$\therefore \quad \%\text{ age of Fe} = \frac{\text{wt. of Fe}}{\text{wt. of ore}} \times 100$$

$$= \frac{0.296 \times 100}{0.804} = 36.82\%$$

(*iii*)

$$\begin{array}{ccc} Fe_3O_4 & \rightleftharpoons & 3Fe \\ (3 \times 56) + (4 \times 16) & & 3 \times 56 \\ = 168 + 64 = 232 & & = 168 \end{array}$$

168 g Fe is obtained from

Fe_3O_4 = 232 g

0.296 g Fe is obtained from

$$Fe_3O_4 = \frac{232 \text{ g}}{168 \text{ g}} \times 0.296 \text{ g} = 0.409 \text{ g}$$

$$\therefore \quad \%\text{ age of } Fe_3O_4 = \frac{\text{wt.}}{\text{wt. of ore}} \times 100$$

$$= \frac{0.409}{0.804} \times 100 = 50.87\%$$

So, the correct answer is (*c*).

Example 203. *0.1 M $KMnO_4$ is used for the following titration. The volume of solution in mL required to react with 0.158 g of $Na_2S_2O_3$ will be :*

(*a*) *26.67 mL*	(*b*) *2.4 mL*
(*c*) *24 mL*	(*d*) *2.7 mL*

$$S_2O_3^{2-} + MnO_4^- + H_2O \longrightarrow MnO_2\,(s) + SO_4^{2-} + OH^-$$

(MLNR, 1992, modified)

Solution. (*i*) **Reaction**

$$S_2O_3^{2-} \longrightarrow SO_4^{2-}$$

or $S_2^{+2}O_3^{2-} \longrightarrow 2S^{+6}O_4^{-2} + 8e^-$ [$\because$ $(2\times+6)-(2\times+2)=8$]

$$\therefore \text{ Eq. wt. of } Na_2S_2O_3 = \frac{\text{Mol. wt.}}{8}$$

$$= \frac{(2\times 23)+(2\times 32)+(3\times 16)}{8} = 19.75$$

$$\therefore \text{ Meq of } Na_2S_2O_3 = \frac{\text{wt.}}{\text{Eq. wt.}}\times 1000$$

$$= \frac{0.158\text{ g}}{19.75}\times 1000 = \mathbf{8}$$

(*ii*) $Mn^{+7}O_4^- + 3e^- \longrightarrow Mn^{+4}O_2$ [$\because$ $+7-4=+3$]

Normality of $KMnO_4$ = Molarity of $KMnO_4$ × $\begin{bmatrix}\text{no. of electrons gained by}\\ \text{one molecule of } KMnO_4\end{bmatrix}$

$= 0.1 \times 3 = 0.3$

But Meq of $KMnO_4$ = Meq of $Na_2S_2O_3$

So : Normality of $KMnO_4$ × volume in mL

= Meq of $Na_2S_2O_3$

$$0.3 \times V = 8\ ;\ V = \frac{8}{0.3} = \mathbf{26.67\ mL}$$

So, the correct answer is (*a*).

Example 204. *A 0.5 g sample containing MnO_2 is treated with HCl, liberating Cl_2. The chlorine is passed through a solution of KI and 30 cm³ of 0.1 M $Na_2S_2O_3$ are required to titrate the liberated iodine. The percentage of MnO_2 in the sample is :*

(*a*) *13.05%*	(*b*) *26.1%*
(*c*) *52.2%*	(*d*) *3%*

(*at. wt., Mn = 55, O = 16*) **(Roorkee 1994 modified)**

Solution. (*i*) **Reactions.**

$$MnO_2 + HCl \longrightarrow Cl_2 \xrightarrow{KI} I_2 \xrightarrow{Na_2S_2O_3} Na_2S_4O_6$$

$$MnO_2 + 2HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$$

or $Mn^{4+}O_2 \longrightarrow Mn^{2+}Cl_2$. O. N. change = 4 – 2 = 2

$$\therefore \text{Eq. wt. of } MnO_2 = \frac{\text{Mol. wt.}}{2} = \frac{55+(2\times 16)}{2}$$

$$= \frac{87}{2} = 43.5$$

$$\therefore \quad \text{Meq of } MnO_2 = \frac{\text{wt. of } MnO_2}{\text{Eq. wt.}}\times 1000$$

$$= \frac{\text{wt. of } MnO_2 \times 1000}{43.5}$$

(*ii*)

$$\begin{array}{ccc} 2S_2O_3^{2-} & \longrightarrow & S_4O_6^{2-} + 2e^- \\ 2\text{ mol} & & 2\ e^- \\ 1\text{ mol} & & 1e^- \end{array}$$

$$\therefore \text{ Eq. wt. of } Na_2S_2O_3 = \frac{\text{Mol. wt. of } Na_2S_2O_3}{1}\ \textit{i.e.}, 0.1\text{ M}$$

$= 0.1$ N

M.eq. of $Na_2S_2O_3$ = Normality × Volume in mL
= 30 × 0.1 = 3

$$\therefore \frac{\text{wt. of } MnO_2 \times 1000}{43.5} = 3\ ;\text{wt. of } MnO_2 = \frac{3\times 43.5}{1000} = 0.1305$$

$$\%\text{ age of } MnO_2 = \frac{0.1305}{0.5}\times 100 = 26.1\%.$$

So, the correct answer is (*b*).

Example 205. *In x mL 0.3 N HCl, firstly addition of 200 mL distilled water and then addition of 100 mL 0.1 N NaOH, gives same final acid strength. Determine, x*

(WB-JEE, 2011)

Solution. First case. $x(0.3) = (x+200)\,y;\ y = 0.3x/200 + x$. Second case. No. of equivalents of HCl after adding NaOH solution $= \frac{0.3x}{1000} - 0.01$

[$\because$ 0.1N NaOH $= \frac{0.1}{1000} \times 100 = 0.01$]

$$\therefore \text{ Concentration} = \frac{\frac{0.3x}{1000} - 0.01}{100+x} \times 1000$$

[$\because$ Total conc. in 1L = 100 + x]

Since both concentrations are equal,

$$\frac{\left[\frac{0.3x}{1000} - 0.01\right]\times 1000}{100+x} = \frac{0.3x}{200+x};\ \frac{0.3x-10}{100+x} = \frac{0.3x}{200+x}$$

or $(200+x)(0.3x-10) = 0.3\,(100+x)$; $60x + 0.3x^2 - 2000 - 10x = 30x + 0.3x^2$ or $20x = 2000$; $x = 100$ mL. **Ans.**

Example 206. *50 cm³ of 0.2 N HCl is titrated against 0.1 N NaOH solution. The titration was discontinued after adding 50 cm³ of NaOH. The remaining titration is completed by adding 0.5 N KOH. The volume of KOH required for completing the titration is:* **(Karnataka, JEE, 2011)**

(*a*) *10 cm³*	(*b*) *12 cm³*
(*c*) *16.2 cm³*	(*d*) *21.0 cm³*

Solution. No. of milliequivalents = $N \times V$ (in mL)

Milliequivalents of NaOH = 0.1 × 50 = 5

Milliequivalents of HCl = 0.2 × 50 = 10

$\therefore$ Milliequivalents of HCl left behind = 10 – 5 = 5

Total volume of solution = 50 + 50 = 100 mL

$$\therefore \text{ Normality of HCl left} = \frac{5}{100} = 0.05\ N$$

Using normality equation N_1V_1 (acid) = N_2V_2 (KOH)

$$0.05 \times 100 = 0.5 \times V_2$$

$\therefore$ $V_2 = (0.05 \times 100)/0.5 = 10\text{cm}^3$.

So, the correct answer is (*a*).

Example 207. *100 mL of 0.1 M acetic acid is completely neutralised using a standard solution of NaOH. The volume of ethane obtained at STP after the complete electrolysis of the resulting solution is:*

(*a*) *112 mL*	(*b*) *56 mL*
(*c*) *224 mL*	(*d*) *560 mL*

(Karnataka, CET, 2012)

Solution. $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$$\underset{\text{2 mol}}{2CH_3COONa} \xrightarrow{\text{Electrolysis}} \underset{\text{1 mol = 22400 mL}}{C_2H_6} + 2CO_2 + 2Na$$

$$\text{no. of mol of} CH_3COOH \text{ given} = \frac{100}{1000} L \times 0.1 = \frac{1}{100}$$

2 mol CH_3COOH form C_2H_6 = 22400 mL

$$\frac{1}{100} \text{ mol } CH_3COOH \text{ form } C_2H_6 = \frac{1}{2} \times \frac{22400}{100} = 112 \text{ mL}$$

So, the correct answer is (*a*).

Example 208. *A given solution containing 20 mg NaCl per mL should be diluted to get a solution containing 8 mg NaCl per mL*

(*a*) *12.0 mL* (*b*) *2.5 mL*
(*c*) *3.0 mL* (*d*) *4.0 mL*

Solution. 20 mg = (20/1000)g ; 8 mg = (8/1000) g. But:

Millequivalent of conc. NaCl ≡ Milliequivalent of Dilute NaCl (Eq. wt. of NaCl = 23 + 35.5 = 58.5). So:

$$\frac{20}{1000} \times \frac{1000}{58.5} \times 1 = \frac{8}{1000} \times \frac{1000}{58.5} \times V; V = 2.5 \text{ mL}.$$

So, the correct answer is (*b*).

Note: Milliequivalents of one solution = Milliequivalent of solid solute

$$\text{Normality} \times \text{volume in mL} = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000$$

$$\frac{\text{Mol wt.} \times \text{Molarity}}{\text{Eq. wt.}} \times \text{Volume in mL} = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000$$

Example 209. *Calculate the volume in millilitre of 0.25 M H_2SO_4 those are needed to dissolve 0.20 g of calcium carbonate.*

(*a*) *7.0 mL* (*b*) *7.5 mL*
(*c*) *8.9 mL* (*d*) *8.0 mL*

(H.P. Board, 2012)

Solution. Mol. wt. of $CaCO_3$ = 40 + 12 + (3 × 16) = 100 g mol$^-$

$$\therefore \text{ Eq. wt. of } CaCO_3 = \frac{100}{\text{Charge on } Ca^{2+}} = \frac{100}{2} = 50.$$

Mol. wt. of H_2SO_4 = (2 × 1) + 32 + (4 × 16) = 98 g mol$^-$

∴ Eq. wt. of H_2SO_4

$$= \frac{\text{Mol. wt. of } H_2SO_4}{\text{Charge on cation, } 2H^+ (= 2)} = \frac{98}{2} = 49$$

But Milliequivalent of H_2SO_4 = Milliequivalent of $CaCO_3$

$$\text{Normality} \times \text{Vol in mL} = \frac{\text{wt.}}{\text{Eq. wt.}} \times 1000$$

$$\frac{\text{Molarity} \times \text{Mol. wt.}}{\text{Eq. wt.}} \times V = \frac{0.2}{50} \times 1000$$

$$\frac{0.25 \times 98}{49} \times V = \frac{0.2}{50} \times 1000;$$

$$\text{So, } V = \frac{0.2 \times 1000 \times 49}{50 \times 0.25 \times 98} = 8.0 \text{ mL}$$

So, the correct answer is (*d*).

Example 210. *Calculate the volume of 0.1 M NaOH to completely neutralise 15.0 mL of 0.2 M H_3PO_3.*

(*a*) *40 mL* (*b*) *50 mL*
(*c*) *60 mL* (*d*) *70 mL*

(Haryana School Board, 2012)

Solution. $H_3PO_3 \rightleftharpoons HPO_3^{2-} + 2H^+$ (Dibasic acid)

$$\underset{\text{2 mol}}{2KOH} + \underset{\text{1 mol}}{H_3PO_3} \longrightarrow K_2HPO_3 + 2H_2O$$

$$\frac{M_1V_1 \text{ of KOH}}{M_2V_2 \text{ of } H_3PO_3} = \frac{\text{no. of moles of KOH}}{\text{no. of moles of } H_3PO_3}$$

$$\frac{0.1 \times V}{0.2 \times 15} = \frac{2}{1}; \; 0.1 \times V = 2 \times 0.2 \times 15;$$

$$V = \frac{2 \times 0.2 \times 15}{0.1} = 60 \text{ mL}$$

So, the correct answer is (*c*).

Example 211. *25 mL of 0.2 M H_3BO_3 solution needs .... mL of 0.1 M NaOH for complete neutralisation*

(*a*) *20 mL* (*b*) *25 mL*
(*c*) *50 mL* (*d*) *60 mL*

(PSEB, 2012)

Solution. $H_3BO_3 + NaOH \longrightarrow NaH_2BO_3 + H_2O$

Monobasic

1 mol 1 mol

$$\frac{\text{Molarity} \times \text{Volume of } H_3BO_3}{\text{Molarity} \times \text{Volume of NaOH}} = \frac{\text{no. of mol of } H_3BO_3}{\text{no. of mol of NaOH}}$$

$$\frac{0.2 \times 25}{0.1 \times V} = \frac{1}{1}; V = \frac{0.2 \times 2.5}{0.1} = 50 \text{ mL}$$

So, the correct answer is (*c*).

Example 212. *What is the volume of CO_2 liberated (in litres) at 1 atmosphere and 0°C when 10 g of 100% pure calcium carbonate is treated with excess dilute sulphuric acid?*

(atomic mass, Ca = 40, C = 12, O = 16).

(*a*) *0.224* (*b*) *2.24*
(*c*) *22.4* (*d*) *224*
(*e*) *11.2*

(Keral PMT, 2012)

Solution. Mol. wt. (or wt. of 1 mol) of $CaCO_3$ = 40 + 12 + (3 × 16) = 100 g mol$^-$

Reaction: $CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2(g) + H_2O$

1 mol 1 mol

100 g 12 + (2 × 16) = 44 g mol$^-$

= 22.4 L at NTP

100 g $CaCO_3$ produce $CO_2(g)$ = 22.4 L

$$10 \text{ g } CaCO_3 \text{ produce } CO_2(g) = \frac{22.4}{100} \times 10 = 2.24 \text{ L}.$$

So, the correct answer is (*b*).

Type. Conversion of molarity of a solution into normality and vice-versa. Use the relation:

$$\boxed{\textbf{Normality} \times \textbf{Eq. wt.} = \textbf{Molarity} \times \textbf{mol. wt.}}$$

EXAMPLE 213. *The volume of 0.1 M $Ca(OH)_2$ required to neutralise 10 mL of 0.1 N HCl is:*

(*a*) 10 mL (*b*) 20 mL (*c*) 5 mL (*d*) 15 mL

(J&K, CET, 2012)

SOLUTION. $\underset{\text{1 mol}}{Ca(OH)_2} \rightleftharpoons Ca^{2+} + \underset{\text{2mol}}{2OH^-}$

$40 + 2(16 + 1)$
$= 74$ g

$$\therefore \text{ Eq. wt. of Ca (OH)}_2 = \frac{\text{Mol. wt.}}{\text{no. of OH}^- \text{ ions}} = \frac{74}{2} = 37$$

$N_1 V_1$ of $Ca(OH)_2 = N_2 V_2$ of HCl.

$$\frac{0.1 \times 74}{37} \times V_1 = 0.1 \times 10; V_1 = 10/2 = 5 \text{ mL}.$$

So, the correct answer is (*c*).

EXAMPLE 214. *25 mL of house hold bleach solution was mixed with 30 mL of 0.50 MKI and 10 mL of 4 N acetic acid. In the titration of liberated iodine, 48 mL of 0.25 N $Na_2S_2O_3$ was used to reach the end point. The molarity of household bleach solution is:*

(*a*) 0.48 M (*b*) 0.96 M (*c*) 0.24 M (*d*) 0.024 M

(IIT-JEE 2012)

SOLUTION. $\underset{\text{Bleaching powder}}{CaOCl_2} + 2CH_3COOH \longrightarrow Ca(CH_3COO)_2 + H_2 + Cl_2$

$Cl_2 + 2KI \longrightarrow 2KCl + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

From above equations, we infer that:

1 millimole of $CaOCl_2$ = 1 millimole of $I_2 = \frac{1}{2}$ millimole of $Na_2S_2O_3$

$\therefore$ Millimoles of $CaOCl_2 = \frac{1}{2} \times 0.25 \times 48 = 6$. Also:

Molarity × volume = 6 millimoles

$\therefore$ Molarity × 25 = 6. So, molarity = 6/25 = 0.24 M

So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. One litre solution contains 4 g of hydroxide of a monovalent metal. Determine volumetrically the atomic weight of the metal. Given N/10 HCl.

   Ans. $(40\ V_1/V_2) - 17$

2. Determine volumetrically the number of molecules of water of crystallisation in oxalic acid, $H_2C_2O_4 \cdot xH_2O$, 6.3 g of which have been dissolved per litre of the given solution. Provided N/10 NaOH solution.

   Ans. 2.

3. You are provided with a solution of a mixture of NaOH and KOH, 9 g of which have been dissolved per litre. Find the % age composition of each. (Given M/10 HNO_3. M_1, is molarity of total solution and x is wt. of NaOH).

   Hints: NaOH = $\frac{100x}{9}$ %;

   KOH = $100 - \left(\frac{100x}{9}\right)$ % **Ans.**

4. You are provided with a solution prepared by dissolving 5.0 g of a copper coin in acid solution making the solution to one litre. Determine the percentage of Cu in the coin. 20 mL of the solution on treatment with Na_2CO_3, CH_3COOH and KI liberated iodine which reacted completely with 16.0 mL of 0.058 N $Na_2S_2O_3$ solution. (at. wt. of Cu = 63.5). **Ans.** 58.93%.

   Hint. Eq. wt. of Cu = 63.5.

5. How will you prepare exactly 3.0 L of 1.0 M HCl by mixing portions of stock solutions of 2.5 M HCl and 0.4 M HCl?

   [**Ans.** 0.857 L of 2.5 M and 2.14 L of 0.4 M HCl should be mixed to get exact 3L of 1.0 M HCl]

6. Calculate the concentration of $Ba(OH)_2$ solution if it takes 40 mL of 3.5 M HNO_3 to neutralise 30.0 mL of this base.

   Hint. $\underset{\text{1 m. mol}}{Ba(OH)_2} + \underset{\text{2 m. mol}}{2HNO_3} \longrightarrow Ba(NO_3)_2 + 2H_2O$

   $$\frac{(30.0 \text{ mL} \times M_1) \text{ of } Ba(OH)_2}{(40 \text{ mL} \times 3.5\ M) \text{ of } HNO_3} = \frac{1 \text{ m. mol}}{2 \text{ m. mol}}; M_1 = \mathbf{2.67\ M}$$

   Ans.

7. Find the ionic strength of the solution containing. 0.1 M $CuSO_4$, 0.2 M $Al_2(SO_4)_3$ and 0.3 M NaCl.

   Ans. 3.7 mol L^-

8. Calculate the equivalent weight of $Mg(OH)_2$ in the following reaction.

   $Mg(OH)_2 + HCl \longrightarrow Mg(OH)Cl + H_2O.$

   Ans. 58

9. Calculate the molar concentration of Na^+ ions when 200 mL of 2.0 M NaCl is diluted to 1/2 litre.

   Ans. 0.8 M

10. 20 mL of 1M KOH solution neutralise

    (*a*) 5 mL (*b*) 10 mL
    (*c*) 15 mL (*d*) 20 mL of 2M H_2SO_4.

    Ans. (*a*)

11. Calculate the molarity of 1.5 N H_2SO_4.

    Ans. (0.75 M)

12. An aqueous solution of NaOH (5.1 M) contains 40% NaOH by weight. The density of solution will be:

    (*a*) 1.6 g mL^- (*b*) 0.1 g $(mL)^-$
    (*c*) 0.51 g $(mL)^-$ (*d*) 10 g $(mL)^-$

    Ans. (*c*)

13. Calculate the molarity of water if its density is 1 kg m^{-3}.

    (*a*) 55.6 (*b*) 16 (*c*) 18 (*d*) 20

    Ans. (*a*)

23

CHAPTER

Physical and Chemical Equilibrium

23.1 EQUILIBRIUM

It represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with passage of time.

Physical equilibrium. If the opposing processes in a reversible reaction involve only physical changes, the equilibrium is called physical equilibrium. e.g.,

$$\text{Solid} \rightleftharpoons \text{liquid; liquid} \rightleftharpoons \text{gas ; solid} \rightleftharpoons \text{gas}$$

Chemical equilibrium. If the opposing processes involve chemical changes (*i.e.*, chemical reactions), the equilibrium is called chemical equilibrium.

23.2 SOME IMPORTANT POINTS REGARDING CHEMICAL EQUILIBRIUM

1. Most of the processes including chemical reactions which take place in a closed vessel, do not go to completion. The reaction **appears to stop** after sometime but the reactants may still be present. The state so reached is called equilibrium state. These are reversible reactions.
2. At equilibrium, the reaction continues both in the forward as well as backward direction *i.e.*, the rate of forward reaction is equal to rate of backward reaction.
3. **Law of mass action** (Proposed by Guldberg and Waage). It states that the rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of active masses of reactants each raised to the power equal to corresponding stoichiometric coefficients in the balanced reaction. For dilute solutions, active masses are equal to concentration. For example, for a reaction :

(*i*)
$$aA + bB \rightleftharpoons cC + dD \text{(reversible)}$$

Rate of forward reaction, $r_f = k_f[A]^a[B]^b$

Rate of backward reaction, $r_b = k_b[C]^c[D]^d$

where k_f and k_b are the rate constant or velocity constants for the forward and backward reactions respectively.

(*ii*) For irreversible reaction, $aA + bB \longrightarrow$ Products.
Rate of forward reaction, $r_f = k_f [A]^a [B]^b$ where k_f is rate constant for the forward reaction.

4. **Equilibrium constant, k_C and k_P. (*i*)** For a reversible reaction, involving solid, solution and gases :

$$a A (s) + b B (g) \rightleftharpoons c C (g) + d D \text{ (solution)}$$

$$\frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where $\frac{k_f}{k_b}$ = equilibrium constant, K.

$$\therefore \qquad K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad \text{... (1)}$$

Since A is a solid, concentration of A (s) = a constant (d/M). So, above relation (1) can be written as :

$$K \times [A\ (s)] = \frac{[C]^c [D]^d}{[B]^b}$$

$$= \text{constant, called } K_C$$

The distinction between K and K_C is that, the word K is used when all the substances in the reaction are involved. The word K_C is used when only solutions and gases are involved. The expression of K_C is devoid of pure liquids and solids.

Note. By convention, concentration of solid = 1; Concentration of liquid = 1; concentration of aqueous, [aq] = 1 **Thus** [solid] = 1 ; (liquid] = 1 ; [aq] = 1.

(*ii*) For a reversible reaction, involving **gases only :**

$$a A(g) + b B(g) \rightleftharpoons c C (g) + d D (g) \qquad \text{... (2)}$$

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

where p_A, p_B, p_C and p_D are the partial pressures (each raised to the power of their respective co-efficients) of gases A, B, C and D respectively. If any one of the reactant or product species is a solid or solution, K_p will be replaced by K_c. The constant K_p is only used for gaseous reactants and products.

> **Note.** K_c is constant at a given temperature irrespective of the initial concentration of *e.g.*, $H_2(g)$, $I_2(g)$ and HI (g) in $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ reaction.

5. **Reaction quotient, Q.** At each point in a reaction, a ratio of concentration terms can be formulated. This formulation is similar to that for equilibrium constant expression shown for K_c and K_p above. This ratio, called reaction quotient (Q) helps to predict the direction of a reaction described below.

(*i*) If $Q < K_c$, the reaction proceeds from left to right direction *i.e.*, in forward direction.

(*ii*) If $Q > K_c$, the reaction proceeds from right to left direction *i.e.*, in backward direction.

(*iii*) If $Q = 0$, the reaction is at equilibrium.

Thus, for a reaction, $a\,A + b\,B \rightleftharpoons c\,C + d\,D$

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

For chemical equilibrium to exist in a reaction mixture, the reaction quotient Q must be equal to the equilibrium constant, K_c.

23.3 CALCULATION OF DEGREE OF DISSOCIATION (OR IONISATION), α

In order to calculate, α of a reactant that undergoes dissociation, use the following concept and use the following relation

Degree of dissociation,

$$\alpha = \frac{\text{no. of mol dissociated}}{\text{Total no. of mol present before dissociation}}$$

Let, x = no. of mol dissociated

(*i*)

$$\begin{array}{llll} & nA & \rightleftharpoons B & + \ C \\ \text{no. of mol at } t=0 & a & 0 & 0 \\ \text{or initial no. of mol} & & & \\ \text{no. of mol at equilibrium} & a-ax & \dfrac{ax}{n} & \dfrac{ax}{n} \end{array}$$

$$\therefore \quad \alpha = \frac{ax}{a} = x$$

For example.

$$\begin{array}{llll} & 2\,HI & \rightleftharpoons H_2 & + \ I_2 \\ \text{no. of mol at } t=0 & a & 0 & 0 \\ \text{no. of mol at equilibrium} & a-ax & \dfrac{ax}{2} & \dfrac{ax}{2} \\ \text{or} & = a(1-x) & & \end{array}$$

$$\therefore \quad \alpha = \frac{ax}{a} = x$$

(*ii*)

$$\begin{array}{llll} & n\,A & \rightleftharpoons B & + \ C \\ \text{no. of mol at } t=0 & a & 0 & 0 \\ \text{no. of mol at equilibrium} & a-x & \dfrac{x}{n} & \dfrac{x}{n} \end{array}$$

$$\therefore \quad \alpha = \frac{x}{a}$$

For example

$$\begin{array}{llll} & 2\,HI & \rightleftharpoons H_2 & + \ I_2 \\ \text{no. of mol at } t=0 & a & 0 & 0 \\ \text{no. of mol at equilibrium} & a-x & \dfrac{x}{2} & \dfrac{x}{2} \end{array}$$

$$\therefore \quad \alpha = \frac{x}{a}$$

(*iii*)

$$\begin{array}{llll} & n\,A & \rightleftharpoons B & + \ C \\ \text{no. of mol at } t=0 & a & 0 & 0 \\ \text{no. of mol at equilibrium} & a-2x & \dfrac{2x}{n} & \dfrac{2x}{n} \end{array}$$

$$\therefore \quad \alpha = \frac{2x}{a}$$

For example.

$$\begin{array}{llll} & 2\,HI & \rightleftharpoons H_2 & + \ I_2 \\ \text{no. of mol at } t=0 & a & 0 & 0 \\ \text{no. of mol at equilibrium} & a-2x & \dfrac{2x}{2} = x & \dfrac{2x}{2} = x \end{array}$$

$$\therefore \quad \alpha = \frac{2x}{a}$$

(*iv*)

$$\begin{array}{llll} & n\,A & \rightleftharpoons B & + \ C \\ \text{no. of mol at } t=0 & 1 & 0 & 0 \\ \text{no. of mol at equilibrium} & 1-x & \dfrac{x}{n} & \dfrac{x}{n} \end{array}$$

$$\therefore \quad \alpha = \frac{x}{1} = x$$

For example.

$$\begin{array}{llll} & 2\,HI & \rightleftharpoons H_2 & + \ I_2 \\ \text{no. of mol at } t=0 & 1 & 0 & 0 \\ \text{no. of mol at equilibrium} & 1-x & \dfrac{x}{2} & \dfrac{x}{2} \end{array}$$

$$\therefore \quad \alpha = \frac{x}{1} = x$$

(*v*)

$$\begin{array}{llll} & nA & \rightleftharpoons B & + \ C \\ \text{no. of mol at } t=0 & 1 & 0 & 0 \\ \text{no. of mol at equilibrium} & 1-2x & \dfrac{2x}{n} & \dfrac{2x}{n} \end{array}$$

$$\therefore \quad \alpha = \frac{2x}{1} = 2x$$

For example.

$$\begin{array}{llll} & 2\,HI & \rightleftharpoons H_2 & + \ I_2 \\ \text{no. of mol at } t=0 & 1 & 0 & 0 \\ \text{no. of mol at equilibrium} & 1-2x & \dfrac{2x}{2} = x & \dfrac{2x}{2} = x \end{array}$$

$$\therefore \qquad \alpha = \frac{2x}{1} = 2x$$

Significance of magnitude of equilibrium constant.

(*i*) If the magnitude of K_c or K_p is very high, the forward reaction goes to completion or nearly so.

(*ii*) If the magnitude of K_c or K_p is very low, the forward reaction does not occur to any significant extent.

(*iii*) If the magnitude of K_c or K_p is neither very high nor very low, the reaction is expected to reach a state of equilibrium.

23.4 HOMOGENEOUS AND HETEROGENEOUS EQUILIBRIA

Type. (*i*) Reactions in homogeneous equilibria are those in which reactants and products are in the same physical state *i.e.*, solid, liquid or gas. e.g., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(*ii*) Reactions in heterogeneous equilibria are those in which reactants and products are in different physical states. e.g., $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Example 1. *Classify the following reversible reactions as systems involving homogeneous equilibria or heterogenous equilibria.*

(*i*) $Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$

(*ii*) $Fe^{3+}(aq) + 3\,OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(*iii*) $2\,NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$

(*iv*) $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$

Solution. Reactions (*iii*) and (*iv*) involve homogeneous equilibria because of same physical states (gas) and aqueous (aq) respectively.

Reactions (*i*) and (*ii*) involve heterogeneous equilibria because of different physical states *i.e.*, in (*i*), solid and aqueous ; in (*ii*) aqueous (aq) and solid (s).

23.5 WRITING EQUILIBRIUM CONSTANT OF REVERSIBLE REACTIONS

Type. (*i*) For a reversible reaction, involving solid, solution and gases e.g.,

$a\,A(s) + b\,B(g) \rightleftharpoons c\,C(g) + d\,D$ (solution), the equilibrium constant K is written as :

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Since A is a solid,

So $\qquad [A] = a$ constant.

$$\text{So,} \qquad [A]^a \times K = K_c \qquad \therefore K_c = \frac{[C]^c\,[D]^d}{[B]^b}$$

(*ii*) For a reversible reaction involving gases only e.g., $a\,A(g) + b\,B(g) \rightleftharpoons c\,C(g) + d\,D(g)$, the equilibrium constant, K_p is written as :

$$K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

where p_A, p_B, p_C and p_D are the **partial pressures** (each raised to the power of their **respective co-efficients**) of gases A, B, C and D respectively.

Example 2. *Write the equilibrium constant expressions for the following reactions.*

(*i*) $Na_2CO_3(s) + SO_2(g) + ½\,O_2(g) \rightleftharpoons Na_2SO_4(s) + CO_2(g)$

(*ii*) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

Solution. For $Na_2CO_3(s) + SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons Na_2SO_4(s) + CO_2(g)$, equilibrium constant, K_c is given as:

$$K_c = \frac{[Na_2SO_4(s)]\,[CO_2(g)]}{[Na_2CO_3(s)]\,[SO_2(g)]\,[O_2(g)]^{1/2}}$$

Since by convention, concentration of solid is taken as 1, we have

$$K_c = \frac{[CO_2(g)]}{[SO_2(g)]\,[O_2(g)]^{1/2}}$$

(*ii*) For $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$, equilibrium constant K_p (for gaseous reactants and products) is given as :

$$K_p = \frac{(p_{H_2O})^2}{(p_{H_2})^2 \times p_{O_2}}$$

It can also be expressed in terms of K_c where

$$K_c = \frac{[H_2O(g)]^2}{[H_2(g)]^2\,[O_2(g)]}$$

Type. Greater the value of K_c, greater will be the tendency of a reaction to proceed farthest towards completion *i.e.*, greater will be the speed of the reaction in the forward direction.

Example 3. *Which of the following reactions will tend to proceed farthest towards completion.*

(*i*) $2\,HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$; $K_c = 7.0 \times 10^{-20}$

(*ii*) $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$; $K_c = 3.4 \times 10^{13}$

(*iii*) $4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O$; $K_c = 5 \times 10^{198}$

Solution. Greater the value of K_c, greater is the speed of reaction. K_c values of given reactions (*i*), (*ii*) and (*iii*) are 7.0×10^{-20}, 3.4×10^{13} and 5×10^{198}. Thus value of K_c of (*iii*) > (*ii*) > (*i*). So, reaction (*iii*) will move farthest towards completion.

Type. When the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original value *i.e.*,

$$K_C' = 1/K_C$$

Similarly, $\qquad K_p' = 1/K_p$

Example 4. *The value of K_p for the reaction, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$ is 41at 400 K. Calculate the value of K_p for the* *reaction,* $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2\,(g)$

SOLUTION. For $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)\,;\, K_p = 41$ ... (1)

The other equation is : $2\,NH_3\,(g) \rightleftharpoons N_2\,(g) + 3\,H_2(g);$

$K'_p = ?$ ... (2)

Since this equation (2) is reverse of the given equation (1) :

$$K'_p = \frac{1}{K_p} = \frac{1}{41} = 2.44 \times 10^{-2}$$

Type. When each of the co-efficients in a balanced equation is divided by factor '*n*', the equilibrium constant value is *n*th root of the previous value.

Thus, $K'_c = (K_c)^{1/n}\,;\; K'_p = (K_p)^{1/n}$

So, when an equation is divided by 2, the new equilibrium constant is the square root of the original value.

Thus, $K'_c = (K_c)^{1/2}$ or $\sqrt{K_c}$;

$K'_p = (K_p)^{1/2}$ or $\sqrt{K_p}$.

EXAMPLE 5. *The value of K_p for the reaction, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3\,(g)$ at 400 K is 41. Find the value of K_p for the reaction, $\frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g) \rightleftharpoons NH_3\,(g)$ at the same temperature.*

SOLUTION. Given

$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)\,;\, K_p = 41$ ... (1)

Required equation:

$\frac{1}{2}N_2\,(g) + \frac{3}{2}H_2\,(g) \rightleftharpoons NH_3\,(g)\;;\; K'_p = ?$ ...(2)

Since equation (2) is obtained by dividing equation (1) by 2, the value of K'_p will be equal to square root of K_p value .

$\therefore$ $K'_p = (K_p)^{1/2} = (41)^{1/2} = 6.4$ **Ans.**

Type. When each of the co-efficients in a balanced equation is multiplied by a factor '*n*', the equilibrium constant value is raised to the same factor.

Thus, $K'_c = (K_c)^n\,;\; K'_p = (K_p)^n$

For example, when an equation is multiplied by 2, the new equilibrium constant is the square of the original value *i.e.,*

$$K'_c = (K_c)^2\,;\quad K'_p = (K_p)^2.$$

EXAMPLE 6. *The value of K_p for the reaction, $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ at 400 K is 41. Find the value of K_p for the reaction,*

$2N_2\,(g) + 6H_2\,(g) \rightleftharpoons 4NH_3\,(g)$

SOLUTION. Given.

$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)\,;\, K_p = 41$ ...(1)

Required equation :

$2N_2\,(g) + 6H_2\,(g) \rightleftharpoons 4NH_3\,(g)\,;\, K'_c = ?$ ... (2)

The equation (2) is obtained by multiplying equation (1) by 2.

So, $K'_p = (K_p)^2$

So, $K'_p = (41)^2 = \mathbf{1681}.$ **Ans.**

Type. When there are two or more partial equations for a net reaction, the individual equations are combined and their equilibrium constant values are multiplied for the net reaction. Suppose K_1, K_2 and K_3 are the stepwise equilibrium constant values for $A \rightleftharpoons B$, $B \rightleftharpoons C$ and $C \rightleftharpoons D$ respectively, then net equilibrium constant, $K = K_1 \times K_2 \times K_3$.

EXAMPLE 7. *Calculate the magnitude of equilibrium constant for the reaction $X \rightleftharpoons Y$ if :*

(*i*) $X \rightleftharpoons A\,;\, K_1 = 2$ (*ii*) $A \rightleftharpoons B\,;\, K_2 = 6$

(*iii*) $B \rightleftharpoons Y\,;\, K_3 = 4.$

SOLUTION.

(*i*) $X \rightleftharpoons A\,;\, K_1 = 2$ (*ii*) $A \rightleftharpoons B\,;\, K_2 = 6$

(*iii*) $B \rightleftharpoons Y\,;\, K_3 = 4$

Net reaction $X \rightleftharpoons Y\,;\, K = 2 \times 6 \times 4 = 48$ **Ans.**

EXAMPLE 8. *Calculate the magnitude of equilibrium constant for the reaction $2N_2 + 4O_2 \rightleftharpoons 4\,NO_2$ if :*

(*i*) $2N_2 + O_2 \rightleftharpoons 2N_2O;\, K_c = K_{c_1}$

(*ii*) $2N_2O + 3O_2 \rightleftharpoons 4NO_2\,;\, K_c = K_{c_2}$

Give Proof also.

SOLUTION. Given :

(*i*) $2N_2 + O_2 \rightleftharpoons 2N_2O\,;\, K_c = K_{c1}$

(*ii*) $2N_2O + 3O_2 \rightleftharpoons 4NO_2\,;\, K_c = K_{c2}$

Adding (*i*) and (*ii*), we get

Net reaction $2N_2 + 4O_2 \rightleftharpoons 4NO_2\,;\, K'_c = ?$ (*iii*)

Since net reaction is obtained by adding the given partial equations, the net equilibrium constant K is given as : $K'_C = K_{C_1} \times K_{C_2}$ **Ans.**

Proof : For reaction (*i*)

$$K_{C_1} = \frac{[N_2O]^2}{[N_2]^2\,[O_2]}$$

(*ii*) $$K_{C_2} = \frac{[NO_2]^4}{[N_2O]^2\,[O_2]^3}$$

(*iii*) $$K'_C = \frac{[NO_2]^4}{[N_2]^2\,[O_2]^4}$$

$\therefore$ $$K_{C_1} \times K_{C_2} = \frac{[N_2O]^2}{[N_2]^2\,[O_2]} \times \frac{[NO_2]^4}{[N_2O]^2\,[O_2]^3}$$

$$= \frac{[NO_2]^4}{[N_2]^2\,[O_2]^1\,[O_2]^3}$$

$$= \frac{[NO_2]^4}{[N_2]\,[O_2]^4}$$

From above we see that

$$K_{C_1} \times K_{C_2} = K'_C$$

EXAMPLE 9. *For $2NO\,(g) \rightleftharpoons N_2(g) + O_2\,(g)$,*

$K_C = 2.4 \times 10^{30}$ at 298 K

For $NO\,(g) + \frac{1}{2}\,Br_2\,(g) \rightleftharpoons NOBr\,(g),$

$$K_C = 1.4 \text{ at } 298\text{ K}.$$

Using above data, calculate the value of K_C for the reaction

$$\frac{1}{2}\,N_2\,(g) + \frac{1}{2}\,O_2\,(g) + \frac{1}{2}\,Br_2\,(g) \rightleftharpoons NOBr\,(g)$$

SOLUTION.

$$NO\,(g) + \frac{1}{2}\,Br_2\,(g) \rightleftharpoons NOBr\,(g) \quad \text{... (1)}$$

$$2\,NO\,(g) \rightleftharpoons N_2\,(g) + O_2(g)]] \times \frac{1}{2} \quad \text{... (2)}$$

Subtract. – – –

$$\frac{1}{2}\,N_2\,(g) + \frac{1}{2}\,O_2\,(g) + \frac{1}{2}\,Br_2\,(g) \rightleftharpoons NOBr\,(g) \quad \text{... (3)}$$

∴ For $N_2(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$ ... (4)

$$K'_C = \frac{1}{K_C}$$

[∵ it is reverse of equation, 2]

Or (*i*) $\frac{1}{2}\,N_2\,(g) + \frac{1}{2}\,O_2\,(g) \rightleftharpoons NO\,(g)$ ... (5)

$$K''_C = (K'_C)^{1/2}$$

[∵ equation 5 is obtained by dividing equation (4) by 2]

$$\therefore \quad K''_C = \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2}$$

$$= 0.6455 \times 10^{-15}$$ **Ans.**

(*ii*) $NO\,(g) + \frac{1}{2}\,Br_2\,(g) \rightleftharpoons NOBr\,(g)\,;\, K'''_C = 1.4$

Since net reaction (3) is obtained by the addition of reactions (*i*) and (*ii*), *K* will be equal to $K''_C \times K'''_C$. Thus we have :

$$K = \frac{[NO\,(g)]}{[N_2\,(g)]^{1/2}\,[O_2\,(g)]^{1/2}} \times \frac{[NOBr\,(g)]}{[NO\,(g)]\,[Br_2\,(g)]^{1/2}}$$

$$= \frac{[NOBr\,(g)]}{[N_2\,(g)]^{1/2}\,[O_2\,(g)]^{1/2}}$$

Or

$$K = K''_C \times K'''_C$$
$$= (0.6455 \times 10^{-15}) \times 1.4$$
$$= 9.037 \times 10^{-16}$$ **Ans.**

23.6 LE-CHATELIER'S PRINCIPLE

It states that when a system in equilibrium is subjected to change in temperature, pressure, concentration etc, the equilibrium shifts in a direction to undo the effect of the change. In order to understand it, consider the following general reaction at equilibrium.

$$c\,A(g) \rightleftharpoons a\,B(g) + b\,C(g)$$

where *c*, *a* and *b* are the moles of *A*, *B* and *C* gases respectively. Let total pressure is P_T. Thus :

$$K_p = \frac{\left[\frac{a}{a+b+c} \times P_T\right]\left[\frac{b}{a+b+c} \times P_T\right]}{\left[\frac{c}{a+b+c} \times P_T\right]}$$

$$= \frac{a\,b\,P_T}{c\,(a+b+c)} \quad \text{...(1)}$$

But $P_T = \frac{n\,RT}{V}$ and $n = a + b + c.$ ... (2)

Hence $P_T = \frac{(a+b+c)\,RT}{V}$

Substituting the value of P_T in (1) from (2), we get :

$$K_p = \frac{a\,b\,RT}{c\,V} \quad \text{... (3)}$$

Or $Q = \frac{a\,b\,RT}{c\,V}$ ...(4)

The equations (3) and (4) are helpful to know the effect of various changes done on equilibrium of a reaction. For example :

(*i*) If volume of the system is increased, *Q* becomes $\frac{a\,b\,RT}{c\,V'}$ where $V' > V$. So, *Q* becomes less than k_p.

Hence reaction would move in the forward direction to attain equilibrium.

(*ii*) If volume of the system is increased by adding noble gas at constant pressure, the reaction would proceed in the forward direction.

(*iii*) If a noble gas is added to the system at constant volume, Q remains as $Q = \frac{a\,b\,RT}{c\,V}$. So, reaction will remain at equilibrium and nothing will happen.

(*iv*) If *d* moles of *C* (*g*) are added, *Q* becomes,

$$Q = \frac{a\,(b+d)\,RT}{c\,V}.$$

Thus Q becomes more than K_p [equation, (3)]. So, the system will move in the backward direction.

EXAMPLE 10. *Write the conditions under which the following reactions proceed in the forward direction.*

(*i*) $C(s) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2(g) + x\,k\,cal$

(*ii*) $N_2O_4(g) \rightleftharpoons 2NO_2(g) - 14\,k\,cal$

SOLUTION.

(*i*) $C\,(s) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g) + x\,k\,\text{cal}$

1 mol 1 mol 1 mol

$$K_C = \frac{[CO_2\,(g)]\,[H_2\,(g)]}{[C\,(s)]\,[H_2O\,(g)]}$$

Since reaction is exothermic and accompanied by decrease in volume, low temperature and high pressure will favour the forward reaction. To keep K_C constant, excess of C and H_2O will favour forward reaction.

(*ii*) $N_2O_4\,(g) + 14\,k\text{ cal} \rightleftharpoons 2\,NO_2\,(g)$

1 mol (1 Vol) 2 mol (2 Vol)

$$K_C = \frac{[NO_2\,(g)]^2}{[N_2O_4\,(g)]}$$

Since reaction is endothermic and accompanied by increase in volume, high temperature and low pressure will favour forward reaction. To keep K_C constant, excess of N_2O_4 (g) will favour forward reaction.

23.7 CALCULATION OF ACTIVE MASSES

Type. Calculation of active mass of substances when their densities are given. For this purpose, use :

(*i*) 1 L substance weighs

$= 1000$ mL substance × density in $\text{g(mL)}^{-} = x\text{ g}$

(*ii*) no. of mol of substance

$$= \frac{x\text{ g}}{g.\text{ mol. wt. of substance}}$$

= Active mass of substance in mol L^{-}.

Example 11. *Calculate the active masses of carbon tetrachloride [density = 1.58 g (mL)⁻].*

Solution. g. mol. wt. of CCl_4

$= 12 + (4 \times 35.5) = 12 + 142.0 = 154$

1L CCl_4 weighs $= 1000\text{ mL} \times$ density in g $(\text{mL})^{-}$

$= 1000\text{ mL} \times 1.58\text{ g (mL)}^{-} = 1580$ g.

∴ no. of mol of CCl_4

$$= \frac{1580}{154} = 10.26\text{ mol L}^{-}$$

or Active mass of CCl_4

$= \mathbf{10.26\text{ mol L}^{-}}$ **Ans.**

23.8 PHYSICAL EQUILIBRIUM

Example 12. *A solid A having molar mass 100 has solubility 0.002 mol L⁻. How much A will remain undissolved ?*

(*i*) *If 0.4 g of it were shaken with 200 cm³ of water till equilibrium is reached ?*

(*ii*) *How much A will be left undissolved if another 200 cm³ of water is added to the above mixture.*

Solution. (*a*) Molar mass of A = 100

Solubility of A $= 0.002\text{ mol L}^{-}$

$= 0.002 \times 100 = 0.2\text{ g L}^{-}$

Wt. of A = 0.4 g

1000 mL H_2O contain A = 0.2 g

200 mL H_2O contain A $= \frac{0.2}{1000} \times 200 = 0.04$ g

∴ Wt. of soluble A = 0.04 g

and Wt. of insoluble A = 0.4 – 0.04 = **0.36 g Ans.**

(*b*) Total volume = 200 mL + 200 mL

= 400 mL

1000 mL water contain A = 0.2 g

∴ 400 mL water contain A $= \frac{0.2}{1000} \times 400 = 0.08$ g

∴ Wt. of undissolved A = 0.4 – 0.08 = **0.32 g Ans.**

Example 13. *If 0.1 g of I_2 [I_2 (aq) at equilibrium = 0.0011 mol L⁻ at 298 K] is stirred in 100 cm³ of water till equilibrium is reached, what will be the mass of iodine found in solution and the mass that is left undissolved ? After equilibrium is reached with 0.1 g of I_2 and 100 cm³ of water, we add 150 cm³ of water to the system. How much iodine will be dissolved and how much will be left undissolved and what will be the concentration of iodine in solution ?*

Solution. Wt. of I_2 = 0.1 g ;

g. molar mass of $I_2 = 2 \times 127 = 254$ g ;

solubility of $I_2 = 1.1 \times 10^{-3}\text{ mol L}^{-}$

$= 1.1 \times 10^{-3} \times 254 = 0.279\text{ g L}^{-}$

$= 0.279$ g per 1000 cm³

∴ Wt. of I_2 dissolved in 100 cm³

$$= \frac{0.279}{1000} \times 100 = 0.0279\text{ g}$$

∴ Wt. of undissolved I_2 in 100 cm³

= 0.1 – 0.0279 = 0.07 g

Total volume after equilibrium when 150 cm³ water is added

= 100 + 150 = 250 cm³

∴ Wt. of I_2 dissolved in 250 cm³ water

$$= \frac{0.279 \times 250}{1000} = 0.0698\text{ g}$$

∴ Wt. of undissolved I_2 = 0.1 – 0.0698 = **0.03 g Ans.**

Example 14. *At 299 K, the data of solubility of O_2 in water is given in the following table.*

Experiment	$[O_2\,(g)]_{eq}$ mol L^{-}	O_2 *pressure* (*k Pa*)	$[O_2\,(aq)]_{eq}$ mol L^{-}	$\frac{[O_2\,(aq)]_{eq}}{[O_2\,(g)]_{eq}}$
1	A	466.1	0.053	B
2	0.08	C	D	0.029
3	0.13	333.3	E	0.029

Calculate the value of A, B, C, D and E.

Solution. Experiment 1. (*a*) We know that

$$PV = n\,RT$$

or $P = \frac{n}{V}RT$ *i.e.*, $P = cRT$ or $c = \frac{P}{RT}$

$$\therefore \quad c = \frac{466.1\text{ k Pa}}{(8.314\text{ k Pa L K}^{-}\text{ mol}^{-}) \times 299\text{ K}}$$

$= 0.1875\text{ mol L}^{-}$

$\therefore \quad A = 0.1875 \text{ mol L}^-$

(*b*) $B = \dfrac{[O_2(aq)]_{eq}}{[O_2(g)]_{eq}} = \dfrac{0.053 \text{ mol L}^-}{0.1875 \text{ mol L}^-}$

$= \mathbf{0.28}$ **Ans.**

Experiment 2.

(*a*) $\dfrac{[O_2\,(aq)]_{eq}}{[O_2\,(g)]_{eq}} = 0.029\,;$

$\therefore \quad \dfrac{D}{0.08 \text{ mol L}^-} = 0.029$

$\therefore \quad D = 0.08 \times 0.029 = 0.002 \text{ mol L}^-$

(*b*) We know $P = C\,RT$ (see experiment 1)

$\therefore \quad P = 0.08 \text{ mol L}^- \times 8.314 \text{ k Pa L K}^- \text{mol}^- \times 299 \text{ K} = 198.9 \text{ k Pa}$

$\therefore \quad C = 198.9 \text{ k Pa}$

Experiment 3.

$\dfrac{[O_2(aq)]_{eq}}{[O_2(g)]_{eq}} = \dfrac{E}{0.13 \text{ mol L}^-} = 0.029\,;$

$\therefore \quad E = 0.13 \text{ mol L}^- \times 0.029$

$= \mathbf{0.0038 \text{ mol L}^-}$ **Ans.**

23.9 HENRY'S LAW

According to this law, the 'mass of a gas dissolved per unit volume of a solvent is directly proportional to the pressure of the gas in equilibrium with the solution at a given temperature. *i.e.*,

$$C = k\,P$$

where C = concentration of dissolved solute, k = constant characteristic of a particular solution and is called Henry's law constant, P = partial pressure of the gaseous solute above the solution.

Also, see section 17.11.

Example 15. *A soda-water bottle contains CO_2 gas at a pressure of 5 atm over the liquid at 298 K. If partial pressure of CO_2 in the atmosphere is 4×10^{-4} atm, what will be the equilibrium concentrations of CO_2 in soda-water both before and after the bottle is opened. The Henry's law constant for CO_2 in aqueous solution is 0.031 mol L^- atm^- at 298 K.*

Solution. (*a*) For sealed bottle, $P = 5$ atm ;

$k = 0.031 \text{ mol L}^- \text{atm}^-$

According to Henry's law,

$C = k\,P$

$\therefore \quad C = 0.031 \text{ mol L}^- \text{atm}^- \times 5 \text{ atm}$

$= 0.155 \text{ mol L}^-$

(*b*) For opened bottle, CO_2 (g) in the bottle comes in equilibrium with the atmospheric CO_2 gas. Thus

$P_{CO_2(g)} = 4 \times 10^{-4}$ atm.

According to Henry's law :

$C = k\,P\,;$

$C = 0.031 \text{ mol L}^- \text{atm}^- \times 4 \times 10^{-4} \text{atm}$

$= \mathbf{1.24 \times 10^{-5} \text{ mol L}^-}$ **Ans.**

Example 16. *At N.T.P., the solubility of a gas is 0.039 g L^-. At what pressure, its solubility will be 2.5 g L^-?*

Solution. $C_1 = 0.039 \text{ g L}^-$

$P_1 = 1$ atm

($\because$ at N.T. P., $P = 1$ atm, $T = 273$ K)

$C_2 = 2.5 \text{ g L}^-;\ P_2 = ?$

According to Henry's law :

$C_1 = k\,P_1;\ C_2 = k\,P_2$

or $\dfrac{C_1}{C_2} = \dfrac{P_1}{P_2}$

Hence : $\dfrac{0.039 \text{ g L}^-}{2.5 \text{ g L}^-} = \dfrac{1 \text{ atm}}{P_2}\,;$

$P_2 = \dfrac{2.5 \text{ g L}^- \times 1 \text{ atm}}{0.039 \text{ g L}^-}$

$= \mathbf{64.1 \text{ atm}}$ **Ans.**

Example 17. *A mixture of gases contains 40% A and 60% B at 25° C and 740 mm pressure. The solubilities of these gases A and B were found to be 0.0475 g L^- and 0.3 g L^- respectively at 0°C and one atmospheric pressure. Find the weight of each gas which dissolves when passed through 500 mL water at 25°C.*

Solution. (*i*) Partial pressure of gas A

$= \dfrac{40}{100} \times 740 = 296 \text{ mm}$

Partial pressure of gas B

$= \dfrac{60 \times 740}{100} = 444 \text{ mm}$

(*ii*) **To find solubility of gas, A.**

1000 mL (= 1L) of water at 760 mm contain,

A = 0.0475 g

Or 1000 mL of water will dissolve A at 296 mm pressure

$= \dfrac{0.0475 \text{ g L}^-}{760 \text{ mm}} \times 296 \text{ mm}$

$= 0.0185 \text{ g L}^-$

Or 500 mL of water will dissolve A

$= \dfrac{0.0185 \text{ g L}^-}{1000 \text{ mL}} \times 500 \text{ mL}$

$= 0.00925 \text{ gL}^-$

(*iii*) **To find solubility of gas, B**

1000 mL (= 1 L) of water at 760 mm contain,

$B = 0.3 \text{ g L}^-$

Or 1000 mL of water will dissolve B at 444 mm pressure

$= \dfrac{0.3 \text{ g L}^-}{760 \text{ mm}} \times 444 \text{ mm}$

$= 0.175 \text{ g L}^-$

Or 500 mL of water will dissolve B

$$= \frac{0.175 \text{ g L}^{-} \times 500 \text{ mL}}{1000 \text{ mL}}$$

$$= \mathbf{0.0875 \text{ g L}^{-}}$$

23.10 FINDING THE VALUE OF K_C AND K_P

Type. Calculation of K_c and K_p for homogeneous gaseous equilibrium reactions involving formation (or synthesis) of product with **change in volume** or having different number of mol of reactants and products.

In order to understand it, consider the synthesis of ammonia.

(*a*) **Determination of K_c**

	N_2	$+\ 3H_2 \rightleftharpoons$	$2NH_3$
Initial conc.	1 mol	3 mol	0
Conc. at equilibrium	$\frac{1-x}{V}$ mol	$\frac{3(1-x)}{V}$ mol	$\frac{2x}{V}$ mol

Let us start with one mol of N_2 and 3 mol of H_2 in a closed vessel of volume of 'V' litre.

V = Volume of the closed vessel in which reaction takes place; x = number of mol of N_2 and $3x$ are the number of mol of H_2 that are used up at equilibrium.

Molar concentrations at equilibrium are :

$$[N_2] = \frac{1-x}{V}; \ [H_2] = \frac{3(1-x)}{V};$$

$$[NH_3] = \frac{2x}{V}$$

Applying law of mass action, we get :

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{3(1-x)}{V}\right)^3}$$

$$= \frac{4x^2}{V^2} \times \frac{V}{1-x} \times \frac{V^3}{27(1-x)^3}$$

$$\therefore \quad K_C = \frac{4x^2 V^2}{27(1-x)^4}$$

(*b*) **Determination of K_p.**

Total number of mol

$$= 1 - x + 3(1-x) + 2x$$

$$= 1 - x + 3 - 3x + 2x = \mathbf{4 - 2x}$$

Let P = Total pressure of the system

Molar concentrations at equilibrium are :

$$p_{N_2} = \frac{(1-x)P}{4-2x}; p_{H_2} = \frac{(3-3x)P}{4-2x};$$

$$p_{NH_3} = \frac{2xP}{4-2x}$$

$$\therefore \quad K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

$$= \frac{\left(\frac{2xP}{4-2x}\right)^2}{\left(\frac{(1-x)P}{4-2x}\right)\left(\frac{3-3x}{4-2x}\cdot P\right)^3}$$

$$= \frac{4x^2P^2}{(4-2x)^2} \times \frac{4-2x}{(1-x)P} \times \frac{(4-2x)^3}{(3-3x)^3 \cdot P^3}$$

$$= \frac{4x^2P^2}{4(2-x)^2} \times \frac{2(2-x)}{(1-x)P} \times \frac{8(2-x)^3}{27(1-x)^3 p^3}$$

$$= \frac{16x^2(2-x)^2}{27P^2(1-x)^4}$$

23.11 FORMATION OF NH_3

Example 18. *A closed vessel contains a mixture of N_2 (g) and H_2 (g) initially in the ratio 1 : 3 at 573 K and 30 atmosphere. If % age of NH_3 (g) by volume at equilibrium is 17.8, find the value of K_p of $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ reaction.*

Solution. Given :

	$N_2(g) +$	$3H_2(g) \rightleftharpoons$	$2NH_3(g)$
Initial Conc.	1 mol	3 mol	0
Conc. at equilibrium	$1-x$	$3-3x$	$2x$

($\because$ x = degree of dissociation)

Total number of moles

$$= 1 - x + 3 - 3x + 2x = 4 - 2x.$$

Since percentage by volume of NH_3 (g) is same as percentage by mole,

$$\frac{2x}{4-2x} = \frac{17.8}{100} \text{ i.e., } 0.178;$$

Or $100 \times 2x = 17.8(4-2x)$ **Or** $200x = 71.2 - 35.6x$

$\therefore$ $200x + 35.6x = 71.2$

Or $x = \frac{71.2}{235.6} = \mathbf{0.302}$

Mole fraction of N_2 (x_{N_2}) at equilibrium

$$= \frac{1-x}{4-2x} = \frac{1-0.302}{4-(2\times 0.302)}$$

$$= \frac{0.698}{3.396} = \mathbf{0.2055}$$

Mole fraction of H_2 i.e., $[x_{H_2}]$ at equilibrium

$$= \frac{3-3x}{4-2x} = \frac{3-(3\times 0.302)}{4-(2\times 0.302)}$$

$$= \frac{2.094}{3.396} = \mathbf{0.6166}$$

Hence, $K_p = \frac{(x_{NH_3} \times P_T)^2}{(x_{N_2} \times P_T) \times (x_{H_2} \times P_T)^3}$

$$= \frac{(0.178 \times 30)^2}{(0.2055 \times 30) \times (0.6166 \times 30)^3}$$

$$= \frac{28.5156}{6.165 \times 6329.57}$$

$\therefore$ K_p = **7.307 × 10^{-4}** **Ans.**

> **Note.** We have taken initial moles of N_2 and H_2 as 1 and 3 respectively. This assumption is valid because K_p will not depend upon the exact number of moles of N_2 and H_2. We can even start with x and $3x$ moles of N_2 and H_2 respectively.

EXAMPLE 19. *One mol of N_2 is mixed with 3 mol of H_2 in a 4 litre container. If 0.0025 mol of N_2 is converted to ammonia by the following reaction*

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

calculate the value of K_c in concentration units. What will be the value of K_c for the following equilibrium.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

(IIT 1981, ISC 1989)

SOLUTION. Mol of N_2 converted to NH_3

= 0.0025 ;

Volume of container = 4 L ;

mol of N_2 = 1; mol of H_2 = 3

Given reaction is :	$N_2(g)$ +	$3H_2(g)$ $\rightleftharpoons$	$2NH_3(g)$
Initial conc.	1 mol	3 mol	0
Conc. at equilibrium	$\frac{1-\alpha}{4}$	$\frac{3-\alpha}{4}$	$\frac{2 \times 0.0025}{4}$

[$\because V = 4L$]

(*i*)
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2 \times 0.0025}{4}\right)^2}{\left(\frac{1-\alpha}{4}\right) \times \left(\frac{3-\alpha}{4}\right)^3}$$

Since α is very small, it is neglected in the denominator. Thus :

$$K_c = \frac{\left(\frac{2 \times 0.0025}{4}\right)^2}{\frac{1}{4} \times \frac{3}{4} \times \frac{3}{4} \times \frac{3}{4}}$$

$$= \frac{\frac{2 \times 0.0025}{4} \times \frac{2 \times 0.0025}{4} \times \frac{4 \times 4 \times 4 \times 4}{1}}{3 \times 3 \times 3}$$

= **1.48 × 10^{-5} atm^2 mol^{2-}**

(*ii*) For the reaction $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$, we have :

$$K_c = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \frac{\frac{0.0025 \times 2}{4}}{\left(\frac{1}{4}\right)^{1/2}\left(\frac{3}{4}\right)^{3/2}}$$

$$= \frac{\frac{0.0025}{2}}{\frac{1}{2} \times \left(\frac{3}{4} \times \frac{3}{4} \times \frac{3}{4}\right)^{1/2}}$$

$$= \frac{0.0025}{2} \times \frac{2}{1} \times \left(\frac{4 \times 4 \times 4}{3 \times 3 \times 3}\right)^{1/2}$$

$$= \frac{0.0025}{2} \times \frac{2}{1} \times \frac{8}{5.196}$$

= 3.85 ×10^{-3} L mol^{-}

EXAMPLE 20. *Calculate the equilibrium concentration of NH_3 after 2 mol of N_2 and 3 mol of H_2 are placed in a 1 L vessel and are allowed to achieve equilibrium. K = 0.444 for the formation of NH_3.*

SOLUTION.	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
(*i*) *n* mol at start	2	3	0
(*ii*) *n* mol produced	–	–	$2x$
(*iii*) *n* mol used up	$-x$	$-3x$	–
(*iv*) *n* mol at equilibrium	$2-x$	$3-3x$	$2x$

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3}; \; 0.444 = \frac{(2x)^2}{(2-x)(3-3x)^3}$$

On solving and ignoring x^2 and x^3 from the denominator, we get:

$$0.444 = \frac{4x^2}{27(2-x)(1-3x)}; \; 4x^2 + 84 - 24 = 0$$

$$\therefore \quad x = \frac{-84 \pm \left[(84)^2 - (4 \times 4 \times -24)\right]^{1/2}}{2 \times 4}$$

= **0.275;**

$2x$ = 2 × 0.275 = **0.55.**

EXAMPLE 21. (*a*) *If helium gas is added to a system containing N_2, H_2 and NH_3 gases, what effect helium gas will have on the partial pressure of each gas ?*

(*b*) *What effect, will the added helium gas have on the position of equilibrium ?*

SOLUTION. Helium gas is an inert gas. So, it will have no effect on the partial pressures of each gas present and (*b*) it does not effect the position of following equilibrium.

$$K_p = \frac{p(NH_3)^2}{p(N_2) \times p(H_2)^3}$$

$$\left[\because N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\right]$$

EXAMPLE 22. *For the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ the value of equilibrium constant at 500°C is 3.9 × 10^{-3} (atm)$^{-}$. If sufficient ammonia is added into an evacuated container at 500°C to give a pressure of 1 atm before any decomposition occurred, calculate the partial pressures of N_2, H_2 and NH_3 at equilibrium?*

SOLUTION.	$\frac{1}{2}N_2$ +	$\frac{3}{2}H_2$ $\rightleftharpoons$	NH_3
(*i*) *n* mol at start	0	0	1

(*ii*) n mol used	–	–	$1-x$
(*iii*) n mol produced	$\frac{1-x}{2}$	$\frac{(3-3x)}{2}$	
– (*iv*) n mol at equilibrium	$0.5-\frac{x}{2}$ $\simeq 0.5$	$1.5-\frac{3x}{2}$ $\simeq 1.5$	x

$$K_p = \frac{p\,(NH_3)}{p\,(N_2)^{1/2}\;p\,(H_2)^{3/2}}\;;$$

$$3.9\times10^{-3} = \frac{x}{(0.5)^{1/2}\,(1.5)^{3/2}}$$

$$3.9\times10^{-3} = \frac{x}{(0.5)^{1/2}\,\sqrt{(1.5)^3}} = \frac{x}{0.707\times\sqrt{3.375}}$$

$$= \frac{x}{0.707\times1.837} = \frac{x}{1.3}$$

$$\therefore \quad x = 3.9\times10^{-3}\times1.3 = 5.07\times10^{-3}\text{ atm}$$

$$= 0.00507\text{ atm}$$

$$\therefore \quad p_{(NH_3)} = x = 5.07\times10^{-3}\text{ atm}\;;$$

$$p_{N_2} = 0.5-\frac{0.00507}{2} = 0.5-0.0025$$

$$= 0.498\text{ atm};$$

$$p_{H_2} = 1.5\text{ atm}$$

EXAMPLE 23. *Assuming that for the reaction*

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

Δ S is independent of temperature and heat capacities of $H_2(g)$, $N_2(g)$ and $NH_3(g)$ do not vary with temperature, calculate the minimum temperature at which this reaction will occur spontaneously with all reactants at unit activity. [ΔH_f° *(NH_3) = –11.04 k cal ; S° (NH_3) = 192.5 J, S° (H_2) = 130.57 J and S° (N_2) = 191 J.*]

SOLUTION. For

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

$$\Delta H = 2\,\Delta H_f^\circ\,(NH_3) - 3\,\Delta H_f^\circ\,(H_2) - \Delta H^\circ_f(N_2)$$

$$= (2\times-11.04\text{ k cal}) - (3\times0) - 0$$

$$= -22.08\text{ k cal}$$

$$= -22.08\times4.148\text{ k J} = -92.38\text{ k J}$$

[∵ 1 k cal = 4.184 k J]

$$\Delta S = 2\,S^\circ\,(NH_3) - 3\,S^\circ\,(H_2) - S^\circ\,(N_2)$$

$$= (2\times192.5\text{ J}) - 3\,(130.57\text{ J}) - 191\text{ J}$$

$$= 385.0 - 391.71 - 191$$

$$= -197.7\text{ J K}^-$$

To find minimum temperature, at which the reaction occurs spontaneously:

$$\Delta G = \Delta H - T\,\Delta S = 0 \textbf{ Or } \Delta H - T\,\Delta S = 0$$

$$\therefore \quad \Delta H = T\,\Delta S \text{ or } T = \frac{\Delta H}{\Delta S} = \frac{-92.38k\,J}{-197.7\,J}$$

$$= \frac{-92.38\times1000\,J}{-197.7\,J}$$

$$\therefore \quad T = \mathbf{467.3\ K} \qquad \textbf{Ans.}$$

EXAMPLE 24. *When a mixture of nitrogen and hydrogen in the volume ratio of 1 : 3 is allowed to attain equilibrium at 400°C and 1000 atm., 0.2491 mole fraction of ammonia is formed. Calculate the equilibrium constant for the above reaction at the experimental temperature and pressure.* **(Kerala, 1968)**

SOLUTION.	N_2 +	$3H_2$ $\rightleftharpoons$	$2NH_3$
(*i*) n mol at start	1	3	0
(*ii*) change by reaction	$-x$	$-3x$	$2x$
(*iii*) n mol at equilibrium	$1-x$	$3-3x$	$2x$

Total number of mol at equilibrium

$$= 1-x+3-3x+2x = 4-2x$$

$$K_p = \frac{p_{(NH_3)^2}}{p_{N_2}\times p_{(H_2)^3}}$$

$$= \frac{\left(\frac{2x}{4-2x}\times P\right)^2}{\left(\frac{1-x}{4-2x}\times P\right)\left(\frac{3-3x}{4-2x}\times P\right)^3}$$

$$= \frac{\frac{4x^2P^2}{(4-2x)^2}}{\frac{(1-x)P}{4-2x}\times\left[\frac{3\,(1-x)}{4-2x}\right]^3}$$

$$= \frac{4x^2\,P^2}{(4-2x)^2}\times\frac{4-2x}{(1-x)P}\times\frac{(4-2x)^3}{27(1-x)^3P^3}$$

$$K_p = \frac{4x^2\,(4-2x)^2}{27(1-x)^4\times P^2} \qquad \text{...(1)}$$

$$\left[\begin{array}{l}\because \text{ for } ax^2+bx+c=0\\ x = \dfrac{-b\pm(b^2-4ac)^{1/2}}{2a}\end{array}\right.$$

But P = 1000 atm and

mole fraction of NH_3

$$= \frac{2x}{4-2x} = 0.2491$$

$$\therefore \quad \frac{2x}{4-2x} = 0.2491\;;$$

$$2x = 0.2491\,(4-2x) = 0.9964 - 0.4982x$$

Or $2x + 0.4982x = 0.9964$; $2.4982x = 0.9963$; $x = 0.4$

Substituting the values of x and P in equation (1), we get :

$$K_p = \frac{4\times(0.4)^2\,[4-(2\times0.4)]^2}{27\,(1-0.4)^4\times(1000)^2}$$

$$= \frac{4\times0.16\times(4-0.8)^2}{27\,(0.6)^4\,(1000)^2}$$

$$= \frac{4\times0.16\times(3.2)^2}{27\,(0.6)^4\,(1000)^2}$$

$$= \frac{6.5536}{27 \times 0.1296 \times 1000000}$$

$$= \mathbf{1.9 \times 10^{-6}}$$ **Ans.**

EXAMPLE 25. *Calculate the value of equilibrium constant, K_c for the reaction*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

from the following data.

Nitrogen and hydrogen are added to a 5 litre flask under pressure. The flask was sealed and heated. The equilibrium mixture contained 18.5 g NH_3, 0.15 g H_2 and 3.3 g N_2

SOLUTION. (*a*) Wt. of N_2 = 3.3 g ;

g. mol. wt. of N_2 = 2 × 14 = 28 g

∴ number of mol of N_2

$$= \frac{3.3}{28} = 0.118\ ; \quad [N_2] = \frac{0.118 \text{ mol}}{5\text{L}}$$

(*b*) Wt. of H_2 = 0.15 g ;

g. mol. wt. of H_2

$$= 2 \times 1 = 2\text{g}$$

∴ number of mol of H_2

$$= \frac{0.15}{2} = 0.075\ ; \quad [H_2] = \frac{0.075 \text{ mol}}{5\text{L}}$$

(*c*) Wt. of NH_3 = 18.5 g ;

g. mol. wt. of NH_3

$$= 14 + (3 \times 1) = 17 \text{ g}$$

∴ number of mol of NH_3

$$= \frac{18.5}{17} = 1.09\ ; \quad [NH_3] = \frac{1.09 \text{ mol}}{5\text{L}}$$

∴ For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_c = \frac{(NH_3)^2}{[N_2][H_2]^3}$$

$$= \frac{\left(\dfrac{1.09 \text{ mol L}^{-}}{5}\right)^2}{\left(\dfrac{0.118 \text{ mol L}^{-}}{5}\right)\left(\dfrac{0.075 \text{ mol L}^{-}}{5}\right)^3}$$

$$= \frac{1.09 \text{ mol}^2 \text{ L}^{-2}}{25} \times \frac{5}{0.118 \text{ mol L}^{-}} \times \frac{125}{0.000422 \text{ mol}^3 \text{ L}^{-3}}$$

$$= 5.97 \times 10^5$$

∴ $$K_c = \mathbf{5.97 \times 10^5 \text{ mol}^{-2} \text{ L}^2}$$ **Ans.**

EXAMPLE 26. *A mixture of 1 mol of N_2 and 3 mol of H_2 react under a constant pressure of 100 atm to form 0.5 mol NH_3 at equilibrium. Calculate K_p for the reaction*

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$$

at the same temperature.

SOLUTION.

	$\frac{1}{2}N_2$ +	$\frac{3}{2}H_2 \rightleftharpoons$	NH_3
(*i*) *n* mol at start	1	3	0
(*ii*) change by reaction	$0.5 \times \frac{1}{2}$ = 0.25	$0.5 \times \frac{3}{2}$ = 0.75	–
(*iii*) *n* mol at equilibrium	1 – 0.25 = 0.75	3 – 0.75 = 2.25	0.5

Total number of mol at equilibrium

$$= 0.75 + 2.25 + 0.5 = 3.5$$

Partial pressure of N_2 (p_{N_2})

$$= \text{mole fraction of } N_2 \times 100$$

$$= \frac{0.75}{3.5} \times 100 = 21.4 \text{ atm.}$$

Partial pressure of H_2 (p_{H_2})

$$= \text{mole fraction} \times 100$$

$$= \frac{2.25}{3.5} \times 100 = 64.3$$

Partial pressure of NH_3 (P_{NH_3})

$$= \text{mole fraction} \times 100$$

$$= \frac{0.5}{3.5} \times 100 = 14.3$$

∴ $$K_p = \frac{p_{NH_3}}{(p_{N_2})^{1/2}\,(p_{H_2})^{3/2}}$$

$$= \frac{14.3}{(21.4)^{1/2} \times \sqrt{(64.3)^3}}$$

$$= \frac{14.3}{4.63 \times \sqrt{265{,}848}}$$

$$K_p = \frac{14.3}{4.63 \times 515.6} = \mathbf{0.00599}$$ **Ans.**

EXAMPLE 27. *For the gas reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ the partial pressures of H_2 and N_2 are 0.4 and 0.8 atm respectively. The total pressure of the entire system is 2.8 atm. What will be the value of K_p if all the concentrations are given in atmospheres.* **(MLNR, 1989)**

SOLUTION.

	N_2 +	$3H_2 \rightleftharpoons$	$2NH_3$
(*i*) Pressure (atm) at start	0.8	0.4	0
(*ii*) Change by reaction	–	–	2.8 – (0.4 + 0.8) = 2.8 – 1.2 = 1.6
(*iii*) Pressure (atm) at equilibrium	0.8	0.4	1.6

$$K_p = \frac{P_{(NH_3)^2}}{P_{N_2} \times P(H_2)^3} = \frac{(1.6)^2}{0.8 \times (0.4)^3}$$

$$= \frac{2.56}{0.0512}$$

$$= \mathbf{50}$$ **Ans**

EXAMPLE 28. *At 773 K, the value of equilibrium constant for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ reaction is 6.4×10^{-2}. If the reaction is started with 1 mol of H_2 and 1 mol of N_2 in a 2L flask at 473K, calculate the concentration of each component in the given reaction.*

SOLUTION. $\qquad N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$

(*i*) n mol L^{-} at start $\quad \frac{1}{2} = 0.5 \quad \frac{1}{2} = 0.5 \quad -$

[∵ Volume = 2L]

(*ii*) change by reaction $\quad -0.5x \quad -0.5x \times 3 = -1.5x \quad 2 \times 0.5x = x$

(*iii*) n mol L^{-} at equilibrium $\quad 0.5 - 0.5x \quad 0.5 - 1.5x \quad x$

$$\therefore \quad K_P = \frac{[NH_3]^2}{[N_2][H_2]^3};$$

$$6.4 \times 10^{-2} = \frac{x^2}{(0.5 - 0.5x)(0.5 - 1.5x)^3}$$

On solving, we get

$$x = 4.9 \times 10^{-2} \text{ mol L}^{-}$$

$$\therefore \quad [N_2] = 0.5 - 0.5x = 0.5 - 0.5 \times 4.9 \times 10^{-2}$$

$$= 0.5 - 0.024 = 0.476 \text{ mol L}^{-}$$

$$[H_2] = 0.5 - 1.5x = 0.5 - 1.5 \times 4.9 \times 10^{-2}$$

$$= 0.5 - 0.073$$

$$= 0.427 \text{ mol L}^{-}$$

$$[NH_3] = x = \mathbf{4.9 \times 10^{-2} \text{ mol L}^{-}}$$

EXAMPLE 29. *One mol of N_2 was treated with 3 mol of H_2 to get ammonia. At 500°C and 10 atm pressure, the mole fraction of NH_3 was 0.012. Find K_p. Also, calculate the pressure at which the mol % of NH_3 will be 10.4 at the same temperature.*

SOLUTION. $\qquad N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$

	N_2	$3H_2$	$2NH_3$
(*i*) n mol at start	1	3	0
(*ii*) Change by reaction	$-x$	$-3x$	$2x$
(*iii*) n mol at equilibrium	$1 - x$	$3 - 3x$	$2x$

Total number of mol at equilibrium

$$= 1 - x + 3 - 3x + 2x = 4 - 2x$$

∴ Mol fraction of NH_3

$$= \frac{2x}{4-2x}; \; 0.012 = \frac{2x}{4-2x};$$

$$0.012(4 - 2x) = 2x$$

$$0.048 - 0.024x = 2x \textbf{ Or } 2x + 0.024x = 0.048;$$

$$2.024x = 0.048; \therefore x = \frac{0.048}{2.024}$$

Or $\qquad x = 0.237; p = 10$ atm.

$$(a) \therefore \quad K_p = \frac{p_{(NH_3)^2}}{p_{N_2} \times p_{(H_2)^3}}$$

$$= \frac{\left(\frac{2x}{4-2x} \times P\right)^2}{\left(\frac{1-x}{4-2x} \times P\right)\left(\frac{3-3x}{4-2x} \times P\right)^3}$$

$$= \frac{4x^2(4-2x)^2}{P^2(1-x)(3-3x)^3}$$

$$\therefore \quad K_p = \frac{4 \times (0.0237)^2 [4 - (2 \times 0.0237)]^2}{(10)^2 (1 - 0.0237)[3 - 3(0.0237)]^3}$$

$$= \frac{4 \times 5.617 \times 10^{-4} \times (4 - 0.0474)^2}{100 \times 0.976 \times (3 - 0.0711)^3}$$

$$= \frac{4 \times 5.617 \times 10^{-4} \times (3.953 \times 3.953)}{100 \times 0.976 \times (2.93)^3}$$

$$= \frac{0.0351}{2455}$$

$$= \mathbf{1.43 \times 10^{-5} \text{ atm}}$$

(*b*) $\qquad N_2 \quad + \quad 3H_2 \rightleftharpoons 2NH_3$

	N_2	$3H_2$	$2NH_3$
(*i*) n mol at start	1	3	0
(*ii*) Change by reaction	$-x$	$-3x$	$2x$
(*iii*) n mol at equilibrium	$1 - x$	$3 - 3x$	$2x$

Total number of mol at equilibrium

$$= 1 - x + 3 - 3x + 2x = 4 - 2x$$

$$\therefore \text{ Mole fraction of } NH_3 = \frac{2x}{4-2x};$$

$$\therefore \quad \frac{2x}{4-2x} = 10.4\,\% = \frac{10.4}{100} = 0.104$$

Or $\qquad 2x = 0.104(4 - 2x);$

$$2x = 0.416 - 0.208x;$$

$$2x + 0.208x = 0.416; \; 2.208x = 0.416;$$

$$\therefore \quad x = \frac{0.416}{2.208} = 0.188$$

But $\qquad K_p = \dfrac{p_{(NH_3)^2}}{p_{N_2} \times p_{(H_2)^3}};$

$$1.43 \times 10^{-5} = \frac{4x^2(4-2x)^2}{P^2(1-x)(3-3x)^3}$$

$$1.43 \times 10^{-5} = \frac{4 \times (0.188)^2 (4 - (2 \times 0.188)^2)}{P^2 (1 - 0.188)[3 - (3 \times 0.188)]^3}$$

$$= \frac{4 \times 0.0353 \times 3.624 \times 3.624}{P^2 \times 0.812 \times 2.436 \times 2.436 \times 2.436}$$

$$= \frac{1.854}{P^2 \times 11.738};$$

Or $\qquad P^2 = \dfrac{1.854}{11.738 \times 1.43 \times 10^{-5}} = 11045.35$

$$\therefore \quad P = \sqrt{11045.35} = \mathbf{105.1 \text{ atm.}} \qquad \textbf{Ans.}$$

EXAMPLE 30. *In an experiment, the concentrations of different species at 1000 K are $[N_2] = 1.1$ mol dm^{-3}, $[H_2] = 1.5$ mol dm^{-3}, $[NH_3] = 0.105$ mol dm^{-3}. Calculate (i) K_c and K_p for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (ii) K_c for $2NH_3 \rightleftharpoons N_2 + 3H_2$ reaction.*

Solution. (*a*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ...(*i*)

n mol dm^{-3} at equilibrium 1.1 1.5 0.105

$$\therefore \quad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(0.105)^2 \text{ mol}^2 \text{ dm}^{-6}}{1.1 \text{ mol dm}^{-3} \times (1.5)^3 \text{ mol}^3 \text{ dm}^{-9}}$$

$$K_c = \frac{0.011}{1.1 \times 3.375} \text{mol}^{-2} \text{ dm}^6$$

$$= 2.96 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6$$

But $K_p = K_c (RT)^{\Delta n}$

In reaction (1),

$$\Delta n = 2 - (1 + 3) = -2 ;$$

$$R = 0.0821 \text{ atm dm}^3 \text{ K}^- \text{mol}^-, T = 1000 \text{ K}$$

$$\therefore \quad K_p = 2.96 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 (0.0821 \text{ atm dm}^3 \text{ K}^- \text{ mol}^- \times 1000 \text{ K})^{-2}$$

$$= \frac{2.96 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6}{(0.0821 \text{ atm dm}^3 \text{ K}^- \text{ mol}^- \times 1000 \text{ K})^2}$$

$$= \frac{2.96 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6}{6740.41 \text{ atm}^2 \text{ dm}^6 \text{ K}^{-2} \text{ mol}^{-2} \text{ K}^2}$$

$$= \mathbf{4.39 \times 10^{-7} \text{ atm}^{-2}}$$ **Ans.**

(*b*) For reverse,

$$2NH_3 \rightleftharpoons N_2 + 3H_2,$$

$$K_c' = \frac{1}{K_c} = \frac{1}{2.96 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6}$$

$$= \mathbf{337.8 \text{ mol}^2 \text{ dm}^{-6}}$$ **Ans.**

23.12 EFFECT OF TEMPERATURE ON THE VALUE OF EQUILIBRIUM CONSTANT

Temperature effect. The magnitude of equilibrium constant changes with change in temperature. Let K_1 and K_2 are the equilibrium constant values for a reversible reaction at temperatures T_1 and T_2 respectively. Then, according to Arrhenius equation :

$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303 \text{ R}} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad ... (1)$$

It is the integrated form of van't Hoff isochore for two temperatures.

Or $K = Ae^{-\Delta H°/RT}$ (for one temperature only)

Where K is equilibrium constant, T is absolute temperature, $\Delta H°$ is heat of reaction, A is frequency factor while R is molar gas constant.

From the above relation (1), it is clear that :

1. If $T_2 > T_1$, ΔH = +ve. Hence, $\log_{10} \frac{K_2}{K_1}$ = +ve i.e., $\log_{10} K_2 > \log_{10} K_1$ or $K_2 > K_1$. Hence for endothermic reactions, equilibrium constant increases with increase in temperature.

2. If $T_2 < T_1$, ΔH = –ve. Hence, log10 $\frac{K_2}{K_1}$ = –ve i.e., $\log_{10} K_2 < \log_{10} K_1$ or $K_2 < K_1$. Hence for exothermic reactions, the equilibrium constant decreases with increase in temperature.

Type. Use the relation,

$$\log K_{P_2} - \log K_{P_1} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_2}{T_1 T_2} \right]$$

Example 31. *At 673 K, the equilibrium constant value for the reaction :*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

is 1.64 × 10^{-4} atm. Calculate K_p at 500°C if the heat of reaction for this temperature range is – 105.2 k J.

Solution. $T_1 = 673 \text{ K} ; T_2 = 500 + 273 = 773 \text{ K} ;$

$$\Delta H = -105.2 \times 1000 \text{ J} = -105200 \text{ J} ;$$

$$K_{p_1} = 1.64 \times 10^{-4} \text{ atm} ;$$

$$K_{p_2} = ? ; R = 8.314 \text{ J K}^-$$

we know :

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta \text{H}}{2.303 \text{ R}} \left[\frac{T_2 - T_1}{T_1 T_2} \right];$$

$$\log K_{p_2} = \log K_{p_1} + \frac{\Delta \text{H}}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore \quad \log K_{p_2} = \log (1.64 \times 10^{-4}) + \frac{-105200}{2.303 \times 8.314} \left[\frac{773 - 673}{773 \times 673} \right]$$

$$= \log 1.64 + (-4) \log 10 - \left(\frac{105200}{19.147} \times \frac{100}{520.229} \right)$$

$$\log K_{p_2} = 0.2148 - 4 - 1.056$$

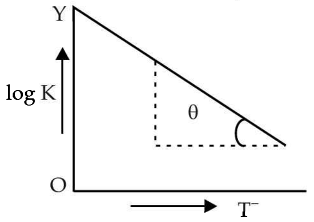
$$= -4.8412 = -4 - 1 + 1 - 0.8412 = \bar{5}.1588$$

$$\therefore \quad K_{p_2} = \text{antilog } \bar{5}.1588 = \mathbf{1.44 \times 10^{-5} \text{ atm}}$$ **Ans.**

Example 32. *According to van't Hoff equation,*

$$\log K = \log A - \frac{\Delta H°}{2.303 \, RT}$$

when a graph is drawn between log K and T$^-$, a straight line was obtained (See Fig below). If tan θ is 0.5 and OY is 10, then find the value of equilibrium constant, K at 298 K and value of K at 700 K if ΔH° is assumed to be independent of temperature.



Solution. (*i*) Since graph is a straight line,

$$\text{slope}, -\tan \theta = \frac{-\Delta H°}{2.303 R} \text{ Or } -0.5 = \frac{-\Delta H°}{2.303 \times 8.314}$$

Hence : $\Delta H° = 0.5 \times 2.303 \times 8.314 \text{ J mol}^-$

$$= 9.574 \text{ J mol}^-.$$

Also, intercept = log A = OY = 10 (given). Thus :

$$\log K = \log A - \frac{\Delta H°}{2.303\,RT};$$

$$\log K = 10 - \frac{9.574}{2.303 \times 8.314 \times 298}$$

$$= 10\,(1.68 \times 10^{-3})$$

$$\log K = 9.998;$$

$$K = \text{antilog } 9.998 = \mathbf{9.95 \times 10^{9}} \qquad \textbf{Ans.}$$

(*ii*) To find *K* at 700 *K*. we have :

$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right];$$

$$\log \frac{K_2}{9.95 \times 10^{9}} = \frac{9.574}{2.303 \times 8.314}\left[\frac{700 - 298}{298 \times 700}\right]$$

$$\log K_2 - \log 9.95 \times 10^{9}$$

$$= 9.6 \times 10^{-4}$$

$$\log K_2 = \log 9.95 + \log 10^{9} + 9.6 \times 10^{-4}$$

$$= 0.9978 + 9 + 9.6 \times 10^{-4}$$

$$= 9.9987$$

$$\therefore \quad K_2 = \text{antilog } 9.9987 = \mathbf{9.97 \times 10^{9}} \qquad \textbf{Ans.}$$

Type. To find K_c or K_p, use the relation

$$K_p = K_c\,(RT)^{\Delta n}$$

where Δn = (no. of mol of products) – (no. of mol of reactants)

$$R = 8.31\ \text{J mol}^{-}\,\text{K}^{-} = 8.31\ \text{k Pa L mol}^{-}\,\text{K}^{-}$$

$$= 0.0831\text{L bar mol}^{-}\,\text{K}^{-}$$

$$\simeq 0.0831\ \text{L atm mol}^{-}\,\text{K}^{-}$$

$$\simeq 0.082\ \text{L atm mol}^{-}\,\text{K}^{-}$$

EXAMPLE 33. *For the following gaseous reaction*

$$2Cl_2(g) + 2H_2O(g) \rightleftharpoons O_2(g) + 4HCl\,(g)$$

the value of K_p *at 673 K is 0.035 atmosphere. Find the value of* K_c *for* $\frac{1}{2}O_2\,(g) + 2HCl\,(g) \rightleftharpoons Cl_2(g) + H_2O(g)$ *(R = 0.082 L atm mol⁻K⁻)*

SOLUTION. For

$$\begin{array}{lcccc} 2Cl_2(g) & + 2H_2O\,(g) & \rightleftharpoons O_2(g) & + 4HCl\,(g) & \quad ...(1) \\ 2\text{ mol} & 2\text{ mol} & 1\text{ mol} & 4\text{ mol} & \end{array}$$

$$\Delta n = (1 + 4) - (2 + 2) = 1\text{ mol};\ T = 673\text{ K}.$$

$$K_p = K_c\,(RT)^{\Delta n}$$

Or $\quad 0.035\text{ atm} = K_c\,(0.082\text{ L atm} \times 673\text{ K})^{1}$

$$\therefore \quad K_c = \frac{0.035\text{ atm}}{0.082\text{ L atm mol}^{-}\,\text{K}^{-} \times 673\text{ K}}$$

$$= 6.342 \times 10^{-4}\text{ mol L}^{-}$$

The other given reaction is reverse of reaction (1)

(*i*) So, $\quad K'_c = \dfrac{1}{K_c} = \dfrac{1}{6.342 \times 10^{-4}\text{ mol L}^{-}}$

$$= 1576.8\text{ L mol}^{-}$$

Also, the other reaction, $\frac{1}{2}O_2\,(g) + 2\,HCl\,(g) \rightleftharpoons Cl_2\,(g) + H_2O\,(g)$ is obtained by dividing the coefficients of reaction (1) by 2, the new equilibrium constant K'_c will be the square root of the value of K_c. Hence :

$$K'_c = (1576.8\text{ L mol}^{-})^{1/2}$$

$$= \mathbf{39.7\ (L\ mol^{-})^{1/2}} \qquad \textbf{Ans.}$$

EXAMPLE 34. *The concentration equilibrium constant* K_c*, for the reaction,* $N_2 + 3H_2 \rightleftharpoons 2NH_3$ *at 673 K is 0.5. Find* K_p*. (R = 0.082 L atm K⁻ mol⁻)* **(MLNR 1996)**

SOLUTION. For

$$\begin{array}{ccccc} N_2 & + & 3\,H_2 & \rightleftharpoons & 2\,NH_3 \\ 1\text{ mol} & & 3\text{ mol} & & 2\text{ mol} \end{array}$$

$$\Delta n = 2 - (1 + 3) = -2$$

$$R = 0.082\text{ L atm K}^{-}\,\text{mol}^{-};\ T = 673\text{ K};$$

$$K_c = 0.5$$

We know $\quad K_p = K_c(RT)^{\Delta n} = 0.5\,(0.082\text{ L atm K}^{-}\,\text{mol}^{-} \times 673\text{ K})^{-2}$

$$\therefore \quad K_p = 0.5 \times (55.186)^{-2}$$

or $\quad K_p = \dfrac{0.5}{55.186 \times 55.186} = \dfrac{0.5}{3045.5}$

$$= \mathbf{1.64 \times 10^{-4}\ atm^{-2}} \qquad \textbf{Ans.}$$

EXAMPLE 35. *The magnitude of* K_p *for the reaction,* $N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$*, is 0.14 bar at 298 K. Calculate the value of* K_c*.*

SOLUTION. $\quad K_p = 0.14\text{ bar};\ K_c = ?;$

$$R = 0.0831\text{ L bar mol}^{-}\,\text{K}^{-};$$

$$T = 298\text{ K}.$$

For the reaction

$$\begin{array}{ccc} N_2O_4(g) & \rightleftharpoons & 2NO_2\,(g) \\ 1\text{ mol} & & 2\text{ mol} \end{array}$$

$$\Delta n = n_p - n_R = 2 - 1 = 1.$$

We know : $\quad K_p = K_c\,(RT)^{\Delta n} = K_c.\,RT$

Or $\quad K_c = \dfrac{K_p}{RT}$

$$\therefore \quad K_c = \frac{0.14}{0.0831 \times 298} = \mathbf{5.65 \times 10^{-3}} \qquad \textbf{Ans.}$$

23.13 DISSOCIATION OF NH_3

Type. Calculation of K_c for homogeneous gaseous dissociation reversible reaction involving change in volume or having different number of mol of reactants and products.

SOLUTION. Dissociation of NH_3.

	$2\,NH_3$	$\rightleftharpoons N_2$	$+\ 3H_2$
(*i*) *n* mol at start	*a*	0	0
(*ii*) Change by reaction	$-x$	$\frac{x}{2}$	$\frac{3x}{2}$
(*iii*) *n* mol at equilibrium	$\frac{a-x}{V}$	$\frac{x}{2V}$	$\frac{3x}{2V}$

x = Amount of NH_3 dissociated;

V = Volume of the reaction vessel.

$$\therefore \quad K_c = \frac{[N_2]\,[H_2]^3}{[NH_3]^2} = \frac{\left(\dfrac{x}{2V}\right)\left(\dfrac{3x}{2V}\right)^3}{\left(\dfrac{a-x}{V}\right)^2}$$

$$= \frac{27x^4}{16\,V^2\,(a-x)^2}$$

$$\therefore \qquad K_c = \frac{27x^4}{16\,V^2\,(a-x)^2}$$

EXAMPLE 36. *4 mol of NH_3 are introduced in one litre container in which it dissociates at high temperature as follows :*

$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2$$

If 2 mol of NH_3 remains undecomposed at equilibrium, find the value of K_c. **(ISC, 2013)**

SOLUTION.	$2\,NH_3 \rightleftharpoons$	$1\,N_2$	$+\,3H_2$
(*i*) *n* mol at start	4	0	0
(*ii*) Change by reaction	$-\,2$	$\frac{1\times 2}{2} = 1$	$\frac{3\times 2}{2} = 3$
(*iii*) *n* mol L⁻ at equilibrium	$\frac{4-2}{V\,(=1\,L)}$	$\frac{1}{V\,(=1L)}$	$\frac{3}{V\,(=1\,L)} = 2$

$$\therefore \qquad K_c = \frac{[H_2]^3\,[N_2]}{[NH_3]^2} = \frac{(3)^3 \times 1}{2\times 2}$$

$$= \mathbf{\frac{27}{4}\,mol^2\,L^{-2}} \qquad \textbf{Ans}$$

EXAMPLE 37. *Pure ammonia (one mol) was injected into a one litre container at a certain temperature. On analysing the equilibrium mixture, $2NH_3 \rightleftharpoons N_2 + 3H_2$, 0.3 mol of H_2 was found. Calculate :*

(*a*) *the concentration of N_2 and*

(*b*) *concentration of NH_3 at equilibrium.*

SOLUTION. Given reaction

$$\begin{array}{l} 2NH_3 \rightleftharpoons N_2 + 3H_2 \\ 2\text{ mol} \end{array}$$

For 1 mol NH_3, the reaction will be

$$NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2 \qquad \ldots(1)$$

$$1\text{ mol} \qquad \frac{1}{2}\text{mol} \quad \frac{3}{2}\text{mol}$$

At equilibrium,

$[H_2] =$ 0.3 mol. From reaction (1), we have:

(*a*) $\frac{3}{2}\text{mol } H_2 \equiv \frac{1}{2}\text{mol } N_2$

$\therefore \quad 0.3\text{ mol } H_2 \equiv \frac{1}{2}\times\frac{2}{3}\times 0.3 = 0.1\text{ mol.}$

(*b*) $\frac{3}{2}\text{mol } H_2 \equiv 1\text{ mol } NH_3$

$\therefore \quad 0.3\text{ mol } H_2 \equiv \frac{2}{3}\times 0.3 = 0.2\text{ mol}$

∴ Amount of undissociated NH_3 at equilibrium or concentration of NH_3 at equilibrium $= 1.0 - 0.2 =$ **0.8 mol.** **Ans**

EXAMPLE 38. *Ammonia under a pressure of 15 atmosphere at 27°C is heated to 374°C in a closed vessel in the presence of a catalyst. Under the conditions, NH_3 is partially decomposed according to the equation :*

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atmosphere. Calculate the percentage of NH_3 actually decomposed. **(MLNR, 1991)**

SOLUTION. $P_1 = 15\text{ atm}, P_2 = ?, T_1 = 27 + 273$
$= 300\text{ K}; T_2 = 347 + 273 = 620\text{ K}.$

Since volume is kept constant,

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}\;;\quad \frac{15}{300} = \frac{P_2}{620}\;;$$

$$P_2 = \frac{15\times 620}{300} = 31\text{ atm.}$$

Considering 1 mol NH_3 in the start, we have.

	$NH_3 \rightleftharpoons$	$\frac{1}{2}N_2 +$	$\frac{3}{2}H_2$
(*i*) no. of mol at start	1	0	0
(*ii*) Change by reaction	$-\,x$	$\frac{x}{2}$	$\frac{3x}{2}$
(*iii*) *n* mol at equilibrium	$1-x$	$\frac{x}{2}$	$\frac{3x}{2}$

Total number of mol at equilibrium

$$= 1 - x + \frac{x}{2} + \frac{3\,x}{2} = 1 + x$$

Thus, 1 + *x* mol concentration corresponds to 50 atm at the same temperature and volume. Thus

$$\frac{\text{No. of mol of } NH_3 \text{ without decomposition}}{\text{No. of mol of } NH_3 \text{ after dissociation}}$$

$$= \frac{1}{1+x}$$

$$\text{Or} \qquad \frac{31\text{ atm}}{50\text{ atm}} = \frac{1}{1+x}\;;\quad 31\,(1+x) = 50\;;$$

$$31 + 31x = 50\;;$$

$$\therefore \qquad 31\,x = 50 - 31 = 19\;;$$

$$\therefore \qquad x = \frac{19}{31} = 0.613$$

∴ percentage decomposition of NH_3

$$= 0.613 \times 100$$

$$= \mathbf{61.3\ \%} \qquad \textbf{Ans.}$$

23.14 DISSOCIATION OF N_2O_4

(*a*) **Determination of K_c**	$N_2O_4 \rightleftharpoons$	$2NO_2$
Original conc.	1mol	0
Conc. at equilibrium	$\frac{1-x}{V}$ mol	$\frac{2x}{V}$ mol

Let us start with one mol of N_2O_4 enclosed in a vessel of volume '*V*' litre

V = Volume of the closed vessel in which reaction takes place

x = number of mol of N_2O_4 that decompose at equilibrium to yield 2*x* mol of NO_2

Molar concentrations at equilibrium are :

$$[N_2O_4] = \frac{1-x}{V} \;;\; [NO_2] = \frac{2x}{V}$$

Applying law of mass action, we get :

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\frac{1-x}{V}} = \frac{4x^2}{V^2} \times \frac{V}{1-x}$$

$$\therefore \quad K_c = \frac{4\,x^2}{V\,(1-x)}$$

(*b*) **Determination of K_p**

Total number of mol

$$= 1 - x + 2x = 1 + x$$

Let P = Total pressure of the system

$$\therefore \quad p_{N_2O_4} = \frac{(1-x)\,P}{1+x} \;;\; p_{NO_2} = \frac{2x\,P}{1+x}$$

$$\therefore \quad K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{2x\,P}{1+x}\right)^2}{\frac{(1-x)\,P}{1+x}}$$

$$= \frac{4x^2\,P^2}{(1+x)\,(1+x)} \times \frac{1+x}{(1-x)\,P}$$

$$\therefore \quad K_p = \frac{4x^2\,P}{1-x^2}$$

Example 39. *At 1 atm and 350 K, N_2O_4 dissociates to 66% as :*

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

Calculate the volume that would 15.0g of N_2O_4 occupy under these conditions.

Solution. α = degree of dissociation

= 66 % = 66/100 = 0.66.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
(*i*) *n* mol at start	1		0
(*ii*) Change by reaction	– 0.66		2 × 0.66 = 1.32
(*iii*) *n* mol at equilibrium	1 – 0.66 = 0.34		1.32

Total number of mol at equilibrium

= 0.34 + 1.32 = 1.66

Wt. of N_2O_4 = 15.0 g ;

g. mol. wt. of N_2O_4

= (2 × 14) + (4 × 16) = 92 g

$\therefore$ Number of mol of $N_2O_4 = \frac{15}{92}$

Or number of mol of N_2O_4 at equilibrium

$$= 1.66 \times \frac{15}{92} = 0.27 = n$$

But $PV = nRT$ (gas equation)

Or $V = \frac{n\,RT}{P}$

$$= \frac{0.27 \text{ mol} \times 0.082 \text{ L atm K}^{-} \text{ mol}^{-} \times 350 \text{ K}}{1 \text{ atm}}$$

V = **7.749 L** **Ans.**

Example 40. *$N_2O_4\,(g)$ dissociates as, $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$. Calculate the equilibrium constant of this reaction if the density of the equilibrium mixture of $NO_2\,(g)$ and $N_2O_4\,(g)$ at 75°C and 1 atmospheric pressure is 1.84 g dm^{-3}.*

Solution.	N_2O_4 (g) $\rightleftharpoons$	2 NO_2 (g)
Initial conc.	C mol	0
Conc. at equilibrium	C – C α	2 C α

($\because$ α = degree of dissociation)

Total moles at equilibrium

= C – C α + 2 C α = C + C α

= C (1 + α)

Initial vapour density, V.D. of N_2O_4

$$= \frac{\text{Mol. wt. of } N_2O_4}{2}$$

$$= \frac{(2 \times 14) + (4 \times 16)}{2} = \frac{92}{2} = \mathbf{46.}$$

We know that :

$$\frac{\text{Total moles at equilibrium}}{\text{Total initial moles}} = \frac{\text{Initial V.D.}}{\text{V.D. at equilibrium } (= d)}$$

$$\therefore \quad \frac{C\,(1+\alpha)}{C} = \frac{46}{d}$$

or $$1 + \alpha = \frac{46}{d} \qquad \text{...(1)}$$

Also, V.D. (d) and actual density (d_1) are related as :

$$d = \frac{d_1\,RT}{2\,P}$$

$$\therefore \quad d = \frac{1.84 \times 0.0821 \times (75 + 273 = 348)}{2 \times 1}$$

$$d = 26.28 \qquad \text{...(2)}$$

From equations (1) and (2), we get

$$1 + \alpha = \frac{46}{26.28} \text{ or } \alpha = \frac{46}{26.28} - 1$$

= 1.75 – 1 = **0.75** **Ans.**

Also $$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left[\frac{2\,C\,\alpha}{C\,(1+\alpha)} \times P_T\right]^2}{\frac{C\,(1-\alpha)}{C\,(1+\alpha)} \times P_T}$$

$$= \frac{\left[\frac{2\,\alpha}{1+\alpha} \times P_T\right]^2}{\frac{1-\alpha}{1+\alpha} \times P_T} = \frac{\left(\frac{2 \times 0.75}{1+0.75} \times 1\right)^2}{\frac{1-0.75}{1+0.75} \times 1}$$

$$= \frac{(0.857)^2}{\frac{0.25}{1.75}} = \frac{0.7344}{0.1428} = \mathbf{5.14 \text{ atm.}} \quad \textbf{Ans.}$$

Example 41. *The K_p for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$ is 640 mm at 775 K. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm. At what pressure, the dissociation will be 50% if its K_p is taken as $4x^2p/_{1-x^2}$*

(Roorkee 1997)

SOLUTION. $N_2O_4(g) \rightleftharpoons 2NO_2$

When $x = 50\%$ or $\frac{50}{100} = 0.5$, $P = ?$

$$\therefore \quad K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}};$$

$$\text{or} \quad 640 = \frac{4x^2\,P}{1-x^2} = \frac{4\times(0.5)^2\,P}{1-(0.5)^2} = \frac{4\times 0.25\,P}{1-0.25};$$

$$640 = \frac{P}{0.75}$$

or $P = 640 \times 0.75 = \mathbf{480\ mm}$ **Ans.**

EXAMPLE 42. *N_2O_4 is 25% dissociated at 37°C and one atmospheric pressure. Calculate (i) K_p and (ii) the percentage dissociation at 1.1 atmosphere and 37°C.* **(IIT 1988)**

SOLUTION. (*a*) $x = 25\% = 25/100 = 0.25$

	$N_2O_4(g)$	$\rightleftharpoons 2NO_2(g)$
(*i*) *n* mol at start	1	0
(*ii*) Change by reaction	-0.25	$2\times 0.25 = 0.5$
(*iii*) *n* mol at equilibrium	$1 - 0.25 = 0.75$	0.5

Total number of mol

$= 0.75 + 0.50 = 1.25$; $P = 1$ atm.

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{0.5}{1.25}\times P\right)^2}{\left(\frac{0.75}{1.25}\times P\right)}$$

$$= \frac{\left(\frac{0.5}{1.25}\times 1\right)^2}{\left(\frac{0.75}{1.25}\times 1\right)}$$

$$K_p = \frac{50}{125}\times\frac{50}{125}\times\frac{125}{75} = 0.267\ \text{atm.}$$

(*b*) α = Degree of dissociation.

	$N_2O_4(g)$	$\rightleftharpoons 2NO_2(g)$
(*i*) *n* mol at start	1	0
(*ii*) Change by reaction	$-\alpha$	2α
(*iii*) *n* mol at equilibrium	$1-\alpha$	2α

Total number of mol

$= 1 - \alpha + 2\alpha = 1 + \alpha$; $P = 1.1$ atm.

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}\times P\right)^2}{\frac{1-\alpha}{1+\alpha}\times P}$$

$$= \frac{2\alpha}{1+\alpha}\times 1.1\times\frac{2\alpha\times 1.1}{1+\alpha}\times\frac{1+\alpha}{(1-\alpha)\times 1.1}$$

$$0.267 = \frac{4\alpha^2\times 1.1}{1-\alpha^2};\ \frac{0.267}{1.1} = \frac{4\alpha^2}{1-\alpha^2};$$

$$0.243 = \frac{4\alpha^2}{1-\alpha^2}$$

$0.243\,(1-\alpha^2) = 4\alpha^2$; $0.243 - 0.243\,\alpha^2 = 4\,\alpha^2$;

$4\,\alpha^2 + 0.243\,\alpha^2 = 0.243$

Or $4.243\,\alpha^2 = 0.243$; $\alpha^2 = \frac{0.243}{4.243} = 0.0573$

Or $\alpha = (0.0573)^{1/2} = 0.239$

$\therefore$ % age dissociation

$= 0.239 \times 100 = \mathbf{23.9\ \%}$ **Ans.**

EXAMPLE 43. *At 25°C and one atmospheric pressure, the partial pressures in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atmosphere respectively. Calculate the partial pressure of these gases when they are in equilibrium at 25°C and at a total pressure of 10 atmosphere.* **(Dhanbad, 1992, MLNR 1990)**

SOLUTION. (*a*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

	$N_2O_4(g)$	$2NO_2(g)$
n mol at equilibrium	0.7	0.3

Total number of mol

$= 0.7 + 0.3 = 1.0$; $P = 1$ atm.

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{0.3}{1}\times 1\right)^2}{\frac{0.7}{1}\times 1} = \frac{0.3\times 0.3}{0.7}$$

$= 0.128$ atm.

(*b*) x = degree of dissociation, $P = 10$ atm.

	$N_2O_4(g)$	$\rightleftharpoons 2NO_2(g)$
(*i*) *n* mol at start	1	0
(*ii*) Change by reaction	$-x$	$2x$
(*iii*) *n* mol at equilibrium	$1-x$	$2x$

Total number of mol at equilibrium

$= 1 - x + 2x = 1 + x$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{2x}{1+x}\times P\right)^2}{\frac{1-x}{1+x}\times P}$$

$$= \frac{4x^2\,P}{1-x^2} = \frac{4x^2\times 10}{1-x^2} = \frac{40x^2}{1-x^2}$$

Or $0.128 = \frac{40x^2}{1-x^2}$;

$0.128\,(1-x^2) = 40x^2$; $0.128 - 0.128\,x^2 = 40\,x^2$

$\therefore\ 40\,x^2 + 0.128\,x^2 = 0.128$; $40.128\,x^2 = 0.128$;

$$x^2 = \frac{0.128}{40.128} = 3.19\times 10^{-3};$$

$$\therefore \quad x = \left(\frac{3.19}{1000}\right)^{1/2} = (0.00319)^{1/2} = 0.056$$

$$\therefore \quad p_{NO_2} = \frac{2x}{1+x}\times 10 = \frac{2\times 0.056\times 10}{1+0.056} = \frac{1.12}{1.056}$$

$= \mathbf{1.06\ atm}$ **Ans.**

$$p_{N_2O_4} = \frac{1-x}{1+x}\times 10 = \frac{(1-0.056)\times 10}{1+0.056} = \frac{9.44}{1.056}$$

$= \mathbf{8.94\ atm}$ **Ans.**

EXAMPLE 44. *The vapour density (hydrogen = 1) of a mixture containing NO_2 and N_2O_4 is 38.3 at 27°C. Calculate the number of mol of NO_2 in 100 g of the mixture.* **(MLNR 1993)**

SOLUTION. (*a*) Mol. wt. of $N_2O_4 = (2 \times 14) + (4 \times 16) = 28 + 64 = 92$

$\therefore$ Vapour density (D) of N_2O_4 before dissociation

$$= \frac{\text{Mol. wt.}}{2} = \frac{92}{2} = 46$$

V.D (d) after dissociation = 38.3.

For $\quad N_2O_4 \rightleftharpoons 2NO_2$

2 mol ; $n = 2$

Let degree of dissociation = α.

But $\quad \alpha = \dfrac{D-d}{d(n-1)}$;

$$\therefore \quad \alpha = \frac{46-38.3}{38.3(2-1)} = \frac{7.7}{38.3} = 0.201$$

(*b*)	N_2O_4	$\rightleftharpoons$ $2NO_2$
(*i*) *n* mol at start	1	0
(*ii*) Change by reaction	$-\alpha\,(=-0.201)$	$2\alpha\,(= 2 \times 0.201) = 0.402$
(*iii*) *n* mol at equilibrium	$1 - 0.201 = 0.799$	0.402

(*c*) $\therefore$ Number of mol of $N_2O_4 = 0.799$;

g. mol. wt. of N_2O_4

$$= (2 \times 14) + (4 \times 16) = 92 \text{ g}$$

$\therefore$ Mass of $N_2O_4 = 0.799 \times 92 = 73.508$ g.

Number of mol of $NO_2 = 0.402$;

g mol. wt. of $NO_2 = 14 + (2 \times 16) = 46$ g

$\therefore$ Mass of $NO_2 = 0.402 \times 46 = 18.492$ g

Total mass of mixture

$$= 73.508 + 18.492 = 92 \text{ g}$$

92 g mixture contain $NO_2 = 18.492$ g

$\therefore$ 100 g mixture contain NO_2

$$= \frac{18.492}{92} \times 100 \text{ g} = 20.1 \text{ g}$$

$\therefore$ Number of mol of NO_2

$$= \frac{\text{Wt. of } NO_2}{\text{g. mol. wt. of } NO_2} = \frac{20.1}{46} = \mathbf{0.437}$$

EXAMPLE 45. *For the $N_2O_4 \rightleftharpoons 2NO_2$, the equilibrium constant, Kp at 25°C is 0.113 atm. Determine the partial pressure of $NO_2(g)$ in a system under a total pressure of 1.0 atmosphere when 0.04 mol of N_2O_4 (g) are sealed in a container and allowed to come to equilibrium at 25°C.*

SOLUTION. $K_p = 0.113$ atm; total pressure, $P = 1.0$ atm.

	N_2O_4	$\rightleftharpoons$ $2NO_2$
(*i*) *n* mol at start	0.04	0
(*ii*) Change by reaction	$-x$	$2x$
(*iii*) *n* mol at equilibrium	$0.04 - x$	$2x$

Total number of mol at equilibrium

$$= 0.04 - x + 2x = 0.04 + x.$$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\dfrac{2x}{0.04+x} \times P\right)^2}{\dfrac{0.04-x}{0.04+x} \times P}$$

$$= \frac{\left(\dfrac{2x}{0.04+x} \times 1\right)^2}{\dfrac{0.04-x}{0.04+x} \times 1} = \frac{4x^2}{(0.04+x)(0.04-x)}$$

Or $\quad 0.113 = \dfrac{4x^2}{(0.04)^2 - x^2} = \dfrac{4x^2}{0.0016 - x^2}$;

$0.113\,(0.0016 - x^2) = 4x^2$

Or $0.00018 - 0.113\,x^2 = 4\,x^2$;

$$4\,x^2 + 0.113\,x^2 = 0.00018$$

Or $\quad 4.113\,x^2 = 0.00018$;

$$x^2 = \frac{0.00018}{4.113} = 0.000044\,;$$

$$x = (0.000044)^{1/2} \;\therefore\; x = 6.63 \times 10^{-3}$$

$$\therefore \quad p_{NO_2} = \frac{2x}{0.04+x} \times P = \frac{2 \times 6.63 \times 10^{-3} \times 1}{0.04 + 6.63 \times 10^{-3}}$$

$$= \frac{13.26 \times 10^{-3}}{0.04 + 0.00663} = \frac{0.01326}{0.04663}$$

$= \mathbf{0.284\ atm}$ **Ans.**

EXAMPLE 46. *An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm pressure respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.* **(Roorkee, 1991)**

SOLUTION. $p_{NO_2} = 1.1$ atm ; $p_{N_2O_4} = 0.28$ atm.

Thus, total pressure = 1.1 + 0.28 = 1.38 atm.

For $\quad N_2O_4 \rightleftharpoons 2NO_2$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{(1.1)^2}{0.28} = \frac{1.21}{0.28} = \frac{121}{28}$$

At constant temperature, since, $V \propto \dfrac{1}{p}$, when volume is doubled, pressure becomes one half.

$\therefore$New pressure $= \dfrac{1.38}{2} = 0.69$ atm.

Let new pressure of $N_2O_4 = P$.

So, $\quad p_{NO_2} = 0.69 - P$

$$\therefore \quad K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{(0.69-P)^2}{P}\,;$$

Or $\quad \dfrac{121}{28} = \dfrac{(0.69-P)^2}{P}$

Or $121\,P = 28\,(0.69 - P)^2\,;$

$$121\,P = 28\,(0.4761 + P^2 - 1.38\,P)$$

$$121\,P = 13.33 + 28\,P^2 - 38.64\,P\,;$$

$$28\,P^2 - 38.64\,P - 121\,P + 13.33 = 0\,;$$

$$28\,P^2 - 159.64\,P + 13.33 = 0$$

$$\therefore \quad P = \frac{-(-159.64) \pm \sqrt{(-159.64)^2 - 4\,(28 \times 13.33)}}{2 \times 28}$$

$$= \frac{159.64 \pm \sqrt{25485 - 1493}}{56}$$

$$= \frac{159.64 \pm \sqrt{23992}}{56}$$

$$= \frac{159.64 \pm 154.89}{56}$$

$$\left[\because \text{for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4\,ac}}{2\,a}\right]$$

$$P = \frac{314.53}{56} = 5.6 \text{ (on addition) or } \frac{4.75}{56}$$

(on subtraction) = 0.085

∴ Partial pressure of N_2O_4

= P = 0.085 atm.

Partial pressure of NO_2

= $0.69 - P = 0.69 - 0.085$

= **0.605 atm.** **Ans.**

Example 47. *The value of Kp at 46°C for $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ is 0.66 atm. Compute the percent dissociation of N_2O_4 at 46°C and a total pressure of 380 torr. What are the partial pressures of N_2O_4 and NO_2 at equilibrium ?* **(Kanpur IIT 1996)**

Solution. (*a*) Total pressure of NO_2 and N_2O_4

$$= 380 \text{ torr} = \frac{380}{760} = 0.5 \text{ atm.}$$

Let partial pressure of $NO_2 = P$

Partial pressure of $N_2O_4 = 0.5 - P$

For $N_2O_4 \rightleftharpoons 2NO_2$

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}}\,;\quad 0.66 = \frac{P^2}{0.5 - P}\,;$$

$$\left[\because \text{for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$0.66\,(0.5 - P) = P^2$$

or $P^2 = 0.33 - 0.66\,P;\ P^2 + 0.66\,P - 0.33 = 0$

$$\therefore \quad P = \frac{-(+0.66) \pm \sqrt{(+0.66)^2 - 4(1 \times -0.33)}}{2 \times 1}$$

$$= \frac{-0.66 \pm \sqrt{0.4356 + 1.32}}{2}$$

$$= \frac{-0.66 \pm \sqrt{1.7556}}{2}$$

$$= \frac{-0.66 \pm 1.32}{2} = \frac{-0.66 + 1.32}{2} = \frac{-0.66 + 1.32}{2} = \frac{0.66}{2} = +0.33;$$

Or $= \dfrac{-0.66 - 1.32}{2} = \dfrac{-1.98}{2} = -0.99$

Since, value cannot be negative, so

$$P = 0.33 \text{ atm.}\ \therefore\ p_{NO_2} = 0.33 \text{ atm}\,;$$

$$p_{N_2O_4} = 0.5 - 0.33 = \mathbf{0.17\ atm.}$$

(*b*) Let degree of dissociation = x

		$N_2O_4 \rightleftharpoons$	$2NO_2$
(*i*)	n mol of start	1	0
(*ii*)	Change by reaction	$-x$	$2x$
(*iii*)	n mol at equilibrium	$1 - x$	$2x$

Total number of mol at equilibrium

= $1 - x + 2x = 1 + x$; P = 0.5 atm.

$$K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\dfrac{2\,x}{1+x} \times P\right)^2}{\dfrac{1-x}{1+x} \times P} = \frac{4\,P\,x^2}{1-x^2}\,;$$

$$0.66 = \frac{4 \times 0.5\,x^2}{1 - x^2} = \frac{2\,x^2}{1 - x^2}$$

Or $0.66\,(1 - x^2) = 2\,x^2\,;$

$$0.66 - 0.66\,x^2 = 2\,x^2\,;$$

$$2\,x^2 + 0.66\,x^2 = 0.66\,;\ 2.66\,x^2 = 0.66$$

$$x^2 = \frac{0.66}{2.66} = 0.248\,;$$

$$\therefore \quad x = \sqrt{0.248} = 0.498\,;$$

∴ % age dissociation

= 0.498 × 100 = **49.8 %** **Ans.**

Example 48. *The V.D. of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.* **(MDU, Pre-med, Pre-engg 1980, UP 1990)**

Solution. g. mol. wt. of N_2O_4

= (2 × 14) + (4 × 16) = 92

∴ *V.D.* (*D*) of undissociated N_2O_4

$$= \frac{\text{Mol. wt.}}{2} = \frac{92}{2} = 46$$

For $N_2O_4 \rightleftharpoons 2NO_2$ (*i.e.*, 2 mol ; $n = 2$)

Degree of dissociation = α (say)

V.D. (*d*) of N_2O_4 at the given temperature = 30

But $$\alpha = \frac{D - d}{d\,(n - 1)} = \frac{46 - 30}{30\,(2 - 1)} = \frac{16}{30} = 0.533$$

∴ % age dissociation

= 0.533 × 100 = **53.3** **Ans.**

Example 49. *The equilibrium constant for $N_2O_4 \rightleftharpoons 2NO_2$ at 27°C and 1 atm is 0.17. What is the extent of dissociation in* *a 69 g sample of N_2O_4 confined in a 20 L vessel at 27°C.*

Solution. g. mol. wt. of N_2O_4

$$= (2 \times 14) + (4 \times 16) = 92\text{ g};$$

$$\text{Wt. of } N_2O_4 = 69\text{ g}$$

$\therefore$ number of mol of N_2O_4

$$= \frac{96}{92} = 0.75\text{ mol}$$

Let α = degree or extent of dissociation.

Thus for :	$N_2O_4 \rightleftharpoons$	$2NO_2$
(*i*) *n* mol at start	0.75	–
(*ii*) Change by reaction	$-0.75\,\alpha$	$+ 2\,(0.75\,\alpha) = 1.50\,\alpha$
(*iii*) *n* mol at equilibrium	$0.75\,(1-\alpha)$ $= 0.75 - 0.75\,\alpha$	$1.50\,\alpha$

Let pressure = P ; $R = 0.082\text{ L atm K}^{-}\text{ mol}^{-}$;

$$T = 27 + 273 = 300\text{ K};\ V = 20\text{ L}$$

But $\quad PV = n\,RT$;

$$\therefore \quad P_{(N_2O_4)} = \frac{n\,(N_2O_4)\,RT}{V}$$

$$= \frac{[0.75\,(1-\alpha)\text{ mol}] \times 0.082\text{ L atm K}^{-}\text{ mol}^{-}) \times 300\text{ K}}{20\text{ L}}$$

or $\quad P_{N_2O_4} = 0.92\,(1-\alpha)$ atm

$$\text{Similarly, } P_{(NO_2)} = \frac{n\,(NO_2)\,RT}{V}$$

$$= \frac{150\,\alpha \times 0.082\text{ L atm mol}^{-}\text{K}^{-} \times 300\text{ K}}{20\text{ L}}$$

$$= 1.84\,\alpha\text{ atm}$$

$$\text{But} \quad K_p = \frac{P_{(NO_2)^2}}{P_{(N_2O_4)}} = \frac{(1.84\,\alpha)^2}{0.92\,(1-\alpha)};$$

$$0.17 = \frac{3.38\,\alpha^2}{0.92 - 0.92\,\alpha};$$

$0.17\,(0.92 - 0.92\,\alpha) = 3.38\,\alpha^2$; $0.16 - 0.16\,\alpha = 3.38\,\alpha^2$;

$3.38\,\alpha^2 + 0.16\,\alpha - 0.16 = 0$

$$\therefore \quad \alpha = \frac{-0.16 \pm \sqrt{(0.16)^2 - 4\,(3.38 \times -0.16)}}{2 \times 3.38}$$

$$= \frac{-0.16 \pm \sqrt{0.026 + 2.16}}{6.76}$$

$$= \frac{-0.16 \pm \sqrt{2.186}}{6.76}$$

$$= \frac{-0.16 \pm 1.48}{6.76}; \quad \left[\because \text{ for } ax^2 + bx + c = 0,\ x = \frac{-b \pm \sqrt{b^2 - 4\,ac}}{2\,a}\right]$$

$$\alpha = \frac{-1.64}{6.76} \text{ (after subtraction)}$$

or $\dfrac{1.32}{6.7}$ (after addition) = –0.24 or 0.197 respectively.

The negative value has to be rejected, So, $\alpha = 0.197$

$\therefore$ % age dissociation

$= 0.197 \times 100 =$ **19.7 %** **Ans.**

Example 50. *20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of equilibrium mixture.* **(Roorkee, 1996)**

Solution. Degree of dissociation,

$$\alpha = 20\,\% = \frac{20}{100} = 0.2$$

	$N_2O_4 \rightleftharpoons$	$2NO_2$
(*i*)*n* mol at start	1	0
(*ii*) Change by reaction	– 0.2	$2 \times 0.2 = 0.4$
(*iii*) *n* mol at equilibrium	$1 - 0.2 = 0.8$	0.4

Total number of mol at equilibrium

$$= 0.8 + 0.4 = 1.2 = n$$

But $\quad P\,V = n\,RT$ (gas equation)

$$\therefore \quad V = \frac{n\,RT}{P}$$

$$= \frac{1.2\text{ mol} \times 0.082\text{ L atm K}^{-}\text{ mol}^{-} \times (27 + 273)\text{ K}}{760\text{ torr } (= 1\text{ atm})}$$

$$\textbf{Or } V = \frac{1.2\text{ mol} \times 0.082\text{ L atm K}^{-}\text{ mol}^{-} \times 300\text{ K}}{1\text{ atm}} = 29.52\text{ L}$$

g. mol. wt. of N_2O_4

$$= (2 \times 14) + (4 \times 16) = 92\text{ g.}$$

$$\text{But} \quad \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{92\text{ g}}{29.52\text{ L}} = \mathbf{3.12\ g\ L^{-}}\ \textbf{Ans.}$$

Example 51. *'a' litre of N_2O_4 decomposes as : $N_2O_4 \rightleftharpoons 2NO_2$ at 273 K and one atmospheric pressure. If original volume is 20% less than that of the existing volume, calculate the extent to which the decomposition has taken place.*

Solution. At constant temperature and pressure, the volume can be taken as mol.

	$N_2O_4 \rightleftharpoons$	$2NO_2$
(*i*) *n* mol at start	*a*	0
(*ii*) Change by reaction	$-x$	$2\,x$
(*iii*) *n* mol at equilibrium	$a - x$	$2\,x$

Total number of mol at equilibrium

$$= a - x + 2x = a + x$$

$$\therefore \text{ Original mol} = \frac{(100 - 20)}{100} \text{ of mol at equilibrium}$$

$$a = \frac{80}{100} \times (a + x)$$

$$\textbf{Or} \quad a = 0.80\,(a + x);\ \frac{a}{0.8} = a + x;$$

$$x = \frac{a}{0.8} - a = a\left(\frac{1}{0.8} - 1\right)$$

$$\textbf{Or} \quad x = a\left(\frac{1 - 0.8}{0.8}\right) = \frac{0.2}{0.8}\,a = 0.25\,a$$

∴ % decomposition

$$= \frac{x}{a} \times 100 = \frac{0.25\,a}{a} \times 100 = \mathbf{25\%}\ \textbf{Ans.}$$

EXAMPLE 52. *0.1 mol of N_2O_4 (g) was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mol of NO_2 (g) present if the equilibrium*

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)\ \ (Kp = 0.14)$$

is reached after some time **(MLNR, 1997)**

SOLUTION.

		$N_2O_4 \rightleftharpoons$	$2NO_2$
(*i*)	*n* mol at start	1	0
(*ii*)	Change by reaction	$-\alpha$	2α
(*iii*)	*n* mol at equilibrium	$1-\alpha$	2α

∴ Total number of mol at equilibrium

$$= 1 - \alpha + 2\alpha = 1 + \alpha$$

Pressure = P

$$\therefore \quad p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P \quad ; \quad p_{NO_2} = \frac{2\alpha}{1+\alpha} \times P$$

$$\text{But} \quad K_p = \frac{p_{(NO_2)^2}}{p_{N_2O_4}} \quad ; \quad 0.14 = \frac{\left(\dfrac{2\alpha P}{1+\alpha}\right)^2}{\dfrac{1-\alpha}{1+\alpha} \times P}$$

$$= \frac{4\alpha^2 P^2}{(1+\alpha)^2} \times \frac{1+\alpha}{P(1-\alpha)}$$

$$0.14 = \frac{4\alpha^2 P}{1-\alpha^2} \quad ; \quad 0.14 = \frac{4\alpha^2 \times 1}{1-\alpha^2}$$

$$\therefore \quad 0.14\,(1-\alpha^2) = 4\alpha^2 ;\ 0.14 - 0.14\,\alpha^2 = 4\alpha^2 ;$$

$$4\alpha^2 + 0.14\,\alpha^2 = 0.14 ;$$

$$4.14\,\alpha^2 = 0.14 ;$$

$$\therefore \quad \alpha = \left(\frac{0.14}{4.14}\right)^{1/2} = 0.18$$

Since 0.1 mol of N_2O_4 is taken, so :

Number of mol of NO_2

$$= 0.1 \times 2\alpha = 0.18 \times 0.1 \times 2 = \mathbf{0.036}\ \textbf{Ans.}$$

EXAMPLE 53. *For the following equilibrium at 450°C and one atmospheric pressure, $N_2O_4\,(g) \rightleftharpoons 2NO_2$, calculate the partial pressure of NO_2 (g). Provided $\Delta G_f^\circ\,(NO_2) = 51.84$ k J, $\Delta G_f^\circ\,(N_2O_4) = 98.29$ k J. Assume that ΔG° does not change. The number of mol of N_2O_4 taken initially is 2.*

SOLUTION. (*a*) Calculation of K_p for

$$N_2O_4(g) \rightleftharpoons 2NO_2\,(g)$$

$$\Delta G^\circ = 2\,\Delta G_f^\circ\,(NO_2) - \Delta G^\circ_f\,(N_2O_4)$$

$$= (2 \times 51.84) - (98.29) = 5.39 \text{ k J}$$

$$= 5.39 \times 1000 = 5390 \text{ J}$$

$$\text{But} \quad \Delta G^\circ = -\,2.303\ RT \log K_p ;$$

$$\log K_p = \frac{-\,\Delta G^\circ}{2.303\,RT}$$

$$\textbf{Or} \quad \log K_p = -\frac{5390}{2.303 \times 8.314 \text{ J K}^{-} \text{ mol}^{-} \times (450 + 273) \text{ K}}$$

$$= (-\,0.3894)$$

$$\therefore \quad K_p = \text{antilog}\,(-\,0.3894)$$

$$= \text{antilog}\,(-\,1 + 1 - 0.3894)$$

$$= \text{antilog}\ \bar{1}.6106 = 0.408$$

(*b*) **To find amount of NO_2 and N_2O_4.**

		$N_2O_4 \rightleftharpoons$	$2NO_2$
(*i*)	*n* mol at start	2	0
(*ii*)	Change by reaction	$-\,2\alpha$	$2\,(2\alpha)$
(*iii*)	*n* mol at equilibrium	$2 - 2\alpha$	4α

Total number of mol at equilibrium

$$2 - 2\alpha + 4\alpha = 2 + 2\alpha ;\ \text{Pressure} = P$$

$$p_{NO_2} = \frac{4\alpha}{2+2\alpha} \times P = \frac{2\alpha P}{1+\alpha} ;$$

$$p_{N_2O_4} = \frac{2-2\alpha}{2+2\alpha} \times P = \frac{2\,(1-\alpha)}{2\,(1+\alpha)} \times P = \frac{(1-\alpha)\,P}{1+\alpha}$$

$$\therefore \quad K_p = \frac{p_{\,(NO_2)^2}}{p_{\,(N_2O_4)}} = \frac{4\alpha^2 P^2}{(1+\alpha)^2} \times \frac{1+\alpha}{(1-\alpha)\,P}$$

$$= \frac{4\alpha^2 P}{(1+\alpha)\,(1-\alpha)} = \frac{4\alpha^2 \times 1}{1-\alpha^2} = \frac{4\alpha^2}{1-\alpha^2}$$

$$\therefore \quad 0.408 = \frac{4\alpha^2}{1-\alpha^2} ;\ 0.408\,(1-\alpha^2) = 4\alpha^2 ;$$

$$0.408 - 0.408\,\alpha^2 = 4\alpha^2$$

$$\textbf{Or} \quad 4\alpha^2 + 0.408\,\alpha^2 = 0.408 ;\ 4.408\,\alpha^2 = 0.408 ;$$

$$\therefore \quad \alpha = \left(\frac{0.408}{4.408}\right)^{1/2} \quad \textbf{Or}\ \alpha = (0.092)^{1/2} = 0.303$$

$$(a) \quad p_{NO_2} = \frac{4\alpha}{2+2\alpha} \times P = \frac{2\,(2\alpha)}{2\,(1+\alpha)} \times P = \frac{2\alpha P}{1+\alpha}$$

$$= \frac{2 \times 0.303 \times 1}{1 + 0.303} = \frac{0.606}{1.303} = \mathbf{0.465\ atm}$$

(*b*) Amount of NO_2 at equilibrium = $4\alpha = 4 \times 0.303 =$ **1.212 mol. Ans.**

(*c*) Amount of N_2O_4 at equilibrium = $2 - 2\alpha$

$$= 2 - (2 \times 0.303) = 2 - 0.606$$

$$= \mathbf{1.394\ mol.} \qquad \textbf{Ans.}$$

EXAMPLE 54. *The K_p value of $N_2O_4 \rightleftharpoons 2NO_2$ reaction at equilibrium is 0.6. The value of degree of dissociation of N_2O_4 at 318 K and a total pressure of 10 bar will be :*

(*a*) 0.02 (*b*) 0.03

(*c*) 0.121 (*d*) 0.242

SOLUTION. Let degree of dissociation of $N_2O_4 = x$. Let the vessel contains one mol of N_2O_4, $K_p = 0.6$, Total pressure, $P = 10$ bar. Thus, for the following reaction, we have :

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial conc.	1	0
Conc. at equilibrium	$1 - x$	$2x$

Total no. of mol at equilibrium

$$= 1 - x + 2x = 1 + x$$

$$\therefore \quad p_{N_2O_4} = \frac{10(1-x)}{1+x};\ p_{NO_2} = \frac{10 \times 2x}{1+x}$$

[$\because$ P = 10 bar]

Using law of chemical equilibrium for the above reaction, we have :

$$K_p = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{20x}{1+x}\right)^2}{\frac{10(1-x)}{1+x}}$$

$$= \frac{400x^2}{(1+x)(1+x)} \times \frac{(1+x)}{10(1-x)} = \frac{40x^2}{(1+x)(1-x)}$$

$$0.6 = \frac{40x^2}{1-x^2};\ 0.6 - 0.6x^2 = 40x^2$$

Or $40x^2 + 0.6x^2 = 0.6$

$$\therefore \quad 40.6x^2 = 0.6 \text{ Or } x^2 = \frac{0.6}{40.6} = 0.0148$$

$$\therefore \quad x = (0.148)^{1/2} = \mathbf{0.121}$$

So, the correct answer is, (*c*)

Example 55. *Find the value of K_c in moles per litre for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_p = 0.15$ atm at 298 K.*

(HP Board, 2007)

Solution. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

no. of mol 1 2

Δn = no. of mol of products – no. of mol of reactants

$= 2 - 1 = 1;\ R = 0.0821$ L atm K^{-} mol^{-};

T = 298 K

But $K_p = K_c(RT)^{\Delta n}$

0.15 atm $= K_c(0.0821 \text{ L atm K}^{-} \text{mol}^{-} \times 298 \text{ K})^1$

$$\therefore \quad K_c = \frac{0.15 \text{ atm}}{0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 298 \text{ K}}$$

$= 6.13 \times 10^{-3}$ mol L^{-} **Ans.**

23.15 SYNTHESIS OF N_2O_4

Example 56. *One mol of NO_2 and 1 mol of N_2O_4 are placed in a one litre flask. At equilibrium, 0.75 mol of N_2O_4 is present in the flask. Calculate the value of K for the reaction :*

$$2\,NO_2 \rightleftharpoons N_2O_4$$

Solution.	$2\,NO_2 \rightleftharpoons$	N_2O_4
(*i*) *n* mol at start	1	1
(*ii*) *n* mol used	–	1 – 0.75 = 0.25
(*iii*) *n* mol produced	2 × 0.25 = 0.5	–
(*iv*) *n* mol at equilibrium	1 + 0.5 = 1.5	0.75

$$K_p = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.75}{(1.5)^2} = \frac{0.75}{1.5 \times 1.5}$$

$= \mathbf{0.33}$ **Ans.**

Example 57. (*i*) *Calculate $\Delta G°$ and K_p for*

$$2NO_2 \rightleftharpoons N_2O_4 \text{ at } 25°C.$$

(*ii*) *Calculate $\Delta G°$ and K_p for the reverse reaction,*

$$N_2O_4 \rightleftharpoons 2NO_2 \text{ at } 25°C$$

(*iii*) *Calculate $\Delta G°$ and K_p for the forward reaction written with different co-efficients.*

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4$$

$$\Delta G_f^\circ (N_2O_4) = 97.82 \text{ kJ mol}^{-};$$

$$\Delta G_f^\circ (NO_2) = 51.30 \text{ kJ mol}^{-};\ R = 8.314 \text{ J K}^{-}.$$

Solution. (*i*) For

$$2NO_2 \rightleftharpoons N_2O_4,\ T = 25 + 273 = 298 \text{ K}$$

$$\Delta G° = \Delta G_f^\circ (N_2O_4) - 2\Delta G_f^\circ (NO_2)$$

$$= 97.82 - 2(51.3) = 97.82 - 102.6$$

$$= -4.78 \text{ kJ}$$

$$= -4.78 \times 1000 = -4780 \text{ J.}$$

But $\Delta G° = -2.303 \text{ RT} \log K_p$

$$\therefore \quad \log K_p = \frac{\Delta G°}{-2.303 \text{ RT}}$$

$$= \frac{-4780 \text{ J}}{-2.303 \times 8.314 \text{ J K}^{-} \times 298 \text{ K}} = 0.837$$

$\therefore$ K_p = antilog 0.837 = **6.87** **Ans.**

(*ii*) We know that (*a*) the value of ΔG is the negative of ΔG for the forward reaction, so,

$$\Delta G = -(-4.78 \text{ kJ})$$

$= +4.78$ kJ for the reverse reaction.

(*b*) the value of K_p for the reverse reaction is reciprocal of the value for forward reaction,

so, $K'_p = \dfrac{1}{K_p} = \dfrac{1}{6.87} = \mathbf{0.146}$ **Ans.**

(*c*) For $NO_2 \rightleftharpoons \frac{1}{2}N_2O_4$

$$\Delta G° = \frac{1}{2}\Delta G_f^o (N_2O_4) - \Delta G_f^o (NO_2)$$

$$= \frac{1}{2}(97.82) - 51.3$$

$$= 48.91 - 51.3 = -2.39 \text{ kJ}$$

$$= -2.39 \times 1000 = -2390 \text{ J}$$

But $\Delta G° = -2.303 \text{ RT} \log Kp$

$$\therefore \quad \log K_p = \frac{\Delta G°}{-2.303 \text{ RT}}$$

$$= \frac{-2390 \text{ J}}{-2.303 \times 8.314 \text{ J K}^{-} \times 298 \text{ K}} = 0.418$$

$\therefore$ K_p = antilog 0.418 = **0.262** **Ans.**

Example 58. *The free energy of formation of NO is 78 kJ mol^{-} at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at 1000 K ?*

(*a*) 8.4×10^{-5} (*b*) 7.7×10^{-9}

(*c*) 4.2×10^{-10} (*d*) 1.7×10^{-19} **(Dumet, 2010)**

SOLUTION. ΔG° = 78 kJ mol^{-}, = 78 × 1000 = 78,000 J mol^{-}. But : K_{equi} = antilog $(-\Delta G^\circ/2.303RT)$ = antilog $(-78000/2.303 \times 1000 \times 8.314)$ = antilog (–4.0737) = 8.4×10^{-5}. So, the correct answer is (*a*)

EXAMPLE 59. *The ΔH° value for the reaction*

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g)$$

is – 13.9 k cal. at 298 K. Calculate the value of equilibrium constant at 273 K, if equilibrium constant value at 298 K is 8.8.

SOLUTION. $T_1 = 298\text{ K},\ T_2 = 273\text{ K},$

$\Delta H^\circ = -13.9$ k cal,

K_1 at 298 K = 8.8 ; K_2 at 273 K = ?.

We know that :

$$\log K_2 - \log K_1 = \frac{-\Delta H^\circ}{2.303\,R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\log K_2 - \log 8.8 = \frac{-(-13.9 \times 1000\text{ cal})}{2.303 \times 2\text{ cal}}\left[\frac{1}{273} - \frac{1}{298}\right]$$

$$\log K_2 - 0.9444 = \frac{13900}{2.303 \times 2} \times \left[\frac{298-273}{273 \times 298}\right]$$

$$= \frac{13900 \times 25}{2.303 \times 2 \times 273 \times 298}$$

$$\log K_2 - 0.9444 = +0.9274\ ;$$

$$\log K_2 = +0.9274 + 0.9444 = 1.8718$$

$\therefore$ K_2 = antilog 1.8718 = **74.4** **Ans.**

EXAMPLE 60. *On mixing NO_2 (g) with NO (g), following equilibria was obtained.*

(*i*) $NO + NO_2 \rightleftharpoons N_2O_3$

(*ii*) $2NO_2 \rightleftharpoons N_2O_4$ $[K_p = 6.8\ (atm)^{-}]$

On mixing NO and NO_2 in the ratio 1 : 2, the total pressure was 5.05 atm and the partial pressure of N_2O_4 was 1.7 atm. Calculate

(*a*) *Partial pressure of NO (g) at equilibrium*

(*b*) *Calculate K_p for the reaction (i).*

SOLUTION. For reaction (*ii*)

$$2\,NO_2 \rightleftharpoons N_2O_4\ ;\ K_p = 6.8\text{ atm}^{-}$$

$$\therefore \quad K_p = \frac{p_{N_2O_4}}{p_{(NO_2)^2}}\ ;\ 6.8\text{ atm}^{-} = \frac{1.7\text{ atm}}{p_{(NO_2)^2}}$$

$$\therefore \quad p_{(NO_2)^2} = \frac{1.7\text{ atm}}{6.8\text{ atm}^{-}} = 0.25\text{ atm}^2\ ;$$

$$p_{NO_2} = (0.25\text{ atm}^2)^{1/2} = \mathbf{0.5\ atm.}$$

For reaction (*i*)

	NO (g) +	NO_2 (g) $\rightleftharpoons$	N_2O_3 (g)
(*i*) Pressure at start	P	2 p	0
(*ii*) Change by reaction	– *x*	– *x* – (2 × 1.7) = – *x* – 3.4	*x*
(*iii*) Pressure at equilibrium	P – *x*	2 P – *x* – 3.4 (= 0.5)	*x*

Since 3.4 atm of NO_2 are used for equilibrium, 2P – *x* – 3.4 will be equal to 0.5 atm. Thus:

Total pressure at equilibrium

$$= p_{NO} + p_{NO_2} + p_{N_2O_3} + p_{N_2O_4}$$

Or $5.05 = P - x + 0.5 + x + 1.7;$

$5.05 = P + 2.2\ ;\ P = 5.05 - 2.2 = 2.85$ atm.

But $2\,P - x - 3.4 = 0.5$.

So, $(2 \times 2.85) - x - 3.4 = 0.5\ ;$

$5.70 - x - 3.4 = 0.5$

Or $x = 5.7 - 3.4 - 0.5 = \mathbf{1.8} = \boldsymbol{p_{N_2O_3}}$

Hence $p_{NO} = P - x = 2.85 - 1.8 =$ **1.05 atm**

For reaction (*i*) :

$$K_p = \frac{p_{N_2O_3}}{p_{NO} \times p_{NO_2}} = \frac{1.8}{1.05 \times 0.5} = \mathbf{3.43\ atm^{-}}$$

23.16 COMPARISON OF THERMAL DECOMPOSITION AND THERMAL DISSOCIATION

Thermal decomposition. Substances like PCl_5, N_2O_4, NH_4Cl, HI when heated in a closed vessel, form two or more simple molecules. When such a reaction is cooled, the original substance is formed. Such a process is called **thermal dissociation.** For example :

$$PCl_5 \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} PCl_3 + Cl_2\ ;\ N_2O_4 \rightleftharpoons 2NO_2$$

$$NH_4Cl \rightleftharpoons NH_3 + HCl\ ;\ 2HI \rightleftharpoons H_2 + I_2$$

Thermal decomposition can be reversible (shown above) or irreversible. For example :

$$2\,KClO_3 \longrightarrow 2\,KCl + 3O_2 \text{ (irreversible).}$$

When the products formed on heating in a closed vessel do not form the original substance on cooling, the process is called **thermal decomposition.**

Degree of dissociation. It is the ratio of number of mol dissociated and total number of mol originally present. Mathematically :

Degree of dissociation,

$$\alpha = \frac{\text{Number of mol or molecules dissociated}}{\text{Total number of mol or molecules taken}}$$

$$= \frac{D-d}{d\,(n-1)}$$

Where D = Vapour density of a substance when there is no dissociation.

$= \frac{1}{2} \times$ Mol. mass of substance.

d = Vapour density of the substance at any temperature at which degree of dissociation is α.

Number of mol of products after dissociation = n

EXAMPLE 61. *The vapour density of nitrogen peroxide at 373 K and under 760 mm pressure is 25.67. Calculate the percentage of NO_2 molecules in the gas at this temperature. (At. mass, N = 14, O = 16).*

SOLUTION. Molar mass of nitrogen peroxide, N_2O_4= (2 × 14) + (4 × 16) = 28 + 64 = 92

$\therefore$ Vapour density (D) of N_2O_4

$$= \frac{1}{2} \times \text{mol. mass} = \frac{1}{2} \times 92 = 46.$$

For $\quad N_2O_4 \rightleftharpoons 2NO_2$

$\qquad\qquad$ 2 mol, $\quad n = 2$

Vapour density (d) of N_2O_4 at 373 K = 25.67

But $\qquad \alpha = \dfrac{D-d}{d\,(n-1)} = \dfrac{46-25.67}{25.67\,(2-1)}$

$$= \frac{20.33}{25.67} = 0.792$$

Let us consider the dissociation of N_2O_4.

	N_2O_4	$\rightleftharpoons 2NO_2$
Initial conc.	1	0
Conc. at equilibrium	$1-\alpha$	2α

Here volume is constant. Since in the reaction, number of mol of reactants and products differ, total number of mol of reaction are taken.

Total number of mol

$$= 1 - \alpha + 2\alpha = 1 + \alpha$$

$\therefore \qquad [NO_2] = \dfrac{2\alpha}{1+\alpha}$ and % of NO_2 in the mixture

$$= \frac{2\alpha}{1+\alpha} \times 100.$$

Since $\qquad \alpha = 0.792,$

$$\% \text{ of } NO_2 = \frac{2 \times 0.792}{1+0.792} \times 100 = \frac{1.584}{1.792} \times 100$$

$$= 88.4\ \%$$ **Ans.**

23.17 ORGANIC ACID + ALCOHOL $\rightleftharpoons$ ESTER + WATER

Type. Calculation of equilibrium constant for reactions involving homogenous liquid systems. In order to understand it, consider the following reaction.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O \ldots(i)$$

Initial conc.	a	b	0	0
Conc. at equilibrium	$a-x$	$b-x$	x	x

Let $\qquad$ V = Total volume of system in litre.

Then :

$$[CH_3COOH] = \frac{a-x}{V} \text{ mol L}^- ; [C_2H_5OH] = \frac{b-x}{V} \text{ mol L}^-$$

$$[CH_3COOC_2H_5] = \frac{x}{V} \text{ mol L}^- ; [H_2O] = \frac{x}{V} \text{ mol L}^-$$

Applying law of chemical equilibrium to reaction (i), we have :

$$K_C = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{\frac{x}{V} \text{ mol L}^- \times \frac{x}{V} \text{ mol L}^-}{\frac{a-x}{V} \text{ mol L}^- \times \frac{b-x}{V} \text{ mol L}^-}$$

$$K_c = \frac{x^2}{(a-x)\,(b-x)}$$

Note I. In order to solve such type of problems, an entry is made on following three lines (given in table) under each substance in the balanced equation. 'n' in the table represents amount of the substance.

Acid, e.g., + Alcohol, e.g. $\quad$ Ester, e.g., $\quad$ + Water

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(i) n mol at start

(ii) Change by reaction

(iii) n mol at equilibrium.

II. Volume (V) of the vessel is not considered because $\Delta n = 0$ in the balanced equation; Δn = number of mol of products (–) number of mol of reactants.

Type. To find the value of equilibrium constant, K for the reaction acid + alcohol $\rightleftharpoons$ ester + water, use the relation :

$$K = \frac{[\text{ester}]\,[\text{water}]}{[\text{acid}]\,[\text{alcohol}]}$$

EXAMPLE 62. *When one mol of acetic acid is mixed with one mol of ethyl alcohol at room temperature, the equilibrium mixture contains 2/3 mol each of ester and water. Calculate the value of equilibrium constant.*

SOLUTION.

CH_3COOH = 1 mol ; C_2H_5OH = 1 mol.

Reaction :

CH_3COOH +	C_2H_5OH $\rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
(i) n mol at start			
1	1	0	0
(ii) Change for reaction			
$-\frac{2}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{2}{3}$
(iii) n mol at equilibrium			
$1-\frac{2}{3}=\frac{1}{3}$	$1-\frac{2}{3}=\frac{1}{3}$	$\frac{2}{3}$	$\frac{2}{3}$

Applying law of chemical equilibrium to the given reaction, we have :

$$K = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4$$

Note. Volume is not considered here because $\Delta n = 0$.

EXAMPLE 63. *When ethanol is mixed with ethanoic acid in equivalent proportion, following equilibrium takes place*

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

and two third of the ethanol and ethanoic acid get consumed. Calculate the amount of ester formed in equilibrium mixture if we start with 115g ethanol and 150 g ethanoic acid.

(MLNR, 1981)

SOLUTION. (*a*)

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(*i*) n mol at start

$1 \qquad 1 \qquad 0 \qquad 0$

(*ii*) Change by reaction

$-\frac{2}{3} \qquad -\frac{2}{3} \qquad \frac{2}{3} \qquad \frac{2}{3}$

(*iii*) n mol at equilibrium

$1-\frac{2}{3}=\frac{1}{3} \qquad 1-\frac{2}{3}=\frac{1}{3} \qquad \frac{2}{3} \qquad \frac{2}{3}$

Since $\Delta n = 0$, volume is not considered.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} =$$

$$= \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4$$

(*b*) Wt. of ethanol

$= 115$ g ;

g. mol. wt. of C_2H_5OH

$= (2 \times 12) + (5 \times 1) + 16 + 1 = 46$ g

$\therefore$ no. of mol of ethanol $= \frac{115}{46} = 2.5$

Wt. of ethanoic acid = 150 g ;

g. mol. wt. of CH_3COOH

$= 12 + (3 \times 1) + 12 + (2 \times 16) + 1$

$= 60$ g

$\therefore$ no. of mol of ethanoic acid $= \frac{150}{60} = 2.5$ mol

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(*i*) n mol at start

$2.5 \qquad 2.5 \qquad 0 \qquad 0$

(*ii*) Change by reaction

$-x \qquad -x \qquad x \qquad x$

(*iii*) n mol at equilibrium

$2.5-x \qquad 2.5-x \qquad x \qquad x$

Since $\Delta n = 0$, Volume is not considered.

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]}$$

$$= \frac{x \times x}{(2.5-x)(2.5-x)} = \frac{x^2}{(2.5-x)^2}$$

Or $\quad 4 = \frac{x^2}{(2.5-x)^2}$

Taking square root of both sides, we get :

$$2 = \frac{x}{2.5-x} \,;\, 2(2.5-x) = x \,;\, 5 - 2x = x$$

Or $\quad x + 2x = 5; 3x = 5$;

$\therefore \quad x = \frac{5}{3} = 1.67$

g. mol. wt. of ester, $CH_3COOC_2H_5 = 12 + (3 \times 1) + 12 + (2 \times 16) + (2 \times 12) + (5 \times 1) = 88$ g

$\therefore$ Amount of ester, ethyl acetate

$= 88 \times 1.67 =$ **146.96 g** **Ans.**

EXAMPLE 64. *The equilibrium constant for the reaction* $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ *is 4. What will be the composition of the equilibrium mixture if one mol of acid is taken along with 8 mol of alcohol ? Equilibrium constant, K = 4*

SOLUTION. Consider the following reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(*i*) n at start

1mol $\qquad$ 8 mol $\qquad 0 \qquad 0$

(*ii*) Change for reaction

$-x \qquad -x \qquad x \qquad x$

(*iii*) n at equilibrium

$1-x \qquad 8-x \qquad x \qquad x$

Applying law of chemical equilibrium, we have :

$$K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$4 = \frac{x \times x}{(1-x)(8-x)} = \frac{x^2}{8 - x - 8x + x^2}$$

$$= \frac{x^2}{x^2 - 9x + 8}$$

$$4x^2 - 36x + 32 = x^2 \quad \text{or} \quad 3x^2 - 36x + 32 = 0$$

$$\therefore \quad x = \frac{-(-36) \pm \sqrt{(-36)^2 - 4(3 \times 32)}}{2 \times 3}$$

$$= \frac{+36 \pm \sqrt{1296 - 384}}{6}$$

$$= \frac{+36 \pm \sqrt{912}}{6} = \frac{+36 \pm 30.2}{6}$$

$$= \frac{66.2}{6} \text{ (when added)}$$

or $\frac{5.8}{6}$ (when subtracted) = 11.03 or 0.967;

$x = 0.967$ respectively.

$$\left[\because x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ for } ax^2 + bx + c = 0\right]$$

x is not equal to 11.03 because minimum number of mol in the reaction is 1 (of CH_3COOH) and x cannot be more than 1.

$\therefore$ $[CH_3COOH] = 1 - x = 1 - 0.967 = \mathbf{0.033}$ **g mol Ans.**

$[C_2H_5OH] = 8 - x = 8 - 0.967 = \mathbf{7.033}$ **g mol Ans.**

$[CH_3COOC_2H_5] = [H_2O] = x = \mathbf{0.967}$ **g mol** **Ans.**

Type. When number of mol of products are also given, add these to x to get 'n' at equilibrium

EXAMPLE 65. *For the following reaction, the value of equilibrium constant is 4.0.*

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Determine the amount of ester present at equilibrium when 1 mol of alcohol reacts with 1 mol of acid in presence of 1 mol of water.

SOLUTION. Consider the reaction.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(i) n at start

$$\begin{array}{llll} 1 \text{ mol} & 1 \text{ mol} & 0 & 1 \end{array}$$

(ii) Change for reaction

$$\begin{array}{llll} -x & -x & x & x \end{array}$$

(iii) n at equilibrium

$$\begin{array}{llll} 1-x & 1-x & x & 1+x \end{array}$$

$$\therefore \quad K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{x(1+x)}{(1-x)(1-x)}$$

$$4 = \frac{x + x^2}{1 + x^2 - 2x};$$

$$4 + 4x^2 - 8x = x + x^2;$$

$$4x^2 - x^2 - 8x - x + 4 = 0$$

or $3x^2 - 9x + 4 = 0$

$$\therefore \quad x = \frac{-(-9) \pm \sqrt{(-9)^2 - 4(3 \times 4)}}{2 \times 3}$$

$$= \frac{9 \pm \sqrt{81 - 48}}{6} = \frac{9 \pm \sqrt{33}}{6}$$

$$x = \frac{9 + 5.74}{6} = 2.45$$

$$\text{or } x = \frac{9 - 5.74}{6} = 0.54.$$

$$\left[\because x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ for } ax^2 + bx + c = 0\right]$$

So, $x = 0.54$ as the second value 2.45 is not admissible.

EXAMPLE 66. *In an experiment, starting with 1 mol of ethyl alcohol, 1 mol of acetic acid and 1 mol of water at 100°C, the equilibrium mixture on analysis shows that 54.3 % of the acid esterified. Calculate the equilibrium constant for this reaction.*

(Roorkee, 1982)

SOLUTION. Reaction

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(i) n at start

$$\begin{array}{llll} 1 \text{ mol} & 1\text{mol} & 0 & 1 \end{array}$$

(ii) Change for reaction

$$\begin{array}{llll} \frac{-54.3}{100} & \frac{-54.3}{100} & \frac{+54.3}{100} & 1+\frac{+54.3}{100} \\ = -0.543 & = -0.543 & = +0.543 & = +1.543 \end{array}$$

(iii) n at equilibrium

$$\begin{array}{llll} 1-0.543 & 1-0.543 & 0.543 & 1.543 \\ = 0.457 & = 0.457 & & \end{array}$$

$$\therefore \quad K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{0.543 \times 1.543}{0.457 \times 0.457}$$

$K = \mathbf{4.01}$ **Ans.**

EXAMPLE 67. *The equilibrium constant for the reaction*

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is 4.0. How much ester will be present in the equilibrium mixture if we start with 240 g of acetic acid and 138 g of ethyl alcohol.

SOLUTION. (i) g. mol. wt. of $CH_3COOH = 12 + (3 \times 1) + 12 + 2(16) + 1 = 60$ g

wt. of $CH_3COOH = 240$ g ;

no. of mol of $CH_3COOH = \frac{240}{60} = 4$ mol

(ii) g. mol. wt. of

$C_2H_5OH = (2 \times 12) + (5 \times 1) + 16 + 1 = 46$ g

wt. of $C_2H_5OH = 138$ g ;

no. of mol of $C_2H_5OH = \frac{138}{46} = 3$ mol

Consider the reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(i) n at start

$$\begin{array}{llll} 4 \text{ mol} & 3 \text{ mol} & 0 & 0 \end{array}$$

(ii) Change for reaction

$$\begin{array}{llll} -x & -x & x & x \end{array}$$

(iii) n at equilibrium

$$\begin{array}{llll} 4-x & 3-x & x & x \end{array}$$

$$\therefore \quad K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$4 = \frac{x \times x}{(4-x)(3-x)} \quad ; \quad 4 = \frac{x^2}{12 - 7x + x^2};$$

$$48 - 28x + 4x^2 = x^2$$

Or $3x^2 - 28x + 48 = 0$

$$x = \frac{-(-28) \pm \sqrt{(-28)^2 - 4\,(3 \times 48)}}{2 \times 3} s$$

$$\left[\because x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ for } ax^2 + bx + c = 0\right]$$

$$= \frac{28 \pm \sqrt{784 - 576}}{6}$$

$$= \frac{28 \pm \sqrt{208}}{6}$$

$$= \frac{28 \pm 14.4}{6} = \frac{42.6}{6} \text{ (when added) or}$$

$\frac{13.6}{6}$ (when subtracted) = 7.06 or 2.26 respectively.

So, $x = 2.26$ mol because second value is not permissible.

g. mol. wt. of ester,

$$CH_3COOC_2H_5 = 12 + (3 \times 1) + 12 + 2\,(16) + (2 \times 12) + (5 \times 1)$$

$$= 12 + 3 + 12 + 32 + 24 + 5 = 88 \text{ g}$$

$\therefore$ Wt. of ester = 2.26 × 88 = **198.88 g** **Ans.**

EXAMPLE 68. *When acetic acid is mixed with ethyl alcohol in equal proportions, 67 % are converted into ethyl acetate ester. Calculate the amount of ester formed when 2 mol of acetic acid is heated with 1 mol of ethyl alcohol.*

SOLUTION. Consider the following reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
(*i*) *n* at start	100	100	0	0
(*ii*) Change for reaction	– 67	– 67	67	67
(*iii*) *n* at equilibrium	100 – 67 = 33	100 – 67 = 33	67	67

$$\therefore \quad K = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{67 \times 67}{33 \times 33} \text{Ă } 4$$

Again consider the reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
(*i*) *n* at start	2 mol	1 mol	0	0
(*ii*) Change for reaction	$-x$	$-x$	x	x
(*iii*) *n* at equilibrium	$2-x$	$1-x$	x	x

$$\therefore \quad K = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$4 = \frac{x \times x}{(2-x)(1-x)} \quad ; \quad 4 = \frac{x^2}{2 - 3x + x^2}$$

$$8 - 12x + 4x^2 = x^2 \quad ; \quad 3x^2 - 12x + 8 = 0$$

$$\therefore \quad x = \frac{-(-12) \pm \sqrt{(-12)^2 - 4\,(3 \times 8)}}{2 \times 3}$$

$$\left[\because x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \text{ for } ax^2 + bx + c = 0\right]$$

$$= \frac{12 \pm \sqrt{144 - 98}}{6} = \frac{12 \pm \sqrt{46}}{6}$$

$$= \frac{12 \pm 6.78}{6}$$

$$= \frac{18.78}{6} \text{ (on addition) or } \frac{5.22}{6} \text{ (on subtraction)}$$

$$= 3.13 \text{ or } 0.87 \text{ respectively.}$$

So, $x = 0.87$ mol because second value is not permissible.

$\therefore$ Amount of ester formed = 0.87 mol.

Type: For problems involving ΔG, RT and equilibrium constant *K*, Use (*i*) $\Delta G^0_f = \Delta G^0_f \text{ (products)} - \Delta G^0_f \text{(reactants)}$ (*ii*) $\Delta G^0 = -2.303\ RT \log K$.

EXAMPLE 69. *Calculate the amount of ester formed when 0.4 mol of n – butyric acid is mixed with 2 mol of ethyl alcohol and allowed to come to equilibrium at 298 K. Given : standard free energies of formation of n-butyric acid, ethyl alcohol, ethyl n-butyrate and water are – 91.5 k. cal, – 41.63 k. cal, –76.0 k. cal and – 56.69 k. cal respectively.*

SOLUTION. Given reaction :

$$CH_3CH_2CH_2COOH + C_2H_5OH \rightleftharpoons CH_3CH_2CH_2COOC_2H_5 + H_2O$$

	$CH_3CH_2CH_2COOH$	C_2H_5OH	$CH_3CH_2CH_2COOC_2H_5$	H_2O
(*i*) *n* at start	0.4 mol	2 mol	0	0
(*ii*) Change for reaction	$-x$	$-x$	$+x$	$+x$
(*iii*) *n* at equilibrium	$0.4-x$	$2-x$	x	x
(*iv*) $\Delta G_f°$ (k. cal)	– 91.5	– 41.63	– 76.0	– 56.69

(*a*) $\Delta G_f° = \Delta G_f° \text{ (Products)} - \Delta G_f° \text{ (reactants)}$

$$= (-76.0 - 56.69) - (-91.5 - 41.63)$$

$$= -132.69 + 133.13$$

$$= 0.44 \text{ k. cal}$$

(*b*) $\Delta G_f° = -2.303\ RT \log K$

$$0.44 = -2.303 \times \frac{1.987}{1000} \times 298 \times \log K$$

$$\left[\because R = \frac{1.987}{1000}\text{ k cal}\right.$$

$$\log K = -\frac{0.44 \times 1000}{2.303 \times 1.987 \times 2.98} = -0.323$$

$$\therefore \quad K = \text{Antilog}\,(-0.323)$$

$$= \text{antilog} -1 + 1 - 0.323 = \bar{1}.677 = 0.48$$

Also, $$K = \frac{[CH_3CH_2CH_2COOC_2H_5]\,[H_2O]}{[CH_3CH_2CH_2COOH]\,[C_2H_5OH]}$$

Or $$0.48 = \frac{x \times x}{(0.4 - x)\,(2 - x)};$$

$$0.48 = \frac{x^2}{0.8 - 2.4\,x + x^2};$$

$$0.384 - 1.152x + 0.48x^2 = x^2$$

$$\therefore x^2 - 0.48\,x^2 + 1.152\,x - 0.384 = 0\,;$$

$$0.52\,x^2 + 1.152\,x - 0.384 = 0$$

$$\therefore \quad x = \frac{-1.152 \pm \sqrt{(1.152)^2 - 4\,(0.52 \times -0.384)}}{2 \times 0.52}$$

$$= \frac{-1.152 \pm \sqrt{1.33 + 0.799}}{1.04}$$

$$= \frac{-1.152 \pm \sqrt{2.129}}{1.04}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4\,ac}}{2\,a}\right]$$

$$= \frac{-1.152 \pm 1.459}{1.04} = 0.295 \text{ mol}$$

Amount of ester ($CH_3CH_2CH_2COOC_2H_5$) formed = **0.295 mol.** **Ans.**

Type. To calculate active masses, calculate the number of mol (n) of substances concerned by using the relation : n = wt. of substance/mol. wt. of the substance.

Active mass = *n*/volume in litre

Example 70. *4.0 g H_2 and 128 g HI were taken in a 2 litre container at 400°C. Calculate their active masses.* **(UP 1980, 1984)**

Solution. (*a*)

Wt. of H_2 = 4.0 g ; g. mol. wt. of H_2 = 2 × 1 = 2g

∴ no. of mol of H_2 = 4/2 = 2

(*b*) Wt. of HI = 128 g ; g. mol. wt. of HI = 1 + 127 = 128 g

∴ no. of mol of HI = 128/128 = 1; Volume of container = 2 L

(*c*) Active mass of

$$H_2 = \frac{\text{no. of mol of } H_2}{\text{Volume in litre}} = \frac{2}{2}$$

= **1 g mol L^{-}** **Ans.**

Active mass of

$$HI = \frac{\text{no. of mol of HI}}{\text{Volume in litre}} = \frac{1}{2}$$

= **0.5 g mol L^{-}** **Ans.**

Type. To know whether equilibrium has reached or not, use the concept :

(*a*) If the value of Q (concentration quotient) is **less** than K (equilibrium constant), the equilibrium has not been reached, and the reaction will proceed in the forward direction.

(*b*) If the value of Q is nearly equal or equal to K, the equilibrium has reached.

(*c*) If Q >> K, the equilibrium has not been reached and the reaction will proceed in the backward direction.

Example 71. *Following two experiments were performed. Predict, whether in these experiments, the equilibrium has reached or not.*

(*a*) *When 1 mol of acetic acid is treated with 0.5 mol of ethyl alcohol, 0.214 mol of ethyl acetate is formed at constant temperature, 298 K. (K = 4).*

(*b*) *When 1 mol of acetic acid is treated with 0.180 mol of ethyl alcohol, 0.170 mol of ethyl acetate is formed after sometime. (K = 4)*

Solution. Given reaction :

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(1) First-Case

(*i*) n mol at start

1.0 mol 0.5 mol 0 0

(*ii*) Change by reaction

− 0.214 mol − 0.214 mol + 0.214 mol + 0.214 mol

(*iii*) n mol at equilibrium

1 − 0.214 = 0.786 mol 0.5 − 0.214 = 0.286 mol 0.214 mol 0.214 mol

∴ Concentration quotient,

$$Q = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

Or $$Q = \frac{0.214 \times 0.214}{0.786 \times 0.286} = 0.2\,;\; K = 4 \text{ (given)}$$

Since the value of Q is less than K, the equilibrium has not reached.

(2) **Second Case.**

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(*i*) n mol at start

1.0 0.18 0 0

(*ii*) Change by reaction

− 0.17 − 0.17 + 0.17 +0.17

(*iii*) n mol at equilibrium

1 − 0.17 = 0.83 0.18 − 0.17 = 0.01 + 0.17 +0.17

$\therefore$ Concentration Quotient,

$$Q = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$$

$$= \frac{0.17 \times 0.17}{0.83 \times 0.01} \simeq 3.5$$

But $K = 4$ (given).

Since the value of Q is very near to the value of K, the equilibrium has reached.

23.18 METHOD TO FIND DEGREE OF DISSOCIATION (α) FROM VAPOUR DENSITY (V.D.) MEASUREMENT OF A GAS

This method is applicable for those reactions only which have no solution but have atleast one gas.

EXAMPLE 72. *The vapour density of PCl_5 was found to be 65 at a certain temperature. Calculate the degree of dissociation at this temperature.*

SOLUTION. Mol. mass of PCl_5

$$= 31 + 5\,(35.5) = 31 + 177.5 = 208.5$$

$\therefore$ Vapour density (D) of PCl_5

$$= \frac{1}{2} \times 208.5 = 104.25$$

For PCl_5, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

1 mol 1 mol] ; $n = 1 + 1 = 2$

Vapour density (d) at a given temperature = $d = 65$

But $\alpha = \dfrac{D-d}{d\,(n-1)}$ **Or** $\alpha = \dfrac{104.25 - 65}{65\,(2-1)}$

$$\alpha = \frac{39.25}{65} = 0.603$$

$= 0.603 \times 100 =$ **60.3 %** **Ans.**

EXAMPLE 73. *3.6 g of PCl_5 volatilises completely at 200 °C and the volume occupied by the vapour is 1 litre under a pressure of 1 atmosphere. A partial dissociation of PCl_5 also takes place giving PCl_3 and Cl_2. Calculate the degree of dissociation of PCl_5 at this temperature. (At. wt. P = 31 ; Cl = 35.5)*

SOLUTION. $P_1 = 1$ atm ; $V_1 = 1$ L ;

$T_1 = 200 + 273 = 473$ K

At N.T. P. ; $P_2 = 1$ atm ; $V_2 = ?$ $T_2 = 273$ K

Applying gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad V_2 = \frac{P_1 V_1 T_2}{P_2 T_1}$$

$$\therefore \quad V_2 = \frac{1\,\text{atm} \times 1\,\text{L} \times 273\,\text{K}}{1\,\text{atm} \times 473\,\text{K}} = 0.577\ \text{L}$$

0.577 L of gaseous mixture weighs = 3.6 g

11.2 L of gaseous mixture weigh

$$= \frac{3.6}{0.577} \times 11.2 = 69.9\ \text{g}$$

$\therefore$ Density (d) of mixture = 69.9

Mol. mass of $PCl_5 = 31 + 5(35.5) = 31 + 177.5 = 208.5$

$$\left[\begin{array}{c} \because \text{g. mol. mass of a gas} \\ \text{occupies volume} = 22.4\ \text{L;} \\ V.D = \frac{1}{2} \times \text{mol. mass ;} \\ \text{Volume occupied} \\ = \frac{1}{2} \times 22.4 = 11.2\ \text{L} \end{array}\right]$$

$\therefore$ Vapour density (D) of $PCl_5 = \dfrac{1}{2} \times 208.5 = 104.25.$

For $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

1 mol 1 mol] $\therefore n = 1 + 1 = 2$

But $\alpha = \dfrac{D-d}{d\,(n-1)}$

$$\therefore \quad \alpha = \frac{104.25 - 69.9}{69.9\,(2-1)} = \frac{34.35}{69.9}$$

$= 0.49 = 0.49 \times 100 =$ **49 %.** **Ans.**

EXAMPLE 74. *At one atmospheric pressure and 127°C, the degree of dissociation of PCl_5 ($PCl_5 \rightleftharpoons PCl_3 + Cl_2$) is 0.4. Assuming ideal behaviour of all the gases, calculate the equilibrium constant at the same temperature and pressure.* **(I.I.T. 1998)**

SOLUTION.	PCl_5	$\rightleftharpoons$	PCl_3	$+ Cl_2$
(*i*) *n* mol at start	1		0	0
(*ii*) Change by reaction	$-\alpha$		α	α
(*iii*) *n* mol at equilibrium	$1-\alpha$		α	α

$\therefore$ Total number of mol $= 1 - \alpha + \alpha + \alpha = 1 + \alpha$

g. mol. wt. of $PCl_5 = 31 + (5 \times 35.5) = 31 + 177.5$

$= 208.5$

$\therefore$ Before dissociation of PCl_5, V.D. of PCl_5

$=$ Mol. Wt./2 = 208.5/2 = 104.25.

Let $d =$ density at equilibrium.

But $\alpha = \dfrac{D-d}{d\,(n-1)}.$

But $\alpha = 0.4$ and $n = 1$ mol PCl_3 + 1 mol Cl_2

$= 2$ mol

$$\therefore \quad 0.4 = \frac{104.25 - d}{d \times 1}\ ;$$

$$0.4\,d = 104.25 - d;$$

$$d + 0.4\,d = 104.25 \ \text{Or}\ 1.4\,d = 104.25\ ;$$

$$\therefore \quad \boldsymbol{d} = \frac{104.25}{1.4} = \mathbf{74.46}\ ;$$

$$T = 127 + 273 = 400\ \text{K}$$

$\therefore$ Mol. wt. of PCl_5 at 127°C = $2 \times d = 2 \times 74.46$

$= 148.92$ g mol^{-}

But $PV = nRT$ or

$$PV = \frac{W}{\text{mol. wt}} \times RT \quad \text{[Ideal gas equation]}$$

Or $\dfrac{W}{V} = \dfrac{P \times \text{mol. wt}}{RT}$

or $$\text{Density} = \frac{1 \text{ atm} \times 148.92 \text{ g mol}^{-}}{0.082 \text{ L atm K}^{-} \text{ mol}^{-} \times 400 \text{ K}}$$

∴ Density = **4.54 g L^{-}** **Ans.**

Example 75. *At 523 K, PCl_5 gets dissociated to 80%. Calculate the vapour density of PCl_5 at 523 K.*

Solution.

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
(*i*) *n* mol at start	100	0	0
(*ii*) Change by reaction	– 80	80	80
(*iii*) *n* mol at equilibrium	100 – 80 = 20	80	80

Total number of mol = 20 + 80 + 80 = 180

Mol. wt. of PCl_5 = 31 + (5 × 35.5) = 31 + 177.5 = 208.5

Density (**D**) of undissociated PCl_5 = Mol. wt/2 = 208.5/2 = **104.25**

We know that :

Densities are inversely proportional to molar volume while molar volume is directly proportional to molar concentration.

$$\therefore \quad D \propto \frac{1}{100} \qquad ...(1)$$

Density (d) at equilibrium of all

$$\text{mol} \propto \frac{1}{180} \qquad ... (2)$$

Dividing (1) and (2), we get :

$$\frac{D}{d} = \frac{180}{100}$$

Or $$d = \frac{D \times 100}{180} = \frac{104.25 \times 100}{180} = \mathbf{57.9}$$ **Ans.**

23.19 DECOMPOSITION OF PCl_5

Example 76. *The equilibrium constant for the reaction :*

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

is 0.041 at 250° C. Calculate the number of mol of Cl_2 produced at equilibrium when 1.0 mol of PCl_5 is heated in a 10 L vessel at 250°C.

Solution. Reaction :

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
(*i*) *n* mol L^{-} at start	$\frac{1 \text{ mol}}{10 \text{ L}}$ = 0.1 mol L^{-}	0	0
(*ii*) Change by reaction	– *x*	*x*	*x*
(*iii*) *n* mol at equilibrium	0.1 – *x*	*x*	*x*

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]};$$

$$0.041 = \frac{x \times x}{0.1 - x} = \frac{x^2}{0.1 - x}$$

Or $0.041(0.1 - x) = x^2$; $0.0041 - 0.041\,x = x^2$

$\therefore \quad x^2 + 0.041x + 0.0041 = 0$;

$$x = \frac{-0.041 \pm \sqrt{(0.041)^2 - 4\,(1 \times 0.0041)}}{2 \times 1}$$

Or $$x = \frac{-0.041 \pm \sqrt{1.681 \times 10^{-3} - 0.0164}}{2}$$

$$\left[\therefore \text{ for } ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$= \frac{-0.041 \pm \sqrt{0.001681 - 0.0164}}{2}$$

$$= \frac{-0.041 + \sqrt{0.0148}}{2}$$

$$= \frac{-0.041 + 0.122}{2} \text{ (on addition)}$$

= 0.0405 mol L^{-}

= 0.0405 mol L^{-} × 10 L;

x = **0.405 mol** **Ans.**

Example 77. *In an experiment, PCl_5 was added into an evacuated chamber. The equilibrium came into being at 2 atm and 250°C. The equilibrium gas contains 40.5 % Cl_2 by volume.*

(*a*) *Calculate the partial pressures of the gaseous components at equilibrium.*

(*b*) *Calculate K_p*

(*c*) *Suppose the gaseous mixture is expanded to 0.2 atm at 250°C, then find :*

  (*i*) *% age of PCl_5 that would be dissociated at equilibrium.*

  (*ii*) *% age by volume of Cl_2 in the equilibrium gaseous mixture.*

  (*iii*) *Partial pressure of Cl_2 in the equilibrium mixture.*

Solution.

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
% age by volume or mol at equilibrium	100 – (40.7 + 40.7) = 18.6	40.7	40.7

(*a*) $$p(Cl_2) = p(PCl_3) = 2 \text{ atm} \times \frac{40.7}{100}$$

= **0.814 atm.** **Ans.**

$$p\,(PCl_5) = 2 \text{ atm} \times \frac{18.6}{100} = \mathbf{0.372 \text{ atm}}$$ **Ans.**

(*b*) $$Kp = \frac{p\,(PCl_3) \times p\,(Cl_2)}{p\,(PCl_5)}$$

$$= \frac{0.814 \text{ atm} \times 0.814 \text{ atm}}{0.372 \text{ atm}}$$

= **1.78 atm.** **Ans.**

(c) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$\therefore K_p = \frac{p\,(PCl_3) \times p\,(Cl_2)}{p\,(PCl_5)}$$

(Law of chemical equilibrium)

or $$p(\text{PCl}_5) = \frac{p\,(\text{PCl}_3)^2}{K_P} \qquad [\because p(\text{PCl}_3) = p(\text{Cl}_2)]$$

$$p(\text{PCl}_5) = \frac{p(\text{PCl}_3)^2}{0.178 \text{ atm}} = 0.562\, p(\text{PCl}_3)^2 \qquad ...(1)$$

But $p(\text{PCl}_3) + p(\text{Cl}_2) + p(\text{PCl}_5) = 0.2$;

$p(\text{PCl}_3) + p(\text{PCl}_3) + 0.562\, p(\text{PCl}_3)^2 = 0.2$

or $0.562\, p(\text{PCl}_3)^2 + 2\, p(\text{PCl}_3) - 0.2 = 0$

$[\because p(\text{PCl}_3) = p(\text{Cl}_2)]$

$$\therefore \quad p(\text{PCl}_3) = \frac{-2 \pm \sqrt{(2)^2 - 4\,(0.562 \times -0.2)}}{2 \times 0.562}$$

$$\left[\because \text{for } ax^2 + bx + c = 0, \quad x = \frac{-b \pm \sqrt{b^2 - 4\,ac}}{2\,a}\right.$$

$$= \frac{-2 \pm \sqrt{4 + 0.4496}}{1.124} = \frac{-2 \pm \sqrt{4.4496}}{1.124}$$

$$= \frac{-2 \pm 2.11}{1.124} = \frac{+0.11}{1.124} \text{ (on adding)}$$

or $$\frac{-4.11}{1.124} \text{ (on subtraction)}$$

But negative value is not possible.

So : $p(\text{PCl}_3) = \frac{+0.11}{1.124} = \mathbf{0.097}$

Thus $p(\text{PCl}_3) = p(\text{Cl}_2) = 0.097$

From equation (1), we get ; $p(\text{PCl}_5) = 0.562 \times (0.097)^2 = 5.29 \times 10^{-3}$ atm. = 0.00529 atm.

Fraction dissociated

$$= \frac{p\,(\text{PCl}_3)}{p\,(\text{PCl}_3) + p\,(\text{PCl}_5)}$$

$$= \frac{0.097}{0.097 + 0.00529} = \frac{0.097}{0.10229} = 0.948$$

Percent dissociated

= 0.948 × 100 = 94.8 %

$$\text{Mol percent Cl}_2 = \frac{p\,(\text{Cl}_2)}{p\,(\text{Cl}_2) + p\,(\text{PCl}_3) + p\,(\text{PCl}_5)} \times 100$$

$$= \frac{0.097 \times 100}{0.097 + 0.097 + 0.00529}$$

$$= \frac{0.097}{0.19929} \times 100$$

$= \mathbf{48.6\ \%\ Cl_2}$ **Ans.**

EXAMPLE 78. *A known amount of PCl_5 was heated at 523 K in a 12 litre container. At equilibrium, the container contains 0.32 mol each of Cl_2 and PCl_3 but 0.21 mol of PCl_5, for the reaction, $PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$. Calculate equilibrium constant (K) for the dissociation of PCl_5 at 523 K when concentrations are measured in 1 mol L^{-}. Also find the value of $\Delta G°$.*

SOLUTION. Volume = 12 L

Reaction	$\text{PCl}_5 \rightleftharpoons$	PCl_3 +	Cl_2
n mol L^{-} at equilibrium	$\frac{0.21}{12}$	$\frac{0.32}{12}$	$\frac{0.32}{12}$

$$\therefore \quad K = \frac{[\text{PCl}_3]\,[\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{0.32}{12} \times \frac{0.32}{12}}{\frac{0.21}{12}}$$

$$= \frac{0.32}{12} \times \frac{0.32}{12} \times \frac{12}{0.21} = 0.041$$

$\therefore \quad \mathbf{K = 0.041}$

Also, $\Delta G° = -2.303 \text{ RT} \log \text{K}$;

$\Delta G° = -2.303 \times 8.314 \text{ J K}^{-} \times 523 \text{ K} \log 0.041$

$= -10{,}014 \log 0.041$

$= (-10014) \times (-1.3872)$

$= 13891 \text{ J} \simeq \mathbf{13.9\ k\ J}$

EXAMPLE 79. *One mol of Cl_2 and 3 mol of PCl_5 are placed in a 100 litre vessel heated to 277°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation of PCl_5 and K_p for the reaction,*

$$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2 \qquad \textbf{(IIT 1984)}$$

SOLUTION. (*a*) P = 2.05 atm ; V = 100 L ;

R = 0.082 L atm (degree)$^{-}$,

T = 227 + 273 = 500 K.

But $PV = n\,RT$;

$$\boldsymbol{n} = \frac{PV}{RT} = \frac{2.05 \times 100}{0.082 \times 500} = \mathbf{5}$$

Reaction :	$\text{PCl}_5 \rightleftharpoons$	PCl_3 +	Cl_2
(*i*) n mol at start	3	0	1
(*ii*) Change by reaction	$-3\,x$	$3\,x$	$3\,x$
(*iii*) n mol at equilibrium	$3 - 3\,x$	$3\,x$	$1 + 3\,x$

∴ Total number of mol (n) at equilibrium

$= 3 - 3\,x + 3\,x + 1 + 3\,x = 3\,x + 4$

Thus $n = 3\,x + 4$ or $5 = 3\,x + 4$;

$3\,x = 1$; $x = \frac{1}{3} = 0.333.$

∴ % age of dissociation

= 0.333 × 100 = **33.3 %.**

(*b*) $$K_p = \frac{[\text{PCl}_3]\,[\text{Cl}_2]}{[\text{PCl}_5]}$$

$$= \frac{\left(\frac{3x}{3x+4} \times P\right)\left(\frac{1+3x}{3x+4} \times P\right)}{\left(\frac{3-3x}{3x+4} \times P\right)}$$

$$= \frac{3x\,(1+3x)\,P}{(3x+4)\,(3-3x)} \qquad ...(1)$$

Substituting the value of $x = \frac{1}{3}$ and P = 2.05 atm in equation (1), we get :

$$K_p = \frac{3 \times \frac{1}{3}\left(1 + 3 \times \frac{1}{3}\right) \times 2.05}{\left[\left(3 \times \frac{1}{3}\right) + 4\right]\left[3 - \left(3 \times \frac{1}{3}\right)\right]}$$

$$= \frac{4.10}{5 \times 2} = \frac{4.1}{10} = \mathbf{0.41} \qquad \textbf{Ans.}$$

EXAMPLE 80. *At 540 K, 0.1 mol of PCl_5 are heated in a 8 L flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.* **(Roorkee 1998)**

SOLUTION.

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2 ...(1)
(*i*) *n* mol at start	0.1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) n mol at equilibrium	$0.1 - x$	x	x

Total number of mol (n) = $0.1 - x + x + x = 0.1 + x$

Also, $P = 1$ atm, $V = 8$ L, $R = 0.082$ L atm K^{-} mol^{-}, $T = 540$ K

But $PV = nRT$; $P = \dfrac{nRT}{V}$;

$$1 = \frac{(0.1 + x) \times 0.082 \times 540}{8}$$

$$0.1 + x = \frac{8}{0.082 \times 540}; \quad 0.1 + x = 0.18;$$

$$x = 0.18 - 0.1 = \mathbf{0.08}$$

But $K_p = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

$$= \frac{\left(\frac{x}{0.1 + x} \times P\right)\left(\frac{x}{0.1 + x} \times P\right)}{\frac{0.1 - x}{0.1 + x} \times P}$$

$$= \frac{x^2 P}{(0.1 - x)(0.1 + x)}$$

$$K_p = \frac{x^2 P}{0.01 - x^2}$$

Substituting, $x = 0.08$, we get : $K_p = \dfrac{(0.08)^2 \times 1}{0.01 - (0.08)^2}$

$$= \frac{0.0064}{0.01 - 0.0064} = \frac{0.0064}{0.0036} = \mathbf{1.78\ atm}$$

In reaction (1),

$$\Delta n = n_P - n_R = (1 + 1) - 1 = 1$$

$\therefore$ $K_p = K_c (RT)^{\Delta n}$

Or $K_c = \dfrac{K_p}{(RT)^{\Delta n}}$

$$= \frac{1.78 \text{ atm}}{[(0.082 \text{ L atm K}^{-}\text{mol}^{-}) \times 540 \text{ K}]}$$

$\therefore$ $K_c = \mathbf{0.0401\ mol\ L^{-}}$ **Ans.**

EXAMPLE 81. *At some temperature and under a pressure of 4 atm, PCl_5 is 10 % dissociated. Calculate the pressure at which PCl_5 will be 20 % dissociated, temperature remaining same.* **(Roorkee 1996)**

SOLUTION.

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$1 - x$	x	x

Total number of mol (n)

$$= 1 - x + x + x = 1 + x$$

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{1+x} \times P\right)\left(\frac{x}{1+x} \times P\right)}{\left(\frac{1-x}{1+x} \times P\right)}$$

$$= \frac{x^2 P}{1 - x^2}$$

$$P = 4 \text{ atm}; \; x = 10\% = \frac{10}{100} = 0.1.$$

Substituting the values, we get :

$$K_p = \frac{(0.1)^2 \times 4}{1 - (0.1)^2} = \frac{0.01 \times 4}{1 - 0.01}$$

$$= \frac{0.04}{0.99} \simeq 0.04 \text{ atm.}$$

When $x = 20\% = \dfrac{20}{100} = 0.2$, $K_p = 0.04$ atm, then,

$$K_p' = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x^2 P'}{1 - x^2} = \frac{(0.2)^2 \times P'}{1 - (0.2)^2}$$

Or $0.04 = \dfrac{0.04 \times P'}{1 - 0.04} = \dfrac{0.04 \times P'}{0.96}$;

$$P' = \frac{0.96 \times 0.04}{0.04} = \mathbf{0.96\ atm}$$

EXAMPLE 82. *At 1 atmospheric pressure and 291 K, PCl_5 gets 41.7 % dissociated. Calculate equilibrium constant as well as the fraction dissociated under three atmospheric pressure.*

SOLUTION. (*a*)

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$1 - x$	x	x

$\therefore$ Total number of mol = $1 - x + x + x = 1 + x$

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\frac{x}{1+x} \times P\right)\left(\frac{x}{1+x} \times P\right)}{\left(\frac{1-x}{1+x}\right) \times P} = \frac{x^2 P}{1 - x^2}$$

Here $P = 1$ atm ; $x = 1 \times \dfrac{41.7}{100} = 0.417$

$\therefore$ $K_p = \dfrac{(0.417)^2 \times 1}{1 - (0.417)^2} = \dfrac{0.174}{1 - 0.174} = \dfrac{0.174}{0.826}$

$= 0.21$

(*b*) $P = 3 \text{ atm}$; $K_p = 0.21$; $x = ?$

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} ; \; 0.21 = \frac{x^2 P}{1-x^2} = \frac{x^2 \times 3}{1-x^2}$$

$$\therefore \; 0.21(1-x^2) = 3x^2 ; \; 0.21 - 0.21x^2 = 3x^2 ;$$

$$3x^2 + 0.21x^2 = 0.21 ;$$

$$3.21x^2 = 0.21 ; \; x^2 = \frac{0.21}{3.21} = 0.0654 ;$$

$$x = \sqrt{0.0654} \; \textbf{Or} \; x = \mathbf{0.256}$$ **Ans.**

EXAMPLE 83. *The K_p value of $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ under a total pressure of 1.5 atmosphere is 0.202. Calculate the volume percent of chlorine at equilibrium.*

SOLUTION.	$PCl_5 \rightleftharpoons$	$PCl_3 +$	Cl_2
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$1-x$	x	x

Total number of mol = $1 - x + x + x = 1 + x$;

Pressure = 1.5 atm

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\frac{x}{1+x} \times P\right)\left(\frac{x}{1+x} \times P\right)}{\left(\frac{1-x}{1+x} \times P\right)} = \frac{x^2 P}{1-x^2}$$

Or $$0.202 = \frac{x^2 \times 1.5}{1-x^2} ; \; 0.202 - 0.202x^2 = 1.5x^2 ;$$

$$1.5x^2 + 0.202x^2 = 0.202 ; \; 1.702x^2 = 0.202$$

$$\therefore \; x^2 = \frac{0.202}{1.702} = 0.119 ; \; x = \sqrt{0.119} = 0.345$$

But volume percent of Cl_2 = mol percent of Cl_2
= mol fraction of Cl_2 × 100

$$= \frac{x}{1+x} \times 100$$

∴ **Volume percent of Cl_2**

$$= \frac{0.345 \times 100}{1+0.345} = \frac{34.5}{1.345} = \mathbf{25.6\ \%}$$ **Ans.**

EXAMPLE 84. *2 g mol of PCl_5 are heated in a closed vessel of 2 litre capacity. When the equilibrium is reached, the pentachloride is 40 % dissociated into PCl_3 and Cl_2. Calculate the equilibrium constant.* **(Rajasthan, 1962, UP 1990)**

SOLUTION.	$PCl_5 \rightleftharpoons$	$PCl_3 +$	Cl_2
(*i*) *n* mol at start	2	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$\frac{2-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)} = \frac{x^2}{(2-x)V}$$

$$V = 2\text{L} ; \; x = 40\,\%\text{ of } 2\text{ mol} = \frac{2 \times 40}{100} = 0.8$$

$$\therefore \; K_p = \frac{(0.8)^2}{(2-0.8) \times 2} = \frac{0.64}{4-1.6} = \frac{0.64}{2.4} = 0.267;$$

$$K_p = \mathbf{0.267}$$ **Ans.**

EXAMPLE 85. *Given that the degree of dissociation of PCl_5 at 523 K under atmospheric pressure is 0.798. Calculate the values of K_p and K_c.* **(Allahabad,1967)**

SOLUTION. (*a*)	$PCl_5 \rightleftharpoons$	$PCl_3 +$	Cl_2
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$1-x$	x	x

Total number of mol = $1 - x + x + x = 1 + x$; Pressure = P

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\frac{x}{1+x} \times P\right)\left(\frac{x}{1+x} \times P\right)}{\left(\frac{1-x}{1+x} \times P\right)} = \frac{x^2 P}{1-x^2}$$

$$x = 0.798 ; \; P = 1 \text{ atm.}$$

$$\therefore \; K_P = \frac{(0.798)^2 \times 1}{1-(0.798)^2} = \frac{0.637}{1-0.637}$$

$$= \frac{0.637}{0.363} = 1.755 \text{ atm.}$$

(*b*) $$K_p = K_c(RT)^{\Delta n}$$

For $$\underset{1\text{ mol}}{PCl_5} \rightleftharpoons \underset{1\text{ mol}}{PCl_3} + \underset{1\text{ mol}}{Cl_2}$$

$$\Delta n = (1+1) - 1 = 1;$$

$$R = 0.0821 \text{ L atm K}^{-}\text{ mol}^{-}, \; T = 523 \text{ K}$$

$$1.755 \text{ atm} = K_c(0.0821 \text{ L atm K}^{-}\text{ mol}^{-} \times 523 \text{ K})^1$$

$$\therefore \; K_C = \frac{1.755 \text{ atm}}{0.0821 \text{ L atm K}^{-}\text{ mol}^{-} \times 523 \text{ K}}$$

$$= \mathbf{0.041\ mol\ L^{-}}$$ **Ans.**

EXAMPLE 86. *The vapour density of PCl_5 at 523 K and one atmospheric pressure is 57.9 . Calculate (i) K_p for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ reaction at 523 K (ii) Pressure at which PCl_5 is half dissociated (iii) % age dissociation when pressure is tripled. (At. wt. P = 31, Cl = 35.5).*

SOLUTION. g. mol. wt. of PCl_5 = 31 + (5 × 35.5)
= 31 + 177.5 = 208.5.

Vapour density (D) of undissociated PCl_5

$$= \frac{\text{Mol. wt.}}{2} = \frac{208.5}{2} = 104.25.$$

Observed V.D. (d) of PCl_5 at 523 K

= 57.9.

For $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

1 mol 1mol $n = 1+1 = 2$

Degree of dissociation,

$$\alpha = \frac{D-d}{d\,(n-1)} = \frac{104.25-57.9}{57.9\,(2-1)} = \frac{46.35}{57.9} = \mathbf{0.8}$$

∴ %age dissociation

= 0.8 × 100 = 80 %

(*b*)	PCl_5	$\rightleftharpoons PCl_3$	$+ Cl_2$
(*i*) *n* mol at start	1		
(*ii*) Change by reaction	– 0.8	0.8	0.8
(*iii*) *n* mol at equilibrium	1 – 0.8 = 0.2	0.8	0.8

Total number of mol = 0.2 + 0.8 + 0.8 = 1.8

$$K_p = \frac{p\,(PCl_3) \times p\,(Cl_2)}{p\,(PCl_5)}$$

$$= \frac{\left(\frac{0.8}{1.8} \times p\right)\left(\frac{0.8}{1.8} \times p\right)}{\left(\frac{0.2}{1.8} \times p\right)} = \frac{\frac{0.8 \times 1}{1.8} \times \frac{0.8 \times 1}{1.8}}{\frac{0.2}{1.8} \times 1};$$

$$K_p = 1.78 \text{ atm.}$$

(*ii*) Let pressure = *p* atm. ;

degree of dissociation, α = 0.5

or % age of dissociation = 0.5 × 100 = 50

	PCl_5	$\rightleftharpoons PCl_3$	$+ Cl_2$
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	– 0.5	0.5	0.5
(*iii*) *n* mol at equilibrium	1 – 0.5 = 0.5	0.5	0.5

Total number of mol = 0.5 + 0.5 + 0.5 = 1.5

$$K_p = \frac{p\,(PCl_3)\, p\,(Cl_2)}{p\,(PCl_5)}$$

$$= \frac{\left(\frac{0.5}{1.5} \times p\right)\left(\frac{0.5}{1.5} \times p\right)}{\left(\frac{0.5}{1.5} \times p\right)} = \frac{p}{3}$$

$$1.78 \text{ atm} = \frac{p}{3};\ p = 3 \times 1.78 = \mathbf{5.34\ atm} \qquad \textbf{Ans.}$$

(*iii*) Pressure, *p* = 3 atm ; α = degree of dissociation :

	PCl_5	$\rightleftharpoons PCl_3$	$+ Cl_2$
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	– α	α	α
(*iii*) *n* mol at equilibrium	1 – α	α	α

Total number of mol = 1 – α + α + α = 1 + α

$$K_p = \frac{p\,(PCl_3) \times p\,(Cl_2)}{p\,(PCl_5)}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha} \times p\right)\left(\frac{\alpha}{1+\alpha} \times p\right)}{\left(\frac{1-\alpha}{1+\alpha} \times p\right)} = \frac{\alpha^2 p}{1-\alpha^2}$$

$$1.78 = \frac{\alpha^2 \times 3}{1-\alpha^2};\ 1.78\,(1-\alpha^2) = 3\alpha^2\,;$$

$$1.78 - 1.78\,\alpha^2 = 3\,\alpha^2\,;\ 3\,\alpha^2 + 1.78\,\alpha^2 = 1.78\,;$$

$$4.78\,\alpha^2 = 1.78;\ \alpha = \frac{1.78}{4.78} = 0.372\,;$$

$$\alpha = \sqrt{0.372} = 0.6099$$

∴ % age dissociation

$$= 0.6099 \times 100 = \mathbf{60.99\ \%} \qquad \textbf{Ans.}$$

EXAMPLE 87. *In which of the following equilibrium, K_c and K_P are not equal ?*

(*a*) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

(*b*) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

(*c*) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(*d*) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$ **(CBSE, PMT, 2010)**

SOLUTION. K_p and K_c are related as : $K_P = K_c\,(RT)^{\Delta n(g)}$ Δn(g) = no. of mol of products — no. of mol of reactants in gaseous states. K_p will not be equal to K_c if Δn(g) is not zero. For reaction (*d*),

$$\Delta n(g) = 2 \text{ mol of } CO_2 - 1 \text{ mol of } O_2 = 1.$$

So, (*d*) is correct answer.

23.20. HETEROGENEOUS EQUILIBRIA

When the species of reactants and products in an equilibrium reaction are present in two or more phases (solid, liquid, gas, aqueous), the equilibrium is called heterogeneous equilibria.

Type. Calculation of K_p from the dissociation of

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

In such cases, the active mass (or concentration) of a solid substance is taken as unity. Thus

$$K_p = \frac{P_{CaO(s)} \times P_{CO_2\,(g)}}{P_{CaCO_3\,(s)}} = \frac{1 \times P_{CO_2}\,(g)}{1}$$

$$= P_{CO_2}\,(g)$$

EXAMPLE 88. *K_p value for the following equilibrium at 393 K*

$$M_2CO_3(s) \rightleftharpoons M_2O\,(s) + CO_2\,(g)$$

is 9.5 × 10^{-3} atm. Would 1 % CO_2 in air is sufficient to prevent any loss of M_2CO_3. How long would the partial pressure of CO_2 have to promote this reaction at 393 K?

SOLUTION. CO_2 (g) pressure of 1 % CO_2 in air $= \frac{1}{100}$ atm $= 10^{-2}$ atm.

For the reaction,

$$M_2CO_3(s) \rightleftharpoons M_2O\,(s) + CO_2(g)$$

$K_p = P_{CO_2(g)}$ because concentration of solids is taken as unity

$\therefore\ 9.5 \times 10^{-3}$ atm, $= P_{CO_2(g)}$

We know $K_p = 9.5 \times 10^{-3}$ atm and decomposition of M_2CO_3 takes place in presence of $P_{CO_2(g)}$ equal to 10^{-2} atm. Thus, practically no decomposition of M_2CO_3 takes place *i.e.*, presence of 1% CO_2 in air is sufficient to prevent any loss in mass.

From above, it is clear that $P_{CO_2(g)}$ must be less than 9.5 $\times\ 10^{-3}$ atm for the reaction to take place.

Example 89. *At 1173 K and 1273 K, the dissociation pressures of $CaCO_3$ are 790 mm and 2940 mm respectively. Calculate the heat of dissociation at this temperature range. $R = 2$ cal K^- mol^-.*

Solution.

$$CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2\,(g)$$

$K_p = p_{CO_2\,(g)}$ because

$[CaO(s)] = [CaCO_3(s)] = 1$

We know that :

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

Or

$$\Delta H = 2.303\,R\,(\log K_{p_2} - \log K_{p_1})\left[\frac{T_1\,T_2}{T_2 - T_1}\right]$$

$$= 2.303 \times 2\,\text{cal K}^{-}\text{mol}^{-}(\log 2940 - \log 790)\left(\frac{1173 \times 1273\ \text{K}^2}{1273 - 1173\ \text{K}}\right)$$

$$= 4.606\ \text{cal K}^{-}\ \text{mol}^{-}\,(3.4683 - 2.8976)\left(\frac{1173 \times 1273\ \text{K}}{100}\right)$$

$$= \frac{4.606\ \text{cal mol}^{-} \times 0.5707 \times 1173 \times 1273}{100}$$

$= 39252$ cal

= 39.252 K cal mol⁻ Ans.

Example 90. *The partial pressure of CO_2 obtained from the dissociation of $CaCO_3$ at 500°C is 0.8 mm (Hg) . If ΔH of the reaction is 43.2 k cal mol^- and it does not change even at 600°C, then calculate K_p at 600 °C. ($R = 2$ cal K^- mol^-).*

Solution.

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

$\therefore\quad K_p = P_{CO_2(g)}$ because

$[CaCO_3(s)] = [CaO(s)] = 1$

We know that :

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta\,H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

$T_1 = 500 + 273 = 773$ K,

$T_2 = 600 + 273 = 873$ K

$$\log K_{p_2} - \log 0.8 = \frac{43.2 \times 1000\ \text{cal}}{2.303 \times 2\ \text{cal K}^{-}\ \text{mol}^{-}}\left[\frac{873 - 773\,\text{K}}{873 \times 773\ \text{K}^2}\right]$$

$\log K_{p_2} - (-\,0.0969)$

$$= \frac{43200}{4.606} \times \frac{100}{873 \times 773} = 1.3898$$

$\log K_{p_2} = 1.3898 - 0.0969 = 1.2929$

$\therefore\quad K_{p_2} =$ antilog $1.2929 =$ **19.63 mm** **Ans.**

Example 91. *In the following chemical equilibrium reaction*

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

at 700 K,

$\Delta G_f^\circ(CaCO_3) = -\,1129$ *k J,*

$\Delta G_f^\circ\,(CaO) = -\,604.2$ *k J*

and $\Delta G_f^\circ(CO_2) = -\,394.6$ *k J.*

Calculate the pressure of CO_2 at 700 K.

Solution. We know that,

$R = 8.314$ J K^- mol^- and :

$$\Delta\,G^\circ\,(\text{reaction}) = \Delta\,G_f^\circ\,(\text{products}) - \Delta G_f^\circ\,(\text{reactants})$$

$$= \Delta G_f^\circ\,(CaO) + \Delta G_f^\circ\,(CO_2) - \Delta G_f^\circ\,(CaCO_3)$$

$$= (-\,604.2 - 394.6 + 1129)\ \text{k J}$$

$$= 130.2\ \text{k J}$$

But $\quad \Delta G = -\,2.303\,RT\log K_p$;

$$\log K_p = \frac{-\,\Delta\,G}{2.303\,RT}$$

or

$$\log K_p = \frac{-130.2 \times 1000\ \text{J}}{2.303 \times 8.314\ \text{J K}^{-}\ \text{mol}^{-} \times 700\ \text{K}}$$

$= -9.7142$

$\therefore\quad K_p =$ antilog $-$ 9.7142

= antilog $-9 - 1 + 1 - 0.7142$

= antilog $\overline{10}.2858 = 1.93 \times 10^{-10}$ atm

Given reaction is :

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

$\therefore\quad K_p = P_{CO_2(g)}$

Thus, $\quad \mathbf{P_{CO_2(g)} = 1.93 \times 10^{-10}}$ **atm.**

Example 92. *For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2\,(g)$, $K_p = 1.16$ atm at 1073 K. If 15.0 g of $CaCO_3$ was put into 10 L flask heated to 1073 K, what % age of $CaCO_3$ would remain unreacted at equilibrium ?*

Solution.

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2(g)$$

$K_p = P_{CO_2(g)}$

Wt. of $CaCO_3$ = 15 g ;

g. mol. wt. of $CaCO_3 = 40 + 12 + (3 \times 16) = 100$ g

$\therefore$ Number of mol of CO_2 at start

$$= \frac{15}{100} = 0.15\ \text{mol}$$

But $PV = nRT$ or $n_{CO_2} = \frac{PV}{RT}$

$$= \frac{1.16 \text{ atm} \times 10 \text{ L}}{0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 1073 \text{ K}}$$

$= 0.132$ mol

% age of $CaCO_3$ decomposed

$$= \frac{0.132 \text{ mol}}{0.15} \times 100 = 88 \%$$

∴ % age of $CaCO_3$ that remained undecomposed

$= 100 - 88 =$ **12 %** **Ans.**

Example 93. *Calculate K_c for the reversible process given below if $K_p = 167$ and $T = 800°C$.*

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.

(*a*) 1.95 (*b*) 1.85

(*c*) 1.89 (*d*) 1.60 **(West Bengal JEE, 2010)**

Solution. $K_p = K_c (RT)^{\Delta n(g)}$.

$$\underset{}{CaCO_3(s)} \rightleftharpoons CaO(s) + \underset{1 \text{ mol}}{CO_2(g)}$$

∴ $\Delta n(g) = n_p - n_r = 1 - 0 = 1$.

$R = 0.0821, T = 273 + 800$

$= 1073\ K, K_p = 167$.

So, $167 = K_c (0.0821 \times 1073)^1$.

Or $K_c = 167/(0.0821 \times 1073) = 1.89$.

So, the correct answer is (*c*).

23.21 DISSOCIATION OF HYDRAZINE (N_2H_4)

Example 94. *0.16 g of N_2H_4 are dissolved in water and total volume made up to 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. The K_p value for N_2H_4 is $4.0 \times 10^{-6} M$* **(Roorkee 1998)**

Solution. g. mol. wt. of $N_2H_4 = (2 \times 14) + (4 \times 1) = 32$ g ;

wt. of $N_2H_4 = 0.16$;

volume of solution = 500 mL.

∴ Molarity of N_2H_4 solution $= \frac{0.16}{32} \times \frac{1000}{500} = 0.01\ M$

α = Amount of N_2H_4 reacted with water.

Reaction.	$N_2H_4 + H_2O$	$\rightleftharpoons N_2H_5^+$	$+ OH^-$
(*i*) *n* mol at start	0.01	0	0
(*ii*) Change by reaction	$-\alpha$	α	α
(*iii*) *n* mol at equilibrium	$0.01 - \alpha$	α	α

$$K_p = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} = \frac{\alpha \times \alpha}{0.01 - \alpha} = \frac{\alpha^2}{0.01}$$

$[\because 0.01 - \alpha \simeq 0.01]$

Or $4 \times 10^{-6} = \frac{\alpha^2}{0.01}$; $\alpha^2 = 4 \times 10^{-6} \times 0.01 = 4 \times 10^{-8}$

∴ $\alpha = (4 \times 10^{-8})^{1/2} = 2 \times 10^{-4}$

∴ % age of N_2H_4 that would react with water

$= \frac{2 \times 10^{-4}}{0.01} \times 100 = 2\%$ **Ans.**

Type involving dissociation of ammonium bisulphide (NH_4HS). Calculation of K_p from the dissociation of ammonium bisulphide, $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$$K_p = \frac{P\,NH_3(g) \times P\,H_2S(g)}{P\,NH_4HS(s)}$$

$$= \frac{P\,NH_3(g) \times P\,H_2S(g)}{1}$$

∴ $K_p = P\,NH_3(g) \times P\,H_2S(g)$

Example 95. *When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.*

(*i*) *Calculate K_c and K_p for the reaction at 27°C.*

(*ii*) *What would happen to the equilibrium when more NH_4HS is introduced into the flask?* **(IIT 1999)**

Solution. Wt. of $NH_4HS = 3.06$ g ;

g. mol. wt. of $NH_4HS = 14 + (4 \times 1) + 1 + 32 = 51$ g ;

volume = 2 L

∴ mol of $NH_4HS = \frac{3.06}{51} = 0.06$; $x = 30$ %

$= \frac{30}{100} = 0.3$.

Reaction.

NH_4HS $\rightleftharpoons$	NH_3 +	H_2S
(*i*) *n* mol at start		
0.06	0	0
(*ii*) Change by reaction		
$-0.06x$	$0.06x$	$0.06x$
$-(0.06 \times 0.3)$	0.06×0.3	0.06×0.3
$= -0.018$	$= 0.018$	$= 0.018$
(*iii*) *n* mol L^- at equilibrium		
$\frac{0.06 - 0.018}{2}$	$\frac{0.018}{2}$	$\frac{0.018}{2}$
$= \frac{0.042}{2} = 0.021$	$= 0.009$	$= 0.009$

∴ $K_c = [NH_3][H_2S] = 0.009 \times 0.009$

$= 8.1 \times 10^{-5}$ mol^2 L^{-2}

But $K_p = K_c (RT)^{\Delta n}$;

$\Delta n = (1 + 1) - 0 = 2$;

$R = 0.0821$ L atm K$^-$ mol$^-$,

$T = 27 + 273 = 300$ K.

∴ $K_p = 8.1 \times 10^{-5}$ mol^2 L^{-2} (0.0821 L atm K$^-$ mol$^-$ × 300 K)^2

$= 8.1 \times 10^{-5}$ mol^2 L^{-2} × (24.63)^2 L^2 atm^2 K^{-2} mol^{-2} K^2

$K_p =$ **0.049 atm^2** **Ans.**

Example 96. *Calculate the equilibrium constant of the following reaction*

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g).$$

Given the observed pressure of mixture equal to 20 atmosphere.

SOLUTION. $P = 20$ atm ;

x = degree of dissociation

	$NH_4HS\ (s) \rightleftharpoons$	$NH_3\ (g)$	$+ H_2S(g)$
(*i*) n mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) n mol at equilibrium	$1-x$	x	x

Total number of mol at equilibrium = $x + x = 2x$

NH_4HS being solid, its mol are not added.

$$\therefore \quad K_p = P\ (NH_3) \times P\ (H_2S)\ ;$$

$$K_p = \left(\frac{x}{2x} \times P\right) \times \left(\frac{x}{2x} \times P\right)$$

$$= \left(\frac{1}{2} \times 20\right)\left(\frac{1}{2} \times 20\right)$$

Or $\quad K_p = 10 \times 10 = \mathbf{100\ atm^2}$. **Ans.**

EXAMPLE 97. *When solid NH_4HS is placed in an evacuated vessel at a certain temperature, it dissociates till total gas pressure is 500 torr.*

(*a*) *Find the value of K_p for the dissociation reaction.*

$$NH_4HS\ (s) \rightleftharpoons H_2S\ (g) + NH_3\ (g)$$

(*b*) *Additional NH_3 is introduced into the equilibrium mixture without change in temperature till partial pressure of NH_3 is 650 torr. Calculate the partial pressure of H_2S (g) and total pressure in the vessel under these conditions.*

SOLUTION. (*a*)$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

n mol at start $\quad 1 \quad 1$

Since NH_3 (g) and H_2S(g) are formed in 1 : 1 ratio,

$$P\ (NH_3) = P\ (H_2S).$$

$$\text{Thus : } P\ (NH_3) = \frac{1}{1+1} \times 500 = 250 \text{ torr}$$

$$= \frac{250}{760} \text{ atm} = P(H_2S) \text{ also}$$

$$\therefore \quad Kp = P\ (NH_3) \times P\ (H_2S)$$

$$= \frac{250}{760} \text{ atm} \times \frac{250}{760} \text{ atm} = \mathbf{0.108\ atm^2}$$

(*b*) The addition of NH_3 at equilibrium will cause the reaction to shift in the backward direction as explained by Le - Chatelier's principle. But K_p value remains constant.

$$650 \text{ torr} = \frac{650}{760} \text{ atm} = P\ (NH_3)$$

$$\therefore \quad K_p = P\ (NH_3) \times P\ (H_2S)\ ;$$

$$P\ (H_2S) = \frac{K_p}{P\ (NH_3)} = \frac{0.108 \text{ atm}^2}{650/760 \text{ atm}}$$

Or $\quad P\ (H_2S) = 0.126 \text{ atm} = 0.126 \times 760 = 95.8$ torr

$\therefore$ Total pressure= $P\ (NH_3) + P\ (H_2S) = 650 + 95.8$

$= \mathbf{745.8\ torr}$ **Ans.**

EXAMPLE 98. *Some solid NH_4HS is placed in flask containing 0.5 atm of NH_3. What would be the pressures of NH_3 and H_2S when equilibrium is reached ?*

$$NH_4HS\ (s) \rightleftharpoons NH_3(g) + H_2S(g)\ ;\ K_p = 0.11$$

(MLNR, 1994)

SOLUTION.	$NH_4HS\ (s) \rightleftharpoons$	$NH_3\ (g)$	$+ H_2S\ (g)$
(*i*) n mol at start		0.5	0
(*ii*) Change by reaction		x	x
(*iii*) n mol at equilibrium		$x + 0.5$	x

$$K_p = 0.11$$

Also, $\quad K_p = P\,NH_3 \times P\,H_2S;\ 0.11 = (x + 0.5) \times x;$

$x^2 + 0.5\,x - 0.11 = 0$

$$\therefore \quad x = \frac{-0.5 \pm \sqrt{(-0.5)^2 - 4\,(1 \times -0.11)}}{2 \times 1}$$

$$= \frac{-0.5 \pm \sqrt{0.25 - 0.44}}{2}$$

$$= \frac{-0.5 \pm \sqrt{0.69}}{2} = \frac{-0.5 \pm 0.83}{2}$$

$$\text{Or} \quad x = \frac{-0.5 + 0.83}{2} \text{ or } \frac{-0.5 - 0.8}{2}$$

$$= 0.165 \text{ or } -0.65$$

The negative value is not possible. So, it is rejected.

So, $\quad x = 0.165$ atm.

$\therefore \quad P_{NH_3} = x + 0.5 = 0.165 + 0.5 = 0.665$ atm ;

$P_{H_2S} = x = \mathbf{0.165\ atm.}$ **Ans.**

Type involving dissociation of ammonium carbamate. Calculation of Kp from the dissociation of ammonium carbamate, $NH_2COONH_4\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$

$$K_p = \frac{(p_{NH_3\,(g)})^2 \times p_{CO_2\,(g)}}{p_{NH_2COONH_4\,(s)}}$$

$$= (p_{NH_3(g)})^2 \times p_{CO_{2}(g)}$$

Let $\quad P$ = total pressure.

	$NH_2COONH_4\ (s) \rightleftharpoons$	$2NH_3\ (g)$	$+ CO_2\ (g)$
Pressure at equilibrium		2 P	P

Total pressure at equilibrium = 2 P + P = 3 P.

$$\therefore \quad p_{NH_3} = \frac{2\,P}{3\,P} \times P = \frac{2\,P}{3}\ ;$$

$$p_{CO_2} = \frac{P}{3\,P} \times P = \frac{P}{3}.$$

$$\therefore \quad K_p = [p_{NH_3\,(g)}]^2 \times p_{CO_2(g)}$$

$$= \left(\frac{2\,P}{3}\right)^2 \times \frac{P}{3}$$

$$\text{Or} \quad \boldsymbol{K_p = \frac{4\,P^3}{27}}$$

EXAMPLE 99. *In a closed vessel containing ammonium carbamate[NH_2COONH_4(s)] in equilibrium*

$$NH_2COONH_4\,(s) \rightleftharpoons 2NH_3\,(g) + CO_2\,(g)$$

ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure to original pressure.

Solution. First case.

$$NH_2COONH_4\,(s) \rightleftharpoons 2NH_3(g) + CO_2\,(g)$$

Pressure at equilibrium 2P P

∴ Total pressure at equilibrium

$$= 2P + P = 3\,P$$

$$\therefore \quad K_p = p_{(NH_3)^2} \times p_{(CO_2)} = (2P)^2 \times P = \mathbf{4P^3}$$

Second Case. When NH_3 is added, pressure of NH_3 at equilibrium = 3 P

$$\therefore \quad K_p = p_{(NH_3)2} \times p_{CO_2} = (3P)^2 \times p_{CO_2}$$

$$\textbf{or} \quad 4\,P^3 = 9P^2 \times p_{CO_2};$$

$$\therefore \quad p_{CO_2} = \frac{4\,P^3}{9\,P^2} = \frac{4\,P}{9}$$

∴ Total pressure in second equilibrium

$$= 3\,P + \frac{4}{9}P = \frac{31\,P}{9}$$

$$\therefore \textbf{Ratio of } \frac{\text{Total pressure in second case}}{\text{Total pressure in first case}}$$

$$= \frac{31\,P/9}{3\,P} = \mathbf{\frac{31}{27}} \qquad \textbf{Ans.}$$

23.22 SYNTHESIS AND DISSOCIATION OF SOME COMPOUNDS

Synthesis of H_2S gas

Example 100. *At 1,200 K, the equilibrium constant value K_p for*

$$H_2(g) + S\,(g) \rightleftharpoons H_2S\,(g)$$

is 20.2 atm. Calculate K_p at 1340 K if heat of reaction in this temperature range is – 21.23 k cal per mol.

Solution. $T_1 = 1200\,K,\ Kp_1 = 20.2$ atm,

$T_2 = 1340\,K,\ Kp_2 = ?$

$\Delta H° = -21.23\text{ k cal mol}^{-},\ R = 2\text{ cal }K^{-}\text{mol}^{-}.$

We know that :

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H°}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

$$\log K_{p_2} - \log 20.2 = \frac{-21.23 \times 1000\text{ cal mol}^{-}}{2.303 \times 2\text{ cal K}^{-}\text{ mol}^{-}} \times \frac{(1340-1200)\text{ K}}{(1200 \times 1340)\text{ K}^2}$$

$$\log K_{p_2} - 1.3054 = -0.4013\,;$$

$$\log K_{p_2} = -0.4013 + 1.3054 = 0.9041$$

$$\therefore \quad K_{p_2} = \text{antilog } 0.9041 = \mathbf{8.02\ atm.} \qquad \textbf{Ans.}$$

Type. Dissociation of H_2S.

Example 101. *Calculate the percentage dissociation of H_2S (g) if 0.1 mol of H_2S is kept in 0.4 litre vessel at 100 K. For the reaction*

$$2H_2S\,(g) \rightleftharpoons 2H_2(g) + S_2\,(g)$$

the value of K_p is 1.0×10^{-6} **(Roorkee, 1994)**

Solution. Vol = 0.4 L.

$$2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$$

(*i*) *n* mol at start

$$0.1 \qquad 0 \qquad 0$$

(*ii*) Change by reaction

$$-0.1x \qquad 0.1x \qquad \frac{0.1x}{2}$$

(*iii*) *n* mol L⁻ at equilibrium

$$\frac{0.1 - 0.1x}{0.4} \qquad \frac{0.1x}{0.4} \qquad \frac{0.1x}{2 \times 0.4}$$

$$= \frac{0.1(1-x)}{0.4} = \frac{1-x}{4} \qquad = \frac{x}{4} \qquad = \frac{x}{8}$$

$$\therefore \quad K_c = \frac{[H_2]^2\,[S_2]}{[H_2S]^2} = \frac{\left(\frac{x}{4}\right)^2 \times \frac{x}{8}}{\left(\frac{1-x}{4}\right)^2} = \frac{\frac{x^2}{16} \times \frac{x}{8}}{\left(\frac{1}{4}\right)^2}$$

[∵ if x is very small, $1 - x \simeq 1$]

$$\therefore \quad K_c = \frac{x^3}{16 \times 8} \times \frac{4 \times 4}{1} = \frac{x^3}{8}\,;$$

$$1.0 \times 10^{-6} = \frac{x^3}{8}\,;$$

$$x^3 = 8 \times 10^{-6} \textbf{ Or } x = (8 \times 10^{-6})^{1/3}$$

$$= 2 \times 10^{-2}$$

∴% age dissociation

$$= 2 \times 10^{-2} \times 100 = 2\,\% \qquad \textbf{Ans.}$$

Example 102. *An equilibrium mixture for the reaction*

$$2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$$

has 1 mol of H_2S, 0.2 mol of H_2 and 0.8 mol of S_2 in a 2 litre vessel. Calculate K_c for the reaction. **(Orissa JEE 1997)**

Solution. $2\,H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$

n mol L⁻ at equilibrium

$$\frac{1\text{ mol}}{2\text{ L}} \qquad \frac{0.2\text{ mol}}{2\text{ L}} \qquad \frac{0.8\text{ mol}}{2\text{ L}}$$

$$= 0.5\text{ mol L}^{-} = 0.1\text{ mol L}^{-} = 0.4\text{ mol L}^{-}$$

$$\therefore \quad K_c = \frac{[H_2]^2\,[S_2]}{[H_2S]^2} = \frac{(0.1)^2 \times 0.4}{(0.5)^2} = \frac{0.01 \times 0.4}{0.25}$$

$$K_c = \mathbf{0.016\ mol\ L^{-}}$$

Type. Dissociation of S_8.

Example 103. *When sulphur in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of the conversion of some S_8 to S_2. Find the value of equilibrium constant for this reaction.* **(Roorkee, 1990)**

SOLUTION. $S_8\,(g) \rightleftharpoons 4\,S_2(g)$

(*i*) Pressure at start

$$1 \qquad\qquad 0$$

(*ii*) Change by reaction

$$-\frac{29}{100} \qquad 4\times\frac{29}{100}=\frac{116}{100}=1.16$$

(*iii*) Pressure at equilibrium

$$1-\frac{29}{100} \qquad 1.16$$

$$=\frac{71}{100}=0.71$$

$$\therefore \qquad K_p=\frac{[p_{S_2(g)}]^4}{[p_{S_8\,(g)}]}=\frac{(1.16)^4\ \text{atm}^4}{0.71\ \text{atm}}\simeq\frac{1.81}{0.71}\text{atm}^3$$

=2.55 atm^{3}Ans.

Type. Dissociation of Se$_6$

EXAMPLE 104. *At 700°C, 0.076 g of selenium vapour occupy a volume of 114 mL and exert a pressure of 185 torr (Hg). Selenium exists in the following equilibrium state.*

$$Se_6\,(g) \rightleftharpoons 3\,Se_2\,(g)$$

(*i*) *Find the value of degree of dissociation of Se and,* (*ii*) *calculate the value of K_c and K_p. (at. wt. of Se = 79 g mol$^-$).*

SOLUTION. (*a*) $P=\frac{185}{760}=0.24$ atm,

$$V=\frac{114}{1000}=0.114\ \text{L},$$

$$R=0.0821\ \text{L atm K}^-\ \text{mol}^-,$$

$$T=700+273=973\ \text{K}.$$

We know that :

$$PV=n\,RT\,;\,n=\frac{PV}{RT}$$

$$=\frac{0.24\ \text{atm}\times0.114\ \text{L}}{0.0821\ \text{L atm K}^-\ \text{mol}^-\times973\ \text{K}}$$

Or $\qquad n=3.4\times10^{-4}$ mol.

(*b*) Wt. of Se = 0.076 g ; Experimental mol. wt. of Se = M.

$$\therefore\ \text{no. of mol of Se}=\frac{0.076}{M}\,;\ 3.4\times10^{-4}=\frac{0.076}{M}$$

Or $\qquad \text{M}=\frac{0.076}{3.4\times10^{-4}}=223.5\ \text{g mol}^-$

∴ Experimental density (*d*) of Se

$$=\frac{\text{mol. wt}}{2}=\frac{223.5}{2}=111.75$$

Theoretical mol. wt. of Se

$$=6\times79\ \text{g mol}^-=474\ \text{g mol}^-$$

∴ Theoretical density D of Se

$$=\frac{474}{2}=237\ \text{g mol}^-$$

In the reaction, $Se_6\,(g) \rightleftharpoons 3\,Se_2\,(g)$

1 mol $\qquad$ 3 mol

1 mol Se_6 (g) produce Se_2 = 3 mol.

So, $n=3$

(*c*) Degree of dissociation,

$$x=\frac{D-d}{d\,(n-1)}=\frac{237-111.75}{111.75\,(3-1)}$$

Or $\qquad x=\frac{125.25}{223.50}=$ **0.5604 mol**

(*d*) $\qquad Se_6\,(g) \rightleftharpoons 3\,Se_2\,(g)$

(*i*) n mol at start $\qquad 1 \qquad 0$

(*ii*) Change by reaction $\qquad -x \qquad 3x$

(*iii*) n mol at equilibrium $\qquad 1-x \qquad 3x$

Total number of mol at equilibrium

$$=1-x+3x=1+2x;\ P=0.24\ \text{atm}.$$

$$K_p=\frac{P\,(Se_2)^3}{P\,Se_6}=\frac{\left(\frac{3x}{1+2x}\times P\right)^3}{\frac{1-x}{1+2x}\times P}$$

$$=\frac{27x^3\,P^3}{(1+2x)^3}\times\frac{1+2x}{(1-x)\,P}$$

$$=\frac{27x^3\,P^2}{(1-x)\,(1+2x)^2}$$

$$\therefore \qquad K_p=\frac{27\times(0.5604)^3\times(0.24)^2}{(1-0.5604)\times[1+(2\times0.5604)^2]}$$

$$=\frac{0.2737}{0.4396\times4.498}=0.138$$

(*e*) $\qquad K_p=K_c\,(RT)^{\Delta n}\,;$

$$\Delta n=n_p-n_R=3-1=2$$

$$R=0.0821\ \text{L atm K}^-\ \text{mol}^-,\ T=973\ \text{K}.$$

$$\therefore \qquad 0.138\ \text{atm}^2=K_c\,(0.0821\ \text{L atm K}^-\ \text{mol}^-\times973\ \text{K})^2$$

$$K_c=\frac{0.138\ \text{atm}^2}{(0.0821\ \text{L atm K}^-\ \text{mol}^-\times973\ \text{K})^2}$$

$$= \mathbf{2.162\times10^{-5}\ mol^2\ L^{-2}} \qquad \textbf{Ans.}$$

Type. Synthesis of SO$_3$.

EXAMPLE 105. *At a certain temperature, the equilibrium constant K_c is 16 for the gaseous reaction :*

$$SO_2+NO_2 \rightleftharpoons SO_3+NO$$

If we take one mol each of all the four gases in a one litre container, what would be the equilibrium concentration of NO and NO$_2$. **(IIT 1987)**

SOLUTION. Vol = 1 L

$$SO_2+NO_2 \rightleftharpoons SO_3+NO$$

(*i*) n mol at start

$$1 \quad 1 \qquad 1 \quad 1$$

(*ii*) Change by reaction

$$-x \quad -x \qquad x \quad x$$

(*iii*) n mol L^{-} at equilibrium

$$\frac{1-x}{1} \quad \frac{1-x}{1} \qquad \frac{1+x}{1} \quad \frac{1+x}{1}$$

x = Amount reacted at equilibrium.

$$\therefore \quad K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]};$$

$$16 = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2}.$$

Taking square root of both sides, we get :

$$(16)^{1/2} = \left[\frac{(1+x)^2}{(1-x)^2}\right]^{1/2}$$

or
$$4 = \frac{1+x}{1-x} \; ; \; 4(1-x) = 1+x \; ;$$

$$4 - 4x = 1 + x \; ; \quad x + 4x = 4 - 1 \; ;$$

$$5x = 3 \; ; \; x = \frac{3}{5} = 0.6$$

$$\therefore \quad [NO] = 1 + x = 1 + 0.6 = \mathbf{1.6\ mol\ L^{-}} \; ;$$

$$[NO_2] = 1 - x = 1 - 0.6 = \mathbf{0.4\ mol\ L^{-}}$$

EXAMPLE 106. *A mixture of SO_2, SO_3 and O_2 gases is maintained in a 10 litre flask at temperature at which the equilibrium constant K_c for the reaction.*

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

is 100. (i) If the number of mol of SO_2 and SO_3 in the flask are equal, how many mol of O_2 are present?

(ii) If the number of mol of SO_2 in the flask is twice the number of mol of SO_3, how many mol of O_2 are present ?

(Roorkee, 1987)

SOLUTION. (*i*) $\quad 2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

n mol L^{-} at equilibrium

$$\frac{1\text{ mol}}{10\text{ L}} \qquad \frac{x\text{ mol}}{10\text{ L}} \qquad \frac{1\text{ mol}}{10\text{ L}}$$

$$= 0.1\text{ mol L}^{-} \quad = 0.1x\text{ mol L}^{-} \quad = 0.1\text{ mol L}^{-}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$= \frac{(0.1\text{ mol L}^{-})^2}{(0.1\text{ mol L}^{-})^2 \times 0.1\,x\text{ mol L}^{-}}$$

$$\therefore \quad 100 = \frac{1}{0.1\,x\text{ mol L}^{-}} = 100 \times 0.1\,x\text{ mol L}^{-} = 1$$

$$\therefore \quad x = \frac{1}{100 \times 0.1} = \mathbf{0.1\ mol.}$$

(*ii*) $\quad 2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

n mol L^{-} at equilibrium

$$\frac{1\text{ mol}}{10\text{ L}} \qquad \frac{2\text{ mol}}{10\text{ L}}$$

$$= 0.1\text{ mol L}^{-} \quad = 0.2\text{ mol L}^{-}$$

$$\therefore \quad K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]};$$

$$100 = \frac{(0.2\text{ mol L}^{-})^2}{(0.1\text{ mol L}^{-})^2\,\frac{[O_2]}{10}}$$

$$\therefore \quad \frac{[O_2]}{10} = \frac{0.04}{0.01 \times 100};$$

$$(O_2) = \frac{10 \times 4}{100} = \mathbf{0.4\ mol} \qquad \textbf{Ans.}$$

EXAMPLE 107. *The equilibrium constant K_p of the reaction*

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

is 900 atm at 1073 K. A mixture containing SO_3 and O_2 having initial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 1073 K. **(IIT 1989)**

SOLUTION. $\quad 2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$

(*i*) Pressure (atm) at start

$$1 \qquad 0 \qquad 2$$

(*ii*) Change by reaction

$$-x \qquad x \qquad \frac{x}{2}$$

(*iii*) Pressure (atm) at equilibrium

$$1-x \qquad x \qquad 2+\frac{x}{2}$$

$$K_p = \frac{p\,(SO_2)^2 \times p\,(O_2)}{p\,(SO_3)^2}$$

$$= \frac{x^2 \times \left(2+\frac{x}{2}\right)}{(1-x)^2} = \frac{2x^2 + \frac{x^3}{2}}{(1-x)^2}$$

Since K_p is very small, $x^3/2$ can be rejected

$$\therefore \quad \frac{1}{900} = \frac{2x^2}{(1-x)^2}.$$

Taking square root of both sides, we get :

$$\frac{1}{30} = \sqrt{2}\left(\frac{x}{1-x}\right); \frac{1}{30} = 1.4142\left(\frac{x}{1-x\,;}\right);$$

$$\frac{x}{1-x} = \frac{1}{30\,(1.4142)};$$

$$\frac{x}{1-x} = 0.0236\,;\, x = 0.0236\,(1-x)$$

$$= 0.0236 - 0.0236x\,;\, 1.0236x$$

$$= 0.0236$$

$$\therefore \quad x = 0.023$$

$$\therefore \quad p\,SO_2 = 0.023\text{ atm}\,;$$

$$p\,SO_3 = 1 - 0.023 = 0.977\text{ atm}\,;$$

$$p\,O_2 = 2 + \frac{x}{2} = 2 + \frac{0.023}{2} = \mathbf{2.0115\ atm.}$$

Type. Dissociation of SO_3

EXAMPLE 108. *For the reaction*

$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$$

$$K_p = 1.8 \times 10^{-3}\text{ k Pa at 700 K.}$$

Calculate the value of K_c in mol per litre for this reaction at the same temperature. **(HP Board, 2007)**

SOLUTION.
$$2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$$
$$\text{2 mol} \qquad \text{2 mol} \qquad \text{1 mol}$$

$$\therefore \quad \Delta n = n_p - n_R$$
$$= (2 + 1) - 2 = 1\,;$$
$$T = 700\text{K},$$
$$R = 8.31\,\text{J K}^{-}\text{mol}^{-}\ (= 8.31\ \text{k Pa L K}^{-}\text{mol}^{-}$$
or
$$0.0831\ \text{L bar K}^{-}\ \text{mol}^{-})$$
$$K_p = 1.8 \times 10^{-3}\ \text{k Pa.}$$
But
$$K_p = K_c\,(RT)^{\Delta n}\,;\ K_p = K_c\,(RT)^1$$
Or
$$K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-3}\ \text{k Pa}}{8.31\ \text{k Pa L K}^{-}\ \text{mol}^{-} \times 700\ \text{K}}$$
$$= \mathbf{3.09 \times 10^{-7}\ mol\ L^{-}}.$$ **Ans.**

Note : $Pa = N\,m^{-2}\,;\,J = Nm.$

EXAMPLE 109. *At a certain temperature, $2SO_2 + O_2 \rightleftharpoons 2SO_3$ reaction was allowed to take place in a vessel of one litre capacity. The equilibrium mixture contains 24.0 g SO_3, 4.8 g O_2 and 6.4 g SO_2. Find the value of K_c.*

SOLUTION. (*a*) Wt. of SO_2 = 6.4 g ;

g. mol. wt. of $SO_2 = 32 + (2 \times 16) = 64$ g

$\therefore$ no. of mol of $SO_2 = 6.4/64 = 0.1$

(*b*) Wt. of O_2 = 4.8 g ; g. mol. wt. of O_2
$$= 2 \times 16 = 32\ \text{g}.$$
$$\therefore \text{ no. of mol of } O_2 = \frac{4.8}{32} = 0.15$$

(*c*) Wt. of SO_3 = 24 g ; g. mol. wt. of SO_3
$$= 32 + (3 \times 16) = 80\ \text{g}$$
$$\therefore \text{ no. of mol of } SO_3 = \frac{24}{80} = 0.3.$$

For the following reaction at equilibrium :
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$
$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$
$$= \frac{0.3 \times 0.3}{0.1 \times 0.1 \times 0.15} = \mathbf{60}$$ **Ans.**

EXAMPLE 110. *For the following reaction at equilibrium,*
$$2\,SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$$
find the value of equilibrium constant. The partial pressures of O_2, SO_2 and SO_3 are 0.1, 0.3 and 0.5 atm respectively.

SOLUTION. $2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$

Pressure (atm) at equilibrium
$$0.5 \qquad 0.3 \qquad 0.1$$
$$K_p = \frac{p\,(SO_2)^2 \times p\,O_2}{p\,(SO_3)^2} = \frac{(0.3)^2 \times 0.1}{(0.5)^2}$$
Or
$$K_p = \frac{0.09 \times 0.1}{0.25}$$
$$= \mathbf{0.036\ atm} \quad \text{or} \quad \mathbf{3.6 \times 10^{-2}\ atm.}$$ **Ans.**

EXAMPLE 111. *SO_3 is partially dissociated into SO_2 and O_2 gases at 1 atm pressure and 900 K. The density of mixture of gases at equilibrium is 0.925 g L^{-}. Find the degree of dissociation of SO_3 (g)*

SOLUTION. $PV = n\,RT$ (gas equation) ;
$$n = \frac{\text{wt. of substance (W)}}{\text{g. mol. wt. of substance, M}}$$
$$\therefore \quad PV = \frac{W}{M} \times RT \quad \text{or} \quad M = \frac{W}{V} \times \frac{RT}{P}$$
Or
$$M = d\,\frac{RT}{P}\ (\because \text{mass/volume} = \text{density}, d).$$
$$M = \frac{0.925\ \text{g L}^{-} \times 0.0821\ \text{L atm K}^{-}\ \text{mol}^{-} \times 900\ \text{K}}{1\ \text{atm}}$$
$$= 68.34\ \text{g mol}^{-}$$
Or Experimental g. mol. wt. of SO_3
$$= 68.34\ \text{g mol}^{-}$$
Theoretical g. mol. wt. of SO_3
$$= 32 + (3 \times 16) = 80\ \text{g mol}^{-}$$

	SO_3	$\rightleftharpoons$ SO_2	$+\ \frac{1}{2}O_2$
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-\alpha$	α	$\frac{1}{2}\alpha$
(*iii*) *n* mol at equilibrium	$1 - \alpha$	α	$\frac{1}{2}\alpha$

Total number of mol at equilibrium
$$= 1 - \alpha + \alpha + 1/2\,\alpha = 1 + 1/2\,\alpha$$
But
$$1 + \frac{\alpha}{2} = \frac{\text{Theoretical molar mass}}{\text{Experimental molar mass}}$$
$$= \frac{80}{68.34} = 1.171$$
$$\therefore \quad \frac{\alpha}{2} = 1.171 - 1 = 0.171$$
Or
$$\alpha = 2 \times 0.171 = 0.342$$
% age degree of dissociation of SO_3
$$= 0.342 \times 100 = \mathbf{34.2\ \%}$$ **Ans.**

EXAMPLE 112. *Sulphur trioxide is 50 % dissociated at 2 atmospheres and 520 K. Calculate the value of K_p.*

SOLUTION. $2SO_3 \rightleftharpoons 2SO_2 + O_2$

(*i*) *n* mol at start
$$1 \qquad 0 \qquad 0$$
(*ii*) Change by reaction
$$-\frac{1 \times 50}{100} = -\,0.5 \qquad 0.5 \qquad \frac{0.5}{2} = 0.25$$
(*iii*) *n* mol at equilibrium
$$1 - 0.5 = 0.5 \qquad 0.5 \qquad 0.25$$

Total number of mol at equilibrium

$$= 0.5 + 0.5 + 0.25 = 1.25 \text{ mol}$$

$$\therefore \qquad K_p = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2}$$

$$= \frac{\left(\frac{0.5}{1.25}\times P\right)^2\left(\frac{0.25}{1.25}\times P\right)}{\left(\frac{0.5}{1.25}\times P\right)^2}$$

$$= \frac{\left(\frac{0.5}{1.25}\times 2\right)^2\left(\frac{0.25}{1.25}\times 2\right)}{\left(\frac{0.5}{1.25}\times 2\right)^2}$$

$$K_p = \frac{0.8\times 0.8\times 0.4}{0.8\times 0.8} = \mathbf{0.4} \qquad \textbf{Ans.}$$

Type. Synthesis of methanol (CH_3OH)

Example 113. *0.15 mol of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place.*

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atmosphere at equilibrium and 0.08 mol of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. **(IIT 1993)**

Solution. $CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$

(*i*) *n* mol at start	0.15	*a*	0
(*ii*) Change by reaction	– 0.08	– (2 × 0.08) = – 0.16	0.08
(*iii*) *n* mol at equilibrium	0.15 – 0.08 = 0.07	*a* – 0.16	0.08

Total number of mol at equilibrium

$$= 0.07 + a - 0.16 + 0.08 = a - 0.01$$

Also, $PV = nRT\,;\; n = \dfrac{PV}{RT}$

$$= \frac{8.5 \text{ atm} \times 2.5 \text{ L}}{0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 750 \text{ K}}$$

$$\simeq 0.345 \text{ mol}$$

$\therefore$ $a - 0.01 = 0.345\,;\; \mathbf{a} = 0.345 + 0.01 = \mathbf{0.355}$

$\therefore$ mol of CO at equilibrium = 0.07

mol of H_2 at equilibrium

$$= a - 0.16 = 0.355 - 0.16 = 0.195$$

mol of CH_3OH at equilibrium = 0.08

(*a*) But $K_c = \dfrac{[CH_3OH]}{[CO]\,[H_2]^2}$

$$= \frac{\dfrac{0.08 \text{ mol}}{2.5 \text{ L}}}{\dfrac{0.07 \text{ mol}}{2.5 \text{ L}} \times \left(\dfrac{0.195 \text{ mol}}{2.5 \text{ L}}\right)^2}$$

$$= \frac{0.08 \text{ mol}}{2.5 \text{ L}} \times \frac{2.5 \text{ L}}{0.07 \text{ mol}} \times \frac{(2.5 \text{ L})^2}{(0.195 \text{ mol})^2}$$

$$K_c = 187.84 \text{ mol}^{-2} \text{ L}^2;\; K_p = K_c\,(RT)^{\Delta n}$$

where $\Delta n = n_P - n_R = 1 - (1+2) = -2;$

$$K_p = 187.84\,(0.0821 \times 750)^{-2}$$

$$= \frac{187.84}{(0.0821\times 750)^2} = \mathbf{0.049}$$

(*b*) To find final pressure :

mol of H_2 = 0.355 ; mol of CO = 0.15

$\therefore$ Total number of mol (*n*) = 0.355 + 0.15 = 0.505

But $PV = nRT\,;$

$$\therefore \qquad P = \frac{nRT}{V} = \frac{0.505 \times 0.0821 \times 750}{2.5}$$

$$\therefore \qquad P = \mathbf{12.4 \text{ atm.}}$$

Type. Reactions involving CO (g) and H_2O (g)

Example 114. *The equilibrium constant for the equation*

$$CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

is 0.63. A mixture of one mol of water vapours and 3 mol of CO is allowed to come to equilibrium at a total pressure of 2 atmosphere.

(*i*) *How many mol of hydrogen are present at equilibrium.*

(*ii*) *What is partial pressure of each gas in the equilibrium mixture.* **(Roorkee, 1992)**

Solution. $CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2(g)$

(*i*) *n* mol at start	3	1	0	0
(*ii*) Change by reaction	– *x*	– *x*	*x*	*x*
(*iii*) *n* mol at equilibrium	3 – *x*	1 – *x*	*x*	*x*

Total number of mol at equilibrium

$$= 3 - x + 1 - x + x + x = 4$$

$$K_p = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}\,;$$

$$0.63 = \frac{\left(\frac{x}{4}\right)\left(\frac{x}{4}\right)}{\left(\frac{3-x}{4}\right)\left(\frac{1-x}{4}\right)} = \frac{x^2}{(3-x)\,(1-x)}$$

Or $\qquad 0.63 = \dfrac{x^2}{3 - 4x + x^2};\; 0.63\,(3 - 4x + x^2) = x^2;$

$$1.89 - 2.52\,x + 0.63\,x^2 = x^2;$$

$$x^2 - 0.63\,x^2 + 2.52\,x - 1.89 = 0$$

Or $$0.37\,x^2 + 2.52\,x - 1.89 = 0$$

$$\therefore \quad x = \frac{-2.52 \pm \sqrt{(2.52)^2 - 4\,(0.37 \times -1.89)}}{2 \times 0.37}$$

$$= \frac{-2.52 \pm \sqrt{6.35 + 2.8}}{0.74}$$

$$= \frac{-2.52 \pm \sqrt{9.15}}{0.74} = \frac{-2.52 \pm 3.02}{0.74}$$

$$= \frac{0.5}{0.74}\text{ (on adding)} \quad \text{or} \quad \frac{-5.54}{0.74}\text{ (on subtraction)}$$

Since x cannot be negative, it is rejected.

$$\therefore \quad x = \frac{0.5}{0.74} = \mathbf{0.68}$$

(*i*) ∴ Mol of H_2 at equilibrium = x = 0.68

$$p_{CO_2\,(g)} = p_{H_2\,(g)} = \frac{x}{4} \times P = \frac{0.68}{4} \times 2 = \mathbf{0.34\ atm}$$

$$p\,CO(g) = \frac{(3-x)}{4} \times P = \frac{(3-0.68)}{4} \times 2 = \frac{2.32 \times 2}{4}$$

$$= \mathbf{1.16\ atm}$$

$$p\,H_2O(g) = \frac{(1-x)\,P}{4} = \frac{(1-0.68)\,2}{4} = \frac{0.32}{4} \times 2$$

$$= \mathbf{0.16\ atm.}$$

EXAMPLE 115. *H_2 (g) (0.3 mol) was injected into a one litre vessel. The composition at equilibrium is shown below.*

$$\begin{array}{cccc} CO + & H_2O & \rightleftharpoons & CO_2 + H_2 \\ 0.1 & 0.1 & & 0.40 \quad 0.1 \end{array}$$

Calculate the new concentration of CO_2 when the equilibrium establishes again.

SOLUTION. $[H_2]$ = 0.3 mol.

First case $CO + H_2O \rightleftharpoons CO_2 + H_2$

mol at equilibrium

0.1 0.1 0.4 0.1

Second case

(*i*) New mol at start

0.1 0.1 0.4; 0.1 + 0.3 = 0.4

(*ii*) Change by reaction

$+x$ $+x$ $-x$ $-x$

(*iii*) mol at equilibrium

$0.1 + x$ $0.1 + x$ $0.4 - x$ $0.4 - x$

$$K_c = \frac{[CO_2][H_2]}{[CO]\,[H_2O]} = \frac{(0.4-x)\,(0.4-x)}{(0.1+x)\,(0.1+x)}$$

Or $$4 = \frac{(0.4-x)^2}{(0.1+x)^2}.$$

Taking square root, we get :

$$2 = \frac{0.4-x}{0.1+x} \quad ; \quad 2\,(0.1+x) = 0.4 - x$$

Or $$2x + x = 0.4 - 0.2\ ;\ 3x = 0.2\ ;$$

$$x = \frac{0.2}{3} = 0.067\text{ mol}$$

∴ New molar concentration of CO_2 = 0.4 − x = 0.4 − 0.067 = **0.333 mol L^{-}** **Ans.**

EXAMPLE 116. *A mixture of 0.5 mol of each of CO and steam were put into a vessel of 2 litre capacity and heated to get the following equilibria*

$$CO\,(g) + H_2(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$$

If K_c is 4, calculate the number of mol of CO_2 at equilibrium.

SOLUTION. $CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2(g) + H_2(g)$

(*i*) n mol at start

0.5 0.5 0 0

(*ii*) Change by reaction

$-x$ $-x$ x x

(*iii*) n mol L^{-} at equilibrium

$$\frac{0.5 - x\text{ mol}}{2\text{ L}} \quad \frac{0.5 - x\text{ mol}}{2\text{ L}} \quad \frac{x\text{ mol}}{2\text{ L}} \quad \frac{x\text{ mol}}{2\text{ L}}$$

$$\therefore \quad K_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]}$$

$$= \frac{\frac{x}{2} \times \frac{x}{2}}{\frac{0.5-x}{2} \times \frac{0.5-x}{2}} = \frac{x^2}{(0.5-x)^2}$$

Or $$4 = \frac{x^2}{(0.5-x)^2}$$

Taking square root of both sides, we get :

$$2 = \frac{x}{0.5-x}\ ;\ 2(0.5-x) = x\ ;\ 1 - 2x = x\ ;$$

$$x + 2x = 1\ ;\ 3x = 1$$

Or $$x = \frac{1}{3} = 0.33$$

∴ number of mol of CO_2 at equilibrium

= **0.33 mol** **Ans.**

Type. Reactions involving H_2 (g) and CO_2 (g)

EXAMPLE 117. *Initially, equal number of moles of CO_2(g) and H_2(g) were put in a flask. The pressure of H_2 (g) at equilibrium is 1.2 atmosphere. If K_p for the reaction, H_2 (g) + CO_2(g) $\rightleftharpoons$ H_2O (g) + CO (g) is 16.0 at a given temperature, the partial pressure of H_2O (g) and CO (g) will be :*

(*a*) *5.0 atm each*
(*b*) *4.8 atm each*
(*c*) *2.6 atm for H_2O (g) and 3.6 atm for CO (g)*
(*d*) *2.5 atm each.*

SOLUTION. For the reaction :

$$H_2(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)$$

Conc. at equilibrium. 1.2 atm 1.2 atm

$$K_p = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}} \quad \textbf{Or} \quad 16 = \frac{p_{H_2O} \times p_{CO}}{1.2 \times 1.2}$$

$\therefore \quad p_{H_2O} \times p_{CO} = 16 \times 1.2 \times 1.2 = 23.04$

Since $\quad p_{H_2O} = p_{CO}, (p_{H_2O})^2 = 23.04$

or $\quad p_{H_2O} = (23.04)^{1/2} = 4.8$

$\therefore \quad p_{H_2O} = p_{CO} = \mathbf{4.8\ atm.}$

So, correct answer is **(*b*)**.

EXAMPLE 118. *The value of K_p for the water gas reaction :*

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is 1.06×10^5 at 298 K. Find the value of standard state free energy change of the reaction at the same temperature. (R = 2 cal).

SOLUTION. $R = 2$ cal, $T = 298$ K,

$K_p = 1.06 \times 10^5$. We know :

$$\Delta G° = -2.303\ RT \log K_p$$
$$= -2.303 \times 2 \times 298 \log (1.06 \times 10^5)$$
$$= -1372.588 [\log 1.06 + \log 10^5]$$
$$= -1372.588 [0.0253 + 5]$$

$\therefore \quad \Delta G° = -1372.588 \times 5.0253 \simeq$ **6898 cal. Ans.**

EXAMPLE 119. *One mol each of a mixture of H_2 and CO_2 is heated to 523 K to get the following equilibrium.*

$$CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$$

If total pressure is 0.1 atm, calculate K_p if final reaction mixture contains 0.16 volume percent of carbon monoxide.

SOLUTION. $CO_2(g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$

(*i*) *n* mol at start

1 1 0 0

(*ii*) Change by reaction

$-x$ $-x$ x x

(*iii*) *n* mol at equilibrium

$1-x$ $1-x$ x x

Total number of mol at equilibrium

$= 1 - x + 1 - x + x + x = 2$

Here , $\Delta n = 0$, so volume is not considered.

Volume % of CO = 0.16

$\therefore$ For CO gas,

$$\frac{x}{\text{Total mol}} = \frac{0.16}{100} ; \frac{x}{2} = \frac{0.16}{100}$$

Or $\quad x = \dfrac{2 \times 0.16}{100} = 0.032$;

$$p_{CO_2} = p_{H_2} = 1 - x = 1 - 0.0032$$

Hence, $\quad K_p = \dfrac{p\,(CO) \times p\ H_2O}{p\ CO_2 \times p\ H_2}$

$$= \frac{0.0032 \times 0.0032}{(1-0.0032)^2} = \frac{1.024 \times 10^{-5}}{(0.9968)^2}$$

$K_p = \dfrac{1.024 \times 10^{-5}}{0.9936} = \mathbf{1.03 \times 10^{-5}}$ **Ans.**

EXAMPLE 120. *0.45 mol each of CO_2 and H_2 gases are heated to 700 K to get the following equilibrium.*

$$CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$$

Equilibrium constant for the reaction is 0.11.

(*i*) *Calculate amount of each gas at equilibrium state.*

(*ii*) *After equilibrium has attained, another 0.34 mol each of CO_2 and H_2 are added to the reaction mixture. Calculate the composition of mixture at the new equilibrium state.* **(Roorkee 1989)**

SOLUTION. First case.

$$CO_2\ (g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$$

(*i*) *n* mol at start

0.45 0.45 0 0

(*ii*) Change by reaction

$-x$ $-x$ x x

(*iii*) *n* mol at equilibrium

$0.45-x$ $0.45-x$ x x

Since , $\Delta n = 0$, volume is not considered.

$$K = \frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} ;$$

$$0.11 = \frac{x \times x}{(0.45-x)\,(0.45-x)} = \frac{x^2}{(0.45-x)^2}$$

Taking square root of both sides, we get :

$$0.33 = \frac{x}{0.45-x} ;\ 0.33\,(0.45-x) = x ;$$

$0.15 - 0.33\,x = x$

Or $\quad 0.33x + x = 0.15$; $\quad 1.33x = 0.15$;

$x = 0.15/1.33 = 0.11$ mol

$\therefore \quad [CO] = x = 0.11 \text{ mol} = [H_2]$;

$[CO_2] = [H_2] = 0.45 - x = 0.45 - 0.11$

$=$ **0.34 mol.**

Second Case

$CO_2(g) + H_2\ (g) \rightleftharpoons CO\ (g) + H_2O\ (g)$

(*i*) *n* mol at start

0.34 + 0.34 0.34 + 0.34 0.11 0.11

= 0.68 = 0.68

(*ii*) Change by reaction

$-x$ $-x$ $+x$ $+x$

(*iii*) *n* mol at equilibrium

$0.68-x$ $0.68-x$ $0.11+x$ $0.11+x$

$\therefore \quad K = \dfrac{[CO]\,[H_2]}{[CO_2]\,[H_2]}$;

$$0.11 = \frac{(0.11+x)\,(0.11+x)}{(0.68-x)\,(0.68-x)} = \frac{(0.11+x)^2}{(0.68-x)^2}$$

Taking square root of both sides, we get :

$$(0.11)^{1/2} = \frac{0.11+x}{0.68-x} ; 0.33 = \frac{0.11+x}{0.68-x}$$

Or $0.33(0.68-x) = 0.11 + x$; $0.22 - 0.33\,x = 0.11 + x$;

$x + 0.33\,x = 0.22 - 0.11$; $1.33\,x = 0.11$;

$$x = 0.11/1.33 = \mathbf{0.083}$$

$$\therefore \quad [CO] = [H_2O] = 0.11 + x = 0.11 + 0.083 = \mathbf{0.193\ mol}$$

$$[CO_2] = [H_2] = 0.68 - x = 0.68 - 0.083 = \mathbf{0.597\ mol}$$

Type. Synthesis of Phosgene or Carbonyl Chloride ($COCl_2$).

Example 121. *Three moles of Cl_2 (g) and two moles of CO (g) were heated in a 5L vessel at a given temperature and allowed to reach the equilibrium, $Cl_2(g) + CO(g) \rightleftharpoons COCl_2$. If one mole of CO (g) is present at equilibrium, the value of equilibrium constant of the reaction would be :*

(*a*) 1.5 (*b*) 2

(*c*) 2.5 (*d*) 3.0

Solution. For the reaction :

	$Cl_2(g)$ +	$CO(g)$ $\rightleftharpoons$	$COCl_2(g)$
Initial conc.	3 mol	2 mol	0
Conc. at equilibrium	$\dfrac{3-1=2\text{ mol}}{\text{Vol.}(=5\text{ L})}$	$\dfrac{2-1=1\text{ mol}}{\text{Vol.}(=5\text{ L})}$	$\dfrac{1\text{ mol}}{\text{Vol.}(=5\text{ L})}$

$$\therefore \quad K_c = \frac{[COCl_2]}{[Cl_2(g)][CO(g)]}$$

$$= \frac{1/5}{2/5 \times 1/5} = \frac{5}{2} = \mathbf{2.5.}$$

Hence, correct answer is (*c*).

Example 122. *The reaction of the formation of phosgene gas from CO and Cl_2 is as follows :*

$$CO + Cl_2 \rightleftharpoons COCl_2$$

In an experiment, starting with equimolar CO and Cl_2 in 250 mL flask, the equilibrium mixture on analysis is found to contain 0.05M CO, 0.05M Cl_2 and 0.15M $COCl_2$. Calculate the equilibrium constant of the reaction. **(UP 1984)**

Solution. Volume of mixture at equilibrium = 250 mL

$$= \frac{250}{1000} = 0.25\text{ L}$$

	CO +	Cl_2 $\rightleftharpoons$	$COCl_2$
mol L^{-} at equilibrium	$\dfrac{0.05\text{ mol}}{0.25\text{ L}}$	$\dfrac{0.05\text{ mol}}{0.25\text{ L}}$	$\dfrac{0.15\text{ mol}}{0.25\text{ L}}$
	$= 0.2\text{ mol L}^{-}$	$= 0.2\text{ mol L}^{-}$	$= 0.6\text{ mol L}^{-}$

$$\therefore \quad K_p = \frac{[COCl_2]}{[CO][Cl_2]}$$

$$= \frac{0.6\text{ mol L}^{-}}{0.2\text{ mol L}^{-} \times 0.2\text{ mol L}^{-}}$$

$$= \mathbf{15\ L\ mol^{-}} \qquad \textbf{Ans.}$$

Type. Dissociation of $COCl_2$ (phosgene)

Example 123. *Phosgene ($COCl_2$) was allowed to decompose at 500°C in a one litre vessel according to the reaction :*

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

If 49.5 g of $COCl_2$ is used initially, find the composition of equilibrium mixture. $K_c = 1.9$.

Solution. Wt. of $COCl_2$ = 49.5 g.

$$\text{g. mol. wt. of } COCl_2 = 12 + 16 + (2 \times 35.5) = 12 + 16 + 71 = 99\text{ g}$$

$$\therefore \text{ number of mol of } COCl_2 = \frac{49.5\text{ g}}{99\text{ g}} = 0.5\text{ mol}$$

	$COCl_2(g)$ $\rightleftharpoons$	$CO(g)$ +	$Cl_2(g)$
(*i*) *n* mol at start	0.5	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$\dfrac{0.5-x}{V}$	$\dfrac{x}{V}$	$\dfrac{x}{V}$

Where V = Volume of vessel = 1 L

$$\therefore \quad K_c = \frac{[CO][Cl_2]}{[COCl_2]};$$

$$1.9 = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{0.5-x}{V}} = \frac{\frac{x}{1} \times \frac{x}{1}}{\frac{0.5-x}{1}} = \frac{x^2}{0.5-x}$$

$$\therefore \quad 1.9\,(0.5 - x) = x^2 \quad ; \quad x^2 + 1.9\,x - 0.95 = 0$$

$$\therefore \quad x = \frac{-1.9 \pm \sqrt{(1.9)^2 - 4\,(1 \times -0.95)}}{2 \times 1}$$

$$\left[\because \textit{for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4\,ac}}{2\,a}\right.$$

$$\therefore \quad x = \frac{0.82}{2} = 0.41$$

$$\therefore \quad [CO] = [Cl_2] = 0.41\text{ mol L}^{-};$$

$$[COCl_2] = 0.5 - x = 0.5 - 0.41 = \mathbf{0.09\ mol\ L^{-}}\ \textbf{Ans.}$$

Type. Synthesis of CO from CO_2 and carbon

Example 124. *A gaseous mixture of CO_2 and CO at 1127 K and 1 atmosphere, in equilibrium with solid carbon has 90.55 % CO by mass in the reaction*

$$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)$$

Calculate the value of K_c for this reaction at the same temperature.

Solution. 90.55 % CO by mass in a mixture of CO and CO_2 gases means :

$$\text{Mass of CO (g)} = 90.55\text{ g};$$

$$\text{mass of } CO_2\text{ (g)} = 100 - 90.55 = 9.45\text{ g}$$

$$\text{g. mol. mass of CO} = 12 + 16 = 28\text{ g}$$

$$\text{g. mol. mass of } CO_2 = 12 + (2 \times 16) = 44\text{ g.}$$

$$\therefore \quad \text{no. of mol CO} = \frac{\text{Mass of CO}}{\text{g. mol. mass of CO}}$$

$$= \frac{90.55}{28} = \mathbf{3.234}$$

$$\text{no. of mol of } CO_2 = \frac{\text{mass of } CO_2}{\text{g. mol. mass of } CO_2}$$

$$= \frac{9.45}{44} = \mathbf{0.215}$$

In the reaction, carbon being a solid, it is not considered. Since the reaction involves change in volume, total number of mol are needed.

$\therefore$ Total number of mol of CO and

CO_2 gases = 3.234 + 0.215 = 3.449

$\therefore$ In the reaction,

$$CO_2\,(g) + C(s) \rightleftharpoons 2CO\,(g)$$

$$p_{CO} = \frac{3.234}{3.449} \times 1 \text{ atm} = 0.938 \text{ atm}\ ;$$

$$p_{CO_2} = \frac{0.215}{3.449} \times 1 \text{ atm} = 0.0623 \text{ atm}$$

$$\therefore \quad K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(0.938 \text{ atm})^2}{0.0623 \text{ atm}}$$

$$= 14.19 \text{ atm.}$$

$$\Delta n = n_P - n_R = 2 - 1 = 1$$

But $\quad K_p = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1$

Or $\quad K_c = \dfrac{K_p}{RT}$

$$= \frac{14.19 \text{ atm}}{0.0821 \text{ L atm K}^{-} \text{ mol}^{-} \times 1127 \text{ K}}$$

$$= 0.153 \text{ L}^{-} \text{ mol}$$

Example 125. *At 817° C, K_p for the reaction between $CO_2(g)$ and excess hot graphite (C) is 10 atm.*

(*a*) *What are the equilibrium concentrations of the gases at 817°C and a total pressure of 5 atm?*

(*b*) *At what total pressure, the gas contains 5 % CO_2 by volume.* **(Roorkee, 2000)**

Solution. K_p = 10 atm.,

α = degree of dissociation.

$$CO_2\,(g) \quad + \quad C\,(s) \quad \rightleftharpoons \quad 2CO\,(g)$$

(*i*) *n* mol at start

1 $\qquad\qquad$ 0

(*ii*) Change by reaction

$-\alpha$ $\qquad\qquad$ 2α

(*iii*) *n* mol at equilibrium

$1-\alpha$ $\qquad\qquad$ 2α

Total number of mol at equilibrium

$$= 1 - \alpha + 2\alpha = 1 + \alpha$$

$$\therefore \quad K_p = \frac{p\,(CO)^2}{p\,CO_2} = \frac{\left(\dfrac{2\alpha}{1+\alpha} \times P\right)^2}{\dfrac{1-\alpha}{1+\alpha} \times P}$$

$$= \frac{4\alpha^2 P^2}{(1+\alpha)^2} \times \frac{1+\alpha}{(1-\alpha)\,P} = \frac{4\alpha^2 P}{1-\alpha^2}$$

Or $\quad 10 = \dfrac{4\alpha^2 \times 5}{1-\alpha^2}$

$$= \frac{20\,\alpha^2}{1-\alpha^2}\ ;\ 10\,(1-\alpha^2) = 20\,\alpha^2\ ;$$

$$1 - \alpha^2 = \frac{20\,\alpha^2}{10} = 2\,\alpha^2$$

Or $\quad 2\alpha^2 + \alpha^2 = 1 \ ;\ 3\alpha^2 = 1\ ;$

$$\alpha^2 = \frac{1}{3} \text{ or } \alpha = \left(\frac{1}{3}\right)^{1/2} = (0.33)^{1/2}$$

$\therefore \quad \alpha$ = 0.577 mol

(*a*) At equilibrium,

$[CO_2] = 1 - \alpha = 1 - 0.577 = 0.423$ mol

$[CO] = 2\,\alpha = 2 \times 0.577 = 1.154$ mol.

(*b*) $\quad CO_2$ = 5 % by volume ;

CO = 100 – 5 = 95 % by volume.

$$\therefore \quad p_{CO_2} = \frac{5}{100} \times P = 0.05\,P\ ;$$

$$p_{CO} = \frac{95}{100} \times P = 0.95\,P$$

$$K_P = \frac{p\,(CO)^2}{p\,CO_2}\ ;$$

$$10 = \frac{(0.95\,P)^2}{0.05\,P} = \frac{0.9025\,P^2}{0.05\,P}$$

Or $\quad 10 \times 0.05 = 0.9025$ P ;

$$P = \frac{10 \times 0.05}{0.9025} = \mathbf{0.554\ atm} \qquad \textbf{Ans.}$$

Type. Dissociation of Carbon dioxide

Example 126. *When the following reaction;*

$$2CO_2\,(g) \rightleftharpoons 2\,CO\,(g) + O_2\,(g)$$

was allowed to take place at 3000 K, the value of K_p was found as 0.15 atm at equilibrium. Calculate the partial pressure of CO_2 at this temperature, if CO and CO_2 gases at partial pressures of 8 and 7 atmosphere at 300 K were brought to equilibrium at 3000 K.

Solution. $\quad 2\,CO_2\,(g) \quad \rightleftharpoons \quad 2\,CO\,(g) + O_2(g)$

(*i*) Pressure at start

7 $\qquad\qquad$ 8

(*ii*) Change by reaction

$-x$ $\qquad\qquad$ $+x$ $\qquad$ $+\dfrac{x}{2}$

(*iii*) Pressure at equilibrium

$7-x$ $\qquad\qquad$ $8+x$ $\qquad$ $\dfrac{x}{2}$

$$\therefore \qquad K_p = \frac{[CO]^2\,[O_2]}{[CO_2]^2} \;;\; 0.15 = \frac{(8+x)^2}{(7-x)^2}\times\frac{x}{2}$$

$$0.15\times 2 = \frac{(8+x)^2\,x}{(7-x)^2} = \frac{(64+x^2+16x)\times x}{49+x^2-14\,x}$$

$$= \frac{64\,x + x^3 + 16\,x^2}{49+x^2-14\,x}$$

Or $0.3\,(49 + x^2 - 14\,x) = 64\,x + x^3 + 16\,x$;
$14.7 + 0.3\,x^2 - 4.2\,x = 64\,x + x^3 + 16x^2$

Neglecting x^3, we have
$15.7\,x^2 + 68.2\,x - 14.7 = 0$. Hence

$$x = \frac{-68.2 \pm \sqrt{(68.2)^2 - (4\times 15.7\times -14.7)}}{2\times 15.7}$$

or $$x = 0.207 \left[\because \text{ for } ax^2+bx+c=0,\; x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}\right]$$

∴ Partial pressure of CO_2, $p\,CO_2\,(g)$ = **0.207 atm.**

Type. Synthesis of methane.

Example 127. *A gaseous mixture contains 0.3 mol CO, 0.1 mol H_2 and 0.02 mol H_2O plus an unknown amount of CH_4 in each litre. This mixture is in equilibrium at 1200 K*

$$CO\,(g) + 3H_2 \rightleftharpoons CH_4\,(g) + H_2O\,(g)$$

What is the concentration of CH_4 in this mixture ? The equilibrium constant $K_c = 3.92$ **(Bihar,CEE.,1995)**

Solution. $CO\,(g) + 3\,H_2\,(g) \rightleftharpoons CH_4\,(g) + H_2O\,(g)$

	$CO\,(g)$	$3\,H_2\,(g)$	$CH_4\,(g)$	$H_2O\,(g)$
n mol at equilibrium	0.3	0.1	x	0.02

$$K_c = \frac{[CH_4]\,[H_2O]}{[CO]\,[H_2]^3} \;;\; 3.92 = \frac{x\times 0.02}{0.3\times(0.1)^3}$$

Or $3.92(0.3)\times(0.1)^3 = 0.02\,x$
$1.176\times 10^{-3} = 0.02\,x\,;\, x = (1.176\times 10^{-3})/0.02$
$= \mathbf{0.0588}$ **Ans.**

Type. Dissociation of I_2

Example 128. *Iodine dissociates as*

$$I_2 \rightleftharpoons 2\,I$$

at 1273 K. As a result, a pressure of 0.112 atm was developed. The expected pressure is, however, 0.074 atm. Find the value of K_p.

Solution. Experimental pressure = 0.112 atm ;
Calculated pressure = 0.074 atm.

	I_2	$\rightleftharpoons$	2I
(*i*) n mol at start	1		0
(*ii*) Change by reaction	$-x$		$2\,x$
(*iii*) n mol at equilibrium	$1-x$		$2\,x$

Total number of mol at equilibrium

$$= 1 - x + 2\,x = 1 + x$$

But $$\frac{1+x}{1} = \frac{\text{Experimental pressure}}{\text{Calculated pressure}} \;;$$

$$1 + x = \frac{0.112}{0.074} = 1.51$$

$$\therefore \qquad x = 1.51 - 1 = 0.51$$

Also, $$K_p = \frac{p\,(I)^2}{p_{I_2}} = \frac{\left(\frac{2\,x}{1+x}\times P\right)^2}{\frac{1-x}{1+x}\times P}$$

$$= \frac{4\,x^2\,P^2}{(1+x)^2}\times\frac{1+x}{(1-x)\,P} = \frac{4\,x^2\,P}{1-x^2}$$

$$K_p = \frac{4\times(0.51)^2\times 0.112}{1-(0.51)^2} = \frac{0.116}{0.7399}$$

$= \mathbf{0.157\ atm.}$

Example 129. *What is the value of K_c for the reaction :*

$$I_2\,(g) \rightleftharpoons 2\,I\,(g)$$

at 1473 K, when one mol of iodine gas introduced into an evacuated one litre flask such that only 5% of it gets dissociated.

(BIT Mesra; Ranchi, 1992)

Solution.	$I_2\,(g)$	$\rightleftharpoons$	$2\,I\,(g)$
(*i*) n mol at start	1		0
(*ii*) Change by reaction	$\frac{-5}{100}$ $= -0.05$		0.05×2 $= 0.1$
(*iii*) n mol at equilibrium	$1 - 0.05$ $= 0.95$		0.1

$$K_c = \frac{[I]^2}{[I_2]} = \frac{(0.1)^2}{0.95} = \frac{0.01}{0.95} = 0.0105$$

$= \mathbf{1.05\times 10^{-2}\ mol\ L^{-}}$

Example 130. *Iodine is highly soluble in KI solution because of the following equilibrium*

$$I_2 + I^- \rightleftharpoons I_3^-$$

But its saturated solution in water is 0.33 g L^-. It is observed that M/10 KI solution (i.e., M/10 I^-) actually dissolves 12.5 g L^- I_2, most of which gets converted to I_3^-. If it is assumed that concentration of I_2 in all saturated solutions is same, what would be the equilibrium constant for the above reaction. Also, describe the effect of adding water to a clear saturated solution of I_2 in KI solution. (at. wt. of I = 127).

Solution. (*a*) Wt. of I_2 in water = 0.33 g ;

g. mol. wt. of I_2 = $2\times 127 = 254$ g mol^-

$$\therefore \text{ Number of mol of } I_2 = \frac{0.33\text{ g}}{254\text{ g mol}^-}$$

$$= 1.3\times 10^{-3}\text{ mol} = 0.0013\text{ mol.}$$

Wt. of I_2 in KI solution = 12.5 g ;
g. mol. wt. of I_2 = 2 × 127 = 254 g mol^-
∴ no. of mol of I_2 in KI solution

$$= \frac{12.5\text{ g}}{254\text{ g mol}^-} = 0.0492\text{ mol}$$

$$\frac{M}{10} I_2 = 0.1\text{ mol } I_2$$

	I_2	$+$	I^-	$\rightleftharpoons$	I_3^-
(*i*) *n* mol at start			0.1		0.0492
(*ii*) Change by reaction			− (0.0492–0.0013) = − 0.0479		− 0.0013
(*iii*) *n* mol at equilibrium	0.0013		0.1 − 0.0479 = 0.0521		0.0492–0.0013 = 0.0479

$$K_p = \frac{[I_3^-]}{[I^-][I_2]} = \frac{0.0479}{0.0521 \times 0.0013} = 707$$

(*b*) If water is added to the saturated solution of I_2 in KI, backward reaction is favoured.

Type. Calculation of K_c and K_p for homogeneous gaseous equilibrium reactions involving synthesis (or formation) of product with **'no change in volume** or having same number of mol of reactants and products'.

In order to understand it, consider the following reactions.

1. Synthesis of HI.

(*a*) **Determination of K_c**

	H_2	$+$	I_2	$\rightleftharpoons$	2HI
Initial conc.	a mol		b mol		0
Conc. at equilibrium	$\frac{a-x}{V}$ mol		$\frac{b-x}{V}$ mol		$\frac{2x}{V}$ mol

Let us start with *a* mol of H_2 and *b* mol of I_2 in a closed vessel having volume of '*V*' litre.

V = Volume of closed vessel in which reaction takes place.
x = Number of mol of each of H_2 and I_2 that are used to form 2 *x* mol of HI at equilibrium.

Molar concentration at equilibrium are :

$$[H_2] = \frac{a-x}{V} \;;\; [I_2] = \frac{b-x}{V} \;;\; [HI] = \frac{2x}{V}$$

Applying law of mass action, we get :

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)}$$

$$= \frac{4x^2}{V^2} \times \frac{V}{a-x} \times \frac{V}{b-x} = \frac{4x^2}{(a-x)(b-x)}$$

$$\therefore \quad K_c = \frac{4x^2}{(a-x)(b-x)}$$

(*b*) **Determination of K_p.**

$K_p = K_c$ (shown above) because the reaction involves no change in volume.

(*c*) **Synthesis of NO.**

(*a*) **Determination of K_c.**

	N_2	$+$	O_2	$\rightleftharpoons$	2NO
Initial conc.	a mol		b mol		0
Conc. at equilibrium	$\frac{a-x}{V}$ mol		$\frac{b-x}{V}$ mol		$\frac{2x}{V}$ mol

Note. (*a*) To find K_c proceed as shown in synthesis of HI above
(*b*) $K_p = K_c$.

EXAMPLE 131. *One mol of H_2, 2 mol of I_2 and 3 mol of HI are injected in a one litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 500°C ? K_c for reaction, $H_2 + I_2 \rightleftharpoons 2HI$ is 45.9.* **(UP SEAT, 1995, MLNR, 1995, Roorkee, 1988)**

SOLUTION. Reaction	H_2	$+$	I_2	$\rightleftharpoons$	2HI
no. of mol at t = 0	1		2		3
no. of mol at equilibrium	1 − *x*		2 − *x*		3 + 2*x*

If volume of container is *V* litre, then :

[∵ *x* = no. of mol dissociated. For 2 HI, HI formed = 2*x*

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{3+2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{2-x}{V}\right)};$$

$$45.9 = \frac{(3+2x)^2}{(1-x)(2-x)};$$

$$45.9 = \frac{9+4x^2+12x}{2-3x+x^2};$$

$$45.9(2-3x+x^2) = 9+4x^2+12x$$
$$= 91.8 - 137.07x + 45.9x^2$$
$$= 9 + 4x^2 + 12x$$

$$41.9x^2 - 149.7x + 82.8 = 0$$

After solving, we find

$$x = 0.684\text{ mol L}^-$$

∴ $[H_2]$ = 1 − 0.684 = **0.316 mol L^-** **Ans.**

[∵ *V* = 1 L]

$[I_2]$ = 2 − 0.684 = **1.316 mol L^-** **Ans.**

$$\left[\begin{array}{l} \because x = \dfrac{-b \pm (b^2 - 4ac)^{1/2}}{2a} \\ \text{for a quadratic equation} \\ ax^2 + bx + c = 0 \end{array}\right]$$

$$[HI] = 3 + 2\,(0.684) = 3 + 1.368$$

$$= \mathbf{4.368\ mol\ L^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 132. *25 cc hydrogen and 18 cc of iodine vapours were heated in a sealed tube at 456°C when at equilibrium 30.8 cc of HI are formed. Calculate the value of equilibrium constant.*

(Modified MLNR, 1984, AIPMT, 2009)

SOLUTION. The reaction is :

$$\begin{array}{lccccc} \textbf{At equilibrium} & H_2 & + & I_2 & \rightleftharpoons & 2HI \\ & \dfrac{a-x}{V} & & \dfrac{b-x}{V} & & \dfrac{2x}{V} \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-x}{V}\right)}$$

$$= \frac{4x^2}{(a-x)(b-x)} \qquad \ldots (1)$$

$$2x = \text{Vol of HI} = 30.8 \text{ cc}$$

$$\therefore \quad x = 30.8/2 = 15.4 \text{ cc;}$$

$$a = \text{Vol. of } H_2 = 25 \text{ cc}$$

$$\therefore \quad a - x = 25 - 15.4 = 9.6 \text{ cc;}$$

$$b = \text{Vol of } I_2 = 18 \text{ cc}$$

$$\therefore \quad b - x = 18 - 15.4 = 2.6 \text{ cc}$$

Substituting these values in equation (1) above, we have :

$$K_c = \frac{4 \times (15.4)^2}{9.6 \times 2.6} = \frac{4 \times 237.16}{9.6 \times 2.6} = 38$$

EXAMPLE 133. *The K_p value for the reaction : $H_2 + I_2 \rightleftharpoons 2\,HI$ at 460° C is 49. If the partial pressure of each of H_2 and I_2 is 0.5 atm, determine the partial pressure of each gas at equilibrium.* **(Roorkee , 1999)**

SOLUTION.

	H_2	+	I_2	$\rightleftharpoons$	2HI
(*i*) *n* atm at start	0.5		0.5		0
(*ii*) Change by reaction	$-x$		$-x$		$2x$
(*iii*) *n* atm at equilibrium	$0.5-x$		$0.5-x$		$2x$

Applying law of chemical equilibrium, we have :

$$K_p = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{(2x)^2}{(0.5-x)(0.5-x)};$$

$$49 = \frac{(2x)^2}{(0.5-x)^2}$$

Taking square root of both sides, we get :

$$7 = \frac{2x}{0.5-x}; \; 3.5 - 7x = 2x \; ; 9x = 3.5$$

$$\therefore \quad x = 3.5/9 = 0.389 \text{ atm.}$$

$$\therefore \quad p_{H_2} = 0.5 - x = 0.5 - 0.389 = \mathbf{0.111\ atm\ Ans.}$$

$$p_{I_2} = 0.5 - x = 0.5 - 0.389 = \mathbf{0.111\ atm\ Ans.}$$

$$p_{HI} = 2x = 2 \times 0.389 = \mathbf{0.778\ atm} \qquad \textbf{Ans.}$$

EXAMPLE 134. *The equilibrium constant for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ is 0.35 at 298 K. Has the equilibrium been reached ? If not, state on which side of the equilibrium, the system is.*

(*i*) *p_{H_2} = 0.55 bar ; p_{HI} = 0.44 bar ; there is solid I_2 in the container.*

(*ii*) *p_{H_2} = 2.5 bar ; p_{HI} = 0.15 bar; there is solid I_2 in the container.*

(*iii*) *p_{H_2} = 0.10 bar ; p_{HI} = 0.80 bar ; there is solid I_2 in the container.*

SOLUTION. The reaction is :

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

(*i*) p_{H_2} = 0.55 bar, p_{I_2} = 1 (being solid) ;

p_{HI} = 0.44 bar.

$\therefore$ Concentration quotient,

$$Q = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{(0.44)^2}{0.55 \times 1} = \frac{0.1936}{0.55} = \mathbf{0.35}$$

K = 0.35 (given). Since the value of *Q* = *K*, *equilibrium has been reached.*

(*ii*) p_{H_2} = 2.5 bar ; p_{I_2} = 1 ; p_{HI} = 0.15 bar

$$\therefore \quad Q = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{0.15 \times 0.15}{2.5}$$

$$= \frac{0.0225}{2.5} = 0.009$$

K = 3.5. Since the value of *Q* is much less than that of *K*, the *equilibrium has not been reached* and the reaction will proceed in the *forward direction*.

(*iii*) p_{H_2} = 0.1 bar, p_{I_2} = 1 ; p_{HI} = 0.8 bar

$$\therefore \quad Q = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{0.8 \times 0.8}{0.1} = 6.4$$

K = 3.5. Since the value of *Q* is much higher than that of *K*, the *equilibrium has not been reached* and the reaction will proceed in the backward direction.

EXAMPLE 135. *A mixture containing H_2 and I_2 in the molar ratio 2 : 3 was heated at 713 K till the reaction $H_2 + I_2 \rightleftharpoons 2\,HI$ reached at the equilibrium state. Calculate the percentage of iodine converted into HI (K_c at 713 K = 0.02).* **(Bihar CEE, 1987)**

SOLUTION. Reaction	H_2	+	I_2	$\rightleftharpoons$	2HI
(*i*) *n* mol at start	2		3		0
(*ii*) Change by reaction	$-x$		$-x$		$2x$
(*iii*) *n* mol at equilibrium	$2-x$		$3-x$		$2x$

Applying law of chemical equilibrium, we have

$$K = \frac{[HI]^2}{[H_2][I_2]} \quad ; \quad 0.02 = \frac{(2x)^2}{(2-x)(3-x)}$$

$$0.02 = \frac{4x^2}{6-5x+x^2} \;;$$

$$= 0.12 - 0.1x + 0.02x^2 = 4x^2 \;;$$

$$4x^2 - 0.02x^2 + 0.1x - 0.12 = 0 \;;$$

$$3.98x^2 + 0.1x - 0.12 = 0$$

$$\therefore \quad x = \frac{-(+0.1) \pm \sqrt{(+0.1)^2 - 4(3.98 \times -0.12)}}{2 \times 3.98}$$

$$\left[\because \text{for } ax^2 + bx + c = 0, \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$x = \frac{-0.1 \pm \sqrt{0.01 + 1.91}}{7.96} = \frac{-0.1 \pm \sqrt{1.92}}{7.96}$$

$$= \frac{-0.1 \pm 1.38}{7.96}$$

$$= \frac{1.28}{7.96} = \mathbf{0.16} \text{ or } \frac{-1.48}{7.96}$$

x cannot be negative, so $\frac{-1.48}{7.96}$ value is rejected.

Total mol of I_2 = 3

$\therefore$ % age of I_2 converted to HI

$$= \frac{0.16 \times 100}{3} = \mathbf{5.33\ \%} \qquad \textbf{Ans.}$$

EXAMPLE 136. *In a 10 L evacuated chamber, 0.5 mol H_2 and 0.5 mol I_2 are reacted at 448°C. At which temperature K = 50 for*

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

For concentration in mol per litre :

(a) What is the value of K_p ?

(b) What is total pressure in the chamber ?

(c) How many mol of iodine remain unreacted at equilibrium ?

(d) What is partial pressure of each component in the equilibrium mixture ?

(e) What is the concentration of each substance at equilibrium ? **(Roorkee, 1985, 1989)**

SOLUTION. (*a*) Since Δn = 0 in this reaction, volume is not considered in this reaction to calculate *K*. Hence,

$$K_p = K_c = 50$$

$$n = \text{Total mol of } H_2 \text{ and } I_2$$

$$= 0.5 + 0.5 = 1.0.$$

$$V = 10\text{ L} \;; \quad R = 0.0821 \text{ L atm mol}^{-} \text{ K}^{-} \;;$$

$$T = 448 + 273 = 721 \text{ K} \quad P = ?$$

(*b*) We know $PV = nRT$;

$$P = \frac{nRT}{V}$$

$$= \frac{1\text{ mol} \times 0.0821 \text{ L atm mol}^{-} \text{ K}^{-} \times 721\text{ K}}{10\text{ L}}$$

$$\therefore \quad P = \mathbf{5.9\ atm = Total\ pressure.} \qquad \textbf{Ans.}$$

Given reaction :	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
(*i*) n mol at start	0.5	0.5	0
(*ii*) Change by reaction	$-x$	$-x$	$2x$
(*iii*) n mol at equilibrium	$0.5-x$	$0.5-x$	$2x$

Applying law of chemical equilibrium, we have.

$$K = \frac{[HI]^2}{[H_2][I_2]} \;;$$

$$50 = \frac{(2x)^2}{(0.5-x)(0.5-x)} = \frac{(2x)^2}{(0.5-x)^2}$$

Taking square root, we get :

$$(50)^{1/2} = \frac{2x}{0.5-x} \;; \quad 7.07 = \frac{2x}{0.5-x}$$

$$3.53 - 7.07x = 2x \;; \quad 2x + 7.07x = 3.53$$

$$9.07x = 3.53 \;; \quad x = \frac{3.53}{9.07} = 0.39$$

(*c*) mol of I_2 remained unreacted at equilibrium

$$= 0.5 - 0.39 = \mathbf{0.11\ mol} \qquad \textbf{Ans.}$$

(*d*)

$$p_{H_2} = \frac{\text{Mol of } H_2}{\text{Total mol}} \times \text{total pressure}$$

$$= \frac{0.11 \times 5.9}{1} = 0.649 \text{ atm}$$

$$p_{I_2} = p_{H_2} = 0.649 \text{ atm}$$

$$p_{HI} = \text{Total pressure} - (p_{H_2} + p_{I_2})$$

$$= 5.9 - (0.649 + 0.649)$$

$$= \mathbf{4.66\ atm}$$

(*e*) $\therefore$

$$[H_2] = [I_2] = 0.5 - 0.39 = 0.11 \text{ mol}$$

$$= \frac{0.11 \text{ mol}}{10 \text{ L}} = \mathbf{0.011\ mol\ L^{-}}$$

Also, $[HI] = 2x = 2 \times 0.39 = \mathbf{0.78\ mol\ L^{-}}$

EXAMPLE 137. *15 g mol of H_2 reacts with 5.2 g mol of I_2 to give 10 g mol of HI. Calculate the equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2HI$.* **(UP, 1980)**

SOLUTION. Reaction :	H_2 +	I_2 $\rightleftharpoons$	2 HI
(*i*) n mol at start	15	5.2	10
(*ii*) Change by reaction	$-x$	$-x$	$2x$
(*iii*) n mol at equilibrium	$15-x$	$5.2-x$	$2x$

$$2x = 10. \quad \text{So,} \quad x = 10/2 = 5$$

$$\therefore \quad [H_2] = 15 - x = 15 - 5 = 10 \;;$$

$$[I_2] = 5.2 - x = 5.2 - 5.0 = 0.2, \quad [HI] = 10$$

Applying law of chemical equilibrium, we get :

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{10 \times 10}{10 \times 0.2} = 50$$

$$\therefore \quad K = \mathbf{50} \qquad \textbf{Ans.}$$

EXAMPLE 138. *25 mL of H_2 and 18 mL of I_2 vapours are heated in a sealed glass tube at 465°C, when at equilibrium, 30.8 mL of HI was formed. Calculate the percentage degree of dissociation of pure 2 mol HI at 465°C.* **(MLNR, 1984)**

SOLUTION. (*a*) K_c = 38 (see example 132...)

(*b*) For $H_2 + I_2 \rightleftharpoons 2HI$,

$$K_c = 38 \qquad \text{...(1)}$$

∴ For $2HI \rightleftharpoons H_2 + I_2,\; K_c' = \dfrac{1}{38}$ ... (2)

For reaction :	$2HI$	$\rightleftharpoons$	H_2	+	I_2, we have
(*i*) *n* mol at start	2		0		0
(*ii*) Change for reaction	-2α		$2\alpha/2 = \alpha$		$2\alpha/2 = \alpha$
(*iii*) *n* mol at equilibrium	$2 - 2\alpha$		α		α

Applying law of chemical equilibrium to equation (2), we have :

$$K_c' = \frac{[H_2][I_2]}{[HI]^2};$$

$$\frac{1}{38} = \frac{\alpha \times \alpha}{(2 - 2\alpha)^2} = \frac{\alpha^2}{4 + 4\alpha^2 - 8\alpha}$$

Or $38\alpha^2 = 4 + 4\alpha^2 - 8\alpha;$

$38\alpha^2 - 4\alpha^2 + 8\alpha - 4 = 0$

Or $34\alpha^2 + 8\alpha - 4 = 0;$

$$\therefore \quad \alpha = \frac{-8 \pm \sqrt{(8)^2 - 4(34 \times -4)}}{2 \times 34}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0,\; x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$\alpha = \frac{-8 \pm \sqrt{64 + 544}}{68} = \frac{-8 \pm \sqrt{608}}{68} = \frac{-8 \pm 24.65}{68}$$

$$\alpha = \frac{-8 \pm 24.65}{68} = \frac{16.65}{68} = 0.244$$

(on addition), $\dfrac{-32.65}{68}$ (on subtraction)

Since α cannot be negative, negative value is neglected.

∴ % age degree of dissociation = 0.244 × 100

= **24.4 %** **Ans.**

> **Note.** According to Avogadro's law, equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure.

EXAMPLE 139. *At a certain temperature, the value of equilibrium constant of the reaction*

$$H_2 + I_2 \rightleftharpoons 2HI$$

is 6.0. If the system is equilibrated at [HI] = 1.23, $[H_2]$ = 0.50 and $[I_2]$ = 0.5 in a one litre flask and suddenly 0.6 mol of HI is removed, calculate the concentration of all species when equilibrium is attained.

SOLUTION. Reaction.	H_2	+	I_2	$\rightleftharpoons$	$2HI$
(*i*) *n* mol at start	0.5		0.5		1.23
(*ii*) Change by reaction	$-x$		$-x$		$+2x - 0.6$
(*iii*) *n* mol at equilibrium	$0.5 - x$		$0.5 - x$		$1.23 + 2x - 0.6 = 0.63 + 2x$

Applying law of chemical equilibrium, we get :

$$K = \frac{[HI]^2}{[H_2][I_2]}; \quad 6 = \frac{(0.63 + 2x)^2}{(0.5 - x)(0.5 - x)}$$

Taking square root of both sides, we get :

$$\sqrt{6} = \frac{0.63 + 2x}{0.5 - x}; \quad 2.45 = \frac{0.63 + 2x}{0.5 - x};$$

$2.45\,(0.5 - x) = 0.63 + 2x$

$1.225 - 2.45\,x = 0.63 + 2x;$

$2x + 2.45\,x + 0.63 - 1.225 = 0$

Or $4.45x - 0.595 = 0;\quad x = \dfrac{0.595}{4.45} = 0.13$

∴ $[H_2] = [I_2] = 0.50 - 0.13 =$ **0.37 mol.** **Ans.**

$[HI] = 0.63 + 2(0.13) = 0.63 + 0.26$

= **0.89 mol.** **Ans.**

EXAMPLE 140. *One mol each of H_2 and I_2 are heated in an evacuated chamber of 30 L capacity to 470°C. If K = 50.*

(*a*) *How many mol of I_2 remain unreacted when equilibrium is established?*

(*b*) *Find the partial pressures of HI and I_2 in the equilibrium mixture.*

(*c*) *Now if one additional mol of H_2 is introduced into this equilibrium mixture, how many mol of the original iodine will remain unreacted ?*

SOLUTION. Reaction :	H_2	+	I_2	$\rightleftharpoons$	$2HI$
(*i*) *n* mol at start	1		1		0
(*ii*) Change by reaction	$-x$		$-x$		$2x$
(*iii*) *n* mol at equilibrium	$1 - x$		$1 - x$		$2x$

Applying law of chemical equilibrium, we get :

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1 - x)(1 - x)} = \frac{(2x)^2}{(1 - x)^2}$$

(*a*) ∴ $$50 = \frac{(2x)^2}{(1 - x)^2}$$

Taking square root of both sides, we get :

$$\sqrt{50} = \frac{2x}{1 - x}; \quad 7.07 = \frac{2x}{1 - x};$$

$7.07 - 7.07\,x = 2x;$

$2x + 7.07\,x = 7.07 \quad ; \quad 9.07x = 7.07;$

Thus $x = 7.07/9.07$

Or $x = 0.78$ mol I_2 reacted.

∴ Mol of I_2 remain unreacted

$= 1 - x = 1 - 0.78 =$ **0.22 mol** **Ans.**

(*b*) Since the number of moles of the gas do not change as the reaction proceeds at 470°C, hence number of mol (*n*) of gas that remains at equilibrium = 1 + 1 = 2.

$P = ?,\quad n = 2,\quad R = 0.0821$ L atm K^{-} mol^{-},

$T = 470 + 273$ K = 743 K and $V = 30$ L.

But $PV = nRT;$

So, $$P = \frac{n\,RT}{V}$$

$$= \frac{2\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 743\text{ K}}{30\text{ L}}$$

∴ $P =$ **4.1 atm.**

$$P_{I_2} = \frac{0.22\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 743\text{ K}}{30\text{ L}}$$

$=$ **0.45 atm.** **Ans.**

no. of mol of HI $= 2\,x = 2 \times 0.78 = 1.56$ mol

∴ $$p_{HI} = \frac{1.56\text{ mol} \times 0.0821\text{ L atm K}^{-}\text{ mol}^{-} \times 743\text{ K}}{30\text{ L}}$$

$=$ **3.17 atm.** **Ans.**

(*c*) H_2	+	I_2 $\rightleftharpoons$	2HI
(*i*) *n* mol at start	$1 + 1$ $= 2$	1	0
(*ii*) Change by reaction	$-x$	$-x$	$2\,x$
(*iii*) *n* mol at equilibrium	$2 - x$	$1 - x$	$2\,x$

Applying law of chemical equilibrium, we have :

$$K = \frac{[HI]^2}{[H_2][I_2]}\ ;$$

$$50 = \frac{(2x)^2}{(2-x)(1-x)} = \frac{4x^2}{2 - 3x + x^2}\ ;$$

$$100 - 150\,x + 50\,x^2 = 4\,x^2 \quad ; \quad 50x^2 - 4x^2 - 150x + 100 = 0$$

$$\therefore\ 46x^2 - 150x + 100 = 0\ ;$$

$$x = \frac{-(-150) \pm \sqrt{(-150)^2 - 4\,(46 \times 100)}}{2 \times 46}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right.$$

∴ $$x = \frac{150 \pm \sqrt{22500 - 18400}}{92}$$

$$= \frac{150 \pm \sqrt{4100}}{92} = \frac{150 \pm 64.03}{92}$$

$$= \frac{214.03}{92} \text{ or } \frac{85.97}{92}$$

$= 2.33$ or 0.93.

Here 2.33 is rejected according to given data. So, $x = 0.93$ mol of I_2 reacted.

∴ Mol of I_2 remained unreacted

= Initial mol of I_2 – mol of I_2 reacted

$= 1.00 - 0.93 =$ **0.07 mol** **Ans.**

EXAMPLE 141. *When one gram of H_2 is heated with 46 g of I_2 at 470°C, the equilibrium mixture contains 1.9 g I_2.*

(*a*) *Calculate the value of equilibrium constant*

(*b*) *How many mol of each gas are present in the equilibrium mixture ?*

SOLUTION. Wt. of $H_2 = 1$ g ;

g. mol. wt. of $H_2 = 2 \times 1 = 2$ g

∴ no. of mol of $H_2 = \frac{1}{2} = 0.5$ mol ;

Wt. of $I_2 = 46$ g ;

g. mol. wt. of $I_2 = 2 \times 127 = 254$ g.

∴ $$\text{no. of mol of } I_2 = \frac{\text{Wt. of } I_2}{\text{g. mol. wt. of } I_2}$$

$$= \frac{46}{254} = 0.181\text{ mol}$$

no. of mol of I_2 produced at equilibrium

$$= \frac{\text{Wt. of } I_2}{\text{g. mol. wt. of } I_2}$$

$$= \frac{1.9\text{ g}}{254\text{ g}} = 0.0075$$

For H_2	+ I_2	$\rightleftharpoons$ 2HI
(*i*) *n* mol at start		
0.5	0.181	0
(*ii*) *n* mol used up		
$0.181 - 0.0075$ $\simeq 0.174$	$0.181 - 0.0075$ $\simeq 0.174$	—
(*iii*) *n* mol produced		
—	—	$2(0.174) = 0.348$
(*iv*) *n* mol at equilibrium		
$0.5 - 0.174$ $= 0.326$	0.0075	0.348

Applying law of chemical equilibrium, we get :

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.348)^2}{0.326 \times 0.0075} = 49.5$$

Or $K =$ **49.5** **Ans.**

Type. ΔG° = – 2.303 RT log K

ΔG° is not the free energy change at equilibrium. It is the free energy change when all the reactants and products are taken at a concentration of 1 Mol L^{-}. ΔG° is related to K_c or K_p as $\Delta G° = -RT \ln K_c$ or $\Delta G° = -RT \ln Kp$. The units of ΔG° depend upon units of R. When R is used as 8.314 J $mol^{-}\ K^{-}$, ΔG° will be in joules. When R is used as 1.99 cal $mol^{-} K^{-}$, ΔG° will be in calories. But K_p must always be in $(atm)^{\Delta n}$.

EXAMPLE 142. *The value of equilibrium constant K is 45.9 at 490°C for the reaction :*

$$H_2 + I_2 \rightleftharpoons 2HI$$

Calculate the value of ΔG° for the reaction at that temperature.

SOLUTION. $\Delta G° = ?$, $R = 1.987$ cal K^{-},

$T = 490 + 273 = 763$ K, $K = 45.9$.

We know that : $\Delta G° = -2.303\text{ RT} \log K$

$$= -2.303 \times 1.987\text{ cal K}^{-} \times 763\text{ K} \log 45.9$$

$$= -3490 \times 1.6618 = -5.79 \times 10^3\text{ cal}$$

$$= \frac{-5.79 \times 10^3}{10^3}\text{ k cal}$$

$\Delta G° =$ **– 5.79 k cal.** **Ans.**

EXAMPLE 143. *When an experiment was performed at 763 K, the following equilibrium composition was obtained for the reaction :* $H_2 + I_2 \rightleftharpoons 2HI + heat$; $[H_2] = 8.62 \times 10^{-4}$ *mol* L^{-} ; $[I_2] = 2.63 \times 10^{-3}$ *mol* L^{-} ; $[HI] = 1.02 \times 10^{-2}$ *mol* L^{-}.

(*a*) *Find equilibrium constant, K*

(*b*) *Find* $\Delta G°$

(*c*) *Predict the effect of increasing temperature on equilibrium*

(*d*) *Predict the effect of increasing volume on the equilibrium.*

SOLUTION. (*a*) Reaction :

$$H_2 \quad + \quad I_2 \quad \rightleftharpoons \quad 2HI + \text{heat}$$

n mol at equilibrium

$$8.62 \times 10^{-4} \qquad 2.63 \times 10^{-3} \qquad 1.02 \times 10^{-2}$$

Applying law of chemical equilibrium, we get :

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1.02 \times 10^{-2})^2}{8.62 \times 10^{-4} \times 2.63 \times 10^{-3}} = \mathbf{45.9} \textbf{ Ans.}$$

(*b*)

$$\Delta G° = -2.303 \text{ RT} \log \text{K}$$

$$= -2.303 \times 1.987 \text{ cal K}^{-} \times 763 \text{ K} \log 45.9$$

$$= -3490 \times 1.6618 = -5.79 \times 10^3 \text{ cal}$$

$$= \mathbf{-5.79 \text{ k cal}} \qquad \textbf{Ans.}$$

(*c*) Since the reaction is exothermic, increase in temperature will favour the backward reaction.

(*d*) Since number of mol of reactants is equal to number of mol of products, volume will have no effect on equilibrium.

EXAMPLE 144. *The value of equilibrium constant for the reaction* $H_2 + I_2 \rightleftharpoons 2HI$ *at 700°C is 54.8. If 0.5 mol* L^{-} *of HI (g) is present at equilibrium at 700°C, what are the concentrations of* H_2 *(g) and* I_2 *(g) assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K.*

(Problem from NCERT Text book)

SOLUTION. For $H_2 + I_2 \rightleftharpoons 2 \text{ HI}$, K = 54.8 . Thus, for $2HI \rightleftharpoons H_2 + I_2$ *i.e.*, reverse reaction, $K' = 1/K_c = 1/54.8$

$\therefore$ For the reaction : $\quad 2 \text{ HI} \rightleftharpoons H_2 + I_2$

n mol at equilibrium $\quad 0.5 \qquad x \qquad x$

Applying law of chemical equilibrium, we get :

$$K = \frac{[H_2][I_2]}{[HI]^2} \ ; \quad \frac{1}{54.8} = \frac{x \times x}{(0.5)^2} = \frac{x^2}{0.25}$$

$$\therefore \qquad 54.8\, x^2 = 0.25 \ ;$$

$$x = \sqrt{\frac{0.25}{54.8}} = \sqrt{0.00456}$$

$$= \mathbf{0.068 \text{ mol L}^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 145. *In the reaction,*

$$H_2 + I_2 \rightleftharpoons 2HI$$

the equilibrium concentration of H_2, I_2 *and HI at 400°C are 0.2 mol, 0.2 mol and 1.6 mol* L^{-} *respectively. Calculate*

(*a*) K_c *and* K_p *for the reaction*

(*b*) *The equilibrium concentrations if 1 mol of* H_2, *2 mol of* I_2 *and 3 mol of HI are heated in a 10 litre flask and 400°C and*

(*c*) *Equilibrium concentrations if one mol of HI is added.*

SOLUTION. (*a*) $\qquad H_2 \quad + \quad I_2 \quad \rightleftharpoons \quad 2 \text{ HI}$

n mol at equilibrium $\quad 0.2 \qquad 0.2 \qquad 1.6$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.6)^2}{0.2 \times 0.2} = 64$$

Since , $\quad \Delta n = 0, \quad K_c = K_p = 64.$

(*b*) Reaction $\qquad H_2 \quad + \quad I_2 \quad \rightleftharpoons \quad 2 \text{ HI}$

(*i*) *n* mol at start $\qquad 1 \qquad 2 \qquad 3$

(*ii*) Change by reaction $\qquad -x \qquad -x \qquad 2x$

(*iii*) *n* mol at equilibrium $\qquad \frac{1-x}{10} \qquad \frac{2-x}{10} \qquad \frac{2x+3}{10}$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x+3}{10}\right)^2}{\left(\frac{1-x}{10}\right)\left(\frac{2-x}{10}\right)}$$

$$= \frac{(2x+3)^2}{(1-x)(2-x)}$$

$$64 = \frac{4x^2 + 9 + 12x}{2 - 3x + x^2} \ ;$$

$$128 - 192x + 64x^2 = 4x^2 + 9 + 12x$$

Or $\quad 64x^2 - 4x^2 - 192x - 12x + 128 - 9 = 0 \quad ;$

$$60x^2 - 204x + 119 = 0$$

$$\therefore \qquad x = \frac{-(-204) \pm \sqrt{(-204)^2 - 4(60 \times 119)}}{2 \times 60}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0, \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$= \frac{204 \pm \sqrt{41616 - 28560}}{120}$$

$$= \frac{204 \pm \sqrt{13056}}{120} = \frac{204 \pm 114}{120}$$

$$= \frac{318}{120} \text{ or } \frac{90}{120} = 2.65 \text{ or } 0.75$$

Since the value cannot be 2.65, we have, $x = 0.75$

$$\therefore \qquad [H_2] = \frac{1-x}{10} = \frac{1-0.75}{10} = \frac{0.25}{10}$$

$$= 0.025 \text{ mol L}^{-}$$

$$I_2 = = \frac{2-x}{10} = \frac{2-0-75}{10} = \frac{1.25}{10} = 0.125 \text{ mol L}^{-}$$

$$[\text{HI}] = \frac{2x+3}{10} = \frac{(2\times 0.75)+3}{10}$$

$$= \frac{1.5+3}{10} = \frac{4.5}{10} = 0.45 \text{ mol L}^{-}$$

	H_2	+	I_2	$\rightleftharpoons$	2HI
(*c*) Reaction	H_2	+	I_2	$\rightleftharpoons$	2HI
(*i*) *n* mol at start	0.2		0.2		1.6
(*ii*) Change by reaction	$-x$		$-x$		$2x$
(*iii*) *n* mol at equilibrium	$0.2-x$		$0.2-x$		$2x+1+1.6$ $= 2x+2.6$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[\text{HI}]^2}{[H_2][I_2]} ;$$

$$64 = \frac{(2x+2.6)^2}{(0.2-x)(0.2-x)} = \frac{(2x+2.6)^2}{(0.2-x)^2}$$

Taking square root of both sides, we get :

$$8 = \frac{2x+2.6}{0.2-x} ; \; 1.6 - 8x = 2x + 2.6 ;$$

$$2x + 8x + 2.6 - 1.6 = 0$$

Or $\quad 10x = -1 \;;\; x = \frac{-1}{10} = -0.1$

$\therefore \quad [H_2] = [I_2] = 0.2 - x = 0.2 - (-0.1)$

$= \mathbf{0.3 \text{ mol L}^{-}}$

$[\text{HI}] = 2x + 2.6 = 2(-0.1) + 2.6 = -0.2 + 2.6$

$= \mathbf{2.4 \text{ mol L}^{-}}$

EXAMPLE 146. *At 700 K, hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5 × 10^8. Calculate the amount of H_2, Br_2 and HBr at equilibrium if a mixture of 0.6 mol of H_2 and 0.2 mol of Br_2 is heated to 700 K.* **(Roorkee, 1995)**

SOLUTION. Reaction

	H_2	+	Br_2	$\rightleftharpoons$	2HBr
(*i*) *n* mol at start	0.6		0.2		0
(*ii*) Change by reaction	$-x$		$-x$		$2x$
(*iii*) *n* mol at equilibrium	$0.6-x$		$0.2-x$		$2x$

Applying law of chemical equilibrium, we have :

$$K_c = \frac{[\text{HBr}]^2}{[H_2][Br_2]} = \frac{2x \times 2x}{(0.6-x)(0.2-x)}$$

$$= \frac{4x^2}{0.12 - 0.8x + x^2}$$

$$\therefore \quad 5\times 10^8 = \frac{4x^2}{x^2 - 0.8x + 0.12} ; \; 5 \times 10^8 x^2 - 5 \times 10^8 \times 0.8x + 5\times 10^8 \times 0.12 = 4x^2 ;$$

$$5 \times 10^8 x^2 - 4x^2 - 4 \times 10^8 x + 0.6 \times 10^8 = 0;$$

$$10^8 (5x^2 - 4 \times 10^{-8} x^2 - 4x + 0.6) = 0$$

Or $5x^2 - 4x + 0.6 = 0;$

[$4 \times 10^{-8} x^2$ being very small, is neglected]

$$x = \frac{-(-4) \pm \sqrt{(-4)^2 - 4(5\times 0.6)}}{2\times 5}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0, \; x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right.$$

Or $$x = \frac{4 \pm \sqrt{16-12}}{10} = \frac{4\pm 2}{10} = 0.6 \text{ or } 0.2.$$

But according to given data, *x* cannot be equal to 0.6.

So, $\quad x = 0.2 \;\; \therefore [H_2] = 0.6 - x = 0.6 - 0.2$

$= \mathbf{0.4 \text{ mol}}$ **Ans.**

$[Br_2] = 0.2 - x = 0.2 - 0.2 \quad = \mathbf{0.0 \text{ mol}}$ **Ans.**

$[\text{HBr}] = 2x = 2 \times 0.2 = \mathbf{0.4 \text{ mol}}$ **Ans.**

Type. Calculation of K_c for homogeneous gaseous **dissociation** reversible reaction involving **"no change in volume or having same number of mol in reactants and products."** In order to understand it, let us consider the **dissociation of HI.**

	2HI	$\rightleftharpoons$	H_2	+	I_2
(*i*) *n* mol at start	1		0		0
(*ii*) Change by reaction	$-x$		$+\frac{x}{2}$		$+\frac{x}{2}$
(*iii*) *n* mol at equilibrium	$\frac{1-x}{V}$		$\frac{x/2}{V} = \frac{x}{2V}$		$\frac{x}{2V}$

Let us start with 1 mol of HI enclosed in a vessel of volume of '*V*' litre.

V = volume of the closed vessel in which reaction takes place.

x = number of mol of HI that decompose at equilibrium to yield *x*/2 mol of H_2 and *x*/2 mol of I_2.

Applying law of mass action, we get,

$$[\text{HI}] = \frac{1-x}{V} ; [H_2] = \frac{x}{2V} ; [I_2] = \frac{x}{2V}$$

$$\therefore \quad K_c = \frac{[H_2][I_2]}{[\text{HI}]^2} = \frac{\left(\frac{x}{2V}\right)\left(\frac{x}{2V}\right)}{\left(\frac{1-x}{V}\right)^2}$$

Or $$K_c = \frac{x^2}{4V^2} \times \frac{V^2}{(1-x)^2} = \frac{x^2}{4(1-x)^2}$$

EXAMPLE 147. *In an equilibrium, 2HI $\rightleftharpoons$ $H_2 + I_2$, 819.2 g of HI, 3.9 g H_2 and 101.6 g I_2 were present in a 4 litre flask. Find the value of K_c. If all the reactants and products are transferred to a 2.5 L flask, calculate the amount of reactants and products at equilibrium. (at. wt. H = 1, I = 127).*

SOLUTION. Reaction. $\quad 2\text{HI} \rightleftharpoons H_2 + I_2$

no. of mol at equilibrium = wt/mol. wt.

2HI	H_2	I_2
$\frac{819.2}{128}$	$\frac{3.9}{2}$	$\frac{101.6}{254}$
$= 6.4$	$= 1.95$	$= 0.4$

If volume of container is *V* litre, then :

$$[\text{HI}] = \frac{6.4}{V} ; [H_2] = \frac{1.95}{V} ; [I_2] = \frac{0.4}{V}$$

$$\therefore \quad K_c = \frac{[H_2][I_2]}{[\text{HI}]^2} = \frac{\frac{1.95}{V} \times \frac{0.4}{V}}{\left(\frac{6.4}{V}\right)^2} = \mathbf{0.019} \;\; \textbf{Ans.}$$

In the given reaction, $\Delta n = 2 - (1 + 1) = 0$. So, if the matter is transferred to attain equilibrium in 2.5 L flask, there will be no effect on equilibrium concentration of reactants and products.

Type. Calculations of **equilibrium constant** (K_c and K_p) for **gaseous reactions** involving "**Change in volume**". To understand it, consider the **dissociation** of AB(g) into A(g) and B(g).

$$AB\,(g) \rightleftharpoons A\,(g) + B\,(g)$$

***(I)* Calculation of K_C.**

Let, 1 = Initial molar concentration of AB, x = Degree of dissociation of AB

V = Total volume of vessel (in litre) in which reaction takes place.

Thus, at equilibrium, we have :

	AB	⇌	A	+	B
Initial conc.	1		0		0
Conc. at equilibrium	$1 - x$		x		x

$$[AB] = \frac{1-x}{V}\text{ mol L}^{-}\,;$$

$$[A] = \frac{x}{V}\text{ mol L}^{-}\,;\,[B] = \frac{x}{V}\text{ mol L}^{-}$$

Applying law of chemical equilibrium, we have :

$$K_c = \frac{[A]\,[B]}{[AB]} = \frac{\left(\frac{x}{V}\text{ mol L}^{-}\right)\times\left(\frac{x}{V}\text{ mol L}^{-}\right)}{\frac{1-x}{V}\text{ mol L}^{-}}$$

$$= \frac{x^2}{(1-x)\,V}\text{ mol L}^{-}$$

Thus K_c value involves also the volume of the vessel in which reaction takes place.

***(II)* Calculation of K_p; $K_p = K_c\,(RT)^{\Delta n}$**

Type. **Calculation** of K_p, pressure, degree of **dissociation for reactions** involving change in volume or **number of mol.** To understand it, consider the dissociation of AB (g) into A (g) and B (g).

I. Calculation of K_p AB (g) ⇌ A (g) + B (g)

Let
1 = Initial molar concentration of AB
x = Degree of dissociation of AB
P = Pressure of vessel (in bar or atm) in which reaction takes place.

Thus, at equilibrium, we have :

	AB (g)	⇌	A (g)	+	B (g)
Initial conc.	1		0		0
Conc. at equilibrium	$1 - x$		x		x

Total number of mol at equilibrium

$$= 1 - x + x + x = 1 + x$$

$$[AB] = \frac{1-x}{1+x}\times P\;;\;[A] = \frac{x}{1+x}\times P\;;$$

$$[B] = \frac{x}{1+x}\times P$$

Applying law of chemical equilibrium, we have :

$$K_p = \frac{[A]\,[B]}{[AB]} = \frac{\left(\frac{x}{1+x}\times P\right)\left(\frac{x}{1+x}\times P\right)}{\left(\frac{1-x}{1+x}\times P\right)}$$

$$= \frac{x^2\,P}{(1+x)\,(1-x)}$$

or $$K_p = \frac{x^2\,P}{1-x^2} \qquad \ldots (1)$$

II. Calculation of pressure (P'). From relation (1), we have :

$$K_p = \frac{x^2\,P'}{1-x^2} \quad or \quad P' = \frac{K_p\,(1-x^2)}{x^2}$$

III. Calculation of degree of dissociation, x. From relation (I), we have :

$$K_p = \frac{x^2\,P'}{1-x^2} \quad or \quad \frac{K_P}{P'} = \frac{x^2}{1-x^2}.$$

So, x can be calculated from this relation.

EXAMPLE 148. *Calculate the degree of dissociation of hydriodic acid if equilibrium constant for $H_2 + I_2 \rightleftharpoons 2HI$ reaction is 38.*

SOLUTION. Let 1 = Initial molar concentration of HI
x = degree of dissociation of HI

This reaction involves no change in volume. So, at equilibrium, we have :

	2HI	⇌	H_2	+	I_2
Initial conc.	1		0		0
Conc. at equilibrium	$1 - x$		$\frac{x}{2}$		$\frac{x}{2}$

$$\left[\begin{array}{llll} \because HI \rightleftharpoons & \frac{1}{2}H_2 & + & \frac{1}{2}I_2 \\ \therefore 1-x & \frac{x}{2} & & \frac{x}{2} \end{array}\right.$$

$$[HI] = 1 - x \;;\; [H_2] = x/2 \;;\; [I_2] = x/2$$

Applying law of chemical equilibrium, we have :

$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{\frac{x}{2}\times\frac{x}{2}}{(1-x)^2} = \frac{x^2}{4\,(1-x)^2}$$

$$\frac{1}{38} = \frac{x^2}{4\,(1-x)^2}$$

Taking square root of both sides, we get :

$$\left(\frac{1}{38}\right)^{1/2} = \frac{x}{2\,(1-x)} \quad \textbf{or} \quad \frac{1}{6.16} = \frac{x}{2\,(1-x)}$$

$$6.16\,x = 2\,(1-x)$$

or $$\frac{6.16}{2}x = 1 - x\,;\,3.08\,x = 1 - x$$

$$\therefore \quad x + 3.08\,x = 1 \quad \text{or} \quad 4.08\,x = 1$$

Hence $$x = \frac{1}{4.08} = 0.245$$

∴ Degree of dissociation

$= 0.245 \times 100 =$ **24.5 %**

23.23 MISCELLANEOUS EXAMPLES

Type. Calculations of *equilibrium constant (K_c and K_p) for gaseous reactions* involving formation (or synthesis) of products with **"no change in volume"**. To understand it, consider the formation of AB (g) from A_2 (g) and B_2 (g).
$A_2 + B_2 \rightleftharpoons 2\,AB$

Let a = Initial molar concentration of A_2

b = Initial molar concentration of B_2

x = no. of mol of A_2 and B_2 that combine to form $2\,x$ mol of AB

V = Total volume of the vessel (in litre) in which reaction takes place.

∴ Thus, at equilibrium, we have :

$$\begin{array}{ccc} A_2 + B_2 & \rightleftharpoons & 2\,AB \\ a-x \quad b-x & & 2\,x \end{array} \qquad \text{...(1)}$$

$$[A_2] = \frac{a-x}{V}\,\text{mol L}^{-}\;;\;[B_2] = \frac{b-x}{V}\,\text{mol L}^{-}$$

$$[AB] = \frac{2\,x}{V}\,\text{mol L}^{-}$$

Applying law of chemical equilibrium to reaction (1), we have :

$$K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{V}\,\text{mol L}^{-}\right)^2}{\frac{a-x}{V}\,\text{mol L}^{-} \times \frac{b-x}{V}\,\text{mol L}^{-}}$$

Or $$K_c = \frac{4\,x^2}{(a-x)(b-x)}$$

Thus K_c is independent of volume of vessel for reactions involving no change in volume.

Calculation of Kp.

$$K_p = K_c (RT)^{\Delta n} \qquad \text{...(2)}$$

Where , Δn = (no. of mol of gaseous products) – (no. of mol of gaseous reactants)

For reactions involving no change in volume, $\Delta n = 0$.

So, in reaction (2)

$$K_p = K_c \qquad [\because (RT)^{\circ} = 1]$$

Here R = gas constant = 0.081 L atm K^{-} mol^{-}

= 0.081 L bar K^{-} mol^{-} and T is absolute temperature in kelvin (K)

EXAMPLE 149. *The equilibrium constant of the reaction :*

$$A_2\,(g) + B_2\,(g) \rightleftharpoons 2AB(g)$$

at 100°C is 50. If one litre flask containing one mol of A_2 is connnected to a two litre flask containing 2 mol of B_2, how many mol of AB will be formed at 373 K. **(IIT, 1985)**

SOLUTION.

	$A_2\,(g)$ +	$B_2\,(g) \rightleftharpoons$	$2\,AB(g)$
(*i*) *n* mol at start	1	2	0
(*ii*) Change by reaction	$-x$	$-x$	$2\,x$
(*iii*) *n* mol at equilibrium	$1-x$	$2-x$	$2\,x$

Total number of mol at equilibrium

$= 1 - x + 2 - x + 2\,x = 3$

$$\therefore \quad K_c = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2\,x}{3}\right)^2}{\left(\frac{1-x}{3}\right)\left(\frac{2-x}{3}\right)}$$

$$= \frac{4\,x^2}{(1-x)(2-x)}$$

Or $$50 = \frac{4\,x^2}{(1-x)(2-x)} = \frac{4\,x^2}{2-3\,x+x^2}\,;$$

$50\,(2 - 3\,x + x^2) = 4\,x^2\,;$

$100 - 150\,x + 50\,x^2 = 4\,x^2\;;$

$46\,x^2 - 150\,x + 100 = 0$

Or $23\,x^2 - 75\,x + 50 = 0$

$$\therefore \quad x = \frac{-(-75) \pm \sqrt{(-75)^2 - 4\,(23 \times 50)}}{2 \times 23}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0,\; x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$x = \frac{+75 \pm 32}{46} = 2.32 \quad \text{or} \quad 0.934.$$

Since x cannot be 2.32, so, $x = 0.934$.

∴ Number of mol of AB formed

$= 2\,x = 2 \times 0.934 =$ **1.868 mol**

EXAMPLE 150. *The value of equilibrium constant for the reaction:*

$$N_2 + 2\,O_2 \rightleftharpoons 2\,NO_2$$

at a certain temperature is 50. Write down the expression for the equilibrium constant in each of the following reactions and also calculate the values of the constants in the two cases.

(*a*) $2\,NO_2 \rightleftharpoons N_2 + 2\,O_2$ (*b*) $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

(UP, 1989, AIEEE, 2012)

SOLUTION. (*a*) $N_2 + 2\,O_2 \rightleftharpoons 2\,NO_2$ ... (1)

$$K_c = \frac{[NO_2]^2}{[N_2]\,[O_2]^2}\;;\;50 = \frac{[NO_2]^2}{[N_2]\,[O_2]^2} \quad \textbf{Ans.}$$

(*b*) $2\,NO_2 \rightleftharpoons N_2 + 2\,O_2$ ...(2)

This reaction is reverse of reaction (1).

So, $$K_c' = \frac{1}{K_c}$$

Or $$K_c' = \frac{[O_2]^2\,[N_2]}{[NO_2]^2} = \frac{1}{50} = \mathbf{0.02} \qquad \textbf{Ans.}$$

(*c*) $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

The number of mol of this equation is 1/2 of that of equation (2). So :

$$K_c'' = \frac{[N_2]^{1/2}\,[O_2]}{[NO_2]}$$

or $\quad K_c'' = (K_c')^{1/2} = (0.02)^{1/2} = 0.1414$

∴ $\quad K_c'' = \mathbf{0.1414}$ **Ans.**

Type. To calculate k_p from the given value of ΔG°, use the relation :

$$\Delta G° = -2.303\ RT \log K_p$$

EXAMPLE 151. *Calculate the value of K_p for the reaction :*

$$N_2 + O_2 \rightleftharpoons 2NO$$

at 2000 K. The standard free energy change ΔG° for the reaction is given by

$$\Delta G° = 22{,}000 - 2.5\ T,\ (R = 1.98\ \text{cal})$$

SOLUTION. $\Delta G° = 22{,}000 - 2.5\ T$ (given)

∴ $\quad \Delta G° = 22{,}000 - (2.5 \times 2{,}000)$

$\quad = 22{,}000 - 5{,}000 = 17{,}000$

But $\quad \Delta G° = -2.303\ RT \log K_p$

$\quad 17{,}000 = -2.303 \times 1.98 \times 2{,}000 \log K_p$

∴ $\quad \log K_p = -\dfrac{17{,}000}{2.303 \times 1.98 \times 2{,}000} = -1.86$

∴ $\quad K_p = \text{antilog} - 1.86 = \text{antilog} -1 -1 +1 -0.86$

$\quad = \text{antilog}\ \bar{2}.14 = \mathbf{0.014}$ **Ans.**

EXAMPLE 152. *A sample of air consisting of N_2 and O_2 was heated at 2,500 K until the equilibrium*

$$N_2 + O_2 \rightleftharpoons 2NO$$

was established with an equilibrium constant, $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mol % age of NO was 1.8. Estimate the initial concentration of air in mol fraction of N_2 and O_2. **(IIT, May 1997)**

SOLUTION.	N_2	+ O_2	$\rightleftharpoons$ 2NO
(*i*) *n* mol at start	a	$100 - a$	0
(*ii*) Change by reaction	$-x$	$-x$	$2x$
(*iii*) *n* mol at equilibrium	$a - x$	$100 - a - x$	$2x$

But $\quad \dfrac{2x}{100} = \dfrac{1.8}{100}$ or $2x = 1.8$; ∴ $x = \dfrac{1.8}{2} = 0.9$

Applying law of chemical equilibrium, we get :

$$K = \frac{[NO]^2}{[N_2][O_2]};$$

$$2.1 \times 10^{-3} = \frac{(2x)^2}{(a-x)(100-a-x)};$$

$$2.1 \times 10^{-3} = \frac{(2 \times 0.9)^2}{(a-0.9)(100-a-0.9)}$$

$$= \frac{3.24}{(a-0.9)(99.1-a)}$$

$$= \frac{3.24}{99.1\,a - a^2 - 89.19 + 0.9a}$$

$$0.0021\,(-a^2 - 100\,a - 89.19) = 3.24 \quad ;$$

$$-a^2 + 100\,a - 89.19 = \frac{3.24}{0.0021} = 1543$$

Or– $a^2 + 100\,a - 89.19 - 1543 = 0$; $a^2 - 100\,a + 1632.19 = 0$

∴ $$a = \frac{-(-100) \pm \sqrt{(-100)^2 - 4\,(1 \times 1632.19)}}{2 \times 1}$$

$$= \frac{-(-100) \pm \sqrt{10{,}000 - 6528.76}}{2}$$

$$\left[\because \text{ for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$= \frac{-100 \pm \sqrt{3471.24}}{2}$$

$$a = \frac{+100 \pm 58.9}{2}$$

$$= \frac{158.9}{2} \text{ or } \frac{41.1}{2} = 79.4 \text{ or } 20.55$$

So, $\quad a = 79.4\ \%$ *i.e.,* % age of N_2 = 79.4 %

% age of O_2 = 100 – 79.4 = 20.6 %.

Since $\dfrac{1.8}{100}$ *i.e.,* 0.018 mol NO is formed at equilibrium, $\dfrac{0.018}{2}$ *i.e.,* 0.009 mol of each N_2 and O_2 have reacted.

Hence, initially,

$O_2 = \dfrac{20.6}{100}$ *i.e.,* 0.206 mol + 0.009 = 0.215 mol.

$N_2 = \dfrac{79.4}{100}$ *i.e.,* 0.794 mol + 0.009 = 0.803 mol.

EXAMPLE 153. *5 moles of SO_2 and 5 moles of O_2 are allowed to react. At equilibrium, it was found that 60 % SO_2 is used up. If the partial pressure of the equilibrium mixture is one atmosphere, the partial pressure of O_2 is :*

(*a*) *0.52 atm* (*b*) *0.21 atm*

(*c*) *0.41 atm* (*d*) *0.82 atm*

(Karnataka CET, 2009)

SOLUTION. Given :	$2SO_2(g)$	+ $O_2(g)$	$\rightleftharpoons$ $2SO_3(g)$
Initial no. of mol.	5	5	0
no of mol reacted	$5 \times \dfrac{60}{100} = 3$	$3 \times \dfrac{1}{2} = 1.5$*	3
no. of mol at equi.	5 – 3 = 2	5 – 1.5 = 3.5	3

$$*\left[\begin{array}{l} \because 2\ \text{mol}\ SO_2 = 1\ \text{mol}\ O_2 \\ 3\ \text{mol}\ SO_2 = \dfrac{3}{2}\text{mol}\ O_2 \\ \qquad = 1.5\ \text{mol} \end{array}\right]$$

Total no. of mol = 2 + 3.5 + 3 = 8.5

∴ $$p_{O_2} = \frac{\text{no. of mol of } O_2}{\text{Total mol}} \times P_{\text{total}},$$

$$p_{O_2} = \frac{3.5 \times 1}{8.5} = 0.41$$

So, the correct answer is (*c*).

EXAMPLE 154. *For the reaction*

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

at 1500°C, the equilibrium constant K_p is 120. If N_2 and O_2 gases at an initial pressure of 0.25 atm each are maintained at 1500°C till equilibrium is established, calculate the partial pressure of N_2, O_2 and NO in the equilibrium.

SOLUTION.

	$N_2(g)$	+ $O_2(g)$	$\rightleftharpoons 2NO(g)$
(*i*) *n* atm at start	0.25	0.25	0
(*ii*) Change by reaction	$-x$	$-x$	$2x$
(*iii*) *n* atm at equilibrium	$0.25-x$	$0.25-x$	$2x$

Applying law of chemical equilibrium, we get :

$$K_p = \frac{(p_{NO})^2}{p_{N_2} \times p_{O_2}} ;$$

$$120 = \frac{(2x)^2}{(0.25-x)(0.25-x)} = \frac{(2x)^2}{(0.25-x)^2}$$

Taking square root of both sides, we get :

$$\sqrt{120} = \frac{2x}{0.25-x} \quad ; \quad 10.95 = \frac{2x}{0.25-x} ;$$

$$2.74 - 10.95\,x = 2x$$

Or $2x + 10.95\,x = 2.74$; $12.95\,x = 2.74$

$$\therefore \quad x = \frac{2.74}{12.95} = 0.21 \text{ atm}$$

$$\therefore \quad p_{N_2} = p_{O_2} = 0.25 - x = 0.25 - 0.21 = \mathbf{0.04\ atm}$$

$$p_{NO} = 2x = 2 \times 0.21 \text{ atm} = \mathbf{0.42\ atm.}$$

EXAMPLE 155. *Bodenstein found that starting with 10.5 mol of HI initially, only 8.2 mol were left at 448°C when equilibrium was attained. Calculate the equilibrium constant for the dissociation of HI. Also calculate how much HI will be obtained when eight mol of H_2 and 27.5 mol of I_2 are heated together for a sufficiently long time at 448°C.*

SOLUTION.

	2 HI	$\rightleftharpoons H_2$	+ I_2
(*i*) *n* mol at start	10.5	0	0
(*ii*) Change by reaction	$-10.5\,x$	$\frac{10.5\,x}{2}$	$\frac{10.5\,x}{2}$
(*iii*) *n* mol at equilibrium	$10.5 - 10.5\,x$	$\frac{10.5\,x}{2}$	$\frac{10.5\,x}{2}$

But $10.5 - 10.5\,x = 8.2$

$$\therefore \quad 10.5\,x = 10.5 - 8.2 = 2.3; \quad x = 2.3/10.5 = 0.219.$$

$$[H_2] = \frac{10.5\,x}{2} = \frac{10.5 \times 0.219}{2} ;$$

$$[I_2] = [H_2] = \frac{10.5 \times 0.219}{2}$$

$$[HI] = 10.5 - 10.5\,x$$

$$= 10.5 - (10.5 \times 0.219) = 10.5\,(1 - 0.219)$$

$$= 10.5 \times 0.781$$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$= \frac{\frac{10.5 \times 0.219}{2} \times \frac{10.5 \times 0.219}{2}}{(10.5 \times 0.781)^2} = \mathbf{0.0196}$$

Second Case.

	H_2	+ I_2	$\rightleftharpoons$ 2HI
(*i*) *n* mol at start	8	27.5	0
(*ii*) Change by reaction	$-x$	$-x$	$2x$
(*iii*) *n* mol at equilibrium	$8-x$	$27.5-x$	$2x$

Applying law of chemical equilibrium, we get :

$$K_c' = \frac{1}{K_c} = \frac{[HI]^2}{[H_2][I_2]} ;$$

$$\frac{1}{0.00196} = \frac{(2x)^2}{(8-x)(27.5-x)} = \frac{4x^2}{(8-x)(27.5-x)}$$

Or $0.0196 \times 4x^2 = 220.0 - 8x - 27.5\,x + x^2$

$$0.0784\,x^2 = x^2 - 35.5\,x + 220 \quad ;$$

$$x^2 - 0.0784\,x^2 - 35.5\,x + 220 = 0$$

Or $0.9216\,x^2 - 35.5\,x + 220 = 0$;

$$x = \frac{-(-35.5) \pm \sqrt{(-35.5)^2 - 4\,(0.9216 \times 220)}}{2 \times 0.9216}$$

Or

$$x = \frac{+35.5 \pm \sqrt{1260.25 - 811}}{1.8432}$$

$$= \frac{35.5 \pm \sqrt{449.5}}{1.8432} = \frac{35.5 \pm 21.2}{1.8432}$$

$$\left[\because \text{For } ax^2 + bx + c = 0, x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}\right]$$

$$= \frac{56.7}{1.8432}$$

or $\frac{14.3}{1.8432} = 30.76$ or 7.76

Out of these only 7.76 is possible.

So, $x = 7.76.$

$\therefore$ $[HI] = 2x = 2 \times 7.76 = \mathbf{15.52\ mol}$ **Ans.**

EXAMPLE 156. *Hydriodic acid undergoes 25 % dissociation at equilibrium. Compare its K_c value with its K_p value for the reaction, $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$.*

SOLUTION.

	HI	$\rightleftharpoons \frac{1}{2}H_2$	+ $\frac{1}{2}I_2$
(*i*) n mol at start	1	0	0
(*ii*) Change by reaction	$\frac{-25}{100}$ $= -0.25$	$\frac{+25}{200}$ $= +0.125$	$\frac{+25}{200}$ $= +0.125$
(*iii*) *n* mol at equilibrium	$1 - 0.25$ $= 0.75$	0.125	0.125

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]} = \frac{(0.125)^{1/2}\times(0.125)^{1/2}}{0.75}$$

$$= \frac{0.125}{0.75} = 0.167$$

∴ $K_c = 0.167$

For the given reaction,

$$\Delta n = \left(\frac{1}{2}+\frac{1}{2}\right) - 1 = 0 \quad i.e., \quad \text{zero.}$$

But $K_p = K_c\,(RT)^{\Delta n} = 0.167\,(RT)^{\circ} = 0.167$

∴ $\mathbf{K_p = K_c}$.

Type. Calculation of dissociation of HI involving titration of I_2 from HI at equilibrium with sodium thiosulphate

The degree of dissociation

$$= \frac{\text{mol of HI dissociated}}{\text{mol of HI taken}}$$

EXAMPLE 157. *A known quantity (0.96 g) of HI was heated to get following equilibrium.*

$$2HI \rightleftharpoons H_2 + I_2$$

The reaction mixture on titration consumed 15.7 mL of 0.1 N sodium thiosulphate solution. Calculate the degree of dissociation of HI. **(Agra, 1961)**

SOLUTION. Wt. of HI = 0.96 g ;

g. mol. wt. of HI = 1 + 127 = 128 g

∴ no. of mol of HI = 0.96/128 = 7.5×10^{-3} mol.

Reaction	$2HI \rightleftharpoons$	H_2 +	I_2
(i) *n* mol at start	7.5×10^{-3}	0	0
(*ii*) Change by reaction	$-x$	$x/2$	$x/2$
(*iii*) *n* mol at equilibrium	$7.5 \times 10^{-3} - x$	$x/2$	$x/2$

1000 m L of 1N - $Na_2S_2O_3$ = g. eq. wt. of I_2 = 127 g

Or 1000 m L of 0.1 N $Na_2S_2O_3$ = 127 × 0.1 = 12.7 g I_2

∴ 15.7 mL of 0.1 N $Na_2S_2O_3$

$$= \frac{12.7}{1000} \times 15.7 \text{ g } I_2$$

But g. mol. wt. of I_2 = 2 × 127 = 254 g

$$\therefore \text{ no. of mol of } I_2 \text{ formed} = \frac{12.7 \times 15.7}{1000 \times 254} = 7.85 \times 10^{-4}$$

$$[H_2] = [I_2] = \frac{x}{2} = 7.85 \times 10^{-4} ;$$

$$x = 2 \times 7.85 \times 10^{-4}$$
$$= 15.70 \times 10^{-4} \text{ mol}$$

no. of mol of HI dissociated = x = 15.7×10^{-4} mol

$$\therefore \quad \text{HI dissociated} = \frac{15.7 \times 10^{-4}}{7.5 \times 10^{-3}} \times 100 = \mathbf{20.93\%}$$

EXAMPLE 158. *In an experiment, the amount of H_2, I_2 and HI in the equilibrium state of the reaction, $2HI \rightleftharpoons H_2 + I_2$ were found to be 7.8 g, 203.2g and 1638.4 g respectively. Calculate the equilibrium constant (H = 1, I = 127)* **(UP, 1982)**

SOLUTION. Wt. of H_2 = 7.8 g ;

g. mol. wt of H_2 = 2 × 1 = 2 g

∴ no. of mol of H_2 = wt. of H_2/g. mol. wt. of H_2

$$= \frac{7.8 \text{ g}}{2 \text{ g}} = 3.9 ;$$

Wt. of I_2 = 203.2 g ;

g. mol. wt. of I_2 = 2 × 127 = 254 g

$$\therefore \quad \text{no. of mol of } I_2 = \frac{203.2 \text{ g}}{254 \text{ g}} = 0.8 ;$$

Wt. of HI = 1638. 4 g ;

g. mol. wt. of HI = 1 + 127 = 128 g

$$\therefore \quad \text{no. of mol of HI} = \frac{1638.4 \text{ g}}{128 \text{ g}} = 12.8$$

Applying law of chemical equilibrium, to the following reaction

$$2\,HI \rightleftharpoons H_2 + I_2$$

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{3.9 \times 0.8}{(12.8)^2} ;$$

K = **0.019** **Ans.**

EXAMPLE 159. *One mol of HI, when heated at 723 K until equilibrium was attained in a volume of one litre, the resultant iodine required 49.6 mL of 5 M $Na_2S_2O_3$ for the reaction. Calculate K_c for $2HI \rightleftharpoons H_2 + I_2$ reaction.*

SOLUTION.	$2HI \rightleftharpoons$	H_2 +	I_2
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	$\frac{x}{2}$	$\frac{x}{2}$
(*iii*) *n* mol at equilibrium	$1-x$	$\frac{x}{2}$	$\frac{x}{2}$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\frac{x}{2}\times\frac{x}{2}}{(1-x)^2} = \frac{x^2}{4(1-x)^2} \quad ...(1)$$

Reaction : $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$
(2 mol) (1mol)

Using above reaction, we have :

$$\frac{(M_1 V_1) \text{ of } I_2}{(M_2 V_2) \text{ of } Na_2S_2O_3} = \frac{1}{2}$$

∴ 49.6 m L of 5 M

$$Na_2S_2O_3 = \frac{1}{2} \times 49.6 \text{ m L of 5 M } I_2$$
$$= 24.8 \text{ mL of 5 M } I_2$$

But 1000 mL of 1 M I_2 = 1 mol of I_2

$$\therefore \quad 24.8 \text{ m L of 5M } I_2 = \frac{1}{1000} \times 24.8 \times 5$$

$$= 0.124 \text{ mol } I_2$$

Or $\frac{x}{2}$ = 0.124 ; x = 2 × 0.124 = 0.248

Substituting the value of x in equation (1), we get :

$$K_c = \frac{(0.248)^2}{4\,(1-0.248)^2} = \frac{(0.248)^2}{4\,(0.752)^2}$$

$$= \frac{0.062}{2.262} = 0.027$$

∴ K_c = **0.027** **Ans.**

EXAMPLE 160. *HI (20 g) was heated to 600 K in a one litre capacity vessel. Calculate the volume percentage of H_2, I_2 and HI at equilibrium. The value of equilibrium constant of the reaction*

$$2\,HI \rightleftharpoons H_2 + I_2$$

is 0.056 at the same temperature when the concentrations are expresssed in mol L^{-}.

SOLUTION. wt. of HI = 20 g ;

g. mol. wt. of HI = 1 + 127 = 128 g

∴ no. of mol of HI = $\frac{20}{128} = 0.156$

	$2HI$	$\rightleftharpoons H_2$	$+\ I_2$
(*i*) *n* mol at start	0.156	0	0
(*ii*) Change by reaction	$-x$	$\frac{x}{2}$	$\frac{x}{2}$
(*iii*) *n* mol at equilibrium	$0.156 - x$	$\frac{x}{2}$	$\frac{x}{2}$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[H_2][I_2]}{[HI]^2} \;;$$

$$0.056 = \frac{\frac{x}{2} \times \frac{x}{2}}{(0.156 - x)^2} = \frac{x^2}{4\,(0.156 - x)^2}$$

Taking square root of both sides, we get :

$$\sqrt{0.056} = \frac{x}{2\,(0.156 - x)} \,;$$

$$0.237 = \frac{x}{0.312 - 2x} \,;\ 0.237\,(0.312 - 2\,x) = x$$

Or $0.074 - 0.474\,x = x \quad ; \quad x + 0.474\,x = 0.074$

Or $1.474\,x = 0.074$;

∴ $x = \frac{0.074}{1.474} = 0.05$

∴ HI dissociated = x = **0.05 mol**;

$[H_2] = [I_2] = \frac{x}{2} = \frac{0.05}{2} = \mathbf{0.025\ mol}$

Amount of HI left behind

$= 0.156 - x = 0.156 - 0.05 = 0.106$ mol.

According to Avogadro's law, equal volume of all gases contain equal number of mol under similar conditions of temperature and pressure. So, ratio by mol will be the ratio by volume.

∴ % age of H_2 and I_2 both by volume

$$= \frac{0.025}{0.156} \times 100 = 16\ \%$$

% age of HI by volume

$$= \frac{0.106}{0.156} \times 100 = 67.9\ \%$$

EXAMPLE 161. *For the reaction : $2\,HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$ the value of equilibrium constant at 764 K and 667 K are 2.18×10^{-2} and 1.64×10^{-2} respectively. Calculate the value of ΔH° for the given reaction.*

SOLUTION. $T_1 = 667$ K, $K_1 = 1.64 \times 10^{-2}$; $T_2 = 764$ K, $K_2 = 2.18 \times 10^{-2}$, ΔH° = ?, R = 2 cal. We know that :

$$\log K_2 - \log K_1 = \frac{-\Delta H^\circ}{2.303\,R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\log 2.18 \times 10^{-2} - \log 1.64 \times 10^{-2}$$

$$= \frac{-\Delta H^\circ}{2.303 \times 2}\left(\frac{1}{764} - \frac{1}{667}\right)$$

$$= \frac{-\Delta H^\circ}{4.606}\left(\frac{667 - 764}{764 \times 667}\right)$$

$$\log 2.18 + \log 10^{-2} - (\log 1.64 + \log 10^{-2})$$

$$= \frac{-\Delta H^\circ}{4.606}\left(\frac{-97}{764 \times 667}\right)$$

$$0.3384 - 2 - 0.2148 + 2$$

$$= \frac{-\Delta H^\circ}{4.606}\left(\frac{-97}{764 \times 667}\right) = 4.13 \times 10^{-5}\ \Delta H^\circ$$

Or $0.1236 = 4.13 \times 10^{-5}\,\Delta H^\circ$;

∴ $\Delta H^\circ = \frac{0.1236}{4.13 \times 10^{-5}}$ = **2998 cal** **Ans.**

EXAMPLE 162. *At 1024 K, the value of equilibrium constant for the reaction $H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g)$ is 1.6×10^5. Calculate the equilibrium pressure of all gases at 10.0 bar if HBr is introduced into a sealed container at the same temperature.*

SOLUTION. For the reaction, $H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr$; $K_p = 1.6 \times 10^5$

∴ For the reaction, $2HBr \rightleftharpoons H_2\,(g) + Br_2\,(g)$;

2 Vol 1Vol 1 Vol

$$K_p' = \frac{1}{1.6 \times 10^5}$$

Let p = Equilibrium pressure.

Since the reaction does not involve change in volume, so total number of mol are not required.

	2HBr (g)	$\rightleftharpoons H_2$ (g) +	Br_2 (g)
Initial conc.	10 bar	0	0
Conc. at equilibrium	$10 - p$	$\frac{p}{2}$	$\frac{p}{2}$

p_{HBr} or $[HBr] = 10 - p$; p_{H_2} or $[H_2] = p/2$; p_{Br_2} or $[Br_2] = p/2$

Applying law of chemical equilibrium, we have :

$$K_p = \frac{[H_2]\,[Br_2]}{[HBr]^2} = \frac{\frac{p}{2} \times \frac{p}{2}}{(10 - p)^2}$$

or $$\frac{1}{1.6 \times 10^5} = \frac{p^2}{4\,(10 - p)^2}$$

Taking square root of both sides, we get :

$$\frac{1}{4\times 10^2} = \frac{p}{2(10-p)} \quad ; \quad \frac{1}{2\times 10^2} = \frac{1}{10-p};$$

$$200\,p = 10 - p \;;\; 200\,p + p = 10$$

or $$201\,p = 10 \quad ; \quad p = \frac{10}{201} = 0.0498$$

$$\therefore \quad P_{\text{HBr}} = 10 - p = 10 - 0.0498 = \mathbf{9.95\ bar}$$

$$p_{\text{H}_2} = \frac{p}{2} = \frac{0.0498}{2} = \mathbf{0.0249\ bar}\;;$$

$$p_{\text{Br}_2} = \frac{p}{2} = \frac{0.0498}{2} = \mathbf{0.0249\ bar}$$

Type. Calculation of K_c and K_p for homogeneous gaseous dissociation reversible reaction involving **"Change in volume or having different number of mol of reactants and products".**

In order to understand it, let us consider :

1. Dissociation of PCl_5

(*a*) **Determination of K_c.**

	PCl_5 ⇌	PCl_3 +	Cl_2
Original conc.	1 mol	0	0
Conc. at equilibrium	$\frac{1-x}{V}$ mol	$\frac{x}{V}$ mol	$\frac{x}{V}$ mol

Let us start with 1 mol of PCl_5 enclosed in a vessel of volume of '*V*' litre.

V = Volume of the closed vessel in which reaction takes place.

x = Number of mol of PCl_5 that decompose at equilibrium to yield *x* mol of PCl_3 and *x* mol of Cl_2.

Molar concentrations at equilibrium are :

$$[PCl_5] = \frac{1-x}{V} \quad ; \quad [PCl_3] = \frac{x}{V} \quad ; \quad [Cl_2] = \frac{x}{V}$$

Applying law of mass action, we get :

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)} = \frac{x^2}{V^2} \times \frac{V}{1-x}$$

$$K_c = \frac{x^2}{V(1-x)} \qquad \text{... (1)}$$

(*b*) **Determination of K_p.**

Total number of mol

$$= 1 - x + x + x = 1 + x$$

Let *P* = Total pressure of the system.

$$\therefore \quad p_{PCl_5} = \frac{(1-x)P}{1+x};\; p_{PCl_3} = \frac{xP}{1+x};\; p_{Cl_2} = \frac{xP}{1+x}$$

$$\therefore \quad K_p = \frac{(p_{PCl_3})(p_{Cl_2})}{p_{PCl_5}} = \frac{\frac{xP}{1+x}\times\frac{xP}{1+x}}{\frac{(1-x)P}{1+x}}$$

$$= \frac{x^2P^2}{(1+x)(1+x)} \times \frac{1+x}{P(1-x)}$$

$$K_p = \frac{x^2P}{1-x^2} \qquad \text{...(2)}$$

(*c*) From equation (2),

$$K_p(1-x^2) = x^2P\;;\; K_p - K_px^2 = x^2P\;;$$

$$x^2P\,z + K_px^2 = K_p\;;\; x^2(P + K_p) = K_p;$$

or $$x^2 = K_p/(P + K_p)$$

$$\therefore \quad x = \sqrt{\frac{K_p}{P+K_p}} \quad \text{or} \quad \left[\frac{K_p}{(P+K_p)}\right]^{1/2}$$

$$x = \left(\frac{K_p}{P+K_p}\right)^{1/2}$$

EXAMPLE 163. *For $PCl_5 \rightleftharpoons PCl_3 + Cl_2$,*

prove that $x = \left(\frac{K_p}{P+K_p}\right)^{1/2}$

Where x is the degree of dissociation at a temperature when equilibrium constant is K_p.

SOLUTION. See derivation in the above given type.

EXAMPLE 164. *At 1 bar pressure and at a certain temperature, the degree of dissociation of PCl_5 is 0.2. Calculate the pressure at which it will be half dissociated at the same temperature.*

SOLUTION. Dissociation of PCl_5 is :

$$\underset{1\ \text{Vol}}{PCl_5} \rightleftharpoons \underset{1\ \text{Vol}}{PCl_3} + \underset{1\ \text{Vol}}{Cl_2}$$

Since the reaction involves change in volume, and pressure is given, so we have to know total number of mol at equilibrium.

Let 1 = Initial molar concentration of PCl_5

P = 1 bar ; *x* = 0.2

Thus, at equilibrium, we have :

	PCl_5 ⇌	PCl_3 +	Cl_2
Initial conc.	1	0	0
Conc. at equilibrium	$1-x$	x	x

Total number of mol at equilibrium

$$= 1 - x + x + x = 1 + x$$

$$[PCl_5] = \frac{1-x}{1+x}\times P\;;\; [PCl_3] = \frac{x}{1+x}\times P\;;$$

$$[Cl_2] = \frac{x}{1+x}\times P$$

Applying law of chemical equilibrium, we have :

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{1+x}\times P\right)\left(\frac{x}{1+x}\times P\right)}{\frac{1-x}{1+x}\times P}$$

$$= \frac{x^2P}{1-x^2} \qquad \text{... (1)}$$

Substituting the values in equation (1), we get :

$$K_p = \frac{0.2\times0.2\times1}{1-(0.2)^2} = \frac{0.04}{1-0.04} = \frac{0.04}{0.96} = 0.041$$

Calculation of pressure, P′. Here, *x* = ½ or 0.5 *i.e.*, half dissociation from relation(1) we have :

$$K_p = \frac{x^2 P'}{1-x^2} \quad \text{or} \quad P' = \frac{K_p(1-x^2)}{x^2}$$

$$= \frac{0.041[1-(0.5)^2]}{0.5 \times 0.5}$$

$$\therefore \quad p' = \frac{0.041 \times (1-0.25)}{0.25} = \frac{0.041 \times 0.75}{0.25}$$

$$= \mathbf{0.123\ bar}$$ **Ans.**

EXAMPLE 165. *The reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$ on heating at 473 K and at 523 K gave density of the mixture 70.2 and 57.9 respectively at equilibrium. What will be the dissociation of PCl_5 at 473 K and 523 K respectively ?*

SOLUTION. V.D. = Mol. Wt/2. Initial vapour density (V.D.) of PCl_5 at 473 K and 523 K will be same and equal to half of the Mol. Wt. of PCl_5.

$$\therefore \quad \text{Initial V.D. of } PCl_5 = \frac{31 + (5 \times 35.5)}{2} = \mathbf{104.25}$$

	$PCl_5\,(g)$	$\rightleftharpoons$	$PCl_3\,(g)$	+	$Cl_2\,(g)$
Initial conc.	1		0		0
Conc. at equilibrium	$1-\alpha$		α		α

[∵ α = degree of dissociation]

Total moles at equilibrium

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha.$$

$$\therefore \frac{\text{Total moles at equilibrium}}{\text{Initial moles}} = \frac{\text{Initial V.D.}}{\text{V.D. at equilibrium}}$$

$$\frac{1+\alpha}{1} = \frac{104.25}{70.2}$$

or $\alpha = 1.485 - 1 = \mathbf{0.485}$

∴ Dissociation of PCl_5 at 473 K = **0.485** **Ans.**

Similarly at 523 K, $1 + \alpha = \frac{104.25}{57.9} = 1.8$

$$\alpha = 1.8 - 1 = 0.8$$

∴ Dissociation of PCl_5 at 523 K = 0.8 **Ans.**

EXAMPLE 166. *One mol of $PCl_3\,(g)$ and 2 mol of $Cl_2\,(g)$ were placed in a 3 litre vessel at a certain temperature. When equilibrium reached, only 0.7 mol of PCl_3 remained. Find the value of equilibrium constant for the reaction*

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5$$

at the same temperature.

SOLUTION.	PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
(*i*) *n* mol L^{-} at start	$\frac{1}{3} = 0.333$		$\frac{2}{3} = 0.667$		0
(*ii*) Change by reaction	-0.1		-0.1		$\frac{1.0-0.7}{3} = 0.1$
(*iii*) *n* mol L^{-} at equilibrium	$0.333-0.1$ $= 0.233$		$0.667-0.1$ $= 0.567$		0.1

[∵ Volume = 3L]

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.1}{0.233 \times 0.567}$$

$$= \mathbf{0.757}$$ **Ans.**

EXAMPLE 167. *Under what pressure must an equimolar mixture of phosphorus trichloride and chlorine be placed at 250°C in order to obtain 80 % conversion of PCl_3 into PCl_5. K_p for dissociation of $PCl_5 = 1.78$*

SOLUTION.	$PCl_3 + Cl_2$		$\rightleftharpoons$	PCl_5
Initial conc.	1	1		0
At. equilibrium	$1-x$	$1-x$		x

Total no. of mol at equilibrium $= 1-x+1-x+x = 2-x$

Applying law of mass action, we have

$$K_p = \frac{p_{PCl_5}}{p_{PCl_3} \times p_{Cl_2}}$$

$$\text{or} \quad 1.78 = \frac{\frac{x}{2-x}P}{\frac{1-x}{2-x}P \times \frac{1-x}{2-x}P} = \frac{x(2-x)}{(1-x)^2 P}$$

$$1.78 = \frac{0.8(2-0.8)}{(1-0.8)^2 P}$$

$$\left[\because x = 80\,\% = \frac{80}{100} = 0.8\right.$$

∴ $P = \mathbf{13.48\ atm.}$

EXAMPLE 168. *The equilibrium composition for the reaction is :*

$PCl_3 + Cl_2$		$\rightleftharpoons$	PCl_5
0.2	0.1		0.4 mol L^{-}

If 0.2 mol of Cl_2 is added at the same temperature, then the equilibrium concentration of PCl_5 will be :

(*a*) *0.46 or 0.08* (*b*) *0.23 or 0.04*

(*c*) *0.86 or 0.49* (*d*) *none of these*

SOLUTION. For	PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
	0.2		0.1		0.4 mol L^{-}

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.4}{0.2 \times 0.1} = 20$$

when 0.2 mol of Cl_2 is added, then ; $[Cl_2] = 0.1 + 0.2 =$ 0.3 mol

Thus :	PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
(*i*) *n* mol at start	0.2		0.3		0.4
(*ii*) Change by reaction	$-x$		$-x$		x
(*iii*) *n* mol at equilibrium	$0.2-x$		$0.3-x$		$0.4+x$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.4+x}{(0.2-x)(0.3-x)}\ ;$$

$$20 = \frac{0.4+x}{0.06 - 0.5\,x + x^2}$$

Or $20x^2 - 10x + 1.2 = 0.4 + x$;

$20x^2 - 10x - x + 1.2 - 0.4 = 0$

Or $20x^2 - 11x + 0.8 = 0$;

$$\therefore \quad x = \frac{-(-11) \pm \sqrt{(-11)^2 - 4(20 \times 0.8)}}{2 \times 20}$$

$$\text{Or} \quad x = \frac{11 \pm \sqrt{121 - 64}}{40}$$

$$= \frac{11 \pm \sqrt{57}}{40} = \frac{11 \pm 7.5}{40}$$

$$= \frac{18.5}{40} \text{ or } \frac{3.5}{40} = 0.46 \text{ or } 0.09$$

∴ Concentration of PCl_5 at equilibrium

$= 0.4 + x = (0.4 + 0.46) =$ **0.86**

Or $(0.4 + 0.09) =$ **0.49** **Ans.**

So, the correct answer is (*c*).

Example 169. *Determine the concentration of NH_3 solution whose one litre can dissolve 0.1 mol AgCl. K_{sp} of AgCl and K_f of $[Ag(NH_3)_2]^+$ are 1.0×10^{-10} M^2 and 1.6×10^7 M^{2-} respectively.*

(Roorkee, 1999)

Solution. (*a*) NH_3 dissolves AgCl(s) as follows.

$$AgCl(s) + 2\,NH_3 \rightleftharpoons Ag(NH_3)_2]^+ + Cl^- \quad ...(1)$$

$$\therefore \quad K_{eq} = \frac{[Ag(NH_3)_2]^+\,[Cl^-]}{[NH_3]^2} \quad ...(2)$$

(*b*) $[Ag(NH_3)_2]^+$ is formed as follows.

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$

$$\therefore \quad K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \quad ...(3)$$

$K_f = 1.6 \times 10^7\ M^{-2}$;

$K_{sp} = 1.0 \times 10^{-10}\ M^2$

$\therefore \quad K_{eq} = K_f \times K_{sp} = 1.6 \times 10^7\ M^{2-} \times 1.0 \times 10^{-10} M^2$

$= 1.6 \times 10^{-3}$

$$AgCl(s) + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

n mol at equilibrium 0.1 0.1

$$\therefore \quad K_{eq} = \frac{[Ag(NH_3)_2]^+\,[Cl^-]}{[NH_3]^2} \ ;$$

$$1.6 \times 10^{-3} = \frac{0.1 \times 0.1}{[NH_3]^2}$$

$$\text{Or} \quad [NH_3]^2 = \frac{0.1 \times 0.1}{1.6 \times 10^{-3}} = 6.25\ ;$$

$[NH_3] = (6.25)^{1/2} = 2.5$ M

Since 0.1×2 (= 0.2) mol of NH_3 is used to dissolve AgCl, so :

Necessary concentration of $NH_3 = 2.5 + 0.2$

= **2.7 M** **Ans.**

Example 170. *For the following reactions*

(*i*) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ *and*

(*ii*) $NO(g) + 1/2\, Br_2(g) \rightleftharpoons NOBr(g)$

the value of K_c for reactions (i) and (ii) are 2.4×10^{30} and 1.4 respectively at 300 K. Calculate the value of K_c for the reaction

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g).$$

Solution. (*i*) $2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$;

$K_c = 2.4 \times 10^{30}$

(*ii*) $NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$; $K_c' = 1.4$

(*iii*) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)$; $K_c'' = ?$

In order to get equation (iii), we have

Equation (ii) $-\frac{1}{2}$ equation (*i*). So, we have :

$$NO(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g) - \frac{1}{2}N_2(g) - \frac{1}{2}O_2(g)\ ; \quad -\frac{1}{2}(2\,NO)$$

$$K''_C = K'_C \times \left(\frac{1}{K_c}\right)^{1/2}$$

$$\therefore \quad \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons NOBr(g)\ ;$$

$$K''_c = 1.4 \times \left(\frac{1}{2.4 \times 10^{30}}\right)^{1/2}$$

Or $K''_c = 1.4 \times 0.646 \times 10^{-15}$

= $\mathbf{0.904 \times 10^{-15}}$ **Ans.**

Example 171. *For a reaction $Br_2(g) + 2NO(g) \rightleftharpoons 2NOBr(g)$, the partial pressure of Br_2 is 41.3 torr while that of NO is 98.3 torr, at 27°C. Calculate the value of standard free energy change and equilibrium constant at the same temperature if the total pressure was 110.5 torr at equilibrium (R = 2.0 cal mol$^-$ K$^-$)*

Solution. T = 273 + 27 = 300 K ; R = 2.0 cal mol$^-$ K$^-$. Let α is the degree of dissociation. For one mol of the given reaction, we have :

$$\frac{1}{2}Br_2(g) + NO(g) \rightleftharpoons NOBr(g)$$

Co-efficients	$\frac{1}{2}$	1	1
Pressure (atm)	41.3	98.3	0

At equilibrium.

p_{Br_2} = Given pressure of Br_2 – (coeff. of Br_2 × α)

$$= 41.3 - \left(\frac{1}{2} \times \alpha\right) = 41.3 - \frac{\alpha}{2}$$

p_{NO} = Given pressure of NO – (coeff. of NO × α)

$$= 98.3 - (1 \times \alpha) = 98.3 - \alpha$$

$$p_{\text{NOBr}} = 0 + (\text{coeff. of NOBr} \times \alpha)$$

$$= 0 + (1 \times \alpha) = \alpha$$

Total pressure = 110.5 torr

$$\therefore 41.3 - \frac{\alpha}{2} + 98.3 - \alpha + \alpha = 110.5\ ;$$

$$\frac{\alpha}{2} = 41.3 + 98.3 - 110.5 = 29.2$$

$$\therefore \quad \alpha = 2 \times 29.2 = 58.4 \text{ torr} = \frac{58.4}{760.4}$$

$$= 7.68 \times 10^{-2} \text{atm.} (\because 760.4 \text{ torr} = 1 \text{ atm})$$

$$\therefore \quad p_{\text{Br}_2} = 41.3 - \frac{58.4}{2} = 12.1 \text{ torr} = \frac{12.1}{760.4} \text{ atm}$$

$$= 1.59 \times 10^{-2} \text{ atm}$$

$$p_{\text{NO}} = 98.4 - 58.4 = 40.0 \text{ torr} = \frac{40}{760.4} \text{ atm}$$

$$= 5.26 \times 10^{-2} \text{ atm}$$

$$p_{\text{NOBr}} = \alpha = 58.4 \text{ torr} = \frac{58.4}{760.4} \text{ atm}$$

$$= 5.26 \times 10^{-2} \text{ atm}$$

But
$$K_p = \frac{[\text{p}_{\text{NOBr}}]^2}{[\text{p}_{\text{Br}_2}]\,[\text{p}_{\text{NO}}]^2}$$

$$= \frac{(7.68 \times 10^{-2})^2}{(1.59 \times 10^{-2})\,(5.26 \times 10^{-2})^2}$$

$$= \frac{58.9824 \times 10^{-4} \text{ atm}}{43.99 \times 10^{-6} \text{ atm}^2}$$

$$= 134.1 \text{ atm}^{-}$$

$$\therefore \quad \Delta G^\circ = -2.303 \text{ RT} \log K_p$$

$$= -2.303 \times 2 \times 300 \times \log 134.1$$

$$= -2.303 \times 2 \times 300 \times 2.1274$$

$$= -2939.6 \text{ cal} = -2939.6 \times 4.184 \text{ J}$$

$$= 12299 \text{ J} = 12.299\text{k J}$$

[When R is used as 8.314 J mol^{-} K^{-}, ΔG° will be in joule and K_p will be in (atm)$^{\Delta n}$].

EXAMPLE 172. *When sulphur is treated with sulphide ions in an alkaline medium, polyvalent sulphide ions are formed. The equilibrium constants for the formation of* S_2^{2-} *and* S_3^{2-} *from S and* S^{2-} *are shown along with the following equilibria reactions.*

(*i*) $S(s) + S^{2-} \rightleftharpoons S_2^{2-}\ ;\ K_{c_1} = 1.7$

(*ii*) $2\,S(s) + S^{2-} \rightleftharpoons S_3^{2-}\ ;\ K_{c_2} = 5.1$

Calculate the equilibrium constant for the following reaction.

$$S(s) + S_2^{2-} \rightleftharpoons S_3^{2-}$$

SOLUTION. (*i*) $\text{S(s)} + \text{S}^{2-} \rightleftharpoons \text{S}_2^{2-}\ ;$

$$K_{C1} = \frac{[\text{S}_2^{2-}]}{[\text{S}^{2-}]}\ ;\ 1.7 = \frac{[\text{S}_2^{2-}]}{[\text{S}^{2-}]} \qquad ...(1)$$

(*ii*) $2\,\text{S(s)} + \text{S}^{2-} \rightleftharpoons \text{S}_3^{2-}\ ;$

$$K_{C_2} = \frac{[\text{S}_3^{2-}]}{[\text{S}^{2-}]}\ ;\ 5.1 = \frac{[\text{S}_3^{2-}]}{[\text{S}^{2-}]} \qquad ...(2)$$

Dividing equation (2) by (1), we get :

$$K_{C_3} = \frac{K_{C_2}}{K_{C_1}} = \frac{[\text{S}_3^{2-}]}{[\text{S}^{2-}]} \times \frac{[\text{S}^{2-}]}{[\text{S}_2^{2-}]} = \frac{5.1}{1.7} = 3$$

EXAMPLE 173. *When 500 mL of 1.09 M* Fe^{2+} *ion were mixed with exact 500 ml of 0.15 M* $AgNO_3$ *solution, following equilibrium was established.*

$$Fe^{2+} + Ag^{+} \rightleftharpoons Fe^{3+} + Ag$$

If 25 mL solution required 30 mL of 0.083 M $KMnO_4$ *at equilibrium for complete oxidation, calculate* K_c *at 298 K.*

SOLUTION. $\text{Fe}^{2+} + \text{Ag}^{+} \rightleftharpoons \text{Fe}^{3+} + \text{Ag(s)}$

	Fe^{2+}	Ag^{+}	Fe^{3+}	Ag(s)
(*i*) milli.equiv. at start	500×1.09 $= 545$	500×0.15 $= 75$	0	0
(*ii*) Change by reaction	$-x$	$-x$	x	x
(*iii*) milliequiv. at equilibrium	$545 - x$	$75 - x$	x	x

Total volume of solution at equilibrium

= 500 + 500 = 1000 mL

$$K_C = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]\,[\text{Ag}^{+}]} = \frac{\frac{x}{1000}}{\frac{545 - x}{1000} \times \frac{75 - x}{1000}}$$

$$= \frac{x}{1000} \times \frac{1000}{545 - x} \times \frac{1000}{75 - x}$$

$$= \frac{1000\,x}{(545 - x)\,(75 - x)}$$

In terms of milliequivalents, molarity should be changed into normality.

$\therefore$ Normality of KMnO_4 = Molarity × 5

$= 0.083 \times 5 = 0.415$ N

$\left[\begin{array}{l}\because \text{5 is valence factor} \\ (= \text{Mol. wt. of KMnO}_4/\text{Eq. wt. of KMnO}_4)\end{array}\right]$

Using normality equation, we have :

Fe^{2+} KMnO_4;

$$\text{N}_1 \times 25 = 0.415 \times 30$$

$$\therefore \quad \text{N}_1 = \frac{0.415 \times 30}{25} = 0.498$$

$\therefore$ Milliequivalents of Fe^{2+}

$= 0.498 \times 1000 = 498$

$\therefore$ At equilibrium, milliequivalents of Fe^{2+} left = 498

Or $498 = 545 - x\ ;\ x = 545 - 498 = 47$

$$\therefore \quad K_c = \frac{1000\,x}{(545 - x)\,(75 - x)} = \frac{1000 \times 47}{(545 - 47)\,(75 - 47)}$$

$$= \frac{47000}{497 \times 28}$$

$\therefore$ K_c = **3.38** **Ans.**

EXAMPLE 174. *120 mL solution was prepared by mixing 15 mL of 4.8 M La(NO$_3$)$_3$, 40 mL of 15 M HNO$_3$, 0.1 mol of La (OH)$_3$ and rest water. Calculate the concentration of each ion in the solution so prepared.*

SOLUTION. $$\begin{array}{lcccc} (i) & La(OH)_3 & \rightleftharpoons & La^{3+} & + \quad 3OH^- \\ n \text{ mol at start} & 0.1 & & 0.1 & 0.1 \times 3 = 0.3 \\ \text{no. of millimol } (= \text{mol} \times 1000) & & & & \\ & 0.1 \times 1000 & & 0.1 \times 1000 & 0.3 \times 1000 \\ & = 100 \text{ m mol} & & = 100 \text{ m mol} & = 300 \text{ m mol} \\ (ii) & La(NO_3)_3 & \rightleftharpoons & La^{3+} & + \quad 3NO_3^- \\ m \text{ mol at start} & 15 \times 4.8 & & 72 \text{ m mol} & 3 \times 72 \\ (= \text{Vol in mL} \times \text{molarity}) & & & & \\ & = 72 \text{ m mol} & & & = 216 \text{ m mol} \\ (iii)\ m \text{ mol at start} & HNO_3 & \rightleftharpoons & H^+ & + \quad NO_3^- \\ (= \text{Vol in mL} \times \text{molairty}) & & & & \\ & 40 \times 15 & & 600 \text{ m mol} & 600 \text{ m mol} \\ & = 600 \text{ m mol} & & & \end{array}$$

Total m mol of H$^+$ ions

$= 600$; OH$^-$ ions $= 300$

$\therefore$ 300 m mol of OH$^-$ react with 300 m mol of H$^+$ to form H$_2$O.

$\therefore$ m mol of H$^+$ ions unreacted

$= 600 - 300$ m mol

$$\therefore \quad \mathbf{M_{H^+}} = \frac{300}{120} = \mathbf{2.5\ m\ mol}\ ;$$

$$\mathbf{M_{La^{3+}}} = (100 + 72)/120 = \mathbf{1.43\ m\ mol.}$$

$$\mathbf{M_{NO_3^-}} = (216 + 600)/120 = \mathbf{6.8\ m\ mol.}$$

EXAMPLE 175. *Calculate the pressure at which CuSO$_4$. 5H$_2$O undergoes efflorescent at 298 K. At 298 K, vapour pressure of water is 23.8 mm Hg. How good CuSO$_4$. 3H$_2$O is a drying agent at the same temperature.At 298 K, the K_p for the reaction*

CuSO$_4$. 5H$_2$O(s) $\rightleftharpoons$ CuSO$_4$. 3H$_2$O(s) + 2H$_2$O(g) is 1.086 $\times$ 10^{-4} atm^2.

SOLUTION.

$$CuSO_4.\ 5H_2O(s) \rightleftharpoons CuSO_4.\ 3H_2O(s) + 2H_2O(g)$$

$\therefore$ $K_p = p(H_2O)^2$ because concentration of solids is taken as unity.

$$\therefore\ 1.086 \times 10^{-4}\ \text{atm}^2 = p(H_2O)^2;$$

$$pH_2O = (1.086 \times 10^{-4}\ \text{atm}^2)^{1/2}$$

$$\therefore \quad pH_2O = 1.042 \times 10^{-2}\ \text{atm}.$$

But $1\ \text{atm} = 760$ mm Hg.

$$\therefore \quad pH_2O = 1.042 \times 10^{-2} \times 760\ \text{mm}$$

$= 7.92$ mm Hg at 298 K.

Vapour pressure of H$_2$O at 298 K

$= 23.8$ mm Hg. So, CuSO$_4$. 3H$_2$O can absorb mixture when P_{H_2O} is above 7.92 mm Hg, in air.

EXAMPLE 176. *At 40°C, $K_p = 9$ atm^2 for the following equilibrium.*

LiCl. 3NH$_3$(s) $\rightleftharpoons$ LiCl. NH$_3$(s) + 2NH$_3$(g)

The reaction was started with 0.1 mol LiCl. NH$_3$ in a 5 L vessel. Calculate the number of mol of NH$_3$ that should be added to the vessel at this temperature so that backward reaction becomes completed.

SOLUTION. The backward reaction will be :

$$\begin{array}{lccc} & LiCl.\ NH_3(s) + & 2NH_3(g) \rightleftharpoons & LiCl.\ 3NH_3(s) \\ (i)\ n \text{ mol at start} & & & \\ & 0.1 & a + (0.1 \times 2) = a + 0.2 & 0 \\ (ii) \text{ Change by reaction} & & & \\ & -0.1 & -0.1 \times 2 = -0.2 & 0.1 \\ (iii)\ n \text{ mol at equilibrium} & & & \\ & 0.1 - 0.1 & a + 0.2 - 0.2 & 0 + 0.1 \\ & = 0 & = a & = 0.1 \end{array}$$

$$\therefore \quad K_p = \frac{1}{P_{(NH_3)^2}}$$

because the partial pressures of solids are taken as unity.

$$\therefore \quad \frac{1}{9\ \text{atm}^2} = \frac{1}{P_{(NH_3)^2}}.$$

Taking square root of both sides,we get :

$$\frac{1}{3\ \text{atm}} = \frac{1}{p_{NH_3}}\ ; \quad p_{NH_3} = 3\ \text{atm}$$

But $PV = n\,RT$ (gas equation) ;

$P = 3$ atm, $V = 5$ L, $n = ?$

$R = 0.0821$ L atm K$^-$ mol$^-$,

$T = 40 + 273 = 313$ K

$$\therefore \quad 3\ \text{atm} \times 5\ \text{L} = n \times 0.0821\ \text{L atm K}^-\ \text{mol}^- \times 313\ \text{K}$$

$$\therefore \quad n = \frac{15\ \text{atm L}}{0.821\ \text{L atm K}^-\ \text{mol}^- \times 313\ \text{K}} = 0.584$$

Or $a = 0.584$

$\therefore$ mol of NH$_3$ to be added at start $= a + 0.2 = 0.584 + 0.2 =$ **0.784 mol Ans.**

EXAMPLE 177. *The composition of the equilibrium mixture (Cl$_2$ $\rightleftharpoons$ 2 Cl) which is attained at 1200°C, is determined by measuring the rate of effusion through a pin-hole. 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 (at. wt. of Kr = 84)* **(IIT, 1995)**

SOLUTION. Let $x =$ Fraction of Cl$_2$ molecules dissociated.

$$\frac{r_{mix}}{r_{Kr}} = \left(\frac{M_{Kr}}{M_{mix}}\right)^{½}$$

(Graham's law of diffusion)

$$\frac{1.16}{1} = \left(\frac{84}{M_{mix}}\right)^{1/2}$$

Squaring both sides, we get :

$$(1.16)^2 = \frac{84}{M_{mix}}\ ; \quad M_{Mix} = \frac{84}{(1.16)^2} = 62.42$$

	$Cl_2 \rightleftharpoons$	$2Cl$
(*i*) *n* mol at start	1	0
(ii) Change by reaction	$-x$	$2x$
(iii) *n* mol at equilibrium	$1-x$	$2x$

Total number of mol at equilibrium

$$= 1 - x + 2x = 1 + x$$

$$M_{mix} = \left(\frac{2x}{1+x} \times \text{at. wt. of Cl}\right) + \frac{1-x}{1+x} \times (\text{mol. wt. of } Cl_2)$$

$$= \left(\frac{2x}{1+x} \times 35.5\right) + \frac{1-x}{1+x} \times (2 \times 35.5)$$

$$= \frac{71x}{1+x} + \frac{71}{1+x} - \frac{71x}{1+x}$$

$$62.42 = \frac{71}{1+x}\ ;\ 62.42\,(1+x) = 71\ ;$$

$$1 + x = \frac{71}{62.42} = 1.137$$

$\therefore$ $x = 1.137 - 1 = \mathbf{0.137}$ **Ans.**

Example 178. *For the reaction :*

$$A + B \rightleftharpoons C$$

the equilibrium concentration of A and B at a particular temperature are 15 mol L^{-} *each. When volume is doubled, the reaction has equilibrium concentration of A as 10 mol* L^{-}*. Calculate (i) Kc for reaction (ii) [C] in the original equilibrium obtained.*

Solution. First Case.	A	+	B	$\rightleftharpoons$	C
n mol at equilibrium	15		15		*a*
			(When volume = *V*)		
Second Case	A	+	B	$\rightleftharpoons$	C
			(When Volume = 2 *V*)		
(*i*) *n* mol at start	$\frac{15}{2}$		$\frac{15}{2}$		$\frac{a}{2}$
	$= 7.5$		$= 7.5$		$= 0.5\,a$
(*ii*) Change by reaction	$+x$		$+x$		$-x$
(*iii*) *n* mol at equilibrium	$7.5 + x$		$7.5 + x$		$0.5\,a - x$

We know that when volume is doubled, the pressure becomes one half. So, the reaction will proceed in a direction where there is an increase in the number of mol, *i.e.*, it will proceed in the backward direction.

Since $7.5 + x = 10\ ;\ \mathbf{x = 10 - 7.5 = 2.5}$

For first case. $K_p = \frac{[C]}{[A][B]} = \frac{a}{15 \times 15} = \frac{a}{225}$

For second case.

$$K_p = \frac{[C]}{[A][B]} = \frac{0.5\,a - x}{(7.5 + x)(7.5 + x)}$$

$$= \frac{0.5\,a - 2.5}{(7.5 + 2.5)^2}$$

Or $\frac{a}{225} = \frac{0.5\,a - 2.5}{100}\ ;\ 100\,a = 225\,(0.5\,a - 2.5)$

$$100\,a - 112.5\,a = -562.5\ ;\ -12.5\,a = -562.5$$

Hence $\mathbf{a = 45\ mol}$

$\therefore$ $K_C = \frac{a}{225} = \frac{45}{225} = \mathbf{0.2\ mol\ L^{-}}$ **Ans.**

Type. *Calculation of concentration of monomers/polymers when equilibrium constant value is given.*

Example 179. *The equilibrium constant for the polymerisation of formaldehyde, HCHO to glucose* $C_6H_{12}O_6$*, in aqueous solution is* 6×10^{22}*.*

$$6\ HCHO \rightleftharpoons C_6H_{12}O_6$$

If 1.0 M solution of glucose were to reach the dissociation equilibrium with respect to the above equation, what would be the concentration of formaldehyde in the solution ?

(MP PMT, 2002)

Solution. Given reaction :

$$6\ HCHO \rightleftharpoons C_6H_{12}O_6$$

$$[C_6H_{12}O_6] = 1.0\ M\ ;\ K = 6 \times 10^{22}$$

For the above reaction :

$$K = \frac{[C_6H_{12}O_6]}{[HCHO]^6}\ ;$$

$$6 \times 10^{22} = \frac{1}{[HCHO]^6}\ ;\ [HCHO]^6 = \frac{1}{6 \times 10^{22}}$$

$$\therefore\quad [HCHO] = \left(\frac{1}{6 \times 10^{22}}\right)^{1/6} = (0.167 \times 10^{-22})^{1/6}$$

Taking logs of both sides, we get :

$$\log [HCHO] = \log (0.167 \times 10^{-22})^{1/6}$$

$$= \frac{1}{6}[\log 0.167 - 22]$$

$$= \frac{1}{6}[-0.7772 - 22] = -3.7962$$

Taking antilogs, we get

$$[HCHO] = \text{antilog} - 3.7962$$

$$= \text{antilog} -3 -1 + 1 - 0.7962$$

$$= \text{antilog}\ \bar{4}.2038 = \mathbf{1.6 \times 10^{-4}}$$ **Ans.**

Example 180. *The equilibrium constant for the reaction*

$$\text{Glycerol} + H_3BO_3 \rightleftharpoons H_3BO_3 - \text{glycerol complex}$$

is 0.90. How much glycerol should be added per litre of 0.1 M H_3BO_3 *solution, so that 70 % of the* H_3BO_3 *is converted to* (H_3BO_3 *– glycerol) complex.*

Solution.

H_3BO_3 + glycerol $\rightleftharpoons$ H_3BO_3 – glycerol complex

n mol at equilibrium

30 70

Applying law of chemical equilibrium, we get :

$$K = \frac{[H_3BO_3 - \text{glycerol}]\ \text{Complex}}{[H_3BO_3]\ [\text{glycerol}]}$$

$$0.9 = \frac{70}{30 \times [\text{glycerol}]}\ ;$$

$$[\text{glycerol}] = \frac{70}{30 \times 0.9} = \mathbf{2.59\ M}$$ **Ans.**

EXAMPLE 181. *For $X_2(g) + Y_2(g) \rightleftharpoons 2XY(g)$ at 373 K, the value of $K_c = 50$. If 1 L vessel containing 1 mol of X_2 is connected with a 2 L flask containing 2 mol of Y_2, calculate the number of mol of XY formed at 373 K.*

SOLUTION. Reaction

Reaction	$X_2(g)$ +	$Y_2(g)$ ⇌	$2XY(g)$
no. of mol at $t = 0$	1	2	0
no. of mol at equilibrium	$1 - x$	$2 - x$	$2x$

Total volume after connecting vessels

$$= 1\text{ L} + 2\text{ L} = 3\text{ L}$$

$$[X_2] = \frac{1-x}{3}, [Y_2] = \frac{2-x}{3}; [XY] = \frac{2x}{3}$$

$$\therefore \quad K_c = \frac{[XY]^2}{[X_2][Y_2]} = \frac{\left(\frac{2x}{3}\right)^2}{\frac{1-x}{3} \times \frac{2-x}{3}}$$

$$= \frac{4x^2}{x^2 - 3x + 2}$$

$$50 = \frac{4x^2}{x^2 - 3x + 2};$$

$$50x^2 - 150x + 100 = 4x^2 \quad ; \quad 46x^2 - 150x + 100 = 0$$

After solving, we get $x = 0.93$ and 2.326. But the value 2.326 is not correct because x cannot be greater than 2.

$\therefore$ no. of mol of XY

$= 2x = 2 \times 0.93 =$ **1.86** **Ans.**

EXAMPLE 182. *The value of K_c at 25°C for the reaction*

$$Hg_2^{2+} + 2\,Fe^{3+} \rightleftharpoons 2Hg^{2+} + 2\,Fe^{2+}$$

is *9.14×10^{-6}. Calculate the concentration of ions at equilibrium if concentrations at the start are, $Hg_2^{2+} = Fe^{3+} = 0.5$ M ; $Hg^{2+} = Fe^{2+} = 0.03$ M.*

SOLUTION.

	Hg_2^{2+} +	$2Fe^{3+}$ ⇌	$2Hg^{2+}$ +	$2Fe^{2+}$
(*i*) *n* mol at start	0.5	0.5	0.03	0.03
(*ii*) Change by reaction	$\frac{-x}{2}$	$-x$	x	x
(*iii*) *n* mol at equilibrium	$0.5 - \frac{x}{2}$	$0.5 - x$	$0.03 + x$	$0.03 + x$

$$K_c = \frac{[Hg^{2+}]^2\,[Fe^{2+}]^2}{[Hg_2^{2+}]\,[Fe^{3+}]^2};$$

$$9.14 \times 10^{-6} = \frac{[Hg^{2+}]^2\,[Fe^{2+}]^2}{[Hg_2^{2+}]\,[Fe^{3+}]^2}$$

$$= \frac{(0.03 + x)^2\,(0.03 + x)^2}{0.5 - (x/2) \times (0.5 - x)^2}$$

After solving the above equation, we get,

$$x = 0.0027$$

$$\therefore \quad [Hg_2^{2+}] = 0.5 - \frac{0.0027}{2} = 0.5 - 0.00135$$

$= \mathbf{0.4986\ M}$ **Ans.**

$[Fe^{3+}] = 0.5 - 0.0027 = \mathbf{0.4973\ M}$ **Ans.**

$[Hg^{2+}] = 0.03 + 0.0027 = \mathbf{0.0327\ M}$ **Ans.**

$[Fe^{2+}] = 0.03 + 0.0027 = \mathbf{0.0327\ M}$ **Ans.**

EXAMPLE 183. *The dissociation equilibrium of a gas AB_2 can be represented as $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$. The degree of dissociation is x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure P is :*

(a) $(2K_p/P)1/2$ *(b)* K_p/P

(c) $2K_p/P$ *(d)* $(2K_p/P)^{1/3}$

(CBSE–PMT, 2008 Prelims)

SOLUTION.

Given :	$2AB_2(g)$ ⇌	$2AB(g)$ +	$B_2(g)$
Initial conc.	2	0	0
Conc. at equilibrium	$2(1-x)$ *i.e.,* $2 - 2x$	$2x$	x

No. of mol at equilibrium

$$= 2(1-x) + 2x + x = 2 + x$$

$$\text{But} \quad K_p = \frac{(P_{AB})^2\left[P_{B_2}\right]}{\left[P_{AB_2}\right]^2} = \frac{\left(\frac{2x}{2+x} \times P\right)^2 \left(\frac{x}{2+x} \times P\right)}{\left[\frac{2(1-x)}{2+x} \times P\right]^2}$$

$$= \frac{\frac{4x^3}{2+x} \times P}{4(1-x)^2}$$

$$= \frac{4x^3 \times P}{2} \times \frac{1}{4}$$

[$\because$ $1 - x = 1$ and $2 + x = 2$, x being very small]

$$\therefore \quad x = \left(\frac{8K_p}{4P}\right)^{1/3} \quad \text{or} \quad x = \left(\frac{2K_p}{P}\right)^{1/3}.$$

So, the correct answer is (*d*).

EXAMPLE 184. *For the reaction*

$$Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-.$$

the K_c at 25°C is 4×10^{-19}. Calculate $[Ag^+]$ in solution which was originally 0.1 M in KCN and 0.03 M in $AgNO_3$.

(IIT 1994)

SOLUTION.

	2KCN +	$AgNO_3$ ⇌	$Ag(CN)_2^-$ +	KNO_3 +	K^+
(*i*) *n* mol at start	0.1	0.03	0	0	0
(*ii*) Change by reaction	$-(2 \times 0.03)$ $= -0.06$	0	$\frac{0.06}{2}$ $= 0.03$	$\frac{0.06}{2}$ $= 0.03$	$\frac{0.06}{2}$ $= 0.03$
(*iii*) *n* mol at equilibrium	$0.1 - 0.06$ $= 0.04$	0	0.03	0.03	0.03

$\therefore$ $[Ag(CN)_2]^- = 0.03.$

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

(*i*) *n* mol at start	0.03	0	0.04
(*ii*) Change by reaction	$-x$	x	$0.04+x$
(*iii*) *n* mol at equilibrium	$0.03-x$	x	$0.04+x$

Since the value of K_c is very small and dissociation of $[Ag(CN)_2]^-$ is very small, $0.03-x=0.03$; $0.04+x=0.04$

But $$K_c=\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]^-}\ ;\ 4\times10^{-19}=\frac{x\times(0.04)^2}{0.03}\ ;$$

$$4\times10^{-19}(0.03)=x\times(0.04)^2\ ;$$

$$x=\frac{4\times10^{-19}\times0.03}{(0.04)^2}=\mathbf{7.5\times10^{-18}}\quad \textbf{Ans.}$$

EXAMPLE 185. *For the equilibrium*

$$AB\,(g) \rightleftharpoons A\,(g)+B\,(g),$$

K_p is equal to four times of total pressure. Calculate the number of mol of A formed. **(BIT Mesra ; Ranchi, 1990)**

SOLUTION.

	AB (g)	A (g)	B (g)
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$1-x$	x	x

Total number of mol at equilibrium

$$=1-x+x+x=1+x$$

$$\therefore\quad K_p=\frac{P_{(B)}\times P_{(A)}}{P_{(AB)}}=\frac{\left(\frac{x}{1+x}\times P\right)\left(\frac{x}{1+x}\times P\right)}{\left(\frac{1-x}{1+x}\times P\right)}$$

$$=\frac{x^2\,P}{1-x^2}$$

Since pressure $=P$, $K_p=4\times P$ (given) $=4$ P

$$\therefore\quad 4\,P=\frac{x^2\,P}{1-x^2}\ ;\ 4(1-x^2)=x^2\ ;$$

$$4-4\,x^2=x^2\ ;\ 5x^2=4$$

$$\therefore\quad x=\left(\frac{4}{5}\right)^{1/2}=0.894$$

Hence number of mol of A formed $=x=$ **0.894 mol.**

EXAMPLE 186. *In the preparation of CaO from $CaCO_3$ using the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s)+CO_2(g)$, K_p is expressed as*

$$\log K_p=7.282-8500/T$$

For the complete decomposition of $CaCO_3$, the temperature in celsius to be used is :

(*a*) *1167* (*b*) *892*

(*c*) *8500* (*d*) *850* **[AMU (engg) 2011]**

SOLUTION. In order to have complete decomposition, $K_p=1$. So, $\log K_p=\log 1=0$. Thus :

$$0=7.282-8500/T\ ;$$

$$T=(8500/7.282)=1167\ K$$

So, the correct answer is (*a*).

EXAMPLE 187. *The value of K_p is 1×10^{-3} atm^- at 25°C for the reaction*

$$2\,NO+Cl_2 \rightleftharpoons 2\,NOCl$$

A flask contains NO at 0.02 atm and at 25°C. Calculate the mol of Cl_2 that must be added if 1 % of the NO is to be converted to NOCl at equilibrium. The volume of flask is such that 0.2 mol of the gas produces 1 atm pressure at 25°C. (Ignore the probable association of NO to N_2O_2). **(Roorkee, 2001)**

SOLUTION. Let initial pressure of Cl_2 = P; $K_p=10^{-3}$

	2NO	Cl_2	2NOCl
(*i*) Pressure (atm) at start	0.02	P	0
(*ii*) Change by reaction	$-\frac{0.02\times1}{100}$ $=-2\times10^{-4}$	$-\frac{1}{2}\times\frac{0.02}{100}$ $=-10^{-4}$	$0.02\times\frac{1}{100}$ $=2\times10^{-4}$
(*iii*) Pressure (atm) at equilibrium	$0.02-2\times10^{-4}$ $=2\times10^{-2}-2\times10^{-4}$ $=2\times10^{-4}(100-1)$ $=198\times10^{-4}$	$P-10^{-4}$ $P-10^{-4}$	2×10^{-4} 2×10^{-4}

$$\therefore\quad K_p=\frac{P(NOCl)^2}{P(NO)^2\times PCl_2}$$

$$=\frac{(2\times10^{-4})^2}{(198\times10^{-4})^2\times(P-10^{-4})}$$

Or $$10^{-3}=\frac{4}{198\times198}\times\frac{1}{P-10^{-4}}\ ;$$

$$P-10^{-4}=\frac{4}{198\times198}\times\frac{1}{10^{-3}}=0.102$$

Or $$P=0.102+10^{-4}=0.102+0.0001$$

$$=0.1021\ \text{atm}$$

But $PV=n\,RT$ (ideal gas equation) ,

$V=$ Volume of vessel.

$$\therefore\quad V=\frac{n\,RT}{P}$$

$$=\frac{0.2\ \text{mol}\times0.082\ \text{L atm K}^-\ \text{mol}^-\times(25+273)\ \text{K}}{1\ \text{atm}}=4.887\ \text{L}$$

Again $$PV=n\,RT\ ;\ n=\frac{PV}{RT}$$

$$=\frac{0.1021\ \text{atm}\times4.877\ \text{L}}{0.082\ \text{L atm K}^-\ \text{mol}^-\times298\ \text{K}}$$

Or $n=$ **0.0204 mol** **Ans.**

EXAMPLE 188. *For a reaction $A(s)+B(g) \rightleftharpoons C(s)+D(g)$ at equilibrium, the value of K_p at 1000°C is 0.45. If B(g) at a pressure of 1 atmosphere and excess C(s) are placed in a container at the same temperature, what will be the pressure of B(g) and D(g), when equilibrium is attained ?*

SOLUTION. The given reaction is :

A(s)	B(g)	C(s)	D(g)
1 mol	1 mol	1 mol	1mol

Here, number of moles of B(g) consumed = Number of moles of D(g) formed. Considering ideal gas behaviour, partial pressures of gases are proportional to number of moles present. Hence, drop in pressure of B(g) will be equal to the partial pressure of D(g) formed. Suppose, partial pressure of D(g) at equilibrium = a atm.

$\therefore$ Partial pressure of B(g) at equilibrium = $(1 - a)$ atm.

But $$K_p = \frac{p_D}{p_B} = \frac{a}{1-a} = 0.45$$

Or $a + 0.45\,a = 0.45$

or $a = 0.31$

Hence $p_B = 1 - a = 1 - 0.31 = \mathbf{0.69\ atm.}$ **Ans.**

and $p_D = \mathbf{0.31 atm.}$ **Ans.**

23.24 AIEEE PATTERN EXAMPLES

Example 189. *A reaction is $A + B \rightleftharpoons C + D$. Initially, we start with equal concentrations of A and B. At equilibrium, we find that the moles of C are two times of A. What is the equilibrium constant of the reaction ?*

(*a*) 1/2 (*b*) 1/4

(*c*) 2 (*d*) 4 **(Karnataka CET, 2000)**

Solution. Given reaction : $A + B \rightleftharpoons C + D$ ...(1)

	A	B	C	D
Initial conc. (mol)	1	1	0	0
At equilibrium, conc.	$1 - x$	$1 - x$	x	x

But at equilibrium no. of mol of C

= 2 × no. of mol of A **Or** $x = 2(1 - x)$

$\therefore \quad x + 2x = 2 \; ; \; x = \frac{2}{3}$

For reaction (1),

$$K_c = \frac{[C][D]}{[A][B]} ; K_C = \frac{x \times x}{(1-x)(1-x)}$$

Or $$K_c = \frac{\frac{2}{3} \times \frac{2}{3}}{\left(1-\frac{2}{3}\right) \times \left(1-\frac{2}{3}\right)} = \frac{2}{3} \times \frac{2}{3} \times \frac{3}{1} \times \frac{3}{1} = \mathbf{4.0.}$$

So, the correct answer is (*d*).

Example 190. *At 1273 K, the value of K_c for the following reactions is given side by side.*

(*i*) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g); K_1 = 0.33$

(*ii*) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g); \; K_2 = 2.2 \times 10^{22}$

The value of K_c for (iii) $2COCl_2(g) + O_2(g) \rightleftharpoons 2CO_2(g) + 2Cl_2(g)$ is :

(*a*) 10^{21} (*b*) 2.3958×10^{21}

(*c*) 239.5×10^{23} (*d*) 4

Solution. For reaction

(*i*) $$K_1 = \frac{[CO(g)][Cl_2(g)]}{[COCl_2(g)]} = 0.33$$

(*ii*) $$K_2 = \frac{[CO_2(g)]^2}{[CO(g)]^2\,[O_2(g)]} = 2.2 \times 10^{22}$$

(*iii*) $$K = \frac{[CO_2(g)]^2\,[Cl_2(g)]^2}{[COCl(g)]^2\,[O_2(g)]} = ?$$

In order to get K, we have $K_1^2 \times K_2$.

So : $$K = \frac{[CO(g)]^2\,[Cl_2(g)]^2}{[COCl_2(g)]^2} \times \frac{[CO_2(g)]^2}{[CO(g)]^2\,[O_2(g)]}$$

$$= (0.33)^2 \times (2.20 \times 10^{22})$$

$$= \mathbf{2.3958 \times 10^{21}}$$ **Ans.**

So, the correct answer is, (*b*).

Example 191. *Equilibrium constants K_1 and K_2 for the following equilibria*

$$NO(g) + ½\,O_2 \xrightleftharpoons{K_1} NO_2(g) \text{ and}$$

$$2NO_2(g) \xrightleftharpoons{K_2} 2NO(g) + O_2(g) \text{ are related as}$$

(*a*) $K_2 = 1/K_1^2$ (*b*) $K_2 = K_1^2$

(*c*) $K_2 = 1/K_1$ (*d*) $K_2 = K_1/K_2$

[CBSE-PMT (Prelim), 2005]

Solution. (*a*) $NO(g) + \frac{1}{2}O_2(g) \xrightleftharpoons{K_1} NO_2(g)$

(*b*) $2NO_2(g) \xrightleftharpoons{K_2} 2NO(g) + O_2(g)$

$$\therefore \quad K_1 = \frac{P_{(NO_2)}}{P_{(NO)} \times P_{(O_2)^{1/2}}} \quad ...(1)$$

$$K_2 = \frac{P_{(NO)^2} \times P_{O_2}}{P_{(NO_2)^2}} \quad ...(2)$$

Equation (*b*) is reverse of equation (*a*) multiplied by 2. So, taking square root on both sides in equation (2), we get :

$$(K_2)^{1/2} = \frac{P_{(NO)} \times P(O_2)^{½}}{P_{(NO_2)}} ;$$

$$(K_2)^{1/2} = \frac{1}{K_1} \quad \textbf{Or} \quad K_2 = \frac{1}{K_1^2}$$

(after squaring both sides).

So, the correct answer is (*a*).

Example 192. *For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, partial pressure of CO_2 at 1000 K is 0.003 atm. $\Delta G^o = 27.2$ k cal. Calculate the value of ΔG.*

(*a*) 12.6 k cal (*b*) 15.6 k. cal

(*c*) 13.4 k. cal (*d*) 14.2 k. cal **(Orissa JEE, 2011)**

Solution. Since in the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, only CO_2 is a gas, so $K_p = P_{CO_2} = 0.003$ atm.

But $$\Delta G = \Delta G^o + 2.303\,RT \log K_p$$

$$= 27.2 + 2.303 \times 2 \times 1000 \times \log 0.003$$

$(\because R = 2 \text{ cal mol}^{-} \text{ K}^{-})$

$$= \mathbf{15.6\ k\ cal}$$

So, the correct answer is (*b*).

Example 193. *You are provided with the reaction, $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $\Delta H = -43.5$ k cal. Which out of the following will be true for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$?*

(*a*) *K varies with the addition of NO*
(*b*) *K is independent of T*
(*c*) *K decreases with the decrease in T*
(*d*) *K increases with the decrease in T.*

Solution. The given reaction is exothermic. So, the given reverse reaction will be endothermic. According to Le-Chatelier's principle, high temperature would favour the forward reaction. It means K increases with increase in T or K decreases with decrease in T. So, the answer is (*c*).

Example 194. *At 5°C, K value of equilibrium constant for the reaction,* $Cu(s) + 2\,Ag^+(aq) \rightleftharpoons 2Cu^{2+}(aq) + 2Ag(s)$ *is* 2.0×10^{15}*. In a solution in which the copper has displaced some silver ions from the solution, concentration of* Ag^+ *ions is* 3.0×10^{-9} *mol* L^- *and of* Cu^{2+} *ions is* 1.8×10^{-2} *mol* L^-*. The system will be :*

(*a*) *At equilibrium*
(*b*) *More to-wards forward*
(*c*) *More to-wards backward*
(*d*) *Can not be predicted.*

Solution.

$[Cu^{2+}(aq)]^{2+} = 1.8 \times 10^{-2}$ mol L^- ;

$[Ag^+(aq)] = 3.0 \times 10^{-9}$ mol L^-. Molar conc. of solids = 1

Applying law of chemical equilibrium for the reaction.

$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$, we have :

$$Q = \frac{[Cu^{2+}(aq)]\,[Ag(s)]^2}{[Cu(s)]\,[Ag^+(aq)]^2}$$

$$= \frac{1.8 \times 10^{-2} \times 1}{1 \times 3.0 \times 10^{-9} \times 3.0 \times 10^{-9}}$$

$$= \mathbf{2.0 \times 10^{15}} \qquad \textbf{Ans.}$$

The value of Q being same as that of K_c, so the correct answer is, (*a*).

Example 195. *For a reaction,* $X + Y \rightleftharpoons Z + E + 50k$ *cal, the value of equilibrium constant at 596K is 900. The value of K in presence of catalyst in the forward reaction would be :*

(*a*) *900 × 596* (*b*) *900*
(*c*) $\dfrac{900}{\textit{conc. of catalyst}}$ (*d*) *Cannot be calculated.*

Solution. Since the value of K varies with temperature only and not by a catalyst, the value will remain same *i.e.*, 900. So, the correct answer is (*b*).

Example 196. *The equilibrium constant, K for the reaction,* $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ *at room temperature is 2.85 and that at 698 K is* 1.4×10^{-2}*. This implies that :*

(*a*) *HI is resonance stabilised*
(*b*) *HI is an exothermic compound*
(*c*) *HI is relatively less stable than* I_2 and H_2
(*d*) *HI is extremely stable at room temperature.*

Solution. The value of K being less (= 1.4×10^{-2}) at high temperature (698K) than (2.85) at room temperature, so the given reaction is exothermic. In other words, the backward reaction is exothermic. So, HI is an endothermic compound. Since the energy of HI is greater than that of constituent elements H_2 and I_2, so HI is relatively unstable. So, the correct answer is, (*c*).

Example 197. *If Henry's law constant for* O_2 *is* 1.28×10^{-3} *mol* L^- *atm*$^-$*, the solubility of* O_2 *in water at a partial pressure of* O_2 *of 190 torr at 298 K will be :*

(*a*) 1.6×10^{-4} *mol* L^- (*b*) 3.2×10^{-4} *mol* L^-
(*c*) 4.8×10^{-6} *mol* L^- (*d*) 10^{-5} *mol* L^- *only.*

Solution. P = 190 torr = 190/760 = 0.25 atm ;
$k = 1.28 \times 10^{-3}$ mol L^- atm$^-$.

According to Henry's law,

$$C = k\,P$$

$$\therefore \quad C = 1.28 \times 10^{-3} \text{ mol } L^- \text{ atm}^- \times 0.25 \text{ atm}$$

$$= \mathbf{3.2 \times 10^{-4}\ mol\ L^-}.$$

So, the correct answer is (*b*).

Example 198. *For a reaction,* $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$*, the value of* K_c *at 127°C is* 4.0×10^{-6}*. The value of* K_p *for the same reaction will be :*

(*a*) 4.0×10^{-2} (*b*) 2.0×10^{-4}
(*c*) $2 \times 10^{-6}\,RT$ (*d*) *none of these.*

Solution. For $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

1 mol 1 mol 2 mol

$\Delta n = 2 - (1 + 1)$ = zero

We know $K_p = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{\circ} = K_c$

or $K_p = K_c$.

Hence the true answer is (*d*).

Example 199. *At 673 K and 10 atmospheric pressure, ammonia was found to be dissociated to 96 % in the equilibrium mixture.*

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

The K_p *for the reaction will be :*

(*a*) *1.1 atm* (*b*) $\simeq 2.3328 \times 10^4$ *atm*^{2}
(*c*) 1.421×10^3 *atm* (*d*) *4 atm.*

Solution.	$2\,NH_3$ $\rightleftharpoons$	$1N_2$ +	$3H_2$
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-96\,\% = \frac{-96}{100}$ $= -0.096$	$\frac{1}{2} \times 0.96$ $= 0.48$	$\frac{3}{2} \times 0.96$ $= 1.44$
(*iii*) *n* mol at equilibrium	$(1 - 0.96)$ $= 0.04$	0.48	1.44

Total number of mol

$$= 0.04 + 0.48 + 1.44 = 1.96$$

$$K_p = \frac{p(H_2)^3 \times p_{N_2}}{p(NH_3)^2}$$

$$= \frac{\left(\frac{1.44}{1.96}\times P\right)^3 \left(\frac{0.48}{1.96}\times P\right)}{\left(\frac{0.04}{1.96}\times P\right)^2}$$

But $P =$ 10 atm. Hence.

$$K_p = \frac{\left(\frac{1.44\times 10}{1.96}\right)^3 \left(\frac{0.48\times 10}{1.96}\right)}{\left(\frac{0.04}{1.96}\times 10\right)^2}$$

$$= \frac{(1.44\times 10)^3}{(1.96)^3}\times\frac{0.48}{1.96}\times 10\times\frac{(1.96)^2}{(0.04\times 10)^2}$$

$$= \frac{2985.98\times 4.8}{3.84\times 0.16} = \mathbf{23328} = 2.3328\times 10^4$$

So, the correct answer is (*b*).

Example 200. *One mol of NH_3 was heated in presence of a catalyst in a half-litre capacity vessel to get equilibrium. The resultant mixture contained 0.7 mol of NH_3. The equilibrium constant at the temperature of experiment will be*

(*a*) *0.1* (*b*) *0.2*

(*c*) *0.8* (*d*) *0.33.*

Solution. mol of NH_3 at equilibrium = 0.7

Volume $= \frac{1}{2}L = 0.5\ L$

	NH_3 $\rightleftharpoons$	$\frac{1}{2}N_2$ +	$\frac{3}{2}H_2$
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$1 - 0.7 = 0.3$	$0.3\times\frac{1}{2} = 0.15$	$0.3\times\frac{3}{2} = 0.45$
(*iii*) *n* mol L^- at equilibrium	$\frac{1-0.3}{0.5} = 1.4$	$\frac{0.15}{0.5} = 0.3$	$\frac{0.45}{0.5} = 0.9$

$\because V = 0.5\ L$

$$K_p = \frac{p(N_2)^{1/2}\times p(H_2)^{3/2}}{p(NH_3)}$$

$$= \frac{(0.3)^{1/2}\times(0.9)^{3/2}}{1.4} = \frac{(0.3)^{1/2}\times\sqrt{(0.9)^3}}{1.4}$$

$$= \frac{0.55\times(0.729)^{1/2}}{1.4} = \frac{0.55\times 0.85}{1.4} = \mathbf{0.33}$$

So, the correct answer is (*d*).

Example 201. *One mol of NH_3 was heated in presence of a catalyst in a one litre capacity flask to get $NH_3 \rightleftharpoons \frac{1}{2}N_2 + \frac{3}{2}H_2$ equilibrium. At equilibrium 0.3 mol of H_2 was left behind. The concentrations of N_2 and NH_3 at equilibrium are respectively :*

(*a*) *0.05, 1 mol* (*b*) *0.1 mol, 0.2 mol*

(*c*) *0.2 mol, 0.1 mol* (*d*) *none of these.*

Solution.

	NH_3 $\rightleftharpoons$	$\frac{1}{2}N_2$ +	$\frac{3}{2}H_2$
(*i*) *n* mol at start	1	0	0
(*ii*) *n* mol at equilibrium	$0.3\times 1\times\frac{2}{3}$	$0.3\times\frac{1}{2}\times\frac{2}{3}$	0.3
	= 0.2	= 0.1	0.3

$\therefore$ $[N_2]$ = 0.1 mol ; $[NH_3]$ = 0.2 mol.

So, the correct answer is (*b*).

Example 202. *1 mol of N_2O_4 is heated in a flask with a volume of 10 dm^3. At equilibrium, 1.708 mol of NO_2 and 0.146 mol of N_2O_4 were found at 407 K. The equilibrium constant value will be :*

(*a*) *200 mol^{-3} dm* (*b*) *2.0 mol dm^{-3}*

(*c*) *100 mol dm^{-3}* (*d*) *50 mol dm^{-3}.*

Solution.

	N_2O_4 $\rightleftharpoons$	$2NO_2$
(*i*) *n* mol at start	1	0
(*ii*) *n* mol dm^{-3} at equilibrium	$\frac{0.146\ \text{mol}}{10\ dm^3}$	$\frac{1.708\ \text{mol}}{10\ dm^3}$
	= 0.0146 mol dm^{-3}	0.1708 mol dm^{-3}

$$\therefore \quad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$= \frac{(0.1708\ \text{mol dm}^{-3})^2}{0.0146\ \text{mol dm}^{-3}}$$

$$= \frac{0.0292\ \text{mol}^2\ \text{dm}^{-6}}{0.0146\ \text{mol dm}^{-3}}$$

$$= \mathbf{2\ mol\ dm^{-3}}$$

So, the correct answer is (*b*).

Example 203. *The concentrations of N_2O_4 and NO_2 for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ are 0.044 mol L^- and 0.015 mol L^- respectively. The equilibrium constant K_c for this reaction at equilibrium will be :*

(*a*) *5.1 × 10^{-3} mol L^-* (*b*) *1.5 × 10^{-4} mol L^-*

(*c*) *10^{-3} mol L^-* (*d*) *10.2 × 10^{-3} mol L^-*

Solution.

$[N_2O_4]$ = 0.044 mol L^- ;

$[NO_2]$ = 0.015 mol L^-.

For the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.015\ \text{mol L}^-)^2}{0.044\ \text{mol L}^-}$$

$$= \frac{0.000225\ \text{mol}^2\ \text{L}^{-2}}{0.044\ \text{mol L}^-}$$

$$K_c = \mathbf{5.1\times 10^{-3}\ mol\ L^-}$$

So, the correct answer is (*a*).

Example 204. *A closed vessel contains one mol of $N_2O_4(g)$ at 27°C and one atmospheric pressure. On heating to 327°C, 20% by mass of this gas decomposed to brown coloured $NO_2(g)$. The resultant pressure will be :*

(*a*) *0.24 atm* (*b*) *2.4 atm*

(*c*) *0.024 atm* (*d*) *0.48 atm.*

SOLUTION. g. mol. mass (= 1 mol) of $N_2O_4(g) = (2 \times 14) + (4 \times 16) = 28 + 64 = 92$ g.

g. mol. mass of $2NO_2 = 2[14 + (2 \times 16)] = 92$ g.
At equilibrium, mass of $N_2O_4(g)$

$$= 92 - \left(92 \times \frac{20}{100}\right) = 92 - 18.4 = 73.6 \text{ g}$$

∴ no. of mol of N_2O_4 (g)

$$= \frac{\text{mass of } N_2O_4}{\text{g. mol. mass of } N_2O_4}$$

$$= \frac{73.6 \text{ g}}{92 \text{ g}} = 0.8 \text{ mol}$$

In the reaction,

$$N_2O_4 \rightleftharpoons 2NO_2 \text{ g}$$

no. of mol of NO_2

$$= \frac{1}{2} \times \text{mol of } N_2O_4 = \frac{1}{2} \times 0.8 \text{ mol}$$

$$= \mathbf{0.4 \text{ mol}}$$

$$T_1 = 27 + 273 = 300\text{K};$$

$$T_2 = 327 + 273 = 600 \text{ K}$$

Total no. of mol = 0.8 + 0.4 = 1.2 mol
Since the volume (V) is constant, thus

(*i*) $P_1 = 0.8$ mol, $V_1 = V$; $T_1 = 300$K, $n_1 = 1$ mol

(*ii*) $P_2 = 0.4$ mol, $V_2 = V$; $T_2 = 600$K, $n_2 = 1.2$ mol

But $$\frac{P_1V_1}{n_1 RT_1} = \frac{P_2V_2}{n_2 RT_2}$$

Or $$\frac{P_1}{n_1T_1} = \frac{P_2}{n_2T_2}; \frac{1}{1 \times 300} = \frac{P_2}{1.2 \times 600}$$

∴ $$P_2 = \frac{1.2 \times 600}{300} = \mathbf{2.4 \text{ atm.}}$$

So, the correct answer is, (*b*).

EXAMPLE 205. *At 27°C and one atmospheric pressure, the equilibrium mixture of* N_2O_4 *(g) and* $NO_2(g)$ *contains 19.8 %* NO_2 *by volume. The value of* K_p *for the equilibrium* N_2O_4 *(g)* $\rightleftharpoons 2NO_2(g)$ *will be :*

(a) 8.49	*(b) 2.22*
(c) 2.89	*(d) 0.0489.*

SOLUTION. Let concentration of N_2O_4 (g) = 1 mol.
concentration of NO_2 at equilibrium

$$= 19.8\ \% = \frac{19.8}{100} = 0.198 \text{ mol}$$

Concentration of N_2O_4 (g) at equilibrium

$$= 1 - \frac{19.8}{100} = 0.802 \text{ mol}$$

Total number of mol of NO_2 and N_2O_4

$$= 0.198 + 0.802 = 1 \text{ mol},$$

Pressure, $P = 1$ atm.

K_p for the reaction $N_2O_4 \text{ (g)} \rightleftharpoons 2NO_2(g)$ is given as:

$$K_p = \left(\frac{p_{NO_2} \times P}{\text{total mol} = 1}\right)^2 \Big/ \left(\frac{p_{N_2O_4} \times P}{\text{total mol} = 1}\right)$$

∴ $$K_p = \frac{0.198 \times 0.198 \times 1}{0.802 \times 1} = 0.0489$$

So, the correct answer is (*d*).

EXAMPLE 206. The dissociation constant of N_2O_4 if it dissociates to the extent of 53% at 60°C and one atmospheric pressure will be :

(*a*) 2.39	(*b*) 9.32
(*c*) 239	(*d*) 23.9

SOLUTION. Dissociation of N_2O_4 = 53 % .

Let initial concentration of N_2O_4 = 1 mol.

P = 1 atm. Thus for the following reaction we have:

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial conc.	1 mol	0
Conc. at. equilibrium	$1 - \frac{53}{100}$	$2 \times \frac{53}{100}$
	= 0.47 mol	= 1.06 mol

$$K_p = \frac{\left(p_{NO_2} \times P\right)^2}{(p_{N_2O_4} \times P)} = \frac{(1.06 \times 1)^2}{(0.47 \times 1)}$$

$$= \frac{(1.06)^2}{0.47} = \mathbf{2.39}$$

So, the correct answer is (*a*).

EXAMPLE 207. *One mol of acetic acid and one mol of ethyl alcohol were mixed at 298 K. At equilibrium, 0.333 mol of acetic acid was found unreacted. The value of equilibrium constant will be :*

(*a*) 2.006	(*b*) 4.012
(*c*) 12.036	(*d*) 1.003

SOLUTION. Concentration of CH_3COOH = 1 mol ;
Concentration of ethyl alcohol = 1 mol ;
mol of CH_3COOH unreacted = 0.333 mol.
Thus for the following reaction, we have :

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

(*i*) no. of mol at start

1 mol	1mol	0	0

(*ii*) Change for reaction

0.333 mol	0.333 mol	– 0.333 mol	–0.333mol

(*iii*) no. of mol at equilibrium

0.333 mol	0.333 mol	1 – 0.333 = 0.667 mol	1 – 0.333 =0.667mol

K_c for the reaction is given as :

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{0.667 \times 0.667}{0.333 \times 0.333} = \mathbf{4.012} \qquad \textbf{Ans.}$$

So, the correct answer is, (*b*).

Example 208. *The equilibrium constant of the reaction*

$$CH_3OH + CH_3COOH \rightleftharpoons CH_3COOCH_3 + H_2O$$

at 298K is 65. The weight of methyl acetate in equilibrium mixture, if 2 mol of methyl alcohol were originally mixed with one mol of acetic acid is :

(*a*) *36.5 g* (*b*) *34.4 g*
(*c*) *72.9 g* (*d*) *17.7 (g)*

Solution. mol of $CH_3COOH = x$. Initial concentration of CH_3OH = 2 mol ; CH_3COOH = 1 mol ; $K_c = 65$. For the following reaction, we have :

$$\begin{array}{lcccc} & CH_3OH + & CH_3COOH & \rightleftharpoons CH_3COOCH_3 + & H_2O \\ (i)\ n \text{ mol at start} & & & & \\ & 2\text{ mol} & 1\text{ mol} & 0 & 0 \\ (ii) \text{ Change for reaction} & & & & \\ & x\text{ mol} & x\text{ mol} & x\text{ mol} & x\text{ mol} \\ (iii)\ n \text{ mol at equilibrium} & & & & \\ & 2-x\text{ mol} & 1-x\text{ mol} & x\text{ mol} & x\text{ mol} \end{array}$$

$$\therefore \qquad K_c = \frac{[CH_3COOCH_3][H_2O]}{[CH_3OH][CH_3COOH]}$$

$$65 = \frac{x \times x}{(2-x)\times(1-x)} = \frac{x^2}{2-3x+x^2}$$

$$130 - 195x + 65x^2 = x^2 \quad ; \quad 65x^2 - x^2 - 195x + 130 = 0$$

$$\therefore\ 64x^2 - 195x + 130 = 0$$

$$\therefore \qquad x = \frac{-(-195) \pm [(-195)^2 - (4 \times 64 \times 130)]^{1/2}}{2 \times 64}$$

$$= \frac{+195 \pm (38025 - 33280)^{1/2}}{128}$$

$$= \frac{+195 \pm (4745)^{1/2}}{128}$$

$$\left[\begin{array}{l} \text{For quadratic equation,} \\ ax^2 + bx + c = 0 \\ x = \dfrac{-b \pm (b^2 - 4\,ac)^{1/2}}{2a} \end{array}\right.$$

$$= \frac{+195 - 68.88}{128} = \frac{126.12}{128}$$

$$x = 0.985 \text{ mol.}$$

$$\left[\begin{array}{l} \text{g. mol. wt. of } CH_3COOCH_3 \\ = 12 + (3 \times 1) + 12 + (2 \times 16) \\ + 12 + (3 \times 1) = 74 \text{ g} \end{array}\right.$$

g. mol. of methyl acetate,

CH_3COOCH_3 weigh = 74 g

Thus 1 mol of CH_3COOCH_3 weigh = 74 g

0.985 mol of CH_3COOCH_3 weigh

$$= 74 \times 0.985 = \mathbf{72.9\ g} \quad \textbf{Ans.}$$

So, the correct answer is, (*c*).

Example 209. *At 427°C, the value of K_c for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.8. If at the same temperature, 0.5 mol L^- of HI (g) is present at equilibrium, the concentration of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI(g) and allowed it to reach equilibrium at same temperature is :*

(*a*) *6.8 mol L^-* (*b*) *68 mol L^-*
(*c*) *0.068 mol L^-* (*d*) *0.34 mol L^-*

Solution. At equilibrium,

$$[H_2] = [I_2] = x \text{ (say) ; [HI] = 0.5 mol}$$

For the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.5 \text{ mol L}^- \times 0.5 \text{ mol L}^-}{x^2}$$

$$54.8 = 0.25/x^2$$

$$\text{Or} \qquad 54.8\,x^2 = 0.25 \text{ mol}^2\text{ L}^{-2}$$

$$\text{Or} \qquad x = \left[\frac{0.25 \text{ mol}^2 \text{ L}^{-2}}{54.8}\right]^{1/2}$$

$$\therefore \qquad x = (0.00456 \text{ mol}^2 \text{ L}^-)^{1/2}$$

$$= \mathbf{0.068\ mol\ L^-} \qquad \textbf{Ans.}$$

So, the correct answer is, (*c*).

Example 210. *0.12 mol of PCl_3 are mixed with 0.9 mol of PCl_5 in a one litre vessel. The vessel contains 0.72 mol of PCl_5 at equilibrium. The value of K_c for the reaction is :*

(*a*) *0.1 mol L^-* (*b*) *0.04 mol L^-*
(*c*) *0.075 mol L^-* (*d*) *0.75 mol L^-*

Solution. Initial no. of mol of PCl_5 = 0.90 ; PCl_3 = 0.12 mol; no. of mol of PCl_5 at equilibrium = 0.72

∴ At equilibrium (*i*) no. of mol of PCl_3 = 0.12 + (0.90 – 0.72) = 0.12 + 0.18 = 0.30 mol

(*ii*) no. of mol of Cl_2

$$= 0.90 - 0.72 = 0.18 \text{ mol}$$

∴ K_c for the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is :

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.3 \times 0.18}{0.72}$$

$$= \mathbf{0.075\ mol\ L^-} \qquad \textbf{Ans.}$$

So, the correct answer is, (*c*).

Example 211. *Phosphorus penta chloride is 82% dissociated into phosphorus trichloride and chlorine, all gaseous at 250°C and 1 atmospheric pressure. The equilibrium constant of dissociation is :*

(*a*) *2.577* (*b*) *3.577*
(*c*) *0.202* (*d*) *2.05*

Solution.	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
(*i*) *n* mol at start	1	0	0
(*ii*) Change by reaction	$-x$	x	x
(*iii*) *n* mol at equilibrium	$1-x$	x	x

Total number of mol

$$= 1 - x + x + x = 1 + x$$

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{\left(\frac{x}{1+x}\times P\right)\left(\frac{x}{1+x}\times P\right)}{\left(\frac{1-x}{1+x}\right)P} = \frac{x^2\,P}{1-x^2}$$

$$x = 82\ \%\ \text{of 1 mol} = \frac{82}{100} \times 1 = 0.82\ ;$$

$$P = 1\ \text{atmosphere}$$

$$\therefore \quad K_p = \frac{(0.82)^2}{1-(0.82)^2} \times 1 = \frac{0.6724}{1-0.6724}$$

$$= \frac{0.6724}{0.3276} = \mathbf{2.05} \qquad \textbf{Ans.}$$

So, the correct answer is (*d*).

Example 212. *Pure PCl_5 was transferred into an evacuated vessel at 473 K. After the attainment of equilibrium, concentration of PCl_5 was found to be 0.05 mol L^{-}. If value of K_c is 8.3×10^{-3}, the concentration of Cl_2 and PCl_3 at equilibrium will be :*

(*a*) *24 mol L^{-}* (*b*) *0.24 mol L^{-}*

(*c*) *0.024 mol L^{-}* (*d*) *0.0024 mol L^{-}*

Solution. $[Cl_2] = [PCl_3] = x$ (say) ; $[PCl_5] = 0.05\ \text{mol}^{-}$

For the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, we have

Conc. at equilibrium : 0.05 mol L^{-} $\quad x \quad x$

$$\therefore \quad K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x \times x}{0.05}$$

$$8.3 \times 10^{-3} = \frac{x^2}{0.05}\ ;\ x^2 = 8.3 \times 10^{-3} \times 0.05$$

$$= 4.15 \times 10^{-4}$$

$$\therefore \quad x = (4.15 \times 10^{-4})^{1/2} = \mathbf{0.024\ mol\ L^{-}}$$

So, the correct answer is, (*c*).

Example 213. *The equilibrium*

$$H_2(g) + S(s) \rightleftharpoons H_2S(g),\ K = 6.8 \times 10^{-2}$$

exists at 363 K. If 0.2 mol of H_2 and 1.0 mol of sulphur are heated to 363 K in a 1.0 L vessel, the partial pressure of H_2S gas at equilibrium will be :

(*a*) *0.21 atm* (*b*) *0.21 atm^2*

(*c*) *0.42 atm* (*d*) *0.42 atm^2.*

Solution.	$H_2(g) + S(s)$ $\rightleftharpoons$	$H_2S(g)$
(*i*) *n* mol at start	0.2	0
(*ii*) Change by reaction	$-x$	x
(*iii*) *n* mol L^{-} at equilibrium	$0.2 - x$ mol/1 L = 0.2 mol L^{-}	x

($\because$ x is very small and can be rejected)

$$K_p = \frac{pH_2S}{pH_2} = \frac{x}{0.2}\ ;\ 6.8 \times 10^{-2} = \frac{x}{0.2}$$

$$\therefore \quad x = 6.8 \times 10^{-2} \times 0.2 = 1.4 \times 10^{-2}\ \text{mol L}^{-}$$

$$P(H_2S) = \left(\frac{n}{V}\right)RT = 1.4 \times 10^{-2}\ \text{mol L}^{-} \times 0.0821$$

$$\text{L atm K}^{-}\ \text{mol}^{-} \times 363\ \text{K}$$

$$P(H_2S) = \mathbf{0.42\ atm} \qquad \textbf{Ans.}$$

So, the correct answer is (*c*).

Example 214. *A container contains CO_2 gas at 0.5 atm pressure and 1000K. On the addition of some graphite, some of the $CO_2(g)$ converted into carbon monoxide. If total pressure at equilibrium is 0.8 atm, the value of equilibrium constant will be:*

(*a*) *0.8 atm* (*b*) *1.8 atm*

(*c*) *2.8 atm* (*d*) *None of these.* **(AIEEE, 2011)**

Solution. Initial pressure of CO_2 = 0.5 atm

At equilibrium ; we have :

$CO_2(g)$ +	$C(s)$ $\rightleftharpoons$	$2CO(g)$
Initial pressure		
0.5 atm	Graphite	0
Conc. at equilibrium		
$0.5 - x$	0	$2x$

Total pressure at equilibrium

$$= 0.5 - x + 2x = 0.5 + x$$

$$0.8 = 0.5 + x\ ;\ \therefore\ x = 0.8 - 0.5 = 0.3$$

$\therefore$ Partial pressure of CO_2 (g), p_{CO_2}

$$= 0.5 - x = 0.5 - 0.3 = \mathbf{0.2\ atm.}$$

Partial pressure of CO(g), p_{CO}

$$= 2x = 2 \times 0.3 = \mathbf{0.6\ atm.}$$

$$\therefore \quad K_p = \frac{(p_{CO})^2}{p_{CO_2}} = \frac{(0.6\ atm)^2}{0.2\ atm} = \frac{0.36\ \text{atm}^2}{0.2\ \text{atm}}$$

$$= \mathbf{1.8\ atm} \qquad \textbf{Ans.}$$

So, the correct answer is, (*b*).

Example 215. *If the equilibrium constants of the following equilibria, $SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$ and $2SO_3 \rightleftharpoons 2SO_2 + O_2$ are given by K_1 and K_2 respectively, which of the following reactions are correct ?*

(*a*) *$K_2 = (1/K_1)^2$* (*b*) *$K_1 = (1/K_2)^3$*

(*c*) *$K_2 = 1/K_1$* (*d*) *$K_2 = (K_1)^2$.* **(WB-JEE, 2011)**

Solution. For $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$, $K_1 = [SO_3]/[SO_2][O_2]$ ...(1)

For $\quad 2SO_3 \rightleftharpoons 2SO_2 + O_2$,

$$K_2 = [SO_2]^2\,[O_2]/[SO_3]^2 \qquad ...(2)$$

From (1) and (2), $K_2 = \dfrac{1}{K_1^2}$ or $K_2 = (1/K_1)^2$

So, the correct answer is (*a*).

EXAMPLE 216. *For the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 400 K, $K_p = 41$. Find the value of K_p for the following reaction.*

$1/2\ N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g)$

(a) 6.4 *(b)* 0.02

(c) 50 *(d)* 4.6 **(J and K CET, 2010)**

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

$$K_p = [p_{NH_3}]^2/[p_{N_2}]\ [p_{H_2}]^3 = 41\ ;$$

$$p_{NH_3} = K_p\ [p_{N_2}]\ [p_{H_2}]^3 \qquad ...(1)$$

For $1/2\ N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g)$

$$K_p' = [p_{NH_3}]/[p_{N_2}]^{1/2}[p_{H_2}]^{3/2} \qquad ...(2)$$

Putting value of (1) in (2), we get :

$$K_p' = (K_p\ p_{N_2} p_{H_2}^3)^{1/2}/p_{N_2}^{1/2}\ p_{H_2}^{3/2} = (41)^{1/2}$$

$= 6.4$. So, correct answer is *(a)*.

EXAMPLE 217. *The value of K_c for the reaction $H_2O\ (g) + CO(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 298 K from the following data*

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)\ ;\ K_{c_1} = 3.3 \times 10^{91}$$

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)\ ;$$

$$K_{c_2} = 9.1 \times 10^{80} \text{ at } 298K \text{ is :}$$

(a) 2.3×10^4 *(b)* 1.9×10^5

(c) 3.1×10^2 *(d)* 1.9×10^{17}

SOLUTION. Given :

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad ...(1)$$

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad ...(2)$$

In order to get $H_2O(g) + CO(g) \longrightarrow CO_2(g) + H_2(g)$, we have :

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)\ ;$$

$$K_{C_1} = 3.3 \times 10^{91}$$

Or $$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)\ ;$$

$K_C' = (K_{C_1})^{½}$ because

When an equation is divided by 2,

new K_C' value $= (K_{C_1})^{½}$

Similarly, write equation (ii) in the reverse direction. So,

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)\ ;$$

$$K_{C_2}'' = \frac{1}{K_{C_2}}$$

Or $$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)\ ;$$

$$K_C'' = \left(\frac{1}{K_{C_2}}\right)^{1/2}$$

because when an equation is divided by 2,

new K_c'' value $= \left(\frac{1}{K_{C_2}}\right)^{1/2}$

Hence net K value is given as :

$$K = K_C' \times K_C'' = \left(\frac{1}{K_{C_1}}\right)^{1/2} \times \left(\frac{1}{K_{C_2}}\right)^{1/2}$$

$$= \left(\frac{3.3 \times 10^{91}}{9.1 \times 10^{80}}\right)^{1/2}$$

$K =$ antilog 5.28 $=$ **1.9×10^5** **Ans.**

So, the correct answer is *(b)*.

EXAMPLE 218. *Iodine vapours contain 40 % by volume of iodine atoms at total pressure of 10^5 Pa and at a certain temperature. The value of K_p for the equilibrium $I_2(g) \rightleftharpoons 2I(g)$ will be :*

(a) 2.67×10^4 *(b)* 0.267×10^4

(c) 5.34×10^8 *(d)* 53.4×10^7

SOLUTION. Iodine vapours contain I–atoms. So, partial pressure of I– atoms

$$= \frac{40}{100} \times 10^5\ Pa = 4.0 \times 10^4\ Pa$$

Also : partial pressure of I_2 – molecules

$$= \frac{(100 - 40)}{100} \times 10^5\ Pa$$

$$= \frac{60}{100} \times 10^5\ Pa$$

$$= 6.0 \times 10^4\ Pa.$$

For the reaction

$$I_2(g) = 2I(g),$$

$$K_p = \frac{[p_I(g)]^2}{(p_{I_2})} = \frac{(4.0 \times 10^4)^2}{6.0 \times 10^4} = \frac{16 \times 10^8}{6.0 \times 10^4}$$

$= \mathbf{2.67 \times 10^4}$ **Ans.**

So, the correct answer is, *(a)*.

EXAMPLE 219. *At 500K, bromine monochloride (BrCl) decomposes to give bromine and chlorine according to the following equilibrium*

$$2BrCl \rightleftharpoons Br_2(g) + Cl_2(g)\ ;\ K_c = 32 \text{ at } 500K$$

If the concentration of BrCl in the beginning was 3.3×10^{-3} mol L^-, its concentration in the mixture at equilibrium will be :

(a) 2.92×10^{-3} *(b)* 2.0×10^{-4}

(c) 6.0×10^{-8} *(d)* 2.92×10^{-4}

SOLUTION. For the following reaction, we have :

2BrCl ⇌	$Br_2(g)$ +	$Cl_2(g)$
Initial conc.		
3.3×10^{-3}	0	0
Conc. at equilibrium		
x	$\frac{1}{2} \times 3.3 \times 10^{-3}$	$\frac{1}{2} \times 3.3 \times 10^{-3}$
	$= 1.65 \times 10^{-3}$	$= 1.65 \times 10^{-3}$

Where $x =$ molar concentration of the mixture at equilibrium.

$$\therefore \quad K_C = \frac{[Br_2]\ [Cl_2]}{[BrCl]^2}$$

$$= \frac{(1.65 \times 10^{-3}) \times (1.65 \times 10^{-3})}{x^2}$$

$$32 = \frac{1.65\times10^{-3}\times1.65\times10^{-3}}{x^2}\ ;$$

$$32x^2 = 1.65\times10^{-3}\times1.65\times10^{-3}$$

$$\therefore \qquad x^2 = \frac{(1.65\times10^{-3})^2}{32}\ ;\ x = \frac{[(1.65\times10^{-3})^2]^{1/2}}{(32)^{1/2}}$$

$$= \frac{1.65\times10^{-3}}{5.656}$$

$$= \mathbf{2.92\times10^{-4}\ mol} \qquad \textbf{Ans.}$$

So, the correct answer is, (*d*).

EXAMPLE 220. *At a total pressure of one atmosphere, SO_2Cl_2 decomposes to the extent of 91.2 % at 102°C according to the reaction.*

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

The value of K_p for the reaction would be :

(*a*) 494 (*b*) 49.4

(*c*) 4.94 (*d*) 0.494

SOLUTION. Total pressure = 1 atm ; % age decomposition of SO_2Cl_2 = 91.2. Initial concentration of SO_2Cl_2 = 1 mol. Thus for the following reaction, we have :

	$SO_2Cl_2(g) \rightleftharpoons$	$SO_2(g)$	$+Cl_2(g)$
Initial conc.	1 mol	0	0
Conc. at equilibrium	$1-\frac{91.2}{100}$ = 0.088	$1\times\frac{91.2}{100}$ = 0.912	$\frac{1\times91.2}{100}$ = 0.912

Total number of mol

$$= 0.08 + 0.912 + 0.912 = 1.912$$

$$K_p = \frac{\left(\dfrac{p_{SO_2}\times P}{\text{Total mol}}\right)\times\left(\dfrac{P_{Cl_2}\times P}{\text{Total mol}}\right)}{\left(\dfrac{p_{SO_2Cl_2}\times P}{\text{Total mol}}\right)}$$

$$= \frac{\dfrac{0.912\times1}{1.912}\times\dfrac{0.912\times1}{1.912}}{\dfrac{0.088\times1}{1.912}}$$

$$= \frac{0.477\times0.477}{0.046} = \mathbf{4.94} \qquad \textbf{Ans.}$$

So, the correct answer is, (*c*).

EXAMPLE 221. *For a reaction of the type, $AB \rightleftharpoons A + B$, the total pressure at which AB gets 50% dissociated will be numerically equal to*

(*a*) 2 Kp (*b*) 3 Kp

(*c*) 4 Kp (*d*) 0.5 Kp.

(Modified PUPET 1986)

SOLUTION. For the following reaction,

total pressure = P (say).

	AB $\rightleftharpoons$	A +	B
no. of mol at equilibrium	$\frac{50}{100}=\frac{1}{2}$	$\frac{50}{100}=\frac{1}{2}$	$\frac{50}{100}=\frac{1}{2}$

$$\text{Total no. of mol} = \frac{1}{2}+\frac{1}{2}+\frac{1}{2}=\frac{3}{2}$$

Partial pressure of a component in a mixture

$$= \frac{\text{no. of mol of component}}{\text{Total no. of mol at equilibrium}}\times P \text{ total}$$

$$\therefore \qquad p_A = \frac{\frac{1}{2}}{\frac{3}{2}}\times P = \frac{1}{2}\times\frac{2}{3}\times P = \frac{1}{3}P$$

Since $\qquad p_A = p_B,$ so $\ p_B = \frac{1}{3}P$;

$$p_{AB} = \frac{\frac{1}{2}}{\frac{3}{2}}\times P = \frac{1}{2}\times\frac{2}{3}\times P = \frac{1}{3}P$$

But $\qquad K_p = \dfrac{[A][B]}{[AB]} = \dfrac{\frac{P}{3}\times\frac{P}{3}}{\frac{P}{3}} = \dfrac{P}{3}$

$$\therefore \qquad P = \mathbf{3\ Kp} \qquad \textbf{Ans.}$$

So, the correct answer is, (*b*).

EXAMPLE 222. *For the reaction at equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-} respectively. The value of K_c for the reaction is :*

(*a*) 3×10^{3} mol L^{-} (*b*) 3.3×10^{2} mol L^{-}

(*c*) 3×10^{-1} mol L^{-} (*d*) 3×10^{-3} mol L^{-} **(AIEEE, 2003)**

SOLUTION. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Rate of forward reaction, $K_f \propto [N_2O_4]$ ...(1)

Rate of backward reaction, $K_b \propto [NO_2]^2$ ...(2)

At equilibrium,

$$K_f = K_b$$

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[NO_2]^2}{[N_2O_4]}$$

Substituting the values we get :

$$K_c = \frac{1.2\times10^{-2}\text{ mol } L^{-}\times1.2\times10^{-2}\text{ mol } L^{-}}{4.8\times10^{-2}\text{ mol } L^{-}}$$

$$= \mathbf{3.0\times10^{-3}\ mol\ L^{-}} \qquad \textbf{Ans.}$$

Hence, the correct answer is (*d*).

EXAMPLE 223. *For the reaction, $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$, K_p/K_c* is :

(*a*) *RT* (*b*) $(RT)^{-1}$

(*c*) $(RT)^{-1/2}$ (*d*) $(RT)^{1/2}$ **(AIEEE, 2002)**

SOLUTION.

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

$$1\text{ mol} \qquad \frac{1}{2}\text{ mol} \qquad 1\text{ mol}\ ;$$

$$\Delta n = 1-\left(1+\frac{1}{2}\right) = 1-1-\frac{1}{2} = -\frac{1}{2}$$

But $K_p = K_c\,(RT)^{\Delta n}$ or $\dfrac{K_p}{K_c} = (RT)^{\Delta n}$

$$\therefore \quad \frac{K_p}{K_c} = (RT)^{-1/2}$$

So, the correct answer is, (*c*).

EXAMPLE 224. *4 moles of CO_2 were heated in 1 dm^3 vessel under conditions which produced at equilibrium 25 % dissociation into carbon monoxide and oxygen. The number of moles of carbon monoxide produced was :*

(a) 0.5 *(b) 1.0*
(c) 1.5 *(d) 2.0*

SOLUTION. Reaction.

$$\begin{array}{llll} & CO_2(g) & \rightleftharpoons CO(g) & + \frac{1}{2}O_2(g) \\ \text{Initial conc.} & 4 \text{ mol} & 0 & 0 \\ \text{At equilibrium} & 4 - \left(4 \times \frac{25}{100}\right) & 4 \times \frac{25}{100} = 1.0 & \end{array}$$

From above we see that number of carbon monoxide produced = 1 mol.

So, the correct answer is, (*b*).

EXAMPLE 225. *For a reaction, $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$, $K_p = 1.7 \times 10^{12}$ at 20°C and 1 atmospheric pressure. The value of K_c will be :*

(a) 7.0×10^{11} *(b) 7.98×10^{12}*
(c) 8.33×10^{9} *(d) 8.33×10^{12}*

SOLUTION. T = 20 + 273 = 293 K ; R = 0.0821 L atm (degree)⁻ mol⁻

$$\begin{array}{llll} \text{For} & SO_2(g) + \frac{1}{2}O_2(g) & \longrightarrow SO_3(g) \\ & 1 \text{ mol} \quad \frac{1}{2}\text{mol} & 1\text{mol} \end{array}$$

$$\Delta n = n_P - n_R = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}\text{ mol}$$

we know $K_p = K_c(RT)^{\Delta n}$

$$\therefore \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.7 \times 10^{12}}{(0.0821 \times 293)^{-1/2}}$$

$$= 1.7 \times 10^{12} \times (0.0821 \times 293)^{1/2}$$

$$= 1.7 \times 10^{12} \times 4.9 = \mathbf{8.33 \times 10^{12}}\ \textbf{Ans.}$$

So, the correct answer is, (*d*).

EXAMPLE 226. *For which of the following shall the ratio of K_p/K_c is unity at 300 K and 1 atmospheric pressure ?*

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(c) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$
(d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

SOLUTION. We know

$$K_p = K_c\,(RT)^{\Delta n} \quad \text{or} \quad K_p/K_c = (RT)^{\Delta n}$$

K_p/K_c will be equal to unity (*i.e.*, 1) when

$$\Delta n = \text{zero}$$

$\Delta n = n_P - n_R$ for reaction (*a*)

$$= 2 - (1 + 3) = -2\,;$$

for reaction (*b*), $\Delta n = 2 - (1 + 1) = 0$; for reaction (*c*),

$\Delta n = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$ and for reaction(*d*),

$$\Delta n = 1 + 1 - 1 = 1.$$

So, for reaction (*b*),

$$K_p/K_c = (RT)^{\circ} = 1.$$

Hence, the correct answer is (*b*).

EXAMPLE 227. *A mixture of NO_2 and N_2O_4 has vapour density 38.5. How many mol of NO_2 are present in 100 g of mixture.*

(a) 0.42 *(b) 4.4*
(c) 33.4 *(d) 3.34*

SOLUTION. Mol. wt. of NO_2 and N_2O_4

$$= 2 \times \text{V.D.} = 2 \times 38.5 = 77$$

Mass of NO_2 in the mixture = *a* g

∴ Mass of N_2O_4 in the mixture = (100 – *a*) g;

Mol. wt. of NO_2 = 14 + (2 × 16) = 46 ;

∴ no. of mol of $NO_2 = \dfrac{a}{46}$

Mol. wt. of N_2O_4 = (2 × 14) + (4 × 16) = 92

∴ no. of mol of $N_2O_4 = \dfrac{100 - a}{92}$

Total no. of mol of mixture $= \dfrac{\text{wt.}}{\text{mol. wt.}} = \dfrac{100}{77}$

$$\therefore \quad \frac{a}{46} + \frac{100 - a}{92} = \frac{100}{77}$$

$$\frac{92a + 4600 - 46a}{46 \times 92} = \frac{100}{77}\ ;\ 46a = \left(\frac{100 \times 46 \times 92}{77}\right)$$

$$-4600 = 5496 - 4600 = 896$$

$$\therefore \quad a = \frac{896}{46} = 19.48$$

$$\therefore \quad \text{No. of mol of } NO_2 = \frac{19.48}{46} = \mathbf{0.42}$$

So, the correct answer is (*a*).

EXAMPLE 228. *For $2A_2(g) + 2B_2(g) \rightleftharpoons 2A_2B_2(g)$, the heat is evolved. The mass of A_2B_2 increases at equilibrium by :*

(a) increasing the total pressure
(b) increasing the temperature
(c) using a catalyst
(d) decreasing the total pressure.

SOLUTION. The reaction $2A_2(g) + 2B_2(g) \rightleftharpoons 2A_2B_2(g)$ is exothermic and is accompanied by decrease in the number of moles from 4(= 2 + 2) to 2 moles. So, low temperature and increase in total pressure will favour the forward reaction. Hence, correct answer is (*a*).

EXAMPLE 229. *For any two reactions, activation energies are E_1 and E_2 respectively. If $E_1 > E_2$, and temperature of the reacting system is increased from T_1 to T_2, then the correct answer is:*

(*a*) $\frac{K_1}{K'_1} = \frac{K_2}{K'_2}$ (*b*) $\frac{K'_1}{K_1} < \frac{K'_2}{K_2}$

(*c*) $\frac{K'_1}{K_1} > \frac{K'_2}{K_2}$ (*d*) $\frac{K'_1}{K_1} = \frac{K'_2}{K_2}$

SOLUTION. The value of equilibrium constant K depends upon temperature. Since $E_1 > E_2$, the first reaction is endothermic. By increase of temperature from T_1 to T_2, the value of K is also increased. So, K'_2/K_2 will become more than K'_1/K if temperature is increased by equal values. So, $(K'_1/K_1) < (K'_2/K_2)$ and correct answer is (*b*).

EXAMPLE 230. *In the reaction $AB(g) \rightleftharpoons A(g) + B(g)$ at 30°C, K_p for the dissociation equilibrium is 2.56×10^{-2} atm. If the total pressure at equilibrium is 1 atm, then the percentage dissociation of AB is*

(*a*) *87 %* (*b*) *13 %*

(*c*) *43.5 %* (*d*) *6 %*

(*e*) *16 %* **(Kerala PMT, 2011)**

SOLUTION.

Given reaction	$AB(g) \rightleftharpoons$	$A(g)$ +	$B(g)$
At start	P	0	0
Change by reaction	$-P\alpha$	$P\alpha$	$P\alpha$
At equilibrium	$P - P\alpha$	$P\alpha$	$P\alpha$
	$= P(1-\alpha)$		

$$\therefore \quad K_p = \frac{[A(g)][B(g)]}{[AB(g)]} = \frac{P\alpha \times P\alpha}{P(1-\alpha)} = \frac{P\alpha^2}{1-\alpha}$$

Substituting the values, we get :

$$2.56 \times 10^{-2} = 1 \times \alpha^2$$

[α being very small, it can be neglected in the denominator]

or $\alpha = [2.56 \times 10^{-2}]^{1/2} = 0.16$

% age dissociation

$$= 0.16 \times 100 = 16\ \%.$$

So, the correct answer is (*e*).

EXAMPLE 231. *The equilibrium constant for the reaction*

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \text{ will be}$$

(*a*) *416* (*b*) *2.40×10^{-3}*

(*c*) *9.8×10^{-2}* (*d*) *4.9×10^{-2}* **(AIEEE, 2006)**

SOLUTION. K_c for $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ is given as :

$$K_c = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 4.9 \times 10^{-2} \qquad ...(1)$$

$$K'_c \text{ for } SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \text{ will be } \frac{1}{4.9 \times 10^{-2}} \qquad ...(2)$$

$\therefore$ For $2SO_2 + O_2 \rightleftharpoons 2SO_3(g)$

$$(K'_1)^2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \left(\frac{1}{4.9 \times 10^{-2}}\right)^2$$

$$= \frac{10^4}{24.01} = \mathbf{416.49}$$

So, the correct answer is (*a*).

EXAMPLE 232. *$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$*

The equilibrium constant for the above reaction is 6.4 at 300 K. If 0.25 mole each of H_2 and I_2 are added to the system, the equilibrium constant will be :

(*a*) *0.8* (*b*) *3.2*

(*c*) *1.6* (*d*) *6.4* **(Karnataka CET, 2009)**

SOLUTION. The value of equilibrium constant does not change even on changing the concentration of the reaction system. So, the correct answer is (*d*).

EXAMPLE 233. *For the reaction $C(s) + CO_2(g) \longrightarrow 2CO(g)$, $K_p = 63$ atm at 1000 K. If at equilibrium, $P_{CO} = 10\ P_{CO_2}$, then the total pressure of the gases at equilibrium is*

(*a*) *6.3 atm* (*b*) *6.93 atm*

(*c*) *0.63 atm* (*d*) *0.693 atm*

(*e*) *69.3 atm* **(Kerala PMT, 2011)**

SOLUTION. Given reaction : $C(s) + CO_2(g) \longrightarrow 2CO(g)$

$$\therefore \quad K_p = \frac{(P_{CO})^2}{[P_{CO_2}]};\ 63 = \frac{(10\ P_{CO_2})^2}{P_{CO_2}};$$

$$63 = \frac{100\ P_{CO_2}^2}{P_{CO_2}}$$

Or $63 = 100\ P_{CO_2};\ P_{CO_2} = \frac{63}{100} = 0.63$ atm.

$$P_{CO} = 10\ P_{CO_2} = 10 \times 0.63 = 6.3 \text{ atm.}$$

$$\therefore \quad P_{total} = P_{CO} + P_{CO_2} = 0.63 + 6.3 = 6.93 \text{ atm.}$$

So, the correct answer is (*b*).

EXAMPLE 234. *Given that the equilibrium constant for the reaction:*

$$2SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$$

has a value of 278 at a particular temperature. What is the value of equilibrium constant for the following reaction at the same temperature?

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$

(*a*) *1.8×10^{-3}* (*b*) *3.6×10^{-3}*

(*c*) *6.0×10^{-2}* (*d*) *1.3×10^{-5}*

(AIPMT Mains, 2012)

SOLUTION. For $2SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ ...(*i*), $K = 278$

On reversing the above equation, we get:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad ...(ii)$$

K' for this reaction $= 1/K = 1/278$

On dividing equation (*ii*) by 2, we get:

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g) \qquad ...(iii)$$

∴ The value of K for this reaction will be:

$$K'' = (K')^{1/2} = \left(\frac{1}{K}\right)^{1/2} = \left(\frac{1}{278}\right)^{1/2} = 0.06 = 6 \times 10^{-2}.$$

So, the correct answer is (*c*).

EXAMPLE 235. *Given the reaction between two gases represented by A_2 and B_2 to give the compound AB(g).*

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

At equilibrium, the concentration of $A_2 = 3.0 \times 10^{-3}$ M; of $B_2 = 4.2 \times 10^{-3}$ M and of AB = 2.8×10^{-3}M. If the reaction takes place in a sealed vessel at 527°C, then the value of K_c will be:

(*a*) 2.0 (*b*) 1.9

(*c*) 0.62 (*d*) 4.5

(AIPMT, Mains, 2012)

SOLUTION. $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

$$\therefore K_c = \frac{[AB]^2}{[A_2][B_2]} \qquad ...(i)$$

Substituting the values in equation (*i*), we get:

$$K_c = \frac{(2.8 \times 10^{-3})^2}{(3.0 \times 10^{-3})(4.2 \times 10^{-3})} = \frac{2.8 \times 2.8}{3.0 \times 4.2} = 0.62.$$

So, the correct answer is (*c*).

EXAMPLE 236. *In the equilibrium $2A \rightleftharpoons B + C$, the equilibrium concentrations of A, B and C at 300K are 3×10^{-4} M, 1×10^{-4} M and 4.5×10^{-4} respectively. The value of Kc for the above equilibrium at 300 K is:*

(*a*) 0.5 (*b*) 0.05

(*c*) 5.0 (*d*) 1.5

(*e*) 0.2 **(Kerala PMT, 2012)**

SOLUTION. Given equilibrium is: $2A \rightleftharpoons B + C$. So:

$$K_c = \frac{[B][C]}{[A]^2};\ [A] = 3 \times 10^{-4}\ M;\ [B] = 1 \times 10^{-4}\ M;$$

$$[C] = 4.5 \times 10^{-4}\ M$$

Substituting these values, we get:

$$K_c = \frac{10^{-4} \times 4.5 \times 10^{-4}}{3 \times 10^{-4} \times 3 \times 10^{-4}} = 0.5.$$

So, the correct answer is (*a*).

EXAMPLE 237. *In the following equilibrium reaction,*

$$2A \rightleftharpoons B + C$$

the equilibrium concentrations of A, B and C are 1×10^{-3} M, 2×10^{-3} M and 3×10^{-3} M respectively at 300 K. The value of K_c for this equilibrium at the same temperature is:

(*a*) 1/6 (*b*) 6

(*c*) 1/36 (*d*) 36

(*e*) 1/24 **(Kerala PET, 2012)**

SOLUTION. For $2A \rightleftharpoons B + C$, $K_c = \frac{[B][C]}{[A]^2}$ ...(1)

Substituting the values of

A (= 10^{-3}), B (= 2×10^{-3}) and C (= 3×10^{-3}) in equation (1), we get:

$$K_c = \frac{2 \times 10^{-3} \times 3 \times 10^{-3}}{(10^{-3})^2} = 6.$$

So, the correct answer is (*b*).

EXAMPLE 238. *Calculate the solubility of lead chloride in water, if its solubility product is 1.7×10^{-5}.*

(ISC, 2012)

SOLUTION. $PbCl_2 \rightleftharpoons Pb^{2+} + 2\,Cl^-$

Solubility S S 2S

∴ Solubility product, $K_{sp} = [Pb^{2+}]\,[Cl^-]^2$

$$1.7 \times 10^{-5} = S \times (2S)^2 = 4S^3$$

$$\therefore S = \left(\frac{1.7 \times 10^{-5}}{4}\right)^{1/3}$$. Taking logs of both sides,

We get:

$$\log S = \log\left(\frac{1.7 \times 10^{-5}}{4}\right)^{1/3} = \frac{1}{3}\left[\log 1.7 + \log 10^{-5} - \log 4\right]$$

$$= \frac{1}{3}[0.2304 - 5 - 0.6020] = \frac{1}{3} \times -5.3716 = 1.7905$$

$$= +1 - 1 - 1 - 0.7905 = \bar{2}.2095$$

Taking antilog of both sides, we get:

$S = \text{antilog}\ \bar{2}.2095 = 0.0162\ g\ L^-$ **Ans.`**

PROBLEMS FOR PRACTICE

1. Give the conditions under which the following reaction proceeds in the forward direction.

(*i*) $PCl_5\,(g) + x\,k\,cal \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

(*ii*) $N_2(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 23\ k\ cal$

(*iii*) $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) + 45\ k\ cal$

(*iv*) $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g) - 43.2\ k\ cal.$

Ans. (*i*)Low *P*, high *T*, excess of PCl_5 (g)

(*ii*) High *P*, low *T*, excess of N_2 and H_2

(*iii*) High *P*, low *T*, excess of SO_2 and O_2

(*iv*) Any *P*, high *T*, excess of O_2 and N_2

2. When 1 mol of ethyl alcohol is mixed with 2.0 mol of acetic acid, 0.428 mol of ester is formed. Will the equilibrium be reached ? K = 4

[Ans. Q = 0.2. So, equilibrium will not reach].

3. What is the percentage decomposition of H_2S if 1.0 mol of H_2S is introduced into a 1.1 litre vessel at 1000°C. K_c for the reaction, $2H_2S\,(g) \rightleftharpoons 2H_2\,(g) + S_2\,(g)$ is 1.0×10^{-6}

[Ans. % age dissociation = 1.3 %] **(Roorkee, 1984)**

4. 16.2 g mol of H_2 and 5.88 g mol of I_2 were heated at constant volume at 444°C, when at equilibrium 11.28 mol of HI are formed. Calculate the equilibrium constant of the reaction. **(UP, 1983)**

[Ans. K = 50.2]

5. For a gaseous phase reaction, $A + 2B \rightleftharpoons AB_2$, $K_c = 0.3475\ L^2\ mol^{-2}$ at 573 K. When 2.0 mol of B are mixed with one mol of A, what total pressure would be needed to convert 60% of A to AB_2 ?

[Hint and Ans.	A	$+\ 2B \rightleftharpoons$	AB_2
no. of mol at $t = 0$	1	2	0
no. of mol at equilibrium	$1 - x$	$2 - 2x$	x

Total no. of mol at equilibrium = $1 - x + 2 - 2x + x = 3 - 2x$

Let P = Pressure at equilibrium

$$\therefore \qquad P'_{AB_2} = \frac{xP}{3-2x};\ P'_A = \frac{(1-x)P}{3-2x};\ P'_B = \frac{(2-2x)P}{3-2x}$$

$$\therefore \qquad K_p = \frac{[AB_2]}{[A][B]}$$

$$= \frac{\dfrac{xP}{3-2x}}{\dfrac{(1-x)P}{3-2x} \times \left(\dfrac{2-2x}{3-2x}\right)^2 P^2}$$

$$= \frac{(3-2x)^2\, x}{(1-x)(2-2x)^2\, P^2} \qquad \textbf{Ans.}$$

6. If the weight of KI and KI_3 at equilibrium in the reaction $KI + I_2 \rightleftharpoons KI_3$ are 1.326g and 0.105g respectively, then calculate the value of K_C. The number of mol of free I_2 at equilibrium is 0.0025 and the volume of solution is $10^3\ cm^3$. (At. wt. K = 39, I = 127). **[Ans. 0.0323]**

Since KI has fully reacted with I_2 and free I_2 will be in the solid state, so $[I_2]$ is taken as constant.

7. Consider the equilibrium reaction $X + Y \rightleftharpoons P + Q$. X and Y are mixed in a vessel at temperature, T. The concentration of X at $t = 0$ is twice the concentration of Y. After the equilibrium has been reached, the concentration of P was three times the equilibrium concentration of Y. Find the value of K_c.

[Ans. $K_c = 1.8$]

8. One mole of FeO(s) and one mole of CO(g) were treated in a closed vessel at 1000°C and the value of Kp was found to be 0.4. The products were $CO_2(g)$ and Fe(s). If CO(g) at one atm and excess FeO(s) are placed in a container at 1000°C, calculate the pressure of CO(g) and $CO_2(g)$ when equilibrium is established.

[Ans. $p_{CO} = 0.714$ atm ; $p_{CO_2} = 0.286$ atm.**]**

9. For which of the reactions, $K_p = K_c$?

(*a*) $H_2 + I_2 \rightleftharpoons 2HI$ (*b*) $PCl_3 + Cl_2 \rightleftharpoons PCl_5$

(*c*) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (*d*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

[Bihar CECE, 2010] (Ans. (a))

10. Calculate the value of K_c for the equilibrium reaction:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g), K_p = 1.8 \times 10^{-2}$ at 500 K.

11. Find the value of K_p for the equilibrium reaction :

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g), K_c = 1.87$ at 1073 K.

[Ans. 164.7]

12. One litre of a solution contains 30 g acetic acid. Calculate its active mass. **[UP 1989]**

[Ans. 0.5 g mol L^{-}]

13. Consider the following gaseous equilibria with equilibrium constants K_1 and K_2 respectively.

$$SO_2(g) + 1/2\, O_2(g) \rightleftharpoons SO_3(g)\ ;$$
$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g).$$

The equilibrium constants are related as:

(*a*) $K_1^2 = 1/K_2$ (*b*) $2K_1 = K_2^2$

(*c*) $K_2 = 2/K_1^2$ (*d*) $K_2^2 = 1/K_1$

[Kerala CET, 2010]

[Ans. (*a*)]

14. For a reaction, $A + 2B \longrightarrow C$, the amount of C formed by starting the reaction with 5 mol of A and 8 mol of B is :

(*a*) 5 mol (*b*) 8 mol

(*c*) 16 mol (*d*) 4 mol

(*e*) 1 mol **[Kerala PMT, 2010]**

24

CHAPTER

Ionic Equilibrium

24.1 SOLUBILITY

Maximum amount of one phase (solute) dissolved by another (solvent) under specified temperature and pressure is called the solubility of the solute.

Type. The solubility of a solute per 100 g of the solvent

$$= \frac{\text{wt. of solute}}{\text{wt. of solvent}} \times 100 .$$

EXAMPLE 1. *A saturated solution weighing 15.2 g gave 3.2g of dry solute. Calculate the solubility of salt.*

SOLUTION. wt. of solute = 3.2 g ; wt. of salt + water (solvent) = 15.2 g

$\therefore$ wt. of solvent = 15.2 – 3.2 = 12.0 g.

$\therefore$ Solubility of salt in 100 g solvent

$$= \frac{3.2}{12} \times 100 = \mathbf{26.7\ g} \qquad \textbf{Ans.}$$

EXAMPLE 2. *A solution of sodium carbonate weighs 6.0 g at 30°C. This solution required 32.8 mL of $\frac{N}{5}$ HCl for complete neutralisation. Calculate the solubility of sodium carbonate at this temperature.*

SOLUTION. 6.0 g Na_2CO_3 (aq) ≡ 32.8 mL of N/5 HCl.

$\therefore$ 32.8 mL of N/5 HCl ≡ 32.8 mL N/5 Na_2CO_3

But 1000 mL of 1N Na_2CO_3 ≡ 53 g Na_2CO_3

$$\left[\because \text{Eq. wt. of } Na_2CO_3 = \frac{\text{Mol. wt}}{2} = \frac{106}{2} = 53\right]$$

$$\therefore \quad 32.8 \text{ mL of N/5 } Na_2CO_3 \equiv \frac{53}{1000} \times 32.8 \times \frac{1}{5} = 0.348 \text{ g}$$

$\therefore$ wt. of Na_2CO_3 in solution = 0.348 g

wt. of Na_2CO_3 solution = 6.0 g

$\therefore$ wt. of solvent = 6.0 – 0.348 = 5.652 g

$\therefore$ Solubility of Na_2CO_3 in 100 g solvent

$$= \frac{0.348}{5.652} \times 100 = \mathbf{6.16\ g} \qquad \textbf{Ans.}$$

EXAMPLE 3. *15.0 g of a solution of $FeSO_4.7H_2O$ is diluted with water to 100 mL. 20 mL of this solution required 22.1 mL of 0.1 N $KMnO_4$ for complete oxidation. Calculate the solubility of $FeSO_4.7H_2O$. (At. wt. Fe = 56, S = 32, O = 16, H = 1)*

SOLUTION. g. eq. wt. of $FeSO_4.7H_2O$

$$= \frac{56 + 32 + (4 \times 16) + 7(18)}{1} = 278 \text{ g}$$

20 mL of dilute $FeSO_4.7H_2O$ solution

≡ 22.1 mL of N/10 $KMnO_4$.

$\therefore$ 100 mL of dilute $FeSO_4.7H_2O$ solution

$$\equiv \frac{22.1}{20} \times 100 = 110.5 \text{ mL of N/10 } KMnO_4$$

$\therefore$ 15 g solution of $FeSO_4.7H_2O$

≡ 110.5 mL of N/10 $KMnO_4$

Also,110.5 mL N/10 $KMnO_4$

≡ 110.5 mL of N/10 $FeSO_4.7H_2O$.

But1000 mL of 1N $FeSO_4$. $7H_2O$

= 278 g $FeSO_4.7H_2O$

$\therefore$ 110.5 mL of N/10 $FeSO_4$. $7H_2O$

$$= \frac{278}{1000} \times 110.5 \times \frac{1}{10} = 3.072 \text{ g}$$

$\therefore$ wt. of $FeSO_4.7H_2O$ = 3.072 g

wt. of $FeSO_4.7H_2O$ solution = 15.0 g

$\therefore$ wt. of solvent = 15.0 – 3.072 = 11.928 g

$\therefore$ Solubility of $FeSO_4.7H_2O$ in 100 g solvent

$$= \frac{3.072}{11.928} \times 100 = \mathbf{25.75 g.} \quad \textbf{Ans.}$$

EXAMPLE 4. *The solubilities of a solute in 120 g of the solvent are given below*

Temperature	*Solubility*
350 K	*140.0 g*
300 K	*85.0 g*

Calculate the amount of crystals of the solute when 100 g of the saturated solution is cooled from 350 K to 300 K.

Solution. (*i*) At 350 K. Solubility of solute = 140 g

wt. of saturated solution = 120 + 140 = 260 g

260 g saturated solution contain solute = 140 g

100 g saturated solution contain solute

$$= \frac{140}{260} \times 100 = 53.85 \text{ g}$$

$\therefore$ wt. of solvent (H_2O) in 100 g saturated solution

$$= 100 - 53.85 = 46.15 \text{ g}$$

Thus, wt. of solute that would be retained by 46.15 g water at 300 K

$$= \frac{85 \times 46.15}{100} = 39.23 \text{ g}$$

$\therefore$ wt. of solute that separates on cooling from 350 K to 300 K

$$= 53.85 - 39.23 = \mathbf{14.62 \text{ g}} \quad \textbf{Ans.}$$

24.2 OSTWALD'S DILUTION LAW

The application of law of chemical equilibrium to **weak electrolytes** is called Ostwald dilution law. Consider the dissociation of weak electrolyte AB in water.

	AB $\rightleftharpoons$	A^+ +	B^-
(1) n. mol at start	C	0	0
(2) Change by reaction	$-C\alpha$	$C\alpha$	$C\alpha$
(α = degree of dissociation at equilibrium)			
(3) n mol at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

Applying law of chemical equilibrium, we get :

$$K_c = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha}$$

K_c is called dissociation (or ionisation) constant and the expression $[K_c = C\alpha^2/(1-\alpha)]$ is the mathematical form of Ostwald dilution law. If α *is very small as compared to unity (= 1),* α *can be neglected.* For such cases, $1 - \alpha = 1$. Thus :

$$K_c = C\alpha^2 \quad \text{Or} \quad \boldsymbol{\alpha = [K_c/C]^{1/2}}$$

where C is molarity.

(*i*) For a *weak monobasic acid* (*HA*), $\alpha = [K_a/C]^{1/2}$ and H^+ ion concentration, $[H^+] = C\alpha = (K_a.C)^{1/2}$; pH = $-\log(C\alpha)$; pH = $-\log(Ka.C)^{1/2}$

(*ii*) For a weak monoacidic base (BOH), $\alpha = (K_b/C)^{1/2}$ and OH^- ion concentration, $[OH^-] = C\alpha$; pOH = $-\log(C\alpha)$

$\therefore$ pOH = $-\log(K_b.C)^{1/2}$

(*iii*) Greater the value of K_a or K_b, greater the strength of acid or base respectively. The values of K_a and K_b depend upon temperature.

Example 5. *Calculate the dissociation constant of a monobasic maleic acid having molarity 0.25 and degree of dissociation 0.95%.* **(Dumet, 2010 modified)**

Solution. Degree of dissociation, $\alpha = 0.95\% = \frac{0.95}{100}$ $= 0.0095$; concentration, $C = 0.25$ mol L^-.

Dissociation constant,

$$\boldsymbol{K_a} = C\alpha^2 = 0.25 \times (0.0095)^2$$

$$= \mathbf{2.26 \times 10^{-5}}$$

Type. To find K_a when normality of a solution is given, use,

$$K_a = \frac{\alpha^2}{(1-\alpha)V}$$

Example 6. *The degree of dissociation of a monobasic acid is 4.5% in N/20 solution at 288 K. Calculate the dissociation constant of the given acid at the same temperature.*

Solution. Degree of dissociation (α)

$$= 4.5\% = \frac{4.5}{100} = 0.045$$

N/20 or 0.05 N solution means that dilution

$$= \frac{L}{0.05} = V \text{ (say).}$$

But, $K_a = \dfrac{\alpha^2}{(1-\alpha)V}$ (Ostwald dilution law)

$$\therefore \qquad K_a = \frac{(0.045)^2 \times 0.05}{(1-0.045)}$$

$$= \frac{2.025 \times 10^{-3} \times 0.05}{0.955}$$

$$= \mathbf{1.06 \times 10^{-4}} \quad \textbf{Ans.}$$

Example 7. *A weak monobasic acid is 1% ionised in 0.1 M solution at 25°C. The percentage ionisation in its 0.025 M solution is :*

(a) 1 *(b)* 2 *(c)* 3 *(d)* 4 *(e)* 5 **(Kerala PET, 2011).**

Solution. Let acid H A ionises as; $HA \rightleftharpoons H^+ + A^-$.

α is the degree of ionisation. Thus:

$$\begin{array}{ccc} HA & \rightleftharpoons & H^+ + A^- \\ C & & C\alpha \quad C\alpha \end{array}$$

$$\therefore \qquad K = \frac{[H^+][A^-]}{[HA]} = \frac{C\alpha \times C\alpha}{C} = C\alpha^2$$

Or $\qquad K = 0.1 \times (1/100)^2; K = 10^{-5}$

Since $\qquad K = C\alpha^2, 10^{-5} = 0.025 \times \alpha^2$

$\therefore \qquad \alpha^2 = 10^{-5}/0.025; \alpha = (4 \times 10^{-3})^{1/2} = 0.02$

$\therefore$ Percentage of ionisation = 0.02 × 100 = 2.

So, the correct answer is (*b*).

Example 8. *The given solution is 1.5 N of HCN. Find the H^+ ion concentration if $K_{HCN} = 4.0 \times 10^{-10}$.*

Solution. HCN solution = 1.5N. So, dilution volume (V) = 1.5 L^-.

But $\qquad K = \dfrac{\alpha^2}{(1-\alpha)V}$

(Ostwald dilution law; α is neglected from denominator because α is very small)

Or $$K = \frac{\alpha^2}{V}\ ;\ \alpha^2 = KV\ ;\ \alpha = (KV)^{1/2}$$

Or $$\alpha = \left(4.0\times10^{-10}\times\frac{1}{1.5}\right)^{1/2}$$
$$= (2.67\times10^{-10})^{1/2} = 1.63\times10^{-5}$$

But $$(H^+) = \frac{\alpha}{V}\ ;\ [H^+] = \frac{1.63\times10^{-5}}{1/1.5}$$
$$= 2.4\times10^{-5}\text{ g. ion L}^-.$$

Type. For Isohydric solution, use, $\frac{\alpha_1^2}{\alpha_2^2} = \frac{V_1}{V_2}$ where as according to Ostwald's dilution law, $\alpha^2 = KV$ Or $\alpha^2 = K/C$

EXAMPLE 9. *At 293 K, dissociation constant of cyanoacetic acid is 0.0037 and that of acetic acid is 0.000018. Calculate the relative dilution of the above acids so that both solutions become isohydric.*

SOLUTION. For isohydric solutions, $$\frac{\alpha_1^2}{\alpha_2^2} = \frac{V_1}{V_2} \qquad ...(1)$$

Where α_1 = dissociation constant of cyanoacetic acid and

α_2 = dissociation constant of acetic acid.

$\therefore$ $\alpha_1^2 = KV_1\ ;\ \alpha_1^2 = 0.0037\times V_1$ ...(2)
[Ostwald dilution law]

$\alpha_2^2 = KV_2\ ;\ \alpha_2^2 = 0.000018\times V_2$ ...(3)
[Ostwald dilution law]

Dividing (2) and (3), we get :

$$\frac{\alpha_1^2}{\alpha_2^2} = \frac{0.0037V_1}{0.000018V_2} \qquad ...(4).$$

Comparing (1) and (4), we get :

$$\frac{V_1}{V_2} = \frac{3700}{18} = 205.56$$

$\therefore$ Relative dilution of cyanoacetic acid and acetic acid is, **205.56 : 1** **Ans.**

EXAMPLE 10. *Calculate the concentration of H_2CO_3, HCO_3^- and CO_3^{2-} in a 0.01M aqueous solution of H_2CO_3 (carbonic acid), having pH 3.98; $K_1 = 4.5\times10^{-7}$; $K_2 = 4.7\times10^{-11}$.*

SOLUTION. $pH = 3.98\ ;\ -\log(H^+) = 3.98\ ;\ \log[H^+] = -3.98 = -3-1+1-0.98 = \bar{4}.02$

$\therefore$ $[H^+] = \text{antilog } \bar{4}.02 = 1.05\times10^{-4}\text{ mol L}^-$

(*a*) H_2CO_3 being a weak acid, its concentration *i.e.*,
$[H_2CO_3] = 0.01M = 10^{-2}$ M **Ans.**

(*b*) $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (Ionisation);

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

Or $$[HCO_3^-] = \frac{K_1\,[H_2CO_3]}{[H^+]}$$
$$= \frac{4.5\times10^{-7}\times10^{-2}}{1.05\times10^{-4}}$$
$$= 4.28\times10^{-5}\text{ mol L}^- \qquad \textbf{Ans.}$$

(*c*) $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$;

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}\ ;$$

$$[CO_3^{2-}] = \frac{K_2\,[HCO_3^-]}{[H^+]}$$

$\therefore$ $$[CO_3^{2-}] = \frac{4.7\times10^{-11}\times4.28\times10^{-5}}{1.05\times10^{-4}}$$
$$= 1.9\times10^{-11}\text{ mol L}^- \qquad \textbf{Ans.}$$

EXAMPLE 11. *If 0.1 M aqueous solution of acetic acid is 1.32 percent ionised, then calculate the following.*

(*i*) *Concentration of $[H_3O^+]$ (ii) Concentration of $[CH_3COO^-]$ (iii) Conc. of acetic acid (iv) Ionisation constant of acetic acid.*

SOLUTION. If M and α represent the molarity and degree of ionisation of ionic substance, then :

	$CH_3COOH + H_2O$	$\rightleftharpoons$ CH_3COO^-	$+ H_3O^+$
(*i*) n mol at start	0.1	0	0
(*ii*) Change by reaction	$-0.1\times\frac{1.32}{100}$	$0.1\times\frac{1.32}{100}$	$0.1\times\frac{1.32}{100}$
	$=-0.1\times0.0132$	$=0.1\times0.0132$	0.1×0.0132
(*ii*) n mol at equilibrium	$0.1-0.1\times0.0132$	0.1×0.0132	$0.1\times0.0.132$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$
$$= \frac{(0.1\times0.0132)\times(0.1\times0.132)}{0.1(1-0.0132)}$$
$$= \frac{0.1(0.0132)^2}{0.9868}$$
$$= \mathbf{1.77\times10^{-5}} \quad \textbf{Ans.}$$

EXAMPLE 12. *The ionisation constant of formic acid (HCOOH) is 1.8×10^{-4}. Calculate the ionisation constant of its corresponding base.*

SOLUTION. $HCOOH \rightleftharpoons H^+ + HCOO^-$
conjugate acid conjugate base

Conjugate acid and its conjugate base differ by H^+ only. K_a for HCOOH $= 1.8\times10^{-4}$; K_b for conjugate base $HCOO^-$ = ? $K_w = 10^{-14}$. For conjugate acid – conjugate base pair :

$$K_a\times K_b = K_w$$

Or $$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8\times10^{-4}}$$
$$= \mathbf{5.6\times10^{-11}} \quad \textbf{Ans.}$$

EXAMPLE 13. *The electrolytic dissociation constants of two acids CH_3COOH and HCOOH are 1.8×10^{-5} and 2.1×10^{-4} respectively. Calculate the relative strength of these acids.* **(UP 1981)**

Solution. Both acids are weak acids. So, their relative strengths can be found by the relation :

$$\frac{\text{Strength of CH}_3\text{COOH}}{\text{Strength of HCOOH}} = \left(\frac{K_{CH_3COOH}}{K_{HCOOH}}\right)^{1/2}$$

$$= \left(\frac{1.8\times10^{-5}}{2.1\times10^{-4}}\right)^{1/2}$$

$$= (0.0857)^{1/2}$$

$$= 0.293$$

∴ Strength of CH_3COOH = 0.293 × strength of HCOOH

Or Strength of HCOOH is $\frac{1}{0.293}$ times or 3.413 times the strength of CH_3COOH.

Example 14. *If in the beginning of the reaction*

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

there are 25 molecules and only 5 molecules out of these dissociate, then calculate the degree of dissociation. **(UP 1983)**

Solution. Degree of dissociation

$$= \frac{\text{no. of molecules which dissociate}}{\text{Total no. of molecules taken}}$$

$$= \frac{5}{25} = 0.2$$

Or *degree of dissociation* = 0.2 × 100 = **20%** **Ans.**

Example 15. *What will be the dissociation constant of 0.1N aqueous ammonia in terms of the degree of dissociation, α. What will be the value if the concentration is 0.01N?* **(DSC, 1988)**

Solution. (*a*)

	NH_4OH	$\rightleftharpoons$ NH_4^+	+ OH^-
Conc. at start	0.1	0	0
Conc. at equilibrium	$0.1 - 0.1\alpha$	0.1α	0.1α

$= 0.1(1-\alpha)$

$= 0.1$

[∵ α is very small, it is neglected]

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{0.1\alpha \times 0.1\alpha}{0.1(1-\alpha)}$$

$$= \frac{\alpha^2}{10(1-\alpha)}$$ **Ans.**

(*b*) For 0.01 N solution ;

$C = 0.01$ N

But $$K_b = \frac{C\alpha^2}{1-\alpha} = \frac{0.01\times\alpha^2}{(1-\alpha)}$$

$$= \frac{\alpha^2}{100(1-\alpha)}$$ **Ans.**

Example 16. *Nicotinic acid ($K_a = 1.4\times10^{-5}$) is represented by the formula HNiC. Calculate its percentage dissociation in a solution which contains 0.1 mol of nicotinic acid per 2.0 litre of solution.*

Solution.

	HNiC	$\rightleftharpoons$ H^+	+ NiC^-
(*i*) n mol at start	$\frac{0.1}{2}$	0	0
(*ii*) Change by reaction	$\frac{-0.1\alpha}{2}$	$\frac{0.1\alpha}{2}$	$\frac{0.1\alpha}{2}$
(*iii*) n mol at equilibrium	$(0.1-0.1\alpha)/2$	$\frac{0.1\alpha}{2}$	$\frac{0.1\alpha}{2}$

[∵ For 2L, [HNiC] = 0.1

$= [0.1(1-\alpha)]/2$

∴ For 1L, $[HNiC] = \frac{0.1}{2}$

$$K_a = \frac{[H^+][NiC^-]}{[HNiC]} ;$$

$$1.4\times10^{-5} = \frac{\frac{0.1\alpha}{2}\times\frac{0.1\alpha}{2}}{\frac{0.1(1-\alpha)}{2}} = \frac{\left(\frac{0.1}{2}\right)^2\alpha^2}{\frac{0.1}{2}}$$

[∵ α is very small, so, 1 − α = 1]

$$\alpha^2 = \frac{1.4\times10^{-5}}{\left(\frac{0.1}{2}\right)} = 2.8\times10^{-4}$$

or $$\alpha = (2.8\times10^{-4})^{1/2} = 1.67\times10^{-2}$$

∴ % age of degree of ionisation

$= 1.67\times10^{-2}\times100 =$ **1.67%** **Ans.**

Example 17. *An aqueous solution contains 10% ammonia and has a density of 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for $NH_4^+ = 5.0\times10^{-10}$ M.* **(Roorkee, 1995)**

Solution. (*i*) Mass of NH_3 = 10%

$$= \frac{10}{100} = 0.1 \text{ g} ;$$

g. mol. wt. of NH_3 = 14 + (3 × 1) = 17g

$$\text{Volume of NH}_3 = \frac{\text{Mass}}{\text{density}} = \frac{0.1 \text{ g}}{0.99 \text{ g cm}^{-3}}$$

$$= \frac{10}{99}\text{cm}^3$$

$$\text{Molarity of NH}_3 = \frac{\text{wt. of NH}_3}{\text{g. mol. wt. of NH}_3} \times \frac{1000}{\text{Volume of solution in cm}^3}$$

$$= \frac{0.1}{17}\times\frac{1000}{10/99} = 58.2$$

(*ii*)

	$NH_3 + H_2O$	$\rightleftharpoons$ NH_4^+	+ OH^-
(*i*) *n* mol at start	*C*	0	0
(*ii*) Change by reaction	$-C\alpha$	$C\alpha$	$C\alpha$
(*iii*) *n* mol at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

$= C(1-\alpha)$

α being very small, it is rejected. Thus $C(1-\alpha) = C$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{C\alpha\times C\alpha}{C}$$

$$= C\alpha^2 ; \quad K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5\times10^{-10}}$$

$$= 0.2\times10^{-4}.$$

Thus $C\alpha^2 = 0.2 \times 10^{-4}$;

$$58.2\,\alpha^2 = 0.2 \times 10^{-4};$$

$$\alpha = \left(\frac{0.2 \times 10^{-4}}{58.2}\right)^{1/2}$$

$$= (0.344 \times 10^{-6})^{1/2}$$

$$= \mathbf{0.586 \times 10^{-3}}$$ **Ans.**

EXAMPLE 18. *Calculate the* $[H_3O^+]$ *and percentage ionisation of 0.1M acetic acid if its ionisation constant value is* 1.8×10^{-5}.

SOLUTION. (*a*) Acetic acid ionises as

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

(*i*)	n mol at start	0.1	0	0
(*ii*)	Change by reaction	$-x$	x	x
	(x = Amount of CH_3COOH ionised)			
(*iii*)	n mol at equilibrium	$0.1 - x$	x	x

$$K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{x \times x}{0.1 - x} = \frac{x^2}{0.1 - x} \qquad ...(1)$$

Substituting these values in equation (1) above, we get

$$K_c = \frac{x \times x}{0.1 - x} = 1.8 \times 10^{-5} \text{ (given)}$$

Since x is extremely small, it can be neglected in the denominator. So, we have :

$$\frac{x^2}{0.1} = 1.8 \times 10^{-5};\ x^2 = 1.8 \times 10^{-6};$$

$$x = (1.8 \times 10^{-6})^{1/2}$$

$\therefore$ $x = 1.34 \times 10^{-3}$

Hence $[H_3O^+] = 1.34 \times 10^{-3}$ g mol L$^-$

(*b*) Ionic concentration = gross concentration × fraction ionised (α).

$$1.34 \times 10^{-3} = 0.1 \times \alpha$$

$\therefore$ $\alpha = 1.34 \times 10^{-2} = 0.0134$

Hence percent ionisation

$= 0.0134 \times 100 =$ **1.34%**

EXAMPLE 19. *Calculate the hydrogen ion concentration of an aqueous solution of formic acid containing 0.92 g of the acid per litre. The ionisation constant of the acid is* 2.4×10^{-4} *at 298 K.*

SOLUTION. Gram molecular weight of formic acid (HCOOH) = 1 + 12 + 16 + 16 + 1 = 46 g

weight of formic acid per litre = 0.92 g

$\therefore$ Molarity of formic acid $= \frac{0.92}{46} = 0.02$ M

= 0.02 g mol L$^-$

HCOOH ionises in water as

$$(HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-)$$

(1)	n g. mol L$^-$ at start	0.02	0	0
(2)	Change by reaction	$-x$	x	x
(3)	n g. mol L$^-$ at equilibrium	$0.02 - x$	x	x

x = mol of formic acid ionised.

$\therefore$ Ionisation constant

$$K_C = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} \qquad ...(1)$$

Substituting these values in equation (1), we get

$$K_C = \frac{x \times x}{0.02 - x} = 2.4 \times 10^{-4} \text{ (given)}$$

Since, 'x' is extremely small, it can be neglected in the denominator. So, we have $\frac{x^2}{0.02} = 2.4 \times 10^{-4}$

$$x^2 = 0.02 \times 2.4 \times 10^{-4};$$

$$x = \sqrt{0.02 \times 2.4 \times 10^{-4}}$$

$$= 2.19 \times 10^{-2}$$

$\therefore$ $[H_3O^+] = \mathbf{2.19 \times 10^{-2}}$ **g mol L$^-$**

EXAMPLE 20. *Find the molar concentration of* $[OH^-]$ *and percentage ionisation of 0.02 M ammonia solution if its ionisation constant value is* 1.8×10^{-5}.

SOLUTION. Ammonia (NH_3) ionises in water as follows.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

(1)	n mol at start	0.02	0	0
(2)	Change by reaction	$-x$	x	x
(3)	n mol at equilibrium	$0.02 - x$	x	x

x = mol of NH_3 ionised

$$\therefore \qquad K_c = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ...(1)$$

Substituting these values in equation (1), we get $K = \frac{x \times x}{0.02 - x} = 1.8 \times 10^{-5}$ (given)

Since 'x' is very small, it can be ignored in the denominator. So, we have :

$$\frac{x^2}{0.02} = 1.8 \times 10^{-5};\ x^2 = 0.02 \times 1.8 \times 10^{-5}$$

$$= 0.02 \times 18 \times 10^{-6}$$

$$x = \sqrt{0.36 \times 10^{-6}} = 0.6 \times 10^{-3}$$

$\therefore$ $[OH^-] = 0.6 \times 10^{-3}$

But ionic concentration

= gross concentration × fraction ionised (α)

$\therefore$ $0.6 \times 10^{-3} = 0.02 \times \alpha;\ \alpha = 0.6 \times 10^{-3}/0.02$

$= 3.0 \times 10^{-2} = 0.03$

or Percent ionisation = 0.03 × 100 = **3.0**

Type. Solution of weak base and salt of a weak base with strong acid.

EXAMPLE 21. *Calculate the percentage ionisation of 0.02M ammonia solution containing 0.02 M NH_4Cl. Also calculate the $[OH^-]$, if K (ionisation constant) of ammonia solution is 1.8 × 10^{-5} and NH_4Cl is 100% ionised with $[OH^-]$ concentration be less or more when no NH_4Cl solution is added in ammonia solution?*

SOLUTION. (*a*) Ammonia solution in water ionises as

	$NH_3 + H_2O \rightleftharpoons$	NH_4^+ +	OH^-
(*i*) n mol at start	0.02	0.02	0.
	$\because$ In $NH_4Cl \rightleftharpoons$	NH_4^+ +	Cl^-
(*ii*) Change by reaction	$-x$	x	x
	common ion $[NH_4^+] = 0.02M$		
(*iii*) n mol at equilibrium	$0.02 - x$	$0.02 + x$	x

x = Degree of ionisation of 0.02 M ammonia.

$$\therefore \quad K_c = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad ...(1)$$

Substituting the values in equation (1), we get :

$$K_c = \frac{(0.02 + x)(x)}{0.02 - x} = 1.8 \times 10^{-5} \text{ (given)}$$

Since x is very small, it can be ignored with respect to 0.02 from numerator as well as denominator. So, we have

$$\frac{0.02x}{0.02} = 1.8 \times 10^{-5}\ ;\ x = 1.8 \times 10^{-5}$$

$$\therefore \quad [OH^-] = 1.8 \times 10^{-5}$$

But degree of ionisation (α)

$$= \frac{\text{Gross ionisation}}{\text{Molar concentration}}$$

$$= 1.8 \times 10^{-5}/0.02 = 9 \times 10^{-4}$$

$\therefore$ % age ionisation in the presence of NH_4Cl = 9 × 10^{-4} × 100 = 0.09%

(*b*)The concentration of OH^- ions will be more when NH_4Cl is not added to NH_4OH because the common ions (NH_4^+) from NH_4Cl suppress the ionisation of NH_4OH due to common ion effect. See previous example for $[OH^-]$ in pure NH_4OH solution.

Type. Weak acid + salt of weak acid with strong base.

EXAMPLE 22. *How will the degree of dissociation of 0.1M solution of CH_3COOH change if 8.2 g of CH_3COONa (mol mass 82 g mol^-) is added to one litre of the solution. (K_a = 1.8 × 10^{-5})* **(WBEngg. 1993)**

SOLUTION. (*a*) wt. of CH_3COONa = 8.2 g ; g. mol. wt. of CH_3COONa = 82 g.

Hence no. of mol of CH_3COONa $= \frac{8.2}{82} = 0.1$ M

	$CH_3COOH \rightleftharpoons$	CH_3COO^- +	H^+
conc in mol L^-	0.1		
conc in mol L^-	$0.1 - 0.1\alpha$		
after change	$= 0.1(1 - \alpha)$	$0.1\alpha'$	$0.1\alpha'$

$\therefore \quad [H^+] = 0.1\alpha'$

Total conc. of CH_3COO^- = $0.1 + 0.1\alpha' = \mathbf{0.1\,(1 + \alpha')}$

$$K_a(CH_3COOH) = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{0.1(1+\alpha') \times 0.1\alpha'}{0.1(1-\alpha')}$$

$$= \frac{(\alpha')^2 + 0.1\alpha'}{1 - \alpha'} = 0.1\alpha'$$

$$\left[\begin{array}{l}\alpha^2 \text{ is neglected because } 0.1\,\alpha \text{ and} \\ \alpha' \text{ are very small as compared to 1}\end{array}\right]$$

$$\therefore \quad \alpha' = \frac{1.8 \times 10^{-5}}{0.1} = 1.8 \times 10^{-4}$$

(*b*) Also, for a weak acid,

$$\alpha = \left(\frac{K_a}{C}\right)^{1/2} = \left(\frac{1.8 \times 10^{-5}}{0.1}\right)^{1/2}$$

$$= (1.8 \times 10^{-4})^{1/2} \therefore \alpha = 1.34 \times 10^{-2}$$

$\therefore$ Decrease in the degree of dissociation = $\alpha - \alpha'$

$$= (1.34 \times 10^{-2}) - (1.8 \times 10^{-4})$$

$$= 10^{-4}(1.34 \times 10^2 - 1.8)$$

$$= 132.2 \times 10^{-4}$$

$$= \mathbf{1.322 \times 10^{-2}} \quad \textbf{Ans.}$$

Type. To calculate rate constant (K) for proton transfer from water to a base (say, NH_3), use the relation

$$K_{(\text{base}-NH_3)} = \frac{K_f}{K_b} = \frac{K_w}{K_{\text{acid}\,(NH_4^+)}}$$

$$[\because K_w = K_{\text{acid}} \times K_{\text{base}}].$$

Here, *f* and *b* represent forward nad backward reactions respectively.

EXAMPLE 23. *The ionisation constant of NH_4^+ in water is 5.6 × 10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4 × 10^{10} lit mol^- s^-. Calculate the rate constant for proton transfer from water to ammonia.* **(I.I.T. 1996)**

SOLUTION.

$$NH_3 + H_2O \underset{K_b}{\overset{K_f}{\rightleftharpoons}} NH_4^+ + OH^-\ ;\ K_b = 3.4 \times 10^{10}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+\ ;\ K_a = 5.6 \times 10^{-10}$$

Equilibrium reaction

$$K_{(\text{base}-NH_3)} = \frac{K_f}{K_b}$$

or

$$\frac{K_w}{K_{\text{acid}\,(NH_4^+)}} = \frac{K_f}{K_b}$$

$$\left[\because K_w = K_{\text{acid}} \times K_{\text{base}}\ ;\ K_{\text{base}} = \frac{K_w}{K_{\text{acid}}}\right]$$

or

$$\frac{10^{-14}}{5.6 \times 10^{-10}} = \frac{K_f}{3.4 \times 10^{10}}\ ;$$

$$K_f = \frac{10^{-14} \times 3.4 \times 10^{10}}{5.6 \times 10^{-10}}$$

$$= \mathbf{6.07 \times 10^5} \quad \textbf{Ans.}$$

Type. Calculation of ionisation constant when vapour pressure of solution is given.

Example 24. *The vapour pressure of 0.01 molal solution of a weak base BOH in water at 293 K is 17.536 torr. What will be the value of K_b of this base if it is assumed that the molality and molarity of this solution are same? (Aqueous tension at 293 K = 17.54 torr).*

Solution. (*a*). We know, molality

$$= \frac{\text{wt}\,(w)}{\text{g.mol.wt.}(m)} \times \frac{1000}{\text{wt}\,(W)\text{ of solvent}}$$

$$= \left(\frac{w}{mW} \times 1000\right)$$

But $\frac{p - ps}{p} = \frac{wM}{mW}$ (Raoult's law)

$$\therefore \quad \frac{w}{mW} = \frac{p - ps}{p\,M} = \frac{17.54 - 17.536}{17.54 \times 18}$$

[∵ mol. wt. of H_2O solvent = (2 × 1) + 16 = 18]

$$\text{or} \quad \frac{w}{mW} = \frac{4 \times 10^{-3}}{17.54 \times 18} = 1.267 \times 10^{-5}$$

$$\therefore \quad \text{Molality} = \text{molarity} = 1.267 \times 10^{-5} \times 1000$$

$$= 1.26 \times 10^{-2} = 0.01267$$

(*b*)

	$BOH \rightleftharpoons$	B^+	+ OH^-
Conc. at start	1	0	0
Conc. at equilibrium	$1 - \alpha$	α	α

∴ Total no. of mol at equilibrium

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

$$\text{But} \quad 1 + \alpha = \frac{\text{Experimental molarity}}{\text{Theoretical molarity}} = \frac{0.01267}{0.01}$$

$$= 1.267$$

Or $\alpha = 1.267 - 1 = 0.267$. For a weak base,

$$\therefore \quad K_b = \frac{C\alpha^2}{1 - \alpha} = \frac{0.01 \times (0.0267)^2}{1 - 0.267}$$

$$= \frac{0.01 \times (0.0267)^2}{0.733} = 9.7 \times 10^{-4}$$

Example 25. *How much concentration of ethanoic acid should be added to 0.5M methanoic acid solution so that the ionisation of both the acids is the same? (K_a for ethanoic acid and methanoic acid are 1.8×10^{-5} and 2.4×10^{-4} respectively.*

Solution. Ethanoic acid = CH_3COOH ; Methanoic acid = $HCOOH$. K_{a_1} (CH_3COOH) = 1.8×10^{-5} ; K_{a_2} ($HCOOH$) = 2.4×10^{-4}. C_1 = ? ; C_2 = 0.5M.

But $\alpha_1 = (K_{a1}C_1)^{1/2}$; $\alpha_2 = (K_{a_2}C_2)^{1/2}$

$HCOOH \rightleftharpoons HCOO^- + H^+$; $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Since the ionisation of both the acids is same, $\alpha_1 = \alpha_2$

$$\therefore \quad (K_{a_2}C_1)^{1/2} = (K_{a_1}C_2)^{1/2} \textbf{ Or } K_{a_1}C_1 = K_{a_2}C_2$$

$$\therefore \quad C_1 = \frac{K_{a_2}C_2}{K_{a_1}} = \frac{2.4 \times 10^{-4} \times 0.5}{1.8 \times 10^{-5}}$$

$$= \mathbf{6.67M} \qquad \textbf{Ans.}$$

Example 26. *An aqueous solution of aniline of concentration 0.24M is prepared. What concentration of NaOH is needed in this solution so that anilinium ion concentration remains at 1×10^{-8}M? (K_a for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$).* **(Roorkee 1996).**

Solution. Reaction

	$C_6H_5NH_2 + H_2O \rightleftharpoons$	$C_6H_5NH_3^+$	$+ OH^-$ ...(1)
Initial conc.	0.24	0	x
Conc. after reaction	$0.24 - \alpha$	α	$x + \alpha$

Where x = Amount of NaOH or OH^- needed to maintain 10^{-8}M concentration of $C_6H_5NH_3^+$. We know :

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{2.4 \times 10^{-5}}$$

$$= 4.17 \times 10^{-10}.$$

$$\text{But for reaction (1),} \quad K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$$

$$= \frac{\alpha\,(x + \alpha)}{0.24 - \alpha} = \frac{10^{-8}\,(x + 10^{-8})}{0.24 - 10^{-8}}$$

$$\textbf{Or} \quad 4.17 \times 10^{-10} = \frac{10^{-8}\,(x + 10^{-8})}{0.24}$$

[∵ 10^{-8} is very small, it is neglected from the denominator]

$$\frac{4.17 \times 10^{-10} \times 0.24}{10^{-8}} = x + 10^{-8} \text{ or } x = 10^{-2}\text{M}$$

Hence $[OH^-] = 10^{-2}$M

Example 27. *0.16 g of N_2H_4 are dissolved in water and the total volume made up to 500 mL. Calculate the percentage of N_2H_4 that has reacted with water in this solution. (K_b for N_2H_4 is 4.0×10^{-6}M)* **(Roorkee, Entrance 1998)**

Solution. wt. of N_2H_4 = 0.16 g ;

g. mol. wt. of N_2H_4 = (2 × 14) + (4 × 1) = 32 g

$$\text{Molarity of } N_2H_4 = \frac{\text{wt.}}{\text{g. mol. wt.}} \times \frac{1000}{\text{volume in mL}}$$

$$= \frac{0.16}{32} \times \frac{1000}{500} = 0.01$$

	$N_2H_4 + H_2O \rightleftharpoons$	$N_2H_5^+$	$+ OH^-$
(*i*) n mol at start	0.01	0	0
(*ii*) Change by reaction	$- 0.01\alpha$	0.01α	0.01α
(*iii*) n mol at equilibrium	$0.01 - 0.01\alpha$ $= 0.01$		

(∵ α is small, it is neglected)

$$\therefore \quad K_b = \frac{[N_2H_5^+][OH^-]}{[N_2H_4]} ;$$

$$4.0 \times 10^{-6} = \frac{0.01\alpha \times 0.01\alpha}{0.01}$$

$$\textbf{Or} \quad 0.01\alpha^2 = 4 \times 10^{-6} ; \alpha = \left(\frac{4 \times 10^{-6}}{0.01}\right)^{1/2}$$

$$= (4 \times 10^{-4})^{1/2} = 2 \times 10^{-2}$$

or Percentage of dissociation

$$= 2 \times 10^{-2} \times 100 = \mathbf{2\%}$$ **Ans.**

24.3 ACIDS AND BASES

According to arrhenius, an acid is that substance which when dissolved in water, gives H^+ ions. A base is a substance which when dissolved in water, gives OH^- ions.

*p*H of a solution is defined as the negative logarithm of its H^+ ion concentration: Mathematically :

$$pH = -\log[H^+] \;\textbf{or}\; pH = \frac{1}{\log[H^+]}$$

Or $\log[H^+] = -pH$

Taking antilog of both sides, we get : $[H^+] = {}_{10}{-}pH$

∴ pH may also be defined as the negative power to which 10 must be raised to equal the hydrogen ion concentration.

(*a*) $[H^+] > 10^{-7}$ or $pH < 7$, the solution is **acidic.**

(*b*) $[H^+] < 10^{-7}$ or $pH > 7$, the solution is **basic.**

(*c*) $[H^+] = 10^{-7}$ or $pH = 7$, the solution is **neutral.**

Sorenson (1909) devised a scale called pH scale (pH = 1 to pH = 14) to represent H^+ ion concentration. Here '*p*' stands for power (French Puissance, German Potenz). pH can be negative also. It will happen when $[H^+]$ (rather the activity) is more than one.

pOH. The pOH of a solution is defined as the negative logarithm of its OH^- ions concentration.

$$\therefore \quad pOH = -\log[OH^-]$$

Ionic product of water, K_w. For :

$H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$ **Or**

$2H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$$\therefore \quad K = \frac{[H^+][OH^-]}{[H_2O]} ;$$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]} ;$$

$$K[H_2O] = [H^+][OH^-] \text{ or}$$

$$K_w = [H^+][OH^-]$$

{∵ H_2O is slightly ionised, $[H_2O]$ is constant. *i.e.*, molar concentration of water, $[H_2O] = \frac{1000}{18} = 55.5 \text{ mol } L^-$

[∵ density of water = 1 g (mL$^-$)]}.

Where K_w is ionic product of water. $\mathbf{pK_w = -\log K_w}$.

At 22°C, $K_w = 1.0 \times 10^{-14} ; K_w = [H^+][OH^-]$;

$$10^{-14} = [H^+][H^+] \; [\because [H^+] = [OH^-] ;$$

$$[H^+] = (10^{-14})^{1/2}$$

$$\therefore \quad [H^+] = 10^{-7}.$$

Hence $[H^+] = [OH^-]$

$$= 10^{-7}.$$

$$pH + pOH = 14.$$

$$pK_w = -\log K_w = -\log 10^{-14} = 14$$

But $[H^+][OH^-] = K_w$. Taking negative log of both sides, we get :

$$-\log H^+ + (-\log OH^-) = -\log K_w \; i.e., -\log 10^{-14} = 14$$

$$\therefore \; pH + pOH = 14.$$

$pK_a + pK_b = pK_w$. Since $K_a \times K_b = K_w$ (where K_a and K_b are the values of conjugate acids and bases respectively), $pK_a + pK_b = pK_w = 14$

24.4 IONIC PRODUCT OF WATER, K_w

Type. To find K_w, use the relation : $K_w = [H^+][OH^-]$

EXAMPLE 28. *A centinormal solution of KOH has pH equal to 12. If KOH is 100% dissociated, calculate the ionic product of water.*

SOLUTION. (*a*) Centinormal (N/100) KOH = 10^{-2}N or 10^{-2}M KOH

$$\underset{10^{-2}\,M}{KOH} \rightleftharpoons K^+ + \underset{10^{-2}\,M}{OH^-}$$

$$\therefore \quad [OH^-] = 10^{-2} \text{ M} \quad \text{...(A)}$$

(*b*) $pH = 12$ (given)

But $pH = -\log(H^+)$

$$\therefore \quad [H^+] = 10^{-12} M; K_w = [H^+][OH^-] \text{...(B)}$$

$$= 10^{-12} \times 10^{-2} = \mathbf{10^{-14}}$$

[From equations (A) and (B)]

EXAMPLE 29. *What is the ionic product of water? If the pH of a solution is 5.5, find out its pOH.* **(UP 1984)**

SOLUTION. Ionic product of water, $K_w = [H^+][OH^-] = 10^{-14}$ at 298K. We know that :

$$pH + pOH = 14 ;$$

$$\therefore \quad pOH = 14 - 5.5 = \mathbf{8.5}$$ **Ans.**

24.5 pH OF SOLUTIONS

EXAMPLE 30. *Calculate the pH of a 1.0×10^{-7} molar solution of HCl. The ionic product of water = 10^{-14}.*

SOLUTION. $K_w = [H^+][OH^-] ; 10^{-14} = [H^+][OH^-]$ ...(1)

$$HCl \rightleftharpoons H^+ + Cl^- \quad \text{(ionisation).}$$

A mass balance on Cl^- ion combined with the charge balance gives the following proton (H^+) condition.

$$[OH^-] = [H^+] - 10^{-7} \quad \text{...(2)}$$

The given HCl solution is very dilute. So, $[OH^-]$ can not be ignored as compared to 10^{-7}. Thus, the equations have to be solved exactly. Thus by substituting the value of $[OH^-]$ from (2) in (1), we get :

$$10^{-14} = [H^+] \times \{[H^+] - 10^{-7}\} = [H^+]^2 - 10^{-7}[H^+]$$

Or $[H^+]^2 - 10^{-7}[H^+] - 10^{-14} = 0$

$$[H^+] = \frac{-(-10^{-7}) \pm \left\{(-10^{-7})^2 - (4 \times 1 \times -10^{-14})\right\}^{1/2}}{2 \times 1}$$

$$\left[\because \text{for } ax^2 + bx + c,\; x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}\right]$$

$$= \frac{+10^{-7} \pm \left\{10^{-14} + (4 \times 10^{-14})\right\}^{1/2}}{2}$$

$$= \frac{+10^{-7} \pm \left\{10^{-14}\,(1+4)\right\}^{1/2}}{2}$$

$$= \frac{+10^{-7} + 2.24 \times 10^{-7}}{2}$$

$$[H^+] = \frac{10^{-7}\,(2.24+1)}{2} = 1.62 \times 10^{-7}$$

(To avoid –ve result out of ±, we take + sign)

$\therefore \quad pH = -\log [H^+] = -\log 1.62 \times 10^{-7}$

$= -(\log 1.62 + \log 10^{-7})$

$pH = -(0.209 - 7) \simeq$ **6.79** **Ans.**

EXAMPLE 31. *At 333K, K_w for $2H_2O \rightleftharpoons H_3O^+ + OH^-$ is 9.62×10^{-14}. Calculate the pH of water at this temperature. What happens to its neutrality?*

SOLUTION. $K_w = [H^+]\,[OH^-]$. For pure water,

$[H^+] = [OH^-]$

$\therefore \quad K_w = [H^+]\,[H^+]\,;\ 9.62 \times 10^{-14} = [H^+]^2.$

Hence : $[H^+] = (9.62 \times 10^{-14})^{1/2} = 3.1 \times 10^{-7}$

$\therefore \quad pH = -\log [H^+] = -\log 3.1 \times 10^{-7}$

$= -(\log 3.1 + \log 10^{-7})$

$= -(0.49 - 7) = 6.51$

Though *p*H of H_2O at 333K has become 6.51 (of acidic solution) yet its nature will remain neutral.

Type. To calculate H^+ ion concentration from the given value of *p*H or *p*OH, use the following relations

(*i*) $pH = -\log [H^+]$ (*ii*) $pH = 14 - pOH$

EXAMPLE 32. *Calculate the H^+ ion concentration of a solution having (i) pH 12.8 and (ii) pOH = 5.7*

SOLUTION. (*i*) Given

$pH = 12.8 \quad \therefore [H^+] = 10^{-12.8}$

$[\because pH = -\log [H^+]]$

Taking logs of both sides, we get

$\log [H^+] = -12.8$ (log 10 = 1

$= -12 - 1 + 1 - 0.8 = \overline{13}.2$

[∵ Mantissa must be positive]

Taking antilogs of both sides, we get

$[H^+] = \text{antilog}\,\overline{13}.2$

$= 1.585 \times 10^{-13}$ g mol L^-

(*ii*) $pOH = 5.7$ (given)

$\therefore \quad pH = 14 - 5.7 = 8.3 \quad [\because pH = 14 - pOH]$

$[H^+] = 10^{-8.3} \quad [\because pH = -\log (H^+)]$

Taking logs of both sides, we get

$\log [H^+] = -8.3 = -8 - 1 + 1 - 0.3 = \overline{9}.7$

(∵ Mantissa must be positive)

Taking antilogs of both sides, we get $[H^+]$

$= \text{antilog}\,\overline{9}.7 \simeq 5.0 \times 10^{-9}$

EXAMPLE 33. *Find the pH of 0.05 M H_2SO_4 solution.*

SOLUTION.

$$\begin{array}{lccc} & H_2SO_4 & \rightleftharpoons 2H^+ + & SO_4^{2-} \\ \text{Conc. before ionisation} & 0.05 \rightleftharpoons & 0 & 0 \\ \text{Conc. after ionisation} & 0 & 2 \times 0.05 & 0.05 \end{array}$$

$\therefore \quad [H^+] = 2 \times 0.05 = 0.1\ M;$

$pH = -\log [H^+] = -\log 0.1$ or 10^{-1}

$= -(-1) \log 10 = +1 \times 1 =$ **1 Ans.**

EXAMPLE 34. *Calculate the pH of 0.2 M $Ca(OH)_2$ which is found to be 90% ionised at 298K.*

SOLUTION. $Ca(OH)_2$ ionises as

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

Since $Ca(OH)_2$ is 90% ionised, the degree of ionisation of $Ca(OH)_2 = \frac{90}{100} = 0.9$

$\therefore \quad [OH^-] = 0.9 \times 2 \times 0.2 = 0.36M$

But $\quad [H^+]\,[OH^-] = K_w = 1.0 \times 10^{-14}$

$\therefore \quad [H^+] = 10^{-14}/[OH^-] = \frac{10^{-14}}{0.36}$

$= 2.78 \times 10^{-14} = 2.78 \times 10^{-14}$

$pH = -\log[H^+] = -[\log 2.78 \times 10^{-14}]$

$= -[\log 2.78 - 14 \log 10$ *i. e.* $- 14]$

$= 14 - \log 2.78 = 14 - 0.44$

$= 13.56$ or **$pH = 13.56$**

I Strong acids such as HCl, HNO_3, H_2SO_4 etc.

Important. *When $[H^+]_{acid} < 10^{-6}$ M, water contribution should be taken. When $[H^+]_{acid} \geq 10^{-6}$ M, water contribution should not be taken.*

EXAMPLE 35. *Calculate the pH of 10^{-8} M HCl.*

(Kanpur IET, 1998, BCECE, Bihar 2005)

SOLUTION.

$$\begin{array}{ccc} HCl & \rightleftharpoons & H^+ + Cl^- \\ 10^{-8}\,M & & 10^{-8}\,M \end{array}$$

Since $(H^+)_{acid} < 10^{-6}$ M, so water contribution should be taken.

$$\therefore \quad \begin{array}{ccc} H_2O & \rightleftharpoons & H^+ + OH^- \\ & & x \quad\ \ x \end{array}$$

[Let $x = [H^+]$ derived from water]

$\therefore \quad K_w = [H^+]_T \times [OH^-]_T$ **or**

$10^{-14} = (10^{-8} + x) \times (x)$

Or $\quad x^2 + 10^{-8}x - 10^{-14} = 0$

$\therefore \quad x = 9.51 \times 10^{-8}$

$\therefore \quad [H^+] = 10^{-8} + x$

$= 10^{-8} + 9.51 \times 10^{-8}$

$= 10^{-8}\,[1 + 9.51]$

$= 10.51 \times 10^{-8}$ g ion L^- **Ans.**

Also, $\quad pH = -\log [H^+]_T$

$= -\log [10.51 \times 10^{-8}]$

$= -[\log 10.51 - 8 \log 10]$

$pH = -[1.0216 - 8]$

$=$ **6.9784** **Ans.**

For general equation $ax^2 + bx + c = 0$,

$$x = \frac{-b+\left[\left(b^2-4ac\right)^{1/2}\right]}{2a}$$

$$\therefore \quad x = \frac{-10^{-8} \pm\left[\left(-10^{-8}\right)^2-\left(4\times1\times-10^{-14}\right)\right]^{½}}{2\times1}$$

$$x = \frac{-10^{-8}+(10^{-16}+4\times10^{-14})^{1/2}}{2}$$

$$= \frac{-10^{-8}+2.002\times10^{-7}}{2}$$

$$= \frac{1.902}{2}\times10^{-7}$$

$$= 0.951\times10^{-7} = 9.51\times10^{-8}$$

Example 36. *Calculate the pH of 10^3 M HCl.*

$$\underset{10^3\text{ M}}{\text{HCl}} \rightleftharpoons \underset{10^3\text{ M}}{\text{H}^+} + \text{Cl}^-$$

$[H^+] = 10^3$ (M) **Or** pH = − log 10^3

= − [3 log 10] = **− 3**

But pH = − 3 is not possible because pH range is from 0 to 14.

∴ pH = − log a_{H^+} × activity coefficient

Hence, unless activity coefficient is given, it is not possible to calculate pH of the solution.

Example 37. *Calculate the pH of a solution containing 0.365 g HCl per litre of water.* **(UP1983).**

Solution. wt. of HCl = 3.65 g ;

g. mol. wt. of HCl = 1 + 35.5 = 36.5 g.

Hence, no. of mol of HCl

$$= \frac{0.365}{36.5} = 0.01 = 10^{-2}$$

$$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$$

Conc. (mol L⁻) 10^{-2}

∴ pH = − log [H⁺] = − (log 10^{-2})

= − (− 2 log 10)

= − (−2 × 1) = **+ 2** **Ans.**

II. Strong Bases such as NaOH, KOH etc.

To find pH of such solutions, having $[OH^-] < 10^{-7}$ *i. e.*, $10^{-8}, 10^{-9}$ etc, add $[OH^-]$ of H_2O ($H_2O \rightleftharpoons H^+ + OH^-$) to given $[OH^-]$. For example, in case of 10^{-8}M NaOH, $[OH^-] = 10^{-8} + x$.

Example 38. *Calculate the pH of 10^{-6} M NaOH.*

Solution. NaOH ⇌ Na⁺ + OH⁻

Conc. after ionisation 10^{-6}

∴ $[OH^-] = 10^{-6}$;

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

∴ pH = − log [H⁺] = − log 10^{-8}

= − (− 8) log 10

= + 8 × 1 = **+ 8** **Ans.**

III Weak bases

Example 39. *Calculate the pH of 0.01N Ba(OH)$_2$.*

Solution. $Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$

Initial conc. 0.01 N or 10^{-2} N 0 0

Conc. at equilibrium 10^{-2} 10^{-2}

∴ $[OH^-] = 10^{-2}$

∴ pH = − log [H⁺]

$$\left[\begin{array}{l} [H^+][OH^-] = 10^{-14} \\ [H^+]\times10^{-2} = 10^{-14} \\ \therefore\ [H^+] = \dfrac{10^{-14}}{10^{-2}} = 10^{-12} \end{array}\right]$$

= − log 10^{-12} = − [− 12 log 10] = **12**

But pH + pOH = 14

∴ ***p*OH** = 14 − pH = 14 − 12 = **2** **Ans.**

Example 40. *2.5 ml of 10N HCl is diluted with water to 500 mL. Calculate the pH of the solution.*

Solution. To find normality of diluted acid, we use normality equation.

∴ Given acid Diluted acid

$N_1V_1 = N_2V_2$; 10 × 2.5 = N_2 × 500

∴ N_2 = 10 × 2.5/500 = 0.50 N

HCl is a strong acid. It ionises completely in water.

∴ [H⁺] = 0.05 g ion L⁻ = 5 × 10^{-2} g ion L⁻

pH = − log [H⁺] = − log 5 × 10^{-2}

= − [log 5 − 2 log 10]

= 2 − log 5 = 2 − 0.699

Or *p*H = 1.301 **Ans.**

Example 41. *Calculate the percentage ionisation of an acid having molarity and pH equal to 0.01 M and 4 respectively.*

Solution. pH = 4.0 (given)

∴ [H⁺] = 10^{-4} g ion L⁻ [∵ pH = − log [H⁺]]

But degree of ionisation,

$$\alpha = \frac{\text{Gross concentration}}{\text{molar concentration}} = \frac{10^{-4}}{0.01} = 10^{-2}$$

∴ Percent ionisation = 10^{-2} × 100 = 1.0

Example 42. *Calculate the pH of a solution which contains 2.01 × 10^{-7} moles of H⁺ ion concentration in 100 ml of the solution.*

Solution. 100 ml solution contains moles of H⁺ ions = 2.01 × 10^{-7}

1000 ml solution contains moles of H⁺ ions =

$$2.01\times10^{-7}\times\frac{1000}{100} = 2.01\times10^{-6}$$

∴ [H⁺] = 2.01 × 10^{-6}; pH = − log [H⁺]

= − log 2.01 × 10^{-6}

$$= -[\log 2.01 - 6 \log 10]$$

$$= -[\log 2.01 - 6]$$

$$pH = 6 - \log 2.01 = 6 - 0.303 = 5.697$$

IV. Weak acids.

A weak acid is that which does not ionise completely in water. For example, acetic acid (CH_3COOH), HCN etc. The equilibrium constant, K_a for $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ is given as :

$$K_a = \frac{[CH_3COOH^-][H^+]}{[CH_3COOH]}$$

	CH_3COOH $\rightleftharpoons$	CH_3COO^- +	H^+
Initial conc.	C	0	0

[Where α = degree of dissociation]

Conc. at equilibrium	$C - C\alpha$ $= C(1 - \alpha)$	$C\alpha$	$C\alpha$

$$\therefore \quad K_a = \frac{[CH_3COOH^-][H^+]}{[CH_3COOH]}$$

$$= \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

> **Note.** If α is ≤ 0.1, α can be ignored in comparison to 1. If α is > 0.1, α can not be ignored and has to be calculated by the use of quadratic equation.

For weak acids, α is very small and can be ignored. Thus :

$$K_a = C\alpha^2 \quad \text{or} \quad \alpha = \left(\frac{K_a}{C}\right)^{1/2}$$

$$[H^+]_{acid} = C\alpha = C\left(\frac{K_a}{C}\right)^{1/2} = \left(\frac{C^2K_a}{C}\right)^{1/2}$$

$$= (K_a.C)^{1/2}$$

If $[H^+]_{acid} < 10^{-6}$ M, H^+ ions coming from water must be taken into consideration. It is clear from following example.

EXAMPLE 43. *(a) Calculate the pH of 10^{-6} M CH_3COOH, with $K_a = 1.8 \times 10^{-5}$.*

$$[H^+]_{acid} = (K_aC)^{1/2} = [(1.8 \times 10^{-5}) \times 10^{-6}]^{1/2}$$

$$= 4.24 \times 10^{-6}$$

$$\therefore \quad pH = -\log 4.24 \times 10^{-6}$$

$$= -[\log 4.24 - 6 \log 10]$$

$$= -(0.6274 - 6) = 5.3726.$$

But pH of 10^{-6} HCl = $-\log 10^{-6} = 6$

This pH value is more than that of CH_3COOH (= 5.3726) having same concentration. It means CH_3COOH gives more H^+ ions than HCl having the same concentration. It is not possible because CH_3COOH is weaker acid than HCl. Hence, we must have done some error.

(*b*) Now, let us calculate degree of dissociation, α.

$$\alpha = (K_a/C)^{1/2} = [(1.8 \times 10^{-5})/10^{-6}]^{1/2}$$

$$= \mathbf{4.24}.$$

But α can not be more than 1. It means we have committed an error by neglecting α from the denominator of $K_a = C\alpha^2/1 - \alpha$. It is because without knowing the value of α, the latter can not be neglected in comparison to 1. Hence α present in denominator must be considered and calculated by using quadratic equation.

$$10^{-6}\alpha^2 + 1.8 \times 10^{-5}\alpha - 1.8 \times 10^{-5} = 0$$

$$\left[\because K_a = \frac{C\alpha^2}{1-\alpha} \textbf{ Or } C\alpha^2 + K_a\alpha - K_a = 0\right]$$

$$\therefore \quad \alpha =$$

$$\frac{-1.8 \times 10^{-5} \pm \left[(1.8 \times 10^{-5})^2 - 4 \times 10^{-6} \times -1.8 \times 10^{-5}\right]^{1/2}}{2 \times 10^{-6}}$$

$$\left[\because \text{for } ax^2 + bx + c = 0,\ x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}\right]$$

$$\alpha = \frac{-1.8 \times 10^{-5} \pm \left[(3.24 \times 10^{-10}) + (7.2 \times 10^{-11})\right]^{1/2}}{2 \times 10^{-6}}$$

$$= \frac{(-1.8 \times 10^{-5}) + \left[10^{-10} \times 3.96\right]^{1/2}}{2 \times 10^{-6}}$$

$$= \frac{-1.8 \times 10^{-5} + 1.9899 \times 10^{-5}}{2 \times 10^{-6}}$$

$$= 0.95$$

$$\therefore \quad \alpha = 0.95. \quad \text{Hence } [H^+]_A$$

$$= C\alpha = 0.95 \times 10^{-6}$$

$$\therefore \quad pH = -\log [H^+]_A = -[\log 0.95 + \log 10^{-6}]$$

$$= -[-0.02227 - 6] = 6.02$$

EXAMPLE 44. *At what molar concentration, the pH of nitrous acid would be 2.0? (K_a of nitrous acid = 4.5×10^{-4}).*

(Dhanbad, 1990)

SOLUTION.	HNO_2 $\rightleftharpoons$	H^+ +	NO_2^-
Conc. at start	*C*	*0*	*0*
Change by ionisation	$-C\alpha$	$C\alpha$	$C\alpha$
Conc. at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$.

$$\text{But} \quad \alpha = \left(\frac{K_c}{C}\right)^{1/2} \quad \text{...(1)}$$

(By Ostwald dilution law)

$$\text{Also,} \quad [H^+] = C\alpha \quad \text{...(2)}$$

From relations (1) and (2), we get :

$$[H^+] = C\left(\frac{K_c}{C}\right)^{1/2} = \left(\frac{C^2K_c}{C}\right)^{1/2} = (CK_c)^{1/2}$$

But $pH = 2.0 ; -\log [H^+] = 2.0 ; [H^+] = 10^{-2}$.

Hence : $10^{-2} = (CK_c)^{1/2} ; (10^{-2})^2 = CK_c$

$$\text{Or} \quad C = \frac{(10^{-2})^2}{K_c} \quad \therefore C \frac{10^{-4}}{4.5 \times 10^{-4}}$$

$= \mathbf{0.222\ M}$ **Ans.**

EXAMPLE 45. *The dissociation constant of HCN is 4×10^{-10}. What will be the concentration of H^+ ions in 1N HCN solution?* **(U.P. 1990)**

SOLUTION. For weak electrolytes, $K = C\alpha^2 ; C = 1N$

$$\therefore \quad 4 \times 10^{-10} = 1 \times \alpha^2 ; \alpha = \left(\frac{4 \times 10^{-10}}{1}\right)^{1/2}$$

$= 2 \times 10^{-2}$ g ion L^-. **Ans.**

EXAMPLE 46. *The pH value of a solution of NaOH is 10. Assuming complete dissociation, calculate the concentration of OH^- ions.* **(UP1990)**

SOLUTION. $pH = 10 ; -\log [H^+] = 10 ; \log [H^+] = -10; [H^+] = 10^{-10}$.

But $[H^+][OH^-] = K_w ; [OH^-] = K_w/[H^+]$

$= 10^{-14}/10^{-10} = 10^{-4}$

Or $[OH^-] = \mathbf{0.0001\ g\ ion\ L^-}$ **Ans.**

EXAMPLE 47. *You are provided with a solution having pH 0.35. Calculate its $[H_3O^+]$ and $[OH^-]$.*

SOLUTION. We know

$$pH = -\log [H^+] \text{ or } -\log [H_3O^+]$$

$\therefore \quad [H_3O^+] = 10^{-pH} = 10^{-0.35}$ $[\because pH = 0.35$ (given)]

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{10^{-0.35}} = 10^{-14+0.35}$$

$= 10^{-13.65}$ g ion L^-

EXAMPLE 48. *How many grams of nitric acid should be dissolved per litre to get its pH 2.6 ?*

SOLUTION. $pH = 2.6$ (given)

$[H^+] = 10^{-2.6}$ $[\because pH = -\log [H^+]]$

Taking logs of both sides, we get $\log H^+ = -2.6$

$= -2 - 1 + 1 - 0.6 = \bar{3}.4$

[$\because$ Mantissa must be positive]

Taking antilogs of both sides, we get

$[H^+] = \text{antilog } \bar{3}.4 = \mathbf{2.5 \times 10^{-3}\ g\ ion\ L^-}$

$= 0.0025$ M

HNO_3 is a strong electrolyte and is supposed to ionise completely in aqueous solution. Hence strength of HNO_3 which corresponds to 0.0025 M $[H^+]$ will be 0.0025 M

$\therefore$ Strength in gL^- = Molecular weight × molarity

$= 63 \times 0.0025\ gL^-$

[$\because$ Mol. wt. of $HNO_3 = 1 + 14 + 3 \times 16 = 63$]

$= 0.1575\ gL^-$

EXAMPLE 49. *Calculate the weight of sodium hydroxide that must be dissolved in 500 ml of solution to give it a pH of 10.*

SOLUTION. $pH = 10$ (given)

$\therefore \quad [H^+] = 10^{-10} ; [pH = -\log [H^+]] ;$

$K_w = [H^+][OH^-]$

$$\therefore \quad [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-10}} = 10^{-4} \text{ g ion } L^-$$

Since NaOH is a strong electrolyte, it is supposed to be 100% ionised. Hence the solution containing 10^{-4} g L^- of OH^- ions, will be 10^{-4} M.

Strength in gL^- = Mol. wt. × molarity $= 40 \times 10^{-4} gL^-$

[$\because$ Mol. wt. of NaOH = 23 + 16 + 1 = 40]

$= 0.0040\ gL^-$

$\because$ 1000 ml solution contain NaOH = 0.004 g

$\therefore$ 500 ml solution would contain NaOH

$$= \frac{0.004 \times 500}{1000} = \mathbf{0.002\ g}$$

EXAMPLE 50. *Calculate the concentration of H_3O^+ and OH^- ions in 0.01 M HNO_3 and 0.01 M KOH solution.*

SOLUTION. (*a*) HNO_3 is a strong electrolyte. It ionises completely in 0.01 M solution.

$$\underset{0.01\,M}{HNO_3} \xrightleftharpoons{H_2O} \underset{0.01M}{H_3O^+} + NO_3^-$$

$\therefore \quad [H_3O^+] = 0.01\ M = 0.01$ g mol L^-

$= 1.0 \times 10^{-2}$ g mol L^-

But $[OH^-] = K_w/[H_3O^+]$ $[\because K_w = [H_3O^+][OH^-]]$

$= 1.0 \times 10^{-14}/1.0 \times 10^{-2}$

$= \mathbf{10^{-12}\ g\ mol\ ion\ L^-}$

(*b*)KOH is a strong electrolyte. It ionises completely in 0.01 M solution

$$\underset{0.01\,M}{KOH} \xrightleftharpoons{H_2O} K^+ + \underset{0.01\,M}{OH^-}$$

$\therefore \quad [OH^-] = 0.01\ M = 1.0 \times 10^{-2}$ g mol L^-

But $K_w = [H_3O^+][OH^-]$

$1.0 \times 10^{-14} = [H_3O^+][1.0 \times 10^{-2}]$

$\therefore \quad [H_3O^+] = 10^{-12}$

Note : From above calculations we see that an acid (HNO_3) solution contains OH^- ions and an alkaline solution (KOH) contains H_3O^+ ions though to very small extent.

Type. To calculate $[H^+]$, K_a or molarity of a solution,

Use $$[H^+] = (K_a \times \text{molarity})^{1/2}$$

EXAMPLE 51. *The pH of a 0.1 M hydrocyanic acid solution is 5.2. What is the value of K_a for hydrocyanic acid?*

(Roorkee entrance, 1988)

SOLUTION. $$pH = 5.2 \text{ (given)}$$

$$\therefore \quad [H^+] = 10^{-5.2} \quad [\because pH = -\log [H^+]]$$

But $$[H^+] = \sqrt{K_a \times \text{Molarity}}$$

Squaring both sides, we get

$$[H^+]^2 = K_a \times \text{Molarity}$$

$$\therefore \quad K_a = [H^+]^2/\text{molarity} = (10^{-5.2})^2/0.1$$

$$K_a = 10^{-10.4} \times 10^1 = 10^{-9.4}$$

Taking logs of both sides, we get

$$\log K_a = \log 10^{-9.4} = -9.4 \log 10 = -9.4$$

$$= -9 - 1 + 1 - 0.4 = \overline{10}.6$$

Taking antilogs, we get

$$K_a = \text{antilog } \overline{10}.6$$

$$\therefore \quad K_a = 3.98 \times 10^{-10}$$

V Strong acid + Weak acid. Let strong acid (HA) and weak acid (HB) have concentrations C_1 and C_2 respectively. Let dissociation of weak acid HB is K_a. Thus, we have

$$\underset{C_1}{HA} \rightleftharpoons H^+ + B^- \quad \text{(complete ionisation)}$$

$$\underset{\substack{C_2 - C_2\alpha \\ = C_2(1-\alpha)}}{HB} \rightleftharpoons \underset{C_2\alpha + C_1}{H^+} + \underset{C_2\alpha}{B^-}$$

(α = degree of dissociation of HB)

$$\therefore \quad K_a = \frac{[H^+][B^-]}{[HB]}$$

$$= \frac{(C_2\alpha + C_1) \times C_2\alpha}{C_2(1-\alpha)} = \frac{(C_2\alpha + C_1)\alpha}{1-\alpha} \quad ...(1)$$

By solving equation (1), α can be calculated. From the value of α, $[H^+]$ and then pH can be calculated.

EXAMPLE 52. *Calculate the pH of a solution obtained by mixing 200 mL of 0.1 M HCl with 800 mL of 0.125 M CH_3COOH. (K_a for $CH_3COOH = 1.8 \times 10^{-5}$).*

SOLUTION. $$\underset{1 \text{ mol}}{HCl} \rightleftharpoons H^+ + Cl^-$$

$$200 \text{ mL of } 0.1 \text{ M HCl} = \frac{200 \times 0.1 \times 1}{1000} = 0.02 \text{ M} = C_1$$

[∵ Total volume of mixture = 200 + 800 = 1000 mL]

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ ; K_a = 1.8 \times 10^{-5}$$

800 mL of 0.125 M CH_3COOH

$$= \frac{800 \times 0.125 \times 1}{1000} = 0.1 \text{ M} = C_2$$

For a mixture of a strong acid (HCl) and weak acid (CH_3COOH),

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= \frac{(C_2\alpha + C_1) \times \alpha}{1-\alpha} \quad ...(1)$$

or $$1.8 \times 10^{-5} = \frac{(0.1\alpha + 0.02) \times \alpha}{(1-\alpha)}$$

$$= \frac{(0.1\alpha + 0.02)\alpha}{1-\alpha}$$

$$\therefore \quad 1.8 \times 10^{-5}(1-\alpha) = (0.1\alpha + 0.02)\alpha ;$$

$$1.8 \times 10^{-5} - 1.8 \times 10^{-5}\alpha = 0.1\alpha^2 + 0.02\alpha$$

$$\therefore \quad 0.1\alpha^2 + 0.02\alpha + 1.8 \times 10^{-5}\alpha - 1.8 \times 10^{-5} = 0$$

Or $$0.1\alpha^2 + 10^{-5}\alpha(2 \times 10^3 + 1.8) - 1.8 \times 10^{-5} = 0$$

$$0.1\alpha^2 + 0.02\alpha - 1.8 \times 10^{-5} = 0$$

$$\therefore \quad \alpha = \frac{-0.02 \pm \left[(0.02)^2 - 4(0.1 \times -1.8 \times 10^{-5})\right]^{1/2}}{2 \times 0.1}$$

$$\left[\because \textit{for } ax^2 + bx + c = 0,\ x = \frac{-b \pm (b^2 - 4ac)^{½}}{2a}\right]$$

$$= \frac{-0.02 \pm (4 \times 10^{-4} + 0.72 \times 10^{-5})^{1/2}}{0.2}$$

$$= \frac{-0.02 \pm \left[10^{-4}(4 + 0.072)^{1/2}\right]}{0.2}$$

$$= \frac{-0.02 \pm 2.02 \times 10^{-2}}{0.2}$$

$$= \frac{-0.02 + 0.0202}{0.2} = \frac{0.002}{0.2}$$

(–ve sign is rejected because α can not be negative)

$$\alpha = 0.01$$

But $$[H^+] = C_2\alpha + C_1 \quad \text{[from equation (1)]}$$

$$= 0.1 \times 0.01 + 0.02$$

$$= 0.001 + 0.02 = \mathbf{0.021\ M}$$

$$\therefore \quad pH = -\log [H^+] = -\log 0.021$$

$$= -(-1.68) = \mathbf{+1.68}$$ **Ans.**

EXAMPLE 53. *K_a for HA is 4.9×10^{-8}. After making the necessary approximation, calculate for its decinormal solution (i) percentage dissociation (ii) OH^- ion conc. and pH.*

(IIT 1983, Kanpur I.I.T 1997)

SOLUTION. (*i*) $K_a = 4.9 \times 10^{-8}$; Degree of dissociation = α = ? Conc, C = N/10 = 0.1 *or* 0.1 M

$$HA \rightleftharpoons H^+ + A^-$$

But $$\alpha = \left(\frac{K_a}{C}\right)^{1/2} = \left(\frac{4.9 \times 10^{-8}}{0.1}\right)^{1/2}$$

$= (49 \times 10^{-8})^{1/2} = 7 \times 10^{-4}$

∴ % age degree of ionisation

$= 7 \times 10^{-4} \times 100 = 7 \times 10^{-2}$

$=$ **0.07% Ans.**

(*ii*) $[H^+] = C\alpha = 0.1 \times 7 \times 10^{-4} = 7 \times 10^{-5}$

(*iii*) $[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{10^{-14}}{7 \times 10^{-5}}$

$= \mathbf{1.43 \times 10^{-10}}$ **Ans.**

(*iv*) $pH = -\log [H^+] = -\log 7 \times 10^{-5}$

$= -[\log 7 + \log 10^{-5}]$

$= -[0.8451 - 5] = \mathbf{4.155}$ **Ans.**

Example 54. *Find the pH of a solution obtained by mixing 15 mL of 0.126 M NaOH and 21.0 mL of 0.051 M H_2SO_4. (Assume that the volume of the mixture is simply the sum of volumes mixed).*

Solution. Total volume of mixture = 15 + 21 = 36 mL

(*i*) 15 mL of 0.126 M NaOH $= 15 \times 0.126$

$= 1.89$ m.eq. NaOH

(*ii*) 21.0 mL of 0.051 M $H_2SO_4 = 21 \times 2 \times 0.051$

$= 2.142$ m.eq. H_2SO_4

[∵ H_2SO_4 in dibasic]

∴ $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

But 1.89 m. eq. of H_2SO_4 exactly neutralise 1.89 m. eq. NaOH.

∴ H_2SO_4 left behind $= 2.142 - 1.89$

$= 0.252$ m. eq.

∴ $[H_2SO_4]$ or $[H^+] = \dfrac{0.252}{36} \times 1000$ m.eq. L^-

$= \dfrac{0.252}{36} \times \dfrac{1000}{1000}$

$= 7 \times 10^{-3}$ M

∴ $pH = -\log [H^+]$

$= -\log [7 \times 10^{-3}]$

$= -[0.845 - 3] = \mathbf{2.15}$ **Ans.**

Type. To find pH of a solution (obtained by mixing a weak acid with a strong base and vice-versa) and K_a or K_b is given, use :

(*i*) $\alpha = (K_a/C$ or molarity$)^{1/2}$ and find molarity *i. e.*, $[H^+]$.
(*ii*) $pH = -\log [H^+]$.

Example 55. *25 mL of 1.0 M acetic acid are completely mixed with 25 mL of 0.5 M caustic potash. Calculate the pH of the mixture ($K_a = 1.8 \times 10^{-5}$).*

Solution. Total volume of mixed solution = 25 + 25 = 50 mL.

(*i*) 25 mL of 1.0 M acetic acid $= 25 \times 1.0 = 25$ m. mol

(*ii*) 25 mL of 0.5 M KOH $= 25 \times 0.5 = 12.5$ m. mol

But 12.5 m. mol acetic acid completely neutralise 12.5 m. mol KOH.

∴ Acetic acid left behind $= 25 - 12.5 = 12.5$ m. mol.

∴ $[CH_3COOH]$ or $[H^+] = \dfrac{12.5}{50} \times 1000$ m. mol L^-

$= \dfrac{12.5}{50} \times \dfrac{1000}{1000}$ mol L^-

$= 0.25$ M

But degree of ionisation,

$\alpha = (K_c/C$ i.e., molarity$)^{½}$

$= \left(\dfrac{1.8 \times 10^{-5}}{0.25}\right)^{1/2}$

$= (72 \times 10^{-6})^{1/2}$

$= 8.48 \times 10^{-3}$

But ionic concentration $= \alpha \times$ molarity

∴ $[H_3O^+] = 8.48 \times 10^{-3} \times 0.25$

$= 2.12 \times 10^{-3}$ g ion L^-

∴ $pH = -\log [H_3O^+]$

$= -[\log 2.12 \times 10^{-3}]$

$= -[0.3263 - 3]$

$= 3 - 0.3263$

∴ $\mathbf{pH = 2.6737}$ **Ans.**

Example 56. *Calculate the pH of a solution of 0.1 M acetic acid. ($K_a = 1.8 \times 10^{-5}$).*

Solution. (*a*) Reaction : $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Conc. at start	0.1 M	0	0
Conc. at equilibrium	$0.1 - x \simeq 0.1$	x	x

$0.1 - x = 0.1$ because x is very small as compared to 0.1 and hence neglected.

∴ $K_a = \dfrac{[CH_3COO^-][H^+]}{[CH_3COOH]}$;

$1.8 \times 10^{-5} = \dfrac{x \times x}{0.1}$

∴ $x = (1.8 \times 10^{-5} \times 0.1)^{1/2}$

$= 1.34 \times 10^{-3}$;

$[H^+] = 1.34 \times 10^{-3}$

or $[H^+] = (K_a \times \text{molarity})^{1/2}$

$= (1.8 \times 10^{-5} \times 0.1)^{1/2}$

$= 1.34 \times 10^{-3}$

∴ $pH = -\log 1.34 \times 10^{-3}$

$= -(\log 1.34 \times 10^{-3})$

$= -(\log 1.34 + \log 10^{-3})$

$pH = -(0.127 - 3) = 2.873$ **Ans.**

Type. To find *p*H of solutions containing weak acid and strong bases but the resulting solution after reaction is **neutral or alkaline**. In other words, at the end point and beyond that, however, [HA] *i.e.*, weak acid concentration, can not be set equal to zero but must be solved for ionic equilibrium conditions.

(*i*) For neutral solution at end point, write hydrolysis reaction of salt and find $[OH^-]$ by supposing $[OH^-] = x$ and, then find H^+, *p*H.

(*ii*) If the resulting solution at end point is basic (*i.e.*, contain excess of OH^- ion), then find $[OH^-]$ and then H^+ and hence *p*H.

EXAMPLE 57. *A 40 mL sample of 0.01 M CH_3COOH is titrated with 0.02 M NaOH. Calculate the pH after the addition of (i) 20 mL (ii) 30.0 mL NaOH solution. ($K_a = 1.8 \times 10^{-5}$)*

SOLUTION. (*i*) Amount of base added (L) = 20 mL = $\frac{20}{1000}$ = 0.02 L

$$\text{Total volume} = \frac{40}{1000} + 0.02$$
$$= 0.04 + 0.02 = 0.06 \text{ L}$$

no. of mol of CH_3COOH before neutralisation

$$= \frac{40}{1000} \times 0.01 = 4 \times 10^{-4}$$

no. of mol of OH^- added

$$= 0.02 \times 0.02 = 4 \times 10^{-4}$$

no. of mol of CH_3COO^- formed = 4×10^{-4}

no. of mol of CH_3COOH left behind

$$= (4 \times 10^{-4}) - (4 \times 10^{-4}) = \text{zero.}$$

Since, neither H^+ nor OH^- ions are present because no. of mol of CH_3COOH left = 0,

$$\therefore \quad M(CH_3COO^-) = \frac{4 \times 10^{-4} \text{ mol}}{\text{Total volume}}$$
$$= \frac{4 \times 10^{-4} \text{ mol}}{0.06 \text{ L}}$$
$$= 6.7 \times 10^{-3} \text{ mol L}^-$$

The solution at the end point is the same as 6.7×10^{-3} M CH_3COONa. Consider the hydrolysis of CH_3COONa.

$$CH_3COO^- + HOH \rightleftharpoons CH_3COOH + OH^-$$

Conc. (mol L^-) 6.7×10^{-3}

Conc. at equilibrium $6.7 \times 10^{-3} - x$ $\quad x \quad x$

But $6.7 \times 10^{-3} - x \simeq 6.7 \times 10^{-3}$ because x is very small as compared to 6.7×10^{-3} and hence neglected.

$$\therefore \quad K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \text{...(1)}$$

$$\text{Also,} \quad K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} \quad \text{...(2)}$$

From (1) and (2), we get :

$$\frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{10^{-14}}{1.8 \times 10^{-5}};$$

$$\frac{x \times x}{6.7 \times 10^{-3}} = \frac{10^{-14}}{1.8 \times 10^{-5}};$$

$$x = \left(\frac{10^{-14} \times 6.7 \times 10^{-3}}{1.8 \times 10^{-5}}\right)^{1/2}$$
$$= (3.7 \times 10^{-12})^{1/2}$$

$$\therefore \quad x = 1.9 \times 10^{-6} \text{ or}$$

$$[OH^-] = 1.9 \times 10^{-6}$$

$$\therefore \quad [H^+] = \frac{10^{-14}}{1.9 \times 10^{-6}} = 5.26 \times 10^{-9};$$

$$pH = -\log[H^+]$$
$$= -(\log 5.26 + \log 10^{-9});$$
$$\mathbf{pH} = -(0.72 - 9) = \mathbf{8.28} \qquad \textbf{Ans.}$$

(*ii*) Amount of base added = 30 mL = $\frac{30}{1000}$ = 0.03 L

$$\text{Total volume} = \frac{40}{1000} \text{ L} + 0.03 \text{ L}$$
$$= 0.04 + 0.03 = 0.07 \text{ L.}$$

no. of mol of CH_3COOH before neutralisation

$$= \frac{40}{1000} \times 0.01 = 4 \times 10^{-4}$$

no. of mol of OH^- added

$$= 0.03 \times 0.02 = 0.0006 = 6 \times 10^{-4}$$

no. of mol of CH_3COO^- formed = 4×10^{-4}

∴ no. of mol of OH^- left behind

$$= (6 \times 10^{-4}) - (4 \times 10^{-4})$$
$$= 2 \times 10^{-4}$$

From above, it is clear that there are excess of OH^- ions beyond that needed for neutralising CH_3COOH. For such a case, we know that :

$$M[OH^-] = \frac{2 \times 10^{-4} \text{ mol}}{\text{Total volume (L)}}$$
$$= \frac{2 \times 10^{-4}}{0.07}$$
$$= 2.86 \times 10^{-3} \text{ mol L}^-$$

$$\therefore \quad [OH^-] = 2.86 \times 10^{-3};$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2.86 \times 10^{-3}}$$
$$= 3.5 \times 10^{-12}$$

$$\therefore \quad pH = -\log[H^+] = -\log(3.5 \times 10^{-12})$$
$$= -(\log 3.5 + \log 10^{-12})$$

$$\textbf{or} \quad \mathbf{pH} = -(0.54 - 12) = \mathbf{11.46} \qquad \textbf{Ans.}$$

EXAMPLE 58. *Calculate the $[OH^-]$ and pH of the following solution : 10 mL of 0.2 M $Ca(OH)_2$ + 25 mL of 0.1 M HCl.*

(CBSE-PMT, 2009)

SOLUTION. Total volume of mixture solution = 10 + 25 = 35 ml

(*i*) 10 mL of 0.2 M $Ca(OH)_2$

$$= 10 \times (2 \times 0.2)$$
$$= 4 \text{ m mol of } Ca(OH)_2$$

$$[\because Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^- \ (\textit{i.e.}, 2 \text{ mol } OH^-)].$$

(*ii*) 25 mL of 0.1 M HCl = 25 × 0.1 = 2.5 m. mol of HCl

But 2.5 m. mol of $Ca(OH)_2$ completely neutralise 2.5 m mol of HCl.

So, m. mol of $Ca(OH)_2$ left behind

$$= 4 - 2.5 = 1.5$$

$$\therefore \quad [Ca(OH)_2] = [OH^-]$$

$$= \frac{1.5}{\text{Total volume}} \times 1000 \text{ m. mol L}^-$$

$$[OH^-] = \frac{1.5}{35} \times \frac{1000}{1000} \text{ mol L}^- = 0.0428 \text{ M}$$

$$\text{But} \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.0428}$$

$$= 2.34 \times 10^{-13} \text{ M}$$

$$\therefore \quad pH = -\log [H^+] = -\log [2.34 \times 10^{-13}]$$

$$= -[0.3692 - 13] = 13 - 0.3692$$

$$\boldsymbol{pH = 12.63} \qquad \textbf{Ans.}$$

EXAMPLE 59. *Calculate the pH of a solution made by mixing 50 mL of 0.01 M $Ba(OH)_2$ solution with 50 mL water.*

(MLNR 1988)

SOLUTION. Total volume of solution = 50 + 50 = 100 mL

Original $Ba(OH)_2$ solution; Diluted $Ba(OH)_2$ solution

$$M_1V_1 = M_2V_2$$

$$0.01 \text{ M} \times 50 \text{ mL} = M_2 \times 100 \text{ mL}$$

$$M_2 = \frac{0.01 \text{ M} \times 50 \text{ mL}}{100 \text{ mL}} = 0.005 \text{ M}$$

$$\underset{1 \text{ mol}}{Ba(OH)_2} \rightleftharpoons Ba^{2+} + \underset{2 \text{ mol}}{2OH^-}$$

$$\therefore \quad [Ba(OH)_2] = [OH^-] = 2 \times 0.005 = 0.01 \text{ M}$$

$$\therefore \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.01} = 10^{-12} \text{ M}$$

$$\therefore \quad pH = -\log 10^{-12} = -[-12 \log 10]$$

$$= -[-12 \times 1] = \mathbf{12} \qquad \textbf{Ans.}$$

Type. *p*H of a solution obtained by **mixing strong acid and strong base.** Use the relation.

no. of mol = Vol (is litre) × molarity (mol L⁻)

EXAMPLE 60. *40 cm³ of a 0.1 molar NaOH was added to 10 cm³ of 0.45 molar HCl. What is the pH of the resulting solution? Both NaOH and HCl are strong electrolytes.* ($K_w = 10^{-14}$ *mol^2L^{-2}*).

SOLUTION. For NaOH, $[OH^-] = 0.1$ M ;

Volume = 40 cm³.

1000 cm³ solution contain $[OH^-] = 0.1$ M

40 cm³ solution contain $[OH^-]$

$$= \frac{0.1}{1000} \times 40 = 0.004 \text{ M.}$$

$$\text{Or} \quad \text{no. of mol of } OH^- = \frac{40}{1000} \times 0.1 = 0.004 \text{ M}$$

For HCl, $[H^+] = 0.45$ M ; Volume = 10 cm³

1000 cm³ solution contain

$$[H^+] = 0.45 \text{ M}$$

10 cm³ solution contain $[H^+]$

$$= \frac{0.45 \times 10}{1000} = 0.0045 \text{ M.}$$

$$\text{Or} \quad \text{no. of mol of } H^+ = \frac{10}{1000} \times 0.45 = 0.0045 \text{ M.}$$

Total volume of mixing = 40 + 10 = 50 cm³

∴ Mol of H^+ ions left unused

$$= 0.0045 - 0.004 = 0.0005 \text{ M.}$$

Mol of H^+ ions in 50 cm³ solution = 0.0005 M

Mol of H^+ ions in 1000 cm³ solution

$$= \frac{0.0005}{50} \times 1000 = 0.01$$

$$= 10^{-2} \text{ M}$$

$$\therefore \quad [H^+] = 10^{-2} \text{ M}$$

$$\text{Hence,} \quad pH = -\log [H^+] = -\log (10^{-2})$$

$$\text{Or} \quad pH = -(-2 \log 10) = -(-2 \times 1)$$

$$= \mathbf{+2} \qquad \textbf{Ans.}$$

EXAMPLE 61. *The pH of a solution prepared by mixing 2.0 mL of HCl solution of pH 3.0 and 3.0 mL of NaOH of pH 10.0 is:*

(a) 2.5 (b) 3.5 (c) 5.5 (d) 6.5

(I.I.T., 1998, AMU med. 2010, J&KCET, 2010)

SOLUTION. (*i*) For HCl, pH = 3. So, $[H^+] = 10^{-3} = M_1$, $V_1 = 2.0$ mL

(*ii*) For NaOH, pH = 10; But $p_H + p_{OH} = 14$, so, 10 + *p*OH = 14 or $p_{OH} = 14 - 10 = 4$; $[OH^-] = 10^{-4} = M_2$, $V_2 = 3.0$ mL; M_R = resultant molarity

$\therefore M_1V_1 - M_2V_2 = M_R(V_1 + V_2)$; $(10^{-3} \times 2) - (10^{-4} \times 3) = M_R(2 + 3)$; $10^{-3}(2 - 0.3) = 5\,M_R$.

or $M_R \times 5 = 1.7 \times 10^{-3}$. So, $M_R = 3.4 \times 10^{-4} = [H^+]$

Hence, pH = $-\log (3.4 \times 10^{-4}) = [\log 3.4 + \log 10^{-4}] = 4 - 0.53 = 3.47 \simeq 3.5$. So, correct answer is (*b*).

EXAMPLE 62. *The pk_{a_1} and pk_{a_2} of an amino acid are 2.3 and 9.7 respectively. The isoelectric point of the amino acid is:*

(a) 12. 0 (b) 7.4 (c) 6.0 (d) 3.7 **(AMUMed.2010)**

SOLUTION. Isoelectric point = 2.3 + 9.7/2 = 6. So, correct answer is (*c*).

EXAMPLE 63. *Calculate the pH of a solution containing 20 mL of 0.1 M H_2SO_4 and 40 mL of 0.2 M HCl.*

SOLUTION. $HCl \rightleftharpoons H^+ + Cl^-$ (ionisation).

∴ Milliequivalent of 40 mL of 0.2 M HCl

$$= 40 \times 0.2 \times 1 = 8$$

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

∴ Milliequivalent of 20 mL 0.1M H_2SO_4

$$= 20 \times 0.1 \times 2 = 4$$

Total number of milliequivalent of H^+ ions (from HCl and H_2SO_4) = 8 + 4 = 12

Total volume of solution

$$= 20 + 40 = 60 \text{ mL}$$

$\therefore \quad [H^+] = \frac{12}{60} = 0.2$

$\therefore \quad pH = -\log [H^+] = -[\log 0.2]$

$= -[-0.6989]$

$= \mathbf{+0.6989}$ **Ans.**

EXAMPLE 64. *Calculate the pH of a solution obtained by mixing 0.063 g nitric acid dissolved in 250 mL solution and 0.049 g sulphuric acid dissolved in 250 mL solution.*

SOLUTION. (*a*) g. mol. wt. of HNO_3

$= 1 + 14 + (3 \times 16) = 63$ g.

Total volume of solution

$= 250 + 250 = 500$ mL

500 mL solution contain HNO_3

$= 0.063$ g

1000 mL HNO_3 contain HNO_3

$= \frac{0.063}{500} \times 1000 = 0.126$ g

$\therefore$ no. of mol of $HNO_3 = \frac{0.126}{63} = 2 \times 10^{-3}$

$\therefore \quad [H^+] = [HNO_3] = 2 \times 10^{-3}\ M \times 1$

$= 2 \times 10^{-3}$ M

$[\because HNO_3 \rightleftharpoons H^+ \text{(1 mol)} + NO_3^-]$

(*b*) g. mol. wt. of $H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98$ g

500 mL solution contain $H_2SO_4 = 0.049$ g

1000 mL solution contain H_2SO_4

$= \frac{0.049}{500} \times 1000 = 0.098$ g

But $\quad H_2SO_4 \rightleftharpoons 2H^+ \text{(2 mol)} + SO_4^{2-}$

$\therefore$ no. of mol of H_2SO_4 or $[H^+]$

$= \frac{0.098}{98} \times 2 = 2 \times 10^{-3}$

$\therefore \quad [H^+] = 2 \times 10^{-3}$ M

$\therefore \quad$ Total $[H^+] = (2 \times 10^{-3}) + (2 \times 10^{-3})$

$= 2 [10^{-3} + 10^{-3}]$

$= 2 \times 2 \times 10^{-3} = 4 \times 10^{-3}$ M

$\therefore \quad pH = -\log [H^+] = -\log 4 \times 10^{-4}$

$= -[\log 4 - 3 \log 10]$

$= -[0.602 - 3]$

$pH = 3 - 0.602 = \mathbf{2.398}$ **Ans.**

EXAMPLE 65. *Calculate the pH of the solution obtained by mixing equal volumes of the solution having pH 2 and 6.*

SOLUTION. (1) $\quad pH = 2 ;\ \therefore\ [H^+] = 10^{-2}$ M

(2) $\quad pH = 6 ;\ [H^+] = 10^{-6}$

Since the resulting solution is obtained by mixing equal volumes of two solutions :

$$[H^+] = \frac{10^{-2} + 10^{-6}}{2} = \frac{10^{-2}[1 + 10^{-4}]}{2}$$

$$= \frac{10^{-2} \times 1.0004}{2}$$

$= 0.5002 \times 10^{-2}$ M

$= 5.002 \times 10^{-3}$ M

$\therefore \quad pH = -\log [H^+]$

$= -\log [5.002 \times 10^{-3}]$

$= -[\log 5.002 + \log 10^{-3}]$

$= -[0.6991 - 3] = \mathbf{2.33}$ **Ans.**

EXAMPLE 66. *How much volume (in mL) of 0.001 M HNO_3 (aq) should be added to 100 cm^3 of 0.001 M KOH to change its pH by one unit ?*

SOLUTION. $\quad KOH \rightleftharpoons K^+ + OH^-$;

$[KOH] = [OH^-] = 0.001M = 10^{-3}$ M

But $\quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-3}} = 10^{-14+3}$

$= 10^{-11}$

$\therefore \quad pH = -\log [H^+] = -\log 10^{-11} = \mathbf{11}$

Change in pH required = 1

$\therefore$ Required pH after adding $HNO_3 = 11 - 1 = \mathbf{10}$

$\therefore \quad [H^+] = 10^{-10}\ M ;\ [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-10}}$

$= 10^{-14+10} = 10^{-4}$

$\therefore$ no. of mol of KOH in 100 cm^3 of 10^{-3} M

$= \frac{10^{-3} \times 100}{1000} = 10^{-4}$

no. of mol of KOH in 100 cm^3 of 10^{-4}M

$= \frac{10^{-4} \times 100}{1000} = 10^{-5}$

no. of mol of KOH to be neutralised by HNO_3

$= 10^{-4} - 10^{-5} = 10^{-5} (10 - 1)$

$= 9 \times 10^{-5}$

Volume of 0.001M HNO_3 containing 9×10^{-5} mol

$HNO_3 = \frac{1000 \times 9 \times 10^{-5}}{0.001} = 90$

$\therefore$ Volume of 0.001 M HNO_3 to be added

$= \mathbf{90\ mL.}$ **Ans.**

EXAMPLE 67. *500 mL of a solution contain 0.28 g of KOH (a) How much water should be added to it to change its original pH by unity?*

(b) How much water should be evaporated from it to change its original pH by unity?

SOLUTION. 500 solution contain KOH = 0.28 g

$\therefore$ 1000 mL solution contain

$KOH = \frac{0.28}{500} \times 1000 = 0.56$ g

g. mol. wt. of KOH = 39 + 16 + 1 = 56 g

$$\therefore \quad [KOH] = [OH^-(aq)] = \frac{0.56}{56} = 10^{-2} M;$$

$$[H^+(aq)] = \frac{K_w}{[OH^-(aq)]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

$$\therefore \quad pH = -\log 10^{-12} = (-)(-12 \log 10)$$
$$= +12 \times 1 = +12$$

(*i*) When KOH solution is diluted, it becomes less concentrated and $[OH^-(aq)]$ decreases *i.e.*, $[H^+(aq)]$ increases and hence pH decreases.

Thus : Desired pH = 12 – 1 = 11.

So, $[H^+(aq)] = 10^{-11}$ M ;

$$[OH^-(aq)] = \frac{K_w}{[H^+(aq)]} = \frac{10^{-14}}{10^{-11}} = 10^{-3}$$

Original $[OH^-(aq)]$ Diluted $[OH^-(aq)]$

$$M_1V_1 = M_2V_2$$

$$10^{-2} \times 500 = 10^{-3} \times V_2\,;\; V_2 = \frac{10^{-2} \times 500}{10^{-3}}$$
$$= 5000 \text{ mL}$$

∴ Volume of water to be added

= 5000 – 500 = 4500 mL

$= \frac{4500}{1000} =$ **4.5 L** **Ans.**

(*ii*) When KOH solution is evaporated, it becomes concentrated and $[OH^-(aq)]$ increases *i.e.*, $[H^+(aq)]$ decreases and hence pH increases.

Desired pH = 12 + 1 = 13.

So, $[H^+(aq)] = 10^{-13}$ M ;

$$[OH^-(aq)] = \frac{K_w}{[H^+(aq)]} = \frac{10^{-14}}{10^{-13}} = 10^{-1}$$

Original $[OH^-(aq)]$ $[OH^-(aq)]$ after evaporation

$$M_3V_3 = M_4V_4$$

$$10^{-2} \times 500 = 10^{-1} \times V_4;\; V_4 = \frac{10^{-2} \times 500}{10^{-1}}$$
$$= 50 \text{ mL}$$

∴ Volume of water to be evaporated

= 500 – 50 = 450 ml

$= \frac{450}{1000} =$ **0.45 L** **Ans.**

EXAMPLE 68. *Calculate the pH value of a solution obtained by mixing 600 mL of 0.1 M NaOH and 400 mL of 0.1M* $Ca(OH)_2$.

SOLUTION. (*i*) 600 mL of 0.1 M NaOH $= \frac{600 \times 0.1}{1000} = 0.06$ M

$$NaOH \xrightleftharpoons{H_2O} Na^+(aq) + OH^-(aq);$$

$[OH^-(aq)] = 0.06$M.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}(aq) + \underset{2 \text{ mol}}{2OH^-(aq)}$$

∴ 400 mL of 0.1M $Ca(OH)_2$

$$= \frac{400 \times 0.1 \times 2}{1000} = 0.8 \text{ M}$$
$$= [OH^-(aq)]$$

∴ Total $[OH^-(aq)] = 0.06 + 0.08 = 0.14$ M

But
$$[H^+(aq)] = \frac{K_w}{[OH^-(aq)]} = \frac{10^{-14}}{0.14}$$
$$= 7.1 \times 10^{-14}$$

$$\therefore \quad pH = -\log [H^+] = -\log 7.1 \times 10^{-14}$$
$$= -[\log 7.1 + \log 10^{-14}]$$

pH = – (0.85 – 14) = 13.15 Ans.

EXAMPLE 69. *A solution has been prepared by mixing 50 mL of 0.05 M* H_2SO_4, *50 mL of 0.05N* HNO_3, *100 mL of 0.1N HCl, 100 mL of 0.2N NaOH and 100 mL of 0.2M* $Ba(OH)_2$. *Calculate the pH of the resulting solution.*

SOLUTION. (*i*) 50 mL of 0.05 M H_2SO_4 = 50 × 0.05 of 1M H_2SO_4 = 2.5 mL of 1M H_2SO_4

= 2.5 × 2 *i.e.*, **5 mL** of 1 N $H^+(aq)$ ions.

$(\because H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-})$

(*ii*) 50 mL of 0.05 N HNO_3 = 50 × 0.05 *i.e.*,

2.5 mL of 1N HNO_3 = **2.5 mL** of 1 N HNO_3

(*iii*) 100 mL of 0.1N HCl = 100 × 0.1 *i.e.*,

10 mL of 1N HCl = **10 mL** of 1N HCl.

(*iv*) 100 mL of 0.2N NaOH = 100 × 0.2 *i.e.*,

20 mL of 1N NaOH = **20 mL** of 1N NaOH

(*v*) 100 mL of 0.2 M $Ba(OH)_2$ = 100 × 0.2 *i.e.*,

20 mL of 1 M $Ba(OH)_2$ = 20 × 2 *i.e.*, **40 mL** of 1N. $Ba(OH)_2$

$[\because Ba(OH)_2 \rightleftharpoons Ba^{2+} + \mathbf{2OH^-}]$

Total volume of 1N $H^+(aq)$ ions

= 5 + 2.5 + 10 = 17.5 mL

Total volume of 1N $OH^-(aq)$ ions

= 20 + 40 = 60 mL

∴ 17.5 mL of 1N $OH^-(aq)$ ions = 17.5 mL of 1N, $H^+(aq)$ ions.

∴ Volume of 1N $OH^-(aq)$ ions left unused

= 60 – 17.5 = 42.5 mL

Actual volume of solution = 50 + 50 + 100 + 100 + 100 = 400 mL

Unused $[OH^-(aq)]$ Mixture $[OH^-(aq)]$

$$N_1V_1 = N_2V_2;\; 1 \times 42.5 = N_2 \times 400$$

$$\therefore \quad N_2 = \frac{42.5}{400}$$

Or $$[OH^-(aq)] = \frac{42.5}{400}\text{ N}$$

∴ $$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{42.5} \times 400$$

$$= 9.4 \times 10^{-14}$$

∴ $$pH = -\log [H^+]$$

$$= -\log 9.4 \times 10^{-14}$$

$$= -[\log 9.4 + \log 10^{-14}]$$

$$pH = -(0.97 - 14)$$

$$= \mathbf{13.03}$$ **Ans.**

EXAMPLE 70. *Calculate the pH of a solution obtained by dissolving 0.28 g of potassium hydroxide in 1.0 L of water.*

(NCERT Book problem)

SOLUTION. g. mol. wt. of KOH = 39 + 16 +1 = 56 g ; wt. of KOH = 0.28 g; 1L = 100 mL.

$$\text{Molarity of KOH} = \frac{\text{wt. (g)}}{\text{g. mol. wt}} = \frac{0.28}{56\text{ g}}$$

$$= 5.0 \times 10^{-3}\text{ M};$$

$$[OH^-] = 5 \times 10^{-3}\text{ M}$$

∴ $$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{5 \times 10^{-3}} = 2 \times 10^{-12}$$

∴ $$pH = -\log [H^+] = -(\log 2 \times 10^{-12})$$

$$= -(\log 2 + \log 10^{-12})$$

$$= -(0.301 - 12) = \mathbf{11.699}$$ **Ans.**

EXAMPLE 71. *Calculate pH for 0.0008 $Mg(OH)_2$*

(Roorkee, 1992)

SOLUTION. 0.0008 M $Mg(OH)_2$ = 8×10^{-4} M $Mg(OH)_2$

	$Mg(OH)_2 \rightleftharpoons$	Mg^{2+} +	$2OH^-$
Original concentration	8×10^{-4} M	0	0
Concentration after ionisation		8×10^{-4} M	$2 \times 8 \times 10^{-4}$ N $= 16 \times 10^{-4}$ N

∴ $$[OH^-] = 16 \times 10^{-4}\text{ N}$$

∴ $$pOH = -\log 16 \times 10^{-4}$$

$$= -[\log 16 + \log 10^{-4}]$$

$$pOH = -(1.204 - 4) = 2.796.$$

Hence $$\mathbf{pH} = 14 - pOH = 14 - 2.796$$

$$= \mathbf{11.204}$$ **Ans.**

EXAMPLE 72. *A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the concentration of S^{2-} and HS^- ions in solution. Given Ka_1 and Ka_2 for H_2S are 10^{-7} and 1.3×10^{-13} respectively.*

(Roorkee, 1992)

SOLUTION. Ionisation.

$$H_2S \rightleftharpoons H^+ + HS^-;\ Ka_1 = 10^{-7}$$

$$HS^- \rightleftharpoons H^+ + S^{2-};\ Ka_2 = 1.3 \times 10^{-13}$$

$$HCl \rightleftharpoons H^+ + Cl^-;\ [H^+] = 0.3\text{ M}$$

H^+ ions are common ions. So, due to addition of HCl, ionisation of H_2S is suppressed. So, $[H^+]$ is due to HCl and thus, $[H^+] = 0.3$.

(*a*) *To find $[HS^-]$.*

$$Ka_1 = \frac{[H^+][HS^-]}{[H_2S]};$$

$$10^{-7} = \frac{0.3 \times [HS^-]}{0.1}$$

∴ $$[HS^-] = \frac{0.1 \times 10^{-7}}{0.3}$$

$$= \mathbf{3.3 \times 10^{-8}\ M}$$ **Ans.**

(*b*) *To find $[S^{2-}]$.* $$Ka_2 = \frac{[H^+][S^-]}{[HS^-]};$$

$$13 \times 10^{-13} = \frac{0.3 \times [S^{2-}]}{3.3 \times 10^{-8}}$$

∴ $$[S^{2-}] = \frac{1.3 \times 10^{-13} \times 3.3 \times 10^{-8}}{0.3}$$

$$= \mathbf{1.43 \times 10^{-20}\ M}$$ **Ans.**

EXAMPLE 73. *Calculate the approximate pH of a 0.1M aqueous H_2S solution. K_1 and K_2 for H_2S are 10^{-7} and 1.3×10^{-13} respectively at 298K.* **(Roorkee,1986)**

SOLUTION. The value of K_1 (= 10^{-7}) is >>> than K_2 (= 1.3×10^{-13}) value. So, $[H^+]$ will be due to first ionisation of H_2S.

$$H_2S \xrightleftharpoons{H_2O} H^+(aq) + HS^-(aq)\text{(First ionisation)}$$

∴ $$K_1 = \frac{[H^+(aq)][HS^-(aq)]}{[H_2S]};$$

$$10^{-7} = \frac{[H^+(aq)][H^+(aq)]}{[H_2S]}$$

$$[\because [H^+(aq)] = [HS^-(aq)]]$$

Or $$10^{-7} = \frac{[H^+(aq)]^2}{0.1};$$

$$[H^+(aq)] = (10^{-7} \times 0.1)^{1/2} = \mathbf{10^{-4}\ M}$$ **Ans.**

$$pH = -\log [H^+] = -\log 10^{-4}$$

$$= -(-4)\log 10 = \mathbf{4}$$ **Ans.**

EXAMPLE 74. *If 0.4 molar aqueous solution of $Ca(OH)_2$ is 85% ionised at 298 K, what will be the pH of this solution at the same temperature ?*

SOLUTION. Degree of ionisation of $Ca(OH)_2$ = 85% = $\frac{85}{100}$ = 0.85

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + \underset{2 \times 0.4 \times 0.85 = 0.68}{2OH^-}$$

∴ $$[OH^-] = 0.68;$$

∴ $$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.68}$$

$$= 1.47 \times 10^{-14}$$

$$\therefore \quad pH = -\log 1.47 \times 10^{-14}$$

$$= -(\log 1.47 + \log 10^{-14})$$

$$= -(0.167 - 14)$$

$$\boldsymbol{pH} = 14 - 0.167 = \mathbf{13.833} \qquad \textbf{Ans.}$$

EXAMPLE 75. *0.1 millimol of $CdSO_4$ are present in 10 mL acid solution of 0.08N HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. What would be the pH of the solution after filtering off precipitate, boiling of H_2S and making the solution 100 mL by adding H_2O?* **(IIT1984)**

SOLUTION. Reaction :

$$CdSO_4 + HCl + H_2S \rightleftharpoons CdS\downarrow + H_2SO_4 + HCl$$

	$CdSO_4$	HCl	H_2S	CdS↓	H_2SO_4	HCl
Millimol at start	0.1	10×0.08 $= 0.8$				
Millimol after reaction	0	0.8			0.1	0.1

$[H^+]$ left in HCl = 0.8 ;

$[H^+]$ in $H_2SO_4 = 2 \times 0.1 = 0.2$

$$[\because H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}]$$

$\therefore$ Total millimol of H^+ ions left = 0.8 + 0.2 = 1.0

Total volume = 100 mL.

Hence : 100 mL solution contain H^+ ions = 1 millimol

$\therefore$ 1000 mL solution contain H^+ ions

$$= \frac{1}{100} \times 1000 = 10 \text{ millimol}$$

But $\quad 10 \text{ millimol} = \dfrac{10}{1000} \text{ mol} = 10^{-2} \text{ mol.}$

$$\therefore \quad [H^+] = 10^{-2}\text{ M} \ \textbf{Or}$$

$$pH = -\log 10^{-2} = -(-2 \log 10)$$

$$= -(-2 \times 1) = \mathbf{2} \qquad \textbf{Ans.}$$

EXAMPLE 76. *Twenty ml of 0.2 M sodium hydroxide is added to 50 ml of 0.2 M acetic acid to give 70 ml of the solution. What is the pH of the solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionisation constant of acetic acid is 1.8×10^{-5}.* **(IIT 1982)**

SOLUTION. (*a*) We know that

$$pH = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]} \qquad ...(1)$$

Since 20 ml of 0.2 M NaOH will completely neutralise 20 ml of 0.2M acetic acid, we shall be left with 30 mL (50 – 20 = 30) of acetic acid. The total volume of solution after mixing is 70 ml. Thus in the mixture :

$$[\text{acid}] = 30 \times 0.2/70 = 0.085;$$

$$[\text{salt}] = 20 \times 0.2/70 = 0.057.$$

Substituting the respective values in equation (1), we get

$$pH = -\log(1.8 \times 10^{-5}) + \log \frac{0.057}{0.085}$$

$$= -[\log 1.8 + \log 10^{-5}]$$

$$+ \log 57 - \log 85$$

$$= -[0.26 - 5] + 1.7559 - 1.9294$$

$$= 5 - 0.26 + 1.7559 - 1.9294$$

$$= 4.74 + 1.7559 - 1.9294$$

$$\mathbf{pH = 4.57}$$

(*b*) To calculate the volume of 0.2 M NaOH to be added to get pH, 4.74. In order to get pH = 4.74, the [salt] should be equal to [acid]. For this purpose, 50/2 ml (= 25 ml) of 0.2M acetic acid must be equal to 50/2 ml (= 25ml) of 0.2 M NaOH.

Volume of 0.2 M NaOH already added = 20 ml

Volume of 0.2 M NaOH to be added for complete neutralisation = 25 ml.

$\therefore$ Additional volume of 0.2 M NaOH to be added for getting pH (4.74) = 25 – 20 = **5 ml**

EXAMPLE 77. *The concentration of hydrogen ions in a 0.2 molar solution of formic acid is 6.4×10^{-3} mole per litre. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution? The dissociation constant of formic acid is 2.4×10^{-4} and degree of dissociation of sodium formate is 0.75.* **(IIT, 1985)**

SOLUTION. (*a*) K_a for formic acid

$$= 2.4 \times 10^{-4} \text{ mol L}^{-};$$

$$[H^+] = 0.2 \text{ M (given)}$$

Let $\quad x = [H^+]$ after the addition of HCOONa.

Formic acid (HCOOH) ionises as :

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

Applying law of mass action, we get

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} \qquad ...(1)$$

Here $\quad [HCOOH]_{\text{final}} = 0.2 - x$

$[HCOO^-]_{\text{final}}$ = $[HCOO^-]$ available from dissociation of HCOONa + $[HCOO^-]$ available from dissociation of HCOOH = $0.75 - x$

Substituting the values in equation (1), we get

$$2.4 \times 10^{-4} = \frac{x \times (0.75 - x)}{0.2 - x}$$

$$2.4 \times 10^{-4} \times 0.2 - 2.4 \times 10^{-4}x = 0.75x - x^2$$

x being small, x^2 and $2.4 \times 10^{-3}x$ are hence neglected.

$$\therefore \quad 0.75x = 0.48 \times 10^{-4} \ x = \frac{0.48 \times 10^{-4}}{0.75}$$

$$= 0.64 \times 10^{-4} \text{ mol L}^{-}$$
$$= 6.4 \times 10^{-5}$$

(*b*) $$pH = -\log[H^+] = -\log(6.4 \times 10^{-5})$$
$$= -(\log 6.4 - 5 \log 10)$$
$$= -0.8062 + 5$$
$$\mathbf{pH = 4.1938 \simeq 4.2}$$

EXAMPLE 78. *What is the pH of a 1.0M solution of acetic acid? To what volume must one litre of its solution be diluted so that the pH of the resulting solution will be twice the original volume? Given $K_a = 1.8 \times 10^{-5}$.* **(IIT, 1990)**

SOLUTION. Acetic acid ionises as,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Applying law of mass action, we have

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$
$$[\because [H^+] = [CH_3COO^-]]$$
$$[H^+]^2 = K_a[CH_3COOH]$$
$$= 1.8 \times 10^{-5} \times 1$$
$$\therefore \quad [H^+] = \sqrt{18 \times 10^{-6}} = 4.24 \times 10^{-3}$$
$$\therefore \quad pH = -\log[H^+] = -\log(4.24 \times 10^{-3})$$
$$= -(\log 4.24 - 3 \log 10)$$
$$= -\log 4.24 + 3$$
$$pH = -0.6274 + 3 = \mathbf{2.3726}$$

Required pH of diluted solution

$$= 2 \times 2.3726 = 4.7452 \simeq 4.74$$
$$\therefore \quad \text{pH required} = 4.74 - \log[H^+] = 4.74$$
$$\log[H^+] = -4.74 = -4 - 1 + 1 - 0.74$$
$$= \bar{5}.26$$

Taking antilogs of both sides,

we get $[H^+] = \text{antilog } \bar{5}.26 = 1.82 \times 10^{-5}$

Substituting $[H^+]$ in the expression K_a

$$= \frac{[H^+]^2}{[CH_3COOH] - [H^+]}$$
$$1.8 \times 10^{-5} = \frac{(1.82 \times 10^{-5})^2}{[CH_3COOH] - 1.82 \times 10^{-5}}$$
$$\therefore \quad [CH_3COOH] \times 1.8 \times 10^{-5} - 1.82 \times 10^{-5} \times 1.8 \times 10^{-5}$$
$$= (1.82 \times 10^{-5})^2$$
$$[CH_3COOH] = \frac{(1.82 \times 10^{-5})^2 + 1.82 \times 10^{-5} \times 1.8 \times 10^{-5}}{1.8 \times 10^{-5}}$$
$$= 3.66 \times 10^{-5}$$

∴ Volume of dil. CH_3COOH containing one mole of

$$\text{acid} = \frac{1}{3.66 \times 10^{-5}} = 2.732 \times 10^4 \text{ L}$$

∴ 1 litre solution should be diluted to 2.732×10^4 litre.

EXAMPLE 79. *A solution of HCl has a pH = 6. If one mL of it is diluted to one litre, what will be the pH of the resulting solution?*

SOLUTION. pH = 6 ; ∴ $[HCl] = 10^{-6}$; original volume= 1.0 mL ; required volume = 1000 mL

Original solution Diluted solution

$$N_1V_1 = N_2V_2 \text{ (normality equation)}$$
$$10^{-6} \times 1 = N_2 \times 1000$$
$$\therefore \quad N_2 = \frac{10^{-6} \times 1}{1000} = 10^{-9};$$
$$\therefore \quad [HCl] = 10^{-9}\text{M}.$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At start : x M xM

At equilibrium, total $[H^+]$: $(x + 10^{-9})$ M xM

But $K_w = [H^+][OH^-]$; ∴ $10^{-14} = (x + 10^{-9})(x)$

Or $x^2 + 10^{-9}x - 10^{-14} = 0$;

$$\therefore \quad x = \frac{-10^{-9} \pm \left[(10^{-9})^2 - 4(1 \times -10^{-14})\right]^{1/2}}{2 \times 1}$$
$$\because \text{ for } ax^2 + bx + c = 0, \; x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

Or $$x = \frac{-10^{-9} \pm (10^{-18} + 4 \times 10^{-14})^{1/2}}{2}$$
$$= \frac{-10^{-9} \pm (10^{-18}(1 + 40000)^{1/2}}{2}$$
$$= \frac{-10^{-9} + 10^{-9} \times 200}{2}$$

(– ive sign of ± is ignored because x can not be negative)

$$= \frac{10^{-9}(-1 + 200)}{2} = 9.95 \times 10^{-8}$$
$$\therefore \quad [H^+] = (x + 10^{-9})\text{ M} = 9.95 \times 10^{-8} + 10^{-9}$$
$$= 10^{-9}(9.95 \times 10 + 1) = 10^{-9}(99.5 + 1)$$
$$= 10^{-9} \times 100.5$$
$$\therefore \quad pH = -\log[H^+] = -\log 10^{-9} \times 100.5$$
$$= -(\log 10^{-9} + \log 100.5)$$
$$pH = -(-9 \log 10 + 2.002)$$
$$= 9 - 2.002 = \mathbf{6.998}$$

Ans.

EXAMPLE 80. *Calculate the pH of a solution which contains 3.01×10^{12} H^+ ions per cm^3 solution.*

SOLUTION. 1 Mol H^+ ions = 6.02×10^{23}

Given : 1 cm^3 solution contains H^+ ions = 3.01×10^{12}

∴ 1000 cm^3 *i.e.*, one litre solution contain H^+ ions

$$= \frac{3.01 \times 10^{12}}{1} \times 1000$$

$$= 3.01 \times 10^{15}$$

$\therefore$ no. of mol of H^+ ions

$$= \frac{3.01 \times 10^{15}}{6.02 \times 10^{23}} = 0.5 \times 10^{-8}$$

$$\therefore \quad pH = -\log [H^+] = -\log 0.5 \times 10^{-8}$$
$$= -(\log 0.5 + \log 10^{-8})$$
$$pH = -(-0.301 - 8) = 8 - 0.301$$
$$= \mathbf{7.699} \qquad \textbf{Ans.}$$

EXAMPLE 81. *The pH value of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionisation constant of the acid and its degree of ionisation in the solution.*

SOLUTION. (*a*) pH = 2.34 ; $\therefore$ – log [H^+] = 2.34 ;

Or [H^+] = antilog (– 2.34)

$$= \text{antilog} - 2 - 1 + 1 - 0.34 = \bar{3}.66 = 4.57 \times 10^{-3}$$

$$HCNO \rightleftharpoons H^+ + CNO^-$$
$$0.1 \qquad C\alpha \qquad C\alpha$$

$$C\alpha = [H^+]; \alpha = \frac{[H^+]}{C} = \frac{4.57 \times 10^{-3}}{0.1}$$
$$= \mathbf{4.57 \times 10^{-2}}$$

But
$$K_a = C\alpha^2 = 0.1 \times (4.57 \times 10^{-2})^2$$
$$= \mathbf{2.09 \times 10^{-4}} \qquad \textbf{Ans.}$$

EXAMPLE 82. *From the equilibrium $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ ($K_a = 4.8 \times 10^{-11}$), $[HCO_3^-] = 9.8 \times 10^{-2}$ M, $[CO_3^{2-}] = 1.1 \times 10^{-3}$M, calculate the pH of the solution.*

SOLUTION. $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

n mol at equilibrium 9.8×10^{-2} ? 1.1×10^{-3}

$$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]};$$

$$4.8 \times 10^{-11} = \frac{[H^+] \times 1.1 \times 10^{-3}}{9.8 \times 10^{-2}}$$

$$\therefore \quad [H^+] = \frac{4.8 \times 10^{11} \times 9.8 \times 10^{-2}}{1.1 \times 10^{-3}}$$
$$= 4.28 \times 10^{-9}$$

$$\therefore \quad pH = -\log [H^+] = -\log 4.28 \times 10^{-9}$$
$$= -[\log 4.28 + \log 10^{-9}]$$
$$pH = -[0.6314 - 9] = \mathbf{8.3686} \quad \textbf{Ans.}$$

EXAMPLE 83. *Calculate the pH value of 0.002 M HBr.*

(HP Board, 2007)

SOLUTION. $HBr \rightleftharpoons H^+ + Br^-$ (ionisation)

Conc. mol L^- 0.002 0.002

$$\therefore \quad (H^+) = 0.002 = \frac{2}{1000} = 2 \times 10^{-3}$$

$$\therefore \quad pH = -\log [H^+] = -\log (2 \times 10^{-3})$$
$$= -[\log 2 + \log 10^{-3}]$$
$$= -[0.301 - 3] = 3 - 0.301$$
$$pH = \mathbf{2.699} \qquad \textbf{Ans.}$$

EXAMPLE 84. *Calculate the molar concentration at which the pH of nitrous acid is 3.0. K_a for nitrous acid = 4.5 × 10^{-4}.*

SOLUTION. pH of HNO_2 = 3 ; $\therefore$ [H^+] = 10^{-3} M.

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$
$$x \qquad 10^{-3}\,M \quad 10^{-3}\,M$$

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]};$$

$$4.5 \times 10^{-4} = \frac{10^{-3} \times 10^{-3}}{x}$$

$$\therefore \quad x = \frac{10^{-3} \times 10^{-3}}{4.5 \times 10^{-4}} = 2.22 \times 10^{-3}\,M$$

$\therefore$ Molar concentration of HNO_2

$$= \mathbf{2.22 \times 10^{-3}\,M} \qquad \textbf{Ans.}$$

EXAMPLE 85. *Will pH value of water be same at temperature 25°C and 4°C. Justify it in not more than 2 or 3 sentences?*

SOLUTION. The pH value of a solution depends upon the hydrogen ion concentration which in turn depends upon the value of K_w. But K_w is a function of temperature. Thus, the change in temperature changes the pH value for a given sample of water.

EXAMPLE 86. *Find the pH, [H^+], [OH^-], [Na^+] and [Cl^-] of a solution obtained by mixing 40 mL of 0.3 M NaOH and 40 mL of 0.6 M HCl.*

SOLUTION. Reaction

$$NaOH + HCl \rightleftharpoons NaCl + H_2O$$

(1) m. equiv (= N_1V_1)

	NaOH	HCl	NaCl	H_2O
(1) m. equiv (= N_1V_1)	40 × 0.3 = 12	40 × 0.6 = 24	0	0
(2) m. equiv. after reaction	12 – 12 = 0	24 – 12 = 12	12	12

Total volume = 40 + 40 = 80 mL

Since both electrolytes (NaOH and HCl) are monovalent,

$$\text{hence molarity} = \text{normality} = \frac{\text{m. equiv.}}{\text{Total volume}}$$

$$\therefore \quad [Na^+] = \frac{12}{40} = 0.3\,M; [Cl^-] = \frac{12 + 12}{40}$$
$$= 0.6\,M$$

$$[H^+] = \frac{12}{40} = \mathbf{0.3\,M};$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{0.3}$$
$$= \mathbf{3.3 \times 10^{-14}\,M}$$

$$pH = -\log [H^+] = -\log 0.3$$
$$= -(-0.52) = \mathbf{0.52} \qquad \textbf{Ans.}$$

EXAMPLE 87. *60 cm^3 of HCl gas at 298 K and 740 mm pressure were dissolved in 500 cm^3 of water. If vapour pressure of water at 298 K is 23.7 mm, calculate the pH of the solution.*

SOLUTION. $$P(\text{HCl}) = \frac{740 - 23.7}{760} = 0.9425 \text{ atm.}$$

500 cm^3 water dissolves HCl gas = 60 cm^3

$\therefore$ 1000 cm^3 (= 1L) water dissolves HCl gas

$$= \frac{60}{500} \times 1000 = 120 \text{ cm}^3$$

Or $$V = \frac{120}{1000} = 0.12 \text{ L}$$

$$T = 298 \text{ K},$$

$$R = 0.0821 \text{ L atm K}^{-} \text{mol}^{-}$$

But $$PV = nRT\,; n = \frac{PV}{RT}$$

$$= \frac{0.9425 \text{ atm} \times 0.12 \text{ L}}{0.0821 \text{ L atm K}^{-}\text{mol}^{-} \times 298 \text{ K}}$$

$$= 4.6 \times 10^{-3} \text{ mol}$$

$$\therefore \quad \text{Molarity of HCl} = \frac{n}{\text{Volume of solution}}$$

$$= \frac{4.6 \times 10^{-3} \text{ mol}}{1 \text{ L}}$$

$$= 4.6 \times 10^{-3} \text{ mol L}^{-}$$

$$\therefore \quad [H^+] = [\text{HCl}] = 4.6 \times 10^{-3}$$

$$\therefore \quad pH = -\log [H^+] = -\log 4.6 \times 10^{-3}$$

$$= -(\log 4.6 + \log 10^{-3})$$

$$\mathbf{pH} = -(0.66 - 3) = 3 - 0.66$$

$$= \mathbf{2.34}$$ **Ans.**

EXAMPLE 88. *pH of a saturated solution of Ba (OH)$_2$ is 12. The value of solubility product (K_{sp}) of Ba(OH)$_2$ is:*

(a) 3.3 × 10^{-7} *(b) 5.0 × 10^{-7}*
(c) 4.0 × 10^{-6} *(d) 5.0 × 10^{-6}*

(AIPMT (Pre.) 2012)

SOLUTION. pH = 12 (given) . So, $[H^+] = 10^{-12}$

$$\therefore [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-12}} = 10^{-2}$$

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

Solubility: S 2S

$$\therefore 2S = 10^{-2}; \quad S = \frac{10^{-2}}{2}$$

$$K_{sp} = [Ba^{2+}]\,[OH^-]^2; K_{sp} = S \times (2S)^2 = 4S^3$$

$$= 4 \times \left(\frac{10^{-2}}{2}\right)^3 = \frac{4 \times 10^{-6}}{8} = 5 \times 10^{-7}.$$

So, the correct answer is (*b*).

EXAMPLE 89. *How many mol of calcium hydroxide must be dissolved to produce 250 mL of aqueous solution of pH 10.65? Assume complete dissociation.* **(Roorkee Entrance, 1987)**

SOLUTION. Given. $$\text{pH} = 10.65\,; \mathbf{pOH} = 14 - \text{pH}$$

$$= 14 - 10.65$$

$$= \mathbf{3.35}; \mathbf{pOH} = -\log [OH^-]$$

Or $$-\log [OH^-] = 3.35\,; \log [OH^-] = -3.35$$

$$= -3 - 1 + 1 - 0.35$$

$= \bar{4}.65$. Taking antilog of both sides, we get :

$$[OH^-] = \text{antilog } \bar{4}.65 = 4.47 \times 10^{-4}.$$

Mol of OH$^-$ ion in 1000 mL solution = 4.47×10^{-4}

Mol of OH$^-$ ion in 250 ml (= 1L) solution

$$= \frac{4.47 \times 10^{-4}}{1000} \times 250$$

$$= 1.12 \times 10^{-4} \text{ M}$$

$$\underset{1\text{ mol}}{Ca(OH)_2} \rightleftharpoons Ca^{2+} + \underset{2\text{ mol}}{2OH^-}$$

2 mol OH$^-$ ions ≡ 1 mol Ca(OH)$_2$

1.12×10^{-4} mol OH$^-$ ions

$$\equiv \frac{1}{2} \times 1.12 \times 10^{-4}$$

$$= \mathbf{5.6 \times 10^{-5}\ mol}$$

$\therefore$ mol of Ca(OH)$_2$ produced

$$= \mathbf{5.6 \times 10^{-5}\ mol}$$ **Ans.**

EXAMPLE 90. *The pH of 0.05 M aqueous solution of diethyl amine is 12. Calculate its K_b.* **(Roorkee entrance, 1993)**

SOLUTION. $[(C_2H_5)_2NH] = 0.05M\,; pH = 12.$

So, $$pOH = 14 - 12 = 2$$

$$\therefore \quad -\log [OH^-] = 2\,; [OH^-] = \text{antilog} - 2 = 0.01$$

$$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$$

(1) Conc. at start	0.05 M	0	0
(2) Change by reaction	− 0.01	0.01	0.01
(3) Conc. at equilibrium	0.05 − 0.01 = 0.04	0.01	0.01

$$\therefore \quad K_b = \frac{[(C_2H_5)_2NH_2^+]\,[OH^-]}{[(C_2H_5)_2NH]}$$

$$= \frac{0.01 \times 0.01}{0.04}$$

$$= \mathbf{2.5 \times 10^{-3}}$$ **Ans.**

EXAMPLE 91. *An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilium ion concentration remains at 1 × 10^{-8} M? K_a for $C_6H_5NH_3^+$ is 2.4 × 10^{-5} M.*

(Roorkee 1996)

SOLUTION. Anilium ion conc. *i.e.*, $[C_6H_5NH_3^+] = 10^{-8}$; $[C_6H_5NH_2] = 0.24M$

For the reaction :

$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$$

$$K_b = \frac{[C_6H_5NH_3^+]\,[OH^-]}{[C_6H_5NH_2]}$$

$$= \frac{10^{-8} \times [OH^-]}{0.24} \qquad ...(1)$$

Also, $$K_b\,(C_6H_5NH_2) = \frac{K_w}{K_a\,[C_6H_5NH_3^+]}$$

$$= \frac{10^{-14}}{2.4 \times 10^{-5}} \qquad ...(2)$$

From (1) and (2),L.H.S. = L.H.S. ; so , R.H.S. = R.H.S.

$$\therefore \quad \frac{10^{-8}\,[OH^-]}{0.24} = \frac{10^{-14}}{2.4 \times 10^{-5}}\,;$$

$$[OH^-] = \frac{10^{-14} \times 0.24}{2.4 \times 10^{-5} \times 10^{-8}} = 0.01$$

$\therefore$ $[OH^-] = [NaOH] = \mathbf{0.01}$ **Ans.**

24.6 INDICATOR

Example 92. *Find the value of pH at which an acid indicator with $K_a = 10^{-5}$ changes colour when the indicator is 10^{-3} M.*

Solution. *Reaction:* $H\,Ind + H_2O \rightleftharpoons Ind^- + H_3O^+$

Concentration $10^{-3}M$ $10^{-3}M$ x

$$\therefore \quad K_a \text{ or } K_{ind} = \frac{[Ind^-]\,[H_3O^+]}{[H\,Ind]}\,;$$

$$10^{-5} = \frac{10^{-3} \times x}{10^{-3}}$$

[At the colour change, $[Ind^-] = [H\,Ind]$]

$\therefore$ $x = [H_3O^+] = 10^{-5}$;

$pH = -\log [H_3O^+] = -\log 10^{-5}$

or **pH** $= -(-5 \log 10) = -(-5 \times 1)$

$= \mathbf{+5}$ **Ans.**

Example 93. *At what pH will a 10^{-3}M solution of an indicator with $K_b = 10^{-10}$ change colour?*

Solution. $Ind + H_2O \rightleftharpoons H\,Ind^+ + OH^-$

Conc. $10^{-3}M$ $10^{-3}M$ x

$$K_b = \frac{[H\,Ind^+]\,[OH^-]}{[Ind]}\,;$$

$$10^{-10} = \frac{10^{-3} \times [OH^-]}{10^{-3}}$$

$\therefore$ $[OH^-] = 10^{-10}$;

$pOH = -\log [OH^-] = -\log 10^{-10}$

$= -(-10 \log 10)$

Or $pOH = -(-10 \times 1) = +10.$

But $pH + pOH = 14$

$\therefore$ $pH = 14 - 10 = \mathbf{4}$ **Ans.**

pH ranges of some indicators

Indicator	pH range	Indicator	pH range
Cresol red (acid)	0.2 – 1.8	Cresol red (base)	7.0 – 9.1
Methyl orange	2.8 – 3.8	Thymol blue	0.8 – 1.8
Congo red	2.8 – 4.8		and 7.6 – 9.2
Methyl red	3.8 – 6.1	Phenolphthalein	8.0 – 9.6
Bromothymol blue	6.0 – 7.9	Thymolphthalein	10.2 – 11.7
Litmus	5.0 – 8.1	Tropeolin O	11.1 – 12.6
Phenol red	6.8 – 8.6		

Example 94. *Find the value of pH at which an indicator with $pK_b = 4$, changes colour.*

Solution. Reaction. $Ind + H_2O \rightleftharpoons H\,Ind^+ + OH^-$

At the colour change, $[H\,Ind^+] = [Ind]$

$$\therefore \quad K_b = \frac{[H\,Ind^+]\,[OH^-]}{[Ind]}\,;\ pK_b = 4.$$

Hence $pK_b = -\log K_b\,; 4 = -\log K_b\,;$

$K_b = 10^{-4}$

$$\therefore \quad 10^{-4} = \frac{[H\,Ind^+]\,[OH^-]}{[Ind]}$$

$= [OH^-]\,;\ pOH = -\log [OH^-]$

$pOH = -\log 10^{-4} = -(-4 \log 10) = 4.$

So, $pH = 14 - pOH = 14 - 4 = 10$

Hence **pH = 10** **Ans.**

Example 95. *The pH range for congo red and methyl red is 2.8 to 4.8 and 3.8 to 6.1 respectively. What indicator should be used for the titration of KH_2BO_3 with 0.1M HCl? ($K_a = 7.3 \times 10^{-10}$).*

Solution. ***Reaction.*** $H_2BO_3^- + H_3O^+ \rightleftharpoons H_3BO_3 + H_2O$

At the equivalence point, concentration of H_3BO_3 produced would be 0.1/2 = 0.05M. Only the first ionisation step of H_3BO_3 is important to the pH determination.

$$H_3BO_3 + H_2O \rightleftharpoons H_2BO_3^- + H_3O^+$$

Conc. at equivalence

point 0.05 x x

$$\therefore \quad K_a = \frac{[H_2BO_3^-]\,[H_3O^+]}{[H_3BO_3]}$$

$$7.3 \times 10^{-10} = \frac{x \times x}{0.05}\,;$$

$x = (7.3 \times 10^{-10} \times 0.05)^{1/2}$

$= (36.5 \times 10^{-12})^{1/2}$

$x = 6 \times 10^{-6}\,;\ [H_3O^+] = 6 \times 10^{-6}$

$\therefore$ $pH = -\log [H_3O^+] = -\log 6 \times 10^{-6}$

$= -(\log 6 + \log 10^{-6})$

$pH = -(0.78 - 6) = 5.22.$

This pH range is the middle of pH range of methyl red indicator. Hence indicator used should be methyl red.

EXAMPLE 96. *At what pH does an indicator change colour if the indicator is a weak acid ? $K_{ind} = 4 \times 10^{-4}$. For which one (s) of the following neutralisations would the indicator be useful? Explain.*

(*i*) $HCl + NH_3 \rightarrow$ (*ii*) $NaOH + HCl \rightarrow$

(*iii*) $NaOH + CH_3COOH \rightarrow$

SOLUTION. Reaction.

$$\underset{\text{conjugate acid}}{H\,Ind} + H_2O \rightleftharpoons \underset{\text{conjugate base}}{Ind} + H_3O^+$$

At colour change,

$$[\text{conjugate acid}] = [\text{conjugate base}]$$

$$\therefore \qquad K_{\text{ind}} = \frac{[Ind^-][H_3O^+]}{[H\,Ind]};$$

$$4 \times 10^{-4} = [H_3O^+]$$

$$\therefore \qquad pH = -\log [H_3O^+]$$

$$= -\log 4 \times 10^{-4};$$

$$-(\log 4 + \log 10^{-4})$$

$$= -(0.6 - 4) \ \textbf{Or}\ \boldsymbol{pH = 3.4.}$$

The indicator is a weak acid (given). In reaction (*i*), NH_4Cl (acidic) is formed and in reaction (*ii*), NaCl (neutral) is formed at the equivalence point. So, the indicator used will be useful. In reaction (*iii*), CH_3COONa (basic) is formed and its pH will be more than 7. So, the indicator which changes colour in acid would not be suitable.

EXAMPLE 97. Name the suitable indicator which indicates the equivalence point when 50 mL of 0.1 M HCN is titrated with 0.1 M NaOH. pH range of indicator for thymolphthalein = 10.2 to 11.7 ; Cresol red = 7.0 to 9.1. $K_a = 6.2 \times 10^{-10}$.

SOLUTION. At the equivalence point, NaCN is formed.

no. of m mol of NaCN, if equal number of m mol NaOH and HCN react completely

$$= 50 \times 0.1 = 5 \text{ m mol}$$

So, the solution is the equivalent of a 0.1/2 or 0.05M solution of HCN. Hence, we have:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Conc. at equivalence point $\quad 0.05 - x \simeq 0.05 \qquad x \qquad x$

$$0.05 - x \simeq 0.05$$

because x is very small as compared to 0.05 and hence ignored.

$$\therefore \qquad K_h = \frac{[HCN][OH^-]}{[CN^-]} \qquad \ldots (1)$$

$$\text{Also,} \qquad K_h = \frac{K_w}{K_a} \qquad \ldots (2)$$

From (1) and (2), we get :

$$\frac{K_w}{K_a} = \frac{[HCN][OH^-]}{[CN^-]};$$

$$\frac{10^{-14}}{6.2 \times 10^{-10}} = \frac{x \times x}{0.05};$$

$$x = \left(\frac{10^{-14} \times 0.05}{6.2 \times 10^{-10}}\right)^{1/2}$$

$$= (80.6 \times 10^{-8})^{1/2} = 8.9 \times 10^{-4}$$

$$\text{or} \qquad [OH^-] = 8.9 \times 10^{-4}; pOH = -\log [OH^-]$$

$$= -\log 8.9 \times 10^{-4}$$

$$= -(\log 8.9 + \log 10^{-4});$$

$$pOH = -(0.95 - 4) = 3.05$$

$$\therefore \qquad pH = 14 - pOH = 14 - 3.05 = \mathbf{10.95}$$

This pH lies in the middle of pH range of thymolphthalein indicator. So suitable indicator is thymolphthalein.

EXAMPLE 98. *The K_a value of an acid indicator, bromophenol blue is 5.84×10^{-5}. Calculate the % age of this indicator in its basic form at a pH of 4.84.*

SOLUTION. $pH = 4.84; -\log [H_3O^+] = 4.84;$

$$\log [H_3O^+] = -4.84$$

$$= -4 - 1 + 1 - 0.84\ \bar{5}.16;$$

$$\therefore \qquad [H_3O^+] = \text{antilog}\ \bar{5}.16 = 1.44 \times 10^{-5}.$$

Reaction $\quad H\,Ind + H_2O \rightleftharpoons Ind^- + H_3O^+$

$$\therefore \qquad K_a = \frac{[Ind^-][H_3O^+]}{[H\,Ind]};$$

$$5.84 \times 10^{-5} = \frac{[Ind^-][H_3O^+]}{[H\,Ind]}$$

$$\therefore \qquad \frac{[Ind^-]}{[H\,Ind]} = \frac{5.84 \times 10^{-5}}{1.44 \times 10^{-5}} = \frac{4.05}{1}$$

$\therefore$ % age of basic form

$$= \frac{[Ind^-]}{[Ind^-] + [H\,Ind]} \times 100$$

$$= \frac{4.05}{4.05 + 1} \times 100$$

$$= \mathbf{80\%}$$

Ans.

EXAMPLE 99. *The K_a value of an indicator is 3.0×10^{-5}. The acidic and basic forms of this indicator have red and blue colour respectively. By how much the pH would change in order to change the indicator from 75% red to 75% blue?*

SOLUTION. (*a*) $\qquad K_a = 3.0 \times 10^{-5};$

[acid] for 75% red = 75 and [base] = 100 − 75 = 25

$$\text{But} \qquad [H^+] = \frac{K_a\,[\text{acid}]}{[\text{base}]}.\ \text{75\% red:}$$

$$[H^+] = \frac{3.0 \times 10^{-5} \times 75}{25} = 9.0 \times 10^{-5}$$

$$\therefore \qquad pH = -\log [H^+]\ -\log 9.0 \times 10^{-5}$$

$$= -(\log 9 + \log 10^{-5})$$

$$= -(0.95 - 5);\ \mathbf{pH = 4.05}$$

(*b*) $K_a = 3.0 \times 10^{-5}$;

[acid] for 75% blue = 100 – 75 = 25, [base] = 75

$$\therefore \quad [H^+] = \frac{K_a\,[\text{acid}]}{[\text{base}]};$$

$$[H^+] = \frac{3.0 \times 10^{-5} \times 25}{75} = 10^{-5}$$

$$\therefore \quad pH = -\log [H^+] = -\log 10^{-5}$$
$$= -(\log 10^{-5}) = -(-5 \log 10)$$
$$= +5.0$$

$\therefore$ Change in $pH = 5.0 - 4.05 = 0.95$.

Example 100. *The pH range of an indicator (weak acid) at which it changes its colour is 3.1 to 4.5. If the neutral point of the given indicator is in the centre of this pH range, calculate the ionisation constant of the indicator.*

Solution. We know that pH values are exponential in form. So, centre of the range may not be calculated by averaging the pH value. Hence, centre of range can be obtained by averaging the corresponding H^+ ion concentration. Hence, we have :

(*a*) $pH = 3.1 ; -\log [H^+] = 3.1$;

$$\log [H^+] = -3.1 = -3 - 1 + 1 - 0.1 = \bar{4}.9$$

$$\therefore \quad [H^+] = \text{antilog } \bar{4}.9 = 7.9 \times 10^{-4}$$

(*b*) $pH = 4.5 ; -\log [H^+] = 4.5 ; \log [H^+]$

$$= -4.5 = -4 - 1 + 1 - 0.5 = \bar{5}.5$$

$$\therefore \quad [H^+] = \text{antilog } \bar{5}.5 = 3.16 \times 10^{-5}$$
$$= 0.316 \times 10^{-4}$$

$\therefore$ Average value of $[H^+] = (7.9 \times 10^{-4} + 0.316 \times 10^{-4})/2$

$$= \frac{10^{-4}\,(7.9 + 0.316)}{2}$$

$[H^+] \simeq 4.1 \times 10^{-4}$. But $[H^+] = K$.

Hence, $\boldsymbol{K = 4.1 \times 10^{-4}}$ **= Ionisation constant.**

Example 101. *An acid type indicator H In differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$)?* **(IIT 1997, Re-exam)**

Solution. $\dfrac{[In]^-}{[H\,In]} = 10 \text{ or } 0.1 \quad (i.e., 10^{-1})$

But $pH = pK_{In} \pm 1$ ...(1)

$(\because \log 10 = 1 \text{ and } \log 10^{-1} = -1)$

Also, $pK_{In} = -\log K_{In} = -\log 10^{-5} = -(-5)$
$= +5$

$\therefore$ From equation (1),

$pH = 5 \pm 1$ *i.e.*, 6 or 4.

$\therefore$ **pH interval** = 6 or 4.

Hence, minimum pH change

= **6 – 4 = 2 pH unit** **Ans.**

Example 102. *Find the pH of a solution obtained at the equivalence point when 0.2M , 20mL CH_3COOH was titrated with 0.1M NaOH solution, K_a (CH_3COOH) = 1.8×10^{-5}.*

Solution. Molarity (M_1) of CH_3COOH = 0.2M ; Volume (V_1) = 20 mL. Molarity (M_2) of NaOH = 0.1M ; Volume (V_2) =?

We know : CH_3COOH NaOH

$$M_1V_1 = M_2V_2$$

$$\therefore \quad 0.2 \times 20 = 0.1 \times V_2$$

Or $V_2 = (0.2 \times 20)/0.1 = 40$ mL.

Concentration of salt formed

$$= \frac{\text{Millimoles of acid}}{\text{Total volume}}$$

$$= \frac{20 \times 0.2}{20 + 40\,(= 60)} = \frac{0.2}{3}$$

We know, $K_w = 10^{-14}$

$$\therefore \quad [H^+] = \left(\frac{K_w . K_a}{C}\right)^{1/2}$$

$$= \left(\frac{10^{-14} \times 1.8 \times 10^{-5}}{0.2/3}\right)^{1/2}$$

$$= (2.7 \times 10^{-18})^{1/2} = 1.6432 \times 10^{-9}$$

$$\therefore \quad pH = -\log [H^+]$$
$$= -(\log 1.6432 \times 10^{-9})$$
$$= [0.2157 - 9] = \mathbf{8.7843} \quad \textbf{Ans.}$$

24.7 COMMON ION EFFECT

Type. For solutions containing common ion, use the relations :

(1) $K_c = \dfrac{C\alpha^2}{1 - \alpha}$;

(2) $\dfrac{\text{Ionic concentration}}{\text{of common ion}}$ = $\dfrac{\text{Gross con-}}{\text{centration}}$ × $\dfrac{\text{fraction}}{\text{ionised}(\alpha)}$

Example 103. *0.1 g mol of ammonium acetate has been dissolved in one litre of 0.1M acetic acid. Calculate $[H_3O^+]$ in this solution. [K (ionisation of acetic acid = 1.8×10^{-5} ; effective ionisation of ammonium acetate = 80%).*

Solution. 0.1 g mol L^- of ammonium acetate in solution = 0.1M

Gross concentration of acetic acid in solution = 0.1M

Acetic acid ionises as

$$(CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-)$$

(1) n mol at start

0.1 – 0 0

(2) Change by reaction

$-x$ x x

(3) n mol at equilibrium

$0.1 - x$ x x

x = mol *i.e.*, amount of CH_3COOH ionised.

$$\therefore \qquad K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} \qquad ...(1)$$

Substituting these values in equation (1), we get

$$K_c = \frac{x \times x}{0.1 - x} = 1.8 \times 10^{-5} \text{ (given)}$$

$$\frac{x^2}{0.1 - x} = 1.8 \times 10^{-5}$$

x being very small, is ignored in the denominator. So, we get :

$$x^2 = 0.1 \times 1.8 \times 10^{-5} = 1.8 \times 10^{-6}$$

$$\therefore \qquad x = \sqrt{1.8 \times 10^{-6}} = 1.3 \times 10^{-3} \qquad ...(2)$$

Ammonium acetate CH_3COONH_4 also ionises to give CH_3COO^- (common ion)

$\therefore$ Ionic concentration of CH_3COO^- = gross concentration × Fraction ionised (α)

$$= 0.1 \times 0.8 = 0.08 \text{ g mol L}^-$$

$$\left[\because 80\% = \frac{80}{100} = 0.8\right]$$

$\therefore$ Total concentration of CH_3COO^- ions in solution

$$= \mathbf{0.8} + x$$

Substituting this value in equation (1), we get

$$K_c = \frac{x \times (0.8 + x)}{0.1 - x} = 1.8 \times 10^{-5} \text{ (given)}$$

In order to avoid quadratic equation in x, x (being very small) is avoided from denominator as well as numerator (*i.e.*, $0.08 + x \simeq 0.08$)

$$\text{So, we have } \frac{x \times 0.08}{0.1} = 1.8 \times 10^{-5};$$

$$x = \frac{0.1 \times 1.8 \times 10^{-5}}{0.08}$$

Or $\qquad x = \mathbf{2.2 \times 10^{-5}}$

Hence $\quad [H_3O^+] = 2.2 \times 10^{-5}$ g mol L$^-$

This value of x is a reduced value of $[H_3O^+]$ (see equation, 2 in acetic acid solution in the presence of ammonium acetate having common ion, CH_3COO^- with acetic acid, (CH_3COO^- + H^+). This reduction value is about one fifty ninth of the original value, 1.3×10^{-3}. The reduction of ionisation of acetic acid in presence of common ion, CH_3COO^- is called common ion effect.

Type Weak acid + salt of weak acid with a strong base.

Example 104. *A 100 mL solution contains 0.01 mol of acetic acid and 0.01 mol of sodium acetate. Calculate its hydronium ion concentration in mol L⁻ if K_a (CH_3COOH) = 1.8×10^{-5}.*

Solution. $[CH_3COOH]$ in mol L$^-$

$$= \frac{0.01}{100} \times 1000 = 0.1 \text{ M}$$

[$\because$ Volume of solution = 100 mL]

$$[CH_3COONa] \text{ in mol L}^- = \frac{0.01}{100} \times 1000 = 0.1 \text{ M}$$

	$CH_3COOH + H_2O$	$\rightleftharpoons$ CH_3COO^-	$+ H_3O^+$
(1) n. mol at start	0.1	0.1	0
(2) Change by reaction	$-x$	x	x
(3) n mol at equilibrium	$0.1 - x$	$0.1 + x$	x

x = Degree of ionisation of CH_3COOH

$$\therefore \qquad K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]};$$

$$1.8 \times 10^{-5} = \frac{(0.1 + x) \times x}{0.1 - x} = \frac{0.1x}{0.1} = x$$

[Since x is very small as compared to 0.1, $0.1 + x \simeq 0.1$ and $0.1 - x \simeq 0.1$] **Or** $x = 1.8 \times 10^{-5}$.

Hence $\qquad [H_3O^+] = x = \mathbf{1.8 \times 10^{-5}}$ **Ans.**

Example 105. *In case of 2×10^{-2}M H_3PO_4, what will be the value of $[H^+]$, $[H_2PO_4^-(aq)]$, $[HPO_4^{2-}(aq)]$ and* $[PO_4^{3-}]$ *K_1, K_2 and K_3 respectively are 8.5×10^{-3}, 7.2×10^{-8} and 5.4×10^{-13}.*

Solution. (*i*) $H_3PO_4 \xrightleftharpoons{H_2O} H^+(aq) + H_2PO_4^-(aq)$;

$$[H_3PO_4] = 2 \times 10^{-2};$$

$$K_1 = \frac{[H^+(aq)][H_2PO_4^-(aq)]}{[H_3PO_4]};$$

$$8.5 \times 10^{-3} = \frac{[H^+(aq)][H^+(aq)]}{[H_3PO_4]};$$

$$[\because [H^+(aq)]] = [H_2PO_4^-(aq)]$$

Or $\quad [H^+(aq)]^2 = 8.5 \times 10^{-3} \times [H_3PO_4]$

$$= 8.5 \times 10^{-3} \times 2 \times 10^{-2}$$

$$\therefore \qquad [H^+(aq)] = (8.5 \times 10^{-3} \times 2 \times 10^{-2})^{1/2}$$

$$= (1.7 \times 10^{-4})^{1/2} = \mathbf{1.3 \times 10^{-2}}$$

Or $\quad [H^+(aq)] = [H_2PO_4^-(aq)] = \mathbf{1.3 \times 10^{-2}}$ **Ans.**

(*ii*) $H_2PO_4^-(aq) \xrightleftharpoons{H_2O} H^+(aq) + HPO_4^{2-}(aq)$

$$\therefore \qquad K_2 = \frac{[H^+(aq)][HPO_4^{2-}(aq)]}{[H_2PO_4^-(aq)]};$$

$$7.2 \times 10^{-8} = [HPO_4^{2-}(aq)]$$

$$[\because [H^+(aq)] = [H_2PO_4^-(aq)]]$$

$\therefore \quad [HPO_4^{2-}(aq)] = \mathbf{7.2 \times 10^{-8}}$ **Ans.**

(*iii*) $HPO_4^{2-}(aq) \xrightleftharpoons{H_2O} H^+(aq) + PO_4^{3-}(aq)$

$$K_3 = \frac{[H^+(aq)][PO_4^{3-}(aq)]}{[HPO_4^{2-}(aq)]};$$

$$5.4 \times 10^{-13} = \frac{1.3 \times 10^{-2} \times [PO_4^{3-}(aq)]}{7.2 \times 10^{-8}}$$

$$\therefore \quad [PO_4^{3-}(aq)] = \frac{5.4 \times 10^{-13} \times 7.2 \times 10^{-8}}{1.3 \times 10^{-2}}$$

$$= \mathbf{2.99 \times 10^{-18}}$$ **Ans.**

IV Weak acid + weak acid. Let weak acid (HA) and weak acid (HB) have concentrations C_1 and C_2 respectively. Let dissociation constants of weak acid HA is Ka_1 and weak acid HB is Ka_2. Thus we have :

	HA	$\rightleftharpoons$	H^+	A^-
Conc. at	$C_1 - C_1\alpha_1$		$C_1\alpha_1$	$C_1\alpha_1$
equilibrium	$= C_1(1-\alpha_1)$			
	HB	$\rightleftharpoons$	H^+	B^-
Conc. at	$C_2 - C_2\alpha_2$		$C_1\alpha_1$	$C_2\alpha_2$
equilibrium	$= C_2(1-\alpha_2)$		$+ C_2\alpha_2$	$+ C_2\alpha_2$

$$\therefore \quad Ka_1 = \frac{[A^-][H^+]}{[HA]}$$

$$= \frac{(C_1\alpha_1)(C_1\alpha_1 + C_2\alpha_2)}{C_1(1-\alpha_1)} \quad ...(1)$$

$$Ka_2 = \frac{[B^-][H^+]}{[HB]}$$

$$= \frac{(C_2\alpha_2)(C_1\alpha_1 + C_2\alpha_2)}{C_2(1-\alpha_2)} \quad ...(2)$$

By solving equations (1) and (2), α can be calculated. From the value of α, $[H^+]$ and then pH can be calculated.

EXAMPLE 106. *500 mL each of two weak monobasic organic acids HA and HB having molarity 1M each were mixed to give one litre solution. Ka_1 for HA = 1.5×10^{-5} and Ka_2 for HB = 1.8×10^{-5}. Calculate the pH of the mixed solution.*

SOLUTION. Since equal volumes (500 mL) of acids HA and HB are mixed to give one litre solution, the concentration of HA and HB in the mixture = 0.5M = C (suppose)

$$\therefore \quad HA \rightleftharpoons \underset{C_1}{H^+} + \underset{C_1}{A^-}$$

$$HB \rightleftharpoons \underset{C_2}{H^+} + \underset{C_2}{B^-}$$

$$\therefore \quad [H^+]_{total} = C_1 + C_2$$

$$K_{HA} = \frac{[H^+][A^-]}{[HA]} = \frac{(C_1 + C_2) \times C_1}{C}; \quad ...(1)$$

$$K_{HB} = \frac{[H^+][B^-]}{[HB]} = \frac{(C_1 + C_2) \times C_2}{C}; \quad ...(2)$$

$$\therefore \quad \frac{K_{HA}}{K_{HB}} = \frac{(C_1 + C_2)C_1}{C} \times \frac{C}{(C_1 + C_2)C_2} = \frac{C_1}{C_2}$$

$$\frac{1.5 \times 10^{-5}}{1.8 \times 10^{-5}} = \frac{C_1}{C_2} \text{ or } 18C_1 = 15C_2 \text{ or } 6C_1 = 5C_2$$

$$\therefore \quad C_1 = \frac{5}{6}C_2.$$

Substituting the value of C_1 is (1), we get :

$$1.5 \times 10^{-5} = \frac{\left(\frac{5}{6}C_2 + C_2\right) \times \frac{5}{6}C_2}{0.5}$$

$$= \frac{\frac{25}{36}C_2^2 + \frac{5}{6}C_2^2}{0.5} = \frac{\frac{25C_2^2 + 30C_2^2}{36}}{0.5}$$

$$1.5 \times 10^{-5} \times 0.5 \times 36 = 55C_2^2$$

$$\text{Or} \quad C_2^2 = \frac{1.5 \times 10^{-5} \times 0.5 \times 36}{55} = 4.909 \times 10^{-6}$$

$$\therefore \quad C_2 = (4.909 \times 10^{-6})^{1/2} = \mathbf{2.21 \times 10^{-3}}$$

$$\text{Since} \quad 6C_1 = 5C_2, 6C_1 = 5 \times 2.21 \times 10^{-3}$$

$$\text{Or} \quad C_1 = \frac{5 \times 2.21 \times 10^{-3}}{6} \quad \therefore \; C_1 = \mathbf{1.84 \times 10^{-3}}$$

$$\text{But} \quad [H^+] = C_1 + C_2 = 1.84 \times 10^{-3} + 2.21 \times 10^{-3}$$

$$= 10^{-3}[1.84 + 2.21] = 10^{-3} \times 4.05$$

$$\therefore \quad pH = -\log[H^+] = -[\log 10^{-3} \times 4.05]$$

$$= -[\log 10^{-3} + \log 4.05]$$

$$\mathbf{pH} = -[-3 + 0.6074] = 3 - 0.6074$$

$$= \mathbf{2.3926}$$ **Ans.**

Type. Weak acid + weak acid

EXAMPLE 107. *A solution contains 0.15M CH_3COOH and 0.25M HCN. Calculate $[H^+]$, $[CN^-]$ and $[CH_3COO^-]$ if K_a $[CH_3COOH] = 1.8 \times 10^{-5}$ and K_a (HCN) = 6.2×10^{-10}.*

SOLUTION.

$$(a) \quad CH_3COOH \xrightleftharpoons{H_2O} CH_3COO^-(aq) + H^+(aq)$$

	CH_3COOH	$CH_3COO^-(aq)$	$H^+(aq)$
(1) n mol at start	0.15	0	0
(2) Change by reaction	$-x$	x	x
(3) n mol at equilibrium	$0.15 - x$	x	x

x = degree of ionisation

$$K_a = \frac{[CH_3COO^-(aq)][H^+(aq)]}{[CH_3COOH]};$$

$$1.8 \times 10^{-5} = \frac{x \times x}{0.15 - x} \text{ or } \frac{x^2}{0.15}$$

$$\therefore \quad x = (1.8 \times 10^{-5} \times 0.15)^{1/2};$$

$$x = (2.7 \times 10^{-6})^{1/2} = 1.64 \times 10^{-3}$$

$$\therefore \quad [H^+(aq)] = [CH_3COO^-(aq)]$$

$$x = \mathbf{1.64 \times 10^{-3}M}$$ **Ans.**

$$(b) \quad HCN \xrightleftharpoons{H_2O} H^+(aq) + CN^-(aq)$$

(1)n mol at start

0.25 $\quad 1.64 \times 10^{-3} \quad$ 0

(2)Change by reaction

$y \quad y \quad y$

(3)n mol at equilibrium

$0.25 + y \quad (1.64 \times 10^{-3}) + y \quad y$

y = degree of ionisation

$$\therefore \quad K_a = \frac{[H^+(aq)][CN^-(aq)]}{[HCN]};$$

$$6.2 \times 10^{-10} = \frac{\left[(1.64 \times 10^{-3}) + y\right] \times y}{0.25 + y};$$

$$6.2 \times 10^{-10} = \frac{1.64 \times 10^{-3} y}{0.25}$$

[$\because$ y being very small, it can be neglected]

Or $$y = \frac{6.2 \times 10^{-10} \times 0.25}{1.64 \times 10^{-3}} = 9.45 \times 10^{-8}$$

$\therefore$ $[CN^-(aq)] = y =$ **9.45×10^{-8}M Ans.**

24.8 BUFFER SOLUTIONS

A buffer solution is that which resists the change in pH of a solution when a small amount of an acid, base or water is added to it. Three types of buffers are :

1. **Acid buffer.** It is solution of weak acid and the salt of this weak acid with a strong base. *e.g.*, $CH_3COOH + CH_3COONa$. The $[H^+]$ and pH of such solutions can be calculated with the help of following relations.

$$[H^+] = K_a \frac{[Acid]}{[Salt]};$$

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

2. **Basic buffer.** It is a solution of a weak base and the salt of this weak base with a strong acid. *e.g.*, $NH_4OH + NH_4Cl$. The pOH and pH of such solutions can be calculated with the help of following relations.

$$pOH = pK_b + \log \frac{[salt]}{[base]};$$

$$pH = 14 - pK_b - \log \frac{[salt]}{[base]}$$

3. **Salt buffer.** It is a solution of a salt which itself acts as a buffer. The salt is of a weak acid with a weak base. *e.g.*, CH_3COONH_4.

Note. When water is added to a buffer solution, no change in the pH of the solution takes place. It is because the volume change caused by the addition of water effects both the concentration of acid and the salt and the volumes, actually cancel each other.

EXAMPLE 108. *Write a relation (a) between pH and pK_a of an acid buffer solution (b) between pH and pK_b of a basic buffer.*

SOLUTION. (*a*) **For acid buffer,**

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

(*b*) **For basic buffer,** $pH = 14 - pK_b - \log \dfrac{[salt]}{[base]}$

Or $\quad p_{OH} = pK_b + \log \dfrac{[salt]}{[base]}$

EXAMPLE 109. *If 100 mL of 0.1 M CH_3COOH is mixed with 200 mL of 0.5 M CH_3 COONa, what will be the pH of the resulting solution? K_a for CH_3 COOH = 1.75×10^{-5}* **(ISC, 2011)**

SOLUTION. (*a*) Total volume of solution = 100 mL + 200 mL = 300 mL; K_a for $CH_3COOH = 1.75 \times 10^{-5}$.

(i) 100 mL of 0.1 M $CH_3COOH = 100 \times 0.1 = 10$ m mol.

(ii) 200 mL of 0.5 M $CH_3COOH = 200 \times 0.5 = 100$ m mol.

$$\therefore \quad [CH_3COOH] = [H^+] = \frac{10}{300} \times \frac{1000}{1000} = \frac{1}{30}$$

$$[CH_3COONa] = \frac{100}{300} \times \frac{1000}{1000} = \frac{1}{3}$$

But $\quad pK_a = -\log K_a = -[\log 1.75 \times 10^{-5}]$

$= -[\log 1.7 - 5 \log 10\ (=1)]$

$= -0.2430 + 5 = 4.757$

$$\therefore \quad pH = pK_a + \log \frac{[salt]}{[acid]};$$

$$pH = 4.757 + \log \frac{1/3}{1/30} \ (= 10)$$

$= 4.757 + 1 = 5.757$ **Ans**

[$\because$ log 10 = 1].

EXAMPLE 110. *Calculate the pH of (i) a solution obtained by mixing (i) 40 mL of 0.05 M NaOH and 40 mL of 0.1N CH_3COOH ($K_a = 1.8 \times 10^{-5}$) (ii) 40 mL of 0.05M HCl and 40mL of 0.1M NH_4OH. ($K_b = 1.8 \times 10^{-5}$)*

SOLUTION. (*i*)Number of millimoles of NaOH

$= 40 \times 0.05 = 2$

Number of millimoles of CH_3COOH

$= 40 \times 0.1 = 4$

$\therefore$ Millimoles of CH_3COOH reacted

= millimoles of NaOH = 2

($\because$ 2 < 4)

$$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$$

Millimoles before

reaction : $\quad 2 \quad 4$

Millimoles after

reaction : $\quad 4 - 2 = 2 \quad 2$

Total volume of solution

= 40 mL + 40 mL = 80 mL.

$$\therefore \quad [CH_3COOH] = \frac{2}{80} M \ ; [CH_3COONa, salt]$$

$$= \frac{2}{80}\,\text{M}.$$

$$\text{Hence, pH} = \text{p}K_a + \log\frac{[\text{salt}, CH_3COONa]}{[\text{acid}, CH_3COOH]} \quad ...(1)$$

$$K_a = 1.8 \times 10^{-5};$$

$$\therefore \quad \text{p}K_a = -\log K_a = -[\log 1.8 + \log 10^{-5}]$$
$$= -[0.2552 - 5]$$
$$\simeq 4.74.$$

Substituting the values in equation (1), we have :

$$\text{pH} = 4.74 + \log\frac{2/80}{2/80}$$
$$= 4.74 + \log 1$$
$$= 4.74 + 0 = \mathbf{4.74} \qquad \textbf{Ans.}$$

(*ii*) Number of millimoles of NH_4OH

$$= 40 \times 0.1 = 4$$

Number of millimoles of HCl

$$= 40 \times 0.05 = 2$$

∴ Millimoles of NH_4OH reacted = number of millimoles of HCl = 2

Total volume of solution = 40 mL + 40 mL = 80 mL.

	NH_4OH +	HCl $\longrightarrow$	NH_4Cl +	H_2O
Millimoles before reaction	4	2		
Millimoles after reaction	4 − 2 = 2		2	

$$\therefore \quad [NH_4OH] = \frac{2}{80}\,\text{M};$$

$$[NH_4Cl\ \text{salt}] = \frac{2}{80}\,\text{M}.$$

$$K_b = 1.8 \times 10^{-5};\ \text{p}K_b = -\log K_b$$
$$= -\log 1.8 \times 10^{-5}$$
$$= -[\log 1.8 + \log 10^{-5}]$$
$$= -[0.2552 - 5] = 4.74$$

Substituting the values in pOH

$$= \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]}, \text{ we have}$$

$$\text{pOH} = 4.74 + \log\frac{2/80}{2/80}$$
$$= 4.74 + \log 1 = 4.74 + 0 = 4.74$$

$$\text{But} \quad \mathbf{pH} = 14 - \text{pOH}$$
$$\textbf{Or} \quad \text{pH} = 14 - 4.74 = \mathbf{9.26} \qquad \textbf{Ans.}$$

EXAMPLE 111. *What is the $[H^+]$ in mol L^- of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH? K_a for acetic acid is 1.8×10^{-5}* **(CBSE, PMT 2010)**

(*a*) 3.5×10^{-4} (*b*) 1.1×10^{-5} (*c*) 1.8×10^{-5} (*d*) 9.0×10^{-6}

SOLUTION.

$$\begin{array}{ccc} CH_3COOH & \rightleftharpoons & CH_3COO^- + H^+ \\ C - x & & x \qquad x \\ CH_3COONa & \rightleftharpoons & CH_3COO^- + Na^+ \\ 0.2\,M & & 0.2M \quad 0.2M \end{array}$$

$$[CH_3COOH] = C - x = 0.1\,M;$$
$$[CH_3COO^-] = 0.2 + x = 0.2\,M$$
$$\therefore \quad [H^+] = K_a \times [CH_3COOH]/[CH_3COO^-]$$
$$= 1.8 \times 10^{-5} \times 10^{-1}/2 \times 10^{-1}$$
$$= 9 \times 10^{-6}\,M.$$

So, correct answer is (*d*).

Note: CH_3COOH being weak, dissociates to least extent.

EXAMPLE 112. *How will you prepare a buffer solution of pH 4.70 using acetic acid and sodium acetate? K_a for $CH_3COOH = 1.75 \times 10^{-5}$.* **(Kanpur I.E.T. 1996)**

SOLUTION. $K_a = 1.75 \times 10^{-5}$. For buffer solution of a weak acid with sodium salt of this weak acid :

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$= -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$4.7 = -\log(1.75 \times 10^{-5}) + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$4.7 = -[\log 1.75 + \log 10^{-5}] + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$4.7 = -[0.24 - 5] + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$\textbf{Or} \quad \log\frac{[\text{salt}]}{[\text{acid}]} = 4.7 + 0.24 - 5 = -0.06$$
$$= -1 + 1 - 0.06 = \bar{1}.94$$
$$\text{or} \quad \frac{[\text{salt}]}{[\text{acid}]} = \text{antilog}\ \bar{1}.94 = 8.7 \times 10^{-1} = \frac{0.87}{1}$$
$$\text{or} \quad \frac{[\text{acid}]}{[\text{salt}]} = \frac{1}{0.87} = 1.15$$

i.e., the ratio in which concentration of acetic acid and sodium acetate should be used is 1 : 1.15.

EXAMPLE 113. *Suppose one litre of a buffer (pH = 5.4) has to be prepared from NH_4Cl and NH_4OH. If 0.1 mol of NH_4Cl is used, how many mol of NH_3 should be added to the solution? Assume an activity co-efficient of one. ($K_b = 1.8 \times 10^{-5}$ mol L^-)*

SOLUTION. $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-;\ [NH_4^+] = 0.1\text{M}$ (given)

$$\text{Also,} \quad \text{pH} = 5.4. \text{ But pH} + \text{pOH} = 14$$
$$\therefore \quad \text{pOH} = 14 - \text{pH} = 14 - 5.4 = 8.6;$$
$$-\log[OH^-] = 8.6.$$
$$\text{Hence :} \quad \log[OH^-] = -8.6 = -8 - 1 + 1 - 0.6 = \bar{9}.4;$$
$$[OH^-] = \text{antilog}\ \bar{9}.4 = \mathbf{2.5 \times 10^{-9}}$$

	NH_4OH $\rightleftharpoons$	NH_4^+ +	OH^-
Conc. (mol L^-) at equilibrium	x	0.1 + 2.5×10^{-9}	2.5×10^{-9}

$$\therefore \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 0.1$$

(∵ 2.5×10^{-9} is very small as compared to 0.1, it is neglected).

Or $$1.8 \times 10^{-5} = \frac{0.1 \times 2.5 \times 10^{-9}}{x};$$

$$x = \frac{0.1 \times 2.5 \times 10^{-9}}{1.8 \times 10^{-5}} = 1.39 \times 10^{-5}$$

∴ Adding 2.5×10^{-9} and 1.39×10^{-5} we get,
13902.5×10^{-9} mol NH_3. **Ans.**

EXAMPLE 114. *Calculate the pH of a solution obtained by mixing 6.0 g of acetic acid and 12.3 g of sodium acetate and making the volume of solution to 500 mL. K_a (CH_3COOH) = 1.8×10^{-5}.*

SOLUTION. g. mol. wt. of CH_3COOH = 12 + (3 × 1) + 12 + (2 × 16) + 1 = 60 g

g. mol. wt. of CH_3COONa

= 12 + (3 × 1) + 12 + (2 × 16) + 23 = 82 g

(*i*) Molarity of CH_3COOH (acid)

$$= \frac{\text{wt.}}{\text{g. mol. wt}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{6}{60} \times \frac{1000}{500} = 0.2\text{M}$$

(*ii*) Molarity of CH_3COONa (salt)

$$= \frac{\text{wt.}}{\text{g. mol. wt}} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{12.3}{82} \times \frac{1000}{500} = 0.3\text{M}$$

But $$p\text{H} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{0.3}{0.2}$$

$$= -[\log 1.8 + \log 10^{-5}] + \log 1.5$$

$$p\text{H} = -[0.2552 - 5] + 0.1761$$

$$= 5 - 0.2552 + 0.1761 = 4.92$$

EXAMPLE 115. *Calculate the pH of a buffer solution containing 0.45 moles of NH_4OH and 0.75 mole of NH_4Cl. K_b for NH_4OH is 1.8×10^{-5}.* **(ISC, 2010)**

SOLUTION. Let volume of buffer solution = one litre. Then: $[NH_4OH] = 0.45\,M$; $[NH_4Cl] = 0.75\,M$. But for a basic buffer solution:

$$p\text{OH} = pK_b + \log_{10}\frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log_{10}(1.8 \times 10^{-5}) + \log_{10}\frac{0.75}{0.45}$$

or $$p\text{OH} = 4.7447 + [-0.1249 + 0.3467]$$

$$= 4.7447 + 0.2218 = 4.9665$$

But $$\text{pH} = 14 - p\text{OH} = 14 - 4.9665$$

$$= 9.0335$$ **Ans.**

EXAMPLE 116. *Calculate the pH of a solution obtained by mixing equal volumes of 0.016N NH_4OH and 0.16N NH_4Cl. K_b (NH_4OH) = 1.8×10^{-5}.*

SOLUTION. Since equal volume of two solutions is mixed, the concentration of each solution becomes one half *i.e.*, 1/2.

∴ $$[NH_4OH] = [\text{Base}] = \frac{0.016}{2} = 0.008\text{N}$$

$$[NH_4Cl] = [\text{Salt}] = \frac{0.16}{2} = 0.08\text{N}$$

For a basic buffer, $$p\text{OH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log K_b + \log\frac{0.008}{0.08}$$

Or $$p\text{OH} = -\log(1.8 \times 10^{-5}) + \log 10$$

$$= -[\log 1.8 + \log 10^{-5}] + 1$$

$$= -[0.2552 - 5] + 1$$

$$= 5 - 0.2552 + 1 = 5.7448$$

But $$\text{pH} + p\text{OH} = 14;$$

∴ $$p\text{H} = 14 - \text{pOH} = 14 - 5.7448$$

Or $$\boldsymbol{p\text{H} = 8.2552}$$ **Ans.**

EXAMPLE 117. *Calculate the amount of $(NH_4)_2SO_4$ in gram which must be added to 500 mL of 0.2M NH_3 to yield a solution with pH = 9.35 (K_b for NH_3 = 1.78×10^{-5}).* **(MLNR 1992)**

SOLUTION. 1000 mL solution contain NH_3 = 0.2M

∴ 500 mL solution contain NH_3

$$= \frac{0.2}{1000} \times 500 = 0.1\text{M}$$

∴ $$[\text{Base}] = [NH_3] = 0.1\text{M}.$$

$$p\text{OH} = 14 - \text{pH} = 14 - 9.35$$

$$= 4.65;\ [(NH_4)_2SO_4] = ?$$

But $$p\text{OH} = pK_b + \log\frac{[\text{salt}]}{[\text{Base}]}$$

(Henderson's equation)

∴ $$4.65 = -\log 1.78 \times 10^{-5} + \log\frac{[\text{salt}]}{0.1};$$

$$4.65 = -[\log 1.78 + \log 10^{-5}] + \log[\text{salt}] - \log 0.1$$

$$4.65 = -[0.25 - 5] + \log[\text{salt}] - (-1);$$

$$\log[\text{salt}] = 4.65 + 0.25 - 5 - 1 = -1.1$$

Or $$\log[\text{salt}] = -1 - 1 + 1 - 0.1 = \bar{2}.9.$$

Taking antilog of both sides we get :

$$[\text{salt}] = 7.9 \times 10^{-2}\ \text{mol};$$

g. mol. wt. of $(NH_4)_2SO_4$ = 2(18) + 32 + (4 × 16) = 132 g

∴ Amount of $(NH_4)_2SO_4$ to be added

= 7.9×10^{-2} mol × Mol. wt. of $(NH_4)_2SO_4$.

= $7.9 \times 10^{-2} \times 132$ g

= **10.5 g** **Ans.**

EXAMPLE 118. *Calculate the pH of a solution prepared by mixing 0.1 mol of sodium acetate with enough water to make 1.0 litre of solution. Assume the activity co-efficient equal to unity* ($K_a = 1.9 \times 10^{-5}$).

SOLUTION.

$$CH_3COO^- + Na^+ + HOH \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

Or $$CH_3COO^- + HOH \rightleftharpoons CH_3COOH + OH^-$$

	CH_3COO^-	CH_3COOH	OH^-
Conc. (mol L⁻)	0.1	0	0
Conc. at equilibrium	$0.1 - x = 0.1$	x	x

($\because$ x is very small as compared to 0.1, it is neglected)

$$\therefore \quad K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \text{...(1)}$$

Also, $$K_h = \frac{K_w}{K_a} \quad \text{...(2)}$$

From (1) and (2), we get :

$$\frac{K_w}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

Or $$\frac{10^{-14}}{1.9 \times 10^{-5}} = \frac{x \times x}{0.1} ; x = \left(\frac{10^{-14} \times 0.1}{1.9 \times 10^{-5}}\right)^{1/2}$$

$$= (53 \times 10^{-12})^{1/2} = 7.3 \times 10^{-6}$$

$$\therefore \quad [OH^-] = 7.3 \times 10^{-6} ;$$

$$[H^+] = \frac{10^{-14}}{7.3 \times 10^{-6}} = 1.37 \times 10^{-9}$$

$$\therefore \quad pH = -\log [H^+] = -(\log 1.37 \times 10^{-9})$$

$$= -(\log 1.37 + \log 10^{-9})$$

$$= -(0.14 - 9) = \mathbf{8.84} \quad \textbf{Ans.}$$

EXAMPLE 119. *A buffer solution was obtained by mixing 8.3 g of acetic acid and 16.0 g of sodium acetate. The buffer is diluted to one litre. Calculate the pH of the solution if mL of 1M HCl is added to it. The dissociation constant of acetic acid is* 1.8×10^{-5}. *(At. wt., C = 12, H = 1, O = 16, Na = 23).*

SOLUTION.

(*a*) wt. of CH_3COOH = 8.3 g ;

g. mol. wt. of CH_3COOH

$$= 12 + (3 \times 1) + 12 + (2 \times 16) + 1 = 60 \text{ g.}$$

$\therefore$ no. of mol of CH_3COOH

$$= \frac{8.3 \text{ g}}{60 \text{ g}} = 0.138 ;$$

$$[CH_3COOH] = \mathbf{0.138}$$

Volume of 1N HCl added = 7 mL

$\therefore$ no. of mol of HCl or H^+ added

$$= \frac{7}{1000} = 0.007 \text{ mol}$$

$$\therefore \quad \text{Total [acid]} = 0.138 + 0.007 = 0.1\,45 \text{ mol L}^-$$

(*b*) wt. of CH_3COONa = 16.0 g.

g. mol. wt. of CH_3COONa

$$= 12 + (3 \times 1) + 12 + (2 \times 16) + 23 = 82$$

$\therefore$ no. of mol L⁻ of CH_3COONa

$$= \frac{16 \text{ g}}{82 \text{ g}} = 0.195$$

$$\therefore \quad [CH_3COONa] = 0.195 \text{ mol} = [\text{salt}]$$

But pH for a mixture of weak acid and salt of weak acid with a strong base is given as:

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{0.195}{0.145}$$

$$= -\log 1.8 \times 10^{-5} + \log 1.345$$

Or $$pH = -[\log 1.8 + \log 10^{-5}] + 0.129$$

$$= -[0.255 - 5] + 0.129$$

$$pH = 5 - 0.255 + 0.129 = \mathbf{4.874} \quad \textbf{Ans.}$$

24.9 BUFFER CAPACITY OR BUFFER INDEX (β)

It is defined as the rate of change of pH with number of mol of acid or base added.

Mathematically : Buffer capacity (Q)

$$= \frac{d_{\text{pH}}}{d_n \text{ acid or base}} \quad \text{Where } d_{\text{pH}} = \text{Change in pH}$$

d_n acid or base = number of mol of acid or base added.

> **Note.** (1) Buffer capacity or buffer index (β) is always positive.
>
> (2) Buffer capacity is maximum near pK_a provided the total number of mol of acid or base remain constant.

EXAMPLE 120. *On adding 0.0012 mol of an acid to 100 mL of a buffer solution, the pH of the solution decreases by 0.04 units. Calculate the buffer capacity of the system.*

SOLUTION. Number of mol of acid added to 100 mL solution = 0.0012

Number of mol of acid added to 1000 mL (= 1L)

$$\text{solution} = \frac{0.0012 \times 1000}{100} = 0.012$$

$\therefore$ Buffer capacity

$$= \frac{\text{no. of mol of acid added per litre}}{\text{Change in pH}}$$

$$= \frac{0.012}{0.04}$$

$$= 0.3 \quad \textbf{Ans.}$$

Example 121. *The value of ionisation constant of formic acid is 1.8 × 10⁻⁴. Calculate the pH value at which its mixture with sodium formate gives a buffer solution of higher capacity. Also, calculate the ratio of sodium formate and formic acid in a buffer of pH 4.32.*

Solution. We know that buffer capacity is maximum near pK_a provided the total number of mol of acid or base remain constant.

(*i*) *To find* pK_a.

$$pK_a = -\log K_a = -\log 1.8 \times 10^{-4}$$
$$= -[\log 1.8 + \log 10^{-4}]$$
$$= -[0.255 - 4] = 3.745$$

∴ pH of high capacity buffer = 3.745.

In order to get buffer solution of pH equal to 4.32, we have

$$\text{pH} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]};$$
$$4.32 = 3.745 + \log\frac{[\text{salt}]}{[\text{acid}]}$$
$$\therefore \quad \log\frac{[\text{salt}]}{[\text{acid}]} = 4.32 - 3.745 = 0.575.$$

Taking antilog of both sides, we get :

$$\frac{[\text{salt}]}{[\text{acid}]} = \text{antilog } 0.575 = \mathbf{3.76} \qquad \textbf{Ans.}$$

Example 122. *Calculate the pH of a buffer solution that contains 0.2M NH_4OH and 0.02 M NH_4Cl per litre ($K_w = 1.0 \times 10^{-14}$, $K_b = 1.8 \times 10^{-5}$).*

Solution. Hint. $[NH_4OH]$ = [Base] = 0.2M ;
$[NH_4Cl]$ = [salt] = 0.02 M

$$p\text{OH} = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$
$$= -\log K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$
$$= -\log(1.8 \times 10^{-5}) + \log\frac{0.02}{0.2}$$
$$\therefore \quad \text{pH} = 14 - p\text{OH} = 14 - 3.745$$
$$= \mathbf{10.26} \qquad \textbf{Ans.}$$

Example 123. *Calculate the composition of a buffer solution of sodium acetate and acetic acid having a total molarity of 0.3 and pH approximately 4.7. [K_a (CH_3COOH) = 1.8 × 10⁻⁵].*

Solution. [salt] + [acid] = 0.3 ; pH = 4.7 ; $K_a = 1.8 \times 10^{-5}$

$$p\text{H} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]};$$
$$4.7 = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

Or
$$4.7 = [\log 1.8 \times 10^{-5}] + \log\frac{[\text{salt}]}{[\text{acid}]};$$
$$4.7 = -[\log 1.8 + \log 10^{-5}] + \log\frac{[\text{salt}]}{[\text{acid}]};$$
$$4.7 = -[0.255 - 5] + \log\frac{[\text{salt}]}{[\text{acid}]};$$
$$\log\frac{[\text{salt}]}{[\text{acid}]} = 4.7 - 5 + 0.255 = -0.045$$
$$= -1 + 1 - 0.045 = \bar{1}.955$$

Taking antilogs of both sides, we get :

$$\frac{[\text{salt}]}{[\text{acid}]} = \text{antilog } \bar{1}.955 = 0.9$$

Or
$$\frac{[\text{salt}]}{[\text{acid}]} + 1 = 1 + 0.9 ; \frac{[\text{salt}] + [\text{acid}]}{[\text{acid}]} = 1.9$$

Or
$$\frac{\text{Total molarity of buffer}}{[\text{acid}]} = 1.9$$

Substituting the values, we get : $\frac{0.3}{[\text{acid}]} = 1.9$;

$$[\text{acid}] = \frac{0.3}{1.9} = \mathbf{0.158} \qquad \textbf{Ans.}$$

Hence **[salt] = 0.3 – 0.158 = 0.142** **Ans.**

Example 124. *A buffer solution with pH 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of mol of NH_4Cl that should be added to one litre of 1.0M NH_4OH. ($K_b = 1.8 \times 10^{-5}$)* **(MLNR 1991)**

Solution. $p\text{H} = 9 ; p\text{OH} = 14 - p\text{H} = 14 - 9 = 5$

$[\text{salt}] = [NH_4Cl] = ?$;
$[\text{Base}] = [NH_4OH] = 1.0\text{M}$.

We know :
$$p\text{OH} = pK_b + \log\frac{[\text{salt}]}{[\text{base}]};$$
$$5 = -\log K_b + \log[\text{salt}] - \log 1$$

Or
$$5 = -\log(1.8 \times 10^{-5}) + \log[\text{salt}] - 0$$
$$= -[\log 1.8 + \log 10^{-5}] + \log[\text{salt}]$$

Or
$$5 = -[0.255 - 5] + \log[\text{salt}]$$
$$= 4.745 + \log[\text{salt}]$$
$$\therefore \quad \log[\text{salt}] = 5 - 4.745 = 0.255.$$

Taking antilog, we get :

$$[\text{salt}] = \mathbf{1.8\ mol\ L^{-}} \qquad \textbf{Ans.}$$

Example 125. *Calculate the change in pH of one litre of buffer solution containing 0.1 mol each of NH_3 and NH_4Cl upon addition of (i) 0.02 mol of dissolved gaseous HCl (ii) 0.02 mol of dissolved NaOH (K_b for $NH_3 = 1.8 \times 10^{-5}$).* **(Roorkee, 1992)**

Solution. $[NH_3]$ = [base] = 0.1 ; $[NH_4Cl]$ = [salt] = 0.1 ;
$K_b = 1.8 \times 10^{-5}$

But
$$p\text{OH} = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$
$$= -[\log 1.8 \times 10^{-5}] + \log\frac{0.1}{0.1}$$

$$= -[\log 1.8 + \log 10^{-2}] + \log 1$$

$$= -[0.255 - 5] + 0 = 4.745$$

$$\therefore \quad pH = 14 - pOH = 14 - 4.745 = \mathbf{9.255.}$$

(*i*) When 0.02 mol HCl is added, we have :

	$NH_3 + HCl \rightleftharpoons$	NH_4Cl
Resulting concentration.	$0.1 - 0.02$ $= 0.08$ mol	$0.1 + 0.02$ $= 0.12$ mol

$$\therefore \quad pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log K_b + \log\frac{0.12}{0.08}$$

$$= -(\log 1.8 \times 10^{-5}) + \log 12 - \log 8$$

$$= -(0.255 - 5) + 1.079 - 0.903$$

$$= 4.921$$

$$\therefore \quad pH = 14 - pOH = 14 - 4.921$$

$$= \mathbf{9.079} \qquad \textbf{Ans.}$$

$\therefore$ Decrease in $pH = 9.255 - 9.079 = \mathbf{0.176}$ **Ans.**

(*ii*) When 0.02 mol NaOH is added, we have :

$$NaOH + NH_4Cl \rightleftharpoons NaCl + NH_3 + H_2O.$$

$$[NH_4Cl] = [\text{salt}] = 0.1 - 0.02 = 0.08 \text{ mol};$$

$$[NH_3] = [\text{base}] = 0.1 + 0.02 = 0.12 \text{ mol}$$

$$pOH = pK_a + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log K_a + \log[\text{salt}] - \log[\text{base}]$$

$$= -\log 1.8 \times 10^{-5} + \log 0.08 - \log 0.12$$

$$= -(\log 1.8 + \log 10^{-5}) - 1.097 + 0.92$$

$$pOH = -(0.255 - 5) - 1.097 + 0.92$$

$$= 5 - 0.255 - 1.097 + 0.92 = 4.568$$

$$\therefore \quad \mathbf{pH} = 14 - 4.568 = \mathbf{9.432} \qquad \textbf{Ans.}$$

Example 126. *The buffers of (X) and (Y) of pH 4.0 and 6.0 are prepared from acid HA and the salt NaA. Both the buffers are 0.50M in HA. What would be the pH of the solution obtained by mixing equal volumes of two buffers.* ($K_{HA} = 1.0 \times 10^{-5}$)

(Roorkee Entrance, 1999)

Solution. K_{HA} or $K_a = 10^{-5}$; $pK_a = -\log K_a = -(\log 10^{-5})$

$$= -(-5 \log 10) = +5$$

$$[\text{salt}] = ? ; [\text{acid}] = 0.5M ; pK_a = 5$$

(*a*) In buffer (*X*),

$$\therefore \quad pH = pK_a + \log\frac{[\text{salt}]}{[\text{base}]};$$

$$4 = 5 + \log[\text{salt}] - \log[\text{acid}]$$

$$4 = 5 + \log[\text{salt}] - \log 0.5$$

$$= 5 + \log[\text{salt}] - (-0.301)$$

$$\therefore \quad \log[\text{salt}] = 4 - 5 - 0.301 = -1.301$$

$$= -1 - 1 + 1 - 0.301 = \bar{2}.699$$

Or $[\text{salt}] = \text{antilog } \bar{2}.699 = 5 \times 10^{-2}$

$$= \mathbf{0.05M} \qquad \textbf{Ans.}$$

(*b*) In buffer (*Y*),

$$pH = pK_a + \log[\text{salt}] - \log[\text{acid}];$$

$$6 = 5 + \log[\text{salt}] - \log 0.5$$

$$= 5 + \log[\text{salt}] - (-0.301)$$

Or $\log[\text{salt}] = 6 - 5 - 0.301 = 0.699$

$$\therefore \quad [\text{salt}] = \text{antilog } 0.699 = 5M$$

$$\therefore \quad [\text{salt}] \text{ in mixture} = \frac{0.05 + 5}{2} = 2.525$$

Hence
$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$= 5 + \log\frac{2.525}{0.5}$$

$$= 5 + \log 2.525 - \log 0.5$$

$$pH = 5 + 0.4 - (-0.301)$$

$$= 5 + 0.4 + 0.301 = \mathbf{5.701} \ \textbf{Ans.}$$

Example 127. *The dissociation constant of an acid HA is 1.34×10^{-5}. How many mol of sodium salt of this acid should be added to one litre of an aqueous solution containing 0.02 mol of this acid to obtain a buffer solution of pH 4.75 ? What will be the pH if 0.01 mol of hydrogen chloride is dissolved in the above buffer solution?*

(MLNR1993)

Solution. (*a*) $K_a = 1.34 \times 10^{-5}$; pH = 4.75 ;

$$[\text{acid}] = 0.02M$$

We know :
$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]};$$

$$4.75 = -\log Ka + \log[\text{salt}] - \log[\text{acid}]$$

$$4.75 = -\log(1.34 \times 10^{-5}) + \log[\text{salt}] - \log 0.02$$

$$= -(\log 1.34 + \log 10^{-5}) + \log[\text{salt}] - (-1.699)$$

$$= -(0.127 - 5) + \log[\text{salt}] + 1.699;$$

$$\log[\text{salt}] = 4.75 + 0.127 - 5 - 1.699$$

$$= -1.822$$

$$\therefore \quad \log[\text{salt}] = -1 - 1 + 1 - 0.822 = \bar{2}.178.$$

Taking antilogs, we get :

$$[\text{salt}] = \text{antilog}\ \bar{2}.178 = 1.5 \times 10^{-2}$$
$$= 0.015\ \text{M}$$

∴ no. of mol of sodium salt to be added

$$= \mathbf{0.015\ mol\ L^{-}} \qquad \textbf{Ans.}$$

(*b*) When HCl is added to salt, we have :

		HCl +	NaA	$\rightleftharpoons$ NaCl + HA
(1)	n mol at start	0.01	0.015	0.02
(2)	Change by reaction	– 0.01	– 0.01	+ 0.01
(3)	n mol at equilibrium	0.01 – 0.01 = 0	0.015 – 0.01 = 0.005	0.02 + 0.01 = 0.03

$$\therefore \quad \text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$
$$= -\log(1.34 \times 10^{-5}) + \log[\text{salt}] - \log[\text{acid}]$$
$$= -(\log 1.34 + \log 10^{-5}) + \log 0.005 - \log 0.03$$
$$= -(0.127 - 5) + (-2.3) - (-1.523) = 4.096$$

$$\therefore \quad \boldsymbol{p}\mathbf{H} = \mathbf{4.096} \qquad \textbf{Ans.}$$

Example 128. *0.15 mol of pyridinium chloride has been added into 500 cm^3 of 0.2M pyridine solution. Calculate pH and hydroxyl ion concentration in resulting solution assuming no change in volume. (K_b for pyridine = 1.5×10^{-9} M)*

(Roorkee Entrance, 1995)

Solution. [Pyridinium chloride]

$$= \frac{\text{no. of mol} \times 1000}{\text{Vol in mL}}$$
$$= \frac{0.15 \times 1000}{500} = 0.3\text{M}$$

[Pyridine] = 0.2M (given)

Since pyridine and pyridinium chloride form a **basic buffer,** we have :

$$\text{pOH} = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$
$$= -\log K_b + \log[\text{salt}] - \log[\text{base}]$$
$$= -\log(1.5 \times 10^{-9}) + \log 0.3 - \log 0.2$$
$$= -(\log 1.5 + \log 10^{-9}) + (-0.523) - (-0.699)$$
$$\text{pOH} = -(0.176 - 9) - 0.523 + 0.699$$
$$= 9$$

But $\quad \text{pH} = 14 - p\text{OH}$ **Or**

$$\text{pH} = 14 - 9 = \mathbf{5} \qquad \textbf{Ans.}$$

Example 129. *The freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer containing 0.25M of NH$_4$Cl and 0.05 M of NH$_4$OH. Calculate the concentration of Al^{3+} and Mg^{2+} ions in a solution. K_b for NH$_4$OH = 1.8×10^{-5}; K_{sp} of Mg(OH)$_2$ = 6×10^{-10}; K_{sp} of Al(OH)$_3$ = 6×10^{-32}.*

(IIT 1989)

Solution. Since NH$_4$Cl (0.25M) and NH$_4$OH (0.05M) form a buffer solution, so :

$$\text{pOH} = pK_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]};$$
$$\text{pOH} = -\log K_b + \log \frac{[\text{NH}_4\text{Cl}]}{[\text{NH}_4\text{OH}]};$$
$$\text{pOH} = -\log(1.8 \times 10^{-5}) + \log \frac{0.25}{0.05};$$
$$\text{pOH} = -(\log 1.8 + \log(10^{-5})) + \log 5$$
$$\text{pOH} = -(0.255 - 5) + 0.699 = 5.444$$

Or $\quad -\log[\text{OH}^-] = 5.444 ; \log[\text{OH}^-] = -5.444$

$$= -5 - 1 + 1 - 0.444 = \bar{6}.556$$

$$\therefore \quad [\text{OH}^-] = \text{antilog}\ \bar{6}.556 = 3.6 \times 10^{-6}.$$

(*i*) $\quad \text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-;$

$$[\text{Al}^{3+}][\text{OH}^-]^3 = K_{\text{sp}}\ i.e., 6 \times 10^{-32}$$
$$\therefore \quad [\text{Al}^{3+}] = \frac{6 \times 10^{-32}}{[\text{OH}^-]^3} = \frac{6 \times 10^{-32}}{(3.6 \times 10^{-6})^3}$$
$$= \mathbf{1.286 \times 10^{-15}} \qquad \textbf{Ans.}$$

(*ii*) $\quad \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-;$

$$[\text{Mg}^{2+}][\text{OH}^-]^2 = K_{\text{sp}}\ i.e., 6 \times 10^{-10}$$
$$\therefore \quad [\text{Mg}^{2+}] = \frac{6 \times 10^{-10}}{[\text{OH}^-]^2} = \frac{6 \times 10^{-10}}{(3.6 \times 10^{-6})^2}$$
$$= \mathbf{46.296M} \qquad \textbf{Ans.}$$

Example 130. *How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.020 mole of propionic acid to obtain buffer solution at pH 4.75? What will be the pH if 0.010 mole of hydrogen chloride is dissolved in the above buffer solution? Compare the last pH value with the pH of 0.010 molar HCl solution. Dissociation constant of propionic acid, K_a at 25°C = 1.34×10^{-5}.* **(IIT, 1981)**

Solution. (*a*) Let moles of sodium propionate (salt) added = *x*

$$p\text{H} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$
$$4.75 = -\log(1.34 \times 10^{-5}) + \log \frac{x}{0.02}$$
$$= -(\log 1.34 + \log 10^{-5}) + \log x - \log 0.02$$
$$= -0.1271 + 5 + \log x - (\log 2 \times 10^{-2})$$
$$= -0.1271 + 5 + \log x - [\log 2 + (-2)\log 10]$$
$$4.75 = -0.1271 + 5 + \log x - \log 2 + 2$$
$$4.75 = -0.1271 + 5 + \log x - 0.3010 + 2$$
$$\log x = 4.75 + 0.1271 - 5 + 0.3010 - 2$$
$$= -1.8219$$

$$= \bar{1}.8219 = \bar{2}.1781$$

Taking antilogs of both sides, we get

$$x = \text{anti log } \bar{2}.1781 = 1.5 \times 10^{-2} \text{ mole} = 0.015 \text{ mole}$$

∴ Number of moles of sodium propionate

$$= x = 1.5 \times 10^{-2}$$

(*b*) When 0.01 mole of HCl is added, we get 0.03 mole (0.01 + 0.02 = 0.03) of propionic acid and 0.005 mole (0.015 – 0.010 = 0.005) of sodium propionate (salt)

$$\therefore \quad p\text{H} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log (1.34 \times 10^{-5}) + \log \frac{0.005}{0.030}$$

$$= -\log 1.34 + 5 + \log 5 - \log 30$$

$$= -0.1271 + 5 + 0.6990 - 1.4771$$

$$\boldsymbol{p\text{H} = 4.09}$$

(*c*) pH of 0.01M HCl or 10^{-2}M HCl

$$= -\log 10^{-2} \qquad \left[\begin{array}{l} \because \text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^- \\ \quad 0.01\text{M} \qquad 0.01\text{M} \end{array}\right]$$

$$\boldsymbol{p\text{H}} = -(-2) \log 10 = \mathbf{+2}$$

EXAMPLE 131. *What is the pH of a solution when 0.20 mole of hydrochloric acid is added to one litre of a solution containing*

(*i*) *1M each of acetic acid and acetate ion?*

(*ii*) *0.1M each of acetic acid and acetate ion?* **(IIT, 1987)**

Assume total volume as one litre and K_a of acetic acid = 1.8 × 10^{-5}.

SOLUTION. HCl ionises as :

$$\underset{0.2 \text{ mole}}{\text{HCl}} \rightleftharpoons \underset{0.2 \text{ mole}}{\text{H}^+ + \text{Cl}^-}$$

$$\therefore \quad [\text{H}^+] = 0.20 \text{ mole} = 0.2 \text{ g L}^-$$

(*i*) Consider $CH_3COOH + CH_3COO^-$ solution.

When HCl *i.e.*, H^+ ions (common ion) are added to above solution, the $[CH_3COO^-]$ will be reduced

$$\therefore \quad \mathbf{[CH_3COO^-] = 1.0 - 0.2 = 0.8 \text{ mole}}$$

The H^+ ions from added HCl will combine with CH_3COO^- ions from CH_3COOH

$$\therefore \quad [CH_3COOH] = 1.0 + 0.2 = 1.2 \text{ mole}$$

We know that : $p\text{H} = -\log K_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

Substituting the values, we get

$$p\text{H} = -\log (1.8 \times 10^{-5}) + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= -\log (1.8 - 5 \log 10) + \log \frac{0.8}{1.2}$$

$$= -(\log 1.8 - 5) + \log 8 - \log 12$$

$$= -(0.2552 - 5) + 0.9031 - 1.0791$$

$$= -0.2552 + 5 + 0.9031 - 1.0791$$

$$\boldsymbol{p\text{H} = 4.5688}$$

(*ii*) When 0.2 mole of HCl (*i.e.*, H^+ ions) are added to 0.1 mole of CH_3COO^- ions present, only 0.1 mole of H^+ ions (from HCl) combine with 0.1 mole of CH_3COO^- ions to form 0.2 mole (0.1 + 0.1 = 0.2) of acetic acid.

$$\therefore \quad [CH_3COOH] = 0.1 + 0.1 = 0.2 \text{ mole};$$

$$[\text{H}^+] = 0.2 - 0.1 = 0.1 \text{ mole}$$

Since CH_3COOH remains unionised due to the presence of H^+ ions, pH of the solution will be due to 0.1 mole HCl.

$$\therefore \quad \boldsymbol{p\text{H}} = -\log [\text{H}^+] = -\log 10^{-1} = \mathbf{1}$$

EXAMPLE 132. *How many gram moles of HCN will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 gram formula weight of NaCN?* **(IIT 1988)**

[*K dissociation (HCN) = 4.1 × 10^{-10}*]

SOLUTION. $p\text{H} = 8.5$ (given)

But $p\text{H} = -\log [\text{H}^+]$

$$\therefore \quad [\text{H}^+] = 10^{-8.5}$$

Taking logs of both sides, we get

$$\log [\text{H}^+] = \log 10^{-8.5} = -8.5 \log 10 = -8.5$$

$$= -8 - 1 + 1 - 0.5$$

$$= \bar{9}.5$$

[∵ mantissa must be positive]

Taking antilogs of both sides, we get $[\text{H}^+]$ = antilog $\bar{9}.5 = 3.16 \times 10^{-9}$ mol L^-

HCN ionises as : $HCN \rightleftharpoons H^+ + CN^-$

Applying law of mass action, we get

$$K_{\text{dissociation}} = [\text{H}^+][\text{CN}^-]/[\text{HCN}]$$

$$4.1 \times 10^{-10} = 3.16 \times 10^{-9} \times \frac{[\text{CN}^-]}{[\text{HCN}]}$$

$$\therefore \quad \frac{[\text{CN}^-]}{[\text{HCN}]} = \frac{4.1 \times 10^{-10}}{3.16 \times 10^{-9}} = 0.129 \qquad ...(1)$$

Let $[\text{HCN}] = C$

$$\therefore \quad [\text{CN}^-] = 0.01 - C$$

[∵ g. formula weight of NaCN = 0.01]

$$\therefore \quad \frac{[\text{CN}^-]}{[\text{HCN}]} = \frac{0.01 - C}{C}$$

$$0.129 = \frac{0.01 - C}{C};$$

$$0.129C = 0.01 - C; \; 1.129C = 0.01$$

$$\therefore \quad C = 0.0089$$

Hence gram mole of HCl required to be added = 0.0089

EXAMPLE 133. *A 40 ml solution of a weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 ml and 20.0 mL of the acid respectively. Find out the dissociation constant of the base.* **(IIT,1991)**

SOLUTION. Let normality of BOH = N

pH of solution = 10.04 and 9.14 (given)

We know that

$$pOH = 14 - pH$$

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$14 - 10.04 = pK_b + \log \frac{[5.0 \times 0.1]}{[40.0 \times N - 5.0 \times 0.1]} \quad ...(1)$$

$$14 - 9.14 = pK_b + \log \frac{[20.0 \times 0.1]}{[40.0 \times N - 20.0 \times 0.1]} \quad ...(2)$$

From expressions (1) and (2), we get

$$pK_b = 3.96 - \log \frac{0.5}{40N - 0.5} \quad ...(3)$$

$$pK_b = 4.86 - \log \frac{2}{40N - 2} \quad ...(4)$$

Equating equations (3) and (4), we get

$$3.96 - \log \frac{0.5}{40N - 0.5} = 4.86 - \log \frac{2}{40N - 2}$$

$$4.86 - 3.96 = \log \frac{2}{40N - 2} - \log \frac{0.5}{40N - 0.5}$$

$$0.9 = \log \frac{2}{40N - 2} \times \log \frac{40N - 0.5}{0.5}$$

$$= \log \frac{4\,(40N - 0.5)}{40N - 2}$$

Taking antilogs of both sides, we get

$$7.943 = \frac{4\,(40N - 0.5)}{40N - 2} \quad \therefore \quad N = 0.088$$

Substituting this value of N in equation (3), we get

$$pK_b = 3.96 - \log \frac{0.5}{40 \times 0.088 - 0.5}$$

$$= 3.96 - \log \frac{0.5}{3.02} = 3.96 - \log \frac{50}{302}$$

$$= 3.96 - [\log 50 - \log 302]$$

$$= 3.96 - 1.6990 + 2.48 = 4.741$$

Or $-\log K_b = 4.74$ or $\log K_b = -4.741$

$$= -4 - 1 + 1 - 0.741 = \bar{5}.259$$

Taking antilogs of both sides we get : $\mathbf{K_b = 1.82 \times 10^{-5}}$

EXAMPLE 134. *The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which in 2M is H_2CO_3 in order to maintain a pH of 7.4? K_a for H_2CO_3 in blood is 7.8×10^{-7}.* **(IIT,1993)**

SOLUTION. Let V = Volume in litres of 5M $NaHCO_3$ to be added to 10 ml (= 0.01 litre) of blood to maintain pH, 7.4

Moles of $NaHCO_3 = 5 \times V = 5V$

Moles of $H_2CO_3 = 2 \times 0.01 = 0.02$

We know that : $pH = -\log K_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

Substituting the values, we get

$$7.4 = -\log 7.8 \times 10^{-7} + \log \frac{5V}{0.02}$$

$$= -[\log 7.8 - 7 \log 10] + \log 5V - \log 2 \times 10^{-2}$$

$$= -[\log 7.8 - 7] + \log 5V - [\log 2 - 2 \log 10]$$

$$7.4 = -0.89 + 7 + \log 5V - 0.301 + 2$$

$$\log 5V = 7.4 + 0.89 - 7 + 0.301 - 2$$

$$= -0.409$$

$$= -1 + 1 - 0.409 = \bar{1}.591$$

Taking antilogs of both sides, we get $5V$

$$= \text{antilog } \bar{1}.591 = 3.9 \times 10^{-1}$$

$$\therefore \quad V = 3.9 \times 10^{-1}/5$$

$$= 0.078 \text{ litre} = \mathbf{78\ mL}$$

EXAMPLE 135. *A buffer solution contains 0.04 mol of Na_2HPO_4 per litre and 0.02 mol of NaH_2PO_4 per litre (i) Calculate pH using $pK_a = 6.84$ (ii) if 1 mL of 1.0 N HCl is added to the buffer, what will be the change in pH? (iii) if the same quantity of HCl is added to one litre of water (having pH = 7), calculate the change in pH.*

SOLUTION. (*i*) $pK_a = 6.84$; [salt] = 0.04 mol L$^-$;

[acid] = 0.02 mol L$^-$

But $pH = pK_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$;

$$pH = 6.84 + \log \frac{0.04}{0.02} \text{ i.e., } 2$$

$$\therefore \quad \mathbf{pH} = 6.84 + 0.301 \simeq \mathbf{7.14}$$

(*ii*) Original solution Dilute solution

$$N_1V_1 = N_2V_2$$

$$1 \times 1 = N_2 \times 1000 \, ; N_2 = \frac{1}{1000} = 10^{-3}$$

$$[\text{salt}] = 0.04 - 10^{-3} ; [\text{acid}] = 0.02 - 10^{-3}$$

$$\therefore \quad pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} ;$$

$$pH = 6.84 + \log \frac{0.04 - 10^{-3}}{0.02 - 10^{-3}}$$

$$pH = 6.84 + \log \frac{0.039}{0.019}\ ;$$

$$pH = 6.84 + \log 39 - \log 19$$

$$= 6.84 + 1.591 - 1.279$$

$$\therefore \quad \mathbf{pH = 7.15.}$$

Thus, **change in pH** = 7.15 – 7.11 = **0.04**

(*iii*) When 1mL of 1N HCl is added to one litre water, $[H^+] = 10^{-3}$ as shown in (*ii*)

$$\therefore \quad pH = -\log [H^+] = -\log 10^{-3}$$

$$= -(-3) = +3$$

$\therefore$ **Change in pH = 7 – 3 = 4** **Ans.**

EXAMPLE 136. *Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 mol L^-. pK_b for NH_3 = 4.7, log 2 = 0.30.* **(Roorkee 1997)**

SOLUTION. $[\text{salt}] = [NH_4Cl] = x\ ;$

$$[\text{base}] = [NH_3] = 0.6 - x$$

We know, $pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}.$

Hence $14 - pH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} \log \frac{[\text{salt}]}{[\text{base}]}$

$$= 14 - pK_b - pH$$

$$= 14 - 4.7 - 9 = 0.3.$$

Taking antilogs, we get : $\frac{[\text{salt}]}{[\text{base}]}$ = antilog 0.3 = 2

Or $\frac{x}{0.6 - x} = 2\ ;\ x = 1.2 - 2x\ ;$

$$3x = 1.2\ ;\ x = \mathbf{0.4}$$

$\therefore$ Amount of salt, $NH_4Cl = x$ = **0.4 mol L⁻** **Ans.**

Amount of base, NH_3 = 0.6 – 0.4 = **0.2 mol L⁻** **Ans.**

EXAMPLE 137. *Calculate the pH of a buffer solution prepared by dissolving 28 g Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1M HCl. (K_a for HCO_3^- = 5.63 × 10^{-11}).*

SOLUTION. g. eq. wt. of Na_2CO_3

$$= \frac{(2 \times 23) + 12 + (3 \times 16)}{2}$$

$$= 53 \text{ g}$$

Reaction $Na_2CO_3 + HCl \rightleftharpoons NaCl + NaHCO_3$

(*i*) m. equiv. $\frac{28 \times 1000}{53}$ 1×150

before reaction = 528 = 150

(2) m. equiv. 528 – 150

after reaction = 378 0 150 150

The above solution is a buffer solution because it contains Na_2CO_3 and $NaHCO_3$.

Hence $pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}\ ;$

$$pH = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore \quad pH = -\log 5.63 \times 10^{-11} + \log \frac{378}{150}$$

$$= -(\log 5.63 + \log 10^{-11}) + \log 378 - \log 150$$

$$\mathbf{pH} = -(0.75 - 11) + 2.58 - 2.18$$

$$= \mathbf{10.65}$$ **Ans.**

EXAMPLE 138. *During a titration of a weak acid (HA) with a strong base (NaOH), the end point was obtained by the addition of 36.0 mL of 0.1N NaOH. After this, 18.0 mL of 0.1N HCl was added to the titrated solution. As a result, pH of solution became 4.5. Find the value of K_a of the weak acid.*

SOLUTION. Reaction. $NaOH + HA \rightleftharpoons NaA + H_2O.$

(*i*) no. of milliequivalent of NaOH

$$= N_1V_1 = 0.1 \times 36 = 3.6$$

no. of milliequivalent of HCl at end point

$$= 0.1 \times 36 = 3.6$$

$\therefore$ no. of milliequivalent of NaA formed

$$= 0.1 \times 36 = 3.6.$$

(*ii*) When 18 mL of 0.1N HCl was added after the end point, we have :

$$NaA + HCl \rightleftharpoons NaCl + HA$$

no. of milliequivalent of NaA

$$= N_2V_2 = 0.1 \times 18 = 1.8$$

no. of milliequivalent of NaCl (= HA) = 1.8

Since weak acid HA and salt (NaA) of weak acid with strong base NaOH is a buffer solution :

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\log K_a = \log \frac{[\text{salt}]}{[\text{acid}]} - pH$$

$$= \log \frac{1.8}{1.8} - 4.5 = 0 - 4.5$$

Or $\log \boldsymbol{K_a} = -4.5 = -4 - 1 + 1 - 0.5 = \bar{5}.5$

$\therefore$ $\boldsymbol{K_a}$ = antilog $\bar{5}.5$ = **3.16 × 10^{-5}** **Ans.**

Type. pH of weak acid + strong alkali

EXAMPLE 139. *To 30 cm^3 of 0.02 mol dm^{-3} acetic acid were added 10 cm^3 of 0.05 mol dm^{-3} potassium hydroxide. Calculate the pH of the solution. pK_a of acetic acid = 4.74.*

SOLUTION. Total volume = 30 + 10 = 40 cm^3

Reaction. $CH_3COOH + KOH \rightleftharpoons CH_3COOK + H_2O.$

m. mol of acetic acid = 30 × 0.02 = 0.6.

m. mol of KOH = 10 × 0.05 = 0.5

(fully ionised because KOH is a strong base)

m. mol of acetic acid left unreacted

= 0.6 – 0.5 = 0.1

$$\therefore \quad [CH_3COOK] = [\text{salt}] = \frac{0.5 \times 40}{1000} = 0.02$$

$$[CH_3COOH] = [\text{acid}] = \frac{0.1 \times 40}{1000} = 0.004$$

Since the reaction is between weak acid and strong base :

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.74 + \log \frac{0.02}{0.004}$$

$$= 4.74 + \log 5 = 4.74 + 0.7$$

Or $pH = \mathbf{5.44}$ **Ans.**

Note.	$1\ cm^3 = 1\ mL$; $mol\ dm^{-3} = mol\ L^-$

EXAMPLE 140. *A solution of 0.1M CH_3COOH (having pH = 3) was titrated against 0.05N NaOH solution. Calculate the pH at 25% and 75% stage of neutralisation of acid.*

SOLUTION. First Case. When 25% or $\frac{25}{100}$ *i.e.*, 1/4th acid is neutralised.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa\ (\text{salt}) + H_2O.$$

(1) Conc. at start $0.1 \quad 0 \quad 0 \quad 0$

(2) Conc. after adding NaOH to have 1/4th neutralisation $0.1 \times \frac{3}{4} = 0.075 \quad 0.1 \times \frac{1}{4} = 0.025$

$$pH = 3 ; -\log [H^+] = 3 ;$$

$$\log [H^+] = -3 ; [H^+] = 10^{-3}.$$

Since $[CH_3COOH] = 0.1\ M, C = 0.1\ M.$

Here $[H^+] = C\alpha$

$$\therefore \quad 10^{-3} = 0.1 \times \alpha ; \alpha = \frac{10^{-3}}{0.1} = 10^{-2}.$$

Also : $K_a = C\alpha^2 ; K_a = 0.1 \times (10^{-2})^2 = 10^{-5}$

$$\therefore \quad pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{0.025}{0.075} \text{ or } \log 0.33$$

$$pH = -\log 10^{-5} - 0.48$$

$= -(-5) - 0.48 = \mathbf{4.52}$ **Ans.**

Second Case

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

(1) Conc. at start $0.1 \quad 0 \quad 0$

(2) Conc. after adding NaOH to have 3/4th neutralisation $0.1 \times \frac{1}{4} = 0.025 \quad 0.1 \times \frac{3}{4} = 0.075$

$K_a = 10^{-5}$ as explained in first case.

$$\therefore \quad pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= \log K_a + \log \frac{0.075}{0.025} \text{ or } \log 3$$

$$pH = -\log 10^{-5} + 0.477$$

$= -(-5) + 0.477 = \mathbf{5.477}$ **Ans.**

EXAMPLE 141. *50 mL of 0.2M CH_3COOH is added to 20 mL of 0.2 M NaOH solution to get exact 70 mL solution. Calculate the pH of solution. Also calculate the additional volume of 0.2M NaOH solution needed to make the pH of the solution equal to 4.71. Ionisation constant of acid = 1.8×10^{-5}.*

SOLUTION. (*a*) Total volume = 50 + 20 = 70 mL.

Reaction :

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

m. mol of CH_3COOH = 50 × 0.2 = 10

m. mol of NaOH = 20 × 0.2 = 4

(fully ionised because NaOH is a strong base)

m. mol of CH_3COOH left unreacted

= 10 – 4 = 6

$$\therefore \quad [CH_3COONa] = \frac{4 \times 70}{1000} = 0.28M = [\text{salt}]$$

$$[CH_3COOH] = \frac{6 \times 70}{1000} = 0.42\ M = [\text{acid}]$$

Since the reaction is between strong base and weak acid,

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{0.28}{0.42}$$

$$= -\log 1.8 \times 10^{-5} + \log 0.67$$

$$= -(\log 1.8 + \log 10^{-5}) - 0.174$$

$$pH = -(0.255 - 5) - 0.174 = 4.571$$

(*b*) After the addition of 0.2M NaOH, *p*H of solution = 4.71

$$\therefore \quad pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$4.71 = -(\log 1.8 \times 10^{-5}) + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -(0.255 - 5) + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore \quad \log \frac{[\text{salt}]}{[\text{acid}]} = 4.71 + 0.255 - 5 = -0.035$$

$$= -1 + 1 - 0.035 = \bar{1}.965$$

$$\therefore \quad \frac{[\text{salt}]}{[\text{acid}]} = \text{antilog } \bar{1}.965$$

$$= \frac{9.2 \times 10^{-1}}{1} \quad \ldots(1)$$

Let volume of 0.2 M NaOH added to get pH 4.71 = x mL

It means, this NaOH solution will neutralise further x mL of 0.2M CH_3COOH and produce x mL of 0.2M CH_3COONa.

$\therefore$ Resulting volume of solution = $(70 + x)$ mL.

This solution would contain :

(i) $(20 + x)$ mL of CH_3COONa

(ii) $(30 - x)$ mL of 0.2M CH_3COOH $\quad (\because 50 - 20 = 30)$

$\therefore$ no. of mol of CH_3COONa $(20 + x)$ mL solution

$$= \frac{0.2\,(20 + x)}{1000}$$

no. of mol CH_3COOH in $(30 - x)$ mL solution

$$= \frac{0.2\,(30 - x)}{1000}$$

$$\frac{[CH_3COONa]}{[CH_3COOH] \text{ or } [\text{acid}]} = \frac{0.2\,(20 + x)/1000}{0.2\,(30 - x)/1000}$$

$$= \frac{20 + x}{30 - x} \quad \ldots(2)$$

From (1) and (2), we get :

$$\frac{9.2 \times 10^{-1}}{1} = \frac{20 + x}{30 - x};$$

$$(30 - x) \times 9.2 \times 10^{-1} = 20 + x$$

$$27.6 - 0.92x = 20 + x;$$

$$1.92x = 7.6 \quad \text{Hence } x = \frac{7.6}{1.92} = 3.96.$$

Thus 3.96 mL of 0.2M NaOH is needed to make pH of solution equal to 4.71.

EXAMPLE 142. *Calculate the ratio of the concentration of salt and the acid to prepare a buffer solution of an acid and its sodium salt, having pH 4.5.* $K_a = 1.7 \times 10^{-5}$ *mol* L^{-}.

SOLUTION. For a buffer solution of an acid and its sodium salt,

$$p\text{H} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

(Henderson's equation)

$$\therefore \quad \log \frac{[\text{salt}]}{[\text{acid}]} = p\text{H} - pK_a$$

$$= 4.5 - (-\log K_a) = 4.5 + \log K_a$$

$$= 4.5 + (\log 1.7 \times 10^{-5})$$

$$= 4.5 + (\log 1.7 + \log 10^{-5})$$

$$= 4.5 + 0.23 - 5 = -0.27$$

$$\therefore \quad \log \frac{[\text{salt}]}{[\text{acid}]} = -0.27 = -1 + 1 - 0.27 = \bar{1}.73$$

$$\therefore \quad \frac{[\text{salt}]}{[\text{acid}]} = \text{antilog } \bar{1}.73 = 5.37 \times 10^{-1} = \frac{0.537}{1}.$$

$$\text{Thus} \quad \frac{[\text{salt}]}{[\text{acid}]} = \frac{0.537}{1}$$ **Ans.**

EXAMPLE 143. *Calculate the weight in g of potassium acetate that should be added to one litre of 0.45M* CH_3COOH *solution so that the* $[H^+]$ *of resultant solution is* 1.5×10^{-4} *g ion* L^{-}. $[K_a(CH_3COOH) = 1.8 \times 10^{-5}]$

SOLUTION. [acid] = 0.45 ; [salt] = ?,

g. mol. wt. of CH_3COOK

$$= 12 + (3 \times 1) + 12 + (2 \times 16) + 39 = 98 \text{ g};$$

$$[H^+] = 1.5 \times 10^{-4}$$

For a buffer solution of CH_3COOH and CH_3COOK,

$$p\text{H} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$-\log [H^+] = -\log (1.8 \times 10^{-5}) + \log \frac{[\text{salt}]}{0.45}$$

$$\therefore \quad \log \frac{[\text{salt}]}{0.45} = \log (1.8 \times 10^{-5}) - \log [H^+]$$

$$= \log 1.8 + \log 10^{-5} - \log 1.5 \times 10^{-4}$$

$$= 0.255 - 5 - (\log 1.5 + \log 10^{-4})$$

$$= 0.255 - 5 - (0.176 - 4)$$

$$= 0.255 - 5 - 0.176 + 4 = -0.921$$

$$= 0 - 1 + 1 - 0.921 = \bar{1}.079$$

$$\therefore \quad \frac{[\text{salt}]}{0.45} = \text{antilog } \bar{1}.079 = 1.2 \times 10^{-1}$$

$$= 0.12 \therefore [\text{salt}] = 0.12 \times 0.45$$

$$= 0.054 \text{ mol L}^{-}$$

$\therefore$ Amount of salt required in g = 0.054×98 g

[$\because$ g. mol. wt. of CH_3COOK = 98 g]

= **5.292 g** **Ans.**

EXAMPLE 144. *Assuming effective ionisation of* CH_3COONH_4 *as 8.0%, calculate the* $[H_3O^+]$ *of a solution containing 0.1 mol of* CH_3COONH_4 *and 0.1M* CH_3COOH. K_a $(CH_3COOH) = 1.8 \times 10^{-5}$.

SOLUTION.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \ldots(1)$$

	CH_3COOH	CH_3COO^-	H_3O^+
Conc. at start (mol L^-)	0.1		
Conc. after reaction	$0.1 - x$	x	x

$$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+ ...(2)$$

$$\text{Conc. (mol L}^-) \quad 80\% = \frac{8}{100} = 0.08$$

$\therefore$ Total $[CH_3COO^-] = x + 0.08$;

$[H_3O^+] = x$; $[CH_3COOH] = 0.1 - x$

From equation (1), $K = \dfrac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$

$$\therefore \quad 1.8 \times 10^{-5} = \frac{(x + 0.08) \times x}{0.1 - x}$$

$$= \frac{x^2 + 0.08\,x}{0.1 - x} = \frac{0.08x}{0.1}$$

($\because$ x is very small as compared to 0.1, it is rejected from the denominator. Also, x^2 being very small, is rejected).

$$\therefore \quad x = \frac{1.8 \times 10^{-5} \times 0.1}{0.08}$$

$$= 2.25 \times 10^{-5} \text{ g ion L}^-$$

or $\quad$ $\mathbf{[H_3O^+] = x = 2.25 \times 10^{-5}}$ **g ion L⁻Ans.**

Example 145. If *the addition of a small amount of solid does not cause the dilution of a solution, what will be the* $[OH^-]$ *in a solution prepared by dissolving 0.02 mol of* NH_4Cl *in 100 mL of 0.15M ammonia.* (K_{eq} *for this reaction* = 1.8×10^{-5})

Solution. $\quad NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

100 mL solution contain $[NH_4^+] = 0.02$ M

1000 mL solution contain $[NH_4^+]$

$$= \frac{0.02 \times 1000}{100} = 0.2 \text{ mol L}^-$$

Reaction $\quad NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Conc. (mol L⁻) $\quad$ 0.15M $\quad$ 0.02M

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]};$$

$$1.8 \times 10^{-5} = \frac{0.02 \times [OH^-]}{0.15}$$

$$\therefore \quad \mathbf{[OH^-]} = \frac{1.8 \times 10^{-5} \times 0.15}{0.02}$$

$$= \mathbf{1.35 \times 10^{-4}\ M} \qquad \textbf{Ans.}$$

Example 146. *Calculate the number of mol of NaOH which can be added to one litre of a solution of 0.1M in* NH_4Cl *and 0.1M in* NH_3 *without changing pOH by more than one unit. Assume that volume does not change.* ($K_b = 1.8 \times 10^{-5}$; $pK_b = 4.75$).

Solution. (*a*) $\quad [NH_4Cl] = [NH_4^+] = 0.1$; $[NH_3] = 0.1$.

We know : $\quad pOH = pK_b + \log \dfrac{[NH_4^+]}{[NH_3]}$;

$$pOH = 4.75 + \log \frac{0.1}{0.1} = 4.75 + \log 1$$

$$\therefore \quad pOH = 4.75 + 0 = 4.75$$

(*b*) Since pOH should not change by more than one unit, so pOH after the addition of NaOH can not be less than 3.75. $\quad$ ($\because$ 4.75 – 1 = 3.75)

$$\therefore \quad pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]};$$

$$3.75 = 4.75 + \log \frac{[NH_4^+]}{[NH_3]}$$

$$\therefore \quad \log \frac{[NH_4^+]}{[NH_3]} = 3.75 - 4.75 = -1 = \bar{1}$$

$$\therefore \quad \frac{[NH_4^+]}{[NH_3]} = \text{antilog } \bar{1} = 10^{-1} = 0.1 \quad ...(1)$$

$\therefore$ NaOH can be added till the ratio of $[NH_4^+]$ and $[NH_3]$ is 0.1

At start, $[NH_4^+] + [NH_3] = 0.1 + 0.1 = 0.2 \quad ...(2)$

From relation (1), $[NH_4^+] = 0.1 \times [NH_3]$.

Substituting this value in relation (2), we get :

$$0.1 \times [NH_3] + [NH_3] = 0.2 \; ; \; [NH_3]\,[0.1 + 1] = 0.2$$

$$\therefore \quad \mathbf{[NH_3]} = \frac{0.2}{1.1} = \mathbf{0.182M}$$

$\therefore$ From relation (2), $[NH_4^+] + 0.182 = 0.2$

$\therefore$ $[NH_4^+] = 0.2 - 0.182 = \mathbf{0.018}$

Assuming no change in volume, hence :

$$\left.\begin{array}{l}\text{no. of mol of NaOH that should}\\ \text{be added without changing } pOH\\ \text{by one unit}\end{array}\right]$$

$$= 0.182 - 0.1 = \mathbf{0.082M.}$$

Example 147. *The concentration of HCN and NaCN in a solution is 0.01M each. Calculate the concentration of hydrogen ad hydroxyl ions if the dissociation constant of HCN is* 7.2×10^{-10}.

(Roorkee, 1991)

Solution. (*a*) $\quad [\text{salt}] = [NaCN] = 0.01M$;

$[\text{acid}] = [HCN] = 0.01M$.

We know that for a solution of weak acid with a strong base :

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]};$$

$$pH = pK_a + \log \frac{0.01}{0.01}$$

Or $\quad pH = pK_a + 0 = pK_a$;

$$-\log [H^+] = -\log K_a$$

$$= -\log 7.2 \times 10^{-10}$$

$$\therefore \quad \mathbf{[H^+] = 7.2 \times 10^{-10}} \qquad \textbf{Ans.}$$

(*b*) We know $[H^+][OH^-] = K_w$; $7.2 \times 10^{-10} \times [OH^-] = 10^{-14}$

Hence : $\quad [OH^-] = \dfrac{10^{-14}}{7.2 \times 10^{-10}}$

$$= \mathbf{1.39 \times 10^{-5}} \qquad \textbf{Ans.}$$

EXAMPLE 148. *How many mol of calcium hydroxide must be dissolved to produce 250 mL of an aqueous solution of pH 10.65. Assume complete dissociation.* **(Roorkee,1989)**

SOLUTION. $pH = 10.65.$

We know $pH + pOH = 14\ ;\ pOH = 14 - pH$

Or $pOH = 14 - 10.65 = 3.35\ ;$

$$-\log [OH^-] = -3.35$$
$$= -3 - 1 + 1 - 0.35 = \bar{4}.65$$

$\therefore$ $[OH^-] = \text{antilog } \bar{4}.65$
$$= 4.47 \times 10^{-4} \text{ mol } L^-$$
$$= 4.47 \times 10^{-4} \text{ mol } (1000 \text{ mL})^-$$

$\therefore$ $[OH^-]$ in 250 mL solution
$$= \frac{4.47 \times 10^{-4} \times 250}{1000} = 1.12 \times 10^{-4} \text{ mol } (250 \text{ mL})^-$$

$\therefore$ no. of mol of $Ca(OH)_2$ dissolved
$$= \frac{1.12 \times 10^{-4}}{2}$$
[$\because$ $Ca(OH)_2$ gives $2OH^-$ ions on dissolution]
$$= \mathbf{0.56 \times 10^{-4} \text{ mol } (250 \text{ mL})^-}$$
Ans.

EXAMPLE 149. *What happens to the 500 mL of solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 mL of 0.1M sodium hydroxide is added? ($K_a = 1.8 \times 10^{-5}$)* **(ISC, 1989)**

SOLUTION. (*a*) Given : 500 mL solution contains 0.1M $CH_3COO^- Na^+$ + 0.1M CH_3COOH.

Hence :

$$[CH_3COO^-] = 0.1 + 0.1 = 0.2 \text{ mol}\ ;$$
$$[CH_3COOH] = 0.1 + 0.1 = 0.2 \text{ mol}$$

Reaction

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$\therefore \quad K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}\ ;$$

$$1.8 \times 10^{-5} = \frac{(0.2) \times [H^+]}{0.2}$$

Or $[H^+] = 1.8 \times 10^{-5}\ ;\ pH = -\log 1.8 \times 10^{-5}$
$$= -(\log 1.8 + \log 10^{-5})$$

Or $pH = -(0.255 - 5) = \mathbf{4.745}$

(*b*) $NaOH \rightleftharpoons Na^+ + OH^-$

Conc. (mol L^-) 0.1 ; $[OH^-] = 0.1 = 10^{-1}$

$$\therefore \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-1}} = 10^{-13}\ ;$$

$$pH = -\log 10^{-13} = 13$$

When 10 mL of 0.1 M NaOH is added, the pH of the solution will increase because the pH of 0.1 M NaOH is 13 as explained above.

EXAMPLE 150. *Calculate the pH of an aqueous solution of 1.0M ammonium formate assuming complete dissociation (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8).* **(IIT 1995)**

SOLUTION. Ammonium formate is a salt of weak acid and weak base. pH of such a salt is given as :

$$pH = 0.5[pK_w + pK_a - pK_b]$$
$$= 0.5\,(-\log K_w + 3.8 - 4.8)$$
$$pH = 0.5[-\log 10^{-14} + 3.8 - 4.8]$$
$$= 0.5\,(14 + 3.8 - 4.8) = \mathbf{6.5}$$
Ans.

Type. Weak acid + strong acid

EXAMPLE 151. *500 mL of 0.2M aqueous solution of acetic acid is mixed with 500 mL of 0.2M HCl at 25°C.*

(*i*) *Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.*

(*ii*) *If 6g of NaOH is added to the above solution, determine the final pH (Assume there is no change in volume on mixing ; K_a of acetic acid is 1.75×10^{-5} mol L^-).* **(IIT 2002 Mains)**

SOLUTION. (*i*) Total volume of solution
$$= 500 + 500 = 1000 \text{ mL}$$

500 mL of 0.2M acetic acid
$$= 500 \times 0.2 = 100 \text{ m mol}$$

$$\therefore \quad [CH_3COOH] = [H^+] = \frac{100}{1000} \times \frac{1000}{1000} = 0.1 \text{ M}$$

500 mL of 0.2M HCl = 500 × 0.2 = 100 m mol

$$\therefore \quad [HCl] = [H^+] = \frac{100}{1000} \times \frac{1000}{1000} = 0.1\text{M}.$$

Let x = degree of dissociation of acetic acid, CH_3COOH

	$CH_3COOH \rightleftharpoons$	CH_3COO^- +	H^+
(1) n mol at start	0.1	0	0.1(of HCl)
(2) Change by reaction	$-x$	x	$x + 0.1$
(3) n mol at equilibrium	$0.1 - x$	x	$x + 0.1$

$$\therefore \quad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}\ ;$$

$$1.75 \times 10^{-5} = \frac{x\,(x + 0.1)}{0.1 - x}$$

Since acetic acid is a weak acid, take $x + 0.1 = 0.1$ and $0.1 - x = 0.1$.

Hence $1.75 \times 10^{-5} = \dfrac{x \times 0.1}{0.1}$; **Or** $\mathbf{x = 1.75 \times 10^{-5}}$

For 0.1M, degree of dissociation of CH_3COOH
$$= 1.75 \times 10^{-5}$$

For 1M, degree of dissociation of CH_3COOH

$$= \frac{1.75 \times 10^{-5}}{0.1} \times 1 = 1.75 \times 10^{-4}$$

(*ii*) wt. of NaOH = 6.0 g ;

g. mol. wt. of NaOH = 23 + 16 + 1 = 40 g

Total volume of mixture solution

= 500 + 500 = 1000 mL

$$\therefore \text{ Molarity of NaOH} = \frac{\text{wt. of NaOH}}{\text{g. mol. wt. of NaOH}} \times \frac{1000}{\text{Vol of solution in mL}}$$

$$= \frac{6}{40} \times \frac{1000}{1000} = \mathbf{0.15M}$$

Molarity of CH_3COOH = 0.1M (found above)

Molarity of NaOH that react with

CH_3COOH = 0.15 – 0.1 = 0.05M

Thus :

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

(1) n mol at start	0.1	0.05	0	0
(2) Change by reaction	– 0.05	+ 0.05		
(3) n mol at equilibrium	0.1 – 0.05 = 0.05	0.05		

Since $CH_3COOH + CH_3COONa$ forms a buffer solution, *p*H of solution can be obtained by the use of Henderson– Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{Acid}]}$$

Or

$$pH = -\log K_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= -\log (1.75 \times 10^{-5}) + \log \frac{0.05}{0.05}$$

$$= -[\log 1.75 + \log 10^{-5}] + 0$$

$$= -[0.243 - 5] = \mathbf{4.757}$$ **Ans.**

Example 152. *What volume of 5M KCN solution must be added to 10mL of 2M HCN solution to maintain pH equal to 9? [K_a(HCN) = 5 × 10^{-10} at 298K].*

Solution. (*a*) HCN + KCN form a buffer solution. For an acidic buffer solution :

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} ;$$

$$9 = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$9 = -[\log 5 \times 10^{-10}] + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -[\log 5 + \log 10^{-10}] + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Or

$$9 = -[0.699 - 10] + \log \frac{[\text{salt}]}{[\text{acid}]} ;$$

$$\log \frac{[\text{salt}]}{[\text{acid}]} = 9 + 0.699 - 10 = -0.3010 ;$$

$$\therefore \quad \frac{[\text{salt}]}{[\text{acid}]} = \text{antilog}(-0.3010)$$

$$= \text{antilog}(-1 + 1 - 0.301 = \bar{1}.699)$$

$$= 5 \times 10^{-1} = 0.5$$

Let volume of 5M KCN to be added = *V* mL

∴ Total volume of KCN + HCN = (*V* + 10)mL

Original KCN KCN in mixture;

$$M_1V_1 = M_2V_2$$

$$5 \times V = M_2 \times (10 + V) ; M_2 = \frac{5V}{10+V} \quad ...(i)$$

Original HCN HCN in mixture

$$M_3V_3 = M_4V_4$$

$$2 \times 10 = M_4 \times (10 + V) ; M_4 = \frac{20}{10+V} \quad ...(ii)$$

But $$\frac{[\text{salt}]}{[\text{acid}]} = \frac{\frac{5V}{10+V}}{\frac{20}{10+V}} \textbf{ Or } 0.5 = \frac{5V}{20}$$ (from (*i*) and (*ii*) above).

Hence $$5V = 20 \times 0.5 \textbf{ Or } V = \frac{20 \times 0.5}{5}$$

Or V = 2 mL.

Hence volume of 5M KCN required to be added to 10 mL of 2M HCN = **2 mL** **Ans.**

Example 153. *Find the value of pH of a solution containing 3.2 mL of 0.1N NaOH and 60mL of 0.01N acetic acid. The effect due to dilution may be neglected. [K_a (CH_3COOH) = 1.7 × 10^{-5} at 298 K]*

Solution. (*i*) 3.2 mL of 0.1N NaOH = $\frac{3.2 \times 0.1}{1000}$ g. eq.

$= 3.2 \times 10^{-4}$ g. eq.

(*ii*) 60 mL of 0.01N CH_3COOH = $\frac{60 \times 0.01}{1000} = 6 \times 10^{-4}$

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

	3.2×10^{-4} g. eq.	3.2×10^{-4} g. eq. (formed)	

∴ Amount of CH_3COOH left behind after neutralisation

$$= (6 \times 10^{-4}) - (3.2 \times 10^{-4})$$

$$= 2.8 \times 10^{-4} \text{ g. eq.}$$

$$\therefore \quad [CH_3COONa] = 3.2 \times 10^{-4} \text{ g. eq} ;$$

$$[CH_3COOH] = 2.8 \times 10^{-4} \text{ g. eq.}$$

But $$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= -\log K_a + \log \frac{3.2 \times 10^{-4}}{2.8 \times 10^{-4}}$$

$$= -\log(1.7 \times 10^{-5}) + \log 3.2 - \log 2.8$$

$$= -[\log 1.7 + \log 10^{-5}] + \log 3.2 - \log 2.8$$

$$p\textbf{H} = -[0.2304 - 5] + 0.5051 - 0.4471 = \mathbf{4.8276} \qquad \textbf{Ans.}$$

24.10 CALCULATION OF pH OF SALTS AND SOLUTIONS DUE TO HYDROLYSIS

When a salt is dissolved in water, ions are formed. If these ions are treated chemically with water, hydrolysis takes place. The salts which undergo hydrolysis are :

(*i*) salts of weak acids and strong bases (*e.g.*, CH_3COONa)

(*ii*) salts of weak bases and strong acids (*e.g.*, NH_4Cl)

(*iii*) salts of weak acids and weak bases (*e.g.*, CH_3COONH_4)

Types : Salts of weak acids and strong bases.

$$\underset{\text{Weak acid}}{CH_3COOH} + \underset{\text{Strong base}}{NaOH} \longrightarrow \underset{\substack{\text{salt of weak acid}\\ \text{and strong base}}}{CH_3COONa} + H_2O.$$

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \qquad ...(1)$$

$$\underset{\substack{\text{Ion}\\ C - C\alpha}}{CH_3COO^-} + H_2O \rightleftharpoons \underset{C\alpha}{CH_3COOH} + \underset{\substack{\text{(hydrolysis)}\\ C\alpha}}{OH^-} \qquad ...(2)$$

[α = degree of hydrolysis]

$$= C(1 - \alpha)$$

Na^+ does not hydrolyse because it reacts with H_2O to give NaOH which ionises completely to give Na^+ and OH^- ions.

∴ Hydrolysis constant,

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \qquad ...(3)$$

[from equation (2)]

Also,
$$K_a = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

$$[\because CH_3COOH \rightleftharpoons CH_3COO^- + H^+]$$

and
$$K_w = [H^+][OH^-][\because H_2O \rightleftharpoons H^+ + OH^-]$$

$$\therefore \quad \frac{K_w}{K_a} = \frac{[H^+][OH^-] \times [CH_3COOH]}{[CH_3COO^-][H^+]}$$

$$= \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = K_h$$

$$\therefore \quad \frac{K_w}{K_a} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$$

$$\left[\because \alpha << 1, \alpha \text{ can be neglected in the denominator}\right]$$

$$\therefore \quad \alpha = \left(\frac{K_w}{K_a.C}\right)^{1/2}. \text{ But } [OH^-] = C\alpha\ ;$$

$$\therefore \quad [OH^-] = C\left(\frac{K_w}{K_aC}\right)^{1/2} = \left(\frac{C^2K_w}{K_aC}\right)^{1/2} = \left(\frac{CK_w}{K_a}\right)^{1/2}$$

Also,
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{K_w}{(CK_w/K_a)^{1/2}}$$

$$= \left(\frac{K^2{}_w \times K_a}{CK_w}\right)^{1/2} = \left(\frac{\boldsymbol{K_wK_a}}{\boldsymbol{C}}\right)^{1/2}$$

Thus, hydrolysis of CH_3COO^- ion gives OH^- ions and hence solution of salts of weak acids and strong bases is **basic** in nature.

EXAMPLE 154. *Calculate the amount of NH_4Cl required to dissolve in 500 mL water to have pH 4.7 of the solution. K_b for $NH_4OH = 1.8 \times 10^{-5}$.*

SOLUTION. Reaction $\quad NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$

Conc. at equilibrium $\quad C - Ch \qquad Ch \qquad Ch$

$$p\text{H} = 4.7\ ; -\log[H^+] = 4.7\ ;$$

$$\log[H^+] = -4.7 = -4 - 1 + 1 - 0.7 = \bar{5}.3$$

Or
$$\log[H^+] = \bar{5}.3\ ; [H^+] = \text{antilog } \bar{5}.3$$

$$= 1.99 \times 10^{-5}$$

Also, $[H^+] = hC$ where h is degree of hydrolysis.

But
$$h = \left(\frac{K_w}{K_bC}\right)^{1/2};$$

Hence
$$[H^+] = \left(\frac{K_w \times C^2}{K_bC}\right)^{1/2} = \left(\frac{K_wC}{K_b}\right)^{1/2}$$

Squaring both sides, we get :

$$[H^+]^2 = \frac{K_wC}{K_b} \text{ Or } C = \frac{[H^+]^2 K_b}{K_w}$$

Hence
$$C = \frac{(1.99 \times 10^{-5})^2 \times 1.8 \times 10^{-5}}{10^{-14}}$$

$$= 0.71 \text{ mol L}^-$$

Thus 1000 mL solution contain NH_4Cl = 0.71 mol

∴ 500 mL solution contain NH_4Cl

$$= \frac{0.71 \times 500}{1000} = 0.355 \text{ mol}$$

g. mol. wt. of NH_4Cl = 14 + (4 × 1) + 35.5 = 53.5 g

∴ Amount of NH_4Cl = 0.355 × 53.5 g = **18.99 g**

Some important formulae on hydrolysis of salts

	Salt of	Examples	Hydrolysis constant, K_h	Degree of hydrolysis, h	pH of solution
1.	Strong acid and strong base	KCl, $NaNO_3$ Na_2SO_4 etc	No hydrolysis takes place		

2.	Strong acid and weak base	NH_4NO_3, NH_4Cl	$\frac{K_w}{K_b}$	$\left(\frac{K_w}{K_bC}\right)^{1/2}$ $= \left(\frac{K_h}{C}\right)^{1/2}$	.5[$pK_w - pK_b -$ log C] Or 7 – 0.5 pK_b – 0.5logC
3.	Weak acid and strong base	Na_2CO_3, CH_3COOK etc	$\frac{K_w}{K_a}$	$\left(\frac{K_w}{K_b.C}\right)^{1/2}$ $= \left(\frac{K_h}{C}\right)^{1/2}$	7 + 0.5 pK_a + 0.5 log COr 0.5 [$pK_w + pK_a$ + log C] Or – log $\left(\frac{K_a.K_w}{C}\right)^{1/2}$
4.	Weak acid and weak base	CH_3COONH_4, NH_4CN	$\frac{K_w}{K_a.K_b}$	$\left(\frac{K_w}{K_a.K_b}\right)^{1/2}$	7 + 0.5 pK_a – 0.5 pK_b Or 0.5[$pK_w + pK_a - pK_b$] Or – log $\left(\frac{K_a.K_w}{K_b}\right)^{1/2}$

Note. (1) $pK_w = -\log K_w$; $pK_a = -\log K_a$; $pK_b = -\log K_b$.

(2) *For salt of weak acid and weak base,* if K_h is not small, then :

(*i*) $$h = \frac{(K_h)^{1/2}}{1+(K_h)^{1/2}}$$

(*ii*) $pH = pK_a - \log h + \log (1-h)$

(3) $$[H^+] = \left(\frac{K_wK_a}{C}\right)^{1/2}$$

(4) $$[OH^-] = \left(\frac{CK_w}{K_a}\right)^{1/2}$$

Type. Salt of strong base and weak acid.

Example 155. *Calculate the amount of potassium cyanide in gram that must be dissolved in 250 mL water to give a solution with a pH of 10.9. K_a (HCN) = 4.0 × 10^{-10}.*

Solution. (*a*) $KCN + H_2O \rightleftharpoons KOH + HCN$

Conc. at equilibrium $C - Ch = C(1-h)$ $\quad Ch \quad Ch$

$$\text{Hydrolysis constant, } K_h = \frac{[KOH][HCN]}{[KCN]};$$

$$K_h = \frac{Ch \times Ch}{C(1-h)} = \frac{(Ch)^2}{C} = \frac{[OH^-]^2}{C}$$

Or $$C = \frac{[OH^-]^2}{K_h} = \frac{[OH^-]^2 \times K_a}{K_w}$$

Or $$C = \frac{K_a[OH^-]^2}{K_w} \quad ...(1)$$

(*b*) $pH = 10.9$; $pOH = 14 - pH$
$= 14 - 10.9 = 3.1$

Or $-\log [OH^-] = 3.1$; $\log [OH^-] = -3.1$
$= -3 - 1 + 1 - 0.1 = \bar{4}.9$

Taking antilog of both sides, we get : $[OH^-]$ =

antilog $\bar{4}.9 = 7.9 \times 10^{-4}$

Substituting the values of $[OH^-]$ in (1), we get :

$$C = \frac{4.0 \times 10^{-10} \times (7.9 \times 10^{-4})^2}{10^{-14}}$$

$= 0.025$

$[KCN] = 0.025$ mol L^-

g. mol. wt. of KCN = 39 + 12 + 14 = 65 g

∴ $[KCN] = 0.025 \times 65 = 1.625$ g L^-

∴ Amount of KCN in 250 mL

$$= \frac{1.625 \times 250}{1000} = \mathbf{0.406\ g} \quad \textbf{Ans.}$$

Example 156. *If the dissociation constant of H_3PO_4 is 1.3 × 10^{-12}, what will be the pH of 0.2M solution of potassium orthophosphate ?*

Solution. Reaction : $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$

But $$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.3 \times 10^{-12}} = 7.7 \times 10^{-5}$$

Also,degree of hydrolysis,

$$h = \left(\frac{K_h}{C}\right)^{1/2} = \left(\frac{7.7 \times 10^{-5}}{0.2}\right)^{1/2}$$

$= (385 \times 10^{-6})^{1/2} = 19.6 \times 10^{-3}$

Also, $[OH^-] = hC$.

Hence $[OH^-] = 19.6 \times 10^{-3} \times 0.2$

∴ $$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{19.6 \times 10^{-3} \times 0.2}$$

$= 2.55 \times 10^{-12}$

∴ $pH = -\log [H^+] = -\log 2.55 \times 10^{-12}$

$= -(\log 2.55 + \log 10^{-12})$

$= -(0.4065 - 12)$ pH

$= \mathbf{11.59}$ **Ans.**

Example 157. *Calculate the pH of 0.03M sodium nitrite solution and also its degree of hydrolysis (ionisation constant of nitrous acid = 4.5 × 10^{-4}).*

Solution.

$K_a(HNO_2) = 4.5 \times 10^{-4}$; $K_w = 10^{-14}$

But hydrolysis constant, $K_h = \frac{K_w}{K_a}$

∴ $$K_h = \frac{10^{-14}}{4.5 \times 10^{-4}} = 2.2 \times 10^{-11}$$

Let h = Degree of hydrolysis

∴ $$K_h = \frac{Ch^2}{1-h} \text{ or } Ch^2$$

[because h being very small, it is ignored from the denominator]

$$2.2 \times 10^{-11} = 0.03\,h^2\,;\,h^2 = \frac{2.2 \times 10^{-11}}{0.03}$$

$$= 7.3 \times 10^{-10}$$

$$\therefore \quad h = (7.3 \times 10^{-10})^{1/2} = 2.7 \times 10^{-5}$$

But $pH = 0.5\,[pK_w + pK_a + \log C]$

$= 0.5\,[-\log K_w - \log K_a + \log C]$

$= 0.5\,[-\log 10^{-14} - [\log 4.5 \times 10^{-4}] + \log 0.03]$

$pH = 0.5\,[14 - 0.6532 + 4 - 1.5229]$

$= 0.5 \times 15.8239$

$= 7.9$ **Ans.**

EXAMPLE 158. *What is the pH of a 0.50M aqueous NaCN solution ? pK_b of CN^- is 4.70.* **(IIT 1996)**

SOLUTION. Concentration of NaCN = 0.5 ; $pK_w = 14$

But $pK_a + pK_b = 14\,;\, pK_a + 4.7 = 14\,;$

$pK_a = 14 - 4.7 = 9.3$

We know that for a salt of weak acid and strong base:

$pH = 0.5\,[pK_w + pK_a + \log C]$

$\therefore \quad pH = 0.5\,[14 + 9.3 + \log 0.5]$

$= 0.5\,[23.3 - 0.301]$

$\boldsymbol{pH = 11.5}$ **Ans.**

EXAMPLE 159. *The pH value of a 0.05 M solution of potassium formate is 9.25 at 25°C. Calculate the degree of hydrolysis, hydrolysis constant and also the dissociation constant of formic acid. (Take K_w at 25°C as 10^{-14}).*

SOLUTION.

(*a*) $K^+ + HCOO^- + H_2O \rightleftharpoons HCOOH + K^+ + OH^-$ (hydrolysis)

Or $\quad HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$

$C = 0.05M$. In case of salt of a weak acid and strong base :

$$pH = -\log\left(\frac{K_w.K_a}{C}\right)^{1/2}$$

$$= -\frac{1}{2}\,[\log K_w + \log K_a - \log C]$$

$$9.25 = -\frac{1}{2}\,[\log 10^{-14} + \log K_a - \log 0.05]$$

$$= -\frac{1}{2}[-14 + \log K_a - (-1.301)]$$

Or $\quad 2 \times 9.25 = -[-14 + \log K_a + 1.301]$

$= 14 - \log K_a - 1.301$

Or $\quad \log K_a = 14 - 1.301 - 18.5 = -5.801$

$= -5 - 1 + 1 - 0.801 = \bar{6}.199$

$\therefore \quad K_a = \text{antilog}\ \bar{6}.199 = 1.581 \times 10^{-6}$

= Dissociation constant of formic acid.

(*b*) Hydrolysis constant,

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.581 \times 10^{-6}}$$

$$= 6.32 \times 10^{-9}$$

(*c*) Degree of hydrolysis,

$$h = \left(\frac{K_h}{C}\right)^{1/2} = \left(\frac{6.32 \times 10^{-9}}{0.05}\right)^{1/2}$$

$$= (12.64 \times 10^{-8})^{1/2}$$

$$= 3.56 \times 10^{-4}$$

Or $\quad h = 3.56 \times 10^{-4} \times 100$

$= \mathbf{0.0356\%}$ **Ans.**

EXAMPLE 160. *Calculate the degree of hydrolysis, hydrolysis constant and pH of a 0.04M solution of sodium acetate. $K_w = 10^{-14}$, $K_a\,(CH_3COOH) = 1.8 \times 10^{-5}$.*

SOLUTION.

$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

Or $\quad CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ (hydrolysis)

$C = 0.04M;\ K_w = 10^{-14},\ K_a = 1.8 \times 10^{-5}.$

(*a*)For the salt of a weak acid and strong base :

$$K_h = \frac{K_w}{k_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = \mathbf{5.56 \times 10^{-10}}$$

(*b*) $\quad h = \text{Hydrolysis constant} = \left(\dfrac{K_w}{k_a C}\right)^{1/2}$

$$= \left(\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.04}\right)^{1/2}$$

$$= (1.39 \times 10^{-8})^{1/2}$$

$$= 1.18 \times 10^{-4}$$

(*c*) $\quad pH = \dfrac{1}{2}\,[pK_w + pK_a + \log C]$

$$= -\frac{1}{2}\,[\log K_w + \log K_a - \log C]$$

$$= -\frac{1}{2}\,[\log 10^{-14} + \log 1.8 \times 10^{-5} - \log 0.04]$$

$$= -\frac{1}{2}\,[-14 + \log 1.8 + \log 10^{-5} - \log 0.04]$$

$$= -\frac{1}{2}\,[-14 + 0.255 - 5 - (-1.398)]$$

$\boldsymbol{pH} = -\dfrac{1}{2}\,[-17.347] = \mathbf{+\,8.674}$ **Ans.**

Type. Salts of strong acids and weak bases

$$\underset{\text{Weak base}}{NH_4OH} + \underset{\text{Strong acid}}{HCl} \longrightarrow \underset{\text{Salt of weak base and strong acid}}{NH_4Cl} + H_2O$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \qquad ...(1)$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \ldots(2) \text{ (hydrolysis)}$$

conc.

at eqbm. $C - C\alpha = C(1-\alpha) \qquad C\alpha \qquad C\alpha$

(α = degree of hydrolysis)

Cl^- does not hydrolyse because it reacts with H_2O to give HCl, which ionises completely to give H^+ and Cl^- ions.

Hydrolysis constant,

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \qquad \ldots(3)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$(\because NH_4OH \rightleftharpoons NH_4^+ + OH^-)$$

$$K_w = [H^+][OH^-] (\because H_2O \rightleftharpoons H^+ + OH^-)$$

$$\therefore \quad \frac{K_w}{K_b} = \frac{[H^+][OH^-] \times [NH_4OH]}{[NH_4^+] \times [OH^-]}$$

$$= \frac{[H^+][NH_4OH]}{[NH_4^+]} = K_h$$

$$\frac{K_w}{K_b} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$$

[$\because \alpha << 1$, α can be neglected from the denominator]

$$\therefore \quad \alpha = \left(\frac{K_w}{CK_b}\right)^{1/2}$$

$$\text{But} \quad [H^+] = C\alpha = \left(\frac{C^2K_w}{CK_b}\right)^{1/2} = \left(\frac{CK_w}{K_b}\right)^{1/2}$$

The hydrolysis of salt of a weak base and a strong acid gives an acidic solution.

Type. ***Salt of strong acid and weak base***

EXAMPLE 161. *Calculate the hydrolysis constant, degree of hydrolysis and hydrogen ion concentration in 0.15N NH_4NO_3 solution. [K_b for $NH_4OH = 1.8 \times 10^{-5}$, $K_w = 1 \times 10^{-14}$]*

SOLUTION. $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

Concentration at equilibrium $C - C\alpha = C(1-\alpha) \qquad C\alpha \qquad C\alpha$

$$\text{Degree of hydrolysis, } h = \left(\frac{K_h}{C}\right)^{1/2} \quad \ldots(1)\ ;\ C = 0.15N$$

$$K_h = \frac{K_w}{K_b}\ ;\ K_h = \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$$= 5.6 \times 10^{-10}$$

Where K_h = Hydrolysis constant.

$\therefore$ From equation (1), we have :

$$h = \left(\frac{5.6 \times 10^{-10}}{0.15}\right)^{1/2} = 6.1 \times 10^{-5}$$

But $[H^+] = Ch\ ;\ [H^+] = 0.15 \times 6.1 \times 10^{-5}$

$= 9.15 \times 10^{-6}$

And $pH = -\log[H^+] = -\log[9.15 \times 10^{-6}]$

$= -[\log 9.15 + \log 10^{-6}]$

$pH = -[0.9614 - 6] = \mathbf{5.04}$ **Ans.**

EXAMPLE 162. *Calculate the hydrolysis constant, pH value and the $[OH^-]$ for NH_4Cl in 0.1M NH_4Cl solution. $K_w = 10^{-14}$ and K (NH_4OH) = 1.75×10^{-5}.* **(CBSE-PMT,2009)**

SOLUTION. (*i*) NH_4Cl is a salt of weak base (NH_4OH) and strong acid (HCl). Thus, the hydrolysis constant :

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.75 \times 10^{-5}}$$

$= \mathbf{5.7 \times 10^{-10}}$ **Ans.**

(*ii*) $pH = 0.5\,[pK_w - pK_b - \log C]$

$= 0.5\,[14 - (-\log 1.75 - \log 10^{-5}) - \log 0.1]$

$pH = 0.5\,[14 + 0.243 - 5 - (-1)]$

$= \mathbf{5.12}$ **Ans.**

$\therefore \quad -\log[H^+] = 5.12\ ;\ \log[H^+] = -5.12$

$= -5 - 1 + 1 - 0.12 = \bar{6}.88$

$\therefore \quad [H^+] = \text{antilog } \bar{6}.88 = 7.58 \times 10^{-6}$

$$\therefore \quad [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{7.58 \times 10^{-6}}$$

$= \mathbf{1.32 \times 10^{-9}}$ **Ans.**

EXAMPLE 163. *Calculate the percentage of hydrolysis in 0.003M aqueous solution of NaOCN (K_a of HOCN = 3.33×10^{-4}M).* **(Roorkee 1996)**

SOLUTION. NaOCN is a salt of strong base NaOH and weak acid HOCN.

Reaction : $OCN^- + H_2O \rightleftharpoons OH^- + HOCN$

Conc. at start 0.003M

Conc. at equilibrium $0.003 - \alpha \qquad \alpha \qquad \alpha$

For such a salt,

$$\alpha = \left(\frac{K_w}{K_aC}\right)^{1/2}$$

$$= \left(\frac{10^{-14}}{3.33 \times 10^{-4} \times 0.003}\right)^{1/2}$$

$$= (10^{-8})^{1/2} = 10^{-4}$$

Or % age hydrolysis = $10^{-4} \times 100 = \mathbf{0.01\%}$ **Ans.**

EXAMPLE 164. *Calculate the ionisation constant of a weak base B, if the pH of its 0.4M BNO_3 solution is 5.*

SOLUTION. $K_b = ?,\ K_w = 10^{-14}\ ;\ pH = 5.$

Hence $[H^+] = 10^{-5}$

Hydrolysis. $BNO_3 + H_2O \rightleftharpoons BOH + HNO_3$

Or $$B^+ + H_2O \rightleftharpoons BOH + \underset{10^{-5}}{H^+}$$

BNO_3 being a salt of a strong acid with a weak base, so hydrolysis constant, K_h is given as:

$$K_h = \frac{K_w}{K_b} \qquad ...(1)$$

But $$K_h = \frac{[BOH][H^+]}{[B^+]}$$

$$= \frac{[H^+][H^+]}{[B^+]} = \frac{[H^+]^2}{[B^+]}$$

$$= \frac{(10^{-5})^2}{0.4} = \frac{10^{-10}}{0.4}$$

Substituting the value of K_h in equation (1), we get :

$$\frac{10^{-10}}{0.4} = \frac{10^{-14}}{K_b} \text{ Or } K_b = \frac{10^{-14} \times 0.4}{10^{-10}}$$

$$= \mathbf{4.0 \times 10^{-5}} \qquad \textbf{Ans.}$$

EXAMPLE 165. *At 298K, how much of a 0.25M solution of sodium acetate should be diluted to get double the degree of hydrolysis?*

SOLUTION. $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

(hydrolysis)

At equilibrium $C - Ch$ $\quad Ch \quad Ch$

$= C(1 - h)$

($\because$ h = degree of hydroysis)

$$\therefore \quad K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$= \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h} = Ch^2 \; ...(1)$$

($\because$ h is very small, it is neglected in the denominator).

Suppose at concentration, C_1, degree of hydrolysis = $2h$.

Hence : $$K_h = C_1(2h)^2 = 4C_1h^2 \qquad ...(2)$$

From equations (1) and (2), we get :

$$4C_1h^2 = Ch^2 \; ; \; C_1 = \frac{C}{4}.$$

Hence solution should be diluted four times.

EXAMPLE 166. *Find out the value of pH of 0.001M $Zn(NO_3)_2$ solution (K_b for $Zn(OH)_2 = 2.2 \times 10^{-12}$).*

SOLUTION. *Reaction :*

$$Zn(NO_3)_2 + 2H_2O \rightleftharpoons Zn(OH)_2 + 2HNO_3$$

Or $$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+ \qquad ...(1)$$

	Zn^{2+}	$Zn(OH)_2$	$2H^+$
Conc. at start	C	0	0
Conc. after the reaction	$C - Ch$	Ch	$2Ch$

Where h = degree of hydrolysis ;

C = 0.001 mol L^-

$$\therefore \quad K_h = \frac{[Zn(OH)_2][H^+]^2}{[Zn^{2+}]} \qquad ...(2)$$

$$= \frac{Ch \times (2Ch)^2}{C - Ch \text{ or } C(1-h)}$$

$$= \frac{4C^3h^3}{C(1-h)} = 4C^2h^3$$

[$\because$ h is very small as compared to 1, so, it is neglected in the denominator]

$$\therefore \quad h = \left(\frac{K_h}{4C^2}\right)^{1/3} \qquad ...(3)$$

Also : $$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$$

$$\therefore \quad K_b = \frac{[Zn^{2+}][OH^-]^2}{[Zn(OH)_2]} \qquad ...(4)$$

From equations (2) and (4), we get

$$K_h \times K_b = [H^+]^2[OH^-]^2 = \{[H^+][OH^-]\}^2$$

$$= K_w^{\,2} \; ; \; K_h = \frac{K_w^2}{K_b}$$

Or $$K_h = \left(\frac{(10^{-14})^2}{2.2 \times 10^{-12}}\right) = 4.5 \times 10^{-17}.$$

Substituting the value of K_h and C in equation (3), we get :

$$h = \left(\frac{4.5 \times 10^{-17}}{4 \times (0.001)^2}\right)^{\frac{1}{3}}$$

$$= (1.125 \times 10^{-11})^{1/3}.$$

Thus, $$\log h = \log (1.125 \times 10^{-11})^{1/3}$$

$$= \frac{1}{3} [\log 1.125 + \log 10^{-11}]$$

$$= \frac{1}{3}(0.051 - 11) = \frac{1}{3} - 10.979$$

$$= -3.6497$$

$$= -3 - 1 + 1 - 0.6497 = \bar{4}.3503$$

Or $$h = \text{antilog } \bar{4}.3503 = \mathbf{2.24 \times 10^{-4}}.$$

But $$[H^+] = 2Ch \text{ [from equation (1)]}$$

$$= 2 \times 0.001 \times 2.24 \times 10^{-4}$$

$$= 4.48 \times 10^{-7}$$

$$\therefore \quad pH = -\log [H^+] = -\log 4.48 \times 10^{-7}$$

$$= -(\log 4.48 \times 10^{-7})$$

$$\boldsymbol{p}\mathbf{H} = -(0.6513 - 7) \simeq \mathbf{6.35} \qquad \textbf{Ans.}$$

Type. Salt of a weak acid and weak base.

EXAMPLE 167. *Find the value of hydrolysis constant, degree of hydrolysis and pH of a 0.02M ammonium cyanide solution at 298K. $K_w = 10^{-14}$, $K_a(HCN) = 4.99 \times 10^{-10}$, K_b (NH_4OH) $= 1.77 \times 10^{-5}$.*

SOLUTION. (*a*) Ammonium cyanide (NH_4CN) is a salt of weak acid and weak base.

Hence : $$K_h = \left(\frac{K_w}{K_aK_b}\right)^{1/2}$$

$$= \left(\frac{10^{-14}}{(4.99 \times 10^{-10}) \times 1.77 \times 10^{-5}}\right)^{1/2}$$

$$= (1.32)^{1/2} = \mathbf{1.06}$$

(*b*) Since the value of K_h is not small :

$$h = \text{degree of hydrolysis} = \frac{(K_h)^{1/2}}{1 + (K_h)^{1/2}}$$

$$= \frac{(1.06)^{1/2}}{1 + (1.06)^{1/2}}$$

$$= \frac{1.03}{1 + 1.03} = \frac{1.03}{2.03} = 0.51$$

(*c*) Since h is very small as compared to unity :

$$pH = pK_a - \log h + \log (1 - h)$$

$$= -\log K_a - \log h + \log (1 - h)$$

$$= -\log (4.99 \times 10^{-10}) - \log 0.51 + \log (1 - 0.51)$$

$$= -[\log 4.99 + \log 10^{-10}] - (-0.29) + (-0.31)$$

$$= -[0.698 - 10] + 0.29 - 0.31$$

$$pH = 9.302 + 0.29 - 0.31 = \mathbf{9.28}$$ **Ans.**

EXAMPLE 168. *Calculate the pH of an aqueous solution of 1.0M ammonium formate assuming complete dissociation. pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.* **(IIT1995)**

SOLUTION. Ammonium formate is a salt of weak acid (formic acid) and weak base (NH_4OH). For such a solution,

$$pH = 0.5[pK_w + pK_a - pK_b]$$

$$= 0.5[14 + 3.8 - 4.8]$$

$[\because$ Given : $pK_a = 3.8, pK_b = 4.8]$

$$= \mathbf{6.5}$$ **Ans.**

EXAMPLE 169. *Calculate the degree of hydrolysis of ammonium acetate if $K_w = 10^{-14}$, $K\ (NH_4OH) = 1.8 \times 10^{-5}$ and $K\ (CH_3COOH) = 1.8 \times 10^{-5}$.*

SOLUTION. Ammonium acetate (CH_3COONH_4) is a salt of weak acid (CH_3COOH) and weak base (NH_4OH).

So, hydrolysis constant,

$$K_h = \frac{K_w}{K_aK_b} = \frac{10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

Or $K_h = 3.09 \times 10^{-5}$

Hydrolysis of salt is given below :

$$\underset{\frac{1-h}{V}}{CH_3COO} + \underset{\frac{1-h}{V}}{NH_4^+} + H_2O \rightleftharpoons \underset{\frac{h}{V}}{CH_3COOH} + \underset{\frac{h}{V}}{NH_4OH}$$

$$\therefore \quad K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]}$$

(law of chemical equilibrium)

$$K_h = \frac{\frac{h}{V} \times \frac{h}{V}}{\frac{1-h}{V} \times \frac{1-h}{V}} = \frac{h^2}{(1-h)^2}.$$

But $$K_h = \frac{K_w}{K_aK_b} = \frac{10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

Or $K_h = 3.09 \times 10^{-5}$

$$\therefore \quad \frac{h^2}{(1-h)^2} = 3.09 \times 10^{-5};$$

$$\frac{h}{1-h} = (3.09 \times 10^{-5})^{1/2} = 5.56 \times 10^{-3}$$

Or $h = 5.56 \times 10^{-3} - 5.56 \times 10^{-3}h$;

$h + 5.56 \times 10^{-3}h = 5.56 \times 10^{-3}$ **Or** $h = 5.56 \times 10^{-3}$

$[\because 5.56 \times 10^{-3}$ is very small, it can be neglected$]$

Hence $h = \mathbf{0.00556}$ **Ans.**

EXAMPLE 170. *At 298K, the values of ionisation constants of water, acetic acid and aniline are respectively 1.008×10^{-14}, 1.75×10^{-5} and 3.83×10^{-10}. Calculate the % age hydrolysis of aniline acetate in the 0.1N and 0.2N solution.*

SOLUTION. Aniline acetate is a salt of weak base and weak acid.

Given $K_w = 1.008 \times 10^{-14}, K_a = 1.75 \times 10^{-5},$
$K_b = 3.83 \times 10^{-10}$

So, we have : Degree of hydrolysis,

$$h = \left(\frac{K_w}{K_aK_b}\right)^{1/2}$$

$$= \left(\frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}}\right)^{1/2}$$

$$= 1.22$$

But h cannot be greater than 1. So, above formula for h cannot be used. So :

$$h = \frac{(K_h)^{1/2}}{1 + (K_h)^{1/2}}$$

Where $$K_h = \frac{K_w}{K_aK_b}$$

$$= \frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}} = 1.5$$

$$\therefore \qquad h = \frac{(1.5)^{1/2}}{1+(1.5)^{1/2}} = \frac{1.22}{1+1.22}$$

$$= \frac{1.22}{2.22} = 0.5495$$

∴ % age degree of hydrolysis

$$= 0.5495 \times 100 = \mathbf{54.95\%} \qquad \textbf{Ans.}$$

We see that in the above case, the degree of hydrolysis (h) is independent of concentration. So, 'h' remains equal to 0.5495 in 0.1 and 0.2N solution.

EXAMPLE 171. *Calculate the dissociation constant of aniline from the given data. (i) K (acetic acid) =* 1.8×10^{-5} *(ii)* $K_w = 10^{-14}$ *(iii) Degree of hydrolysis of 0.01N aniline acetate is 55% at 291K.*

SOLUTION. *Aniline acetate is a salt of weak acid (acetic acid) and weak base (aniline). So,* $K_b = ?$ $K_a = 1.8 \times 10^{-5}$; $h = 55\% = 55/100 = 0.55$.

But (a) $$K_h = \frac{h^2}{(1-h)^2} \qquad \text{...(1)}$$

(b) $$K_h = \frac{K_w}{K_a \times K_b} \qquad \text{...(2)}$$

From equations (1) and (2), we get

$$\frac{h^2}{(1-h)^2} = \frac{K_w}{K_a \times K_b}\,;\; K_b = \frac{K_w \times (1-h)^2}{K_a h^2}$$

Or $$K_b = \frac{10^{-14}\,(1-0.55)^2}{1.8 \times 10^{-5} \times (0.55)^2} = \frac{10^{-9} \times (0.45)^2}{1.8\,(0.55)^2}$$

$$= \mathbf{3.7 \times 10^{-10}} \qquad \textbf{Ans.}$$

EXAMPLE 172. *Calculate for 0.01N solution of sodium acetate (i) hydrolysis constant (ii) degree of hydrolysis (iii) pH* ($K_a = 1.9 \times 10^{-5}$). **(MLNREC Allahabad, 1991)**

SOLUTION. $K_w = 10^{-14}$; C = 0.01N

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

Concentration $\qquad Ch$

(i) $$K_h = \text{hydrolysis constant}$$

$$= \frac{K_w}{K_a} = \frac{10^{-14}}{1.9 \times 10^{-5}}$$

$$= \mathbf{5.26 \times 10^{-10}} \qquad \textbf{Ans.}$$

(ii) Degree of hydrolysis,

$$h = \left(\frac{K_h}{C}\right)^{1/2}$$

$$= \left(\frac{5.26 \times 10^{-10}}{0.01}\right)^{1/2}$$

$$= (5.26 \times 10^{-8})^{1/2}$$

$$\therefore \qquad h = 2.29 \times 10^{-4} \qquad \textbf{Ans.}$$

(iii) $\qquad pH = ?$;

$$[OH^-] = Ch = 0.01 \times 2.29 \times 10^{-4}$$

$$= 0.0229 \times 10^{-4} M$$

$$\therefore \qquad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.0229 \times 10^{-4}}$$

$$= 4.37 \times 10^{-9}$$

$$\therefore \qquad pH = -\log [H^+] = -\log 4.37 \times 10^{-9}$$

$$= -[\log 4.37 + \log 10^{-9}]$$

$$= -[0.64 - 9]$$

$$\mathbf{pH = 8.36} \qquad \textbf{Ans.}$$

EXAMPLE 173. *When 0.2M acetic acid is neutralised with 0.2M NaOH in a 0.5 litre of water, the resulting solution is slightly alkaline. Calculate the pH of the resulting solution.* *(K_a for acetic acid =* 1.8×10^{-5}*).* **(Roorkee, 1989)**

SOLUTION.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

Volume of water = 0.5 L = 0.5 × 1000 = 500 ml

0.2M CH_3COOH is neutralised by 0.2 M NaOH in 500 mL water.

$$\therefore \qquad [CH_3COONa] = \frac{0.2\text{ M} \times 500\text{ mL}}{1000\text{ mL}} = 0.1\text{ M}$$

	$CH_3COO^- + H_2O$	$\rightleftharpoons CH_3COOH$	$+ OH^-$
(1) Conc. at start	0.1M	x	x
(2) Change by reaction	$-x$	x	x
(3) Conc. at equilibrium	$0.1 - x$ $= 0.1$	x	x

(∵ x is very small, $0.1 - x = 0.1$)

$$\therefore \qquad K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$= \frac{x \times x}{0.1} = \frac{x^2}{0.1} \qquad \text{...(1)}$$

But $$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10} \qquad \text{...(2)}$$

From (1) and (2), we get :

$$\frac{x^2}{0.1} = 5.5 \times 10^{-10}$$

$$\therefore \qquad x = (5.5 \times 10^{-10} \times 0.1)^{1/2}$$

$$= (55 \times 10^{-12})^{1/2} = 7.4 \times 10^{-6}$$

Or $$[OH^-] = 7.4 \times 10^{-6}$$

$$\therefore \qquad [H^+(aq)] = \frac{K_w}{[OH^-(aq)]} = \frac{10^{-14}}{7.4 \times 10^{-6}}$$

$$= 1.35 \times 10^{-9}$$

$$pH = -\log [H^+] = -\log 1.35 \times 10^{-9}$$

$$= -[\log 1.35 + \log 10^{-9}]$$

$$= -(0.13 - 9) = \mathbf{8.87} \qquad \textbf{Ans.}$$

EXAMPLE 174. *Calcium lactate is a salt of weak acid and is represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.13 mol of salt in 0.5 litre solution. The pOH of this is 5.6. Assuming complete dissociation of salt, calculate K_a of lactic acid.* **(Roorkee Entrance 1991)**

SOLUTION. $Ca(LaC)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HLaC$

Or $2LaC^- + 2H_2O \rightleftharpoons 2OH^- + 2HLaC$.hydrolysis

Conc. after hydrolysis $C - Ch$ $\quad Ch \quad Ch$

$$[OH^-] = Ch = C\left(\frac{K_h}{C}\right)^{1/2}$$

$$= \left(C^2 \frac{K_w}{K_a C}\right)^{1/2} = \left(\frac{K_w C}{K_a}\right)^{1/2}$$

0.5L solution contain $Ca(LaC)_2 = 0.13M$

$\therefore$ 1L solution contain $Ca(LaC)_2 = \frac{0.13}{0.5} \times 1 = 0.26M.$

$\therefore$ C = Concentration of $2LaC^-$ anion that undergoes hydrolysis = 0.26M × 2 = 0.52 M

We know $$[OH^-] = \left(\frac{CK_w}{K_a}\right)^{1/2};$$

$$[OH^-] = \left(\frac{0.52 \times 10^{-14}}{K_a}\right)^{1/2} \qquad ...(1)$$

But $\quad pOH = 5.6$ (given) ;

$- \log [OH^-] = 5.6$;

$\log [OH^-] = -5.6 = -5 - 1 + 1 - 0.6 = \bar{6}.4.$

Taking antilog of both sides, we get :

$[OH^-] = 2.5 \times 10^{-6}.$

Substituting the value $[OH^-]$ in equation (1), we get :

$$2.5 \times 10^{-6} = \left(\frac{0.52 \times 10^{-14}}{K_a}\right)^{1/2}$$

Squaring both sides, we get

$$(2.5 \times 10^{-6})^2 = \frac{0.52 \times 10^{-14}}{K_a};$$

$$K_a = \frac{0.52 \times 10^{-14}}{2.5 \times 10^{-6} \times 2.5 \times 10^{-6}}$$

$\therefore$ $\mathbf{K_a = 8.32 \times 10^{-4}}$ **Ans.**

EXAMPLE 175. *Calculate the pH at the equivalence point when a solution of 0.1M acetic acid is titrated with a solution of 0.1M NaOH. K_a for acetic acid is 1.9×10^{-5}.* **(Roorkee Entrance, 1990)**

SOLUTION. $[CH_3COOH] = [NaOH] = 0.1M$ (given)

Let V ml of 0.1M CH_3COOH and V mL of 0.1M NaOH are used.

$\therefore$ Total volume of solution = $V + V = 2V$ mL

$\therefore$ Initial concentration of CH_3COOH

$$= \frac{0.1 \times V}{2V} = 0.05M = C$$

Also, Initial concentration of NaOH

$$= \frac{0.1 \times V}{2V} = 0.05M \backsimeq C$$

Reactions :

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$ [neutralisation]

$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$ [Hydrolysis]

Concentration after reaction, $C \quad Ch \quad Ch$

$$\therefore \quad [OH^-] = Ch = C\left(\frac{K_h}{C}\right)^{1/2}$$

$$= \left(\frac{CK_w}{K_a}\right)^{1/2} = \left(\frac{0.05 \times 10^{-14}}{1.9 \times 10^{-5}}\right)$$

$= (26.3 \times 10^{-12})^{1/2}$ or

$[OH^-] = 5.13 \times 10^{-6}$

$\therefore$ $pOH = -\log [OH^-]$

$= -[\log 5.13 \times 10^{-6}]$

$= -[\log 5.13 + \log 10^{-6}]$

$= -[0.71 - 6]; pOH = 5.29$

$\therefore$ **pH** $= 14 - pOH = 14 - 5.29$

$= \mathbf{8.71}$ **Ans.**

EXAMPLE 176. *What is the pH of a 0.5M aqueous NaCN solution? pK_b of $CN^- = 4.70$.* **(IIT 1996)**

SOLUTION.	$NaCN + H_2O$	$\rightleftharpoons$ NaOH	+ HCN
(1) n mol at start	C	0	0
(2) Change by reaction	$-Ch$	Ch	Ch
(3) n mol after hydrolysis	$C - Ch$	Ch	Ch

$\therefore$ $[OH^-] = Ch$

$$[OH^-] = (K_h.C)^{1/2} = \left(\frac{K_w.C}{K_a}\right)^{1/2} \qquad ...(1)$$

But $\quad pOH = 0.5 [pK_w - pK_a - \log C]$

$= 0.5 [-\log K_w - pK_a - \log C]$

$= 0.5 [-\log 10^{-14} - 9.3 - \log 0.5]$

$= 0.5 [14 - 9.3 - (-0.301)]$

$\because$ $pK_a = 14 - pK_b = 14 - 4.7 = 9.3$

Also, $C = 0.5$ M

$pOH = 2.5$

$\therefore$ **pH** $= 14 - pOH = 14 - 2.5$

$= \mathbf{11.5}$ **Ans.**

Example 177. *A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.* **(IIT 1984)**

Solution. Let weak acid = HA ; strong base = BOH

For weak acid,

$$HA \underset{}{\overset{H_2O}{\rightleftharpoons}} H^+(aq) + A^-(aq) ;$$

$$K_a = \frac{[H^+(aq)]\,[A^-(aq)]}{[HA]}$$

Reaction of weak acid with strong base is :

$$HA + B^+(aq) + OH^-(aq) \rightleftharpoons H_2O + B^+(aq) + A^-(aq)$$

$$\therefore \quad K_{eq} = \frac{[A^-(aq)]}{[HA]\,[OH^-(aq)]}$$

Or $$K_{eq} = \frac{[A^-(aq)]}{[HA]\,[OH^-(aq)]} \times \frac{H^+(aq)}{H^+(aq)}$$

$$= \frac{[A^-(aq)]\,[H^+(aq)]}{[HA]} \times \frac{1}{[OH^-(aq)]\,[H^+(aq)]} = \frac{K_a}{K_w}$$

Or $$K_{eq} = \frac{K_a}{K_w} \text{ which is reverse of } K_h$$

$$\left[\because K_h = \frac{K_w}{K_a}\right]$$

$$\therefore \quad K_{eq} = \frac{10^{-4}}{10^{-14}} = 10^{-4+14} = \mathbf{10^{10}}$$ **Ans.**

Example 178. *K_a for ascorbic acid (HAsc) is 5×10^{-5}. Calculate the hydrogen ion concentration and percentage of hydrolysis in an aqueous solution in which the concentration of the AsC^- ions is 0.02M.* **(Roorkee, 1997)**

Solution. We know $K_b = \frac{K_w}{K_a}$; $K_b = \frac{10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10}$

Reaction : $AsC^- + H_2O \rightleftharpoons HAsC + OH^-$

Conc. at start 0.02M 0 0

Conc. after reaction $0.02 - x$ x x

$$\therefore \quad K_b = \frac{[HAsC]\,[OH^-]}{[AsC^-]}$$

$$= \frac{x \times x}{0.02 - x} = \frac{x^2}{0.02}$$

[$\because$ x is very small as compared to 0.02, it is rejected in the denominator]

Or $$\frac{x^2}{0.02} = 2 \times 10^{-10}$$

($\because$ $K_b = 2 \times 10^{-10}$ found above)

$$\therefore \quad x = (2 \times 10^{-10} \times 0.02)^{1/2}$$

$$= 0.2 \times 10^{-5} ; \textbf{ Or}$$

$$[OH^-] = 0.2 \times 10^{-5}$$

$$\therefore \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.2 \times 10^{-5}}$$

$$= 5 \times 10^{-9} M$$

$$\therefore \quad \text{Degree of hydrolysis} = \frac{0.2 \times 10^{-5}}{0.02} \times 100$$

$$= \mathbf{0.01\%}$$ **Ans.**

Example 179. *The sodium salt of a weak acid is hydrolysed to the extent of 3.5% in 0.1M solution in water at 298K. Calculate the ionic product of water. (K_a of acid = 1.3×10^{-10}).*

Solution. ionic, C = 0.1M ; x = degree of hydrolysis = $3.5\% = \frac{3.5}{100} = 0.035$.

But hydrolysis constant,

$$K_h = Cx^2 ; K_h = 0.1 \times (0.035)^2$$

$$= 1.2 \times 10^{-4} \qquad \text{...(1)}$$

Also, $$K_h = \frac{K_w}{K_a} = \frac{K_w}{1.3 \times 10^{-10}} \qquad \text{...(2)}$$

Equating (1) and (2), we get :

$$\frac{K_w}{1.3 \times 10^{-10}} = 1.2 \times 10^{-4} ;$$

$$K_w = 1.2 \times 10^{-4} \times 1.3 \times 10^{-10}$$

$$= \mathbf{1.56 \times 10^{-14}}$$ **Ans.**

Example 180. *Calculate the amount of sodium acetate in gram that must be added to 500 mL water to give a pH of 8.4. ($K_a = 1.8 \times 10^{-5}$)*

Solution. We know that for a salt of weak acid (acetic acid) and strong base (NaOH):

$$pH = 0.5\,(pK_w + pK_a + \log C) ;$$

$$8.4 = 0.5\,\{14 + (-\log K_a) + \log C\}$$

$$8.4 = 0.5\,\{14 - (\log 1.8 \times 10^{-5}) + \log C\}$$

$$= 0.5\,\{\log 1.8 + \log 10^{-5} + \log C\}$$

$$8.4 = 0.5\,\{14 - (0.26 - 5) + \log C\} ;$$

$$\frac{8.4}{0.5} = 14 - 0.26 + 5 + \log C$$

$$16.8 - 14 + 0.26 - 5 = \log C$$

or $$\log C = -0.94$$

$$= -1 - 1 + 1 - 1.94 = \bar{2}.06$$

$$\therefore \quad C = \text{antilog } \bar{2}.06 = 1.15 \times 10^{-2} \text{ mol L}^-$$

$$= 1.15 \times 10^{-2} \text{ mol } (1000 \text{ mL})^-.$$

g. mol. wt. of CH_3COONa

$$= 12 + (3 \times 1) + 12 + (2 \times 16) + 23$$

$$= 82 \text{ g.}$$

$\therefore$ Amount of CH_3COONa in 500 mL

$$= \frac{1.15 \times 10^{-2} \times 500 \times 82}{1000} = \mathbf{0.472 \text{ g}}$$ **Ans.**

Example 181. *Calculate the pH of a 0.2M solution of NH_4Cl. The ionisation constant of $NH_4^+ = 1.8 \times 10^{-5}$.*

Solution. Hydrolysis reaction.

$$\begin{array}{lcccc} & NH_4^+ + HOH & \rightleftharpoons & NH_3 + & H_3O^+ \\ \text{Conc. (mol L}^-\text{)} & 0.2\text{M} & & & \\ \text{Conc. at} & & & & \\ \text{equilibrium} & 0.2 - x & & x & x \end{array}$$

But $0.2 - x \simeq 0.2$ because as compared to 0.2, x is very small and hence neglected.

$$\therefore \quad K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \qquad \text{...(1)}$$

$$\text{Also,} \quad K_h = \frac{K_w}{K_b} \qquad \text{...(2)}$$

From (1) and (2) we get :

$$\frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{K_w}{K_b}; \frac{x \times x}{0.2}$$

$$= \frac{10^{-14}}{1.8 \times 10^{-5}}; x = \left(\frac{10^{-14} \times 0.2}{1.8 \times 10^{-5}}\right)^{1/2}$$

$$\textbf{Or} \quad x = (1.1 \times 10^{-10})^{1/2}$$

$$= 1.05 \times 10^{-5} = [H_3O^+]$$

$$\therefore \quad pH = -\log 1.05 \times 10^{-5}$$

$$= -(\log 1.05 + \log 10^{-5})$$

$$= -(0.02 - 5) = \mathbf{4.98} \qquad \textbf{Ans.}$$

Example 182. *Calculate the percent hydrolysis of 1N solution of sodium acetate. K_a (CH_3COOH) = 1.8×10^{-5} at 298K. K_w at 298K = 1.2×10^{-14}.*

Solution. Sodium acetate is a salt of strong base (NaOH) and weak acid (CH_3COOH). Hence, hydrolysis constant :

$$K_h = \frac{K_w}{K_a} = \frac{1.2 \times 10^{-14}}{1.8 \times 10^{-5}} = 6.67 \times 10^{-10}.$$

$$h = \left(\frac{K_h}{C}\right)^{1/2} \Rightarrow h = \left(\frac{6.67 \times 10^{-10}}{1}\right)^{1/2}$$

$$= 2.58 \times 10^{-5}$$

$\therefore$ % age hydrolysis

$$= 2.58 \times 10^{-5} \times 100 = 2.58 \times 10^{-3}$$

$$= \mathbf{0.00258\%} \qquad \textbf{Ans.}$$

Example 183. *K_a for butyric acid is 2×10^{-5}. Calculate pH and hydroxyl ion concentration of 0.2M aqueous solution of sodium butyrate.* **(Roorkee Entrance, 1994)**

Solution. *Sodium butyrate is a salt of strong base (NaOH) and weak acid (butyric acid).*

$$\text{So :} \quad pOH = 0.5\,[pK_w - pK_a - \log C]$$

$$\text{But} \quad pH = 14 - pOH.$$

$$\text{Hence :} \quad pH = 14 - 0.5\,[-\log K_w - (-\log K_a) - \log C]$$

$$= 14 - 0.5\,[-\log 10^{-14} - (-\log 2 \times 10^{-5})]$$

$$- \log C$$

$$\therefore \quad pH = 14 - 0.5\,[14 - (\log 2 - \log 10^{-5}) - \log 0.2]$$

$$= 14 - 0.5\,[14 - (-0.301 + 5) - (-0.699)]$$

$$pH = 14 - 0.5\,[14 + 0.301 - 5 + 0.699]$$

$$= 14 - 5 = 9 \qquad \textbf{Ans.}$$

$$\text{Since} \quad pH = 9; -\log[H^+] = 9; [H^+] = 10^{-9}$$

$$\text{But} \quad [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-9}} = 10^{-14+9} = \mathbf{10^{-5}} \qquad \textbf{Ans.}$$

24.11 SOLUBILITY AND SOLUBILITY PRODUCT

Solubility. The concentration (mol L⁻) of a saturated solution of a salt at a given temperature is called solubility of a salt.

Solubility product and ionic product. Suppose AgCl salt is dissolved in water to get its saturated solution. It ionises as $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Applying law of chemical equilibrium we have :

$$K = \frac{[Ag^+][Cl^-]}{[AgCl(s)]}$$

$$\textbf{Or} \quad K \times [AgCl(s)] = [Ag^+][Cl^-]$$

$$\textbf{Or} \quad K_c, \text{ called } K_{sp} = [Ag^+][Cl^-];$$

K_{sp} = solubility product while $[Ag^+][Cl^-]$ is called ionic product.

(*i*) If ionic product > K_{sp}, precipitation takes place

(*ii*) If ionic product < K_{sp}, no precipitation takes place and more of the salt dissolves.

(*iii*) If ionic product = K_{sp}, the solution is saturated.

I. *Calculation of solubility of a salt of a strong base and a strong acid in pure water e.g.,* AgCl

Let solubility of salt = s mol L⁻,

$$\begin{array}{lcc} & AgCl \rightleftharpoons Ag^+ + & Cl^- \\ \text{Solubility (mol L}^-\text{)} & s & s \end{array}$$

$$\therefore \quad K_{sp} = [Ag^+][Cl^-] = s \times s = s^2$$

$$\text{then,} \quad \mathbf{s = (K_{sp})^{1/2}}$$

II. Calculation of solubility of a salt of a strong base and strong acid in a solution which already contains a common ion. *e.g.*, {[Ag^+] common ion = '*a*' mol L⁻} in AgCl solution.

$$\begin{array}{lcc} \text{Thus :} & AgCl \rightleftharpoons Ag^+ + & Cl^- \\ & s' + a & s' \end{array}$$

Here, $K_{sp} = [Ag^+][Cl^-]$

Or $K_{sp} = (s' + a) \times s'$

III. *Calculation of solubility of a salt of a weak acid with a strong base in* ***pure water****. e.g.,* CH_3COOAg.

Since the salt is of weak acid and strong base, it will get hydrolysed. Suppose, solubility of $CH_3COOAg = x$ mol L^-; amount of CH_3COO^- that gets hydrolysed = y mol L^-.

Thus :
$$CH_3COOAg \rightleftharpoons \underset{x-y}{CH_3COO^-} + \underset{x}{Ag^+} \quad ...(1)$$
$$\underset{x-y}{CH_3COO^-} + H_2O \rightleftharpoons \underset{y}{CH_3COOH} + \underset{y}{OH^-} \quad ...(2)$$

$\therefore$ From equation (1),
$$K_{sp} = [CH_3COO^-][Ag^+]$$
$$= (x-y) \times x = x(x-y) \quad ...(3)$$

Similarly from equation (2) :
$$K_h (= K_w/K_a) = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$
$$= \frac{y \times y}{x-y} = \frac{y^2}{x-y} \quad ...(4)$$

After solving equations (3) and (4), the volume of x can be calculated.

IV. *Calculation of solubility of a salt (e.g., CH_3COOAg) of a weak acid (e.g., CH_3COOH) and a strong base (e.g., AgOH) in an* ***acidic buffer*** *solution.* CH_3COOAg ionises as :
$$CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+$$

The given condition is that the solution is acidic. So, CH_3COO^- ions would react with H^+ ions to form CH_3COOH

Suppose solubility of CH_3COOAg = x mol L^- and
Concentration of CH_3COO^- combined with H^+ ions $= y$
$$\underset{x}{CH_3COOAg} \rightleftharpoons \underset{x-y}{CH_3COO^-} + \underset{x}{Ag^+} \quad ...(1)$$
$$\underset{x-y}{CH_3COO^-} + H^+ \rightleftharpoons \underset{y}{CH_3COOH} \quad ...(2)$$

$\therefore$ From equation (1),
$$K_{sp} = [CH_3COO^-][Ag^+]$$
$$= (x-y) \times x = x(x-y) \quad ...(3)$$

Similarly, from equation (2) :
$$K_a = \frac{[CH_3COOH]}{[CH_3COO^-][H^+]}$$
$$= \frac{y}{(x-y)[H^+]} \quad ...(4)$$

Solving equation (3) and (4), value of x can be calculated. This value of x will be more than that of x, found in pure water.

V. *Calculation of solubility of a salt of a weak acid (e.g., CH_3COOH) and a strong base (e.g., AgOH) in a* ***basic buffer****.* CH_3COOAg ionises as :
$$CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+ \quad ...(1)$$

Since the solution is basic (given), the $[H^+]$ will be less and very less amount of CH_3COO^- would react with H^+ ions. Also, the hydrolysis would get suppressed by already existing OH^- ions.

Let solubility of $CH_3COOAg = x$ mol L^-.

So, from equation (1),
$$[CH_3COO^-] = [Ag^+] = x \text{ mol } L^-.$$

Hence $K_{sp} = [CH_3COO^-][Ag^+]$
$$= x \times x = x^2 \text{ mol}^2 \text{ L}^{-2}.$$

> **Note 1.** The decreasing order of solubility of such salts is :
>
> In acidic solution > in pure water> in basic solution.
>
> **2.** For salts (*e.g.*, $C_6H_5NH_3^+Cl^-$) of a strong acid (*e.g.*, HCl) with a weak base (*e.g.*, aniline, $C_6H_5NH_2$), the decreasing order of solubility of such salts is :
>
> In basic solution > in pure water > in acidic solution.

VI. *Calculation of solubility of a salt of weak acid (e.g., HCN) with a weak base (e.g., NH_4OH), in pure water. NH_4CN ionises as :*
$$NH_4CN \rightleftharpoons \underset{x-y}{NH_4^+} + \underset{x-y}{CN^-} \quad \text{(Ionisation)}...(1)$$
$$\underset{x-y}{NH_4^+} + \underset{x-y}{CN^-} + H_2O \rightleftharpoons \underset{y}{NH_4OH} + \underset{y}{HCN} \quad \text{(Hydrolysis)} \quad ...(2)$$

$\therefore$ From equation (1), we have :
$$K_{sp} = [NH_4^+][CN^-] = (x-y)(x-y)$$

Or $K_{sp} = (x-y)^2$ ...(3)

From equation (2), we have :
$$\frac{K_w}{K_aK_b} = \frac{[NH_4OH][HCN]}{[NH_4^+][CN^-][H_2O]}$$
$$= \frac{y \times y}{(x-y) \times (x-y)} = \frac{y^2}{(x-y)^2}$$

or
$$\frac{K_w}{K_aK_b} = \frac{y^2}{(x-y)^2} \quad ...(4)$$

Solving equations (3) and (4), solubility of salt can be found.

VII. *Calculation of solubility of a salt (e.g., NH_4CN) of a weak acid (e.g., HCN) and weak base (e.g., NH_4OH) in an acidic buffer and in a basic buffer.*

In acidic buffer medium
$$NH_4CN \rightleftharpoons \underset{x}{NH_4^+} + \underset{x-y}{CN^-} \quad ...(1)$$
$$\underset{x-y}{CN^-} + H^+ \rightleftharpoons \underset{y}{HCN} \quad ...(2)$$

Where solubility of salt = x mol L$^-$ and concentration of CN$^-$ combined with H$^+$ is $x - y$.

$\therefore$ $[CN^-] = x - y$; $[HCN] = y$; $[NH_4^+] = x$

$\therefore$ From equation (1) we have :

$$K_{sp} = [NH_4^+]\,[CN^-] = x\,(x - y)$$

From equation (2) using CN$^-$ of product of equation (1), we have :

$$K_a^{-1} = \frac{[HCN]}{[CN^-]\,[H^+]} = \frac{y}{(x-y)\,(H^+)}$$

In basic buffer medium

$$NH_4CN \rightleftharpoons \underset{x-y}{NH_4^+} + \underset{x}{CN^-} \qquad ...(1)$$

$$\underset{x-y}{NH_4^+} + OH^- \rightleftharpoons \underset{y}{NH_4OH} \qquad ...(2)$$

Where solubility of salt = x mol L$^-$ and concentration of NH$_4^+$ combined with OH$^-$ is $x - y$.

$\therefore$ $[NH_4^+] = x - y$; $[CN^-] = x$;

$[NH_4OH] = y$

$\therefore$ From equation (1) we have :

$$K_{sp} = [NH_4^+]\,[CN^-] = (x - y)x$$

From equation (2) using NH$_4^+$ of product of equation (1), we have :

$$K_b^{-1} = \frac{[NH_4OH]}{[NH_4^+]\,[OH^-]} = \frac{y}{(x-y)\,(OH^-)}$$

EXAMPLE 184. *A cation A$^+$ and anion B$^-$ react to give salts of the type (i) AB (ii) AB$_2$ and A$_2$B (iii) A$_3$B$_2$ and A$_2$B$_3$. If S is the solubility of the salt in mol L$^-$, calculate the value of solubility product of these types of salts.*

SOLUTION. (*i*) AB ionises as : $AB \rightleftharpoons A^+ + B^-$

Solubility $\quad S \quad S$

$\therefore$ $K_{sp} = [A^+]\,[B^-] = S\ mol\ L^- \times S\ mol\ L^-$
$= S^2\ mol^2\ L^{-2}$

(*ii*) AB$_2$ ionises as : $AB_2 \rightleftharpoons A^+ + 2B^-$

Solubility $\quad$ S mol L$^-$ $\quad$ 2 S mol L$^-$

$\therefore$ $K_{sp} = [A^+]\,[B^-]^2$
$= (S\ mol\ L^-) \times (2\ S\ mol\ L^-)^2$
$= 4S^3\ mol^3\ L^{-3}$

(*iii*) A$_2$B ionises as : $A_2B \rightleftharpoons 2A^+ + B^-$

Solubility $\quad$ 2S mol L$^-$ $\quad$ S mol L$^-$

$\therefore$ $K_{sp} = [A^+]^2\,[B^-]$
$= (2\ S\ mol\ L^-)^2 \times (S\ mol\ L^-)$
$= 4S^3\ mol^3\ L^{-3}$

(*iv*) A$_3$B$_2$ ionises as : $A_3B_2 \rightleftharpoons 3A^+ + 2B^-$

Solubility $\quad$ 3 S mol L$^-$ $\quad$ 2 S mol L$^-$

$\therefore$ $K_{sp} = [A^+]^3\,[B^-]^2$
$= (3\ S\ mol\ L^-)^3 \times (2\ S\ mol\ L^-)^2$
$= \mathbf{108\ S^5\ mol^5\ L^{-5}}$

(*v*) A$_2$B$_3$ ionises as : $A_2B_3 \rightleftharpoons 2A^+ + 3B^-$

Solubility]$\rightarrow$ $\quad$ 2S mol L$^-$ $\quad$ 3S mol L$^-$

$\therefore$ $K_{sp} = [A^+]^2\,[B^-]^3$
$= (2S\ mol\ L^-)^2 \times (3S\ mol\ L^-)^3$
$= \mathbf{108\ S^5\ mol^5\ L^{-5}}$

EXAMPLE 185. *Calculate the solubility of strontium fluoride in 0.1M NaF solution. K$_{sp}$ for SrF$_2$ in water = 8 × 10^{-10}.*

(Roorkee, 1997)

SOLUTION. SrF$_2$ ionises as :

$$SrF_2 \xrightleftharpoons{\text{in 0.1 M NaF}} Sr^{2+} + 2F^-$$

Solubility $\quad$ S mol L$^-$ $\quad$ 2S mol L$^-$

NaF ionises as $\quad NaF \rightleftharpoons Na^+ + F^-$

Concentration $\quad$ 0.1M $\quad$ 0.1M

$\therefore$ $[Sr^{2+}] = S\ mol\ L^-$; $[F^-] = 2S + 0.1$

Hence, $K_{sp} = [Sr^{2+}]\,[F^-]^2 = S\,(2S + 0.1)^2$

$8 \times 10^{-10} = S \times (0.\ 1)^2$

[Since $S << 0.1$, $(2S + 0.1)^2 = (0.1)^2$]

$= S \times (0.1)^2 = S \times 10^{-2}$

or $\quad S = \dfrac{8 \times 10^{-10}}{10^{-2}} = 8 \times 10^{-10+2}$

$= \mathbf{8 \times 10^{-8}}$ **Ans.**

EXAMPLE 186. *Calculate the maximum pH of a given solution of 0.1M Mg^{2+} ions from which Mg(OH)$_2$ is not precipitated [K$_{sp}$ of Mg(OH)$_2$ = 1.2 × 10^{-11}].*

SOLUTION. $[Mg(OH)_2] = 0.1$ M (given) ;

$K_{sp} = 1.2 \times 10^{-11}$

For $\quad Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

Concentration $\quad$ 0.1M $\quad$ x

$K_{sp} = [Mg^{2+}]\,[OH^-]^2$;

$1.2 \times 10^{-11} = 0.1\,[OH^-]^2$

$\therefore$ $[OH^-] = \left(\dfrac{1.2 \times 10^{-11}}{0.1}\right)^{1/2}$

$= (1.2 \times 10^{-10})^{1/2} = 1.1 \times 10^{-5}$

But $\quad [H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{10^{-14}}{1.1 \times 10^{-5}}$

$= 9.09 \times 10^{-10}$ M

$\therefore$ $pH = -\log 9.09 \times 10^{-10}$
$= -[\log 9.09 + \log 10^{-10}]$
$= -[0.9586 - 10]$

$pH = 10 - 0.9586 = \mathbf{9.04}$ **Ans.**

EXAMPLE 187. *The solubility product of PbF$_2$ is 3.2 × 10^{-8}. Calculate the solubility of PbF$_2$ in (i) mol L$^-$ or mol dm^{-3} (ii) in gL$^-$ (at. wt. Pb = 207, F = 19).*

SOLUTION. (*i*) K_{sp} $\therefore$ 3.2×10^{-8} ; (*i*) Solubility of

$PbF_2 = S = ?$ (*ii*) in gL^-

g. mol. wt. of $PbF_2 = 207 + (2 \times 19) = 245$ g.

$$PbF_2 \rightleftharpoons Pb^{2+} + 2F^-$$

Solubility S mol S mol 2S mol

$$K_{sp} = [Pb^{2+}][F^-]^2;$$

$$3.2 \times 10^{-8} = S \times (2S)^2 = 4S^3$$

$$\therefore \quad S = (3.2 \times 10^{-8})^{1/3}.$$

Taking logs, we get :

$$\log S = \log (3.2 \times 10^{-8})^{1/3}$$

$$= \frac{1}{3}[\log 3.2 + \log 10^{-8}]$$

$$= \frac{1}{3}[0.505 - 8] = 2.498$$

$$= -2 - 1 + 1 - 0.498 = \bar{3}.502$$

Taking antilogs of both sides, we get :

$$S = 3.18 \times 10^{-3} \text{ mol L}^-$$

$(\text{or } 3.18 \times 10^{-3} \text{ mol dm}^{-3})$ **Ans.**

(*ii*) Solubility in gL^- = no. of mol × g. mol. wt. of PbF_2

$$= 3.18 \times 10^{-3} \times 245 \text{ g}$$

$= \mathbf{0.779\ g\ L^-}$ **Ans.**

EXAMPLE 188. *At 25°C, the solubility product of Hg_2Cl_2 in water is 3.2×10^{-17} mol^3 dm^{-9}. What is the solubility of Hg_2Cl_2 in water at 25 ° C?*

(a) 1.2×10^{-12} M (b) 3.0×10^{-6} M (c) 2×10^{-6} M

(d) 1.2×10^{-16} M (e) 5.2×10^{-6} M

(MLNR 1985, HP Board 2007, UP 1986, 89 Kerala PMT, 2011)

SOLUTION. $Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$

Concentration 2 x $2x$

$$\therefore \quad K_{sp} = [Hg_2^{2+}][Cl^-]^2; 3.2 \times 10^{-17}$$

$$= x \times (2x)^2 = 4x^3$$

$$\therefore \quad x = \left[\frac{3.2 \times 10^{-17}}{4}\right]^{1/3}$$

$$= (8 \times 10^{-18})^{1/3}$$

$$= [2^3 \times (10^{-6})^3]^{1/3} = 2 \times 10^{-6}.$$

So, the correct answer is (*c*)

EXAMPLE 189. *If the solubility product of $BaSO_4$ at 25°C be 1×10^{-10}, find out the solubility is gL^-. (Mol. wt. = 233.3).*

(UP 1989, H.P. Board 2012)

SOLUTION. $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

Solubility, mol L^- S S

$$K_{sp} = [Ba^{2+}][SO_4^{2-}];$$

$$10^{-10} = S \times S ; S = (10^{-10})^{1/2}$$

$$= 10^{-5} \text{ mol L}^-$$

Or $S = 10^{-5} \times 233.3$

$= \mathbf{2.333 \times 10^{-3}\ g\ L^-}$ **Ans.**

EXAMPLE 190. *Calculate the solubility of $BaSO_4$ in 0.05 M $BaCl_2$ solution, K_{sp} of $BaSO_4 = 1.1 \times 10^{-10}$.* **(HP Board, 2007)**

SOLUTION. $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ (ionisation)

Solubility, (mol L^-) S S

$$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$$

Conc. (mol L^-) 0.05

$$\therefore \quad [Ba^{2+}] = S + 0.05; SO_4^{2-} = S$$

Hence $K_{sp} = [Ba^{2+}][SO_4^{2-}] = (S + 0.05) \times S$

$$1.1 \times 10^{-1} = 0.05\,S$$

$$[\because S << 0.12, K_{sp} = 0.05\,S]$$

$$\therefore \quad S = \frac{1.1 \times 10^{-10}}{0.05}$$

$= \mathbf{2.2 \times 10^{-9}}$ **Ans.**

TYPE. *To predict precipitation or non-precipitation of a compound when two different solutions are mixed.*

EXAMPLE 191. *In 1L solution of AgCl [K_{sp} (AgCl) = 1.6×10^{-10}], 0.1 mol of CuCl [K_{sp} (CuCl)] = 1.0×10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of x is :* **(IIT-JEE, 2011)**

SOLUTION. (*i*) Suppose, solubility of AgCl = *a* mol L^-

$$AgCl \rightleftharpoons Ag^+ + Cl^- \quad \ldots(1)$$

a a

(*ii*) Suppose solubility of CuCl = *b* mol L^-

$$CuCl \rightleftharpoons Cu^+ + Cl^-$$

b b ...(2)

$$\therefore \quad K_{sp} \text{ of AgCl} = [Ag^+][Cl^-]$$

$$1.6 \times 10^{-10} = a(a + b) \quad \ldots(3)$$

[from equations (1) and (2)]

Similarly, K_{sp} of CuCl = $[Cu^+][Cl^-]$

$$1.0 \times 10^{-6} = b(a + b) \quad \ldots(4)$$

Solving equations (3) and (4) by dividing, we get :

$$\frac{1.6 \times 10^{-10}}{1.0 \times 10^{-6}} = \frac{a(a+b)}{b(a+b)};$$

$$1.6 \times 10^{-4} = \frac{a}{b}; \; a = b\,(1.6 \times 10^{-4}) \quad \ldots(5)$$

Substituting the value of *a* in equation (3), we get :

$$1.6 \times 10^{-10} = b(1.6 \times 10^{-4})\,[b(1.6 \times 10^{-4}) + b];$$

$$\frac{1.6 \times 10^{-10}}{1.6 \times 10^{-4}} = b^2(1.6 \times 10^{-4}) + b^2$$

or $10^{-6} = b^2\,(1.6 \times 10^{-4} + 1);$

$$b = \sqrt{10^{-6} / (1.6 \times 10^{-4} + 1)}$$

$$= 10^{-3}$$

Substituting the value of $b (= 10^{-3})$ in equation (5), we get:

$$\therefore \quad a = 10^{-3}\,(1.6 \times 10^{-4}) = 1.6 \times 10^{-7}$$

$$\therefore \quad [Ag^+] = a = 1.6 \times 10^{-7} \quad \ldots(6)$$

Thus from 1.6×10^{-x} (given) and 1.6×10^{-7}, the value of ***x* is 7**.

EXAMPLE 192. *Will a precipitate exist at equilibrium if 1/2 litre of a 4×10^{-3}M solution of NaOH and 1/2 litre of 2×10^{-3}M* *solution of $AlCl_3$ are mixed and diluted to 10^3 litre with water at room temperature (K_{sp} for $Al(OH)_3 = 5 \times 10^{-33}$)?*

SOLUTION. $K_{sp} = 5 \times 10^{-33}$; Total volume = 10^3 L

For NaOH $M_1V_1 = M_2V_2$; $4 \times 10^{-3} \times \frac{1}{2} = M_2 \times 10^3$

$$\therefore \quad M_2 = \frac{4 \times 10^{-3} \times \frac{1}{2}}{10^3} = 2 \times 10^{-6}$$

Since $\quad NaOH \rightleftharpoons Na^+ + OH^-$

$\therefore \quad [OH^-] = 2 \times 10^{-6} M$

For $AlCl_3$ $M_3V_3 = M_4V_4$

$$2 \times 10^{-3} \times \frac{1}{2} = M_4 \times 10^3$$

$$\therefore \quad M_4 = \frac{2 \times 10^{-3}}{10^3} \times \frac{1}{2} = 10^{-6} M$$

$$AlCl_3 \rightleftharpoons \underset{10^{-6}M}{Al^{+3}} + 3Cl^-$$

$\therefore \quad [Al^{+3}] = 10^{-6}$ M.

$$AlCl_3 + 3NaOH \longrightarrow Al(OH)_3 + 3NaCl$$

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

$$\text{Ionic Product} = [Al^{+3}][OH^-]^3 = (10^{-6})(2 \times 10^{-6})^3 = 8.0 \times 10^{-24}$$

Since ionic product (= 8.0×10^{-24}) is greater than solubility product (= 5×10^{-33}), so precipitation will take place.

EXAMPLE 193. *The solubility of $Ca_3(PO_4)_2$ in water is y mol L^-. Its solubility product is:*

(a) 6 y^4 (b) 36 y^4 (c) 64 y^5 (d) 108 y^5

[WB-JEE, 2011, Karnataka CET, 2011]

SOLUTION. $Ca_3(PO_4)_2$ ionises as:

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$$

Concentration : $\quad 3y \quad 2y$

$\therefore$ Solubility product,

$$K_{sp} = (3y)^3 (2y)^2 = 27y^3 \times 4y^2 = 108\, y^5.$$

So, the correct answer is (*d*).

EXAMPLE 194. *Decide if a precipitation occurs on mixing together, 10 mL of 0.02M solution of $CaCl_2$ and 5mL of 0.1M solution of K_2CrO_4. (K_{sp} for $CaCrO_4 = 2.3 \times 10^{-2}$).*

(WB Engg. 1993)

SOLUTION. Total volume = 10 + 5 = 15 mL

For $CaCl_2$: $M_1V_1 = M_2V_2$;

$$10 \times 0.02 = M_2 \times 15 \,; M_2 = \frac{10 \times 0.02}{15} = 0.013$$

$\therefore \quad [Ca^{2+}] = 0.013$

$$[\because CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-]$$

For K_2CrO_4 :

$$M_3V_3 = M_4V_4$$

$$5 \times 0.1 = M_4 \times 15 \,; M_4 = \frac{5 \times 0.1}{15} = 0.03M$$

$\therefore \quad K_2CrO_4 \rightleftharpoons 2K^+ + CrO_4^{2-}$; $[CrO_4^{2-}] = 0.03M$

$\therefore$ Ionic product of $CaCrO_4$

(*i.e.*, $CaCrO_4 \rightleftharpoons Ca^{2+} + CrO_4^{2-}$)

$$= [Ca^{2+}][CrO_4^{2-}] = 0.013 \times 0.03 = 3.9 \times 10^{-4}$$

Since ionic product (= 3.9×10^{-4}) is less than solubility product (= 2.3×10^{-2}), no precipitation of $CaCrO_4$ will take place.

Type. To calculate percentage error in washing of precipitate with (*i*) water (*ii*) acid solution.

EXAMPLE 195. *The solubility of $BaSO_4$ in water is 2.3×10^{-3} g L^-. Calculate the percentage loss/or error in washing 0.25 g of $BaSO_4$ with (i) 1L H_2O and (ii) N/250 H_2SO_4.*

SOLUTION. (*i*) Solubility of $BaSO_4 = 2.3 \times 10^{-3}$ gL^-.

It means, 0.25 g of $BaSO_4$ must be less from 2.3×10^{-3} g when dissolved in 1L pure water.

$$\text{Hence : } \quad \%\text{ age error} = \frac{2.3 \times 10^{-3}\text{ g}}{0.25\text{ g}} \times 100 = 0.92\%$$

(*ii*) Solubility of $BaSO_4 = 2.3 \times 10^{-3}$ g L^- ;

g. mol. wt. of $BaSO_4$ = 137 + 32 + (4 × 16) = 233 g mol^-

$$\therefore \quad \text{Solubility of } BaSO_4 = \frac{2.3 \times 10^{-3}\text{ g}L^-}{233\text{ g mol}^-} = 9.87 \times 10^{-6}\text{ mol L}^-$$

$\therefore \quad BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$$\therefore \quad K_{sp}(BaSO_4) = [Ba^{2+}][SO_4^{2-}] = (9.87 \times 10^{-6})(9.87 \times 10^{-6})$$

$$[\because [Ba^{2+}] = [SO_4^{2-}]]$$

$$= 97.4 \times 10^{-12}$$

Suppose solubility of $BaSO_4$ in 1L N/250 H_2SO_4 = xg $= \frac{x}{233}$ g mol.

$$\therefore \quad [Ba^{2+}] = [SO_4^{2-}] = \frac{x}{233}$$

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

$$\text{Molarity} \quad \frac{1}{250} \times \frac{1}{2} = 0.002$$

$$\therefore \quad \text{Total } [SO_4^{2-}] = \frac{x}{233} + 0.002$$

But $\quad K_{sp} = [Ba^{2+}][SO_4^{2-}]$;

$$97.4 \times 10^{-12} = \frac{x}{233}\left(\frac{x}{233} + 0.002\right)$$

$$= \frac{x}{233} \times 0.002$$

[∵ Value of $\frac{x}{233}$ is very small as compared to 0.002, it is rejected]

$$\therefore \quad x = \frac{97.4 \times 10^{-12} \times 233}{0.002}$$

$$= 1.13 \times 10^{-5}$$

$$\therefore \quad \%\text{ age loss} = \frac{1.13 \times 10^{-5}}{0.25} \times 100$$

$$= 4.52 \times 10^{-3} = \mathbf{0.00452\%}$$

EXAMPLE 196. *Calculate the solubility of $BaSO_4$ in (i) pure water and (ii) is 0.1M $BaCl_2$ [K_{sp} ($BaSO_4$) = 1.5×10^{-9}].*

(Roorkee, 1989)

SOLUTION. (*i*) $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ ...(1)

Solubility in pure water (mol L^{-}) S S S

$$\therefore \quad K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]\,;$$

$$1.5 \times 10^{-9} = S \times S = S^2$$

$$\therefore \quad S = (1.5 \times 10^{-9})^{1/2}$$

$$= (15 \times 10^{-10})^{1/2} = 3.87 \times 10^{-5}.$$

∴ Solubility of $BaSO_4$ in pure water = 3.87×10^{-5} mol L^{-}.

(*ii*) $BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$ ...(2)

Conc. (mol L^{-}) 0.1

∴ From equations (1), and (2),

$$[Ba^{2+}] = S + 0.1\,;\ [SO_4^{2-}] = S$$

$$\therefore \quad K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]\,;$$

$$1.5 \times 10^{-9} = (S + 0.1)\,(S)$$

$$= S^2 + 0.1\,S$$

$$= 0.1S$$

(∵ S being very small, S^2 is neglected).

$$\text{or} \quad S = \frac{1.5 \times 10^{-9}}{0.1}$$

$$= 1.5 \times 10^{-8}\ \text{mol L}^{-}$$

∴ Solubility of $BaSO_4$ in 0.1M $BaCl_2$ = 1.5×10^{-8} mol L^{-}

EXAMPLE 197. *In qualitative analysis, the metals of group 1 can be separated from other ions by precipitating them as chloride salts. A solution initially contains Ag^+ and Pb^{2+} at a concentration of 0.10 M. Aqueous HCl is added to this solution until the Cl^- concentration is 0.10 M. What will be the concentrations of Ag^+ and Pb^{2+} be at equilibrium? (K_{sp} for AgCl = 1.8×10^{-10}; K_{sp} for $PbCl_2$ = 1.7×10^{-5})*

(a) $[Ag^+] = 1.8 \times 10^{-7}$ M, $Pb^{2+} = 1.7 \times 10^{-6}$ M

(b) $[Ag^+] = 1.8 \times 10^{-11}$ M, $[Pb^{2+}] = 8.5 \times 10^{-5}$ M

(c) $[Ag^+] = 1.8 \times 10^{-9}$ M, $[Pb^{2+}] = 1.7 \times 10^{-3}$ M

(d) $[Ag^+] = 1.8 \times 10^{-11}$ M, $[Pb^{2+}] = 1.7 \times 10^{-4}$ M

(AI PMT, 2011)

SOLUTION. (*i*) For AgCl, K_{sp} [AgCl] = $[Ag^+][Cl^-]$

$$[Ag^+] = \frac{K_{sp}[AgCl]}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{10^{-1} = 0.1}$$

$$= \mathbf{1.8 \times 10^{-9}\ M}$$

(*ii*) For $PbCl_2$, K_{sp} $[PbCl_2] = [Pb^{2+}][Cl^-]^2$

$$\therefore \quad [Pb^{2+}] = \frac{K_{sp}[PbCl_2]}{[Cl^-]^2} = \frac{1.7 \times 10^{-5}}{0.1 \times 0.1}$$

$$= 1.7 \times 10^{-3}\ \text{M}$$

So, the correct answer is (*c*).

EXAMPLE 198. *Calculate the minimum volume of water needed to dissolve 1.5 g of calcium sulphate at 298K. $K_{sp}(CaSO_4) = 9.1 \times 10^{-6}$. (at. wt., Ca = 40, S = 32, O = 16)*

SOLUTION. $CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$

Solubility (mol L^{-}) S S S

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}]\,;$$

$$9.1 \times 10^{-6} = S \times S = S^2$$

$$\therefore \quad S = (9.1 \times 10^{-6})^{1/2}$$

$$= 3.017 \times 10^{-3}\ \text{mol L}^{-}$$

g. mol. wt. of $CaSO_4$ = 40 + 32 + (4 × 16) = 136 g

∴ Solubility in gL^{-} = no. of mol × g. mol. wt. of $CaSO_4$

$$= 3.017 \times 10^{-3} \times 136 = 0.41\ \text{gL}^{-}$$

Volume of water used to dissolve 0.41 g $CaSO_4$ = 1L

∴ Volume of water used to dissolve 1.5 g $CaSO_4$

$$= \frac{1}{0.41} \times 1.5 = \mathbf{3.66\ L} \quad \textbf{Ans.}$$

EXAMPLE 199. *The values of solubility product of AgBr and Ag_2CrO_4 are 5.0×10^{-13} and 1.1×10^{-12} respectively. Calculate the ratio of the molarities of their saturated solutions.*

SOLUTION. (*i*) For AgBr $AgBr \rightleftharpoons Ag^+ + Br^-$

Solubility (mol L^{-}) S S S

$$K_{sp} = [Ag^+]\,[Br^-]\,;$$

$$5.0 \times 10^{-13} = S \times S = S^2$$

$$\therefore \quad S = (5.0 \times 10^{-13})^{1/2}$$

$$= (50 \times 10^{-14})^{1/2}$$

$$= 7.07 \times 10^{-7}\ \text{mol L}^{-}$$

(*ii*) For Ag_2CrO_4. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

Solubility (mol L^{-}) S $2S$ S

$$K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]\,;$$

$$1.1 \times 10^{-12} = (2S)^2 \times S = 4S^3$$

$$\therefore \quad S = \left(\frac{1.1 \times 10^{-12}}{4}\right)^{1/3}$$

$$= (0.275 \times 10^{-12})^{1/3}.$$

Taking logs, we get :

$$\begin{aligned}
\log S &= \log (0.275 \times 10^{-4})^{1/3} \\
&= \frac{1}{3} \log (0.275 \times 10^{-4}) \\
&= \frac{1}{3} (\log 0.275 + \log 10^{-4}) \\
&= \frac{1}{3} (0.561 - 4) \\
&= -1.52 = -1 - 1 + 1 - 0.52 \\
&= \bar{2}.48 \\
\therefore \quad S &= \text{antilog } \bar{2}.48 = 3.02 \times 10^{-2}
\end{aligned}$$

$$\therefore \quad \text{Ratio of molarities} = \frac{3.02 \times 10^{-2}}{7.07 \times 10^{-7}} = \frac{42715}{1}$$

EXAMPLE 200. *Calculate the solubility product of Ag_2CrO_4 if its solubility at 85°C is 8.0×10^{-5} mol L^{-}.*

SOLUTION. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

Solubility (mol L^-) $\quad S \quad 2S \quad S$

$$\begin{aligned}
K_{sp} &= [Ag^+]^2 [CrO_4^{2-}] \\
&= [2S]^2 \times S = 4S^3 \\
&= 4 \times (8.0 \times 10^{-5})^3 \\
K_{sp} &= \mathbf{2.048 \times 10^{-12}\ mol^3\ L^{-3}} \quad \textbf{Ans.}
\end{aligned}$$

EXAMPLE 201. 0.*00094 g of AgCl is dissolved in 500 cm^3 water at 298K to form saturated solution. Calculate the solubility product of AgCl (At. wt. Ag = 108, Cl = 35.5).*

SOLUTION. 500 mL solution contain AgCl = 0.00094 g

∴ 1000 mL (= 1L) solution contain

$$AgCl = \frac{0.00094}{500} \times 1000 = 0.00188 \text{ g.}$$

g. mol. wt. of AgCl = 108 + 35.5 = 143.5 g.

143.5 g AgCl ≡ 1 mol AgCl

$$\begin{aligned}
0.00188 \text{ g AgCl} &\equiv \frac{1}{143.5} \times 0.00188 \\
&= 1.31 \times 10^{-5} \text{ mol}
\end{aligned}$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

Solubility (mol L^-) $\quad 1.31 \times 10^{-5} \quad 1.31 \times 10^{-5}$

$$\begin{aligned}
K_{sp} &= [Ag^+][Cl^-] \\
&= (1.31 \times 10^{-5}) \times (1.31 \times 10^{-5}) \\
&= \mathbf{1.71 \times 10^{-10}} \quad \textbf{Ans.}
\end{aligned}$$

EXAMPLE 202. H*ow much KBr should be added to one litre of 0.05M $AgNO_3$ solution just to start the precipitation of AgBr ? K_{sp} (AgBr) = 5×10^{-13}. (at. wt., K = 39, Br = 80)*

SOLUTION. Precipitation will start if ionic product $[Ag^+][Br^-] > K_{sp}$ value.

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

Solubility (mol L^-) $\quad 0.05$

$$\begin{aligned}
K_{sp} &= [Ag^+][Br^-] \\
\therefore \quad [Br^-] &= \frac{K_{sp}}{[Ag^+]} = \frac{5 \times 10^{-13}}{0.05} \\
&= 10^{-11} \text{ mol } L^-
\end{aligned}$$

g. mol. wt. of KBr = 39 + 80 = 119 g.

∴ Amount of KBr = $10^{-11} \times 119 = 11.9 \times 10^{-9}$ g L^-

Type. To know *p*H at which precipitation would start.

EXAMPLE 203. *Calculate the pH at which $Mg(OH)_2$ starts precipitating from a solution containing 0.1M Mg^{2+} ions. K_{sp} for $Mg(OH)_2 = 10^{-11}$.* **(Roorkee Entrance 1992)**

SOLUTION. $[Mg^{2+}] = 0.1M$, $K_{sp} = 10^{-11}$

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

$$0.1 \qquad ?$$

$$K_{sp} = [Mg^{2+}][OH^-]^2 \,;\; 10^{-11} = 0.1 \times [OH^-]^2 \,;$$

$$\therefore \quad [OH^-] = \left(\frac{10^{-11}}{0.1}\right)^{1/2} = 10^{-5} \text{ M}$$

$$\text{But} \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-5}} = 10^{-14+5} = 10^{-9} \text{ M}$$

$$\begin{aligned}
\therefore \quad pH &= -\log [H^+] = -\log 10^{-9} \\
&= -(-9) \log 10 = \mathbf{+9} \quad \textbf{Ans.}
\end{aligned}$$

EXAMPLE 204. *The solubility product of AgCl is 1.8×10^{-10}. Calculate the concentration of Cl^- ions when one drop of $AgNO_3$ solution is added to one litre of N/50 HCl solution.*

SOLUTION. (*a*) $\quad AgCl \rightleftharpoons Ag^+ + Cl^-$

Solubility $\quad x \quad x \quad x$

$$\begin{aligned}
\therefore \quad K_{sp} &= [Ag^+][Cl^-] \,; \\
1.8 \times 10^{-10} &= x \times x \,;\; x^2 = 1.8 \times 10^{-10} \\
\therefore \quad x &= (1.8 \times 10^{-10})^{1/2} = 1.342 \times 10^{-5} \\
\text{Or} \quad [Ag^+] &= x = 1.342 \times 10^{-5}
\end{aligned}$$

∴ $[Ag^+]$ before adding HCl

$$= 1.342 \times 10^{-5} \text{ g ion } L^-$$

(*b*) $[Cl^-]$ ion in 1L of N/50 HCl

$$= 1 \times \frac{1}{50} = 0.02 \text{ g ion } L^-$$

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

Solubility (g ion L^-) $\quad 0.02$

$$\begin{aligned}
\therefore \quad K_{sp} &= [Ag^+][Cl^-] \,; \\
1.8 \times 10^{-10} &= [Ag^+] \times 0.02 \\
\therefore \quad [Ag^+] \text{ on adding HCl} &= \frac{1.8 \times 10^{-10}}{0.02} \\
&= 9.0 \times 10^{-9} \text{ g ion } L^-
\end{aligned}$$

$$AgNO_3 \rightleftharpoons \underset{\text{Common ion}}{Ag^+} + NO_3^-$$

Since ion added to AgCl is common ion Cl^-, the ionisation of AgCl is suppressed. Hence, concentration of Ag^+ on the addition of one drop of N/50 HCl = 9.0×10^{-9} g ion L^-.

EXAMPLE 205. *If a metal (II) fluoride salt is 60% dissociated in its saturated solution, calculate its solubility product. (At. wt.*

of metal = 40, K_{sp} of metal fluoride = 3.6×10^{-11}).

SOLUTION. $MF_2 \rightleftharpoons M^{2+} + 2F^-$

Solubility mol L^- $\quad x \quad x \quad 2x$

$$\therefore \quad K_{sp} = [M^{2+}][F^-]^2 ;$$

$$3.6 \times 10^{-11} = x \times (2x)^2 = 4x^3$$

$$\therefore \quad x^3 = \frac{3.6 \times 10^{-11}}{4} = 0.9 \times 10^{-11} ;$$

$$x = (0.9 \times 10^{-11})^{1/3}$$

Taking logs of both sides, we get :

$$\log x = \log (0.9 \times 10^{-11})^{1/3}$$

$$= \frac{1}{3} [\log 0.9 + \log 10^{-11}]$$

$$= \frac{1}{3} [-0.046 - 11]$$

$$= -3.682 = -3 - 1 + 1 - 0.682$$

$$= \bar{4}.318$$

Taking antilog of both sides we get :

$$x = 2.08 \times 10^{-4}$$

$\therefore$ Solubility of MF_2 = $x = 2.08 \times 10^{-4}$ mol L^-

g. mol. wt. of MF_2 = $40 + (2 \times 19) = 78$ g.

$\therefore$ Solubility of MF_2 = $2.08 \times 10^{-4} \times 78$

$= 162.24 \times 10^{-4}$ g L^-

Since MF_2 is 60% dissociated. so :

$$\text{solubility of } MF_2 = 162.24 \times 10^{-4} \times \frac{60}{100}$$

$= \mathbf{9.7 \times 10^{-3}}$ **g L^-** **Ans.**

EXAMPLE 206. *A solution of Mn salt is mixed with 0.025 M $(NH_4)_2S$ solution. Calculate the amount of Mn^{2+} that will remain unprecipitated in 15 mL of the solution (K_{sp} of Mn S = 3.0×10^{-22}).*

SOLUTION. $(NH_4)_2S \rightleftharpoons 2NH_4^+ + S^{2-}$

Conc. (mol L^-) $\quad 0.025 \quad 0.025$

$MnS \rightleftharpoons Mn^{2+} + S^{2-}$

Conc. (mol L^-) $\quad 0.025$

$$K_{sp} = [Mn^{2+}][S^{2-}] ;$$

$$3.0 \times 10^{-22} = [Mn^{2+}] \times 0.025$$

$$\therefore \quad [Mn^{2+}] = 1.2 \times 10^{-20} \text{ M.}$$

At. wt. of Mn = 55

$\therefore$ Mn^{2+} ions left in solution = $1.2 \times 10^{-20} \times 55$

$= 6.6 \times 10^{-19}$ g

$\therefore$ 15 mL solution will contain Mn^{2+} ions

$$= \frac{6.6 \times 10^{-19}}{1000} \times 15$$

$$= 9.9 \times 10^{-21} \text{ g}$$

EXAMPLE 207. *Calculate the highest concentration of iodide ions that can exist in equilibrium with 0.02M of Ag^+ ions. [K_{sp} (AgI) = 8.3×10^{-17}].*

SOLUTION. $AgI(s) \xrightleftharpoons{\text{water}} Ag^+(aq) + I^-(aq)$

Conc. mol L^- $\quad 0.02 \quad x$

$$K_{sp} = [Ag^+][I^-] ;$$

$$8.3 \times 10^{-17} = 0.02 \times x$$

$$\therefore \quad x = \frac{8.3 \times 10^{-17}}{0.02} = 4.15 \times 10^{-15}$$

$\therefore$ $[I^-] = x = \mathbf{4.15 \times 10^{-15}}$ **mol L^- Ans.**

EXAMPLE 208. *A saturated solution of a mixture of silver chromate and silver oxalate was prepared. Calculate the [Ag^+] in this solution. (K_{sp} of silver chromate = 1.2×10^{-12} and that of silver oxalate = 6×10^{-12}).*

SOLUTION. Solubility of Ag_2CrO_4 = x mol$^-$; that of $Ag_2C_2O_4$ = y mol L^-

$$Ag_2CrO_4(s) \xrightleftharpoons{\text{water}} 2Ag^+(aq) + CrO_4^{2-}(aq)$$

Solubility $\quad 2x \quad x$

$$Ag_2C_2O_4(s) \xrightleftharpoons{\text{water}} 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

Solubility $\quad 2y \quad y$

Total $[Ag^+] = 2x + 2y$

(*a*) For Ag_2CrO_4 ; $K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$$1.2 \times 10^{-12} = (2x + 2y)^2 \times x ;$$

$$(2x + 2y)^2 = \frac{1.2 \times 10^{-12}}{x} \qquad ...(1)$$

For $Ag_2C_2O_4$; $K_{sp} = [Ag^+]^2 [C_2O_4^{2-}]$;

$$6 \times 10^{-12} = (2x + 2y)^2 \times y$$

$$\therefore \quad (2x + 2y)^2 = \frac{6 \times 10^{-12}}{y} \qquad ...(2)$$

In equations (1) and (2), L.H.S = L.H.S., so, R.H.S. = R.H.S.

$$\therefore \quad \frac{1.2 \times 10^{-12}}{x} = \frac{6 \times 10^{-12}}{y} \text{ or } y = \frac{6 \times 10^{-12} x}{1.2 \times 10^{-12}}$$

$$= 5x$$

Substituting the value of $y = 5x$ in equation (1), we get:

$$(2x + 10x)^2 = \frac{1.2 \times 10^{-12}}{x} ;$$

$$144x^3 = 1.2 \times 10^{-12} ;$$

$$x = \left(\frac{1.2 \times 10^{-12}}{144}\right)^{1/3}$$

Taking logs of both sides, we get :

$$\log x = \frac{1}{3} [\log 1.2 + \log 10^{-12} - \log 144]$$

$$= \frac{1}{3} [0.079 - 12 - 2.158]$$

$$= -4.693$$

$$= -4 - 1 + 1 - 0.693 = \bar{5}.307$$

Taking antilog of both sides, we get :

$$\mathbf{x = 2.03 \times 10^{-5}}$$

But $y = 5x$. So, $y = 5 \times 2.03 \times 10^{-5}$

$$= 10.15 \times 10^{-5}$$

$$\therefore \quad [Ag^+(aq)] = 2x + 2y = (2 \times 2.03 \times 10^{-5}) + (2 \times 10.15 \times 10^{-5})$$

$$[Ag^+(aq)] = 4.06 \times 10^{-5} + 20.3 \times 10^{-5}$$

$$= \mathbf{24.36 \times 10^{-5}}$$ **Ans.**

EXAMPLE 209. *A solution has 0.05M Mg^{2+} and 0.05M NH_3. Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in the solution. K_{sp} of $Mg(OH)_2$ is 9.0×10^{-12} and ionisation constant of NH_3 is 1.8×10^{-5}.* **(Roorkee Entrance 1993)**

SOLUTION. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ ...(1)

$$Mg^{2+} + 2OH^- \rightleftharpoons Mg(OH)_2 \quad ...(2)$$

$$\therefore \quad K_{sp} = [Mg^{2+}]\,[OH^-]^2 ;$$

$$9 \times 10^{-12} = 0.05\,[OH^-]^2$$

Or $$[OH^-] = \left(\frac{9 \times 10^{-12}}{0.05}\right)^{1/2}$$

$$= (180 \times 10^{-12})^{1/2} = 13.4 \times 10^{-6}$$

From equation (1), $$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

$$\therefore \quad [NH_4]^+ = \frac{K_b\,[NH_3]}{[OH^-]}$$

$$= \frac{1.8 \times 10^{-5} \times 0.05}{13.4 \times 10^{-6}} = 0.067M$$

$$[\because [NH_3] = 0.05M \text{ (given)}]$$

$\therefore$ 0.067M NH_4^+ ions must be produced by 0.067M NH_4Cl ($NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$) to prevent the formation of NH_4^+ ions and hence OH^- ions from NH_3.

EXAMPLE 210. *Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by the formula HSaC. A 4×10^{-4} mol amount of Saccharin is dissolved in 200 cm^3 water of pH 3. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium.* **(Roorkee, 1994)**

SOLUTION. [HSaC] no. of mol $\times \dfrac{1000}{\text{vol in mL}}$

$$= \frac{4 \times 10^{-4} \times 1000}{200}$$

$$= 2 \times 10^{-3}\text{ M}$$

$$pH = 3 ; -\log[H^+] = 3 ;$$

$$\log[H^+] = -3 ;$$

$$[H^+] = \text{antilog}(-3) = 10^{-3}$$

$$HSaC \rightleftharpoons H^+ + SaC^-$$

Concentration 2×10^{-3} M 10^{-3} M

H^+ ions are common ions. So, due to common ion effect, the dissociation of HSaC is almost negligible.

Hence : $$[H^+] = \frac{[H^+]\,[SaC^-]}{[HSaC]} ;$$

$$2 \times 10^{-12} = \frac{10^{-3}\,[SaC^-]}{2 \times 10^{-3}}$$

$$\therefore \quad [SaC^-] = \frac{2 \times 10^{-12} \times 2 \times 10^{-3}}{10^{-3}}$$

$$= \mathbf{4.0 \times 10^{-12}\ M}$$ **Ans.**

EXAMPLE 211. *Calculate the pH value of a saturated solution of $Mg(OH)_2$. K_{sp} for $Mg(OH)_2 = 10^{-11}$.*

SOLUTION. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

Solubility (mol L^-) S S $2S$

$$K_{sp} = [Mg^{2+}]\,[OH^-]^2 = S \times (2S)^2$$

$$= 4S^3 ; 10^{-11} = 4S^3$$

Hence $$S = \left(\frac{10^{-11}}{4}\right)^{1/3} ;$$

$$\log S = \log(0.25 \times 10^{-11})^{1/3}$$

$$= \frac{1}{3}[\log 0.25 + \log 10^{-11}]$$

$$= \frac{1}{3}(-0.6 - 11) = -3.87$$

$$= -3 - 1 + 1 - 0.87 = \bar{4}.13$$

$$\therefore \quad S = \text{antilog}\,\bar{4}.13 = 1.35 \times 10^{-4}\text{ M.}$$

$$\therefore \quad [OH^-] = 2S = 2 \times 1.35 \times 10^{-4}$$

$$= 2.7 \times 10^{-4}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{2.7 \times 10^{-4}}$$

$$= 3.7 \times 10^{-11}$$

Hence $$pH = -\log 3.7 \times 10^{-11}$$

$$= -(\log 3.7 + \log 10^{-11})$$

$$= -(0.57 - 11)$$

$$\mathbf{pH = 10.43}$$ **Ans.**

EXAMPLE 212. *If we increase the solubility of $Mg(OH)_2$ by the addition of ammonium ions, then calculate :*

(i) K_c for the reaction,

$$Mg(OH)_2 + 2NH_4^+ \rightleftharpoons Mg^{2+} + 2NH_3 + 2H_2O$$

(ii) Solubility of $Mg(OH)_2$ in a solution containing 0.6M NH_4Cl before $Mg(OH)_2$ has been added. [K_b for $NH_3 = 1.8 \times 10^{-5}$; K_{sp} for $Mg(OH)_2 = 10^{-11}$].

SOLUTION. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$;

$$\therefore \quad K_{sp} = [Mg^{2+}]\,[OH^-]^2 \quad ...(1)$$

For $NH_4OH \rightleftharpoons NH_4^+ + OH^-$;

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_4OH]}$$

For $Mg(OH)_2 + 2NH_4^+ \rightleftharpoons Mg^{2+} + 2NH_3 + 2H_2O$;

$$K_c = \frac{[Mg^{2+}]\,[NH_3]^2}{[NH_4^+]^2}$$

$$= \frac{[Mg^{2+}]\,[NH_4OH]^2}{[NH_4^+]^2}$$

$$\therefore \quad K_c \times K_b^2 = \frac{[Mg^{2+}]\,[NH_4OH]^2}{[NH_4^+]^2} \times \frac{[NH_4^+]^2\,[OH^-]^2}{[NH_4OH]^2}$$

$$= [Mg^{2+}]\,[OH^-]^2$$

$$K_c \times K_b^2 = K_{sp} \quad \text{[see equation (1)]}$$

$$\therefore \quad K_c = \frac{K_{sp}}{K_b^2} = \frac{10^{-11}}{(1.8 \times 10^{-5})^2} = 0.03$$

Let $Mg(OH)_2$ dissolved in presence of 0.6M NH_4Cl = x mol L^-

$$\therefore \quad Mg(OH)_2 + 2NH_4^+ \rightleftharpoons Mg^{2+} + 2NH_3 + 2H_2O$$

(1) Conc. at start	0.6	0	0
(2) Change by reaction	$-2x$	$\frac{2x}{2} = x$	$2x$
(3) Conc. at equilibrium	$0.6 - 2x$	x	$2x$

$$\therefore \quad K_c = \frac{[Mg^{2+}]\,[NH_3]^2}{[NH_4^+]^2}$$

$$= \frac{x(2x)^2}{(0.6 - 2x)^2} = \frac{4x^3}{0.6}$$

[2x is neglected from the denominator because it is very small as compared to 0.6]

$$\therefore \quad 0.03 = \frac{4x^3}{0.6}\ ;\ x = \left(\frac{0.03 \times 0.36}{4}\right)^{1/3}$$

$$= (2.7 \times 10^{-3})^{1/3}$$

$$\therefore \quad \log x = \log (2.7 \times 10^{-3})^{1/3}$$

$$= \frac{1}{3}\,[\log 2.7 + \log 10^{-3}]$$

$$= \frac{1}{3}\,[0.43 - 3] = -0.86$$

$$= -1 + 1 - 0.86 = \bar{1}.14$$

$$\therefore \quad x = \text{antilog } 1.14 = 1.38 \times 10^{-1}$$

$$= \mathbf{0.138\ M}$$ **Ans.**

EXAMPLE 213. *Determine the number of mol of AgI which may be dissolved in 1.0M CN^- solution. K_{sp} for AgI and K_c for $Ag(CN)_2^-$ are 1.2×10^{-17} M^2 and 7.1×10^{19} M^{2-} respectively.*

(Roorkee Entrance 1998)

SOLUTION. $[CN^-] = 1.0M$

(*i*) $$AgI(s) \underset{}{\overset{H_2O}{\rightleftharpoons}} Ag^+(aq) + I^-(aq) \quad \text{(given)}$$

$$\therefore \quad K_{sp} = [Ag^+(aq)]\,[I^-(aq)]$$

$$= 1.2 \times 10^{-17}\ M^2$$

(*ii*) $Ag^+(aq) + 2CN^-(aq) \rightleftharpoons [Ag(CN)_2]^-$

(formation process)

$$\therefore \quad K_f = \frac{[Ag(CN)_2]^-}{[Ag^+(aq)]\,[CN^-(aq)]^2}$$

$$= 7.1 \times 10^{19}\ M^{2-}$$

But $$K_{eq} = K_{sp} \times K_f$$

$$\therefore \quad K_{eq} = \frac{[Ag^+(aq)]\,[I^-(aq)]\,[Ag(CN)_2]^-}{[Ag^+(aq)]\,[CN^-(aq)]^2}$$

$$= \frac{[I^-(aq)]\,[Ag(CN)_2]^-}{[CN^-(aq)]^2}$$

Or $$K_{eq} = 1.2 \times 10^{-17} \times 7.1 \times 10^{19} = 852$$

Let x = no. of mol of AgI that dissolve in CN^- solution.

Thus : $$AgI(s) + 2CN^- \rightleftharpoons [Ag(CN)_2]^- + I^-$$

(1) n mol at start	1	0	0
(2) Change by reaction	$-2x$	x	x
(3) n mol after reaction	$1 - 2x$	x	x

$$\therefore \quad K_{eq} = \frac{[Ag(CN)_2]^-\,[I^-]}{[CN^-]^2}$$

$$= \frac{x \times x}{(1 - 2x)^2} = \frac{x^2}{(1 - 2x)^2}$$

Or $$852 = \frac{x^2}{(1 - 2x)^2}$$

Taking square root of both sides, we get :

$$(852)^{1/2} = \frac{x}{1 - 2x}\ ;$$

$$29.19 = \frac{x}{1 - 2x}\ ;\ 29.19\,(1 - 2x) = x$$

$$29.19 - 58.38x = x\ ;\ 59.38x = 29.19\ ;$$

$$x = \frac{29.19}{59.38} = 0.49 \text{ mol}$$

∴ no. of mol of AgI which may be dissolved in 1.0M CN^- = **0.49 mol.**

EXAMPLE 214. *A solution contains a mixture of Ag^+(0.1M) and Hg_2^{2+} (0.1M) which are to be separated by relative precipitation. Calculate the maximum concentration of iodide ions at which one of these gets precipitated almost completely. What percentage of metal ion is precpitated? K_{sp} of AgI and Hg_2I_2 are 8.5×10^{-17} and 2.5×10^{-26} respectively.* **(IIT 1984)**

SOLUTION. (*i*) $$AgI(s) \overset{H_2O}{\rightleftharpoons} Ag^+(aq) + I^-(aq)$$

(dissociation)

$$\therefore \quad K_{sp} = [Ag^+(aq)]\,[I^-(aq)]\ ;$$

$$8.5 \times 10^{-17} = [Ag^+(aq)]\,[I^-(aq)]$$

or $$8.5 \times 10^{-17} = 0.1\,[I^-(aq)]\ ;$$

$$\therefore \quad [I^-(aq)] = \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16}$$

(*ii*) $Hg_2I_2(s) \xrightleftharpoons{H_2O} Hg_2^{2+}(aq) + 2I^-(aq)$ (dissociation)

$$\therefore \qquad K_{sp} = [Hg_2^{2+}(aq)]\,[I^-(aq)]^2\,;$$

$$2.5 \times 10^{-26} = 0.1\,(I^-(aq))^2$$

$$\text{or} \qquad [I^-(aq)] = \left(\frac{2.5 \times 10^{-26}}{0.1}\right)^{1/2}$$

$$= (25 \times 10^{-26})^{1/2} = 5 \times 10^{-13}$$

Since $[I^-(aq)]$ required to precipitate AgI is less ($= 8.5 \times 10^{-16}$) than that of Hg_2I_2 ($= 5 \times 10^{-13}$), AgI gets precipitated first. During the precipitation of AgI, Hg_2I_2 exists is solution and for which maximum concentration of I^- ions is 5×10^{-13} M found above. This concentration of I^- ions exist until Hg_2I_2 gets precipitated.

(*iii*)To find % age of Ag^+ ion precipitated.

To find $[Ag^+(aq)]$ left in solution when

$$[I^-(aq)] = 5 \times 10^{-13}\ \text{M},$$

$$\text{We have} \qquad K_{sp} = [Ag^+(aq)]\,[I^-(aq)]\,;$$

$$8.5 \times 10^{-17} = [Ag^+(aq)] \times 5 \times 10^{-13}$$

$$\therefore \qquad [Ag^+(aq)] = \frac{8.5 \times 10^{-17}}{5 \times 10^{-13}} = 1.7 \times 10^{-4}\ \text{M}.$$

Since 0.1M $Ag^+(aq)$ will leave 1.7×10^{-4} M Ag^+ ions in solution :

$\therefore$ 100 M $Ag^+(aq)$ leave $Ag^+(aq)$ ions in solution

$$= \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17\ \text{M}$$

$\therefore$ % age of Ag^+ ions precipitated

$$= 100 - 0.17 = \mathbf{99.83\ M} \qquad \textbf{Ans.}$$

EXAMPLE 215. *The K_{sp} of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3L^{-3}. A solution of $K_2C_2O_4$ containing 0.152 mol in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the equilibrium is reached. $Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$.*

At equilibrium, the solution contains 0.0358 mol of K_2CO_3. Assuming degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be same, calculate K_{sp} of Ag_2CO_3. **(IIT1991)**

SOLUTION. *Reaction*

(*a*)	$Ag_2CO_3 +$	$K_2C_2O_4 \rightleftharpoons$	$Ag_2C_2O_4 +$	K_2CO_3
(1) n mol at start	Excess	0.152	0	0
(2) Change by reaction		− 0.0358	+ 0.0358	+0.0358
(3) n mol at equilibrium		0.152 − 0.0358 = 0.1162	0.0358	0.0358

(*i*) 500 mL solution contain $K_2C_2O_4$ = 0.1162 M

$\therefore$ 1000 mL solution contain

$$K_2C_2O_4 = \frac{0.1162}{500} \times 1000 = 0.2324\ \text{M}$$

Similarly, $[CO_3^{2-}]$ in 1000 mL

$$= \frac{0.0358 \times 1000}{500} = 0.0716\ \text{M}$$

(*ii*) 500 mL solution contain $K_2C_2O_4$ = 0.152 mol

$\therefore$ 1000 mL solution contain $K_2C_2O_4$

$$= \frac{0.152 \times 1000}{500} = 0.304\ \text{mL}^-$$

(*b*)	$Ag_2C_2O_4 \rightleftharpoons$	$2Ag^+$ +	$C_2O_4^{2-}$
Concentration		2×0.0716	0.304

$$\therefore \qquad \text{Ionic product} = [Ag^+]^2\,[C_2O_4^{2-}]$$

$$= (2 \times 0.0716)^2 \times 0.304$$

$$= 6.23 \times 10^{-3}$$

Since ionic product $[Ag^+]^2\,[C_2O_4^{2-}]$ ($= 6.23 \times 10^{-3}$) is greater than solubility product [$= 1.29 \times 10^{-11}$ (given)], $Ag_2C_2O_4$ will be precipitated.

Since $Ag_2C_2O_4$ is almost precipitated and Ag_2CO_3 is solid, for the precipitation of $Ag_2C_2O_4$.

$$[Ag^+]^2\,[C_2O_4^{2-}] = K_{sp}\,(Ag_2C_2O_4)\,;$$

$$[Ag^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$$

$$\text{or} \qquad [Ag^+] = \left(\frac{0.129 \times 10^{-11}}{0.2324}\right)^{1/2}$$

$$= (56 \times 10^{-12})^{1/2} = 7.48 \times 10^{-6}$$

$$(c) \qquad Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$$

$$K_{sp} = (Ag^+)^2\,[CO_3^{\,2-}]$$

$$= (7.48 \times 10^{-6})^2 \times 0.0716$$

$$= \mathbf{4.0 \times 10^{-12}\ mol^3\ L^{-3}} \qquad \textbf{Ans.}$$

EXAMPLE 216. *Given $[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3\,;\ K_c = 6.2 \times 10^{-8}$ and K_{sp} of AgCl $= 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.*

(IIT, 1998)

SOLUTION. $[Ag(NH_3)_2^+] = ?\ ;\ [NH_3] = 1.0$ M

$$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag^+(aq) + 2NH_3(aq) \quad ...(1)$$

n mol at start		$a + b$	$2a$M = 1M (given)

$$AgCl(s) \xrightleftharpoons{water} Ag^+(aq) + Cl^-(aq) \qquad ...(2)$$

$$a + b \qquad b$$

$[Ag^+] = a + b$ because the solution contains Ag^+ ions due to $Ag(NH_3)_2^+(aq)$ and AgCl(s). In case of simultaneous solubility, Ag^+ ions remain same in solution.

$$\therefore \qquad K_c = \frac{[Ag^+(aq)]\,[NH_3(aq)]^2}{[Ag(NH_3)_2(aq)]^+}$$

$$= \frac{(a+b) \times 1^2}{b}$$

$$\because [Ag(NH_3)_2^+(aq)] = [Cl^-(aq)] = b$$

Also, K_{sp} for equation (2) = $[Ag^+(aq)]\,[Cl^-(aq)]$ $= (a + b) \times b$

$$\text{Hence} \qquad \frac{K_c}{K_{sp}} = \frac{a+b}{b} \times \frac{1}{(a+b) \times b}$$

$$= \frac{1}{b^2} ; \frac{6.2 \times 10^{-8}}{1.8 \times 10^{-10}} = \frac{1}{b^2}$$

Or $b^2 = 29 \times 10^{-4} ; b = 5.38 \times 10^{-2}$

$= 0.538$

Or $[Ag(NH_3)_2^+(aq)] = \mathbf{0.0538}$ **Ans.**

EXAMPLE 217. *For the reaction* $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$*, the equilibrium constant at 25°C is* 4×10^{-19}*. Calculate the silver ion concentration in a solution which was originally 0.1 molar in KCN and 0.03 molar in* $AgNO_3$*.* **(IIT JEE. 1994)**

SOLUTION. (*a*) $Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2^-]$ ...(1)

$[CN^-] = 0.1\ M ; [CN^-]$ used

$= 2\,[CN^-] = 2 \times 0.03 = 0.06$

$\therefore$ $[CN^-]$ left in solution $= 0.1 - 0.06 = 0.04$ M

Also, $[Ag(CN)_2^-]$ formed in solution = 0.03M

Since reaction (1) is reverse of reaction

$[Ag(CN)_2^-] \rightleftharpoons Ag^+ + 2CN^-$, so :

$$K' = \frac{1}{K} = \frac{1}{4.0 \times 10^{-19}}$$

Hence
$$\frac{1}{4.0 \times 10^{-19}} = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2}$$

$$= \frac{0.03}{[Ag^+] \times (0.04)^2}$$

$$\therefore \quad [Ag^+] = \frac{0.03 \times 4 \times 10^{-19}}{(0.04)^2}$$

$= \mathbf{7.5 \times 10^{-18}\ M}$ **Ans.**

EXAMPLE 218. *A sample of AgCl was treated with 5.0 mL of 1.5 M* Na_2CO_3 *solution to give* Ag_2CO_3*. The remaining solution contained 0.0026 g of* Cl^- *per litre. Calculate the solubility product of AgCl* (K_{sp} *of* $Ag_2CO_3 = 8.2 \times 10^{-12}$). **(IIT 1997)**

SOLUTION. (*i*) *To find* $[Ag^+]$.

$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

$\therefore$ $K_{sp} = [Ag^+]^2\,[CO_3^{2-}]$;

$$[Ag^+]^2 = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{8.2 \times 10^{-12}}{1.5}$$

$= 5.47 \times 10^{-12}$

$\therefore$ $[Ag^+] = (5.47 \times 10^{-12})^{1/2}$

$= 2.34 \times 10^{-6}$ M

(2) wt. of Cl^- = 0.0026 g ;

g. at. wt. of Cl^- = 35.5 g

$$\therefore \quad [Cl^-] = \frac{\text{wt.}}{\text{g. at. wt}} = \frac{0.0026\ \text{g}}{35.5\ \text{g}}$$

$= 7.32 \times 10^{-5}$

$\therefore$ K_{sp} of AgCl $= [Ag^+]\,[Cl^-]$

$= 2.34 \times 10^{-6} \times 7.32 \times 10^{-5}$

$= \mathbf{1.7 \times 10^{-10}}$ **Ans.**

EXAMPLE 219. *The* K_{sp} *of* $Ca(OH)_2$ *is* 4.42×10^{-5} *at 25°C. A 500 mL of saturated solution of* $Ca(OH)_2$ *is mixed with equal volume of 0.4M NaOH. How much* $Ca(OH)_2$ *in mg is precipitated.* **(IIT 1992)**

SOLUTION. Let s = Solubility of $Ca(OH)_2$

$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

Solubility s $2s$

$\therefore$ $K_{sp} = [Ca^{2+}]\,[OH^-]^2$;

$4.42 \times 10^{-5} = s \times (2s)^2 = 4s^3$

$$\therefore \quad s = \left(\frac{4.42 \times 10^{-5}}{4}\right)^{1/3}$$

$= (1.105 \times 10^{-5})^{1/3}$

Taking logs of both sides, we get :

$\log s = \log (1.105 \times 10^{-5})^{1/3}$

$= \frac{1}{3}\,[\log 1.105 + \log 10^{-5}]$

$= \frac{1}{3}\,(0.043 - 5) = -1.652$

$\log s = -1 - 1 + 1 - 0.652 = \bar{2}.348.$

Taking antilogs, we get :

$s = \text{antilog}\ \bar{2}.348 = 2.23 \times 10^{-2}$

$= 0.0223$ M

When $Ca(OH)_2$ is mixed with NaOH solution, some Ca^{2+} ions are precipitated.

On mixing (*i*)
$$[Ca^{2+}] = \frac{0.0223\ M \times 500\ mL}{1000\ mL}$$

$= 0.01115$ M

$$[OH^-] = \frac{0.0223\ M \times 2 \times 500}{1000} + \frac{0.4\ M \times 500}{1000}$$

$= 0.2223$ M

$\therefore$ $K_{sp} = [Ca^{2+}\ (\text{left})]\,[OH^-]^2$

$$\therefore \quad Ca^{2+}\ (\text{left}) = \frac{K_{sp}}{[OH^-]^2} = \frac{4.42 \times 10^{-5}}{(0.2223)^2}$$

$= 8.84 \times 10^{-4}$ mol L^-.

$\therefore$ mol of $Ca(OH)_2$ precipitated

$= \text{Total}\ [Ca^{2+}] - [Ca^{2+}\ (\text{left})]$

$= 111.5 \times 10^{-4} - 8.84 \times 10^{-4}$

$= 10^{-4} \times (111.5 - 8.84)$

$= 102.56 \times 10^{-4}$ mol L^-

g. mol. wt. of $Ca(OH)_2 = 40 + 2\,(16 + 1) = 74$ g

$= 74 \times 1000 = 74000$ mg

$\therefore$ wt. of $Ca(OH)_2$ precipitate in 1L solution

$= 102.56 \times 10^{-4} \times 74000$

$= \mathbf{758.9\ mg}$ **Ans.**

EXAMPLE 220. *The solubility of* $Mg(OH)_2$ *in pure water is* 9.57×10^{-3} *g*L^-*. Calculate its solubility in g*L^- *in 0.02M* $Mg(NO_3)_2$*.* **(IIT 1986)**

SOLUTION. g. mol. wt. of $Mg(OH)_2$

$$= 24 + 2\,(16 + 1) = 58 \text{ g mol}^{-}$$

$$\therefore \quad [\text{Mg(OH)}_2] = \frac{9.57 \times 10^{-3}}{58}$$

$$= 1.65 \times 10^{-4} \text{ mol L}^{-}$$

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

$$\therefore \quad [\text{OH}^-] = \frac{2 \times 9.57 \times 10^{-3}}{58}$$

$$= 3.30 \times 10^{-4} \text{ mol L}^{-}$$

$$\therefore \quad K_{\text{sp}} = [\text{Mg}^{2+}]\,[\text{OH}^-]^2$$

$$= (1.65 \times 10^{-4})\,(3.3 \times 10^{-4})^2$$

$$= 1.797 \times 10^{-11}$$

In presence of $\text{Mg(NO}_3)_2$, let solubility of Mg(OH)_2 = x mol L$^-$

$$\therefore \quad [\text{Mg}^{2+}]\,[\text{OH}^-]^2 = K_{\text{sp}} \textit{ i.e., } 1.797 \times 10^{-11}$$

$$\therefore \quad (0.02 + x)\,(2x)^2 = 1.797 \times 10^{-11}$$

$$[\because \text{Mg(OH)}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-]$$

$$0.08x^2 + 4x^3 = 1.797 \times 10^{-11}$$

or
$$0.08x^2 = 1.797 \times 10^{-11}$$

$$[\because x \text{ is very small, } x^3 \text{ is neglected}]$$

$$\therefore \quad x = \left(\frac{1.797 \times 10^{-11}}{0.08}\right)^{1/2}$$

$$= (2.246 \times 10^{-10})^{1/2}$$

$$\log x = \frac{1}{2} \log 2.246 \times 10^{-10}$$

$$= \frac{1}{2} (\log 2.246 + \log 10^{-10})$$

$$= \frac{1}{2} (0.351 - 10) = -4.824$$

$$= -4 - 1 + 1 - 0.824 = \bar{5}.176$$

$$\therefore \quad x = \text{antilog } \bar{5}.176 \simeq 1.5 \times 10^{-5}$$

$$\therefore \quad \text{Solubility of Mg(OH)}_2 = 1.5 \times 10^{-5} \times \text{mol. wt.}$$

$$= 1.5 \times 10^{-5} \times 58$$

$$= \mathbf{87 \times 10^{-5} \text{ g L}^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 221. *Calculate the solubility of AgCl in 0.2 M solution of sodium chloride. K_{sp} of AgCl = 1.2×10^{-10}.*

(ISC, 2007)

SOLUTION. AgCl ionises as: $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

Solubility (mol L$^-$) $\quad S \quad S$

NaCl ionises as : $\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$

Concentration $\quad$ 0.2M $\quad$ 0.2M

$$\therefore \quad [\text{Ag}^+] = S;\ [\text{Cl}^-] = S + 0.2$$

$$= 0.2 \quad \because S <<< 0.2, S + 0.2 \simeq 0.2)$$

Hence
$$K_{\text{sp}} = [\text{Ag}^+]\,[\text{Cl}^-]$$

$$1.2 \times 10^{-10} = S \times 0.2; \quad S = \frac{1.2 \times 10^{-10}}{0.2}$$

$$= 6.0 \times 10^{-10} \text{ mol L}^{-}$$

$$\therefore \quad \text{Solubility of AgCl} = \mathbf{6.0 \times 10^{-10} \text{ mol L}^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 222. *The values of equilibrium constant for the dissociation of H_2S are as follows :*

(*i*) $H_2S \rightleftharpoons H^+ + HS^-$; $Ka_1 = 9.0 \times 10^{-8}$

(*ii*) $HS^- \rightleftharpoons H^+ + S^{-2}$; $Ka_2 = 10^{-12}$

Find the maximum concentration of Zn^{2+} ions in water (at 27°C) that is saturated with H_2S (0.1 M at 27°C) and maintained at pH 3 with HCl. K_{sp} (ZnS) = 4.51×10^{-24}.

SOLUTION. We know, overall dissociation constant, K_a is equal to multiple of dissociation constants of step wise reactions. Thus :

$$K_a = Ka_1 \times Ka_2\,;$$

$$K_a = 9.0 \times 10^{-8} \times 10^{-12} = 9.0 \times 10^{-20}$$

Also,
$$\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-};$$

$$\therefore \quad K_a = \frac{[\text{H}^+]^2\,[\text{S}^{2-}]}{[\text{H}_2\text{S}]} \qquad \text{...(1)}$$

Given $\quad pH = 3$; $\therefore\ -\log\,[\text{H}^+] = 3$;

Or $\quad [\text{H}^+] = 10^{-3}$

From equation (1), we have :

$$9.0 \times 10^{-20} \simeq \frac{(10^{-3})^2\,[\text{S}^{2-}]}{0.1}\,;$$

$$[S^{2-}] = \frac{9.0 \times 10^{-20} \times 0.1}{(10^{-3})^2}$$

Or $\quad [\text{S}^{2-}] = 9.0 \times 10^{-15}$

Also, $\quad \text{ZnS} \rightleftharpoons \text{Zn}^{2+} + \text{S}^{2-}$

$$K_{\text{sp}} = [\text{Zn}^{2+}]\,[\text{S}^{2-}]\,;$$

$$[\text{Zn}^{2+}] = \frac{K_{sp}}{[\text{S}^{2-}]} = \frac{4.51 \times 10^{-24}}{9.0 \times 10^{-15}}$$

Or $\quad [\text{Zn}^{2+}] = \mathbf{5.01 \times 10^{-10}\ M} \qquad$ **Ans.**

EXAMPLE 223. *The given nickel sulphide solution contains concentration of Ni^{2+} ions as 0.18×10^{-5} mol L$^-$. Calculate the minimum concentration of S^{2-} ions that could cause the precipitation of nickel sulphide. K_{sp} for nickel sulphide is 1.4×10^{-14}.*

SOLUTION. $\quad \text{NiS} \rightleftharpoons \text{Ni}^{2+} + \text{S}^{2-}$

Conc. (mol L$^-$) $\quad 0.18 \times 10^{-5}$

But $\quad K_{\text{sp}} = [\text{Ni}^{2+}]\,[\text{S}^{2-}]\,;$

$$[\text{S}^{2-}] = \frac{K_{sp}}{[\text{Ni}^{2+}]} = \frac{1.4 \times 10^{-14}}{0.18 \times 10^{-5}}$$

$$= 7.7 \times 10^{-9} \text{ mol L}^{-}.$$

So any value of concentration of S^{2-} ions greater than 7.7×10^{-9} mol L$^-$ will cause NiS to get precipitated.

EXAMPLE 224. *When a lead salt was dissolved in HCl, it was found to ionise up to 90%. It contains H^+ and Pb^{2+} ions respectively as 0.25 M and 0.12 M respectively. The solution is saturated with H_2S. Find the amount of Pb^{2+} ions those could not be precipitated. K_{sp} (H_2S) = 10^{-22} ; K_{sp} (PbS) = 4×10^{-29}.*

SOLUTION. HCl ionises to 90%.

So, $$[H^+] = \frac{0.25 \times 90}{100} = 0.225 \text{ M}$$

(*i*) $$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

∴ $$K_{sp} = [H^+]^2\,[S^{2-}]\,;$$

$$[S^{2-}] = \frac{K_{sp}}{[H^+]^2} = \frac{10^{-22}}{(0.225)^2}$$

$$= 1.98 \times 10^{-21} \text{ M}$$

(*ii*) $$PbS \rightleftharpoons Pb^{2+} + S^{2-}$$

∴ $$K_{sp} = [Pb^{2+}]\,[S^{2-}]\,;$$

$$[Pb^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{4 \times 10^{-29}}{1.98 \times 10^{-21}}$$

$$= \mathbf{2 \times 10^{-8}\ mol\ L^{-}}$$ **Ans.**

EXAMPLE 225. *The dissociation constant of carbonic acid is 4.31×10^{-7} and the solubility product of silver carbonate is 6.15×10^{-12}. What will happen to the concentration of hydrogen ions in a 0.01 molar carbonic acid solution and also its pH if 10^{-3} mol of silver nitrate powder is added to the solution ? Why ?* **(ISC 1996)**

SOLUTION. (*a*) $Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}; [Ag^+] = 10^{-3}$ M

$$K_{sp} = [Ag^+]^2\,[CO_3^{2-}]\,;$$

$$[CO_3^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{6.15 \times 10^{-12}}{(10^{-3})^2}$$

$$= 6.15 \times 10^{-6}$$

(*b*) $$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}\,;\ [H_2CO_3] = 0.01$$

∴ $$K = \frac{[H^+]^2\,[CO_3^{2-}]}{[H_2CO_3]}\,;$$

$$[H^+]^2 = \frac{K \times [H_2CO_3]}{[CO_3^{2-}]}$$

$$= \frac{4.31 \times 10^{-7} \times 0.01}{6.15 \times 10^{-6}}$$

∴ $$[H^+]^2 = 7 \times 10^{-4}\,;\ \therefore\ [H^+] = (7 \times 10^{-4})^{1/2}$$

$$= 2.646 \times 10^{-2}$$

∴ $$pH = -\log\,[H^+]$$

$$= -\log\,(2.646 \times 10^{-2})$$

$$= -(\log 2.646 + \log 10^{-2})$$

$$pH = -(0.422 - 2) = \mathbf{1.578}$$ **Ans.**

Type. Calculation of simultaneous solubilities of salts when their solubility products are given and when their K_{sp} values are very near to each other.

EXAMPLE 226. *Calculate the simultaneous solubility of AgSCN and AgBr. The solubility products of AgSCN and AgBr are 1.0×10^{-12} and 5.0×10^{-13} respectively.* **(MLNR 1995)**

SOLUTION. Data of K_{sp} values indicate that the solubilities of AgSCN and AgBr are very close to each other. So, the contribution of AgBr (less soluble) can not be ignored.

(*a*) For $AgSCN \rightleftharpoons Ag^+ + SCN^-\,;\ K_{sp} = [Ag^+]\,[SCN^-]\,;$

$$10^{-12} = [Ag^+]\,[SCN^-] \qquad ...(i)$$

(*b*) For $AgBr \rightleftharpoons Ag^+ + Br^-\,;\ K_{sp} = [Ag^+]\,[Br^-]\,;$

$$5 \times 10^{-13} = [Ag^+]\,[Br^-] \qquad ...(ii)$$

Dividing (*i*) by (*ii*), we get

$$\frac{[SCN^-]}{[Br^-]} = \frac{10^{-12}}{5 \times 10^{-13}} = 2 \qquad ...(iii)$$

Because of the need to balance electrical charge :

$$[SCN^-] + [Br^-] = [Ag^+] \qquad ...(iv)$$

Dividing (*iv*) by $[Br^-]$, we get :

$$\frac{[SCN^-]}{[Br^-]} + \frac{[Br^-]}{[Br^-]} = \frac{[Ag^+]}{[Br^-]}$$

Or $$2 + 1 = \frac{[Ag^+]}{[Br^-]}$$

$$\left\{\because \text{from } (iii)\,\frac{[SCN^-]}{[Br^-]} = 2\right\}$$

∴ $$[Ag^+] = 3[Br^-] \qquad ...(v)$$

Substituting the value of $[Ag^+]$ from (*v*) in (*ii*), we get :

$$5 \times 10^{-13} = 3[Br^-]\,[Br^-] = 3[Br^-]^2;$$

$$[Br^-] = \left(\frac{5 \times 10^{-13}}{3}\right)^{1/2}$$

∴ $$[Br^-] = (16.7 \times 10^{-14})^{1/2} = 4.1 \times 10^{-7}$$

(*c*) Substituting the value of $[Br^-]$ in (*iii*) and (*iv*), we get :

$$[SCN^-] + [Br^-] = 3[Br^-]\,;\ [SCN^-] = 2[Br^-]$$

$$= 2 \times 4.1 \times 10^{-7} = 8.2 \times 10^{-7}$$

$$5 \times 10^{-13} = [Ag^+] \times 4.1 \times 10^{-7}$$

∴ $$[Ag^+] = \frac{5 \times 10^{-13}}{4.1 \times 10^{-7}} = 1.2 \times 10^{-6}$$

∴ Solubility of AgSCN $= 8.2 \times 10^{-7}$ mol L^-

Solubility of AgBr $= 4.1 \times 10^{-7}$ mol L^-

EXAMPLE 227. *Assuming no hydrolysis of F^- ions, what will the $[F^-]$ in a solution saturated with respect to both SrF_2 and MgF_2. (K_{sp} of $SrF_2 = 2.8 \times 10^{-9}$ and K_{sp} of $MgF_2 = 6.5 \times 10^{-9}$)*

SOLUTION. $$\frac{K_{sp}\,[MgF_2]}{K_{sp}\,[SrF_2]} = \frac{[Mg^{2+}]\,[F^-]^2}{[Sr^{2+}]\,[F^-]^2} = \frac{[Mg^{2+}]}{[Sr^{2+}]}$$

Or $$\frac{6.5 \times 10^{-9}}{2.8 \times 10^{-9}} = \frac{[Mg^{2+}]}{[Sr^{2+}]}\,;\ 2.32 = \frac{[Mg^{2+}]}{[Sr^{2+}]}$$

∴ $$[Mg^{2+}] = 2.32\,[Sr^{2+}]$$

(*a*) $$SrF_2 \rightleftharpoons Sr^{2+} + 2F^-$$

Solubility (mol L^-) $\qquad S \qquad 2S$

$$MgF_2 \rightleftharpoons Mg^{2+} \quad + \quad 2F^-$$

Solubility (mol L^-) $\qquad 2.32S \qquad 2 \times 2.32S = 4.64S$

$$\begin{aligned} K_{sp}\,[\mathrm{SrF_2}] &= [\mathrm{Sr^{2+}}]\,[\mathrm{F^-}]^2 \\ 2.8 \times 10^{-9} &= S\,(2S + 4.64S)^2 \\ &= S\,(6.64S)^2 = 44.09S^3 \\ \therefore \quad S &= \left(\frac{2.8 \times 10^{-9}}{44.09}\right)^{1/3}; \\ \log S &= \log\,(0.063 \times 10^{-9})^{1/3} \\ &= \frac{1}{3}\,(\log 0.063 + \log 10^{-9}) \\ &= \frac{1}{3}\,(-1.2 - 9) = -3.4 \\ &= -3 - 1 + 1 - 0.4 = \bar{4}.6 \\ \therefore \quad S &= \text{antilog}\ \bar{4}.6 = 3.98 \times 10^{-4} \\ \therefore \quad [\mathrm{F^-}] &= 6.64S = 6.64 \times 3.98 \times 10^{-4} \\ &= \mathbf{2.64 \times 10^{-3}\ M} \qquad \textbf{Ans.} \end{aligned}$$

EXAMPLE 228. *You are provided with a 250 mL of a sample of hard water containing 0.0025 mol of* $CaCl_2$ *and a sample of 0.001 M* H_2SO_4*. Will this sample of* H_2SO_4 *precipitate out* Ca^{2+} *ions?* K_{sp} *of* $CaSO_4$ *in water at 298K is* 2.4×10^{-5}.

SOLUTION. (*a*) $[\mathrm{Ca^{2+}}] = \dfrac{\text{no. of mol} \times 1000}{\text{Volume of solution in mL}}$

$$= \frac{0.0025 \times 1000}{250} = 0.01\ \text{mol L}^{-}$$

(*b*) Let equal volumes of hard water and H_2SO_4 are used. As a result, the volume becomes double.

Hence : $[\mathrm{Ca^{2+}}]$ in solution after adding $H_2SO_4 = \dfrac{0.01}{2}$

$$= 0.005\ \text{mol L}^{-}$$

In $\qquad H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

Conc. mol L^- $\quad$ 0.001M $\qquad$ 0.001M

$\therefore$ $[SO_4^{2-}]$ in solution obtained after mixing

$$= \frac{0.001}{2} = 0.0005\ \text{M}$$

Hence $\quad$ *ionic product* $= [\mathrm{Ca^{2+}}]\,[\mathrm{SO_4^{2-}}]$

$$= 0.005 \times 0.0005 = 2.5 \times 10^{-6}$$

But Solubility product,

$$K_{sp} = 2.4 \times 10^{-5}\ \text{(given)}$$

Since ionic product is less than solubility product, no precipitation of $CaSO_4$ would take place.

EXAMPLE 229. *A sample of hard water contains 0.005 mol of* $CaCl_2$ *per litre. What is the maximum concentration of* Na_2SO_4 *which must be added for removing* Ca^{2+} *ions from this sample.* K_{sp} *for* $CaSO_4$ *is* 2.4×10^{-5} *at 25°C.* **(Rookee, 1986)**

SOLUTION. $\qquad CaCl_2 \xrightleftharpoons{H_2O} Ca^{2+}(aq) + 2Cl^-(aq)$

Conc. (mol L^-) $\quad$ 0.005

$$Na_2SO_4 \xrightleftharpoons{H_2O} 2Na^+(aq) + SO_4^{2-}(aq)$$

Conc. (mol L^-) $\quad x$

$$\therefore \quad K_{sp} = [\mathrm{Ca^{2+}(aq)}]\,[\mathrm{SO_4^{2-}(aq)}];$$

$$\begin{aligned} 2.4 \times 10^{-5} &= 0.005 \times x \\ \therefore \quad x = [\mathrm{SO_4^{2-}(aq)}] &= \frac{2.4 \times 10^{-5}}{0.005} \\ &= 4.8 \times 10^{-3}\ \text{mol L}^{-} \end{aligned}$$

So, maximum concentration of Na_2SO_4 to be added

$$= \mathbf{4.8 \times 10^{-3}\ mol\ L^{-}} \qquad \textbf{Ans.}$$

EXAMPLE 230. *Powdered silver nitrate solid is added bit by bit to a solution which is 0.001 M each of KCl, KBr and KI,*

(*i*) *Find the concentration of* Ag^+ *ions needed to initiate the precipitation of AgCl, AgBr and AgI.*

(*ii*) *Find the percentage of* I^- *ions precipitated before the precipitation of AgBr.*

(*iii*) *Find the % age of* I^- *ions precipitated before the precipitation of* Cl^- *ions. (*K_{sp} *AgCl, AgBr and AgI =* 1.8×10^{-10} 3.3×10^{-13} *and* 1.5×10^{-16} $mol^2\ L^{-2}$ *respectively).*

SOLUTION. (*i*) KCl, KBr and KI are strong electrolytes.

Hence, $\qquad [\mathrm{Cl^-}] = [\mathrm{Br^-}] = [\mathrm{I^-}] = 0.001$ M

(*a*) For $\quad AgCl \rightleftharpoons Ag^+ + Cl^-, K_{sp}\,[AgCl] = [Ag^+]\,[Cl^-]$.

Thus : $\qquad [\mathrm{Ag^+}] = \dfrac{K_{sp}}{[\mathrm{Cl^-}]} = \dfrac{1.8 \times 10^{-10}}{0.001}$

$$= \mathbf{1.8 \times 10^{-7}\ M} \qquad \textbf{Ans.}$$

(*b*) For $\quad AgBr \rightleftharpoons Ag^+ + Br^-, K_{sp}\,[AgBr] = [Ag^+]\,[Br^-]$.

Thus : $\qquad [\mathrm{Ag^+}] = \dfrac{K_{sp}}{[\mathrm{Br^-}]} = \dfrac{3.3 \times 10^{-13}}{0.001}$

$$= \mathbf{3.3 \times 10^{-10}\ M} \qquad \textbf{Ans.}$$

(*c*) For $\quad AgI \rightleftharpoons Ag^+ + I^-, K_{sp}\,[AgI] = [Ag^+]\,[I^-]$.

Hence : $\qquad [\mathrm{Ag^+}] = \dfrac{K_{sp}}{[\mathrm{I^-}]} = \dfrac{1.5 \times 10^{-16}}{0.001}$

$$= \mathbf{1.5 \times 10^{-13}\ M} \qquad \textbf{Ans.}$$

(*ii*) When AgBr just begins to precipitate, then, $[Ag^+] = 3.3 \times 10^{-10}$ (found above). At this stage, $[I^-]$ can be calculated as follows :

$$K_{sp}\,[AgI] = [Ag^+]\,[I^-]\,;\ [I^-] = \frac{K_{sp}\,[AgI]}{[Ag^+]}$$

$$= \frac{1.5 \times 10^{-16}}{3.3 \times 10^{-10}} = \mathbf{4.5 \times 10^{-7}}$$

$\therefore$ Percentage of I^- ions, not precipitated

$$= \frac{4.5 \times 10^{-7}}{0.001} \times 100 = 0.045\%$$

$\therefore$ Percentage of I^- ions precipitated before AgBr begins to precipitate

$$= 100 - 0.045 = \mathbf{99.955\%}\ \textbf{Ans.}$$

(*iii*) When AgCl just begins to precipitate, then, $[Ag^+] = 1.8 \times 10^{-7}$ (found above). At this stage, $[I^-]$ can be calculated as follows :

$$K_{sp}\,[AgI] = [Ag^+]\,[I^-]\,;$$

$$[I^-] = \frac{K_{sp}\,[AgI]}{[Ag^+]} = \frac{1.5 \times 10^{-16}}{1.8 \times 10^{-7}}$$

$$= \mathbf{8.3 \times 10^{-10}\ M}$$

∴ Percentage of I^- ions, not precipitated

$$= \frac{8.3 \times 10^{-10}}{0.001} \times 100$$

$$= 8.3 \times 10^{-5}\ M = 0.000083$$

∴ Percentage of I^- ions precipitated before AgCl begins to precipitate

$$= 100 - 0.000083$$

$$= \mathbf{99.999917\ \%} \qquad \textbf{Ans.}$$

EXAMPLE 231. *A given sample of hard water contains 0.03 mol L$^-$ of $CaCl_2$. Predict which of the following solutions of Na_2SO_4 will cause precipitation with hard water if equal volumes of both solutions are mixed? [K_{sp} ($CaSO_4$) = 2.4×10^{-4}].*

(*i*) *0.01 M* (*ii*) *0.008 M*

SOLUTION. Let volume of hard water ($CaCl_2$) = x mL; Volume of Na_2SO_4 = x mL

∴ Total volume of solution = $x + x = 2x$ mL

First case.

Hard water ($CaCl_2$) (before mixing) — Hard water (after mixing)

$$M_1V_2 = M_2V_2;\ 0.03 \times x = M_2 \times 2x$$

$$\therefore \quad M_2 = \frac{0.03 \times x}{2x} = 0.015\,;$$

$$[Ca^{2+}] = 0.015$$

Na_2SO_4 (before mixing) — Na_2SO_4 (after mixing)

$$M_1V_1 = M_2V_2;\ 0.01 \times x = M_2 \times 2x$$

$$\therefore \quad M_2 = \frac{0.01 \times x}{2x} = 0.005\,;$$

$$[SO_4^{2-}] = 0.005\ M$$

$$\therefore \quad \text{Ionic product} = [Ca^{2+}]\,[SO_4^{2-}] = 0.015 \times 0.005$$

$$= 7.5 \times 10^{-5}$$

Given $K_{sp} = 2.4 \times 10^{-4}$. Since ionic product is less than solubility product, **no precipitation of $CaSO_4$ will take place.**

Second Case.

Hard water ($CaCl_2$) (before mixing) — Hard water (after mixing)

$$M_1V_1 = M_2V_2;\ 0.08 \times x = M_2 \times 2x$$

$$\therefore \quad M_2 = \frac{0.08x}{2x} = 0.04 = [SO_4^{2-}]$$

$$\therefore \quad \text{Ionic product} = [Ca^{2+}]\,[SO_4^{2-}] = 0.015 \times 0.04$$

$$= 0.0060 = 6.0 \times 10^{-3}$$

Given $K_{sp} = 2.4 \times 10^{-4}$. Since ionic product is greater than solubility product, precipitation of $CaSO_4$ will take place.

EXAMPLE 232. *A few determinations of the solubility of AgCl in water at 298 K were recorded. Their average value is 0.00194 g L$^-$. Using this value, calculate the K_{sp} value of AgCl.*

SOLUTION. $AgCl(s) \rightleftharpoons Ag^+ + Cl^-\,;\ K_{sp} = [Ag^+]\,[Cl^-]$

Conc. $\qquad\qquad C \quad C$

$$\therefore \quad [Ag^+] = [Cl^-] = C\,;$$

$$\text{g. mol. wt. of AgCl} = 108 + 35.5 = 143.5\ \text{g mol}^-$$

$$= 1.435 \times 10^2\ \text{g mol}^-;$$

$$\text{wt. of AgCl} = 0.00194 = 1.94 \times 10^{-3}\ \text{g mol}^-$$

$$C = \frac{\text{wt. of AgCl}}{\text{g. mol. wt. of AgCl}}$$

$$= \frac{1.94 \times 10^{-3}}{1.435 \times 10^{+2}}$$

$$= 1.35 \times 10^{-5}\ \text{mol L}^-$$

$$\therefore \quad K_{sp} = [Ag^+]\,[Cl^-]$$

$$= (1.35 \times 10^{-5}) \times 1.35 \times 10^{-5}$$

$$= 1.82 \times 10^{-10}$$

$$K_{sp} = -\log Ks$$

$$= -(\log 1.82 + \log 10^{-10})$$

$$= -(0.26 - 10) = \mathbf{9.74} \qquad \textbf{Ans.}$$

EXAMPLE 233. *Silver nitrate is slowly added to a 0.02 M solution. of $NaC_2H_3O_2$.*

(*a*) *Will a precipitate of $AgC_2H_3O_2$ form when concentration of Ag^+ ions = 0.5×10^{-2}M?*

(*b*) *Calculate the approximate [Ag^+] at which precipitate starts forming. [K_{sp} ($AgC_2H_3O_2$)] = 2×10^{-3}.*

SOLUTION. (*a*) $NaC_2H_3O_2$ or CH_3COONa (sodium acetate) ionises as :

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+\ ;\ [CH_3COO^-] = 0.02M$

$AgC_2H_3O_2$ Or

$CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+\,;\ [Ag^+] = 0.5 \times 10^{-2}$

∴ Ionic product, $[Ag^+]\,[CH_3COO^-]$

$$= (0.5 \times 10^{-2}) \times (0.02) = 1 \times 10^{-4}$$

$$K_{sp} = 2 \times 10^{-3}.$$

Since ionic product is less than K_{sp}, no precipitate of silver acetate is formed.

(*b*) Since, we need precipitate to begin with, ionic product $[Ag^+]\,[CH_3COO^-]$ should be equal to K_{sp} *i.e.*, equilibrium value. So, we have :

$$K_{sp} = [Ag^+]\,[CH_3COO^-]\,;$$

$$2 \times 10^{-3} = [Ag^+] \times 0.02$$

$$\therefore \quad [Ag^+] = \frac{2 \times 10^{-3}}{0.02} = 0.1\ M$$

Hence the minimum concentration of Ag^+ ion at which precipitate of silver acetate would start forming is 0.1 M. At concentration, higher than 0.1M, precipitation of silver acetate will occur and sufficient amount of CH_3COO^- ions will be removed from solution to maintain K_{sp} value.

Example 234. *A litre of a solution contains 0.1 mol of Ag^+ and 0.1 mol of Hg_2^{2+} ion/litre. Calculate the concentration of I^- ions at which, one of them gets precipitated most completely. What %age of that metal ion is precipitated?*

$(K_{sp}\,(AgI) = 8.5 \times 10^{-17} = ;\ K_{sp}\,(Hg_2I_2) = 2.5 \times 10^{-26})$

(IIT, 1984)

Solution. (*a*) $AgI \rightleftharpoons Ag^+ + I^-\ ;\ K_{sp} = [Ag^+]\,[I^-]\ ;$

$$[I^-] = \frac{K_{sp}}{[Ag^+]}$$

$$\therefore \quad [I^-] = \frac{8.5 \times 10^{-17}}{0.1}$$

$$= 8.5 \times 10^{-16} \text{ g ion L}^-$$

(*b*) $Hg_2I_2 \rightleftharpoons Hg_2^{+2} + 2I^-\ ;\ K_{sp} = [Hg_2^{2+}]\,[I^-]^2\ ;$

$$[I^-] = \left[\frac{K_{sp}}{[Hg_2^{2+}]}\right]^{1/2} \left(\frac{2.5 \times 10^{-26}}{0.1}\right)^{1/2}$$

$$\therefore \quad [I^-] = 5 \times 10^{-13} \text{ g ion L}^-.$$

Since ionic product of AgI is greater than its K_{sp}, so AgI will precipitate first.

(*c*) When $[I^-] = 5 \times 10^{-13}$ g ion L^-, *i.e.*, when Hg_2I_2 starts precipitating out, then :

$$[Ag^+] = \frac{K_{sp}\,[AgI]}{[I^-]\text{ of }Hg_2I_2} = \frac{8.5 \times 10^{-17}}{5 \times 10^{-13}}$$

$$= 1.7 \times 10^{-4}\text{M}$$

$$\therefore \quad \%\text{ age of } Ag^+ \text{ left} = \frac{1.7 \times 10^{-4}}{0.1} \times 100 = 0.17$$

% age of Ag^+ precipitated

= 100 – 0.17 = 99.83 Ans.

Example 235. *The given solution of one litre contains 0.01 mol $Cr_2O_7^{2-}$ ions and 0.01 mol Cl^- ions. If Ag^+ ions are added dropwise, will AgCl or $Ag_2Cr_2O_7$ be precipitated first? $[K_{sp}\,(AgCl) = 1.56 \times 10^{-10}\ ;\ K_{sp}\,(Ag_2Cr_2O_7) = 2.83 \times 10^{-11}]$.*

Solution. (*a*) $AgCl \rightleftharpoons Ag^+ + Cl^-\ ;\ K_{sp} = [Ag^+]\,[Cl^-]\ ;$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]}$$

$$\text{Or} \quad [Ag^+] = \frac{1.56 \times 10^{-10}}{0.01} = 1.56 \times 10^{-8} \text{ g ion L}^-$$

(*b*) $Ag_2Cr_2O_7 \rightleftharpoons 2Ag^+ + Cr_2O_7^{2-}\ ;\ K_{sp} = [Ag^+]^2\ Cr_2O_7^{2-}]\ ;$

$$[Ag^+] = \left[\frac{K_{sp}}{[Cr_2O_7]^{2-}}\right]^{1/2}$$

$$\textbf{Or} \quad [Ag^+] = \left(\frac{2.83 \times 10^{-11}}{0.01}\right)^{1/2}$$

$$= (0.283 \times 10^{-8})^{1/2} = 0.53 \times 10^{-4} \text{ g ion L}^-.$$

Since the concentration of Ag^+ ions required to precipitate as AgCl (= 1.56×10^{-8} g ion L^-) is much less than that of Ag^+ ion in $Ag_2Cr_2O_7$ (= 0.53×10^{-4}), AgCl will precipitate first.

Example 236. *The pH of a 0.1M solution of monoprotic weak acid is 4.0. Calculate its $[H^+]$ and K_a value.*

Solution. Let HA = monoprotic acid ; α = degree of dissociation.

	HA ⇌	H^+	+ A^-
(1) n mol at start	0.1	0	0
(2) Change by reaction	–0.1α	0.1α	0.1α
(3) n mol after ionisation	0.1 – 0.1α	0.1α	0.1α

$$pH = 4\ ;\ -\log\,[H^+] = 4$$

$$\log\,[H^+] = -4$$

$$\therefore \quad [H^+] = \mathbf{10^{-4}} \qquad \textbf{Ans.}$$

$$\therefore \quad \text{But} \quad [H^+] = 0.1\alpha\ ;\ 10^{-4} = 0.1\alpha\ ;$$

$$\alpha = \frac{10^{-4}}{0.1} = 10^{-3}$$

$$\text{But} \quad K_a = \frac{[H^+]\,[A^-]}{[HA]} = \frac{0.1\alpha \times 0.1\alpha}{0.1 - 0.1\alpha}$$

$$= \frac{0.1 \times 0.1\alpha^2}{0.1(1-\alpha)} = 0.1\alpha^2$$

[∵ α is very small as compared to 1, so, α is rejected from the denominator]

$$\text{Or} \quad K_a = 0.1 \times (10^{-3})^2 = \mathbf{10^{-7}} \qquad \textbf{Ans.}$$

Example 237. *Find the value of equilibrium constant at 298K for the disproportionation of 3 mol HNO_2 to yield NO (g) and aqueous NO_3^-. The standard potential for the reduction of HNO_2 to NO is 0.99 V ; that for the reduction of NO_3^- to HNO_2 is 0.94V. Also, comment on the stability of HNO_2.*

Solution. The given reduction reactions are as follows.

(*i*) $HNO_2 + H_3O^+ + e^- \rightarrow NO + 2H_2O\ ;\ E° = +\,0.99V$

(*ii*) $NO_3^- + 3H_3O^+ + 2e^- \rightarrow HNO_2 + 4H_2O\ ;\ E° = +\,0.94V.$

In order to get the required equation,

$3HNO_2 \rightarrow 2NO + NO_3^- + H_3O^+;\ E° = ?$

we have 2 × Equation (*i*) – Eqation (*ii*). Thus

$2HNO_2 + 2H_3O^+ + 2e^- - NO_3^- \rightarrow 2NO + 4H_2O$

$\quad - 3H_3O^+ - 2e^- \qquad\qquad - HNO_2 - 4H_2O$

$E° = +\,0.099V - 0.94\text{ V} = +\,0.05V$

$$\text{Or} \quad 3HNO_2 \rightarrow 2NO + NO_3^- + H_3O^+\ ;$$

$$E° = +\,0.05V$$

$$\text{But} \quad E°nF = 2.303RT/\log K$$

$$\text{where} \quad n = \text{no. of electrons} = 2\ ;$$

$$R = 8.31\ JK^-$$

$$\text{Or} \quad \log K = \frac{2.303\,RT}{E^{\circ}\,nF}$$

$$= \frac{2.303 \times 8.31\text{ J K}^- \times 298\text{ K}}{0.05\text{ V} \times 2\text{ F} \times 96500\text{ CF}}$$

$$= 0.59$$

$$\text{Or} \quad K = \text{antilog } 0.59 = 3.89$$

The value of *K* being very small, HNO_2 is not very stable and decomposes on standing.

EXAMPLE 238. *The pH of hydrogen electrode is made 10. What will be its electrode potential?*

SOLUTION. $pH = \frac{E_{cell}}{0.0591}$; $E_{cell} = 0.0591 \times 10 = 0.591$

EXAMPLE 239. *An ammonia solution gives the following values of equivalent conductivity at different dilutions.*

V (in litre)	8	16	32	64	∞
g $(\text{ohm}^{-}\ \text{cm}^2\ (\text{equiv})^{-}$	3.2	4.45	6.62	8.9	2.37

From the above data, calculate the ionisation constant of ammonia.

SOLUTION. Let α = degree of ionisation ; K = ionisation constant = ?

Expt. no	Volume (V)	$\alpha = \frac{\alpha/\lambda_V}{\lambda_\infty}$	$K = \frac{\alpha^2}{(1-\alpha)V}$
(*i*)	8	$\frac{3.2}{237} = 0.0135$	$\frac{(0.0135)^2}{(1-0.0135)8} = 2.31 \times 10^{-5}$
(*ii*)	16	$\frac{4.45}{237} = 0.0188$	$\frac{(0.0188)^2}{(1-0.0188)16} = \frac{(0.0188)^2}{0.9812 \times 16}$ $= 2.25 \times 10^{-5}$
(*iii*)	32	$\frac{6.62}{237} = 0.0279$	$\frac{(0.0279)^2}{(1-0.0279)32} = \frac{(0.0279)^2}{0.9721 \times 32}$ $= 2.5 \times 10^{-5}$
(*iv*)	64	$\frac{8.9}{2.37} = 0.0375$	$\frac{(0.0375)^2}{(1-0.0375) \times 64} = \frac{(0.0375)^2}{0.9625 \times 64}$ $= 2.28 \times 10^{-5}$

$$\therefore \text{ Average value of } K = \frac{10^{-5}(2.31 + 2.25 + 2.5 + 2.28)}{4}$$

$$= \mathbf{2.34 \times 10^{-5}} \qquad \textbf{Ans.}$$

24.12 MISCELLANEOUS EXAMPLES

EXAMPLE 240. *What is the conjugate acid of* HS^-*?*

SOLUTION. Since conjugate acid and conjugate base pair differ by H^+, so the conjugate acid of HS^- will be H_2S.

EXAMPLE 241. *Aniline,* $C_6H_5NH_2$ *is a weak organic base in aqueous solutions. Suggest a solvent in which this compound would become a strong base.*

SOLUTION. The needed solvent should be such which has appreciably stronger acid properties than water. One such solvent is liquid acetic acid.

EXAMPLE 242. *At 298K, the self-ionisation constant,* $K = [HCOO^-]\,[HCOOH_2^+]$ *is* 10^{-6}*. Calculate the percentage of formic acid molecules in pure formic acid (HCOOH) that can be converted to formate ion,* $HCOO^-$*. (density of formic acid* $= 1.22\ g\ cm^{-3}$*).*

SOLUTION. wt. of formic acid = 1.22 g ;

g. mol. wt. of HCOOH = 1 + 12 + (2 × 16) + 1 = 46 g ; $1L = 10^{-3}\ cm^3$.

$\therefore$ no. of mol L^- of HCOOH

$$= \frac{1.22\ g}{cm^3} \times \frac{10^3\ cm^3}{L} \times \frac{1\ mol\ HCOOH}{46\ g\ HCOOH}$$

$$= 26.5\ mol\ L^-$$

Also $2HCOOH \rightleftharpoons HCOO^- + HCOOH_2^+ ; K = 10^{-6}$

Conc. mol L^- $\qquad x \qquad x$

$$\therefore \quad K = [HCOO^-]\,[HCOOH_2^+] ;$$

$$10^{-6} = x^2 ;$$

$$x = (10^{-6})^{1/2} = 10^{-3}$$

$$\therefore [HCOO^-] = 10^{-3}\ M$$

Hence percent dissociated to formate ion

$$= \frac{10^{-3}}{26.5} \times 100 = \mathbf{0.0038} \qquad \textbf{Ans.}$$

EXAMPLE 243. *At –50°C the ionic product of weakly ionised* NH_3 *is given as* $K = [NH_2^-]\,[NH_4^+] = 10^{-30}$*. Calculate the number of amide ions that are present per* mm^3 *of pure liquid ammonia.*

SOLUTION. $2NH_3 \rightleftharpoons NH_2^- + NH_4^+ ; K = 10^{-30}$

Conc. (mol L^-) $\qquad x \qquad x$

$$\therefore \quad K = [NH_2^-]\,[NH_4^+] ;\ 10^{-30} = x \times x ;$$

$$x = (10^{-30})^{1/2} = 10^{-15}$$

$\therefore$ no. of amide ions (NH_2^-) present per mm^3 of pure liquid ammonia

$$= \frac{10^{-15} mol}{L} \times \frac{1L}{10^6 mm^3} \times \frac{6.02 \times 10^{23}}{mol}$$

$$= 602 \text{ ions per } mm^3.$$

EXAMPLE 244. *Calculate the pH of* 7.0×10^{-8} *M acetic acid. Also calculate the concentration of unionised acetic acid.* $(K_a = 1.8 \times 10^{-5})$*.*

SOLUTION. (*a*) Given concentration of acetic acid indicates that the acid solution is very dilute. So, complete ionisation of acid can be considered but ionisation of water must be considered. Thus, we have :

$H_2O \rightleftharpoons H^+ + OH^- ; CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Conc. (mol L^-)

$x \qquad x \qquad\qquad 7 \times 10^{-8} \quad 7 \times 10^{-8}$

$$\therefore \quad [H^+] = x + (7 \times 10^{-8}) ; [OH^-] = x.$$

Thus : $\quad K_w = [H^+]\,[OH^-] ;$

$$10^{-14} = [x + (7 \times 10^{-8})] \times x ;$$

$$x^2 + (7 \times 10^{-8})x - 10^{-14} = 0$$

$$\therefore \quad x = \frac{-7 \times 10^{-8} + [(7 \times 10^{-8})^2 - 4(1 \times -10)^{-14}]^{1/2}}{2}$$

$$= \frac{-7 \times 10^{-8} + (49 \times 10^{-16} + 4 \times -10^{-14})^{1/2}}{2}$$

$$x = \frac{-7 \times 10^{-8} + [10^{-16}(49 + 400)^{1/2}}{2}$$

$$= \frac{-7\times10^{-8} + 21.2\times10^{-8}}{2} = 7.1\times10^{-8}$$

∵ for $ax^2 + bx + c = 0$

$$x = \frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

$$\therefore \quad [OH^-] = 7.1\times10^{-8}; [H^+] = x + 7\times10^{-8}$$
$$= 7.1\times10^{-8} + 7\times10^{-8}$$
$$= 14.1\times10^{-8}$$

$$\therefore \quad pH = -\log 14.1\times10^{-8}$$
$$= -(\log 14.1 + \log 10^{-8})$$
$$= -1.15 + 8 = \mathbf{6.85} \qquad \textbf{Ans.}$$

(*b*) From electroneutrality, we have :

$$[CH_3COO^-] + [OH^-] = [H^+]; [CH_3COO^-]$$
$$= [H^+] - [OH^-]$$
$$= 14.1\times10^{-8} - 7.1\times10^{-8}$$
$$= 7\times10^{-8}$$

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]};$$

$$1.8\times10^{-5} = \frac{7\times10^{-8}\times14.1\times10^{-8}}{[CH_3COOH]}$$

$$\therefore \quad [CH_3COOH] = \frac{7\times10^{-8}\times14.1\times10^{-8}}{1.8\times10^{-5}}$$
$$= \mathbf{5.5\times10^{-10}\,M} \qquad \textbf{Ans.}$$

EXAMPLE 245. *Calculate the pH of a 1.0L of 0.1M pyridine solution to which 0.12 mol of pyridinium chloride, $C_5H_5NH^+Cl^-$ has been added, assuming no change is volume. (K_b of pyridine = 1.52×10^{-9}).*

SOLUTION. $C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$

Conc. at start 0.1

Conc. at equilibrium $0.1 - x$ $\quad x \quad x$

$C_5H_5NH^+Cl^- \rightleftharpoons C_5H_5NH^+ + Cl^-$

Conc. at start 0.12

$$\therefore \quad [C_5H_5NH^+] = x + 0.12 = 0.12;$$
$$[OH^-] = x; [C_5H_5N] = 0.1 - x = 0.1$$

$$\therefore \quad K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]};$$

$$1.52\times10^{-9} = \frac{0.12x}{0.1};$$

$$x = \frac{1.52\times10^{-9}\times0.1}{0.12}$$

Or $\quad x = 1.27\times10^{-9};$
$\quad [OH^-] = 1.27\times10^{-9};$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.27\times10^{-9}}$$
$$= 7.8\times10^{-6}$$

$$\therefore \quad pH = -\log 7.8\times10^{-6}$$
$$= -(\log 7.8 + \log 10^{-6})$$
$$= -(0.89 - 6) = \mathbf{5.11} \qquad \textbf{Ans.}$$

EXAMPLE 246. *Calculate the pH and extent of hydrolysis of 0.1M NH_4NO_3 solution. ($K_b = 1.8\times10^{-5}$).*

SOLUTION. $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
$[\because NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^-]$

Conc. at start 0.1

Conc. at equilibrium $0.1 - x$ $\quad x \quad x$
$\simeq 0.1$

$$\therefore \quad K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x\times x}{0.1} \quad ...(1)$$

$$\text{But} \quad K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8\times10^{-5}} \quad ...(2)$$

From (1) and (2), we get :

$$\frac{x^2}{0.1} = \frac{10^{-14}}{1.8\times10^{-5}};$$

$$x = \left(\frac{10^{-14}}{1.8\times10^{-5}}\times0.1\right)^{1/2}$$

$$x = (0.55\times10^{-10})^{1/2}$$
$$= 0.74\times10^{-5} = [H_3O^+]$$

$$\therefore \quad pH = -\log[H_3O^+]$$
$$= -\log 0.74\times10^{-5}$$
$$= -(\log 0.74 + \log 10^{-5})$$
$$pH = -(-0.13 - 5) = \mathbf{5.13} \qquad \textbf{Ans.}$$

$$\%\ \text{hydrolysed} = \frac{\text{Amount hydrolysed}}{\text{Total amount}}\times100$$
$$= \frac{0.74\times10^{-5}}{0.1}\times100$$
$$= 0.0074\%$$

EXAMPLE 247. *A 10^{-2} M solution of $PuO_2(NO_3)_2$ has pH 3.8. Calculate the hydrolysis constant K_h for PuO_2^{2+} and K_b for PuO_2OH^+. ($K_w = 10^{-14}$).*

SOLUTION. $PuO_2^{2+} + H_2O \rightleftharpoons PuO_2(OH)^+ + H_3O^+$

Conc. $\quad 10^{-2} \qquad x$

$$K_h = \frac{[PuO_2(OH)^+][H_3O^+]}{[PuO_2^{2+}]};$$

$$pH = 3.8; -\log[H_3O^+] = 3.8$$

$$\therefore \quad \log[H_3O^+] = -3.8 = -3 - 1 + 1 - 0.8 = \bar{4}.2.$$

Or $\quad [H_3O^+] = \text{antilog}\ \bar{4}.2$

Or $\quad [H_3O^+] = 1.58\times10^{-4} = x = [PuO_2(OH)^+].$

$$\text{Hence} \quad K_h = \frac{1.58\times10^{-4}\times1.58\times10^{-4}}{10^{-2}}$$
$$= \mathbf{2.5\times10^{-6}} \qquad \textbf{Ans.}$$

Also, $K_b = \frac{K_w}{K_h} = \frac{10^{-14}}{2.5 \times 10^{-6}} = \mathbf{4 \times 10^{-9}}$ **Ans.**

Type. Polyprotic acids and bases

Example 248. *Calculate the $[SO_4^{2-}]$ in 0.12M H_2SO_4. K for $(HSO_4^-) = 1.02 \times 10^{-2}$.*

Solution. (*i*) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ (complete ionisation)

(*ii*) $HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$ (hydrolysis)

For reaction (*ii*) $K = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]}$;

$$1.02 \times 10^{-2} = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} \qquad ...(1)$$

For reaction (*ii*) at equilibrium,

$$[SO_4^{2-}] = x\ ;\ [H_3O^+] = 0.12 + x$$

$[HSO_4^-] = 0.12 - x$. Hence, from reaction (1), we have :

$$1.02 \times 10^{-2} = \frac{x\,(0.12 + x)}{0.12 - x}\ ;$$

$$0.0102(0.12 - x) = x^2 + 0.12x$$

$$0.0012 - 0.0102x = x^2 + 0.12x\ ;$$

$$x^2 + 0.13x - 0.0012 = 0$$

$\because$ for $a\,x^2 + bx + c = 0$,

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

$$\therefore \quad x = \frac{-\,0.13 + [(0.13)^2 + (4 \times 0.0012)]^{1/2}}{2}$$

$$= \frac{-\,0.13 + 0.147}{2} = 8.5 \times 10^{-3}$$

$\therefore$ $[SO_4^{2-}] = \mathbf{8.5 \times 10^{-3}}$ **Ans.**

Example 249. *Calculate the pH of a solution containing 0.12M HCO_3^- and 0.16M CO_3^{-2}. $(K = (HCO_3^-) = 4.7 \times 10^{-11})$*

Solution. $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$

Conc. 0.12M 0.16M

$$\therefore \quad K = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}\ ;$$

$$4.7 \times 10^{-11} = \frac{[H^+] \times 0.16}{0.12}$$

$$\therefore \quad [H^+] = \frac{4.7 \times 10^{-11} \times 0.12}{0.16} = 3.50 \times 10^{-11}.$$

Hence : $pH = -\log[H^+] = -\log(3.5 \times 10^{-11})$

$= -(\log 3.5 + \log 10^{-11}) = -(0.54 - 11)$

$pH = \mathbf{10.46}$ **Ans.**

Example 250. *What will be the $[H_3PO_4]$ and $[OH^-]$ of a solution prepared by dissolving 0.12 mol of $[NH_4]_3PO_4$ in sufficient water to make one litre solution? K_1, K_2 and K_3 which refer to the ionisation constants for H_3PO_4 are 7.1×10^{-3}, 6.3×10^{-8} and 4.5×10^{-13} respectively.*

Solution. PO_4^{3-} hydrolyses in three steps.

(*i*) $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$;

$$K = \frac{K_w}{K_3} = \frac{10^{-14}}{4.5 \times 10^{-13}} = 0.022$$

(*ii*) $HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$;

$$K' = \frac{K_w}{K_2} = \frac{10^{-14}}{6.3 \times 10^{-8}}$$

$$= 1.6 \times 10^{-7}$$

(*iii*) $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$;

$$K'' = \frac{K_w}{K_1} = \frac{10^{-14}}{7.1 \times 10^{-3}}$$

$$= 1.4 \times 10^{-12}$$

(*a*) Out of all the above reactions, reaction (*i*) is used to calculate $[OH^-]$ because OH^- ions from this reaction suppress the ionisation of second and third steps due to common ion effect.

$$\therefore \quad K = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]}\ ;$$

$$0.022 = \frac{x \times x}{0.12 - x}\ ;\ x^2 = 0.022\,(0.12 - x)$$

$$x^2 + 0.022x - 0.00264 = 0;$$

$$\left[\begin{array}{l}\because \text{for } ax^2 + bx + c = 0 \\ x = \dfrac{-b \pm (b^2 - 4ac)^{1/2}}{2a}\end{array}\right]$$

$$x = \frac{-\,0.022 + [(0.022)^2 - (4 \times 1 \times -\,0.00264)]^{1/2}}{2}$$

$$x = \frac{-\,0.022 + (0.000484 + 0.1056)^{1/2}}{2}$$

$$= \frac{-\,0.022 + 0.105}{2} = 0.0415\ M$$

Or $[OH^-] = 0.0415$ M

(*b*) Concentration of H_3PO_4 is calculated with the help of K' and K''values.

Thus : $K' = \frac{[H_2PO_4^-][OH^-]}{[HPO_4^{2-}]}$;

$$1.6 \times 10^{-12} = \frac{[H_2PO_4^-] \times x}{x}\ ;$$

$$[H_2PO_4^-] = 1.6 \times 10^{-7}$$

$$K'' = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]}\ ;$$

$$1.4 \times 10^{-12} = \frac{[H_3PO_4] \times x}{x} ;$$

$$[H_3PO_4] = \mathbf{1.4 \times 10^{-12}\ M} \qquad \textbf{Ans.}$$

Example 251. *Calculate the concentration of sulphide ions in a solution that is 0.045 M H_2S and 0.01M HCl. K_1 and K_2 for H_2S are 10^{-7} and 10^{-14} respectively.*

Solution. HCl is a strong acid and ionises completely. So, it suppresses the ionisation of both H_2S and HS^-. So, in case of HCl, $[H_3O^+] = 0.01M$.

(*i*) $H_2S \rightleftharpoons H^+ + HS^-$;

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} ;$$

$$10^{-7} = \frac{0.01\,[HS^-]}{0.045}$$

$$\therefore \quad [HS^-] = \frac{10^{-7} \times 0.045}{0.01}$$

$$= \mathbf{4.5 \times 10^{-7}\ M} \qquad \textbf{Ans.}$$

(*ii*) $HS^- \rightleftharpoons H^+ + S^{2-}$;

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} ;$$

$$10^{-14} = \frac{0.01\,[S^{2-}]}{4.5 \times 10^{-7}}$$

$$\therefore \quad [S^{2-}] = \frac{4.5 \times 10^{-7} \times 10^{-14}}{0.01}$$

$$= \mathbf{4.5 \times 10^{-19}\ M} \qquad \textbf{Ans.}$$

Example 252. *Calculate the $[H^+]$ of 0.1M H_2S solution. K_1 and K_2 for H_2S are 10^{-7} and 10^{-14} respectively.*

Solution. (*a*) $H_2S \rightleftharpoons H^+ + HS^-$ (primary ionisation)

	H_2S	H^+	HS^-
Conc.	0.1		
Conc. at equilibrium	$0.1 - x$ $\simeq 0.1$	x	x

$$\therefore \quad K_1 = \frac{[H^+][HS^-]}{[H_2S]} ; 10^{-7} = \frac{x \times x}{0.1} ;$$

$$x = (10^{-7} \times 0.1)^{1/2} = 10^{-4}$$

$$\therefore \quad [H^+] = [HS^-] = 10^{-4}$$

(*b*) $HS^- \rightleftharpoons H^+ + S^{2-}$ (second ionisation)

	HS^-	H^+	S^{2-}
Conc.	10^{-4}		
Conc. at equilibrium	10^{-4}	10^{-4}	

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} ;$$

$$10^{-14} = \frac{10^{-4}\,[S^{2-}]}{10^{-4}} ; [S^{2-}] = 10^{-14}$$

As calculated from first ionisation, the second ionisation is so limited that it does not appreciably lower $[H^+]$ or $[HS^-]$. In general, the [conjugate base] resulting from the second ionisation is numerically equal to K_2 whenever the extent of second ionisation is less than 5%.

Example 253. *Calculate the $[CO_3^{2-}]$ in a 0.001M Na_2CO_3 solution after the hydrolysis reactions have come to equilibrium. $K_2 = 4.7 \times 10^{-11}$.*

Solution. $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

Conc. at equilibrium $0.1 - x$ $\quad x \quad x$

Note: First hydrolysis supresses the second

$$\therefore \quad K_h = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} ;$$

$$K_h = \frac{x \times x}{0.001 - x} \qquad ...(1)$$

Also, $$K_h = \frac{K_w}{K_2} = \frac{10^{-14}}{4.7 \times 10^{-11}}$$

$$= 2.1 \times 10^{-4} \qquad ...(2)$$

From (1) and (2) we get :

$$\frac{x^2}{0.001 - x} = 2.1 \times 10^{-4}$$

$$x^2 = 2.1 \times 10^{-4}(0.001 - x) ;$$

$$x^2 + 2.1 \times 10^{-4}x - 2.1 \times 10^{-7} = 0$$

$$\textbf{Or } x = \frac{-2.1 \times 10^{-4} + [(2.1 \times 10^{-4})^2 - (4 \times 1 \times -2.1 \times 10^{-7})]}{2}$$

$$\textbf{Or } x = \frac{-2.1 \times 10^{-4} + [4.41 \times 10^{-8} + 8.4 \times 10^{-7}]^{1/2}}{2}$$

$$= \frac{-2.1 \times 10^{-4} + [10^{-8}(4.41 + 8.4 \times 10)]^{1/2}}{2}$$

$$= \frac{-2.1 \times 10^{-4} + 9.4 \times 10^{-4}}{2}$$

$\because$ for $ax^2 + bx + c = 0$

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}$$

$$x = 3.65 \times 10^{-4} = [OH^-]$$

$$\therefore [CO_3^{2-}] = 0.001 - x = 0.001 - 3.65 \times 10^{-4}$$

$$= \mathbf{0.000635} \qquad \textbf{Ans.}$$

Example 254. *The pH of blood is 7.4. Assuming that the buffer in blood is CO_2, HCO_3^- and CO_3^{2-}, calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH. Also, write the effect of rapid forced breathing on the blood pH. ($K_1 = 4.5 \times 10^{-7}$).*

Solution. $pH = 7.4 ; -\log[H^+] = 7.4 ; \log[H^+] = -7.4 = -7 - 1 + 1 - 0.4 = \bar{8}.6$

$$\therefore \quad [H^+] = \text{antilog}.\bar{8}.6 = 3.98 \times 10^{-8} = [H_3O^+]$$

$$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[CO_2]};$$

$$4.5 \times 10^{-7} = \frac{3.98 \times 10^{-8}\,[HCO_3^-]}{[CO_2]}$$

$$\therefore \quad \frac{[HCO_3^-]}{[CO_2]} = \frac{4.5 \times 10^{-7}}{3.98 \times 10^{-8}} = \mathbf{11.3}$$

Rapid breathing would lower $[CO_2]$. It will shift the equilibrium and pH also to some extent. Some dizziness may take place.

EXAMPLE 255. *Calculate the pH of 0.01 M NaHCO$_3$. $K_1 = 4.5 \times 10^{-7}$; $K_2 = 4.7 \times 10^{-11}$.*

SOLUTION. Reaction. (*i*) $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (Ionisation, acidic solution, $K_2 = 4.7 \times 10^{-11}$)

(*ii*) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ (hydrolysis, basic solution, $K_1 = 4.5 \times 10^{-7}$)

$$\text{Hydrolysis constant, } K_h = \frac{K_w}{K_1} = \frac{10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8}$$

It may be noted that K_h for reaction (*ii*) is related to K_1 because both hydrolysis and K_1 equilibrium involve H_2CO_3 and HCO_3^-. Since equilibrium constant for reaction (*ii*) is greater than that of reaction (*i*), the pH is definite to exceed 7. We assume that after self neutralisation, both H^+ and OH^- will be very small. Thus, there will be no appreciable effect on the *ionic charge balance.* Since the cationic charge remains at 0.01M, the $[Na^+]$, regardless of the acid and base equilibria, electrical neutrality can be preserved only by maintaining a fixed total anionic charge among the various carbonate species. In other words, for every negative charge removed by converting HCO_3^- to H_2CO_3, another charge must be created by converting HCO_3^- to CO_3^{2-}. As a result, following conditions are observed.

$$[CO_3^{2-}] = [H_2CO_3] = x;$$

$$[HCO_3^-] = 0.01 - 2x \approx 0.01$$

$$\therefore \quad K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]};$$

$$4.7 \times 10^{-11} = \frac{H^+ \times x}{0.01} \qquad ...(iii)$$

$$K_h = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]};$$

$$2.2 \times 10^{-8} = \frac{x \times [OH^-]}{0.01} \qquad ...(iv)$$

Multiply (*iii*) and (*iv*), we get :

$$4.7 \times 10^{-11} \times 2.2 \times 10^{-8} = \frac{[H^+]x \times x[OH^-]}{0.01 \times 0.01}$$

$$= \frac{[H^+][OH^-]x^2}{10^{-4}};$$

$$1.034 \times 10^{-18} = \frac{10^{-14}x^2}{10^{-4}}$$

$$[\because [H^+][OH^-] = K_w = 10^{-14}]$$

$$\therefore \quad x = \left(\frac{1.034 \times 10^{-18} \times 10^{-4}}{10^{-14}}\right)^{1/2}$$

$$= (1.034 \times 10^{-8})^{1/2}$$

$$= 1.02 \times 10^{-4}$$

From equation (*iii*), we have :

$$4.7 \times 10^{-11} = \frac{[H^+]x}{0.01};$$

$$[H^+] = \frac{4.7 \times 10^{-11} \times 0.01}{x}$$

$$= \frac{4.7 \times 10^{-11} \times 0.01}{1.02 \times 10^{-4}}$$

Or $[H^+] = 4.6 \times 10^{-9}$

$$\therefore \quad pH = -\log[H^+] = -\log(4.6 \times 10^{-9})$$

$$= -(\log 4.6 + \log 10^{-9})$$

$$pH = -(0.66 - 9) = \mathbf{8.34} \qquad \textbf{Ans.}$$

EXAMPLE 256. *Calculate the percent hydrolysis in a 10^{-2}M KCN solution. ($K_a = 6.2 \times 10^{-10}$)*

SOLUTION. Reaction. $CN^- + H_2O \rightleftharpoons HCN + OH^-$

Conc. at equilibrium 10^{-2} x x

$= 0.01M$

(hydrolysis ; $KCN \rightleftharpoons K^+ + CN^-$)

$$K_h = \frac{[HCN][OH^-]}{[CN^-]} = \frac{x \times x}{0.01} \qquad ...(1)$$

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2 \times 10^{-10}}$$

$$= 1.6 \times 10^{-5} \qquad ...(2)$$

From (1) and (2), we have :

$$\frac{x^2}{0.01} = 1.6 \times 10^{-5};$$

$$x = (1.6 \times 10^{-5} \times 0.01)^{1/2}$$

Or $x = (16 \times 10^{-8})^{1/2} = 4 \times 10^{-4}$

$$\therefore \quad \%\ \text{Hydrolysis} = \frac{4 \times 10^{-4}}{0.01} \times 100 = \mathbf{4.0\%} \quad \textbf{Ans.}$$

EXAMPLE 257. *Calculate the pH and extent of hydrolysis of 0.01 M CH$_3$COONH$_4$. [K_b(NH$_3$) = 1.8×10^{-5} ; K_a(CH$_3$COOH) = 1.8×10^{-5}].*

SOLUTION. $CH_3COONH_4 \rightleftharpoons NH_4^+ + CH_3COO^-$

In this case NH_4^+ as well as CH_3COO^- hydrolyse. Thus:

$$\text{For } NH_4^+, \quad K_h = \frac{K_w}{K_b\,(NH_3)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\text{For } CH_3COO^-, \; K_h = \frac{K_w}{K_a\,(CH_3COOH)}$$

$$= \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Here K_h for cation and anion are identical. Hence $[H^+]$ from NH_4^+ hydrolysis = $[OH^-]$ from CH_3COO^- hydrolysis and solution will be neutral. Thus $[H^+] = [OH^-] = 10^{-7}$; $pH = 7$

$\therefore$ For NH_4^+ hydrolysis : $NH_4^+ \rightleftharpoons H^+ + NH_3$

Conc. at equilibrium $\quad 0.01 - x \quad 10^{-7} \quad x$

$$K_h = \frac{[H^+]\,[NH_3]}{[NH_4^+]};$$

$$5.6 \times 10^{-10} = \frac{10^{-7}x}{0.01 - x}$$

$$5.6 \times 10^{-10}\,(0.01 - x) = 10^{-10}x \,;\, 5.6 \times 10^{-12} - 5.6 \times 10^{-10}\,x = 10^{-7}x$$

Or $10^{-7}x + 5.6 \times 10^{-10}x = 5.6 \times 10^{-12}$;

$$10^{-10}x\,(10^3 + 5.6) = 5.6 \times 10^{-12}$$

Or $$x = \frac{5.6 \times 10^{-12}}{10^{-10} \times 1005.6} = 5.6 \times 10^{-5}$$

$\therefore$ % age of NH_4^+ hydrolysed

$$= \frac{5.6 \times 10^{-5}}{0.01} \times 100 = \mathbf{0.56\%} \quad \textbf{Ans.}$$

EXAMPLE 258. *Calculate the pH in a 0.1M NH_4OCN solution.* $[K_b\,(NH_3) = 1.8 \times 10^{-5}\,;\, K_a\,(HOCN) = 3.0 \times 10^{-4}]$.

SOLUTION. $NH_4OCN \rightleftharpoons NH_4^+ + OCN^-$

Both NH_4^+ and OCN^- hydrolyse. NH_3 is a weaker base than HOCN which is an acid. However, NH_4^+ hydrolyses more than OCN^- and pH is less than 7. In order to preserve electrical neutrality, there can not be appreciable difference between $[NH_3]$ and $[HOCN]$. Thus we assume $[NH_3] = [HOCN] = x$; $[NH_4^+] = [OCN^-] = 0.1 - x$.

(*a*) For NH_4^+; $NH_4^+ \rightleftharpoons H^+ + NH_3$

$$K_h = \frac{[H^+]\,[NH_3]}{[NH_4^+]} \quad ...(1)$$

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$$= 5.6 \times 10^{-10} \quad ...(2)$$

From (1) and (2), we get :

$$\frac{[H^+]\,[NH_3]}{[NH_4^+]} = 5.6 \times 10^{-10}$$

or $$\frac{[H^+] \times x}{0.1 - x} = 5.6 \times 10^{-10} \,;$$

$$[H^+] = \frac{5.6 \times 10^{-10}(0.1 - x)}{x} \quad ...(3)$$

(*b*) For OCN^- ; $H_2O + OCN^- \rightleftharpoons HOCN + OH^-$

$$\therefore \quad K_h = \frac{[HOCN]\,[OH^-]}{[OCN^-]} = \frac{x[OH^-]}{0.1 - x} \quad ...(4)$$

Also $$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{3.0 \times 10^{-4}}$$

$$= 3.3 \times 10^{-11} \quad ...(5)$$

From (4) and (5), we get,

$$\frac{x[OH^-]}{0.1 - x} = 3.3 \times 10^{-11}$$

$$\therefore \quad [OH^-] = \frac{3.3 \times 10^{-11}(0.1 - x)}{x} \quad ...(6)$$

Dividing (3) and (6), we get,

$$\frac{[H^+]}{[OH^-]} = \frac{5.6 \times 10^{-10}(0.1 - x)}{x} \times \frac{x}{3.3 \times 10^{-11}(0.1 - x)}$$

Or $$\frac{[H^+]}{[OH^-]} = 17 \quad ...(7)$$

But $\quad [H^+]\,[OH^-] = K_w = 10^{-14} \quad ...(8)$

Multiplying (7) and (8), we get

$$\frac{[H^+]\,[H^+]\,[OH^-]}{[OH^-]} = 17 \times 10^{-14} \,;\, [H^+]^2 = 17 \times 10^{-14} \,;$$

$$[H^+] = (17 \times 10^{-14})^{1/2}$$

Or $\quad [H^+] = 4.1 \times 10^{-7}$.

Hence, $\quad pH = -\log\,[H^+] = -\log 4.1 \times 10^{-7}$

$= -(\log 4.1 + \log 10^{-7})$

$= -(0.61 - 7) = 6.39.$

So, $\quad pH = \mathbf{6.39} \quad$ **Ans.**

EXAMPLE 259. *Calculate the* $[OH^-]$ *in a 0.005M solution of* $Na_2C_2O_4$. K_1 *and* K_2 *for oxalic acid,* $H_2C_2O_4$ *are* 5.6×10^{-2} *and* 5.4×10^{-5} *respectively.*

SOLUTION. $Na_2C_2O_4 \rightleftharpoons 2Na^+ + C_2O_4^{2-}$

$C_2O_4^{2-} + H_2O \rightleftharpoons HC_2O_4^- + OH^-$ (hydrolysis)

Conc. at equilibrium

$0.005 - x \quad x \quad x$

≈ 0.005

$$\therefore \quad K_h = \frac{[HC_2O_4^-]\,[OH^-]}{[C_2O_4^{-2}]} = \frac{x \times x}{0.005} \quad ...(1)$$

Also, $$K_h = \frac{K_w}{K_2} = \frac{10^{-14}}{5.4 \times 10^{-5}}$$

$$= 1.85 \times 10^{-10} \quad ...(2)$$

From (1) and (2), we get :

$$\frac{x^2}{0.005} = 1.85 \times 10^{-10} \,;$$

$x = (1.85 \times 10^{-10} \times 0.005)^{1/2}$

Or $x = (92.5 \times 10^{-14})^{1/2} = 9.6 \times 10^{-7}$

Or $[OH^-] = \mathbf{9.6 \times 10^{-7}\,M}$ **Ans.**

EXAMPLE 260. *To a solution buffered at pH 9.0, 5 × 10^{-4} mol of $NaHCO_3$ is added. Calculate the material that would exist in each of the three forms, $H_2CO_3^-$, HCO_3^- and CO_3^{2-}. K_1 and K_2 are 4.5 × 10^{-7} and 4.7 × 10^{-11} respectively.*

SOLUTION. (*a*) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ (hydrolysis)

$$K_h = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} \quad ...(1)$$

$$K_h = \frac{K_w}{K_1} = \frac{10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8} \quad ...(2)$$

From (1) and (2),

$$\frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = 2.2 \times 10^{-8} \quad ...(3)$$

(*b*) $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ (hydrolysis)

$$K_2 = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]};$$

$$4.7 \times 10^{-11} = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \quad ...(4)$$

(*c*) $pH = 9; -\log[H^+] = 9;$

$\log[H^+] = -9; [H^+] = 10^{-9}$ M.

$$\therefore \quad [OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-9}} = 10^{-5}\text{ M}$$

(*d*) From equation (3)

$$\frac{[H_2CO_3] \times 10^{-5}}{[HCO_3^-]} = 2.2 \times 10^{-8};$$

$$\frac{[H_2CO_3]}{[HCO_3^-]} = \frac{2.2 \times 10^{-8}}{10^{-5}}$$

Or $$\frac{[H_2CO_3]}{[HCO_3^-]} = 2.2 \times 10^{-3} \quad ...(5)$$

$$[H_2CO_3] = 2.2 \times 10^{-3}[HCO_3^-] \quad ...(6)$$

(*e*) Also, from equation (4),

$$4.7 \times 10^{-11} = \frac{[CO_3^{2-}] \times 10^{-9}}{[HCO_3^-]}$$

$$\therefore \quad \frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{4.7 \times 10^{-11}}{10^{-9}} = 4.7 \times 10^{-2} \quad ...(7)$$

$$[CO_3^{2-}] = 4.7 \times 10^{-2}[HCO_3^-] \quad ...(8)$$

All the species being in the same solution, their concentration ratios are equal to their molar ratio.

But $[NaHCO_3] = 0.0005\text{ M} = 5 \times 10^{-4}$ mol.

(*a*) $n[H_2CO_3] + n[HCO_3^-] + n[CO_3^{2-}] = 5 \times 10^{-4}$ mol.

$n \times 2.2 \times 10^{-3}[HCO_3^-] + n[HCO_3^-] + n \times 4.7 \times 10^{-2}[HCO_3^-] = 5 \times 10^{-4}$ mol.

Or $0.0022\,n[HCO_3^-] + n[HCO_3^-] + 0.047\,n[HCO_3^-] = 0.0005$

$1.05\,n[HCO_3^-] = 0.0005$

hence $n[HCO_3^-] = \frac{0.0005}{1.05} = \mathbf{4.76 \times 10^{-4}\,mol}$ **Ans.**

But $[H_2CO_3] = 2.2 \times 10^{-3}[HCO_3^-]$;

$\therefore$ $[H_2CO_3] = 2.2 \times 10^{-3} \times 4.76 \times 10^{-4}$

Or $[H_2CO_3] = 1.05 \times 10^{6}$ mol **Ans.**

(*c*) $[CO_3^{2-}] = 4.7 \times 10^{-2}[HCO_3^-]$

[from equation (8)]

Hence $[CO_3^{2-}] = 4.7 \times 10^{-2} \times 4.76 \times 10^{-4}$

$= \mathbf{2.2 \times 10^{-5}\,mol}$ **Ans.**

EXAMPLE 261. *Calculate the $[H^+]$, concentrations of monovalent anion, divalent anion and trivalent anion in 0.01M polyprotic citric acid. pK_1, pK_2 and pK_3 of citric acid are 3.13, 4.76 and 6.4 respectively.*

SOLUTION. (*a*) Let citric acid is represented as H_3A.

$\therefore \quad H_3A + H_2O \rightleftharpoons H_2A^- + H_3O^+$;

Conc. $0.01 - x \qquad x \qquad x$

$$K_1 = \frac{[H_2A^-][H_3O^+]}{[H_3A]} \quad ...(1)$$

But $pK_1 = 3.13; -\log K_1 = 3.13;$

$\log K_1 = -3.13$

$= -3 - 1 + 1 - 0.13 = \bar{4}.87$.

Hence $K_1 = \text{antilog } \bar{4}.87 = 7.4 \times 10^{-4}$.

$\therefore$ From (1), we have $7.4 \times 10^{-4} = \frac{x \times x}{0.01 - x}$;

$x^2 = 7.4 \times 10^{-4}(0.01 - x)$

$x^2 + 7.4 \times 10^{-4}x - 7.4 \times 10^{-6} = 0;$

$$\left[\because \text{for } ax^2 + bx + c = 0,\; x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a}\right]$$

$$x = \frac{-7.4 \times 10^{-4} + [(7.4 \times 10^{-4})^2 - (4 \times 1 \times -7.4 \times 10^{-6})]^{1/2}}{2}$$

Or $$x = \frac{-7.4 \times 10^{-4} + (54.76 \times 10^{-8} + 29.6 \times 10^{-6})]^{1/2}}{2}$$

$$= \frac{-7.4 \times 10^{-4} + (10^{-8}(54.76 + 29.6 \times 100)]^{1/2}}{2}$$

$$x = \frac{-7.4 \times 10^{-4} + 54.9 \times 10^{-4}}{2} = 0.0024$$

$= \mathbf{[H_3O^+]}$ **Ans.**

(*b*) $H_2A^- + H_2O \rightleftharpoons HA^{2-} + H_3O^+$;

$$K_2 = \frac{[HA^{2-}][H_3O^+]}{[H_2A^-]} \quad ...(2)$$

$pK_2 = 4.76; -\log K_2 = 4.76;$

$\log K_2 = -4.76$

$$= -4 - 1 + 1 - 0.76 = \bar{5}.24$$

$$\therefore \quad K_2 = \text{antilog } \bar{5}.24 = 1.74 \times 10^{-5}$$

∴ From (2), we have,

$$K_2 = \frac{[HA^{2-}] \times x}{x};$$

$$1.74 \times 10^{-5} = \mathbf{[HA^{2-}]} \qquad \textbf{Ans.}$$

(*c*) $HA^{2-} + H_2O \rightleftharpoons A^{3-} + H_3O^+$;

$$K_3 = \frac{[A^{3-}][H_3O^+]}{[HA^{2-}]} \qquad ...(3)$$

$$pK_3 = 6.4 \,;\, -\log K_3 = 6.4 \,;\, \log K_3 = -6.4$$

$$= -6 - 1 + 1 - 0.4 = \bar{7}.6$$

$$\therefore \quad K_3 = \text{antilog } \bar{7}.6 = 3.98 \times 10^{-7}$$

∴ From (3), we have :

$$3.98 \times 10^{-7} = \frac{[A^{3-}] \times 0.0024}{1.74 \times 10^{-5}}$$

$$\therefore \quad [A^{3-}] = \frac{3.98 \times 10^{-7} \times 1.74 \times 10^{-5}}{0.0024}$$

$$= \mathbf{2.9 \times 10^{-9}\ M} \qquad \textbf{Ans.}$$

Example 262. *If 10^{-4} M H_3PO_4 is added to a one litre solution buffered at pH = 7, calculate the relative proportions of the four forms H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. K_1, K_2 and K_3 values of respective species are 7.1 × 10^{-3}, 6.3 × 10^{-8} and 4.5 × 10^{-13} respectively.*

Solution. The given solution being well buffered, *p*H value does not change on adding H_3PO_4. So, if $[H^+]$ is fixed, the ratio of the two desired concentrations from each of the ionisation constant equations will be:

(*a*) $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$;

$$K_1 = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]};\ \frac{[H_3PO_4]}{[H_2PO_4^-]} = \frac{[H^+]}{K_1}$$

$$\text{or} \quad \frac{[H_3PO_4]}{[H_2PO_4^-]} = \frac{10^{-7}}{7.1 \times 10^{-3}} = 1.4 \times 10^{-5} \qquad ...(1)$$

(*b*) $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$;

$$K_2 = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\text{or} \quad \frac{[H^+]}{K_2} = \frac{[H_2PO_4^-]}{[HPO_4^{2-}]};\ \frac{10^{-7}}{6.3 \times 10^{-8}} = \frac{[H_2PO_4^-]}{[HPO_4^{2-}]};$$

$$\frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 1.59 \qquad ...(2)$$

(*c*) $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$;

$$K_3 = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$\frac{[HPO_4^{2-}]}{[PO_4^{3-}]} = \frac{[H^+]}{K_3} = \frac{10^{-7}}{4.5 \times 10^{-13}}$$

$$= 2.2 \times 10^{5} \qquad ...(3)$$

Out of these, the ratio $\frac{[H_3PO_4]}{[H_2PO_4^-]}$ is very small but that of $\frac{[HPO_4^{2-}]}{[PO_4^{3-}]}$ is very large. Hence, practically all the material will exist as $H_2PO_4^-$ and HPO_4^{2-}. These sum of amounts of these species will, thus be practically equal to 10^{-4}M or 0.0001 M.

$$\text{Let} \quad [HPO_4^{2-}] = x \,;\, [H_2PO_4^-] = 0.0001 - x.$$

$$\text{But} \quad \frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = 1.59 \,;$$

$$\therefore \quad \frac{0.0001 - x}{x} = 1.59$$

$$\textbf{Or} \quad 1.59x + x = 0.0001 \,;\, 2.59x = 0.0001.$$

$$\text{Hence} \quad x = \frac{0.0001}{2.59} = 3.88 \times 10^{-5} \ \textit{i.e.,}$$

$$[HPO_4^{2-}] = x = \mathbf{3.86 \times 10^{-5}} \qquad \textbf{Ans.}$$

$$[H_2PO_4^-] = 0.0001 - 3.86 \times 10^{-5}$$

$$= \mathbf{6.14 \times 10^{-5}} \qquad \textbf{Ans.}$$

$$\text{Also,} \quad \frac{[H_3PO_4]}{[H_2PO_4^-]} = 1.4 \times 10^{-5} \,;$$

$$[H_3PO_4] = 1.4 \times 10^{-5}\,[H_2PO_4^-]$$

$$\text{Hence} \quad [H_3PO_4] = 1.4 \times 10^{-5} \times 6.14 \times 10^{-5}$$

$$= \mathbf{8.6 \times 10^{-10}} \qquad \textbf{Ans.}$$

Similarly, from (3),

$$[PO_4^{3-}] = \frac{[H_2PO_4^{2-}]}{2.2 \times 10^5} = \frac{3.86 \times 10^{-5}}{2.2 \times 10^5}$$

$$= \mathbf{1.75 \times 10^{-10}} \qquad \textbf{Ans.}$$

Example 263. *Calculate the equilibrium $[CO_3^{2-}]$ after equal volumes of 1.0M HCl and 1.0M Na_2CO_3 are mixed together. K_1 and K_2 are 4.5 × 10^{-7} and 4.7 × 10^{-11} respectively.*

Solution. $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

Since the solution is same as that of $\frac{0.1}{2}$ *i.e.*, 0.5 M $NaHCO_3$ and 0.5M NaCl (when volume becomes double, molarity becomes one half), HCO_3^- reacts with water in the following two ways.

(*i*) $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$;

$$K_a \text{ or } K_2 = 4.7 \times 10^{-11}$$

$$= \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]} \qquad ...(1)$$

(*ii*) $HCO_3^- \rightleftharpoons CO_2 + OH^-$;

$$K_h = \frac{[CO_2][OH^-]}{[HCO_3^-]} \qquad ...(2)$$

The magnitude of both of these constants are small. It is, therefore, supposed that the $[HCO_3^-]$ remains 0.5M within experimental error. Thus $[CO_2] \approx [CO_3^{2-}]$.

Multiplying (1) and (2) we get :

$$K_2K_h = \frac{[CO_3^{2-}][H_3O^+][CO_2][OH^-]}{[HCO_3^-]^2}$$

$$= \frac{[CO_3^{2-}][CO_2] \times K_w}{[HCO_3^-]}$$

But $$K_h = \frac{K_w}{K_1}$$

So, $$K_2 \times \frac{K_w}{K_1} = \frac{[CO_3^{2-}][CO_2] \times K_w}{[HCO_3^-]^2}$$

Or $$\frac{K_2}{K_1} = \frac{[CO_3^{2-}][CO_2]}{[HCO_3^-]^2} = \frac{[CO_3^{2-}][CO_3^{2-}]}{[HCO_3^-]^2}$$

$$[\because [CO_3^{2-}] = [CO_2]]$$

Taking square root of both sides, we get :

$$\therefore \quad \frac{[CO_3^{2-}]}{[HCO_3^-]} = \left(\frac{K_2}{K_1}\right)^{1/2};$$

$$[CO_3^{2-}] = \left(\frac{4.7 \times 10^{-11}}{4.5 \times 10^{-7}}\right)^{1/2} \times [HCO_3^{2-}]$$

$$\therefore \quad [CO_3^{2-}] = (1.04 \times 10^{-4})^{1/2} \times 0.5$$

$$= 1.01 \times 10^{-2} \times 0.5 = \mathbf{5 \times 10^{-3}} \text{ Ans.}$$

EXAMPLE 264. *0.01 mol of $AgNO_3$ is added to one litre of a solution which is 0.1M in Na_2CrO_4 and 0.005M in $NaIO_3$. Calculate the mol of precipitate formed at equilibrium and the concentration of Ag^+, IO_3^- and CrO_4^{2-}. (K_{sp} values of Ag_2CrO_4 and $AgIO_3$ are 10^{-8} and 10^{-13} respectively.)* **(Roorkee 2001)**

SOLUTION. The chemical reactions involved are :

$$\underset{0.1\ \text{mol}}{2AgNO_3 + Na_2CrO_4} \longrightarrow Ag_2CrO_4 + 2NaNO_3$$

$$\underset{0.005\ \text{mol}}{AgNO_3 + NaIO_3} \longrightarrow AgIO_3 + NaNO_3$$

Thus, the molar conc. of $AgNO_3$ that will react with

$NaIO_3$ = 0.005 mol.

∴ Precipitate of $AgIO_3$ formed = 0.005 mol

Number of moles of $AgNO_3$ left

= 0.01 – 0.005 = 0.005 mol.

The whole of $AgNO_3$ left will react completely with Na_2CrO_4.

Na_2CrO_4 reacted = 0.005/2 = 0.0025 mol.

Hence, Na_2CrO_4 left = 0.1 – 0.0025 = 0.0975 mol.

Precipitate of $AgNO_3$ formed = 0.0025 mol.

Thus, $[CrO_4^{2-}]$ = 0.0975 + CrO_4^{2-} (obtained from Ag_2CrO_4 which can be neglected)

= 0.0975 mol = 9.75×10^{-2} M.

$$Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$$

$$K_{sp}(Ag_2CrO_4) = [Ag^+]^2 [CrO_4^{2-}]$$

$$10^{-8} = [Ag^+]^2 \times (9.75 \times 10^{-2})$$

$$[Ag^+]^2 = \frac{10^{-8}}{9.75 \times 10^{-2}} = 0.1 \times 10^{-6}$$

or $$[Ag^+] = (0.1 \times 10^{-6})^{1/2} = 0.32 \times 10^{-3}\ M$$

$$= 3.2 \times 10^{-4}.$$

Total precipitate formed = 0.005 + 0.0025 = 0.0075 mol

Clearly, it is the total Ag^+ ion conc. present in the solution which is obtained from Ag_2CrO_4 and $AgIO_3$.

$$AgIO_3 \longrightarrow Ag^+ + IO_3^-$$

$$K_{sp}(AgIO_3) = [Ag^+][IO_3^-];$$

$$10^{-13} = (3.2 \times 10^{-4})[IO_3^-]$$

$$[IO_3^-] = \frac{10^{-13}}{3.2 \times 10^{-4}} = 0.3125 \times 10^{-9}$$

$$= 3.125 \times 10^{-10}\ M$$

EXAMPLE 265. *What $[H_3O^+]$ must be maintained in a saturated H_2S solution to precipitate Pb^{2+} but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01M?*

(K_{sp} H_2S = 1.1×10^{-22} and K_{sp} ZnS = 1.0×10^{-21})

(Roorkee 2000)

SOLUTION. Given that K_{sp} for ZnS = 1.0×10^{-21}

and $[Zn^{2+}]$ = 0.01 M = 10^{-2} M

But we know that

$$K_{sp}\ ZnS = [Zn^{2+}][S^{2-}] \text{ or } 10^{-21} = (10^{-2})(S^{2-})$$

or $$[S^{2-}] = 10^{-21}/10^{-2} = 10^{-19}\ M.$$

Clearly to prevent precipitation of Zn^{2+} ions, S^{2-} ion conc. must be less than 10^{-19} M.

Again $H_2S + 2H_2O \longrightarrow 2H_3O^+ + S^{2-}$

$$K_{sp}(H_2S) = [H_3O^+]^2[S^{2-}]$$

$$1.1 \times 10^{-22} = [H_3O^+]^2[S^{2-}]$$

or $$1.1 \times 10^{-22} = [H_3O^+]^2 \times 10^{-19}$$

$$\therefore \quad [H_3O^+]^2 = \frac{1.1 \times 10^{-22}}{10^{-19}} = 1.1 \times 10^{-3}$$

or $$[H_3O^+] = (1.1 \times 10^{-3})^{1/2} = 3.32 \times 10^{-2}\ M$$

Thus, the molar conc. of hydronium ion equal to 3.32×10^{-2} M must be maintained.

EXAMPLE 266. *The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 mole lit^{-1} and the pK_a of H_2SO_3 is 1.92. Estimate the pH of rain on that day.* **(IIT 2000 mains)**

SOLUTION. The chemical equation involved is

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Thus, the molar conc. of SO_2 in the molar conc. of H_2SO_3.

$$[H_2SO_3] = [SO_2] = 1.3653 \text{ mole lit}^{-1}$$

$$H_2SO_3 \rightleftharpoons 2H^+ + SO_3^{2-}$$

Let us suppose that the molar conc. of H^+ ion at equilibrium = x mol L^{-1}

Then, $[H_2SO_3] = (1.3653 - x/2)$ and

$[SO_3^{2-}] = x/2$ mol L^{-1}

Applying the law of chemical equilibrium

$$K_a = \frac{[H^+][SO_3^{2-}]}{[H_2SO_3]} = \frac{x^2 \times x/2}{1.3653 - x/2} \quad ...(i)$$

Given $pK_a = 1.92$ or $-\log K_a = 1.92$

or $\log K_a = -1.92$ or $K_a = 10^{-1.92}$

Equation (i) can be written as $\dfrac{x^3}{2 \times 1.3653} = 10^{-1.92}$

($x/2$ may be neglected compared to 1.3653)

$$\begin{aligned}
\text{or} \quad x^3 &= 2 \times 1.363 \times 10^{-1.92} \\
\text{or} \quad x^3 &= 2.7306 \times 10^{-1.92} \\
\text{Taking logs } \log x^3 &= \log (2.7306 \times 10^{-1.92}) \\
&= 0.4348 - 1.92 \\
3 \log x &= -1.4852 \\
\text{or} \quad -\log x &= \frac{1.4852}{3} = 0.485 \\
\text{or} \quad -\log [H^+] &= pH = \mathbf{0.485}
\end{aligned}$$

EXAMPLE 267. *When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_p and K_c for the reaction at 27°C (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ?* **(IIT 1999)**

SOLUTION. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$$\text{Initial moles} = \frac{3.06}{51} = 0.06$$

Moles at equilibrium,

$$\frac{0.06 \times 70}{100} = 0.042 \quad \frac{0.06 \times 30}{100} = 0.018 \quad \frac{0.06 \times 30}{100} = 0.018$$

$$\begin{aligned}
K_c &= [NH_3]\,[H_2S] = \left(\frac{0.018}{2}\right)\left(\frac{0.018}{2}\right) \\
&\qquad\qquad \because \text{Volume} = 2\text{L}] \\
&= (0.009 \times 0.009)\ \text{mole}^2\ \text{litre}^{-2} \\
&= 8.1 \times 10^{-5}\ \text{mol}^2\ \text{litre}^{-2} \\
K_p &= K_c(RT)^{\Delta n}\ ;\ \Delta n = (1 + 1) - 0 = 2 \\
\therefore \quad K_p &= 8.1 \times 10^{-5} \times (0.082 \times 300)^2 = 0.049
\end{aligned}$$

Addition of NH_4HS does not change the position of equilibrium.

EXAMPLE 268. *We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution, find the conductivity (specific conductance of this solution in terms of 10^{-7} Sm^{-} units. Given $\lambda°_{(Ag+)} = 6 \times 10^{-3}$ Sm^2/mol; $\lambda°_{(Br-)} = 8 \times 10^{-3}$ Sm^2/mol, $\lambda°_{(NO^-{}_3)} = 6 \times 10^{-3}$ Sm^2/mol.)* **(IIT-JEE, 2006)**

SOLUTION. *Reaction* $AgBr \rightleftharpoons Ag^+ + Br^-$

Solubility, mol L^- $\quad S \quad S$

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$

Solubility, mol L^- $\quad 10^{-7} \quad 10^{-7}$

$\therefore$ Solubility of $Ag^+ = S + 10^{-7}$

$$K_{sp} = [Ag^+]\,[Br^-] = (S + 10^{-7}) \times S$$

$$\text{or} \quad 12 \times 10^{-14} = S^2 + 10^{-7}S\ ;$$

$$S^2 + 10^{-7}S - 12 \times 10^{-14} = 0$$

$$\therefore S = \frac{-10^{-7} \pm [(-10^{-7})^2 - (4 \times 1 \times -12 \times 10^{-14})]^{1/2}}{2 \times 1}$$

$$\left[\because \text{for } ax^2 + bx + c = 0,\quad x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} \right.$$

$$\begin{aligned}
&= \frac{-10^{-7} \pm [10^{-14} + 48 \times 10^{-14}]^{1/2}}{2 \times 1} \\
&= \frac{-10^{-7} \pm (49 \times 10^{-14})^{1/2}]}{2} \\
&= \frac{-10^{-7} + 7 \times 10^{-7}}{2} = 3 \times 10^{-7}
\end{aligned}$$

$$\begin{aligned}
\therefore \quad [Br^-] &= S = 3 \times 10^{-7} \times 10^3 = 3 \times 10^{-4}\ \text{m}^3; \\
[NO_3^-] &= 10^{-7} \times 10^3 = 10^{-4}\ \text{m}^3\ ; \\
[Ag^+] &= S + 10^{-7} = 3 \times 10^{-7} + 10^{-7} \\
&= 10^{-7}\,(3 + 1) = 4 \times 10^{-7} \\
&= 4 \times 10^{-7} \times 10^3 = 4 \times 10^{-4}\ \text{m}^3
\end{aligned}$$

$$\begin{aligned}
\text{But} \quad {}^\wedge m &= \frac{K \times 1000}{C}; \\
K &= \frac{{}^\wedge m \times C}{1000} = {}^\wedge mC \times 10^{-3} \\
\therefore \quad K_{(Ag+)} &= 6 \times 10^{-3} \times 4 \times 10^{-4} = 24 \times 10^{-7} \\
K_{(Br-)} &= 8 \times 10^{-3} \times 3 \times 10^{-4} = 24 \times 10^{-7} \\
K_{(NO_3^-)} &= 7 \times 10^{-3} \times 10^{-4} = 7 \times 10^{-7} \\
\therefore \quad K_{(total)} &= K_{Ag+} + K_{Br-} + K_{(NO_3^-)} \\
&= 24 \times 10^{-7} + 24 \times 10^{-7} + 7 \times 10^{-7} \\
&= 10^{-7}\,[24 + 24 + 7] = 55 \times 10^{-7}\ Sm^- \\
&= \mathbf{55\,Sm^-}(\text{in terms of } 10^{-7} Sm^-)\ \textbf{Ans.}
\end{aligned}$$

24.13 AIEEE PATTERN EXAMPLES

EXAMPLE 269. *2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $^2/_{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) is*

(*a*) 3.7×10^{-13} M (*b*) 3.2×10^{-7} M
(*c*) 3.2×10^{-2} M (*d*) 2.7×10^{-2} M

(IIT-JEE, 2008)

SOLUTION. Reaction : $BOH + HCl \rightarrow BCl + H_2O$

Conc. $\quad$ C

$B^+ + H_2O \rightleftharpoons BOH + H^+$

Conc. $\quad C\,(1 - h) \quad ch \quad ch$

We know that : $N_{acid} \times V_{acid} = N_{base} \times V_{base}$

$$2/15 \times V = 2.5 \times 2/5$$

$$\therefore \quad V = \frac{2.5 \times 2 \times 15}{2 \times 5} = 7.5\ \text{mL (acid used)}$$

In the resulting solution, concentration of salt [BCl]

$$= \frac{2/5 \times 2.5}{10} = 0.1$$

But $$\frac{[BOH][H^+]}{[B^+]} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{1-h} = Ch^2$$

[∵ h is very small as compared to 1]

$$Ch^2 = \frac{K_w}{K_b}$$

or $$h = \left(\frac{K_w}{K_b \times C}\right)^{1/2}$$

$$= \left(\frac{10^{-14}}{10^{-12} \times 0.1}\right)^{1/2} = \left(\frac{1}{10}\right)^{1/2}$$

But $$(H^+) = Ch = 0.1\ C\left(\frac{1}{10}\right)^{1/2}$$

$$= 0.1 \times 0.316 \simeq 3.2 \times 10^{-2}\ \text{M}$$

So, the correct answer is (*c*).

EXAMPLE 270. *The dissociation constant of an acid, the pH of whose molar solution in 5, is :*

(*a*) 10^{-7} (*b*) 10^{-8}

(*c*) 10^{-9} (*d*) 10^{-10}

SOLUTION. $pH = 5\ ;\ -\log [H^+] = 5\ ;$

$\log [H^+] = -5\ ;\ [H^+] = 10^{-5}$

$HA \rightleftharpoons H^+ + A^-\ ;\ [HA] = 1M$

$$\therefore \quad K_a = \frac{[H^+][A^-]}{[HA]};$$

$$K_a = \frac{[H^+][H^+]}{[HA]} \qquad [\because [H^+] = [A^-]]$$

$$\therefore \quad K_a = \frac{10^{-5} \times 10^{-5}}{1} = 10^{-10}.$$

So, the correct answer is (*d*).

EXAMPLE 271. *The pH of 10^{-2} M $Ca(OH)_2$ is*

(*a*) 12 (*b*) 12.3

(*c*) 11.3 (*d*) 2 **(Orissa JEE, 2011)**

SOLUTION. $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

10^{-2} M $\qquad 2 \times 10^{-2}$ M

$\therefore$ $(OH^-) = 2 \times 10^{-2}$. But $pOH = -\log [OH^-]$

$\therefore$ $pOH = -\log (2 \times 10^{-2}) = -[\log 2 + \log 10^{-2}]$

$= -[0.3010 - 2] = 1.6990.$

$\therefore$ $pH = 14 - pOH;$

$pH = 14 - 1.6990 = 12.3010.$

So, the correct answer is (*b*).

EXAMPLE 272. *At a certain temperature, the value of K_w is 9.55×10^{-14}. So, the pH value of water will be :*

(*a*) 7 (*b*) 7.9

(*c*) 6.51 (*d*) 8.51

SOLUTION. In $H_2O \rightleftharpoons H^+ + OH^-$, $[H^+] = [OH^-]$

$K_w = 9.55 \times 10^{-14}.$

But $K_w = [H^+][OH^-] = [H^+][H^+] = [H^+]^2$

$\therefore$ $9.55 \times 10^{-14} = [H^+]^2$ **Or** $[H^+] = (9.55 \times 10^{-14})^{1/2}$

$$\therefore \quad pH = -\log [H^+] = -\log (9.55 \times 10^{-14})^{1/2}$$

$$= -\frac{1}{2}[\log 9.55 + \log 10^{-14}]$$

$$= -\frac{1}{2}[0.98 - 14] = 6.51.$$

So, the correct answer is (*c*).

EXAMPLE 273. *The pH of a solution that contains 6.02×10^{11} H^+ ions per mL solution is :*

(*a*) 7 (*b*) 8

(*c*) 9 (*d*) 10

SOLUTION. 1 mL solution contains H^+ ions = 6.02×10^{11}

$\therefore$ 1000 mL (= 1L) solution contains H^+ ions

$= 6.02 \times 10^{11} \times 1000$

$= 6.02 \times 10^{11} \times 1000 = 6.02 \times 10^{14}$

$$\therefore \text{ no. of mol of } H^+ \text{ ions} = \frac{6.02 \times 10^{14}}{6.02 \times 10^{23}}$$

[∵ 1 mol = 6.02×10^{23} particles]

$= 10^{14-23} = 10^{-9}$

Or $[H^+] = 10^{-9}\ ;\ pH = -\log [H^+]$

$= -\log 10^{-9} = (-)(-9) \log 10$

Or **pH** = 9

So, the correct answer is (*c*).

EXAMPLE 274. *For an aqueous solution to be neutral, it must have :*

(*a*) $[H^+] < OH^-$ (*b*) $[H^+] = (Kw)^{1/2}$

(*c*) $pH = 7$ (*d*) $[H^+] = [OH^-]$

SOLUTION. For an aqueous solution to be neutral, $[H^+]$ must always be equal to $[OH^-]$. Hence, (*d*) is correct.

EXAMPLE 275. *Assume that the dissociation constant for ammonia and acetic acid are same. The pOH of an ammonia solution, when that of acetic acid of equal strength is 3.27, would be :*

(*a*) 3.27 (*b*) 10.8

(*c*) 7 (*d*) 1.6635

SOLUTION. pK_a of acetic ccid = 3.2 ; pK_b of ammonia = ?

We know, $pK_a + pK_b = 14$. Substituting the values, we get :

$3.2 + pK_b = 14$

$\therefore$ $pK_b = 14 - 3.2 = 10.8.$

Hence, correct answer is (*b*).

EXAMPLE 276. *The values of K_{p_1} and K_{p_2} for the reactions: $X \rightleftharpoons Y + Z$...... (i) and $A \rightleftharpoons 2B$ .....(ii)*

are in the ratio 9 : 1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (i) and (ii) are in the ratio :

(*a*) 36 : 1 (*b*) 1 : 1

(*c*) 3 : 1 (*d*) 1 : 9

(CBSE–PMT, 2008 Prelims)

Solution. Given : $X \rightleftharpoons Y + Z$ ...(*i*)

Initial mol $1 \quad 0 \quad 0$

mol at equilibrium $1-\alpha \quad \alpha \quad \alpha$

$\therefore$ Total no. of mol at equilibrium

$$= 1-\alpha+\alpha+\alpha = 1+\alpha$$

Also : $A \rightleftharpoons 2B$ ...(*ii*)

Initial mol $1 \quad 0$

Mol at equilibrium $1-\alpha \quad 2\alpha$

$\therefore$ Total no. of mol at equilibrium $= 1-\alpha+2\alpha = 1+\alpha$

Hence
$$k_{p_1} = \frac{p_y \times p_z}{p_x} = \frac{\frac{\alpha}{1+\alpha}\times p_1 \times \frac{\alpha}{1+\alpha}\times p_1}{\frac{1-\alpha}{1+\alpha}\times p_1}$$

$$k_{p_2} = \frac{(P_B)^2}{P_A} = \frac{\left(\frac{2\alpha}{1+\alpha}\times P_2\right)^2}{\frac{1-\alpha}{1+\alpha}\times P_2};$$

$$\frac{K_{p_1}}{K_{p_2}} = \frac{P_1}{4P_2}; \frac{9}{1} = \frac{P_1}{4P_2}$$

i.e., $\frac{P_1}{P_2} = \frac{36}{1}$ *i.e.,* 36 : 1. So, the correct answer is (*a*).

Example 277. *An acidic indicator HIn ionises as,* $HIn \rightleftharpoons H^+ + In^-$. *The maximum pH value at which its solution will have distinct colour characteristic of HIn will be :*

(*a*) pK_{In+1} (*b*) pK_{In-1}

(*c*) 6 (*d*) 5

Solution. For the colour characteristic of acidic indicator, HIn.

$$pH = pK_{In} - \log\frac{[HIn]}{[In^-]} = pK_{In+1}$$

$$[\because HIn \rightleftharpoons H^+ + In^-]$$

So, the correct answer is (*a*).

Example 278. *At 298K, an aqueous solution has thrice as many* OH^- *ions as pure water. Its pOH will be :*

(*a*) 7 (*b*) 6.5229

(*c*) 7.312 (*d*) 4.921

Solution. $[H^+]$ of water $= 10^{-7}$ $\therefore$ $[OH^-] = 3\times10^{-7}$

Taking logs of both sides, we have :

$$\log[OH^-] = \log 3\times10^{-7}$$

Or $$-\log[OH^-] = -\log 3\times10^{-7}$$

$$\therefore \quad pOH = -[\log 3 + \log 10^{-7}]$$
$$= -[0.4771 - 7\log 10]$$
$$= -[0.4771 - (7\times1)]$$
$$= 7 - 0.4771 = 6.5229$$

$\therefore$ The correct answer is (***b***).

Example 279. *The hydrolysis constant* (K_h) *for zinc chloride will be :*

(*a*) $K_h = \frac{K_a}{K_b}$ (*b*) $\frac{K_a}{K_w^2}$

(*c*) $\frac{K_w^2}{K_b}$ (*d*) $\frac{K_b}{K_w^2}$

Where K_b is the effective dissociation constant of the base, $Zn(OH)_2$.

Solution. $ZnCl_2 \rightleftharpoons Zn^{2+} + 2Cl^-$

$Zn^{2+} + 2H_2O \rightleftharpoons Zn(OH)_2 + 2H^+$ (hydrolysis)

$$\therefore \quad K_h = \frac{[Zn(OH)_2][H^+]^2}{[Zn^{2+}]} \quad ...(1)$$

$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$ (ionisation)

Base

$$\therefore \quad K_b = \frac{[Zn^{2+}][OH^-]^2}{[Zn(OH)_2]} \quad ...(2)$$

Also, $K_w = [H^+][OH^-]$

From equations (1) and (2), we have

$$K_h \times K_b = \frac{[Zn(OH)_2][H^+]^2 \times [Zn^{2+}][OH^-]^2}{[Zn^{2+}][Zn(OH)_2]}$$
$$= [H^+]^2[OH^-]^2 = K_w^2$$

$$\therefore \quad K_h = \frac{K_w^2}{K_b}$$

Hence, the correct answer is (*c*).

Example 280. *Solubility of AgCl in water, 0.01M* $BaCl_2$, *0.01M KCl and 0.05M* $AgNO_3$ *are* S_1, S_2, S_3, *and* S_4 *respectively. Then :*

(*a*) $S_4 > S_3 > S_2 > S_1$ (*b*) $S_3 > S_4 > S_1 > S_2$

(*c*) $S_2 > S_3 > S_4 > S_1$ (*d*) $S_1 > S_3 > S_2 > S_4$

Solution. $AgCl \rightleftharpoons Ag^+ + Cl^-$ (in water)

$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$ (in $BaCl_2$)

$0.01 \quad 0.01 \quad 2\times0.01 = 0.02$

$KCl \rightleftharpoons K^+ + Cl^-$ (in KCl)

$0.01 \quad 0.01 \quad 0.01$

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$ (in $AgNO_3$)

$0.05 \quad 0.05 \quad 0.05$

Common ion effect suppresses the degree of ionisation *i.e.,* solubility. This effect is maximum in $AgNO_3$. So, AgCl will be least soluble in $AgNO_3$ and maximum soluble is water. Considering KCl and $BaCl_2$ also, the order of solubility will be, $\longrightarrow S_1 > S_3 > S_2 > S_4$. So, the correct answer is (***d***).

Example 281. 10^{-3} *mol of KOH was added to 10 litre of water. The pH of the solution will change by :*

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 4

Solution. In the beginning, pH for water = 7

$$[OH^-] = 10^{-3}\times\frac{1}{10} = 10^{-4}.$$

But $[H^+][OH^-] = K_w = 10^{-14}$

$\therefore$ $[H^+]\times10^{-4} = 10^{-14}$

$$\text{Or} \qquad [H^+] = \frac{10^{-14}}{10^{-4}} = 10^{-14+4} = 10^{-10}$$

$$\therefore \qquad pH = -\log 10^{-10}$$

$$\text{or} \quad -(-10)\log 10 = -(-10)\times 1 = +10$$

$\therefore$ pH change $= 10 - 7 = 3$. So, true answer is **(*c*)**.

EXAMPLE 282. *A solution of benzonic acid was titrated with NaOH solution. When half of the solution was neutralised, the pH of the solution was found to be 4.2. The dissociation constant of the acid is :*

(*a*) 6.31×10^{-4} (*b*) 1.585×10^{-4}
(*c*) 6.31×10^{-5} (*d*) 7.23×10^{-6}

SOLUTION. Benzoic acid reacts with NaOH as follows :

$$C_6H_5COOH + NaOH \rightleftharpoons C_6H_5COONa + H_2O.$$

Conc. after neutralisation 0.5 (weak acid) 0.5 Salt

The above solution is a buffer solution of weak acid and its salt. So, we have :

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$4.2 = pK_a + 0 \ \text{Or}\ pK_a = -4.2$$

$$\text{or} \qquad -\log K_a = 4.2. \text{ Thus } \log K_a = -4.2$$

$$\therefore \qquad K_a = \text{antilog of } -4.2 = -4 - 1 + 1 - 0.2$$

$$= \bar{5}.8 = 6.31 \times 10^{-5}.$$

Hence the correct answer is **(*c*)**.

EXAMPLE 283. *The pH of a solution having $[H_3O^+]$ equal to 4×10^{-2} g ion L^- is :*

(*a*) -1 (*b*) 2.7
(*c*) 1.398 (*d*) None of these

SOLUTION. $[H_3O^+] = 4 \times 10^{-2}$;

$$pH = -\log [H_3O^+] = -(\log 4 \times 10^{-2})$$

$$\text{Or} \qquad pH = -(\log 4 + \log 10^{-2})$$

$$= -(0.602 - 2) = \mathbf{1.398} \qquad \textbf{Ans.}$$

So, the correct answer is (*c*).

EXAMPLE 284. *H_2S is passed into one dm^3 of a solution containing 0.1 mol of Zn^{2+} and 0.01 mol of Cu^{2+} till the sulphide ion concentration reaches 8.1×10^{-19} moles. Which of the following statement is true?*

(*a*) *Only ZnS precipitates*
(*b*) *both CuS and ZnS precipitate*
(*c*) *Only CuS precipitates*
(*d*) *No precipitation takes place*

[K_{sp} ZnS = 3×10^{-22}; CuS = 8×10^{-36}]

(Karnataka CET, 2011)

SOLUTION. A precipitate is formed when ionic product becomes greater than the solubility product. 1 dm^3 (= 1L) solution contains, 0.1 mol Zn^{2+}, 0.01 mol Cu^{2+} and 8.1×10^{-19} mol of S^{2-} ions. Thus

(*i*) **For ZnS,** ionic product = $(Zn^{2+})\,[S^{2-}] = 0.1 \times 8.1 \times 10^{-19} = 8.1 \times 10^{-20}$ K_{sp} of Zn S = 3×10^{-22}. Since ionic product > K_{sp}, ZnS will be precipitated.

(*ii*) For CuS, ionic product = $[Cu^{2+}]\,[S^{2-}] = 0.01 \times 8.1 \times 10^{-19} = 8.1 \times 10^{-21}$ K_{sp} of CuS = 8×10^{-36}. Since ionic product > K_{sp}, CuS will be precipitated. So, the correct answer is (*b*).

EXAMPLE 285. *The solubility product (K_{sp}) of the following compounds are given at 25° C.*

The most soluble and least soluble compounds are:

Compounds	K_{sp}
AgCl	1.1×10^{-10}
AgI	1.0×10^{-16}
$PbCrO_4$	4.0×10^{-14}
Ag_2CO_3	8.0×10^{-12}

(*a*) *AgCl and $PbCrO_4$* (*b*) *Ag I and Ag_2CO_3*
(*c*) *AgCl and Ag_2CO_3* (*d*) *Ag_2CO_3 and AgI*
(*e*) *Ag_2CO_3 and $PbCrO_4$* **(Kerala, PET, 2011)**

SOLUTION. (*i*) Consider solubility equilibrium of AgCl.

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

Solubility at equi. S mol S mol S mol

$$\therefore \qquad K_{sp} = [Ag^+][Cl^-];\ 1.1 \times 10^{-10} = S \times S = S^2.$$

$$\text{So,} \qquad S = (1.1 \times 10^{-10})^{1/2} = \mathbf{1.0 \times 10^{-5}}$$

(*ii*) Consider solubility equilibrium of Ag I

$$AgI \rightleftharpoons Ag^+ + I^-$$

Solubility at equi. S mol S mol S mol

$$\therefore K_{sp} = [Ag^+]\,[I^-];$$

$$1.0 \times 10^{-16} = S \times S = S^2;$$

$$S = (1.0 \times 10^{-16})^{1/2} = \mathbf{1.0 \times 10^{-8}}$$

(*iii*) Consider solubility equilibrium of $PbCrO_4$.

$$Pb\,CrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{2-}$$

Solubility at equi. S mol S mol S mol

$$\therefore \qquad K_{sp} = [Pb^{2+}]\,[CrO_4^{2-}] = S \times S = S^2;$$

$$S = (4.0 \times 10^{-14})^{1/2} = \mathbf{2.0 \times 10^{-7}}$$

(*iv*) Consider solubility equilibrium of Ag_2CO_3.

$$Ag_2\,CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$$

Solubility at eqm. S mol 2 S mol S mol

$$\therefore \qquad K_{sp} = [Ag^+]^2\,[CO_3^{2-}] = (2\,S)^2 \times S = 4\,S^3;$$

$$S = \left(\frac{8.0 \times 10^{-12}}{4}\right)^{1/3}$$

$$= (2 \times 10^{-12})^{1/2} = \mathbf{1.26 \times 10^{-4}}$$

From above (*i*), (*ii*), (*iii*) and (*iv*) values, it is clear that Ag_2CO_3 is most soluble and Ag I is least soluble. So, the correct answer is (*d*).

EXAMPLE 286. *Let the solubility of an aqueous solution of $Mg(OH)_2$ be x, then its K_{sp} is :*

(*a*) $9x$ (*b*) $27x^4$
(*c*) $4x^3$ (*d*) $108x^5$

(AIEEE, 2003)

Solution. $Mg(OH)_2$ ionises as :

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

Solubility $\qquad x \qquad\qquad x \qquad 2x$

But $\qquad K_{sp} = [Mg^{2+}][OH^-]^2.$

Substituting the values, we get :

$$K_{sp} = x \times (2x)^2 = 4x^3$$

So, the correct answer is, (*c*).

Example 287. *The value of equilibrium constant of the reaction, HI(g)* $\rightleftharpoons \frac{1}{2}$ *$H_2(g)$ +* $\frac{1}{2}$ *I_2 (g) is 8.0. The equilibrium constant of the reaction*

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ will be

(*a*) *16* (*b*) *1/8*

(*c*) *1/16* (*d*) *1/64*

(CBSE–PMT, 2008 Prelims)

Solution. For $HI(g) \rightleftharpoons \frac{1}{2} H_2(g) + \frac{1}{2} I_2(g)$

$$K = \frac{(H_2)^{1/2}[I_2]^{1/2}}{[HI]} = 8$$

For $H_2(g) + I_2(g) \rightleftharpoons 2HI$,

$$K' = \frac{[HI]^2}{[H_2][I_2]} = \left(\frac{1}{8}\right)^2 \text{ or } K' = \frac{1}{64}.$$

So, the correct answer is (*d*).

Example 288. *The pH of 10^{-10} molar solution of HCl solution at 25°C is approximately :*

(*a*) *6* (*b*) *5*

(*c*) *11* (*d*) *7*

Solution. $\qquad HCl \rightleftharpoons H^+ + Cl^-; [H^+] = 10^{-10}$

For such solutions in which *p*H > 7, the concentration of H^+ ions of water can not be neglected. Thus :

Total H^+ ion concentration

$$\begin{aligned} &= 10^{-10} \text{ (of HCl)} + 10^{-7} \text{ (of } H_2O) \\ &= 10^{-10}(1 + 10^3) = 10^{-10} + 1001 \\ \therefore \quad pH &= -\log[H^+] = -\log(10^{-10} + 1001) \\ &= (-)[\log 10^{-10} + \log 1001] \\ &= (-)[-10 \log 10 + 3] \\ &= -[-10 \times 1 + 3] = 10 - 3 = 7 \end{aligned}$$

So, the correct answer is, **(*d*)**.

Example 289. *200 mL water is added to 500 mL of 0.2 M solution. What is the molarity of this diluted solution?*

(*a*) *0.501 M* (*b*) *0.2897 M*

(*c*) *0.4005 M* (*d*) *0.1428 M*

(Kerala PET, 2010)

Solution. No. of millimoles = 500 × 0.2 = 100. So, molarity of diluted solution = 100/700 = 0.1428 M. So, correct answer is (*d*).

Example 290. *If a mol L^- is the solubility of $KAl(SO_4)_2$, then K_{sp} is equal to*

(*a*) a^4 (*b*) $2a^4$

(*c*) $3a^4$ (*d*) $4a^4$

Solution. $KAl(SO_4)_2$ ionises as :

$$KAl(SO_4)_2 \rightleftharpoons K^+ + Al^{3+} + 2SO_4^{2-}$$

Solubility $\qquad a \qquad a \qquad 2a$

$$\begin{aligned} \therefore \quad K_{sp} &= [K^+][Al^{3+}][SO_4^{2-}]^2 \\ &= a \times a \times (2a)^2 = a \times a \times 4a^2 = 4a^4. \end{aligned}$$

So, the correct answer is, (*d*).

Example 291. *The pH of a solution is 6. If H^+ ion concentration is reduced by 100, the resulting solution will be :*

(*a*) *more acidic* (*b*) *less acidic*

(*c*) *neutral* (*d*) *can not say*

Solution. $\qquad pH = 6 ; \therefore pH = -\log[H^+],$

Or $\qquad [H^+] = 10^{-6}$

On, diluting 100 times,

$$\begin{aligned} [H^+] &= \frac{10^{-6}}{10^2} = 10^{-8} \\ \therefore \quad pH &= -\log[H^+] = -\log 10^{-8} \\ &= -[-8 \log 10] \\ &= -[-8 \times 1] = 8 \end{aligned}$$

The solution being acidic, *p*H value should be less than 7 but it is more than 7 (= 8).

So, answer is less acidic and correct answer is (*b*).

Example 292. *The % age ionisation of 0.2 M CH_3COOH will be :*

(*a*) *1* (*b*) *0.8*

(*c*) *0.95* (*d*) *6.7*

($K_a = 1.8 \times 10^{-5}$)

Solution. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (ionisation)

Conc. (mol L⁻) $\qquad 0.2$

Conc. at equilibrium $\qquad 0.2 - x \qquad x \qquad x$

$$\therefore \quad K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x \times x}{0.2 - x}$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.2 - x} = \frac{x^2}{0.2}$$

$$\therefore \quad x^2 = 0.2 \times 1.8 \times 10^{-5}; x = (3.6 \times 10^{-6})^{1/2}$$

Or $\qquad x = 1.9 \times 10^{-3} = [H^+]$

Let fraction of CH_3COOH (0.2 M) ionised = *y*

$$\therefore \quad 0.2y = 1.9 \times 10^{-3};$$

$$y = \frac{1.9 \times 10^{-3}}{0.2} = 9.5 \times 10^{-3}$$

∴ % age ionisation of $CH_3COOH = 9.5 \times 10^{-3} \times 100$ = 0.95%

So, the correct answer is (*c*).

Example 293. *1.96 g of H_2SO_4 is present in 200 mL of the solution. The pH value of this solution will be :*

(*a*) *1.7* (*b*) *10*

(*c*) *0.699* (*d*) *14*

Solution. wt. of H_2SO_4 = 1.96 g ;

g. mol. wt. of $\quad H_2SO_4 = (2 \times 1) + 32 + (4 \times 16) = 98$ g

Volume of solution in mL = 200 mL.

$$\text{But : Molarity of } H_2SO_4 = \frac{\text{wt. of } H_2SO_4}{\text{g. mol. wt. of } H_2SO_4} \times \frac{1000}{\text{Volume of solution in mL}}$$

$$= \frac{1.96}{98} \times \frac{1000}{200} = 0.1 \text{ M}$$

Also, $H_2SO_4 \rightleftharpoons 2H^+ \text{ (2 mol)} + SO_4^{2-}$

$\therefore$ $[H^+] = 2 \times 0.1 \text{ M} = 0.2 \text{ M}$

$\therefore$ $pH = -\log[H^+] = -\log 0.2$

$= -[-0.699] = 0.699$

So, the correct answer is (*c*).

EXAMPLE 294. *The pH of a solution obtained by mixing equal volumes of N/10 NaOH and N/20 HCl is:*

(*a*) *13.4* (*b*) *12.4*

(*c*) *7.6* (*d*) *1.6*

(AMU, med. 2010)

SOLUTION. Let V = volume of both acid and base; total volume = V + V = 2V, N_1V_1(Base) = N_2V_2 (acid); 1/10 × V –1/20 V = N_R × 2V; N_R = 0.025

$\therefore$ $[H^+]$ = 0.025. Hence pH = –log [0.025] = **1.6.** So, correct answer is (*d*).

EXAMPLE 295. *The pH value of* 10^2*M KOH is :*

(*a*) *14* (*b*) *15*

(*c*) *2* (*d*) *None of these.*

Explain also.

SOLUTION. $KOH \rightleftharpoons K^+ + OH^-$

Conc. at start 10^2M 0 0

Conc. after ionisation 0 10^2M 10^2M

$\therefore$ $[OH^-] = 10^2\text{M}$;

$$\text{But } [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^2} = 10^{-16}$$

$\therefore$ $pH = -\log [H^+] = -\log 10^{-16}$

$= -(-16) \log 10$

$= 16 \times 1 = 16$

But *p*H value can not be 16 (*i.e.,* more than 14). So, the correct answer is (*d*). The reason is same as shown in above example. So, *p*H of 10^{2} M KOH can not be calculated. It can, thus, be concluded that *p*H of 10^2 M KOH lies near to 14.

EXAMPLE 296. *The hydrogen ion concentration of a solution having a pH value of 4.32 is*

(*a*) *4.79 × 10*$^{-5}$ (*b*) *3.8 × 10*^{2}

(*c*) *2 × 10*$^{-6}$ (*d*) *11 × 10*$^{-9}$

SOLUTION. $pH = -\log [H^+] ; \log [H^+] = -pH = -4.32$

$= -4 - 1 + 1 - 0.32 = \bar{5}.68$.

$\therefore$ $[H^+] = \text{antilog } \bar{5}.68 = 4.79 \times 10^{-5}$.

So, the correct answer is (*a*).

EXAMPLE 297. *Solution of 0.8 M NH*$_4$*Cl and 0.1M Mg*$^{2+}$ *ions when mixed in equal volumes, just gave precipitate. The concentration of NH*$_3$ *in solution will be :*

(*a*) *0.74* (*b*) *0.37*

(*c*) *1.11* (*d*) *2.0*

$(K_b \text{ (NH}_4\text{OH)} = 1.8 \times 10^{-5}$;

$K_{sp} = [Mg(OH)_2] = 1.4 \times 10^{-11})$.

SOLUTION. Let V = volume of each solution of NH_4Cl and Mg^{2+}.

Total volume = $V + V = 2V$

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

$$\text{Conc. at start } \left(\frac{N_1V_1}{\text{total vol}}\right) = \frac{0.1 \times V}{2V} = 0.05$$

$\therefore$ $K_{sp} = [Mg^{2+}] [OH^-]^2$;

$1.4 \times 10^{-11} = 0.05 \times [OH^-]^2$

$$\therefore \quad [OH^-] = \left(\frac{1.4 \times 10^{-11}}{0.05}\right)^{1/2} = (2.8 \times 10^{-10})^{1/2}$$

$= 1.67 \times 10^{-5}$ M.

It means when $[OH^-]$ is 1.67×10^{-5} M, $Mg(OH)_2$ will form precipitate on the addition of NH_4Cl and NH_3. For such a buffer solution of NH_4Cl and NH_3,

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} ;$$

$$-\log [OH^-] = -\log K_b + \log \frac{[NH_4Cl]}{[NH_3]}$$

Or $-\log (1.67 \times 10^{-5}) = -\log 1.8 \times 10^{-5} + \log [NH_4Cl] - \log [NH_3]$ ...(1)

$$[NH_4Cl] = \frac{N_1V_1}{\text{Total volume}} = \frac{0.8 \times V}{2V} = 0.4 \text{ M}$$

$$[NH_3] = \frac{N_2V_2}{\text{Total volume}} = \frac{xV}{2V} = 0.5x$$

[$\because x = [NH_3]$ suppose]

Substituting these values in equation (1), we get :

$-\log (1.67 \times 10^{-5}) = -\log 1.8 \times 10^{-5} + \log 0.4 - \log 0.5x$

$-(\log 1.67 + \log 10^{-5}) = -(\log 1.8 + \log 10^{-5} + \log 10^{-5}$

$- 0.398 - \log 0.5x)$

$-(0.223 - 5) = -(0.255 - 5) - 0.398 - \log 0.5x$

$\therefore$ $\log 0.5x = 5 - 0.255 - 0.398 + 0.223 - 5 = -0.43$

$= -0.43 = -1 + 1 - 0.43 = \bar{1}.57$

$\therefore$ $0.5x = \text{antilog } \bar{1}.57 = 3.7 \times 10^{-1}$

Or $[NH_3] = 0.5x = 3.7 \times 10^{-1} = 0.37\text{M}$.

So, the correct answer is **(*b*)**.

EXAMPLE 298. *The value of pH at which the 1.2 × 10*$^{-3}$ *M solution of an indicator having K*$_b$ *value 10*$^{-10}$ *will change colour is :*

(*a*) *2* (*b*) *3*

(*c*) *4* (*d*) *5*

SOLUTION. An indicator changes colour when its conjugate acid and base concentrations are equal. Since K_b is given, indicator is basic in nature. Reactions is :

$$InOH \rightleftharpoons In^+ + OH^-$$

$$\therefore \quad K_b = \frac{[In^+][OH^-]}{[InOH]};\ K_b = [OH^-]$$

$$[\because [In^+] = [InOH] = 1.2 \times 10^{-3}]$$

$$\text{But} \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-10}} = \log 10^{-4}$$

$$\therefore \quad pH = -\log [H^+] = -\log 10^{-4}$$

$$= -(-4 \log 10) = 4 \times 1 = 4$$

So, the correct answer is (*c*).

EXAMPLE 299. *A buffer solution contains 0.1 mol of sodium acetate dissolved in 1000 cm^3 of 0.1 M acetic acid. To the above buffer solution, 0.1 mol of sodium acetate is further added and dissolved. The pH of the resulting buffer is:*

(*a*) pK_a (*b*) $pK_a + 2$

(*c*) $pK_a - \log 2$ (*d*) $pK_a + \log 2$

(Karnataka CET, 2011)

SOLUTION. Moles of acetic acid (CH_3COOH) added = 0.1 M in 1L (= 1000 cm^3). Total no. of mol of sodium acetate, CH_3COONa = 0.1 + 0.1 = 0.2

$$\therefore \quad pH = pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

$$= pK_a + \log \frac{0.2}{0.1}$$

$$pH = pK_a + \log 2.$$

So, the correct answer is (*d*)

EXAMPLE 300. *The maximum pH value that could be used so that at least 90% of total Fe(III) in a dilute solution exists as Fe^{3+} is :*

(*a*) 4 (*b*) 6

(*c*) 7 (*d*) 1.23

[K_a for acid ionisation of Fe^{3+} to $[Fe(OH)]^{2+}$ and H_3O^+ is 6.5×10^{-3}]

SOLUTION. Reaction

	$Fe^{3+} + 2H_2O$	$\rightleftharpoons$ $Fe(OH)^{2+}$	+ H_3O^+
Conc. is mol L^-	$\frac{90}{100} = 0.90$	100 – 90 = 10%	x
		$= \frac{10}{100} = 0.1$	

$$\therefore \quad K_a = \frac{[Fe(OH)^{2+}][H_3O^+]}{[Fe^{3+}]};$$

$$6.5 \times 10^{-3} = \frac{0.1 \times x}{0.9}$$

$$\therefore \quad x = \frac{6.5 \times 10^{-3} \times 0.9}{0.1}$$

$$= 0.0585;\ [H_3O^+] = [H^+] = 0.0585$$

$$\therefore \quad pH = -\log [H^+] = -\log 0.585$$

$$= -(-1.23) = 1.23.$$

So, the correct answer is (*d*).

EXAMPLE 301. *The composition [salt] and [acid] of an acid buffer solution of total molarity 0.29 having pH 4.5 is : ($K_a = 1.8 \times 10^{-5}$)*

(*a*) 0.1, 0.19 (*b*) 0.2, 0.09

(*c*) 3, 2 (*d*) None of these

SOLUTION. Let x = [salt] ; [acid] = 0.29 – x.

$$\text{For an acid buffer, } pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$4.5 = -\log K_a + \log [\text{salt}] - \log [\text{acid}]$$

$$4.5 = -\log (1.8 \times 10^{-5}) + \log x - \log (0.29 - x)$$

$$= -[\log 1.8 + \log 10^{-5}] + \log x - \log (0.29 - x)$$

$$4.5 = -(0.255 - 5) + \log x - \log (0.29 - x).$$

$$4.5 + 0.255 - 5 = \log \frac{x}{0.29 - x};$$

$$-0.245 = \log \frac{x}{0.29 - x};$$

$$-1 + 1 - 0.245 = \log \frac{x}{0.29 - x};\ \bar{1}.755 = \log \frac{x}{0.29 - x}$$

Taking antilogs we have :

$$\text{Antilog } \bar{1}.755 = \frac{x}{0.29 - x};$$

$$0.57 = \frac{x}{0.29 - x};\ 0.57\,(0.29 - x) = x$$

$$0.16 - 0.57x = x;\ x + 0.57x = 0.16;\ 1.57x = 0.16$$

$$\therefore \quad x = \frac{0.16}{1.57} \simeq 0.1$$

$$\text{Hence} \quad [\text{salt}] = x = 0.1;$$

$$[\text{acid}] = 0.29 - x = 0.29 - 0.1 = 0.19$$

So, the correct answer is (*a*).

EXAMPLE 302. *The pH of a solution, one litre of which contains 0.1 mol CH_3COOH and 0.1 mol HCOOH is :*

(*a*) 4.1 (*b*) 2.36

(*c*) 3.7 (*d*) 1.43

[K_a (HCOOH)] = 1.8×10^{-4} and

K_a for CH_3COOH = 1.8×10^{-5}]

SOLUTION. let mol of CH_3COOH dissociated = x ; mol of HCOOH dissociated = y.

Thus :	CH_3COOH	$\rightleftharpoons$ CH_3COO^-	+ H^+
Conc. at start	0.1	0	0
Conc. after change	0.1 – x = 0.1	x	x

($\because$ x is very small as compared to 0.1, it is neglected)

	HCOOH	$\rightleftharpoons$ $HCOO^-$	+ H^+
Conc. at start	0.1	0	0
Conc. after change	0.1 – y = 0.1	y	y

($\because$ y is very small as compared to 0.1, it is neglected)

$$\therefore \text{ For } CH_3COOH\ ; K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{x(x+y)}{0.1} \qquad ...(1)$$

$[\because [H^+] = x \text{ (of } CH_3COOH) + y \text{ (of HCOOH)}]$

For HCOOH ; $K_a = \dfrac{[HCOO^-][H^+]}{[HCOOH]}$

$$1.8 \times 10^{-4} = \frac{y(x+y)}{0.1} \qquad ...(2)$$

$[\because [H^+] = x \text{ (of } CH_3COOH) + y \text{ (of HCOOH)}]$

(*a*) Dividing (1) and (2), we get :

$$\frac{1.8 \times 10^{-5}}{1.8 \times 10^{-4}} = \frac{x(x+y)}{0.1} \times \frac{0.1}{y(x+y)} = \frac{x}{y}$$

Or $$10^{-1} = \frac{x}{y} ; y = 10x.$$

(*b*) Substituting the value of $y = 10x$ is (1), we get :

$$1.8 \times 10^{-5} = \frac{x(x+10x)}{0.1};$$

$$1.8 \times 10^{-5} \times 0.1 = 11x^2 ;$$

$$x^2 = \frac{1.8 \times 0.1 \times 10^{-5}}{11}$$

Or $$x^2 = 1.6 \times 10^{-7} = 16 \times 10^{-8} ;$$

$$x = (16 \times 10^{-8})^{1/2} = 4 \times 10^{-4}$$

$\therefore$ $$y = 10x = 10 \times 4 \times 10^{-4} = 4 \times 10^{-3}.$$

Hence $$[H^+] = x + y = 4 \times 10^{-4} + 4 \times 10^{-3}$$
$$= 4 \times 10^{-4}(1 + 10) = 44 \times 10^{-4}$$

$\therefore$ $$pH = -\log [H^+] = -\log 44 \times 10^{-4}$$
$$= -(\log 44 + \log 10^{-4})$$
$$pH = -(1.64 - 4) = 2.36.$$

So, the correct answer is (*b*).

EXAMPLE 303. *The pH of a solution obtained by mixing 50 cm^3 of 0.4M NH_3 and 50 cm^3 of 0.3M HCl is :*

(*a*) *8.778*	(*b*) *11*
(*c*) *14*	(*d*) *2.5*

(K_b *for* $NH_4OH = 1.8 \times 10^{-5}$)

SOLUTION. m. mol of $NH_3 = M_1V_1 = 0.4 \times 50 = 20$

m. mol of HCl $= M_2V_2 = 0.3 \times 50 = 15$

$\therefore$ m. mol of NH_3 left unreacted = 20 – 15 = 5

Total volume = 50 + 50 = 100 cm^3

$\therefore$ m. mol of NH_4^+ produced = 15

Hence the solution contains, NH_4^+ ions

$$= \frac{15 \times 1000}{1000 \times 100} = 0.15 \text{ M}$$

The solution contains NH_3 unreacted

$$= \frac{5 \times 1000}{100 \times 1000} = 0.05\text{M}$$

Reaction $NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$

Conc. after reaction 0.05 M 0.15M

But $$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$
$$= -\log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Or $$pOH = -\log 1.8 \times 10^{-5} + \log \frac{0.15}{0.05}$$
$$= -(\log 1.8 + \log 10^{-5}) + \log 3$$
$$= -(0.255 - 5) + 0.477$$
$$= 5 - 0.255 + 0.477 = 5.222$$

But $pH + pOH = 14$;

$\therefore$ $pH = 14 - 5.222 = 8.778.$

So, the correct answer is (*a*).

EXAMPLE 304. *The pH of a solution formed by mixing 20 mL of 0.05 M H_2SO_4 with 5.0 mL of 0.45 M NaOH at 298 K is:*

(*a*) *6*	(*b*) *2*
(*c*) *12*	(*d*) *7*

(J and K-CET, 2011)

SOLUTION. Reaction $2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$
2 m. mol 1 m. mol

Millimoles of NaOH = 5 × 0.45 = 2.25 m. mol

Millimoles of H_2SO_4 = 20 × 0.05 = 1 m. mol

Total volume of solution = 5 + 20 = 25 mL

For H_2SO_4 containing $2H^+$, millimoles = 2 × 1 = 2 m. mol.

Millimoles of NaOH = 2.25

$\therefore$ millimoles of OH^- ions left behind = 2.25 – 2.0 = 0.25

$\therefore$ Concentration of OH^- ions in solution

$$= \frac{0.25}{25} = 0.01 = 10^{-2} \text{ M}$$

$\therefore$ $$pOH^- = -\log (10^{-2}) = -(-2) \log 10$$
$$= +2 \times 1 = +2$$

$\therefore$ $$pH = 14 - pOH^- = 14 - 2 = 12.$$

So, correct answer is (*c*).

EXAMPLE 305. *The solubility of AgCN in a buffer solution of pH = 3 in mol L$^-$ (mol dm^{-3}) is :*

(*a*) 0.58×10^{-10}	(*b*) 1.58×10^{-5}
(*c*) 2.58×10^{-5}	(*d*) 10^{-7}

[K_{sp} *(AgCN)* $= 1.2 \times 10^{-16}$; K_a *(HCN)* $= 4.8 \times 10^{-10}$]

SOLUTION. (*a*) $AgCN + H^+ \rightleftharpoons Ag^+ + HCN$

Solubility (mol L$^-$) s s

$\therefore$ $[Ag^+] = s, [HCN] = s$

where s = solubility of AgCN in mol L$^-$

(*b*) For HCN, $HCN \rightleftharpoons H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]}; [CN^-] = \frac{K_a [HCN]}{[H^+]}$$

Or $$[CN^-] = \frac{(4.8 \times 10^{-10}) \times s}{10^{-3}} = 4.8 \times 10^{-7} s$$

$\{\because pH = 3 ; -\log [H^+] = 3$ **or** $[H^+] = 10^{-3}\}$

(*c*) For $AgCN \rightleftharpoons Ag^+ + CN^- ; K_{sp} = [Ag^+][CN^-]$;

$$1.2 \times 10^{-16} = (s) \times 4.8 \times 10^{-7}s$$

$$\therefore \quad s^2 = \frac{1.2\times10^{-16}}{4.8\times10^{-7}} = 2.5\times10^{-10}\ ;$$

$$s = (2.5\times10^{-10})^{1/2}$$

$$= \mathbf{1.58\times10^{-5}\ mol\ L^{-}\ (mol\ dm^{-3})\ Ans.}$$

So, the correct answer is (*b*).

EXAMPLE 306. *1.0 M Al(NO$_3$)$_3$ solution is found to have a pH value 2.7. The K_a for the reaction*

$$Al^{3+} + HOH \rightleftharpoons [AlOH]^{2+} + H^+ \textit{ will be :}$$

(*a*) 10^{-6} (*b*) 2×10^{-6}

(*c*) 3×10^{-6} (*d*) 4×10^{-6}

SOLUTION. pH = 2.7 ; $-\log[H^+] = 2.7$;

$$\log[H^+] = -2.7$$

$$= -2-1+1-0.7 = \bar{3}.3$$

Or $\log[H^+] = \bar{3}.3$.

Hence $[H^+] = \text{antilog } \bar{3}.3 = 2.0\times10^{-3}$

For the given reaction

	$Al^{3+} + HOH \rightleftharpoons$	$[AlOH]^{2+}$	$+ \quad [H^+]$
Conc. at start	1M		
Conc. at equilibrium	$1-(2\times10^{-3})$ $=1$	2×10^{-3}	2×10^{-3}

($\because$ 2×10^{-3} is very small as compared to 1)

$$\therefore \quad K_a = \frac{[AlOH]^{2+}[H^+]}{[Al^{3+}]}$$

$$= \frac{(2\times10^{-3})\times(2\times10^{-3})}{1} = 4\times10^{-6}$$

So, the correct answer is (*d*).

EXAMPLE 307. *The concentration of S^{2-} ion in an acid solution is 1.7×10^{-21} g/litre. A litre of 0.1 M ZnSO$_4$ solution is added to one litre of above solution. As a result, ZnS :*

(*a*) *gets precipitated*

(*b*) *does not form ppt* (*c*) *gets hydrolysed*

(*K_{sp} of ZnS = 2.5×10^{-22}*)

SOLUTION. Total volume = 1 + 1 = 2L ;

$$\therefore \quad [Zn^{2+}] = \frac{0.1M}{2} = 0.05M$$

$$[S^{2-}] = \frac{1.7\times10^{-21}}{2} = 0.85\times10^{-21}\ g\ L^{-}$$

$$\therefore \quad \text{Ionic product} = [Zn^{2+}][S^{2-}] = 0.05\times0.85\times10^{-21}$$

$$= 4.25\times10^{-23}]$$

Since ionic product is less than K_{sp}, ZnS does not form precipitate. So, the correct answer is **(*b*)**.

EXAMPLE 308. *When one litre of a saturated solution of PbCl$_2$ is evaporated to dryness, the residue is found to weigh 4.5 g. The K_{sp} for PbCl$_2$ will be :*

(*a*) 1.6×10^{-5} (*b*) 2.7×10^{-6}

(*c*) 1.0×10^{-7} (*d*) *None of these.*

(*Mol. wt. of PbCl$_2$ = 278*).

SOLUTION. wt. of PbCl$_2$ = 4.5 g ;

g. mol. wt. of PbCl$_2$ = 278 g.

$$\therefore \quad \text{no. of mol of PbCl}_2 = \frac{4.5}{278} = 0.(016$$

	$PbCl_2 \rightleftharpoons$	Pb^{2+}	$+ \quad 2Cl^-$
Solubility (mol L$^-$)		0.016	$2\times0.016 = 0.032$

$$\therefore \quad K_{sp} = [Pb^{2+}][Cl^-]^2 = 0.016\times(0.032)^2$$

$$= 1.6\times10^{-5}.$$

So, the correct answer is (*a*).

EXAMPLE 309. *At 20°C, 0.016N solution of acetic acid is 4% ionised. The ionisation constant of acetic acid will be :*

(*a*) 2.66×10^{-5} (*b*) 10^{-5}

(*c*) 5.32×10^{-5} (*d*) 10^{-6}

(Modified UP 1984)

SOLUTION. $\alpha = 4\% = \frac{4}{100} = 0.04$;

$C = 0.016$.

$$\text{For a weak acid : } K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.016\times(0.04)^2}{1-0.04}$$

$$= \frac{0.016\times0.0016}{0.96} = 2.66\times10^{-5}$$

So, the correct answer is (*a*).

EXAMPLE 310. *The degree of dissociation of 0.1M NH$_4$OH solution will be :*

(*a*) *34%* (*b*) *3.4%*

(*c*) *1.34%* (*d*) *1.8%*

$K_b = 1.8\times10^{-5}$

SOLUTION. [NH$_4$OH] = C = 0.1M ; $K_b = 1.8\times10^{-5}$

For a weak base : $K_b = C\alpha^2$; $1.8\times10^{-5} = 0.1\times\alpha^2$

$$\therefore \quad \alpha = \left(\frac{1.8\times10^{-5}}{0.1}\right)^{1/2} = (1.8\times10^{-4})^{1/2}$$

$$= 1.34\times10^{-2}$$

$\therefore$ % age degree of dissociation

$$= 1.34\times10^{-2}\times100 = 1.34\%$$

So, the correct answer is (*c*).

EXAMPLE 311. *The degree of dissociation of NH$_4$OH in a solution which is 0.2 M with respect to NH$_4$Cl and 0.1M with respect to NH$_4$OH is :*

(*a*) $9\times10^{-3}\%$ (*b*) $0.9\times10^{-30}\%$

(*c*) $2\times10^{-3}\%$ (*d*) *None of these*

SOLUTION. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Conc. at start C $C\alpha$ $C\alpha$

Conc. at equilibrium $C = (1-\alpha)\ C\alpha$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

Conc. at equilibrium 0.2

$\therefore$ $[NH_4OH] = C(1-\alpha) = C$ (assuming α to be very small).

$$[NH_4^+] = C\alpha + 0.2\ ;\ [OH^-] = C\alpha.$$

$$\therefore \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]};$$

$$1.8 \times 10^{-5} = \frac{(C\alpha + 0.2) \times C\alpha}{C}$$

or $\quad 1.8 \times 10^{-5} = 0.2\alpha$

[$\because$ α is very small, $C\alpha + 0.2 = 0.2$]

$$\therefore \qquad \alpha = \frac{1.8 \times 10^{-5}}{0.2} = 9 \times 10^{-5}$$

or $\quad \alpha = 9 \times 10^{-5} \times 100 = 9 \times 10^{-3}\%$

So, the correct answer is (*a*).

Example 312. *0.1M NH_4OH solution is 1.34% dissociated. Its K_b value will be*

(*a*)	1.8×10^{-4}	(*b*)	2.9×10^{-5}
(*c*)	1.8×10^{-5}	(*d*)	1.8×10^{-12}

Solution. $[NH_4OH] = C = 0.1M$;

$$\alpha = 1.34\% = \frac{1.34}{100} = 1.34 \times 10^{-2}$$

We know that for a weak base,

$$K_b = C\alpha^2 = 0.1 \times (1.34 \times 10^{-2})^2$$

Or $\quad K_b = 1.8 \times 10^{-5}$.

So, the correct answer s (*c*).

Example 313. *The equilibrium constant for the reaction $2X(g) + Y(g) \rightleftharpoons 2Z(g)$ is 2.25. The concentration of y at equilibrium with 2 moles of X and 3 moles of Z in one litre vessel is :*

(*a*)	1.0 mol	(*b*)	2.25 mole
(*c*)	2.0 mol	(*d*)	4.0 mole

(SCRA, 2000)

Solution. Reaction $\quad 2X(g) + Y(g) \rightleftharpoons 2Z(g)$

$$\therefore \qquad K = \frac{[Z]^2}{[X]^2\,[Y]}$$

But $\quad [X] = 2$ mole, $[Z] = 3$ mole ; K = 2.25

$$\therefore \qquad 2.25 = \frac{(3)^2}{(2)^2 \times Y};\ Y = \frac{9}{4 \times 2.25};\ Y = 1$$

So, the correct answer is (*a*).

Example 314. *At 50°C, pure water has $[H_3O^+] = 10^{-6}$ mole litre$^-$. The value of K_w at 50°C is :*

(*a*)	10^{-14}	(*b*)	10^{-6}
(*c*)	10^{-8}	(*d*)	10^{-12}

(SCRA, 2000)

Solution. In pure water, $[H_3O^+] = [OH^-]$.

We know that : $K_w = [H_3O^+]\,[OH^-]$.

But $[H_3O^+] = 10^{-6}$ mole litre$^-$

$$\therefore \qquad K_w = 10^{-6} \text{ mole litre}^- \times 10^{-6} \text{ mole litre}^- = 10^{-12} \text{ mol}^2 \text{ L}^{-2}$$

So, the correct answer is (*d*).

Example 315. *The solubility of a sparingly soluble salt AB_3 of molecular weight M, is x gL^- and therefore, its K_{sp} is :*

(*a*) $27x^4$ (*b*) $27(x/M)^4$ (*c*) $(x/M)^4$ (*d*) $9(x/M)^4$

(SCRA, 2000)

Solution. For AB_3 molecule, $\quad AB_3 \rightleftharpoons A^{+3} + 3B^-$

Solubility (gL^-) $\qquad S \qquad S \qquad 3S$

$$\therefore \qquad K_{sp} = [A^{3+}]\,[B^-]^3 ;$$

$$K_{sp} = S \times (3S)^3 = S \times 27S^3 = 27S^4$$

But $\quad S = \dfrac{x}{M}$. Hence $K_{sp} = 27\left(\dfrac{x}{M}\right)^4$.

So, the correct answer is (*b*).

Example 316. *Will the pH of water be same at 4°C and 25°C? Explain.* **(IIT 2003)**

Solution. At 25°C, $K_w = 10^{-14}$. Hence $pK_w = -\log 10^{-14} = -(-14)\log 10$ or $pK_w = 14 \times 1 = 14$. But $pH + pOH = 14$. Pure water is neutral.

Hence, $pH = pOH$. Hence $pH = pOH = 7$.

As the temperature decreases, K_w decreases due to low ionisation of H_2O and ΔH = +ve while pK_w increases. But pH of water = $pK_w/2$. so, pH of water will increase. Hence pH of water at 4°C will be more than that at 25°C but H_2O remains neutral.

Example 317. *The hydroxyl ion concentration in a solution having pH value 3 will be :*

(*a*)	10^{-11}	(*b*)	10^{-7}
(*c*)	10^{-3}	(*d*)	10^{-14} **(BET, 2003)**

Solution. We know,

$$pH + pOH = 14. \text{ Given } pH = 3$$

$$\therefore \qquad pOH = 14 - pH = 14 - 3 = 11$$

i.e., $\quad pOH = 11$

$$\therefore \qquad -\log [OH^-] = 11 ; \log [OH^-] = -11 ;$$

$$[OH^-] = 10^{-11}.$$

So, the correct answer is **(*a*)**.

Example 318. *The K_a of a weak monobasic acid is 1×10^{-5}. The percentage of ionisation in a decimolar acid solution is:*

(*a*)	0.1	(*b*)	10
(*c*)	0.01	(*d*)	0.5
(*e*)	1		**(Kerala PMT, 2010)**

Solution. $K_a = 10^{-5}$, C = 1/10 or 10^{-1} M. So, $\alpha = (K_a/C)^{1/2} = (10^{-5}/10^{-1})^{1/2}$.

$(10^{-4})^{1/2} = 10^{-2}$. % age ionisation $= 10^{-2} \times 100 = 1$. So, correct answer is (*e*).

Example 319. K_{sp} *[AB] = 1×10^{-10}. If $[A^+] = 1 \times 10^{-5}$, which of the following solution of $[B^-]$ can not be precipitated.*

(*a*)	1×10^{-5}	(*b*)	5×10^{-6}
(*c*)	2×10^{-5}	(*d*)	5×10^{-5}

(IMS – BHU 2003)

Solution. $K_{sp}(AB) = 10^{-10}$ *i.e.*, $[A^+]\,[B^-] = 10^{-10}$.

But $\quad [A^+] = 10^{-5}$, so $[B^-] = \dfrac{10^{-10}}{10^{-5}}$

$$= 10^{-10+5} = 10^{-5}.$$

AB can not be precipitated if $[A^+]\,[B^-] < K_{sp}$. It is possible only if $[B^-] < 10^{-5}$ *i.e.*, $[B^-]$ is 10^{-6}, 10^{-7} etc. Out of the answers given, 5×10^{-6} is less than 10^{-5}. So, the correct answer is (*b*).

EXAMPLE 320. *The pK_a of a certain weak acid is 4.0. What should be the [salt] to [acid] ratio if we have to prepare a buffer with pH = 5 using the acid and one of the salts?*

(*a*) 1 : 10	(*b*) 10 : 1
(*c*) 5 : 4	(*d*) 4 : 5

(Karnataka CET, 2000)

SOLUTION.
$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$
(Hendersons's equation)
$$\therefore \quad 5 = 4 + \log\frac{[\text{salt}]}{[\text{acid}]};$$
$$5 - 4 = \log\frac{[\text{salt}]}{[\text{acid}]};\ 1 = \log\frac{[\text{salt}]}{[\text{acid}]}$$

Taking antilog of both sides, we get :
$$\text{antilog } 1 = \frac{[\text{salt}]}{[\text{acid}]} \quad \textbf{Or} \quad \frac{10}{1} = \frac{[\text{salt}]}{[\text{acid}]}$$

Hence [salt] to [acid] ratio is 10 : 1. So, the correct answer is (*b*).

EXAMPLE 321. *By adding 20 mL of 0.1N HCl to 20mL of 0.001N KOH, the pH of the obtained solution will be :*

(*a*) 1.3	(*b*) 2
(*c*) 7	(*d*) 0

(Karnataka CET, 2000)

SOLUTION. Total volume = 20 mL + 20 mL = 40 mL.

Let N = normality of the resulting solution.

So, milliequivalents of resulting solution = 40 N

(*i*) Milliequivalents of HCl (N_1V_1) = 0.1 × 20 = 2

(*ii*) Milliequivalents of KOH (N_2V_2) = 0.001 × 20 = 0.02

∴ Milliequivalents of HCl left behind = 2 – 0.02 = 1.98
$$\therefore \quad 40\text{N} = 1.98 ;\ \text{N} = \frac{1.98}{40} = 0.0495$$
$$\underset{}{\text{HCl}} \rightleftharpoons \underset{0.0495}{\text{H}^+} + \underset{0.0495}{\text{Cl}^-}$$
$$\therefore \quad pH = -\log[\text{H}^+] = -\log 0.0495$$
$$= -(-1.3054) = +1.3054 \simeq 1.3.$$

So, the correct answer is (*a*).

EXAMPLE 322. *What is the $[H^+]$ in a 0.4 M solution of HOCl, $K_a = 3.5 \times 10^{-8}$?* **(DU met, 2010)**

(*a*) 1.4×10^{-8} M	(*b*) 1.2×10^{-4} M
(*c*) 1.9×10^{-9} M	(*d*) 3.7×10^{-4} M

SOLUTION. V = 1/0.4 L = 2.5 L; $K_a = 3.5 \times 10^{-8}$. So, $\alpha = (K_a\ V)^{1/2} = (3.5 \times 10^{-8} \times 2.5)^{1/2} = 2.95 \times 10^{-4}$; $[H^+] = \alpha/V = 2.95 \times 10^{-4}/2.5 \simeq 1.2 \times 10^{-4}$ M

So, the correct answer is (*b*).

EXAMPLE 323. *In a solution of weak acid having concentration 'c' and dissociation constant K_a, the H^+ ion concentration is almost equal to*

(*a*) $(K_a/C)^{1/2}$	(*b*) $\sqrt{K_a.C}$
(*c*) $\sqrt{C/K_a}$	(*d*) K_a/C

(Kerala CET, 2010)

SOLUTION. Let α = degree of dissociation.

Thus	HA	$\rightleftharpoons$	$H^+ + A^-$
Initial conc.	C		0 0
After dissociation, conc :	$C - C\alpha$		$C\alpha$ $C\alpha$

$$\therefore \quad K_a = \frac{[H^+][A^-]}{[HA]}$$
$$= \frac{C\alpha \times C\alpha}{C - C\alpha \text{ or } C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If α is very small,1 – α = 1.
$$\text{Thus :} \quad K_a = C\alpha^2 ;\ \alpha = \left(\frac{K_a}{C}\right)^{1/2}$$
$$\text{Thus} \quad [H^+] = C\alpha = C \times \left(\frac{K_a}{C}\right)^{1/2} = \left(\frac{K_aC^2}{C}\right)^{1/2}$$
$$\text{or} \quad [H^+] = (K_aC)^{1/2}$$

So, the correct answer is **(*b*)**.

EXAMPLE 324. *The dissociation constant of two acids HA_1 and HA_2 are 3.4×10^{-14} and 1.8×10^{-5} respectively. The relative strength of the acids will approximately be :*

(*a*) 1 : 4	(*b*) 4 : 1
(*c*) 1 : 16	(*d*) 16 : 1

(Rajasthan Pre. med. 2000)

SOLUTION.
$$\frac{\text{Strength of } HA_1}{\text{Strength of } HA_2} = \left(\frac{Ka_1}{Ka_2}\right)^{1/2} = \left(\frac{3.4 \times 10^{-4}}{1.8 \times 10^{-5}}\right)^{1/2}$$
$$= (18.88)^{1/2} \simeq \frac{4}{1}$$

So, the correct answer is (*b*).

EXAMPLE 325. *The equilibrium constant for equilibria $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ and $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ are K_1 and K_2 respectively. Then :*

(*a*) $K_2 = K_1^2$	(*b*) $K_2 = \dfrac{1}{K_1^2}$
(*c*) $K_2 = K_1$	(*d*) $K_2 = \dfrac{1}{K_1}$

(Kerala CET, 2010)

SOLUTION. For $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$,
$$K_1 = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} \quad \text{...(1)}$$

For $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$,
$$K_2 = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} \quad \text{...(2)}$$

Squaring (1), we get :
$$K_1^2 = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} \quad \text{...(3)}$$

Since $K_2 = K_1^2$, the correct answer is **(*a*)**.

EXAMPLE 326. *If the solubility product K_{sp} of a sparingly soluble salt MX_2 at 25°C is 1.0×10^{-11}, the solubility of salt in mole $litre^{-}$ at this temperature will be :*

(*a*) 2.46×10^{14} (*b*) 1.36×10^{-4}
(*c*) 2.60×10^{-7} (*d*) 1.20×10^{-10}

(Rajasthan Pre-med. 2000)

SOLUTION. $MX_2 \rightleftharpoons M^{2+} + 2X^-$

$$\text{S} \quad \text{2S} \qquad \text{(solubilities)}$$

$$K_{sp} = [M^{2+}]\,[X^-]^2 ;$$

$$1.0 \times 10^{-11} = S \times (2S)^2 = 4S^3$$

$$\therefore \quad S = \left(\frac{10^{-11}}{4}\right)^{1/3} .$$

Taking logs of both sides, we get :

$$\log S = \log\left(\frac{10^{-11}}{4}\right)^{1/3}$$

$$= \frac{1}{3}\,[\log 10^{-11} - \log 4]$$

$$= \frac{1}{3}\,[-11 - 0.602] = -3.8673$$

$$= -3 - 1 + 1 - 0.8673 = \bar{4}.1327 .$$

Taking antilog of both sides, we get :

$$S = 1.36 \times 10^{-4}\ \text{mol L}^{-}.$$

So, the correct answer is (*b*).

EXAMPLE 327. *10^{-6} M NaOH is diluted 100 times. The pH of the diluted base is:*

(*a*) *between 5 and 6* (*b*) *between 6 and 7*
(*c*) *between 10 and 11* (*d*) *between 7 and 8*

(Karnataka CET, 2009)

SOLUTION. $NaOH \rightleftharpoons Na^+ + OH^-$. So, given $[OH^-] = 10^{-6}$. On diluting the solution 100 *i.e.*, 10^2 times,

$$[OH^-] = \frac{10^{-6}}{10^2} = 10^{-6-2} = 10^{-8}$$

Since the base is weak, autoprotolysis of water will also take place. So, the OH^- ions available from water will also be considered.

$\therefore$ Total $[OH^-] = 10^{-8} + [OH^-]$ water. So, the correct answer is (*d*).

EXAMPLE 328. *When 0.1 mol of CH_3NH_2 (ionisation constant $K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol HCl and the volume is made up to 1 lit., the $[H^+]$ of resulting solution is:*

(*a*) 8×10^{-2} (*b*) 2×10^{-11}
(*c*) 1.23×10^{-4} (*d*) 8×10^{-11}

[IIT-JEE (screening), 2005]

SOLUTION. *Reaction.* $CH_3NH_2 + HCl \rightleftharpoons CH_3NH_3^+Cl^-$

Initial conc. (mol)	0.1	0.08	0
After the reaction	0.1 – 0.08	0.08 – 0.08	0.08
	= 0.02	= 0	
	(base)	(acid)	(salt)]

According to Hendersons's equation :

$$pOH = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log 5 \times 10^{-4} + \log\frac{0.08}{0.02}$$

$$= -[\log 5 + \log 10^{-4}] + \log 4$$

$$= -(0.6989 - 4) + 0.602$$

$$pOH = -0.6989 + 4 + 0.602 = 3.903$$

But $pH + pOH = 14$. Hence $pH = 14 - pOH$

$$= 14 - 3.903 = 10.097$$

But $pH = -\log[H^+]$. So, $[H^+] = 10^{-pH} = 10^{-10.097}$

$$\therefore \quad [H^+] = \text{antilog} - 10.097$$

$$= \text{antilog}\,(-10 - 1 + 1 - 0.097 = \overline{11}.903)$$

Or $[H^+] = 8 \times 10^{-11}$.

So, the correct answer is **(*d*)**.

EXAMPLE 329. *For the reaction, $AB(g) \rightleftharpoons A(g) + B(g)$, AB is 33% dissociated at a total pressure of P. Therefore, P is related to K_p by one of the following options.*

(*a*) $P = K_p$ (*b*) $P = 3K_p$
(*c*) $P = 4K_p$ (*d*) $P = 8K_p$

(AMU Med. 2010)

SOLUTION. $AB(g) \rightleftharpoons A(g) + B(g)$

At start (mol)	1	0	0
At eqmb.	1–0.33	0.33	0.33;

Total mol = 1 –0.33 + 0.33 + 0.33 = 1.33.

$\therefore$ $p_A = (0.33/1.33)$ P; $p_B = (0.33/1.33)$ P; $p_{AB} = (0.67/1.33)$ P; $K_p = p_A \times p_B/p_{AB}$

$\therefore$ $K_p = 0.33 \times 0.33 \times P/0.67 \times 1.33$; $P = 8\,K_p$.

So, the correct answer is (*d*).

EXAMPLE 330. *At 25°C, the dissociation constant of a base, BOH, is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be :*

(*a*) 1.0×10^{-5} *mol* L^- (*b*) 1.0×10^{-6} *mol* L^-
(*c*) 2.0×10^{-6} *mol* L^- (*d*) 1.0×10^{-7} *mol* L^-

(CBSE - PMT (screening), 2005)

SOLUTION. *Reaction.* $BOH \rightleftharpoons B^+ + OH^-$

Initial conc.	C	0	0
Conc. at equilibrium	C – Cα	Cα	Cα

$\therefore$ $[OH^-] = C\alpha$. Also, $K_b = 1.0 \times 10^{-12}$;

$$C = 0.01 = \frac{1}{100} = 10^{-2}$$

But $[OH^-] = (K_bC)^{1/2} = (1.0 \times 10^{-12} \times 10^{-2})^{1/2}$

$$= (10^{-14})^{1/2}$$

$$= 10^{-7}\ \text{mol L}^-$$

$\therefore$ Correct answer is **(*d*)**.

EXAMPLE 331. *The absolute enthalpy of neutralisation of the reaction :*

$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$ will be :

(*a*) *– 57.33 kJ* mol^-
(*b*) *greater than – 57.33 kJ* mol^-

(*c*) *less than –57.33 kJ mol⁻*

(*d*) *57.33 kJ mol⁻* **(CBSE.PMT (Prelims), 2005)**

SOLUTION. Since some energy is used up to break MgO(s), enthalpy is less than – 57.33 kJ mol⁻. So, the correct answer is **(*c*)**.

EXAMPLE 332. *On adding 0.1M solution each of* $[Ag^+]$, $[Ba^{2+}]$, $[Ca^{2+}]$ *in a* Na_2SO_4 *solution, species first precipitated is:*

$(K_{sp}\ BaSO_4 = 10^{-11}, K_{sp}\ CaSO_4 = 10^{-6}, K_{sp}\ Ag_2SO_4 = 10^{-5})$

(*a*) Ag_2SO_4	(*b*) $BaSO_4$
(*c*) $CaSO_4$	(*d*) *all of these*

(DCE, 2005)

SOLUTION. (*a*) $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-};$

$$K_{sp} = [Ag^+]^2\,[SO_4^{2-}]$$

$$\therefore \quad [SO_4^{2-}] = K_{sp}/[Ag^+]^2 = \frac{10^{-5}}{0.1 \times 0.1} = 10^{-3}$$

(*b*)
$$BaSO_4 \rightleftharpoons Ba^{+2} + SO_4^{2-};\ K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$[SO_4^{2-}] = K_{sp}/[Ba^{2+}]$$

$$\therefore \quad [SO_4^{2-}] = \frac{10^{-11}}{0.1} = 10^{-10}$$

(*c*)
$$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-};$$

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}];$$

$$[SO_4^{2-}] = K_{sp}/[Ca^{2+}]$$

$$\therefore \quad [SO_4^{2-}] = \frac{10^{-6}}{0.1} = 10^{-5}$$

Since the ionic product of $BaSO_4$ is less, so Ba^{2+} will be precipitated first. So, the correct answer is (*b*).

EXAMPLE 333. *Partial pressure of* O_2 *in the reaction :*

$$2Ag_2O(s) \rightleftharpoons 4Ag(s) + O_2(g) \text{ is :}$$

(*a*) K_p	(*b*) $\sqrt{K_p}$
(*c*) $3\sqrt{K_p}$	(*d*) $2K_p$ **(DCE, 2005)**

SOLUTION. We know that : $[Ag_2O(s)] = [Ag(s)] = 1$.
Hence K_p for the reaction

$$2Ag_2O(s) \rightleftharpoons 4Ag(s) + O_2(g) \text{ is :}$$

$$\frac{(pAg(s))^4 \times pO_2}{(pAg_2O(s))^2} = \frac{1 \times pO_2}{1}$$

$$\therefore \quad K_p = pO_2.$$

So, the correct answer is **(*a*)**.

EXAMPLE 334. $A(g) + 3B(g) \rightleftharpoons 4C(g)$. *Initial concentration of A is equal to that of B. The equilibrium concentrations of A and C are equal.* $K_c =$

(*a*) 0.08	(*b*) 0.8
(*c*) 8	(*d*) 80
(*e*) 1/8	**(Kerala PET, 2005)**

SOLUTION. Given reaction :

	A	+	3B	⇌	4C
Conc. at start :	*a*		*b*		*0*
Conc. at equilibrium	*a – x*		*b – 3x*		*4x*

$$\therefore \quad K_c = \frac{[C]^4}{[A]\,[B]^3} - \frac{(4x)^4}{(a-x)\,(b-3x)^3}$$

But we are given that,

$$a = b\ ;\ a - x = 4x \text{ i.e., } a = 4x + x = 5x$$

$$\therefore \quad a = b = 5x.$$

Substituting the values, we get :

$$K_c = \frac{(4x)^4}{(5x-x)\,(5x-3x)^3} = \frac{(4x)^4}{4x \times (2x)^3}$$

$$= \frac{4x \times 4x \times 4x \times 4x}{4x \times 8x^3} = 8$$

So, the correct answer is **(*c*)**.

EXAMPLE 335. *Two mol of* PCl_5 *are heated in a closed vessel of 2 litre capacity. When the equilibrium is attained, 40% of it has been found to be dissociated. What is the value of* K_c *in mol/dm*^{3}*?*

(*a*) 0.532	(*b*) 0.266
(*c*) 0.133	(*d*) 0.174
(*e*) 0.25	**(Kerala PET, 2005, 2011)**

SOLUTION. Degree of dissociation,

$$\alpha = 40\% = \frac{40}{100} = 0.40$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$\text{Initial conc.}\ \frac{2\text{mol}}{V = 2L} = 1 \text{ mol L}^- \text{ or } 1 \text{ mol dm}^{-3}$$

According to Ostwald dilution law :

$$K_c = \frac{\alpha^2 C}{1 - \alpha}$$

$$\therefore \quad K_c = \frac{(0.4)^2 \times 1\text{mol dm}^{-3}}{1 - 0.4 = 0.6}$$

$$= 0.266 \text{ mol/dm}^3$$

So, the correct answer is (*b*).

EXAMPLE 336. *For the reaction,* $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ ($K_c = 1.8 \times 10^{-6}$ *at 184°C, R = 0.0831 kJ/mol K). When* K_p *and* K_c *are compared at 184°C, it is found that*

(*a*) K_p *is greater than* K_c (*b*) K_p *is less than* K_c

(*c*) $K_p = K_c$

(*d*) *Whether* K_p *is greater than, less than or equal to* K_c *depends upon total gas pressure.* **(AIEEE, 2005)**

SOLUTION. We know that

$$K_p = K_c\,(RT)^{\Delta n}.$$

For
$$\underset{2\text{ mol}}{2NO_2(g)} \rightleftharpoons \underset{2\text{ mol}}{2NO(g)} + \underset{1\text{ mol}}{O_2(g)}$$

$$\Delta n = (2 + 1) - 2 = 1.$$

$$T = 184 + 273 = 457 \text{ K}$$

$$\frac{K_p}{K_c} = (0.0831 \text{ kJ mol}^-\text{K}^- \times 457\text{K}) \simeq 38$$

Hence K_p is greater than K_c. So, the correct answer is **(*a*)**.

EXAMPLE 337. *An amount of solid* NH_4HS *is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide* *decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4HS decomposition at this temperature is :*

(*a*) *0.30* (*b*) *0.18* (*c*) *0.17* (*d*) *0.11*

(AIEEE 2005)

Solution.	$NH_4HS(s) \rightleftharpoons$	$NH_3(g)$ +	$H_2S(g)$
Initial pressure	0	0.5	0
Pressure at equilibrium	0	$0.5 + p$	p

$$\therefore \quad 0.5 + p + p = 0.84 ; 2p = 0.84 - 0.5 = 0.34$$

$$\therefore \quad p = \frac{0.34}{2} = 0.17 \text{ atm.}$$

$$\therefore \quad p_{NH_3} = 0.5 + p = 0.5 + 0.17 = 0.67 \text{ atm}$$

$$\therefore \quad K_p = p_{NH_3} \times p_{H_2S}$$
$$= 0.67 \text{ atm} \times 0.17 \text{ atm} = 0.11 \text{ atm}^2$$

So, the correct answer is (*d*).

Example 338. *Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15} respectively. Solubility (mol dm^{-3}) of the salts at temperature T are in the order.*

(*a*) $MX > MX_2 > M_3X$

(*b*) $M_3X > MX_2 > MX$

(*c*) $MX_2 > M_3X > MX$

(*d*) $MX > M_3X > MX_2$ **(IIT-JEE, 2008)**

Solution. Let solubility of MX, MX_2 and M_3X are x_1, x_2 and x_3 respectively.

(*i*) $MX \rightleftharpoons \underset{x_1}{M^+} + \underset{x_1}{X^-}; K_{sp} = (M^+)(X^-) = x_1 \times x_1 = x_1^2$

$$\therefore x_1^2 = K_{sp}; x_1 = (K_{sp})^{1/2} = (4 \times 10^{-8})^{1/2} = 2 \times 10^{-4}.$$

(*ii*) $MX_2 \rightleftharpoons \underset{x_2}{M^+} + \underset{2x_2}{2X^-}; K_{sp} = (M^+)(X^-)^2 = x_2 \times (2x_2)^2$

$$\text{or} \quad 4x_2^3 = K_{sp}; x_2 = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2 \times 10^{-14}}{4}\right)^{1/3}$$

$$\text{or} \quad x_2 = \mathbf{2 \times 10^{-5}}$$

(*iii*) $M_3 X \rightleftharpoons \underset{3x_3}{3M^+} + \underset{x_3}{X^-}; K_{sp} = (M^+)^3 (X^-) = (3x_3)^3 \times x_3$

$$= 27\, x_3^4 ; x_3 = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

$$= \left[\frac{2.7 \times 10^{-15}}{27} = 10^{-16}\right]^{1/4} = 10^{-4}$$

From the values in (*i*), (*ii*) and (*iii*) above, we see that $x_1 > x_3 > x_2$ *i.e.*, $MX > M_3X > MX_2$.

So, the correct answer is (*d*).

Example 339. *The pH value of which one of the following is not equal to one.*

(*a*) *0.1 M CH_3COOH* (*b*) *0.1 M HNO_3*

(*c*) *0.05 M H_2SO_4*

(*d*) *50 cm^3 0.4 M HCl + 50 cm^3 0.2 M NaOH.*

(BCECE, 2005, Karanataka CET, 2011)

Solution. Out of all the given options, only CH_3COOH is a weak acid which does not dissociate completely. So, pH is not equal to one.

Example 340. *Given pH of a solution is 3 and it is mixed with another solution B having pH 2. If both mixed, the resultant pH of the solution will be :*

(*a*) *3.2* (*b*) *1.96*

(*c*) *3.4* (*d*) *3.5*

(IMS-BHU 2005)

Solution. (*i*)*p*H of solution, *A* = 3.

But $\quad pH = -\log [H^+]$

$\therefore \quad [H^+] = 10^{-pH} = 10^{-3}M$ ...(1)

(*ii*) *p*H of solution, *B* = 2.

But $\quad pH = -\log [H^+]$.

Hence : $\quad [H^+] = 10^{-pH} = 10^{-2}$ M ...(2)

$\therefore$ Total $[H^+]$ from (1) and (2)

$$= 10^{-3}M + 10^{-2}M = 10^{-3}(1 + 10)M$$
$$= 11 \times 10^{-3}M$$

$\therefore$ *p*H of resultant solution

$$= -\log [H^+] = -[\log 11 \times 10^{-3}]$$
$$= -[\log 11 + \log 10^{-3}] = -[1.04 - 3]$$
$$= 3 - 1.04 = 1.96$$

So, the correct answer is (*b*).

Example 341. *$A + B \rightleftharpoons C + D$. If initially the concentration of A and B are both equal but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction ?*

(*a*) *4/9* (*b*) *9/4*

(*c*) *1/9* (*d*) *4*

(IMS – BHU, 2005)

Solution. *Reaction.*	*A*	+ *B* $\rightleftharpoons$	*C* + *D*
Initial conc.	*x* mol	*x* mol	0 0
Conc. at equilibrium			2*x* 2*x*

Applying law of chemical equilibrium, we have :

$$K_c = \frac{[C][D]}{[A][B]}; \; K_c = \frac{2x \times 2x}{x \times x} = 4$$

So, the correct answer is (*d*).

Example 342. *$Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$;*

$$K_1 = 6.8 \times 10^{-3}$$

$[Ag(NH_3)^+] + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$;

$$K_2 = 1.6 \times 10^{-3}$$

Then the formation constant of $[Ag(NH_3)_2]^+$ is :

(*a*) *1.08×10^{-7}* (*b*) *1.08×10^{-5}*

(*c*) *1.08×10^{-9}* (*d*) *none of these*

(IIT-JEE, 2006)

Solution. Since the reaction takes place in two steps :

$$k = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3}$$
$$= 1.08 \times 10^{-5}.$$

So, the correct answer is (*b*).

EXAMPLE 343. *If the concentration of OH^- ions in the reaction*

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by :

(*a*) *64 times* (*b*) *4 times* (*c*) *8 times* (*d*) *16 times*

(CBSE-PMT 2008 (Prelims))

SOLUTION. For the reaction :

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

$$K = \frac{[Fe^{3+}][OH^-]^3}{[Fe(OH)_3]} = [Fe^{3+}][OH^-]^3$$

[∵ activity of solids is one]

From above relation of K, it is clear that if the concentration of OH^- is decreased by 1/4 times, the equilibrium concentration of Fe^{3+} will be increased by 4^3 *i.e.*, 64 times, in order to keep the value of K as constant.

EXAMPLE 344. *Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed is a vessel. What will be the H^+ ion concentration in the mixture ?*

(*a*) *3.7×10^{-3} M* (*b*) *1.11×10^{-3} M*

(*c*) *1.11×10^{-4} M* (*d*) *3.7×10^{-4} M*

(CBSE-PMT, 2008 Prelims)

SOLUTION. Since pH = $-\log(H^+)$, So, $(H^+) = 10^{-pH}$

(*i*) For solution 1, pH = 3. So, $(H^+) = 10^{-3}$

(*ii*) For solution 2, pH = 4. So, $(H^+) = 10^{-4}$

(*iii*) For solution 3, pH = 5. So, $(H^+) = 10^{-5}$

∴ Total concentration of $(H^+) = 10^{-3} + 10^{-4} + 10^{-5}$

$$= 10^{-3}(1 + 10^{-1} + 10^{-2})$$

$$= 10^{-3}\left(1 + \frac{1}{10} + \frac{1}{100}\right)$$

$$= 10^{-3}\left(\frac{100+10+1}{100} = \frac{111}{100}\right)$$

$$= 1.11 \times 10^{-3}$$

Hence (H^+) is a mixture containing equal volume of these acids solution

$$= \frac{1.11 \times 10^{-3}}{3} = 3.7 \times 10^{-4} M.$$

So, the correct answer is (*d*).

EXAMPLE 345. *30 c.c. of M/3 HCl, 20 c.c. of M/2 HNO_3 and 40 c.c. of M/4 NaOH solutions are mixed and the volume was made up to 1 dm^3. The pH of the resulting solution is:*

(*a*) *2* (*b*) *1*

(*c*) *3* (*d*) *8*

(Karnataka CET, 2009, HP Board, 2007)

SOLUTION. Total milliequivalents of H^+ ions = (Volume of HCl × molarity of HCl) + (Volume of HNO_3 × molarity of HNO_3) $= \left(30 \times \frac{1}{3}\right) + \left(20 \times \frac{1}{2}\right) = 20$

Total milliequivalents of NaOH *i.e.*, OH^- ions = volume of NaOH × molarity of NaOH

$$= 40 \times \frac{1}{4} = 10$$

∴ Milliequivalents of H^+ ions left = 20 – 10 = 10

Total volume of solution = 1 dm^3 = 1000 c.c.

∴ $[H^+] = 10/1000 = 10^{-2}$

∴ $pH = -\log[H^+] = -\log 10^{-2}$

$= (-)(-2)\log 10 = 2 \times 1 = 2.$

So, the correct answer is (*a*).

EXAMPLE 346. *The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium*

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$, would be :

(*a*) *3.0×10^{-5}* (*b*) *3.0×10^{-4}* (*c*) *3.0×10^{4}* (*d*) *3.0×10^{5}*

(CBSE-PMT, 2009)

SOLUTION. (*i*) For $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$;

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.5 \times 10^{-5}$$

(*ii*) For $HCN \rightleftharpoons H^+ + CN^-$;

$$K_2 = \frac{[H^+][CN^-]}{[HCN]} = 4.5 \times 10^{-10}$$

Given: $CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$;

$$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$$

But $K = \frac{K_1}{K_2} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} = 0.3 \times 10^5$

or $K = 3.0 \times 10^4$.

So, the correct answer is (*c*).

EXAMPLE 347. *0.023 g of sodium metal is reacted with 100 cm^3 of water. The pH of the resulting solution is:*

(*a*) *10* (*b*) *8* (*c*) *9* (*d*) *12*

(Karnataka, 2011)

SOLUTION. Wt. of Na-metal = 0.023 g; Volume of water = 100 cm^3; At. wt. (or mol. wt.) of Na = 23 g mol^-.

∴ Molarity of solution

$$= \frac{\text{wt.}}{\text{mol. wt}} \times \frac{1000}{\text{Volume in mL}}$$

$$= \frac{0.023}{23} \times \frac{1000}{100} = 0.01\text{ M} = 10^{-2}\text{ M}$$

Reaction. $Na + H_2O = Na^+ + OH^- + \frac{1}{2}H_2$

Here, $[OH^-] = 10^{-2}$ M. we know that:

$pOH = -\log[OH^-] = -\log 10^{-2}$

$= (-)(-2)\log 10 = +2 \times 1 = +2$

∴ pH = 14 – pOH = 14 – 2 = 12.

So, the correct answer is (*d*).

Type: Strong alkali + Strong alkali .

To calculate (H^+) and pH of a mixtrue of alkali solutions (say v_1mL of x M alkali + v_2 mL of y M alkali + ...) Use the relation :

(*i*) $[OH^-]$

$$= \frac{\text{Total no. of milli equivalents of all the alkalies}}{\text{Total volume of solution } (= v_1 + v_2 + ...) \text{ in mL}} \times 1000$$

Where no. of milliequivalents of the alkali.

= volume × molarity × acidicity of base

= volume × normality (if normalities are given).

(*ii*) $(H^+) = Kw/[OH^-] = \{10^{-14}/[OH^-]\} = x$ (say)

(*iii*) $pH = -\log [H^+] = -\log x$.

Type: Strong acid + strong alkali .

To calculate the $[H^+]$ and pH of a mixture of solution of a strong acid (e.g. v_1 mL of $x\,M$ of HCl, HNO_3 or H_2SO_4) and strong alkali (e.g. v_2 mL of $y\,M$ NaOH or KOH), Use the relations:

(*i*) no. of milliequivalents of alkali = $v_1 \times x \times$ acidity of base = p

(*ii*) no. of milliequivalents of acid = $v_2 \times y \times$ basicity of acid = q

(*iii*) If $p > q$, no. of milliequivalents of alkali left behind $= p - q$

(*iv*) If $q > p$, no. of milliequivalents of acid left behind $= q - p$

Then for (*iii*), $[OH^-] = \dfrac{p-q}{v_1+v_2} \times 1000$ m.eq. $L^- = Z$

$\therefore [H^+] = [Kw^2/(OH^-)] = 10^{-14}/Z$; $pH = -\log [H^+]$.

For (iv), $(H^+) = \dfrac{q-p}{v_1+v_2} \times 1000$ m.eq. L^-; $pH - \log [H^+]$.

> **Note.** If normalities of solutions are given, then: no. of milliequivalents = volume × normality of solution.

EXAMPLE 348. *5mL of 0.4 N NaOH is mixed with 20 mL of 0.1N HCl. the pH of the resulting solution will be:*

(*a*) 6 (*b*) 7

(*c*) 8 (*d*) 5

(Karnataka, CET, 2012)

SOLUTION. no. of millieqiuivalents of NaOH = 5 × 0.4 = 2.0

no. of millieqiuivalents of HCl = 20 × 0.1 = 2.0

Since the no. of millieqiuivalents of NaOH and HCl are Equal the solution is mental . So, the pH of the solution = 7. So, the correct answer is (*b*).

EXAMPLE 349. *Which one of the following will decrease the pH of 50 mL of 0.01 M hyrochloric acid?*

(*a*) Addition of 50 mL of 0.01 M HCl

(*b*) Addition of 50 mL of 0.002 M HCl

(*c*) Addition of 150 mL of 0.002 M HCl

(*d*) Addition of 5 mL of 1 M HCl

(*e*) Addition of metallic zinc. **(Kerala PMT, 2012)**

SOLUTION. For 0.01 M HCl or $10^{-2}[H^+]$, $pH = -\log (H^+)$ or $pH = -\log 10^{-2} = -(-2) \log 10 = +2$. For the pH of the mixture of solutions (for total volume, $V_1 + V_2$) We have:

$$N_1V_1 + N_2V_2 = N_3 (V_1 + V_2)$$

$\therefore$ For (*a*), $50 \times 0.01 + 50 \times 0.01 = N_3 \times (50 + 50)$;

$$N_3 = \frac{0.5 + 0.5}{100} = 10^{-2}$$

$pH = -\log 10^{-2} = -(-2) \log 10 = +2 \times 1 = +2$ (same pH)

For (*b*) $50 \times 0.01 + 50 \times 0.002 \times N_3 (50 + 50)$;

$$N_3 = \frac{0.5 + 0.1}{100} = 6 \times 10^{-3}$$

$pH = -\log (6 \times 10^{-3}) = 2.2$ (pH increased)

(*c*) $50 \times 0.01 + 150 \times 0.002 = N_3 (50 + 150)$; $N_3 = \dfrac{0.5 + 0.3}{200}$

$$= 4\ 0 \times 10^{-3}$$

$\therefore pH = -\log 4 \times 10^{-3} = 2.39$ (pH increased)

(*d*) $50 \times 0.01 + 5 \times 1 = N_3 (50 + 5)$; $N_3 = \dfrac{0.5 + 5}{55} = 0.1$

$$= 10^{-1}$$

$pH = -\log 10^{-1} = 1$ (pH decreased)

Type: Strong acid + strong acid:

To calculate $[H^+]$ and pH of a mixture of acid solutions (say v_1 mL of $x\,M$ acid + v_2 mL of $y\,M$ acid), use the relations:

$$(i)\ [H^+] = \frac{\text{Total no. of milliequivalent of all the acids}}{\text{Total valume of solution } (= v_1 + v_2) \text{ in mL}} \times 1000$$

Where no. of milliequivalent of an acid = Volume × molarity × basicity of acid = volume × normality of acid if normalities are given.

e.g. no. of milliequivalents of 100 mL of 0.2M H_2SO_4 = (100 × 0.2 × 2 = 40 ($\because$ H_2SO_4 is dibasic acid).

> **Note:** For HCl and HNO_3, basicity = 1 for each acid

EXAMPLE 350. *The pK_a of an acid HA is 4.77 and pK_b of a base BOH is 4.75. The pH of 0.1 M aqueous solution of the salt is:*

(*a*) 7.02 (*b*) 7.01

(*c*) 6.99 (*d*) 7.00

(*e*) 6.98

(Karnataka, CET, 2012)

SOLUTION. $HA + BOH \longrightarrow AB \text{ (salt)} + H_2O$.

AB is a salt of a weak acid and a weak base. So:

$$pH = 7 + \frac{1}{2}\,pK_a - \frac{1}{2}\,pK_b;\ pK_a = 4.77;\ pK_b = 4.75$$

$$\therefore pH = 7 + \left(\frac{1}{2} \times 4.77\right) - \frac{1}{2}(4.75) = 7 + 2.385 - 2.375$$

= 7.01. So the correct answer is (*b*)

EXAMPLE 351. *The pH of a 0.1 molar solution of the acid, HQ is 3. The value of ionisation constant, Ka of this acid is:*

(*a*) 1×10^{-3} (*b*) 1×10^{-5}
(*c*) 1×10^{-7} (*d*) 3×10^{-1}

(AIEEE, 2012)

SOLUTION. pH = 3. So, $[H^+] = 10^{-pH} = 10^{-3}$

$\{\because pH = -\log [H^+]\}$

Concentration, $C = 0.1\ M$. But:

$[H^+] = (KaC)^{1/2}; 10^{-3} = (KaC)^{1/2}$. Squaring both sides, we get:

$$(10^{-3})^2 = K_a \times 0.1. \text{ So, } K_a = \frac{10^{-6}}{0.1} = 10^{-5}.$$

So, the correct answer is (*b*).

Type. When v_1 mL solution of pH = *x*, is mixed with v_2 mL solution of pH = *y*, then resulting [H⁺] and pH of solution can be found by using the relations:

(*i*) $$[H^+] = \left[\frac{v_1 \times 10^{-x}}{1000} + \frac{v_2 \times 10^{-y}}{1000}\right] \times \frac{1000}{v_1 + v_2} = R(\text{say})$$

(*ii*) $pH = -\log R$

EXAMPLE 352. *The pH of a solution obtained by mixing 100 mL of a solution of pH = 3 with 400 mL of a solution of pH = 4 is:*

(*a*) 3 – log 2.8 (*b*) 7–log 2.8
(*c*) 4 – log 2.8 (*d*) 5 – log 2.5

(Karnataka, CET, 2012)

SOLUTION. Total volume of solution = 100 + 400 = 500 mL.

(*i*) pH = 3. So, $[H^+] = 10^{-3}\ M$

1000 mL solution = $10^{-3}\ M$

$$100 \text{ mL solution} = \frac{10^{-3}}{1000} \times 100 = 10^{-4}\ M$$

(*ii*) pH = 4. So, $[H^+] = 10^{-4}\ M$

1000 mL solution = $10^{-4}\ M$

$$\therefore \quad 400 \text{ mL solution} = \frac{10^{-4}}{1000} \times 400 = 4 \times 10^{-5}\ M$$

Total [H⁺] of mixed solution = $[10^{-4} + 4 \times 10^{-5}]\ M = 10^{-5}[10 + 4]\ M = 14 \times 10^{-5}\ M$

Now 500 mL solution has $[H^+] = 14 \times 10^{-5}\ M$

$$\therefore \quad 1000 \text{ mL solution has } [H^+] = \frac{14 \times 10^{-5}}{500} \times 1000 = 28 \times 10^{-5}\ M = 2.8 \times 10^{-4}\ M$$

$\therefore$ pH = – log [H⁺] = – [log 2.8 ×10⁻⁴] = – [log 2.8 – 4 log 10]

= 4 – log 2.8 $[\because \log 10 = 1]$

So, the correct answer is (*c*).

Second method. $$[H^+] = \frac{v_1 \times 10^{-x} + v_2 \times 10^{-y}}{1000} \times \frac{1000}{v_1 + v_2}$$

$$= \frac{100 \times 10^{-3} + 400 + 10^{-4}}{1000} \times \frac{1000}{500} = 2.8 \times 10^{-4}$$

$\therefore pH = -\log 2.8 \times 10^{-4} = 4 - \log 2.8$

EXAMPLE 353. *If the solubility of pb Br$_2$ is S g-mole per liter, its solubility product,considering it to be 80% ionised is:*

(*a*) 2.048 S² (*b*) 20.48 S²
(*c*) 2.048 S³ (*d*) 2.048 S⁴

(AMU. Engg. 2012)

SOLUTION. $$\text{Pb Br}_2 \rightleftharpoons Pb^{2+} + 2\,Br^-$$

$$\text{Solubility} \quad S \qquad \frac{S \times 80}{100} \qquad \frac{2S \times 80}{100}$$

$[\because$ Pb Br$_2$ gets 80% ionised]

$$\therefore \quad K_{sp} = [Pb^{2+}] \times [Br^-]^2$$

$$= \frac{S \times 80}{100} \times \frac{2S \times 80}{100} \times \frac{2S \times 80}{100} = 2.048\ S^3$$

So, the correct answer is (*c*).

EXAMPLE 354. *A buffer solution is prepared by mixing equal concentration of weak base and its salt with strong acid. For the base, K_b is given as 10^{-9}. The pH of the buffer solution is:*

(*a*) 3 (*b*) 5
(*c*) 8 (*d*) 9

(Odisha, JEE, 2012)

SOLUTION. For a buffer salt:

$$pOH = pKb + \log \frac{[\text{Salt}]}{[\text{Base}]}.$$

Since $K_b = 10^{-9}$, $pK_b = -\log K_b = -\log 10^{-9}$

= (–) (– 9 log 10) = + 9 × 1 = 9

$\therefore$ pOH = 9, pH = 14 – 9 = 5.

So, the correct answer is (*b*).

EXAMPLE 355. *A solution has $[H_3O^+]$ as 10^{-4}. This solution is ;*

(*a*) natural (*b*) basic
(*c*) acidic (*d*) amphoteric

(Odisha. JEE. 2012)

SOLUTION. $[H_3O^+] = 10^{-4}$. So, $pH = -\log [H_3O^+] = -\log 10^{-4}$

= – (– 4)log 10 = 4 × 1 = 4.

Since pH is less tham 7, it is acidic. So, the correct answer is (*c*).

EXAMPLE 356. *The number of moles of Ca(OH)$_2$ that must be dissolved to make 250 mL solution in water of pH 10.65 is:*

(*a*) 5.6×10^{-5} (*b*) 6.5×10^{-5}
(*c*) 4.5×10^{-5} (*d*) 5.4×10^{-5}

(AMS, Engg. 2012)

SOLUTION. We know pH + pOH = 14; 10.65 + pOH = 14; pOH = 14 – 10.65 = 3.35. Since pOH = – log[OH⁻]; $[OH^-] = 10^{-3.35}$

Taking logs of both sides, we get, $\log [OH^-] = \log 10^{-3.35} = -3.35 \log 10 = -3.35$.

Taking antilogs of both sides, [OH⁻] = antilog – 3.35 + 1 – 1 i.e., $\bar{4}.65 = 4.47 \times 10^{-4}$ M.

$$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$$

2 mol

$$\therefore\ [Ca(OH)_2] = \frac{4.47 \times 10^{-4}}{2} M = 2.235 \times 10^{-4} M$$

$$\therefore\ \text{No. of moles in 250 mL} = \frac{2.235 \times 10^{-4} \times 250}{1000} = 5.58$$

$\times\ 10^{-5} \simeq 5.6 \times 10^{-5}$. So, the correct answer is (*a*).

EXAMPLE 357. *20 mL of 0.1N acetic acid is mixed with 10 mL of 0.1N solution of NaOH. The pH of the resulting solution is (pK of acetic acid is 4.74):*

(*a*) 3.74 (*b*) 4.74

(*c*) 5.74 (*d*) 6.74

(WB. JEE. 2012)

SOLUTION. Moles of acetic acid

$$= \frac{\text{Normality} \times \text{volume in mL}}{1000} = \frac{0.1 \times 20}{1000} = 0.002$$

$$\text{Moles of NaOH} = \frac{0.1 \times 10}{1000} = 0.001$$

	CH_3COOH	$+\ NaOH \longrightarrow$	CH_3COONa	$+\ H_2O$
	1mol	1mol	1mol	1mol
Initial mol	0.002	0.001		
Mol after reaction	0.002 − 0.001 = 0.001	0	0.001	0.001

But $\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$ (Henderson's equaiton)

$$= 4.74 + \log \frac{(0.001)}{(0.001)}$$

$= 4.74 + \log 1 = 4.74 + 0 = 4.74$

So, the correct answer is (*b*).

EXAMPLE 358. *On adding which of the following, the pH of 20 mL of 0.1 NHCl will not alter?*

(*a*) *1 mL of 1NHCl*

(*b*) *20 mL of distilled water*

(*c*) *1 mL of 0.1NaOH*

(*d*) *500 mL of HCl of pH = 1* **(Karnataka, CET, 2012)**

SOLUTION. For 0.1 NHCl, $[H^+] = 10^{-1}$. So, $\text{pH} = -\log [H^+] = -\log 10^{-1} = (-)(-1) \log 10 = 1 \times 1 = 1$

(*a*) $N_1V_1 + N_2V_2 = N_3 (V_1 + V_2)$

$(20 \times 0.1) + (1 \times 1) = N_3 (20 + 1); N_3 = \frac{3}{21}; [H^+] = 10^{-3/21}$

(*b*) Solution will become dilute and pH will change.

(*c*) $(20 \times 0.1) + (0.1 \times 1) = N_3 (20 + 1); N_3 = 2.1/21 = 10^{-1}; [H^+] = 10^{-1}$

$\therefore\ \text{pH} = -\log [H^+] = -\log 10^{-1} = (-)(-1) \log 10 = 1 \times 1 = 1$. This pH is same as that of given solution. So, correct answer is (*c*).

(*d*) $\text{pH} = 1 ; [H^+] = 10^{-1}$ mol L^- *i.e.*,

1000 mL solution contain $[H^+] = 10^{-1}$

$$\text{500 mL solution contain } [H^+] = \frac{10^{-1}}{1000} \times 500 = 0.5 \times 10^{-1}$$

Since $[H^+]$ is not same as that of given solution, its pH will be different from that of given solution.

EXAMPLE 359. *Which of the following acids is stronger than benzoic acid ($K_a = 6.3 \times 10^{-5}$):*

(*a*) $A\ (K_a = 1.67 \times 10^{-8}$

(*b*) $B\ (pK_a = 6.0)$

(*c*) $C\ (pK_a = 4.0)$

(*d*) $D\ (K_a = 1.0 \times 10^{-5})$

(AMU, Engg. 2012)

SOLUTION. An acid having greater value of K_a than that of benzoic acid will be stronger acid than benzoic acid.

(*a*) K_a value is less than benzoic acid

(*b*) $pK_a = 6.0; -\log K_a = 6.0: K_a = -\text{antilog } 6.0 = 1 \times 10^{-6}$. This value is less than that of benzoic acid

(*c*) $pK_a = 4.0 ; -\log K_a = 4.0 ; K_a = -\text{antilog } 4.0 = 10^{-4}$. This value is more than that of benzoic acid.

(*d*) $K_a = 10^{-5}$. Out of all K_a values, value of K_a of (*c*) is more than that of benzoic acid. So, the correct answer is (*c*).

EXAMPLE 360. *pH of 0.0002 M formic acid (HCOOH, Ka = 2 × 10^{-4}) approximately is :*

(*a*) 1.35 (*b*) 0.5

(*c*) 3.7 (*d*) 1.85

(J&K, CET, 2012)

SOLUTION.	$HCOOH + H_2O \rightleftharpoons$	H_3O^+	$+\ HCOO^-$
Moles at start	0.0002M	0	0
Change by reaction	$-x$	x	x
At equilibrium	$0.0002 - x$	x	x

$$K_c = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

$$2 \times 10^{-4} = \frac{x \times x}{0.0002 - x}$$

x being very small, it can be ignored from denominator.

$\therefore\ 2 \times 10^{-4} \times 0.0002 = x^2 ; x^2 = 4 \times 10^{-8} ; x = [4 \times 10^{-8}]^{1/2} = 2 \times 10^{-4}$

$\therefore\ [H^+] = 2 \times 10^{-4} ; \text{pH} = -\log [H^+]$

or $\text{pH} = -\log 2 \times 10^{-4} = -[\log 2 + \log 10^{-4}] = -(0.3010 - 4)$

$= 3.699 \approx 3.7$. So, the correct answer is (*c*).

EXAMPLE 361. *If 40 mg of NaOH is dissolved in 10 litre of water, what is the resulting pH of of the solution?*

(*a*) 4 (*b*) 13

(*c*) 10 (*d*) 1 **(AFMC,2012)**

SOLUTION. $40 \text{ mg} = \frac{40}{1000} g = 0.04$ g; mol. wt. of NaOH

$= 23 + 16 + 1 = 40 \text{ g mol}^-$; no. of mol of NaOH $= \frac{0.04}{40} = 0.001$.

molarity of solution $= \frac{0.001}{10} = 10^{-4}$. So, $[OH^-] = 10^{-4}$.

$$\therefore \; [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-4}} = 10^{-10}.$$

Hence pH = – log 10^{-10} = (–) (–10) log 10 = 10.

So, the correct answer is (*c*).

Example 362. *The solubility product of a sparingly soluble salt AB is* 1.21×10^{-6}. *Its molar solubility is*:

(*a*) 1.1×10^{-3} *mol* L^-
(*b*) 1.21×10^{-6} *mol* L^-
(*c*) 1.01×10^{-3} *mol* L^-
(*d*) 1.1×10^{-4} *mol* L^-

(AFMC, 2012)

Solution.

Given:	AB	$\rightleftharpoons$	A^+	+	B^-
Solubility	s		s		s

Solubility product = $[A^+]\,[B^+] = s \times s = s^2$

$\therefore \; s^2 = 1.21 \times 10^{-6}; \; s = [1.21 \times 10^{-6}]^{1/2}$

$= 1.1 \times 10^{-3}$ mol L^-

So, the correct answer is (*a*).

Example 363. *At temperature, T, a compound* $AB_2(g)$ *dissociates according to the reaction;* $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ *with a degree of dissociation, x which is small as compared to unity. The expression for* K_p *in terms of x and the partial pressure, P is:*

(*a*) $\frac{Px^3}{2}$
(*b*) $\frac{Px^2}{3}$
(*c*) $\frac{Px^3}{3}$
(*d*) $\frac{Px^2}{2}$

(AFMC,2012)

Solution.	$2AB_2$	$\rightleftharpoons$	$2AB_{(g)}$	+	$B_{2(g)}$
Initial mol.	1		0		0
At equilibrium	$1-x$		x		$x/2$

Total no. of mol = $1 - x + x + x/2 = (2 + x)/2$

$$\therefore \; K_p = \frac{p^2AB \times pB_2}{p^2AB_2}$$

$$= \frac{\left[\frac{x}{(2+x)/2}\right]^2 \times \frac{x/2}{(2+x)/2}}{\left[\frac{1-x}{(2+x)/2}\right]^2} = \frac{px^3}{(2+x)\,(1-x)^2}$$

Since $x <<< 1$, so $1 - x$ can be neglected and $2 + x \simeq 2$

$$\therefore \; K_p = \frac{Px^3}{2}.$$

So, the correct answer is (*a*).

Example 364. *How many liters of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution of pH of 2 ?*

(*a*) 0.9L
(*b*) 2.0 L
(*c*) 9.0 L
(*d*) 0.1 L **(JEE Main, 2013)**

Solution. (*i*) pH = – log [H^+] = 1. So, [H^+] = $10^{-1}\,M = M_1$

(*ii*) pH = – log [H^+] = 2. So, [H^+] = $10^{-2}\,M = M_2$

V_1 = Volume of HCl = 1 L, Let volume of water added V_2L.

$\therefore \; M_1V_1 = M_2\,(V_1 + V_2)$

$10^{-1} \times 1 = 10^{-2}\,(1 + V_2)$

$\frac{0.1}{0.01} = 1 + V_2\,;\; V_2 = 10 - 1 = 9$ L.

So the correct answer is (3)

PROBLEMS FOR PRACTICE

1. Calculate the pH of 10^4 M HCl

   [**Ans.** pH = – 4 but it is not possible because pH range is from 0 to 14.]

2. 3.65×10^{-2} g of HCl is dissolved in 100 mL of water. Calculate the pH of the solution. **(UP 1984)**

   [**Hint.** 100 mL solution contain HCl = 3.65×10^{-2} g. Hence 1000 mL solution will contain HCl = 0.365 g. Now this question is same as example, 37.]

   Ans. pH = +2

3. The concentration of H^+ ions in water is 10^{-7} g ion per litre. Even then, it is neutral. Why?

   Ans. [H^+] = [OH^-] = 10^{-7} in water. So, water is neutral.

4. The H^+ ion concentration of a solution is 0.001 M. What will be the OH^- ion concentration of the solution?

   [**Hint.** [H^+] = 0.001 = 10^{-3} ; [OH^-] = K_w/[H^+]
   = $10^{-14}/10^{-3} = 10^{-11}$] **Ans.** 10^{-11}

   (UP 1989)

5. Calculate the H^+ ion concentration of a solution, which has a pH 4.5. **(UP 1985).**

   Ans. 3.16×10^{-5} g ion L^-

6. Find the pH of the solution obtained by dissolving 3.2 g of hydrogen chloride in 1.0 L of water. **(NCERT Text book problem).**

   [**Hint.** g. mol. wt. of HCl = 1 + 35.5 = 36.5 g ;
   [H^+] = 3.2/36.5 = 8.77×10^{-2} ; *p*H = **1.057 Ans.**]

7. When 0.001 mol of a base is added to 250 mL of a buffer solution, the pH of a buffer solution increases by 0.01 units. Calculate the buffer capacity of the system.

   [**Hint.** Buffer capacity = $\left(\frac{0.001 \times 1000}{250}\right) \times \frac{1}{0.01}$
   = 0.4 units. Ans.]

8. Calculate the pH of a buffer solution containing 0.25 mol NH_4Cl and 0.15 mol NH_4OH ($K_b = 1.8 \times 10^{-5}$).

   Ans. 9.034

9. Calculate the hydrolysis constant of a salt containing NO_2^- ions. [K_a (HNO_2) = 4.5×10^{-5}]. **Hint.** $K_h = K_w/K_a$ = $10^{-14}/4.5 \times 10^{-10}$). **Ans. 2.2×10^{-5}**

10. Calculate the solubility of silver chloride in 0.1M KCl. Given K_{sp} for AgCl equal to 2.8×10^{-10} at 25°C.

Ans. 2.8×10^{-9} mol L^{-}

11. The solubility of silver chromate (Ag_2CrO_4) is 2.2×10^{-2} gL^{-}. Determine the solubility product of Ag_2CrO_4. **Ans. 1.1×10^{-12} mol^3 L^{-3}**

12. Determine the solubility of Hg_2I_2 at 298K if K_{sp} (Hg_2I_2) = 4.5×10^{-29}. (**Hint.** $Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$)

Ans. $[Hg_2^{2+}] = 2.24 \times 10^{-10}$ M ; $[I^-] = 4.48 \times 10^{-10}$

13. The solubility of $PbSO_4$ in water is 0.038 gL^{-} at 25°C. Calculate its solubility product at the same temperature (mol. wt. of $BaSO_4$ = 303).

Ans. 1.57×10^{-8}

(UP 1981)

[**Hint,** solubility = $\dfrac{0.038}{303}$ mol L^{-}]

14. The equivalent conductivity of a weak acid at dilution of 256000 cm^3 is 23.82 ohm^{-} cm^2 $(equiv)^{-}$ at 298 K. At infinite dilution, it is 364 ohm^{-} cm^2 $(equiv)^{-}$. Calculate the dissociation constant of the acid. (**Hint.** $K = \alpha^2/(1-\alpha)V$ where $V = 256{,}000/1000$ = 256L ; $a = 23.82/364 = 0.0654$). **Ans. 1.788×10^{-7}**

15. 10^{-2} mol of NaOH was added to 10 litre of water. The *p*H of the solution will change by :

(*a*) *4* (*b*) *3*
(*c*) *2* (*d*) *1* **Ans.** (*a*)

16. 0.023 g of sodium metal is reacted with 100 cm^3 of water. The pH of resulting solution is:

(*a*) 10 (*b*) 11
(*c*) 9 (*d*) 12 **Ans.** (*d*)

(Karnataka CET, 2010)

17. A buffer solution contains 0.1 mol of sodium acetate in 100 cm^3 of 0.1 M acetic acid. To the above buffer solution, 0.1 mol of sodium acetate is further added and dissolved. The pH of the resulting buffer is:

(*a*) $pK_a - \log 2$ (*b*) pK_a
(*c*) $pK_a + 2$ (*d*) $pK_a + \log 2$

Ans. (*d*) **(Karnataka CET, 2010)**

18. One dm^3 solution containing 10^{-5} mol each of Cl^- ions and CrO_4^{2-} ions is treated with 10^{-4} mol of silver nitrate. Which one of the following observations is made; K_{sp} $Ag_2CrO_4 = 4 \times 10^{-12}$; K_{sp} (AgCl) = 1×10^{-10}

(*a*) Precipitation does not occur
(*b*) Ag_2CrO_4 is precipitated first
(*c*) AgCl is precipitated first
(*d*) Both Ag_2CrO_4 and AgCl get precipitated simultaneously. **Ans.** (*c*)

(Karnataka CET 2010)

19. The pH value of which of the following is not equal to one?

(*a*) 0.1 M HNO_3 (*b*) 0.05 M H_2SO_4
(*c*) 0.1 M CH_3COOH
(*d*) 50 cm^3 of 0.4 M HCl + 50 cm^3 of 0.2 M NaOH

Ans. (*c*)

(Karnataka CET, 2010)

20. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 Mg^{2+} ions?

(*a*) 8 (*b*) 9
(*c*) 10 (*d*) 11 **Ans.** (*c*)

(AIEEE, 2010)

21. Solubility product of $Mg(OH)_2$ is 4×10^{-12} mol L^{-}. Solubility of $Mg(OH)_2$ is:

(*a*) 4×10^{-4} mol L^{-} (*b*) 1×10^{-12} mol L^{-}
(*c*) 1×10^{-4} mol lit^{-} (*d*) 2×10^{-6} mol L^{-}

Ans. (*c*) **(Orissa JEE, 2010)**

22. The pH of 10^{-3} M NaOH is

(*a*) 3 (*b*) 11
(*c*) 4 (*d*) 12 **Ans.** (*b*)

(Orissa JEE, 2010)

23. The concentration of $[H^+]$ and $[OH^-]$ of 0.1 M aqueous solution of 2% ionised weak acid is: [K_{sp} (H_2O) = 1×10^{-14}]

(*a*) 2×10^{-3} and 5×10^{-12} M
(*b*) 1×10^{-3} M and 3×10^{-11} M
(*c*) 0.02×10^{-3} M and 5×10^{-11} M
(*d*) 3×10^{-2} M and 4×10^{-13} M **Ans.** (*a*)

(BHU, 2010)

24. If pH of a saturated solution of $Ba(OH)_2$ is 12, the value of its K_{sp} is:

(*a*) 4.0×10^{-6} M^3 (*b*) 4.0×10^{-7} M^3
(*c*) 5.0×10^{-6} M^3 (*d*) 5.0×10^{-7} M^3

Ans. (*d*) **(CBSE, PMT, 2010)**

25. In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is:

(*a*) 10 (*b*) 7
(*c*) 6 (*d*) 4 **Ans.** (*d*)

(CBSE, PMT, 2010)

25

CHAPTER

Estimation of Elements in Organic Compounds

25.1 ESTIMATION OF CARBON AND HYDROGEN BY LIEBIG'S METHOD

A known weight of an organic compound is burnt in excess of oxygen. Carbon and hydrogen present in it get oxidised to CO_2 and H_2O respectively.

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

The weights of CO_2 and water are determined from the increase in the weights of potash bulbs and $CaCl_2$ u-tube respectively. From the weights of CO_2 and H_2O formed, the percentage of carbon and hydrogen are then calculated.

EXAMPLE 1. *In a Liebig's method, an organic compound weighing 0.198 g produced 0.524 g CO_2 and 0.132 g H_2O. Calculate the percentage of carbon and hydrogen in the given compound.*

SOLUTION. Wt. of compound = 0.198 g;

wt. of CO_2 = 0.524 g;

wt. of H_2O = 0.132 g.

(*i*) *To find % age of carbon.* $\underset{12+(2\times16)=44g}{CO_2} \equiv \underset{12g}{C}$

44 g CO_2 contain carbon

= 12g

0.524 g CO_2 contain carbon

$$= \frac{12}{44} \times 0.524 \text{ g}$$

∴ % age of carbon

$$= \frac{\text{wt. of C}}{\text{wt. of substance}} \times 100$$

$$= \frac{12 \times 0.524}{44} \times \frac{100}{0.198}$$

= **72.18%** **Ans.**

(*ii*) *To find % age of hydrogen.* $\underset{(2\times1)+16=18\,g}{H_2O} \equiv \underset{2\,g}{2H}$

18g H_2O contain hydrogen

= 2 g

0.132g H_2O contain hydrogen

$$= \frac{2}{18} \times 0.132 \text{ g}$$

∴ % age of hydrogen

$$= \frac{\text{wt. of H}}{\text{wt. of substance}} \times 100$$

$$= \frac{2 \times 0.132}{18} \times \frac{100}{0.198} = \mathbf{7.4\%}$$ **Ans.**

EXAMPLE 2. *An organic compound contains carbon, hydrogen and oxygen. In a Liebig's method, 0.2475 g of it was analysed. The increase in the weight of U-tube and the potash bulb at the end of operation was found to be 0.2025 g and 0.4950 g respectively. Calculate the percentage composition of the compound.*

SOLUTION. Wt. of compound = 0.2475 g;

wt. of CO_2 = increase in the wt. of potash bulb

= 0.4950 g;

wt. of H_2O = increase in the wt. of U-tube (containing $CaCl_2$) = 0.2025 g.

(*i*) *To find % age of carbon.* $\underset{12+(2\times16)=44g}{CO_2} \equiv \underset{12g}{C}$

44 g CO_2 contain carbon = 12 g

0.495 g CO_2 contain carbon $= \frac{12}{44} \times 0.495$ g

$$\%\text{ age of C} = \frac{\text{wt. of C}}{\text{wt. of substance}} \times 100$$

$$= \frac{12 \times 0.495}{44} \times \frac{100}{0.2475}$$

= **54.54%** **Ans.**

(*ii*) *To find percentage of hydrogen.* $\underset{(2\times1)+16=18\,g}{H_2O} \equiv \underset{2\times1=2\,g}{2H}$

18 g H_2O contain hydrogen = 2 g

0.2025 g H_2O contain hydrogen $= \frac{2}{18} \times 0.2025$ g

$$\therefore \quad \%\text{ age of hydrogen} = \frac{\text{wt. of hydrogen}}{\text{wt. of substance}} \times 100$$

$$= \frac{2\times 0.2025}{18}\times\frac{100}{0.2475} = 9.09\%$$

∴ % age of oxygen $= 100 - (54.54 + 9.09)$

$= \mathbf{36.37\%}$ **Ans.**

Example 3. *An organic compound contains 52.18% carbon and 13.04% hydrogen, the rest being oxygen. Calculate the masses of CO_2 and H_2O produced when 0.2346 g of this compound is subjected to complete combustion.*

Solution. We know that :

(*i*) % age of carbon

$$= \frac{12}{44}\times\frac{\text{mass of } CO_2 \text{ formed}}{\text{mass of organic compound}}\times 100$$

$$\left[\because \underset{12+(2\times 16)=44\,g}{CO_2} \equiv \underset{12\,g}{C}\right]$$

$$\therefore \quad 52.18 = \frac{12}{44}\times\frac{\text{mass of } CO_2 \text{ formed}}{0.2346}\times 100$$

$$\therefore \quad \text{Mass of } CO_2 \text{ formed} = \frac{52.18\times 44\times 0.2346}{12\times 100}$$

$= \mathbf{0.4488\ g}$ **Ans.**

(*ii*) % age of hydrogen

$$= \frac{2}{18}\times\frac{\text{mass of } H_2O \text{ formed}}{\text{mass of organic compound}}\times 100$$

$$\left[\because \underset{(2\times 1)+16=18\,g}{H_2O} \equiv \underset{2\times 1=2\,g}{2H}\right]$$

$$13.04 = \frac{2}{18}\times\frac{\text{mass of } H_2O \text{ formed}}{0.2346}\times 100$$

$$\therefore \text{Mass of } H_2O \text{ formed} = \frac{13.04\times 18\times 0.2346}{2\times 100} = \mathbf{0.2753\ g.}$$

25.2 ESTIMATION OF NITROGEN BY DUMA'S METHOD

A known weight of organic compound is mixed with CuO and heated in an atmosphere of CO_2. Volume of N_2 gas set free is collected over 40% KOH to absorb CO_2 and H_2O formed. This N_2 gas is now converted to N.T.P.

$$C_xH_yN_z + \left(2x+\frac{y}{2}\right)CuO \rightarrow xCO_2 +$$

$$\frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x+\frac{y}{2}\right)\text{Cu compound}$$

Example 4. *0.2 g of an organic compound on combustion with CuO, gave 30.1 cm^3 of moist nitrogen at 15°C and 730.7 mm pressure. Calculate the percentage of nitrogen in the compound. (Aqueous tension at 15°C = 12.7 mm).*

Solution. Wt. of organic compound = 0.2 g.

$P_1 = 730.7 - 12.7 = 718$ mm, $V_1 = 30.1$ cm^3, $T_1 = 15 + 273 = 288$ K; at NTP, $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K.

$$\text{We know, } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (Gas equation)}$$

$$\therefore \quad V_2 = \frac{P_1V_1T_2}{T_1\times P_2} = \frac{718\,\text{mm}\times 30.1\,\text{cm}^3\times 273\text{ K}}{288\text{ K}\times 760\,\text{mm}}$$

$= 26.96$ mL

But, 22400 mL of

N_2 weighs = g. mol. wt. of N_2 = 28 g

26.96 mL of

$$N_2 \text{ weighs} = \frac{28}{22400}\times 26.96 \text{ g}$$

$$\therefore \quad \%\text{ age of } N_2 = \frac{28\times 26.96}{22400}\times\frac{100}{0.2} = \mathbf{16.85\%} \quad \textbf{Ans.}$$

Example 5. *An organic compound having molecular formula C_4H_9N was analysed by Duma's method for the estimation of nitrogen in this compound. Calculate the volume of nitrogen liberated at N.T.P. from 2.1 g of the substance (at. wt., C = 12, H = 1, N = 14).*

Solution. Mol. wt. of

$C_4H_9N = (4 \times 12) + (9 \times 1) + 14 = 71$

Reaction :

$$\underset{1\,\text{mol}=71\,g}{C_4H_9N} \xrightarrow[\Delta]{CuO} 4CO_2 + \frac{9}{2}H_2O + \underset{\frac{1}{2}\text{mol}=\frac{1}{2}\times 22400=11200\text{ mL at NTP}}{\frac{1}{2}N_2}$$

71 g of C_4H_9N produce

N_2 at NTP = 11200 mL

∴ 2.1 g of C_4H_9N would produce

$$N_2 \text{ at NTP} = \frac{11200}{71}\times 2.1 = \mathbf{331.3\ mL}$$

Volume of

N_2 at N.T.P. = **331.3 mL** **Ans.**

Example 6. *An organic compound containing carbon, hydrogen, oxygen and nitrogen gave the following results on analysis. 0.27 g of the compound gave 0.396 g of CO_2 and 0.216 g water. 0.36 g of the same compound gave 48.88 mL of N_2 at 17°C and 740 mm pressure by Duma's method. Calculate the percentage composition of the compound.*

Solution. (*i*) Wt. of compound = 0.27 g

(*a*) *To find % age of C.* $\underset{12+(2\times 16)=44\,g}{CO_2} \equiv \underset{12\,g}{C}$

44 g CO_2 contain carbon = 12 g

$$0.396 \text{ g } CO_2 \text{ contain carbon} = \frac{12}{44}\times 0.396 \text{ g}$$

$$\therefore \quad \%\text{ age of C} = \frac{12\times 0.396}{44}\times\frac{100}{0.27}$$

$= \mathbf{40\%}$ **Ans.**

(*b*) *To find % age of hydrogen.* $\underset{(2\times 1)+16=18\,g}{H_2O} \equiv \underset{2\times 1=2\,g}{2H}$

18 g H_2O contain H = 2 g

$$0.216 \text{ g } H_2O \text{ contain H} = \frac{2}{18} \times 0.216 \text{ g}$$

$$\therefore \text{ \% age of H} = \frac{2 \times 0.216}{18} \times \frac{100}{0.27} = \mathbf{8.89\%}$$

(*c*) *To find % age of nitrogen.*

Wt. of substance = 0.36 g; $P_1 = 740$ mm, $V_1 = 48.88$ mL, $T_1 = 17 + 273 = 290$ K; at N.T.P., $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K. We know,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (gas equation);}$$

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$\therefore \quad V_2 = \frac{740 \text{ mm} \times 48.88 \text{ mL} \times 273 \text{ K}}{290 \text{ K} \times 760 \text{ mm}}$$

$$= 44.8 \text{ mL}$$

22400 mL of N_2 at N.T.P. weighs

$$= \text{g. mol. wt. of } N_2 = 2 \times 14 = 28 \text{ g}$$

44.8 mL of N_2 at N.T.P. weighs

$$= \frac{28}{22400} \times 44.8 \text{ g}$$

$$\therefore \text{ \% age of nitrogen} = \frac{28 \times 44.8}{22400} \times \frac{100}{0.36} = \mathbf{15.56\%}$$

Ans.

$$\therefore \text{ \% age of oxygen} = 100 - (40 + 8.89 + 15.56)$$

$$= \mathbf{35.55\%}$$ **Ans.**

25.3 ESTIMATION OF NITROGEN BY KJELDAHL'S METHOD

A known weight of organic compound is digested with conc. H_2SO_4 to convert nitrogen present in the compound to $(NH_4)_2SO_4$. The latter is heated with alkali to get ammonia gas which is passed through excess of standard acid. The volume of unreacted acid is determined with standard alkali. From the amount of NH_3 evolved, the percentage of nitrogen is calculated.

Example 7. *0.45 g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 20 mL of 0.1 M H_2SO_4. Calculate the percentage of nitrogen in the compound.*

SOLUTION. Wt. of organic compound = 0.45 g.

Volume of 0.1 M H_2SO_4 required to neutralise NH_3 = 20 mL.

$$\underset{\substack{2\text{mol}\\2\text{vol}}}{2NH_3} + \underset{\substack{1\text{mol}\\1\text{vol}}}{H_2SO_4} \rightarrow (NH_4)_2SO_4$$

20 mL of 0.1 M H_2SO_4 = 2 × 20 mL of 0.1 M NH_3 = 40 mL of 0.1 M NH_3

$$= \frac{40 \times 0.1 \text{M}}{1 \text{M}}$$

$$= 4 \text{ mL of 1 M } NH_3$$

But 1000 mL of 1 M NH_3 = 14 g N

$$\therefore \quad 4 \text{ mL of 1 M } NH_3 = \frac{14}{1000} \times 4 \text{ gN}$$

$$\therefore \quad \text{\% age of nitrogen} = \frac{14 \times 4}{1000} \times \frac{100}{0.45} = \mathbf{12.4\%} \quad \textbf{Ans.}$$

or 1000 mL of 1 M NH_3 = 14 g N

$$40 \text{ mL of 0.1 M } NH_3 = \frac{14}{1000} \times 40 \times 0.1 = 0.056 \text{ g of N.}$$

$$\therefore \quad \text{\%age of nitrogen} = \frac{0.056}{0.45} \times 100 = \mathbf{12.4\%} \quad \textbf{Ans.}$$

Example 8. *An organic compound weighing 0.354 g on analysis by Kjeldahl's method gave ammonia which was absorbed in 70 mL of M/10 H_2SO_4. The excess of the acid required 40 mL of M/5 NaOH for complete neutralisation. (i) The percentage of nitrogen in the compound and (ii) amount of NH_3 formed is:*

(*a*) 25, 0.4
(*b*) 27, 0.5
(*c*) 23.73, 0.102
(*d*) 18.1, 0.9
(*e*) 11.11, 0.8

(Kerala, PMT, 2012)

Solution. (*i*) Volume of H_2SO_4 of molarity M/10 taken = 70 mL.

$$\frac{(M_1V_1) \text{ Residual } H_2SO_4}{(M_2V_2) \text{NaOH}} = \frac{1}{2}$$

$$\left(\because \ \underset{2\text{mol}}{2\text{NaOH}} + \underset{1\text{mol}}{H_2SO_4} \rightarrow Na_2SO_4 + 2H_2O \right)$$

$$\frac{\frac{1}{10} \times V_1}{40 \times \frac{1}{5}} = \frac{1}{2}; \ V_1 = 40 \times \frac{1}{5} \times \frac{10}{2} = 40 \text{ mL}$$

$\therefore$ Volume of M/10 acid left unused = 40 mL

Volume of M/10 H_2SO_4 used by NH_3

$$= 70 - 40 = 30 \text{ mL}$$

$$\therefore \quad 30 \text{ mL of } \frac{M}{10} H_2SO_4 \equiv 2 \times 30 \text{ mL of } \frac{M}{10} NH_3$$

$$= 60 \text{ mL of } \frac{M}{10} NH_3$$

$$(\because 2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4)$$

But, 1000 mL of
1 M NH_3 contain nitrogen = 14 g

$$60 \text{ mL of } \frac{M}{10} H_2SO_4 \text{ contain nitrogen} = \frac{14}{1000} \times 60 \times \frac{1}{10} \text{g}$$

$$\therefore \quad \text{\% age of nitrogen} = \frac{14 \times 60}{1000} \times \frac{1}{10} \times \frac{100}{0.354}$$

$$= \mathbf{23.73\%}$$ **Ans.**

(*ii*) *To find weight of NH_3 formed*

1000 mL of 1 M NH_3 contain NH_3

$$= \text{g. mol. wt. of } NH_3 = 14 + (3 \times 1) = 17 \text{ g}$$

∴ 60 mL of $\frac{M}{10}$ NH_3 contain NH_3

$$= \frac{17}{1000} \times 60 \times \frac{1}{10} = \mathbf{0.102\ g}$$

∴ **Wt. of NH_3 formed = 0.102g** **Ans.**

So, the correct answer is (*c*).

EXAMPLE 9. *An organic compound weighing 0.4 g was Kjeldahlised and ammonia gas produced was absorbed in 50 mL of M/4 H_2SO_4. The residual acid solution was diluted with distilled water and the volume was made up to 150 mL. The 20 mL of this diluted solution required 31mL of 0.05 M NaOH for complete neutralisation. Calculate the percentage of nitrogen in the compound.*

SOLUTION.

Wt. of compound = 0.4 g.

Volume of $\frac{M}{4}$ H_2SO_4 required to absorb ammonia

= 50 mL

(*i*) $\underset{2\,\text{mol}}{2NaOH} + \underset{1\,\text{mol}}{H_2SO_4} \rightarrow Na_2SO_4 + 2H_2O$

$$\frac{M_1V_1 \text{ (diluted acid)}}{M_2V_2 \text{ (NaOH)}} = \frac{1\,\text{mol}}{2\,\text{mol}}; M_1 \times 20 = \frac{0.05 \times 31}{2};$$

$$M_1 \text{ (dil. acid)} = \frac{0.05 \times 31}{2 \times 20}$$

(*ii*) To find volume of $\frac{M}{4}$ original H_2SO_4 left used

$$M_3V_3 \text{ (dil. acid)} = M_4V_4 \text{ (original acid)}$$

$$\frac{0.05 \times 31}{2 \times 20} \times 150 = \frac{1}{4} \times V_4;$$

$$V_4 = \frac{0.05 \times 31 \times 150 \times 4}{2 \times 20} = 23.25 \text{ mL}$$

∴ Volume of $\frac{M}{4}$ H_2SO_4 used = 50 – 23.25 = 26.75 mL

Now, 26.75 mL of $\frac{M}{4}$ H_2SO_4 = 2 × 26.75 mL of $\frac{M}{4}$ NH_3

$$\left(\because \underset{2\,\text{mol}}{2NH_3} + \underset{1\,\text{mol}}{H_2SO_4} \rightarrow (NH_4)_2SO_4 \right)$$

But, 1000 mL of 1M NH_3 contain nitrogen

= g. at. wt. of N = 14 g

∴ 2 × 26.75 mL of $\frac{1}{4}$ M NH_3 contain nitrogen

$$= \frac{14}{1000} \times 2 \times 26.75 \times \frac{1}{4} \text{g}$$

$$\therefore \quad \text{\% age of nitrogen} = \frac{14 \times 2 \times 26.75}{1000 \times 4} \times \frac{100}{0.4}$$

= **46.81%** **Ans.**

Type. To find % age of N_2 when normality of H_2SO_4 is given.

EXAMPLE 10. *Ammonia gas evolved in Kjeldahl estimation from 1.61 g of organic compound, was passed through 250 mL of seminormal H_2SO_4. The residual acid was diluted to one litre with distilled water. 25 mL of the diluted acid required 25.5 mL of decinormal NaOH for complete neutralisation. Calculate the percentage of nitrogen in the organic compound and also the amount of ammonia produced.*

SOLUTION. Wt. of organic compound = 1.61 g

Volume of original $\frac{N}{2}$ H_2SO_4 taken = 250 mL

(*i*) *To find normality of diluted H_2SO_4.*

Diluted acid NaOH solution

$$N_1V_1 = N_2V_2$$

$$N_1 \times 25 = \frac{1}{10} \times 25.5;$$

$$N_1 = \frac{25.5}{10 \times 25} = 0.102$$

(*ii*) *To find volume of used $\frac{N}{2}$ H_2SO_4 by NH_3*

Diluted acid Original acid

$$N_3V_3 = N_4V_4$$

$$0.102 \times 1000 = \frac{1}{2} \times V_4;$$

$$V_4 = 2 \times 0.102 \times 1000 = 204 \text{ mL}$$

Volume of unused $\frac{N}{2}$ H_2SO_4 = 204 mL

∴ Volume of used $\frac{N}{2}$ H_2SO_4 = 250 – 204 = 46 mL

∴ 46 mL of $\frac{N}{2}$ H_2SO_4 ≡ 46 mL of $\frac{N}{2}$ NH_3.

(*iii*) *To find % age of nitrogen.*

1000 mL of 1N NH_3 contain nitrogen

= g. at. wt. of N = 14 g

∴46 mL of $\frac{N}{2}$ NH_3 contain nitrogen

$$= \frac{14}{1000} \times 46 \times \frac{1}{2} \text{g}$$

$$\therefore \quad \text{\% age of nitrogen} = \frac{14 \times 46 \times 1}{1000 \times 2} \times \frac{100}{1.61} = \mathbf{20\%} \quad \textbf{Ans.}$$

(*iv*) *To find amount of ammonia NH_3.*

[mol. wt. = 14 + (3 × 1) = 17g]

1000 mL of 1N NH_3 ≡ g. eq. wt. of NH_3 = 17g

$$\therefore \quad 46 \text{ mL of } \frac{N}{2} NH_3 \equiv \frac{17}{1000} \times 46 \times \frac{1}{2} = \mathbf{0.391\ g}$$

Ans.

EXAMPLE 11. *0.236 g of an organic compound on distillation with caustic soda solution yielded ammonia which required 40 mL of decinormal sulphuric acid for complete neutralisation. Calculate the percentage of nitrogen in the compound.*

Solution.

Wt. of substance = 0.236 g

$$40 \text{ mL of } \frac{N}{10} H_2SO_4 \equiv 40 \text{ mL of } \frac{N}{10} NH_3$$

But, 1000 mL of 1 N NH_3 contain nitrogen

= g. at. wt. of nitrogen = 14 g

∴ 40 mL of $\frac{N}{10}$ NH_3 contain nitrogen

$$= \frac{14}{1000} \times 40 \times \frac{1}{10} = 0.056 \text{ g}$$

$$\therefore \quad \% \text{ age nitrogen} = \frac{\text{wt. of nitrogen}}{\text{wt. of substance}} \times 100$$

$$= 0.056 \times \frac{100}{0.236} = \mathbf{23.73\%} \textbf{ Ans.}$$

Example 12. *0.26 g of an organic compound was Kjeldahlised and NH_3 gas evolved was absorbed in 45 mL of decinormal hydrochloric acid which further required 18.0 mL of decinormal NaOH for complete neutralisation. Calculate the percentage of nitrogen in the compound.*

Solution. Wt. of organic compound = 0.26 g

(*i*) *To find volume of HCl used by NH_3.*

$$\begin{aligned} &\text{HCl} \quad \text{NaOH} \\ N_1V_1 &= N_2V_2 \text{ (normality equation)} \\ \frac{1}{10} \times V_1 &= \frac{1}{10} \times 18\,; \\ V_1 &= \frac{1}{10} \times 18 \times 10 = 18 \text{ mL} \end{aligned}$$

∴ Volume of unused

HCl = 18 mL

Hence, volume of used

HCl by NH_3 = 45 – 18 = 27 mL

$$27 \text{ mL of } \frac{N}{10} \text{ HCl} = 27 \text{ mL of } \frac{N}{10} NH_3$$

But, 1000 mL of 1N NH_3 contain nitrogen

= g. at. wt. of nitrogen = 14 g

∴ 27 mL of $\frac{N}{10}$ NH_3 contain nitrogen

$$= \frac{14}{1000} \times 27 \times \frac{1}{10} \text{g}$$

$$\% \text{ age of nitrogen} = \frac{14 \times 27}{1000 \times 10} \times \frac{100}{0.26}$$

$$= \mathbf{14.54\%} \qquad \textbf{Ans.}$$

25.4 ESTIMATION OF HALOGENS (Cl, Br AND I) BY CARIUS METHOD

A known weight of organic compound is heated with fuming nitric acid and solid $AgNO_3$ in a sealed tube called carius tube. The halogens (Cl, Br or I) present in the organic compound changes into silver halide (AgCl, AgBr or AgI) precipitate. The latter is separated, washed, dried and weighed. From the weight of silver halide, the percentage of halogen in the compound is calculated.

Example 13. *In a carius method, 0.24 g of an organic substance was heated with fuming nitric acid and solid $AgNO_3$. As a result, 0.31 g of dry silver chloride was obtained. Calculate the percentage of Cl in the given substance. (at. wt., Ag = 108, Cl = 35.5).*

Solution. Wt. of organic substance= 0.24 g.

Wt. of AgCl ppt = 0.31 g.

$$\text{We know,} \quad \underset{108+35.5=143.5\text{g}}{\text{AgCl}} \equiv \underset{35.5\text{g}}{\text{Cl}}$$

143.5 g AgCl contain Cl= 35.5 g

$$0.31 \text{ g AgCl contain Cl} = \frac{35.5}{143.5} \times 0.31\text{g}$$

$$\% \text{ age of Cl} = \frac{\text{wt. of Cl}}{\text{wt. of substance}} \times 100$$

$$= \frac{35.5 \times 0.31}{143.5} \times \frac{100}{0.24}$$

$$= \mathbf{31.95\%} \qquad \textbf{Ans.}$$

Example 14. *In a carius method, 0.31 g of an organic compound yielded 0.296 g of silver bromide. Calculate the percentage of bromine in the organic compound. (At. wt. Ag = 108, Br = 80).*

Solution. Wt. of

organic substance = 0.31 g.

Wt. of AgBr ppt = 0.296 g

$$\text{We know :} \quad \underset{108+80=188\text{g}}{\text{AgBr}} \equiv \underset{80\text{g}}{\text{Br}}$$

188 g AgBr contain Br = 80 g;

$$0.296 \text{ g AgBr contain Br} = \frac{80}{188} \times 0.296\text{g}$$

$$\% \text{ age of Br} = \frac{\text{wt. of Br}}{\text{wt. of substance}} \times 100$$

$$= \frac{80 \times 0.296}{188} \times \frac{100}{0.31}$$

$$= \mathbf{40.63\%} \qquad \textbf{Ans.}$$

Example 15. *An organic compound weighing 0.197 g was heated with fuming nitric acid and solid $AgNO_3$ in a carius tube. As a result, 0.3525 g of dry silver iodide was obtained. Calculate the percentage of iodine in the given compound.*

(At. wt. Ag = 108, I = 127).

Solution. Wt. of

organic compound = 0.197 g;

Wt. of Ag I ppt = 0.3525 g

$$\text{We know :} \quad \underset{108+127=235\text{g}}{\text{Ag I}} \equiv \underset{127\text{g}}{\text{I}}$$

235 g Ag I contain I = 127 g

$$0.3525 \text{ g Ag I contain I} = \frac{127}{235} \times 0.3525\text{g}$$

$$\therefore \quad \%\text{ age of I} = \frac{\text{wt. of I}}{\text{wt. of substance}} \times 100$$

$$= \frac{127 \times 0.3525}{235 \times 0.197} \times 100$$

$$= \mathbf{96.7\%}$$ **Ans.**

25.5 ESTIMATION OF SULPHUR BY CARIUS METHOD

A known weight of organic compound is heated with fuming nitric acid in a carius tube. Sulphur present in the organic substance is oxidised to sulphuric acid. The resulting solution is treated with excess of barium chloride solution to get barium sulphate precipitate. From the weight of dry $BaSO_4$ ppt, the percentage of sulphur can be calculated.

Example 16. *An organic compound weighing 0.3198 g was heated with fuming nitric acid in a carius tube. The resulting solution was treated with excess of* $BaCl_2$ *solution to get 0.2330 g dry* $BaSO_4$*. Calculate the percentage of sulphur in the organic compound (at. wt., Ba = 137, S = 32, O = 16).*

Solution. Wt. of organic substance = 0.3198 g;
Wt. of $BaSO_4$ = 0.233 g

$$\underset{\substack{137+32+(4\times16)\\=233\text{ g}}}{BaSO_4} \equiv \underset{32\text{g}}{S}$$

233 g $BaSO_4$ contain sulphur = 32 g

$$0.233 \text{ g } BaSO_4 \text{ contain sulphur} = \frac{32}{233} \times 0.233 \text{ g}$$

$$\%\text{ age of sulphur} = \frac{\text{wt. of S}}{\text{wt. of substance}} \times 100$$

$$= \frac{32 \times 0.233}{233} \times \frac{100}{0.3198}$$

$$= \mathbf{10.0\%}$$ **Ans.**

Example 17. *An organic compound contains C, H, O and sulphur. Its analysis was done as under :*

(i) 0.167 g of it on combustion gave 0.456 g CO_2 *and 0.0666 g* H_2O.

(ii) 0.125 g of the substance on being heated with nitric acid and barium chloride gave 0.13 g barium sulphate. Calculate the percentage of C, H, O and sulphur in the given compound.

Solution. (*i*) Wt. of organic substance = 0.167 g;
Wt. of CO_2 = 0.456 g

$$\underset{12+(2\times16)=44\text{ g}}{CO_2} \equiv \underset{12\text{g}}{C}$$

44 g CO_2 contain carbon = 12 g

$$0.456 \text{ g } CO_2 \text{ contain carbon} = \frac{12}{44} \times 0.456 \text{ g}$$

$$\%\text{ age of carbon} = \frac{\text{wt. of C}}{\text{wt. of substance}} \times 100$$

$$= \frac{12 \times 0.456}{44} \times \frac{100}{0.167} = \mathbf{74.47\%}$$

(*ii*) Wt. of substance = 0.167 g;
Wt. of H_2O = 0.0666 g

$$\underset{(2\times1)+16=18\text{g}}{H_2O} \equiv \underset{2\times1=2\text{g}}{2H}$$

18 g water contain H = 2 g

0.0666 g water contains

$$H = \frac{2}{18} \times 0.0666 \text{g}$$

$$\therefore \quad \%\text{ age of hydrogen} = \frac{\text{wt. of H}}{\text{wt. of substance}} \times 100$$

$$= \frac{2 \times 0.0666}{18} \times \frac{100}{0.167} = 4.43\%$$

(*iii*) Wt. of substance = 0.125 g;
Wt. of $BaSO_4$ = 0.13 g

$$\underset{\substack{137+32+(4\times16)\\=233\text{ g}}}{BaSO_4} \equiv \underset{32\text{g}}{S}$$

233 g $BaSO_4$ contain sulphur = 32 g;

$$0.13 \text{ g } BaSO_4 \text{ contain sulphur} = \frac{32}{233} \times 0.13 \text{g}$$

$$\therefore \quad \%\text{ age of sulphur} = \frac{\text{wt. of S}}{\text{wt. of substance}} \times 100$$

$$= \frac{32 \times 0.13}{233} \times \frac{100}{0.125} = 14.28\%$$

(*iv*) $\therefore$ % age of oxygen = 100 – (74.47 + 4.43 + 14.28)
= **6.82%** **Ans.**

25.6 ESTIMATION OF PHOSPHORUS BY CARIUS METHOD

A known weight of organic compound is heated with fuming nitric acid in a carius tube to get phosphoric acid. The latter is treated with magnesia mixture ($MgCl_2$ + NH_4Cl + NH_4OH) to get precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$. The latter precipitate is heated to get magnesium pyrophosphate $Mg_2P_2O_7$ from which the percentage of phosphorus can be calculated.

Example 18. *0.298 g of an organic compound containing phosphorus gave 0.5314 g* $Mg_2P_2O_7$*, in a carius estimation. Calculate the percentage of phosphorus in this compound. (At. wt., Mg = 24, P = 31, O = 16).*

Solution. Wt. of organic substance = 0.298 g;
Wt. of $Mg_2 P_2O_7$ = 0.5314 g

$$\underset{\substack{(2\times24)+(2\times31)+(7\times16)\\=222\text{g}}}{Mg_2P_2O_7} \equiv \underset{2\times31=62\text{g}}{2P}$$

222 g $Mg_2P_2O_7$ contain phosphorus = 62 g

$$0.5314 \text{ g } Mg_2P_2O_7 \text{ contain phosphorus} = \frac{62}{222} \times 0.5314 \text{ g}$$

$$\therefore \text{ \% age of phosphorus} = \frac{\text{Wt. of P}}{\text{Wt. of substance}} \times 100$$

$$= \frac{62 \times 0.5314 \times 100}{222 \times 0.298}$$

$$= \mathbf{49.8\%} \qquad \textbf{Ans.}$$

Note: Oxygen element can be estimated as:

$$\text{\% age of oxygen} = 100 - \left[\begin{array}{l}\text{sum total of \% ages of all the other} \\ \text{elements in the given organic compound.}\end{array}\right]$$

25.7 AIEEE PATTERN EXAMPLES

Example 19. *In a Liebig's method to estimate carbon in an organic compound, 0.2 g of the latter produced 0.532g CO_2. The percentage of carbon in this compound is :*

(1) 36.27 *(2) 72.54*

(3) 90 *(4) 45*

Solution. Wt. of organic substance = 0.2 g;

Wt. of CO_2 = 0.532g

$$\underset{\substack{12+(2\times16)\\=44\,g}}{CO_2} \equiv \underset{12g}{C}$$

44 g CO_2 contain carbon = 12 g

0.532 g CO_2 contain carbon

$$= \frac{12}{44} \times 0.532 \text{ g}$$

$$\therefore \quad \text{\% age of carbon} = \frac{\text{wt. of C}}{\text{wt. of substance}} \times 100$$

$$= \frac{12 \times 0.532}{44 \times 0.2} \times 100 = \mathbf{72.54\%}$$

So, the correct answer is (2)

Example 20. *0.316 g of an organic compound containing hydrogen and carbon produced 0.272 g water. The % age of hydrogen in the compound is*

(1) 9.56 *(2) 4.78*

(3) 2.39 *(4) 19.12*

Solution. Wt. of organic substance = 0.316 g

Wt. of H_2O = 0.272 g

$$\underset{(2\times1)+(1\times16)=18\,g}{H_2O} \equiv \underset{2\times1=2g}{2H}$$

18 g H_2O contain H = 2 g

$$0.272 \text{ g } H_2O \text{ contains H} = \frac{2}{18} \times 0.272 \text{ g}$$

$$\text{\% age of H} = \frac{\text{wt. of H}}{\text{wt. of substance}} \times 100$$

$$= \frac{2 \times 0.272}{18} \times \frac{100}{0.316} = \mathbf{9.56\%}$$

So, the correct answer is (1).

Example 21. *0.246 g of an organic compound yielded 31.2 mL of N_2 gas at N.T.P. by Duma's method. The percentage of N_2 in the organic compound is*

(1) 31.70 *(2) 3.17*

(3) 15.85 *(4) 1.6*

Solution.

Wt. of substance = 0.246 g;

Volume of N_2 gas at N.T.P. = 31.2 mL.

22400 mL of N_2 weighs = g. mol. wt. of N_2 = 2 × 14 = 28 g

$$31.2 \text{ mL of } N_2 \text{ weighs} = \frac{28}{22400} \times 31.2\text{g}$$

$$\therefore \quad \text{\% age of } N_2 = \frac{\text{wt. of } N_2}{\text{wt. of substance}} \times 100$$

$$= \frac{28 \times 31.2}{22400} \times \frac{100}{0.246} = \mathbf{15.85\%}$$

So, the correct answer is (3).

Example 22. *1.2 g of organic compound on Kjeldahlization liberates ammonia which consumes 30 cm^3 of 1 M HCl. The percentage of nitrogen in the compound is :*

(a) 30 *(b) 35*

(c) 46.67 *(d) 20.8* **(Karnataka CET, 2011)**

Solution.

Wt. of organic compound = 1.2 g;

normality of acid = 1,

volume consumed for NH_3 = 30 cm^3.

% age of nitrogen = 1.4 × normality of acid × volume of acid used for NH_3

$$= \frac{1.4 \times 1 \times 30}{1.2} = 35.$$

So, the correct answer is (*b*).

Example 23. *0.5 g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 25 mL of 0.08 M H_2SO_4. The % age of nitrogen in the compound is :*

(1) 1.9 *(2) 1.8*

(3) 10.7 *(4) 11.2*

Solution. Wt. of organic substance = 0.5 g

Volume of 0.08 M H_2SO_4 required to neutralise NH_3 = 25 mL.

$$\underset{2\,mol}{2NH_3} + \underset{1\,mol}{H_2SO_4} \rightarrow (NH_4)_2SO_4$$

25 mL of 0.08 M H_2SO_4 = 2 × 25 mL of 0.08 M NH_3 = 50 mL of 0.08 M NH_3

But 1000 mL of 1 M NH_3 = 14 g N

$$50 \text{ mL of 0.08 M } NH_3 = \frac{14}{1000} \times 50 \times 0.08 \text{ g nitrogen}$$

$$\therefore \quad \text{\% age of nitrogen} = \frac{\text{wt. of nitrogen}}{\text{wt. of substance}} \times 100$$

$$= \frac{14 \times 50 \times 0.08 \times 100}{1000 \times 0.5} = \mathbf{11.2\%}$$

So, the correct answer is (4).

Example 24. *An organic compound weighing 0.2562 g gave 0.2998 g of silver bromide. The percentage of bromine in this compound is :*

(1) 36.36 (2) 18.18

(3) 40.34 (4) 49.79

Solution. Wt. of organic compound = 0.2562 g;

Wt. of silver bromide = 0.2998 g

$$\underset{108+80=188\text{ g}}{\text{AgBr}} \equiv \underset{80\text{g}}{\text{Br}}$$

188 g AgBr contain Br = 80 g; 0.2998 g AgBr contains

$$\text{Br} = \frac{80}{188} \times 0.2998 \text{ g}$$

$$\% \text{ age of bromine} = \frac{\text{wt. of Br}}{\text{wt. of substance}} \times 100$$

$$= \frac{80 \times 0.2998}{188} \times \frac{100}{0.2562} = \mathbf{49.79\%}$$

So, the correct answer is (4).

Example 25. *In Kjeldahl method, ammonia from 5.0 g of food neutralises 30 cm^3 of 0.1 N acid. The % age of nitrogen in the food is :*

(*a*) 0.84 (*b*) 8.4

(*c*) 16.8 (*d*) 1.68 **(Karnataka CET, 2010)**

Solution. % age of N = 1.4 × N_1 × V/w = 1.4 × 0.1 × 30/5 = **0.84%**. So, the correct answer is (*a*)

Example 26. *In a carius determination of sulphur, 0.16g of an organic compound gave 0.4908g of barium sulphate. The % age of sulphur in the compound is :*

(1) 42.13 (2) 84.26

(3) 60.1 (4) 17.98

(AFMC, 2012)

Solution.

Wt. of substance = 0.16g;

Wt. of $BaSO_4$ = 0.4908 g

$$\underset{\substack{137+32+(4\times16)\\=233\text{g}}}{BaSO_4} \equiv \underset{32\text{g}}{S}\ ; \quad 233 \text{ g } BaSO_4 \text{ contain sulphur} = 32 \text{ g}$$

0.4908 g $BaSO_4$ contains sulphur

$$= \frac{32}{233} \times 0.4908 \text{ g}$$

$$\therefore \quad \% \text{ age of sulphur} = \frac{32 \times 0.4908}{233} \times \frac{100}{0.16} = \mathbf{42.13\%}$$

So, the correct answer is (1).

Example 27. *0.155 g of an organic compound containing phosphorus gave 0.275 g of $Mg_2P_2O_7$ in a carius estimation. The percentage of phosphorus in the compound is :*

(1) 98.1 (2) 24.75

(3) 49.55 (4) 73.75

Solution. Wt. of

organic substance = 0.155 g;

Wt. of $Mg_2P_2O_7$ = 0.275 g

$$\underset{\substack{(2\times24)+(2\times31)+(7\times16)\\=222\text{ g}}}{Mg_2P_2O_7} \equiv \underset{2\times31=62\text{ g}}{2P}$$

222 g $Mg_2P_2O_7$ contain phosphorus

= 62 g

0.275 g $Mg_2P_2O_7$ contains phosphorus

$$= \frac{62}{222} \times 0.275 \text{ g}$$

$$\% \text{ age of phosphorus} = \frac{62 \times 0.275}{222} \times \frac{100}{0.155} = \mathbf{49.55\%}$$

So, the correct answer is (3).

PROBLEMS FOR PRACTICE

1. An organic compound weighing 0.354 g containing C, H, N and oxygen gave on combustion by Liebig's method, 0.528 g CO_2 and 0.27 g water. Calculate the percentage of carbon and hydrogen in this compound. (**Ans.** C = 40.68%, H = 8.48%)

Hint. Consult example, 1.

2. An organic compound weighing 0.25 g contains carbon, hydrogen and oxygen. On analysis by Liebig's method, an increase in weights of calcium chloride U-tube and potash bulbs were found to be 0.15 g and 0.1837 g respectively. Calculate the percentage composition of the compound.

(**Ans.** % C = 20.04; % H = 6.66%; O = 73.3)

Hint. Consult example, 2.

3. An organic nitrogenous compound has molecular formula C_3H_7N. It was analysed by Duma's method. Calculate the volume of N_2 gas at NTP produced from 1.5 g of this compound. (**Ans.** 294.74 mL)

Hint. Consult example, 5.

4. In a Duma's method for the estimation of nitrogen, 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K temperature and 715 mm pressure. (Aqueous tension at 300 K = 15 mm). Calculate the percentage of nitrogen in the compound.

(**Ans.** 17.46%)

Hint. Consult example, 4.

5. During the estimation of nitrogen by Kjeldahl's method, the NH_3 gas evolved from 0.5 g of the compound neutralised 10 mL of 1M H_2SO_4. Calculate the percentage of nitrogen in the compound.

(**Ans.** 56%)

Hint. Consult example, 7.

6. An organic compound weighing 0.35 g was Kjeldahlised and NH_3 gas evolved was absorbed in 100 mL of 0.1 M H_2SO_4. The residual acid required

154 mL of M/40 NaOH for complete neutralisation. Calculate the % age of nitrogen in the compound. **(Ans.** 18.4%**)**

Hint. Consult example, 8.

7. An organic compound weighing 0.5 g was Kjeldahlised and ammonia gas produced was absorbed in 45 mL of M/4 H_2SO_4. The residual solution was diluted to 100 mL. The 20 mL of this diluted solution required 35 mL of M/20 NaOH for complete neutralisation. Calculate the percentage of nitrogen in the compound. **(Ans.** 38.5%**)**
8. An organic compound weighing 0.246 g gave 0.248 g dry silver chloride. Calculate the percentage of chlorine in the compound. (At. wt., Ag = 108, Cl = 35.5). **(Ans.** 24.94% Cl**)**

   Hint. Consult example, 13.
9. In a carius determination of halogens, 0.18 g of an organic compound gave 0.145 g of silver bromide. Calculate the percentage of bromine in the compound. (At. wt., Ag = 108, Br = 80). **(Ans.** 34.28% Br**)**

   Hint. Consult example, 14.
10. 0.229 g of an organic compound when heated with excess of strong HNO_3 and solid $AgNO_3$ yielded 0.41 g of silver iodide. Calculate the percentage of iodine in the organic compound. (At. wt., Ag = 108, I = 127). **(Ans.** 96.76%**)**

    Hint. Consult example, 15.
11. In a carius method, 0.2746 g of an organic compound gave 0.37 g of barium sulphate. Calculate the percentage of sulphur in the compound. **(Ans.** 18.5%**)**

    Hint. Consult example, 16.
12. An organic compound weighing 0.375 g and containing phosphorus was heated with conc. HNO_3 in the carius tube. The phosphoric acid thus formed was precipitated with magnesia mixture as $MgNH_4PO_4$. The latter when ignited after washing and drying left a residue of 0.6273 g of $Mg_2P_2O_7$. Calculate the % age of phosphorus in the given compound (At. wt. Mg = 24, P = 31, O = 16) **(Ans.** 46.72%**)**

    Hint. Consult example, 18.

Note. For more problems and their solution, see appendix (*i*).

26

CHAPTER

Empirical and Molecular Formulae

26.1 PERCENTAGE COMPOSITION

The percentage composition of a compound is a relative weight of each of its constituent elements in 100 parts of it. Mathematically :

% age composition of each component in the compound

$$= \frac{\text{wt. of each component}}{\text{mol. wt.}} \times 100$$

Type. To find mol. wt.

Example 1. *Calculate the molecular weight of the following compounds (i) Green vitriol or ferrous sulphate crystals ($FeSO_4$. 7 H_2O). (At. wt. S = 32, O = 16, Fe = 56, H = 1).*

Solution. (*i*) ***$FeSO_4 . 7H_2O$.***

1 atom of Fe = 1 × 56 = 56 a.m.u. or 56 u
1 atom of S = 1 × 32 = 32 a.m.u.
11 atoms of O = 11 × 16 = 176 a.m.u.
14 atoms of H = 14 × 1 = 14 a.m.u.

∴ Mol. wt. of $FeSO_4 . 7H_2O$

= 56 + 32 + 176 + 14

= **278 a.m.u.** Ans.

Example 2. *Blood contains red coloured compound haemoglobin. The latter contains 0.355% of iron (at. wt. 56). Calculate the mol. wt. of haemoglobin if four atoms of iron are present in one molecule of it.*

Solution. ***Haemoglobin.*** 4 atoms of

Fe = 4 × 56 = 224 a.m.u.

0.355 parts of Fe correspond to haemoglobin

= 100 parts

∴ 224 parts of Fe correspond to haemoglobin

$$= \frac{100}{0.355} \times 224 = 63098$$

∴ Mol. wt. of haemoglobin

= **63098 a.m.u.** Ans.

Type. % age composition of a compound

$$= \frac{\text{wt. of each component}}{\text{mol. wt.}} \times 100$$

Example 3. *Calculate the percentage composition of $BaCl_2 . 2H_2O$. Also find the weight of barium and water of crystallisation in 20 g of the crystals. (At. wt., Ba = 137.5, Cl = 35.5, H = 1, O = 16).*

Solution. Mol. wt. of $BaCl_2 . 2H_2O$ = 137.5 + (2 × 35.5) + 2 [(2 × 1) + 16)] = 137.5 + 71 + 36 = 244.5 a.m.u.

$$\therefore \quad \text{\% age of Ba} = \frac{137.5 \times 100}{244.5} = 56.24\,;$$

$$\text{\% age of Cl} = \frac{71 \times 100}{244.5} = 29.04$$

$$\text{\% age of H} = \frac{4 \times 100}{244.5} = 1.64\,;$$

$$\text{\% age of O} = \frac{32 \times 100}{244.5} = 13.08;$$

$$\text{\% age of } H_2O = \frac{36}{244.5} \times 100 = 14.72$$

Wt. of Ba in 20 g of $BaCl_2 . 2\,H_2O$

$$= \frac{137.5 \times 20}{244.5} = 11.25 \text{ g}$$

$$\left[\because \underset{244.5}{BaCl_2.2H_2O} \equiv \underset{137.5}{Ba}\right]$$

Wt. of H_2O in 20 g of $BaCl_2 . 2H_2O$

$$= \frac{36 \times 20}{244.5} = 2.94 \text{ g}$$

$$\left[\because \underset{244.5}{BaCl_2.2H_2O} \equiv \underset{36}{2H_2O}\right]$$

Example 4. *Calculate the percentage composition of microcosmic salt (sodium ammonium hydrogen phosphate tetrahydrate) $NaNH_4HPO_4$; 4 H_2O; Cr = 52, P = 31, Na = 23, N = 14, O = 16].*

Solution.

Mol. wt. of $NaNH_4\,HPO_4 . 4\,H_2O$ = 23 + 14 + 4 × 1 + 1 + 31 + 4 × 16 + 4 (2 + 16) = 209

$$\begin{aligned}
\text{1 atom of Na} &= 23 \times 1 = 23 \text{ a.m.u.}\\
\text{\% age of Na} &= \frac{23}{209} \times 100 = 11\\
\text{1 atom of N} &= 14 \times 1 = 14 \text{ a.m.u.}\\
\text{\% age of N} &= \frac{14}{209} \times 100 = 6.7\\
\text{5 atom of H} &= 5 \times 1 = 5 \text{ a.m.u.}\\
\text{\% age of H} &= \frac{5 \times 100}{209} = 2.39\\
\text{1 atom of P} &= 31 \times 1 = 31 \text{ a.m.u.}\\
\text{\% age of P} &= \frac{31 \times 100}{209} = 14.83\\
\text{4 atoms of O} &= 16 \times 4 = 64\\
\text{\% age of O} &= \frac{64 \times 100}{209} = 30.62\\
\text{4 molecules of } H_2O &= 18 \times 4 = 72 \text{ a.m.u.}\\
\text{\% age of } H_2O &= \frac{72 \times 100}{209} = 34.45
\end{aligned}$$

26.2 EMPIRICAL FORMULA (E.F.)

It is the simplest formula that represents the relative whole number ratio of atoms of different elements present in one molecule of the substance *e.g.*, the E.F. of glucose ($C_6H_{12}O_6$) = CH_2O (after dividing by common factor, 6); E.F. of ethene (C_2H_4) is CH_2 (after dividing by common factor, 2).

26.3 MOLECULAR FORMULA (M.F.)

The molecular formula of a compound is the formula that represents the actual number of atoms of different elements present in one molecule of the compound. *For example,* M.F. of glucose is $C_6H_{12}O_6$, that of ethene is C_2H_4 and that of benzene is C_6H_6.

26.4 RELATION BETWEEN EMPIRICAL FORMULA AND MOLECULAR FORMULA

Molecular formula (M.F.) = $n \times$ Empirical formula (E.F).

$$\text{where} \qquad n = \frac{\text{Mol. wt.}}{\text{Empirical formula weight (E.F.wt)}}$$

In order to find the E.F., use the following table.

Element	% age	at. wt.	Relative number of atoms = $\frac{\%\text{ age}}{\text{at. wt}}$ or $\frac{\text{wt.}}{\text{At. wt.}}$	Simple ratio	Whole number ratio.

(*i*) Simple ratio is obtained by dividing relative number of atoms by least value of relative number of atoms.

(*i*) If simple (or least) ratio is in 0.5, 1.5, 2.5, etc., multiply all ratios by 2 to get nearest whole number ratio.

(*ii*) If simple (or least) ratio is in 0.33, 0.66, 1.33, 1.66, etc., multiply all ratios by 3 to get nearest whole number ratio.

(*iii*) If simple (or least) ratio is in 0.14, 1.14, etc., multiply all ratios by 7 to get nearest whole number.

EXAMPLE 5. *Assuming the at. wt. of a metal M to be 56, find the E.F. of its oxide containing 30% of oxygen.*

SOLUTION. % age of M = 100 – 30 = 70; %age of O = 30.

To find E.F.

Element	*%age*	*At.wt.*	*Relative number of atoms = % age/At. wt.*	*Least ratio*	*Whole no. ratio*
Metal, M	70	56	$\frac{70}{56} = 1.25$	$\frac{1.25}{1.25} = 1$	1 × 2 = 2
O	30	16	$\frac{30}{16} = 1.875$	$\frac{1.875}{1.25} = 1.5$	1.5 × 2 = 3

$\therefore$ E.F. = M_2O_3.

EXAMPLE 6. *An organic compound contains C, H and O. 1.80 g of the substance on combustion gave 2.64 g of CO_2 and 1.08 g of water. Calculate the E.F. of the compound.*

SOLUTION. (*i*) To find %age of C

$$\underset{12+2\times16=44\,g\,CO_2}{CO_2} \equiv \underset{12\,g\,C}{C} \qquad \text{Wt. of substance} = 1.8 \text{ g}$$

$$\begin{aligned}
\therefore \quad 44 \text{ g } CO_2 &\equiv 12 \text{ gC}\\
2.64 \text{ g } CO_2 &= \frac{12}{44} \times 2.64 = 0.72 \text{ g}\\
\text{\% age of C} &= \frac{0.72}{1.8} \times 100 = 40
\end{aligned}$$

(*ii*) To find %age of H

$$\underset{2\times1+16=18}{H_2O} \equiv \underset{2\times1=2\,g}{2H}$$

$$\begin{aligned}
18 \text{ g } H_2O &\equiv 2 \text{ gH}\\
1.08 \text{ g } H_2O &\equiv \frac{2}{18} \times 1.08 = 0.12 \text{ g}\\
\text{\% age of H} &= \frac{0.12}{1.8} \times 100 = 6.66\%
\end{aligned}$$

(*iii*) % age of O = 100 – (%age of C + %age of H)

= 100 – (40 + 6.66) = 53.34.

(*iv*) **To find E.F.**

Element	*%age*	*At.wt.*	*Relative number of atoms = % age/At. wt.*	*Least ratio*	*Whole no. ratio*
C	40	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$	1

Element	*%age*	*At.wt.*	*Relative number of atoms = % age/At. wt.*	*Least ratio*	*Whole no. ratio*
H	6.66	1	$\frac{6.66}{1} = 6.66$	$\frac{6.66}{3.33} = 2$	2
O	53.34	16	$\frac{53.34}{16} = 3.33$	$\frac{3.33}{3.33} = 1$	1

$\therefore$ E.F. = CH_2O.

Example 7. *100 g of a hydrated salt contains 25.45 g of copper, 12.82 g of sulphur, 25.65 g of oxygen and 36.07 g of water of crystallisation. Calculate the E.F. of the salt. (At. wt., Cu = 63.5, S = 32, O = 16, H = 1).*

Solution. Calculation of E.F.

Element or compound	*Weight*	*At. wt. (or mol. wt.*	*Relative no. of atoms = wt./At. wt or wt./mol. wt.*	*Simple ratio*	*Whole no. ratio*
Cu	25.45	63.5	$\frac{25.45}{63.5} = 0.4$	$\frac{0.4}{0.4} = 1$	1
S	12.82	32	$\frac{12.82}{32} = 0.4$	$\frac{0.4}{0.4} = 1$	1
O	25.65	16	$\frac{25.65}{16} = 1.6$	$\frac{1.6}{0.4} = 4$	4
H_2O	36.07	18	$\frac{36.07}{18} = 2.0$	$\frac{2.0}{0.4} = 5$	5

$\therefore$ E.F. of salt = $Cu_1S_1O_4 . 5H_2O$ *Or* $\mathbf{CuSO_4 . 5\,H_2O}$ **Ans.**

Example 8. *A carbohydrate containing C, H and O has atomic ratio of H and O as 2 : 1. When heated in absence of air, 155 g of it gave 62 g of carbon. Calculate its empirical and molecular formula if 0.167 mol of it contain 2.0 g hydrogen. (At. wt. C = 12, H = 1, O = 16).*

Solution. (*i*) To calculate E.F.,

wt. of H_2O = 155 – 62 = 93 g.

Element or compound	*Weight*	*At. wt. (or mol. wt.*	*Relative no. of atoms = wt./at. wt or wt./mol. wt.*	*Simple ratio*	*Whole no. ratio*
C	62	12	$\frac{62}{12} = 5.17$	$\frac{5.17}{5.17} = 1$	1
H_2O	93	18	$\frac{93}{18} = 5.17$	$\frac{5.17}{5.17} = 1$	1

$\therefore$ E.F. of carbohydrate

$$= C_1(H_2O)_1 = CH_2O.$$

(*ii*) **To calculate M.F.**

0.167g mol of carbohydrate contain hydrogen

= 2g or 2 mol atoms.

1 mol of carbohydrate contain hydrogen

$$= \frac{2}{0.167} \simeq 12 \text{ mol atoms}$$

or 1 molecule of carbohydrate contain H-atoms = 12.

In order to get 12-atoms of hydrogen, the E.F. CH_2O should be multiplied by $\frac{12}{2}$ *i.e.*, 6 to get M.F. Hence, M.F.

= 6 × CH_2O = $\mathbf{C_6H_{12}O_6}$ **Ans.**

Example 9. *An inorganic compound mixed with sand has the following % age composition. K = 26.57%, Cr = 35.36%, O = 38.07%. Calculate the molecular formula of the compound if its molecular mass is 294 (K = 39, Cr = 52, O = 16).*

Solution. To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
K	26.57	39	$\frac{26.57}{39} = 0.68$	$\frac{0.68}{0.68} = 1$	1 × 2 = 2
Cr	35.36	52	$\frac{35.36}{52} = 0.68$	$\frac{0.68}{0.68} = 1$	1 × 2 = 2
O	38.07	16	$\frac{38.07}{16} = 2.379$	$\frac{2.379}{0.68} = 3.5$	3.5 × 2 = 7

$\therefore$ E.F. = $K_2Cr_2O_7$.

E.F. wt. = 2 × 39 + 2 × 52 + 7 × 16 = 294

$$\text{M.F.} = \frac{\text{mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.}$$

$$= \frac{294}{294} \times K_2Cr_2O_7 = \mathbf{K_2Cr_2O_7}$$ Ans.

Note. The impurity (sand) does not affect the relative ratio of atoms.

Example 10. *A crystalline salt on being rendered anhydrous loses 45.6% of its weight. The percentage composition of the anhydrous salt is Al = 10.5%, K = 15.1%, S = 24.96% and O = 49.92%. Find the simplest formula of anhydrous and crystalline salt (K = 39, Al = 27, S = 32, O = 16).*

Solution. (*i*) To find E.F. of anhydrous salt.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
K	15.1	39	$\frac{15.1}{39} = 0.39$	$\frac{0.39}{0.39} = 1$	1
Al	10.5	27	$\frac{10.5}{27} = 0.39$	$\frac{0.39}{0.39} = 1$	1
S	24.96	32	$\frac{24.96}{32} = 0.78$	$\frac{0.78}{0.39} = 2$	2

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
O	49.92	16	$\frac{49.92}{16}=3.12$	$\frac{3.12}{0.39}=8$	8

$\therefore$ E.F of anhydrous salt = K Al S_2O_8.

(*ii*) To find E.F. of hydrated salt.

E.F. wt. of anhydrous salt,

$$KAlS_2O_8 = 39 + 27 + 2 \times 32 + 8 \times 16 = 258 \text{ a.m.u.}$$

Let wt. of hydrated salt = 100 g

wt. of water lost = 45.6 g

wt. of anhydrous salt = 100 – 45.6 = 54.4 g

E.F. mass of hydrated salt

$$= \frac{\text{wt. of hydrated salt}}{\text{wt. of anhydrous salt}} \times \begin{array}{c}\text{E.F. wt of}\\ \text{anhydrous salt}\end{array}$$

$$= \frac{100 \times 258}{54.4} = 474.3 \text{ g}$$

E.F. mass of anhydrous salt = 258 g

$\therefore$ wt. of water lost = 474.3 – 258 = 216.3 g

Mol. wt. of H_2O molecule = 2 × 1 + 16 = 18 g

$\therefore$ no. of water molecules in the hydrated salt

$$= \frac{216.3}{18} \simeq 12$$

$\therefore$ E.F. of hydrated salt = $KAlS_2O_8 \cdot 12\,H_2O$.

EXAMPLE 11. *A compound on analysis gave the following % age composition. Na = 14.31%; S = 9.97%; H = 6.22% and O = 69.5%. Calculate the molecular formula of the compound on the assumption that all the hydrogens in the compound are present in combination with oxygen as water of crystallisation. The molecular mass of the compound is 322. [At. mass Na = 23, S = 32, H = 1, O = 16].*

SOLUTION. (*i*) To find empirical formula of the compound.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
Na	14.31	23	$\frac{14.31}{23}=0.62$	$\frac{0.62}{0.31}=2$	2
S	9.97	32	$\frac{9.97}{32}=0.31$	$\frac{0.31}{0.31}=1$	1
H	6.22	1	$\frac{6.22}{1}=6.22$	$\frac{6.22}{0.31}=20$	20
O	69.5	16	$\frac{69.5}{16}=4.34$	$\frac{4.34}{0.31}=14$	14

$\therefore$ E.F. of compound = $Na_2S\,H_{20}\,O_{14}$.

E.F. of compound containing water molecules

$$= Na_2SO_4 \cdot 10\,H_2O$$

$$\text{E.F. wt.} = 2 \times 23 + 32 + 4 \times 16 + 10\,(18) = 322$$

$$\text{Mol. formula} = \frac{\text{mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.}$$

$$= \frac{322}{322} \times Na_2SO_4.10H_2O$$

$$= Na_2SO_4.10H_2O$$

EXAMPLE 12. *A compound on analysis gave the following percentage composition by weight. H = 9.09%; O = 36.36% and C = 54.55%. Its V.D. is 44. Find the molecular formula of the compound. (At. wt. H = 1, O = 16, C = 12).*

SOLUTION. (*i*) **To find E.F.**

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
H	9.09	1	$\frac{9.09}{1}=9.09$	$\frac{9.09}{2.27}=4$	4
O	36.36	16	$\frac{36.36}{16}=2.27$	$\frac{2.27}{2.27}=1$	1
C	54.55	12	$\frac{54.55}{12}=4.55$	$\frac{4.55}{2.27}=2$	2

$\therefore$ E.F. = C_2H_4O.

E.F. wt. = 2 × 12 + 4 × 1 + 16 = 44.

(*ii*) To find M.F.

Mol. wt. = 2 × V.D. = 2 × 44 = 88

$$\text{M.F.} = \frac{\text{Mol. wt.}}{\text{E.F. wt}} \times \text{E.F.} = \frac{\cancel{88}^{\,2}}{\cancel{44}} \times C_2H_4O$$

$$= \mathbf{C_4H_8O_2}$$ **Ans.**

EXAMPLE 13. *An inorganic substance has the following %age composition. N = 35%, H = 5%, O = 60%. On being heated, it yielded a gaseous compound containing N = 63.63% and O = 36.37%. Suggest formula for each substance and write equation for the chemical change.*

SOLUTION. (*i*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
N	35	14	$\frac{35}{14}=2.5$	$\frac{2.5}{2.5}=1$	1 × 2 = 2
H	5	1	$\frac{5}{1}=5$	$\frac{5}{2.5}=2$	2 × 2 = 4

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
O	60	16	$\frac{60}{16} = 3.75$	$\frac{3.75}{2.5} = 1.5$	$1.5 \times 2 = 3$

$\therefore$ E.F. = $N_2H_4O_3$.

(*ii*) To find E.F. of gaseous compound.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
N	63.63	14	$\frac{63.63}{14} = 4.55$	$\frac{4.55}{2.27} = 2$	2
O	36.37	16	$\frac{36.37}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1

$\therefore$ E.F. = N_2O (nitrous oxide).

Since the compound formed is N_2O, the original compound is expected as NH_4NO_3.

(*ii*) *Reaction* : $NH_4NO_3 \xrightarrow{\Delta} N_2O + 2\,H_2O$.

Example 14. *A compound of carbon, hydrogen and nitrogen contains three elements in the respective ratio 9 : 1 : 3.5. Calculate its empirical formula. If the mol. wt. is 108, what is its molecular formula ?* **(I.I.T., 1973)**

Solution. (*i*) To find E.F.

Element	*Ratio by wt.*	*At.wt*	*Relative number of atoms = Ratio by wt./At. wt.*	*Simple ratio*	*Whole no. ratio*
C	9	12	$\frac{9}{12} = 0.75$	$\frac{0.75}{0.25} = 3$	3
H	1	1	$\frac{1}{1} = 1$	$\frac{1}{0.25} = 4$	4
N	3.5	14	$\frac{3.5}{14} = 0.25$	$\frac{0.25}{0.25} = 1$	1

$\therefore$ E.F. = C_3H_4N.

E.F. wt. = $3 \times 12 + 4 \times 1 + 14 = 54$.

(*ii*) To find M.F.

$$\text{M.F.} = \frac{\text{Mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.}$$

$$= \frac{\cancel{108}}{\cancel{54}} \times C_3H_4N = 2 \times C_3H_4N$$

$$= C_6H_8N_2$$

Example 15. *A certain compound contains 23.7% sulphur, 23.7% oxygen and rest chlorine. 0.182 g of its vapours occupy 36 mL at 27°C and 700 mm pressure. Calculate the molecular formula of the compound. Also, name the compound.*

Solution. $P_1 = 700$ mm, $V_1 = 36$ mL, $T_1 = 27 + 273 = 300$ K; At. N.T.P., $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K. Using gas equation :

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

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{700\,\text{mm} \times 36\,\text{mL} \times 273\,\text{K}}{300\,\text{K} \times 760\,\text{mm}}$$

or V_2 (at N.T.P.) = 30.2 mL. We know :

$$\text{Mol. wt.} = \frac{\text{Wt.}}{V_{\text{NTP}}} \times 22400;$$

$$\text{Mol. wt.} = \frac{0.182\,\text{g}}{30.2\,\text{mL}} \times 22400\,\text{mL} = 135\,\text{g}$$

(*i*) To find E.F. % age of Cl

= 100 – (23.7 + 23.7) = 52.6.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
S	23.7	32	$\frac{23.7}{32} = 0.74$	$\frac{0.74}{0.74} = 1$	1
O	23.7	16	$\frac{23.7}{16} = 1.48$	$\frac{1.48}{0.74} = 2$	2
Cl	52.6	35.5	$\frac{52.6}{35.5} = 1.48$	$\frac{1.48}{0.74} = 2$	2

$\therefore$ E.F. of compound = SO_2Cl_2.

E.F. wt. of SO_2Cl_2

= 32 + (2 × 16) + (2 × 35.5) = 135.

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}} = SO_2Cl_2 \times \frac{135}{135}$$

= $\mathbf{SO_2Cl_2}$ **Ans.**

Name of the compound is sulphuryl chloride.

Example 16. *Determine the molecular formula of the compound which contains H = 2.1%, C = 12.8%, Br = 85.1%. One gram of it occupies 119 cc at N.T.P. = (C = 12, H = 1, Br = 80).*

Solution. (*i*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
H	2.1	1	$\frac{2.1}{1} = 2.1$	$\frac{2.1}{1.06} = 2$	2

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	12.8	12	$\frac{12.8}{12} = 1.07$	$\frac{1.07}{1.06} = 1$	1
Br	85.1	80	$\frac{85.1}{80} = 1.06$	$\frac{1.06}{1.06} = 1$	1

$\therefore$ E.F. = CH_2Br

E.F. wt. = $12 + 2 \times 1 + 80 = 94$.

(*ii*) To find M.F.

$\therefore$ g. mol. wt. of gas

$$= \frac{\text{wt}}{V_{NTP}} \times 22400 = \frac{1 \times 22400}{119} = 188.2\text{ g}$$

$$\text{M.F.} = \frac{\text{Mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.} = \frac{\cancel{188.2}^{2}}{\cancel{94}} \times CH_2Br$$

$\therefore$ M.F. = $C_2H_4Br_2$

Example 17. *Calculate the formula of kaolin, the composition of which is as follows. Al_2O_3 = 39.5%; SiO_2 = 46.6% and H_2O = 13.9% (At. wt. Al = 27, Si = 28, O = 16, H = 1).*

Solution. To find E.F. of kaolin.

Element	*% age*	*Mol. wt.*	*Relative number of molecules = % age/mol. wt.*	*Simple ratio*	*Whole no. ratio*
Al_2O_3	39.5	2 × 27 + 3 × 16 = 102	$\frac{39.5}{102} = 0.387$	$\frac{0.387}{0.387} = 1$	1
SiO_2	46.6	28 + 2 × 16 = 60	$\frac{46.6}{60} = 0.777$	$\frac{0.777}{0.387} = 2$	2
H_2O	13.9	2 × 1 + 16 = 18	$\frac{13.9}{18} = 0.772$	$\frac{0.772}{0.387} = 2$	2

$\therefore$ E.F. = $Al_2O_3 . 2\,SiO_2 . 2\,H_2O$.

Example 18. *2.5 g of a sample of a metal was heated in air. The resulting oxide weighed 2.95g. Determine the empirical formula of the oxide (At. wt. of metal is 238).*

Solution. Wt. of metal = 2.5 g

wt. of metal oxide = 2.95 g

$\therefore$ wt. of oxygen = 2.95 – 2.5 = 0.45 g

To find E.F.

Element	*Weight*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
M	2.5	238	$\frac{2.5}{238} = 0.0105$	$\frac{0.0105}{0.0105} = 1$	1 × 3 = 3
O	0.45	16	$\frac{0.45}{16} = 0.028$	$\frac{0.028}{0.0105}$ = 2.66	2.66 × 3 = 7.98 ≃ 8

$\therefore$ E.F. = M_3O_8.

Example 19. *9.7g of a hydrate of $CuSO_4$ loses 3.5 g of water on heating. What is the empirical formula of the hydrate ? (Cu = 63.5, S = 32, O = 16).*

SOLUTION. E.F. wt. of $CuSO_4$ anhydrous = 63.5 + 32 + 4 × 16 = 159.5 g

Wt. of hydrated compound = 9.7 g

Wt. of water = 3.5 g

Wt. of anhydrous compound = 9.7 – 3.5 = 6.2 g

$\therefore$ E.F. wt. of hydrated $CuSO_4$

$$= \frac{\text{wt. of hydrated salt}}{\text{wt. of anhydrous compound}} \times \begin{array}{c}\text{E.F. Wt. of}\\ \text{anhydrous compound}\end{array}$$

$$= \frac{9.7}{6.2} \times 159.5 = 249.5\text{ g}$$

E.F. wt. of anhydrous $CuSO_4$ = 159.5 g

$\therefore$ Wt. of water = 249.5 – 159.5 = 90

$\therefore$ No. of water molecules = $\frac{90}{18} = 5$

$\therefore$ Formula of hydrated copper sulphate

= $CuSO_4 . 5H_2O$

Example 20. *1g of hydrated compound of iron contains 0.2014 g of Fe, 0.1153g of S, 0.231g of O and 0.4532g of water of crystallisation. Find the E.F. of the compound (Fe = 56, S = 32, O = 16, H = 1).*

Solution. To find E.F.

Element or compound	*Weight*	*At.wt or mol. wt.*	*Relative number of atoms = % age/At. wt. or mol. wt.*	*Simple ratio*	*Whole no. ratio*
Fe	0.2014	56	$\frac{0.2014}{56} = 0.0035$	$\frac{0.0035}{0.0035} = 1$	1
S	0.1153	32	$\frac{0.1153}{32} = 0.0036$	$\frac{0.0036}{0.0036} = 1$	1
O	0.231	16	$\frac{0.231}{16} = 0.0144$	$\frac{0.0144}{0.0035} = 4$	4
H_2O	0.4532	18	$\frac{0.4532}{18} = 0.0251$	$\frac{0.0251}{0.0035} = 7$	7

$\therefore$ E.F. = $FeSO_4 . 7H_2O$.

Example 21. *A dibasic acid containing C, H and O was found to contain C = 26.7% and hydrogen 2.2%. The vapour density of diethyl ester was found to be 73. What is the molecular formula of the acid ? (At. wt. C = 12, O = 16,. H = 1).*

(P.U.C.E.T. 1989)

Solution. To find E.F.; % age of O

= 100 – (26.7 + 2.2 = 28.9) = 71.1%.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	26.7	12	$\frac{26.7}{12}=2.2$	$\frac{2.2}{2.2}=1$	1
H	2.2	1	$\frac{2.2}{1}=2.2$	$\frac{2.2}{2.2}=1$	1
O	71.1	16	$\frac{71.1}{16}=4.4$	$\frac{4.4}{2.2}=2$	2

∴ E.F. = CHO_2.

E.F. wt. = 12 + 1 + 2 × 16 = 45.

Mol. mass of acid

= Mol. mass – mol. mass of two + at. mass of two
of ester ethyl (C_2H_5)groups H-atoms

= 2 × (V.D) – mass of two + mass of two
C_2H_5 groups H-atoms

= (2 × 73) – 2 (2 × 12 + 5 × 1) + (2 × 1)

= 146 – 58 + 2 = 90.

$$\text{M.F.} = \frac{\text{Mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.} = \frac{\cancel{90}^{2}}{\cancel{45}} \times CHO_2$$

$= C_2H_2O_4$ **Ans.**

Type. Determination of M.F. of monobasic acid when V.D. of its ethylester is given.

Example 22. *The empirical formula of monobasic acid is CH_2O. The vapour density of its* ***ethyl ester*** *is found to be 44. Calculate the molecular formula of the acid.*
(C = 12, H = 1, O = 16).

Solution. E.F. = CH_2O.

E.F. wt. of

CH_2O = 12 + 2 × 1 + 16 = 30.

Mol. mass of

acid = Mol. mass of – Mol. wt. of + at. mass of
ethyl ester one ethyl one H-atom
(C_2H_5)

= (2 × (V.D) – (2 × 12 + 5 × 1) + 1

i.e., 2 × 44 = 88

= 88 – 29 + 1 = 60

$$\text{M.F.} = \frac{\text{Mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.} = \frac{\cancel{60}^{2}}{\cancel{30}} \times CH_2O$$

$= C_2H_4O_2$ **Ans.**

Example 23. *In case of a hydrocarbon, it was found from analysis that the hydrogen content is $\frac{1}{12}$ of that of carbon by weight. What is the empirical formula of the compound ? (C = 12, H = 17).*

Solution. To find E.F.

Element	*Wt.*	*At.wt*	*Relative number of atoms = Wt./ At. wt*	*Simple ratio*	*Whole no. ratio*
C	12	12	$\frac{12}{12}=1$	$\frac{1}{1}=1$	C
H	1	1	$\frac{1}{1}=1$	$\frac{1}{1}=1$	H

∴ E.F. = CH.

Example 24. *The empirical formula of a compound is $FeSH_{14}O_{11}$, write its formula if all the hydrogen atoms are present in it as water of crystallisation.*

Solution. E.F. = $FeS\,H_{14}O_{11} = FeSO_4 . 7H_2O$

$[\because 7H_2O = H_{14}O_7 \ \therefore\ H_{14}O_7 + 4O = H_{14}O_{11}]$

Example 25. *An organic acid contain C, H and O. A 4.24 mg of the sample is burnt completely. It gives 8.45 mg CO_2 and 3.46 mg H_2O. What is the mass percentage of each ? Calcualte the empirical formula of the compound (C = 12, O = 16, H = 1).*

Solution. (*i*) To find % age of C.

$$\text{\% age of C} = \frac{\text{Wt. of C}}{\text{Wt. of compound}} \times 100$$

$$= \frac{2.304}{4.24} \times 100 = 54.34$$

(*ii*) To find % age of H

$$\text{\% age of H} = \frac{\text{Wt. of H}}{\text{Wt. of compound}} \times 100$$

$$= \frac{0.384}{4.24} \times 100 = 9.06$$

% age of O = 100 – (54.34 + 9.06)

= 36.60.

$CO_2 \equiv C$

12 + 2 × 16 = 44 mg ≡ 12 mg

44 mg CO_2 ≡ 12 mg C

$$8.45 \text{ mg } CO_2 \equiv \frac{12}{44} \times 8.45 = 2.304 \text{ mg}$$

$H_2O \equiv 2H$

2 × 1 + 16 = 18 mg 2 × 1 = 2 mg

18 mg H_2O ≡ 2 mgH

$$3.46 \text{ mg } H_2O \equiv \frac{2}{18} \times 3.46 = 0.384 \text{ mg}$$

(*iii*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	54.34	12	$\frac{54.34}{12} = 4.52$	$\frac{4.52}{2.26} = 2$	2
H	9.06	1	$\frac{9.06}{1} = 9.06$	$\frac{9.06}{2.26} = 4$	4
O	36.60	16	$\frac{36.60}{16} = 2.26$	$\frac{2.26}{2.26} = 1$	1

∴ E.F. = C_2H_4O.

Example 26. *A hydrocarbon contains 10.5 g of carbon per gram of hydrogen. One litre of the vapour of the hydrocarbon at 127°C and 1 atm pressure weighs 2.8 g. Find the molecular formula.* **(I.I.T. 1980)**

Solution. (*i*) To find E.F.

Element	*Wt.*	*At.wt*	*Relative number of atoms = wt./At. wt.*	*Simple ratio*	*Whole no. ratio*
C	10.5 g	12	$\frac{10.5}{12} = 0.875$	$\frac{0.875}{0.875} = 1$	1 × 7 = 7
H	1 g	1	$\frac{1}{1} = 1$	$\frac{1}{0.875}$ = 1.143	1.143 × 7 ≃ 8

∴ E.F. of hydrocarbon = C_7H_8

∴ E.F. wt. = (7 × 12) + (8 × 1) = 92.

(*ii*) To find molecular weight. We know :

$$PV = nRT; \; PV = \frac{\text{Wt.}}{\text{mol. wt.}} \times RT;$$

$$\text{Mol.wt.} = \frac{\text{wt.} \times RT}{PV}$$

But P = 1 atm, V = 1L, wt. = 2.8g,

R = 0.0821L atm K^{-} mol^{-};

T = 127 + 273 = 400K.

Substituing the values, we get :

$$\text{Mol. wt.} = \frac{2.8\text{g} \times 0.0821\text{L atm K}^{-}\text{mol}^{-} \times 400\text{K}}{1\text{atm} \times 1\text{L}}$$

$$\simeq 92 \text{ g mol}^{-}$$

(*iii*) To find M.F.

$$\text{M.F.} = \text{E.F.} \times \frac{\text{mol. wt.}}{\text{E.F. wt.}} = C_7H_8 \times \frac{92}{92} = C_7H_8$$

∴ M.F. of hydrocarbon = $\mathbf{C_7H_8}$ **Ans.**

Example 27. *A certain compound containing only carbon and oxygen has an approximate molecular weight of 290. On analysis, it is found to contain exactly 50 per cent by weight of each element. What is the molecular formula of the compound ?* **(I.I.T. 1970)**

Solution. (*i*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	50	12	$\frac{50}{12} = 4.16$	$\frac{4.16}{3.125} = 1.33$	1.33 × 3 ≃ 4
O	50	16	$\frac{50}{16} = 3.125$	$\frac{3.125}{3.125} = 1$	1 × 3 = 3

∴ E.F. of compound = C_4O_3.

E.F. wt. = (4 × 12) + (3 × 16) = 96.

But
$$\text{M.F.} = \text{E.F.} \times \frac{\text{mol. wt.}}{\text{E.F. wt.}} = \text{E.F.} \times \frac{290}{96}$$

$$= C_4O_3 \times 3$$

$$= \mathbf{C_{12}O_9}$$ **Ans.**

Example 28. *A compound 'X' contains 36.5% Na, 25.4% S and rest oxygen. Calculate the molecular formula of X if its mol. wt. is 126. 'X' is also easily oxidised to give a compound 'Y'. Calculate the percentage composition of 'Y'.*

(At. wt. Na = 23, S = 32, O = 16).

Solution. % age of oxygen = 100 – (36.5 + 25.4) = 38.1%

(*i*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
Na	36.5	23	$\frac{36.5}{23} = 1.587$	$\frac{1.587}{0.793} = 2.001$	2
S	25.4	32	$\frac{25.4}{32} = 0.793$	$\frac{0.793}{0.793} = 1$	1
O	38.1	16	$\frac{38.1}{16} = 2.381$	$\frac{2.381}{0.793} = 3.001$	3

∴ E.F. of compound = Na_2SO_3.

On oxidation, Na_2SO_3 forms Na_2SO_4. So, compound 'Y' is Na_2SO_4. Mol. wt. of Na_2SO_4 = (2 × 23) + 32 + (4 × 16) = 142 because in Na_2SO_4; 2 atoms of Na = 2 × 23 = 46 a.m.u., 1 atom of S = 32 a.m.u. and 4 atoms of oxygen = 4 × 16 = 64 a.m.u. Hence :

$$\text{\% age of Na} = \frac{46 \times 100}{142} = \mathbf{32.39}$$ **Ans.**

$$\text{\% age of S} = \frac{32 \times 100}{142} = \mathbf{22.54}$$ **Ans.**

$$\text{\% age of O} = \frac{64 \times 100}{142} = \mathbf{45.07}$$ **Ans.**

Example 29. *18.488g of Epsom salt lost 9.459 g water of crystallisation on heating and left behind $MgSO_4$. Find the formula of Epsom salt. (At. wt., Mg = 24, S = 32, O = 16, H = 1).*

SOLUTION. Wt. of water, H_2O = 9.459g; g. mol. wt. of $H_2O = (2 \times 1) + 16 = 18$g;

Wt. of $MgSO_4 = 18.488 - 9.459 = 9.029$ g.

To find E.F.; mol. wt. of

$$MgSO_4 = 24 + 32 + (4 \times 16) = 120.$$

Compound	*Wt.*	*Mol. wt.*	*Relative number of molecules = Wt./Mol. wt.*	*Simple ratio*	*Whole no. ratio*
$MgSO_4$	9.029	120	$\frac{9.029}{120} = 0.075$	$\frac{0.075}{0.075} = 1$	1
H_2O	9.459	18	$\frac{9.459}{18} = 0.526$	$\frac{0.526}{0.075} = 7$	7

∴ E.F. of Epsom salt = $MgSO_4 . 7H_2O$ **Ans.**

EXAMPLE 30. *An organic compound on qualitative analysis was found to contain C, H and N. One gram of it on oxidation with CuO and oxygen gave 1.239 g of CO_2 and 0.1269g of H_2O. 2.0g of the sample was digested with conc. H_2SO_4 and the residue was distilled after the addition of excess solution of sodium hydroxide. The ammonia gas evolved was absorbed in 50 mL of 1.0N sulphuric acid. The resulting solution was diluted to 500 mL in a measuring flask. 25 mL of this solution required 21.8 mL of 0.05N NaOH for complete neutralisation. Calculate the empirical formula of the compound.* **(I.I.T., 1971)**

SOLUTION. Wt. of compound = 1.0 g;

Wt. of CO_2 = 1.239g; wt. of H_2O = 0.1269g.

(*a*) $CO_2 \equiv C$

$$12 + (2 \times 16) = 44\text{g} \quad 12\text{g}$$

$$44 \text{ g } CO_2 \equiv 12\text{g C}$$

$$1.239\text{g } CO_2 \equiv \frac{12}{44} \times 1.239 \text{ g C}$$

$$\therefore \quad \%\text{ age of C} = \frac{12 \times 1.239}{44} \times \frac{100}{1} = \mathbf{33.79\%}$$

(*b*) $H_2O \equiv 2H$

$$(2 \times 1) + 16 = 18\text{g} \quad 2 \times 1 = 2\text{g}$$

$$18\text{g } H_2O \equiv 2 \text{ g H}$$

$$0.1269 \text{ g } H_2O \equiv \frac{2}{18} \times 0.1269\text{g H}$$

$$\therefore \quad \%\text{ age of } H_2 = \frac{2}{18} \times \frac{0.1269 \times 100}{1} = \mathbf{1.41\%}$$

(*c*) To find %age of nitrogen.

(*i*) To find normality of dil H_2SO_4

Dil. H_2SO_4 NaOH solution

$$N_1V_1 = N_2V_2;$$

$$N_1 \times 25 = 21.8 \times 0.05;$$

$$N_1 = 0.0436$$

(*ii*) To find volume of original acid unused

Dil. H_2SO_4 Original H_2SO_4

$$N_3V_3 = N_4V_4;$$

$$0.0436 \times 500 = 1 \times V_4;$$

$$V_4 = 21.8 \text{ mL}$$

(*iii*) To find volume of original acid used by ammonia = 50 – 21.8 = 28.2 mL.

(*iv*) To find weight and % age of nitrogen.

28.2 mL of 1N H_2SO_4 ≡ 28.2 mL of 1N NH_3

Now

1000 mL of 1N NH_3 ≡ 14 g N

$$\therefore \quad 28.2 \text{ mL of 1N } NH_3 \equiv \frac{14}{1000} \times 28.2 \times 1 = 0.3948 \text{ g}$$

$$\therefore \quad \%\text{ age of nitrogen} = \frac{0.3948}{2.0} \times 100 = 19.74$$

$$\%\text{ age of oxygen} = 100 - (33.79 + 1.41 + 19.74) = 45.06\%$$

(*v*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	33.79	12	$\frac{33.79}{12} = 2.816$	$\frac{2.816}{1.41} = 2$	2
H	1.41	1	$\frac{1.41}{1} = 1.41$	$\frac{1.41}{1.41} = 1$	1
N	19.74	14	$\frac{19.74}{14} = 1.41$	$\frac{1.41}{1.41} = 1$	1
O	45.06	16	$\frac{45.06}{16} = 2.816$	$\frac{2.816}{1.41} \simeq 2$	2

∴ E.F. of the compound = C_2HNO_2 **Ans.**

EXAMPLE 31. (*i*) *An organic mono-acid base contains 78.6% C and 8.4% hydrogen. (ii) 1.070 g of the base needed 25.0 mL of N/2.5 H_2SO_4 for complete neutralisation. (iii) 0.6g of the base gave 65.4 mL N_2 at 15°C and one atmospheric pressure. Calculate the molecular formula of the base.*

SOLUTION. (*i*) To find % age of nitrogen. P_1 = 1 atm = 760 mm, V_1 = 65.4 mL, T_1 = 15 + 273 = 288 K. At. N.T.P., P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

Using gas equation, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \textbf{ Or } V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$\therefore \quad V_2 = \frac{760 \times 65.4 \times 273}{288 \times 760} = 62 \text{ mL}$$

22400 mL of N_2 weighs = g. mol. wt. of N_2
= 2 × 14 = 28 g

$$62 \text{ mL of } N_2 \text{ weighs} = \frac{28}{22400} \times 62\text{g}$$

$$\therefore \quad \%\text{ age of } N_2 = \frac{28 \times 62}{22400} \times \frac{100}{0.6} = 12.92\%$$

(*ii*) To find E.F.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	78.6	12	$\frac{78.6}{12} = 6.55$	$\frac{6.55}{0.92} = 7$	7
H	8.4	1	$\frac{8.4}{1} = 8.4$	$\frac{8.4}{0.92} \simeq 9$	9
N	12.92	14	$\frac{12.92}{14} = 0.92$	$\frac{0.92}{0.92} = 1$	1

$\therefore$ E.F. of base = C_7H_9N **Ans.**

E.F. wt. of base = (7 × 12) + (9 × 1) + 14 = 107.

(*iii*) To find mol. wt. of base

25.0 mL of $\frac{N}{2.5}$ H_2SO_4 neutralised base

$$= 1.07 \text{ g}$$

1000 mL of 1N H_2SO_4 neutralised base

$$= \frac{1.07}{25} \times 1000 \times 2.5 = 107\text{g}$$

$\therefore$ Eq. wt. of base = 107;

Mol. wt. = Eq. wt. × acidity

= 107 × 1 = 107.

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= C_7H_9N \times \frac{107}{107} = \mathbf{C_7H_9N}$$

Ans.

EXAMPLE 32. *(i) 0.203 g of an organic liquid in a victor meyer apparatus displaced 55.92 mL of dry air measured at 15°C and 750 mm pressure. (ii) In a Kjeldahl's apparatus, the ammonia gas obtained from 2.02 g of the compound was neutralised by 23.2 mL of 1N H_2SO_4. (iii) In a carius estimation of sulphur, 0.4132 g of the substance resulted in the precipitation of 1.1088 g of $BaSO_4$. The compound also contains 41.37% C and 5.75% hydrogen. Calculate the molecular formula of the organic liquid. (At. wt., Ba = 137, S = 32, O = 16).*

SOLUTION. (*i*) Wt. of substance = 0.203 g; P_1 = 750 mm; V_1 = 55.92 mL, T_1 = 15 + 273 = 288 K; at N.T.P, P_2 = 760 mm, V_2 = ?, T_2 = 273 K.

Using gas equation :

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

$$V_2 = \frac{P_1V_1T_2}{T_1P_2} = \frac{750 \times 55.92 \times 273}{288 \times 760}$$

or $\quad V_2 = 52.31$ mL

$$\therefore \quad \text{Mol. wt.} = \frac{W}{V_2} \times 22400 = \frac{0.203}{52.31} \times 22400$$

$$= 86.93 \text{ g mol}^{-}$$

(*i*) To find % age of nitrogen.

23.2 mL of 1N H_2SO_4 ≡ 23.2 mL of 1N NH_3

1000 mL of 1N NH_3 contain nitrogen

= At. wt. of nitrogen = 14 g

23.2 mL of 1N NH_3 contain nitrogen

$$= \frac{14}{1000} \times 23.2 \text{ g}$$

$$\therefore \quad \text{\% age of nitrogen} = \frac{14 \times 23.2 \times 100}{1000 \times 2.02} = 16.08\%$$

(*ii*) To find % age of sulphur.

$BaSO_4$ ≡ S

137 + 32 + (4 × 16) = 233 g 32 g

233 g $BaSO_4$ contain S = 32 g

1.1088 g $BaSO_4$ contains S

$$= \frac{32}{233} \times 1.1088 \text{ g}$$

$$\therefore \quad \text{\% age of S} = \frac{32 \times 1.1088 \times 100}{233 \times 0.4132} = 36.85$$

(*iii*) To find E.F.

Element	*% age*	*at.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	41.37	12	$\frac{41.37}{12} = 3.45$	$\frac{3.45}{1.15} = 3$	3
H	5.75	1	$\frac{5.75}{1} = 5.75$	$\frac{5.75}{1.15} = 5$	5
N	16.08	14	$\frac{16.08}{14} = 1.15$	$\frac{1.15}{1.15} = 1$	1
S	36.85	32	$\frac{36.85}{32} = 1.15$	$\frac{1.15}{1.15} = 1$	1

$\therefore$ E.F. of compound = C_3H_5NS

E.F. wt. of compound = (3 × 12) + (5 × 1) + 14 + 32

= 87

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= C_3H_5NS \times \frac{86.93}{87}$$

$$\simeq C_3H_5NS \times 1$$

M.F. = $\mathbf{C_3H_5NS}$ **Ans.**

EXAMPLE 33. *(a) A solution of a 1.25g of the non-volatile substance in 25g of water boiled at 100.26°C. The value of 'K', the molecular elevation for 100 g of water is 5.2 °C. (b) 2g of the substance when Kjeldahlised produced 0.34g of NH_3. If the percentage of carbon and hydrogen in the compound are 48% and 5% respectively, what would be the molecular formula of the compound.*

SOLUTION. (*a*) Elevation in b.pt, ΔT = 100.26 – 100 = 0.26 °C = 0.26 K, Mol. wt. of solute, M_2 = ?,

W = wt. of substance = 1.25 g;

$$W = \text{wt. of solvent} = 25\text{ g} \times \frac{1\text{kg}}{1000\text{ g}} = 0.025\text{ kg};$$

K = 5.2 °C kg mol^{-}/100 g = 0.52 °C or 0.52K kg mol^{-}.

$$\text{Mol. wt., } M_2 \text{ of substance} = \frac{K \times w}{W \times \Delta T}$$

$$= \frac{0.52\text{K kg mol}^{-} \times 1.25\text{g}}{0.025\text{kg} \times 0.26\text{ K}} = 100\text{g mol}^{-}\cdot$$

(*b*) To find % age of nitrogen.

Mol. wt. of NH_3 = 14 + (3 × 1) = 17

17g NH_3 contain N = 14 g (∵ at. wt. of N = 14)

$$0.34\text{g } NH_3 \text{ contain N} = \frac{14}{17} \times 0.34\text{ g}$$

$$\therefore \quad \% \text{ age of N} = \frac{14 \times 0.34}{17} \times \frac{100}{2} = \mathbf{14\%}$$

(*c*) To find E.F., C = 48%, H = 5%,

N = 14%,

O = 100 – (48 + 5 + 14) = 33 %.

Element	*% age*	*at.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	48	12	$\frac{48}{12} = 4$	$\frac{4}{1} = 4$	4
H	5	1	$\frac{5}{1} = 5$	$\frac{5}{1} = 5$	5
N	14	14	$\frac{14}{14} = 1$	$\frac{1}{1} = 1$	1
O	33	16	$\frac{33}{16} = 2$	$\frac{2}{1} = 2$	2

∴ E.F. of substance = $C_4H_5NO_2$

E.F. wt. of substance = (4 × 12) + (5 × 1) + 14 + (2 × 16) = 99

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= C_4H_5NO_2 \times \frac{100}{99}$$

$$= C_4H_5NO_2 \times 1$$

$$= \mathbf{C_4H_5NO_2}$$ **Ans.**

EXAMPLE 34. *A sample of an organic substance weighing 1.0g having the empirical formula CH_2O was vaporised at 220°C and 760 mm pressure. Its vapours occupied 560 mL volume. The same volume was occupied by 0.5g of C_2H_6 (ethane) gas under similar conditions of temperature and pressure. Calculate the molecular formula of the substance.*

SOLUTION. The given organic substance as well as C_2H_6 occupy the same volume (560 mL) under similar conditions of temperature and pressure. So, according to ***Avogadro's law***, equal volume of both gases would contain equal number of molecules. So, the ratio of their weights (of equal volume) would give the ratio of the weights of single molecules or mol. wt. *i.e.,*

	Sample	C_2H_6
wt.	1.0	0.5
Ratio of wts.	$\frac{1.0}{0.5} = 2$	$\frac{0.5}{0.5} = 1$

Mol. wt. of C_2H_6 = (2 × 12) + (6 × 1) = 30

∴ Mol. wt. of sample = 2 × 30 = 60

E.F. of sample = CH_2O;

E.F. wt. of sample = 12 + (2 × 1) + 16 = 30

$$\therefore \quad \text{M.F. of sample} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

(= 2)

$$= CH_2O \times \frac{60}{30}$$

$$= \mathbf{C_2H_4O_2}$$ **Ans.**

EXAMPLE 35. *The element composition of an unknown compound of molecular mass 86 is found to be carbon 69.75%, hydrogen 11.65% and the balance oxygen. What is the molecular formula of the compound ? Also specify the group to which it belongs.* **(P.b. C.E.T. 1998)**

SOLUTION. Percentage of oxygen = 100 – (% of C + % of H) = 100 – (69.75 + 11.65) = 18.6%.

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	69.75	12	$\frac{69.75}{12} = 5.8125$	$\frac{5.8125}{1.1625} = 5$	5
H	11.65	1	$\frac{11.65}{1} = 11.65$	$\frac{11.65}{1.1625} = 10.02$	10
O	18.6	16	$\frac{18.6}{16} = 1.1625$	$\frac{1.1625}{1.1625} = 1$	1

Empirical formula = $C_5H_{10}O$

Empirical formula mass

= 12 × 5 + 1 × 10 + 16 × 1 = 86

Molecular mass = 86

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

$$= \frac{86}{86} = 1.$$

Molecular formula = *n* × Emp. formula

= 1 × $C_5H_{10}O$ =$C_5H_{10}O$

The molecular formula indicates that the given compound can be aldehyde or ketone. Therefore, the functional group present is >C = O.

EXAMPLE 36. *An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess acid required 25 mL of 0.1 M sodium hydroxide for neutralisation. Determine the molecular formula of the compound if its molecular weight is 121. Draw two possible structures for this compound.* **(I.I.T. 1982)**

SOLUTION. (*i*) *Calculation of the percentage of nitrogen.*

Since, eq. wt. of H_2SO_4 is half its mol. wt., therefore, molarity of H_2SO_4 is half its normality.

$\therefore$ 50 mL of 0.05 M sulphuric acid = 50 mL of 2 × 0.05 (= 0.1 N) sulphuric acid.

Excess acid requires 25 mL of 0.1 M or 0.1N NaOH (normality of NaOH = molarity of NaOH) for neutralisation.

$\therefore$ 0.1N H_2SO_4 neutralised by 25 mL of 0.1 N NaOH = 25 mL.

Acid used up for the neutralisation of ammonia evolved is :

$$= 50 \text{ mL of } 0.1\text{N } H_2SO_4 - 25 \text{ mL of } 0.1\text{N } H_2SO_4$$

$$= 25 \text{ mL of } 0.1\text{N } H_2SO_4$$

$$25 \text{ mL of } 0.1\text{N } H_2SO_4 \equiv 25 \text{ mL } 0.1 \text{ N } NH_3$$

$$\equiv 2.5 \text{ mL } (= 25 \times 0.1 = 2.5) \text{ of } 1 \text{ N } NH_3$$

$$1000 \text{ mL } 1\text{N } NH_3 \equiv 17 \text{ g } NH_3 = 14 \text{ g nitrogen}$$

$$\therefore \quad 2.5 \text{ mL } 1\text{N } NH_3 = \frac{14}{1000} \times 2.5 = \frac{7}{200} \text{ g nitrogen}$$

Thus, 0.303 g of aromatic compound contains $\frac{7}{200}$ g of nitrogen.

Hence,percentage of nitrogen

$$= \frac{7 \times 100}{200 \times 0.303} = 11.55$$

(*ii*) *Calculation of empirical formula*

Percentage of carbon = 69.40

Percentage of hydrogen = 5.80

Percentage of nitrogen = 11.55

Percentage of oxygen = 100 – (69.4 + 5.8 + 11.55) = 13.25

$$\therefore \quad C : H : N : O = \frac{69.40}{12} : \frac{5.80}{1} : \frac{11.55}{14} : \frac{13.25}{16}$$

$$= 5.8 : 5.80 : 0.825 : 0.828$$

$$= 7 : 7 : 1 : 1$$

(by dividing each with 0.825)

$\therefore$ The empirical formula of the aromatic compound is C_7H_7NO.

(*iii*) *Calculation of molecular formula*

The empirical formula weight of the aromatic compound, C_7H_7NO, is 7 × 12 + 7 × 1 + 14 + 16 = 121.

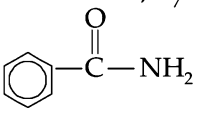
$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{121}{121} = 1$$

Hence, molecular formula of the compound is the same as the empirical formula *i.e.*, C_7H_7NO. ($\because$ M.F. = *n* × E.F. = 1 × C_7H_7NO = C_7H_7NO)

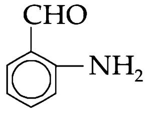
(*iv*) *Structure of the compound.*

Since, the aromatic compound must contain a benzene ring, the two possible structures for the compound with molecular formula, C_7H_7NO are :

(*i*)



(*ii*)



26.5 AIEEE PATTERN EXAMPLES

EXAMPLE 37. *The empirical formula of a non-electrolyte is CH_2O. A solution containing 3 g of the compound exerts the same osmotic pressure as that of 0.05 M glucose solution. The molecular formula of the compound is :*

(*a*) CH_2O (*b*) $C_2H_4O_2$

(*c*) $C_4H_8O_4$ (*d*) $C_3H_6O_3$

(Karnatka CET, 2011)

SOLUTION.

Empirical formula = CH_2O. So, E.F. mass = 12 + (2 × 1) + 16 = 30

wt. of glucose = 3 g.

1 M of glucose, $C_6H_{12}O_6$ = (6 × 12) + (12 × 1) + (6 × 16) = 180 g mol$^-$

$\therefore$ 0.05 M glucose, 180 × 0.05 = 9 g

$$\text{For isotonic solution, } \frac{W_a}{M_a} = \frac{W_{C_6H_{12}O_6}}{M_{C_6H_{12}O_6}};$$

$$\frac{3}{M_a} = \frac{9}{180}$$

$$\therefore \quad M_a = 3 \times 180/9 = 60$$

But Molecular formula = *n* × Empirical formula

where *n* = M.wt./E.F. wt = 60/30 = 2.

$\therefore$ Molecular formula = 2 × CH_2O = $C_2H_4O_2$.

So, the correct formula is (*b*).

EXAMPLE 38. *An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating, it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is :*

(1) CH_3NCO (2) CH_3CONH_2

(3) $(NH_2)_2CO$ (4) $CH_3CH_2CONH_2$

(AIEEE, 2005)

SOLUTION. C = 20%, H = 6.67%,

N = 46.67%,

$$O = 100 - (20 + 6.67 + 46.67)$$
$$= 26.66.$$

Element	*% age*	*At.wt*	*Relative number of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
C	20	12	$\frac{20}{12} = 1.67$	$\frac{1.67}{1.67} = 1$	1
H	6.67	1	$\frac{6.67}{1} = 6.67$	$\frac{6.67}{1.67} = 4$	4
N	46.67	14	$\frac{46.67}{14} = 3.33$	$\frac{3.33}{1.67} = 2$	2
O	26.66	16	$\frac{26.66}{16} = 1.67$	$\frac{1.67}{1.67} = 1$	1

$\therefore$ E.F. of compound = $C_1H_4N_2O_1 = CH_4N_2O$.

Since the compound gives out NH_3 on heating and it gives violet colour with alkaline copper sulphate (Biuret test), it appears to be urea, NH_2CONH_2.

$$2NH_2CONH_2 \xrightarrow{\Delta} NH_2CONHCONH_2 + NH_3 \uparrow$$

So, the correct answer is (3).

EXAMPLE 39. *A solution containing 1.8 g of a compound (empirical formula CH_2O) in 40 g water is observed to freeze at –0.465°C. The molecular formula of the compound is : (K_f for water = 1.86 kg K mol⁻) :*

(*a*) $C_2H_4O_2$ (*b*) $C_3H_6O_3$ (*c*) $C_4H_8O_4$

(*d*) $C_5H_{10}O_5$ (*e*) $C_6H_{12}O_6$ **(Kerala PET, 2011)**

SOLUTION. Let M = molar mass of compound ;

E.F. = CH_2O ;

$$\text{Molality, } m = \frac{\text{wt.}}{\text{Mol. wt}} \times \frac{1000}{\text{wt. of solvent}}$$

$$= \frac{1.8 \text{ g}}{\text{M}} \times \frac{1000}{40 \text{ g}} = \frac{45}{\text{M}} \text{ mol kg}^{-}$$

$$\Delta T_f = 0.465°\text{C or } 0.465 \text{ K}.$$

We know that

$$\Delta T_f = K_f \times m \text{ ;}$$

$$0.465 \text{ K} = 1.86 \text{ kg K mol}^{-} \times \frac{45}{\text{M}} \text{ mol kg}^{-}$$

$$\therefore \qquad \text{M} = \frac{1.86 \text{ kg K mol}^{-} \times 45 \text{ mol kg}^{-}}{0.465 \text{ K}}$$

$= 180$ [E.F. wt. of CH_2O = 12 + (2 × 1) + 16 = 30]

Molecular formula = n × empirical formula

$$\text{where} \qquad n = \frac{\text{Molecular mass (wt.)}}{\text{E.F. weight}}$$

$$= \frac{180}{30} = 6$$

$\therefore$ Molecular formula = 6 × CH_2O = $C_6H_{12}O_6$.

Hence the correct answer is (*e*).

EXAMPLE 40. *A hydrocarbon contains 80% carbon. What is the empirical formula of the compound ?*

(*a*) CH_4 (*b*) CH_3 (*c*) CH_4

(*d*) CH (*e*) C_2H_3 **(Kerala PMT, 2011)**

SOLUTION. % age of C = 80 ; % age of H = 100 – 80 = 20

To find empirical formula (E.F.), we use the following table.

Element	*% age*	*At.wt*	*Relative no. of atoms = % age/At. wt.*	*Simple ratio*	*Whole no. ratio*
Carbon, C	80	12	80/12 = 6.67	$\frac{6.67}{6.67} = 1$	1
Hydrogen, H	20	1	20/1 = 20	$\frac{20}{6.67} = 2.99$	3

$\therefore$ E.F. of hydrocarbon = C_1H_3 or CH_3.

So, the correct answer is (*b*).

EXAMPLE 41. *In the estimation of sulphur by carius method, 0.480 g of an organic compound gives 0.699 g of barium sulphate. The percentage of sulphur in this compound is (atomic mass, Ba = 137, S = 32, O = 16):*

(*a*) 20 % (*b*) 15 % (*c*) 35 %

(*d*) 30 % (*e*) 40 % **(Kerala PET, 2012)**

SOLUTION. $BaSO_4 \equiv S$

137 + 32 + (4 × 16)

= 233 g 32g

233 g $BaSO_4$ contain S = 32 g

$$0.699 \text{ g BaSO}_4 \text{ contain S} = \frac{32}{233} \times 0.699 \text{ g}$$

$$\therefore \text{ \% age of S} = \frac{\text{wt. of S}}{\text{wt. of substance}} \times 100$$

$$= \frac{32}{233} \times \frac{0.699}{0.48} \times 100 = 20.$$

So, the correct answer is (*a*).

EXAMPLE 42. *A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g of CO_2. The empirical formula of hydrocarbon is:*

(1) C_3H_4 (2) C_6H_5

(3) C_7H_8 (4) C_2H_4 **(JEE Main, 2013)**

SOLUTION. Mol wt. of H_2O $(2 \times 1) + 16 = 18$g mol^{-}; mol. wt. of $CO_2 = 12 + (2 \times 16) = 44$ g mol^{-}.

$$\text{No. of mol of } H_2O \text{ produced} = \frac{\text{wt}}{\text{mol . wt}} = \frac{0.72}{18} = 0.04$$

$$\text{No. of mol of } CO_2 \text{ produced} = \frac{\text{wt}}{\text{mol. wt.}} = \frac{3.08}{44} = 0.07$$

Equation to show combustion of hydrocarbon C_xH_y is:

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}\, H_2O \text{ ....(1)}$$

From equation (1), $x = 0.07$ and $\frac{y}{2} = 0.04$ i.e.,

$y = 2 \times 0.04 = 0.08$

$\therefore \ \frac{x}{y} = \frac{0.07}{0.08} = \frac{7}{8}$. Hence the empirical formula of hydrocarbon is C_7H_8.

So, the correct answer is (3).

PROBLEMS FOR PRACTICE

1. Calculate the empirical formula of the following molecular formulae.

   (*i*) C_6H_6 (*ii*) N_2O_4

   (*iii*) H_2O (*iv*) Na_2CO_3

   [**Ans** (*i*) CH (*ii*) NO_2 (*iii*) H_2O (*iv*) Na_2CO_3]

2. Calculate the % age of Na in Na_2CO_3. **Ans.** 43.4%

3. A hydrocarbon is composed of 75 % carbon. The empirical formula of the compound is :

   (*a*) CH_2 (*b*) CH_3 (*c*) C_2H_5

   (*d*) C_2H_7 (*e*) CH_4 **(Kerala PMT, 2010)**

   Ans. (*e*)

4. In an experiment, 4 g of M_2O_x oxide was reduced to 2.8 g of the metal. If the atomic mass of the metal is 56 g mol^{-}, the number of O-atoms in the oxide is :

   (*a*) 1 (*b*) 2

   (*c*) 3 (*d*) 4

   (AFMC, 2010)

   Ans. (*c*).

5. 1.0 g of a hydrated compound of iron contains 0.2014 g of Fe, 0.1153 g of S, 0.231 g O and 0.4532 g of water of crystallisation. Find the empirical formula of the compound. (**Ans.** $FeSO_4 \cdot 7H_2O$)

6. When anhydrous salt of zinc weighing 1.615 g. was placed in moist air, it got fully hydrated and weighed 2.875 g. Calculate the molecular formula of the hydrated compound, if it contains Zn = 40.6%, O = 39.6% and S = 19.8%. (At. wt. Zn = 65, S = 32, O = 16, H = 1)

   (**Ans.** $ZnSO_4.7H_2O$).

7. The chloride of a platinum contains 42.1 % chlorine. Calculate its empirical formula (At. wt. Pt = 195, Cl = 35.5)

   (**Ans.** Pt Cl_4)

8. Calculate he molecular formula of an organic compound having mol. wt. 30 g mol^{-} and percentage of C and H as 80% and 20% respectively. (At. wt. C = 12, H = 1)

   (**Ans.** C_2H_6).

9. Copper chloride weighing 4.0 g on analysis was found to contain 2.11 g chlorine (Cl) and 1.89 g copper (Cu). Calculate the empirical formula of the compound.

   (At. wt. Cu = 63.5, Cl = 35.5)

   (**Ans.** Cu Cl_2)

10. The molecular weight of an organic compound is 78 g mol^{-} and its percentage composition is 92.3% C and 7.69% H. Find its molecular formula.

    (**Ans.** C_6 H_6)

27

CHAPTER

Structure and Reaction Based Problems

27.1 SOME BASIC CONCEPTS

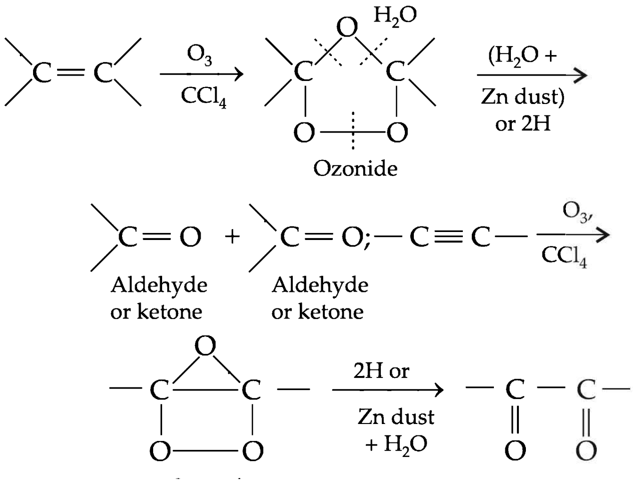
In order to elucidate structure of organic compounds based on certain given reactions, some specific reactions of organic compounds are given for the help of students. The students are advised to go through these reactions before attempting the concerned problem.

1. **Saturated hydrocarbons** (C_nH_{2n+2}). These usually undergo **substitution** reactions. e.g.,

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

2. Unsaturated hydrocarbons [C_nH_{2n} *i.e.*, $C=C$ **double bond** ; C_nH_{2n-2} *i.e.*, $C\equiv C$ **triple bond**]. These undergo **addition reactions.** For example :

(*a*) Ozonolysis reactions.



The process helps to decide nature of unsaturation in the compound. It also helps to locate the position of unsaturation in a compound. For example; the **terminal alkynes** give the following reactions.

(*i*) Reaction with ammoniacal Cu_2Cl_2 to give red precipitate of Cu(I) acetylide

$$\underset{\text{Terminal Carbon}}{2[-C\equiv CH]} + Cu_2Cl_2 \longrightarrow \underset{\text{Red ppt.}}{[-C\equiv C.Cu]} + 2HCl$$

(*ii*) Reaction with Na to give H_2 gas

$$-C\equiv CH \xrightarrow[NH_3]{\text{Na in}} -C\equiv C.\,Na + \frac{1}{2}H_2$$

(*iii*) Reaction with ammoniacal silver nitrate to give white ppt. of silver alkylide.

$$-C\equiv CH + Ag_2O \longrightarrow \underset{\text{Silver alkylide (white ppt.)}}{-C\equiv C.\,Ag} + H_2O$$

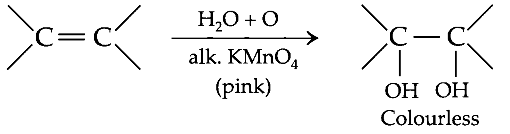
Note. **Ozonolysis of** (*i*) **Symmetrical alkenes** (e.g., $CH_2=CH_2$, $CH_3CH=CHCH_3$ etc) give two mole of same carbonyl compound ($>C=O$).

(*ii*) **Alkynes** give one product having two carbonylic groups.

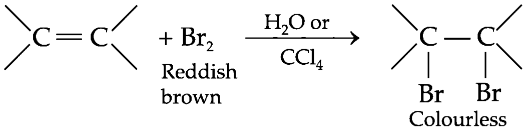
(*iii*) **Cycloalkenes** give one product having two carbonyl groups.

(*b*) **Halogenation of alkenes.** These follow anti-addition. Br_2 adds to cis-2-butene to give a racemic mixture of 2,3-dibromobutane. Br_2 adds to trans-2-butene to give a meso-derivative of 2, 3-dibromobutane.

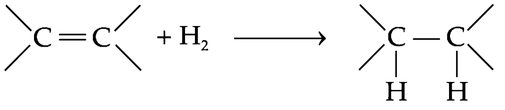
(*c*) **Decolorises Baeyer's reagent** (1% cold alkaline $KMnO_4$ solution).



(*d*) Decolorises bromine water or Br_2 solution in CCl_4.

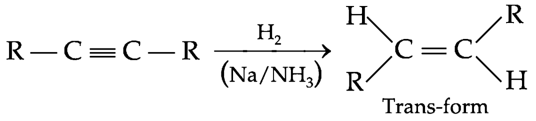


(*e*) **Addition of H_2** to form saturated hydrocarbon.

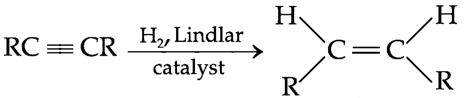


(*f*) **Hydrogenation of alkynes**

(*i*) With Na/NH_3, trans-form is formed.



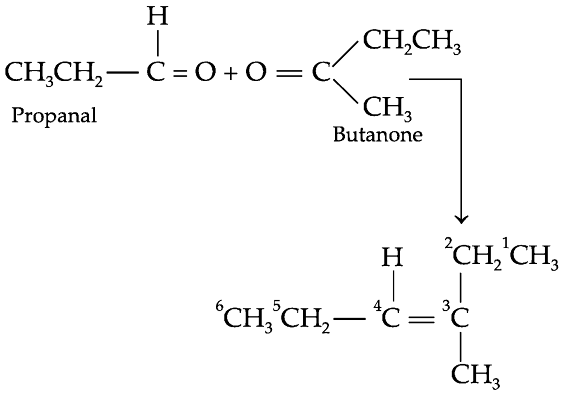
(*ii*) With H_2 in presence of **Lindlar catalyst,** cis form is obtained.



$$RC \equiv CR \xrightarrow[\text{catalyst}]{H_2,\text{ Lindlar}} \text{(H)(R)C} = \text{C(H)(R)}$$

Cis-form

Location of C ═ C in alkenes : The structure of alkene can be obtained by removing the oxygen atoms of the two carbonyl carbons of products and making a double bond between the carbonyl carbon atoms. *e.g.,* if an alkene on ozonolysis followed by action with Zn-dust and water gives propanal and butanone, the structure of alkene will be:



3-Methyl-hex-3-ene

3. Halides

(*i*) **Monohalides.** (a) with KOH(aq), these give **alcohols**

$$RX + KOH(aq) \longrightarrow ROH + KX$$

(*b*) **With KOH (alcoholic),** these give **alkene**

$$RCH_2 - CH_2X + KOH\ (alc) \longrightarrow RCH = CH_2 + KX + H_2O$$

(*ii*) **Dihalides.** (a) with KOH (aq), **vicinal** dihalides (*i.e.,* halogens on different carbon atoms), give diol.

$$CH_2X - CH_2X \xrightarrow{KOH\,(aq)} CH_2OH - CH_2OH\ (diol)$$

(*b*) **With KOH(aq), gem** dihalides (*i.e.,* halogens on the same carbon atom) with **terminal** position to halogens, give **aldehydes.**

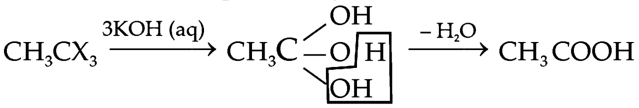
$$CH_3CH_2CHX_2 \xrightarrow{KOH\,(aq)} CH_3CH_2CHO \quad \text{(Propanal)}$$

(*c*) **With KOH(aq),** gem dihalides with **non-terminal position** to halogens give **ketones**

$$CH_3.CX_2.CH_3 \xrightarrow{KOH\,(aq)} CH_3COCH_3\ \text{(Acetone)}$$

(*iii*) **Trihalides.** When all the three halogens are on terminal carbon atoms then :

(*a*) With KOH (aq), **carboxylic acid** is formed,



$$CH_3CX_3 \xrightarrow{3KOH\,(aq)} CH_3C(OH)_3 \xrightarrow{-H_2O} CH_3COOH$$

Unstable Acetic acid

(*b*) With primary amine and alc. KOH, these give **carbylamine reaction.** As a result, unpleasant odour is produced.

$$CHCl_3 + RNH_2 + 3KOH\,(alc) \longrightarrow RN \equiv C + 3KCl + 3H_2O$$

Chloroform Carbylamine (unpleasant smell)

4. Alcohols.

(*i*) These give esters (having fruity odour) when warmed with carboxylic acids.

$$ROH + RCOOH \xrightarrow{\text{Warm}} RCOOR + H_2O.$$

(*ii*) These give red colour with ceric ammonium nitrate

(*iii*) These evolve H_2 gas with effervescence when treated with Na or K metal.

$$2ROH + 2Na \longrightarrow 2RONa + H_2\,(g).$$

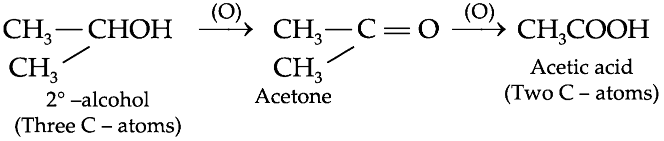
Distinction among primary (1°), secondary (2°) and tertiary (3°) alcohols.

Oxidation test (*a*) 1°- alcohols on oxidation give firstly aldehyde and finally carboxylic acid having same number of carbon atoms as that of 1°-alcohol

$$RCH_2OH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH$$

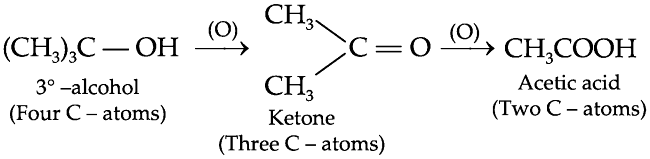
1°-alcohol Aldehyde Carboxylic acid.

(*b*) 2°–alcohols (on oxidation) give first of all ketones (with same number of carbon atoms as of 2°–alcohol) and finally carboxylic acid (having one carbon atom less than the parent 2°–alcohol)



$$(CH_3)_2CHOH \xrightarrow{(O)} (CH_3)_2C = O \xrightarrow{(O)} CH_3COOH$$

(*c*) **3°-alcohols** (on drastic oxidation) give first of all ketones (with one C-atom less than the parent 3°-alcohol) and finally carboxylic acid (with two C-atoms less than the parent 3°-alcohol)



$$(CH_3)_3C - OH \xrightarrow{(O)} (CH_3)_2C = O \xrightarrow{(O)} CH_3COOH$$

(B) **Lucas Test.** Lucas reagent is 'anhydrous $ZnCl_2$ + Conc. HCl'.

(*i*) Primary alcohols donot give white ppt. or cloudiness with Lucas reagent within 15 minutes but give separate layer of alkyl chloride on heating.

$$CH_3CH_2OH \xrightarrow[\text{conc,HCl, }\Delta]{\text{anhy. }ZnCl_2,} CH_3CH_2Cl$$

(*ii*) **Secondary alcohols** give ppt. or cloudiness in 5-10 minutes with Lucas reagent.

$$(CH_3)_2CHOH \xrightarrow[\text{conc,HCl}]{\text{Anhy. }ZnCl_2,} (CH_3)_2\,CHCl$$

(Isopropyl chloride)

(*iii*) **Tertiary alcohols** give ppt. or cloudiness immediately.

$$(CH_3)_3COH \xrightarrow[\text{conc,HCl}]{\text{Anhyd. }ZnCl_2,} (CH_3)_3CCl$$

(tert. butyl chloride)

(C) Victor Meyer's method

(*i*) Primary, secondary and tertiary alcohols on treatment with P + I_2, $AgNO_2$ and alkali, give blood red colour, blue colour and no colour respectively.

(D) Action of dehydration reagent. At low temperature, these give ether.

$$2ROH \xrightarrow[\text{temp.}]{\text{low}} R\text{–}OR(\text{ether}) + H_2O$$

At higher temperature, alkene is formed. The order of reaction is : tert. alcohol > sec. alcohol > primary alcohol.

$$CH_3CH_2OH \longrightarrow CH_2 = CH_2 + H_2O.$$

(E) Action with Cu at 200–300°C. 1°, 2° and 3° alcohols give aldehyde, ketone and alkene respectively.

5. Ethers.

(*i*) These donot change the colour of litmus.

(*ii*) **Action with conc.** HI.

(*a*) **In cold,** alkyl iodide is formed.

$$ROR + HI \longrightarrow RI + ROH$$

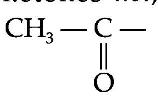
(*b*) **In hot,** two mol of alkyl iodide are formed

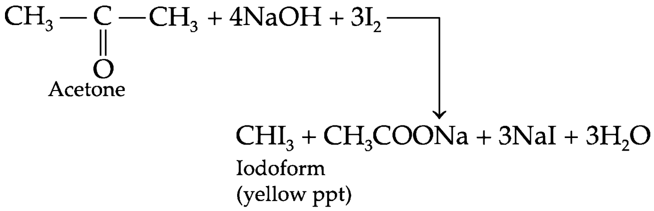
$$ROR' + 2HI \longrightarrow RI + R'I + H_2O$$

(*c*) With mixed ethers, the iodide gets attached to alkyl group having less number of carbon atoms.

$$CH_3OC_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

6. Carbonyl ($>C=O$) compounds (aldehydes and ketones)

(*i*) **Iodoform test.** Acetaldehyde and all methyl ketones *i.e.*, organic compounds containing  $CH_3-\underset{\underset{O}{\|}}{C}-$ unit bonded to H or carbon give yellow *ppt.* with NaOH + I_2 solution.



$$\underset{\text{Acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + 4NaOH + 3I_2 \longrightarrow \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + CH_3COONa + 3NaI + 3H_2O$$

(*ii*) Action with DNP *i.e.*, 2, 4-dinitrophenyl hydrazine. Both aldehyde and ketone give orange-yellow solid with DNP.

(*iii*) **Aldehydes.** (*a*) Reduce Schiff's reagent to give pink colour.

(*b*) Reduce Benedict reagent to give red ppt. of Cu_2O.

(*c*) Reduce Fehling solution to give red ppt. of Cu_2O

$$R\,CHO + 2CuO \longrightarrow R\,COOH + Cu_2O\downarrow \text{(red ppt.)}.$$

Benzaldehyde does not give this test.

(*d*) Reduce Tollen's reagent (ammoniacal silver nitrate solution) to give silver mirror test.

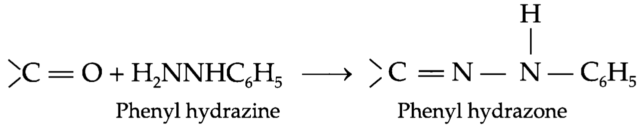
$$RCHO + Ag_2O \longrightarrow RCOOH + 2Ag\downarrow \text{(silver mirror)}$$

(*e*) Give primary alcohols on reduction.

(*f*) **Addition reactions.** All aldehydes (and only methyl ketones) give white ppt. with sodium bisulphite.

(*g*) Carbonyl compounds give oxime with hydroxylamine and hydrazone with phenylhydrazine.

$$>C=O + \underset{\text{Hydroxylamine}}{H_2NOH} \longrightarrow \underset{\text{Oxime}}{>C=NOH} + H_2O$$



$$>C=O + \underset{\text{Phenyl hydrazine}}{H_2NNHC_6H_5} \longrightarrow \underset{\text{Phenyl hydrazone}}{>C=N-\overset{\overset{H}{|}}{N}-C_6H_5}$$

Note 1. Like aldehydes, ketones form addition products with $NaHSO_3$, 2, 4-dinitrophenyl hydrazine, HCN, NH_3. Ketones donot reduce Fehling solution, Benedict solution, donot give pink colour with Schiff's reagent, give secondary alcohol on reduction, on oxidation give carboxylic acid with one carbon atom less than the parent ketone.

2. An aldehyde when warmed with dilute alkali undergoes aldol condensation. Such an aldehyde must contain an α-hydrogen.

7. Carboxylic acids.

(*i*) These turn blue litmus red.

(*ii*) These give effervescence with $NaHCO_3$ solution.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2\uparrow + H_2O$$

(*iii*) When heated with soda-lime (NaOH + CaO), CO_2 gas is evolved along with alkane.

$$RCOOH \xrightarrow[\Delta]{CaO + NaOH} RH + CO_2.$$

(*iv*) **With NH_3.** When heated with NH_3, amide is formed which on further heating with P_2O_5 form cyanide.

$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{-H_2O}$$

$$\underset{\text{Amide}}{RCONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Cyanide}}{RCN}$$

(*v*) With alcohol and conc. H_2SO_4, acids give esters having fruity odour.

$$RCOOH + R'OH \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\text{ester}}{RCOOR'} + H_2O.$$

(*vi*) **On dry distillation** (*a*) Calcium formate gives formaldehyde.

$$Ca(HCOO)_2 \longrightarrow CaCO_3 + HCHO \text{ (formaldehyde)}$$

(*b*) Calcium acetate gives acetaldehyde.

$$Ca(CH_3COO)_2 \longrightarrow CaCO_3 + CH_3CHO \text{ (acetaldehyde)}$$

(*c*) A mixture of $Ca(HCOO)_2$ and $Ca(CH_3COO)_2$ give acetaldehyde.

$$Ca(HCOO)_2 + Ca(CH_3COO)_2 \longrightarrow 2CaCO_3 + 2CH_3CHO.$$

(*d*) If a mixture contains $Ca(HCOO)_2$, only aldehydes are formed. See reaction (*c*) above

(*e*) Mixed calcium salts of acids give all possible products.

8. Acid derivatives

(*i*) **Acid anhydrides.** (*a*) These form carboxylic acid on hydrolysis.

$$RCO.O.COR + H_2O \longrightarrow 2RCOOH$$

(*b*) These form ester and carboxylic acid with alcohol.

$$\text{RCO.O.COR} + \text{R'OH} \longrightarrow \text{RCOOH} + \underset{\text{(ester)}}{\text{R COOR'}}$$

(*ii*) **Acid amides.** (*a*) Form ammonia, when boiled with alkali, NH_3 gives brown ppt. with Nessler's reagent.

$$\text{RCONH}_2 + \text{NaOH} \longrightarrow \text{RCOONa} + \text{NH}_3$$

(*b*) **Hofmann's bromamide reaction.** These give primary amine when heated with KOH (aq) and Br_2.

$$\text{RCONH}_2 + 4\text{KOH} + \text{Br}_2 \longrightarrow \underset{\text{Primary amine}}{\text{RNH}_2} + \text{K}_2\text{CO}_3 + 2\text{KBr} + 2\text{H}_2\text{O}$$

(*c*) Form **nitrogen gas,** when heated with nitrous acid (HNO_2)

$$\text{RCONH}_2 + \text{HONO} \longrightarrow \text{RCOOH} + \text{N}_2\uparrow + \text{H}_2\text{O}$$

(*d*) Form cyanides *i.e.*, nitriles when heated with dehydrating agents like P_2O_5, $KHSO_4$ etc.

$$\text{RCONH}_2 \xrightarrow[\Delta]{\text{P}_2\text{O}_5} \text{RCN} + \text{H}_2\text{O}$$

(*iii*) **Esters.** (*a*) These possess fruity smell.

(*b*) Decolorise pink colour of phenolphthalein when boiled with aqueous alkali.

(*c*) On **reduction,** form two molecules of alcohol.

$$\text{RCOOR'} \xrightarrow{\text{Reduction}} \text{RCH}_2\text{OH} + \text{R'OH}$$

(*d*) On **hydrolysis,** form an alcohol and carboxylic acid.

$$\text{RCOOR'} + \text{HOH} \longrightarrow \text{R'OH} + \text{RCOOH}$$

(*iv*) **Acid chlorides.** (*a*) These fume in moist air due to their hydrolysis into HCl(g) and corresponding acid.

$$\text{RCOCl} + \text{HOH} \longrightarrow \text{HCl(g)}\uparrow + \text{RCOOH}$$

(*b*) On Rosenmund's reduction, these form aldehydes.

$$\text{RCOCl} + \text{H}_2 \xrightarrow[\text{S}]{\text{Pd, BaSO}_4} \text{RCHO} + \text{HCl}$$

9. Amines

(*i*) **Primary amines.** (*a*) Aliphatic as well as aromatic amines (*e.g.,*) aniline, $C_6H_5NH_2$, give carbylamine reaction (see serial no. 3, halides)

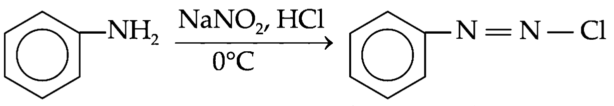
(*b*) **Action with HNO_2**($NaNO_2$ + HCl, 0°C). These give N_2 gas with HNO_2.

$$\text{RNH}_2 + \text{HONO} \longrightarrow \text{ROH} + \text{N}_2\uparrow + \text{H}_2\text{O}$$

(*c*) **Action with Hinsberg's reagent,** $C_6H_5SO_2Cl$. These give sulphonamide with $C_6H_5SO_2Cl$ which is soluble in an alkali

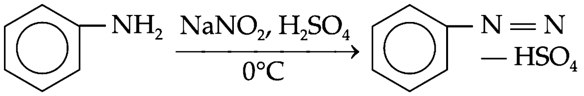
$$\text{RNH}_2 + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \longrightarrow \text{RNHSO}_2\text{C}_6\text{H}_5 \xrightarrow{\text{NaOH}} \text{RN NaSO}_2\text{C}_6\text{H}_5 \text{ (Solution)}$$

(*d*) **Diazotization.** Aromatic amines having $-NH_2$ group undergo diazotization with HNO_2 *i.e.*, $NaNO_2$ + HCl at 0°C (or $NaNO_2$ + H_2SO_4 at 0°C) to form diazonium salt

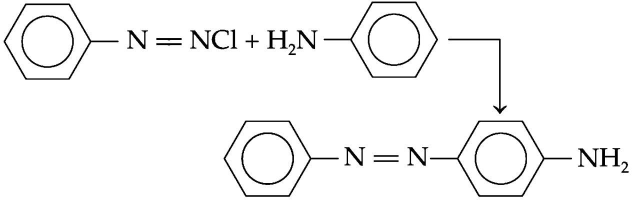


Aniline Benzene diazonium chloride

or



These diazonium salts undergo coupling reaction to form dye



p-Aminoazobenzene (yellow dye)

(*ii*) **Secondary amines.** (*a*) These react with nitrous acid HNO_2 ($NaNO_2$ + HCl) to give yellow oily substance, called nitrosamine.

$$\text{R}_2\text{NH} \xrightarrow{\text{HNO}_2} \underset{\text{(Yellow oily substance)}}{\text{R}_2\text{N}-\text{N}=\text{O}}$$

(*b*) **With Hinsberg's reagent,** $C_6H_5SO_2Cl$. These give sulphonamide with $C_6H_5SO_2Cl$ which is insoluble in an alkali.

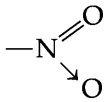
$$\text{R}_2\text{NH} + \text{C}_6\text{H}_5\text{SO}_2\text{Cl} \longrightarrow \text{R}_2\text{NSO}_2\text{C}_6\text{H}_5 \xrightarrow{\text{alkali}} \text{no action.}$$

(*iii*) **Tertiary amines.** (*a*) These react with HNO_2 ($NaNO_2$ + HCl) to give following products.

$$\text{R}_3\text{N} \xrightarrow{\text{HONO}} \text{R}_3\text{N.HNO}_2 \xrightarrow{\Delta} \text{R}_2\text{N.NO} + \underset{\text{(alcohol)}}{\text{ROH}}$$

(*b*) With Hinsberg's reagent $C_6H_5SO_2Cl$, these amines donot react.

10. Nitro compounds



(*i*) These form yellow coloured substance with NaOH solution.

(*ii*) Reduction with Sn + HCl. These form primary amine on reduction with Sn and HCl.

$$\text{RNO}_2 \xrightarrow[\text{(Sn + HCl)}]{6\text{H}} \text{RNH}_2 + 2\text{H}_2\text{O}$$

(*iii*) These give acids and hydroxylamine on hydrolysis.

11. Alkyl nitrite (R — O — N = O)

(*i*) On **hydrolysis,** these give corresponding alcohols giving nitrous acid.

(*ii*) On **reduction, these** form corresponding alcohols, liberating ammonia.

12. Cyanids.

(*i*) On **reduction,** these form primary amines.

$$\text{RCN} + 2\text{H}_2 \xrightarrow{\text{Pt}} \text{RCH}_2\text{NH}_2$$

(*ii*) On **hydrolysis** by an acid or alkali, acids are formed,

$$RCN + H_2O \xrightarrow{H^+} RCONH_2 \xrightarrow{H_2O, H^+} RCOOH + NH_4^+$$

13. **Isocyanides.**

(*i*) On **reduction**, these form secondary amines.

$$RNC + 2H_2 \longrightarrow RNHCH_3$$

(*ii*) On **hydrolysis**, these give primary amines.

$$RNC + 2HOH \longrightarrow HCOOH + RNH_2$$

14. **Aromatic compounds.**

(*a*) Such compounds obey $(4n + 2)\ \pi$ electron rule (*i.e.*, **Huckel's rule**) in planar ring system. Here, *n* is any integer, 0, 1, 2 etc.

(*b*) Groups such as $-OH$, $-NH_2$, $-OR$, $-NHCOCH_3$, $-SH$, $-CH_3$, $-X$, NH_3^+, $-NC$ etc, already present in the nucleus, are **ortho and para dircting** groups.

(*c*) Groups such as $-NO_2$(nitro), $-CN$, $-CHO$, $-COOH$, $-SO_3H$, $-CCl_3$ etc are **meta–directing** groups

15. **Carbohydrates.**

(*i*) **Molish's test.** 2 mL carbohydrate (aq) is firstly mixed with 1 or 2 drops of alcoholic solution of α – naphthol. Now 1mL of conc. H_2SO_4 is added along the sides of the tube. Violet ring at the junction confirms carbohydrate.

(*ii*) **Osazone formation.** When glucose or fructose ($C_6H_{12}O_6$) is heated with phenylhydrazine in presence of acetic acid, a yellow crystalline compound called osazone (m.p. 205°C) is formed.

16. **Phenols**

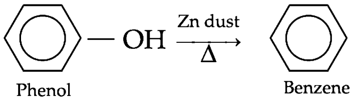
(*i*) These turn moist blue litmus red

(*ii*) These donot give effervescence with $NaHCO_3$

(*iii*) These are soluble in alkali

(*iv*) These give characteristic colour with aqueous $FeCl_3$ solution.

(*v*) Phenol when heated with zinc dust forms benzene.



17. **Ammonium salts of acids.**

(*i*) When ammonium salts of monocarboxylic acid are heated, acid amides are formed. For test of amides, see acid amides on previous pages.

(*ii*) When ammonium salts of dicarboxylic acids (having — COOH groups on adjacent C–atoms) of aliphatic and aromatic compounds are heated, amides are formed which further lose ammonia molecule to give imides.

27.2 SOME TYPICAL FACTS

1. A compound which undergoes haloform reaction, must contain CH_3CO- group.
2. A compound which does not answer iodoform test, does not contain CH_3CO- group.
3. A compound which forms mono-ozonide contains a $C=C$ double bond. A mono-ozonide of the type shown in Fig. 1 undergoes hydrolysis in presence of zinc dust to give RCHO (aldehyde) and $\begin{matrix}R\\R'\end{matrix}\!\!>C=O$ (a ketone) where R′ = alkyl group and not H; if R′ = H, then aldehyde is obtained.

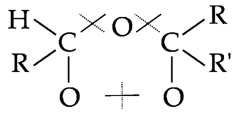
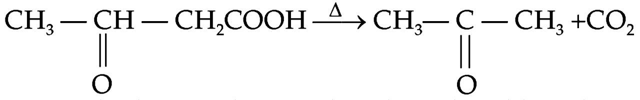


Fig. 1.

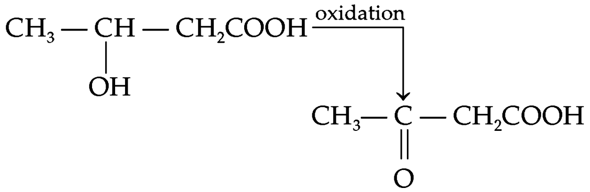
4. To assign position to keto group in carbon chain, keto acids on careful oxidation undergo C — C bond fission at a place where $>C=O$ is situated.

   Further keto-group is also converted into–COOH and remains with acid having smaller number of C-atoms
5. Only β – hydroxy acids (and not α – hydroxy acids) lose H_2O on heating
6. Compounds like $CH_3CH_2CHOHCOOH$ or $CH_3CHOHCH_2COOH$ lose optical activity on strong heating because of the formation of alkene.
7. β - keto-substituted acids when heated give out CO_2 gas, *e.g.*,



$$CH_3-\underset{\underset{O}{\|}}{C}H-CH_2COOH \xrightarrow{\Delta} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CO_2$$

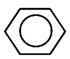
8. β - hydroxy substituted acids with mild oxidants will give β-keto-acids. *e.g.*,



$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2COOH \xrightarrow{\text{oxidation}} CH_3-\underset{\underset{O}{\|}}{C}-CH_2COOH$$

9. Hydrolysis of tertiary alkyl halides is independent of nucleophilic concentration.
10. Phenols give Libermann as well as Reimer-Tiemann ($CHCl_3/KOH$ or CCl_4/KOH) reaction to introduce —CHO or COOH groups in the ring at ortho and para positions.
11. An organic compound which on heating with NaOH or KOH gives NH_3 (giving white fumes with a rod dipped in HCl) will contain—$CONH_2$ group or — CN group.

    Compounds which give red colour with ceric ammonium nitrate contain an alcoholic group, — OH
12. An optically active compound contains asymmetric C–atom. Geometrical isomers contain $C=C-$ β or δ.
13. Tollen's reagent converts compounds like $CH_3CH=CHCHO$ to $CH_3CH=CHCOOH$
14. Carbylamine test is only performed for primary amines with $CHCl_3$ + KOH, to get obnoxious smelling isocyanide.

15. Symmetrical aromatic hydrocarbons like CH_3 —  — CH_3 give only one monosubstituted (*e.g.*, mononitro) derivative.
16. An organic compound that has an asymmetric (or chiral) carbon atom as well as a C $=$ C, will show optical as well as geometrical isomerisms. e.g., $CH_3CH = CH — CH^*(Br)\ CH_3$. Here C* is the chiral carbon. A chiral C–atom is that which is bonded to four different atoms or groups.
17. Compounds which do not reduce Fehling solution but form oxime are ketones; give Beilstein test, are usually alkyl halides; give ppt. with ammonical Cu_2Cl_2, will have $C \equiv CH$ at the corner; aldol condensation takes place in aldehydes and ketones having α-hydrogen; give silver mirror test and reduce Fehling solution, are aldehydes.
18. Degree of unsaturation = [No. of C– atoms] – [No. of H–atoms] + 1.

27.3. OPTICAL ISOMERS

Type. To calculate number of optical isomers.

1. For molecules having no symmetry.

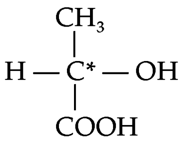
(*a*) no. of *d* and *l* forms, $a = 2^n$ where n = no. of asymmetric carbon atoms.

(*b*) no. of meso *l*-forms, $m = 0$

$\therefore$ Total no. of optical isomers $= a + m = 2^n + 0 = 2^n$

EXAMPLE 1. *Calculate the total number of optical isomers of lactic acid.*

SOLUTION. Lactic acid is :



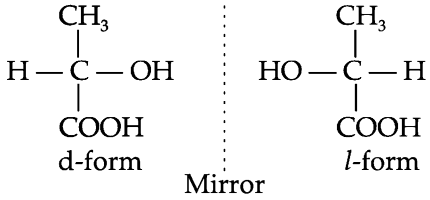
$$H — \overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C^*}} — OH$$

no plane of symmetry

no. of asymmetric C–atoms = 1

$\therefore$ *d* and *l* forms, $a = 2^n = 2^1 = 2$

Meso forms, $m = 0$ $\therefore$ Total number of optical isomers $= a + m = 2 + 0 = 2$



$$H — \overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}} — OH \qquad HO — \overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C}} — H$$

d-form Mirror *l*-form

Mirror images are also called enantiomers.

Type. For molecules having symmetry.

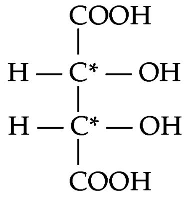
(*a*) no. of *d* and *l* forms, $a = 2^{n-1}$ where n is the number of asymmetric C–atoms.

(*b*) no. of meso *l*-forms, $m = 2^{\frac{n}{2}-1}$; Total no. of optical isomers $= a + m = 2^{n-1} + 2^{\frac{n}{2}-1}$

(*c*) No. of racemic forms $= a/2$.

EXAMPLE 2. *Calculate the total number of optical isomers of tartaric acid.*

SOLUTION. Tartaric acid is :



$$\begin{array}{c} COOH \\ | \\ H — C^* — OH \\ | \\ H — C^* — OH \\ | \\ COOH \end{array}$$

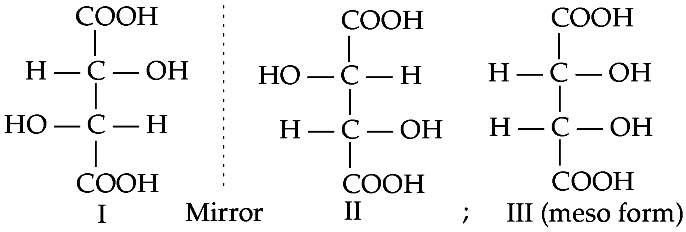
Plane of symmetry
$n = 2$

no. of asymmetric C-atoms = 2 ; *d* and *l* forms,

$$a = 2^{n-1} = 2^{2-1} = 2$$

Meso forms, $m = 2^{\frac{n}{2}-1} = 2^{\frac{2}{2}-1} = 2^{1-1} = 2^0 = 1$

$\therefore$ Total no. of optical isomers $= a + m = 2 + 1 = 3$



$$\begin{array}{c} COOH \\ | \\ H — C — OH \\ | \\ HO — C — H \\ | \\ COOH \end{array} \qquad \begin{array}{c} COOH \\ | \\ HO — C — H \\ | \\ H — C — OH \\ | \\ COOH \end{array} \qquad \begin{array}{c} COOH \\ | \\ H — C — OH \\ | \\ H — C — OH \\ | \\ COOH \end{array}$$

I Mirror II ; III (meso form)

Structures I and III or II and III which are not mirror images of each other, are called **diastereoisomers**.

Type. Specific rotation $[\alpha]_{\lambda}^{T} = \dfrac{\alpha}{l \times C}$

Where, l = length of tube in decimeters (dm)

C = concentration in g cm^{-3}, for a solution, density is in g cm^{-3} for a pure liquid,

λ = wave length of light used.

EXAMPLE 3. *The specific rotation of R–(–)–2–bromooctane was found to be–36°. Calculate the percentage composition of a mixture of enantiomers of 2 – bromooctane where rotation is + 18°.*

SOLUTION. Let mole fraction of $R = x$

$$\begin{aligned} \therefore \quad \text{mole fraction of } S &= 1 - x \\ \therefore \quad x(-36°) + (1 - x)\,36° &= 18° \\ \therefore \quad -36°x + 36° - 36°x &= 18°; \\ -72°x &= 18 - 36 = -18° \\ \therefore \quad x &= \frac{-18°}{-72°} = \frac{1}{4} \\ \therefore \quad \%\text{ age of } R &= \frac{1}{(1+4)} \times 100 = 25\%; \\ \%\text{ age of } S &= 100 - 25 = 75\% \end{aligned}$$

27.4 MISCELLANEOUS PROBLEMS

EXAMPLE 4. *A compound (X) containing only C, H and O is unreactive to-wards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydriodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted to (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives carboxylic acid. The equivalent weight of this acid is 60. What are the compounds (X), (Y) and (Z) ? Write chemical equations leading to the conversion of (X) to (Y).* **(IIT, 1981)**

Solution. (*X*) does not react with Schiff's base. So, it is not an aldehyde. (*Z*) on oxidation gives carboxylic acid, so it should be an alcohol. (*X*) reacts with HI to give iodide. Also, (*Z*) gives (*Y*) with P_4 and I_2. So, (*X*) is expected to be an ether. Thus :

$$\underset{\text{Diethyl ether } (= X)}{CH_3CH_2OCH_2CH_3} \xrightarrow{HI} \underset{(Y)}{CH_3CH_2I} + \underset{(Z)}{CH_3CH_2OH}$$

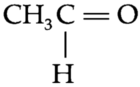
$$\underset{(Z)}{CH_3CH_2OH} \xrightarrow[\text{Red P, } I_2]{HI,} \underset{(Y)}{CH_3CH_2I} + H_2O$$

$$\underset{Z}{CH_3CH_2OH} \xrightarrow{2[O]} \underset{\text{Carboxylic acid (acetic acid)}}{CH_3COOH + H_2}$$

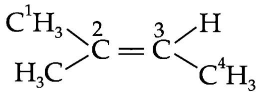
∴ (*X*) = Diethyl ether ;

(*Y*) = Ethyl iodide ; (*Z*) = Ethyl alcohol.

Example 5. *One mole of a hydrocarbon (A) reacts with one mole of bromine giving a dibromo compound $C_5H_{10}Br_2$. Substance (A) on treatment with cold, dilute alkaline potassium permanganate solution forms a compound $C_5H_{10}O_2$. On ozonolysis, (A) gives equimolar quantities of propanone and ethanal. Deduce the structural formula of (A).* **(IIT, 1981)**

Solution. Since (*A*) reacts with Br_2 and alkaline $KMnO_4$, (A) must contain a C = C double bond. The products of (*A*) on ozonolysis are $(CH_3)_2\,C = O$ and  $CH_3\underset{\underset{H}{|}}{C} = O$. So, the compound (*A*) can be the compound as shown below:

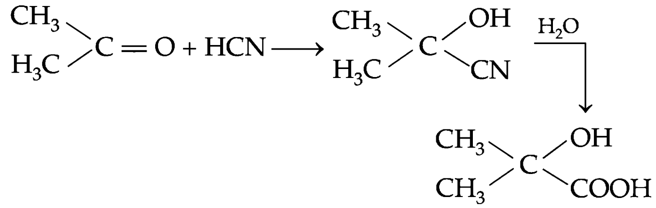
$$(CH_3)_2C = \underset{\text{remove}}{\boxed{O+O}} = C\,(H)\,(CH_3) \text{ i.e.,}$$



or 2 - Methyl but-2-ene.

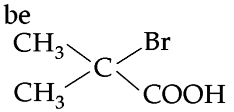
Example 6. *An alkene (A) on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid (B). When (B) is treated with bromine in the presence of phosphorus, it yields a compound (C) which an hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.* **(IIT, 1982)**

Solution. (*i*) (*D*) is obtained by the action of acetone on HCN followed by hydrolysis. So, we have :

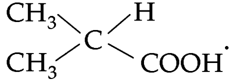


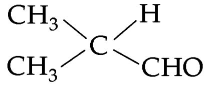
(D)

(*ii*) Since (*D*) is also obtained by the hydrolysis of (*C*), so (*C*) will be

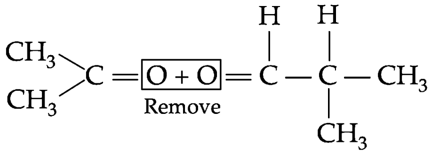


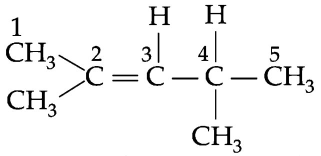
(C)

(*iii*) (*C*) is obtained by treating (*B*) with Br_2 and P. So, (*B*) must contain α – hydrogen. Hence, (*B*) is  . The aldehyde from (***B***) will be



(*iv*) Alkene (*A*) on ozonolysis gives acetone (CH_3COCH_3) and the aldehyde (B). So, the alkene will be:





2, 4-Dimethyl pent -2-ene. (**A**)

Example 7. *An alcohol (A) when heated with conc. H_2SO_4 gives an alkene (B). When (B) is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodalime, a new compound (C) is obtained. The compound (C) gives (D) when treated with warm dil. H_2SO_4, in presence of $HgSO_4$. (D) can also be obtained by either oxidising A with $KMnO_4$ or from acetic acid through its calcium salt. Identify A, B, C and D.* **(IIT, 1983)**

Solution. (A) is an alcohol. (D) is obtained from oxidation of A or from CH_3COOH through its calcium salt. So, (*A*) will contain two carbon atoms. Thus :

(*i*) (*A*) is C_2H_5OH (ethyl alcohol).

(*ii*) $C_2H_5OH + H_2SO_4 \xrightarrow{170°C} \underset{\text{Ethene } (B)}{CH_2 = CH_2} + H_2O$

(*iii*) $CH_2 = CH_2 \xrightarrow{Br_2} CH_2Br - CH_2Br$

$$\xrightarrow[\substack{\text{with sodalime} \\ (-\ 2HBr)}]{\text{Dehydrohalogenated}} \underset{\substack{\text{Ethyne} \\ (C)}}{CH \equiv CH}$$

(*iv*) $CH \equiv CH \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{(D)}{CH_3CHO}$. Also ,

$$C_2H_5OH \xrightarrow[KMnO_4]{[O]} \underset{(D)}{CH_3CHO} + H_2O$$

Example 8. *A certain hydrocarbon (A) was found to contain 85.7 % carbon and 14.3 percent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon (B). 1.0 g of hydrocarbon (A) just decolorised 38.05 g of a 5 percent solution (by weight) of Br_2, in CCl_4. Compound (A) on oxidation with concentrated $KMnO_4$, gave compound (C) (molecular formula C_4H_8O) and acetic acid. Compound (C) could easily be prepared by the action of acidic aqueous mercuric sulphate on 2– butyne. Determine the molecular formula of (A) and deduce the structures of A, B and C.* **(IIT, 1984)**

Solution. At. wt. of $C = 12 ; H = 1 ; Br = 80$

Given : $C = 85.7\ \% ; H = 14.3\% ;$

wt. of $(A) = 1.0$ g ;

Wt. of Br_2 decolorised = 38.05 g of 5% Br_2.

(*i*) Number of carbon atoms $= \frac{85.7}{12} = 7.14$

(*ii*) Number of *H*–atoms $= \frac{14.3}{1} = 14.3$

$\therefore$ Atomic ratio of C : H is 7 . 14 : : 14.3

or $\frac{7.14}{7.14} : \frac{14.3}{7.14}$ or **1 : 2**

$\therefore$ Empirical formula $= C_1H_2$ Or $\mathbf{CH_2}$.

(*A*) consumes 1 molar equivalent of H_2. So, (*A*) will have only one $C = C$. Thus :

1 g of (*A*) consumes $Br_2 = \frac{38.05}{100} \times 5 = 1.9025$ g ;

Mol. wt. of $Br_2 = 2 \times 80 = 160$

$\therefore$ 1.9025 g of Br_2 is consumed by $A = 1.0$ g

160 g of Br_2 is consumed by

$$A = \frac{1}{1.9025} \times 160 = 84.1\text{g} \approx 84\text{ g}$$

No. of C–atoms in 84 g

$$A = \frac{\text{Wt}}{\text{Mol. wt. of } CH_2}$$

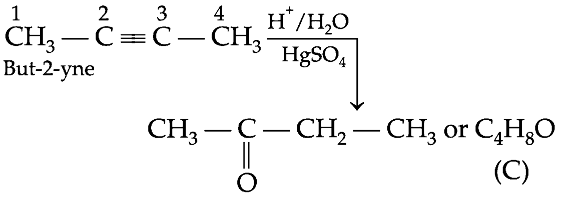
$$= \frac{84}{[12 + (2 \times 1)] = 14} = 6$$

$\therefore$ No. of H–atoms in $A = 84 - (12 \times 6) = 12$

$\therefore$ Molecular formula of $A = \mathbf{C_6H_{12}}$

(*iii*) (*A*) on oxidation with $KMnO_4$ gives (*C*) and acetic acid, CH_3COOH. (*C*) has molecular formula C_4H_8O. Thus :

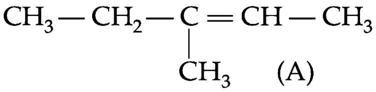
$(A) \xrightarrow{KMnO_4} (C) + CH_3COOH$. Also, (*C*) is formed from the reaction.



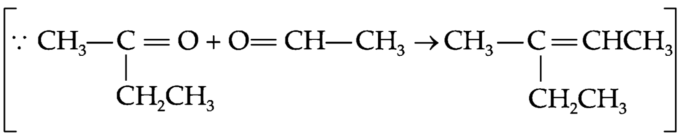
$$\overset{1}{C}H_3 - \overset{2}{C} \equiv \overset{3}{C} - \overset{4}{C}H_3 \xrightarrow[HgSO_4]{H^+/H_2O} CH_3 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3 \text{ or } C_4H_8O$$

But-2-yne (C)

(*iv*) The molecular formula of (*A*) will thus be :



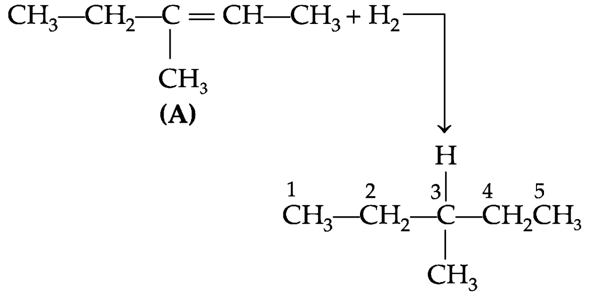
$$CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{C} = CH - CH_3 \quad (A)$$



$$\left[\because CH_3 - \underset{\underset{CH_2CH_3}{|}}{C} = O + O = CH - CH_3 \rightarrow CH_3 - \underset{\underset{CH_2CH_3}{|}}{C} = CHCH_3 \right]$$

; CH_3CHO gives CH_3COOH on oxidation.

But $A + H_2 \longrightarrow B$. So, (*B*) will be :

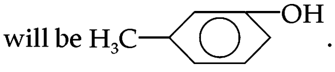


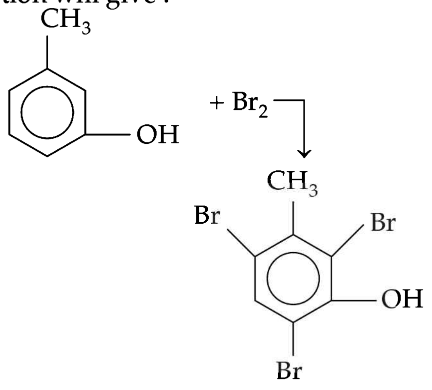
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{C} = CH-CH_3 + H_2 \longrightarrow \overset{1}{C}H_3-\overset{2}{C}H_2-\overset{\overset{H}{|}}{\overset{3}{C}}-\overset{4}{C}H_2\overset{5}{C}H_3 \text{ with } CH_3 \text{ on } C_3$$

(A)

3-Methyl pentane (**B**).

Example 9. *A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate but dissolves in aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Write down the structure of the compound.* **(IIT, 1985)**

Solution. The compound is insoluble in water and $NaHCO_3$ but soluble in NaOH (aq). So, the compound is expected to be a phenol. The formula of this compound will be . This compound on bromination will give :



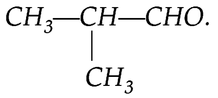
or $C_7H_5OBr_3$ **Ans.**

1-Methyl-2, 4, 6,-tribromophenol.

Example 10. *A white precipitate was formed slowly when silver nitrate was added to compound (A) with molecular formula $C_6H_{13}Cl$. Compound (A) on treatment with hot alcoholic KOH gave a mixture of two isomeric alkenes (B) and (C) having formula C_6H_{12}. The mixture of (B) and (C) on ozonolysis furnishes four compounds :*

(*i*) CH_3CHO (*ii*) C_2H_5CHO

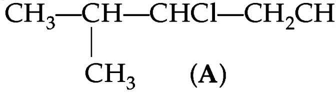
(*iii*) CH_3COCH_3 *and*

(*iv*) 

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CHO.$$

Write the structures of A, B and C. **(IIT, 1986)**

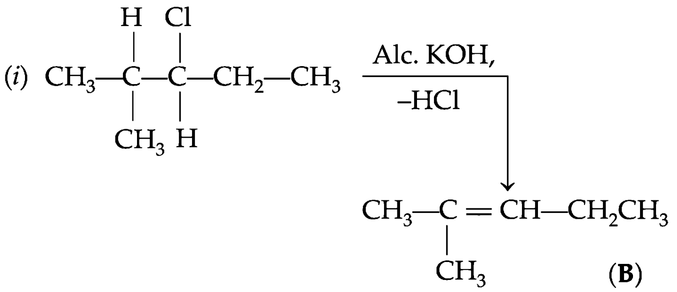
Solution. (*a*) The structure of (*A*) having molecular formula $C_6H_{13}Cl$ will be



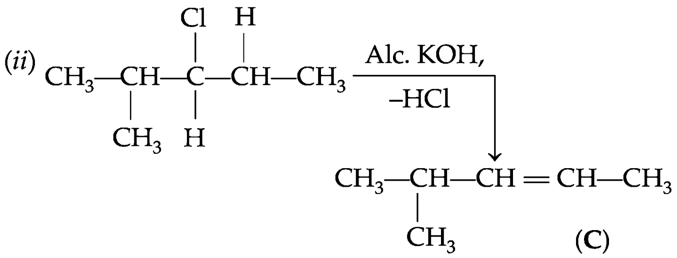
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CHCl-CH_2CH_3 \quad (A)$$

because it gives white precipitate of AgCl with $AgNO_3$.

(*b*) (*A*) gives following two isomers when treated with alcoholic KOH because alcoholic KOH removes HCl.

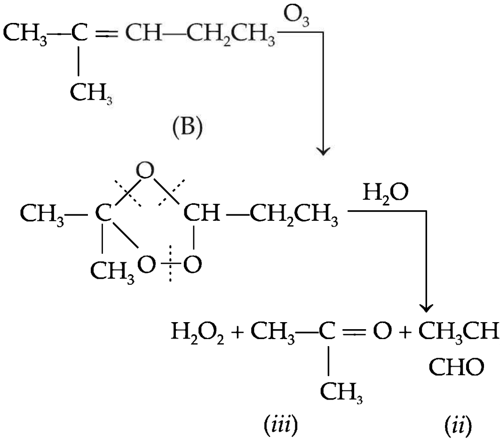


(*i*) $CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_2-CH_3 \xrightarrow[-HCl]{Alc.\ KOH,} CH_3-\underset{CH_3}{C}=CH-CH_2CH_3$ (**B**)



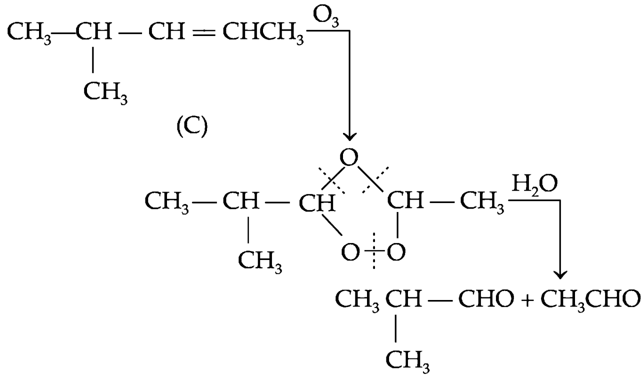
(*ii*) $CH_3-\underset{CH_3}{\overset{Cl}{CH}}-\underset{H}{\overset{H}{C}}-CH-CH_3 \xrightarrow[-HCl]{Alc.\ KOH,} CH_3-\underset{CH_3}{CH}-CH=CH-CH_3$ (**C**)

(*c*) (*B*) and (*C*) on ozonolysis followed by hydrolysis gives the following compounds as required in question.



$CH_3-\underset{CH_3}{C}=CH-CH_2CH_3 \xrightarrow{O_3}$ (B) ozonide $\xrightarrow{H_2O} H_2O_2 + CH_3-\underset{CH_3}{C}=O + CH_3CH_2CHO$

(*iii*) (*ii*)

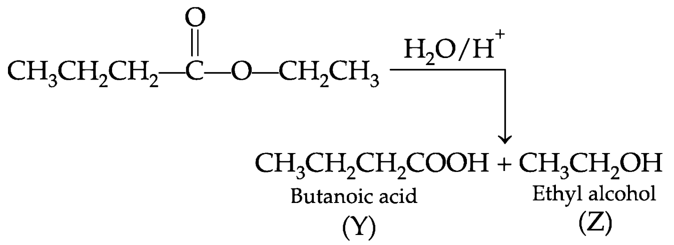


$CH_3-\underset{CH_3}{CH}-CH=CHCH_3 \xrightarrow{O_3}$ (C) ozonide $\xrightarrow{H_2O} CH_3\underset{CH_3}{CH}-CHO + CH_3CHO$

(*iv*) (*i*)

Example 11. *A liquid (X) having a molecular formula $C_6H_{12}O_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are the structures of X, Y and Z ?* **(IIT, 1986)**

Solution. (*X*) gives a carboxylic acid (*Y*) and an alcohol (*Z*), so (*X*) will be an ester. So, $C_6H_{12}O_2$ will be an ester. (*X*), $CH_3CH_2CH_2-COO-CH_2CH_3$ *i.e.*, ethyl propyl ester. Oxidation of (*X*) gives the following compounds.



$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 \xrightarrow{H_2O/H^+} \underset{\text{Butanoic acid (Y)}}{CH_3CH_2CH_2COOH} + \underset{\text{Ethyl alcohol (Z)}}{CH_3CH_2OH}$

Example 12. *An unknown compound of carbon, hydrogen and oxygen contain 69.77 % carbon and 11.63% hydrogen and has a molecular weight of 86. It does not reduce Fehling solution but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures ?* **(IIT, 1987)**

Solution. At. wt. of C = 12 ; H = 1 ; O = 16 ; C = 69.77%, H = 11.63%, O = 100 –(69.77 + 11.63 = 81.40) = 18.6%.

∴ No. of C–atoms = 69.77/12 = 5.81 ;

No. of H–atoms = 11.63/1 = 11.63

No. of O–atoms = 18.6/16 = 1.16. The ratio of atoms of C : H : O is :

$$5.81 : 11.63 : 1.16 \quad \text{or} \quad \frac{5.81}{1.16} : \frac{11.63}{1.16} : \frac{1.16}{1.16}$$

or 5 : 10 : 1. Hence:

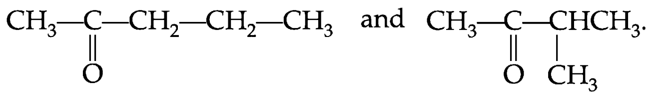
Empirical formula (E.F.) of unknown compound $= C_5H_{10}O$

E.F. wt. of $C_5H_{10}O = (5 \times 12) + (10 \times 1) + (1 \times 16)$
$= 60 + 10 + 16 = 86$

Given mol. wt. = 86.

Hence, molecular formula = E.F. *i.e.*, $\mathbf{C_5H_{10}O}$.

The compound does not reduce Fehling solution. So, it is not an aldehyde *i.e.*, —CHO group is absent. The compound forms a bisulphite. So, it should be a ketone. Since the ketone gives iodoform test, $CH_3-\underset{O}{\underset{\|}{C}}-$ group is a must. So, the possible structures of the keto compounds will be :



$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-CH_2-CH_3$ and $CH_3-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{CH}CH_3$.

Example 13. *An organic compound (A) on treatment with acetic acid in the presence of sulphuric acid produces an ester (B). (A) on mild oxidation gives (C). (C) with 50% potassium hydroxide followed by acidification with hydrochloric acid generates (A) and (D). (D) with phosphorus pentachloride followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.* **(IIT, 1987)**

Solution. The sequence of reactions given in the question is :

(*a*) $A + CH_3COOH \xrightarrow{H_2SO_4} B$ (ester)

(*b*) $A \xrightarrow[\text{Oxidation}]{\text{Mild}} (C) \xrightarrow[\text{(ii) HCl}]{\text{(i) 50\% KOH}} (A) + (D)$

(*c*) $(D) \xrightarrow[\text{(ii) } NH_3]{\text{(i) } PCl_5} (E) \xrightarrow[(-H_2O)]{\text{Dehydration}} HCN$

Since (E) on dehydration gives HCN, it suggests that (E) will be an amide with one C–atom only. So, (E) is $HCONH_2$ (formamide). Also, (A gives the ester (B) with CH_3COOH, so (A) will be an alcohol with one C–atom *i.e.*, CH_3OH. So, the reactions will be as follows :

$$\underset{(A)}{CH_3OH} + CH_3COOH \xrightarrow[-H_2O]{H_2SO_4} \underset{\text{Dimethyl ester }(\mathbf{B})}{CH_3COOCH_3}$$

$$CH_3OH \xrightarrow[\text{oxidation}]{\text{Mild}} \underset{\text{Formaldehyde }(\mathbf{C})}{HCHO}$$

$$\underset{(C)}{2HCHO} \xrightarrow[\text{(ii) Dil. HCl}]{\text{(i) 50\% KOH}} \underset{(\mathbf{A})}{CH_3OH} + \underset{\text{Formic acid }(\mathbf{D})}{HCOOH}$$

$$\underset{(\mathbf{D})}{HCOOH} \xrightarrow[\text{(ii) } NH_3]{\text{(i) } PCl_5} \underset{\text{Formamide }(\mathbf{E})}{HCONH_2} \qquad \underset{(\mathbf{E})}{HCONH_2} \xrightarrow{-H_2O} HCN$$

EXAMPLE 14. *An organic compound (A) containing C,H,N and O, on analysis gives 49.32% carbon, 9.59% hydrogen and 19.18% nitrogen. (A) on boiling with NaOH gives off* NH_3 *and a salt which on acidification gives a monobasic nitrogen free acid (B). The silver salt of (B) contains 59.67% silver. Deduce the structures of (A) and (B).* **(IIT, 1988)**

SOLUTION. To calculate empirical formula (E.F.) of (A).
% age of O = 100 – (% age of C, H, N) = 100 – (49.32 + 9.59 + 19.18) = 21.91

Element	*At. wt.*	*% age*	*Relative no. of atoms = % age/ At.wt.*	*Simple ratio*	*Whole no. ratio*
C	12	49.32	49.32/12 = 4.11	4.11/1.37 = 3	3
H	1	9.59	9.59/1 = 9.59	9.59/1.37 = 7	7
N	14	19.18	19.18/14 = 1.37	1.37/1.37 = 1	1
O	16	21.91	21.19/16 = 1.37	1.37/1.37 = 1	1

∴ E.F. of (A) = C_3H_7NO.

(A) when boiled with NaOH gives off NH_3. So, (A) will be an amide. But % age of Ag in silver salt, (B) = 59.67

$$\text{But Eq. wt. of acid} = \left[\frac{\text{Eq. wt. of Ag}}{\text{wt. of Ag}} \times 100\right] - 107$$

$$= \left[\frac{108 \times 100}{59.67}\right] - 107$$

$$= 181 - 107 = 74$$

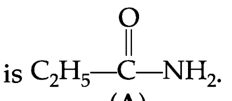
Mol. wt. of monobasic acid

$$= \text{Eq. wt. of acid} \times \text{basicity}$$

$$= 74 \times 1 = 74$$

∴ Mol. wt. of acid = $C_3H_6O_2$ (mol. wt. = 74)

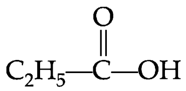
So, **structure of amide,** C_3H_7NO is



$C_2H_5-\overset{\overset{\large O}{\|}}{C}-NH_2$.

(A)

Structure of acid is



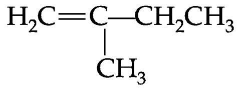
$C_2H_5-\overset{\overset{\large O}{\|}}{C}-OH$

(B)

EXAMPLE 15. *A hydrocarbon (molecular formula* C_5H_{10}*) yields 2-methyl butane on catalytic hydrogenation. (A) adds HBr (in accordance with Markownikoff's rule) to form a compound (B) which on reaction with silver hydroxide forms an alcohol (C),* $C_5H_{12}O$*. Alcohol (C) on oxidation gives a ketone (D). Deduce the structures of A, B, C and D and show the reactions involved.* **(IIT, 1988)**

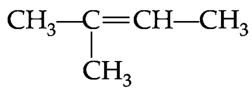
SOLUTION. C_5H_{10} is an alkene (A) because it gives an alkane (2–methyl butane) on catalytic hydrogenation. So, (A) must have a C = C double bond. The alkene will, thus, have the following possible structures.

(*i*)



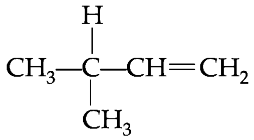
$H_2C{=}\underset{\underset{\large CH_3}{|}}{C}-CH_2CH_3$

(*ii*)



$CH_3-\underset{\underset{\large CH_3}{|}}{C}{=}CH-CH_3$

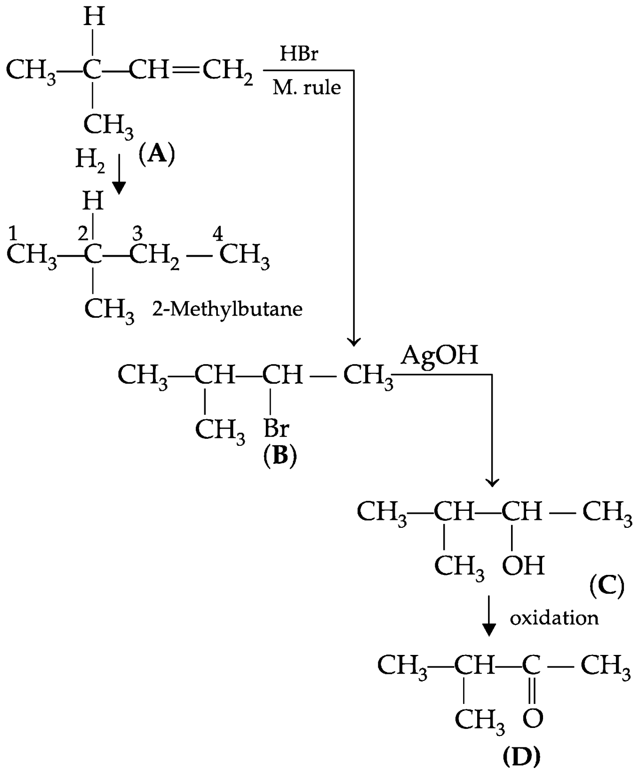
(*iii*)



$CH_3-\overset{\overset{\large H}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH{=}CH_2$

(*C*) gives a ketone on oxidation. So, (C) must be a secondary alcohol. The corresponding bromide (B) should also be a secondary bromide. But secondary bromide is fomed by the addition of HBr to alkene by Markownikoff's rule. So, the alkene (A) will have the structure, (*iii*).

Thus :



EXAMPLE 16. *An organic compound (X) on analysis gives 24.24 percent carbon and 4.04 percent hydrogen. Further, sodium extract 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound (X) may be represented by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous potassium hydroxide solution gives dihydroxy com-*

pound while (Z) gives ethanal. Find out the molecular formula of (X) and give the structures of (Y) and (Z). **(IIT, 1989)**

Solution. Given : C = 24.24% ; H = 4.04%. At. wt. of C = 12, H = 1, Cl = 35.5, Ag = 108, molar mass of AgCl = 108 + 35.5 = 143.5. We know that :

Mass percent of chlorine

$$= \frac{\text{at. mass of Cl}}{\text{mol. mass of AgCl}} \times \frac{\text{Mass of AgCl obtained}}{\text{Mass of compound taken}} \times 100$$

$$= \frac{35.5}{143.5} \times \frac{2.9}{1.0} \times 100 = \mathbf{71.74\%}$$

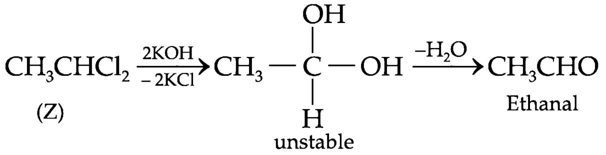
Calculation of empirical formula (E.F.)

Element	At. wt.	% age	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	12	24.24	24.24/12 = 2.02	2.02/2.02 = 1	1
H	1	4.04	4.04/1 = 4.04	4.04/2.02 = 2	2
Cl	35.5	71.74	71.74/35.5 = 2.02	2.02/2.02 =1	1

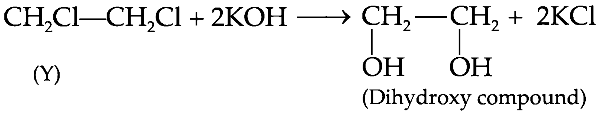
∴ E.F. of compound (X) = $\mathbf{CH_2Cl}$.

(Y) on treatment with KOH (aq) gives dihydroxy compound. So, (X) must have two Cl atoms. So, (X) will be $(CH_2Cl)_2$, or $C_2H_4Cl_2$. *i.e.*, **[X] =** $\mathbf{C_2H_4Cl_2}$

Two isomers of $C_2H_4Cl_2$ will be, CH_3CHCl_2 and $CH_2Cl—CH_2Cl$. These react with KOH as follows.



$$\underset{(Z)}{CH_3CHCl_2} \xrightarrow[-2KCl]{2KOH} \underset{\text{unstable}}{CH_3—\overset{OH}{\overset{|}{C}}(H)—OH} \xrightarrow{-H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$



$$\underset{(Y)}{CH_2Cl—CH_2Cl} + 2KOH \longrightarrow \underset{\text{(Dihydroxy compound)}}{\underset{OH}{CH_2}—\underset{OH}{CH_2}} + 2KCl$$

Example 17. *n-Butane is produced by the monobromination of ethene followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g n-butane, if the bromination takes place with 90% yield and the Wurtz reaction with 85% yield.* **(IIT 1989)**

Solution. $\underset{\text{Ethene (1 mol)}}{CH_2 = CH_2} \xrightarrow[\text{HBr}]{\text{Monobromination}} \underset{\text{(1 mol)}}{CH_3CH_2Br}$ ...(1)

$\underset{\text{1 mol}}{CH_3CH_2Br} + Zn + \underset{\text{1 mol}}{BrCH_2CH_3} \xrightarrow[\text{reaction}]{\text{Wurtz}} \underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} + ZnBr_2$ ...(2)

Volume of ethane = ? ; Mass of *n*-butane = 55 g.

∴ no. of moles of *n*-butane to be prepared

$$= \frac{\text{Wt.}}{\text{mol. wt}} = \frac{55\text{ g}}{58\text{ g mol}^-}$$

= 0.948 mol

From reaction (2), 1 mol *n*-butane ≡ 1 + 1 *i.e.*, 2 mol C_2H_5Br

$$\left[\begin{array}{l} \because \text{Mol. wt of } C_4H_{10} \\ = (4 \times 12) + (10 \times 1) \\ = 58\text{ g mol}^- \end{array}\right.$$

0.948 mol *n*-butane ≡ 2 × 0.948 mol = 1.896 mol

Since the conversion is only 85%

∴ Amount of C_2H_5Br required

$$= 1.896 \times \frac{100}{85} = 2.23\text{ mol}$$

Also, $\underset{\text{Ethane (1 mol)}}{C_2H_6} + Br_2 \longrightarrow \underset{\text{1 mol}}{C_2H_5Br} + HBr$ ...(3)

From reaction (3), we see that 1 mol ethane ≡ 1 mol C_2H_5Br. But %age conversion of C_2H_6 to C_2H_5Br is 90. So :

Amount of C_2H_6 required

$$= 2.23 \times \frac{100}{90} = 2.478\text{ mol}$$

1 mol C_2H_6 at NTP requires volume = 22.4 L

∴ 2.478 mol C_2H_6 at NTP requires volume

≡ 22.4 L × 2.478 = **55.51 L.**

Example 18. *The sodium salt of a carboxylic acid, (A) was produced by passing a gas, (B) into an aqueous solution of caustic alkali at an elevated temperature and pressure. (A) on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid, (C). A sample of 0.4 g of acid (C) on combustion gave 0.08 g of water and 0.39 g of carbon dioxide. The silver salt of the acid weighing 1.0 g on ignition yielded 0.71 g of silver as residue. Identify A, B, and C.* **(IIT, 1990)**

Solution. At. wt. of Ag = 108, C = 12, H = 1, O = 16. Since the given acid is dibasic, so:

$$\text{1 mol dicarboxylic acid} \xrightarrow{\Delta} \text{2 mol of Ag (= 2 × 108 = 216 g).}$$

0.71 g silver is obtained from silver salt = 1.0 g

216 g silver is obtained from silver salt

$$= \frac{1}{0.71} \times 216 = 304.2$$

But Mol. wt. of acid = Mol. wt. of silver salt–2 (at. wt. of Ag) + 2(at. wt. of H)

= 304.2 – (2 × 108) + 2(1)

= 304.2 – 216 + 2 = 90.2 g

So, th dicarboxylic acid (Mol. wt. 90.2) is HOOC—COOH (**C**).

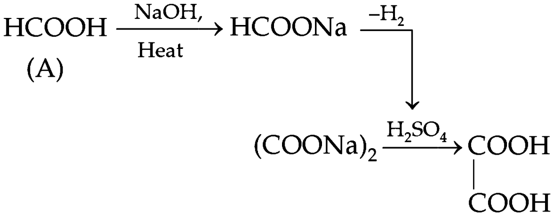
This acid is obtained as given below :

$$A \xrightarrow[\text{Heat}]{\text{NaOH,}} \text{Intermediate compound}$$

$$\xrightarrow{H_2SO_4} HOOC—COOH$$

To find empirical formula (E.F.) of compound (try yourself). Use the method shown in example 21. %age of C = 2.22, H = 26.6, O = 100 – (2.22 + 26.6) = 71.18. So, E.F. = HCO_2 or HCOOH.

The compound (A) should be formic acid because HOOC—COOH is obtained from it as follows.



$$\underset{(A)}{HCOOH} \xrightarrow[\text{Heat}]{\text{NaOH,}} HCOONa \xrightarrow{-H_2} (COONa)_2 \xrightarrow{H_2SO_4} \underset{COOH}{\overset{|}{COOH}}$$

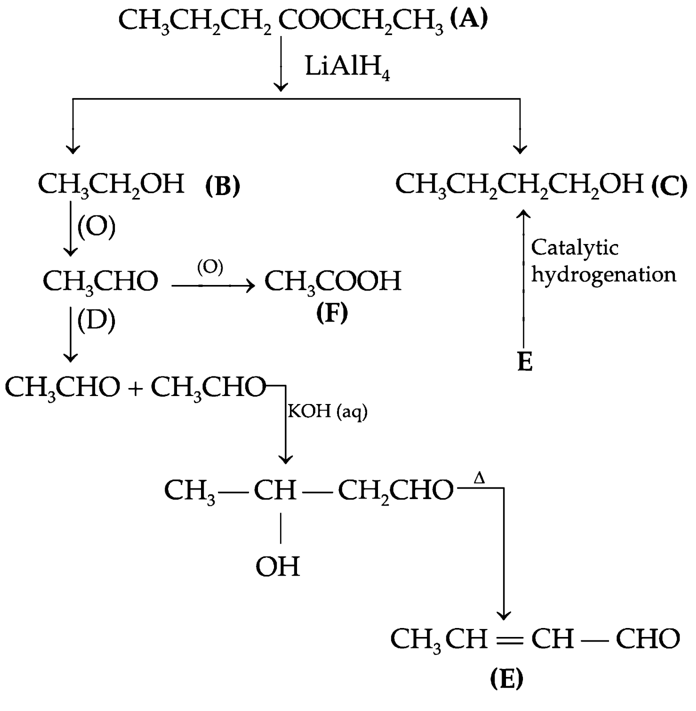
(A) *i.e.*, HCOOH (formic acid) is prepared as follows :

$$NaOH + \underset{(B)}{CO} \xrightarrow[\text{and pressure}]{\text{High temp.}} HCOONa$$

Hence, A = HCOOH ; B = CO gas ; C is COOH—COOH

Example 19. *Compound (A) ($C_6H_{12}O_2$) on reduction with Li AlH_4 yielded two compounds (B) and (C). The compound (B) on oxidation gave (D), which on treatment with aqueous alkali and subsequent heating furnished (E). The latter on catalytic hydrogenation gave (C). The compound (D) was oxidised further to give (E) which was found to be monobasic acid (molecular formula weight = 90.0). Deduce the structures of A, B, C, D, E and F.* **(IIT, 1990)**

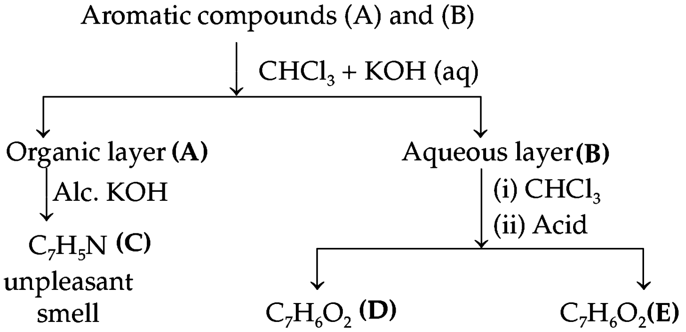
Solution. The compound (A) *i.e.*, $C_6H_{12}O_2$ contains two oxygen atoms. So, it should be an **ester**, $CH_3CH_2CH_2COOCH_2CH_3$. It is propyl ethyl ester. It gives two different alcohols on reduction. The overall reactions are given below.



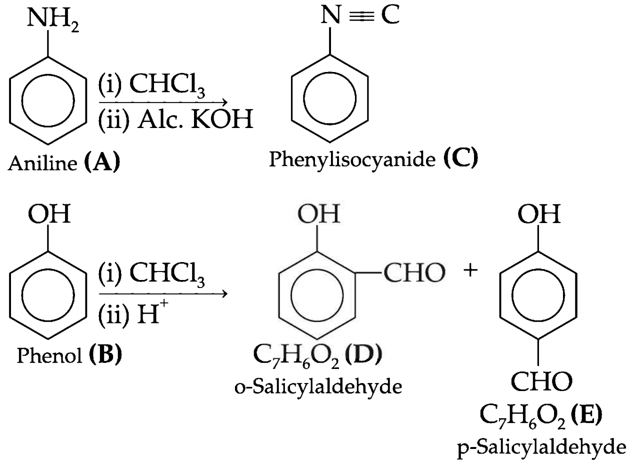
So, A, B, C, D, E and F compounds are those as shown above.

Example 20. *A mixture of two aromatic compounds (A) and (B) was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound (A), when heated with alcoholic solution of KOH produced a compound (C), (C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds (D) and (E) of molecular formula $C_7H_6O_2$. Identify the compounds A, B, C, D, E and write their structures.* **(IIT, 1990)**

Solution. The flow sheet of the given data is :



We know that aromatic compounds which have unpleasant smell are isocyanides. These isocyanides are obtained from the action of aromatic compounds containing NH_2 group, on $CHCl_3$ and alcoholic KOH. So, the compound (A) should be aniline. The other aromatic compound (B) should be a phenol because phenol reacts with $CHCl_3$ followed by acidification, gives a mixture of ortho and para salicylaldehydes. Thus :



Example 21. *An organic compound containing C, H and O exists in two isomeric forms (A) and (B). An amount of 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. (A) is insoluble in NaOH and $NaHCO_3$ while (B) is soluble in NaOH. (A) reacts with Conc. HI to give compounds (C) and (D). (C) can be separated from (D) by the ethanolic $AgNO_3$ solution and (D) is soluble in NaOH. (B) reacts readily with bromine water to give compound (E) of molecular formula $C_7H_5OBr_3$. Identify A, B, C, D, and E with justification and give their structures.* **(IIT, 1991)**

Solution. To find percentage of C, H and O in the compound.

(*i*) $$\underset{\substack{12 + (2 \times 16)\\ = 44\text{ g}}}{CO_2} \equiv \underset{12\text{ g}}{C}$$

44 g CO_2 contain C ≡ 12g;

$$0.308 \text{ g } CO_2 \text{ contain } C \equiv \frac{12}{44} \times 0.308\text{g}$$

$$\therefore \quad \%\text{ age of C} = \frac{\text{Wt. of } C}{\text{Wt. of substance}} \times 100$$

$$= \frac{12}{44} \times \frac{0.308 \times 100}{0.108} = 77.78$$

(*ii*) $H_2O \equiv 2H$

$(2 \times 1) + 16 = 18$ g $\quad (2 \times 1) = 2$ g

18 g H_2O contain H = 2 g; 0.072 g

$$H_2O \text{ contain H} = \frac{2}{18} \times 0.072\text{g}$$

$$\therefore \quad \% \text{ age of H} = \frac{\text{Wt. of } H}{\text{Wt. of substance}} \times 100$$

$$= \frac{2}{18} \times \frac{0.072}{0.108} \times 100 = 7.41$$

(*iii*) $\% \text{ age of O} = 100 - (\% \text{ age of C} + \% \text{ age of H})$

$= 100 - (77.78 + 7.41)$

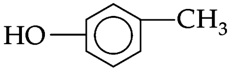
$= 100 - 85.19 = 14.81$

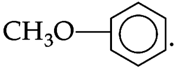
(*b*) To find empirical formula (E.F.) of the compound.

Element	At. wt.	% age	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	12	77.78	77.78/12 = 6.48	6.48/0.926 = 6.99	7
H	1	7.41	7.41/1 = 7.41	7.41/0.926 = 8	8
O	16	14.81	14.81/16 = 0.926	0.926/0.926 = 1	1

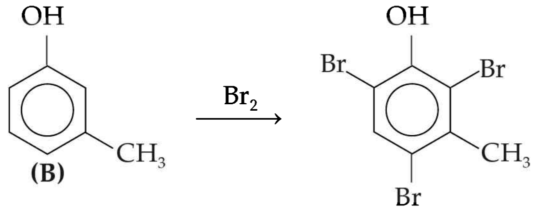
$\therefore$ E. F. of the compound = C_7H_8O.

The carbon content in this compound is very high. So, it will be an aromatic compound. (B) reacts readily with bromine water to give compound (E) of molecular formula $C_7H_5OBr_3$. It indicates that (A) and (B) have same molecular formula.

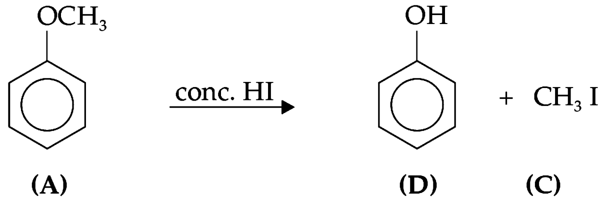
Compound (B) is soluble in NaOH, so, it appears to be a phenol of the formula  (**B**)

The compound (A) is insoluble in NaOH and $NaHCO_3$. So, the other isomer (A) will not be a phenol. So, (**A**) is .

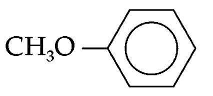
Since (E) is $C_7H_5O\ Br_3$ and contains three Br– atoms, OH and CH_3 groups must be at meta positions in (B). Thus:



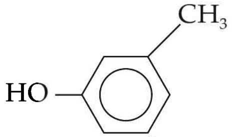
Action of (A) with HI will be:



Since (C) can be separated from (D) by ethanolic $AgNO_3$ solution, (C) will be soluble in it, while (D) is insoluble. (D) is soluble in NaOH. The compounds A, B, C, D and E will be :

(A) 

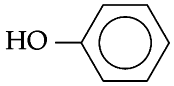
Anisol

(B) 

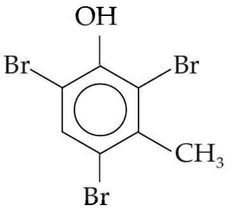
m-cresol

(C) CH_3I

Methyl iodide

(D) 

Phenol

(E) 

m-Methyl 2, 4, 6 - tribromophenol

Example 22. *Compound (X) containing chlorine, on treatment with strong ammonia gives a solid (Y) which is free from chlorine. (Y) analysed as : C = 49.31%, H = 9.59% and N = 19.18 % and reacts with* Br_2 *and caustic soda to give a basic compound (Z). (Z) reacts with* HNO_2 *to give ethanol. Suggest structures of (X), (Y) and (Z).* **(IIT, 1992)**

Solution. C = 49.31%, H = 9.59%, N = 19.18%, O = 100 – (49.31 + 9.59 + 19.18) = 100 – 78.08 = 21.92 (*a*) To calculate empirical formula (E.F.) of (Y).

Element	At. wt.	% age	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	12	49.31	49.31/12 = 4.11	4.11/1.37 = 3.2	3
H	1	9.59	9.59/1 = 9.59	9.59/1.37 = 7	7
N	14	19.18	19.18/14 = 1.37	1.37/1.37 = 1	1
O	16	21.92	21.92/16 = 1.37	1.37/1.37 = 1	1

$\therefore$ E.F. of (*Y*) = C_3H_7NO.

Since (Z) reacts with HNO_2 to give ethanol, CH_3CH_2OH, (Z) will be $CH_3CH_2NH_2$ (ethylamine). So, the sequence of reaction is $(X) \xrightarrow{NH_3} Y \xrightarrow{Br_2/KOH} Z \xrightarrow{HNO_2} C_2H_5OH$

Since *Z* is obtained from (*Y*) and Br_2/KOH, *Y* will be an amide, $C_2H_5CONH_2$. Since (*X*) contains Cl, (*X*) will be C_2H_5COCl. So ; (X) = C_2H_5COCl ; (Y) = $C_2H_5CONH_2$; (Z) = $C_2H_5NH_2$.

Example 23. *An organic compound (A) on treatment with ethyl alcohol gives a carboxylic acid (B) and compound (C). Hydrolysis of (C) under acidic conditions gives (B) and (D). Oxidation of (D) with* $KMnO_4$ *also gives (B). (B) on heating with* $Ca(OH)_2$ *gives (E) (molecular formula* C_3H_6O*). (E) does not give Tollen's test and does not reduce Fehling solution but forms a 2, 4–dinitrophenyl hydrazone. Identify A, B, C, D and E.* **(IIT, 1992)**

Solution. (E) does not give Tollen's test and does not reduce Fehling solution and forms 2, 4-dinitrophenyl hydrazone. So, (E) is not an aldehyde but a ketone. The ketone having given formula C_3H_6O will be CH_3COCH_3 *i.e.*, acetone.

(B) on heating with $Ca(OH)_2$ gives (E) *i.e.*, acetone. So, (B) must be acetic acid, CH_3COOH as $Ca\ (CH_3COO)_2$ on heating gives acetone. (D) will be ethyl alcohol because it gives acetic acid on oxidation.

(C) on hydrolysis under acidic conditions gives (B) *i.e.*, CH_3COOH and (D) *i.e.*, C_2H_5OH. So, (C) will be an ester *i.e.*, $CH_3COOC_2H_5$. (A) reacts with ethyl alcohol (D) to give carboxylic acid (B) and an ester. So, (A) will be acetic anhydride, $CH_3CO.O.COCH_3$.

$$\underset{(A)}{CH_3CO.O.COCH_3} + \underset{(D)}{C_2H_5OH} \rightarrow \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$$

Example 24. *Compound (X) (molecular formula, C_5H_8O) does not react appeciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of Me Mg Br, 0.42 g of (X) gives 224 mL of CH_4 at S.T.P. Treatment of (X) with H_2 in presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest, structure for (X) and write the equations involved.* **(IIT, 1992)**

Solution. The compound (*X*) [C_5H_8O, mol. wt. = $(5 \times 12) + (8 \times 1) + 16 = 84$] does not react with Lucas reagent appreciably. So, (*X*) will be a primary alcohol.

(*i*) No. of moles of

$$(X) = \frac{\text{Wt. of } (X)}{\text{Mol. wt. of } (X)}$$

$$= \frac{0.42}{84} = 5 \times 10^{-3} = 0.005 \text{ mol.}$$

(*ii*) No. of moles of CH_4

$$= \frac{\text{Volume of } CH_4 \text{ (mL)}}{22400 \text{ mL}}$$

$$= \frac{224}{22400} = 0.01 \text{ mol}$$

Thus : 0.01 mol of CH_4 contain H–atoms = 4

∴ 0.005 mol of CH_4 obtained from (*X*) will contain

$$\text{active H–atoms} = \frac{4}{0.01} \times 0.005 = 2$$

Out of these two active H-atoms, one must be of —OH group. Since (*X*) gives a precipitate with $AgNO_3$, the other active H-atom will be from — C ≡ CH. Also, (*X*) reacts with H_2/Pt followed by boiling with HI gives *n*-pentane. So, (*X*) will contain a straight chain. So, structure of (*X*) will be

$$\overset{5}{HC} \equiv \overset{4}{C}—\overset{3}{CH_2}—\overset{2}{CH_2}—\overset{1}{CH_2OH}$$

Pent-4-yn-1-ol.

Reactions involved are :

(*i*) $HC \equiv C — CH_2CH_2CH_2OH \xrightarrow{AgNO_3}$ $Ag\,C \equiv C — CH_2CH_2CH_2OH$

(*ii*) $HC \equiv C — CH_2CH_2CH_2OH \xrightarrow{MeMgBr}$ BrMg $C \equiv CCH_2CH_2CH_2O\,MgBr + 2CH_4$

(*iii*) $HC \equiv C — CH_2CH_2CH_2OH \xrightarrow{H_2/Pt}$ $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{Boil}]{HI,}$ $CH_3CH_2CH_2CH_2CH_3$

Example 25. *A basic, volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance, dissolved in aq. HCl and treated with $NaNO_2$ solution at 0°C, liberated a colourless, odourless gas whose volume corresponded to 112 mL at S.T.P. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N–atom per molecule.* **(IIT, 1993)**

Solution. Since the compound is basic and gives a foul smelling gas with chloroform and alc. KOH, it must be a primary amine, $R\,NH_2$ because it contains one N-atom. Its reaction with $NaNO_2$ and HCl at 0°C will be:

$$\underset{\text{Mol. wt.} = M}{R\,NH_2} + NaNO_2 + HCl \longrightarrow ROH + NaCl + \underset{22.4 \text{ L or } 22400 \text{ mL}}{N_2\uparrow} + H_2O.$$

Wt. of substance = 0.295 g

112 mL gas is obtained from substance = 0.295 g

22400 mL gas is obtained from substance

$$= \frac{0.295}{112} \times 22400 = 59 \text{ g}$$

∴ Mol. wt. of substance = 59 g mol^{-}.

But, $R = C_n\,H_{2n+1}$.

So, $R\,NH_2 = C_n\,H_{2n+1}.\,NH_2$

Or $(12 \times n) + 1(2n + 1) + 14 + (2 \times 1) = 59$

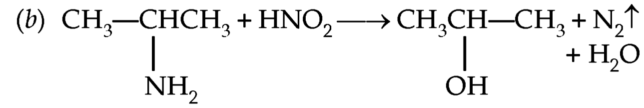
$12n + 2n + 1 + 14 + 2 = 59$ **Or** $14n = 59 - 17 = 42$

Or $n = 42/14 = 3$

∴ The given compound = $\mathbf{C_3H_7NH_2}$. The possible amines can be :

(I) $CH_3CH_2CH_2NH_2$ (II) $CH_3CH(NH_2)CH_3$.

(*a*) $CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2CH_2OH + N_2\uparrow + H_2O$

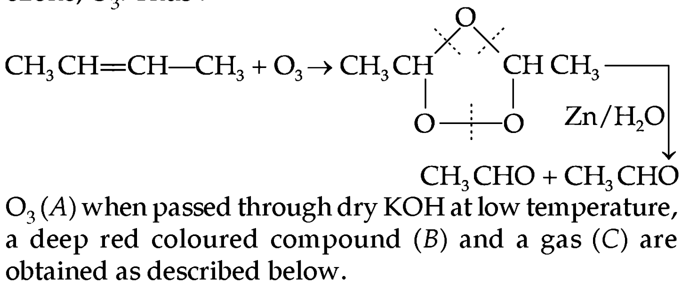


(*b*) $CH_3—\underset{NH_2}{CH}CH_3 + HNO_2 \longrightarrow CH_3\underset{OH}{CH}—CH_3 + N_2\uparrow + H_2O$

The product from (II) is $CH_3CH\ (OH)\ CH_3$ which yields yellow precipitate, with alkali and I_2. Hence the unknown compound is $\mathbf{CH_3CH\ (NH_2)\ CH_3}$.

Example 26. *When gas (A) is passed through dry KOH at low temperature, a deep red–coloured compound, (B) and a gas (C) are obtained. The gas (A), on reaction with but–2–ene, followed by treatment with Zn/H_2O yields acetaldehyde. Identify A, B and C.* **(IIT, 1994)**

Solution. (*A*) reacts with but–2–ene followed by action with Zn/H_2O gives acetaldehyde. So, (*A*) is expected to be ozone, O_3. Thus :



O_3 (*A*) when passed through dry KOH at low temperature, a deep red coloured compound (*B*) and a gas (*C*) are obtained as described below.

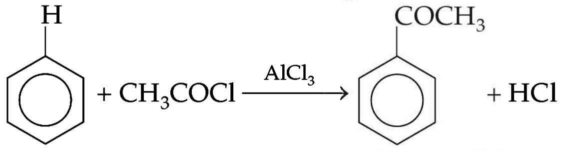
$$3\,KOH + 2O_3 \longrightarrow \underset{\underset{(B)}{\text{Potassium ozide (red)}}}{2KO_3\,(s)} + KOH.\,H_2O(s) + \underset{(C)}{½\,O_2(g)}$$

Example 27. *An organic compound (A), C_8H_6 on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound (B) which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound (B), when treated with iodine in aqueous KOH, yields (C) and a yellow compound, (D). Identify A, B, C and D with justification. Show how (B) is formed from (A).* **(IIT, 1994)**

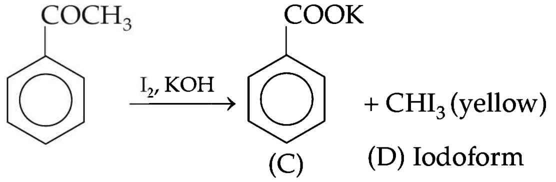
Solution. The sequence of various reactions required in the question is :

$$\begin{tikzcd} C_8H_6 \arrow[r, "\text{Dil. } H_2SO_4", "HgSO_4"'] & B \arrow[r, "I_2\text{, KOH (aq)}"] & C + D \text{ (yellow compound)} \\ & C_6H_6 \text{ (Benzene)} \arrow[u, "CH_3COCl/AlCl_3"'] & \end{tikzcd}$$

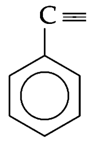
The reaction of C_6H_6 with CH_3COCl and $AlCl_3$ is :



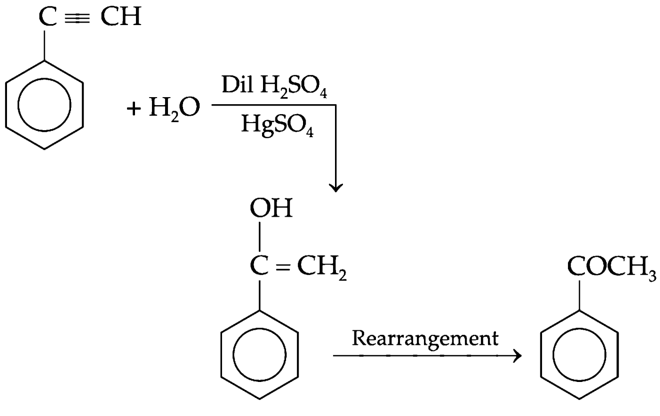
Acetophenone (**B**)



Since (A) reacts with dil. H_2SO_4 and $HgSO_4$, there must be $-C \equiv CH$ bond in (A). C_8H_6 formula indicates a benzene ring. So, (A) will be



Hence :



∴ (A) $= C_6H_5C\equiv CH$ (B) $C_6H_5COCH_3$

(C) C_6H_5COOK (D) CHI_3

Example 28. *An alkanone (A) that undergoes a haloform reaction, gives a compound (B) on reduction. When (B) is heated with H_2SO_4, forms the compound (C) which gives mono-ozonide (D). (D) on hydrolysis in presence of zinc dust forms only ethanal. Identify A, B, C and D. Also, write the reactions involved.* **(IIT, 1989)**

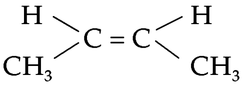
Solution. The given general reactions are :

$$A \xrightarrow{\text{Reduction}} B \xrightarrow[\text{(dehydration)}]{H_2SO_4,\Delta} C\,;$$

(C) forms mono-azonide (D) and

$$D \xrightarrow{Zn/H_2O} CH_3CHO$$

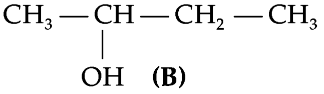
(A) undergoes, haloform reaction. So, it will contain CH_3CO group. (C) forms mono-ozonide (D), so (C) contains a C = C double bond. (D) on hydrolysis in presence of Zn dust gives only CH_3CHO. So, structure of (C) will be :



(But-2-ene)

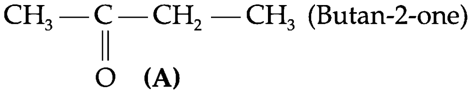
(C)

(C) is obtained by the action of H_2SO_4 *i.e.*, by dehydration of (B), so (B) will be a secondary alcohol.



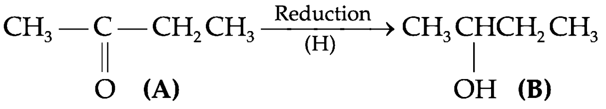
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \quad \textbf{(B)}$$

But (B) is obtained by the reduction of (A). So (A) should have the structure



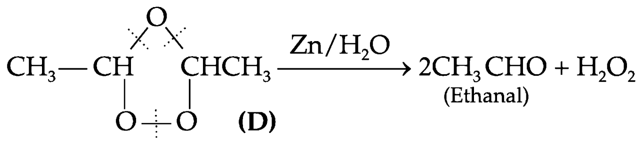
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3 \text{ (Butan-2-one)} \quad \textbf{(A)}$$

Hence the reactions involved are :



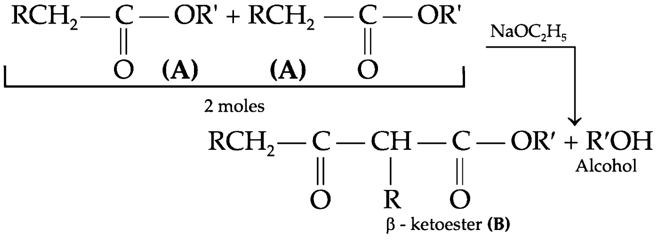
$$\underset{\textbf{(A)}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_2CH_3} \xrightarrow[\text{(H)}]{\text{Reduction}} \underset{\textbf{(B)}}{CH_3\underset{\underset{OH}{|}}{CH}CH_2CH_3}$$

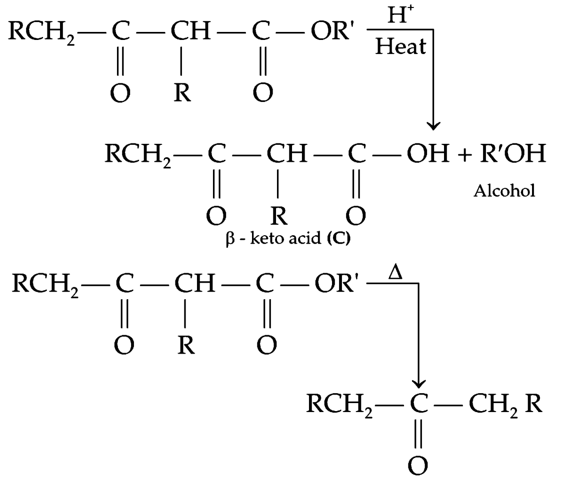
$$\xrightarrow[(-H_2O)]{H_2SO_4} CH_3-CH=CHCH_3 \xrightarrow{O_3}$$



Example 29. *An alkyl alkanoate (2 moles) when condensed in presence of sodium ethoxide gave ethanol and a β-keto ester (B). (B) on heating in acidic medium, gave ethanol and a β–keto acid (C). On decarboxylation, (C) formed pentan–3–one. Identify A, B and C with appropriate reasoning.* **(Roorkee, 1992)**

Solution. Alkyl alkanoate is called an ester. The action of an ester with sodium ethoxide to give an alcohol and β-keto ester is called Claisen condensation reaction. So, the reaction is ;

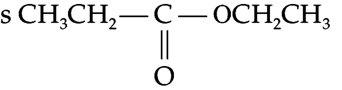




In order to get the required product,

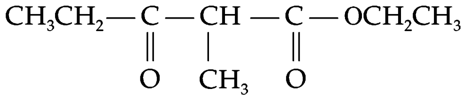
$R = -CH_3\ ;\ R' = -CH_2CH_3$

∴ (A) is



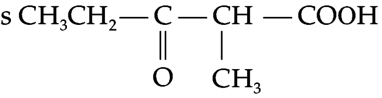
$CH_3CH_2-\underset{\underset{O}{\|}}{C}-OCH_2CH_3$

(B) is



$CH_3CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OCH_2CH_3$

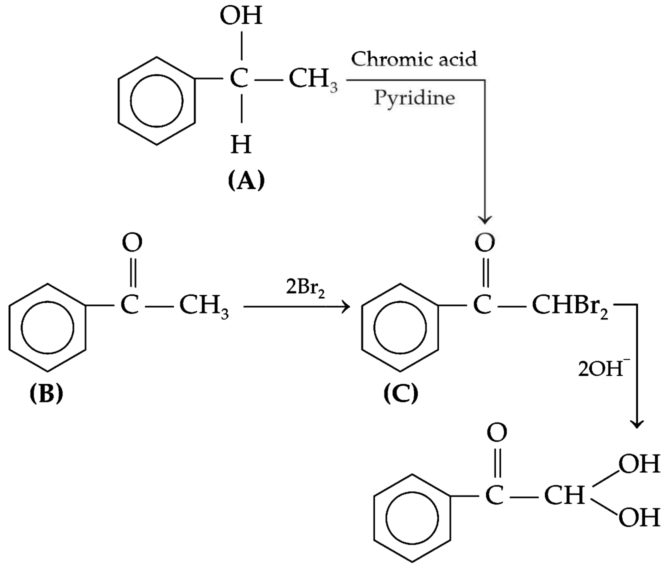
(B) is

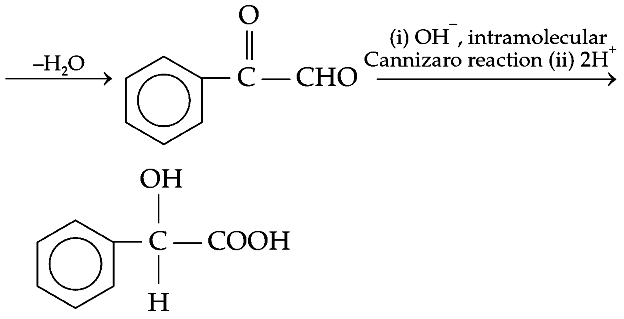


$CH_3CH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-COOH$

EXAMPLE 30. *A compound (A) $C_8H_{10}O$ when treated with chromic acid, pyridine give a compound (B) C_8H_8O. When (B) is treated with two equivalents of Br_2 gives (C) $C_8H_6O\ Br_2$ which on treatment with NaOH followed by acidification forms compound (D) $C_8H_8O_3$. (D) when treated with $NaHCO_3$ liberate CO_2 and is resolvable. Identify A, B, C and D.*

SOLUTION. Since (B) C_8H_8O is formed from (A) $C_8H_{10}O$, (B) must have been formed by the reduction of a secondary alcohol. Number of 8 carbon atoms indicate an aromatic ring. So, we have :



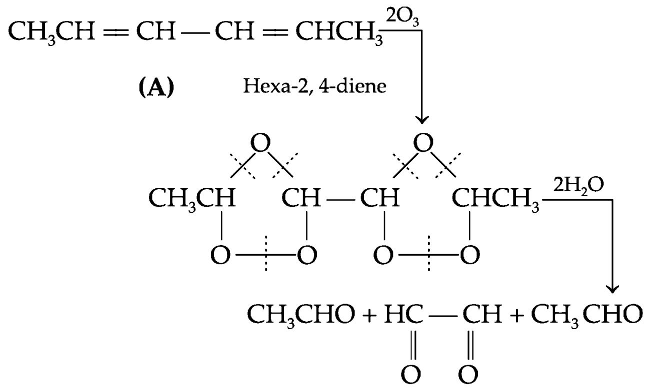


(D)

EXAMPLE 31. *When an organic compound (A) C_6H_{10} was reduced, first of all it forms B (C_6H_{12}) and finally (C) (C_6H_{14}). On ozonolysis, and followed by hydrolysis, (A) gives two aldehydes, D (C_2H_4O) and E ($C_2H_2O_2$). When (B) was oxidised with acidified $KMnO_4$, F ($C_4H_8O_2$) which is an acid was formed. Determine the structures of A, B,C, D, E and F along with reasons.*

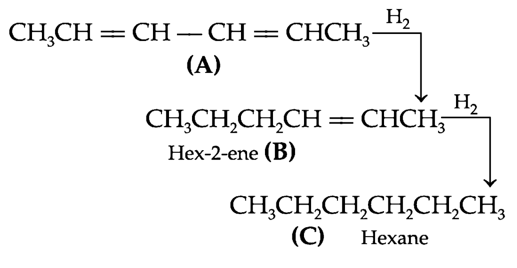
(Roorkee1993)

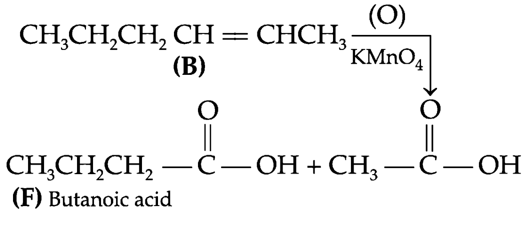
SOLUTION. (A) on reduction gives two compounds (B) and (C). Also, (A) on ozonolysis followed by hydrolysis forms two aldehydes. So, (A) must have two C = C double bonds. It means there will be two molecules of D (CH_3CHO) and one molecule of E (OHC – CHO). The above reactions can be represented as :



(D) (E) (D)

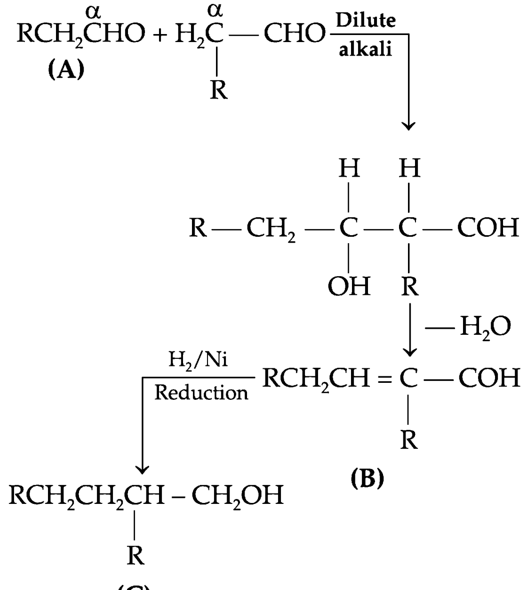
Elucidation of structures of (B) and (C) is explained below.





Example 32. *An organic compound (A) gives positive silver mirror test and reduces Fehling's solution. On warming with dilute alkali, followed by dehydration, it gives the product (B), which also responds to both the above tests. In addition, it decolorises the colour of bromine water. On treatment with hydrogen in the presence of nickel under pressure, the compound (B) is converted to (C) which does not give anyone of the above three tests. Molecular weight of (C) is 74 g mol⁻. Identify A and B, give reactions involved and draw their structures.*

Solution. (A) gives silver mirror test and reduces Fehling's solution. So, (A) must be an aldehyde. Warming (A) with dilute alkali indicates that (A) undergoes aldol condensation to give (B). So, it must have an α–hydrogen. (B) decolorises bromine water. So, (B) will contain unsaturation *i.e.*, C = C double bond. So, (A) will have the structure, RCH_2CHO. The reaction can be :



(C)

The mol. wt. of (C) is 74 g mol⁻. Thus :

R + 12 + (2 × 1) + 12 + (2 × 1) + 12 + 1 + R + 12 + (2 × 1) + 16 + 1 = 74

2R + 72 = 74 Or 2R = 74 – 72 = 2 *i.e.*,

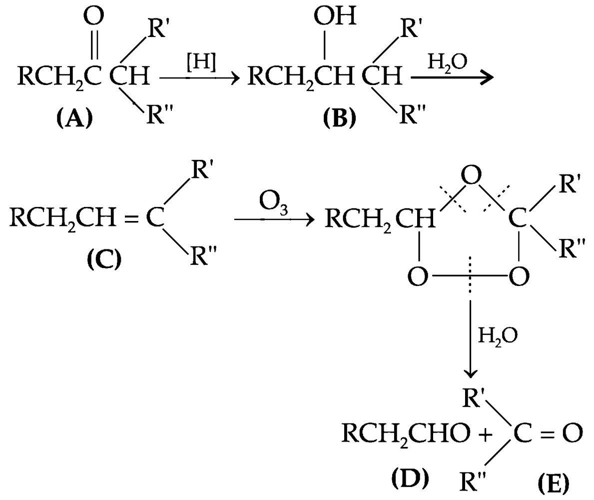
R = 2/2 = 1. Hence,

R is H. Substituting R = H in (A), (B) and (C), the structures of (A), (B) and (C) will be :

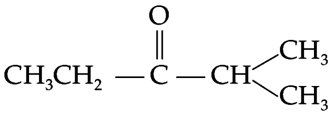
(A) is CH_3CHO ; (B) is $CH_3CH = CHCHO$ (C) is $CH_3CH_2CH_2CH_2OH$.

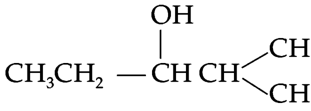
Example 33. *An organic compound (A) $C_6H_{12}O$ does not reduce Tollen's reagent but forms an oxime. On reduction with Na/Hg, (A) forms an alcohol (B) which on dehydration forms mainly a single alkene (C). The ozonolysis of (C) produces (D) and (E). The compound (D) reduces Tollen's reagent but does not give iodoform test. Explain the reactions involved and write the structures of A, B, C, D, and E compounds.*

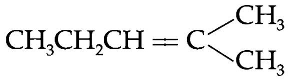
Solution. (A) does not reduce Tollen's reagent. So, it is not an aldehyde. It forms an oxime, so, it must be a ketone. (D) does not give iodoform test. So, it does not contain CH_3CO-group. So, (D) will be an aldehyde while (E) will be a ketone. Suppose (D) is RCH_2CHO and (E) is RCOR′ where R, R′ and R″ are alkyl groups. The sequence of reactions will be as follows.



Since the compound (A) contains six carbon atoms, R, R′ and R″ must be CH_3. So, the structures of A, B, C, D and E will be :

(A):

$CH_3CH_2—\overset{O}{\overset{\|}{C}}—CH(CH_3)_2$

(B): is

$CH_3CH_2—\overset{OH}{\overset{|}{C}H}\,CH(CH_3)_2$

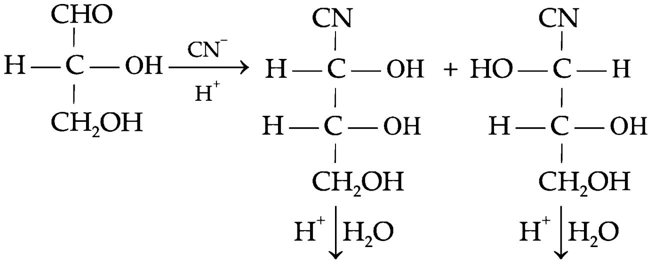
(C): is

$CH_3CH_2CH = C(CH_3)_2$

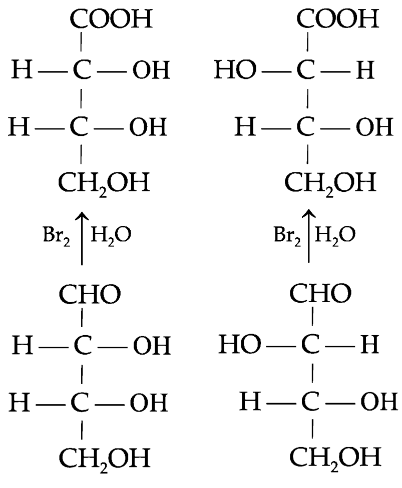
(D): is CH_3CH_2CHO and

(E): is CH_3COCH_3

Example 34. *When $CH_2OHCH(OH)CHO$ (R glyceraldehyde) is treated with cyanide and the resulting product is hydrolysed, two monocarboxylic acids are formed. These acids are identical with the acids obtained by the oxidation of (–) erythrose and (–) threose. Assign single structure to (–) threose and (–) erythrose.*

Solution. We know that a threose isomer is convertible to a racemic modification, while a erythrose isomer is convertible (in principle at least) into a meso structure. The names of these compounds are the basis to designate erythro and threo acids to specify certain configurations of compounds containing two chiral carbons. The various reactions involved are as follows :

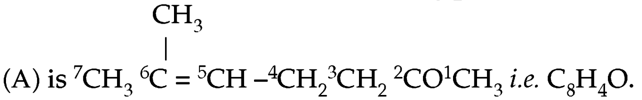




(–) Erythrose (–) Threose

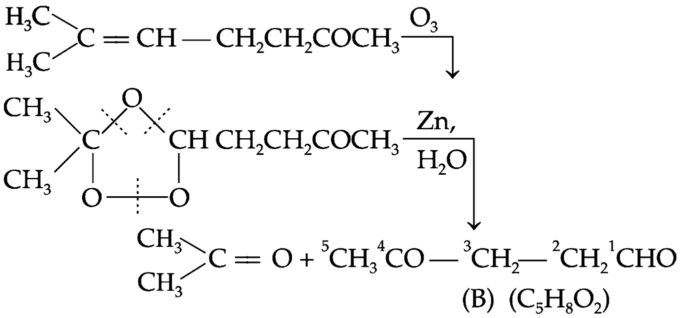
EXAMPLE 35. *An organic compound (A) $C_8H_{14}O$ gives a positive haloform reaction and forms an oxime. (A) on ozonolysis forms a compound (B) and acetone. (B) $C_5H_8O_2$ forms a dioxime and on subjecting to haloform reaction forms an acid (C), $C_4H_6O_4$. On treatment with excess of ammonia and strong heating, (C) gives a neutral compound (D) $C_4H_5O_2N$. When (D) was distilled with Zn-dust, pyrrole was formed. Suggest the sructures and give IUPAC names of A, B, C and D compounds.*

SOLUTION. A compound which gives a positive haloform reaction and forms an oxime, must contain CH_3CO–group. Also, it undergoes ozonolysis to give acetone and a compound (B). Since one of the products is acetone, so C = C double bond must be present as $(CH_3)_2$ C =. Hence :



(A) is $^7CH_3\,{}^6\overset{\overset{CH_3}{|}}{C} = {}^5CH - {}^4CH_2{}^3CH_2\,{}^2CO{}^1CH_3$ *i.e.* C_8H_4O.

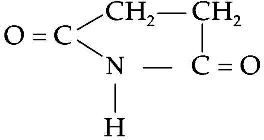
Its IUPAC name is 6– Methyl hept-5-en-2-one.



I.U.P.A.C. Name is 4-oxopentanal

Since (B) forms a dioxime and on subjecting to haloform reaction, forms an acid (C) $C_4H_6O_4$, so (C) will be HOOC. $CH_2.CH_2$.COOH. Its IUPAC name is butan –1, 4–dioic acid.

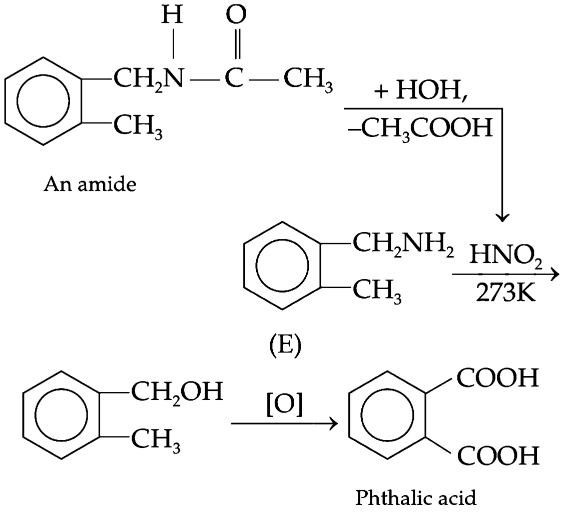
(C) reacts with excess NH_3 and on strong heating gives a neutral compound (D) $C_4H_5O_2N$ which forms pyrrole on distillation with Zn. So, (D) is



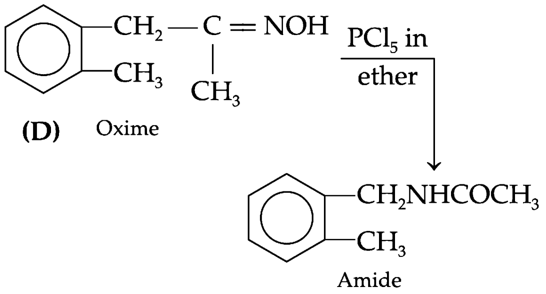
Its IUPAC name is succinimide.

EXAMPLE 36. *An organic compound (A) $C_{18}H_{20}O$ gives (B) $C_{10}H_{12}O$ and (C) $C_8H_8O_2$ on ozonolysis. (B) gives iodoform reaction and gives oxime (C) $C_{10}H_{13}ON$ with NH_2OH. The oxime undergoes rearrangement to form an amide when treated with PCl_5 in dry ether. This amide on hydrolysis gives a compound (E) $C_8H_{11}N$ and acetic acid. (E) with nitrous acid at 273 K gives an aromatic alcohol $C_8H_{10}O$, oxidation of which gives phthalic acid. (C) gives a carboxylic acid $C_8H_8O_2$ which is degraded by HI to CH_3I and p-hydroxybenzoic acid. Describe various reactions involved and identify A, B, C, D and E.* **(Roorkee, 1998)**

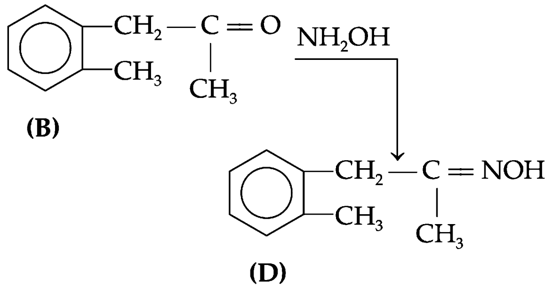
SOLUTION. (B) gives iodoform test and forms an oxime. So, it must contain CH_3CO–group. (E) obtained after hydrolysis of amide must contain aliphatic amine, $-NH_2$ group as it gives an alcohol at 273 K with HNO_2. The oxidation of above alcohol gives phthalic acid. So, the alcoholic substituent must be at the ortho position to the another substituent. Keeping the above facts in view, we proceed as follows :



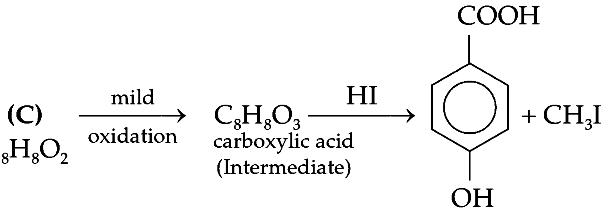
Above amide is formed by the rearrangement of oxime (D) as shown below.



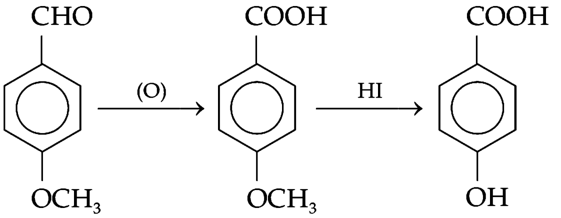
The structure of (B) would be :



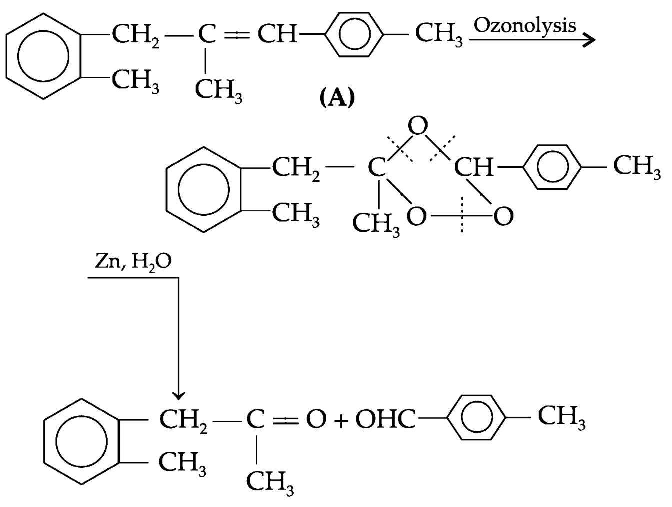
From the given data, reactions on (C) would be



The above intermediate must be an ether. Also, (C) must be containing $>C = O$ keto group because it is the ozonolysis product of (A). Keeping in view the above facts, the reactions can be given as :

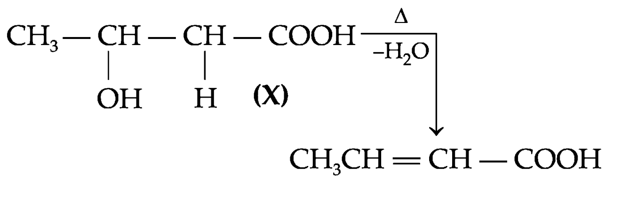


The structure of (A) can finally be written as :



EXAMPLE 37. *An organic compound (X) ($C_4H_8O_3$), acidic in reaction is oxidised with mild oxidants to give (A) (unstable), syrupy compound. It easily forms (B) C_3H_6O and CO_2 gas. (X) alone gives (C), $C_4H_6O_2$ having an acid neutralisation equivalent of 104 on simply heating. Write the structural formulae of X, A, B and C.*

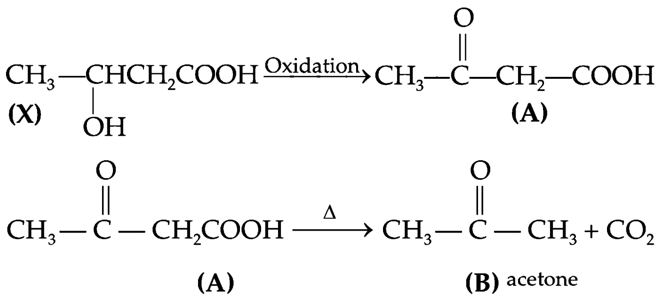
SOLUTION. Since (X) is acidic in reaction, $C_4H_8O_3$ must contain —COOH group. So, $C_4H_8O_3$ can be written as C_3H_7O—COOH. Here, C_3H_7O contains one O-atom. The product (C) C_3H_5COOH is an unsaturated acid that is obtained by heating X.



$$\underset{\text{OH}}{\underset{|}{CH_3-CH}}-\underset{\text{H}}{\underset{|}{CH}}-COOH\ (X)\ \xrightarrow[-H_2O]{\Delta}\ CH_3CH=CH-COOH$$

(C) $C_4H_6O_2$ Buten-2-oic acid

We know β-hydroxy substituted acids form substituted acids on heating. Thus, (X) should be β-hydroxy substituted acid. *i.e.*, $CH_3-\underset{\text{OH}}{\underset{|}{{}^{\beta}CH}}\,{}^{\alpha}CH_2-COOH$ (X). (X) on oxidation with mild oxidant give the following compound.

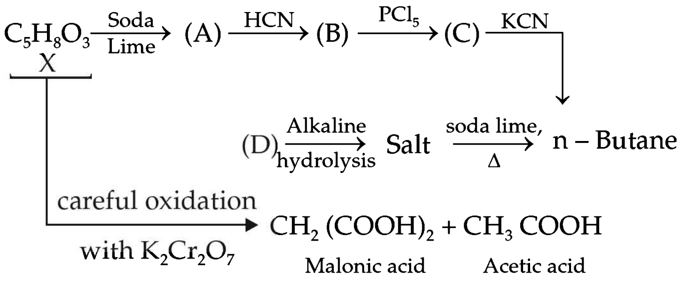


$$\underset{(X)}{CH_3-\underset{\text{OH}}{\underset{|}{CH}}CH_2COOH}\xrightarrow{\text{Oxidation}}\underset{(A)}{CH_3-\overset{\text{O}}{\overset{\|}{C}}-CH_2-COOH}$$

$$\underset{(A)}{CH_3-\overset{\text{O}}{\overset{\|}{C}}-CH_2COOH}\xrightarrow{\Delta}\underset{(B)\ \text{acetone}}{CH_3-\overset{\text{O}}{\overset{\|}{C}}-CH_3}+CO_2$$

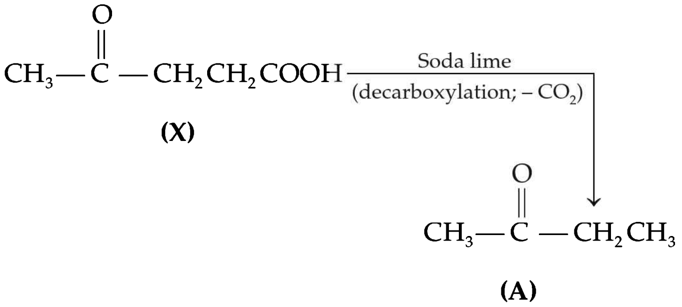
EXAMPLE 38. *An organic compound (X) $C_5H_8O_3$ gives a compound (A) on heating with soda-lime. (A) reacts wih HCN to form (B). (B) gives (C) on treating with PCl_5. (C) reacts with KCN to form (D). D gives a salt on alkaline hydrolysis. This salt is isolated and gives n-butane when heated with soda-lime. (X) when oxidised carefully with potassium dichromate, formed malonic acid and CH_3COOH. What are X, A, B, C, and D. Write their structural formula.* **(Roorkee, 1999)**

SOLUTION. The flow sheet of reactions as required in the given data are:

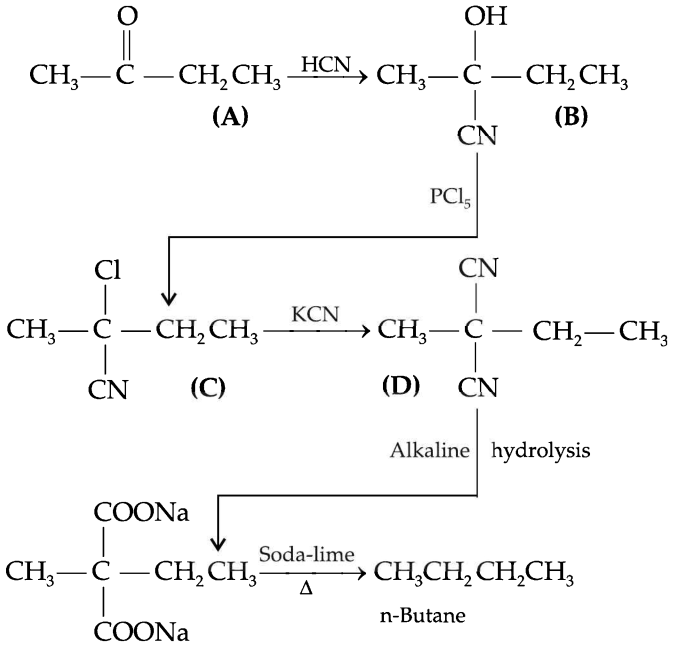


(X) on careful oxidation gives CH_3COOH and $CH_2(COOH)_2$ *i.e.*, three COOH groups. We know that on oxidaton, only two —COOH groups can be introduced *i.e.*, one to each carbon undergoing C—C fission. It confirms that (X) initially contains one —COOH group. So, $C_5H_8O_3$—COOH *i.e.*, C_4H_7O will be the remaining group of (X). This group will have a keto substituted alkyl group, $C_3H_7-\underset{|}{C}=O$. Hence, (X) is keto substituted acid.

In order to assign $>C = O$ keto group in carbon chain, we know that keto acids on careful oxidation undergo C—C bond fission at a place where $>C = O$ is situated. Keto group is also converted to —COOH group and remains with acid having small number of carbon atoms. It means CH_3COOH must have formed from $CH_3{>}C = O$ arrangement. So, $C_3H_7\overset{|}{C} = O$ will have the structure $CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2-$ and compound (X) will be $\underset{(X)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2COOH}$



$$\underset{\textbf{(X)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_2COOH} \xrightarrow[\text{(decarboxylation; }-CO_2)]{\text{Soda lime}} \underset{\textbf{(A)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3}$$



$$\underset{\textbf{(A)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3} \xrightarrow{HCN} \underset{\textbf{(B)}}{CH_3-\overset{OH}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2CH_3}$$

$$\xrightarrow{PCl_5} \underset{\textbf{(C)}}{CH_3-\overset{Cl}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2CH_3} \xrightarrow{KCN} \underset{\textbf{(D)}}{CH_3-\overset{CN}{\overset{|}{\underset{CN}{\underset{|}{C}}}}-CH_2-CH_3}$$

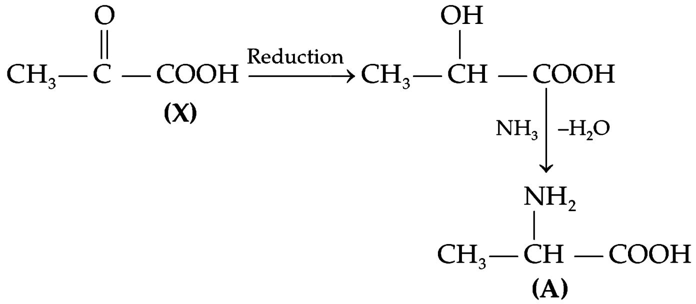
$$\xrightarrow{\text{Alkaline hydrolysis}} CH_3-\overset{COONa}{\overset{|}{\underset{COONa}{\underset{|}{C}}}}-CH_2CH_3 \xrightarrow[\Delta]{\text{Soda-lime}} \underset{\text{n-Butane}}{CH_3CH_2CH_2CH_3}$$

EXAMPLE 39. *An organic acid (X) $C_3H_4O_3$ gives the product (A) when catalytically reduced in presence of ammonia. (A) $C_3H_7NO_2$ reacts with acetyl chloride, HCl and alcohols. When treated with HNO_2, it gives another compound (B) $C_3H_6O_3$ along with N_2 gas. Citing reasons, identify (X), A and B compounds.*

SOLUTION. (X) is an acid. So, it contains one COOH group. The remaining part of (X) will be C_2H_3O or $CH_3-C{\overset{\nearrow O}{\searrow}}$. The structural formula of (X) will be:

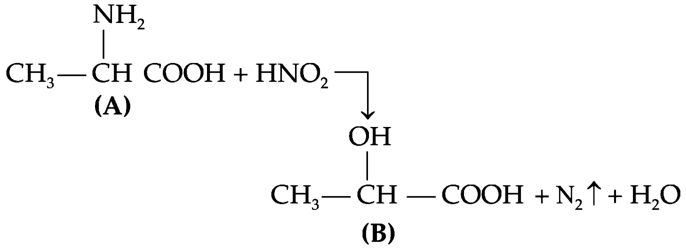
$CH_3-\overset{O}{\overset{\|}{C}}-COOH$ **(X)**.

(*i*) Catalytic reduction of keto group gives secondary alcohol which gives amino acid with ammonia. Thus:



$$\underset{\textbf{(X)}}{CH_3-\overset{O}{\overset{\|}{C}}-COOH} \xrightarrow{\text{Reduction}} CH_3-\overset{OH}{\overset{|}{CH}}-COOH \xrightarrow{NH_3,\ -H_2O} \underset{\textbf{(A)}}{CH_3-\overset{NH_2}{\overset{|}{CH}}-COOH}$$

(A) reacts with HNO_2 to give (B) and N_2 gas.

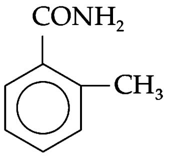


$$\underset{\textbf{(A)}}{CH_3-\overset{NH_2}{\overset{|}{CH}}\ COOH} + HNO_2 \longrightarrow \underset{\textbf{(B)}}{CH_3-\overset{OH}{\overset{|}{CH}}-COOH} + N_2\uparrow + H_2O$$

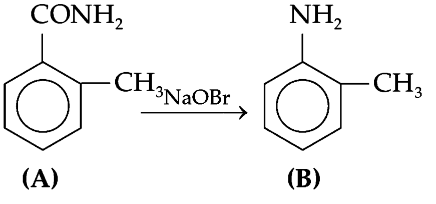
EXAMPLE 40. *An organic neutral compound (A) C_8H_9ON when treated with NaOBr forms an acid soluble substance C_7H_9N (B). (B) reacts with $NaNO_2$ and dil HCl at 0 to –5°C to give an ionic compound (C) $C_7H_7N_2Cl$. (C) reacts with alkaline β-naphthol solution to give red dye. When treated wih potassium cuprocyanide, (C) yields a neutral substance (D) C_8H_7N. (D) gives (E) $C_8H_8O_2$ on hydrolysis. (E) reacts with $NaHCO_3$ to produce CO_2 gas. Also, (E) on oxidation with permanganate gives (F). When (F) was nitrated, two isomeric mononitroderivatives (G) and (H) having molecular formula $C_8H_5NO_6$ were formed. Write various reactions involved and identify A, B, C, D, E, F, G and H.*

SOLUTION. Since (A) reacts with NaO Br, to form a base C_7H_9N (B), so, A should be an aromatic amide and (B) should be an amine. Thus :

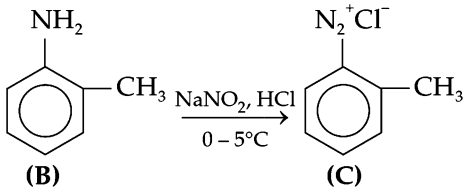
(*i*) A is

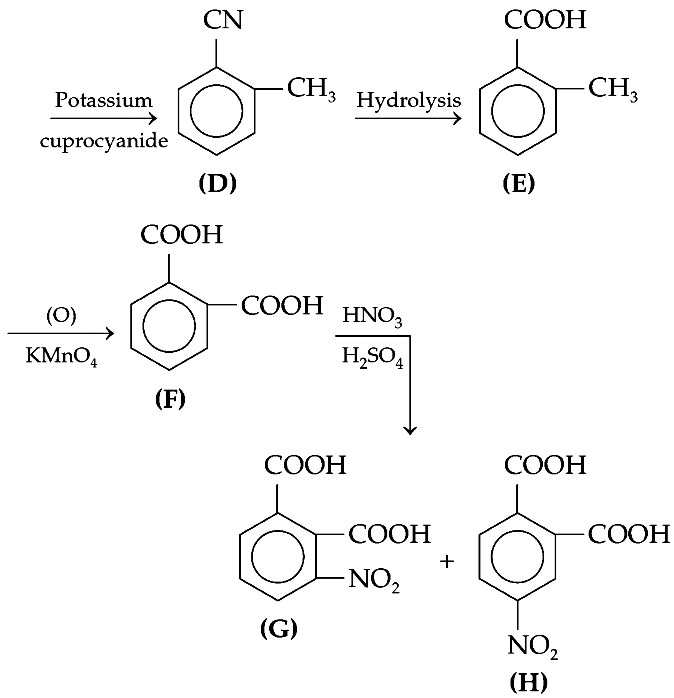


(*ii*)



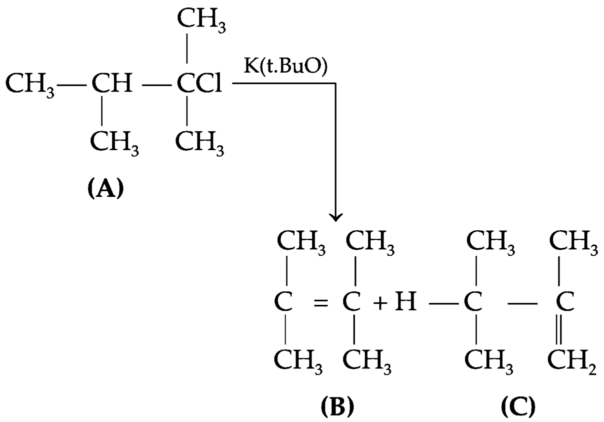
(*iii*)



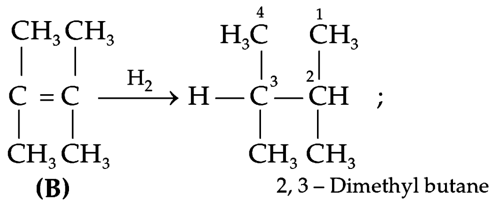


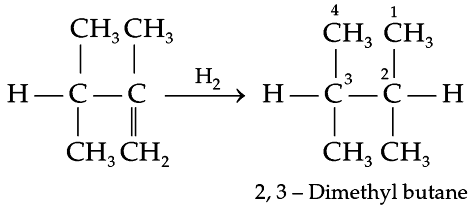
EXAMPLE 41. *An alkylhalide (A) having molecular formula $C_6H_{13}Cl$ when treated with potassium tertiary butoxide gave two isomeric alkenes (B) and (C) (C_6H_{12}). Both alkenes on hydrogenation gives 2, 3-dimethyl butane. Assign structures to A, B and C compounds.* **(IIT, 1996)**

SOLUTION. The given alkyl halide (A) $C_6H_{13}Cl$ gives two isomeric alkenes. It shows that the 'Cl' should not be bonded to the C-atom of terminal alkyl group. So, the reactions can be shown as follows :



(B) and (C) on hydrogenation give 2, 3–dimethyl butane as shown below:





EXAMPLE 42. *An alcohol ROH having mass 0.37 g was added to CH_3MgI and a gas evolved measured 112 mL at N.T.P. Calculate the molecular mass of ROH. This alcohol on dehydration forms an alkene which on ozonolysis gave acetone as one of the products. Also, this alcohol on oxidation easily gives an acid containing same number of carbon atoms. Assign structures to the acid as well as the alcohol with reasons.* **(Roorkee, 1994)**

SOLUTION. Wt (W) of ROH = 0.37 g ;

$$\text{Volume (V)} = 112\text{ mL} = 112/1000 = 0.112\text{ L}$$

$$T = 273\text{K} ;\ \text{Mol. wt. (M)} = ? ;$$

$$R = 0.0821\text{ L atm. K}^{-}\text{ mol}^{-};\ P = 1\text{ atm.}$$

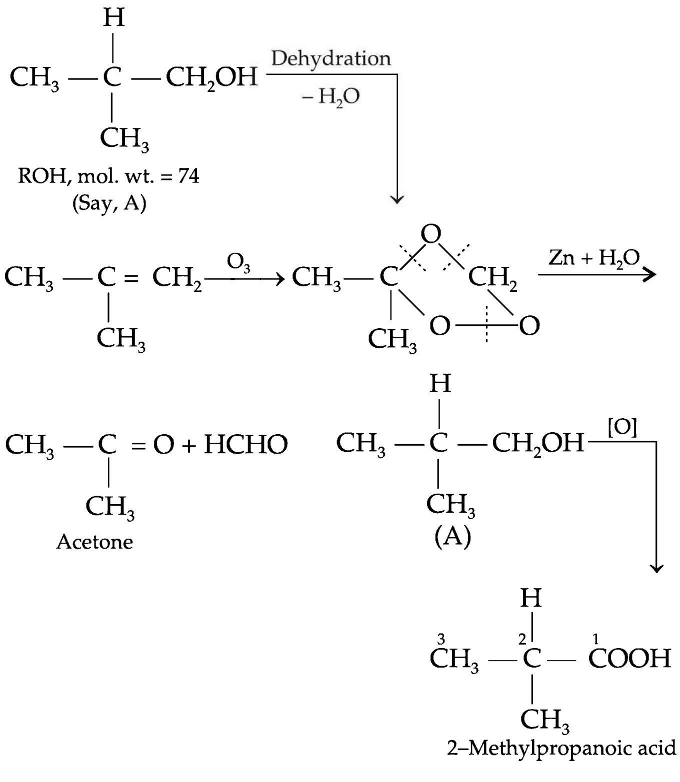
We know, $PV = nRT$ or $PV = \frac{W}{M}RT$

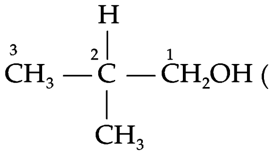
Or $M = \frac{WRT}{PV}$

$$= \frac{0.37\text{g} \times 0.0821\text{ L atm mol}^{-}\text{ K}^{-} \times 273\text{ K}}{1\text{ atm} \times 0.112\text{ L}} = 74\text{ g mol}^{-}$$

∴ Mol. wt. of ROH = **74 g mol⁻.** **Ans.**

ROH on dehydration gives alkene, which on ozonolysis gives acetone, CH_3COCH_3. Thus the reactions will be :

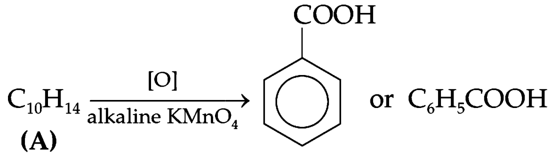




and alcohol is $\overset{3}{C}H_3-\overset{2}{C}(H)(CH_3)-\overset{1}{C}H_2OH$ (2 – methyl propanol)

Example 43. *An organic chiral compound (A) $C_{10}H_{14}$ gives C_6H_5COOH when oxidised with alkaline $KMnO_4$. But the achiral compound (B) $C_{10}H_{14}$ is inert to oxidation under the same conditions. Assign structures to (A) and (B).*

Solution. From the given data, we have :

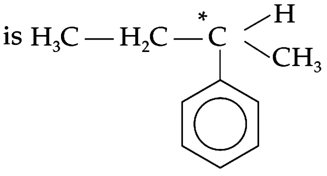


(*i*) $\underset{(A)}{C_{10}H_{14}} \xrightarrow[\text{alkaline KMnO}_4]{[O]}$ or C_6H_5COOH

(*ii*) $\underset{(B)}{C_{10}H_{14}} \xrightarrow[\text{alkaline KMnO}_4]{[O]}$ no action *i.e.*, inert to oxidation.

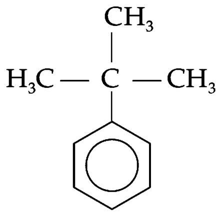
From (i), it is clear that C_6H_5COOH is the only product. So, (A) should be monosubstituted compound *i.e.*, $C_{10}H_{14} - C_6H_5$ or C_4H_9 group should be present in the monosubstituted benzene. Thus :

(A) is



Chiral and prone to oxidation

(B)



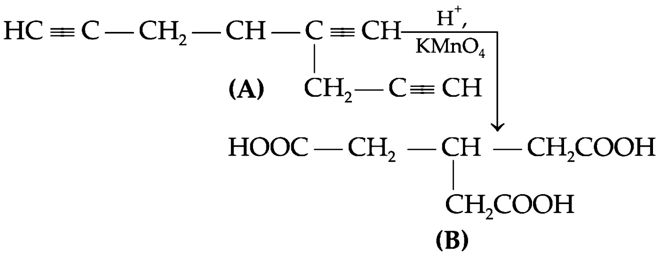
Achiral and inert to oxidation

Example 44. An organic compound (A) $C_{10}H_{10}$ gives only one organic compound $HOOC.\,CH_2.\,\underset{\displaystyle CH_2COOH}{CH}\,CH_2COOH$ (B) on oxidative cleavage. Deduce the structural formula of $C_{10}H_{10}$ compound.

Solution. (A) on oxidative cleavage gives only one compound containing COOH groups. So, the degree of unsaturation in the compound can be calculated by the relation :

$$\text{Degree of unsaturation} = (\text{No. of C-atoms}) - \frac{\text{No. of H - atoms}}{2} + 1 = 10 - \frac{10}{2} + 1 = 10 - 5 + 1 = 6$$

So, the compound (A) contains 6 bonds. Since on oxidative cleavage, (A) gives only one compound, so, all the multiple bonds should be on the terminal atom. Hence, we have :



Example 45. *An organic compound (A) containing chlorine showed the following properties.*

(*i*) *when vaporised, 1.49g of (A) produced 448 mL of vapour at N.T.P.*

(*ii*) *gives a precipitate with ammonical cuprous chloride*

(*iii*) *decolorises bromine in CCl_4 liquid.*

(*iv*) *absorbs H_2 in the presence of a catalyst.*

Identify (A).

Solution. At N.T.P., $P = 1$ atm ; $T = 273$ K., $V = 448$ mL $= 448/1000 = 0.448$ L ; $R = 0.0821$ L atm. K^- mol^-; Mol. wt. (M) = ? ; $W = 1.49$ g.

$$\text{We know } PV = n\,RT = \frac{W\,RT}{M}$$

$$\textbf{Or } M = \frac{W\,RT}{PV}.$$

Substituting the values, we get :

$$M = \frac{1.49\text{g} \times 0.0821 \text{ L atm. } K^-.\text{mol}^-. \times 273 \text{ K}}{1 \text{ atm} \times 0.448 \text{ L}}$$

$$= \mathbf{74.54\ g\ mol^-}$$

(A) gives a ppt. with ammonical cuprous chloride, decolorises bromine water and absorbs H_2 in presence of a catalyst. So, (A) must have terminal $C \equiv C$.

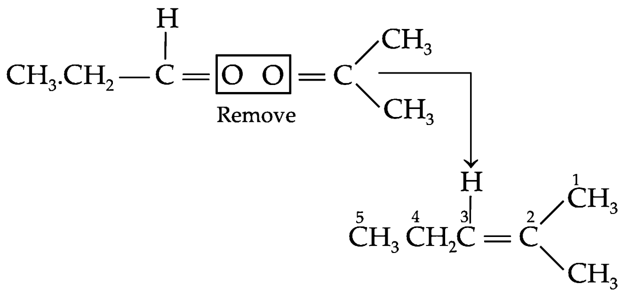
Mol. wt. of (A) *i.e.*, R. Cl = 74.45

$\therefore$ Mol. wt. of R = 74.45 – at. wt. of Cl (= 35.5) = 38.95 ≃ 39.

R contains C and H atoms. The number of C–atoms are obtained by dividing the mol. wt. by at. wt. of C (= 12) and the remainder represents number of H–atoms. So, 39/12 = 3 with remainder 3 which represents H–atoms. So, the formula of R is C_3H_3. Thus, the molecular formula of RCl is C_3H_3Cl *i.e.*, $CH_2Cl—C \equiv CH$.

Example 46. *On ozonolysis, an alkene C_6H_{12} gives two products. One of the products gave a positive iodoform test while a negative Tollen's test. The other product gave a positive Tollen's test but a negative iodoform test. Identify the alkene and give its I.U.P.A.C name.*

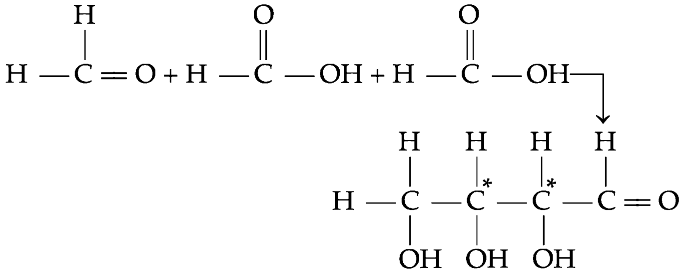
Solution. One product gives positive iodoform test but negative Tollen's test. So, it will contain CH_3CO – group or it will be methyl ketone. The other product gives a positive Tollen's test and a negative iodoform test. So, it will be an aldehyde and will not contain methyl group. Hence the products will on ozonolysis be $CH_3CO\,CH_3$ and CH_3CH_2CHO. The alkene can be obtained by removing O–atoms from $C = O$ groups of aldehyde and ketone and joining them by $C = C$.



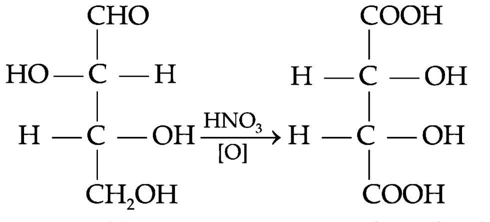
2 – Methyl pent-2-ene (IUPAC name)

EXAMPLE 47. *An organic compound, (–) erythrose* $C_4H_8O_4$ *gives tests with Benedict's solution and Tollen's reagent. It is also oxidised to an optically active acid,* $C_4H_8O_5$*. Treatment with ethanoic anhydride yields* $C_{10}H_{14}O_7$*. It consumes 3 moles of periodic acid and yields one mole of methanal and 3 moles of methanoic acid. Oxidation of erythrose by* HNO_3 *gives an optically inactive compound* $C_4H_8O_5$*. (–) threose, an isomer of erythrose, shows similar chemical behaviour except that* HNO_3 *oxidation yields an optically active compound* $C_4H_8O_6$*. On the basis of these evidences what structure or structures are possible for (–) threose and for (–) erythrose.*

SOLUTION. We know that erythrose is an aldehyde and contains three –OH groups. Cleavage by 3 moles of HIO_3 show that it has the following structure containing two chiral carbon* atoms.

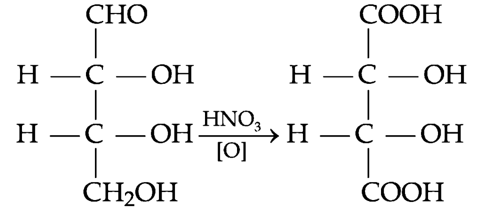


When (–) erythrose is oxidised, a dicarboxylic acid, HOOC – *CH– (OH) CH (OH) COOH is formed. This acid being optically inactive, it must have meso configuration, showing that (–) erythrose has either structure I or II as shown below :



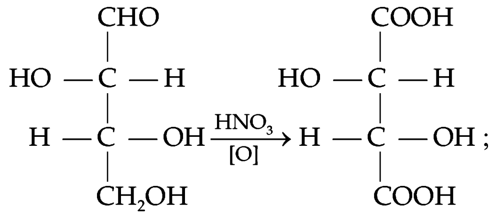
(I) Meso form of acid

or

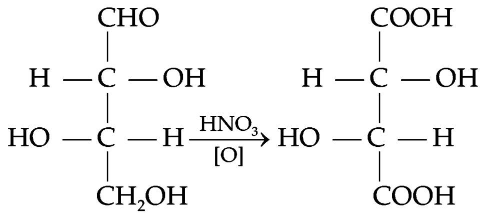


(II) Same meso form of acid

Also, (–) threose must be a diasteroisomer of erythrose, having either structure (III) or (IV) as shown below :



(III) Active acid



(IV) Active acid

EXAMPLE 48. *A compound having molecular formula* C_2HCl_3O *forms an addition product with sodium bisulphite and yields chloroform when warmed wih caustic soda solution. Derive the structural formula of the compound.*

SOLUTION. Molecular formula is C_2HCl_3O.

Structural formula. Since the compound forms an addition product with $NaHSO_3$, it must be a carbonyl compound containing either aldehyde (–CHO) or keto group (>C = O). First member of a ketone is CH_3COCH_3 that contains 3 carbon atoms. So, the given compound containing 2 carbon atoms cannot be a ketone. It will be an aldehyde. So, the compound will be CCl_3 – CHO *i.e.,* **trichloroacetaldehyde** or chloral.

It forms chloroform when heated with NaOH solution.

$$CCl_3.CHO + NaOH \longrightarrow \underset{\text{Chloroform}}{CHCl_3} + HCOONa$$

It gives addition compound with sodium bisulphite.

EXAMPLE 49. *An organic compound A having molecular formula* C_7H_8O *when oxidised on controlled condition, firstly gave an aldehyde (B) and then an acid (C). Sodium salt of the (C) gave benzene on distillation with soda-lime. Determine the structural formula of the compound A.*

SOLUTION. Since A on oxidation firstly gives an aldehyde B and then an acid (C) whose sodium salt on distillation with soda-lime gives benzene, A may be an alcohol *i.e.,* $C_6H_5CH_2OH$. A on oxidation gives aldehyde C_6H_5CHO (B) which on oxidation gives C_6H_5COOH (C).

EXAMPLE 50. *An organic compound gave the following results on analysis. (a) C = 26.08%, H = 4.34% (b) vapour density = 23. The compound gave brisk effervescence with sodium bicarbonate and reduced* $HgCl_2$ *solution. Write a suitable structure for the compound giving reasons.* **(KU 1978)**

SOLUTION. C = 26.08%, H = 4.34%,

O = 100 – (26.08 + 4.34) = 69.58%

(*i*) To find E.F.

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	26.08	12	$\frac{26.08}{12} = 2.17$	$\frac{2.17}{2.17} = 1$	1
H	4.34	1	$\frac{4.34}{1} = 4.34$	$\frac{4.34}{2.17} = 2$	2
O	69.58	16	$\frac{69.58}{16} = 4.35$	$\frac{4.35}{2.17} = 2$	2

$\therefore$ E. F. of compound = CH_2O_2 ;

E.F. wt. = 12 + (2 × 1) + (2 × 16) = 46

(*ii*) **To find M.F.** Mol. wt.

= 2 × V.D. = 2 × 23 = 46

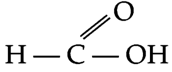
$$\therefore \quad M.F. = E.F. \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= CH_2O_2 \times \frac{46}{46} = CH_2O_2$$

(*iii*) To find structural formula. Since the compound gives brisk effervescence with $NaHCO_3$, it may be a carboxylic acid with one C – atom *i.e.*, HCOOH (formic acid). It reduces $HgCl_2$ to Hg_2Cl_2 and itself gets oxidised to CO_2.

$$2HgCl_2 + HCOOH \longrightarrow Hg_2Cl_2 + CO_2 + 2\,HCl.$$

So, the structural formula of acid is HCOOH

or 

$H-\overset{\overset{O}{\|}}{C}-OH$

EXAMPLE 51. *A monobasic organic acid on analysis gave the following results.*

(*a*) *0.315 g required 33.33 mL of N/10 NaOH for complete neutralisation*

(*b*) *0.2079 g of carious determination gave 0.3157 g silver chloride*

(*c*) *0.189g gave 0.1761 g CO_2 and 0.054g H_2O on analysis. Derive the molecular as well as structural formula of the compound.*

SOLUTION. (*i*) **To find mol. wt. of acid.** 33.33mL of N/10 NaOH ≡ 0.315g acid

$$1000\text{mL of 1N NaOH} \equiv \frac{0.315}{33.33} \times \frac{10}{1} \times 1000$$

= 94.51g acid.

$\therefore$ Eq. wt. of acid = 94.51

$\therefore$ Mol. wt. of acid = Basicity × Eq. wt.

= 1 × 94.51 = 94.51

[$\because$ acid given is monobasic]

(*ii*) To calculate E.F.

(*a*) Wt. of AgCl = 0.3157g.

AgCl ≡ Cl

108 + 35.5 35.5g

= 143.5g

143.5g AgCl ≡ 35.5g Cl

$$0.3175\text{g AgCl} \equiv \frac{35.5}{143.5} \times 0.3175 = 0.0781\text{g of Cl}$$

$$\therefore \quad \%\text{ age of Cl} = \frac{0.0781}{0.2079} \times 100 = \mathbf{37.57\%}$$

(*b*) $CO_2 \equiv C$;

12 + (2 × 16) 12g

= 44g

44g CO_2 ≡ 12g C

$$0.1761\text{g } CO_2 \equiv \frac{12}{44} \times 0.1761 = 0.048\text{g};$$

$$\therefore \%\text{ age of C} = \frac{0.048}{0.189} \times 100 = \mathbf{25.4\%}$$

(*c*) $H_2O \equiv 2H$

(2 × 1) + 16 2 × 1 = 2g

= 18 g

18g H_2O ≡ 2g H

$$0.054\text{g } H_2O \equiv \frac{2}{18} \times 0.054 = 6 \times 10^{-3}$$

$$\therefore \quad \%\text{ age of H} = \frac{6 \times 10^{-3}}{0.189} \times 100 = 3.17\%;$$

$$\%\text{ age of O} = 100 - (37.57 + 25.4 + 3.17) = 33.86\%$$

Element	% age	At. Wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	25.4	12	$\frac{25.4}{12} = 2.1$	$\frac{2.1}{1.058} = 2$	2
H	3.17	1	$\frac{3.17}{1} = 3.17$	$\frac{3.17}{1.058} = 3$	3
Cl	37.57	35.5	$\frac{37.57}{35.5} = 1.058$	$\frac{1.058}{1.058} = 1$	1
O	33.86	16	$\frac{33.86}{16} = 2.1$	$\frac{2.1}{1.058} = 2$	2

$\therefore$ E. F. of compound = $C_2H_3ClO_2$

E.F. wt. of $C_2H_3ClO_2$ = (2 × 12) + (3 × 1) + 35.5 + (2 × 16) = 94.5

$$\therefore \quad M.F. = E.F. \times \frac{\text{Mol. wt}}{\text{E.F. wt}}$$

$$= C_2H_3ClO_2 \times \frac{94.51}{94.5} = C_2H_3ClO_2$$

(*iii*) **Structural formula.** The given compound is monobasic acid. So, it contains one —COOH group. So, $C_2H_3ClO_2$ can be written as ; CH_2Cl COOH *i.e.*, monochloroacetic acid.

EXAMPLE 52. *An organic compound (A) containing C, H and O with boiling point 78°C and possessing a rather pleasant odour, on heating with conc. H_2SO_4 gives a gaseous product (B) with the empirical formula CH_2. 'B' decolorises bromine water as well as alkaline $KMnO_4$ solution and takes up one mol of H_2 (per mol of 'B') in the presence of finely-divided nickel at high temperature. Identify the substances A and B.* **(IIT 1979)**

SOLUTION. The empirical formula CH_2 indicates that its general formula will be $(CH_2)_n$ or C_nH_{2n} *i.e.*, alkene. Alkenes also decolorise Br_2 water as well as alkaline $KMnO_4$ and also adds up H_2 at high temperature. So, B is alkene. Compound A contains C, H and O. It is pleasant smelling with b.p. 78°C. So, it will be ethyl alcohol (C_2H_5OH). It gives ethene (C_2H_4) when heated with conc. H_2SO_4. So, A is C_2H_5OH ; B is C_2H_4

Reactions. $C_2H_5OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2 = CH_2$

$\xrightarrow[\text{water}]{Br_2} CH_2Br\text{–}CH_2Br ; CH_2 = CH_2 \xrightarrow[\substack{KMnO_4(H_2O + O) \\ \text{Pink}}]{\text{Alkaline}}$

$\underset{\text{glycol (colourless)}}{CH_2OH - CH_2OH} ; CH_2 = CH_2 \xrightarrow[\text{Catalyst}]{H_2, \Delta} \underset{\text{Ethane}}{CH_3 - CH_3}$

Example 53. *An organic compound having molecular formula $C_4H_8O_2$ on treatment with sodium hydroxide gave ethyl alcohol and sodium salt of an acid. When heated with sodalime, the sodium salt gave methane. Derive the structural formula of the compound.*

Solution. The given compound gives C_2H_5OH and sodium salt of acid. So, the compound may be an ester. The sodium salt of the acid gave methane (CH_4) with soda lime. So, the acid produced by the hydrolysis of ester should be CH_3COOH and ester should be $CH_3COOC_2H_5$.

Reactions :

(*i*) $CH_3COOC_2H_5 + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$

(*ii*) $CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$.

Example 54. *An organic compound A (V.D., 46.25) gave a positive Beilstein test. When A was treated with alcoholic KOH, another compound B was formed which did not give Beilstein test. B on oxidation with acidic $KMnO_4$ yielded an acid C (V.D., 37). Derive the structural formula of A and name it.*

Solution. (*i*) Mol. wt. of A = 2 × V.D. = 2 × 46.25 = 92.50. Since it gives a positive Beilstein test, it must be alkyl chloride (not bromide and iodide because their mol. wt. will be much higher than 92.5). So, the expected alkyl chloride is C_4H_9Cl (mol. wt. = 4 × 12 + 9 × 1 + 35.5 = 92.5).

(*ii*) C_4H_9Cl when treated with alc. KOH gives an olefin (C_4H_8).

$$\underset{\text{(A)}}{C_4H_9Cl} \xrightarrow[-\,HCl]{\text{alc. KOH}} \underset{\text{(B)}}{C_4H_8}$$

(*iii*) The olefin on oxidation with acidic $KMnO_4$ gets oxidised at C = C to give following two monocarboxylic acids.

$$CH_3CH_2CH = CH_2 \xrightarrow{O} \underset{\text{(C) Propanoic acid}}{CH_3CH_2COOH} + HCOOH$$

Mol. wt. of compound C = 2 × V.D. = 2 × 37 = 74.

Also, mol. wt. of CH_3CH_2COOH = 12 + (3 × 1) + 12 + (2 × 1) + 12 + (2 × 16) + 1 =74. So, C is CH_3CH_2COOH

(*iv*) If C_4H_8 is taken as $CH_3CH = CHCH_3$, then on oxidation, we get CH_3COOH which has mol. wt. (= 60 ; 12 + (3 × 1) + 12 + (2 × 16) + 1 = 60). So, this structure is rule out. Hence the structure of A is $CH_3CH_2CH_2CH_2Cl$ *i.e.*, **1–chlorobutane.**

Example 55. *An organic liquid A (C_2H_6O) on oxidation gives an acid B having empirical formula CH_2O. Both A and B form a sweet smelling liquid C (Mol. wt. 88), when treated with conc–H_2SO_4. Calculate the structural formula of A, B and C.*

Solution. Organic liquid A is C_2H_6O. It can be either CH_3OCH_3 (dimethyl ether) or C_2H_5OH (ethyl alcohol).

(*i*) If CH_3OCH_3 is oxidised, HCOOH (E.F. = CH_2O_2) is formed which does not correspond to given E.F. (CH_2O). So, it is not CH_3OCH_3.

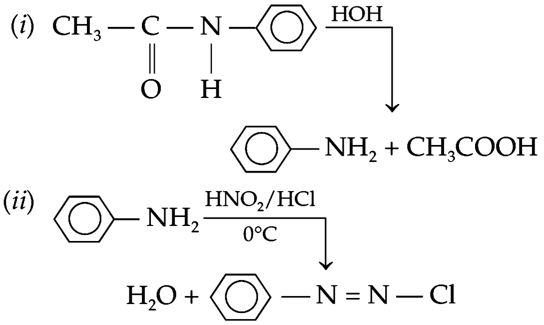
If C_2H_5OH is oxidised, CH_3COOH (B) (E.F. = CH_2O) is formed which has the same E.F. as required. So, A is ethyl alcohol.

B *i.e.*, CH_3COOH reacts with A (C_2H_5OH) in presence of conc. H_2SO_4 to give a sweet smelling substance (C), ethyl acetate [$CH_3COOC_2H_5$, mol. wt. = 12 + (3 × 1) + 12 + (2 × 16) + (2 × 12) + (5 × 1) = 88] whose mol. wt. is same as given in the question. So, C is **ethyl acetate,** $CH_3COOC_2H_5$.

Example 56. *An organic compound having molecular formula C_8H_9NO on hydrolysis yields acetic acid and a primary amine. If the amine is diazotisable, name the compound and assign structural formula to it.*

Solution. The compound C_8H_9NO gives acetic acid (CH_3COOH) and an amine on hydrolysis. But amine is diazotisable. So, the compound may be the derivative of acetic acid and aromatic amine (aniline). So, the expected compound is $CH_3CO.NH.C_6H_5$ (acetanilide)

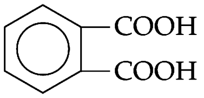
Reactions.



(Benzene diazonium chloride)

Example 57. *An organic acid (mol. formula $C_8H_6O_4$) when heated with its sodium salt formed benzene. It also formed two series of salts and two series of esters. It also forms an anhydride on simple heating. Derive the structural formula from the above data.*

Solution. Since $C_8H_6O_4$ compound gives two series of salts and two series of esters, the given acid will be a dibasic acid. When heated with sodalime, it gives benzene. So, it is a benzene derivative and may be benzene dicarboxylic acid, $C_6H_4(COOH)_2$. Also, it forms an anhydride on simple heating. So, it may be **ortho-phthalic acid,**



Example 58. *An organic compound $C_6H_5NO_2$ when heated with Sn and HCl gave a compound B (C_6H_7N). B on treatment with $NaNO_2$ and HCl followed by treatment with KCN gave a compound C which on hydrolysis yielded benzoic acid. Name the compounds B and C.*

Solution. (*i*) $C_6H_5NO_2$ on reduction with Sn/HCl gives amine.

$$C_6H_5NO_2 \xrightarrow[H]{Sn/HCl} \underset{\text{B (aniline)}}{C_6H_5NH_2}$$

So, compound B is aniline, $C_6H_5NH_2$ *i.e.*, C_6H_7N.

(*ii*) $C_6H_5NH_2$ on treatment with $NaNO_2$ and HCl gives benzene diazonium chloride, $C_6H_5N_2Cl$. The latter reacts

$$C_6H_5NH_2 \xrightarrow[0°C]{NaNO_2/HCl} C_6H_5N_2Cl$$

with KCN to give phenyl cyanide, C_6H_5CN (compound, C)

$$C_6H_5N_2Cl + KCN \longrightarrow C_6H_5CN + N_2 + KCl.$$

C_6H_5CN on hydrolysis gives benzoic acid, C_6H_5COOH

$$\underset{(C)}{C_6H_5CN} \xrightarrow{HOH} C_6H_5COOH + NH_3$$

Example 59. *A compound X reduces Fehling solution but does not react with sodium bicarbonate. On the otherhand, a compound Y does not reduce Fehling solution but reacts with sodium bicarbonate. Derive the structures of X and Y if their empirical formulae are same but their vapour densities are 15 and 30 respectively. Give reactions also.*

Solution. (*i*) The E.F. of X = CH_2O. Since X compound reduces Fehling solution but does not react with $NaHCO_3$, it will be an aldehyde with E.F. CH_2O. But mol. wt. of aldehyde is 2 × V.D. = 2 × 15 = 30. So, **X = HCHO** (mol. wt. = 30) *i.e.*, formaldehyde.

$$HCHO + \underset{\text{(From Fehling solution)}}{2CuO} \longrightarrow \underset{\text{Red ppt}}{Cu_2O\downarrow} + HCOOH$$

$$HCHO + NaHCO_3 \longrightarrow \text{No action.}$$

(*ii*) The E.F. of Y = CH_2O. Y compound does not reduce Fehling solution but reacts with $NaHCO_3$. So, it will be an acid and not an aldehyde. The acid may be acetic acid, CH_3COOH ($C_2H_4O_2$) having E.F., CH_2O. So **Y is CH_3COOH.**

$$CH_3COOH + \underset{\text{From Fehling solution}}{CuO} \longrightarrow \text{No action}$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COO\,Na + CO_2 + H_2O.$$

Example 60. *An organic substance A (mol. wt., 135) contains 71.13% carbon, 10.35% nitrogen and 6.67% hydrogen. 'A' on hydrolysis forms a monobasic acid B and an amine. The acid B contains 40% carbon and 6.6% hydrogen. 0.167g of its silver salt on ignition left behind 0.108g silver. Calculate the molecular formula of the compounds and write the various reactions involved.*

Solution. C = 71.13% , N = 10.35%, H = 6.67% and O = 100 – (71.13 + 10.35 + 6.67) = 11.85.

(*i*) **To find E.F.**

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	71.13	12	$\frac{71.13}{12} = 5.928$	$\frac{5.928}{0.739} = 8$	8
H	6.67	1	$\frac{6.67}{1} = 6.67$	$\frac{6.67}{0.739} = 9$	9
N	10.35	14	$\frac{10.35}{14} = 0.739$	$\frac{0.739}{0.739} = 1$	1
O	11.85	16	$\frac{11.85}{16} = 0.740$	$\frac{0.740}{0.739} = 1$	1

∴ E.F. of compound = C_8H_9NO

$$\text{E.F. wt.} = (8 \times 12) + (9 \times 1) + 14 + 16 = 135$$

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}} = C_8H_9NO \times \frac{135}{135}$$

$$= \mathbf{C_8H_9NO}$$

(*ii*) Eq. wt. by silver salt method

$$= \frac{\text{wt. of Ag-salt}}{\text{wt. of Ag}} \times 108 - 107$$

$$= \frac{0.167 \times 108}{0.108} - 107 = 60$$

$$\therefore \quad \text{Mol. wt.} = \text{Eq. wt.} \times \text{basicity} = 60 \times 1 = 60.$$

To find E.F., C = 40%, H = 6.6%,

O = 100 – (40 + 6.6) = 53.4%

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	40	12	$\frac{40}{12} = 3.33$	$\frac{3.33}{3.33} = 1$	1
H	6.6	1	$\frac{6.6}{1} = 6.66$	$\frac{6.66}{3.33} = 2$	2
O	53.4	16	$\frac{53.4}{16} = 3.33$	$\frac{3.33}{3.33} = 1$	1

$$\therefore \quad \text{E.F.} = CH_2O;$$

$$\text{E.F. wt.} = 12 + (2 \times 1) + 16 = 30.$$

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= CH_2O \times \frac{60}{30} = C_2H_4O_2.$$

The substance A on hydrolysis gives acid B with molecular formula $C_2H_4O_2$ or CH_3COOH (acetic acid) because carboxylic acid group is –COOH. It also gives amine. So, A is an acetyl derivative of an amine with the formula, $C_6H_5NH_2$ (aniline).

Hence A = acetanilide, $C_6H_5NHCOCH_3$

Reaction :

$$C_6H_5NHCOCH_3 + H_2O \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Aniline}}{C_6H_5NH_2}$$

EXAMPLE 61. *Two compounds A and B, both having same molecular weight (= 58) contain C = 62% , H = 10.4% and oxygen = 27.6%. A on oxidation gives a mixture of two acids containing one and two atoms of carbon per molecule respectively while B compound gives a monobasic acid containing three carbon atoms in the molecule. What are the compounds A and B? Give their reaction with (i) ammonical silver nitrate (ii) ammonia and (iii) sodium bisulphite.*

SOLUTION. (*i*) **To find E.F.**

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	62	12	$\frac{62}{12} = 5.17$	$\frac{5.17}{1.725} = 3$	3
H	10.4	1	$\frac{10.4}{1} = 10.4$	$\frac{10.4}{1.725} = 6$	6
O	27.6	16	$\frac{27.6}{16} = 1.725$	$\frac{1.725}{1.725} = 1$	1

$\therefore$ E.F. of compound $= C_3H_6O$.

$$\text{E.F. wt.} = (3 \times 12) + (6 \times 1) + 16 = 58$$

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt.}}$$

$$= C_3H_6O \times \frac{58}{58} = C_3H_6O$$

(*ii*) 'A' compound on oxidaton gives a mixture of acids (– COOH) with one (HCOOH) and two (CH_3COOH) carbon atoms per molecule respectively. So, A must be a ketone having formula **CH_3COCH_3 (acetone or propanone)**
Compound 'B' on oxidation gives an acid with 3 carbon atoms and it can be CH_3CH_2COOH which has same number of C–atoms as B has. So, **B** may be an aldehyde with formula CH_3CH_2CHO *i.e.*, **propanal** or propionaldehyde

Reactions

(*i*) $CH_3COCH_3 + Ag_2O \longrightarrow$ no action

$CH_3CH_2CHO + Ag_2O \longrightarrow CH_3CH_2COOH + 2Ag$

(*ii*) $2CH_3COCH_3 + NH_3 \longrightarrow \underset{\text{(Diacetone amine)}}{(CH_3)_2C(NH_2)CH_2COCH_3}$

$CH_3CH_2CHO + NH_3 \longrightarrow \underset{\text{Propionaldehyde ammonia}}{CH_3CH_2CH(OH)NH_2}$

(*iii*) $CH_3COCH_3 + NaHSO_3 \longrightarrow \underset{\text{Acetone bisulphite compound}}{(CH_3)_2C(OH)SO_3Na}$

$CH_3CH_2CHO + NaHSO_3 \longrightarrow \underset{\text{Propionaldehyde bisulphite compound.}}{CH_3CH_2CH(OH)\ SO_3Na}$

EXAMPLE 62. *An organic liquid 'X' having molecular formula C_2HCl_3O (i) undergoes oxidaton to give a monobasic acid Y (containing C = 14.68%, H = 0.612% and Cl = 65.13%) and also reduces Fehling solution. Y gives a sweet smelling liquid (Z) containing 89.12% chlorine, when distilled with sodalime. (Z) can also be obtained by heating 'X' with alkali. Derive the structural formulae of X, Y and Z, using various reactions involved.*

SOLUTION. (*i*) Molecular formula of X = C_2HCl_3O.

To find E.F. of Y. C = 14.68%, H = 0.612%, Cl = 65.13%, O = 100–(14.68 + 0.612 + 65.13) = 19.578%

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	14.68	12	$\frac{14.68}{12} = 1.223$	$\frac{1.223}{0.612} \simeq 2$	2
H	0.612	1	$\frac{0.612}{1} = 0.612$	$\frac{0.612}{0.612} = 1$	1
Cl	65.13	35.5	$\frac{65.13}{35.5} = 1.835$	$\frac{1.835}{0.612} \simeq 3$	3
O	19.578	16	$\frac{19.578}{16} = 1.223$	$\frac{1.223}{0.612} \simeq 2$	2

$\therefore$ E.F. of $Y = C_2HCl_3O_2$

'**X**' compound reduces Fehling solution and on oxidation gives monobasic acid '*Y*'. So, ***X* will be** an aldehyde *i.e.*, **CCl_3CHO** (trichloroacetaldehyde) while ***Y* will be $CCl_3.COOH$** (trichloroacetic acid)

Reactions. $CCl_3CHO \xrightarrow{O} CCl_3COOH$

$\underset{\text{(from Fehling solution)}}{CCl_3CHO + 2CuO} \longrightarrow CCl_3COOH + \underset{\text{Reddish brown ppt}}{Cu_2O\downarrow}$

(*ii*) '*Y*' gives sweet smelling liquid '*Z*' as shown below.

$$CCl_3COONa + NaOH \xrightarrow{CaO} \underset{\text{Z (Chloroform)}}{CHCl_3} + Na_2CO_3$$

Mol. wt. of $CHCl_3 = 12 + 1 + (35.5 \times 3) = 119.5$

$\therefore$ % age of Cl in $CHCl_3$

$$= \frac{(3 \times 35.5)}{119.5} \times 100 = 89.12\%$$

This value is in agreement with given percentage of chlorine.

Also, compound 'X' gives $CHCl_3$ on heating with alkali, NaOH.

$$CCl_3CHO + NaOH \longrightarrow CHCl_3 + \underset{\text{(Sodium formate)}}{HCOONa}$$

EXAMPLE 63. *An organic compound 'X' (chemical formula CH_2O) reduces Fehling solution as well as forms phenyl hydrazone. When 2 molecules of X react in presence of conc. NaOH solution, one molecule of a neutral compound 'Y' and a sodium salt of monobasic acid 'Z' are formed. Derive the structures of A, B and C and also, the various reactions involved in these.*

SOLUTION. (*i*) Compound 'X' reduces Fehling solution and forms phenyl hydrazone. So 'X' may be an aldehyde.

The formula CH_2O corresponds to the **formaldehyde, HCHO.** So, X = HCHO. Reactions are :

$$HCHO + 2CuO \longrightarrow HCOOH + Cu_2O \text{ (red ppt).}$$

(from Fehling solution)

$$HCHO + C_6H_5NHNH_2 \longrightarrow HCH = NNHC_6H_5$$

(phenyl hydrazone)

(*ii*) HCHO undergoes Cannizaro's reaction to form a neutral compound (CH_3OH = Y) and sodium salt of monobasic acid (HCOONa, sodium formate) *i.e.*, Z compound.

$$\underset{(X)}{2HCHO} + NaOH \longrightarrow \underset{(Y)}{CH_3OH} + \underset{(Z)}{HCOONa}$$

EXAMPLE 64. *An organic compound (CH_2O) gave two compounds A and B when treated with conc. NaOH. 'A' on oxidation gives original compound CH_2O while 'B' compound reduces ammoniacal silver nitrate. Name the compounds CH_2O, A and B and write the various reactions involved in it.*

SOLUTON. CH_2O reacts with conc. NaOH to give A which on oxidation gives CH_2O. It also gives B which reduces ammoniacal silver nitrate. So, CH_2O will be an aldehyde which gives Cannizaro's reaction. So, CH_2O is aldehyde *i.e.*, **formaldehyde (HCHO).** The reactions are :

(*i*) $2HCHO + NaOH \longrightarrow \underset{(A)}{CH_3OH} + \underset{(B)}{HCOONa}$

(*ii*) $CH_3OH \xrightarrow{O} HCHO + H_2O$

(*iii*) $HCOONa + Ag_2O$ (from ammoniacal silver nitrate solution) $\longrightarrow 2Ag\downarrow + CO_2 + NaOH.$

EXAMPLE 65. *A dibasic organic acid contains 26.59% C, 2.22% hydrogen and rest oxygen. 2.40g of a silver salt on ignition gave 1.704 g silver as residue. Calculate the molecular formula of the acid and write its structural formula.*

SOLUTION. Wt. of Ag–salt = 2.40g ;

wt. of silver = 1.704g. we know that :

$$\text{Eq. wt. of acid} = \left[\frac{\text{Wt. of Ag-salt}}{\text{Wt. of Ag}} \times 108\right] - 107$$

$$= \frac{2.4 \times 108}{1.704} - 107$$

$$= 152.1 - 107 = 45.1$$

$\therefore$ Mol. wt. of acid = Eq. wt. × basicity = 45.1 × 2 = 90.2

To find E.F. C = 26.59%, H = 2.22%, O = 100 – (26.59 + 2.22) = 71.19%

Element	% age	At. wt.	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	26.59	12	$\frac{26.59}{12} = 2.2$	$\frac{2.2}{2.22} = 1$	1
H	2.22	1	$\frac{2.22}{1} = 2.22$	$\frac{2.22}{2.22} = 1$	1
O	71.19	16	$\frac{71.19}{16} = 4.44$	$\frac{4.44}{2.22} = 2$	2

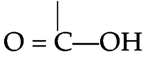
$\therefore$ E.F. of organic acid = CHO_2 ;

$$\text{E.F. wt.} = 12 + 1 + (2 \times 16) = 45$$

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E.F. wt}}$$

$$= CHO_2 \times \frac{90.2}{45} = C_2H_2O_4.$$

The given acid is a dibasic acid, so, it wll contain two COOH groups. Hence the structure of the organic acid is



$$\begin{array}{l} O = C\text{—}OH \\ \quad\ | \\ O = C\text{—}OH \end{array}$$

i. e., **oxalic acid**

EXAMPLE 66. *An organic compound (0.6g) on combustion gave 1.32g CO_2 and 0.72g H_2O. Calculate its molecular formula if its vapour density is 30. Write the structure of three compounds having this formula.*

SOLUTION. (*i*) $CO_2 \equiv C$

$44g\ CO_2 \equiv 12g\ C$

$12 + (2 \times 16) \quad 12g$

$= 44$ g

$$1.32g\ CO_2 \equiv \frac{12}{44} \times 1.32 = 0.36g$$

$$\therefore \quad \%\text{ age of C} = \frac{0.36}{0.6} \times 100 = 60\%$$

(*ii*) $H_2O \equiv 2H$

$18g\ H_2O \equiv 2g\ H$

$(2 \times 1) + 16 \quad 2 \times 1$

$= 18g \quad = 2g$

$$0.72g\ H_2O \equiv \frac{2}{18} \times 0.72 = 0.08g$$

$$\therefore \quad \%\text{ age of H} = \frac{0.08 \times 100}{0.6} = 13.33\%$$

$$\%\text{ age of O} = 100 - (60 + 13.33) = 26.67$$

To Find E.F.

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	60	12	$\frac{60}{12} = 5$	$\frac{5}{1.67} \simeq 3$	3
H	13.33	1	$\frac{13.33}{1} = 13.33$	$\frac{13.33}{1.67} \simeq 8$	8
O	26.67	16	$\frac{26.67}{16} = 1.67$	$\frac{1.67}{1.67} = 1$	1

$\therefore$ E.F. of compound = C_3H_8O *i.e.,* $C_nH_{2n+2}O$.

E.F. wt. = (3 × 12) + (8 × 1) + 16 = 60 ;

Mol. wt. = 2 × V.D. = 2 × 30 = 60.

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E. F. wt.}}$$

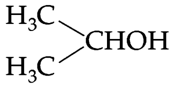
$$= C_3H_8O \times \frac{60}{60} = C_3H_8O$$

C_3H_8O may be an ether or an alcohol. Among alcohols, it cannot be tertiary alcohol because the latter contains

4 carbon atoms. Keeping in view valencies of C (= 4), O (= 2) and H (= 1), following structures can be suggested for C_3H_8O.

(*i*) $CH_3OC_2H_5$ (ethyl methyl ether)

(*ii*) $CH_3CH_2CH_2OH$ (*n* – propyl alcohol *i.e.*, 1° or primary alcohol.

(*iii*) 
$\begin{matrix}H_3C\\H_3C\end{matrix}\!>CHOH$ Isopropyl alcohol or propan – 2 – ol.

Example 67. *An organic compound on analysis was found to contain 64% oxygen, 4% hydrogen and rest being carbon. Calculate the molecular formula if 6 oxygen atoms per molecule of the compound are present.*

Solution. O = 64%, H = 4%, C = 100 – (64 + 4) = 32%

To find E.F.

Element	% age	At. wt.	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	32	12	$\frac{32}{12} = 2.67$	$\frac{2.67}{2.67} = 1$	1 × 2 = 2
H	4	1	$\frac{4}{1} = 4$	$\frac{4}{2.67} = 1.5$	1.5 × 2 = 3
O	64	16	$\frac{64}{16} = 4$	$\frac{4}{2.67} = 1.5$	1.5 × 2 = 3

∴ E.F. of the compound = $C_2H_3O_3$.

To find M.F. Since each molecule of compound contains six atoms of oxygen, M.F. = 2 × $C_2H_3O_3$ = $\mathbf{C_4H_6O_6}$ **Ans.**

Example 68. *A nitrogen containing organic compound gave the following results on analysis. 0.93g of it on combustion gave 2.64g CO_2 and 0.630g water. 0.465g of the substance liberated 55.6 cm^3 of nitrogen at N.T.P. (1 cm^3 of N_2 weighs 0.00126g). Calculate the empirical formula of the substance. write its structure if it gives tests of diazotisation.*

Solution. (*i*) wt. of compound = 0.93g; wt. of CO_2 = 2.64g and wt. of H_2O = 0.63 g.

(*a*)
$$\begin{array}{rl} CO_2 & \equiv C \\ 44g\ CO_2 & \equiv 12g\ C \\ 12 + (2 \times 16) & \ \ 12g \\ = 44g & \\ 2.64g\ CO_2 & \equiv \frac{12}{44} \times 2.64 = 0.72 \end{array}$$

$$\therefore \ \% \text{ age of C} = \frac{0.72}{0.93} \times 100 = 77.42$$

(*b*)
$$\begin{array}{rl} H_2O & = 2H \\ 18g\ H_2O & \equiv 2g\ H \\ (2 \times 1) + 16 & \ \ 2 \times 1 \\ = 18\ g & \ \ = 2g \\ 0.63g\ H_2O & \equiv \frac{2}{18} \times 0.63 = 0.07g \end{array}$$

$$\therefore \ \% \text{ age of H} = \frac{0.07}{0.93} \times 100 = \mathbf{7.53\%}$$

(*c*) 1 cm^3 of N_2 weighs = 0.00126g

55.6 cm^3 of N_2 weighs = 0.00126 × 55.6g

$$\therefore \ \% \text{ age of nitrogen} = \frac{0.00126 \times 55.6}{0.465} \times 100 = 15.07\%$$

To find E.F.

Element	% age	At. wt.	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	77.42	12	$\frac{77.42}{12} = 6.45$	$\frac{6.45}{1.08} = 6$	6
H	7.53	1	$\frac{7.53}{1} = 7.53$	$\frac{7.53}{1.08} = 7$	7
N	15.07	14	$\frac{15.07}{14} = 1.08$	$\frac{1.08}{1.08} = 1$	1

∴ E.F. = C_6H_7N

The compound gives diazotisation test. So, it contains NH_2 group. The compound will thus be aniline, $C_6H_5NH_2$.

Example 69. *0.5g of the chloroplatinate of organic mono-acid base on ignition left 0.195g of platinum residue. (b). 0.36g of the base in Kjeldahl's experiment liberated 0.136g of NH_3 Derive the molecular formula as well as structural formula of the base if it contains 53.33% C and 15.56% hydrogen. (at. wt., Pt = 195). Also, give action of base on nitrous acid.*

Solution. (*i*) **To find mol. wt. of base (B).** We know that :

$$\frac{\text{Wt. of chloroplatinate}}{\text{Wt. of Pt residue}} = \frac{\text{Mol. wt. of chloroplatinate } (B_2H_2\ Pt\,Cl_6)}{\text{At. wt. of Pt } (= 195)}$$

$$\frac{0.5}{0.195} = \frac{\text{Mol. wt. of } B_2H_2\ Pt\,Cl_6}{195}$$

$$\therefore \text{Mol. wt. of } B_2H_2\ Pt\,Cl_6 = \frac{0.5 \times 195}{0.195} = 500$$

∴ Eq. wt. of base (B)

$$= \frac{\text{Mol. wt. of } B_2H_2\ Pt\,Cl_6 - \text{mol. wt. of } H_2\ Pt\,Cl_6}{2}$$

$$= \frac{500 - 410}{2} = 45$$

$$\left[\because \text{mol. wt. of } H_2PtCl_6 = (2 \times 1) + 195 + (6 \times 35.5) = 410\right]$$

∴ Mol. wt. = Eq. wt. × basicity = 45 × 1 = 45

(*ii*) **To find % age of nitrogen.** g. mol. wt. of

$$NH_3 = 14 + (3 \times 1) = 17g$$

17g NH_3 contain nitrogen = 14g

[∵ at. wt. of N = 14]

∴ 0.136g NH_3 contain nitrogen

$$= \frac{14}{17} \times 0.136g$$

$$\therefore \text{ \% age of nitrogen } = \frac{14 \times 0.136}{17} \times \frac{100}{0.36} = 31.11$$

(*iii*) **To find E.F.**, C = 53.33%, H = 15.56%, N = 31.11%

Element	% age	At. wt.	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	53.33	12	$\frac{53.33}{12} = 4.44$	$\frac{4.44}{2.22} = 2$	2
H	15.56	1	$\frac{15.56}{1} = 15.56$	$\frac{15.56}{2.22} = 7$	7
N	31.11	14	$\frac{31.11}{14} = 2.22$	$\frac{2.22}{2.22} = 1$	1

$\therefore$ E.F. of the base = C_2H_7N

E.F. wt. of C_2H_7N = (2 × 12) + (7 × 1) + 14 = 45

$$\therefore \quad \text{M.F.} = \text{E.F.} \times \frac{\text{Mol. wt.}}{\text{E. F. wt.}}$$

$$= C_2H_7N \times \frac{45}{45} = C_2H_7N.$$

The structural formula of compound can be anyone of the following compounds.

(*i*) $C_2H_5NH_2$ (ethyl amine, 1° – amine)

(*ii*) $(CH_3)_2$ NH (dimethyl amine, 2°–amine)

Reactions.

(*i*) $C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2 + H_2O$

(*ii*) $(CH_3)_2\,NH + HONO \longrightarrow (CH_3)_2\,N.\,NO + H_2O$

Dimethyl nitrosoamine

EXAMPLE 70. *An organic compound A on heating with PCl_5 gives B which gives C when heated with NH_3. 'C' gives 'D' when distilled wih P_2O_5. The substance D containing 0.205g of 'D' gave 65mL of N_2 gas at N.T.P. The substance 'D' gives 'A' on complete hydrolysis. Calculate the molecular formula and structural formula of the compound. Also, identify A, B, C and D compounds if the percentage of C and H in 'D' are 58.54 and 7.32 respectively.*

SOLUTION. To find the % age of nitrogen ; g. mol. wt. of N_2 = 2 × 14 = 28g.

22400mL of N_2 weighs = 28g

$$56\text{mL of } N_2 \text{ weighs} = \frac{28}{22400} \times 56 = 0.07\text{g}$$

$$\therefore \text{ \% age of nitrogen} = \frac{0.07}{0.205} \times 100 = 34.14\%$$

To find E.F. of the compound.

Element	% age	At. wt.	Relative no. of atoms = % age/At. wt.	Simple ratio	Whole no. ratio
C	58.54	12	$\frac{58.54}{12} = 4.88$	$\frac{4.88}{2.44} = 2$	2
H	7.32	1	$\frac{7.32}{1} = 7.32$	$\frac{7.32}{2.44} = 3$	3
N	34.14	14	$\frac{34.14}{14} = 2.44$	$\frac{2.44}{2.44} = 1$	1

$\therefore$ E.F. of the compound = C_2H_3N

The structural formula may be represented as

$CH_3—C \equiv N$ or $CH_3—N \rightleftarrows C$.

CH_3CN = Methyl cyanide or acetonitrile ;

$CH_3—N \rightleftarrows C$ is Methyl isocyanide.

(*i*) $CH_3CN + 2H_2O \xrightarrow{\text{Hydrolysis}} CH_3COOH + NH_3$

(*ii*) $CH_3NC + 2H_2O \longrightarrow HCOOH + CH_3NH_2$

(*a*) CH_3CN = D ; CH_3COOH = A

Reactions :

(*i*) $\underset{(A)}{CH_3COOH} + PCl_5 \longrightarrow \underset{(B)}{CH_3COCl} + POCl_3 + HCl$

$\underset{(B)}{CH_3COCl} + NH_3 \longrightarrow \underset{(C)}{CH_3CONH_2} + HCl$

$\underset{(C)}{CH_3CONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{(D)}{CH_3CN}$

$\underset{(D)}{CH_3CN} + 2H_2O \longrightarrow \underset{(A)}{CH_3COOH} + NH_3$

EXAMPLE 71. *A hydrocarbon A, adds one mole of hydrogen in presence of platinum catalyst to form n-hexane. When A is oxidised vigorously with $KMnO_4$, a single carboxylic acid containing three carbon atoms is isolated. Give the structure of A and explain.* **(IIT 1997)**

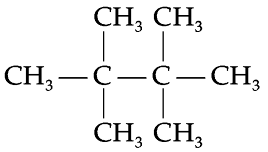
SOLUTION. Since hydrocarbon A adds a single molecule of hydrogen, it must be an alkene *i.e.*, hexene.

On vigorous oxidation with $KMnO_4$, it forms only one acid containing three carbon atoms. Clearly, it must be a symmetrical hexene *i.e.*, 3-hexene. The reaction is shown below :

$$\underset{\text{3-Hexene}}{CH_3—CH_2—CH=CH—CH_2—CH_3} \xrightarrow[\text{(O)}]{\text{alk. KMnO}_4} \underset{\text{Propanoic acid}}{2CH_3CH_2COOH}$$

EXAMPLE 72. *An organic compound C_8H_{18} on monochlorination gives a single monochloride. Write the structure of the hydrocarbon.* **(Roorkee 1999)**

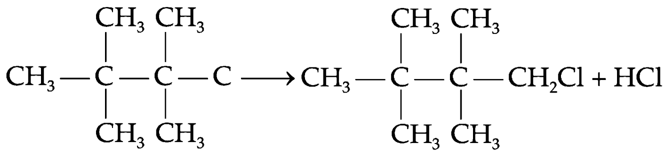
SOLUTION. As C_8H_{18} forms one and only one monochloride, it is clear that all the hydrogen atoms in C_8H_{18} are all alike. Such hydrogens are all primary H-atoms and the probable structure of alkane is given below :



$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\underset{CH_3}{\overset{CH_3}{C}}—CH_3$$

2, 2, 3, 3-tetra methyl butane

Since all hydrogen atoms are equivalent, Cl_2 reacts with it to form the following monochloroproduct.



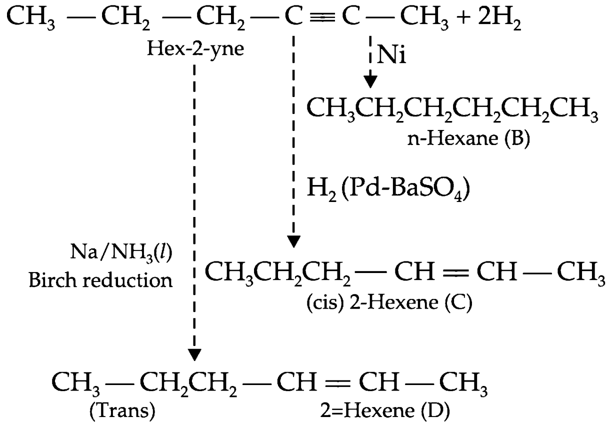
$$CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\underset{CH_3}{\overset{CH_3}{C}}—C \longrightarrow CH_3—\underset{CH_3}{\overset{CH_3}{C}}—\underset{CH_3}{\overset{CH_3}{C}}—CH_2Cl + HCl$$

1 – chloro – 2, 2, 3,
3 – tetra methyl butane

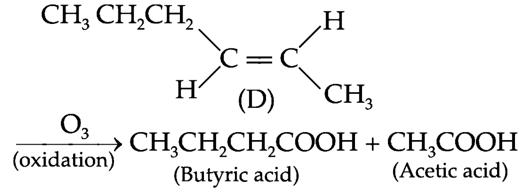
Example 73. *Hydrocarbon (A) C_6H_{10} on treatment with H_2/ Ni, H_2/Lindlar's catalyst and Na/NH_3 (l) forms three different products (B), (C) and (D) respectively. (A) forms salt (E) on heating with $NaNH_2$ in inert solvent but it does not form salt with ammonical $AgNO_3$ solution. Compound (E) further reacts with CH_3I to form (F). Compound (D) on oxidation ozonolysis gave butyric acid along with other products.*

Give the structures from (A) to (F) with proper reasoning. **(Roorkee 1998)**

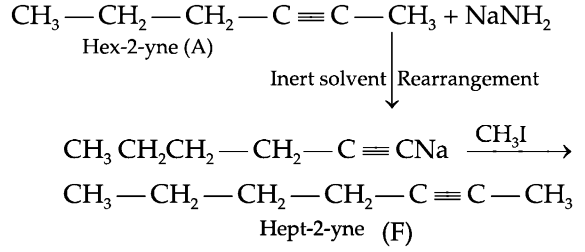
Solution. The hydrocarbon (A) C_6H_{10} appears to be hex-2-yne. Its reduction under different conditions is shown below :



(D) On oxidative ozonolysis gives butyric acid



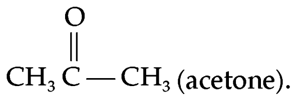
When hex-2-yne is heated wth $NaNH_2$ in inert solvent, then hex-2-yne rearranges to hex-1-yne which further reacts with $NaNH_2$ to form sodium salt. It then reacts with CH_3I to form hept-2-yne.



Example 74. *Ozonolysis of an alkene 'X' followed by decomposition with zinc and water gave two isomeric compounds of the formula C_3H_6O. Give the structure of the alkene and write the IUPAC name of this compound.*

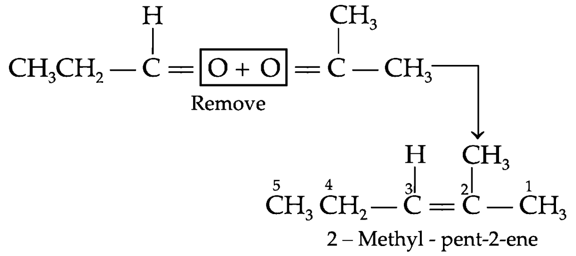
Solution. Since ozonolysis of an alkene gives an aldehyde or ketone or a mixture of aldehyde and ketone, so the isomers of C_3H_6O will be :

(*i*) CH_3CH_2CHO (propanal) and



(*ii*) $CH_3\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ (acetone).

The structure of alkene can be obtained by removing the oxygen atoms of the two carbonyl carbons of propanal and butanone and making a double bond between the carbonyl carbon atoms. Thus, we have :



Example 75. $A(C_6H_{12}) \xrightarrow{HCl} B + C$

$C_6H_{13}Cl$

$B \xrightarrow{Alc.\,KOH}$ *D (isomer of A)*

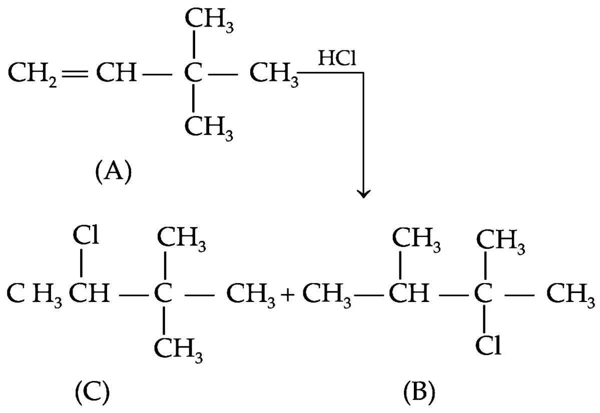
$D \xrightarrow{ozonolysis}$ *E (it gives negative test with Fehling solution but responds to iodoform test)*

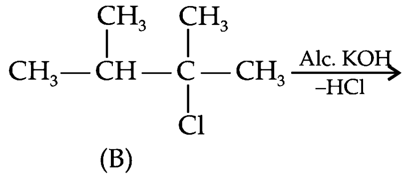
$A \xrightarrow{ozonolysis}$ *F + G (both give positive Tollen's test but donot give iodoform test)*

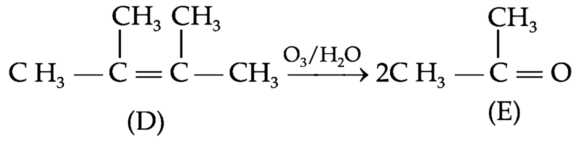
$F + G \xrightarrow{Conc.\,NaOH}$ *HCOONa + a primary alcohol).*

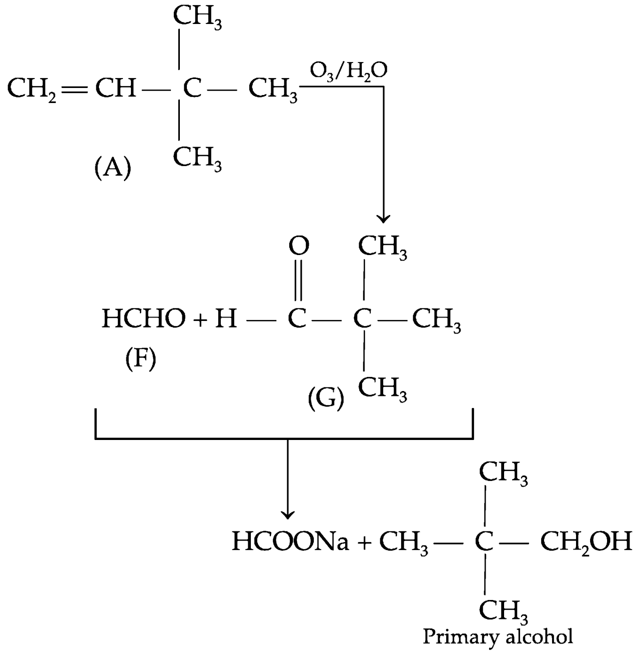
Identify A to G. **(IIT, 2003)**

Solution. Formation of $C_6H_{13}Cl$ from C_6H_{12} indicates one C = C bond, at which HCl is added. So, we have :





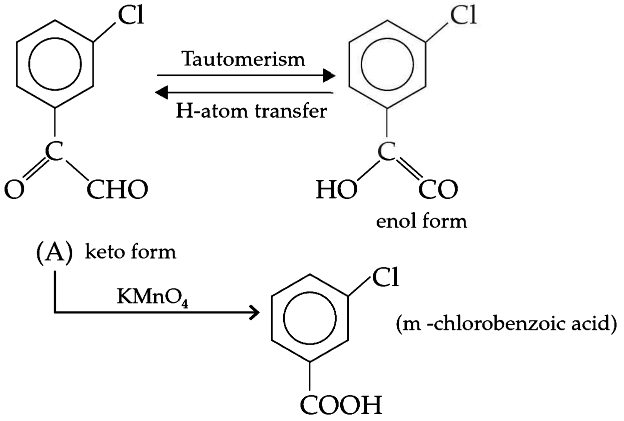




F and G donot give iodoform test because these donot contain $CH_3\overset{|}{C}=O$ group.

EXAMPLE 76. *A compound A of molecular formula $C_9H_7O_2Cl$ exists in ketoform and predominantly in enolic form 'B'. On oxidation with $KMnO_4$, A gives m-chlorobenzoic acid. Identify A and B.* **(IIT, 2003)**

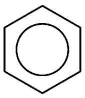
SOLUTION. Keto form contains >C = O group, while enol form contains –OH group. So, the tautomeric forms of $C_9H_7O_2Cl$ can be written as :



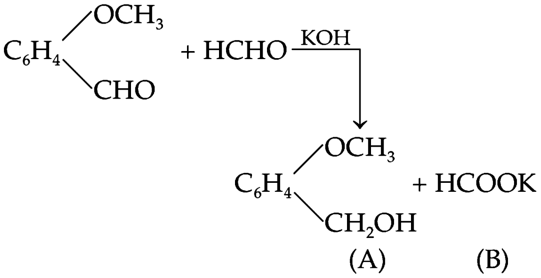
EXAMPLE 77. *Complete the following*

(*a*) 
$C_6H_4\left\langle\begin{matrix}OCH_3\\CHO\end{matrix}\right. + HCHO \xrightarrow{KOH} A + B$

(*b*) $C_6H_5\,CONH_2 \xrightarrow{P_2O_5} A \xrightarrow{H^+, H_2O, \Delta} B$

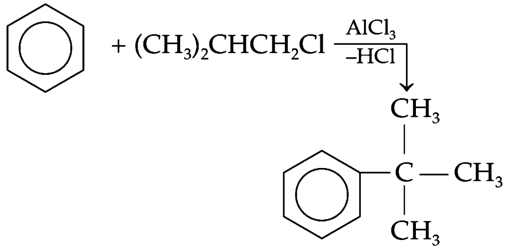
(*c*)  $+ (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3} A$ **(IIT, 1992)**

SOLUTION. (*a*)

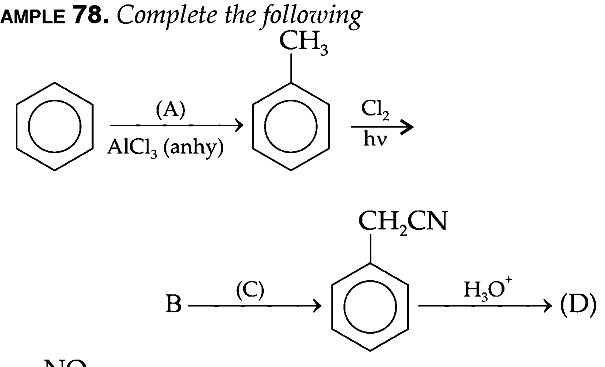


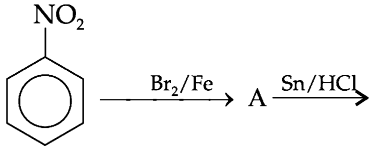
(b) $C_6H_5CONH_2 \xrightarrow[-H_2O]{P_2O_5} C_6H_5CN \xrightarrow[\text{Hydrolysis}]{H^+, H_2O, \Delta}$

$C_6H_5COOH + NH_3$

(c) 

EXAMPLE 78. *Complete the following*

(*a*) 

(*b*) 

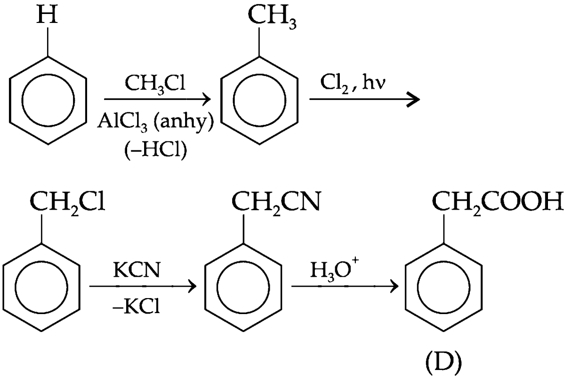
$B \xrightarrow[HCl,\ 0-5°C]{NaNO_2} C \xrightarrow{Cu_2Cl_2} D$

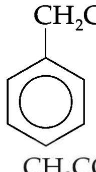
(*c*) $CH_3CH_2CH_2OH \xrightarrow{P + Br_2} A \xrightarrow{KOH(alc.)}$

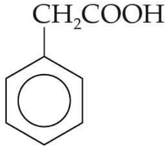
$B \xrightarrow{HBr} C \xrightarrow[\Delta]{NH_3(g)} D$

(*d*) $C_6H_5COOC_6H_5 \xrightarrow{\text{mononitration}} A$ **(IIT, 1993)**

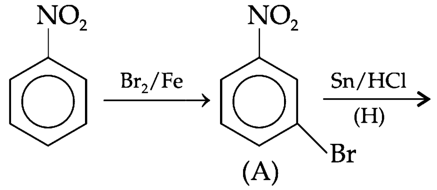
SOLUTION.

(*a*) 

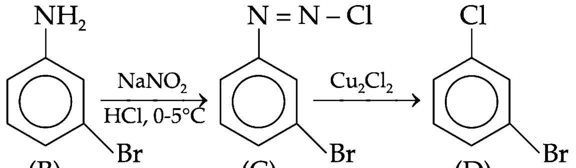
So A = CH_3Cl, B =  ,

(C) = KCN, D = 

(*b*) NO_2, group is meta- directing. So,



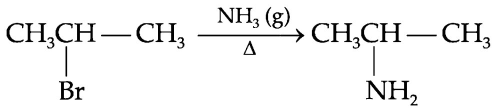
(A)



(B) (C) (D)

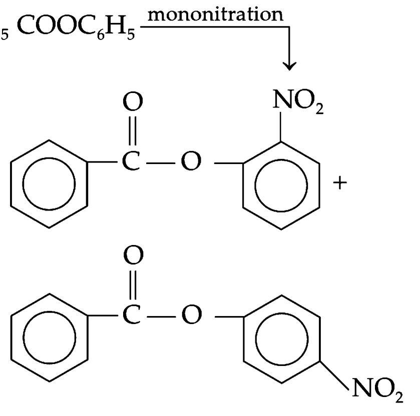
(*c*) $CH_3CH_2CH_2OH \xrightarrow{P + Br_2}$

$$\underset{(A)}{CH_3CH_2CH_2Br} \xrightarrow[-HBr]{Alc.\ KOH} \underset{(B)}{CH_3CH = CH_2} \xrightarrow[M.\ rule]{HBr}$$



$$\underset{(C)}{CH_3\underset{\underset{Br}{|}}{CH}—CH_3} \xrightarrow[\Delta]{NH_3\ (g)} \underset{(D)}{CH_3\underset{\underset{NH_2}{|}}{CH}—CH_3}$$

(*d*) $C_6H_5\ COOC_6H_5 \xrightarrow{mononitration}$



EXAMPLE 79. *Predict the major product in the following reactions.*

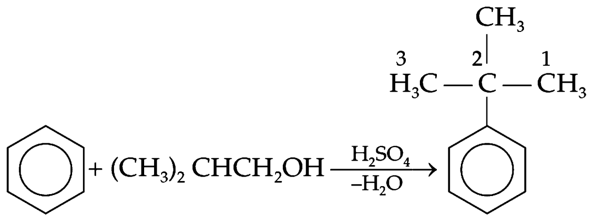
(*a*) $C_6H_6 + (CH_3)_2\ CHCH_2OH \xrightarrow{H_2SO_4}$

(*b*) $C_6H_5CH_2COOCH_3 \xrightarrow[2.\ 2H^+]{1.\ CH_3Mg\ Br\ (excess)}$

(*c*) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1.\ Br_2,\ heat,\ light}$ **(ITT, 1994)**

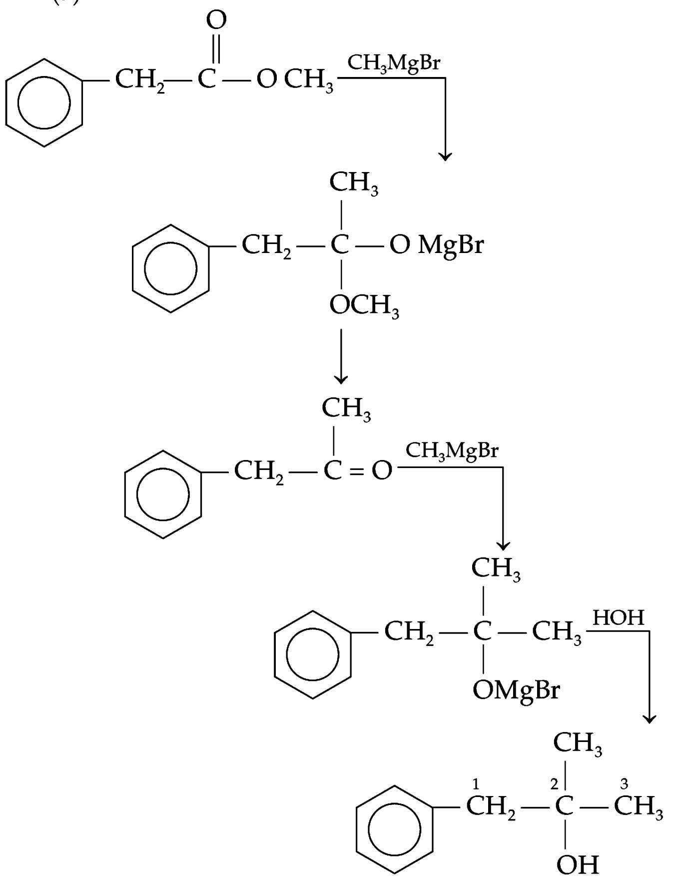
SOLUTION.

(*a*)



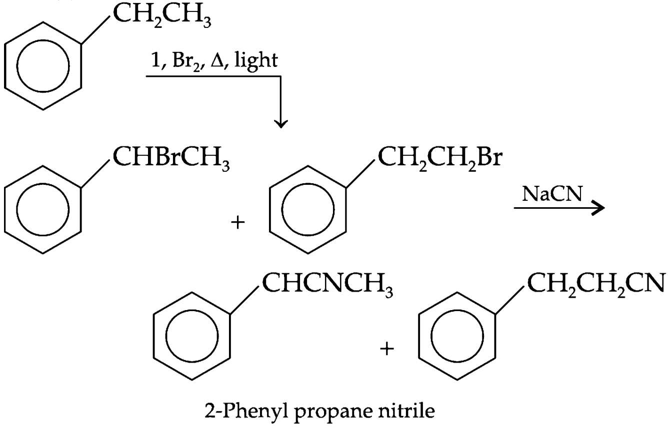
2 - Methyl-2-phenylpropane

(*b*)



(2-Methyl -1-phenyl - propan-2-ol.)

(*c*)



2-Phenyl propane nitrile

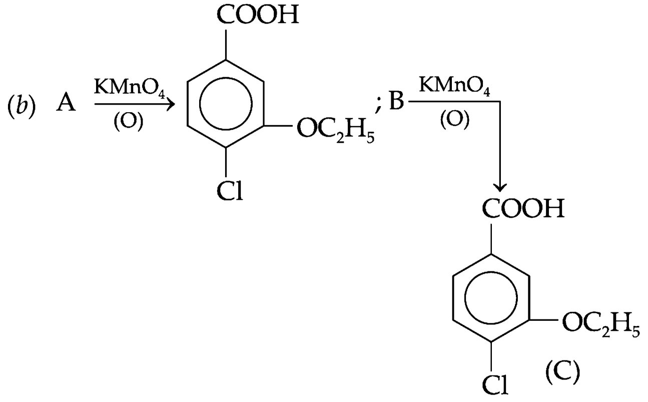
(Major) (Minor)

EXAMPLE 80. *Two isomeric compounds A and B have the same formula $C_{11}H_{13}OCl$. Both are unsaturated, yield the same compound (C) on catalytic hydrogenation and produce 4-chloro-*

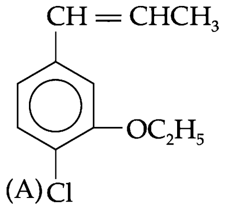
3-ethoxybenzoic acid on vigorous oxidation. (A) exists in geometrical isomers, (D) and (E) but not (B). Give structures of (A) to (E) with proper reasoning. **(Roorkee, 1994)**

SOLUTION. Both isomers A and B have the formula $C_{11}H_{13}OCl$ and are unsaturated. Hence :

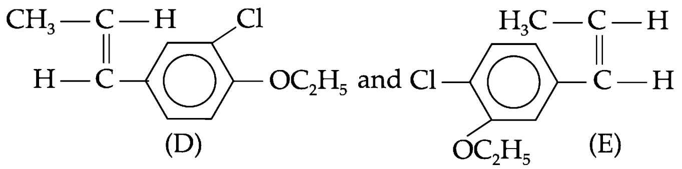
(*a*) $A \xrightarrow[\text{hydrogenation}]{\text{Catalytic}} C \; ; \quad B \xrightarrow[\text{hydrogenation}]{\text{Catalytic}} C$



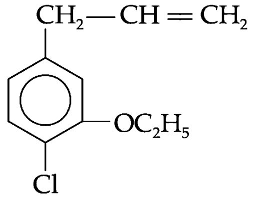
Since the side chain at carbon no. 1 is oxidised to —COOH, the compound (A) will be



which has following two isomers.



So, (B) will be simply



EXAMPLE 81. *Complete the following.*

$$CH_3CH_2COOH \xrightarrow{P + Br_2} A. \xrightarrow[2.\ H^+]{1.\ Alc.\ KOH\ (excess)} B$$

(IIT, 1995)

SOLUTION.

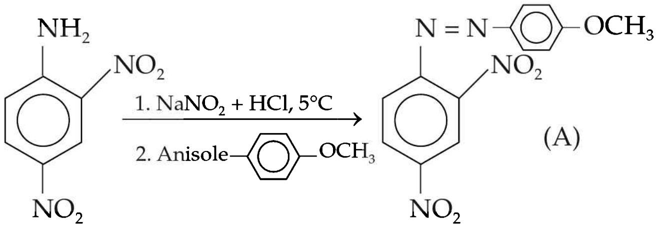
$$CH_3CH_2COOH \xrightarrow{P + Br_2} \underset{(A)}{CH_3CHBrCOBr} \xrightarrow[2.\ H^+]{1.\ KOH\ (alc)} \underset{(B)}{CH_2 = CH.COOH} + HBr$$

EXAMPLE 82. *Complete the following.*

$$2,\ 4\text{-}Dinitroaniline \xrightarrow[\text{at } 5°\ C,\ anisole]{NaNO_2 \text{ and } HCl} A$$

(IIT, 1995)

SOLUTION.



EXAMPLE 83. *Complete the following.*

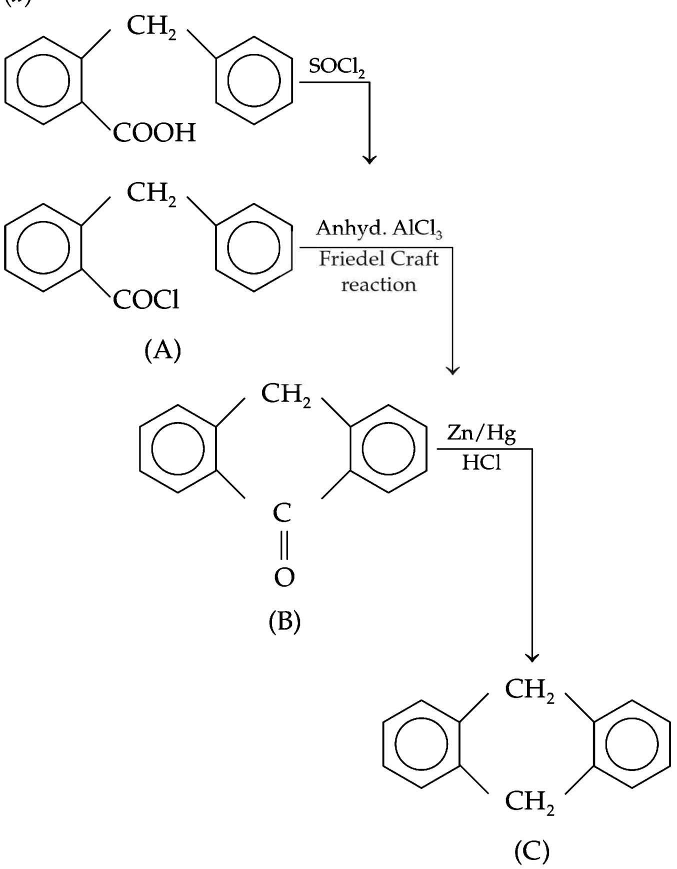
(*a*) $o - HOOC - C_6H_4 - CH_2 - C_6H_5 \xrightarrow{SOCl_2} A \xrightarrow{Anhyd.\ AlCl_3} B \xrightarrow[HCl]{Zn/Hg} C$

(*b*) $C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH \text{ and heat}]{NaOC_2H_5 \text{ in absolute}} A$

(ITT, 1995)

SOLUTION.

(*a*)

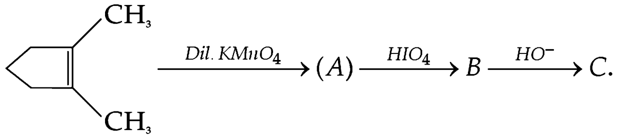


(*b*) $C_6H_5CHO + CH_3COOC_2H_5 \xrightarrow[C_2H_5OH \text{ and heat}]{NaOC_2H_5 \text{ in absolute}}$

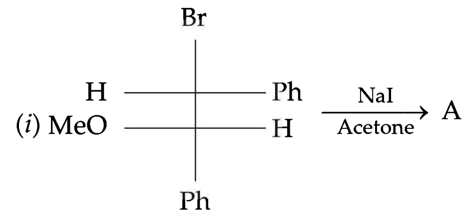
(Claisen condensation)

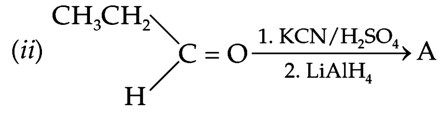
$$\underset{(A)}{C_6H_5CH = CHCOOC_2H_5}$$

EXAMPLE 84. (*a*) Suggest appropriate structures of the missing compounds. The number of carbon atoms remain same throughout the reactions



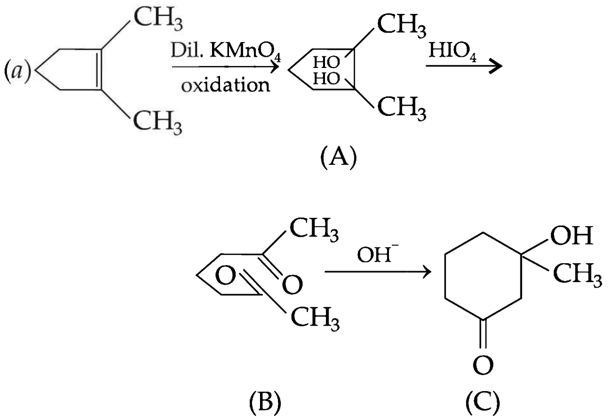
(*b*) Predict the structure of the product in the following reactions



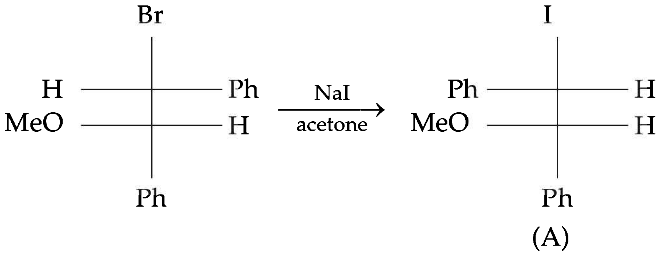


(ITT, 1996)

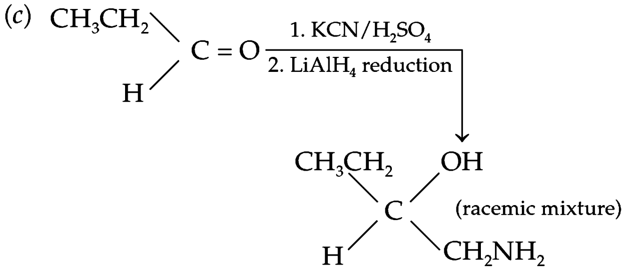
SOLUTION.



(*b*)



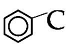
The product (A) is formed because enantiomer of original compound is formed involving SN^2 mechanism.

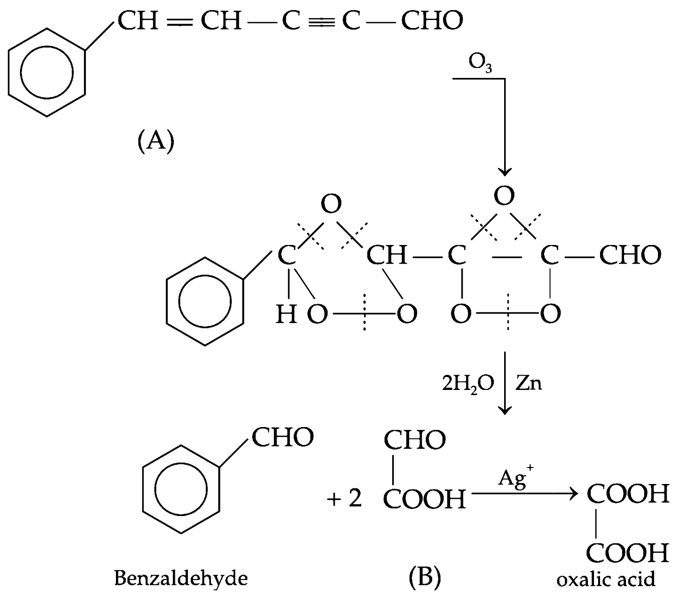


(A)

EXAMPLE 85. *An aldehyde (A) ($C_{11}H_8O$) which does not undergo self aldol condensation, gives benzaldehyde and two mol of (B) on ozonolysis. Compound (B), on oxidation with silver ion, gives oxalic acid. Identify the compounds A and B.*

(IIT, 1998)

SOLUTION. Since the compound does not undergo self aldol condensation, the compound will be $CH=CH—C\equiv C—CHO$ because it gives benzaldehyde on ozonolysis.

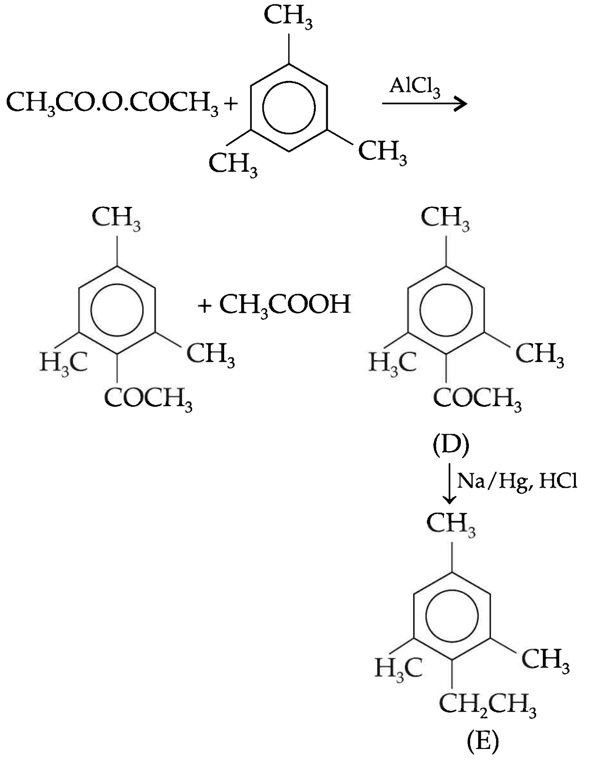


EXAMPLE 86. *An organic acid (A) on heating with $AlPO_4$ at 700°C forms (B). Compound (B) also reacts with (A) to give (C). Compound (C) on reaction with 1, 3, 5- trimethyl benzene in presence of $AlCl_3$ gives a ketone (D) and CH_3COOH. (D) on treatment with Na/Hg/HCl gives an aromatic hydrocarbon (E). Give structures of (A) to (E) with proper reasoning.*

(Roorkee, 1998)

SOLUTION. When an organic acid is heated with $AlPO_4$, a ketene is formed. Ketene reacts with organic acid to give a ketone. So, A is expected to be acetic acid.

$$\underset{(A)}{CH_3COOH} \xrightarrow{AlPO_4,\,700°C} \underset{\substack{(B)\\ \text{Ketene}}}{CH_2=C=O} \xrightarrow{CH_3COOH} \underset{(C)}{CH_3CO.O.COCH_3}$$

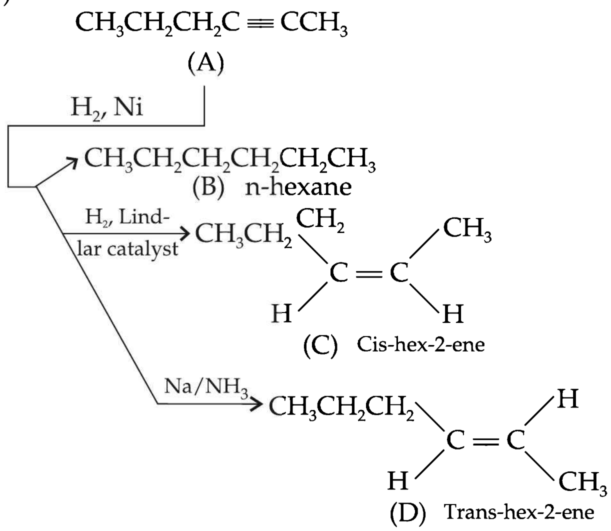


EXAMPLE 87. *Hydrocarbon (A), C_6H_{10} on treatment with H_2/Ni, H_2/Lindlar's catalyst and Na/liquid ammonia forms three different reduction products (B), (C) and (D) respectively. (A) does not form any salt with ammoniacal $AgNO_3$ solution but forms a salt (E) on heating with $NaNH_2$ in an inert solvent. Compound E reacts with CH_3I to give (F). Compound (D) on oxidative ozonolysis gives n-butanoic acid along with other product. Give structures of (A) to (F) with proper reasoning.*

(Roorkee, 1998)

SOLUTION. The formula C_6H_{10} corresponds to the general formula of an alkyne. Also, (A) does not form salt with ammoniacal $AgNO_3$. So, ≡ C does not contain ≡ CH. So, alkyne (A) is, $CH_3CH_2CH_2C \equiv CCH_3$. Its reactions will be:

(*i*)



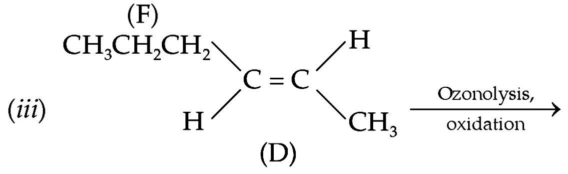
(*ii*) (A) gives (E) with $NaNH_2$ which *i.e.*, E reacts with CH_3I to form F. Thus :

$$CH_3CH_2CH_2C \equiv CCH_3 \xrightarrow[\Delta]{NaNH_2,}$$

$$CH_3CH_2CH_2CH_2C \equiv CNa \xrightarrow{CH_3I}$$

$$\underset{(F)}{CH_3CH_2CH_2CH_2C \equiv CCH_3}$$

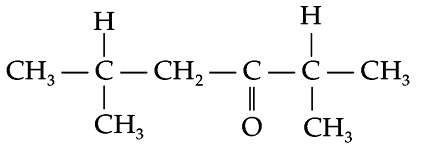
(*iii*)



$$\underset{n\text{-Butanoic acid}}{CH_3CH_2CH_2COOH} \quad + \quad \underset{\text{Ethanoic acid}}{CH_3COOH}$$

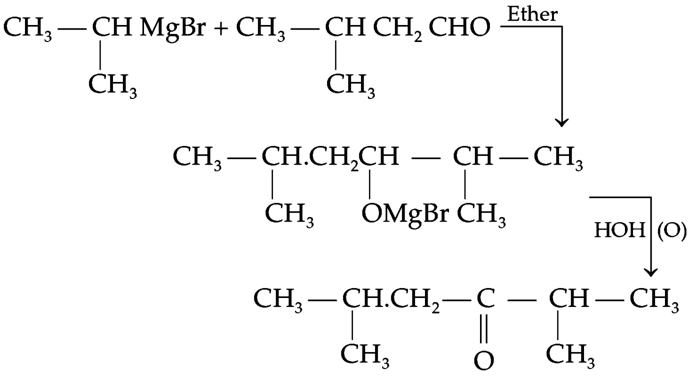
EXAMPLE 88. *Compounds (A) and (B) on reaction in ether medium and subsequent acidification and oxidation gave 2, 5-dimethyl-3-hexanone. What are (A) and (B).* **(Roorkee, 1998)**

SOLUTION. 2, 5-dimethyl-3-hexanone is



$$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2-\underset{O}{\overset{\|}{C}}-\overset{H}{\underset{CH_3}{C}}-CH_3$$

Since this compound is obtained from (A) and (B) compounds in ether medium and subsequent acidification and oxidation, (A) or (B) can be as follows :



2, 5 - Dimethyl -3-hexanone.

EXAMPLE 89. *A chlorocompound (A) showed the following properties.*

(*i*) *Decolorised bromine in CCl_4*
(*ii*) *Absorbed hydrogen catalytically*
(*iii*) *Gave a precipitate with ammoniacal cuprous chloride*
(*iv*) *When vaporised 1.49g of (A) gave 448 mL of vapours at STP. Identify (A) and write down the equations of reactions.* **(Roorkee, 1991)**

SOLUTION. (*i*) Mol. wt. of (A)

$$= \frac{\text{wt.}}{\text{volume at STP}} \times 22400$$

$$= \frac{1.49}{448} \times 22400 = \mathbf{74.5}$$

(*ii*) Since the compound decolorises Br_2 in CCl_4 and absorbs H_2 catalytically, it will be an unsaturated compound having double or triple bond.
Also, it gives a ppt. with ammoniacal Cu_2Cl_2. So, it will have a triple bond at the corner.

(*iii*) Since the compound has a ≡ CH at the corner, a Cl– atom, and mol. wt. 74.5, so, we have :

$$RCl\,C \equiv CH = 74.5$$

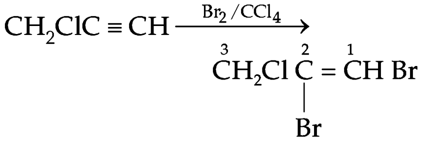
$$R + 35.5 + 12 + 12 + 1 = 74.5\,;$$

$$R + 60.5 = 74.5\,;\ R = 14 \text{ or R is } CH_2$$

∴ Compound is $\mathbf{CH_2Cl.\ C \equiv CH.}$

Reactions :

(*i*)



$$CH_2ClC \equiv CH \xrightarrow{Br_2/CCl_4} \overset{3}{C}H_2Cl\,\underset{Br}{\overset{2}{C}} = \overset{1}{C}H\,Br$$

1, 2 Dibromo-3-chloroprop-1-ene

(*ii*) $$CH_2ClC \equiv CH \xrightarrow{H_2} \overset{1}{C}H_2Cl\overset{2}{C}H_2 - \overset{3}{C}H_3$$

1-chloropropane

(*iii*) $$2CH_2ClC \equiv CH \xrightarrow[Cu_2Cl_2\ i.e.,\ Cu_2O]{\text{Ammoniacal}} 2CH_2ClC \equiv CCu + H_2O$$

Red ppt.

EXAMPLE 90. *A hydrocarbon (A) [C = 90.56%, vapour density = 53] was subjected to vigorous oxidation to give a dibasic acid (B). 0.10g of (B) required 24.1mL of 0.05 N NaOH for complete neutralisation. When (B) was heated strongly with sodalime, it gave benzene. Nitration of benzene gave a single* *mono nitroderivative. Identify (A) and (B) with proper reasoning and also give their structure.* **(Roorkee, 1991)**

SOLUTION. (*i*) To find empirical formula.

Element	At. wt.	% age	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	12	90.56	$\frac{90.56}{12} = 7.55$	$\frac{7.55}{7.55} = 1$	1 × 4 = 4
H	1	100 – 90.56 = 9.44	$\frac{9.44}{1} = 9.44$	$\frac{9.44}{7.55} = 1.25$	1.25 × 4 = 5

$\therefore$ E.F. $= C_4H_5$;

E.F. wt. = (4 × 12) + (5 × 1) = 53

Given mol. wt. = 2 × V.D. = 2 × 53 = 106

$$\therefore \text{Molecular formula} = \frac{\text{Mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.}$$

$$= \frac{106}{53} \times C_4H_5 = C_8H_{10}$$

(*ii*) 24.1mL of 0.05 N dibasic acid = 0.1 g

1000mL of 1N dibasic acid

$$= \frac{0.1}{24.1 \times 0.05} \times 1000 = 82.98 \simeq 83$$

$\therefore$ Eq. wt. of dibasic acid,

$R(COOH)_2 = 83$ Or Mol. wt. of

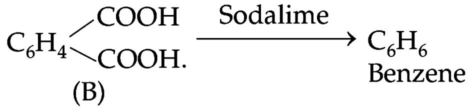
$R(COOH)_2 = 2 \times 83 = 166.$

$\therefore$ Mol. wt. of $R = 166 - 2(12 + 16 + 16 + 1) = 76$

Also, mol. wt. of $C_6H_4 = (6 \times 12) + (4 \times 1) = 76$

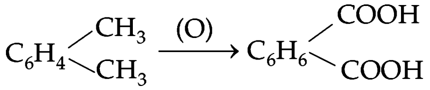
$\therefore R(COOH)_2 = C_6H_4\begin{smallmatrix}\diagup COOH\\ \diagdown COOH\end{smallmatrix}$ and hance

$(B) = C_6H_4\begin{smallmatrix}\diagup COOH\\ \diagdown COOH.\end{smallmatrix}$

(*iii*) 

$$C_6H_4\begin{smallmatrix}\diagup COOH\\ \diagdown COOH.\end{smallmatrix} \xrightarrow{\text{Sodalime}} \underset{\text{Benzene}}{C_6H_6}$$

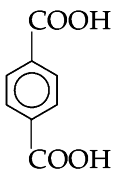
(B)

(*iv*) 

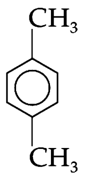
$$C_6H_4\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix} \xrightarrow{(O)} C_6H_6\begin{smallmatrix}\diagup COOH\\ \diagdown COOH\end{smallmatrix}$$

(A) (B)

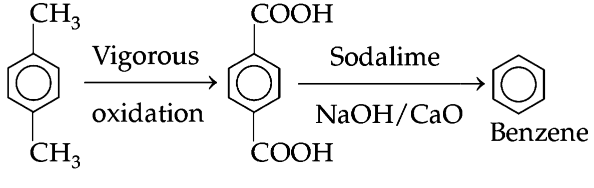
Since (B) shows mononitroderivative, so, (B) is



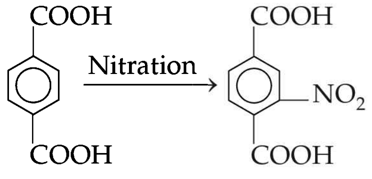
while (A) is



Reactions. (*v*)



(A) p-xylene **(B)** Terephthalic acid

(*v*) 

(B)

EXAMPLE 91. *An ester has molecular weight 102. On aqueous hydrolysis, it produces a monobasic acid and an alcohol. If 0.185g of the acid produced, completely neutralises 25mL of 0.1N NaOH, find out the structural formula of the produced alcohol, acid and the ester with proper reasoning.* **(Roorkee, 1990)**

SOLUTION. Mol. wt. of ester RCOOR′ = 102

Thus $R + 12 + 16 + 16 + R' = 102$;

$R + R' = 102 - 44 = 58$

$RCOOR' + HOH \longrightarrow R\,COOH + R'\,OH$

25mL of 0.1N or 0.1M NaOH neutralise acid

RCOOH = 0.185g

1000mL of 1M NaOH neutralise

$$RCOOH = \frac{0.185}{25 \times 0.1} \times 1000 = 74$$

$\therefore$ Mol. wt. of R in

$RCOOH = R + 12 + 16 + 16 + 1$;

$74 = R + 45$;

$\therefore R = 74 - 45 = 29$

But $R + R' = 58$; $29 + R' = 58$;

$R' = 58 - 29 = 29$

$\therefore R = R'$; $C_n H_{2n+1} = R = R' = 29$;

$12n + 1(2n + 1) = 29$;

$14n = 29 - 1 = 28$; $n = 2.$

Hence $R = R' = C_nH_{2n+1} = \mathbf{C_2H_5}$

$\therefore$ Ester $= C_2H_5COOC_2H_5$

Reaction :

$$C_2H_5COOC_2H_5 + HOH \longrightarrow \underset{\text{Propanoic acid}}{C_2H_5COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

EXAMPLE 92. *An organic compound (A) of mol. wt. 140.5 has 68.32% C and 6.4% H and 25.26% Cl. Hydrolysis of (A) with dilute acid gives compound (B), $C_8H_{10}O$. Compound (B) can be oxidised under mild conditions to compound (C), C_8H_8O. Compound (C) forms a phenyl hydrazone (D) with $PhNHNH_2$ and gives positive iodoform test. Deduce the structures of (A) to (D) with proper reasoning.* **(Roorkee, 1990)**

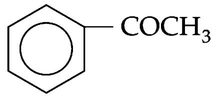
SOLUTION. (*i*) To Find empirical formula of (A)

Element	At. wt.	% age	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	12	68.32	$\frac{68.32}{12} = 5.59$	$\frac{5.59}{0.71} \simeq 8$	8
H	1	6.4	$\frac{6.4}{1} = 6.4$	$\frac{6.4}{0.71} \simeq 9$	9
Cl	35.5	25.26	$\frac{25.26}{35.5} = 0.71$	$\frac{0.71}{0.71} = 1$	1

$$\begin{aligned}\therefore \quad \text{E.F.} &= C_8H_9Cl,\ \text{E.F. wt.}\\ &= (8 \times 12) + (9 \times 1) + (35.5 \times 1)\\ &= 140.5\\ \text{Given mol. wt.} &= 140.5\\ \therefore \text{Molecular formula} &= \frac{\text{Mol. wt.}}{\text{E.F. wt.}} \times \text{E.F.}\\ &= \frac{140.5}{140.5} \times C_8H_9Cl = C_8H_9Cl.\end{aligned}$$

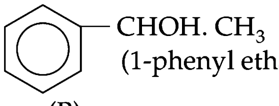
(*ii*) $\underset{\textbf{(A)}}{C_8H_9Cl} \xrightarrow{HOH} \underset{\textbf{(B)}}{C_8H_9OH} \xrightarrow{\text{Oxidation}} \underset{\textbf{(C)}}{C_8H_8O}$

Since (C) reacts with phenyl hydrazine, it will be a carbonyl compound. Since (C) gives a positive iodoform test, it will have $-CH_3CO$ group. Hence (C) is



(C) Acetophenone

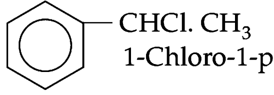
(*iii*) Since secondary alcohol >CHOH group on oxidation gives ketone >C = O, so (B) will be



(1-phenyl ethanol)

(B)

(*iv*) Since (B) is obtained by the hydrolysis of (A), so (A) will be

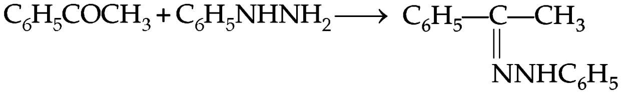


1-Chloro-1-phenyl ethanol.

(A)

Possible reactions.

$$\underset{(A)}{C_6H_5CHClCH_3} \xrightarrow[H^+]{H_2O,} \underset{(B)}{C_6H_5CHOH.CH_3} \xrightarrow{(O)} \underset{(C)}{C_6H_5COCH_3}$$



$$C_6H_5COCH_3 + C_6H_5NHNH_2 \longrightarrow C_6H_5-\underset{\underset{NNHC_6H_5}{\|}}{C}-CH_3$$

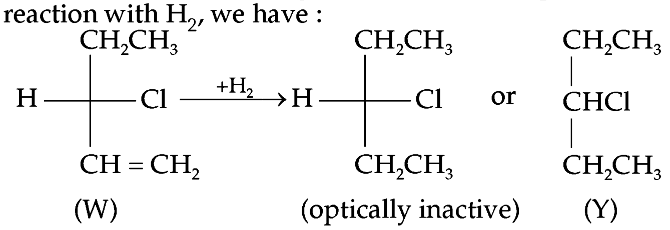
(Phenyl hydrazone)

$$C_6H_5COCH_3 + 4NaOH + 3I_2 \longrightarrow CHI_3 + C_6H_5COONa + 3NaI + 3H_2O$$

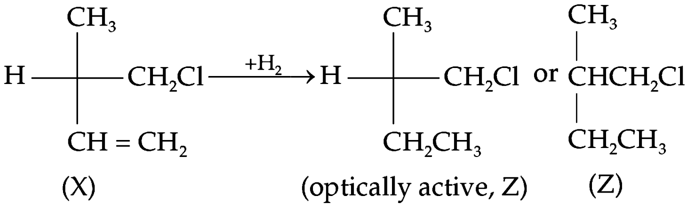
Iodoform (Yellow ppt.)

EXAMPLE 93. *(W) and (X) are optically active isomers of C_5H_9Cl. (W) on treatment with one mol of H_2 is converted to an optically inactive compound (Y), but (X) gives an optically active compound (Z) under the same conditions. Give structure of (Y) and configurations of (W), (X) and Z in Fischer projections.* **(Roorkee, 2000)**

SOLUTION. Under the given conditions in question for reaction with H_2, we have :



$$\underset{(W)}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH=CH_2}{|}}{C}}-Cl} \xrightarrow{+H_2} \underset{\text{(optically inactive)}}{H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-Cl} \text{ or } \underset{(Y)}{\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{CHCl}}}$$



$$\underset{(X)}{H-\overset{\overset{CH_3}{|}}{\underset{\underset{CH=CH_2}{|}}{C}}-CH_2Cl} \xrightarrow{+H_2} \underset{\text{(optically active, Z)}}{H-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-CH_2Cl} \text{ or } \underset{(Z)}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{CHCH_2Cl}}}$$

EXAMPLE 94. $(A) \xrightarrow[250°C]{Al_2O_3} B \xrightarrow[(ii)\ AgOH]{(i)\ HI} (C) \xrightarrow[150°C]{Al_2O_3,} (B) \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6,} (A).$

In the above reactions, compounds (A) and (C) are isomers. (B) has a formula of C_5H_{10}, which can also be obtained from the product of the reactions of CH_3CH_2MgBr and $(CH_3)_2CO$. Give structures of (A), (B) and (C). **(Roorkee, 2000)**

SOLUTION. (B) is C_5H_{10}. So, the data suggests :

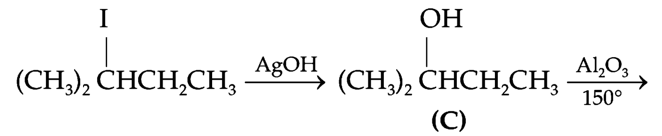
$$\underset{(A)}{C_5H_{11}OH} \xrightarrow[250°]{Al_2O_3} \underset{(B)}{\underset{(-H_2O)}{}\ C_5H_{10}} \xrightarrow[AgOH]{HI} \underset{(C)}{C_5H_{11}OH}$$

$$\xrightarrow[150°]{Al_2O_3,} \underset{(B)}{C_5H_{10}} \xrightarrow[H_2O_2,\ OH^-]{B_2H_6,} \underset{(A)}{C_5H_{11}OH}$$

$-H_2O$

The above reactions are possible if (A) is $(CH_3)_2 CH.CHOH.CH_3$. Thus :

(*i*) $(CH_3)_2\,CH.CHOH\,CH_3 \xrightarrow[250°]{Al_2O_3} \underset{\textbf{(B)}}{(CH_3)_2\,CH = CHCH_3} \xrightarrow{HI}$

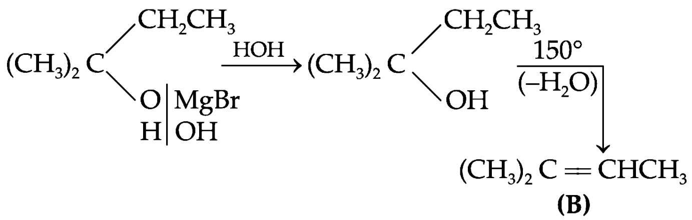


$$(CH_3)_2\overset{\overset{I}{|}}{C}HCH_2CH_3 \xrightarrow{AgOH} \underset{\textbf{(C)}}{(CH_3)_2\overset{\overset{OH}{|}}{C}HCH_2CH_3} \xrightarrow[150°]{Al_2O_3}$$

$$\underset{\textbf{(B)}}{(CH_3)_2\,CH = CHCH_3} \xrightarrow[OH]{B_2H_6,\ H_2O_2} \underset{\textbf{(A)}}{(CH_3)_2\,CHCHOHCH_3}$$

(*ii*)

$$(CH_3)_2\,C = O + CH_3CH_2MgBr \longrightarrow$$



EXAMPLE 95. *Give structures of (W). (X), (Y) and (Z) in the following reactions.*

$$H_2C = CH—CH_2OH \xrightarrow[(CH_2Cl_2)]{CrO_3.2C_5H_5N} (W)$$

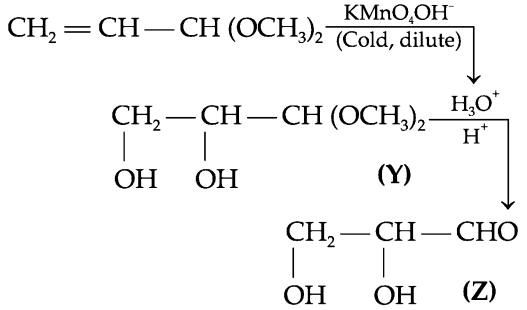
$$\xrightarrow{CH_3OH,\ H^+} (X)\ C_5H_{10}O_2 \xrightarrow[\text{Cold, dilute}]{KMnO_4,\ OH^-} (Y)\ C_5H_{12}O_4$$

$$\xrightarrow[H_2O]{H_3O^+,} (Z)\ C_3H_6O_3.$$

(Roorkee, 2000)

SOLUTION. $CH_2 = CH—CH_2OH \xrightarrow[(CH_2Cl_2)]{CrO_3.\ 2C_5H_5N}$

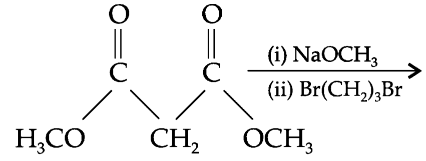
$$\underset{\textbf{(W)}}{CH_2 = CH\ CHO} \xrightarrow{CH_3OH,\ H^+}$$



$$CH_2{=}CH{-}CH(OCH_3)_2 \xrightarrow[\text{(Cold, dilute)}]{KMnO_4, OH^-} \underset{OH\quad OH}{CH_2{-}CH{-}CH(OCH_3)_2}\ (Y) \xrightarrow[H^+]{H_3O^+} \underset{OH\quad OH}{CH_2{-}CH{-}CHO}\ (Z)$$

EXAMPLE 96. What are (A) to (L) in the scheme of reactions given below ?

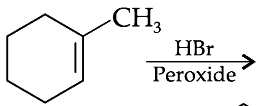
(*a*)



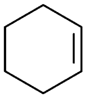
$(A) \xrightarrow{NaOCH_3} (B) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) NaOH}} (C) \xrightarrow{-CO_2}$

(D) (cycloalkane carboxylic acid)

(*b*)



(E); (c)



$\xrightarrow[(CH_2Cl_2)]{Br_2} (F) \xrightarrow[\text{Acetic acid}]{Zn}$

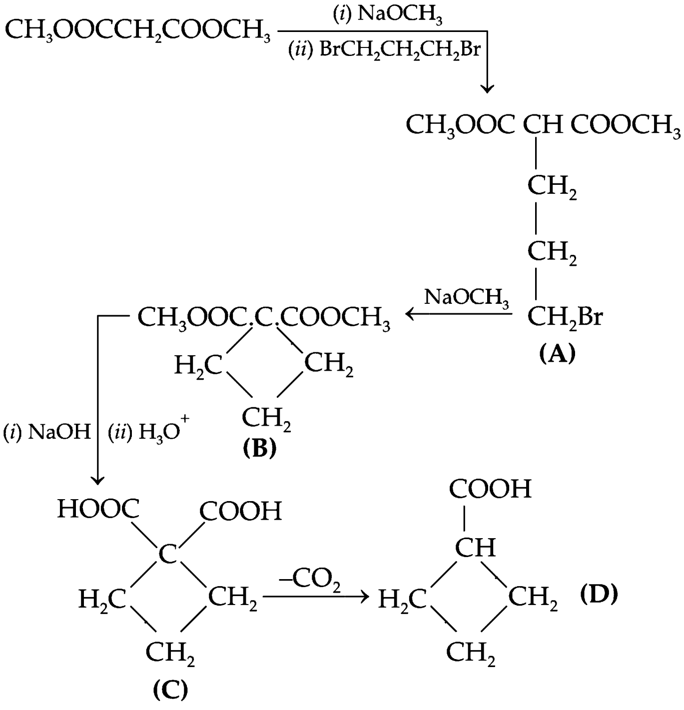
$(G)C_6H_{10} \xrightarrow[(ii)\ H_2O_2;OH^-]{(i)\ (Br_3)_2} (H)$

(*d*) $(J) \xleftarrow[H_2O]{HCrO_4} (I) \xrightarrow[\text{(Pyridine)}]{CrO_3} CH_3CHO$

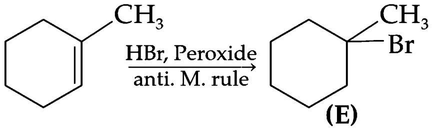
(*e*) Acetone (2 mol) $\xrightarrow{OH^-} (K) \xrightarrow[\textit{Heat}]{NaHSO_4} (L)$

(Roorkee, 2000)

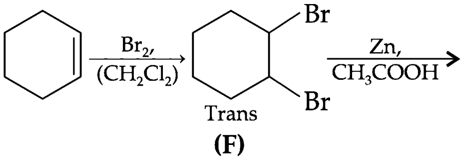
SOLUTION. (*a*)

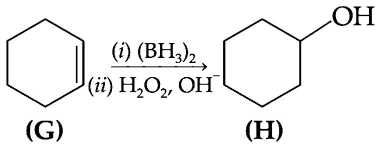


(*b*)



(*c*)





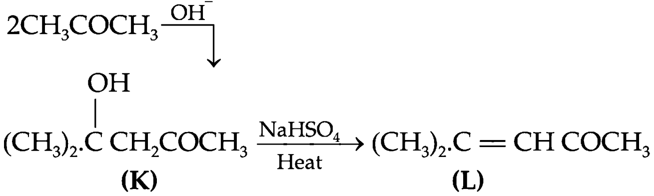
(*d*) $CH_3CH_2OH \xrightarrow[H_2O]{HCrO_4} CH_3COOH$

(I) (J)

$\downarrow CrO_3$, pyridine

CH_3CHO

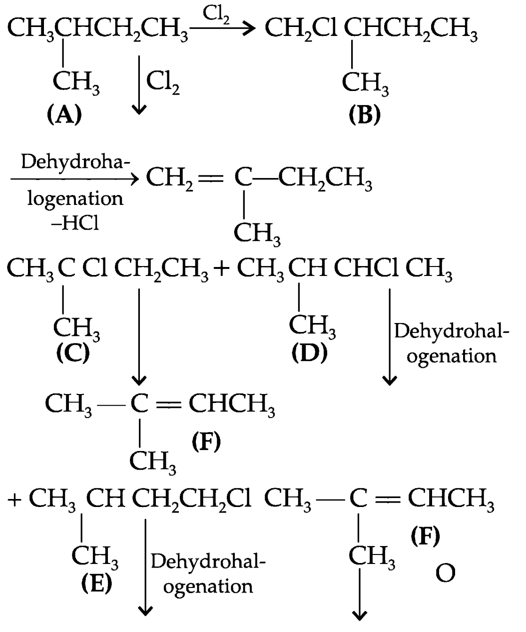
(*e*)



$$2CH_3COCH_3 \xrightarrow{OH^-} (CH_3)_2.\overset{OH}{C}\,CH_2COCH_3\ (K) \xrightarrow[\text{Heat}]{NaHSO_4} (CH_3)_2.C = CH\,COCH_3\ (L)$$

EXAMPLE 97. *An alkane (A), C_5H_{12} on chlorination at 300°C gives a mixture of four different monochlorinated derivatives, (B), (C), (D) and (E). Two of these derivatives give the same stable alkene (F) on dehydrohalogenation. On oxidation with hot alkaline $KMnO_4$, followed by acidification, (F) gives two products (G) and (H). Give the structures of (A) to (H) with proper reasoning.* **(Roorkee, 1995)**

SOLUTION. Alkane C_5H_{12} gives four different monochloroderivatives. So, alkane will be a branched chain alkane. So, it will be isopentane,



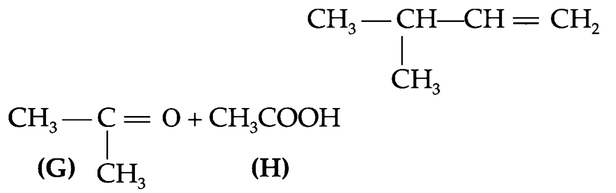
$$\underset{CH_3}{CH_3CHCH_2CH_3}\ (A) \xrightarrow{Cl_2} \underset{CH_3}{CH_2Cl\,CHCH_2CH_3}\ (B) \xrightarrow[\text{logenation } -HCl]{\text{Dehydroha-}} \underset{CH_3}{CH_2{=}C{-}CH_2CH_3}$$

$$\downarrow Cl_2$$

$$\underset{CH_3}{CH_3C\,Cl\,CH_2CH_3}\ (C) + \underset{CH_3}{CH_3CH\,CHCl\,CH_3}\ (D) \xrightarrow{\text{Dehydrohalogenation}}$$

$$\underset{CH_3}{CH_3{-}C{=}CHCH_3}\ (F)$$

$$+ \underset{CH_3}{CH_3\,CH\,CH_2CH_2Cl}\ (E) \xrightarrow{\text{Dehydrohalogenation}} \quad \underset{CH_3}{CH_3{-}C{=}CHCH_3}\ (F) \quad O$$



$CH_3—CH—CH = CH_2$ (CH_3 on CH)

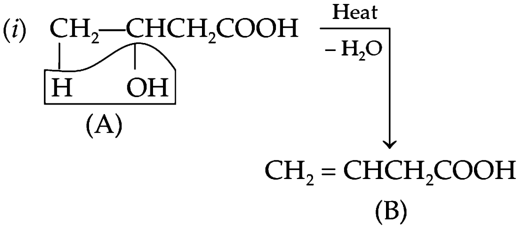
$CH_3—C = O + CH_3COOH$ (CH_3 on C)

(G) **(H)**

Example 98. *An acidic compound (A),$C_4H_8O_3$ loses its optical activity on strong heating yielding (B), $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$ which on reaction with $(CH_3)_2$ NH gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylates readily to give (F), C_3H_6O. The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning.* **(Roorkee, 1995)**

Solution. Since (A) *i.e.*, $C_4H_8O_3$ loses its optical activity on strong heating to give B *i.e.*, $C_4H_6O_2$, (A) is expected to be $CH_3CHOHCH_2COOH$ or $CH_3CH_2CHOHCOOH$. Also, since (B) is $C_4H_6O_2$ (formed) by loss of H_2O, (A) is β-hydroxy acid *i.e.*, $CH_3CHOH\ CH_2COOH$. It cannot be α-hydroxy acid because only β-hydroxy acid loses water on strong heating. Thus :

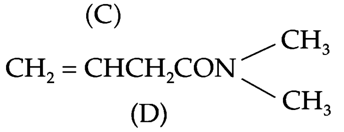
(*i*)



(*ii*) $CH_2 = CHCH_2COOH \xrightarrow{SOCl_2}$

$CH_2 = CHCH_2COCl \xrightarrow{(CH_3)_2NH}$

(C)



$CH_2 = CHCH_2CON(CH_3)_2$

(D)

(*iii*) $CH_3CHOHCH_2COOH \xrightarrow{[O]}$

(A)

$CH_3COCH_2COOH \xrightarrow[(-\ CO_2)]{\text{Decarboxylation}} CH_3COCH_3$

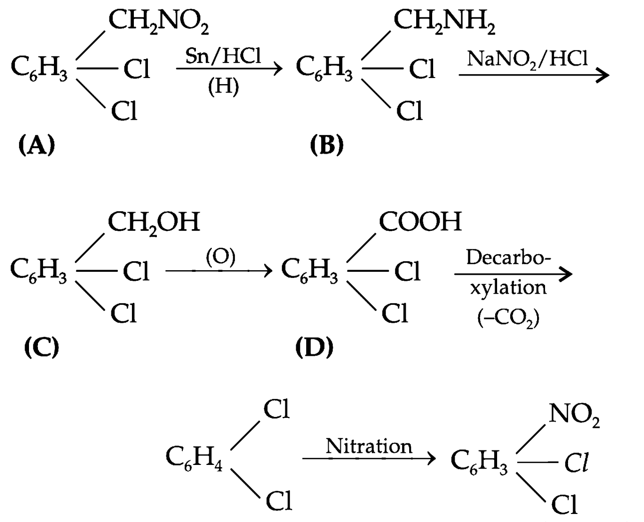
(E) **(F)**

$\xrightarrow[\text{Reduction}]{Zn/HCl} CH_3CH_2CH_3$

n-Propane, **(G)**

Example 99. *An aromatic compound (A), $C_7H_5NO_2Cl_2$ on reduction with Sn/HCl gives (B) which on reaction with $NaNO_2$/HCl gives (C). Compound (B) does not form a dye with β-naphthol. However, (C) gives red colour with ceric ammonium nitrate and on oxidation gives an acid (D) of equivalent weight 191. Decarboxylation of (D) gives (E) which forms a single mononitroderivative, (F) on nitration. Give structures of (A) to (F) with proper reasoning.* **(Roorkee, 1995)**

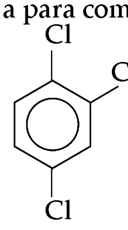
Solution. (A) contains NO_2 group which on reduction gives NH_2 group. The latter changes to OH with $NaNO_2$/ HCl. Thus, the data suggests :



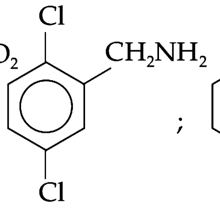
i.e., One product only.

(E) **(F)**

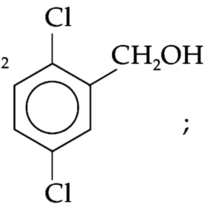
Since the compound (F) is only one product, so (E) will be a para compound. Hence :



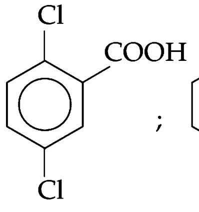
(A)



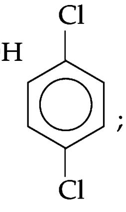
(B)



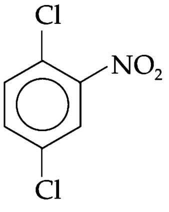
(C)



(D)



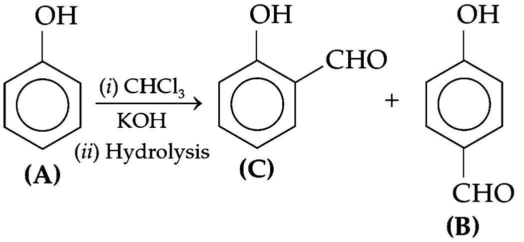
(E)



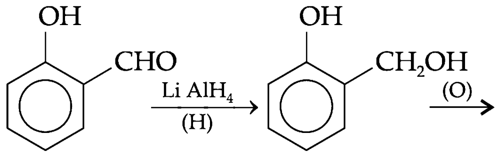
(F)

Example 100. *An organic compound (A) gives positive Libermann reaction and on treatment with $CHCl_3$/KOH followed by hydrolysis gives (B) and (C). Compound (B) gives colour with Schiff's reagent but not (C) which is steam volatile. (C) on treatment with $LiAlH_4$ gives (D) $C_7H_8O_2$ which on oxidation gives (E). Compound (E) reacts with $(CH_3CO)_2O/CH_3COOH$ to give a pain reliever (F). Give structures of (A) to (F) with proper reasoning.* **(Roorkee, 1995)**

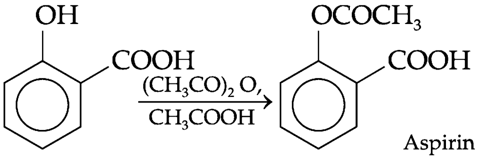
Solution. (*i*) Since (A) gives Libermann as well as Riemer-Tiemann reaction ($CHCl_3$/KOH), it can be a phenol. So:



(*ii*) (C) is steam volatile and does not reduce Schiff's reagent due to intramolecular hydrogen bonding. The reactions of (C) as given in data are:



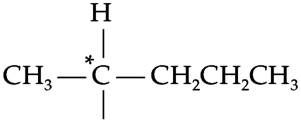
(C) **(D)**



(E) **(F)** Aspirin (a pain reliever)

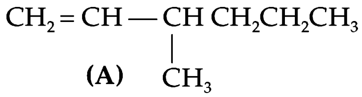
EXAMPLE 101. *There are six different alkenes (A), (B), (C), (D), (E) and (F). Each on addition of one mol of hydrogen gives (G) which is the lowest molecular weight hydrocarbon containing only one asymmetric carbon atom. None of the alkenes give acetone as a product on ozonolysis. Give structures of (A) to (F). Identify the alkene which is likely to give a ketone containing more than five carbon atoms on-treatment with a warm concentrated solution of alkaline $KMnO_4$. Show various configurations of (G) in Fischer projections.* **(Roorkee, 1992)**

SOLUTION. (*i*) An alkene on the addition of one mol of H_2 gives (G) which has lowest mol. wt. and contains one asymmetric carbon atom. So, it should be 3-methyl hexane which has one asymmetric C*-atom



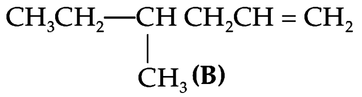
$$CH_3-\underset{\underset{\displaystyle CH_2CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{\overset{*}{C}}}-CH_2CH_2CH_3$$

(G). Six different alkenes from this compound will be the following which donot give acetone on ozonolysis.



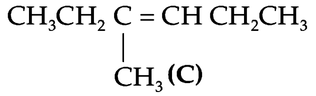
$$CH_2=CH-\underset{\underset{\displaystyle CH_3}{|}}{CH}\,CH_2CH_2CH_3$$

(A) 3-Methyl hex-1-ene



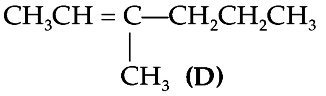
$$CH_3CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}\,CH_2CH=CH_2$$

(B) 4-Methyl hex-1-ene



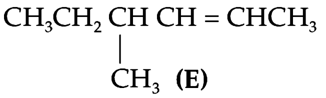
$$CH_3CH_2\,\underset{\underset{\displaystyle CH_3}{|}}{C}=CH\,CH_2CH_3$$

(C) 3-Methyl hex-3-ene



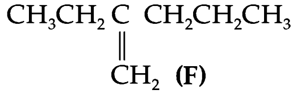
$$CH_3CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_2CH_2CH_3$$

(D) 3-Methyl hex-2-ene



$$CH_3CH_2\,\underset{\underset{\displaystyle CH_3}{|}}{CH}\,CH=CHCH_3$$

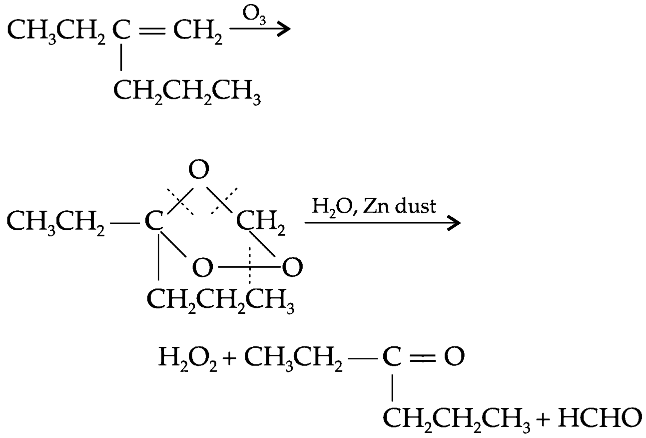
(E) 4-Methyl hex-2-ene



$$CH_3CH_2\,\underset{\underset{\displaystyle CH_2}{\|}}{C}\,CH_2CH_2CH_3$$

(F) 2-Ethyl pent-1-ene

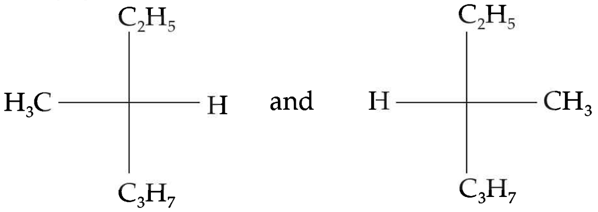
(*ii*) Alkene (F) on ozonolysis gives ketone with more than five C-atoms as shown below:



$$CH_3CH_2\,\underset{\underset{\displaystyle CH_2CH_2CH_3}{|}}{C}=CH_2\xrightarrow{O_3}$$

$$H_2O_2+CH_3CH_2-\underset{\underset{\displaystyle CH_2CH_2CH_3}{|}}{C}=O+HCHO$$

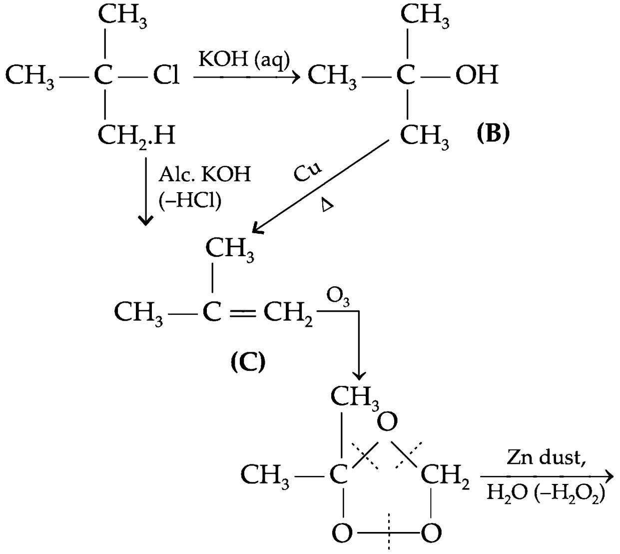
Various configurations of (G) in Fischer projections are :

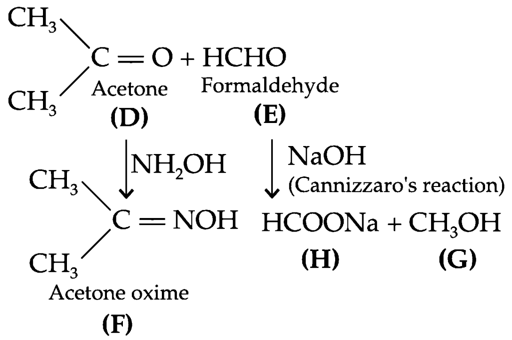


EXAMPLE 102. *An organic compound (A), C_4H_9Cl on reacting with aqueous KOH gives (B) and on reaction with alcoholic KOH gives (C) which is also formed on passing the vapours of (B) over heated copper. The compound (C) readily decolorises bromine water. Ozonolysis of (C) gives two compounds (D) and (E). Compound (D) reacts with NH_2OH to give (F) and the compound (E) reacts with NaOH to give an alcohol (G) and sodium salt (H) of an acid. (D) can also be prepared from propyne on treatment with water in presence of Hg^{2+} and H_2SO_4. Identify (A) to (H) with proper reasoning.* **(Roorkee, 1996)**

SOLUTION. Aqueous KOH forms an alcohol while alc. KOH on dehydrohalogenation forms an alkene. Such an alkene is also formed on passing vapours over heated copper. So, C_4H_9Cl is $(CH_3)_3CCl$.

Thus ; (**A**) = $(CH_3)_3$ CCl,





Note: Since (E) undergoes Cannizzaro's reaction, so (D) and (E) are formed from ozonolysis.

Formation of (D) from propyne:

$$CH_3{-}C\equiv CH \xrightarrow[H_2O]{Hg^{2+},\, H_2SO_4,} \underset{(D)}{CH_3COCH_3}$$

Example 103. *An aliphatic hydrocarbon A on treatment with sulphuric acid in the presence of $HgSO_4$ yields a liquid B with molecular formula C_2H_4O. B on oxidation with acidified potassium dichronate yields C which gives effervescence with sodium bicarbonate. C when treated with $SOCl_2$ gives D. WHen D reacts with ethanol, it gives a sweet smelling liquid E. E is also formed when C reacts with ethanol in presence of Conc. H_2SO_4. Identify A, B, C, D and E.* **(ISC, 2012)**

Solution. (*a*) C_2H_4O appears to be CH_3CHO (acetaldehyde) which is a liquid. It is formed from acetylene, $HC\equiv CH$:

$$HC{\equiv}CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_2 = CHOH \xrightarrow[\text{ment}]{\text{Rearrange-}} CH_3CHO$$

So, A is acetylene and B is acetaldehyde.

(*b*) Since C gives effervescence with $NaHCO_3$, it appears to be an acid. So:

$$\underset{(B)}{CH_3CHO} \xrightarrow[K_2Cr_2O_7,\, H^+]{[O]} \underset{(C)}{CH_3COOH}$$

So, C is acetic acid.

(*c*) $$\underset{(C)}{CH_3COOH} + SOCl_2 \longrightarrow \underset{(D)}{CH_3COCl} + SO_2 + HCl$$

$$CH_3COCl + C_2H_5OH \longrightarrow \underset{\text{Ethyl acetate (ester) (E)}}{CH_3COOC_2H_5} + HCl$$

D will be CH_3COCl (acetyl chloride) because it gives an ester E which is a sweet smelling liquid.

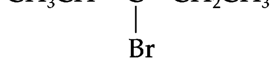
(*d*) $$\underset{(C)}{CH_3COOH} + C_2H_5OH \longrightarrow \underset{(E)}{CH_3COOC_2H_5} + H_2O$$

So, A = Acetylene; B = Acetaldahyde; C = Acetic acid; D = Acetyl Chloride; E = Ethyl acetate.

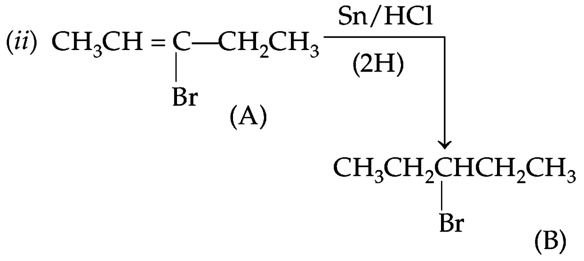
Example 104. *An organic compound (A), C_5H_9Br which readily decolorises bromine water and $KMnO_4$ solution, gives (B), $C_5H_{11}Br$ on treatment with Sn/HCl. The reaction of (A) with $NaNH_2$ produces (C), with evolution of ammonia. (C) neither reacts with sodium nor forms any metal acetylide but reacts with Lindlar's catalysts to give (D) and on reaction with Na/NH_3(liq.) produces (E). Both the compounds (D) and (E) are isomeric. Give structures of (A) to (E) with proper reasoning.*

(Roorkee, 1997)

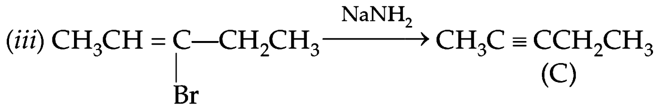
Solution. (*i*) Decolorisation of Br_2 water and $KMnO_4$ indicates unsaturation in C_5H_9Br. So, (A) can be



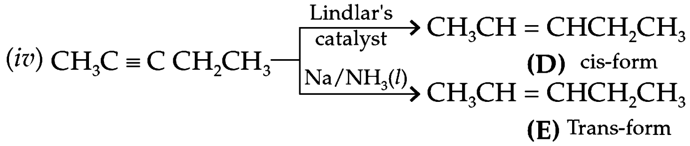
$$CH_3CH = \underset{Br}{\underset{|}{C}}{-}CH_2CH_3$$



(*ii*) $$\underset{(A)}{CH_3CH = \underset{Br}{\underset{|}{C}}{-}CH_2CH_3} \xrightarrow[(2H)]{Sn/HCl} \underset{(B)}{CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_2CH_3}$$



(*iii*) $$CH_3CH = \underset{Br}{\underset{|}{C}}{-}CH_2CH_3 \xrightarrow{NaNH_2} \underset{(C)}{CH_3C\equiv CCH_2CH_3}$$



(*iv*) $$CH_3C\equiv C\,CH_2CH_3 \begin{cases} \xrightarrow{\text{Lindlar's catalyst}} \underset{\text{(D) cis-form}}{CH_3CH = CHCH_2CH_3} \\ \xrightarrow{Na/NH_3(l)} \underset{\text{(E) Trans-form}}{CH_3CH = CHCH_2CH_3} \end{cases}$$

(D) and (E) are geometrical isomers

The compound (C) is not a terminal alkyne. So, it will neither react with Na nor it will form metal acetylide.

Example 105. *Dehydrobromination of compounds (A) and (B) yield the same alkene (C). Alkene (C) can regenerate (A) and (B) by the addition of HBr in the presence and absence of peroxide respectively. Hydrolysis of (A) and (B) give isomeric products, (D) and (E) respectively. 1,1-diphenyl ethane is obtained on reaction of (C) with benzene in presence of H^+. Give structures of (A) to (E) with reasons.* **(Roorkee, 1997)**

Solution. (*i*) Dehydrobromination suggests that (*A*) and (*B*) should be bromoderivatives of an alkane which on reaction with alc. KOH undergo dehydrobromination. So, expected compounds having a phenyl group will be (*A*) = $C_6H_5CH_2CH_2$ Br and (B) = $C_6H_5CHBrCH_3$, Thus :

(*ii*) $$\underset{(A)}{C_6H_5CH_2Br} \xrightarrow[-HBr]{\text{Alc. KOH}}$$

$$\underset{(C)}{C_6H_5CH = CH_2} \xrightarrow[\substack{\text{Peroxide} \\ \text{(anti M.Rule)}}]{+\,HBr}$$

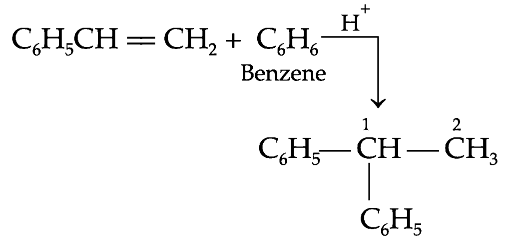
$$\underset{(A)}{C_6H_5CH_2CH_2Br} \xrightarrow{HOH} \underset{(D)}{C_6H_5CH_2CH_2OH}$$

(*iii*) $C_6H_5CHBrCH_3 \xrightarrow[-HBr]{\text{Alc. KOH}}$

$\underset{(C)}{C_6H_5CH = CH_2} \xrightarrow[\text{M. Rule}]{HBr}$

$\underset{(B)}{C_6H_5CHBrCH_3} \xrightarrow{HOH} \underset{(E)}{C_6H_5CH(OH)CH_3}$

From above, we see that (*D*) and (*E*) are isomeric alcohols

(*iv*)


$C_6H_5CH = CH_2 + \underset{\text{Benzene}}{C_6H_6} \xrightarrow{H^+} C_6H_5-\overset{1}{C}H(C_6H_5)-\overset{2}{C}H_3$

1, 1- Diphenyl ethane

EXAMPLE 106. *An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometrical isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiff's test but F does not. Give structures of (A) to (F) with reasons.*

(Roorkee, 1997)

SOLUTION. Since (*A*) reacts with $Br_2 + P_4$ *i.e.*, it gives Hell Volhard Zelinsky reaction, so acid (*A*) will be *R* CH_2COOH.

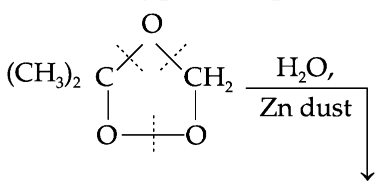
(*i*) $\underset{(\mathbf{A})}{R\,CH_2COOH} \xrightarrow{Br_2 + P_4} \underset{(\mathbf{B})}{R\,\overset{*}{C}HBr\,COOH}$ where $R = C_3H_7$ and C^* is asymmetric *C*– atom.

(*ii*) $\underset{(C)}{R\,CHBr\,COOH} \xrightarrow{-HBr} (C).$

Since (C) has not geometrical isomers, so (C) can be $\underset{(C)}{(CH_3)_2C = CHCOOH}$.

(*iii*) $(CH_3)_2C = CHCOOH \xrightarrow[\text{boxylation}(-CO_2)]{\text{Decar-}} \underset{\mathbf{(D)}}{(CH_3)_2C = CH_2}$

(*iv*) $(CH_3)_2C = CH_2 \xrightarrow{\text{Ozonolysis}}$

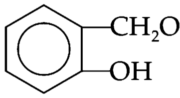


$(CH_3)_2CO \quad + \quad HCHO$

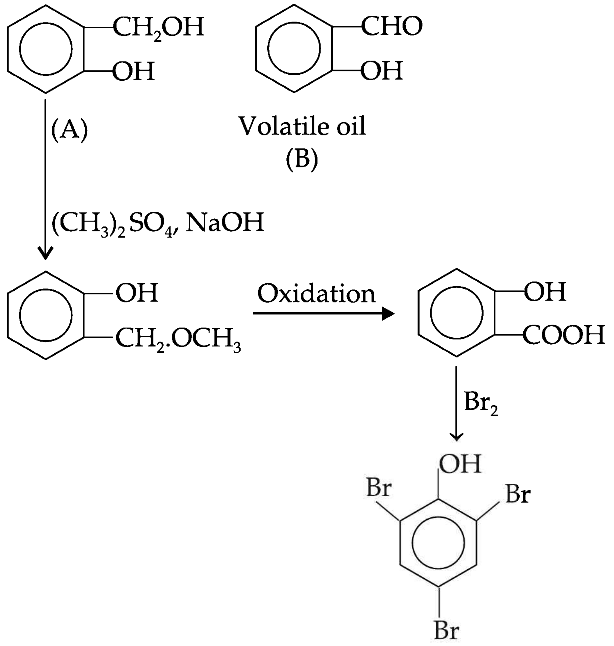
Acetone, (F) negative test with Schiff's reagent	(E) positive test with Schiff's reagent.

Thus, (C) is $(CH_3)_2C = CH.COOH$.

EXAMPLE 107. *A phenolic compound (A), $C_7H_8O_2$ on mild oxidation gives a highly volatile oil (B). (A) forms (C) on reaction with dimethylsulphate in alkali. Oxidation of (C) with hot $KMnO_4$ gives (D) which then reacts with bromine water to give (E) containing about 72% bromine. Give structures of (A) to (E) with proper reasoning.* **(Roorkee, 1997)**

SOLUTION. Compound (A), $C_7H_8O_2$ with phenolic group –OH is


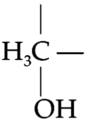
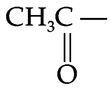
. Writing reactions as required in question, we have :

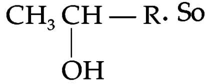


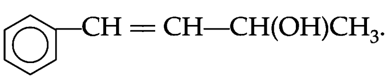
72% bromine in this (E) compound

EXAMPLE 108. *Compound (A) $C_{12}H_{12}O$ gives off hydrogen on treatment with sodium metal and also decolorises Br_2 in CCl_4 to give (B), $C_{10}H_{12}OBr_2$. (A) on treatment with I_2 in NaOH gives iodoform and acid (C) after acidification. Give structures of (A) to (C) and also of all the geometrical and optical isomers of (A).*

(Roorkee, 1997)

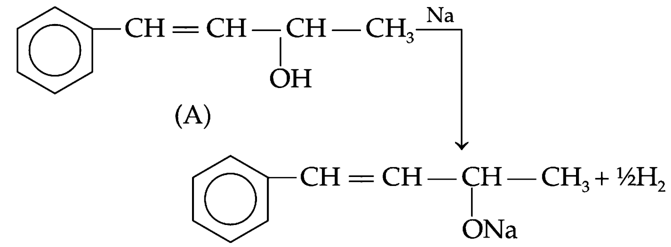
SOLUTION. (*a*) We know iodoform test is given by compounds having

$CH_3\underset{OH}{C}-$ group,

$CH_3\underset{O}{\overset{\|}{C}}-$ etc groups.

So (A) should have the structure,

$CH_3\underset{OH}{CH}-R$. So, (A)

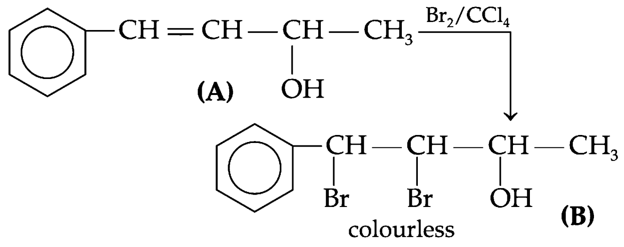
$C_{12}H_{12}O$ is expected to be :


The double bonds indicate the decoloration of Br_2/CCl_4 solution because of unsaturation. – OH group indicates evolution of H_2 with Na-metal. So, reactions involved will be :

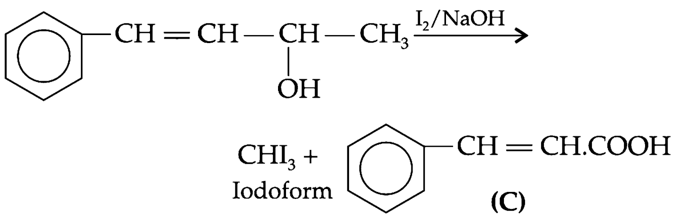
(*i*)



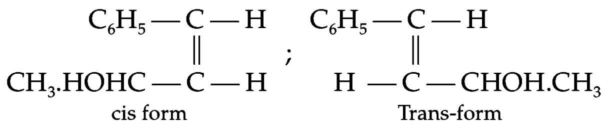
(*ii*)



(*iii*)

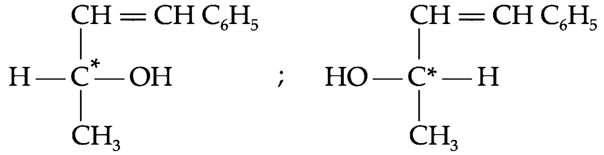


(*b*) **Geometrical isomers** of (A) are cis and trans as shown below.



$$\begin{array}{c} C_6H_5—C—H \\ \| \\ CH_3.HOHC—C—H \\ \text{cis form} \end{array} \quad ; \quad \begin{array}{c} C_6H_5—C—H \\ \| \\ H—C—CHOH.CH_3 \\ \text{Trans-form} \end{array}$$

(*c*) Optical isomers of (A) are :



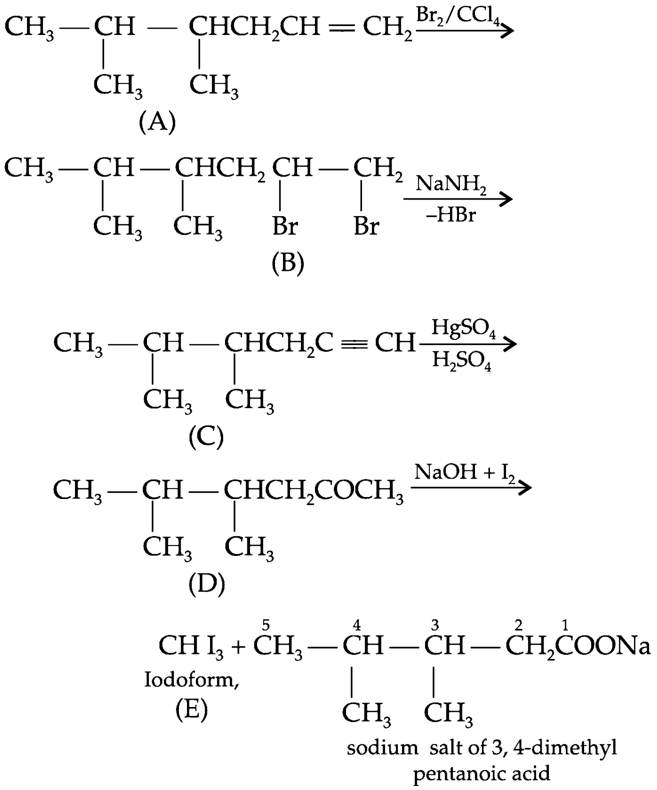
$$\begin{array}{c} CH=CH\,C_6H_5 \\ | \\ H—C^*—OH \\ | \\ CH_3 \end{array} \quad ; \quad \begin{array}{c} CH=CH\,C_6H_5 \\ | \\ HO—C^*—H \\ | \\ CH_3 \end{array}$$

C* indicate asymmetric carbon atom.

EXAMPLE 109. *An alkene (A) on passing through Br_2/CCl_4 gives a compound (B), which on dehydrobromination in presence of $NaNH_2$ gives a hydrocarbon (C). Compound (C) yields (D) when warmed with dilute H_2SO_4 in the presence of $HgSO_4$. (D) gives a yellow ppt. of (E) on treatment with I_2 and NaOH and also forms sodium salt of 3, 4–dimethyl pentanoic acid. Give structures of (A) to (E) with reasons.* **(Roorkee, 2001)**

SOLUTION. Action of alkene (A) with Br_2/CCl_4 indicates unsaturation in (A). Dehydrobromination in presence of $NaNH_2$ indicates terminal $C\equiv CH$ etc. The last compound has seven C-atoms and iodoform CHI_3. So, the data suggests that :

(A) is



$$\underset{(A)}{CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{C}}HCH_2CH=CH_2} \xrightarrow{Br_2/CCl_4}$$

$$\underset{(B)}{CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{C}}HCH_2\,\underset{Br}{\underset{|}{CH}}—\underset{Br}{\underset{|}{CH_2}}} \xrightarrow[-HBr]{NaNH_2}$$

$$\underset{(C)}{CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{C}}HCH_2C\equiv CH} \xrightarrow[H_2SO_4]{HgSO_4}$$

$$\underset{(D)}{CH_3—\underset{CH_3}{\underset{|}{CH}}—\underset{CH_3}{\underset{|}{C}}HCH_2COCH_3} \xrightarrow{NaOH + I_2}$$

$$\underset{\text{Iodoform, (E)}}{CH\,I_3} + \overset{5}{C}H_3—\underset{CH_3}{\underset{|}{\overset{4}{C}H}}—\underset{CH_3}{\underset{|}{\overset{3}{C}H}}—\overset{2}{C}H_2\overset{1}{C}OONa$$

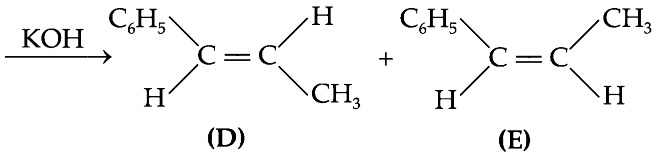
sodium salt of 3, 4-dimethyl pentanoic acid

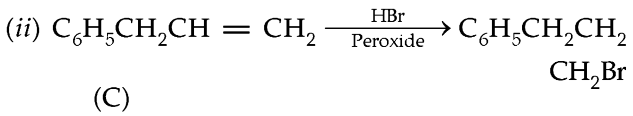
EXAMPLE 110. *A Grignard reagent (A) and a haloalkene (B) react to give (C). Compound (C) on heating with KOH yields a mixture of two geometrical isomers, (D) and (E), of which (D) predominates. (D) and (E) have the same molecular formula and (C) gives I-bromo-3-phenylpropane on reaction with HBr in the presence of peroxide. Give structures of (A), (B) and (C) and configurations of (D) and (E) with reasons.* **(Roorkee, 2001)**

SOLUTION. Since (C) gives 1-bromo-3-phenyl propane when treated with HBr in presence of peroxide (anti Markownikoff's rule), so (C) will be an alkene. This suggests the following.

(*i*)

$$\underset{\textbf{(A)}}{C_6H_5MgX} + \underset{\textbf{(B)}}{CH_2=CHCH_2X} \longrightarrow \underset{\textbf{(C)}}{C_6H_5CH_2CH=CH_2}$$

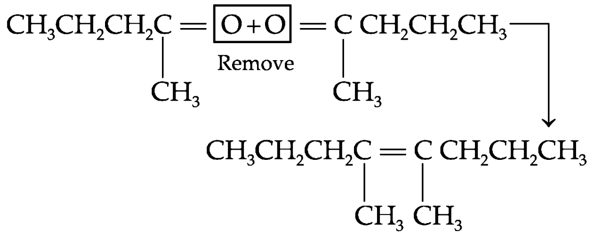




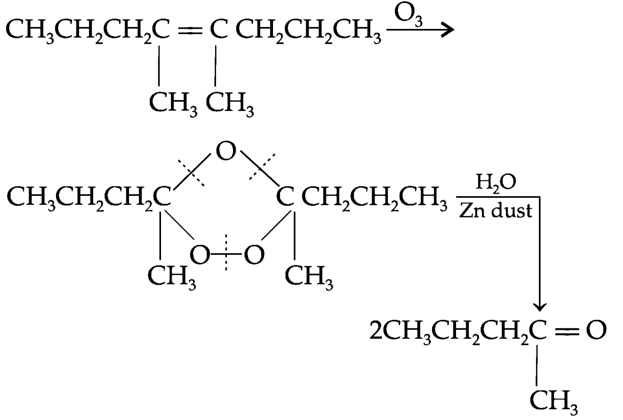
$$(ii)\ \underset{(C)}{C_6H_5CH_2CH=CH_2} \xrightarrow[\text{Peroxide}]{HBr} \underset{CH_2Br}{C_6H_5CH_2CH_2}$$

EXAMPLE 111. *Write the structure and give IUPAC name of the alkene which gives only pentan-2-one on ozonolysis.* **(Roorkee, 1985)**

SOLUTION. Product is $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$ on ozonolysis. So, the alkene should be :



It is confirmed from the following reactions.



(Pentan-2-one).

EXAMPLE 112. *Compound (A) contains only carbon and hydrogen. It decolorises Br_2 in CCl_4 solution and reacts slowly with Conc. H_2SO_4. Compound (A) reacts with HBr to form (B). (B) reacts with NaOH to form (C). On oxidation, (C) gives hexanone-3. write the structures of (A), (B) and (C) and give reactions.* **(Roorkee, 1986)**

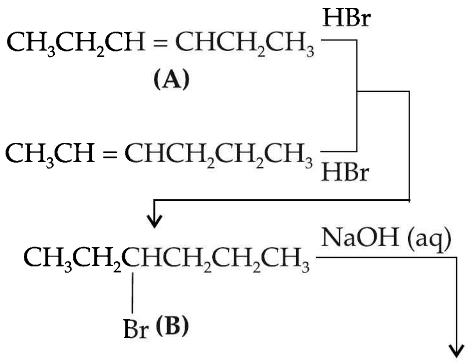
SOLUTION. Since (A) decolorises Br_2 in CCl_4, (*A*) is unsaturated hydrocarbon. Also, (*C*) on oxidation gives a ketone *i.e.*, hexanone-3, so, (*C*) should be a secondary alcohol. Also, position of keto group $>C = O$ should be 3. Thus, (C) is ;

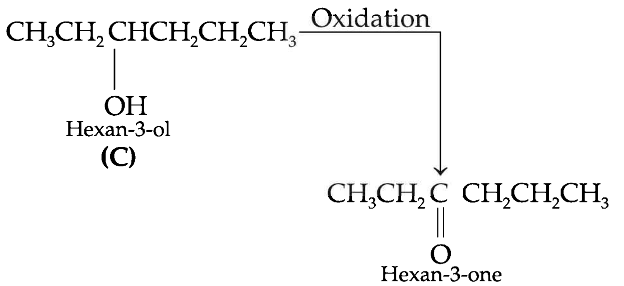
$$CH_3CH_2\underset{\underset{OH}{|}}{C}H\,CH_2CH_2CH_3.$$

Since (C) is formed from (B) on hydrolysis with NaOH, so (B) is $CH_3CH_2\underset{\underset{Br}{|}}{C}H\,CH_2CH_2CH_3$. Also , (A) reacts with HBr to form (B), so (A) should be

$CH_3CH{=}CHCH_2CH_2CH_3$ or $CH_3CH_2CH{=}CHCH_2CH_3$
(A) Hex-2-ene Hex-3-ene (A)

Reactions are :





EXAMPLE 113. *It required 0.7g of a hydrocarbon (A) to react completely with Br_2(2.0g). On treatment of (A) with HBr, it yielded monobromoalkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structural formula of (A) and (B) and explain the reactions involved.* **(Roorkee, 1987)**

SOLUTION. Since (A) reacts completely with Br_2, (A) should be an alkene.

Mol. wt. of $Br_2 = 2 \times 80 = 160.$

2.0g of Br_2 react with

(A) = 0.7g

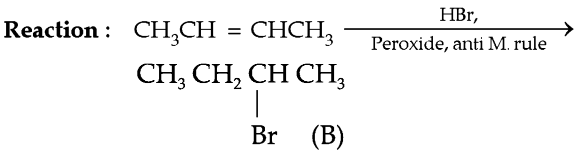
160.0g of Br_2 react with (A)

$$= \frac{0.7}{2.0} \times 160 = 56.0\text{g (A)}$$

$\therefore$ Mol. wt. of alkene,

$$C_nH_{2n} = 56\ ;\ 12n + 2n(1) = 56\ ;\ n = 4.$$

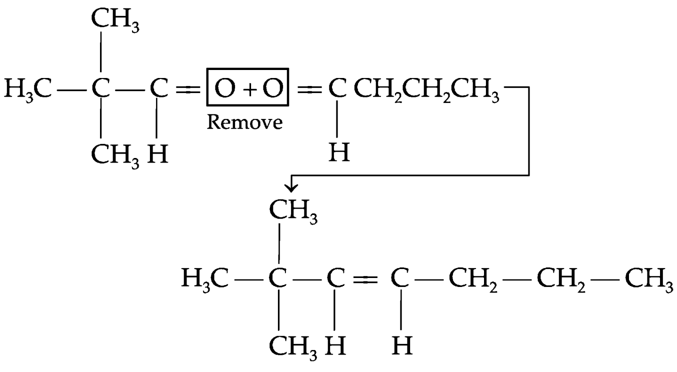
$\therefore$ Alkene = C_4H_8 or $CH_3CH = CHCH_3$
But - 2 - ene, (A)



Reaction : $CH_3CH = CHCH_3 \xrightarrow[\text{Peroxide, anti M. rule}]{\text{HBr,}} CH_3\,CH_2\,\underset{\underset{Br}{|}}{C}H\,CH_3$ (B)

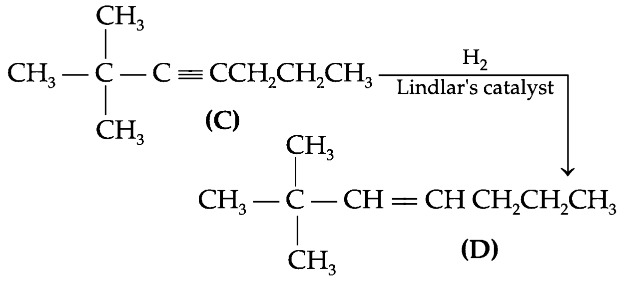
EXAMPLE 114. *An unsaturated hydrocarbon (A), C_6H_{10} readily gives (B) on treatment with $NaNH_2$ in liquid NH_3. When (B) is allowed to react with 1-chloropropane, a compound (C) is obtained. On partial hydrogenation in the presence of Lindlar's catalyst, (C) gives (D), C_9H_{18}. On ozonolysis, (D) gives 2, 2-dimethyl propanal and 1-butanal. Give structures of (A), (B), (C) and (D) with proper reasoning.* **(Roorkee, 1992)**

SOLUTION. (*i*) (D) is an alkene which on ozonolysis gives 2,2-dimethyl propanal and 1-butanal. So, (D) is :



(D)

(*ii*) Since (D) is formed by the partial hydrogenaton of (C) in presence of Lindlar's catalyst, so (C) will be:



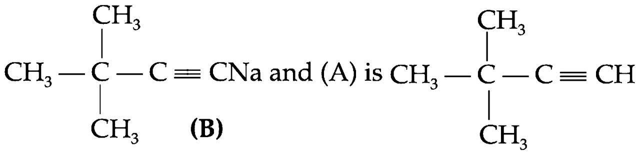
$$\underset{\textbf{(C)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CCH_2CH_2CH_3} \xrightarrow[\text{Lindlar's catalyst}]{H_2} \underset{\textbf{(D)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH\,CH_2CH_2CH_3}$$

(*iii*) Since (B) reacts with 1-chloropropane to form (C), so (B) will be :

$$\underset{(B)}{CH_3CH_2CH_2CH_2C\equiv CNa} + ClCH_2CH_2CH_3 \longrightarrow$$

$$\underset{(C)}{CH_3CH_2CH_2CH_2C\equiv C-CH_2CH_2CH_3}$$

But the actual structure of (C) is as shown in (ii) above. So, the comparison of two structures of (C) suggests that (B) should be :



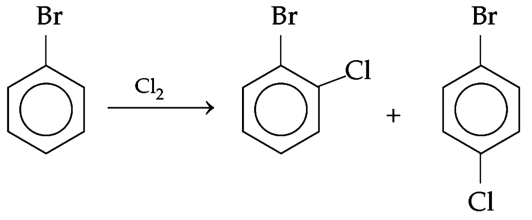
$$\underset{\textbf{(B)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CNa} \text{ and (A) is } CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C\equiv CH$$

3, 3 – Dimethyl but – 1 – yne, **(A)**

EXAMPLE 115. *When bromobenzene is monochlorinated, two isomeric compounds (A) and (B) are obtained. Monobromination of (A) gives several isomeric products of formula* $C_6H_3ClBr_2$ *while monobromination of (B) yields only two isomers (C) and (D). Compound (C) is identical with one of the compounds obtained from the bromination of (A), however, (D) is totally different from any of the isomeric compounds obtained from the bromination of (A). Give structures of (A), (B), (C) and (D) and also suggest structures of four isomeric monobrominated products of (A). Support your answer with reasoning.*

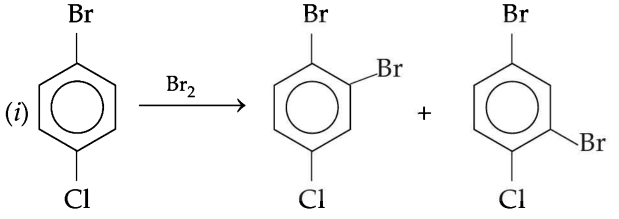
(Roorkee, 1992)

SOLUTION. –Br group in bromobenzene is ortho and para directing group. So, we have :



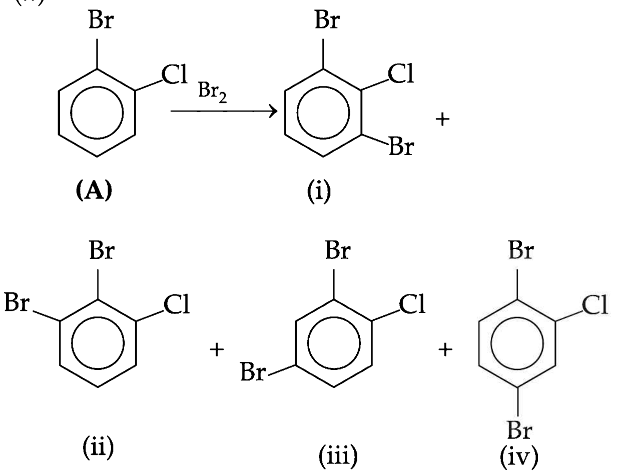
(A) **(B)**

Since (B) gives only two isomers while (A) gives several products on monobromination, so, we have :



(B) **(D)** **(C)**

(*ii*)



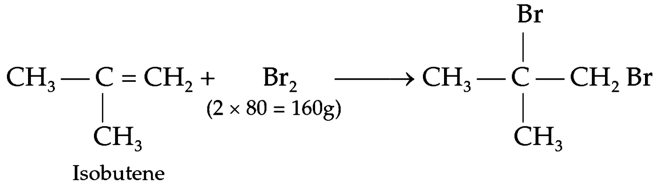
Structure (C) is identical to structure (*iii*) but structure (D) is different from the structures (*i*), (*ii*) and (*iv*)

EXAMPLE 116. *A 10g mixture of isobutane and isobutene requires 20g of* Br_2 *(in* CCl_4*) for complete addition. If 10g of the mixture is catalytically hydrogenated and the entire alkane is monobrominated in the presence of light at 127°C, which is the exclusive product and how much of it would be formed ? (atomic weight of bromine = 80).* **(Roorkee, 1998)**

SOLUTION. (*i*) Wt. of isobutane + isobutene = 10g.

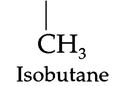
Let wt. of isobutene $= x$ g ; wt. of isobutane = 10 – x g.

Reactions :



$$\underset{\text{Isobutene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} + \underset{(2\times 80\,=\,160g)}{Br_2} \longrightarrow CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2\,Br$$

(Mol. wt. = 12 + 3 + 12 + 12 + 3 + 12 + 2 = 56g)



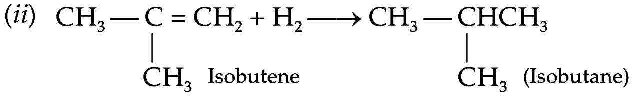
$$\underset{\text{Isobutane}}{CH_3-\underset{\underset{CH_3}{|}}{C}HCH_3} \xrightarrow{Br_2} \text{no action}$$

160g Br_2 is needed for isobutene = 56g

∴ 20g Br_2 is needed for isobutene $= \frac{56}{160} \times 20 = 7g$

∴ Wt. of isobutene = 7g

Wt. of isobutane = 10 – 7 = 3g

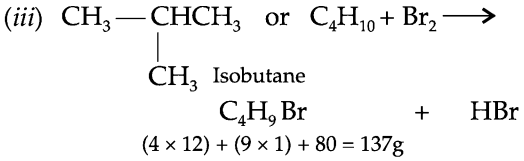


(*ii*) $$\underset{\text{Isobutene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2} + H_2 \longrightarrow \underset{\text{(Isobutane)}}{CH_3-\underset{\underset{CH_3}{|}}{C}HCH_3}$$

Mol. wt. = 56 Mol. wt. = 58

56g isobutene forms isobutane = 58g

7g isobutene forms isobutane $= \frac{58}{56} \times 7 = 7.25g$



(*iii*) $$\underset{\text{Isobutane}}{CH_3-\underset{\underset{CH_3}{|}}{C}HCH_3} \text{ or } C_4H_{10} + Br_2 \longrightarrow$$

$$\underset{(4\times 12)+(9\times 1)+80\,=\,137g}{C_4H_9Br} + HBr$$

mol. wt. = 58g

58g isobutane forms C_4H_9Br = 137g

$\therefore$ 7.25 + 3 *i.e.*, 10.25g C_4H_{10} forms product

$$= \frac{137}{58} \times 10.25 = \mathbf{24.21g\ C_4H_9Br.}$$

EXAMPLE 117. *An organic compound $C_3H_6O_2$ has two isomers, (A) and (B). (B) gives effervescence with $NaHCO_3$ while (A) does not do so. (B) gives out H_2 when treated with metallic zinc but (A) has no reaction with it. (A) on treatment with excess of NaOH yields two compounds (C) and (D). Compound (C) when treated with dil. H_2SO_4 gives (E) which reduces Tollen's reagent. (D), however, can form iodoform with I_2 and alkali. Identify (A) to (E).*

SOLUTION. (*i*) Since (*B*) gives effervescence with $NaHCO_3$, it will be an acid. Since (*A*) and (*B*) are isomers, (*A*) may be an ester. Thus, $C_3H_6O_2$ may be an acid or ester. (*A*) is $HCOOC_2H_5$ or $H_3CCOOCH_3$; (*B*) is CH_3CH_2COOH (*ii*) (*A*) reacts with NaOH to form (*C*) and (*D*). Since (*D*) gives iodoform test, the ester is $HCOOC_2H_5$

$$HCOOC_2H_5 \xrightarrow{NaOH} HCOONa + C_2H_5OH\,(Ethanol)$$

(*A*), Ethyl formate — (*C*) Sodium formate — (D), gives iodoform test.

$$(ii)\ HCOONa \xrightarrow[H_2SO_4]{H_2O,} HCOOH\ (formic\ acid) + NaOH$$

(*C*) — (*F*), reduces Tollen's reagent

EXAMPLE 118. *An organic compound (A), $C_6H_{12}O_3$ on treatment with conc. H_2SO_4 gives CO_2, H_2O and (B). Compound (B) can be prepared by passing vapours of pentanol–1 over heated copper at 570K. Compound (A) on heating gives (C), $C_{12}H_{20}O_4$. Give structures of (A) to (C) with proper reasoning.*

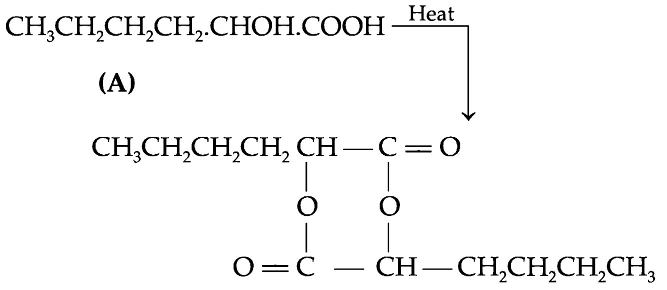
(Roorkee, 1998)

SOLUTION. (*i*) Since primary alcohols on heating with Cu at 570K give aldehyde, so, (B) will be aldehyde as it is obtained from pentanol–1.

$$\underset{\text{Pentanol–1}}{CH_3CH_2CH_2CH_2CH_2OH} \xrightarrow[570K]{Cu,} \underset{\text{(B), Pentanal – 1}}{CH_3CH_2CH_2CH_2CHO}$$

Since on treating (A) with conc. H_2SO_4, we get CO_2, H_2O and (B), so (A) will be $CH_3CH_2CH_2CH_2CHOHCOOH$

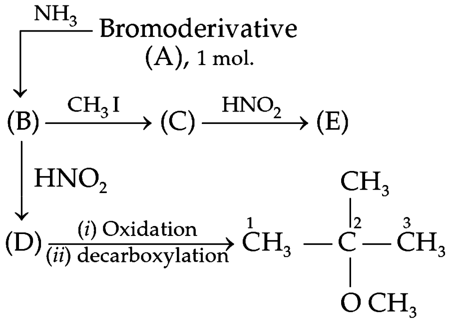
(*ii*) $CH_3CH_2CH_2CH_2CHOHCOOH \xrightarrow{Conc.\ H_2SO_4} CH_3CH_2CH_2CH_2CHO + CO_2 + H_2O$. Also (A) gives (C) on heating. Thus



(C) Lactide

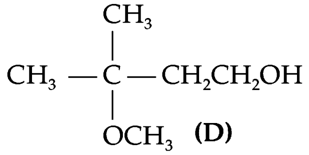
EXAMPLE 119. *One mole of each bromoderivative (A) and NH_3 react to give one mole of an organic compound (B). (B) reacts with CH_3I to give (C). Both (B) and (C) react with HNO_2 to give compounds (D) and (E) respectively. (D) on oxidation and subsequent decarboxylation gives 2-methoxy-2-methyl propane. Give structures of (A) to (E) with proper reasoning.* **Roorkee, 1994)**

SOLUTION.



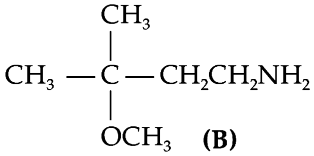
2-Methoxy-2-methyl propane

(*i*) Since 1°-alcohols on oxidation give carboxylic acid and the latter on decarboxylation results in the loss of one carbon atom, so (D) will be



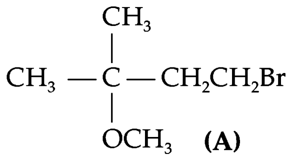
$$CH_3-\underset{OCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2OH\quad \mathbf{(D)}$$

(*ii*) Since alcohol is formed by the action of HNO_2 on $-NH_2$ group, so, (B) will be



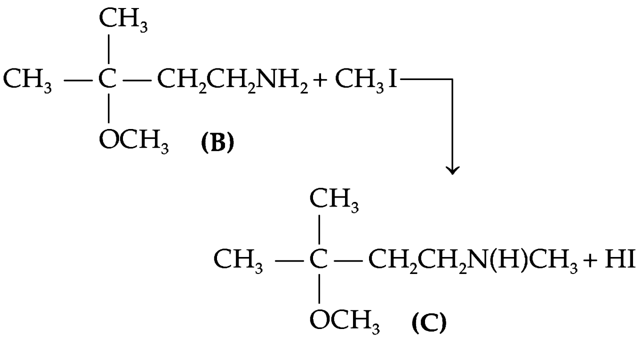
$$CH_3-\underset{OCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2NH_2\quad \mathbf{(B)}$$

(*iii*) Since (B) is formed by the action of NH_3 on (A) which is a bromoderivative, so (A) will be :



$$CH_3-\underset{OCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2Br\quad \mathbf{(A)}$$

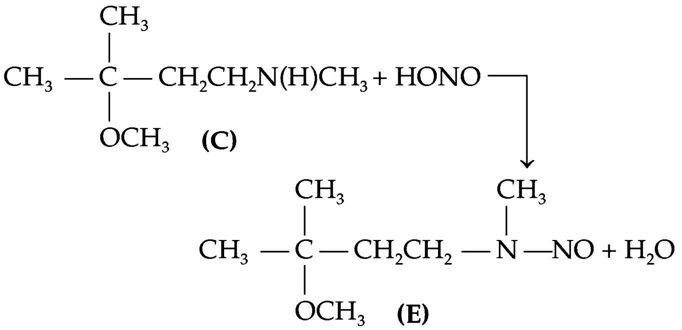
(*iv*) Since (D) is formed by the action of (B) on CH_3I, so, we have.



$$CH_3-\underset{OCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2NH_2 + CH_3I \longrightarrow CH_3-\underset{OCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2N(H)CH_3 + HI$$

(B) — **(C)**

(*v*) Action of (C) on HNO_2 gives (E). Thus :



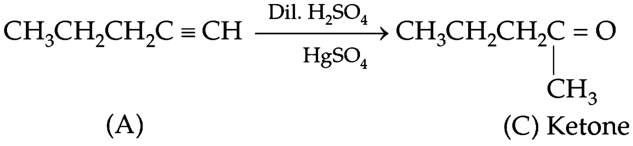
$$\underset{\text{(C)}}{CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2N(H)CH_3} + HONO \longrightarrow \underset{\text{(E)}}{CH_3-\underset{\underset{OCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2-\overset{\overset{CH_3}{|}}{N}-NO} + H_2O$$

EXAMPLE 120. *An organic compound (A) of molecular formula C_5H_8 when treated with Na in liquid ammonia followed by reaction with n-propyl iodide yields (B), C_8H_{14}. (A) gives a ketone (C), $C_5H_{10}O$ when treated with dil. H_2SO_4 and $HgSO_4$. (B) on oxidation with alkaline $KMnO_4$ gives two isomeric acids (D) and (E), $C_4H_8O_2$. Give structures of compounds (A) to (E) with proper reasoning.* **(Roorkee, 1994)**

SOLUTION. The formula C_5H_8 is of alkyne C_nH_{2n-2}. Since (A) reacts with Na/NH_3, it will be terminated alkyne, $CH_3CH_2CH_2C\equiv CH$. (**A**)

(*i*) $CH_3CH_2CH_2C\equiv CH \xrightarrow{Na} CH_3CH_2CH_2C\equiv CNa \xrightarrow{CH_3CH_2CH_2I} \underset{(B)}{CH_3CH_2CH_2C\equiv C-CH_2-CH_2-CH_3}$.

(*ii*)

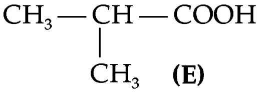


$$\underset{(A)}{CH_3CH_2CH_2C\equiv CH} \xrightarrow[HgSO_4]{Dil.\ H_2SO_4} \underset{\text{(C) Ketone}}{CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}=O}$$

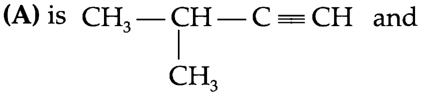
(*iii*) $CH_3CH_2CH_2C\equiv CCH_2CH_2CH_3 \xrightarrow[[O]]{KMnO_4,}$

$\underset{(D)}{CH_3CH_2CH_2COOH} + \underset{(E)}{CH_3CH_2CH_2COOH}$

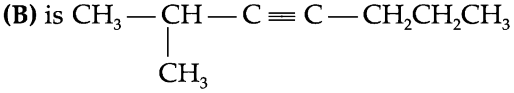
But (D) and (E) are isomeric. So, (E) can be



$$\underset{(E)}{CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH}$$



(A) is $CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv CH$ and



(B) is $CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv C-CH_2CH_2CH_3$

EXAMPLE 121. *Hydrocarbon (X), C_7H_{12} on reaction with boron hydride followed by treatment with CH_3COOH yields (A). On reduction ozonolysis, (A) yields a mixture of two aldehydes, (B) and (C). Of these, only (B) can undergo Cannizzaro's reaction. (A) exists in two geometrical isomers (A – I) and (A – 2) of which (A–2) is more stable. Give structures of (X), (A), (B), (C), (A – I) and (A – 2) with proper reasoning.* **(Roorkee, 2000)**

SOLUTION. (*i*) $A \xrightarrow[(ii)\ H_2O,\ Zn\ dust]{(i)\ O_3} \underset{(B)}{R\ CHO} + \underset{(C)}{R'\ CHO}$

(*ii*) If (*B*) is HCHO, it will give Cannizzaro's reaction because of the presence of α–H atom in it. But, then (*A*) must have $R'\ C=CH_2$ structure which is not possible because it will not give geometrical isomers.

(*iii*) $\underset{(X)}{C_7H_{12}}$ is an alkyne of formula C_nH_{2n-2}. Its reaction is :

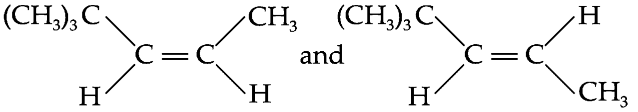
$$\underset{(X)}{C_7H_{12}} \xrightarrow[CH_3COOH]{B_2H_6,} \underset{\text{Alkene}}{C_7H_{14}}$$

But reaction of an alkyne to form alkene takes place through vinylic boranes as intermediate and cis-alkene is the main product. Hence, we have :

$$\underset{(A)}{(CH_3)_3CCH=CHCH_3} \xrightarrow[(ii)\ H_2O,\ Zn\ dust]{(i)\ O_3} \underset{(B)}{(CH_3)_3\ C.CHO} + \underset{(C)}{CH_3CHO}$$

(B) does not have α–H atom but gives Cannizzaro's reaction

(*iv*) Two geometrical isomers of (A) are



cis, (A-1) Trans, (A-2)

EXAMPLE 122. *An organic compound (A) reacts with ethanol to give (B) and (C). On acid hydrolysis, (C) yields (B) and (D). Oxidation of (D) gives (B). (B) is an acid and forms a salt with $Ca(OH)_2$ which on dry distillation gives (E), C_3H_6O. Give structures of (A) to (E) with proper reasoning.* **(Roorkee, 2000)**

SOLUTION. (*i*) (B) is an acid and forms a salt with $Ca(OH)_2$ which on dry distillation gives (E), C_3H_6O *i.e.*, acetone. So, (B) is acetic acid, CH_3COOH.

Reactions.

$2CH_3COOH + Ca(OH)_2 \longrightarrow Ca(CH_3COO)_2 + 2H_2O$

$Ca(CH_3COO)_2 \xrightarrow{\text{Dry distillation}} CaCO_3 + CH_3COCH_3$ *i.e.*, C_3H_6O.

(*ii*) Since (A) reacts with C_2H_5OH to give (B) and (C), so (A) will be acetic anhydride.

$$\underset{\text{Acetic anhydride}}{CH_3CO.O.COCH_3} + \underset{\text{Ethanol}}{C_2H_5OH} \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(C)}{CH_3COOC_2H_5}$$

(*iii*) (C) on acid hydrolysis gives (B) *i.e.*, CH_3COOH and (D) and (D) on oxidation gives (B). So, we have :

$$CH_3COOC_2H_5 + HOH \longrightarrow \underset{(B)}{CH_3COOH} + \underset{(D)}{C_2H_5OH}$$

$$C_2H_5OH \xrightarrow{[O]} \underset{(B)}{CH_3COOH} + H_2O.$$

EXAMPLE 123. *Compound (A), $C_5H_{11}NO$ is not soluble in cold dilute alkaline or acidic solutions. When (A) is refluxed in*

NaOH solution, a gas (B) is evolved and a salt (C) is formed. Acetyl chloride reacts with (B) to give (D), C_4H_9NO. (B) reacts with HNO_2 to give a yellow oil (E). Give structures of (A) to (E) with reactions. **(Roorkee, 2000)**

SOLUTION. Since (B) reacts with HNO_2 to give a yellow oil (E), so, (B) is expected to be secondary amine. Also (A) gives a salt (C) when refluxed with NaOH. So, (C) is sodium salt of an acid. Thus, the given data suggest that, (A) is $(CH_3)_2N.\ COCH_2CH_3$.

(*i*) $\underset{\textbf{(A)}}{(CH_3)_2N.COCH_2CH_3} + NaOH \xrightarrow{\text{Reflux}} \underset{\textbf{(B)}}{(CH_3)_2NH} + \underset{\textbf{(C)}}{CH_3CH_2COONa}$

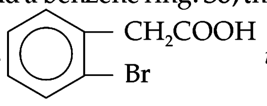
(*ii*) $\underset{\textbf{(B)}}{(CH_3)_2NH} + HONO \longrightarrow \underset{\text{Yellow oil }\textbf{(E)}}{(CH_3)_2N.\ NO}$

(*iii*) $\underset{\textbf{(B)}}{(CH_3)_2NH} + \underset{\text{Acetyl chloride}}{CH_3COCl} \longrightarrow \underset{\textbf{(D)}}{(CH_3)_2N.\ COCH_3}$

EXAMPLE 124. *An acid (A) $C_8H_7O_2$ Br on bromination with $FeBr_3$ gives two isomers (B) and (C) of formula $C_8H_6O_2Br_2$. Vigorous oxidation of (A), (B) and (C) gives acids (D), (E) and (F) respectively. (D) $C_7H_5O_2$ Br is the strongest acid among all of its isomers, whereas (E) and (F) each has a molecular formula of $C_7H_4O_2Br_2$. Give structures of (A) to (F) with justification.*

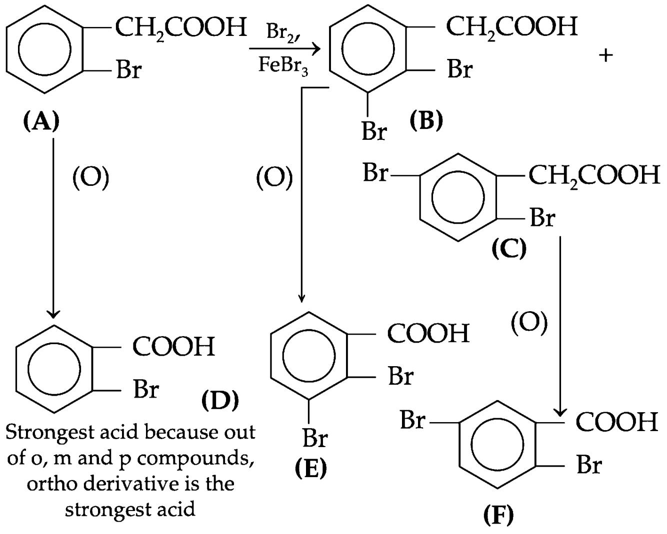
(Roorkee, 2000)

SOLUTION. The formula $C_8H_7O_2Br$ of acid (A) suggests a–COOH group and a benzene ring. So, the given reactions suggest that **(A)** is



i.e. $C_8H_7O_2$ Br.

Hence:



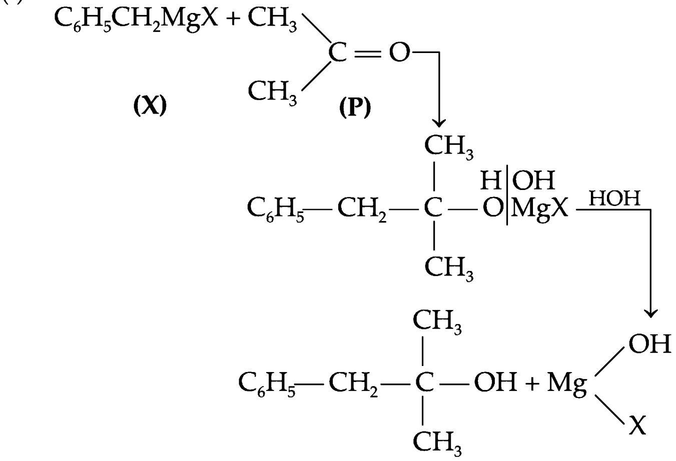
Strongest acid because out of o, m and p compounds, ortho derivative is the strongest acid

EXAMPLE 125. *Two different Grignard reagents, (X) and (Y) produce $C_6H_5CH_2C(CH_3)_2$ OH on reaction with (P) and (Q) respectively. Give structures of (X), (Y), (P) and (Q).*

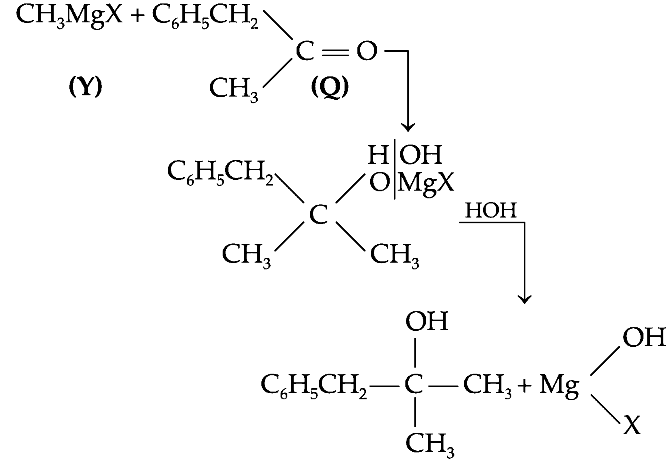
(Roorkee, 2000)

SOLUTION. The product $C_6H_5CH_2C(CH_3)_2OH$ indicates that (X) should be $C_6H_5CH_2MgX$ and (Y) should be CH_3MgX. Since Grignard reagents react with ketones followed by hydrolysis give alcohols, so keeping in view the groups present in the product, we have :

(*i*)

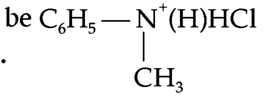


(*ii*)



EXAMPLE 126. *The aqueous solution of a nitrogen and chlorine containing organic compound (A) is acidic to litmus. (A) on treatment with aqueous NaOH gives a compound (B) containing nitrogen, but not chlorine. Compound (B), on treatment with $C_6H_5SO_2Cl$ in the presence of NaOH gives an insoluble product $C_{13}H_{13}NO_2S$. Give structures of (A) and (B).* **(Roorkee, 2000)**

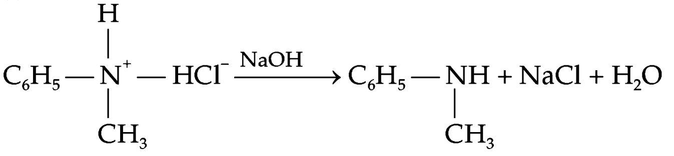
SOLUTION. Since (A) contains N and Cl and is acidic to litmus, it can be



$C_6H_5 - \underset{\underset{\displaystyle CH_3}{|}}{N^+}(H)HCl$

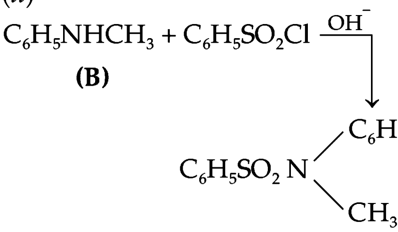
Reaction.

(*i*)



$C_6H_5 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}} - HCl^- \xrightarrow{NaOH} C_6H_5 - \underset{\underset{\displaystyle CH_3}{|}}{NH} + NaCl + H_2O$

(*ii*)



(Insoluble in NaOH as there is no H-atom with N-atom)

EXAMPLE 127. *Compound (A) gives positive Lucas test in 5 minutes. When 6.0g of (A) is treated with sodium metal, 1120mL of hydrogen is evolved at S.T.P. Assuming (A) to contain one atom of oxygen per molecule, write structural formula of (A). Compound (A) when treated with PBr_3 gives (B) which when treated with benzene in presence of anhydrous aluminium chloride gives (C). What are (B) and (C) ?* **(Roorkee, 1990)**

SOLUTION. (*i*) 1120 mL of H_2 is produced from (A) = 6.0 g

11200 mL of H_2 is produced from (A) = $\frac{6}{1120} \times 11200 = 60$ g

Since (A) gives Lucas test within 5 minutes, it will be a secondary alcohol, $>CHOH$. Also, (A) contains one O-atom. So, there will be only one – OH group in (A).

(*ii*) Since one mol of alcohol having one OH group gives 11200 mL H_2 at S.T.P., mol. wt. of (A) = 60.

$$\left[\because\ -OH + Na \rightarrow -ONa + \frac{1}{2}H_2\ (i.e., \frac{1}{2} \times 22400 = 11200\ mL\ H_2)\right]$$

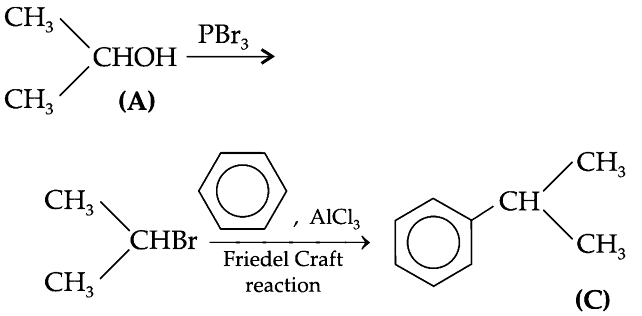
∴ Mol. wt. of

$$C_nH_{2n+1}OH = 60;\ 12n + (2n + 1) \times 1 + 16 + 1 = 60;$$

$$14n = 42;\ n = 3.$$

So. alcohol is C_3H_7OH *i.e.*, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH$ (Isopropyl alcohol)

Reactions.



(A)

(B)
2-Bromopropane

(C)
2-Phenyl propane

EXAMPLE 128. *When 0.0088g of a compound (A) was dissolved in 0.5g of camphor, the melting point of camphor was lowered by 8°C. Analysis of (A) gave 68.18% C and 13.16% H. Compound (A) showed the following reactions.*

(*i*) *It reacted with acid chloride and evolved hydrogen with Na.*

(*ii*) *When reacted with HCl + $ZnCl_2$, a dense oily layer separated out immediately.*

Compound (A) was passed over Al_2O_3 at 350°C to give compound (B). (B) on ozonolysis followed by hydrolysis gave two neutral compounds (C) and (D), which gave positive test with carbonyl reagents but only (C) gave a positive test with Fehling solution and resinous substance with NaOH. Identify (A), (B), (C) and (D) with proper reasoning. K_f for camphor = 40K mol⁻ kg **(Roorkee, 1990)**

SOLUTION. (*i*) To find empirical formula, E.F.,

Element	At. wt.	% age	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	12	68.18	$\frac{68.18}{12} = 5.68$	$\frac{5.68}{1.17} = 4.8$	5
H	1	13.16	$\frac{13.16}{1} = 13.16$	$\frac{13.16}{1.17} = 11.2$	11
O	16	100 – (68.18 + 13.16) = 18.66	$\frac{18.66}{16} = 1.17$	$\frac{1.17}{1.17} = 1$	1

∴ E.F. = $C_5H_{11}O$;

E.F. wt. = (5 ×12) + (11 × 1) + 16 = 87

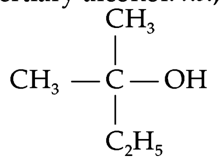
(*ii*) Mol. wt. of (*A*) = $\frac{1000 \times K_f \times \text{wt. of } (A)}{\Delta T \times \text{wt. of camphor solvent}}$

$$= \frac{1000 \times 40K\ mol^{-}\ Kg \times 0.0088g}{8K \times 0.5g} = 88Kg\ mol^{-}$$

∴ Molecular formula = E.F. × $\frac{\text{Mol. wt.}}{\text{E.F. wt.}}$

$$= C_5H_{11}O \times \frac{88}{77} \approx C_5H_{11}O$$

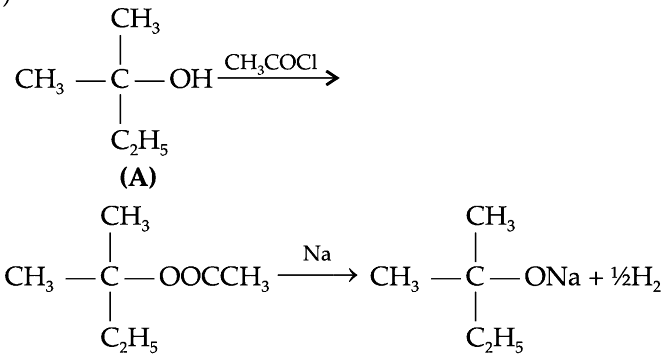
(*iii*) Since (A) reacts with acetyl chloride and liberates H_2 with Na, so (A) is an alcohol. But (A) reacts with Lucas reagent ($ZnCl_2$ + HCl) to give an oily layer, so (A) is a tertiary alcohol. *i.e.*,



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{C}}-OH$$

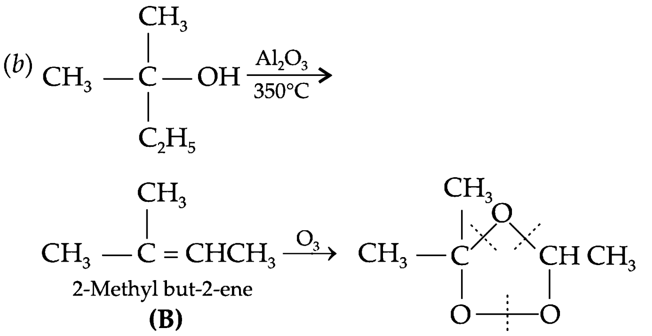
Reactions.

(*a*)



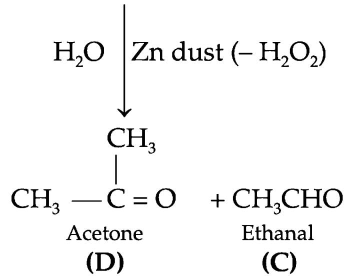
(A)

Methyl 2, 2-dimethyl butanoate



(*b*)

2-Methyl but-2-ene
(B)



$$\xrightarrow[H_2O]{\text{Zn dust } (-H_2O_2)} \underset{\substack{\text{Acetone}\\ \textbf{(D)}}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=O} + \underset{\substack{\text{Ethanal}\\ \textbf{(C)}}}{CH_3CHO}$$

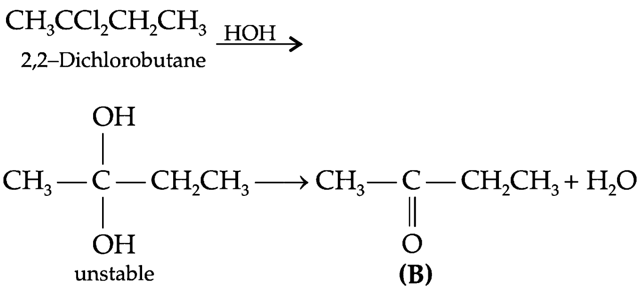
Out of (C) and (D), only (C) gives Fehling solution test. Thus (C) is an aldehyde while (D) will be a ketone because both(C) and (D) give test with carbonyl reagents like $NaHSO_3$, NH_2OH etc.

Example 129. *The compound $C_4H_8Cl_2$ (A) on hydrolysis gives a compound C_4H_8O, (B). The compound (B) reacts with hydroxylamine and gives a negative test with Tollen's reagent. What are (A) and (B)? Support your answer by proper reasoning and give the equations of reactions.* **(Roorkee,1985)**

Solution. (*i*) Since (B) reacts with NH_2OH, it is expected to be a carbonyl compound having aldehyde (–CHO) or keto (>C = O) group. Since (B) gives a negative test with Tollen's reagent, (B) is expected to be a ketone.

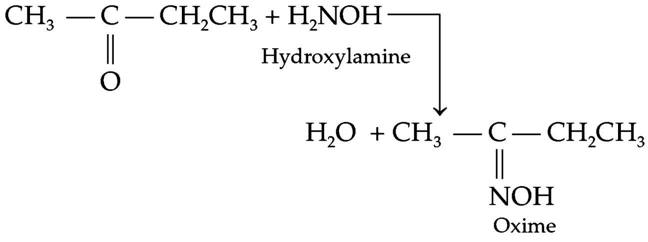
(*ii*) Since (B) is obtained by the hydrolysis of (A), so, both Cl-atoms will be of a gem-dihalide *i.e.*, Cl-atoms are bonded to the same C- atom which is not a corner C-atom. So, (A) is, $CH_3CCl_2CH_2CH_3$.

Reaction :

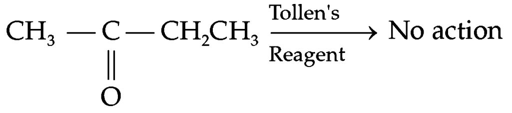


$$\underset{\text{2,2–Dichlorobutane}}{CH_3CCl_2CH_2CH_3} \xrightarrow{HOH}$$

$$\underset{\text{unstable}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CH_3} \longrightarrow \underset{\textbf{(B)}}{CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2CH_3} + H_2O$$



$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2CH_3 + \underset{\text{Hydroxylamine}}{H_2NOH} \longrightarrow H_2O + \underset{\text{Oxime}}{CH_3-\underset{\underset{\displaystyle NOH}{\|}}{C}-CH_2CH_3}$$



$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2CH_3 \xrightarrow[\text{Reagent}]{\text{Tollen's}} \text{No action}$$

Example 130. *A mixture of an anhydride (A) and a monobasic acid (B) on heating produces another monobasic acid (C) of equivalent weight 74 and an anhydride (D). The acids and anhydrides remain in equilibrium. The anhydride (D) contains two identical fluoroalkyl groups. The acid (B) contains a trifluoromethyl group and has an equivalent weight of 128. Give structures of (A) to (D) with proper reasoning. (at. wt. of fluorine = 19).* **(Roorkee, 1998)**

Solution. Monobasic acid (B) having equivalent weight, 74 = CH_3CH_2COOH. The acid (B) containing trifluoromethyl group having equivalent weight, 128 = CF_3CH_2COOH ($\because$ at. wt. C = 12, H = 1, F = 19, O = 16). This data suggests that the required reaction is ;

$$\underset{(A)}{(CH_3CH_2CO)_2O} + \underset{(B)}{2CF_3CH_2COOH} \longrightarrow \underset{(C)}{2CH_3CH_2COOH} + \underset{(D)}{(CF_3CH_2CO)_2O}$$

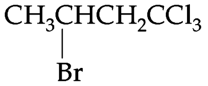
Example 131. *Write the products of the following reactions.*

(*i*) $CH_3CH = CH_2 + Br\,CCl_3 \xrightarrow{\text{Peroxide}}$

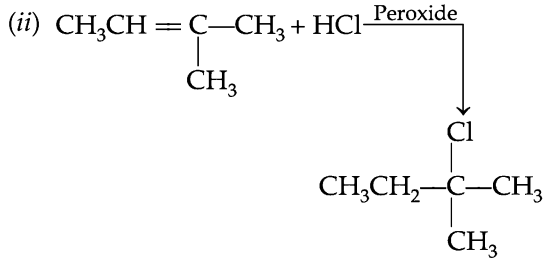
(*ii*) $CH_3CH = C(CH_3)_2 + HCl \xrightarrow{\text{Peroxide}}$

(Roorkee, 1998)

Solution. (*i*) $CH_3CH = CH_2 + Br\,CCl_3 \xrightarrow{\text{Peroxide}}$

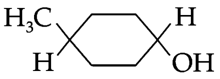


$$CH_3\underset{\underset{\displaystyle Br}{|}}{C}HCH_2CCl_3$$



$$(ii)\ CH_3CH=\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3 + HCl \xrightarrow{\text{Peroxide}} CH_3CH_2-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

Example 132. (*a*) *Dehydration of*



gives a compound which exists in two isomeric forms. Give the structure of both the isomers.

(*b*) *Explain in not more than 2, 3 lines.*

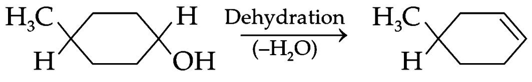
(*i*) Aniline does not undergo Friedel–Crafts reaction

(*ii*) Mineral acid is added in excess in diazotisation of arylamines.

(*c*) *Complete the reaction,* $(CH_3)_2\,C = CH_2$ + *isobutane* $\xrightarrow[273K]{HF}$ **(Roorkee, 1999)**

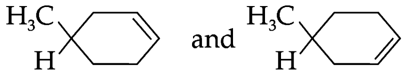
Solution.

(*a*)



(I)

The above compound (I) has following two optically active forms.



(*b*) (*i*) The question is wrong because aniline does undergo Friedel Crafts reaction although the yield is poor. Aniline (base) reacts with Lewis acid ($AlCl_3$) to form $C_6H_5NH_2 . AlCl_3$, and thus resists the attack of carbocation. The formation of carbocation is also hindered because aniline reacts with $AlCl_3$.

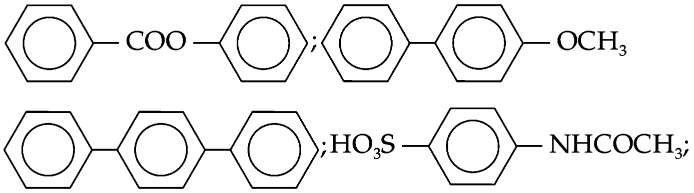
(*ii*) $C_6H_5NH_2 \xrightarrow{NaNO_2\,+\,2HCl\,(\text{excess})} C_6H_5N = NCl$

Excess of HCl is required because reaction needs

HNO_2 and HCl. So, HCl is needed more to get complete reaction. Also, excess of HCl does not allow the coupling of diazonium salt with aniline. The excess of HCl also prevents the hydrolysis of salt formed.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2.$$

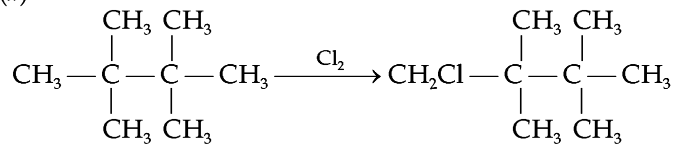
EXAMPLE 133. *(a) An organic compound C_8H_{18} on monochlorination gives a single monochloride. Write the structure of the hydrocarbon. (b) Write the structures of the possible major monosubstituted products formed when Br^+ attacks the following molecules.*



(Roorkee, 1999)

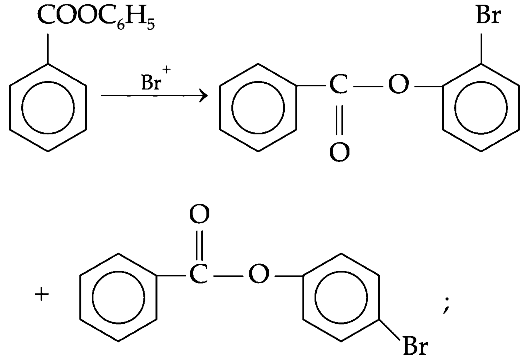
SOLUTION. C_8H_{18} indicates alkane ($C_n H_{2n+2}$). Since, it gives only one monochloride on subsitution, so, there will be all CH_3 groups bonded to C–atoms. Thus.

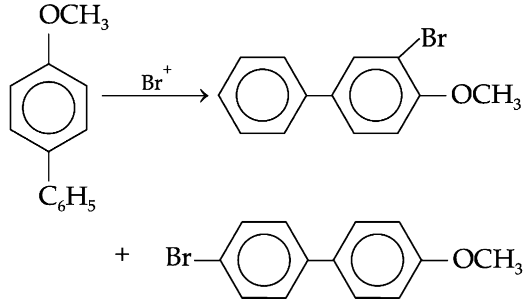
(*a*)

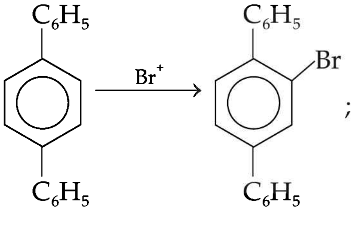


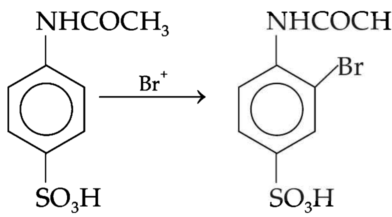
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{Cl_2} CH_2Cl-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

(*b*)







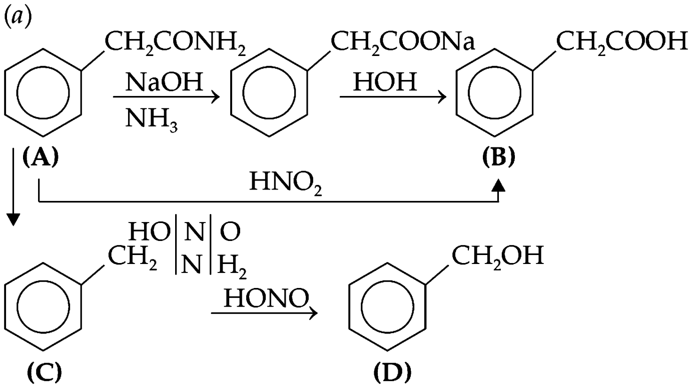


EXAMPLE 134. *An organic compound (A) of molecular weight 135, on boiling with NaOH evolves a gas which gives white dense fumes on bringing a rod dipped in HCl near it. The alkaline solution thus obtained on acidification gives the precipitate of a compound (B) having mol. wt. 136. Treatment of (A) with HNO_2 also yields (B), whereas its treatment with Br_2/KOH gives red colour with ceric ammonium nitrate. On the other hand, (E) an isomer of (A) on boiling with dil. HCl gives an acid (F), having mol. wt. 136. On oxidation followed by heating, (F) gives an anhydride (G) which condenses with benzene in presenece of $AlCl_3$ to give anthraquinone. Give structures of (A) to (G) with proper reasoning.* **(Roorkee, 1996)**

SOLUTION. The organic compound which gives NH_3 on heating with NaOH will contain —$CONH_2$ group. So, (A) compound having mol. wt. 135, should be $C_6H_5CH_2CONH_2$.

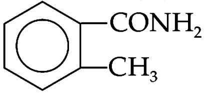
So, reactions are :

(*a*)



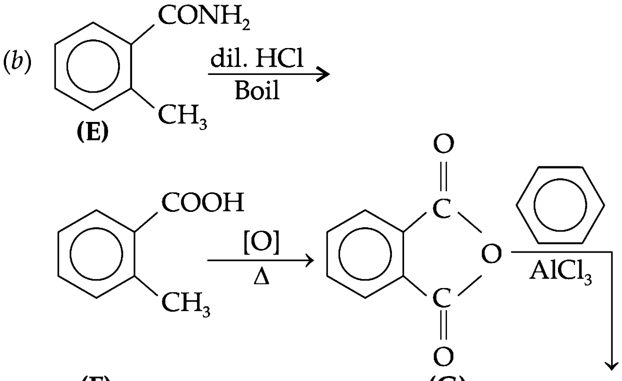
(contains alcoholic group. So, it gives red colour with ceric ammonium nitrate)

Since (E) is an isomer of (A), so (E) will be

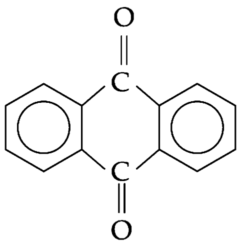


(E)

(*b*)

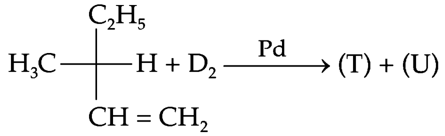


(F) **(G)**

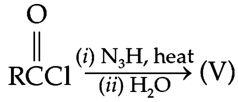


Anthraquinone

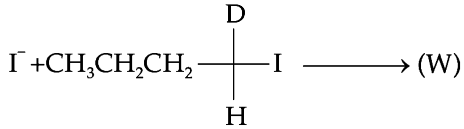
EXAMPLE 135. *Give the structures/configurations of the products (T) to (Z) of the following reactions.*

(*a*) 

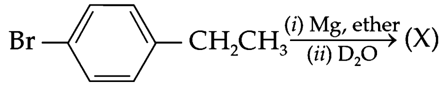
$$H_3C-\overset{C_2H_5}{\underset{CH=CH_2}{C}}-H + D_2 \xrightarrow{Pd} (T) + (U)$$

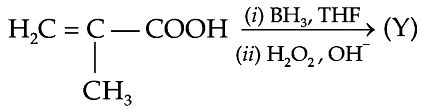
(*b*) 

$$R\overset{O}{\overset{\|}{C}}Cl \xrightarrow[(ii)\ H_2O]{(i)\ N_3H,\ heat} (V)$$

(*c*) 

$$I^- + CH_3CH_2CH_2-\overset{D}{\underset{H}{C}}-I \longrightarrow (W)$$

(*d*) 

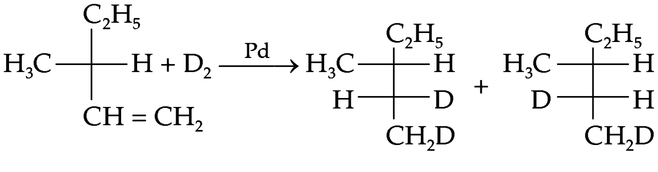
(*e*) 

$$H_2C=\underset{CH_3}{C}-COOH \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ BH_3,\ THF} (Y)$$

(*f*) $2HC \equiv CH \xrightarrow[O_2]{Cu^{2+}} (Z)$

SOLUTION.

(*a*)



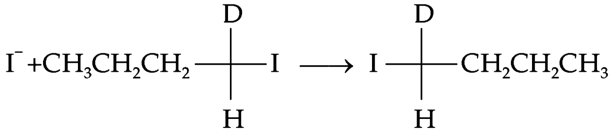
$$H_3C-\overset{C_2H_5}{\underset{CH=CH_2}{C}}-H + D_2 \xrightarrow{Pd} H_3C-\begin{array}{c}C_2H_5\\ C \\ C \\ CH_2D\end{array}\begin{array}{l}\\ -H\\ -D\\ \\\end{array} + H_3C-\begin{array}{c}C_2H_5\\ C \\ C \\ CH_2D\end{array}\begin{array}{l}\\ -H\\ -H\\ \\\end{array}$$

(T) **(U)**

(*b*) $RCOCl \xrightarrow[(ii)\ H_2O]{(i)\ N_3H,\ \Delta} RNH_2$

(V)

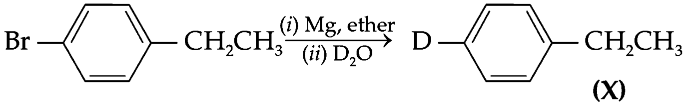
(*c*)



$$I^- + CH_3CH_2CH_2-\overset{D}{\underset{H}{C}}-I \longrightarrow I-\overset{D}{\underset{H}{C}}-CH_2CH_2CH_3$$

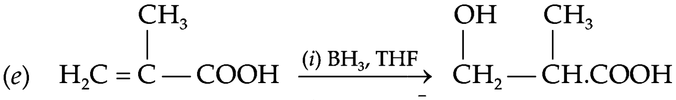
(W)

(*d*)



(X)

(*e*)



$$H_2C=\overset{CH_3}{C}-COOH \xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ BH_3,\ THF} \overset{OH}{CH_2}-\overset{CH_3}{CH}.COOH$$

(Y)

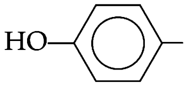
(*f*) $2CH \equiv CH \xrightarrow[O_2]{Cu^{2+}} HC \equiv C-C \equiv CH$

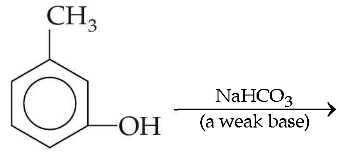
(Z)

EXAMPLE 136. *Compound (A) C_7H_8O is insoluble in aqueous sodium bicarbonate but dissolves in equeous sodium hydroxide and gives a characteristic colour with aqueous ferric chloride. When treated with bromine, (A) forms a compound (B) $C_7H_5OBr_3$*

(*i*) *Give structural formula of (A) and (B)*

(*ii*) *What would be the structure of (A) if it neither dissolves in aqueous sodium hydroxide nor gives a characteristic colour with $FeCl_3$.* **(Roorkee, 1993)**

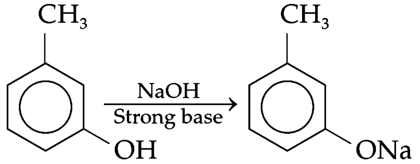
SOLUTION. Since (A) is insoluble in $NaHCO_3$ but dissolves in NaOH; also gives characteristic colour with $FeCl_3$ (aq), so, (A) has a phenolic group, –OH. Also, (A) forms $C_7H_5OBr_3$ with Br_2. Considering molecular formula of (A), (A) appears to have CH_3 group. So, we have; $C_6H_4(CH_3)$ (OH) *i.e.*, cresol. Considering bromination, (A) can be  because meta position can form tribromoderivative as shown below.

(*i*) 

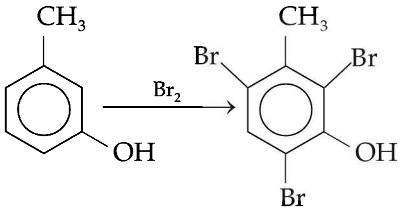
no reaction as NaHCO$_3$ is a weak base.

m-cresol

(A)

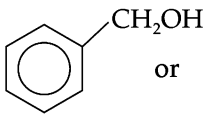
(*ii*) 

(A)

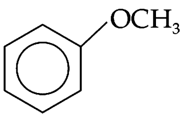
(*iii*) 

(B)

(*iii*) If (A) neither dissolves in NaOH (aq) nor gives characteristic colour with $FeCl_3$, it will be a neutral compound. So, (A) can be



or



Benzyl alcohol Methoxy benzene or anisol

EXAMPLE 137. *(A), (B), (C), (D), (E), (F), and (G) are amines, each of which forms a hydrochloride containing 32.42% chlorine. (A), (B), (C) and (D) evolve N_2 on reaction with HNO_2 but (E), (F) and (G) donot. Give structures of (A) to (G) with reasons.* **(Roorkee, 2001)**

SOLUTION. Amines hydrochloride = C_nH_{2n+3}. N. HCl

Also, since all amines have fixed Cl = 32.42%, so :

For 32.42 Cl, amine = (100 – (32.42 + 1) = 66.58

[∵ HCl = 1 + 32.42 (given)]

$$\text{For 35.5 Cl, amine} = \frac{66.58 \times 35.5}{32.42} = 72.9$$

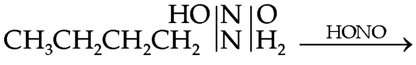
∴ In C_nH_{2n+3} N ; 12n + 1(2n + 3) + 14

= 72.9 ; 14n = 55.9 ≃ 56 ; *n* = 4

∴ Amine = $C_4H_{11}N$.

The expected isomers will be on the basis that some amines evolve N_2 with HNO_2 *i.e.*, some are primary amines which will have NH_2 group. Thus :

(*i*)

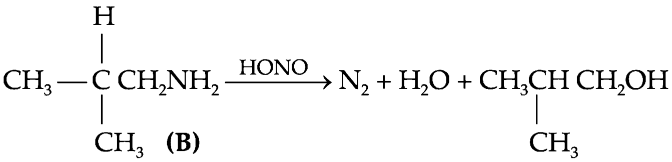


$$CH_3CH_2CH_2CH_2\,\overset{HO}{N}\overset{N}{N}\overset{O}{H_2} \xrightarrow{HONO}$$

(A)

$N_2 + H_2O + CH_3CH_2CH_2CH_2OH$

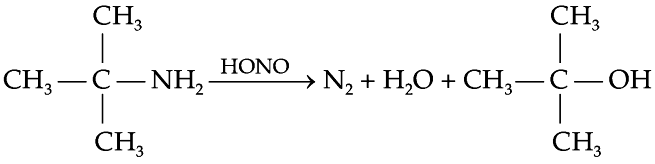
(*ii*)



$$CH_3-\underset{CH_3}{\overset{H}{C}}CH_2NH_2 \xrightarrow{HONO} N_2 + H_2O + CH_3\underset{CH_3}{CH}\,CH_2OH$$

(B)

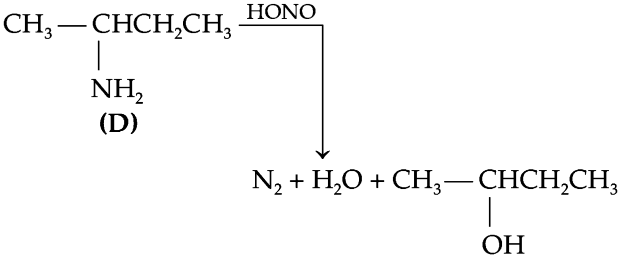
(*iii*)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-NH_2 \xrightarrow{HONO} N_2 + H_2O + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

(C)

(*iv*)

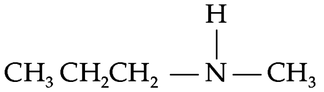


$$CH_3-\underset{NH_2}{CH}CH_2CH_3 \xrightarrow{HONO} N_2 + H_2O + CH_3-\underset{OH}{CH}CH_2CH_3$$

(D)

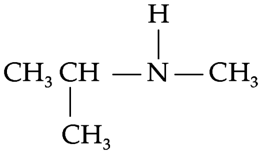
Other amines which donot give N_2 with HNO_2 will be 2° and 3° amines. Thus, we have.

(*v*)



$$CH_3CH_2CH_2-\overset{H}{N}-CH_3$$

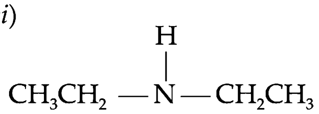
or



$$CH_3\underset{CH_3}{CH}-\overset{H}{N}-CH_3$$

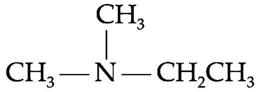
(E) **(E)**

(*vi*)



$$CH_3CH_2-\overset{H}{N}-CH_2CH_3$$

or



$$CH_3-\overset{CH_3}{N}-CH_2CH_3$$

(F)

EXAMPLE 138. *The percentage of carbon, hydrogen and nitrogen in a disubstituted aromatic compound (A) is 71.11, 6.67 and 10.37 respectively. Its molecule contains a single atom of nitrogen. Compound (A) evolves NH_3 when heated with NaOH to form salt (B), from which an acid (C) is obtained on acidification. If an electrophilic substitution is carried on (C), an entering electrophile can occupy either of the two identical positions available in the ring. Acid (C) on heating with PCl_5, gives (D) which reacts with (B) to give an organic product (E). Give structures of (A) to (E) with proper reasoning.*

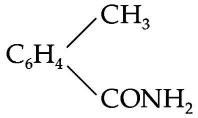
(Roorkee, 1996)

SOLUTION. (*i*) To find empirical formula of (A)

Element	% age	At. wt.	Relative no. of atoms = % age/at. wt.	Simple ratio	Whole no. ratio
C	71.11	12	$\frac{71.11}{12} = 5.92$	$\frac{5.92}{0.74} = 8$	8
H	6.67	1	$\frac{6.67}{1} = 6.67$	$\frac{6.67}{0.74} = 9$	9
N	10.37	14	$\frac{10.37}{14} = 0.74$	$\frac{0.74}{0.74} = 1$	1
O	100 – (71.11 + 6.67 + 10.37) = 11.85	16	$\frac{11.85}{16} = 0.74$	$\frac{0.74}{0.74} = 1$	1

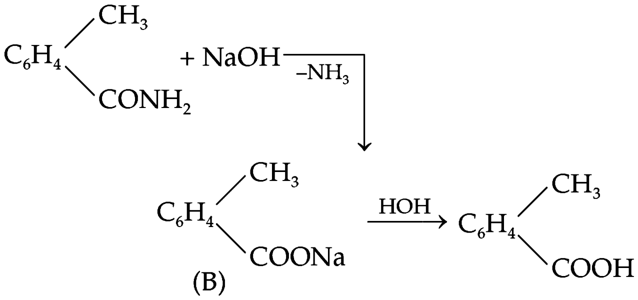
∴ E.F. = C_8H_9NO

(*ii*) Since (A) gives NH_3 when heated with NaOH, it will contain $-CONH_2$ group. Hence (A) is expected to be



$$C_6H_4\begin{matrix} CH_3 \\ CONH_2 \end{matrix}$$

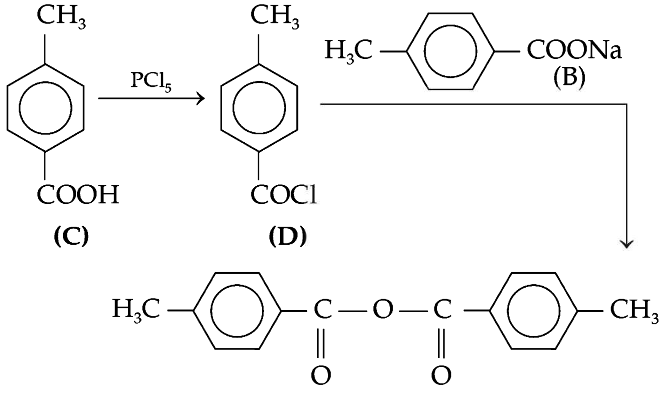
Reaction.



$$C_6H_4\begin{matrix} CH_3 \\ CONH_2 \end{matrix} + NaOH \xrightarrow{-NH_3} C_6H_4\begin{matrix} CH_3 \\ COONa \end{matrix} \xrightarrow{HOH} C_6H_4\begin{matrix} CH_3 \\ COOH \end{matrix}$$

(B)

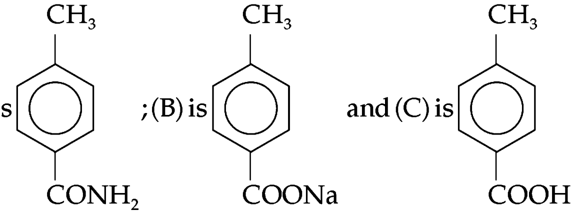
(*iii*) Since (C) on electrophilic substitution gives one product only, (C) will be para derivative. So, we have :



(C) **(D)**

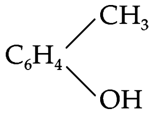
(E)

∴ (A) is ;(B) is and (C) is

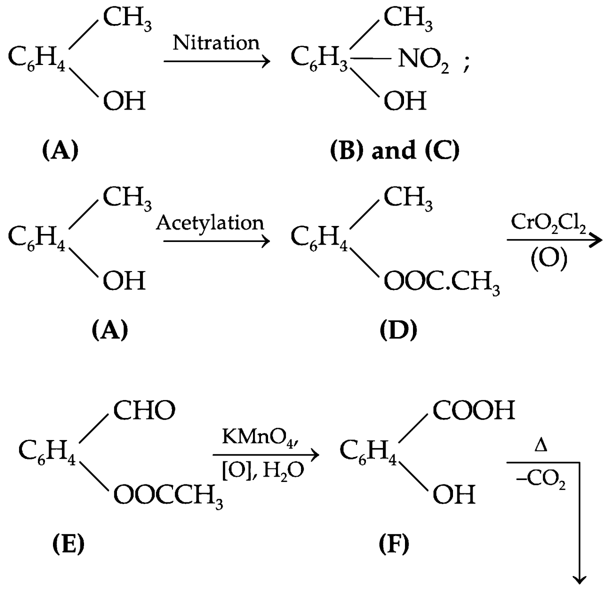


Example 139. *Two isomeric mononitroderivatives (B) and (C) are obtained by the nitration of an organic compound (A), C_7H_8O. Treatment of (A) with acetyl chloride produces (D), which on reaction with CrO_2Cl_2 gives (E) whose oxidation with neutral $KMnO_4$ followed by acdificaton gives, (F). The compound (F) on heating gives phenol. (A) on treatment with alkaline $C_6H_5SO_2Cl$ produces (G) which on oxidation with $KMnO_4$ gives (H). Hydrolysis of (H) also gives (F). Give structures of (A) to (H) with proper reasoning.* **(Roorkee, 1996)**

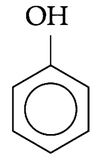
Solution. The reactions given in question suggest that C_7H_8O should contain a C_6H_4 group *i.e.*, (A) can be



$C_6H_4(CH_3)(OH)$ Thus :

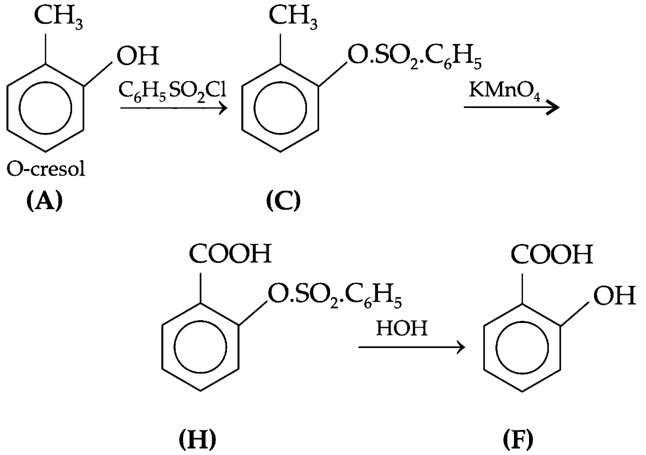


C_6H_5OH or

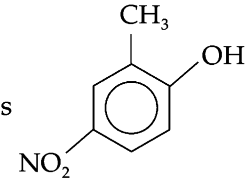


Phenol

It is given that (F) on heating gives phenol. So, (F) is orthoderivative and it is salicylic acid. Hence, (A), (D) and (E) are orthoderivatives, as shown below

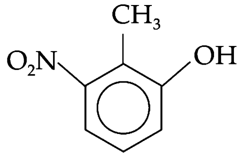


Similarly, **(B)** is



;

(C) is



Example 140. *An organic compound (A), $C_9H_{12}O$ was subjected to a series of tests in the laboratory. It was found that this compound*

(*i*) *rotates the plane of polarised light*

(*ii*) *evolves H_2 with sodium*

(*iii*) *reacts with I_2 and NaOH to produce a pale yellow solid compound*

(*iv*) *does not react with Br_2/CCl_4*

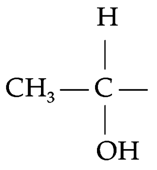
(*v*) *reacts wth hot $KMnO_4$ to form compound (B) $C_7H_6O_2$ which can also be synthesised by the reaction of benzene and carbonyl chloride followed by hydrolysis*

(*vi*) *loses optical activity as a result of formation of compound (C) on being heated with HI and P*

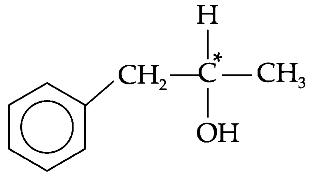
(*vii*) *reacts with Luca's reagent in about 5 minutes.*

Give structures of (A) to (C) with proper reasoning and draw Fischer projections for (A). Give reactions for steps, wherever, necessary. **(Roorkee, 1999)**

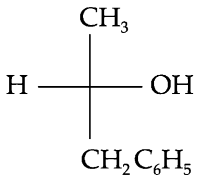
Solution. (*i*) Since the compound (A), $C_9H_{12}O$ rotates the plane of polarised light, it will have an asymmetric C*–atom. It forms iodoform (yellow ppt.) with NaOH and

I_2, it will have  $CH_3—\underset{OH}{\overset{H}{C}}—$ group. which also gives H_2 with Na(due to – OH group).

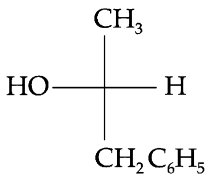
So, (A) can be



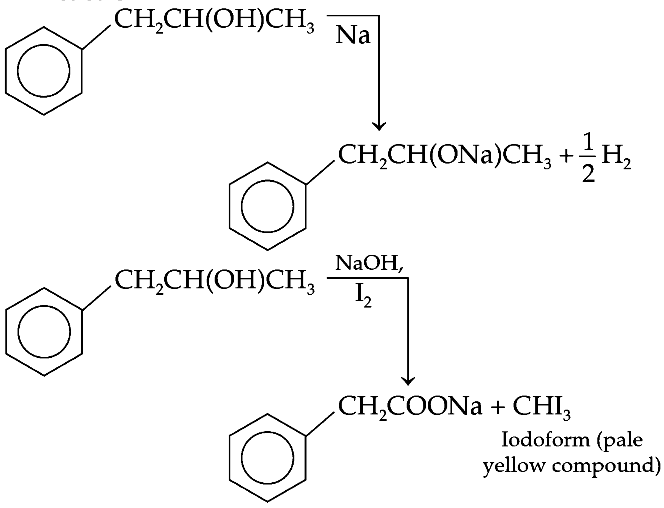
or



and

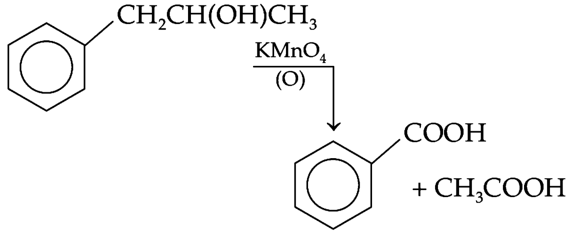


Reaction.

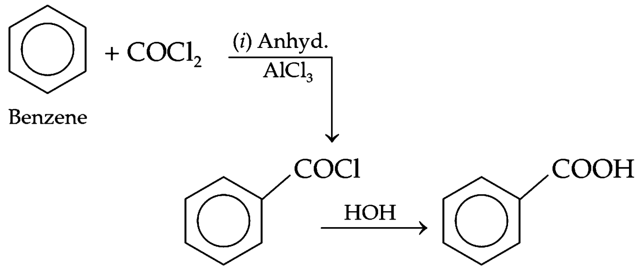


(*ii*) It does not react with Br_2/CCl_4

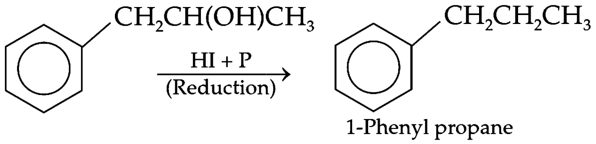
(*iii*)



Also,



(*iv*)



1-Phenyl propane (optically inactive)

(*v*) Since (A) reacts with Lucas reagent in about 5 minutes, it will contain secondary alcoholic group, – CHOH

EXAMPLE 141. *An organic compound (A) containing C = 81.6%, H = 4.8%, N = 13.6% has vapour density 51.5. It gives off ammonia upon heating with KOH. Reaction of (A) with Na and ethanol gives a basic compound (B) which gives off N_2 and forms an alcohol (C) when reacted with HNO_2. The alcohol (C) can be oxidised to benzoic acid. Identify (A). (B) and (C) and explain the reactions.* **(UPSEAT, 1994)**

SOLUTION. (*i*) To find empirical formula of (A) compound.

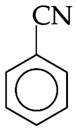
Element	% age	At. wt.	Relative no. of atoms = % age/ at. wt.	Simple ratio	Whole no. ratio
C	81.6	12	$\frac{81.6}{12}=6.8$	$\frac{6.8}{0.97}=7$	7
H	4.8	1	$\frac{4.8}{1}=4.8$	$\frac{4.8}{0.97}=5$	5
N	13.6	14	$\frac{13.6}{14}=0.97$	$\frac{0.97}{0.97}=1$	1

$\therefore$ E.F. = C_7H_5N ;

$$\text{E.F. wt.} = (7 \times 12) + (5 \times 1) + (1 \times 14) = 103$$

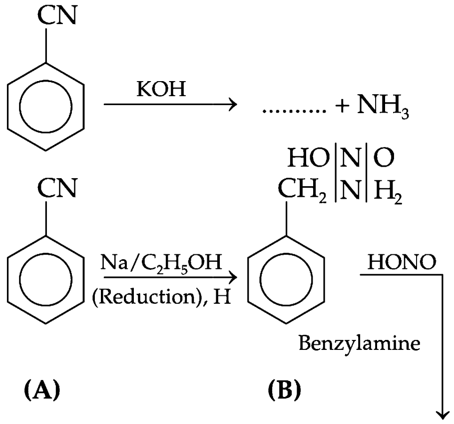
$$\text{M.F.} = \frac{\text{Mol. wt.}}{\text{E.F. wt}} \times \text{E.F.} = \frac{2 \times \text{V.D}}{\text{E.F. wt.}} \times \text{E.F.}$$

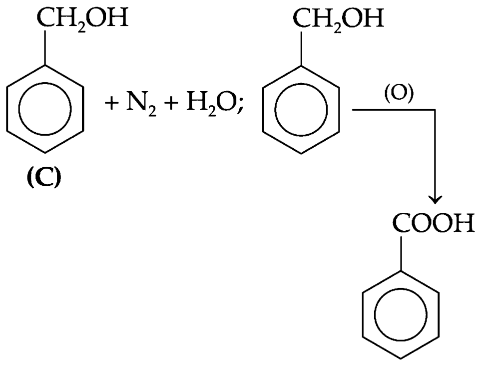
$$= \frac{2 \times 51.5}{103} \times C_7H_5N = C_7H_5N$$

$\therefore$ (A) can be 

Since (A) gives off NH_3 on heating with KOH, it can have —CN group.

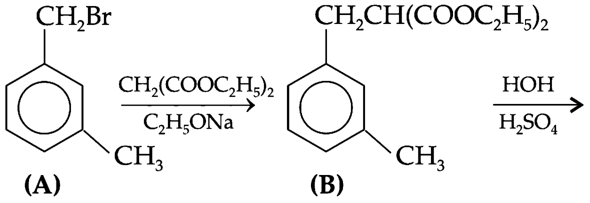
(*ii*) The reactions can be :

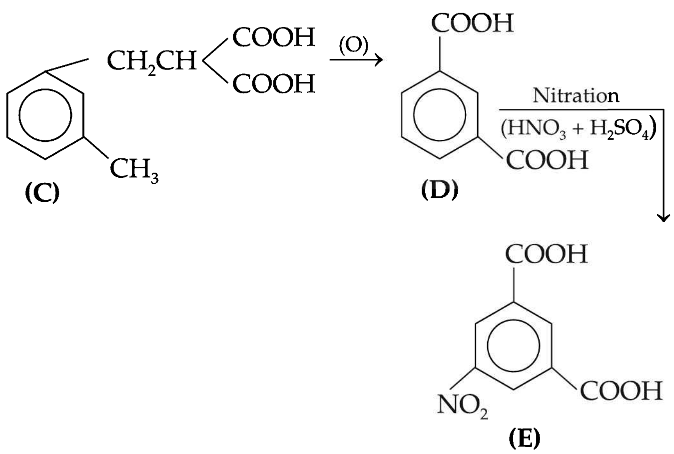




EXAMPLE 142. *An aromatic compound (A), C_8H_9Br reacts with $H_2C\ (COOC_2H_5)_2$ in the presence of C_2H_5ONa to give (B). Compound (B) on refluxing with dil. H_2SO_4 gives (C) which on vigorous oxidation gives (D). The compound (D) is a dibasic acid but on heating does not give an anhydride. It forms a mononitro-derivative (E), in which all the substituents are at equidistant from one another. Give structures of (A) to (E) with proper reasoning.* **(Roorkee, 1998)**

SOLUTION. The molecular formula of (A), C_8H_9Br indicates that the substituents are bonded to the benzene ring. Since it reacts with a bulky group $CH_2(COOC_2H_5)_2$ and other given data, the substituents are expected at meta position. Thus :



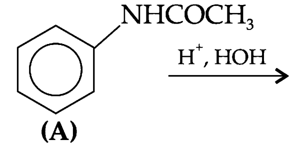


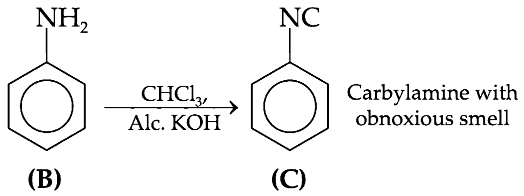
Since (E) is mono-nitroderivative in which all the substituents are at equidistant from each other, it will be a symmetrical trisubstituted (1, 3, 5) product indicating that the two substituents in compounds (A) to (D) are at the meta position.

EXAMPLE 143. *A colourless substance (A) is sparingly soluble in water and gives (B) on heating with mineral acids. Compound (B) on reaction with $CHCl_3$ and alcoholic potash produces an obnoxious smell of carbylamine due to the formation of (C). Compound (A), on reaction with chlorosulphonic acid gives (D) which on treatment with ammonia gives (E). Compound (E) on acid hydrolysis gives sulphanilamide, a well known drug. Give structures of (A) to (E) with proper reasoning.* **(Roorkee, 1998)**

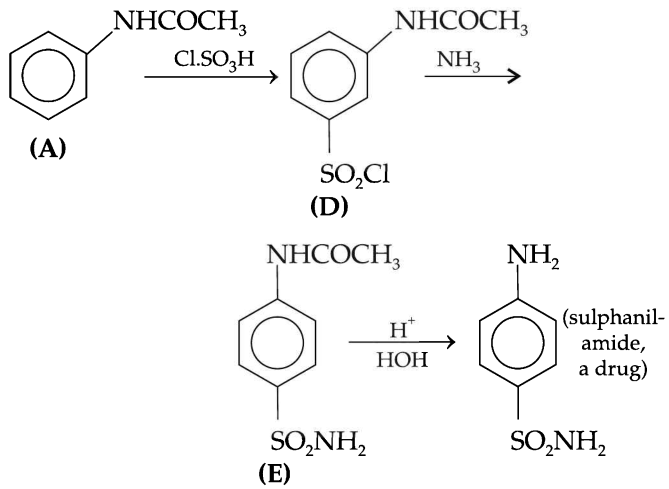
SOLUTION. Since the compound (C) having unpleasant smell is formed by the action of (A) on $CHCl_3$/alc. KOH, (A) should have NH_2 group (1°–amine). Since (A) gives a mineral acid on heating and (A) is also, insoluble in water, it is expected to be acetanilide. So, we have :

(*i*)

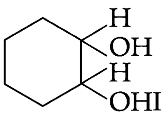
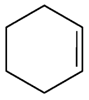
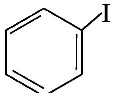
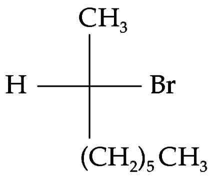
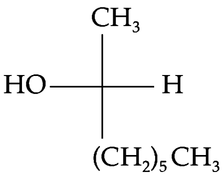


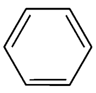


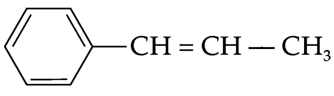
(*ii*)

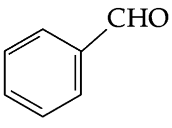


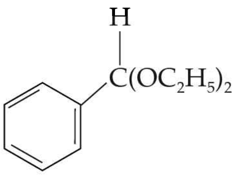
EXAMPLE 144. *Structures of some reactants and products are given in columns I and II respectively. Firstly match the appropriate reactant product pair from columns I and II and then suggest another suitable reagent for each pair.*

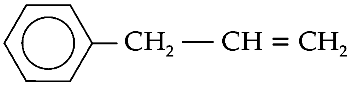
Column I		**Column II**	
(*a*)	$R—CH=CH_2$	(*i*)	
(*b*)		(*ii*)	
(*c*)		(*iii*)	

(d)


(iv)


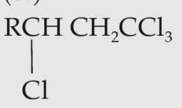
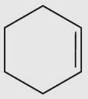
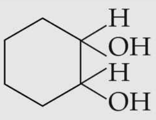
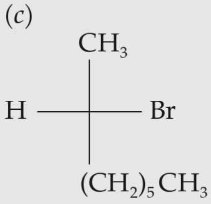
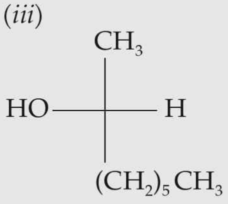
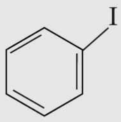
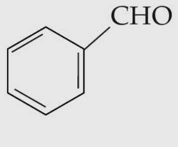
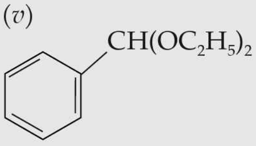
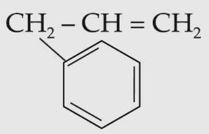
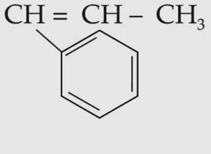
(e)


(v)


(f)


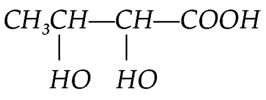
(vi) R — $CHClCH_2CCl_3$ **(Roorkee, 2003)**

SOLUTION.

Column I	Column II	Other Reagent
(*a*) R—CH = CH_2	(*vi*)  $\underset{\displaystyle Cl}{RCH}\,CH_2CCl_3$	CCl_4/ Peroxide
(*b*) 	(*i*) 	HCOOH or Baeyer's reagent or OsO_4 (aq) + $NaHSO_3$
(*c*) 	(*iii*) 	KOH(aq)
(*d*) 	(*ii*) 	ICl or I_2 + HNO_3
(*e*) 	(*v*) 	C_2H_5OH + dry HCl
(*f*) 	(*iv*) 	KOH + heat

EXAMPLE 145. *Read the statements given below and write 'true' against correct statements. If any of the statements is wrong, rectify the mistake/mistakes and give a correct statement in its place*

(*a*) *Tollen's reagent converts* $CH_3CH = CH—CHO$ *to*



$$\underset{\displaystyle HO}{CH_3CH}—\underset{\displaystyle HO}{CH}—COOH$$

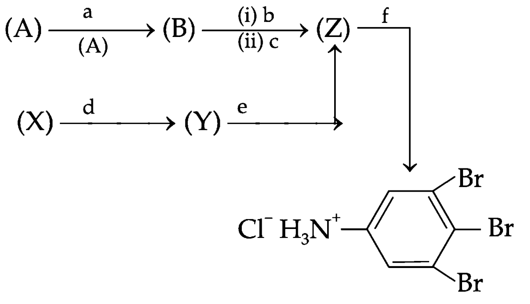
(*b*) *Total number of optical isomers of 3, 4 –dichlorohexane is 3.*

(*c*) *When heated with dil.* H_2SO_4, $C_6H_5\,SO_3H$ *undergoes further sulphonation to give* $C_6H_4\,(SO_3H)_2$.

(*d*) *Addition of HI to 3, 3 – dimethyl - 1- butene not only gives 1-iodo-3, 3-dimethyl butane but also 2-iodo-2, 3-dimethyl butane.* **(Roorkee, 2001)**

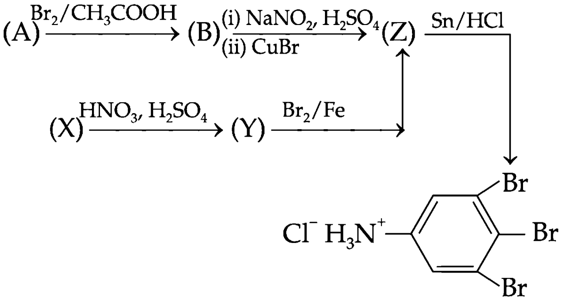
SOLUTION. (*a*) It is not true because Tollen's reagent converts $CH_3CH = CH—CHO$ to $CH_3CH = CH\,COOH$. (*b*) It is true (*c*) It is not correct because desulphonation takes place to form benzene. (*d*) It is not correct because it not only gives 3-iodo-2, 2-dimethyl butane but also 2-iodo-2, 3-dimethyl butane or 3-iodo-2, 3-dimethyl butane.

EXAMPLE 146.

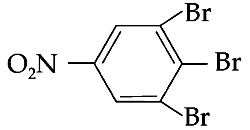


Give structures of (A), (B), (X), (Y) and (Z) in the above scheme of reactions. If reagents a, b, c, d, e and f are Br_2/ CH_3COOH, $NaNO_2/H_2SO_4$ + CuBr, HNO_3/H_2SO_4, Br_2/Fe *and Sn/HCl respectively.* **(Roorkee, 2001)**

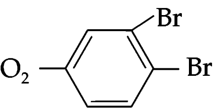
SOLUTION.



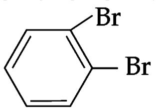
(*i*) Since last compound obtained by the reduction of (Z) with Sn/HCl,(Z) should contain $–NO_2$ group in place of $Cl^-–H_3N^+$. So :

(Z) is


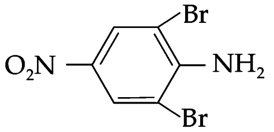
(*ii*) Since (Z) is obtained by the action of (Y) on Br_2/ Fe, (Y) should have one Br-atom less than (Z). So :

(Y) is


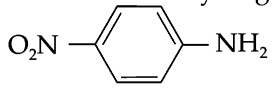
(*iii*) Since (Y) is obtained by the nitration of (X), so (X) should have no $–NO_2$ group. hence:

(X) is


(*iv*) Since (Z) is obtained by the action of (*i*) $NaNO_2$ + H_2SO_4 and (*ii*) Cu Br, (B) should also contain $-NH_2$ group. So :

(B) is 

(*v*) Since (B) is obtained by the bromination of (A), so (A) should not have any Br group. So :

(A) is 

EXAMPLE 147. *A hydrocarbon (A) of molecular weight 54 reacts with an excess of Br_2 in CCl_4 to give a compound (B) whose molecular weight is 593% more than that of (A). However, on catalytic hydrogenation, with excess of hydrogen, (A) forms (C) whose molecular weight is only 7.4% more than that of (A). (A) reacts with CH_3CH_2Br in the presence of $NaNH_2$ to give another hydrocarbon (D) which on ozonolysis yields diketone (E). (E) on oxidation gives propionic acid. Give structures of (A) to (E) with reasons.* **(Roorkee, 1997)**

SOLUTION. Step1. Calculation of molcular mass of (B) and (C)

The mol. wt. of compound A = 54

Mol. wt. of compound (B) formed by treatment of A

$$\text{with } Br_2 \text{ in } CCl_4 = \frac{(100+593)}{100} \times 54 = 374.22$$

Thus the increase in weight due to addition of Br atoms

$$= 374.22 - 54.0 = 320.22$$

Therefore, the number of bromine atoms added

$$= \frac{320.22}{80} = 4 \quad [\because \text{ At. wt. of Br} = 80]$$

Hence, the hydrocarbon must be an alkyne.

Mol. wt. of compound (C) formed by hydrogenation of A

$$= \left(\frac{100+7.4}{100}\right) \times 54 = 57.994$$

$$= 58 \text{ (approx)}$$

Thus, the increase in weight due to addition of H atoms

$$= 58 - 54 = 4$$

$$\text{Number of H-atoms added} = \frac{4}{1} = 4$$

This also suggests that hydrocarbon A must be an alkyne.

Step 2. *Structures of (A), (B), (C) and (D)*

Molecular formula of an alkyne having molecular mass

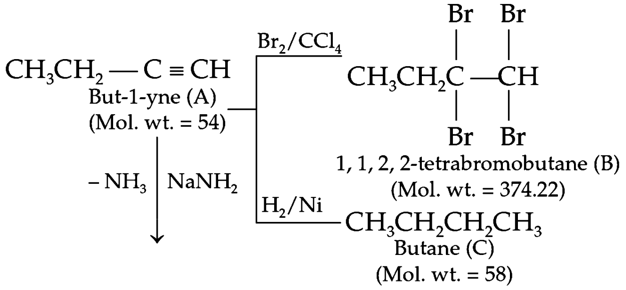
$$54 = C_4H_6$$

Two possible structures for an alkyne are :

$$\underset{\text{But-1-yne}}{CH_3CH_2C\equiv CH} \qquad \underset{\text{But-2-yne}}{CH_3\text{—}C\equiv C\text{—}CH_3}$$

Since (A) reacts with CH_3CH_2Br in presence of Na NH_2 to give another hydrocarbon (D), therefore (A) must be But-1-yne which is a terminal alkyne.

Considering (A) as But-1-yne, the structures of (B), (C) and (D) can be derived as follows:

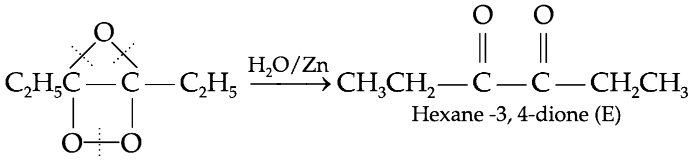


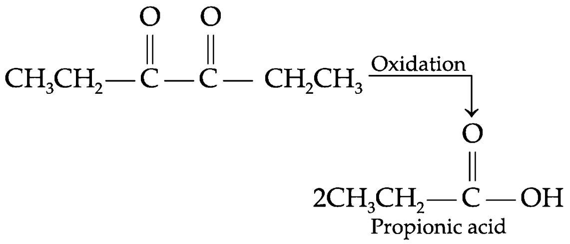
$$CH_3CH_2—C\equiv C^- Na^+ \xrightarrow[-\text{Na Br}]{CH_3CH_2Br} \underset{\text{Hex-3-yne (D)}}{CH_3CH_2C\equiv C.\,CH_2CH_3}$$

Step 3. *Structure of diketone E*

Since the hydrocarbon (D) *i.e.*, Hex-3-yne on ozonolysis gives a diketone (E), which on further oxidation gives propionic acid, therefore, E must be hexane-3, 4-dione as explained below :

$$CH_3CH_2C\equiv C.\,CH_2CH_3 \xrightarrow{O_3}$$





Thus A = but-1-yne, B = 1, 1, 2, 2-tetrabromobutane, C = Butane, D = Hex-3-yne, E = Hexane-3, 4-dione.

EXAMPLE 148. *Compound (A) with molecular weight 108 contained 88.89% C and 11.11% H. It gave a white precipitate with ammoniacal silver nitrate. Complete hydrogenation of (A) gave another compound (B) with molecular weight 112. Oxidation of (A) gave an acid with equivalent weight 128. Decarboxylation of acid gave cyclohexane. Give structures of (A) and (B) and write the equations of the reactions involved.* **(Roorkee, 1988)**

SOLUTION. Calculation of empirical formula

Element	% age	Atomic mass	Relative no. of atoms = % age/at. mass	Simplest ratio	Simple Whole no. ratio
C	88.89	12	$\frac{88.89}{12} = 7.4$	$\frac{7.4}{7.4} = 1$	1 × 2 = 2
H	11.11	1	$\frac{11.11}{1} = 11.11$	$\frac{11.11}{7.4} = 1.5$	1.5 × 2 = 3

∴ Empirical formula = C_2H_3

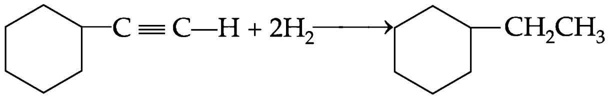
Empirical formula wt. = $2 \times 12 + 1 \times 3 = 27$

Molecular wt. = 108

$n = 108/27 = 4$

∴ Molecular formula = $n \times \text{E.F.} = 4 \times C_2H_3 = C_8H_{12}$(A)

As the hydrocarbon (A) gives white ppt. with $AgNO_3$, it should be an alkyne which on hydrogenation should give C_8H_{16} (B) having molecular weight 112. Oxidation of (A) gave an acid having equivalent weight 128 which on decarboxylation gave cyclohexane. Hence (A) is hydrocarbon having six membered ring and an unsaturated side chain. The structures of A and B and the reactions involved are :



EXAMPLE 149. *448mL of hydrocarbon (A) having C, 87.80% ; H, 12.19% weigh 1.64g at STP. On hydrogenation it gives 2-methylpentane. Treatment of (A) with acidic $HgSO_4$ gives a new compound (B) having molecular formula $C_6H_{12}O$. Compound (A) does not react with ammoniacal $AgNO_3$. Find out the structure of (A) and explain the reactions involved.*

(Roorkee, 1989)

SOLUTION. 448mL of (A) at STP weighs 1.64g.

$$22400\text{mL of A at STP weigh} = \frac{1.64}{448} \times 22400 = 82\text{g}$$

∴ Molecular weight of A = 82

Calculation of empirical formula

Element	% age	Atomic mass	Relative no. of atoms = % age/at. mass	Simple ratio	Whole no. ratio
C	87.8	12	87.8/12 = 7.31	7.31/7.31 = 1	1 × 3 = 3
H	12.19	1	12.19/1 = 12.19	12.19/7.31 = 1.66	1.66 × 3 = 4.98 ≃ 5

Empirical formula = C_3H_5

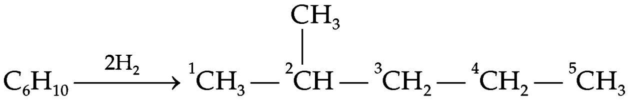
Empirical formula mass = $12 \times 3 + 1 \times 5 = 41$

$$n = \frac{\text{Mol. mass}}{\text{Emp. formula mass}} = \frac{82}{41} = 2$$

∴ Molecular formula of

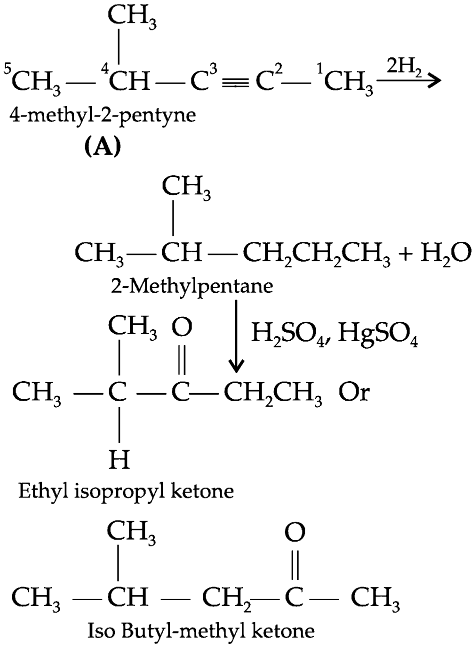
$$A = n \times \text{E.F.} = 2 \times C_3H_5 = C_6H_{10}$$

Treatment of (A) with acidic $HgSO_4$ gives (B) having molecular formula $C_6H_{10}O$. Conversion of (A) to (B) involves the addition of a water molecule and is a characteristic reaction of alkyne. Hence (A) is an alkyne. Further (A) does not react with ammonical $AgNO_3$ indicating the absence of a terminal carbon-carbon triple bond. The exact position of the triple bond in (A) is established by the fact that (A) on hydrogenation gives 2-methylpentane.



$$C_6H_{10} \xrightarrow{2H_2} {}^{1}CH_3-{}^{2}\underset{}{\overset{CH_3}{\overset{|}{C}H}}-{}^{3}CH_2-{}^{4}CH_2-{}^{5}CH_3$$

Since triple bond is not possible between C_2 and C_3 and hence it must be between C_3 and C_4. Thus the compound (A) is 4-methyl-2-pentyne which explains all the given reactions.



27.5 AIEEE PATTERN EXAMPLES

EXAMPLE 150. *Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled as A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dil. HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this statement ?*

(*i*) *Addition of HNO_3 was unnecessary*

(*ii*) *A was C_6H_5I*

(*iii*) *A was $C_6H_5CH_2I$*

(*iv*) *B was C_6H_5I* **(AIEEE, 2003)**

SOLUTION. According to the given data, we have :

(*i*) $C_6H_5I \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{HNO_3} C_6H_5OH \xrightarrow{AgNO_3}$ No yellow ppt.

(*ii*) $C_6H_5CH_2I \xrightarrow{NaOH} C_6H_5CH_2ONa$

So, A is C_6H_5I and B is $C_6H_5CH_2I$.

EXAMPLE 151. *An aromatic compound 'Y' having molecular formula C_7H_7NO produces ammonia on heating with alkali. When Y is treated with bromine and alkali, the product will be :*

(*a*) *Aniline* (*b*) *Benzonitrile*

(*c*) *Benzoic acid* (*d*) *Benzamide.*

Solution. The compound produces ammonia on heating with alkali. So, C_7H_7NO must be an amide *i.e.*, benzamide. Since amide is treated with Br_2 and alkali, it must be Hofmann bromamide reaction to form aniline.

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + NaOH \xrightarrow{\text{Boil}} C_6H_5COONa + NH_3$$

$$C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} C_6H_5NH_2 \text{ (aniline)}$$

Example 152. *An alkene with molecular formula C_8H_{16} on oxidation with hot $KMnO_4$ gives acetone and 3-pentanone. The structure of the alkene is :*

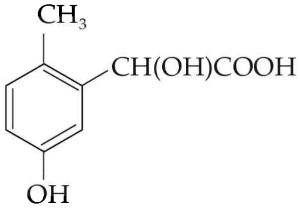
(*a*) $(CH_3)_2C = C(C_2H_5)_2$
(*b*) $(CH_3)(C_2H_5)C = C(CH_3)(C_2H_5)$
(*c*) $CH_3CH_2CH_2CH = C(C_2H_5)_2$
(*d*) $(CH_3)_2C = CH(CH_2)_3CH_3$

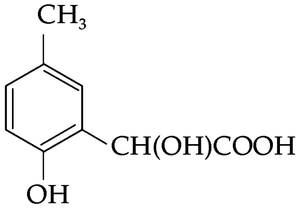
Solution. Since the given compound is alkene and it gives a mixture of ketones, the alkene must have undergone ozonolysis followed by action with H_2O. For such an ozonide reaction, the O–atoms of both keto groups facing each other are removed to get the unknown alkene. So, we have

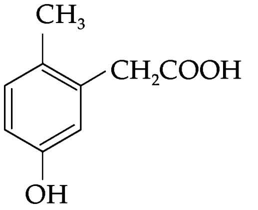
$$\underset{\text{Acetone}}{(CH_3)_2C =}\boxed{O + O}\underset{\text{Pentanone}}{= C(C_2H_5)_2} \longrightarrow (CH_3)_2C = C(C_2H_5)_2$$

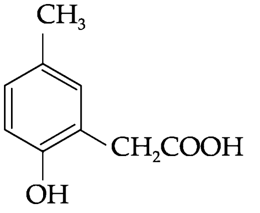
So, the correct answer is, (*a*).

Example 153. *p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is :*

(*a*)


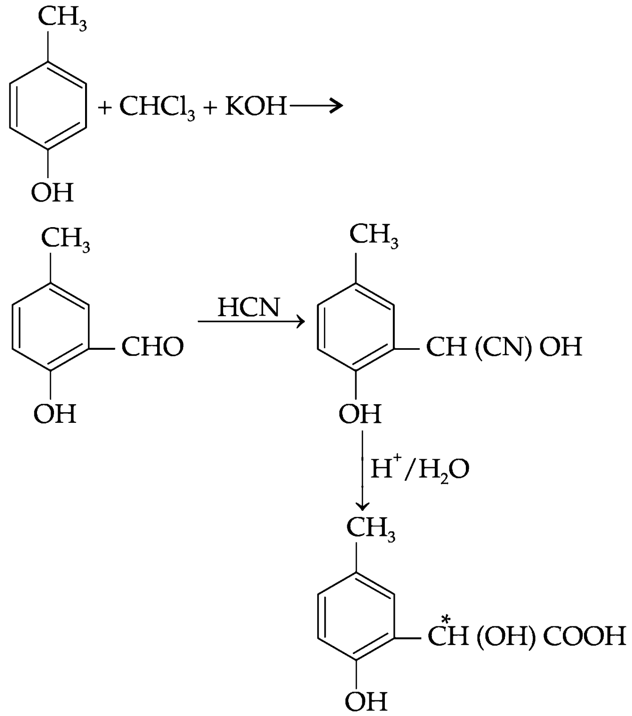
(*b*)


(*c*)


(*d*)


(AIEEE, 2005)

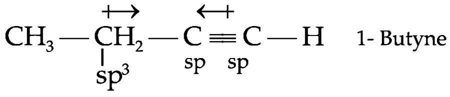
Solution.



So, the correct answer is (*b*)

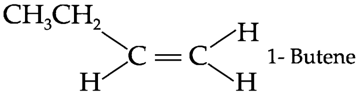
Example 154. *Which of the following has larger dipolemoment? Explain; 1-Butyne or 1-Butene.* **(Roorkee, 1999)**

Solution. Dipolemoment is a vector quantity. The direction of dipolemoment of individual bonds in 1-Butyne and 1-Butene are shown below :



$$CH_3 — \underset{sp^3}{\overset{+\!\!\rightarrow}{CH_2}} — \underset{sp}{\overset{\leftarrow\!\!+}{C}} \equiv \underset{sp}{C} — H$$

1- Butyne



1- Butene

In case of 1-Butyne, the resultant or net dipolemoment is due to the dipolemoments of C—H and CH_3CH_2—C bonds. These oppose each other. Since *sp* hybridised carbon atom is more electronegative than sp^2 carbon, we say that CH_3—CH_2—C (*sp*) is more polar than that of $CH_3—\underset{sp^3}{CH_2}—C(sp^2)$ in 1-Butene. Hence, 1-Butyne has more dipolemoment than that of 1-Butene.

Example 155. *When 32.25g of ethyl chloride is subjected to dehydrohalogenation reaction, the yield of the alkene formed is 50%. The mass of product formed is (atomic mass of chlorine is 35.5):*

(*a*) *14g* (*b*) *28g*
(*c*) *64.5g* (*d*) *56g*
(*e*) *7g*.

(Kerala PET, 2005)

Solution. Reaction

$$C_2H_5Cl \xrightarrow{-HCl} C_2H_4$$

$$(2 \times 12) + (5 \times 1) + 35.5 \qquad (2 \times 12) + (4 \times 1)$$

$$= 64.5g \qquad = 28g$$

Alkene C_2H_4 formed = 50%

Wt. of ethyl chloride = 32.25g

64.5g C_2H_5Cl form C_2H_4 = 28g

$$32.25\text{g } C_2H_5Cl \text{ form } C_2H_4 = \frac{28}{64.5} \times 32.25 = 14\text{g}$$

Since the yield is 50%, so mass of alkene (C_2H_4) formed

$$= 14 \times \frac{50}{100} = 7\text{g}$$

So, the correct answer is (*e*)

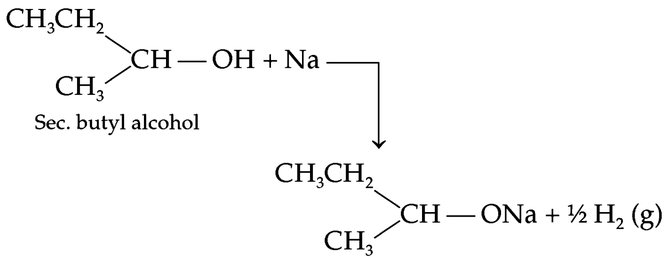
EXAMPLE 156. *A compound of the formula $C_4H_{10}O$ reacts with sodium and undergoes oxidation to give a carbonyl compound which does not reduce Tollen's reagent. The original compound is :*

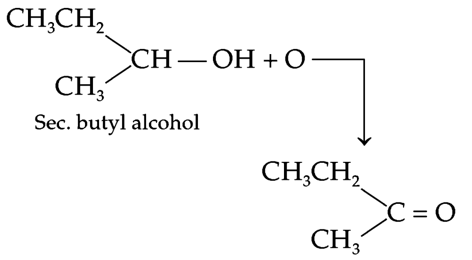
(*a*) *Diethyl ether* (*b*) *n-Butyl alcohol*

(*c*) *Isobutyl alcohol* (*d*) *Sec. butyl alcohol*

(JIPMER-Pondicherry, 2000)

SOLUTION. The given compound $C_4H_{10}O$ is an alcohol because an alcohol reacts with Na to form alkoxide and H_2 gas. Its oxidation product should be a ketone because ketones donot reduce Tollen's reagent.





Butan-2-one (ketone), a carbonyl compound

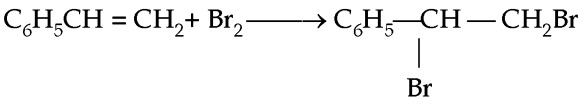
So, the correct answer is (*d*).

EXAMPLE 157. *Complete the following :*

$$C_6H_5CH = CH_2 \xrightarrow{Br_2} [A] \xrightarrow[(ii)\,CH_3I]{(i)\,NaNH_2\,(3.0\,eq)} [B]$$

(Styrene)

SOLUTION. Styrene adds a molecule of Br_2 to form 1, 2-dibromo product.

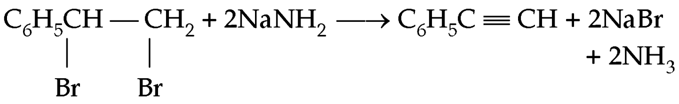


$$C_6H_5CH = CH_2 + Br_2 \longrightarrow C_6H_5\text{—}\underset{\substack{|\\ Br}}{CH}\text{—}CH_2Br$$

Phenyl-1, 2-dibromoethane

(A)

Like other dihalocompounds, (A) also reacts with $NaNH_2$ to form an alkyne.



$$C_6H_5\underset{\substack{|\\ Br}}{CH}\text{—}\underset{\substack{|\\ Br}}{CH_2} + 2NaNH_2 \longrightarrow C_6H_5C \equiv CH + 2NaBr + 2NH_3$$

$$C_6H_5C \equiv CH + NaNH_2 \longrightarrow C_6H_5C \equiv C.Na + NH_3$$

$$C_6H_5C \equiv C.Na + CH_3I \longrightarrow C_6H_5C \equiv C\text{—}CH_3 + NaI$$

1-Phenyl prop-1-yne

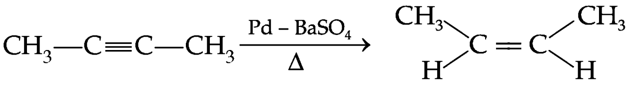
EXAMPLE 158. *When 2-butyne is treated with Pd-BaSO$_4$, the product formed will be :*

(*a*) *Cis-2-butene* (*b*) *trans-2-butene*

(*c*) *1-butene* (*d*) *2-hydroxy butane*

(DCE, 2005)

SOLUTION.



cis-2-butene

The product is cis-form because the reduction from $C \equiv C$ to $C == C$ bond is a syn type

So, the correct answer is (*a*).

EXAMPLE 159. *Which of the following gives iodoform test ?*

(*a*) *$CH_3CH_2(OH)$* (*b*) *C_2H_5CHO*

(*c*) *$(CH_2OH)_2$* (*d*) *none of these.*

(DCE, 2005)

SOLUTION. We know that compounds containing CH_3CO— group or compounds (like CH_3CH_2OH) which on oxidation with halogen and alkali gives CH_3CO— group, give haloform reaction *i.e.*, iodoform test.

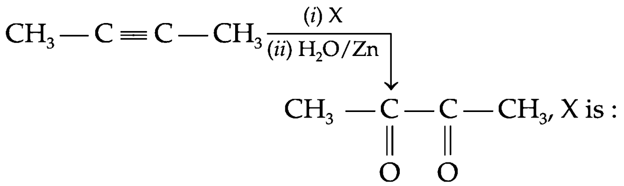
$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + 5NaI + 5H_2O$$

Iodoform + HCOONa

Sodium formate

So, the correct answer is (*a*).

EXAMPLE 160. *In the reaction,*



$$CH_3\text{—}C \equiv C\text{—}CH_3 \xrightarrow[(ii)\,H_2O/Zn]{(i)\,X} CH_3\text{—}\underset{\substack{\|\\ O}}{C}\text{—}\underset{\substack{\|\\ O}}{C}\text{—}CH_3, \text{ X is :}$$

(*a*) *HNO_3* (*b*) *O_2*

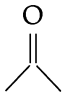
(*c*) *O_3* (*d*) *$KMnO_4$*

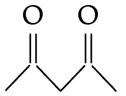
(DCE, 2005)

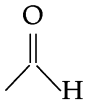
SOLUTION. Since ozonolysis of $\text{—}C \equiv C\text{—}$ followed by H_2O/Zn action gives $\text{—}\underset{\substack{\|\\ O}}{C}\text{—}\underset{\substack{\|\\ O}}{C}\text{—}$, *X* will be ozone, O_3.

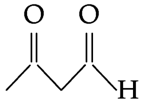
So, the correct answer is (*c*).

EXAMPLE 161. *Maximum enol content is in :*

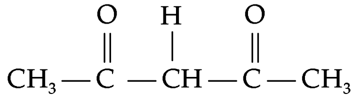
(*a*)


(*b*)


(*c*)


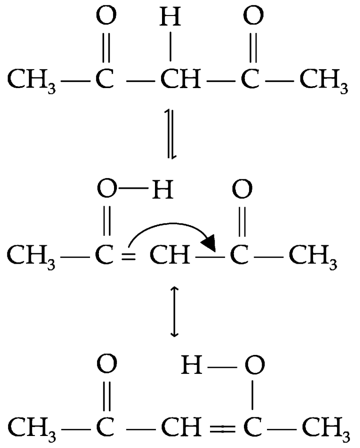
(*d*)


SOLUTION. The compound (*b*) is



$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_3$$

which can be represented by the following structures.



It may be noted that the enol content further increases if the enol form gets stabilised by H–bonding as well as by conjugation *i.e.*, enolic double bond is in conjugation with a multiple bond or a benzene ring. So, the correct answer is (*b*).

EXAMPLE 162. *Which of the following is most reactive towards nucleophilic substitution reaction ?*

(*a*) $CH_2 = CH—Cl$

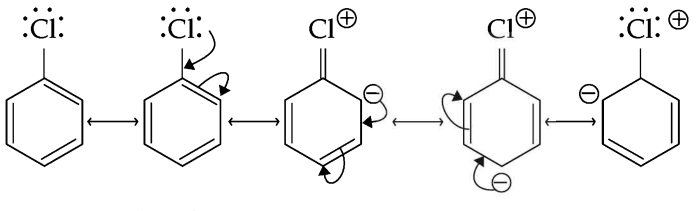
(*b*) C_6H_5Cl

(*c*) $ClCH_2—CH = CH_2$

SOLUTION. The compound (c) is the most reactive out of all the given compounds because in allyl chloride

$$\overset{3}{C}H_2 = \overset{2}{C}H\overset{1}{C}H_2Cl,$$

the π-electrons of carbon-carbon double bond increase the electron density at $\overset{1}{C}$ and help in breaking the carbon-halogen bond. In (*a*) *i.e.*, vinyl chloride ($CH_2 = CH—Cl$), each C–atom is sp^2 hybridised. There is also a partial double bond character between carbon and chlorine due to resonance. So, it is less reactive than (*d*). In (*b*) *i.e.*, C_6H_5Cl, there is a delocalisation of electron cloud and C—Cl bond is difficult to break.



So, order of reactivity is (*c*) > (*a*) > (*b*)

So, the correct answer is (*c*).

EXAMPLE 163. $[A] \xleftarrow[\textit{Catalyst}]{\textit{Lindlar's}} CH_3-C\equiv CH \xrightarrow[liq.\,NH_3]{\textit{Na in}} [B]$

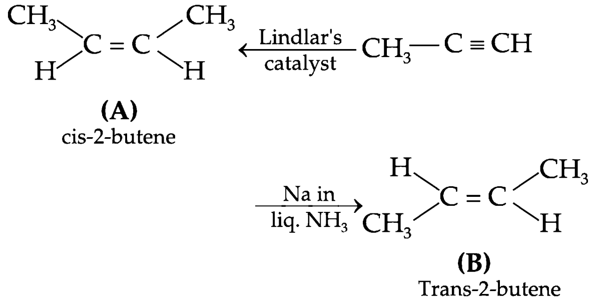
[A] and [B] are respectively

(*a*) *cis, trans-2-butene* (*b*) *both trans-2-butene*

(*c*) *trans-cis-2-butene* (*d*) *both cis - 2- butene.*

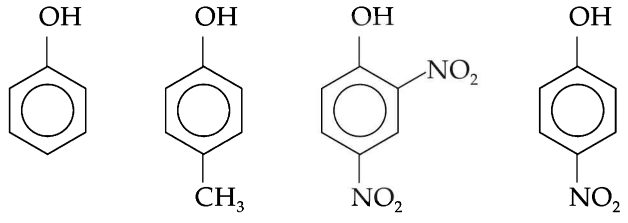
(DCE, 2005)

SOLUTION. Using Lindlar's catalyst (Pd deposited on $BaSO_4$ or $CaCO_3$, and partially poisoned by sulphur, Pb $(CH_3COO)_2$ or quinoline) or nickel boride (called P-2 catalyst), cis-alkenes are formed but with Na in liquid ammonia at 200K (Birch reduction), trans alkenes are formed.



So, the correct answer is (*a*).

EXAMPLE 164. *Strength of acidity is in order*



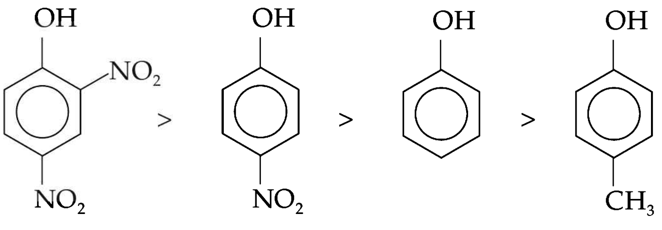
I II III IV

(*a*) *II > I > III > IV* (*b*) *III > IV > I > II*

(*c*) *I > IV > III > II* (*d*) *IV > III > I > II*

(DCE, 2005)

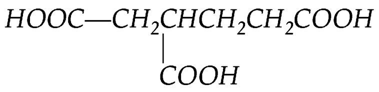
SOLUTION. —NO_2 is electron withdrawing group. Greater the number of electron withdrawing groups, greater the ease with which a proton is released. Hence greater the acidity. —CH_3 is electron releasing group. It increases the electron density on O—H bond. As a result, H^+ ions are not easily released. This causes reduced acidity. So, the strength of acidity is in the following order :



III IV I II

So, the correct answer is (*b*).

EXAMPLE 165. *The IUPAC name of the compound is :*



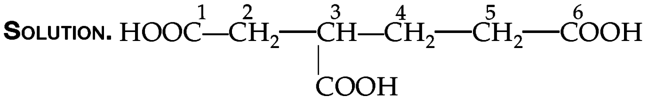
$$HOOC-CH_2\underset{\underset{COOH}{|}}{CH}CH_2CH_2COOH$$

(*a*) *2(carboxymethyl)-pentane 1, 5-dioic acid*

(*b*) *3-carboxyhexane-1, 6-dioic acid*

(*c*) *butane-1, 2, 4-tricarboxylic acid*
(*d*) *4-carboxy hexane-1, 6-dioic acid*
(*e*) *1, 2-dicarboxy pentanoic acid.* **(Kerala PET, 2005)**

SOLUTION.



$$\overset{1}{\text{HOOC}}-\overset{2}{\text{CH}_2}-\underset{\text{COOH}}{\overset{3}{\text{CH}}}-\overset{4}{\text{CH}_2}-\overset{5}{\text{CH}_2}-\overset{6}{\text{COOH}}$$

3–Carboxy hexane–1, 6–dioic acid,

So, the correct answer is (*b*).

EXAMPLE 166. *Propyne and propene can be distinguished by :*

(*a*) Conc. H_2SO_4		(*b*) Br_2 in CCl_4	
(*c*) alk. $KMnO_4$		(*d*) $AgNO_3$ in NH_3	

(DCE, 2005)

SOLUTION.

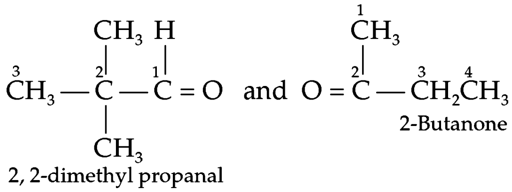
Action of	Propyne	Propene
(*a*) Conc. H_2SO_4	Addition	addition
(*b*) Br_2 in CCl_4	Colour discharges	Colour discharges
(*c*) alk. $KMnO_4$	Colour discharges	Colour is discharged
(*d*) $AgNO_3$ in NH_3	White ppt is formed $2CH_3.C \equiv CH + AgNO_3 + 2\,NH_4OH \longrightarrow 2CH_3C{\equiv}C\,Ag\downarrow + 2H_2O + 2NH_4NO_3$	No action

So, the correct answer is (*d*).

EXAMPLE 167. *An alkene having the molecular formula C_9H_{18} on ozonolysis gives 2, 2-dimethyl propanal and 2-butanone. The alkene is :*

(*a*) *2, 2, 4–trimethyl –3–hexene*
(*b*) *2, 2, 6–trimethyl–3–hexane*
(*c*) *2, 3, 4–trimethyl –2–hexene*
(*d*) *2, 2, 4– trimethyl –2–hexene*
(*e*) *2, 2–dimethyl –3–heptene.* **(Kerala PET, 2005)**

SOLUTION. The compounds formed on ozonolysis are :

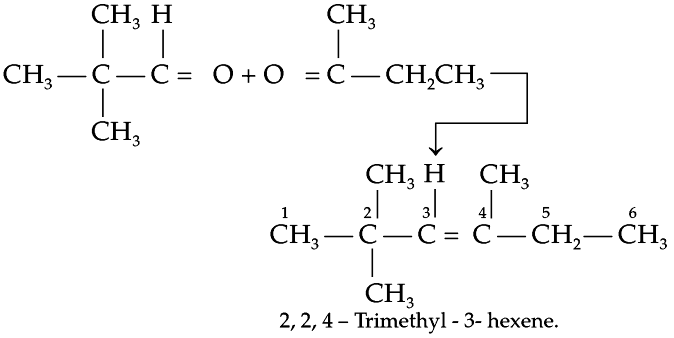


$$\overset{3}{\text{CH}_3}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\overset{2}{\text{C}}}}-\overset{\text{H}}{\overset{1}{\text{C}}}=\text{O} \quad \text{and} \quad \text{O}=\overset{\overset{1}{\text{CH}_3}}{\overset{2}{\text{C}}}-\overset{3}{\text{CH}_2}\overset{4}{\text{CH}_3}$$

2, 2-dimethyl propanal

2-Butanone

The structure of alkene can be obtained by removing the oxygen atoms of the two carbonyl carbons of products and making a double bond between the carbonyl carbon atoms. So, the alkene will be :



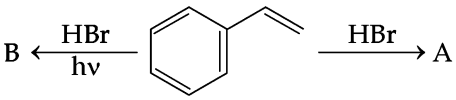
$$\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\overset{\text{H}}{\text{C}}=\ \text{O}+\text{O}\ =\overset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{CH}_3$$

$$\overset{1}{\text{CH}_3}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\overset{2}{\text{C}}}}-\overset{\text{H}}{\overset{3}{\text{C}}}=\overset{\text{CH}_3}{\overset{4}{\text{C}}}-\overset{5}{\text{CH}_2}-\overset{6}{\text{CH}_3}$$

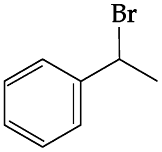
2, 2, 4 – Trimethyl - 3- hexene.

So, the correct answer is (*a*).

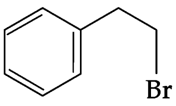
EXAMPLE 168. *Observe the following reactions and predict the nature of A and B*



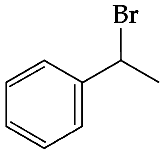
(*a*) *A and B both are*



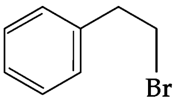
(*b*) *A and B both are*



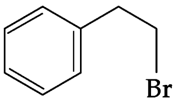
(*c*) *A is*



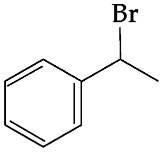
and B is



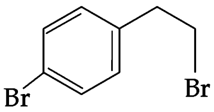
(*d*) A is



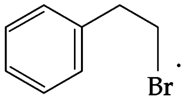
and B is



(*e*) *A is*



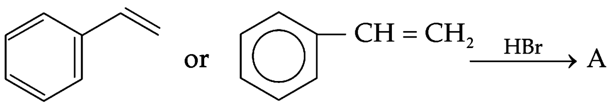
and B is



.

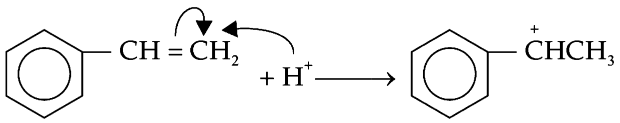
(Kerala PET, 2005)

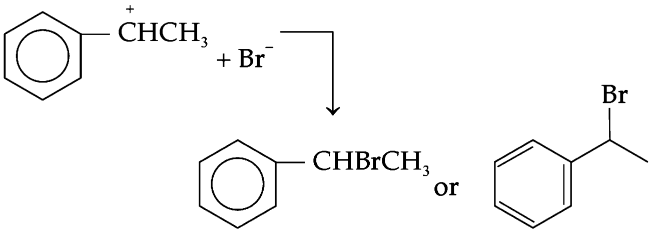
SOLUTION.



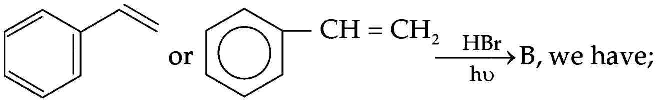
(*i*) HBr ⟶ $H^+ + Br^-$

(*ii*)

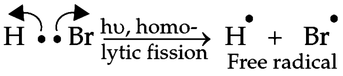




For



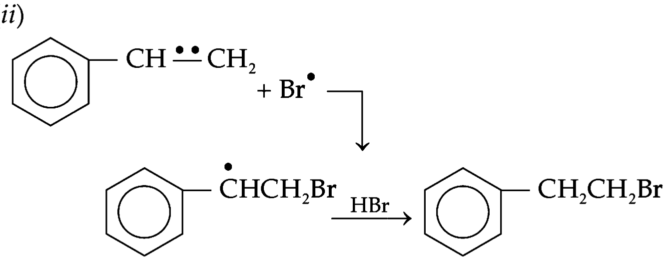
(*i*)

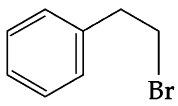


$$\text{H}\,{:}\,\text{Br} \xrightarrow[\text{lytic fission}]{\text{hυ, homo-}} \overset{\bullet}{\text{H}} + \overset{\bullet}{\text{Br}}$$

Free radical

(*ii*)



or  . So, the correct answer is (C).

Example 169. *Nitration of aniline in strongly acidic medium, results in the formaton of m–nitroaniline also. This is because :*

(*a*) *amino group is meta orienting during electrophilic substitution reaction*

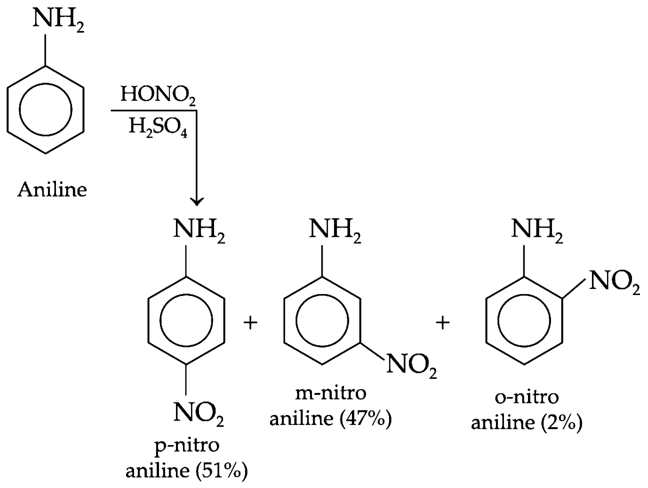
(*b*) *nitrogroup goes always to the meta position irrespective of the substituents.*

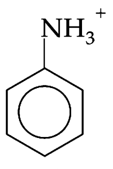
(*c*) *nitration of aniline is a nucleophilic substitution reaction in strongly acidic medium*

(*d*) *in strongly acidic solutions, aniline is present in anilinium ion.*

(*e*) *strong acids generate nitrite ion which can only attack the meta position.* **(Kerala PET, 2005)**

Solution.

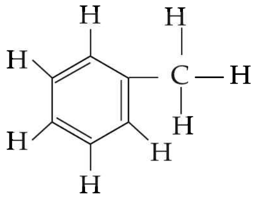


In strongly acidic medium, the protonation of $-NH_2$ group results in the formation of anilinium cation  which is deactivating and m-directing. So, the correct answer is (*d*).

Example 170. *How many sigma and pi bonds are present in toluene ?*

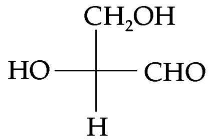
(*a*) $3\pi + 15\sigma$
(*b*) $3\pi + 6\sigma$
(*c*) $3\pi + 10\sigma$
(*d*) $6\pi + 3\sigma$
(*e*) $6\pi + 6\sigma$

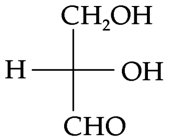
Solution.

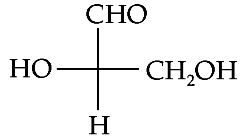
Toluene is 

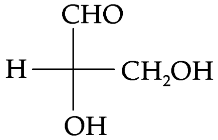
So, there are 3π and 15σ bonds. So, the correct answer is (*a*).

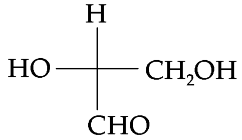
Example 171. *Which of the following Fischer's projection formula is identical to D-glyceraldehyde?*

(*a*) 

(*b*) 

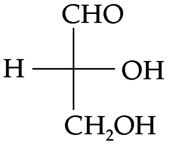
(*c*) 

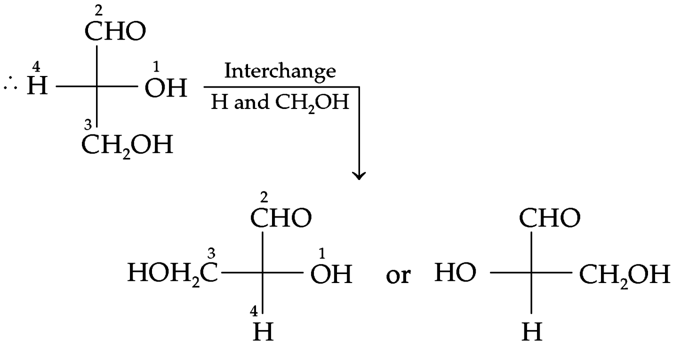
(*d*) 

(*e*) 

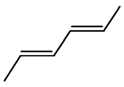
(Kerala, PET, 2005)

Solution. In a D-glyceraldehyde configuration, –CHO group lies at the top, $-CH_2OH$ group lies at the bottom, H–atom to-wards the left while OH group lies to-wards the right of the Fischer projection. Thus, the D-glyceraldehyde configuration would be





So, the correct answer is (*c*)

Example 172. *The name of compound*  *is :*

(*a*) *(2Z, 4Z) –2, 4–hexadiene*

(*b*) *(2Z, 4E) –2, 4–hexadiene*

(*c*) *(2E, 4Z) –2, 4–hexadiene*

(*d*) *(4E, 4Z) –2, 4–hexadiene*

(*e*) *(2E, 4E) –2, 4–hexadiene* **(Kerala PET, 2005)**

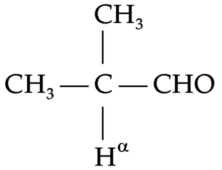
Solution. The rules to assign configuration are if the atoms or groups of higher priority on each carbon atom of double bond are (*i*) on the opposite side of the double bond, the configuration is designated as E and (*ii*) if these are on the same side, the configuration is designated as Z. So, the configuration in the present case is (2E, 4E) –2, 4–hexadiene. Hence the correct answer is (*e*).

Example 173. *Which of the following does not undergo Cannizzaro's reaction ?*

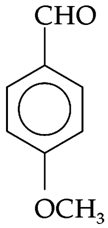
(*a*) *benzaldehyde*
(*b*) *2– methyl propanal*
(*c*) *p– methoxybenzaldehyde*
(*d*) *2, 2–dimethyl propanal*
(*e*) *formaldehyde.* **(Kerala PET, 2005)**

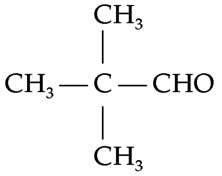
Solution. Aldehydes which donot have α-hydrogen, undergo self oxidation and reduction in presence of concentrated aqueous or alcoholic solution of alkali. (KOH)

(*a*) C_6H_5CHO
no α - H atom

(*b*)

$CH_3-\underset{H^{\alpha}}{\overset{CH_3}{C}}-CHO$

Has α - H atom

(*c*)

no α - H atom

(*d*)

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CHO$

no α - H atom

(*e*) HCHO
no α - H atom

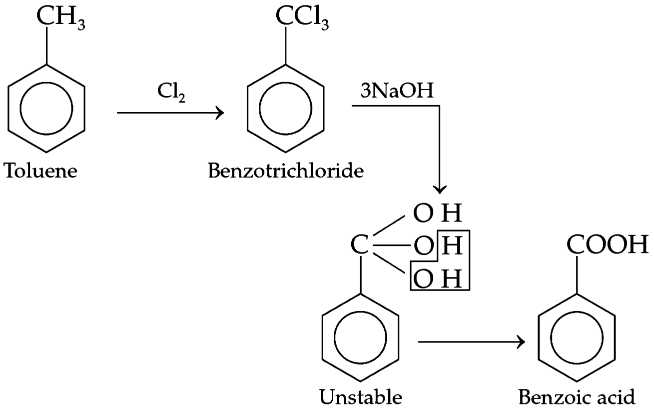
So, the correct answer is (*b*).

Example 174. *Chlorination of toluene in presence of light and heat followed by treatment with aqueous NaOH gives :*

(*a*) *o–cresol*	(*b*) *p–cresol*
(*c*) *mixture of o–cresol and p–cresol*	
(*d*) *benzoic acid*	(*e*) *1, 3, 5– trihydroxy toluene.*

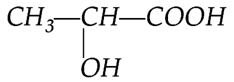
(Kerala PET, 2005)

Solution.

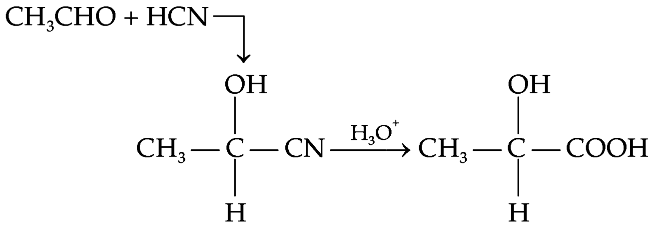


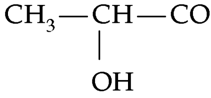
So, the correct answer is (*d*).

Example 175. *CH_3—CHO + HCN ⟶ A. Compound A on hydrolysis gives :*

(*a*) *CH_3CH_2COOH*
(*b*) *$CH_3CH_2CH_2NH_2$*
(*c*) *$CH_3CO.\ COOH$*
(*d*) *$CH_3COCH = NOH$*
(*e*)

$CH_3-\underset{OH}{CH}-COOH$ **(Kerala PET, 2005)**

Solution.


$$CH_3CHO + HCN \longrightarrow CH_3-\underset{H}{\overset{OH}{C}}-CN \xrightarrow{H_3O^+} CH_3-\underset{H}{\overset{OH}{C}}-COOH$$


i.e., $CH_3-\underset{OH}{CH}-COOH$. So, the correct answer is (e)

Example 176. *Among the amines :*

(*i*) *$C_6H_5NH_2$*	(*ii*) *CH_3NH_2*
(*iii*) *$(CH_3)_2NH$*	(*iv*) *$(CH_3)_3N$*

the order of basicity is :

(*a*) *(i) < (iv) < (ii) < (iii)*
(*b*) *(iv) < (iii) < (ii) < (i)*
(*c*) *(i) < (ii) < (iii) < (iv)*
(*d*) *(ii) < (iii) < (iv) < (i)*
(*e*) *(iv) < (iii) < (ii) < (i)* **[Kerala PET, 2005]**

Solution. From the combined effects of steric effect, inductive effect, and solvation of ions, secondary amines are the strongest bases while tertiary amines are the least basic. So, actual basic strength of 1°, 2° and 3° amines is ;

Secondary amine (*iii*) > Primary amine, (*ii*) > Tertiary amine, (*iv*)

In case of aniline $C_6H_5NH_2$ *i.e.*, compound (*i*), the phenyl group (– C_6H_5) exerts – I (inductive) effect. *i.e.*, it withdraws electrons. As a result, the lone pair of electron on N–atom is not easily available for protonation. So, it is least basic. So, the correct answer is

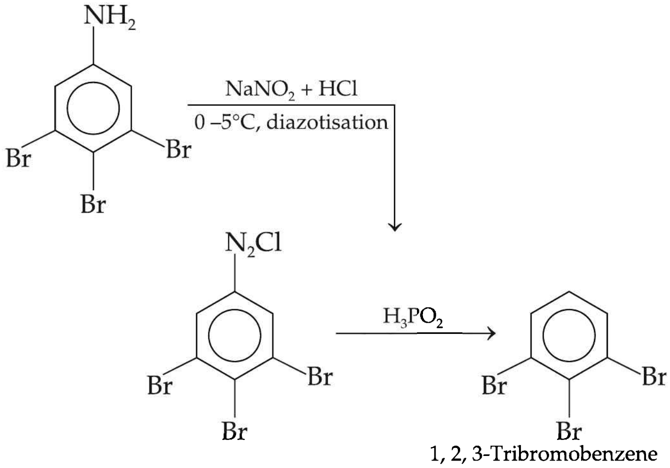
(*i*) < (*iv*) < (*ii*) < (*iii*) *i.e.*, (*a*).

Example 177. *Identify the product in the following equation.*

$$\text{3, 4, 5–tribromoaniline} \xrightarrow[(ii)\,H_3PO_2]{(i)\,diazotisation} ?$$

(*a*) *3, 4, 5–tribromobenzene*
(*b*) *1, 2, 3–tribromobenzene*
(*c*) *2, 4, 6–tribromobenzene*
(*d*) *3, 4, 5– tribromonitrobenzene*
(*e*) *3, 4, 5–tribromophenol.* **(Kerala PET, 2005)**

SOLUTION.



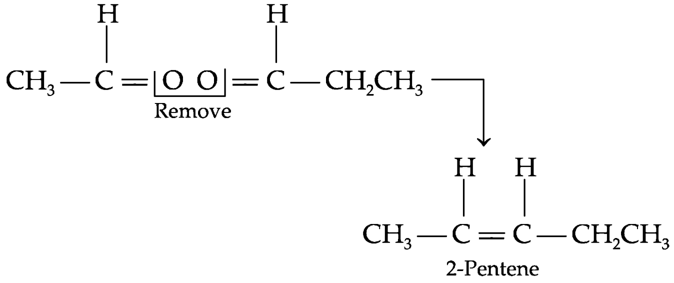
So, the correct answer is (*b*).

EXAMPLE 178. *The olefin which on ozonolysis gives* CH_3CHO *and* CH_3CH_2CHO *is :*

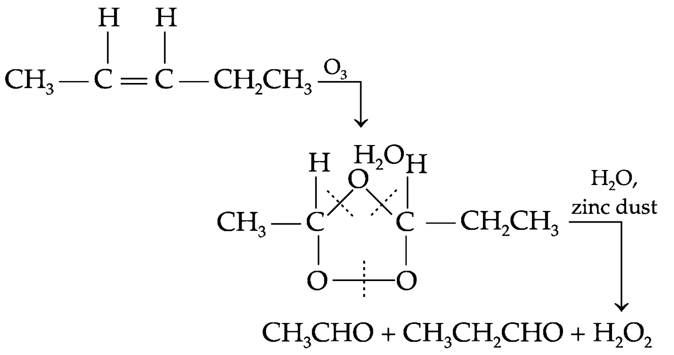
(*a*) *1–Butene* (*b*) *2–Butene*
(*c*) *1–Pentene* (*d*) *2–Pentene*

(Rajasthan Pre-Med. 2000)

SOLUTION. The required alkene can be obtained as :



Confirmation.



So, the correct answer is (*d*).

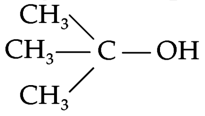
EXAMPLE 179. *Which of the following reagents is used to distinguish between aldehyde and ketone ?*

(*a*) *Ammonical* $AgNO_3$ (*b*) *Phenyl hydrazine*
(*c*) *Hydroxylamine* (*d*) *Semicarbazide*

SOLUTION. Since aldehydes give silver mirror test and Ketones do not, so the correct answer is (*a*)

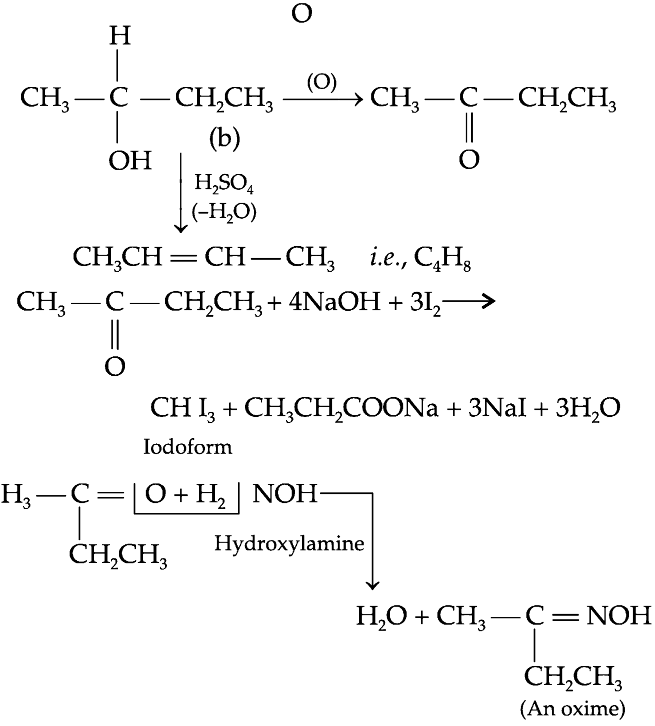
$$\underset{\text{Aldehyde}}{RCHO} + \underset{\substack{\text{(From ammonical}\\\text{silver nitrate)}}}{Ag_2O} \longrightarrow RCOOH + \underset{\text{Silver mirror}}{2Ag\downarrow}$$

EXAMPLE 180. *A substance* $C_4H_{10}O$ *yields on oxidation a compound,* C_4H_8O*, which gives an oxime and a positive iodoform test. The original substance on treatment with Conc.* H_2SO_4 *gives* C_4H_8*. The structure of the compound is :*

(*a*) $CH_3CH_2CH_2CH_2OH$
(*b*) $CH_3CHOHCH_2CH_3$
(*c*)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$
(*d*) $CH_3CH_2OCH_2CH_3$ **(SCRA, 2000)**

SOLUTION. The compound which gives positive iodoform test should contain $CH_3-\underset{\overset{\|}{O}}{C}-$ group which also contains keto group $\rangle C=O$ (that reacts with an oxime).

Considering compound (*b*), we find that this compound on oxidation gives $CH_3-\underset{\overset{\|}{O}}{C}$ group. So, we have:

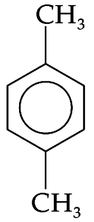


So, the correct answer is (*b*).

EXAMPLE 181. *An aromatic hydrocarbon of molecular formula* C_8H_{10} *forms only one mononitroderivative. The hydrocarbon is :*

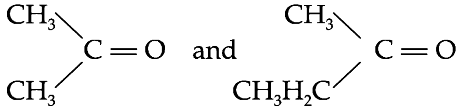
(*a*) *1, 4–dimethyl benzene*
(*b*) *1, 2–dimethyl benzene*
(*c*) *1, 3–dimethyl benzene*
(*d*) *ethyl benzene* **(SCRA, 2000)**

SOLUTION. Since the aromatic compound C_8H_{10} forms only one mononitro derivative, the compound should be symmetrical in structure *i.e.*,



because in this sructure, each position is ortho with respect to the methyl group, —CH_3. So, the correct answer is (*a*) *i.e.*, 1, 4–dimethyl benzene.

Example 182. *An alkene having molecular formula* C_7H_{14} *was subjected to ozonolysis in the presence of zinc dust. An equimolar amount of following two compounds was obtained.*



The IUPAC name of the compound is :

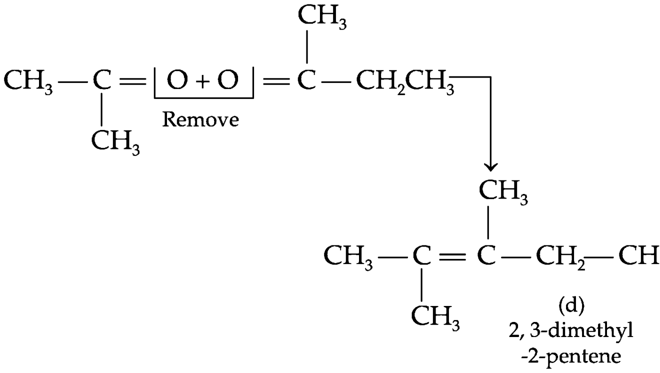
(*a*) *3, 4–dimethyl –3–pentene*

(*b*) *3, 4 – dimethyl –2–pentene*

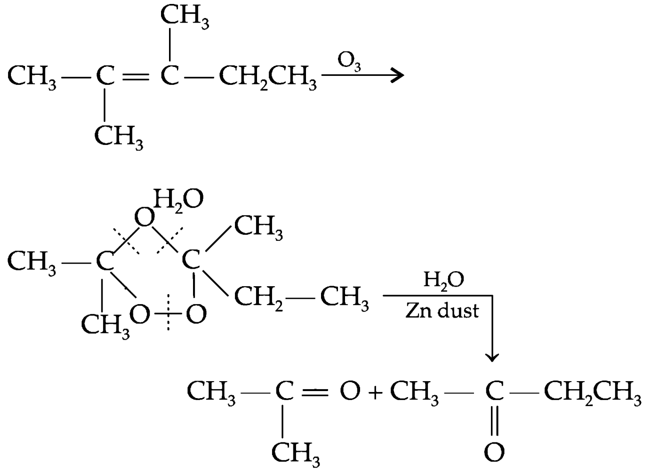
(*c*) *2, 3–dimethyl –3–pentene*

(*d*) *2, 3–dimethyl –2–pentene.* **(SCRA, 2000)**

Solution. The alkene is obtained by removing O–atoms from both compounds. So, we have :

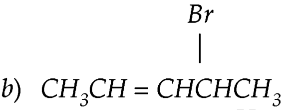


Confirmation of above compound, (*d*) is :

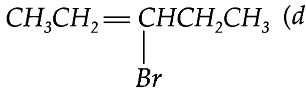


Example 183. *Which one of the following will show optical as well as geometrical isomerism?*

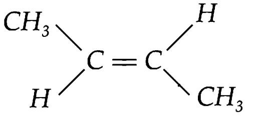
(*a*) *$CH_3(CH_2)_2CH_2OH$*

(*b*) 

$CH_3CH=CHCH(Br)CH_3$

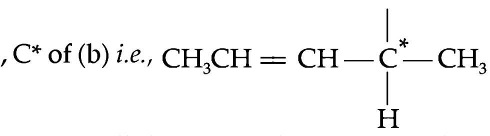
(*c*) 

$CH_3CH_2=CH(Br)CH_2CH_3$

(*d*) 

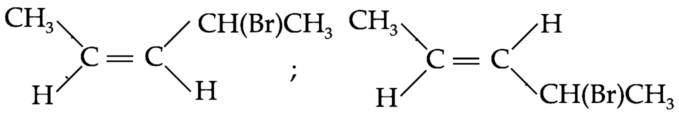
(CSRA, 2000)

Solution. An organic compound which has atleast one chiral carbon atom as well as a C = C will show optical as well as geometrical isomerism. Out of the above given compounds, C* of (b) *i.e.*,



$CH_3CH=CH-C^*H(Br)-CH_3$

is a chiral carbon. So, it will show optical isomerism. The presence of C = C indicates that it will show following geometrical isomers.



cis-form ; Trans-form

Example 184. *Equal quantities of an alkyl halide,* C_4H_9Cl *were treated with equal volume of 0.1 molar and 0.2 molar solutions of caustic soda respectively at the same temperature in two separate experiments. In both these experiments, the times taken for the reactions of exactly fifty percent of the alkyl halide were the same. The most likely structure of halide is :*

(*a*) *$CH_3CH(Cl)CH_2CH_3$* (*b*) *$(CH_3)_3CCl$*

(*c*) *$(CH_3)_2CHCH_2Cl$* (*d*) *$CH_3(CH_2)_3Cl$.*

Solution. The alkyl halide is treated with equal volumes of different concentrations (0.1 M and 0.2 M) of NaOH. But the times taken for the reactions are of exactly 50% of alkyl halide. So, the hydrolysis of alkyl halide is independent of nucleophilic concentration. It means the alkyl halide will be tertiary alkyl halide because hydrolysis of tertiary alkyl halide is independent of nucleophilic concentration. Thus, the true answer is (*b*).

Type. If *n* = number of asymmetric carbon atoms and molecule has **no symmetry** (*i.e.*, molecule cannot be divided into two equal parts); *a* = number of optically active isomers, then:

(*i*) Number of meso forms (optically inactive), *m* = zero

(*ii*) Number of optically active isomers, $a = 2^n$

(*iii*) Total number of racemic forms, $r = \frac{a}{2}$

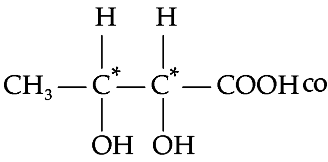
(*iv*) Total number of optical isomers = *a* + *m*.

Asymmetric carbon atom is that which is bonded to four different atoms or groups. For example, C* in lactic acid C*(H) (OH) (CH_3) (COOH) is an asymmetric carbon atom.

EXAMPLE 185. *The total number of optical isomers in CH_3. CHOH. CHOH. COOH are :*

(*a*) 1 (*b*) 2

(*c*) 3 (*d*) 4



$CH_3-\overset{H}{\underset{OH}{C^*}}-\overset{H}{\underset{OH}{C^*}}-COOH$

SOLUTION. $CH_3—C^*—C^*—COOH$ contains two asymmetric C* – atoms. So, $n = 2$ and no. of meso forms, $m = 0$

no. of optically active isomers, $a = 2^n = 2^2 = 4$

So, the correct answer is (*d*).

Type. If n = Even number of asymmetric carbon atoms and molecule **has symmetry** (*i.e.*, the molecule can be divided into two equal halves) then:

(*i*) no. of meso forms,

$$m = 2^{\frac{n}{2}-1}$$

(*ii*) no. of optically active isomers, $a = 2^{n-1}$

(*iii*) no. of racemic forms, $r = \dfrac{a}{2}$

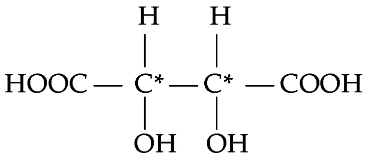
(*iv*) Total number of optical isomers = $a + m$.

EXAMPLE 186. *The total number of optical isomers in CO_2H. CHOH.CHOH, CO_2H are*

(*a*) 1 (*b*) 4

(*c*) 3 (*d*) 2

SOLUTION.



$HOOC-\overset{H}{\underset{OH}{C^*}}-\overset{H}{\underset{OH}{C^*}}-COOH$

The compound $HOOC—C^*—C^*—COOH$ contains two asymmetric C* – atoms.

So, $n = 2$. Hence

(*i*) no. of meso forms, $m = 2^{\frac{n}{2}-1} = 2^{1-1} = 2^\circ = 1$

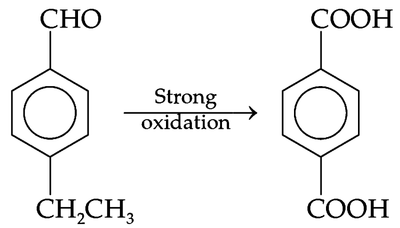
(*ii*) no. of optically active isomers, $a = 2^{n-1} = 2^{2-1} = 2^1 = 2$

$\therefore$ Total number of optical isomers = $a + m = 2 + 1 = 3$.

So, the correct answer is (*c*).

EXAMPLE 187. *An organic compound with molecular formula $C_9H_{10}O$ forms 2, 4 – DNP derivative, reduces Tollen's reagent and undergoes Cannizaro's reaction. On vigorous oxidation, it gives a dicarboxylic acid which is used in the preparation of terylene. Identify the organic compound.* **(WB-JEE, 2011)**

SOLUTION. The data shows that the organic compound gives positive Brady's test which shows carbonyl compound. Tollen's test and Cannizzaro's test shows the presence of aldehyde group without α-hydrogen. The end product being terylene, the organic compound should be



p-ethyl benzaldehyde Terephthalic acid

EXAMPLE 188. *A compound A treated with $NaNH_2$ followed by CH_3CH_2 Br gave compound B. Partial hydrogenation of compound B produced compound C, which on ozonolysis gave carbonyl compound D, C_3H_6O. Compound D did not respond to iodoform test with I_2/KI and NaOH. Find out the structures of A, B, C and D.* **(WB-JEE, 2011)**

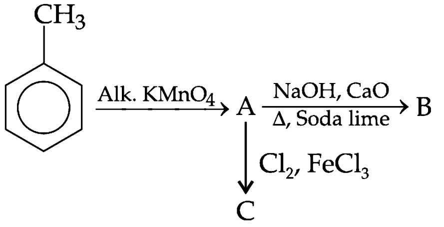
SOLUTION.

$$\underset{(A)}{CH_3CH_2C{\equiv}CH} \xrightarrow[(ii)\,CH_3CH_2\,Br]{(i)\,NaNH_2} \underset{(B)}{CH_3CH_2C{\equiv}C{-}CH_2CH_3}$$

$$\xrightarrow{\text{Partial hydrogenation}} \underset{(C)}{CH_3CH_2CH = CHCH_2CH_3} \xrightarrow[(ii)\,Zn + H_2O]{(i)\,O_3\text{ (ozonolysis)}} \underset{(D)}{2CH_3CH_2CHO}$$

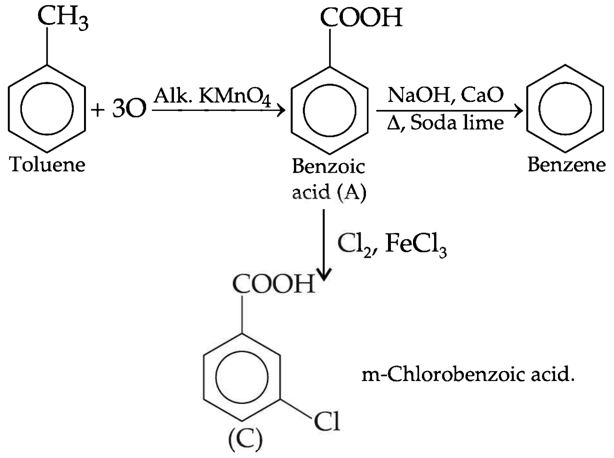
$\xrightarrow[(ii)\,NaOH]{(i)\,I_2/KI}$ no iodoform test because CH_3CH_2CHO does not have CH_3CO – group.

EXAMPLE 189. *Identify the products A, B and C.*



(ISC, 2012)

SOLUTION.



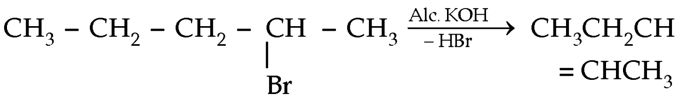
EXAMPLE 190. *2-Bromopentane is treated with alcoholic KOH solution. The major product formed in this reaction and the type of reaction, respectively are:*

(a) pent-2-ene (β-elimination)

(b) pent-1-ene (β-elimination)
(c) 2-pentanol (nucleophilic substitution)
(d) pent-1-ene (nucleophilic substitution)
(e) pent-2-ene (nucleophilic substitution)

(Kerala, PMT, 2012)

SOLUTION.



$$CH_3-CH_2-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[-\,HBr]{Alc.\ KOH} CH_3CH_2CH=CHCH_3$$

2-Bromopentane 2-Pentene

It is a β-elimination reaction.

PROBLEMS FOR PRACTICE

1. In the following reaction,

$$CH_3-C(CH_3)_2\,CH=CH_2 \xrightarrow{H_2O/H^+} \underset{\text{Major Product}}{A} + \underset{\text{Minor Product}}{B}$$

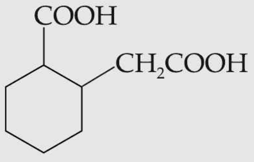
the major product is:

(*a*) $C(CH_3)_2\,(OH)-CH\,(CH_3)_2$
(*b*) $CH_2OH\,C(CH_3)_2\,CH_2\,CH_3$
(*c*) $C(CH_3)_3\,CH(OH)\,CH_3$
(*d*) $C(CH_3)_3\,CH_2CH_2OH$ **Ans.** (*a*)

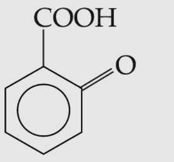
(AIPMT, Prelim, 2012)

2. The compound that undergoes decarboxylation most readily under mild conditions is:

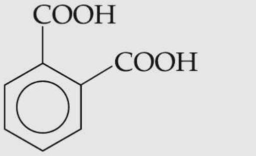
(*a*)



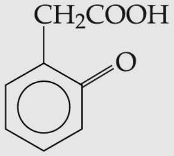
(*b*)



(*c*)



(*d*)



Ans. (*c*)

(IIT, JEE, 2012)

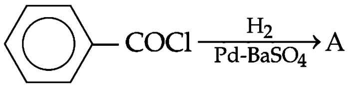
3. An organic compound (C_3H_9N) (A), When treated with nitrous acid, gave an alcohol and N_2 gas was evolved. (A) on warming with $CHCl_3$ and caustic potash gave (C) which on reduction gave isopropylmethylamine. Predict the structure of (A)

(*a*) $(CH_3)_2CHNH_2$ (*b*) $CH_3CH_2NHCH_3$
(*c*) $CH_3N(CH_3)_2$ (*d*) $CH_3CH_2CH_2NH_2$

Ans. (*a*)

(AIPMT (mains), 2012)

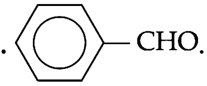
4. Consider the following reaction:



The product (A) is:

(*a*) C_6H_5CHO (*b*) C_6H_5OH
(*c*) $C_6H_5COCH_3$ (*d*) C_6H_5Cl

(**Ans.**



CHO. It is Rosenmund reaction)

5. One mole of propanone and one mole of formaldehyde are the products of ozonolysis of one mole of alkene. The alkene may be:

(*a*) 2-methylpropene (*b*) 2, 2-dimethyl-1-butene
(*c*) propene (*d*) 2-butene
(*e*) 1-butene **Ans.** (*a*)

(Kerala, PMT, 2012)

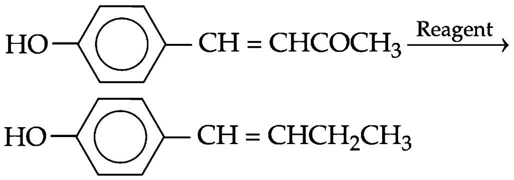
6. How many chiral compounds are possible on monochlorination of 2-methylbutane?

(*a*) 2 (*b*) 4 (*c*) 6 (*d*) 8

Ans. (*a*), **(AIEEE, 2012)**

Hint. Out of 4 compounds, $C_2H_5\,C^*(CH_3)\,CH_2Cl$ and $CH_3C^*(H)(Cl)\,CH(CH_3)_2$ have chiral C* atoms.

7. In the given transformation, which of the following is the most appropriate reagent?



(*a*) Zn–Hg/HCl (*b*) Na,liq. NH_3
(*c*) $NaBH_4$ (*d*) NH_2-NH_2, OH^-

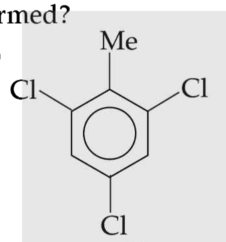
Ans. (*d*)

(AIEEE, 2012)

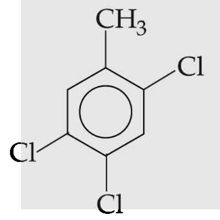
Hint. – OH group and alkene are acid sensitive groups. So, Clemmensen reduction cannot be used and $NaBH_4$ reduces $\rangle C=O$ to – CHOH only.

8. By passing excess Cl_2(g) in boiling toluence, which one of the following compounds is exclusively formed?

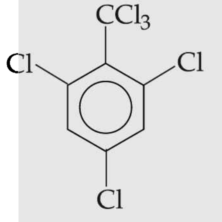
(*a*)



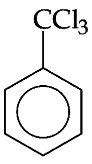
(*b*)



(*c*)



(*d*)



Ans. (*d*)

(W.Bengal JEE, 2012)

9. Iodoform reaction is shown by:
   (*a*) $CH_3CH_2CH_2CH(OH)CH_3$
   (*b*) $C_2H_5OC_2H_5$
   (*c*) $CH_3CH_2CH_2CH_2OH$
   (*d*) (CH_3) COH

[**Ans.** (*a*), **(Odisha JEE, 2012)**]

Hint. All alcohols containing  $>CH-OH$ with CH_3 segment respond to iodoform reaction

10. Ethanoic acid on heating with ammonia forms compound (A) which on treatment with bromine and sodium hydroxide gives compound B. Compound (B) on treatment with $NaNO_2$/dil. HCl gives compound (C). The compounds (A), (B) and (C) respectively are:
   (*a*) ethanamide, methanamine, methanol
   (*b*) Propanamide, ethanamine, ethanol
   (*c*) N-ethylpropanamide, methane isonitrile, methanamine
   (*d*) ethanamine, bromoethane, ethanediazonium chloride
   (*e*) methanamine, ethanamide, methanol

[**Ans.** (*a*), **(Kerala PET, 2012)**]

28

CHAPTER

Water and Hydrogen Peroxide

28.1 HARD WATER

The water sample that contains mainly chlorides and sulphates of calcium and magnesium is called hard water. Such a water gives curdy white precipitate with soap solution in alcohol.

28.2 SOFT WATER

The water sample that contains mainly bicarbonates of calcium and magnesium is called soft water. Such a water gives lather with soap solution in alcohol.

28.3 HARDNESS OF WATER

It is always calculated in terms of calcium carbonate although $CaCO_3$ is not all responsible for causing hardness of water. It is because $CaCO_3$ is insoluble in water. The reason why $CaCO_3$ is chosen for calculating hardness of water is that its molar mass is exact 100 g mol⁻. Following relations are used to calculate amounts of various hardness causing substances in terms of $CaCO_3$.

1. 1 g mol or 162 g of $Ca(HCO_3)_2$ = 1 g mol or 100 g $CaCO_3$
   [∵ Mol. wt. of $Ca(HCO_3)_2$ = 162 g mol⁻]
2. 1 g mol or 146 g of $Mg(HCO_3)_2$ = 1 g mol or 100 g $CaCO_3$
   [∵ Mol. wt. of $Mg(HCO_3)_2$ = 146 g mol⁻]
3. 1 g mol or 111g of $CaCl_2$ = 1 g mol or 100 g $CaCO_3$
   [∵ Mol. wt. of $CaCl_2$ = 111g mol⁻]
4. 1 g mol or 95 g of $MgCl_2$ = 1 g mol or 100 g $CaCO_3$
   [∵ Mol. wt. of $MgCl_2$ = 95 g mol⁻]
5. 1 g mol or 136 g of $CaSO_4$ = 1 g mol or 100 g $CaCO_3$
   [∵ Mol. wt. of $CaSO_4$ = 136 g mol⁻]
6. 1 g mol or 120 g of $MgSO_4$ = 1 g mol or 100 g $CaCO_3$
   [∵ Mol. wt. of $MgSO_4$ = 120 g mol⁻]

Temporary and permanent hardness of water can be calculated as follows :

1. ***Temporary hardness***. Hardness due to $Ca(HCO_3)_2$ + Hardness due to $Mg(HCO_3)_2$.
2. ***Permanent hardness.*** Hardness due to $CaCl_2$ + hardness due to $MgCl_2$ + Hardness due to $CaSO_4$ + Hardness due to $MgSO_4$.

28.4 DEGREE OF HARDNESS

It is expressed in ppm (parts per million) and is defined as the number of parts by weight of $CaCO_3$ (equivalent to Ca and Mg-salts) present in a million (10^6) parts by weight of water. Thus : 1 ppm = 1 part of $CaCO_3$ in 10^6 parts of water.

Also, **1 ppm = 1 mg L⁻**

Equations to be used to determine hardness of water.

1. $\underset{\substack{1\,\text{g mol}\\=111\text{g}}}{CaCl_2} \equiv \underset{\substack{1\,\text{g mol}\\=100\text{g}}}{CaCO_3}$
2. $\underset{\substack{1\,\text{g mol}\\=95\text{g}}}{MgCl_2} \equiv \underset{\substack{1\,\text{g mol}\\=100\text{g}}}{CaCO_3}$
3. $\underset{\substack{1\,\text{g mol}\\=136\text{g}}}{CaSO_4} \equiv \underset{\substack{1\,\text{g mol}\\=100\text{g}}}{CaCO_3}$
4. $\underset{\substack{1\,\text{g mol}\\=120\text{g}}}{MgSO_4} \equiv \underset{\substack{1\,\text{g mol}\\=100\text{g}}}{CaCO_3}$

EXAMPLE 1. *A sample of water contains 25 ppm of $CaCl_2$. Find the degree of hardness of this water.*

SOLUTION. We know that :

$$\underset{\substack{1\,\text{g mol}\\=111\text{g}\\=111\,\text{ppm}}}{CaCl_2} \equiv \underset{\substack{1\,\text{g mol}\\=100\text{g}\\=100\,\text{ppm}}}{CaCO_3}$$

[Mol. wt. of $CaCl_2$ = 40 + (2 × 35.5) = 111g mol⁻
Mol. wt. of $CaCO_3$ = 40 + 12 + (3 × 16) = 100 g mol⁻]

$$111 \text{ ppm } CaCl_2 \equiv 100 \text{ ppm } CaCO_3$$

$$\therefore \quad 25 \text{ ppm } CaCl_2 \equiv \frac{100}{111} \times 25 = 22.52 \text{ ppm } CaCO_3$$

Ans.

EXAMPLE 2. *One litre sample of hard water contains 1 mg $CaCl_2$ and 1 mg $MgCl_2$. Calculate total hardness in terms of $CaCO_3$ per 10^6 parts water by weight.* **(IIT, 1980)**

SOLUTION. Density of water = 1g (mL)⁻;

Volume of water = 1 L = 1000 mL

∴ Wt. of water = Volume × density

= 1000 mL × 1g (mL)⁻ = 1000g

(*i*) Mol. wt. of $CaCl_2$ = 40 + (2 × 35.5) = 111 g mol⁻

$$\text{Wt. of } CaCl_2 = 1\text{mg} \times \frac{1\text{g}}{1000\,\text{mg}} = 0.001\text{g}$$

$$\text{No. of mol. of } CaCl_2 = \frac{\text{wt.}}{\text{mol. wt}} = \frac{0.001\text{g}}{111\text{g mol}^{-}}$$

$$= \frac{0.001}{111}\text{mol}$$

$$1\text{g mol. } CaCl_2 = 1 \text{ g mol } CaCO_3 = 100 \text{ g } CaCO_3$$

$$[\because \text{Mol. wt. of } CaCO_3 = 40 + (3 \times 16) = 100 \text{ g mol}^{-}]$$

$$\therefore \frac{0.001}{111}\text{mol}\, CaCl_2 = \frac{0.001}{111} \times 100\text{g}\, CaCO_3$$

Thus, 1000g H_2O contain $CaCl_2$

$$= \frac{0.001}{111} \times 100 \text{ g } CaCO_3$$

10^6 g H_2O contain $CaCl_2$

$$= \frac{0.001}{111} \times \frac{100}{1000} \times 10^6\text{g}\, CaCO_3$$

$$= 0.9 \text{ g } CaCO_3$$

∴ Hardness of water = 0.9 ppm.

(*ii*) Mol. wt. of $MgCl_2 = 24 + (2 \times 35.5) = 95$ g mol^{-}

$$\text{Wt. of } MgCl_2 = 1\text{mg} \times \frac{1\text{g}}{1000\,\text{mg}} = 0.001\text{g}$$

No. of mol. of $MgCl_2$

$$= \frac{\text{Wt.}}{\text{Mol. wt.}} = \frac{0.001\text{g}}{95\text{g mol}^{-}} = \frac{0.001}{95}\text{mol}$$

$$1\text{g mol } MgCl_2 = 1\text{g mol } CaCO_3 = 100 \text{ g } CaCO_3$$

$$\text{Thus : 1000 g } H_2O \text{ contain } MgCl_2 = \frac{0.001}{95} \times 100\text{g}\, CaCO_3$$

10^6 g H_2O contain $MgCl_2$

$$= \frac{0.001}{95} \times \frac{100}{1000} \times 10^6\text{g}\, CaCO_3$$

$$= 1.05 \text{ g } CaCO_3$$

∴ Hardness of water = 1.05 ppm

∴ Total hardness of water

= 0.9 ppm + 1.05 ppm = **1.95 ppm**

or 1.95 g per 10^6 part water by weight **Ans.**

Example 3. *A sample of water contains 8 mg of calcium sulphate per kilogram of water. Calculate the degree of hardness of this hard water.*

Solution. Mol. wt. of

$$CaSO_4 = 40 + 32 + (4 \times 16) = 136 \text{ g mol}^{-}$$

$$\text{Wt. of } CaSO_4 = 8\,\text{mg} \times \frac{1\text{g}}{1000\,\text{mg}} = 0.008\text{g}$$

∴ no. of mol. of $CaSO_4$

$$= \frac{\text{Wt.}}{\text{Mol. wt.}} = \frac{0.008\text{g}}{136\text{g mol}^{-}}$$

$$= 5.88 \times 10^{-5} \text{ mol.}$$

But 1 g mol $CaSO_4 \equiv$ 1 g mol $CaCO_3 \equiv$ 100 g $CaCO_3$.

∴ 5.88×10^{-5} mol $CaSO_4$

$$= 5.88 \times 10^{-5} \times 100 \text{ g}$$

$$CaCO_3 = 5.88 \times 10^{-3}\text{g}\, CaCO_3$$

Wt. of hard water = 1 kg = 1000 g

∴ 1000 g water contains $CaSO_4$ equivalent to

$$CaCO_3 = 5.88 \times 10^{-3} \text{ g.}$$

∴ 10^6g (*i.e.*, one million) water contains $CaSO_4$ equivalent to $CaCO_3$

$$= \frac{5.88 \times 10^{-3}\text{g}}{1000\text{g}} \times 10^6 \text{ g}$$

$$= 5.88\text{g}\, CaCO_3$$

∴ Hardness of water = 5.88 ppm

Example 4. *A certain sample of water was found to contain 12 ppm of $MgSO_4$ and 42 ppm of $CaCl_2$. Calculate the total hardness in the given sample of water.*

Solution. Mol. wt. of

$$MgSO_4 = 24 + 32 + (4 \times 16) = 120 \text{ g mol}^{-}$$

$$\text{Mol. wt. of } CaCl_2 = 40 + (2 \times 35.5) = 111 \text{ g mol}^{-};$$

$$\text{Mol. wt. of } CaCO_3 = 40 + 12 + (3 \times 16) = 100 \text{ g mol}^{-}$$

We know that hardness of water is expressed in terms of $CaCO_3$. Hence :

(*i*) 1 g mol $MgSO_4 \equiv$ 1 g mol $CaCO_3$

120 g   100 g

120 g $MgSO_4 \equiv$ 100 g $CaCO_3$

or 120 ppm $MgSO_4 \equiv$ 100 ppm $CaCO_3$

$$12 \text{ ppm } MgSO_4 \equiv \frac{100}{120} \times 12 = 10\,\text{ppm}$$

(*ii*) 1 g mol $CaCl_2 \equiv$ 1 g mol $CaCO_3$

111 g   100 g

111 ppm   100 ppm

or 111 ppm $CaCl_2 \equiv$ 100 ppm $CaCO_3$

$$42 \text{ ppm } CaCl_2 = \frac{100}{111} \times 42 = 37.84\,\text{ppm}$$

∴ Total hardness = Hardness due to $MgSO_4$ + Hardness due to $CaCl_2$

= 10 ppm + 37.84 ppm

= **47.84 ppm** **Ans.**

Example 5. *0.45 dm^3 of a sample of hard water contains 0.5 mg of $MgCl_2$ and 0.55 mg of $CaCl_2$. Calculate the total hardness of water in terms of $CaCO_3$ per 10^6 parts of water by mass (at. wt. Ca = 40, Mg = 24, Cl = 35.5).*

Solution. Mol. mass of $CaCl_2$

$$= 40 + (2 \times 35.5) = 111$$

Molar mass of $MgCl_2$

$$= 24 + (2 \times 35.5) = 95 \text{ g mol}^{-}$$

Molar mass of $CaCO_3$

$$= 40 + 12 + (3 \times 16) = 100 \text{ g mol}^{-}$$

(*a*) We know that $CaCl_2 \equiv CaCO_3$

111 parts   100 parts

111 parts $CaCl_2 \equiv$ 100 parts $CaCO_3$

$$0.55 \text{ mg } CaCl_2 \equiv \frac{100}{111} \times 0.55\,\text{mg} = 0.4955\,\text{mg}$$

(*b*) $MgCl_2 \equiv CaCO_3$

95 parts   100 parts

95 parts $MgCl_2 \equiv$ 100 parts $CaCO_3$

$$0.5 \text{ mg } MgCl_2 \equiv \frac{100}{95} \times 0.5\,\text{mg} = 0.5263\,\text{mg}$$

0.45 dm^3 of hard water contain

$$CaCO_3 = 0.4955 + 0.5263 = 1.0218 \text{ mg}$$

∴ 1 dm^3 of hard water contain

$$CaCO_3 = \frac{1.0218}{0.45} = 2.27 \text{ mg}$$

But 1 dm^3 (*i.e.,*, 1L) of water weighs

$$= 1000 \text{ g} \times \frac{1000 \text{ mg}}{1\text{g}} = 10^6 \text{ mg}$$

[∵ density of water = 1g (mL)$^{-}$]

∴ Degree of hardness in water

= 2.27 mg per 10^6 parts of water by mass.

Example 6. *What will be the weight of CaO needed to remove hardness of 10^6 litre of water containing 0.81 g of calcium bicarbonate per litre ?*

Solution. Reaction. $Ca(HCO_3)_2 + CaO \rightarrow 2\ CaCO_3 + H_2O$.

$$\underset{\substack{40+2[1+12+(3\times16)]\\=162=\text{mol. wt.}}}{Ca(HCO_3)_2} \rightleftharpoons \underset{\substack{(i)\,\text{mol}=1\\(ii)\,\text{oxidation state of } Ca^{2+}=2}}{Ca^{2+}} + 2HCO_3^-$$

∴ Eq. wt. of Ca $(HCO_3)_2$

$$= \frac{\text{Mol. wt.}}{\substack{\text{no. of mol. of } Ca^{2+} \text{in}\\ \text{one mol of Ca } (HCO_3)_2} \times \substack{\text{oxidation state}\\ \text{of } Ca^{2+}}} = \frac{162}{1\times2} = 81$$

$$\underset{40+16=56}{CaO} \rightleftharpoons \underset{\substack{(i)\,\text{mol}=1\\(ii)\,\text{oxidation state of } Ca^{2+}=2}}{Ca^{2+}} + O^{2-}$$

∴ Eq. wt. of CaO

$$= \frac{\text{Mol. wt.}}{\substack{\text{no. of mol. of } Ca^{2+} \text{in}\\ \text{one mol of CaO}} \times \substack{\text{oxidation state}\\ \text{of } Ca^{2+}}} = \frac{56}{1\times2} = 28$$

No. of equivalents (eq.) of $Ca(HCO_3)_2$ in 1L hard water

$$= \frac{\text{Wt.}}{\text{Eq. wt.}}$$

$$= \frac{0.81}{81} = 0.01 \qquad \left[\because \text{Eq.} = \frac{\text{Wt.}}{\text{Eq.wt.}}\right]$$

∴ no. of equivalents of CaO needed to remove $Ca(HCO_3)_2$ in 1 L = 0.01

[∵ eq. CaO ≡ eq. $Ca(HCO_3)_2$]

∴ no. of equivalents of CaO needed to remove $Ca(HCO_3)_2$ in 10^6L water = 0.01 × 10^6

Hence, wt. of CaO needed

= no. of equivalents × Eq. wt.

= 0.01 × 10^6 × 28 = **2.8 × 10^5g** **Ans.**

Example 7. *A precipitate of 0.19 g of calcium oxalate ($CaC_2O_4 . H_2O$) was obtained from 300 cm^3 of hard water. Calculate the calcium content in it in ppm (at. wt., Ca = 40, C = 12, O = 16)*

Solution. $CaC_2O_4 . H_2O$ ≡ Ca

40 + (2 × 12) + (4 × 16) + (2 × 1) + 16 40 g

= 146 g

Wt. of $CaC_2O_4 . H_2O$ ppt = 0.19 g

146 g $CaC_2O_4 . H_2O$ ≡ 40 g Ca

$$0.19 \text{ g Ca } C_2O_4 . H_2O \equiv \frac{40}{146} \times 0.19 \text{g}$$

Wt. of 300 cm^3 water = Volume × density

= 300 cm^3 × 1g cm^{-3} = 300 g

$$\therefore \text{ Ca content in ppm} = \frac{\text{Wt. of component, Ca}}{\text{Total wt. of water}} \times 10^6$$

$$= \frac{40}{146} \times \frac{0.19 \times 10^6}{300} = 173.5 \qquad \textbf{Ans.}$$

Type. For softening hard water :

Lime, *i.e.,* $Ca(OH)_2$ required

$$= \frac{\text{Mol. wt. of } Ca(OH)_2}{100} \times \begin{bmatrix} \text{Temporary hardness} \\ + \text{Permanent Mg hardness} \end{bmatrix}$$

Soda *i.e.,* Na_2CO_3 required

$$= \frac{\text{Mol. wt. of } Na_2CO_3}{100} \times [\text{Permanent hardness}]$$

Example 8. *How much soda and lime would be needed to soften 12,000 L of hard water analysed as, permanent hardness = 15 ppm, permanent magnesium hardness = 12 ppm and temporary hardness = 18 ppm ?*

Solution. (*i*) Soda requirement

$$= \frac{\text{Mol. wt. of } Na_2CO_3}{100} \times [\text{Permanent hardness}]$$

$$= \frac{(2\times23)+12+(3\times16)}{100} \times 15$$

$$= \frac{106}{100} \times 15 = 15.9 \text{ ppm} = 15.9 \text{ mgL}^{-}$$

∴ Amount of soda required for 12,000 L water

$$= 15.9 \times 12{,}000 \text{ mg} = \frac{15.9 \times 12{,}000}{1000} \text{g}$$

= **190.8 g** **Ans.**

(*ii*) Lime *i.e.,* $Ca(OH)_2$ required

$$= \frac{\text{Mol. wt. of } Ca(OH)_2}{100} \times \begin{bmatrix} \text{Temporary hardness +} \\ \text{permanent Mg hardness} \end{bmatrix}$$

$$= \frac{40 + 2(16+1)}{100} \times [18 + 12] = \frac{74}{100} \times 30$$

= 22.2 ppm = 22.2 mg L^{-}

∴ Amount of lime required for 12,000 L water

$$= 22.2 \times 12{,}000 \text{mg} = \frac{22.2 \times 22{,}000}{1000} \text{g}$$

= **266.4 g** **Ans.**

Type. For softening hard water :
Lime *i.e.*, $Ca(OH)_2$ required

$$= \frac{\text{Mol. wt. of Ca(OH)}_2}{100} \times \left[\begin{array}{c}\text{CaCO}_3 \text{ equivalent of CO}_2,\\ \text{HCO}_3^- , \text{Mg}^{2+} \text{ and FeSO}_4.7\text{H}_2\text{O}\\ \text{(as coagulent)}\end{array}\right]$$

Soda *i.e.*, Na_2CO_3 required

$$= \frac{\text{Mol. wt. of Na}_2\text{CO}_3}{100} \times \left[\begin{array}{c}\text{Chemical equivalent of}\\ \text{Ca}^{2+} + \text{Mg}^{2+} + \text{FeSO}_4.7\text{H}_2\text{O}\\ -\text{HCO}_3^-\end{array}\right]$$

> **Note** 1. SiO_2, NaCl, KCl etc., do not contribute to hardness.
>
> 2. $CaCO_3$ equivalent = no. of ppm of constituent × $\dfrac{100}{\text{at. wt. or mol. wt. of constituent}}$

Example 9. *A sample of hard water from a lake on analysis gave the following results:* Ca^{2+} *= 45 ppm,* Mg^{2+} *= 50 ppm, 2* HCO^-_3 *= 400 ppm and* CO_2 *= 20 ppm. If 145 ppm of* $FeSO_4 . 7H_2O$ *is used as a coagulant, find the amount of soda and lime used to soften above hard water (at. wt., Ca = 40, Mg = 24, C = 12, H = 1, O = 16, Fe = 56, S = 32).*

Solution. Mol. Wt. of $CO_2 = 12 + (2 \times 16) = 44$; $Ca^{2+} = 40$, $Mg^{2+} = 24$, $2\,HCO^-_3 = 2\,[1 + 12 + (3 \times 16)] = 122$, $FeSO_4 . 7\,H_2O = 56 + 32 + (4 \times 16) + 7\,(2 \times 1 + 16) = 278$. To calculate $CaCO_3$ equivalent :

Constituent	Mol. wt./At. wt.	Amount	$CaCO_3$ equivalent
Ca^{2+}	40	45 ppm	$\frac{(45 \times 100)}{40} = 112.5$
Mg^{2+}	24	50 ppm	$\frac{(50 \times 100)}{24} = 208.3$
$2\,HCO_3^-$	122	400 ppm	$\frac{(400 \times 100)}{122} = 327.9$
CO_2	44	20 ppm	$\frac{(20 \times 100)}{44} = 45.45$
$FeSO_4 . 7H_2O$	278	145 ppm	$\frac{(145 \times 100)}{278} = 52.16$

1. Soda requirement

$$= \frac{\text{Mol. wt. of Na}_2\text{CO}_3}{100} \times \left[\begin{array}{c}\text{CaCO}_3 \text{ equivalent of Ca}^{2+} + \text{Mg}^{2+}\\ + \text{FeSO}_4.7\text{H}_2\text{O} - 2\text{HCO}_3^-\end{array}\right]$$

$$= \frac{106}{100} \times [112.5 + 208.3 + 52.16 - 327.9]$$

$$= \frac{106}{100} \times 45.06 = \mathbf{47.76\ ppm} \qquad \textbf{Ans.}$$

2. Lime requirement

$$= \frac{\text{Mol. wt. of Ca(OH)}_2}{100} \times \left[\begin{array}{c}\text{CaCO}_3 \text{ equivalent of Mg}^{2+}\\ + \text{CO}_2 + 2\text{HCO}_3^- + \text{FeSO}_4.7\text{H}_2\text{O}\end{array}\right]$$

$$= \frac{74}{100} \times [208.3 + 45.45 + 327.9 + 52.16]$$

$$= \frac{74}{100} \times 633.81 = \mathbf{469\ ppm} \qquad \textbf{Ans.}$$

Example 10. *How much soda and lime would be required to soften 900L of hard water from the following data.* Ca^{2+} *= 40 ppm,* Mg^{2+} *= 10 ppm,* CO_2 *= 45 ppm, 2* HCO^-_3 *= 160 ppm ? (at. wt. Ca = 40, Mg = 24, C = 12, O = 16).*

Solution. At. wt. of Ca = 40, Mg = 24, Mol. wt. of $CO_2 = 12 + (2 \times 16) = 44$, $2HCO^-_3 = 2\,[1 + 12 + (3 \times 16)] = 122$.

To calculate $CaCO_3$ equivalent.

Constituent	Mol. wt./At. wt.	Amount	$CaCO_3$ equivalent
Ca^{2+}	40	40 ppm	$\frac{(40 \times 100)}{40} = 100$
Mg^{2+}	24	10 ppm	$\frac{(10 \times 100)}{24} = 41.67$
CO_2	44	45 ppm	$\frac{(45 \times 100)}{44} = 102.27$
$2\,HCO^-_3$	122	160 ppm	$\frac{(160 \times 100)}{122} = 131.14$

1. Soda requirement

$$= \frac{\text{Mol. wt. of Na}_2\text{CO}_3}{100} \times \left[\begin{array}{c}\text{CaCO}_3 \text{ equivalents of Ca}^{2+} + \text{Mg}^{2+}\\ - 2\text{HCO}_3^-\end{array}\right]$$

$$= \frac{106}{100} \times [100 + 41.67 - 131.14]$$

$$= \frac{106 \times 10.53}{100}$$

$$= \mathbf{11.16\ ppm\ or\ mg\ L^-} \qquad \textbf{Ans.}$$

∴ Amount of soda required for 900 L water

$$= 11.16 \times 900 \text{ mg}$$

$$= \frac{11.16 \times 900}{1000} \text{ g} \simeq \mathbf{10g} \qquad \textbf{Ans.}$$

2. Lime *i.e.*, $Ca(OH)_2$ requirement

$$= \frac{\text{Mol. wt. of Ca(OH)}_2}{100} \times \left[\begin{array}{c}\text{CaCO}_3 \text{ equivalent of Mg}^{2+}\\ + \text{CO}_2 + 2\text{HCO}_3^-\end{array}\right]$$

$$= \frac{74}{100} \times [41.67 + 102.27 + 131.14]$$

$$= 203.56 \text{ ppm or mg L}^-$$

∴ Amount of lime required for 900 L water = 203.56 × 900 mg

$$= \frac{203.56 \times 900}{1000} \text{g} = \mathbf{183.204\ g\ \ Ans.}$$

EXAMPLE 11. *A sample of hard water contains Ca^{2+} ions as the only cations, 183 ppm of HCO^-_3 and 96 ppm of SO_4^{2-}. (one ppm means one part of the substance in one million part of water, mass/mass). Calculate the number of moles of CaO needed to remove HCO^-_3 from one thousand kilogram of this water. If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions ? If the Ca^{2+} ions in one litre of the treated water are completely exchanged with H^+ ions, what will be its pH ? (Assume that $CaCO_3$ is completely insoluble in water).*

SOLUTION. (*a*) Molecular mass of

$$HCO_3^- = 1 + 12 + (3 \times 16) = 61\text{g}.$$

Mass of HCO_3^- in 1000 kg of H_2O = 183 kg

$$\therefore \text{ Mass of } HCO_3^- = \frac{183}{61} = 3\,\text{mol}.$$

(*b*) Molecular mass of SO_4^{2-} = 32 + (4 × 16) = 96 g

Mass of SO_4^{2-} in 1000 g of H_2O = 96 g

$$\therefore \text{ Moles of } SO_4^{2-} = \frac{96}{96} = 1\,\text{mol}.$$

Action of Ca^{2+} ions with HCO_3^- and SO_4^{2-} ions is given below :

$$\underset{\substack{1\,\text{mol}\\ \frac{1}{2}\text{mol}}}{CaO} + \underset{\substack{2\,\text{mol}\\ 1\,\text{mol}}}{2HCO_3^-} \rightarrow Ca(HCO_3)_2 + H_2O \qquad ...(1)$$

$$\underset{1\,\text{mol}}{Ca^{2+}} + \underset{1\,\text{mol}}{SO_4^{2-}} \rightarrow CaSO_4 \qquad ...(2)$$

(*c*) Moles of HCO_3^- = 3 mol

From reaction (1), moles of CaO required to remove all $HCO_3^- = \frac{1}{2} \times 3 = 1.5$ moles

∴ Moles of SO_4^{2-} ions + moles of Ca^{2+} ions

= 1 + 1.5 = 2.5 moles

Reaction of CaO with $Ca(HCO_3)_2$ is : $CaO + Ca(HCO_3)_2 \rightarrow 2CaCO_3 + H_2O$.

(*d*) Moles of Ca^{2+} ions required to remove all

SO_4^{2-} ions = 1 mol

∴ Moles of Ca^{2+} ions left in solution = 2.5 – 1.5 = 1 mol.

∴ Mass of Ca^{2+} ions = 1 mol × mol. mass of Ca^{2+}

= 1 × 40 = 40 g

[At. mass or mol. mass of Ca^{2+} = 40]

(*e*) Moles of Ca^{2+} ions in one litre (= 1000 mL) water

$$= \frac{1}{1000} = 10^{-3}$$

∴ Moles of H^+ ions that will be exchanged with

Ca^{2+} ions $= 10^{-3} \times 2$ [∵ $Ca^{2+} \equiv H_2O$]

Or $[H^+] = 2 \times 10^{-3}$. Hence, $2H^+$

$pH = -\log(H^+)$.

Or $pH = -\log[2 \times 10^{-3}]$

$= -[\log 2 + \log 10^{-3}]$

$= -[0.3010 - 3] = 3 - 0.3010$

pH = 2.699 **Ans.**

28.5 VOLUME STRENGTH OF HYDROGEN PEROXIDE, H_2O_2

Type. Volume strength of H_2O_2 = 5.6 × normality.

x volume H_2O_2 means that one litre (or 1 mL) of *x* volume H_2O_2 liberates oxygen on decomposition = *x* litre (or *x* mL). Thus 20 volume H_2O_2 means that 1 mL of 20 volume H_2O_2 liberates oxygen = 20 mL. Thus :

$$\underset{\substack{2[(2\times1)+(2\times16)\\ =68\,g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22.4\,L\,at\,N.T.P.}{O_2} \qquad ...(1)$$

Calculation of x volume strength of H_2O_2.

From equation (1), it is clear that :

22.4 L O_2 is liberated from H_2O_2 = 68 g

∴ *x* volume O_2 is liberated from

$$H_2O_2 = \frac{68}{22.4} \times x = \frac{17x}{5.6}\text{g}$$

Hence, ***x volume strength of*** $\mathbf{H_2O_2} = \boldsymbol{\frac{17x}{5.6}\,g}$

But *x* volume strength of H_2O_2 = Normality × Eq. wt.

$$\therefore \quad \text{Normality} = \frac{\text{Strength of } x \text{ volume } H_2O_2}{\text{Eq. wt. of } H_2O_2}$$

$$\left[\text{Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2} = 17\right]$$

$$\textbf{Or} \quad \textbf{Normality} = \frac{17x}{5.6 \times 17} = \frac{x}{\mathbf{5.6}}$$

$$\text{Or} \quad \text{normality} = \frac{\text{Volume strength}}{5.6} = \frac{x}{5.6}$$

But molarity × mol. wt. = Normality × Eq. wt.

$$\therefore \quad \text{Molarity} \times 34 = \frac{x}{5.6} \times 17$$

[∵ Mol. wt. of H_2O_2 = (2 × 1) + (2 × 16) = 34]

$$\therefore \textbf{ Molarity of } \mathbf{H_2O_2} = \frac{x}{5.6} \times \frac{17}{34} = \frac{x}{\mathbf{11.2}}.$$

EXAMPLE 12. *20 mL of H_2O_2 solution were added to excess of acidified potassium iodide solution. The liberated iodine required 18.0 mL of 0.1N $Na_2S_2O_3$ solution for titration. Calculate the strength of H_2O_2 in terms of normality and volume.*

SOLUTION. We know :

Meq. of H_2O_2 = Meq. of I_2 = Meq. of $Na_2S_2O_3$

Meq. of H_2O_2 = Volume of H_2O_2 × normality of H_2O_2 (= N say)

Meq. of H_2O_2 = 20 × N ...(1)

Meq. of $Na_2S_2O_3$ = Vol. of $Na_2S_2O_3$ × normality of $Na_2S_2O_3$

Meq. of $Na_2S_2O_3$ = 18 × 0.1 = 1.8 ...(2)

Equating equations (1) and (2), we have :

$$20\ N = 1.8 \text{ Or } \mathbf{N} = \frac{1.8}{20} = \frac{18}{200} = \frac{9}{100} = \mathbf{0.09}$$

Volume strength of H_2O_2 $\underset{\substack{2[(2\times1)+(2\times16)]\\=68\,g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22.4L}{O_2}$

Or 22.4 L O_2 is liberated from H_2O_2 = 68 g

xL O_2 is liberated from

$$H_2O_2 = \frac{68}{22.4} \times x$$

∴ x volume strength of

$$H_2O_2 = \frac{68x}{22.4}$$

But x volume strength of H_2O_2 = Normality × Eq. wt.

$$\therefore \quad \frac{68x}{22.4} = 0.09 \times 17$$

$$\left[\because \text{ Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2} = 17\right]$$

$$\therefore \quad x = \frac{0.09 \times 17 \times 22.4}{68} = 0.504$$

∴Volume strength of H_2O_2 = **0.504 volume.**

EXAMPLE 13. *A bottle containing 20 volume H_2O_2 was left open. As a result, some of the H_2O_2 decomposed. In order to get new volume strength of H_2O_2, 10 mL of the solution was taken and diluted to 100 mL. 10 mL of this diluted solution consumed 25 mL of 0.025 M $KMnO_4$ solution in acidic medium. Calculate the volume strength of H_2O_2 solution.*

SOLUTION. Let normality of H_2O_2 = N

∴ 1 L (= 1000 mL) solution of H_2O_2 contains

H_2O_2 = N equivalents.

∴ 1 mL solution of H_2O_2 contains

$$H_2O_2 = \frac{N}{1000}\text{equivalents}$$

$$\text{Moles of } H_2O_2 \text{ in 1 mL} = \frac{1}{2} \times \frac{N}{1000}$$

$$\left[\because \text{ Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2}\right]$$

Moles of O_2 that H_2O_2 gives

$$= \frac{1}{2} \times \frac{1}{2} \times \frac{N}{1000}$$

$$\left[\begin{array}{l}\because\ H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \\ \textbf{Or}\ \ \frac{1}{2}O_2^{2-} \rightarrow \frac{1}{2}O_2 + 1\bar{e}\end{array}\right]$$

At N.T.P., volume of O_2 in mL

$$= 22400 \times \frac{1}{2} \times \frac{1}{2} \times \frac{N}{1000} = 5.6 \times \text{Normality}$$

[∵ 1 mol of O_2 occupy volume = 22400 mL at N.T.P.]

Or Volume strength = 5.6 × normality ...(1)

From titration of 10 mL H_2O_2, 25 mL of 0.025 M $KMnO_4$ is used.

Equivalents of H_2O_2 = Vol × normality

= 10 × normality. ...(2)

Equivalents of $KMnO_4$ = Vol. × molarity × n

= 25 × 0.025 × 5 ...(3)

$$\left[MnO_4^- + 8H^+ + \underset{n=5}{5e^-} \rightarrow Mn^{2+} + 4H_2O\right]$$

Equating (2) and (3), we get :

10 × normality of H_2O_2= 25 × 0.025 × 5

$$\therefore \text{ Normality of } H_2O_2 = \frac{25 \times 0.025 \times 5}{10} = 0.3125$$

Or Normality of 100 mL H_2O_2 diluted solution = 0.3125

∴ Normality of original 10 mL H_2O_2 solution

$$= 0.3125 \times \frac{100}{10} = 3.125$$

Substituting this normality value in equation (1), we get :

Volume strength = 5.6 × 3.125 = **17.5** **Ans.**

Type. % age strength of H_2O_2 in a sample marked

$$\textbf{'}x\textbf{ volume'} = \frac{68x}{22400} \times 100$$

EXAMPLE 14. *Find the percentage strength of H_2O_2 in a sample marked "10 volume".* **(Roorkee, 1989)**

SOLUTION. 10 volume H_2O_2 means that 1 mL of 10 volume H_2O_2 at N.T.P. liberates oxygen = 10 mL at N.T.P.

Reaction : $\underset{2[(2\times1)+(2\times16)]=68g}{2H_2O_2} \rightarrow 2H_2O + \underset{22400\,mL}{O_2}$

22400 mL O_2 is liberated from H_2O_2 = 68 g

∴ 10 mL O_2 is liberated

$$\text{from } H_2O_2 = \frac{68g}{22400\,mL} \times 10\,mL = \frac{68}{2240}g$$

$$\text{Thus : 1 mL } H_2O_2 \text{ contains } H_2O_2 = \frac{68}{2240}g$$

100 mL H_2O_2 contains

$$H_2O_2 = \frac{68}{2240} \times 100 = \mathbf{3.03\%}$$ **Ans.**

EXAMPLE 15. *Calculate the volume strength of 12% solution of H_2O_2.*

SOLUTION. 12% H_2O_2 means that :

100 mL H_2O_2 contains H_2O_2 = 12 g

∴ 1L (= 1000 mL) H_2O_2 contains

$$H_2O_2 = \frac{12}{100} \times 1000 = 120\,g$$

Reaction: $\underset{2[(2\times1)+(2\times16)]=68g}{2H_2O_2} \rightarrow 2H_2O + \underset{22400\,mL\,at\,N.T.P=22.4L}{O_2}$

68g H_2O_2 produce O_2 = 22.4 L

120 g H_2O_2 produce $O_2 = \frac{22.4\,L}{68} \times 120$

$\therefore$ 1 L solution gives O_2 at NTP

$$= \frac{22.4 \times 120}{68} L = 39.53\,L$$

Hence volume strength of 12% solution of H_2O_2 = 39.53.

Type. Normality of H_2O_2 solution

$$= \frac{\text{strength (of } x \text{ volume } H_2O_2) \text{ in } gL^-}{\text{Eq. wt. of } H_2O_2 (=17)}$$

Or Volume strength = 5.6 × Normality

EXAMPLE 16. *Calculate the normality of 20 volume H_2O_2.*

(AMU, medical, 2012)

SOLUTION. *Reaction* :

$$\underset{2[(2\times1)+(2\times16)]=68g}{2H_2O_2} \rightarrow 2H_2O + \underset{22.4\text{ L or }22400\text{ mL at N.T.P.}}{O_2} \quad ...(1)$$

20 volume H_2O_2 means that 1 L H_2O_2 produces O_2 = 20 L.

Thus, from equation (1), we see that :

22.4 L O_2 is produced from H_2O_2 = 68 g

$\therefore$ 20 L O_2 is produced from

$$H_2O_2 = \frac{68\,g}{22.4\,L} \times 20\,L = 60.71\,g$$

$\therefore$ Strength of H_2O_2 = 60.71 gL^-

$$\text{But, Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2} = 17$$

$$\text{Strength} = \text{Normality} \times \text{Eq. wt.}$$

$$\text{Normality} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{60.71}{17} = 3.57\,N$$

$$\textbf{Or} \quad \textbf{Normality} = \frac{\text{Volume strength of } H_2O_2}{5.6}$$

$$= \frac{20}{5.6} = 3.57\,N \qquad \textbf{Ans.}$$

Type. To find molarity of H_2O_2 solution, proceed, as follows :

(*i*) $\text{Normality} = \frac{\text{Strength of } x \text{ volume } H_2O_2 \text{ in } gL^-}{\text{Eq. wt. of } H_2O_2}$

Or $\text{Normality} = \frac{\text{Volume strength}}{5.6}$

(*ii*) Molarity of

$$H_2O_2 = \frac{\text{Normality} \times \text{Eq. wt. of } H_2O_2}{\text{Mol. wt. of } H_2O_2}$$

EXAMPLE 17. *Calculate the molarity of 5 volume H_2O_2.*

SOLUTION. *Reaction* :

$$\underset{2[(2\times1)+(2\times16)]=68g}{2H_2O_2} \rightarrow 2H_2O + \underset{22.4\,L\,at\,N.T.P}{O_2} \quad ...(1)$$

5 volume H_2O_2 means that 1 L H_2O_2 produces O_2 = 5L

Thus, from equation (1), we see that :

22.4 L O_2 is produced from H_2O_2 = 68 g

5 L O_2 is produced from

$$H_2O_2 = \frac{68g}{22.4\,L} \times 5L = 15.18\ gL^-$$

$\therefore$ Strength of 5 vol = 15.18 gL^-

$$\text{Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2}$$

$$= \frac{34}{2} = 17$$

Mol. wt. of H_2O_2 = 34 g mol^-

$$\text{Normality} = \frac{\text{Strength}}{\text{Eq. wt.}} = \frac{15.18}{17}$$

But, Molarity × mol. wt. = Normality × Eq. wt.

$$\therefore \quad \text{Molarity} = \frac{\text{normality} \times \text{Eq. wt.}}{\text{Mol. wt.}}$$

$$= \frac{15.18}{17} \times \frac{17}{34} = \mathbf{0.446\ M} \qquad \textbf{Ans.}$$

EXAMPLE 18. *What volume of 25 volume H_2O_2 should be decomposed to get 400 mL of O_2 at S.T.P. ?*

SOLUTION. 25 volume H_2O_2 means that :

1 mL of 25 volume H_2O_2 produces oxygen = 25 mL

$\therefore$ 25 mL of O_2 is produced from 25 volume

H_2O_2 = 1 mL

$\therefore$ 400 mL of O_2 is produced from 25 volume

$$H_2O_2 = \frac{1mL}{25mL} \times 400\text{ mL} = \mathbf{16\ mL} \quad \textbf{Ans.}$$

Type. To calculate strength of H_2O_2 solution.

EXAMPLE 19. *Calculate the strength of 10 cm^3 of a 20 volume solution of hydrogen peroxide in g per litre.*

SOLUTION. Volume of H_2O_2 = 10 cm^3; label of H_2O_2 = 20 volume. 20 volume H_2O_2 means that :

1 cm^3 H_2O_2 produce O_2 = 20 cm^3

10 cm^3 H_2O_2 produce O_2 = 20 × 10 = 200 cm^3

$$\text{But,} \quad \underset{\substack{2[(2\times1)+(2\times16)]\\=68g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400cm^3}{O_2}$$

22400 cm^3 O_2 is produced from H_2O_2 = 68 g

200 cm^3 O_2 is produced from

$$H_2O_2 = \frac{68}{22400} \times 200 = 0.607\,g$$

Thus, 10 cm^3 H_2O_2 contain H_2O_2 = 0.607 g

1000 cm^3 H_2O_2 contain

$$H_2O_2 = \frac{0.607}{10} \times 1000 = 60.7g$$

$\therefore$ Concentration of H_2O_2 = **60.7 g L^-** **Ans.**

Type. To calculate volume strength of H_2O_2.

EXAMPLE 20. *Calculate the strength in volumes of a solution containing 60.7 g L^- of hydrogen peroxide.*

SOLUTION. *Reaction* : $\underset{\substack{2[(2\times1)+(2\times16)]\\=68g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22.4\,L\,at\,N.T.P.}{O_2}$

68 g H_2O_2 produce O_2 = 22.4 L

60.7 g H_2O_2 produce $O_2 = \frac{22.4}{68} \times 60.7 \simeq 20L$

We know that : 1 L O_2 is produced from

H_2O_2 = 1 volume

∴ 20 L O_2 is produced from H_2O_2 = **20 volume** **Ans.**

Example 21. *A 5.0 cm^3 of H_2O_2 liberates 0.508 g of iodine from an acidified KI solution. Calculate the strength of H_2O_2 solution in terms of volume strength at S.T.P.* **(IIT, 1995)**

Solution. Volume of H_2O_2 = 5.0 cm^3; Wt. of I_2 = 0.508 g. Strength of H_2O_2 solution in terms of volume = ?

Reaction :

$$2KI + H_2SO_4 + \underset{(2\times1)+(2\times16)=34g}{H_2O_2} \rightarrow K_2SO_4 + 2H_2O + \underset{2\times127=254g}{I_2}$$

254 g I_2 is formed from H_2O_2 = 34 g

0.508 g I_2 is formed from

$$H_2O_2 = \frac{34}{254} \times 0.508 = 0.068 \text{ g}$$

It means : 5 cm^3 H_2O_2 solution contain

H_2O_2 = 0.068 g

∴ 1 cm^3 H_2O_2 solution contain

$$H_2O_2 = \frac{0.068}{5} = 0.0136g$$

But, $\underset{\substack{2[(2\times1)+(2\times16)]\\=68g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400cm^3}{O_2}$

68 g H_2O_2 produce O_2 = 22400 cm^3

0.0136 g H_2O_2 produce O_2

$$= \frac{22400}{68} \times 0.0136 = 4.48 \text{ cm}^3 \text{ at S.T.P.}$$

Since 1 cm^3 H_2O_2 produce O_2 = 4.48 cm^3

∴ Strength of H_2O_2 solution = **4.48 volume** **Ans.**

Type. To calculate percentage, normality and molarity of H_2O_2 solution.

Example 22. *The label on a bottle of hydrogen peroxide solution reads as 30 volume. Calculate the concentration of hydrogen peroxide in percentage. Also, calculate the molarity and normality of this solution.* **(Roorkee, 1989)**

Solution. (*a*) 30 volume H_2O_2 means that :

1 L H_2O_2 liberates O_2 = 30 L

But, $\underset{\substack{2[(2\times1)+(2\times16)]\\=68g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22.4L\,at\,N.T.P.}{O_2}$

Thus, 22.4 L O_2 is produced from H_2O_2 = 68 g

30 L O_2 is produced from

$$H_2O_2 = \frac{68g}{22.4L} \times 30L = 91.07gL^{-}$$

∴ Concentration of H_2O_2 = 91.07 g L^{-}.

Thus : 1000 mL H_2O_2 solution contain

H_2O_2 = 91.07 g

∴ 100 mL H_2O_2 solution contain

$$H_2O_2 = \frac{91.07}{1000} \times 100 = 9.107 \text{ g}$$

∴ Conc. of H_2O_2 in percentage = 9.107%

(*b*) To calculate normality of H_2O_2 :

$$\text{Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2} = 17$$

$$\therefore \quad \text{Normality} = \frac{\text{Wt. of } H_2O_2}{\text{g. eq. wt. of } H_2O_2} \times \frac{1000}{\text{Vol. of solution in mL}}$$

$$= \frac{91.07g}{17g} \times \frac{1000}{1000} = \mathbf{5.36} \qquad \textbf{Ans.}$$

(*c*) To calculate molarity of H_2O_2.

g. mol. wt. of H_2O_2 = (2 × 1) + (2 × 16) = 34 g. We know :

Molarity × Mol. wt. = normality × Eq. wt.

$$\therefore \quad \text{Molarity} = \frac{\text{normality} \times \text{Eq. wt.}}{\text{Mol. wt.}}$$

$$= \frac{5.36 \times 17}{34} = \mathbf{2.68\ M} \qquad \textbf{Ans.}$$

Example 23. *Calculate the mass of hydrogen peroxide present in 0.5 litre of a 2.5 M solution. Also, find the volume of oxygen at N.T.P. liberated upon the complete decomposition of 60 cm^3 of the above solution.*

Solution. (*a*) Volume = 0.5 L = 0.5 × 1000 = 500 cm^3; wt. of H_2O_2 = ? Volume of O_2 at N.T.P. = ?, molarity of H_2O_2 = 2.5 M; g. mol. wt. of H_2O_2 = (2 × 1) + (2 × 16) = 34 g.

$$\text{Molarity} = \frac{\text{wt.}}{\text{g. mol. wt.}} \times \frac{1000}{\text{Vol. of solution in cm}^3}$$

Or Wt. of H_2O_2

$$= \frac{\text{molarity} \times \text{g. mol. wt.} \times \text{vol. of solution in cm}^3}{1000}$$

$$= \frac{2.5 \times 34 \times 500}{1000} = \mathbf{42.5\ gL^{-}} \qquad \textbf{Ans.}$$

(*b*) $\underset{\substack{2[(2\times1)+(2\times16)]\\=68g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400cm^3 at N.T.P.}{O_2}$ ...(1)

1000 cm^3 H_2O_2 contain H_2O_2 = 42.5 g

60 cm^3 H_2O_2 contain $H_2O_2 = \frac{42.5}{1000} \times 60 = 2.55g$

From equation (1), we have :

68 g H_2O_2 liberate O_2 = 22400 cm^3

2.55 g H_2O_2 liberate O_2

$$= \frac{22400}{68} \times 2.55 = \mathbf{840\ cm^3} \qquad \textbf{Ans.}$$

Example 24. *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 thisulphate solution. Calculate the volume strength of H_2O_2 solution.* **(IIT, 1997)**

Solution. (*i*) Let N_1 = normality of H_2O_2 solution. Thus:

$$\begin{array}{ll} H_2O_2 \text{ solution} & Na_2S_2O_3 \text{ solution} \end{array}$$

$$N_1V_1 = N_2V_2\,;\; N_1 \times 25 = 0.3 \times 20$$

$$\therefore \quad N_1 = \frac{0.3 \times 20}{25} = 0.24$$

(*ii*) To find amount of H_2O_2 in 25 mL H_2O_2 solution.

$$\text{Eq. wt. of } H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times 1)+(16\times 2)}{2} = 17$$

We know that : 1000 mL 1N

$$H_2O_2 \equiv \text{g. eq. wt. of } H_2O_2 = 17\text{g}$$

$\therefore$ 25 mL of 0.24 N H_2O_2

$$\equiv \frac{17}{1000} \times 25 \times 0.24 = \mathbf{0.102\ g.}$$

(*iii*) To find volume strength of H_2O_2

$$\underset{\substack{2[(2\times1)+(2\times16)]\\=68\,\text{g}}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400\,\text{mL}}{O_2}$$

68g H_2O_2 liberate O_2 = 22400 mL

0.102 g H_2O_2 liberate

$$O_2 = \frac{22400}{68} \times 0.102 = 33.6\,\text{mL at N.T.P.}$$

25 mL H_2O_2 liberate O_2 = 33.6 mL

1 mL H_2O_2 liberate O_2

$$= \frac{33.6}{25} = 1.344\,\text{mL}$$

$\therefore$ Volume strength of H_2O_2 = **1.344** **Ans.**

Example 25. *Hydrogen peroxide solution (20 mL) reacts quantitatively with the solution of $KMnO_4$ (20 mL) acidified with dilute sulphuric acid. The same volume of the $KMnO_4$ solution is just decolorised 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 conditions in presence of dilute sulphuric acid. Write the balanced equations involved in the reaction and calculate the molarity of H_2O_2.* **(IIT, 2001)**

Solution. The balanced equations are :

(*i*) In acidic medium :

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-] \times 5$$

$$\text{Adding: } 2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

(*ii*) In neutral medium :

$$MnO_4^- + 2H_2O + 3e^- + \rightarrow MnO_2 + 4OH^-] \times 2$$

$$Mn^{2+} + 4OH^- \rightarrow MnO_2 + 2H_2O + 2e^-] \times 3$$

$$\text{Adding : } 2MnO_4^- + 3Mn^{2+} + 4OH^- \rightarrow \underset{\text{Brown ppt}}{5MnO_2} + 2H_2O$$

(*iii*) To dissolve MnO_2ppt in sodium oxalate ($Na_2C_2O_4$) and dil. H_2SO_4.

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$$\text{Adding : } MnO_2 + C_2O_4^{2-}\ 4H^+ \rightarrow Mn^{2+} + 2CO_2 + 2H_2O$$

We know that 20 mL H_2O_2 reacts quantitatively with 20 mL $KMnO_4$. Also from equation (*iii*) we find that :

x equivalents sodium oxalate $\equiv x$ eqivalents of MnO_2 $\equiv x$ equivalents of H_2O_2 ...(*iv*)

$$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

$$\therefore \text{ Eq. wt. of } Na_2C_2O_4 = \frac{\text{Mol. wt.}}{2}$$

$\therefore$ Normality of

$$\begin{aligned} Na_2C_2O_4 &= \text{Molarity} \times \text{no. of electrons} \\ \text{involved} &= 0.2 \times 2 = 0.4 \end{aligned}$$

$\therefore$ Milliequivalent of $Na_2C_2O_4$

$$\begin{aligned} &= \text{Normality} \times \text{volume in mL} \\ &= 0.4 \times 10 = 4 \end{aligned}$$

Hence using relation (*iv*), no. of milliequivalents of H_2O_2 in 20 mL = 4.

Or *no. of milliequivalents of H_2O_2 in 1 mL*

$$= \frac{4}{20} = \mathbf{0.2.}$$

Or No. of millimol of

$$H_2O_2 \text{ in 1 mL} = \text{no. of milliequivalents} \times \frac{\text{Eq. wt. of } H_2O_2}{\text{Mol. wt. of } H_2O_2}$$

$$= \frac{0.2 \times 17}{34} = \mathbf{0.1}$$

[$\because$ Mol. wt. of H_2O_2 = (2 × 1) + (2 × 16) = 34; eq. wt. of

$$H_2O_2 = \frac{\text{Mol. wt.}}{\substack{\text{Total valency}\\ \text{of } 2H^+(=2)}} = \frac{34}{2} = 17]$$

Hence molarity of H_2O_2 = 0.1 M **Ans.**

28.6 AIEEE PATTERN EXAMPLES

Example 26. *The hardness of water containing 24 ppm of $MgSO_4$ is :*

(a) 10 ppm	*(b) 20 ppm*
(c) 30 ppm	*(d) 40 ppm*

Solution. Mol. wt. of $MgSO_4$

$$= 24 + 32 + (4 \times 16) = 120\ \text{g mol}^-.$$

Mol. wt. of $CaCO_3$ = 40 + 12 + (3 × 16) = 100 g mol^-

We know that : 1 g mol

$$\begin{array}{rl} MgSO_4 & \equiv 1 \text{ g mol } CaCO_3 \\ 120\text{ g} & 100\text{ g} \\ 120\text{ ppm} & 100\text{ ppm} \end{array}$$

Since the hardness of water is expressed in terms of $CaCO_3$, thus :

$$120 \text{ ppm } MgSO_4 \equiv 100 \text{ ppm } CaCO_3$$

$$24 \text{ ppm } MgSO_4 \equiv \frac{100}{120}\times 24 = 20\,\text{ppm}$$

So, the correct answer is (*b*).

Example 27. *The temporary hardness of water containing 20 ppm of Ca $(HCO_3)_2$ and 10 ppm of $MgSO_4$ is :*

(*a*) *8.2 ppm* (*b*) *9.2 ppm*

(*c*) *12.3 ppm* (*d*) *24.6 ppm*

Solution. Mol. wt. of

$$Ca\,(HCO_3)_2 = 40 + 2\,[1 + 12 + (3 \times 16)]$$
$$= 162 \text{ g mol}^-$$

Mol. wt. of $CaCO_3$ = 40 + 12 + (3 × 16) = 100 g mol$^-$

Since temporary hardness of water is due to $Ca(HCO_3)_2$ only and it is expressed in terms of $CaCO_3$, so we have :

g. mol. of $Ca(HCO_3)_2 \equiv$ 1 g. mol $CaCO_3$

162 g 100 g

162 ppm 100 ppm

162 ppm $Ca(HCO_3)_2 \equiv$ 100 ppm $CaCO_3$

$$\therefore\ 20 \text{ ppm } Ca(HCO_3)_2 \equiv \frac{100}{162}\times 20 = 12.3\,\text{ppm}$$

So, the correct answer is (*c*).

Example 28. *The permanent hardness of water containing 12 mg of $MgCl_2$ and 24 ppm of $Mg(HCO_3)_2$ per 1/2 kg of water is :*

(*a*) *25.2 ppm* (*b*) *12.6 ppm*

(*c*) *126 ppm* (*d*) *1.26 ppm*

Solution. Out of $MgCl_2$ and $Mg(HCO_3)_2$, the permanent hardness is due to $MgCl_2$ only.

Mol. wt. of $MgCl_2$ = 24 + (2 × 35) = 95 g mol$^-$;

Mol. wt. of $CaCO_3$ = 40 + 12 + (3 × 16) = 100 g mol$^-$

Since the hardness is expressed in terms of $CaCO_3$, so, we have :

$$\text{Wt. of } MgCl_2 = 12\text{mg}\times\frac{1\text{g}}{1000\,\text{mg}} = 12\times10^{-3}\text{g}$$

$$\text{No. of mol. of } MgCl_2 = \frac{\text{wt.}}{\text{mol. wt.}} = \frac{12\times10^{-3}\text{g}}{95\text{g mol}^-}$$
$$= 1.26 \times 10^{-4} \text{ mol}$$

But, 1 g mol $MgCl_2 \equiv$ 1 g mol $CaCO_3 \equiv$ 100 g $CaCO_3$

1.26×10^{-4} mol $MgCl_2$ = $1.26 \times 10^{-4} \times 100$ g $CaCO_3$

= 1.26×10^{-2} g $CaCO_3$

$$\text{Wt. of hard water} = \frac{1}{2}\text{kg} = \frac{1}{2}\times 1000 = 500\,\text{g}.$$

∴ 500 g hard water contains $MgCl_2$ equivalent to $CaCO_3$ = 1.26×10^{-2}g $CaCO_3$

∴ 10^6 g (= one million) water contains $MgCl_2$ equivalent to $CaCO_3$

$$= \frac{1.26\times10^{-2}\text{g}}{500\,\text{g}}\times10^6\text{g} = 25.2\text{g}.$$

∴ Permanent hardness of water = 25.2 ppm. So, the correct answer is (*a*).

Example 29. *The 'volume strength' of 1.5 N H_2O_2 solution is :*

(*a*) *4.8* (*b*) *8.4*

(*c*) *3.0* (*d*) *8.0*

(CBSE, 1997, IIT, 1991)

Solution. g. eq. wt. of

$$H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2} = 17\text{g}$$

1N H_2O_2 contain

H_2O_2 = 1 g eq. wt. of H_2O_2= 17 g

1.5 N H_2O_2 contain H_2O_2 = 17 × 1.5 = 25.5 g

$$\underset{\substack{2[(2\times1)+(2\times16)]\\=68\,\text{g}}}{2H_2O_2} \rightarrow \underset{22.4\text{L}}{O_2} + 2H_2O$$

68 g H_2O_2 liberate O_2 = 22.4 L

$$25.5 \text{ g } H_2O_2 \text{ liberate } O_2 = \frac{22.4}{68}\times 25.5 = 8.4 \text{ L}$$

So, the correct answer is (*b*).

Example 30. *The amount of H_2O_2 present in one litre of 2.2 N H_2O_2 solution is :*

(*a*) *74.8* (*b*) *37.4*

(*c*) *18.7* (*d*) *9.35*

Solution. g. eq. wt. of

$$H_2O_2 = \frac{\text{Mol. wt.}}{2} = \frac{(2\times1)+(2\times16)}{2} = 17\text{g}$$

1 N H_2O_2 contain H_2O_2 = g. eq. wt. of H_2O_2 = 17 g

2.2 N H_2O_2 contain H_2O_2 = 17 × 2.2 = 37.4 g

So, the correct answer is (*b*).

Example 31. *20 volume of H_2O_2 solution has a strength of about*

(*a*) *30%* (*b*) *6%*

(*c*) *3%* (*d*) *10%*

Solution. $\underset{\substack{2[(2\times1)+(2\times16)]\\=68\,\text{g}}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400\,\text{mL}}{O_2}$

20 volume H_2O_2 solution means that 1 mL H_2O_2 liberate 20 mL oxygen.

22400 mL O_2 is liberated from H_2O_2 = 68 g.

$$20 \text{ mL } O_2 \text{ is liberated from } H_2O_2 = \frac{68}{22400}\times 20 = 0.06$$

$$\%\text{ age of } H_2O_2 = \frac{0.06}{1}\times 100 = 6\%$$

So, the correct answer is (*b*).

Example 32. *Commercially 10 volume H_2O_2 is a solution with strength of approximately*

(*a*) *30 gL$^-$* (*b*) *6 gL$^-$*

(*c*) *3 gL$^-$* (*d*) *10 gL$^-$*

(BET, 2003)

Solution. 10 volume H_2O_2 means that :

1 mL of H_2O_2 at N.T.P. gives O_2 gas = 10 mL

Reaction : $\underset{\substack{2[(2\times1)+(2\times16)]\\=68\,g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400\,mL}{O_2}$

22400 mL O_2 at N.T.P. ≡ 68 g H_2O_2

$\therefore$ 10 mL O_2 at N.T.P. = $\dfrac{68}{22400}\times10 = 0.0303\,g$

$\therefore$ 1mL of H_2O_2 (volume) weighs
= 0.0303 g

$\therefore$ 1000 mL of H_2O_2 (10 volume) weighs
= 0.0303 × 1000 = 30.3 ≃ 30 gL^-.

So, the correct answer is (*a*).

Exampe 33. *The percent strength (W/V) and normality of 15 mL of a 40 volume H_2O_2 solution is respectively.*

(*a*) *6%, 6.1 N* (*b*) *7%, 9.2 N*
(*c*) *12.13%, 7.14 N* (*d*) *20%, 2N*

Solution. 40 volume H_2O_2 means that :

1 mL of 40 volume H_2O_2 produces O_2 = 40 mL

$\therefore$ 15 mL of 40 volume H_2O_2 produces

$$O_2 = \frac{40\,mL}{1\,mL}\times15\,mL = 600\,mL$$

Reaction : $\underset{\substack{2[(2\times1)+(2\times16)]\\=68\,g}}{2H_2O_2} \rightarrow 2H_2O + \underset{22400\,mL\,at\,N.T.P.}{O_2}$

22400 mL of O_2 at N.T.P. is obtained from
H_2O_2 = 68 g

$\therefore$ 600 mL of O_2 at N.T.P. is obtained from

$$H_2O_2 = \frac{68g}{22400\,mL}\times600\,mL = 1.82g$$

(*i*) 15 mL of given H_2O_2 solution contains
H_2O_2 = 1.82 g

1000 mL (or 1L) of given H_2O_2 solution contains H_2O_2

$$= \frac{1.82g}{15\,mL}\times1000\,mL = 121.3\,gL^-$$

$\therefore$ Strength of given 40 volume
H_2O_2 solution = 121.3 gL^-

Similarly : 15 mL of given H_2O_2 solution contains
H_2O_2 = 1.82 g

$\therefore$ 100 mL of given H_2O_2 solution contains

$$H_2O_2 = \frac{1.82\,g}{15\,mL}\times100\,mL$$

= 12.13 g per 100 mL

$\therefore$ Percent strength of given
H_2O_2 = 12.13 % (W/V)

(*ii*) Eq. wt. of H_2O_2 = $\dfrac{\text{Mol. wt. of } H_2O_2}{2}$

$$= \frac{(2\times1)+(2\times16)}{2} = 17$$

$[\because H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-]$

$$\therefore \quad \text{Normality} = \frac{\text{Strength in gL}^-}{\text{Eq.wt.}} = \frac{12.13}{17}$$

= 7.14 N **Ans.**

So, the correct answer is (*c*).

Example 34. *7.5 cm^3 of '10 volume' H_2O_2 solution was acidified with dil. H_2SO_4 and titrated with N/20 $KMnO_4$ solution. It was found that 15 cm^3 of N/20 $KMnO_4$ was needed to exactly oxidise the given H_2O_2 solution. The % age of H_2O_2 in the solution is :*

(*a*) *20%* (*b*) *21%*
(*c*) *17%* (*d*) *0.17%*

Solution. For H_2O_2 ,
N_1 = ?, V_1 = 7.5 cm^3; For $KMnO_4$,
N_2 = 1/20, V_2 = 15 cm^3.

Using normality equation, we have:

$$\begin{aligned} &H_2O_2 \quad KMnO_4 \\ N_1V_1 &= N_2V_2 \\ N_1\times7.5\,cm^3 &= \frac{1}{20}\times15\,cm^3; N_1 \\ &= \frac{1}{20}\times\frac{15\,cm^3}{7.5\,cm^3} = 0.1N \end{aligned}$$

H_2O_2 (reductant) was oxidised by $KMnO_4$ according to the reaction:

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$$

$\therefore$ Eq. wt. of H_2O_2 = $\dfrac{\text{Mol. wt.}}{2} = \dfrac{(2\times1)+(2\times16)}{2} = 17$

$\therefore$ Strength of H_2O_2 = Normality × Eq. wt.
= 0.1 × 17 = 1.7 g L^-

Hence,% age of H_2O_2= $\dfrac{1.7\times100}{1000} = 0.17\%$

So, the correct answer is (*d*).

Example 35. *The normality of 30 volume H_2O_2 is:*

(*a*) *2.678 N* (*b*) *5.35 N*
(*c*) *8.034 N* (*d*) *6.685 N*

(WB-JEE, 2011)

Solution. We know:
Volume strength = 5.6 × normality
$\therefore$ 30 = 5.6 × Normality;
Normality = 30/5.6 = 5.35

So, the correct strength is (*b*).

Example 36. *An ion exchange resin RH_2 displaces Mg^{2+} ions in hard water as:*

$Mg^{2+} + RH_2 \rightarrow R\,Mg + 2H^+$

When exact one litre of hard water was passed through the resin, the water was found to have pH = 3. So, the hardness of Mg^{2+} in ppm will be:

(*a*) *4 ppm* (*b*) *8 ppm*
(*c*) *12 ppm* (*d*) *16 ppm*

(PSEB, 2012)

Solution. pH = 3. So, $[H^+] = 10^{-3}$ and $[Mg^{2+}] = 10^{-3}/2$

$= \dfrac{24 \times 10^{-3}}{2}$ g L^- ($\because$ at. wt. of Mg = 24 amu.). Hence:

$$\text{Hardness} = \frac{24 \times 10^{-3}}{2 \times 1000} \times 10^6 = 12 \text{ ppm.}$$

[$\because$ 1 L = 1000mL]

Example 37. *150 mL of a given hard water (density 1 g cm^{-3}) needs 31.2 mL of 0.04 N H_2SO_4 for complete reaction. The hardness of water will be:*

(a) *208 ppm* *(b)* *416 pm*
(c) *624 pm* *(d)* *832 ppm*

(H.P. Board, 2012)

Solution. The hardness is calculated in terms of $CaCO_3$, mol. wt. = 100 [*i.e.*, 40 + 12 + (3 × 16) = 100] and equivalent weight = 100/Valency of Ca^{2+} = 2

= 50. Thus:

Milliequivalents of H_2SO_4 = Milliequivalents of $CaCO_3$.

$$31.2 \times 0.04 = \frac{\text{wt. of } CaCO_3\ (= w)}{\text{Eq. wt. of } CaCO_3} \times 1000 = \frac{w \times 1000}{50}$$

$$\therefore w = \frac{31.2 \times 0.04 \times 50}{1000} = 0.0624$$

$$\text{Hence hardness} = \frac{0.0624 \times 10^6}{150} = 416 \text{ ppm}$$

So, the correct answer is (*b*).

Example 38. *Calculate the degree of hardness (in ppm) of a sample of water containing 6 mg of $MgSO_4$ per kg of water. (Mol. wt. of $MgSO_4$ = 120 g mol^-)*

Solution.

Mol. wt. of $MgSO_4$ = 120 g mol^- = 1 g mol^- of $MgSO_4$

(*i*) 120 g $MgSO_4 \equiv$ 1 g mol of $CaCO_3$ or 100 g $CaCO_3$

$$6 \times 10^{-3} \text{ g } MgSO_4 = \frac{100 \times 6 \times 10^{-3}}{120} = 5 \times 10^{-3} \text{ g } CaCO_3$$

$$\left[\begin{array}{l} \because \text{Mol. wt. of } CaCO_3 = 40 + 12 + 3\,(16) = 100 \\ \text{Also, } 6 \text{ mg} = 6 \times 10^{-3} \text{ g} \\ \quad 1 \text{ kg} = 1000 \text{ g} \end{array}\right]$$

(*ii*) 1000 g water contains $MgSO_4$ equivalent to 5×10^{-3} g $CaCO_3$

$$\therefore 10^6 \text{ g of water will contain } CaCO_3 = \frac{5 \times 10^{-3}}{1000} \times 10^6$$

$= 5$ g $CaCO_3$

$\therefore$ Hardness of water sample = **5 ppm** **Ans.**

PROBLEMS FOR PRACTICE

1. Volume strength of hydrogen peroxide is 22.4. What volume of this sample is required for the oxidation of 3.4 g of hydrogen sulphide?

(*a*) 50 mL (*b*) 200 mL
(*c*) 100 mL (*d*) 5 mL **Ans.** (*a*)

2. The normality of 30 volume H_2O_2 is:

(*a*) 1.1 (*b*) 2.2
(*c*) 5.36 (*d*) 6.2 **Ans.** (*c*)

3. A sample of water contains 30 ppm of $CaCl_2$. Find the degree of hardness of this water.

Ans. (27.03 ppm $CaCO_3$)

4. Calculate the molarity of 10 volume H_2O_2.

Ans. (3.57 M)

5. What volume of 30 volume H_2O_2 be decomposed to get 100 mL of oxygen at N.T.P.?

Ans. (3.33 mL)

6. Calculate the strength in volumes of a solution containing 60.7 gL^- of hydrogen peroxide.

Ans. (20 Volume)

7. The temporary hardness of water containing 15 ppm of $Ca(HCO_3)_2$ and 10 ppm of $MgSO_4$ is:

(*a*) 9.26 ppm (*b*) 1 ppm
(*c*) 2 ppm (*d*) 1.97 ppm

Ans. (*a*)

8. The hardness of water containing 10 ppm $MgSO_4$ is:

(*a*) 5.1 (*b*) 7.7
(*c*) 8.33 (*d*) 2.67 **Ans.** (*c*)

9. Calculate the volume strength of 0.16 N H_2O_2.

Ans. (0.896)

10. Find the volume strength of 0.2 M H_2O_2.

Ans. (2.24)

Note: For more numericals on hard water, see chapter 23, page.. 662.

29

CHAPTER

Polymers, Co-ordination Compounds and Surface Chemistry

29.1 POLYMERS

These are the high molecular mass compounds, obtained by joining to-gether a large number of simple molecules through covalent bonds in a regular fashion. The simple molecules which combine to form a polymer are called monomers. The process of the formation of polymers from the simple starting materials is called polymerisation.

29.2 NUMBER AVERAGE MOLECULAR WEIGHTS ($\overline{\mathbf{M}}_\mathbf{n}$)

It is defined as the total mass (or weight) of the material of a polymer sample divided by the number of moles of various polymer molecules present in the sample.

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + ... n_iM_i + ...}{n_1 + n_2 + ... n_i + ...}$$

$$= \overline{M}_n = \frac{\sum_i niM_i}{\sum_i n_i}$$

Where $n_1\ n_2\ .....\ n_i$ ..... are the number of moles of the polymer molecule of molecular weight M_1, M_2 ..... M_i respectively.

Or $$\overline{M}_n = \frac{\text{wt. of polymer sample}}{\text{Total number of moles of various molecules present in the sample}}$$

In other words, $\overline{M}_n$ is simply the arithmetic mean of molecular weights of all molecules in a sample.

If *xi* is the mole fraction of polymer species '*i*', with molar mass 'M_i' then :

$$\overline{M}_n = \sum_i xiMi$$

29.3 WEIGHT AVERAGE MOLECULAR WEIGHTS ($\overline{\mathbf{M}}_\mathbf{w}$)

It is defined as the total contribution of various weight fractions of molecules to-wards the total molecular mass of the polymeric sample. *i.e.,*

$$\overline{M}_w = \sum_i w_iM_i = w_1M_1 + w_2M_2 + ...w_iM_i + ... \qquad (1)$$

Where w_i is the weight or mass fraction of polymeric species with molecular mass M_i *i.e.,*

$$w_i = \frac{\text{Mass of species '}i\text{'}}{\text{Total mass of polymer sample}}$$

$$= \frac{m_i}{\Sigma m_i} = \frac{n_iM_i}{\Sigma n_iM_i} \qquad ...(2)$$

Combining equations (1) and (2), we get :

$$\overline{M}_w = \frac{n_1M_1 \times M_1}{\Sigma n_iM_i} + \frac{n_2M_2 \times M_2}{\Sigma n_iM_i} + ... \frac{n_iM_i \times M_i}{\Sigma n_iM_i}$$

Or $$\overline{M}_w = \frac{\Sigma n_iM_i^2}{\Sigma n_iM_i}$$

29.4 CO-ORDINATION OR COMPLEX COMPOUNDS

These are such compounds which retain their identities even when dissolved in water or any other solvent and having properties completely different from those of the constituents. The branch of inorganic chemistry which deals with the study of co-ordination compounds is called co-ordination chemistry.

In co-ordination or complex compounds, the ligands that are written along with the central metal in square brackets *i.e.,* [] are non-ionisable while those which are written outside the square brackets are ionisable. *e.g.,*

(*i*) When the complex $[Co(NH_3)_6]Cl_3$ is dissolved in water, we get three Cl^- ions as shown below.

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$

(*ii*) When the complex $[Co(NH_3)_5Cl]Cl_2$ is dissolved in water, we get two Cl^- ions as shown below.

$$[Co(NH_3)_5Cl]Cl_2 \rightleftharpoons [Co(NH_3)_5Cl]^{2+} + 2Cl^-$$

Adsorption. The phenomenon of higher concentration of molecular species (gases or liquids) at the surface of a solid than in the bulk is called adsorption.

Freundlich adsorption isotherm. The curves obtained by plotting the amount of gas adsorbed ($a = x/m$) against gas pressure at a constant temperature are called adsorption isotherms. Mathematically, $\frac{x}{m} = a = kp^{1/n}$. This relation is called Freundlich isotherm. $\frac{x}{m}$ is the amount of gas adsorbed per gram of the adsorbent at a pressure P. K and n are the constants depending upon the nature of the gas and the adsorbent.

Example 1. *A sample of human blood plasma contains 40.0 g albumin with molecular weight, $M_1 = 69000$ and 20.0 g of globulin with molecular weight, $M_2 = 162000$. Calculate $\overline{M_n}$ and $\overline{M_w}$.*

Solution. Wt. of albumin, $W_1 = 40.0$g ; mol. wt, $M_1 = 69000$. So, no. of moles of albumin, $n_1 = \frac{40}{69000}$; Wt. of globulin, $W_2 = 20.0$g ; mol. wt., $M_2 = 162000$. So, $n_2 = \frac{20}{162000}$.

Hence (*i*) $\overline{M_n} = \frac{\sum_i niMi}{\sum_i ni}$

$$= \frac{[(40/69000) \times 692000 + [(20/162000) \times 162000]}{(40/69000) + (20/162000)}$$

$$= (40 + 20)/(5.7971 \times 10^{-4}) + (1.2346 \times 10^{-4})$$

$$= 60/10^{-4}(5.7971 + 1.2346) = \frac{60 \times 10^4}{7.0317} = 85328$$

(*ii*) $\overline{M_w} = \sum_i niM_i^2 / \sum_i niMi.$

$$= \frac{(40/69000) \times (69000)^2 + (20/162000) \times (162000)^2}{(40/69000) \times 69000 + (20/162000) \times 162000}$$

$$= 6 \times 10^6/60 = \mathbf{10^5}$$ **Ans.**

Example 2. *Calculate the number average molecular mass $\overline{M_n}$ and weight average molecular mass ($\overline{M_w}$) of a polymer in which 30% molecules have a molecular mass 20,000; 40% have 30,000 and the rest 30% have 60,000.*

Solution. The polymer contains $n_1 = 30, M_1 = 20{,}000$; $n_2 = 40, M_2 = 30{,}000$ and $n_3 = 30, M_3 = 60{,}000$.

So, $\overline{M_n} = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$

$$= \frac{30 \times 20{,}000 + 40 \times 30{,}000 + 30 \times 60{,}000}{30 + 40 + 30}$$

$$= \frac{10{,}000\,(60 + 120 + 180)}{100} = 36{,}000$$ **Ans.**

$$\overline{M_w} = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2}{n_1M_1 + n_2M_2 + n_3M_3}$$

Substituting the values, we get ;

$$\frac{30(20{,}000)^2 + 40(30{,}000)^2 + 30(60{,}000)^2}{30 \times 20000 + 40 \times 30{,}000 + 30 \times 60{,}000}$$

$$= \frac{10^8(120 + 360 + 1080)}{10^4(60 + 120 + 180)}$$

$$= 10^4(1560/360) = 43333$$ **Ans.**

Example 3. *1 kg of a polymer with molar mass 10,000 g and the same amount of polymer with molar mass 20,000 g are mixed. Calculate $\overline{M_n}$ and $\overline{M_w}$.* **(GNDU 1998)**

Solution. (*i*) Wt. of one polymer, $W_1 = 1$ kg $= 1000$ g ; molar mass of one polymer, $M_1 = 10{,}000$ g.

So, n_1 = no. of moles of one polymer

$$= \frac{\text{wt.}}{\text{molar mass}} = \frac{1000\text{g}}{10{,}000\text{g}} = 0.1$$

(*ii*) Wt. of second polymer $W_2 = 1$ kg $= 1000$ g ; molar mass. of second $M_2 = 20{,}000$g.

So, n_2 = no. of moles of second polymer

$$= \frac{\text{wt.}}{\text{molar mass}} = \frac{1000\text{g}}{20{,}000\text{g}} = 0.05.$$

$\therefore$ $\overline{M_n} = \frac{\sum_i n_iM_i}{\sum_i n_i}$

$$= \frac{0.1 \times 10000 + 0.05 \times 20000}{0.1 + 0.05} = \frac{2000}{0.15}$$

$$= \mathbf{13333}$$ **Ans.**

Also, $\overline{M_w} = \frac{\sum_i n_iM_i^2}{\sum_i n_iM_i}$

$$= \frac{0.1 \times (10000)^2 + 0.05 \times (20{,}000)^2}{0.1 \times 10{,}000 + 0.05 \times 20{,}000}$$

$$= \frac{10^7 + 2 \times 10^7}{2000} = \frac{10^7(1 + 2)}{2000} = \frac{3 \times 10^7}{2 \times 10^3}$$

$$= \mathbf{15{,}000}$$ **Ans.**

Example 4. *A solution containing 4.22 g $PtCl_4.5NH_3$ was passed through a cation exchanger. The solution so obtained was treated with $AgNO_3$ solution. As a result 4.305 g of AgCl precipitate was obtained. Calculate the formula of the complex. (Molar mass of $PtCl_4.5NH_3$ = 422 g mol^{-} ; at. wt. of Ag = 108, Cl = 35.5).*

Solution. (*i*) Molar mass of AgCl = 108 + 35.5 = 143.5g mol$^-$; wt. of AgCl ppt = 4.305g.

We know that :

$$AgCl \equiv Cl$$
$$143.5 \text{ g} \quad 35.5 \text{ g}$$

143.5 g AgCl contain Cl = 35.5 g

$$4.305 \text{ g AgCl contain Cl} = \frac{35.5}{143.5} \times 305 = 1.065 \text{ g}$$

(*ii*) Let *n* = no. of Cl$^-$ ions (ionisable) outside the coordination sphere. Hence

422 g of $PtCl_4.5NH_3$ contain ionisable

Cl$^-$ ions = $n \times 35.5$ g

∴ 4.22 g of $PtCl_4.5NH_3$ contain ionisable

$$Cl^- \text{ ions} = \frac{n \times 35.5}{422} \times 4.22$$

$$\text{Hence} \quad \frac{n \times 35.5 \times 4.22}{422} = 1.065$$

$$\therefore \quad n = \frac{1.065 \times 422}{35.5 \times 4.22} = 3.0$$

∴ no. of Cl$^-$ ions outside the co-ordination sphere = 3

∴ Formula of the complex = **$[Pt(NH_3)_6]Cl_3$** **Ans.**

Example 5. *A solution containing 1 g of the complex $[Co(NH_3)_6]Cl_3$ was passed through a cation exchanger. The acid liberated was made up to one litre. Find out the strength of the acid solution. (At. wt., Co = 58.9, Cl = 35.5, N = 14, H = 1)*

Solution. Molar mass of complex $[Co(NH_3)_6]Cl_3$ = 58.9 + 6[14 + (3 × 1)] + 3 (35.5) = 266.4 g mol$^-$.

When solution of above complex is passed through cation exchanger, HCl is produced according to the following reactions.

$$\underset{1 \text{ mol}}{[Co(NH_3)_6]Cl_3} \rightleftharpoons \underset{3 \text{ mol}}{[Co(NH_3)_6]^{3+}} + \underset{3 \text{ mol}}{3Cl^-}$$

$$\underset{\text{(From cation exchanger)}}{3H^+} + 3Cl^- \longrightarrow \underset{3 \text{ mol}}{3HCl}$$

∴ 3 mol of HCl are produced from 1 mol of the complex *i.e.*,

$$[Co(NH_3)_6]Cl_3 \equiv 3HCl$$
$$266.4 \text{ g} \quad 3(1 + 35.5) = 109.5 \text{ g}$$

266.4 g complex liberated HCl = 109.5 g

$$1 \text{ g complex liberated HCl} = \frac{109.5}{266.4} \text{g} = 0.411 \text{ g}$$

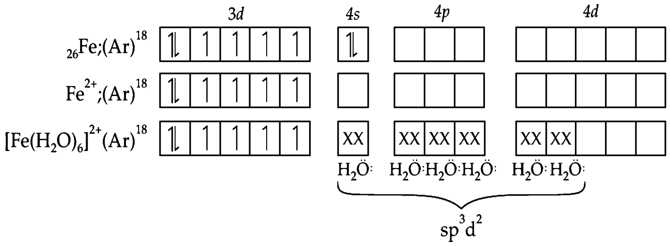
Hence one litre solution contain HCl = **0.411 g** **Ans.**

Example 6. *Describe for any two of the following complex-ions, the type of hybridisation, shape and magnetic properties.*

(*i*) $[Fe(H_2O)_6]^{2+}$ (*ii*) $[Co(NH_3)_6]^{3+}$

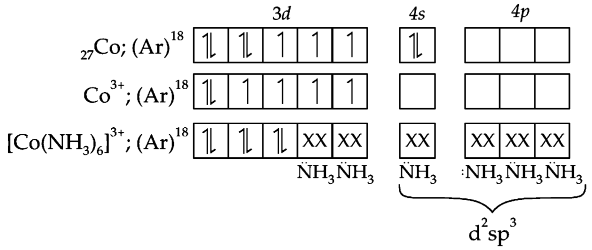
(At. no. Fe = 26, Co = 27, Ni = 28) **(CBSE, 2007)**

Solution. (*i*) $[Fe(H_2O)_6]^{2+}$. Here, oxidation state of Fe = +2



The complex has sp^3d^2 hybridisation and hence has octahedral shape. It is paramagnetic due to four unpaired electrons.

(*ii*) $[Co(NH_3)_6]^{3+}$. Here oxidation state of Co = +3

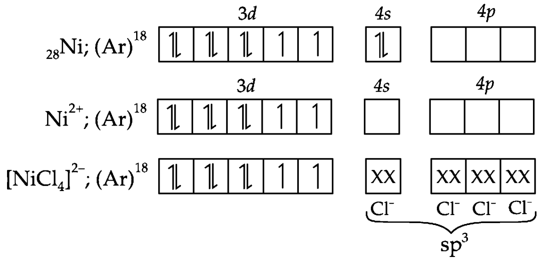


The complex has d^2sp^3 hybridisation and hence has octahedral shape. It is diamagnetic because all electrons are paired.

Example 7. *The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is.*

(*a*) 1.82 BM	(*b*) 5.46 BM
(*c*) 2.82 BM	(*d*) 1.41 BM **(AIEEE, 2011)**

Solution. $[NiCl_4]^{2-}$. Here oxidation state of Ni = + 2



The complex has sp^3 hybridisation and hence has tetrahedral shape. It is paramagnetic due to two unpaired electrons. *i.e.*, $\mu_{BM} = [n(n + 2]^{1/2} = [2\ (2 + 2)]^{1/2} = 8^{1/2} =$ 2.82 B.M.

So, correct answer is (c)

Example 8. *A decapeptide (mol. wt. 796) on complete hydrolysis gives glycine (mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is :* **(IIT-JEE, 2011)**

Solution. Given : Decapeptide + $9H_2O$ → glycine + alanine + phenylalanine. Thus total wt. of amino acids after addition of 9 mol H_2O = 796 + (9 × 18) = 958. Let *n* = no. of units of glycine. So:

$$\frac{n \times 75}{958} \times 100 = 47.0 \; ; n = \frac{47 \times 958}{75 \times 100} = 6.003 \simeq 6$$

Example 9. *In a coagulation experiment, a sol of As_2S_3 is mixed with distilled water and 0.2 m solution of an electrolyte,* *AB so that total volume is 20 mL. It was found that all solutions containing more than 4.5 mL of AB get coagulated within two minutes. What is the flocculation value of AB for As_2S_3 ?* **(PSEB, 2008)**

Solution. Given : Concentration of AB = 0.2 m; Volume needed to coagulate 20 mL solution = 4.5 mL.

wt. of AB needed to coagulate 20 mL solution

$$= \frac{4.5 \times 0.2}{1000} \text{mol}$$

$$= \frac{4.5 \times 0.2}{1000} \times 1000 \text{ millimol}$$

$$= 0.9 \text{ millimol}$$

∴ Millimole of AB needed to coagulate 1 L (= 1000 mL)

$$\text{solution} = \frac{0.9 \times 1000}{20 \text{ for } As_2S_3} = 45$$

Hence flocculation value of AB = 45

Example 10. *On the addition of 2 mL of 5% NaCl to 10 mL gold sol in the presence of 0.025 g starch, the coagulation is just prevented. What is the gold number of starch ?* **(PSEB, 2008)**

Solution. Given : 2 mL of 5% NaCl solution means 1 mL of 10% NaCl solution. Thus:

0.025 g of starch just prevents the coagulation of 10 mL of gold sol on the addition of 1 mL of 10% NaCl.

∴ Milligram of starch which just prevent the coagulation of 10 mL gold sol on the addition of 1 mL of

$$10\% \text{ NaCl} = 0.025 \text{ g} \times \frac{1000 \text{ mg}}{1 \text{g}} = 25 .$$

∴ Gold number of starch = 25.

29.5 AIEEE PATTERN EXAMPLES

Example 11. *The number average molecular mass and mass average molecular mass of a polymer are respectively 30,000 and 40,000. The polydispersity index of the polymer is :*

(a) < 1 *(b)* > 1

(c) 1 *(d)* 0

(e) – 1 **(Kerala, PET, 2005)**

Solution. $\overline{M_n}$ = Number average molecular mass = 30,000

$\overline{M_w}$ = Mass average molecular mass = 40,000

$$\therefore \text{ polydispersity index (PDI)} = \frac{\overline{M_w}}{\overline{M_n}} = \frac{40{,}000}{30{,}000} = 1.33$$

So, the correct answer is **(*b*)**.

Example 12. *Which of the following complexes exhibits the highest paramagnetic behaviour?*

(a) $[Co(ox)_2(OH)_2]^-$ *(b)* $[Ti(NH_3)_6]^{3+}$

(c) $[V(gly)_2(OH)_2(NH_3)_2]^+$

(d) $[Fe(en)(bpy)(NH_3)_2]^{2+}$

Where gly = glycine, en = ethylenediamine and bpy = bipyridyl moities (At. no., Ti = 22, V = 23, Fe = 26, Co = 27) **(CBSE-PMT, 2008, Prelims)**

Solution. (*a*) Oxidation state (O.S) of Co is $[Co(ox)_2(OH)_2]^-$:

$x + 2(-2) + 2(-1) = -1; x - 4 - 2 = -1; x = 5$. or $_{27}Co^{5+} = (Ar)^{18}\, 3d^4$. The +5 oxidation state of Co is not possible because O.S. of Co is usually +2, +3 or +4.

(*b*) O.5 of Ti is $[Ti(NH_3)_6]^{3+}$. $x + 6 \times 0 = +3; x = +3$.

So, $_{22}Ti^{3+} = Ar^{18}\, 3d^1$, So, no. of unpaired electrons = 1.

(*c*) O.S of V is $[V(gly)_2(OH)_2(NH_3)_2]^+$. $x + (2 \times 0) + 2 \times (-1) + 2 \times 0 = +1; x - 2 = +1; x = +3$, So, $_{23}V^{3+} = (Ar)^{18}\, 3d^2$. So, no. of unpaired electrons = 2.

(*d*) O.S of Fe is $[Fe(en)(bpy)(NH_3)_2]^{2+}$. $x + 0 + 0 + 2 \times 0 = +2; x = +2$.

So, $_{26}Fe^{2+} = (Ar)^{18} 3d^6$ with 4 unpaired electrons ($3d^{2+1+1+1+1}$).

Since (*d*) has maximum no. of unpaired electrons, correct answer is (*d*).

Example 13. *Excess of silver nitrate solution is added to 100 mL of 0.01 M pentaaquachlorochromium (III) chloride solution. The mass of silver chloride obtained in gram is : (atomic mass of silver is 108).*

(a) 287×10^{-3} *(b)* 143.5×10^{-3}

(c) 143.5×10^{-2} *(d)* 287×10^{-2}

(Karnataka CET, 2011)

Solution.

$$[Cr(H_2O)_5Cl]Cl_2 \xrightarrow[\text{of } AgNO_3]{\text{Excess}} [Cr(H_2O)_5Cl]^{+2}_{+2NO_3^-} + 2AgCl\downarrow$$

2 mol, Cl 2 mol, Cl

∴ milliequivalents of Cl^- in complex = Milliequivalent of Cl^- in AgCl

But number of mol of Cl^- ions in 100 mL of 0.01 m complex.

$$= (2 \times 100 \times 0.01)/1000 = 0.002 \text{ mol.}$$

$$\therefore \text{Mass of AgCl} = 0.002 \times 143.5 \; [\because \text{Mol. wt. of AgCl} = 108 + 35.5 = 143.5]$$

$$= 0.287 \text{ g} = 287 \times 10^{-3} \text{ g.}$$

So, the correct answer is (*a*)

Example 14. *The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$ as silver chloride is close to ml :* **(IIT-JEE, 2011)**

Solution. (*i*) The precipitation reaction is :

$$[Cr(H_2O)_5Cl]Cl_2 + 2AgNO_3 \rightarrow 2AgCl\downarrow + [Cr(H_2O)_5Cl](NO_3)_2$$

Here, the number of ionisable Cl^- ions =2. Thus :

No. of millimoles = 2 × molarity × volume (in mL)

$$= 2 \times 0.01 \times 30 = 0.6$$

∴ Ag^+ ions needed for precipitation = 0.6 millimoles.

But Millimoles = molarity × volume (in mL)

∴ 0.6 = 0.1 × volume ;

or volume = 0.6/0.1 = 6 mL

Example 15. *What is the equation form of Langmuir isotherm under high pressure?*

(a) $\frac{x}{m} = \frac{a}{b}$ *(b)* $\frac{x}{m} = aP$

(*c*) $\frac{x}{m} = \frac{1}{aP}$ (*d*) $\frac{x}{m} = \frac{b}{a}$ **(Gujarat, 2006)**

Solution. According to Langmuir adsorption isotherm,

$$\frac{x}{m} = \frac{aP}{1+bP} \qquad ...(A)$$

Where x = mass of gas adsorbed on mass m g of the adsorbent. a and b are constants while p is the pressure of the gas. At high pressure, $bP >>> 1$.

So, Equation (*A*) changes to

$$\frac{x}{m} = \frac{aP}{1+bP} = \frac{a}{b}$$

So, the correct answer is (***a***).

Example 16. *The volume of a colloidal particle, Vc as compared to the volume of a solute particle in a true solution Vs could be :*

(*a*) $\frac{Vc}{Vs} \simeq 1$ (*b*) $\frac{Vc}{Vs} \simeq 1023$

(*c*) $\frac{Vc}{Vs} = 10$ to 3 (*d*) $\frac{Vc}{Vs} \simeq 1003$ **(AIEEE, 2005)**

Solution. (*i*) For a true solution, the diameter of the solute particle ranges from 1 to 10A° and for colloidal solution, the diameter of colloidal particle range is 10 to 1000 A°. Taking the lower limits :

$$\frac{Vc}{Vs} = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi r_s^3} = \left(\frac{rc}{rs}\right)^3$$

Substituting the values of diameters in place of rc and rs, we have

$$\frac{Vc}{Vs} = \left(\frac{10}{1}\right)^3 = 1000 \simeq 1003.$$

So, the correct answer is (*d*).

Example 17. *1 g of charcoal adsorbs 100 mL of 0.5M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49. The surface area of charcoal is 3.01×10^2 m²/g. The surface area of the charcoal adsorbed by each molecule of acetic acid is :*

(*a*) 2.5×10^{-19} (*b*) 5.0×10^{-19}

(*c*) 13.2×10^{-18} (*d*) 1.32×10^{-19}

(IIT 2003 modified)

Solution. (*i*) At start, no, of millimol of CH_3COOH adsorbed = 100 × 0.5 = 50

(*ii*) At the end, no. of millimol of CH_3COOH adsorbed = 100 × 0.49 = 49

∴ no. of millimole of CH_3COOH actually adsorbed = 50 – 49 = 1

But $1 \text{ millimol} = \frac{1}{1000} \text{ mol} = \frac{1}{10^3}$

∴ no. of molecules of CH_3COOH that adsorbed

$$= \frac{6.02 \times 10^{23}}{10^3} = 6.02 \times 10^{20}$$

Area of 1 g charcoal = 3.01×10^2 m²

6.02×10^{20} molecules of CH_3COOH get adsorbed in area = 3.01×10^2 m²

∴ 1 molecule of CH_3COOH get adsorbed in area

$$= \frac{3.01 \times 10^2}{6.02 \times 10^{20}} = \mathbf{5.0 \times 10^{-19}} \qquad \textbf{Ans.}$$

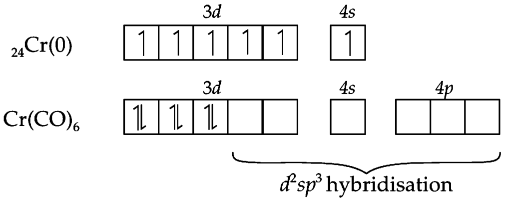
Example 18. *The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is :*

(*a*) 0 (*b*) 2.84

(*c*) 4.90 (*d*) = 5.92

(AIEEE, 2006; IIT-JEE, 2009)

Solution. In $Cr(CO)_6$, Cr (at. no. 24) has 24 e^- and CO is a neutral strong ligand. So, CO causes pairing of electrons.



∴ number of unpaired electrons, $n = 0$

∴ Magnetic moment, $\mu = [n(n+2)]^{1/2}$

$= [0(0+2)]^{1/2} = 0$

So, the correct answer is (*a*)

Example 19. *There are 20 naturally occurring aminoacids. The maximum number of tripeptides that can be obtained is :*

(*a*) 6470 (*b*) 7465

(*c*) 5360 (*d*) 8000. **(Karnataka CET, 2009)**

Solution. Given: no. of naturally occurring amino acids is 20. So, the maximum number of tripeptides that can be obtained = $(20)^3$ = 8000. So, the correct answer is (*d*).

Example 20. *The magnetic moment of a transition metal ion is $\sqrt{15}$ B.M. Therefore, the number of unpaired electrons in it is :*

(*a*) 4 (*b*) 1

(*c*) 2 (*d*) 3 **(Karnataka CET, 2009)**

Solution. We know that magnetic moment, $\mu = [n(n+2)]^{1/2}$ where n is the number of unpaired electrons. Since:

$$\mu = (15)^{1/2}, \text{ so, } \sqrt{15} = \sqrt{n(n+2)};$$

$$15 = n(n+2)$$

or $n^2 + 2n - 15 = 0$. After factorising, we get $n = 3$.

So, the correct answer is (*d*).

Example 21. *The spin only magnetic moment of Fe^{3+} ion (in BM) is approximately*

(*a*) 4 (*b*) 7

(*c*) 5 (*d*) 6 **(Karnatka CET, 2011)**

Solution. ${}_{26}Fe = (Ar)^{18}3d^6 4s^2; Fe^{2+} = (Ar)^{18} 3d^{2+1+1+1+1}$. So, Fe^{2+} has 4 unpaired electrons. Hence its magnetic moment, $\mu = [n(n+2)]^{1/2} = [4(4+2)]^{1/2} = (24)^{1/2} = 4.899 \simeq 5$. B.M. So, the correct answer is (*c*).

Example 22. *When 0.01 mol of a cobalt complex is treated with excess silver nitrate solution, 4.305 g silver chloride is precipitated. The formula of the complex is :*

(*a*) $[Co(NH_3)_3Cl_3]$ (*b*) $[Co(NH_3)_5Cl]Cl_2$

(*c*) $[Co(NH_3)_6]Cl_3$ (*d*) $[Co(NH_3)_4Cl_2]NO_3$

(*e*) $[Co(NH_3)_4Cl_2]Cl.$ **(Kerala PET, 2011)**

Solution. Wt. of AgCl = 4.305 g; mol. wt. of AgCl =108 + 35.5 = 143.5 g mol^{-}.

No. of mol of 4.305 g AgCl

$$= \text{wt./Mol.wt.} = \frac{4.305}{143.5} = 0.03 \text{ mol}$$

It shows that one mol of compound gives 3 mol of Cl^- ions in solution. So, the correct answer is (c) because when this compound is dissolved in water, 3 mol of Cl^- ions will be formed.

Example 23. *50 mL of oxalic acid is shaken with 0.5 g of wood charcoal. The final concentration of the solution after adsorption of the solution is 0.5 M. Amount of oxalic acid adsorbed per gram of charcoal is:*

(*a*) *3.15 g* (*b*) *3.45 g*

(*c*) *6.3 g* (*d*) *none of these*

(M.P. PMT, 2004)

Solution. 50 mL of 1M oxalic acid contains oxalic acid

$$= \frac{50 \times 1}{1000} = 0.05 \text{ mol}$$

∴ 50 mL of 0.5 M oxalic acid contains oxalic acid = 0.05 × 0.5 = 0.025 mol

Amount adsorbed = 0.05 – 0.025 = 0.025 mol

$$\text{Amount adsorbed per gram} = \frac{0.025}{0.5} \times 1 = 0.05 \text{ mol}$$

= 0.05 × 126 (= mol. wt. of oxalic acid)

= 6.3 g **Ans.**

∴ (*c*) is correct.

Example 24. *On addition of 1mL of 10% NaCl solution to 10 mL gold sol in the presence of 0.25 g of starch, the coagulation is just prevented. Starch has gold number*

(*a*) *0.025* (*b*) *0.25*

(*c*) *2.5* (*d*) *none of these*

(M.P. PMT, 2004)

Solution. 0.25 g of starch just prevents the coagulation of 10 mL of gold sol on adding one mL of 10% NaCl.

$$\therefore \text{Gold number} = 0.25 \text{ g} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 250 \text{ mg} = \mathbf{250}$$

So, the correct answer is (*d*).

Example 25. *10^{-4} g of gelation is required to be added to 100 cm^3 of a standard gold solution to just prevent its precipitation by the addition of 1 cm^3 of 10% NaCl solution to it. Hence the gold number of gelation in mg is:*

(*a*) *10* (*b*) *1.0*

(*c*) *0.1* (*d*) *0.01*

(Kerala PMT, 2005)

Solution. $10^{-4} \text{ g} = 10^{-4} \text{ g} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 0.1 \text{ mg}$

Gelatin required to prevent the coagulation of $10cm^3$ of gold sol $= \frac{0.1 \times 10}{100} = 0.01$ mg

[$10cm^3$ sol. = 0.01 mg = gold number]

∴ Gold number = **0.01.**

Example 26. *1 g of charcoal adsorbs 100 mL of 0.5 M CH_3COOH to form a monolayer, and thereby the molarity of CH_3COOH reduces to 0.49. Calculate the surface area of the charcoal adsorbed by each molecules of acetic acid. Surface area of charcoal is 3.01×10^2 m^2/g.* **(I.I.T. 2003)**

Solution. No. of moles of CH_3COOH in 100 mL before the addition of charcoal

$$= \frac{0.5 \times 100}{1000} = 0.05$$

No. of moles of CH_3COOH in 100 mL after adding charcoal

$$= \frac{0.49}{1000} \times 100 = 0.049$$

∴ No. of moles of CH_3COOH adsorbed on the surface of charcoal

= 0.050 – 0.049 = 0.001

No. of molecules of CH_3COOH adsorbed on the surface of charcoal

$= 0.001 \times 6.02 \times 10^{23} = 6.02 \times 10^{20}$

(∵ 1 mol = 6.02×10^{23} particles)

Surface area of charcoal = 3.01×10^2 m^2

∴ Area occupied by single acetic acid molecule on the surface of charcoal $= \frac{3.01 \times 10^2}{6.02 \times 10^{20}} = 5 \times 10^{-19}$ m^2.

Example 27. *20% of the surface sites are occupied by N_2 molecules. The density of surface site is 6.023×10^{14} cm^{-2} and total surface area is 1000 cm^2. The catalyst is heated to 300 K while N_2 is completely desorbed into a pressure of 0.001 atm and volume of 2.46 cm^3. Find the number of active sites occupied by each N_2 molecule.* **(I.I.T. 2005)**

Solution. Total number of surface sites = [Total surface area × density]

$= 1000 \times 6.023 \times 10^{14} = 6.023 \times 10^{17}$

Sites occupied by N_2 molecules

$$= \frac{6.023 \times 10^{17} \times 20}{100} = 12.04 \times 10^{16}$$

Pressure of desorbed N_2 = 0.001 atm, Temperature = 300K

Volume = 2.46 cm^3 = 2.46×10^{-3} L, R = 0.082 1 L atm K^- mol^-

But $PV = nRT$. Hence,

$$n = \frac{PV}{RT} = \frac{0.001 \text{ atm} \times 2.46 \times 10^{-3} L}{0.0821 \, L \text{ atm } K^- \text{ mol}^- \times 300 \, K} = 10^{-7} \text{ mol}$$

$\therefore$ No. of N_2 molecules $= 10^{-7} \times 6.023 \times 10^{23}$

$= 6.023 \times 10^{16}$

$\therefore$ No. of sites occupied by each molecule

$$= \frac{12.04 \times 10^{16}}{6.023 \times 10^{16}} = 2$$ **Ans.**

EXAMPLE 28. *The mass (m) of an adsorbed solute on a solid is given by a form of the Freumdlich isotherm as, $m = kC^n$ where C is the concentration in molarity and the values of k and n that give m in units of (g acetic acid, HAc) and (g blood charcoal)$^{-}$ are k = 0.160 and n = 0.431. Calculate the amount of acetic acid that 1 kg of charcoal would adsorb from0.837 M vinegar (acetic acid) solution.* **(PSEB, 2012)**

SOLUTION. $m = 0.160\ (0.837)^{0.431} = 0.148$ (g HAc) (g charcoal)$^{-}$

[Hint. Use log on both side to solve]

= 148 (g HAc) (kg charcoal)$^{-}$

$$= \frac{148 \text{ (g HAc) (kg charcoal)}^{-}}{60.05 \text{ g mol}^{-} \text{ (= mol wt. of HAc)}}$$

= 247 (mol HAc) (kg charcoal)$^{-}$ **Ans.**

EXAMPLE 29. *The adsorption of a dye from a solution on charcoal is governed by Freundlich isotherm as, $m = kC^n$ where C is the concentration in millimoles per c.c., m in millimoles per g, n = 2 and k = 6.8. If 10 g of charcoal is shaken with a 0.1 M solution of a dye, what will be the equilibrium concentration of the solution?* **(H.P.Board, 2012)**

SOLUTION. Given: $\frac{x}{m} = k\,C^n$; Initial concentration = 0.1 mol L^{-} = 0.1 millimol (cm^3)$^{-}$.

Let x millimoles have been adsorbed.

$\therefore$ Equilibrium conc. = 0.1 – x millimoles

But $\frac{x}{10} = 6.8 \times (0.1 - x)^2$ or $x = 68 \times (0.1 - x)^2$

Or $x^2 = 462.4 + 4624\,x$ Or $x = 0.09$

Hence eqm. conc. = 0.1 – 0.09 = 0.01 mollimoles /c.c = 0.01 M **Ans.**

EXAMPLE 30. *Low spin complex of d^6–cation in an octahedral field will have the following energy?*

(a) $\frac{-12}{5}\Delta_0 + P$ (b) $\frac{-12}{5}\Delta_0 + 3P$

(c) $\frac{-2}{5}\Delta_0 + 2P$ (d) $\frac{-2}{5}\Delta_0 + P$

(H.P.Board, 2012)

SOLUTION. Since it is low spin octahedral complex, the distribution of electrons in t_{2g} and e_g orbits = $t_{2g}^{2+2+2}\,e_g^{\,0}$.

So, total number of pairs of electrons, $P = 3$. But:

CFSE = $(-\,0.4\,x + 0.6\,y)\,\Delta_0 + zP$ ...(1)

x = no. of electrons occupying t_{2g} orbitals, y = no. of electrons occupying e_g orbitals and z = no. of pairs of electrons. Substituting these values in equation (1), we get:

$$\text{CFSE} = [(-\,0.4 \times 6) + (0.6 \times 0)]\,\Delta_0 + 3P \text{ or } \frac{-12}{5}\Delta_0 + 3P.$$

So, the correct answer is (*b*).

EXAMPLE 31. *The spin only magnetic moment of $(CrF_6)^{4-}$ (at. no. of Cr = 24) is:*

(a) 0 (b) 1.73 BM

(c) 2.83 BM (d) 4.9 BM

(J&K CET, 2012)

SOLUTION. Cr in $[CrF_6]^{4-}$ is Cr^{2+}.

$_{24}Cr = (Ar)^{18}\,3d^5\,4s^1$; $Cr^{2+} = 3d^4 = 3d^{1+1+1+1}$ *i.e.*, four unpaired electrons. So, $n = 4$

Magnetic moment = $(n\,(n + 2))^{1/2} = [4\,(4 + 2)]^{1/2} = (24)^{1/2}$ = 4.9 BM. So, the correct answer is (*d*).

EXAMPLE 32. *The effective atomic number of the central metal ion, Pt, in the complex $[Pt\,(NH_3)_6]^{4+}$ is: (at. no. of Pt = 78):*

(a) 74 (b) 90

(c) 86 (d) 84

(AMU (medical), 2012)

SOLUTION. Effective at. no. (EAN) = At. no. of metal + no. of $\bar{e}$s gained from donor atoms of the ligands –no. of $\bar{e}$s lost in ion formation.

$\therefore$ EAN of Pt in $[Pt(NH_3)_6]^{4+} = 78 + (6 \times 2) - 4 = 86$.

So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. The number average molecular mass and mass average molecular mass of a polymer are 20,000 and 30,000 respectively. The polydispersity index of the polymer is :

(*a*) > 1 (*b*) 1

(*c*) < 1 (*d*) 0 **Ans** (*a*)

2. On the addition of 2 mL of 5% NaCl to 10 mL gold sol in the presence of 0.04 g of a compound, the coagulation is just prevented. What is the gold number of the compound ? **Ans.** (40)

3. What is the type of hybridisation of Ni in nickel carbonyl ? **Ans.** (sp^3)

4. A polymer sample contains 25% molecules of molar mass, 20,000, 30% molecules of molar mass 30,000 and 45% molecules of molar mass, 40,000. Calculate $\overline{M_n}$. **Ans.** (32,000)

5. One kg of a polymer with molar mass, 20,000 g and 500 g of another polymer with molar mass, 25,000 g are mixed. Calculate $\overline{M_w}$. **Ans.** ($\simeq$ 21667)

6. The magnetic moment (spin only) of $[Fe(H_2O)_6]^{2+}$ in B.M. is :

(*a*) 4.89 (*b*) 3.99

(*c*) 1.5 (*d*) 4.01 **Ans.** (*a*)

7. The magnetic moment of a transition metal ion is $\sqrt{35}$. Therefore, the number of unpaired electrons in it are :

(*a*) 3 (*b*) 4

(*c*) 5 (*d*) 6 **Ans.** (5)

8. Excess of silver nitrate solution is added to 200 mL of 0.05 M pentaaquachloridochromium (III) obtained in gram is :

(*a*) 0.175 (*b*) 1.9

(*c*) 1.1 (*d*) 0.287 g **Ans.** (*d*)

9. The volume (in mL) of 0.2 M $AgNO_3$ needed for the complete precipitation of chloride ions present in 40 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$ as silver chloride is close to :

(*a*) 2 mL (*b*) 3 mL

(*c*) 4 mL (*d*) 5 mL **Ans.** (*c*)

10. Suppose there are x naturally occurring aminoacids. Calculate the maximum number of tripeptides that can be obtained. **Ans.** (x^3)

30

CHAPTER

Distribution Law

30.1 SOLVENT EXTRACTION

Solvent extraction or liquid - Liquid extraction is a partitioning process which involves the distribution of a solute between two immiscible liquid phases. It is a standard method of purification of organic compounds and for quantitative separation of both inorganic and organic compounds.

30.2 NERNST DISTRIBUTION LAW

This law states that 'When a solute (liquid or solid) is added to a heterogeneous system of two immiscible liquids (in both of which solute is soluble), the solute distributes itself between the two solvents in such a way that the ratio of the concentrations in the two liquid phases is constant at a constant temperature provided the solute has same molecular weight in each phase and this ratio is independent of the amount of solute or solvent.

Mathematically, when a solute does not undergo dissociation or association in a solvent, then:

$$\frac{\text{Concentration of solute } x \text{ in phase } A \text{ or solvent, } A}{\text{Concentration of solute } x \text{ in phase } B \text{ or solvent, } B} = \frac{C_1}{C_2} = K$$

where **K** is constant called **Partition co-efficient** or **distribution-co-efficient.**

30.3 WHEN THE SOLUTE NEITHER UNDERGOES DISSOCIATION NOR ASSOCIATION IN THE SOLVENTS

Use : $\frac{C_1}{C_2} = K$

Note: When K is required in favour of solvent A (or phase A), the concentration of solute in solvent A should be taken in the numerator.

EXAMPLE 1. *When boric acid was shaken with a mixture of water and amyl alcohol solvents at constant temperature, the following data was recorded.*

	I	*II*	*III*
Equilibrium conc. of boric acid in H_2O	*0.087*	*0.54*	*0.90*
Equilibrium conc. of boric acid in amyl alcohol	*0.024*	*0.15*	*0.25*

Show that the data illustrates the distribution law considering distributing co-efficient in favour of amyl alcohol.

SOLUTION.

$$\frac{C_{\text{Boric acid} - \text{amyl alcohol}}}{C_{\text{Boric acid} - \text{water}}} = K$$

$$\textbf{I. } \frac{0.024}{0.087} = \mathbf{0.276}; \quad \textbf{II. } \frac{0.15}{0.54} = 0.278; \textbf{III. } \frac{0.25}{0.90} = 0.274$$

Since the value of K is constant, the distribution law is obeyed.

EXAMPLE 2. *When a mixture of 70cm^3 ether and 150 cm^3 water was shaken with succinic acid, at equilibrium, water layer contained 3.0g while ether layer contained 0.2 g of succinic acid. Calculate the partition co-efficient in favour of ether.*

SOLUTION.

$$C_{\text{succinic acid} - \text{ether}} = \frac{0.2}{70} \text{ g cm}^{-3} = C_1$$

$$C_{\text{succinic acid} - \text{water}} = \frac{3}{150} \text{ g cm}^{-3} = C_2$$

$$\therefore \quad \frac{C_1}{C_2} = K; \ \frac{0.2/70}{3.0/150} = \frac{0.2 \times 150}{3.0 \times 70}$$

Or $K = \mathbf{0.1428}$ **Ans.**

EXAMPLE 3. *The partition co-efficient of boric acid between water and amyl alcohol in favour of water is 3.3. How much amyl alcohol is needed to decrease the concentration of boric acid in 50 ml water from 6% to 2%?*

SOLUTION.

(*i*) Conc. of boric acid in H_2O = 6%

$\therefore$ Wt. of boric acid in 50 ml water $= \frac{50 \times 6}{100} = 3.0g$

(*ii*) Conc. of boric acid in H_2O after the use of amyl alcohol = 2%

$\therefore$ Wt. of boric acid in 50 ml

$$H_2O = \frac{50 \times 2}{100} = 1.0 \text{ g}$$

Let volume of amyl alcohol required = V mL

$\therefore$ At equilibrium, wt. of boric acid in

H_2O = 1.0 g per 50 mL H_2O

Wt. of boric acid in ether = 3.0 – 1.0

= 2.0 g per VmL ether

But $$K = \frac{\text{Conc. of boric acid in water}}{\text{Conc. of boric acid in amyl alcohol}}$$

$$3.3 = \frac{1/50}{2/V};\ 3.3 = \frac{1}{50} \times \frac{V}{2};$$

$V = 3.3 \times 50 \times 2 =$ **330 mL** **Ans.**

Example 4. *25 mL of ether was shaken with 100 mL of M/10 aqueous solution of quinine ($C_{20}H_{24}O_2N_2$) till equilibrium was established. If distribution co-efficient of quinine is 22 in favour of ether, find the concentration of quinine in the ether layer.*

Solution. Conc. of quinine in

$$H_2O = \frac{1}{10}\ M = \frac{1}{10} \text{ mol L}^{-}$$

Thus : Conc. of quinine in 1000 mL

$$H_2O = \frac{1}{10}$$

Conc. of quinine in 100 mL

$$H_2O = \frac{1}{10} \times \frac{100}{1000} = \frac{1}{100} = 10^{-2}$$

Let quinine extracted in 25 mL ether = a mol

$\therefore$ Conc. of quinine in 25 mL ether = $\frac{a}{25}$

At equilibrium, conc. of quinine in

$$100 \text{ mL water} = \frac{10^{-2} - a}{100}$$

But $$\frac{\text{Conc. of quinine in ether}}{\text{Conc. of quinine in } H_2O} = K$$

$$\frac{a/25}{\left(10^{-2} - a\right)/100} = 22;\ \frac{a}{25} \times \frac{100}{10^{-2} - a} = 22$$

$$22(10^{-2} - a) = 4a;\ 0.22 = 26a$$

$\therefore$ $a = \frac{0.22}{26} =$ **0.00846 mol per 25 mL Ans.**

Example 5. *10 mL of CCl_4 was shaken with 100 mL of a saturated solution of I_2 in water to attain equilibrium. The solubility of I_2 in water is 0.7g L^-. Calculate the amount of I_2 in CCl_4 if partition co-efficient of I_2 in favour of CCl_4 is 85.*

Solution. Solubility of

I_2 in H_2O = 0.7g L^- = 0.7g (1000 mL^-)

1000 mL H_2O contain I_2 = 0.7 g

$$100 \text{ mL } H_2O \text{ contain } I_2 = \frac{0.7}{1000} \times 100 = 0.07 \text{ g}$$

Let wt. of I_2 extracted by

10 mL CCl_4 = a g

$$\therefore \text{Conc. of } I_2 \text{ in 10 mL } CCl_4 = \frac{a}{10} \text{ g} (\text{mL})^- = C_1$$

Wt. of I_2 in 100 mL H_2O = $(0.07 - a)$g

$\therefore$ Conc. of I_2 in

$$100 \text{ mL } H_2O = \frac{0.07 - a}{100} \text{ g} (\text{mL})^- = C_2$$

But $$\frac{C_1}{C_2} = K;\ \frac{a/10}{(0.07 - a)/100} = 85$$

Or $$\frac{a}{10} \times \frac{100}{0.07 - a} = 85;$$

$$10\,a = 85(0.07 - a) = 5.95 - 85a$$

or $$95\,a = 5.95;\ a = 5.95/95$$

= **0.0626 g in 10 mL CCl_4 Ans.**

Example 6. *Benzoic acid exists as a monomer in water but gives a higher value in benzene. Calculate the complexity of benzoic acid in benzene from the following distribution experimental data.*

	I	*II*	*III*
$C_1(H_2O)$	*0.015*	*0.022*	*0.029*
$C_2(C_6H_6)$	*0.24*	*0.55*	*0.93*

Solution. Suppose n = complexity of benzoic acid in C_6H_6

$$\therefore \quad K = \frac{C_1}{(C_2)^{1/n}}$$

Taking logs of both sides, we get :

$$\log K = \log C_1 - \frac{1}{n} \log C_2 \quad ...(i)$$

Substituting the values in equation (*i*), we get :

I $$\log K = \log 0.015 - \frac{1}{n} \log 0.24$$

$$= -1.82 - \frac{1}{n}(-0.62)$$

$$= -1.82 + \frac{0.62}{n} \quad ...\text{(ii)}$$

II $$\log K = \log 0.022 - \frac{1}{n} \log 0.55$$

$$= -1.66 - \frac{1}{n}(-0.26)$$

$$= -1.66 + \frac{0.26}{n} \quad ...\text{(iii)}$$

III $$\log K = \log 0.029 - \frac{1}{n}\log 0.93$$

$$= -1.54 - \frac{1}{n}(-0.032)$$

$$\log K = -1.54 + \frac{0.032}{n} \quad \ldots (iv)$$

(*a*) Equating equation (*ii*) and (*iii*), we get

$$-1.82 + \frac{0.62}{n} = -1.66 + \frac{0.26}{n};\ \frac{0.62}{n} - \frac{0.26}{n}$$

$$= 1.82 - 1.66 = 0.16$$

or $$\frac{0.36}{n} = 0.16.\ \text{Hence } n = \frac{0.36}{0.16} \approx 2.$$

(*b*) Equating equation (*iii*) and (*iv*), we get

$$-1.66 + \frac{0.26}{n} = -1.54 + \frac{0.032}{n};\ \frac{0.26}{n} - \frac{0.032}{n}$$

$$= 1.66 - 1.54 = 0.12$$

or $$\frac{0.228}{n} = 0.12.\ \text{Hence } n = \frac{0.228}{0.12} \approx 2.$$

Since the value of n is almost equal to 2, benzoic acid exists as a dimer in benzene.

EXAMPLE 7. *5.0g of oxalic acid is distributed between* ***a mixture*** *of one litre water and 100 mL of ether. If partition co-efficient of* ***oxalic acid*** *in water and ether is 10, find the* ***concentration*** *of oxalic acid in both the solvents.*

SOLUTION.

Suppose, wt. of oxalic acid in ether = x g

Total wt. of oxalic acid added = 5 g

∴ Wt. of oxalic acid in H_2O phase = $(5 - x)$ g.

Volume of ether = 100 mL

∴ Conc. (C_1) of

acid in ether layer = $\frac{x}{100}\text{g}(\text{mL})^{-}$

Also, conc. (C_2) of acid in water layer

$$= \frac{5-x}{1000}\text{g}\,(\text{mL})^{-}$$

[∵ 1L = 1000 mL]

But $\frac{C_1}{C_2} = K$ (By Nernst distribution law)

$$\therefore \quad \frac{x/100}{(5-x)/1000} = 10;\ \frac{x}{100} \times \frac{1000}{5-x} = 10$$

$$10x = 10(5 - x);\ \boldsymbol{x = 2.5\ \text{g}}$$

(*i*) wt of acid in 100 mL ether = 2.5 g

∴ conc of acid in 1000 mL ether

$$= \frac{2.5}{100} \times 1000 = \mathbf{25\ gL}$$ **Ans.**

(*ii*) wt of acid in

1000 mL water = $5 - x = 5 - 2.5 = 2.5$ g

or wt of acid in H_2O = **2.5 gL^{-}** **Ans.**

EXAMPLE 8. *The solubility ratio of an organic substance in between water and benzene is 4.1. 100 cm^3 of an aqueous solution having 0.75 g per 500 cm^3 of the substance is shaken with 50 mL of benzene till equilibrium is attained. Calculate the amount of substance extracted by benzene from aqueous solution.*

SOLUTION.

(*i*) *Aqueous solution.*

500 cm^3 solution contain substance = 0.75 g

100 cm^3 solution contain substance

$$= \frac{0.75 \times 100}{500} = 0.15\ \text{g}$$

(*ii*) *C_6H_6 solution.*

Let wt. of substance extracted in

50 cm^3 benzene = xg

∴ Wt. of substance extracted in

100 cm^3 H_2O = $(0.15 - x)$g

Conc. of substance in benzene = $\frac{x}{50} = C_1$

Conc. of substance in H_2O

$$= \frac{0.15 - x}{100} = C_2 \quad \text{But } \frac{C_1}{C_2} = K.\ \text{So,}$$

$$\left(\frac{x}{50}\right)\Big/\left(\frac{0.15 - x}{100}\right) = 4.1;\ \frac{x}{50} \times \frac{100}{0.15 - x} = 4.1;$$

$$2x = 0.615 - 4.1x$$

$$\therefore \quad x = \frac{0.615}{6.1} = \mathbf{0.1g}$$ **Ans.**

30.4 WHEN THE SOLUTE DISSOCIATES

In case, a solute dissociates in solvent 1 and α_1 is the degree of dissociation of the solute in solvent, then :

$$K = \frac{C_1(1-\alpha)}{C_2}$$

Where C_1 and C_2 are the concentrations of the solute in solvent 1 and solvent 2 respectively.

30.5 WHEN THE SOLUTE DISSOCIATES IN BOTH OF THE SOLVENTS

In case, a solute dissociates in both the solvents 1 and 2, and α_1 and α_2 are the degrees of dissociation of the solute in solvent 1 and 2 respectively, then :

$$K = \frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)}$$

where K is the partition co-efficient or distribution co-efficient.

Type: *To calculate degree of dissociation.*

EXAMPLE 9. *An organic compound is five times more soluble in water than in a solvent, X. When 10.0 g of the compound was mixed with 50 mL water and 40 ml of X, 0.5 g of the compound* *was found to be present in 20 mL of X. Find the degree of dissociation of the compound in water.*

Solution.

$$\frac{\text{Solubility in } H_2O}{\text{Solubility in solvent}, X} = K;\ K = \frac{5}{1} = 5$$

Suppose degree of dissociation of compound in

$H_2O = \alpha$

Compound present in

20 mL of X = 0.5g

∴ Compound present in 40 mL of X

$$= \frac{0.5}{20} \times 40 = 1.0 \text{ g}$$

Total compound mixed = 10g

∴ Compound present in 50 mL H_2O

= 10 – 1 = 9g

Conc. of compound in

$$H_2O = \frac{9(1-\alpha)}{M \times 50} = C_1$$

Conc. of compound in solvent,

$$X = \frac{1.0}{M \times 40} = C_2$$

But $\frac{C_1}{C_2} = K$. So, $\dfrac{\dfrac{9(1-\alpha)}{50M}}{\dfrac{1}{40M}} = 5$

$$\frac{9(1-\alpha) \times 40}{50} = 5;\ 1 - \alpha = \frac{5 \times 50}{40 \times 9} = 0.69$$

∴ $\alpha = l - 0.69 = 0.31$

Or $\alpha = 0.31 \times 100 = $ **31%** **Ans.**

30.6 WHEN THE SOLUTE ASSOCIATES IN ONE OF THE TWO SOLVENTS

Suppose a solute (molecular formula, X) exists as such (i.e., X) in solvent I but is associated in solvent II as $(X)_n$. Then :

$$(X)_n = nX$$

where n is the degree of association. Then according to distribution law

$$K = \frac{C_1}{(C_2)^{1/n}}$$

Example 10. *Using the following data, prove that acetic acid exists as a dimer in CCl_4 if it exists as single molecules in water.*

$C_1(H_2O)$	2.51	3.99	5.45
$C_2(CCl_4)$	0.146	0.362	0.705

Solution.

$$\frac{C_1(H_2O)}{[C_2(CCl_4)]^{1/2}} = K \qquad \left[\because \frac{C_1}{(C_2)^{1/n}} = K\right]$$

I $\quad \dfrac{2.51}{(0.146)^{1/2}} = K;\quad K = \dfrac{2.51}{0.382} = 6.57$

II $\quad \dfrac{3.99}{(0.362)^{1/2}} = K;\quad K = \dfrac{3.99}{0.62} = 6.44$

III $\quad \dfrac{5.45}{(0.705)^{1/2}} = K;\quad K = \dfrac{5.45}{0.839} = 6.49$

The constant value of K indicates that acetic acid exists as a dimer in CCl_4.

Example 11. *Phenol was shaken with a mixture of water and $CHCl_3$. Their distribution ratio gave the following results.*

	I	*II*	*III*
$C_1(H_2O)$	0.188	0.508	0.872
$C_2(CHCl_3)$	0.508	3.70	10.86

What conclusion can be drawn from above results regarding molecular condition of phenol in $CHCl_3$.

Solution. (*a*) Suppose phenol exists as a monomer. Then :

I $\quad \dfrac{C_1(H_2O)}{C_2(CHCl_3)} = K;\quad \dfrac{0.188}{0.508} = K;\quad K = 0.37$

II $\quad \dfrac{C_1(H_2O)}{C_2(CHCl_3)} = K;\quad \dfrac{0.508}{3.70} = K;\quad K = 0.137$

III $\quad \dfrac{C_1(H_2O)}{C_2(CHCl_3)} = K;\quad \dfrac{0.872}{10.86} = K;\quad K = 0.08$

Since the value of K is not constant, phenol does not exist as monomer or normal molecule in $CHCl_3$.

(*b*) Suppose phenol exists as a dimer in $CHCl_3$. Then :

$$\frac{C_1(H_2O)}{[C_2(CHCl_3)]^{1/n}} = K \quad \text{where n is the degree of association}$$

I

$$\frac{C_1(H_2O)}{[C_2(CHCl_3)]^{1/n}} = K;\ \frac{0.188}{(0.508)^{1/2}} = K;\ K = \frac{0.188}{0.712} = 0.26$$

II

$$\frac{C_1(H_2O)}{[C_2(CHCl_3)]^{1/n}} = K;\ \frac{0.508}{(3.70)^{1/2}} = K;\ K = \frac{0.508}{1.923} = 0.26$$

III

$$\frac{C_1(H_2O)}{[C_2(CHCl_3)]^{1/n}} = K;\ \frac{0.872}{(10.86)^{1/2}} = K;\ K = \frac{0.872}{2.295} = 0.26$$

Since the value of K is constant, phenol exists as a double molecule or dimer in $CHCl_3$.

30.7 SOLVENT EXTRACTION METHOD.

It has been found experimentally that the process of extraction is very economical if carried out in several operations with the given volume of solvent than by using the same volume in one lot.

Consider a mixture of two immiscible solvents containing a solute.

Let Wt. of the solute = Wg; Volume of the mixture solution = V_1 mL

Volume of the pure immiscible solvent shaken repeatedly for extraction = V_2mL

No. of extractions done = n

Then :

(*a*) **Wt. of solute left unextracted** after the end of n extractions = W_n. Then :

$$W_n = W\left[\frac{KV_1}{KV_1 + V_2}\right]^n$$

(*b*) Wt. of solute extracted will be :

$$W - W_n = W - W\left[\frac{KV_1}{KV_1 + V_2}\right]^n = W\left[1 - \left(\frac{KV_1}{KV_1 + V_2}\right)^n\right];$$

where K = Partition co-efficient

Example 12. *12 g of hydrogen peroxide is present in a 140 mL solution of hydrogen peroxide in amyl alcohol. The partition co-efficient of hydrogen peroxide between amyl alcohol and water is 1:7. Calculate the amount of H_2O_2 extracted out with 90 mL of H_2O (i) in one lot and (ii) in three lots of 30 mL each.*

Solution.

(*i*) Volume of mixture solution, V_1 = 140 mL

Volume of pure solvent used, V_2 = 90 mL

Wt. of H_2O_2 = 12 g

Partition co-efficient,

$$K = \frac{C_1 \text{ of } H_2O_2 \text{ in amyl alcohol}}{C_2 \text{ of } H_2O_2 \text{ in water}} = \frac{1}{7}$$

Wt. of H_2O_2 extracted when extraction is done in one lot of 90 mL will be given by the relation :

$$W_n = W\left[1 - \left(\frac{KV_1}{KV_1 + V_2}\right)^n\right]$$

$$W_1 = 12\left[1 - \left(\frac{\frac{1}{7}\times 140}{\left(\frac{1}{7}\times 140\right) + 90}\right)^1\right]$$

$$= 12\left[1 - \frac{20}{110}\right] = 12 \times \frac{9}{11} = \mathbf{9.82\ g\ Ans.}$$

(*ii*) wt. of H_2O_2 extracted when extraction is done in three lots of 30 mL each i.e., when V_2 = 30 mL

$$W_n = W\left[1 - \left(\frac{KV_1}{KV_1 + V_2}\right)^n\right]$$

$$= 12\left[1 - \left(\frac{\frac{1}{7}\times 140}{\left(\frac{1}{7}\times 140\right) + 30}\right)^3\right]$$

$$= 12\left[1 - \left(\frac{20}{50}\right)^3\right]$$

$$= 12\left(1 - \frac{8}{125}\right) = 12 \times \frac{117}{125}$$

= **11.23 g** **Ans.**

Example 13. *The solubility of a substance (A) is two times more in other liquid than in water. Compare the quantities of A extracted from 120 mL of aqueous solution by (i) 100 mL of CCl_4 in one operation and (ii) four extractions using 25 mL in each extraction. Also calculate the amount of A unextracted in each case.*

Solution.

Volume of mixture solution,

V_1 = 120 mL

Volume of pure solvent,

V_2 = 100 mL

Wt. of substance,

$$A = W; K = \frac{1}{2}.$$

(*i*) Wt. of A unextracted when extraction is done in one lot of 100 mL will be given as :

$$W_n = W\left(\frac{KV_1}{KV_1 + V_2}\right)^n;$$

$$W_1 = W\left(\frac{\frac{1}{2}\times 120}{\left(\frac{1}{2}\times 120\right) + 100}\right)^1$$

$$W_1 = W\left(\frac{60}{160}\right) = \frac{3}{8}\times 100$$

= **37.5% of W** **Ans.**

(*ii*) Wt. of A unextracted when extraction is done in four lot of 25 mL each will be given as:

$$W_n = W\left(\frac{KV_1}{KV_1 + V_2}\right)^n;$$

$$W_4 = W\left(\frac{\frac{1}{2}\times 120}{\left(\frac{1}{2}\times 120\right) + 25}\right)^4$$

$$W_4 = W\left(\frac{60}{85}\right)^4 = 0.2489\,W \quad \text{(See below)}$$

$$= 0.2489 \times 100$$

$$= \mathbf{24.89\%\ of\ W} \qquad \textbf{Ans.}$$

Let $x = \left(\frac{60}{85}\right)^4$. Taking logs of both sides, we get:

$$\log x = \log\left(\frac{60}{85}\right)^4$$

$$= 4[\log 60 - \log 85]$$

$$= 4[1.778 - 1.929]$$

$$= 4 \times -0.151$$

$$= -0.604 = -1 + 1 - 0.604$$

$$= \bar{1}.396.$$

Taking antilog of both sides, we get $x = 0.2489$

Example 14. *2.0 grams of a solute are contained is 100 ml of an aqueous solution. Determine the quantity of the solute left in aqueous phase after :*

(i) single extraction with 90 ml of an organic solvent with appropriate reagents;

(ii) a single extraction with 30 ml solvent and

(iii) three successive extractions with 30 ml of solvent, assuming that the distribution ratio of solute between ether and water is 10 : 1.

Solution. Weight (W) of solute in 100 ml of aqueous solution = 2.0 gm

Volume (V_1) of solution containing the solute = 100 ml

Volume (V_2) of extracting solvent in (*i*) 90 ml (*ii*) 30 ml (*iii*) three successive extractions of 30 ml.

Number (n) of extractions in (*i*) 1, (*ii*) 1, (*iii*) 3.

Let weight of solute left after the extraction with V_2 ml of solvent = W gm.

Distribution co-efficient

$$(K) = \frac{1}{10}.$$

We know that $W_n = W\left[\frac{KV_1}{KV_1 + V_2}\right]^n$

$\therefore$ For (*i*) $W_1 = 2.0 \times \left(\frac{\frac{1}{10}\times 100}{\left(\frac{1}{10}\times 100\right) + 90}\right)^1$

$$= 0.20 \text{ gm}$$

(*ii*) $W_1 = 2.0 \times \left(\frac{\frac{1}{10}\times 100}{\left(\frac{1}{10}\times 100\right) + 30}\right)^1$

$$= 0.50 \text{ gm.}$$

For (*iii*) $W_3 = 2.0 \times \left(\frac{\frac{1}{10}\times 100}{\left(\frac{1}{10}\times 100\right) + 30}\right)^3$

$$= 0.0312 \text{ gm.}$$

Hence percent solute extracted in (*i*) = $\frac{2-0.2}{2} \times 100 = 90$; percent solute extracted in (*ii*) = $\frac{2-0.5}{2} \times 100 = 75$; percent solute extracted in (*iii*) = $\frac{2-0.0312}{2} \times 100 = 98.4$

Example 15. *100 ml of 0.01 M solution of NH_3 in chloroform was shaken with 10.0 ml of H_2O until distribution equilibrium was attained at 291 K. Calculate the number of moles of NH_3 left in the chloroform layer after extraction ($K_e = 27.5$).*

Solution. Volume of

$$NH_3 = 100 \text{ mL} = \frac{100}{1000} \text{ L} = 0.1 \text{ L};$$

molarity of $NH_3 = 0.01\ ML^-$

$\therefore$ No. of mol of

NH_3 = [Volume of NH_3] × [Molarity of NH_3]

$= 0.1\ L \times 0.01\ mol\ L^- = 0.001$ mol

Suppose x = no. of mol of NH_3 left in the chloroform layer after extraction.

$\therefore$ No. of mol of NH_3 extracted by water

$$= 0.001 - x$$

$\therefore$ Molarity of NH_3 in aqueous layer

$$= \frac{(0.001 - x) \text{ mole}}{0.01 \text{ litre}}$$

$$= 0.1 - 100x \text{ mole litre}^-$$

$$= [NH_3]_{H_2O}$$

Molarity of NH_3 in chloroform layer

$$= \frac{x}{0.1} \text{ mole litre}^- = 10x \text{ mole litre}^-$$

$$= [NH_3]_{CHCl_3}$$

Assuming that the volumes of the two liquid phases are unaffected by transfer of NH_3, the equilibrium condition is :

$$27.5 = \frac{[NH_3]_{H_2O}}{[NH_3]_{CHCl_3}}$$

$$= \frac{0.1 - 100x \text{ mole litre}^-}{10x \text{ mole litre}^?};$$

$$\therefore \quad x = 2.67 \times 10^{-4} \text{ mole.}$$

30.8 DISTRIBUTION RATIO

A different term, the distribution ratio, D is more meaningful than distribution co-efficient. It is because it does not account for any equilibrium steps which might take place in either of the two phases. **Due to this reason, the distribution law is redefined in terms of distribution ratio, *D* as follows :**

"It is the ratio of the concentration of all the species of solute in each phase. The concentrations in the two phases are expressed as total concentrations rather equilibrium concentrations".

EXAMPLE 16. *40 ml of an aqueous solution of 0.20 M butanoic acid are shaken with 20 ml of ether. After the aqueous and ether layers separated, it was found by titration that 1.0 millimoles of butanoic acid remained in the aqueous layer. Find the distribution ratio (D) and percent of solute extracted.*

SOLUTION. Number of moles of butanoic acid

$$= 40 \text{ ml} \times 0.20 \text{ M} = 8.0 \text{ millimoles.}$$

Number of millimoles of butanoic acid left in aqueous solution = 1.0

∴ Number of millimoles of butanoic acid extracted in ether = 8.0 – 1.0 = 7.0

Concentration of the acid in ether layer

$$= \frac{7.0 \text{ mil lim oles}}{20\text{ml}} = 0.35\, M$$

Concentration of the acid in aqueous layer

$$= \frac{1.0}{40} = 0.025\, M$$

∴ Distribution ratio,

$$D = \frac{\text{Concentration of acid in ether layer}}{\text{Concentration of acid in aqueous layer}}$$

$$= \frac{0.35}{0.025} = 14$$

Since 7.0 millimoles of the acid were extracted in ether; the percent extracted (% E) $= \frac{7}{8} \times 100 = 87.5\%$

or % $E = \dfrac{100D}{D + V_\alpha / V_o}$ where V_α = volume of aqueous solution and V_0 = volume of ether solvent $= \dfrac{100 \times 14}{14 + 40/20}$

$$= \frac{1400}{16} = 87.5\%.$$

EXAMPLE 17. *An aqueous solution of an organic compound contains 10 g of solute per litre. When one litre of this solution is treated with 100 mL of ether, 6g of the organic solute is extracted. How much of the solute will be extracted from the aqueous solution by adding further 100 ml of ether? (Assume that molecular state of the solute is the same in ether and water). (ISC, 2007)*

SOLUTION. $k_d = \dfrac{C_e}{C_w} = \dfrac{w/100}{(a-w)/100}$

$$= \frac{6/100}{(10-6)/1000} = 15$$

Let, w_1 = Amount extracted with further 100 mL of ether.

$$\therefore \quad k_d = \frac{C_e}{C_w};\ 15 = \frac{w_1/100}{(4-w_1)/1000}$$

$$= \frac{10w_1}{4-w_1};\ 60 - 15\, w_1 = 10\, w_1;$$

$$25\, w_1 = 60$$

$$\therefore \quad w_1 = 60/25 = 2.49$$ **Ans.**

30.9 AIEEE PATTERN EXAMPLES

EXAMPLE 18. *The concentrations of iodine between CCl_4 and water solvents in g/200 mL are 10.2 and 0.12 respectively. The value of partition co-efficient in favour of water will be :*

(*a*) 85 (*b*) 0.01176

(*c*) 42.5 (*d*) 21.25

SOLUTION. According to distribution law.

$$\frac{C_{I_2 - H_2O}}{C_{I_2 - CCl_4}} = K;\ \frac{0.12}{10.2} = K$$

∴ $K = 0.01176$. So, the correct answer is (*b*)

EXAMPLE 19. *The partition co-efficient of I_2 in-between CCl_4 and H_2O is 85 in favour of CCl_4 solvent at 298 K. If solubility of I_2 in CCl_4 at 298 K is 28.05 gL^{-}, the solubility of I_2 in water at 298 K will be :*

(*a*) 33.0 gL^{-} (*b*) 0.66 gL^{-}

(*c*) 0.33 gL^{-} (*d*) 66 gL^{-}

SOLUTION. Let solubility of I_2 in water = $x\, gL^{-}$

$$\text{But} \quad \frac{C_{I_2 - CCl_4}}{C_{I_2 - H_2O}} = K;\ \frac{28.05}{x} = 85$$

$$\therefore \quad x = \frac{28.05}{85} = 0.33 \text{gL}^{-}.$$

So, the correct answer is (*c*)

EXAMPLE 20. *The distribution co-efficient of lactic acid between water and chloroform in favour of chloroform is 0.02. Half litre of aqueous solution of lactic acid in water having 25 g was mixed with 250 ml of chloroform. The concentration of lactic acid in gram in chloroform will be :*

(*a*) 0.02 (*b*) 0.01

(*c*) 1.5 (*d*) 0.247

SOLUTION. $K = 0.02$ in favour of chloroform ($CHCl_3$)

Let lactic acid comes out in $CHCl_3$ at equilibrium = xg

∴ Conc. of lactic acid in

$$CHCl_3 = \frac{x}{250} \text{g}(\text{mL})^{-}$$

Conc. of lactic acid in

$$H_2O = \frac{250 - x}{500} \text{g}(\text{mL})^{-} \quad \left[\because \frac{1}{2} \text{L} = 500\text{mL}\right]$$

$$\text{But} \quad \frac{\text{Conc. of lactic acid in } CHCl_3}{\text{Conc. of lactic acid in } H_2O} = K$$

$$\frac{\frac{x}{250}}{\frac{25-x}{500}} = 0.02 \quad \text{Or} \quad \frac{x}{250}\times\frac{500}{25-x} = 0.02;$$

$$\frac{2x}{25-x} = 0.02;\ 2x = 0.5 - 0.02x$$

Or $2.02x = 0.5$

Hence $x = (0.5/2.02) = 0.247$ g

So, the correct answer is (*d*).

EXAMPLE 21. *A mixture of equal volumes of bromoform and water was thoroughly mixed with 7.52g of Br_2 till equilibrium was attained. Now, excess of phenol was added to bromoform layer after separation. As a result, 10.2 g of tribromophenol, $C_6H_2Br_3OH$ (mol. mass = 331 g mol⁻) precipitate was obtained. The partition co-efficient in favour of water is :*

(*a*) 0.0162 (*b*) 4.21

(*c*) 1.24 (*d*) 0.0531

SOLUTION. Given, $C_6H_2Br_3OH = 3Br$

$$331 \text{ g} = 3 \times 80 = 240 \text{ g}$$

331 g $C_6H_2Br_3OH$ has Br_2 = 240 g

10.2 g $C_6H_2Br_3OH$ has $Br_2 = \frac{240}{331}\times 10.2 = 7.4$ g

$\therefore$ Br_2 in $C_6H_2Br_3OH$ = 7.4 g

Total Br_2 = 7.5 g (given)

$\therefore$ Br_2 in aqueous layer

$= 7.52 - 7.4 = 0.12$ g

Volume of bromoform

= Volume of H_2O = V (say)

But $$\frac{\text{Conc. of } Br_2 \text{ in } H_2O}{\text{Conc. of } Br_2 \text{ in bromoform layer}} = K$$

Or $$\frac{0.12/V}{7.4/V} = K; \quad K = 0.0162$$

So, the correct answer is (*a*)

EXAMPLE 22. *When benzoic acid was shaken with a mixture of water and benzene, following data was obtained.*

	I	*II*	*III*
Concentration of benzoic acid in water (C_1) in g/100 cm^3	0.016	0.024	0.03
Concentration of benzoic acid in benzene (C_2) in g/100 cm^3	0.242	0.56	0.95

The above data indicates that in benzene, benzoic acid exists as :

(*a*) monomer (*b*) dimer

(*c*) trimer (*d*) tetramer

SOLUTION. (*i*) *For monomer :*

I $$\frac{C_1}{C_2} = K; \quad K = \frac{0.016}{0.242} = 0.066$$

II $$\frac{C_1}{C_2} = K; \quad K = \frac{0.024}{0.56} = 0.043$$

III $$\frac{C_1}{C_2} = K; \quad K = \frac{0.03}{0.95} = 0.0316$$

Since the values of K are not constant, benzoic acid does not exist as a monomer.

(*ii*) *For dimer :*

I $$\frac{C_1}{(C_2)^{1/2}} = K; \quad K = \frac{0.016}{(0.242)^{1/2}} = \frac{0.016}{0.49} = 0.0326$$

II $$\frac{C_1}{(C_2)^{1/2}} = K; \quad K = \frac{0.024}{(0.56)^{1/2}} = \frac{0.024}{0.748} = 0.0321$$

III $$\frac{C_1}{(C_2)^{1/2}} = K; \quad K = \frac{0.03}{(0.95)^{1/2}} = \frac{0.03}{0.97} = 0.031$$

The constant values of K suggest that benzoic acid exists as a dimer in benzene solvent.

EXAMPLE 23. *An organic compound containing nitrogen was shaken with a mixture of water and ether at 273K. The following data was obtained.*

C_1(Conc. in H_2O layer)	*0.042*	*0.047*	*0.051*
C_2(Conc. in ether layer)	*0.913*	*1.028*	*1.1208*

If the organic compound exists as monomer in ether it will exist as one of the following in water.

(*a*) *trimer* (*b*) *dimer*

(*c*) *monomer* (*d*) *tetramer*

SOLUTION.

I $$\frac{C_1}{C_2} = K; \quad K = \frac{0.042}{0.913} = 0.046$$

II $$\frac{C_1}{C_2} = K; \quad K = \frac{0.047}{1.028} = 0.046$$

III $$\frac{C_1}{C_2} = K; \quad K = \frac{0.051}{1.1208} = 0.0455$$

Since the values of K are constant, the organic compound exists as a monomer in water. So, the correct answer is (*c*).

EXAMPLE 24. *The distribution co-efficient of an organic compound in ethoxyethane and water is 3:1. The weight of organic compound extracted from 200 mL of aqueous solution containing 20 g of organic compound by 100 mL ethoxyethane is :*

(*a*) *0.0012 g* (*b*) *1.2 g*

(*c*) *6 g* (*d*) *12 g*

SOLUTION.

Volume of mixture solution,

$$V_1 = 200 \text{ mL}$$

Volume of pure solvent (ethoxyethane) used

$$V_2 = 100 \text{ mL}$$

Wt of organic compound,

$$W = 20 \text{ g}$$

Distribution co-efficient,

$$K = \frac{C_1(H_2O)}{C_2(\text{ethoxyethane})} = \frac{1}{3}$$

We know that :

$$W_n = W\left[1-\left\{\frac{KV_1}{KV_1+V_2}\right\}^n\right]$$

$$= 20\left[1-\left\{\frac{\frac{1}{3}\times 200}{\left(\frac{1}{3}\times 200\right)+100}\right\}^1\right]$$

$$= 20\left[1-\frac{200/3}{500/3}\right] = 20(1-0.4)$$

$$= 20 \times 0.6 = 12 \text{ g}$$

So, the correct answer is (*d*)

EXAMPLE 25. *100 mL of an aqueous solution contains 5.6 g of an organic compound. The partition co-efficient of this compound between water and $CHCl_3$ is 1:5. The weight of organic compound extracted by 120 mL of $CHCl_3$ in four separate extractions using 30 ml of $CHCl_3$ for* each extraction will be:

(*a*) 5.6 g (*b*) 4.6 g

(*c*) 5.46 (*d*) 1.2 g (**Ans.** (*c*))

SOLUTION.

Hint. Consult example, 24.

EXAMPLE 26. *The partition co-efficient of iodine between CCl_4 and H_2O in favour of CCl_4 is 85. When 15 g of I_2 is shaken with the mixed solvents, the approximate ratio between the volumes of CCl_4 and H_2O if 8 g of I_2 is left in aqueous layer will be:*

(*a*) 85 : 1 (*b*) 1 : 85

(*c*) 97 : 1 (*d*) 1 : 97

SOLUTION.

Wt of I_2 in mixed solution = 15.0 g

Wt. of I_2 in water layer = 8.0 g

∴ Wt. of I_2 in CCl_4 layer = 15 – 8 = 7 g

Let Volume of H_2O taken = *a* litre

Volume of CCl_4 taken = *b* litre

∴ Conc. of I_2 in CCl_4 = $\frac{7}{b}\,\text{gL}^{-} = C_1$

Conc. of I_2 in H_2O = $\frac{8}{a}\,\text{gL}^{-} = C_2$

$$\therefore\ K = \frac{C_1}{C_2};\ 85 = \frac{7/b}{8/a};\ \frac{a}{b} = \frac{85\times 8}{7} = 97$$

∴ Ratio between volumes of H_2O and CCl_4 = 97 : 1; between CCl_4 and H_2O = 1 : 97

So, the correct answer is (*d*).

EXAMPLE 27. *One gram of silver gets distributed between 10 cm^3 of molten zinc and 100 cm^3 of molten lead at 800°C. The percentage of silver still left in the lead layer is approximately : Partition co-efficient of Ag in Zn and Pb = 300*

(*a*) 2 (*b*) 5

(*c*) 3 (*d*) 1 **[Karnataka CET 2011]**

SOLUTION. Let mass of Ag in Zn at equilibrium = *x*

Mass of Ag in Pb = 1 – *x*

$$\text{But partition co-efficient} = \frac{\text{Conc. of Ag in molten Zn}}{\text{Conc. of Ag is molten Pb}}$$

$$\text{or} \qquad 300 = \frac{x/10}{(1-x)/100} = \frac{10x}{1-x};$$

$$30(1-x) = x;\ 30 - 30x = x \text{ or } 31x = 30;$$

x = 30/31. So, mass of

Ag in Pb = 1 – 30/31 = 1/31

or % age of Ag = 1/31 × 100 ≃ 3.2% ≃ 3

So, the correct answer is (*c*).

PROBLEMS FOR PRACTICE

1. When a solute A was shaken with a mixture of water and an alcohol solvents at constant temperature, the following data was recorded.

	I	II	III
Equilibrium concentration of solute A in H_2O	0.174	1.08	1.80
Equilibrium concentration of solute A in alcohol	0.048	0.30	0.50

Show that the data illustrates the distribution law considering distribution co-efficient in favour of alcohol

2. Using data of above question 1, show that the data illustrates the distribution law considering distribution co-efficient in favour of water.
3. When a mixture of 60 cm^3 ether and 120 cm^3 water was shaken with succinic acid, at equilibrium, water layer contained 2.5 g while ether layer contained 0.15 g of succinic acid. Calculate partition co-efficient in favour of ether. (**Ans.** 0.1202)
4. Calculate partition co-efficient in favour of water in the above question, 3. (**Ans.** 8.32)
5. 20 mL of ether was shaken with 80 mL of M/5 aqueous solution of an organic compound till equilibrium was established. If distribution co-efficient of compound is 18 in favour of ether, find the concentration of organic compound in ether layer. (**Ans.** 0.013)
6. An organic compound is six times more soluble in water than in a solvent, S. When 9.0 g of the compound was mixed with 40 mL water and 30 mL of S, 0.4 g of the compound was found to be present in 18.0 mL of S. Find the degree of dissociation of the compound in water. (**Ans.** 35.65 %)
7. Using following data, prove that benzoic acid exists as a dimer in C_6H_6 if it exists as a single molecule in water.

$C_1(H_2O)$	5.02	7.98	10.90
$C_2(C_6H_6)$	0.146	0.362	0.705

8. 1.0 gm of a substance is dissolved in 100 ml of water. This solution is shaken repeatedly with 10 ml of $CHCl_3$ four times. The distribution ratio of the substance is 10 in favour of $CHCl_3$. Calculate the amount of substance left in water after four shakings and left if only once with 40 ml of $CHCl_3$. The substance has same molecular weight in both the solvents.

Ans. (*i*) 0.0625 g (*ii*) 0.20 g]

Hint. Consult example 1, 2.

9. 1.0 gram of a solute is contained in 100 ml of an aqueous solution. Calculate the quantity of solute left in aqueous phase after single extraction with 70 ml of an organic solvent (*ii*) two successive extractions with 35 ml of solvent assuming that the distribution ratio of the solute between organic solvent and water is 10. Also calculate the percent solute extracted.

Ans. (*i*) 0.125 gm left and 87.5% extracted (*ii*) 0.049 gm left and 95.1% extracted]

Hint. Consult example 14.

10. 20 mL of an aqueous solution of 0.1 M organic acid are shaken with 10 ml of chloroform. After the layers are separated, it is found by titration that 0.5 millimoles of the organic acid remains in the aqueous layer. Calculate the distribution ratio and percent of organic acid extracted. **Ans. D = 6.0%; extracted = 75%**

Hint. Consult example 16.

Appendix (i)

Hints and Answers to Practice Problems

CHAPTER – 1

1. **Hint.** $\left(\text{Speed} = \frac{1.60 \times 10^3\ \text{m}}{1\ \text{mile}} \times \frac{1\ \text{hr}}{3.6 \times 10^3 \text{s}} \times \frac{100\ \text{miles}}{\text{hr}}\right)$

   [**Ans.** 44 ms^{-}.]
2. Pm = petameter = 10^{15}; 41 $pm = 41 \times 10^{15}\ m$
3. 1 pico, $p = 10^{-12}$; $7p = 7 \times 10^{-12}\ m$
7. $2 \times 10^{-2}\ m^3 = (1L/10^{-3}\ m^3) \times 2 \times 10^{-2}\ m^3 = 20\ L$
8. $(10^{-10}\ m/\text{Å}) \times 0.50\ \text{Å} = 5.0 \times 10^{-11}\ m$.
9. $-25°\text{C} = 273 - 25 = 248\ K$
10. 1 yotta, $Y = 10^{24}$. So, $2Y = 2 \times 10^{24}$ cm.

CHAPTER – 2

3. 8.01 + 10.11 + 9.123 = 27.243 = 27.24 (up to least no. of decimal places in given data) = 4 significant figures.
4. $2.1\ \text{m} \times 1.50\ \text{m} = 3.15\ \text{m}^2 = 3.2\ \text{m}^2$
5. 0.1246 ÷ 3.6 = 0.03461 = 0.034 i.e., upto least no. of significant figures in question.
6. Significant figures in 2.2315 are four because preceding digit to 5 is odd. Thus, we have 2.232.
7. Significant figures in 1.12225 are five because preceding digit to 5 is even. Thus, we have 1.1222.
8. 1.1 × 1.111 = 1.2221 = 1.2 because significant figures the least precise factor 1.1 is 2.
9. $4000 = 4.0 \times 10^3$. No. of significant figures in 4.0 are two when the value is determined up to two significant figures.
10. 245 × 0.0125 + 55 = 3.062 + 55 = 58.062 = 58 since 55 contains only number up to two decimal places.

CHAPTER – 3

1. $2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{e}^-$; or $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1\text{e}^-$.

   Eq. wt. of Fe SO_4 = Mol. wt. of
   Fe SO_4 (= 56 + 32 + (4 × 16) = 152)/(no.
   of e^- s = 1) = 152 ; $\text{Cl}^{5+} + 6e^- \rightarrow \text{Cl}^-$;
   Eq. wt. of KClO_3 = Mol. wt. of KClO_3
   [= 39 + 35.5 + (3 × 16)
   = 122.5/no. of e^{-s} (= 6)] = 20.42
2. Eq. wt. of Na_2HPO_4 = Mol. wt. of Na_2HPO_4
   = (2 × 23) + 1 + 31 + (4 × 16)
   = 142/no. of replaceable H-atoms
   (= 1) = 142.
3. $\frac{E_1}{E_2} = \frac{\text{wt. of metal, 1}}{\text{wt. of metal, 2}}$; $\frac{E_1}{E_2} = \frac{x}{y}$; $E_1 = \frac{x\,E_2}{y}$
4. $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$; Eq. wt. of
   I_2 = [Mol. wt. of
   I_2 (= 2 × 127)/No. of e^-s gained (= 2)]
   = 127
5. Eq. wt. of metal = [(wt. of metal/wt. of H_2)] × Eq.
   wt. of H_2 = (2.5 × 1.008)/0.21 = 12
6. Eq. wt. = At. wt./valency = 40/2 = 20
7. Eq. wt. = (strength in g L^-/normality) = 5.3/0.1 = 53
8. In $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$, no. of H^+ ions that react with one molecule of NaOH is 1. So, equivalent wt. of NaOH = mol. wt. of NaOH (= 23 + 16 + 1 = 40)/1 = 40
9. Eq. wt. of KHCO_3 = [mol. wt. of KHCO_3/no. of
   replaceable H-atom] = $\frac{100}{1} = 100$
   [∵ Mol. wt. of KHCO_3 = 39 + 1 + 12 + (3 × 16) = 100].
10. 1 mol HCl = 1 mol H^+ ions. So, eq. wt. of
    HCl = mol. wt. of HCl = 1 + 35.5 = 36.5
    ∴ Milliequivalents of
    HCl = (wt./eq. wt.) × 1000
    = (3.65/36.5) × 1000 = 100.

CHAPTER – 4

1. Mol. wt. of KClO_4 = m + 35.5 + (4 × 16)
   = m + 99.5;
   m = at. wt. of K. Hence,
   28.26 = m/(m + 99.5) × 100; m = 39
2. At. wt. = $23 \times 1.66 \times 10^{-24} \times 6.023 \times 10^{23} = 23$
3. Mean at. wt. of Cl = [(35 × 3) + (37 × 1)/3 + 1] = 35.5
4. App. at. wt. = 6.4/0.05 = 128;
   1/3 = E/E + 80 [∵ at. wt. of Br = 80]
   ∴ E = 40; valency = 128/40 = 3.2 = 3;
   at. wt. = 40 × 3 = 120
5. wt. of metal/wt. of oxygen
   = Eq. wt. of metal/Eq. wt. of

oxygen; 60/40 = E/8
∴ E = 12; Mol. wt. of MClx
= $E_x + 35.5x$ where x is valency.
So, $12x + 35.5\,x = 2 \times 47.5$; $x = 2$;
At. wt. = 12 × 2 = 24

6. At. wt. = $3.82 \times 10^{-23} \times 6.023 \times 10^{23} = 23$

7. 1120 mL weighs 3.55 g. So, 22400 mL weighs (3.55/1120) × 22400 = 71 g mol. wt.
But mol. wt. = Atomicity of Cl_2 × at. wt.
So, 71 = 2 × at. wt. Thus, at. wt. = 35.5

8. E = Eq. wt. of Mg ; (Wt. of Mg/wt. of MgO) $= \dfrac{\text{Eq. wt. of Mg (E)}}{\text{Eq. wt. of MgO}}$
$\dfrac{1.2}{2} = \dfrac{E}{E+8}$; E = 12 ; At. wt. of Mg
= E × valency = 12 × 2 = 24.

9. γ = Cp/Cv
= 1.33. So, atomicity of gas is 3.
So, at. wt. of gas = Mol. wt./atomicity = 48/3 = 16

10. Cp − Cv = R ; Cp − 24.6 = 8.3 ; Cp = 32.9;
Cp/Cv $= \dfrac{32.9}{24.6} = 1.33$
So, gas is triatomic. So, at. wt.
= (Mol. wt./atomicity) = 48/3 = 16

CHAPTER – 5

1. Volume = $4/3\, \pi r^3 = 4/3 \times 22/7 \times (8.8/2)^3$
= 357 mm^3; density = mass/volume
= 2.0 g/357 mm^3
= 2.0×10^{-3} kg/357×10^{-9} m^3
= 5.602×10^3 kg m^{-3}.

2. Volume = (Mass/density)
= 18kg × (1000g/1kg) × (1cm^3/1.5g) × 1L/1000cm^3 = 12 L

3. V.D. = 11200 mL of H_2 × sp. gr ;
V.D. = $11200 \times 1.29 \times 10^{-3} = 14.48$

4. Density = Mass/volume
= 1500 g/10 × 8 × 1.5 cm^3
= 12.5 g cm^{-3}.

5. wt. = vol. × density
= 15 cm^3 × 1.1 g cm^{-3}
= 16.5 g; %age by wt. of HNO_3 = (5.2 g/16.5 g) × 100 = 31.5%

6. 500 mL = (500/1000) L
= 0.5 L ; d = 1.18 g cm^{-3}
= 1.18 kg L^{-}.

Pure HCl $= 0.5\text{L} \times \dfrac{1.81\text{ kg}}{1\text{L}} \times \dfrac{28\text{ kg acid}}{100\text{ kg acid}} = 0.344$ g

7. Density = mass/volume
= 120 g / 100,000 mL
= 1.2×10^{-3} g mL^{-1}

8. wt. of KOH = Molarity × mol. wt.
= 5.6 × 5.6 = 313.6 of L^{-}
1000 mL solution contain alkali = 313.6 g.
100 mL solution contain alkali = (313.6/1000) × 100
= 31.36 g
[∵ wt. = 25 g, volume is 100 mL]
∴ 31.36 g alkali is present in solution
= (100/25) × 31.36 = 125.44 g

9. wt. of liquid = 25 g; wt. of solution
= 100 g . 45 g of liquid is present
in solution = (100/25) × 45
= 180 g. So, volume
= (mass/density)
= 180/1.09 = 165.1 mL

10. Density = (1.9 g/cm^3) × (1 kg/1000 g) × (100 cm/1 m)^3 = 1900 kg m^{-3}

CHAPTER – 6

1. Molar mass of base
= $n/2\,[(195\, m_1/m_2) - 410]$
= 1/2 [(195 × 100)/33.4] − 410]
= 86.9 g mol

2. Molar mass = 2 [(108 × 0.8/0.51) − 107]
= 124.8 g mol^{-}.

3. 1000 mL of 1 N NaOH neutralise acid
= (0.24 × 1000)/30 × 0.1
= 80 g = g. eq. wt. of acid
∴ Molar mass = Eq. wt. × basicity
= 80 × 2 = 160 g mol^{-}

4. 1000 mL of 1 NHCl neutralise base
$= \left[(0.12 \times 1000)/\left(10 \times \dfrac{1}{2}\right)\right]$
= 24 g = g. eq. wt. of base.
So, molar mass = Eq. wt. × acidity
= 24 × 1 = 24 g mol^{-}.

5. 300 mL weighs = 0.368 g. So, 22400 mL weighs
= (22400 × 0.368)/300 = 27.5 g

6. $V_2 = (P_1V_1T_2/T_1P_2)$
= [(750 mm × 0.056 dm^3 × 273 K)/
(25 + 273 = 298 K) × 760 mm]
= 0.05 dm^3; 0.05 dm^3 weighs 0.073

g. So, 22.4 dm^3 weighs equal to $(0.073\ g \times 22.4\ dm^3)/0.05\ dm^3$ i.e., 32.7 g mol^-

7. $V_2 = (P_1V_1T_2/T_1P_2)$
$= [(1.1\ atm \times (36\ L/1000) \times 273\ K/$
$(107 + 273 = 280\ K) \times 1\ atm]$
$= 0.038$ L. So, wt. of 0.038 L H_2
$= 0.09\ g \times 0.038 = 3.42 \times 10^{-3}\ g$
$\therefore$ $V.D. = 36$; Mol. wt. = 2 × V.D.
$= 2 \times 36 = 72\ g\ mol^-$.

8. $P_1 = 35/76$ atm.,
$V_1 = 72/1000 = 0.072$ L,
$T = 25 + 273 = 298$ K.
But $PV = nRT$ or $PV = wRT/M$.
So, $M = WRT/PV$
$= (0.059\ g \times 0.0821\ L\ atm\ K^-mol^- \times 298\ K \times 76)/35\ atm \times 0.072\ L)$
$= 43.5\ g\ mol^-$

9. 0.4 L of a gas weighs 0.57 g. So, 22.4 L of gas weighs equal to $(0.57 \times 22.4/0.4) = 31.92\ g\ mol^-$.

10. $P_1 = 755.7 - 26.7 = 729.0$ mm,
$V_1 = 20.8$ mL, $T_1 = 27 + 273 = 300$ K;
At NTP, $P_2 = 760$ mm, $V_2 = ?$, $T_2 = 273$ K. So,
$V_2 = (P_1V_1T_2/T_1P_2)$
$= (729\ mm \times 20.8\ mL \times 273\ K/\ 300$
$K + 760\ mm) = 18.16$ mL;
V.D. $= (0.054/18.16 \times 0.00009)$
$= 33$; Mol. wt. = 2 × V.D. = 2 × 33
$= 66\ g\ mol^-$

CHAPTER – 7

1. $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$;
0.65 g 1.5 g x 0.635 g
Using law of conservation of mass, 0.65 + 1.5
$= x + 0.635$. So, $x = 1.515$ g.

2. (*i*) Ratio of I : Cl = 3.5 : 1; K : I = 1 : 3.237; K : Cl
= 1 : 0.923. Keeping wt. of K constant,
I : Cl = 3.237/0.923 : 0.923/0.923
= 3 . 5 : 1 which is same as of (*i*).
So, correct answer is (*b*).

3. (*i*) wt. of CO_2 = (44 × 1120)/22400)
= 2.2 g ($\because$ mol. wt. of CO_2 = 44 g);
wt. of oxygen = 2.2 – 0.6 = 1.6 g;
So, C : O = 0 . 6 : 1.6 = 3 : 8 ...(1)
(*ii*) C = 27.3%, O = 100 – 27.3 = 72.7 %.
Thus C : O = 27.3 : 72.7 or (27.3/27.3)
: (72.7/27.3)
= 1 : 2.66 or (3 × 1) : 3 × 2.66
= 3 : 8 ...(2)
the ratio in (1) and (2) is same.

4. When 5 mL of O_2 are treated with 10 mL of H_2, water is formed. When 100 mL of H_2 at N.T.P are passed over heated cupric oxide, the cupric oxide loses 0.072 g of its weight. Show that the results are in agreement with the law of constant composition.

(**Ans.** In both experiments, the ratio by wt. of $H_2 : O_2$ to form H_2O is 1 : 8. So, the law of constant composition is obeyed).

Hint. wt. of 5 mL

$$O_2 = \frac{32}{22400} \times 5\ g = 71 \times 10^{-4}\ g;$$

$$\text{wt. of } H_2 = \frac{2 \times 10}{22400}\ g = 8.9 \times 10^{-4}\ g.$$

$$\text{wt. of 100 mL } H_2 = \frac{2 \times 100}{22400} = 8.9 \times 10^{-3}\ g$$

$$\text{wt. of } O_2 = 0.072\ g = 72.0 \times 10^{-3}\ g$$

Ratio by wt. of H : O in both cases is same *i.e.*, 1 : 8.

5. In H_2O, ratio by wt. of H : O
= 11.2 : (100 – 11.2 = 88.8) = 1 : 7.92
In H_2O_2, the ratio by wt. of H : O
= 5.93 : (100 – 5.93 = 94.07)
= (5.93/5.93) : (94.07/5.93)
= 1 : 15.86. Keeping wt. of H
= 1 fixed, the ratio by wt. of O in H_2O and H_2O_2 is 7.92 : 15.86 or 1 : 2 which is simple multiple ratio.

6. (*i*) 0.2/0.2 : 0.4/0.2 = 1 : 2 (*ii*) 6/6 : 24/6 = 1 : 4 (*iii*) 20/20 : 120/20 = 1 : 6. Keeping wt. of A = 1 fixed, wts. of B are multiple of each other, 2 : 4 : 6 or 1 : 2 : 3

7. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
1L 2L
1L CH_4 uses O_2 = 2L. So, 6 L CH_4 uses
O_2 = 6 × 2
= 12 L. So, volume of air used
= (12 × 100/20.9) = 38.27 L.

8. $NaHCO_3 + CH_3COOH \longrightarrow \underbrace{CH_3COONa + H_2O} + 2CO_2$
2.1 g 1.5 g 2.05 g x
$\therefore$ 2.1 + 1.5 = 2.05 + x ;
x = 2.1 + 1.5 – 2.05
= 1.55 g
(law of conservation of mass)

9. (*i*) In PCl_3, P : Cl = [(22.57/22.57) : 77.43/22.57]
= 1 : 3.43; (*ii*) In PH_3, P : H

= [91.18/91.18 : 8.82/91.18]
= 1 : 0.096
In (*i*) and (*ii*) ratio of H : Cl
= 0.096 : 3.43 = 1 : 35. In (*iii*) H : Cl
= [2.77/2.77 : 97.23/2.77]
= 1 : 35.
In both cases, the ratio is same.

10. (*i*) In NH_3, N : H = (82.35/17.65 : 17.65/17.65)
= 4.66 : 1 (*ii*) In H_2O, O : H
= (88.9/11.1 : 11.1/11.1) = 8 : 1. So,
in (*i*) and (*ii*) N : O = (4.66/4.66 : 8/4.66)
= 1 : 1.71. In (*iii*), N : O
= (36.85/36.85 : 63.15/36.85)
= 1 : 1.71. In both cases, ratio is same.

CHAPTER – 8

20. $n = PV/RT$
$= 3170\ \text{Pa} \times 1\ \text{dm}^3/8.314 \times 10^3\ \text{Pa}$
$\text{dm}^3\ \text{K}^-\ \text{mol}^- \times 300\ \text{K} = 1.27 \times 10^{-3}$ mol.

21. $P_A = d_A\, RT/M_A = 2d_B\, RT/M_{B/2}$
$= 4\, d_B\, RT/M_B$;
$P_B = d_B\, RT/M_B$.
So, $P_A/P_B = [4\, d_B\, RT/M_B]/d_B\, RT/M_B] = 4/1$

22. Vol = mass/density
= (144 – 50 = 94 g)/0.47 g mL^-
= 0.2L ; PV = nRT
= (m/M)RT. So, 1 atm × 0.2 L
= (0.5 g/M) × 0.0821 L atm $\text{K}^-\ \text{mol}^-$
× 300 K. So, M = 61.575 g mol^-.

23. $U_{rms}(H_2) = (3RT/M)^{1/2} = (3R \times 300/2)^{1/2}$
$= 1.9 \times 10^3\ \text{ms}^-$; $U_{rms}(O_2)$
$= (3RT/M)^{1/2} = (3R \times 1200/32)^{1/2}$
$= (3R \times 4 \times 300/16 \times 2)^{1/2}$
$= \dfrac{2}{4}\ (3R \times 300/2)^{1/2}$
$= 0.95 \times 10^3\ \text{ms}^-$

24. $P_1V_1/T_1 = P_2V_2/T_2$; [1.5 atm × V_1/15 + 273
= 298 K] = 1.0 atm × V_2/288;
$V_2 = 1.55\ V_1 \simeq 1.6\ V_1$.

25. $PV = nRT = mRT/M$; 1 atm × 22.4 *L*
= (4.4 g/M) × 0.0821 L atm $\text{K}^-\ \text{mol}^-$
× 273.15 K; *M* = 44.05 g
[∵ *p* = 101.325 *k* Pa = 101325 Pa = 1 atm].
So, gas is C_3H_8 (3 × 12 + 8 = 44).

26. Greater the volume of vander Waal constant, '*a*' stronger will be the intermolecular forces and easily that gas will liquify. So, the correct answer is (*d*).

27. Average velocity of gas = $(8RT/M)^{1/2}$, On doubling the temperature, the average velocity will be $(2)^{1/2}$ i.e., 1.414 times.

28. $r_{HCl}/r_{NH_3} = (M_{NH_3}/M_{HCl})^{1/2} = (17/36.5)^{1/2} = 1/1.46$.

29. $r_{H_2}/r_{H.C.} = (M_{HC}/M_{H_2})^{1/2} = 3(3)^{1/2}$;
$(M_{HC/2})^{1/2} = 3(3)^{1/2}$;
$M_{HC} = 2 \times 27 = 54$.
So, the hydrocarbon (H.C.)
= C_4H_6 i.e., 54/12
= 4C + 6H = C_4H_6.

CHAPTER – 9

11. 22.4 L SO_2 at N.T.P.
= 6.023×10^{23} molecules; 5.6 L SO_2
= $6.023 \times 10^{23} \times 5.6/22.4$
= 1.5×10^{23} molecules.

12. 11.2 L (= 22.4/2) $O_2 \equiv (6.02 \times 10^{23}/2)$
= 3.01×10^{23} molecules; 8 g (= 32/4)
O_2 = $(6.02 \times 10^{23}/4)$ or 1.505×10^{23}
molecules; 0.1 mol O_2 = $0.1 \times 6.02 \times 10^{23}$
= 6.02×10^{22} molecules ;
2.24×10^4 mL of O_2 = $6.02 \times 10^{23} \times 2.24 \times 10^4/22400$
= 6.02×10^{23}.

13. Molarity of acid = Normality/basicity ;
Molarity = 0.02/2 = 0.01 M ; 1000 mL
= 0.01 mol, so 100 mL
= 0.01 × 100/1000 mL
= 0.001 mol or $6.02 \times 10^{23} \times 0.001$
= 6.02×10^{20}.

14. 1 mol $(NH_4)_2Cr_2O_7$
= Total no. of atoms × 6.023×10^{23}
= 19 atoms (= 2 N + 8H + 2 Cr +
7O = 19) × 6.023×10^{23}
= 114.437×10^{23} atoms.

15. Time in hours to distribute 10^{20} grains
= $(6.023 \times 10^{23})/10^{20} \times 60 \times 60$
= 1.673 hours.

16. No. of atoms in 0.1 mol of triatomic gas
= $0.1 \times 3 \times 6.02 \times 10^{23} = 1.806 \times 10^{23}$.

17. 1 mol CO_2 = 12 + (2 × 16) = 44 g; 88 g CO_2
= 2 mol ; no. of O-atoms in 1 molecule of CO_2
= 2 ; no. of O-atoms in 2 mol of
CO_2 = $2 \times 2 \times 6.02 \times 10^{23}$
= 24.08×10^{23} ;
One CO molecule contains O-atoms = 1
1 mol CO (= 12 + 16 = 28 g) contain O-atoms
= 6.02×10^{23}.

So, mass of CO containing 24.08×10^{23} oxygen atoms

$= (28/6.02 \times 10^{23}) \times 24.08 \times 10^{23}$

$= 112$ g. So, (*d*) is correct.

18. 22400 cm^3 contain Ar-atoms = Atomicity of Ar × 6.02×10^{23} atoms

∴ 100 cm^3 contain Ar-atoms

$= 1 \times 6.02 \times 10^{23} \times 100/22400$

$= 2.7 \times 10^{21}$. So, (*d*) is correct.

19. wt. of A $= 20 \times 10{,}000 = 20{,}000$ g; 1 g atom

of A $= 6.02 \times 10^{23}$ atoms. So, g. atoms of

A $= 3.01 \times 10^{-23} \times 6.02 \times 10^{23}$

$= 18.1$ g; 18.1 g of A

$= 1$ g atom of A. So, 20,000 g of A

contain g atoms $= 20{,}000/18.1 = 1105$ g atoms.

20. $V_2 = (P_1V_1T_2/P_2T_1)$

$= (2 \times 400 \times 273/1 \times 273)$

$= 800\ cm^3$. 22400 cm^3 gas weighs (1 g × 22400/800) = 28 g ; wt. of one atom of gas = [1 g. mol. wt. of gas/ atomicity of gas × 6.02×10^{23}]

$= [28\ g/2 \times 6.02 \times 10^{23}]$

$= 2.3 \times 10^{-23}$ g.

CHAPTER – 10

2. Suppose no. of O^{2-} ions = 30. So, no. of octahedral voids = 30.

∴ Ratio of $Al^{3+} : O^{2-} = (30 \times 2/3) : 30 = 20 : 30 = 2 : 3$

∴ Formula $= Al_2O_3$.

3. **AB:** $r^+/r^- = 1/1 = 1$. So, b.c.c. struture ;

$2 \times (r_A^{\ +} + r_B^{\ -}) = \sqrt{3} \times a$.

∴ $a = (2/\sqrt{3})\ (1 + 1)$

$= 4/\sqrt{3}$; vol. $a^3 = (4/\sqrt{3})^3$

$= 12.32\ cm^3$.

AC : $r^+/r^- = 1/2 = 0.5$; so octahedral structure ; $a = 2\ (r^+/r^-) = 6$ pm. So, volume, $a^3 = (6\ pm)^3$

$= 216\ pm^3$.

4. $d = [(4 \times 58.5)/6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3] = 2.1805\ g\ cm^{-3}$;

Due to misssing of some ions, observed density 2.164 $g\ cm^{-3}$ is less than calculated 2.1805 $g\ cm^{-3}$. Thus:

$Z = 2.164 \times 6.023 \times 10^{23} \times (0.5627 \times 10^{-7})^3/58.5 = 3.969$; missing units

$= 4 - 3.969 = 0.031$; % missing

$Na^+, Cl^- = 0.031 \times 100/4 = 0.775$.

5. (*i*) Length, *a*. $4r = \sqrt{2}.a$; $4 \times 130 = \sqrt{2}\ .\ a$

So, $a = 367.64$ pm; (*ii*) volume

$= a^3 = 4.94 \times 10^{-23}\ cm^3$ (*iii*) for fcc,

$Z = 4$ (*iv*) $d = [(4 \times 63.54)/6.023 \times 10^{23} \times (3.67 \times 10^{-8})^3] = 8.54\ g\ cm^{-3}$.

6. For fcc, Z = 4; for bcc, Z = 2. Use

$d = n$ M/No. a^3. So, d_{fcc}/d_{bcc}

$$= 4/2 \times \frac{3^3}{(3.5)^3} = 1.259$$

7. $2r^+ + 2r^- = 600$ pm, $r^+ + r^-$

$= 300$; For octahedral, r^+/r^-

$= 0.414$. From r^+/r^-

$$= 300,\ r^-\left(\frac{r^+}{r^-} + 1\right) = 300;$$

r^- of $A^- = 212.164$ and r^+ of M^+

$= 212.164 \times 0.414 = 87.84$ pm.

8. $n\lambda = 2d \sin\theta$; $d = n\lambda/2 \sin 60$

$= 2 \times 1\ Å/2 \times \sqrt{3}/2 = 1.15Å$.

9. Radius ratio $= r^+/r^- = 88/200$

$= 0.44$. So, co-ordination number

$= 6$.

10. $a = 2d/\sqrt{3} = 2 \times 452/1.732$

$= 522$ pm; for bcc, $Z = 2$. So,

$d = Z\ M/N_c \times a^3 \times 10^{-30} = 910\ kg\ m^{-3}$.

So, (*c*) is correct.

11. For fcc, $r^+/r^- = a/2 = 508/2 = 254$ pm.

So, $r^- = 254 - 110 = 144$ pm.

CHAPTER – 11

1. Use example, 1 at page, 182.

2. $CO_2 \equiv C$; H_2O : 2H

44 g   12 g   18 g   2 g

wt. of H_2 in 0.69 g H_2O

$= [(2 \times 0.69)/18] = 0.0767$ g

wt. of carbon in 3.38 g CO_2

$= (12 \times 3.38/44) = 0.9218$ g; mass

of fuel gas $= 0.9218 + 0.0767$

$= 0.9985$ g; mass percent of carbon

$= (0.9218 \times 100/0.9985)$

$= 92.32\%$; mass percent of H_2

$= (0.0767 \times 100/0.9985)$

$= 7.68\%$. To find E.F. we have:

Element	*% age*	*At. mass*	*relative no. of atoms*	*simple ratio*	*whole no. ratio*
C	92.32	12	92.32 = 7.69	7.69/7.69 = 1	1
H	7.68	1	7.68/1 = 7.68	7.68/7.68 = 1	1

So, E.F. = CH

3. 10 L gas weighs = 11.6 g. So, 22.4 L gas weighs
= (11.6 × 22.4/10) = 26 g

4. M.F. = n × E.F.; n = [molar mass/E.F. mass of CH (= 12 + 1 = 13)] = 26/13
= 2. So, M.F. 2 × CH = C_2H_2

5. $H_2 + Br_2 \longrightarrow 2HBr$
1 vol 1 vol 2 vol
3L 3L 2 × 3 = 6L

Vol. of H_2 gas taken = 3.2 L ; Vol of H_2 gas used is 3.0 L. So, vol. of H_2 gas left behind = 3.2 – 3.0 = 0.2 L; vol of HBr formed = 2 × 3 = 6 L. Here, Br_2 being less, is limiting reagent.

6. $2\,Na + 2HCl \longrightarrow 2NaCl + H_2$
2 vol 1 vol
Decrase in volume = 2 – 1 = 1V. Actual decrease in vol
= 48 – 40 = 8 mL. Vol of HCl in 48 mL
mixture = 8 × 2 = 16 mL; vol of
H_2 = 48 – 16 = 32 mL; 98 mL of mixture
contain HCl (g) = 16 × 2 = 32 mL and
H_2 = 98 – 32 = 66 mL.
$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$; [32 mL NH_3 = 32 mL HCl]
32 mL 32 mL
Residual NH_3 = 48 – 32 = 16 mL ; residual
H_2 = 98 – 32 = 66 mL

7. $C_xH_y + (x + y/4)\,O_2 \longrightarrow x\,CO_2 + y/2\,H_2O.$
250 mL 250 $(x + y/4)$ 250 x 250 × y/2
= 125 y
= 1250 mL = 1500
[∵ 1.5 L = 1.5 × 1000 = 1500 mL]
250 x = 1250; x = 5 ; 125 y = 1500.
So, y = 1500/125 = 12 .
Thus, the formula of hydrocarbon = C_5H_{12}.

8. Use example 23 for calculations.

9. Use example 27 for calculations.

10. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
22400 mL 2 × 22400 mL
22400 mL CH_4 use O_2 = 2 × 22400 mL
112 mL CH_4 use O_2 = [2 × 22400 × 112/22400] = 224 mL. So, (b) is correct.

CHAPTER – 12

1. No. of atoms in NH_3
= 1 N + (3 × 1) H
= 4. Mol. wt. of NH_3
= 14 + (3 × 1) = 17 g mol⁻
17 g NH_3 ≡ 4 × 6.023 × 10^{23} atoms
4.25 g NH_3 ≡ [4 × 6.023 × 10^{23}/17] × 4.25
= 6.023 × 10^{23} atoms.
So, correct answer is (a).

2. 22400 mL H_2O ≡ 6.023 × 10^{23} molecules.
1 mL H_2O ≡ (6.023 × 10^{23}/22400) = 20 drops.
∴ 1 drop H_2O ≡ [6.023 × 10^{23}/22400 × 20]
= 1.344 × 10^{18} molecules.

3. $(NH_4)_2Cr_2O_7$ contains atoms
= 2N + 8H + 2Cr + 7O
= 19. So, 1 mol contains 19 × 6.023 × 10^{23} = 114.437 × 10^{23} atoms.
So, (c) is correct.

5. no. of emitted spectral lines when electron jumps from n_2 to n_1 orbit
= $[(n_2 - n_1)(n_2 - n_1 + 1)/2]$
= (5 – 1) (5 – 1 + 1)/2 = 10

6. $\bar{v} = R_H\,[1/n_1^2 - 1/n_2^2]$
= 8/9 R_H; $1/n_1^2 - 1/n_2^2$
= 8/9. So, n_1 = 2, n_2 = 3.
So, (a) is correct.

7. n = no. of photons ;power
= 600 W or 600 J s^{-}; E = n hc/λ
= 600 Js^{-}.
600 = [n × 6.626 × 10^{-34} × 3 × 10^8/331.3 × 10^{-9}]; n = 1 × 10^{21} photons.

8. ΔE = $N_A\,hc/\lambda$; 242 × 10^3
= [6.02 × 10^{23} × 6.62 × 10^{-34} × 3.0 × 10^8/λ]
or λ = 4.94 × 10^{-7} m = 494 nm.

9. Z for He = 2; for Li = 3. I.E. of He^+
= I.E. of H × Z^2 ; I.E. of H
= 19.6 × 10^{-18}/Z^2 = 4
= 4.9 × 10^{-18} J atom⁻. I.E. of Li^{2+}
= I.E. of H atom × Z^2 = 4.9 × 10^{-18} × $(3)^2$ = 4.41 × 10^{-17} J
= – 4.41 × 10^{-17} J.

10. $_{24}Cr = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^4$.
So, 19th electron goes to 4s-energy level.

CHAPTER – 13

1. $_{27}Co = (Ar)^{18}\,3d^7\,4s^2$; $Co^{3+} = (Ar)^{18}\,3d^6$

2. $_7N = (He)^2\,2s^2\,2p^1_x\,2p^1_y\,2p^1_z$ **Ans.** Try others yourself e.g. ; $_{12}Mg^{2+} = (Ne)^{10}$ has no unpaired electron.

3. $\chi_B - \chi_A$ = 1.0. Use the calculations of example 25, page 258 to get the result.

4. Extra ionic resonance energy
= 103.2 – $[104.2 \times 58]^{1/2}$
= 103.2 – $(6043.6)^{1/2}$
= 103.2 – 77.7 = 25.5 cal mol⁻

5. %age ionic character

$= 16\,\Delta x + 3.5\,(\Delta x)^2$

$= 16\,(3.0 - 2.8) + 3.5\,(3.0 - 2.8)^2$

$= 3.34.$

6. $\Delta H = E.A. + I.P. = -3.7\text{ eV} + 4.3\text{ eV}$

$= 0.6\text{ eV}.\ \Delta H\text{ mol}^{-}$

$= 0.6 \times 6.02 \times 10^{23}\text{ eV} \times 1.602 \times 10^{-19}$

$\times 10^{-3}\text{ kJ/1 eV} = 57.86\text{ kJ}.$

7. I.P. of K $= 4.3\text{ eV atom}^{-} \times 6.023 \times 10^{23} \times 1.602 \times 10^{-19}\text{ J mol}^{-}/1\text{eV atom}^{-}$

$= 414.9 \times 10^{3}\text{ J mol}^{-}$. For 3.0 mol K,

I.P. $= 3 \times 414.9 \times 10^{3} = 1244.7 \times 10^{3}$ J.

8. Bond length = 0.28 Å + 0.99 Å = 1.27 Å.

9. ${}_{19}K = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$. Highest no. of shell = no. of period = 4.

CHAPTER – 14

1. $4Al + 3O_2 \longrightarrow 2Al_2O_3$

4 × 27 = 108 g   3 mol

3 mol O_2 ≡ 108 g Al ; 1.5 mol O_2

≡ (108 × 1.5)/3 = 54 g

2. 1 kg sea water ≡ 10^6 mg; 10^6 mg H_2O contain dissolved O_2

= 6 mg. So, concentration of O_2

$= 6 \times 10^6\text{ ppm}/10^6 = 6$ ppm.

3. Mol. wt. of Na_2CO_3

= 106; Molarity

$$= \frac{25.3 \times 1000}{106 \times 250}$$

= 0.955 M;

$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$

∴ $Na^+ = 2 \times 0.955 = 1.910$ M;

$CO_3^{2-} = 0.955$ M.

4. $NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl$

23 + 35.5	108 + 14 + 48	108 + 35.5
= 58.5	= 170	= 143.5
5g	20 g (given)	
5g	14.5g (see (*i*) below)	
5 – 5 = 0	20 – 14.5 = 5.5 (difference)	
Less	more	

= Limiting reagent

(*i*) 58.5 g NaCl ≡ 170 g $AgNO_3$

5 g NaCl = 170 × 5/58.5 = 14.5 g

(*ii*) 58.5 g NaCl ≡ 143.5 g AgCl

5 g NaCl = (143.5 × 5/58.5) = 12.26 g

5. $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$

23 + 1 + 12 + (3 × 16) = 84 g   22400 mL

84 g $NaHCO_3$ form CO_2 = 22400 mL

8.4 g $NaHCO_3$ form CO_2 = (22400 × 8.4/84) = 2240 mL

6. $Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2 + 2NaNO_3$

207 + 2 (14 + 148)	2(23 + 35.5)
= 331 g	= 117 g
3.31 g	1.0 g (given)
3.31 g	1.17 (Calculated)
0	– 0.17 Difference

Since – 0.17 < 0, NaCl is the limiting reactant.

3.31 g Pb $(NO_3)_2$ ≡ 117 g NaCl

3.31 g Pb $(NO_3)_2$ = 117 × 3.31/331 = 1.17 g

7. Acidity of Ca $(OH)_2$

= 2; Molarity of Ca $(OH)_2$

= Normality/acidity = 0.2/2 = 0.1

$[M_1\,V_1\,(H_2SO_4)/M_2V_2\,Ca(OH)_2]$

= no. of mol of H_2SO_4/no. of mol. of Ca $(OH)_2$; 0.4 × V_1/0.1 × 20

= 1/1 ; V_1 = 20 × 0.1/0.4 = 5 mL

$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$

1 mol   1 mol

8. $Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$

1 mol   1 mol

0.1 mol   0.1 mol

Moles of Mg = (wt/g at. wt.) = 2.4/24 = 0.1

1 mol   1 mol

Vol of H_2SO_4 in litre = Mol/molarity

= 0.1/0.4 = 0.25 L

9. Consult example 70.

10. Consult example 68.

CHAPTER – 15

11. At equilibrium, ΔG

= 0; ΔG (= 0) = ΔH – TΔS ; T

$= \Delta H/\Delta S = (-743.1\text{ J mol}^{-}/$

$-17\text{ J k}^{-}\text{ mol}^{-}) = 43.7$ K

12. $\Delta S = \Delta H v/T$;

$\Delta S = (-35.3 \times 1000\text{ J mol}^{-}/273 + 80$

$= 353\text{ K}) = -100\text{ JK}^{-}\text{ mol}^{-}$

13. $\Delta S^\circ = S^\circ(XY_3) - 1/2\,S^\circ(X_2) - 3/2\,S^\circ(Y_2)$

$= 50 - 1/2(60) - 3/2(40) - 40\text{ JK}^{-}\text{mol}^{-}$

$T = \Delta H^\circ/\Delta S^\circ = (-30 \times 10^{3}\text{ J mol}^{-}/$

$-40\text{ JK}^{-}\text{ mol}^{-}) = 750$ K.

15. For $1/2\ H_2\ (g) + 1/2\ Cl_2\ (g) \rightarrow HCl\ (g)$,
$\Delta_r H = \Delta H$ (Products) – ΔH (reactants) ;
$\Delta_r H = (-92.3) - ((1/2 \times 218) + 1/2 \times 121.68) = -262.14$ kJ mol$^-$

16. Moles of HCl; $= 0.1 \times 500/1000 = 0.05$ mol; mol of NaOH $= 0.2 \times 200/1000 = 0.04$ mol
0.04 mol NaOH $\equiv$ 0.04 HCl ; Heat of neutralisation $= 0.04 \times 57.1 = 2.284 \simeq 2.29$ kJ.

17. $H-H + O=O \rightarrow H-O-O-H$;
$\Delta_r H$ = B.E. (reactants) – B.E. (Products) $= (438) + (498) - [2\ (464 + 138)] = -130$ kJ mol$^-$.

18. Given equations are (*i*) $1/2\ N_2\ (g) + 3/2\ H_2\ (g) \rightarrow NH_3\ (g)$;
$\Delta H = -46$ kJ (*ii*) $2\ H\ (g) \rightarrow H_2(g)$;
$\Delta H = -436$ kJ; (*iii*) $2N\ (g) \rightarrow N_2(g)$;
$\Delta H = -712$ kJ. In order to get equation,
$NH_3(g) \rightarrow N(g) + 3/2\ H\ (g)$,
we have, 1/2 equation (*iii*) + 3/2 × equation (*ii*) –equation (*i*), we get
$\Delta H = 1056$ kJ for three N-H bonds.
So, average bond energy (N – H) = 1056/3 = 352 kJ.

19. At equilibrium $\Delta G = 0$; $\Delta G\ (= 0) = \Delta H - T\Delta S$;
$\Delta S = \Delta H/T = [21.3 \times 1000$ J mol$^-/82 + 273 = 355] = 60$ JK$^-$ mol$^-$

20. External pressure, $P = 0$; $W = P \times \Delta V = 0 \times \Delta V =$ zero.

CHAPTER – 16

6. H_2SO_4. 2 × O.N. of H + O.N. of S (= x) + 4 × O.N. of O = 0; $(2 \times +1) + x + 4\ (-2) = 0$; $x = +6$

7. Let O.N. of I $= x$; (*c*) IO_3^-; $x + 3\ (-2) = -1$; $x = +5$; IO_4^- ; $x + 4\ (-2) = -1$. So, $x = +7$; $K^+ I^-$; $x = -1$; I^0_2 ; I = 0.

8. $Ag^+ + e^- \rightarrow Ag$, $E° = +0.80$ V; $Cu^{2+} + 2e^- \rightarrow Cu$, $E° = +0.34$. Since E° (reduction) value + 0.80 V > + 0.34 V, Ag^+ is stronger oxidant than Cu^{2+}.

9. $Zn^{2+} + 2e^- \rightarrow Zn$, $E° = -0.76$ V ; $Cu^{2+} + 2e^- \rightarrow Cu$, $E° = +0.34$ V.
Since E° (reduction) value – 0.76 V < + 0.34 V, Zn is stronger reducing agent than Cu.

10. $MnO_4^- + 8H^+\ 5e^- \rightarrow Mn^{2+} + 4H_2O] \times 2$
$\underline{FeC_2O_4 \rightarrow Fe^{2+} + 2CO_2 + 2e^-] \times 5}$
$5\ FeC_2O_4 + 2\ MnO_4^- + 16\ H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5\ Fe^{2+} + 10CO_2$
$\therefore$ 5 mol $FeC_2O_4 \equiv$ 2 mol MnO_4^-. So, 2 mol FeC_2O_4 $\equiv$ 2/5 or 0.6 mol MnO_4^-.

11. $Mn^{7+}\ O_4^- + N^{3-} \rightarrow N^{5+} + Mn^{4+}$. Here O.N. of Mn $= +4 - 7 = -3$; O.N. change of N $= +5 - (-3) = +8$. So, $x = 8$, $y = 3$.

12. Let x = O.N. of Hg. So, in Hg_2Cl_2, $2x + 2$ (O.N. of Cl) = 0; $2x + 2\ (-1) = 0$; $x = +1$.

13. (*i*) PO_4^{3-} ; $x + 4\ (-2) = -3$. So, $x = +5$ (*ii*) SO_4^{2-} ; $x + 4\ (-2) = -2$. So, $x = +6$ (*iii*) $Cr_2O_7^{2-}$; $2x + 7\ (-2) = -2$. So, $x = +6$.

14. (*c*) $Cl^{+1}\ O^- + Cl^{+1}\ O^- \rightarrow Cl^{+5}\ O_3^- + Cl^-$. Here one Cl^{+1} is oxidised to +5 while the second Cl^+ is reduced to Cl^-.

15. In Mohr's salt, $FeSO_4\ (NH_4)_2\ SO_4$. 24 H_2O, oxidation state of Fe in $FeSO_4$ is + 2 i.e., x + O.N. of $SO_4^{2-} = 0$; $x - 2 = 0$; $x = +2$

CHAPTER – 17

1. Molarity of solution = (25.3 × 1000/106 × 250) = 0.955 M; $Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$
$\therefore$ $[Na^+] = 2 \times 0.955 = 1.910$ M; $CO_3^{2-} = 1 \times 0.955 = 0.955$ M.

2. 0.08 g S is present in insulin = 100 g; so, 32 g S (at. wt. of S = 32) is present in insulin = (100 × 32/0.08) = 40,000.

3. Mass of NO_2 gas = (46 × 112/22400) = 0.3 g; Volume of liquid = 0.23/1.15 = 0.20 mL; no. of molecules = no. of moles × Avogadro's no. $= (0.23/0.46) \times 6.02 \times 10^{23} = 3.01 \times 10^{21}$.

10. Mole fraction $I_2 = 0.2$; $C_6H_6 = 0.8$. Mass of C_6H_6 (mol. wt. 78) = 0.8 × 78 = 62.4. So, molarity of I_2 = (0.2 × 1000/62.4) = 3.2.

CHAPTER - 18

3. $\Delta T_f = i\ k_f \times m$. For $Na_2SO_4 \rightleftharpoons 2Na^+$ (2 mol) + SO_4^{2-} (1 mol), $i = 2 + 1 = 3$.
Molality, m = (0.01/1 kg) = 0.01 m;
$\Delta T_f = 3 \times 1.86$ K kg mol$^- \times 0.01$ mol kg$^-$ = 0.0558.

4. $x_{\text{solute}} = (p^{\circ} - p/p^{\circ}) = (0.8 - 0.6/0.8) = \mathbf{0.25}.$

5. $\pi = \text{CRT}$

$= 0.002 \times 1000 \text{ mol m}^{-3} \times 8.314 \text{ JK}^{-}$

$\text{mol}^{-} \times (273 + 20 = 293 \text{ K})$

$= 4872.004 \text{ J m}^{-3} = 4872.004 \text{ Pa}$

6. Molality, m = [mol. of solute/mass of solvent

(g)] $= [(1/250)/51.2] \times 1000 = 0.078$

$\therefore \quad \Delta T_f = k_f \times m = 5.12 \times 0.078 = 0.4$

7. Electrolytes with maximum degree of dissociation in diluted solution have maximum van't it off value. So, correct result is (*a*).

8. Relative lowering of V.P., $(p^{\circ} - p_s/p^{\circ})$

$= (w_A/m_A) \times (m_B/w_B)$; $(10/100)$

$= [x/60)/(180/18)]$

$\therefore \quad x = 60$. So, 60 g of solute should be added.

9. (*i*) Osmotic pressure, π

$= hdg = (2.6/10 \text{ cm}) \times 1 \text{g cm}^{-3} \times 980$

dynes cm^{-2} (*ii*) $\pi = \text{WRT/V}m$. Hence $(2.6 \times 1 \times$

$980/10) = 0.75 \times 8.314 \times 10^7 \times (273 + 4$

$= 277)/125 \times m$. So, $m = 5.4 \times 10^5$.

10. Such solutions are isotonic which have same molar concentration.

In 0.1 M Ba $(NO_3)_2$, $Ba(NO_3)_2 \rightleftharpoons Ba^{2+}$ (0.1 M) + 2 NO_3^- (0.2 M).

$\therefore$ Molar concentration of 0.1 M $Ba(NO_3)_2$ = 0.1 + 0.2 = 0.3 M. In 0.1 M Na_2SO_4, Na_2SO_4 (0.1 M) $\rightleftharpoons$ 2 Na^+ (0.2 M) + SO_4^{2-} (0.1 M).

$\therefore$ Molar concentration of 0.1 M Na_2SO_4 = 0.1 M + 0.2 M = 0.3 M. Since molar concentrations are same, (*d*) is correct.

11.
$$\begin{array}{cccc} \text{Na I} & \rightleftharpoons & \text{Na}^+ & + \quad \text{I}^- \\ 1 - \alpha & & \alpha & \alpha \end{array}$$

Total no. of mol $= 1 - \alpha + \alpha + \alpha$

$= 1 + \alpha$; Observed osmotic pressure,

$\pi_{\text{obs}} = \pi_{\text{Theoretical}} \times (1 + \alpha)$

$= 0.01 \text{ RT } (1 + \alpha)$; π_{glucose}

$= 0.016$ RT. So, $0.01 \text{ RT } (1 + \alpha)$

$= 0.016$ RT. Hence, α

$= 0.6$ or $0.6 \times 100 = 60$ %.

12. $\Delta T_b = K_b \times W_2/M_2 \, W_1$ in kg

$= [0.513°\text{C kg mol}^{-} \times 20 \text{ g}/78 \text{ g mol}^{-} \times 400/1000 \text{ kg}]$

$= 0.329°$C. So, b. pt. of solution

$= 99.834°\text{C} + 0.329°\text{C} = 100.163°\text{C}.$

CHAPTER – 19

19. Resistivity = 1/conductance = 1/18.5 ;

$\lambda_0 = 438 \text{ ohm}^{-} \text{ cm}^2 \text{ eq}^{-1}$

$\lambda_c = K \times 1000/C = (1/18.5 \times 1000)/15/49;$

$$\alpha = \lambda_c/\lambda_0 = \frac{1 \times 1000 \times 49}{18.5 \times 15} \times \frac{1}{438} = 0.403$$

$\therefore \quad \alpha = 0.403 \times 100 = 40.3\%.$

So, correct answer is (*d*).

20. 0.1 millifaraday $= (0.1 \times 1/1000)$ F

But 1 Faraday = 1g equivalent of Al

$$= \frac{\text{At. wt. of Al}}{\text{Valency}} = \frac{27}{3} = 9$$

$= 9 \times 1000 \text{ mg} = 9000 \text{ mg}$

$= 0.1 \times \dfrac{1}{1000} F = 9000 \times 0.1 \times 1/1000$

$= 0.9$ mg

So. the correct answer is (*d*).

21. $E_{\text{cell(2)}} = E°_{\text{Cell}} - (0.059/1) \log (0.0025/1)$

$= -\,0.059 \log 0.0025;$

$E_{\text{cell(1)}} = E°_{\text{cell}} - (0.059/1) \log (0.05/1)$

$= -\,0.059 \log 0.05;$ $(E_{\text{cell(2)}}/E_{\text{cell(1)}})$

$= [-0.59 \log 0.0025/-0.59 \log 0.05]$

$= (-\,2.6/-\,1.3) = 2$. So, $E_{\text{cell (2)}}$

$= 2 \times 70 \text{ mV} = 140 \text{ mV}.$

22. W = Z It; $Z_H = 1/96500$;

$Z_{\text{oxygen}} = 8/96500$;

$W_H = 0.504$ g, t = 2 hrs, W_{oxygen} = ?

$(W_H/W_{\text{oxygen}}) = Z_H \text{ It}/Z_{\text{oxygen}} \text{ It} = Z_H/Z_{\text{oxygen}}$;

$(0.504/W_{\text{oxygen}}) = (1/96500)/(8/96500)$

$\therefore \quad W_{\text{oxygen}} = 4.032 \simeq 4\text{g}$

23. g eq. wt. of Cu = At. wt/Valency

= 63.5/2 g i.e., 0.5 mol ;

1 mol Cu = 63.5 g; 0.5 mol Cu is deposited

from = 1Faraday.So,1molCuisdeposited

from = $(1/0.5) \times 1 = 2$ **Ans**

24. $\lambda_\infty = \lambda_c + \lambda_a = 315 + 35$

$= 350 \text{ mho cm}^2 \text{ eq}^-.$

25.
$$\begin{array}{lll} Al^{3+} + 3e^- \rightarrow Al \,; & Cu^{2+} + 2e^- \rightarrow Cu \,; & Na^+ + 1e^- \rightarrow Na \\ 3F \quad 1 \text{ mol} & 2F \quad 1 \text{ mol} & 1F \quad 1 \text{ mol} \\ 1F \quad 1/3 \text{ mol} & 1F \quad 1/2 \text{ mol} & \end{array}$$

$\therefore$ Mole ratio = 1/3 : 1/2 : 1 or 2 : 3 : 6

26. Percent ionisation, $\mu = \Lambda_c/\Lambda_\infty = (14/238) \times 100 = 5.9$

27.
$$\begin{array}{ccccc} Cu^{2+} & + & 2e^- & \rightarrow & Cu \\ 1 \text{ mol} & & 2 \text{ mol} & & 1 \text{ mol } (63.5 \text{ g}) \end{array}$$

Charge to deposit 2.0 g Cu

= (2 × 96500 × 2.5/63.5)
= 7598.4 Coulomb ;
t = (no. of coulombs/current in
ampere) = [7598.4/2.5] = 3039.36 s/60 × 60
= 0.844 hours.

28. 1 coulomb = 3×10^9 esu. So, electrostatic
charge on Na^+ ions = (96500 coulomb/6.023×10^{23})
= [96500 × 3 × 10^9 e.s.u./6.023×10^{23}] = 4.8×10^{-10} e.s.u.

CHAPTER – 20

3. ΔH = E_a (forward) – E_a (back ward) for a reversible reaction
∴ ΔH = 150 –260 = – 110 kJ mol^-

4. $2\,A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$

	2 A(g)	B(g)	3C(g)	D(g)
Initial :	1 mol	1 mol	0	0
At eqm	1 – (2 × 0.25) = 0.5	1 – 0.25 = 0.75	3 × 0.25 = 0.75	0.25

∴ Eqm. constant, K= $[C]^3\,[D]/[A]^2[B]$
= $(0.75)^3\,(0.25)/(0.5)^2\,(0.75)$

5. k = (2.303/t) log $a/a - x$ and
k = $0.693/t_{1/2}$; $t_{1/2}$ = 69.3 min.
∴ k = 0.693/69.3
= 2.303/t log 100/10. So,
t = 230.3 min.

6. A + 2B → C
1 mol 2 mol 1 mol

8 mol of B need 4 mol of A, so B, is limiting reagent. 2 mol B give 1 mol of C, so 8 mol of B give 1/2 × 8 = 4 mol of C.

7. k = (2.303/t) log $a/a - x$; 4.5×10^{-3}
= (2.303/60) log $1/a - x$
∴ $a - x$ = 0.7634, So, rate after 1 hr (= 60
min) = $k\,(a - x) = 4.5 \times 10^{-3} \times 0.7634$
= 3.4354×10^{-3}

8. Rate = k (A) ; 0.08 = $k\,[A]_{15}$;
0.06 = $k[A]_{25}$; $[A]_{15}/[A]_{25}$
= 0.08/0.06 = 4/3.

For first order reaction,
t = 2.303 log $[A]_{15}/[A]_{25}$. But
t = 25 – 15 = 10 min. So,
10 = 2.303/k log 4/3. So,
k = 0.0288 min^{-}. Hence,
$t_{1/2}$ = 0.693/k = 0.693/0.0288
= 24.06 min.

9. log $k(s^-)$ = 12.14 – (1.41×10^4/T) (given).
Also, log k = log A – E_a/2.303 RT.

Comparing both equations, we have (E_a/2.303 RT)
= 1.41×10^4. So,
E_a = $1.41 \times 10^4 \times 2.303 \times 8.314 \times 10^{-3}$
= 269.97 kJ mol^-
∴ log $k\,(s^-)$ = 12.14 – (1.41×10^4/800)
= – 5.485. So, k = antilog – 5.485
= 3.27×10^{-6}.

10. $t_{1/2}$ = 0.693/0.03465 = 20; concentartion,
C = $C_0(1/2)^n$; $n = t/t_{1/2}$, so, n = 40/20
= 2; C_0 = 2M. Hence, C = 2 × $(1/2)^2$
= 1/2 M; rate of reaction in the
beginning = $k_1 \times C_0$ = 20 × 0.03465 × 2
= 1.386 M min^- ; rate after 40 min
= k_1 C = 0.03465 × 1/2 = 0.017325.

11. Arrhenius parameters are activation energy, E_a and pre-exponential factor, A.
log k_2/k_1 = $E_a/R\,[T_2 - T_1/T_1T_2]$.
E_a = [2.303 $RT_1T_2/T_2 - T_1$] log k_2/k_1
= [2.303 × 8.314 × 10^{-3} × (273 + 20
= 293) × (273 + 45 = 318)/ 318 – 293
= 25] log $1.2 \times 10^{-2}/3.0 \times 10^{-3}$
= 3 × 10^{-3} × 1/2.303 antilog 42.96/8.314 × 10^{-3} × 293
= 3 × 10^{-3} × 1/2.303 antilog 17.43
= 3 × 10^{-3} × (1/2.303) × 2.69 × 10^{17}
= 3.5 × 10^{14}

12. E_a'/T_1 = E_a/T_2 ; (20/273 + 25 = 298)
= $30/T_2$; T_2 = 447 K

CHAPTER – 21

12. ${}^{x}_{y}A \rightarrow {}^{m}_{n}B + a\,{}^{4}_{2}He + b\,{}^{0}_{-1}\beta$;
$x = m + 4a + (b \times 0); a = x - m/4;$
$y = n + 2\,a - b;$
$y = n + (2 \times x - m/4) - b\,;$
$b = n + (x - m/2)\; - y.$

13. ${}^{235}_{92}U \rightarrow {}^{142}_{54}Xe + {}^{90}_{38}Sr + x\,{}^{1}_{0}n$;
235 = 142 + 90 + x ; x = 3

14. Rate of decay of Ra
= λ × no. of nuclei of Ra in 1 g
$$= \frac{0.693}{1600 \times 365 \times 60 \times 60} \times 1.6023$$
10^{23}/226 [∵ $t_{1/2}$ = 0.693/λ] = 3.7×10^{10} dps.
= ($3.7 \times 10^{10}/10^6$) = 3.7×10^4.

15. Ac : $\frac{227}{4}$ = 56 + remainder, 3. So, it belongs to 4n + 3 series.

16. $^{39}_{19}K \rightarrow {}_{+1}^{0}\beta + {}^{39}_{18}A$;
= [At. mass of A/at. no. of A]
= 39/18 = 2.16

17. Amount left = 100 – 93.75 = 6.25 ;
N/N_0 = 6.25/100 = 1/16. So, 1/16
= $(1/2)^n = (1/2)^4$; $n = 4$;
$t_{1/2}$ = 30 min/4 = 7 min. 30 seconds.

18. Radius of $_{40}Ar$ = $(40)^{1/3} \times 1.4 \times 10^{-15}$ *m*
= 5.1×10^{-15} *m*.

19. Packing fraction = $(34.96903 - 35) \times 10^4/35 = -8.848$

20. Half-life is independent of initial concentration of radioactive subtances of first order reaction. So, half-life of 1 g = half-life of 15 g = 25 days.

21. No. of half-lives = 18 days/6 days
= 3. So, amount of radioactivity left
behind = $2 \times (1/2)^3$ = 1/4 millicurie.

CHAPTER – 22

1. $40V_1/V_2 - 17$. Where V_1 = volume of hydroxide taken for each titration and V_2 is volume of HCl used for neutralising V_1 ml of given hydroxide solution.

2. Mol. wt. of hydrated oxalic acid found experimentally {*i.e.* 6.3 × basicity of oxalic acid (2)/Normality of oxalic acid} (–) Mol. wt. of anhydrous oxalic acid *i.e.* 90/18

3. RCOOH + NaOH $\longrightarrow$ RCOONa + H_2O; find normality (N_1) of organic acid ; then Eq. wt. of org. acid = $5.25/N_1$ = *a* (say) ; basicity of org. acid = 126/*a*]

4. $MHCO_3$ + HCl $\longrightarrow$ MCl + CO_2 + H_2O ; find normality (N_1) of $MHCO_3$; Eq. wt. of
$MHCO_3$ = $10/N_1$ = *a* (say) ; Eq. wt. of
$MHCO_3$ = at. wt. of M (*i.e. m*) + 1 + 12 + (3 × 16) or *m* + 61; *a* = *m* + 61 ; ∴ *m* = *a* – 61]

8. Eq. wt. of Mg $(OH)_2$ = (Mol. wt. of Mg $(OH)_2$/no. of replacement OH^- groups) = 24 + 2(16 + 1)/1 = 58

9. Total volume = 1/2 L = 1/2 × 1000
= 500 mL; NaCl $\rightleftharpoons$ $Na^+ + Cl^-$
No. of m. mol of NaCl
= (2.0 m. mol/mL) × 200 mL
= 400 m. mol; Na^+ = 400/500
= 0.8 M.

10. KOH $\rightleftharpoons$ $K^+ + OH^-$. One OH^- gives valency factor
= 1; $H_2SO_4 \rightleftharpoons SO_4^{2-} + 2H^+$ (two H^+
give valency factor = 2). N_1 KOH
= 1 M × valency factor
= 1 × 1 = 1 ; $N_2(H_2SO_4)$
= 2 M × Valency factor
= 2 × 2 = 4 M. Thus:
$N_1 V_1$ (KOH) = N_2V_2 (H_2SO_4); 1 × 20
= 4 × V_2 ; V_2 = 5 mL

11. Molarity = Normality/valence factor; For $H_2SO_4 \rightleftharpoons SO_4^{2-} + 2H^+$ (Valency factor = 2); Molarity = 1.5/2 = 0.75 M

12. Wt. of NaOH = 40 g, wt. of solution
= 100 g; vol of solution
= 100/density, *d*.
Molarity = (40 × 1000 d/40 × 100) = 5.1 ;
d = 0.51 g $(mL)^-$

13. Molarity of H_2O = (wt. of H_2O × 1000)/(mol. wt. of
H_2O × Vol in mL) = [100 g × 1000/18 g mol^- × 1000]
= 55.6.

CHAPTER – 23

1. $Kp = Kc\,(RT)^{\Delta n(g)}$. *Kp* will be equal to
Kc; if Δn(g) = 0.
In reaction (*a*), Δn(g)
= no. of mol of products – no. of
mol of reactants = 2 – 2 = zero. $Kp = Kc\,(RT)^{\circ}$;
Kp = *Kc*. So, correct answer is (*a*).

2. $Kp = Kc\,(RT)^{\Delta n(g)}$; $\Delta n(g) = n_p - n_r$
= (2 + 1) – 2 = 1; 1.8×10^{-2}
= *Kc* (0.0821 L atm K^- mol^- × 500).
So, *Kc* = $1.8 \times 10^{-2}/0.0821 \times 500$
= 4.38×10^{-4}

3. $Kp = Kc\,(RT)^{\Delta n(g)}$;
$\Delta n(g) = n_p - n_r$ = (1 + 0) – 0 = 1;
$Kp = Kc\,(RT)^{\Delta n(g)}$
∴ *Kp* = $1.87\,(0.0821 \times 1073)^1$ = 164.73

4. Molar mass of
CH_3COOH = 12 + (3 × 1) + 12 + 2 (16) + 1
= 60 g mol^-, wt. of CH_3COOH
= 30 g. No. of mol of CH_3COOH
= 30/60 = 0.5. Hence, active mass
= no. of mol / vol in litre
= 0.5 mol/1 L = 0.5 mol L^-.

5. Calculate the percentage dissociation of H_2S (g) if 0.1 mol of H_2S is kept in 0.4 litre vessel at 100 K. For the reaction $2H_2S\,(g) \rightleftharpoons 2H_2(g) + S_2\,(g)$ the value of K_p is 1.0×10^{-6} **(Roorkee, 1994)**

Ans. Vol = 0.4 L.

	$2H_2S$ (g) ⇌	$2H_2$ (g) +	S_2 (g)
(*i*) n mol at start	0.1	0	0
(*ii*) Change by reaction	$-0.1x$	$0.1x$	$\frac{0.1x}{2}$
(*iii*) *n* mol L^- at equilibrium	$\frac{0.1-0.1x}{0.4}$	$\frac{0.1x}{0.4}$	$\frac{0.1x}{2\times 0.4}$
	$= \frac{0.1\,(1-x)}{0.4}$	$= \frac{x}{4}$	$= \frac{x}{8}$
	$= \frac{1-x}{4}$		

$$\therefore \quad K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left(\frac{x}{4}\right)^2 \times \frac{x}{8}}{\left(\frac{1-x}{4}\right)^2} = \frac{\frac{x^2}{16} \times \frac{x}{8}}{\left(\frac{1}{4}\right)^2}$$

[∵ if x is very small, $1 - x \simeq 1$]

$$\therefore \quad K_c = \frac{x^3}{16 \times 8} \times \frac{4 \times 4}{1}$$

$$= \frac{x^3}{8};\ 1.0 \times 10^{-6} = \frac{x^3}{8};$$

$$x^3 = 8 \times 10^{-6}$$

Or $\quad x = (8 \times 10^{-6})^{1/3} = 2 \times 10^{-2}$

∴ % age dissociation

$= 2 \times 10^{-2} \times 100 =$ **2 %** **Ans.**

7. *15 g mol of H_2 reacts with 5.2 g mol of I_2 to give 10 g mol of HI. Calculate the equilibrium constant of the reaction $H_2 + I_2 \rightleftharpoons 2HI$.* **(UP, 1980)**

Ans. Reaction :	H_2	+	I_2	$\rightleftharpoons$	2 HI
(*i*) *n* mol at start	15		5.2		10
(*ii*) Change by reaction	$-x$		$-x$		$2x$
(*iii*) *n* mol at equilibrium	$15 - x$		$5.2 - x$		$2x$

$2x = 10.$ So, $x = 10/2 = 5$

$\therefore \quad [H_2] = 15 - x = 15 - 5 = 10;$

$[I_2] = 5.2 - x = 5.2 - 5.0 = 0.2,\ [HI] = 10$

Applying law of chemical equilibrium, we get :

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{10 \times 10}{10 \times 0.2} = 50$$

$\therefore \quad$ **$K = 50$** **Ans.**

9. If the weight of KI and KI_3 at equilibrium in the reaction $KI + I_2 \rightleftharpoons KI_3$ are 1.326g and 0.105g respectively, then calculate the value of K_C. The number of mol of free I_2 at equilibrium is 0.0025 and the volume of solution is 10^3 cm³. (At. wt. K = 39, I = 127).

Hint and Ans.

$$\begin{array}{lccc} & KI\,(aq) & + \ I_2(s) \rightleftharpoons & KI_3(aq) \\ \text{no. of mol at } t = 0 & \frac{1.326}{166} & & 0 \\ \text{no. of mol at equilibrium} & \frac{1.326}{166} - \frac{0.105}{420} & 0.0025 & \frac{0.105}{420} \\ & = 7.738 \times 10^{-3} & 0.0025 & 2.5 \times 10^{-4} \end{array}$$

$$\therefore \quad K_c = \frac{[KI_3]}{[KI][I_2(s)]} = \frac{2.5 \times 10^{-4}}{7.738 \times 10^{-3}}$$

$=$ **0.0323** **Ans.**

Since KI has fully reacted with I_2 and free I_2 will be in the solid state, so $[I_2]$ is taken as constant.

10. Consider the equilibrium reaction $X + Y \rightleftharpoons P + Q$. X and Y are mixed in a vessel at temperature, T. The concentration of X at $t = 0$ is twice the concentration of Y. After the equilibrium has been reached, the concentration of P was three times the equilibrium concentration of Y. Find the value of K_c.

Hint and Ans.

	X	+	Y	$\rightleftharpoons$	P	+	Q
no. of mol at $t = 0$	$2a$		a		0		0
no. of mol at equilibrium	$(2a - x)$		$a - x$		x		x

But $\quad [X] = 2\,[Y] = 2a$

$$\text{Hence} \quad K_c = \frac{x \times x}{(2a - x)(a - x)} \qquad \text{... (1)}$$

At equilibrium, $\quad [P] = 3\,[Y]$

$$x = 3\,(a - x)\,;\ x = \frac{3a}{4} \qquad \text{...(2)}$$

Putting $\quad x = \dfrac{3a}{4}$ in equation (1),

$K_c = 1.8$ **Ans.**

11. When an equation for a reaction is multiplied by a factor '*n*' , then the new equilibrium constant (k') becomes $k''$and also if the reaction is reversed, the value of equilibrium constant gets inverted. Thus:

$k_2 = 1/k_1^2$. So, (*a*) is correct.

12.

A	+	2B	→	C
1 mol		2 mol		1 mol
5 mol		5 × 2 = 10 mol		5 mol

Since 8 mol of B are given instead of 10 mol, so, B acts as a limiting reagent. Since;

2 mol of B give mol of $C = 1$

∴ 8 mol of B give mol of

$C = 1/2 \times 8 = 4$ mol.

So, the correct answer is (*d*).

CHAPTER – 24

16. Molarity, M $= [0.023 \times 1000/(23 \times 100)]$

$= 0.01$ M; $NaOH \rightleftharpoons Na^+ + OH^-$.

So, $[OH^-] = 0.01 = 10^{-2}$ M;

$p_{OH} = -\log 10^{-2} = -(-2)\log 10$

$= 2.\ p_H + p_{OH} = 14;\ p_H = 14 - 2 = 12.$

17. $p_H = pKa + \log\,[\text{salt}]/[\text{Acid}]$. So, [salt]

$= [0.1 + 0.1/1000 \text{ mL}] = \dfrac{0.2}{1\text{L}} = 0.2$

mol L^-. [Acid] $= 0.1/1000 \text{ mL} = 0.1/1\text{L} = 0.1 \text{ mL}^-$.

Hence, $p_H = pKa + \log 0.2/0.1 = pKa + \log 2.$

18. Ionic product of AgCl

$= 10^{-4} \times 10^{-5} = 10^{-9}$; ionic product

of $Ag_2CrO_4 = 10^{-8} \times 10^{-5} = 10^{-13}$; Ionic product of AgCl > *Ksp*, so AgCl will precipitate. Ionic product of Ag_2CrO_4 < *Ksp* of Ag_2CrO_4. So, it will not precititate.

19. $p_H = -\log\,[H^+]$ (*a*) $p_H = -\log\,(0.1)$

$= 1$ (*b*) $p_H = -\log\,(2 \times 0.05)$

= 1 (*c*) p_H of CH_3COOH is not equal to one because it is a weak acid and does not ionise completely (*d*) Milliequivalent of acid
= 50 × 0.4 = 20; milliequivalent of
NaOH = 50 × 0.2 = 10. So, acid left behind
= 20 – 10 = 10 milliequivalent.

20. $Ksp\ [Mg(OH)_2] = [Mg^{2+}]\ [OH^-]^2;\ 10^{-11}$
$= (0.001)\ [OH^-]^2;\ [OH^-]^2$
$= (10^{-8})^{1/2};\ [OH^-] = 10^{-4}$
$\therefore\quad p_{OH} = -(-4) \log 10 = 4;\ p_H + p_{OH}$
$= 14 \therefore p_H = 14 - 4 = 10.$

21. $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-.$
Let s = solubility of $Mg(OH)_2$ in mol L^-
$k_{sp} = [Mg^{2+}]\ [OH^-]^2 = s \times (2s)^2 = 4s^3;\ s$
$= (K_{sp}/4)^{1/3} = (4 \times 10^{-12}/4)^{1/3}$
$= 10^{-4}$ mol L^-.

22. $p_{OH} = -\log [OH^-] = (-) \log 10^{-3}$
$= -(-3) \log 10 = 3;\ p_H = 14 - p_{OH}$
$= 14 - 3 = 11$

23. $\because [H^+] = C\alpha = 0.1 \times 0.02$
$= 2 \times 10^{-3}$ M
($\because$ degree of dissociation = 2 % = 2/100 = 0.02)
Hence, $[OH^-] = 10^{-14}/2 \times 10^{-3} = 5 \times 10^{-12}$ M

24. $p_H + p_{OH} = 14;\ 12 + p_{OH} = 14;\ p_{OH} = 14 - 12$
$= 2;\ [OH^-] = 10^{-2}$
$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-;$
$\qquad\qquad s \qquad 2s$
$2s = [OH^-] = 10^{-2};\ s = 10^{-2}/2 = 5 \times 10^{-3}$
$Ksp = [Ba^{2+}]\ [OH^-]^2$
$= (5 \times 10^{-3}\ M) \times (10^{-2}\ M)^2$
$= 5 \times 10^{-7}\ M^3.$

25. $p_{OH} = pK_b + \log [B^-]/[HB]$. Since $[B^-]$
= [HB] (given), the $p_{OH} = pK_b$ or p_{OH}
$= -\log 10^{-10} = -(-10) \log 10$
$= 10;\ p_H = 14 - p_{OH} = 14 - 10 = 4.$

CHAPTER – 25

1. An organic compound contains carbon, hydrogen and oxygen. In a Liebig's method, 0.2475g of it was analysed. The increase in the weight of U-tube and the potash bulb at the end of operation was found to be 0.2025g and 0.4950g respectively. Calculate the percentage composition of the compound.

wt. of compound = 0.2475g; wt. of CO_2
= increase in the wt. of potash
bulb = 0.4950g; wt. of H_2O
= increase in the wt. of U-tube
(containing $CaCl_2$) = 0.2025g.

(*i*) *To find % age of carbon.* $\underset{12+(2\times16)=44g}{CO_2} \equiv \underset{12g}{C}$

44g CO_2 contain carbon = 12g

0.495g CO_2 contain carbon $= \dfrac{12}{44} \times 0.495g$

$$\%\text{ age of C} = \frac{\text{wt. of C}}{\text{wt. of substance}} \times 100$$
$$= \frac{12 \times 0.495}{44} \times \frac{100}{0.2475}$$
= 54.54% **Ans.**

(*ii*) *To find percentage of hydrogen.* $\underset{(2\times1)+16=18g}{H_2O} \equiv \underset{2\times1=2g}{2H}$

18g H_2O contain hydrogen
= 2g

0.2025 g H_2O contain hydrogen $= \dfrac{2}{18} \times 0.2025g$

$$\therefore\ \%\text{ age of hydrogen} = \frac{\text{wt. of hydrogen}}{\text{wt. of substance}} \times 100$$
$$= \frac{2 \times 0.2025}{18} \times \frac{100}{0.2475} - 9.09\%$$ **Ans.**

$\therefore$ % age of oxygen = 100−(54.54+9.09)=36.37% **Ans.**

2. 0.2 g of an organic compound on combustion with CuO, gave 30.1 cm^3 of moist nitrogen at 15°C and 730.7 mm pressure. Calculate the percentage of nitrogen in the compound. (Aqueous tension at 15°C = 12.7 mm).
Wt. of organic compound = 0.2 g.
P_1 = 730.7 – 12.7 = 718 mm,
V_1 = 30.1 cm^3, T_1 = 15 + 273
= 288 K; at NTP, P_2 = 760 mm,
V_2 = ?, T_2 = 273 K.

We know, $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$ (Gas equation)

$$\therefore\quad V_2 = \frac{P_1V_1T_2}{T_1 \times P_2}$$
$$= \frac{718\,\text{mm} \times 30.1\,\text{cm}^3 \times 273\text{K}}{288\,\text{K} \times 760\,\text{mm}}$$
= 29.96 mL But, 22400 mL of
N_2 weighs = g. mol. wt. of
N_2 = 28g

26.96 mL of N_2 weighs $= \dfrac{28}{22400} \times 26.96$ g

$$\therefore\quad \%\text{ age of } N_2 = \frac{28 \times 26.96}{22400} \times \frac{100}{0.2} = \mathbf{16.85\%}$$ **Ans.**

3. An organic compound having molecular formula C_4H_9N was analysed by Duma's method for the estimation of nitrogen in this compound. Calculate the volume of nitrogen liberated at N.T.P. from 2.1 g of the substance (at. wt., C = 12, H = 1, N = 14).
Mol. wt. of C_4H_9N = (4 × 12) + (9 × 1) + 14 = 71
Reaction :

$$\underset{1\,\text{mol}=71\,\text{g}}{C_4H_9N} \xrightarrow[\Delta]{CuO} 4CO_2 + \frac{9}{2}H_2O + \underset{\frac{1}{2}\text{mol}=\frac{1}{2}\times 22400=11200\,\text{mL at NTP}}{\frac{1}{2}N_2}$$

71g of C_4H_9N produce N_2 at NTP= 11200 mL

$\therefore$ 2.1g of C_4H_9N would produce N_2 at NTP

$$= \frac{11200}{71} \times 2.1 = \mathbf{331.3\ mL}$$

Volume of N_2 at N.T.P. = **331.3 mL Ans.**

4. 0.45g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralise 20mL of 0.1 M H_2SO_4. Calculate the percentage of nitrogen in the compound.

Wt. of organic compound = 0.45 g.

Volume of 0.1 M H_2SO_4 required to neutralise

NH_3 = 20 mL.

$$\underset{\substack{2\,\text{mol}\\2\,\text{vol}}}{2NH_3} + \underset{\substack{1\,\text{mol}\\1\,\text{vol}}}{H_2SO_4} \rightarrow (NH_4)_2SO_4$$

20 mL of 0.1 M H_2SO_4

$= 2 \times 20$ mL of 0.1 M NH_3

$= 40$ mL of 0.1 MNH_3

$$= \frac{40 \times 0.1\text{M}}{1\text{M}} = 4\,\text{mL of } 1\text{M}\,NH_3$$

But 1000 mL of 1 M NH_3 = 14 g N

$$\therefore 4\text{ mL of 1 M } NH_3 = \frac{14}{1000} \times 4\,\text{gN}$$

$$\therefore \%\text{ age of nitrogen} = \frac{14 \times 4}{1000} \times \frac{100}{0.45} = \mathbf{12.4\%} \qquad \textbf{Ans.}$$

or 1000 mL of 1 M

NH_3 = 14 g N

$$40\text{ mL of 0.1 M } NH_3 = \frac{14}{1000} \times 40 \times 0.1 = 0.056\,\text{g of N.}$$

$$\therefore \%\text{age of nitrogen} = \frac{0.056}{0.45} \times 100 = \mathbf{12.4\%} \qquad \textbf{Ans.}$$

5. An organic compound weighing 0.354g on analysis by Kjeldahl's method gave ammonia which was absorbed in 70mL of M/10 H_2SO_4. The excess of the acid required 40 mL of M/5 NaOH for complete neutralisation. Calculate the per*centage of nitrogen in the compound.*

Volume of H_2SO_4 of molarity M/10 taken = 70 mL.

$$\frac{(M_1V_1)\text{ Residual } H_2SO_4}{(M_2V_2)\text{NaOH}} = \frac{1}{2}$$

$$\left(\because\ \underset{2\,\text{mol}}{2NaOH} + \underset{1\,\text{mol}}{H_2SO_4} \rightarrow Na_2SO_4 + 2H_2O\right)$$

$$\frac{\frac{1}{10} \times V_1}{40 \times \frac{1}{5}} = \frac{1}{2};$$

$$V_1 = 40 \times \frac{1}{5} \times \frac{10}{2} = 40\,\text{mL}$$

$\therefore$ Volume of M/10 acid left unused = 40 mL

Volume of M/10 H_2SO_4 used = 70 – 40 = 30 mL

$\therefore$ 30 mL of $\frac{M}{10}$ $H_2SO_4 \equiv 2 \times 30$ mL of $\frac{M}{10}$

NH_3 = 60 mL of $\frac{M}{10}$ NH_3

$(\because 2\,NH_3 + H_2SO_4 \rightarrow (NH_4)_2\,SO_4)$

But, 1000 mL of 1 M NH_3 contain nitrogen = 14 g

60 mL of $\frac{M}{10}$ H_2SO_4 contain nitrogen

$$= \frac{14}{1000} \times 60 \times \frac{1}{10}\,\text{g}$$

$$\therefore \%\text{ age of nitrogen} = \frac{14 \times 60}{1000} \times \frac{1}{10} \times \frac{100}{0.354}$$

$= \mathbf{23.73\%}$ **Ans.**

6. An organic compound weighing 0.4g was Kjeldahlised and ammonia gas produced was absorbed in 50 mL of M/4 H_2SO_4. The residual acid solution was diluted with distilled water and the volume was made up to 150 mL. The 20mL of this diluted solution required 31mL of 0.05M NaOH for complete neutralisation. Calculate the percentage of nitrogen in the compound.

Wt. of compound = 0.4g.

Volume of $\frac{M}{4}$ H_2SO_4 required to absorb ammonia = 50 mL

(*i*) $\underset{2\,\text{mol}}{2NaOH} + \underset{1\,\text{mol}}{H_2SO_4} \rightarrow Na_2SO_4 + 2H_2O$

$$\frac{M_1V_1\text{ (diluted acid)}}{M_2V_2\text{ (NaOH)}} = \frac{1\,\text{mol}}{2\,\text{mol}};\quad M_1 \times 20 = \frac{0.05 \times 31}{2};$$

$$M_1\text{ (dil. acid)} = \frac{0.05 \times 31}{2 \times 20}$$

(*ii*) To find volume of $\frac{M}{4}$ original H_2SO_4 left used

M_3V_3 (dil. acid) = M_4V_4 (original acid)

$$\frac{0.05 \times 31}{2 \times 20} \times 150 = \frac{1}{4} \times V_4;$$

$$V_4 = \frac{0.05 \times 31 \times 150 \times 4}{2 \times 20} = 23.25\,\text{mL}$$

$\therefore$ Volume of $\frac{M}{4}$ H_2SO_4 used = 50 – 23.25 = 26.75 mL

Now, 26.75 mL of $\frac{M}{4}$ H_2SO_4 = 2 × 26.75 mL of $\frac{M}{4}$ NH_3

$$\left(\because\ \underset{2\,\text{mol}}{2NH_3} + \underset{1\,\text{mol}}{H_2SO_4} \rightarrow (NH_4)_2SO_4\right)$$

But, 1000 mL of 1M NH_3 contain nitrogen = g. at. wt. of N = 14 g

$\therefore$ 2 × 26.75 mL of $\frac{1}{4}$ M NH_3 contain nitrogen

$$= \frac{14}{1000} \times 2 \times 26.75 \times \frac{1}{4}\,\text{g}$$

$$\therefore \%\text{ age of nitrogen} = \frac{14 \times 2 \times 26.75}{1000 \times 4} \times \frac{100}{0.4}$$

= 46.81% **Ans.**

7. In a carius method, 0.24 g of an organic substance was heated with fuming nitric acid and solid $AgNO_3$. As a result, 0.31 g of dry silver chloride was obtained. Calculate the percentage of Cl in the given substance. (at. wt., Ag = 108, Cl = 35.5).

Wt. of organic substance = 0.24 g.

Wt. of AgCl ppt = 0.31 g. We know, $\underset{108+35.5=143.5\,g}{AgCl} \equiv \underset{35.5\,g}{Cl}$

143.5 g AgCl contain

$$Cl = 35.5\ g$$

$$0.31\ g\ AgCl\ contain\ Cl = \frac{35.5}{143.5}\times 0.31\,g$$

$$\%\ age\ of\ Cl = \frac{\text{wt. of Cl}}{\text{wt. of substance}}\times 100$$

$$= \frac{35.5\times 0.31}{143.5}\times\frac{100}{0.24}$$

$$= \mathbf{31.95\%} \qquad \textbf{Ans.}$$

8. In a carius method, 0.31 g of an organic compound yielded 0.296 g of silver bromide. Calculate the percentage of bromine in the organic compound. (At. wt. Ag = 108, Br = 80).

Wt. of organic substance = 0.31 g.

Wt. of AgBr ppt = 0.296 g

We know : $\underset{108+80=188\,g}{AgBr} \equiv \underset{80\,g}{Br}$

188 g AgBr contain Br = 80 g;

$$0.296\ g\ AgBr\ contain\ Br = \frac{80}{188}\times 0.296\,g$$

$$\%\ age\ of\ Br = \frac{\text{wt. of Br}}{\text{wt. of substance}}\times 100$$

$$= \frac{80\times 0.296}{188}\times\frac{100}{0.31} = \mathbf{40.63\%}\ \ \textbf{Ans.}$$

9. An organic compound weighing 0.197 g was heated with fuming nitric acid and solid $AgNO_3$ in a carius tube. As a result, 0.3525 g of dry silver iodide was obtained. Calculate the percentage of iodine in the given compound. (At. wt. Ag = 108, I = 127).

Wt. of organic compound = 0.197 g;

Wt. of Ag I ppt = 0.3525 g

We know : $\underset{108+127=235\,g}{Ag\,I} \equiv \underset{127\,g}{I}$

235 g Ag I contain I = 127 g

$$0.3525\ g\ Ag\ I\ contain\ I = \frac{127}{235}\times 0.3525\,g$$

$$\therefore\quad \%\ age\ of\ I = \frac{\text{wt. of I}}{\text{wt. of substance}}\times 100$$

$$= \frac{127\times 0.3525}{235\times 0.197}\times 100 = \mathbf{96.7\%\,Ans.}$$

CHAPTER – 26

1. (*i*) MF. = n × E.F; C_6H_6 = 6 × CH. So, E.F = CH (*ii*) N_2O_4 has E.F. = NO_2 (*iii*) and

(*iv*) E.F. and M.F. are same as their atoms do not have comman factor for division.

2. Mol. wt. of

Na_2CO_3 = (2 × 23) + 12 + (3 + 16)

= 106 g mol^{-}. % age of Na

= (2 × 23/106) × 100 = 43.39 %.

3.

Element	*% age*	*At. mass*	*Relative no. of atoms*	*Simple ratio*	*whole no. ratio*
C	75	12	75/12 = 6.25	6.25/6.25 = 1	1
H	25	1	25/1 = 25	25/6.25 = 4	4

So, E.F. is CH_4.

4. $M_2O_x \xrightarrow{\text{Reduction}} M$; eq. wt. of

M_2O_x = eq. wt. of metal; wt. of M_2O_x/Eq.

wt. of M_2O_x = wt. of metal/Eq. wt. of metal;

$4/(2 \times 56 + x \times 16/2x) = 2.8/(5.6/x)$

On solving, we get x = 3. So, oxide is M_2O_3.

5. %age of Fe = (0.2014/1.0) × 100

= 20.14. Similarly,

S = 11.53%, O = 23.1%, H_2O = 45.32%

Element	*% age*	*At. mass*	*Relative no. of atoms*	*Simple ratio*	*whole no. ratio*
Fe	20.14	56	20.14/56 = 0.3596	0.3596/0.3596 = 1	1
S	11.53	32	1253/32 = 0.3603	0.3603/0.3596 ≃ 1	1
O	23.1	16	23.1/16 = 1.4438	1.4438/0.3596 = 4	4
H_2O	45.32	18	45.32/18 = 2.518	2.518/0.3596 = 7	7

∴ E.F. = $FeSO_4 \cdot 7H_2O$.

6. wt. of H_2O = 2.875 g – 1.615 g

= 1.260 g. %age of H_2O

= (1.260 × 100)/1.165 = 78%

Use method of question 5 and get $ZnSO_4 \cdot 7H_2O$.

7. %age of Pt = 100 – 42.1 = 57.9%.

Now find M.F. as Pt Cl_4.

9. %age of Cu = (1.89/4) × 100

= 47.25%; %age of Cl

= 2.11 × 100/4 = 52.75%.

Try yourself.

CHAPTER – 28

1. H_2S + H_2O_2 $\longrightarrow$ $2H_2O + S$

$(2 \times 1 + 32)$ $(2 \times 1) + (2 \times 16)$

$= 34$ g $= 34$ g

34 g H_2S react with $H_2O_2 = 34$ g

3.4 g H_2S react with $H_2O_2 = (34/34 \times 3.4 = 3.4$ g)

Volume strength 22.4 means : $22.4 \times 3.035 = 67.98$ gL⁻

67.98 g are present in volume = 1000 mL

3.4 g are present in volume $= 1000 \times 3.4/67.98$

$= 50.00$ mL

2. Volume strength = 5.6 × normality. Thus, 30 = 5.6 × normality

So, normality = 30/5.6 = 5.36. So, the correct answer is (*c*).

3. $CaCl_2$ ≡ $CaCO_3$

$40 + (2 + 35.5)$ $40 + 12 + (3 \times 16)$

$= 111$g $= 100$g

111 ppm $CaCl_2$ = 100 pm $CaCO_3$

30 ppm $CaCl_2$ = 100 × 30/111 = 27.03 ppm

4. Volume strength = 5.6 × normality.

So, 10 = 5.6 × Normality

∴ Normality = 10/56. But Molarity

= Normality × Eq. wt./Mol. wt.

So, Molarity = (10/5.6) × 17/34 = 3.57.

5. 30 mL O_2 is produced from 30 volume

H_2O_2 = 1 mL; 100 mL O_2 is produced from

30 volume H_2O_2 = 1 ×100/30 = 3.33 mL

6. $2\,H_2O_2$ $\rightarrow$ $2H_2 + O_2$

$2[(2 \times 1) + (2 \times 16)]$ 22.4L at NTP

$= 68$ g

68 g H_2O_2 produce

O_2 = 22.4 L; 60.7 g H_2O_2 produce

O_2 = 22.4 × 60.7/68

= 20 L; 1 L O_2 is produced from

H_2O_2 = 1 volume; 20 L O_2 is produced

from H_2O_2 = 20 volume

7. Ca $(HCO_3)_2$ ≡ $CaCO_3$

$40 + 2\,(1 + 12 + 48)$ $40 + 12 + 48$

$= 162$ g $= 100$ g

162 ppm 100 ppm

162 ppm Ca $(HCO_3)_2$ ≡ 100 ppm $CaCO_3$

15 ppm Ca $(HCO_3)_2$ ≡ 100 × 15/162 = 9.26 ppm.

Note. Temporary hardness is only due to $Ca(HCO_3)_2$

8. $MgSO_4$ ≡ $CaCO_3$

$24 + 32 + 64$ $40 + 12 + 48 = 100$ g

$= 120$ g

120 ppm 100 pm

120 ppm $MgSO_4$ ≡ 100 ppm $CaCO_3$

10 ppm $MgSO_4$ ≡ 100 × 10/120 = 8.33 ppm

9. Volume strength = 5.6 × normality = 5.6 × 0.16 = 0.896

10. $$\text{Volume strength} = 5.6 \times \frac{\text{Molarity} \times \text{Mol. wt.}}{\text{Eq. wt. of } H_2O_2}$$

$= 5.6 \times 0.2 \times 34/17 = 2.24$

CHAPTER – 29

1. Polydispersity index = $\overline{M_w}/\overline{M_n}$ = 30,000/20,000 = 1.5

2. 2 mL of 5% NaCl means that 1 mL of 10% NaCl solution. Thus, the milligram of compound which prevents co-agulation = 0.04 g × 1000 mg/1 g = 40 mg.

3. In $Ni(CO)_4$, Ni is in zero oxidation state. $_{28}Ni^0 = (Ar)^{18}$ $3d^{2+2+2+1+1}\,4s^2$. In $Ni(CO)_4$, we have $(Ar)^{18}\,3d^{2+2+2+2+2}\,4s^0\,4p^0$. So, Ni is sp^3 hybridised.

4. $\overline{M_n}$ = 25 × 20,000 + 30 × 30,000 + 45 × 40,000/(25 + 30 + 45) = 32,000.

5. $w_1 = 1$ kg $= 1000$ g; $n_1 = 1000/20{,}000$

$= 0.05$; $w_2 = 500$ g; n_2

$= 500/25000 = 0.02$

$\overline{M_w} = 0.05 \times (20{,}000)^2 + 0.02 \times (25{,}000)^2/(0.05 \times 20{,}000) + (0.02 \times 25{,}000) = 21667$

6. $_{26}Fe = (Ar)^{18}\,3d^6\,4s^2$;

$Fe^{2+} = (Ar)^{18}\,3d^{2+1+1+1+1}\,4s^0$

= 4 unpaired electrons

$= n$; $\mu_{B.M.} = (n\,(n + 2))^{1/2}$

$= [4\,(4 + 2)]^{1/2} = 4.89$ B.M.

7. $\sqrt{35} = \sqrt{n\,(n + 2)}$. So, $n\,(n + 2) = 35$; $n^2 + 2n - 35 = 0$. After factorising, we get $n = 5$.

8. $$[Cr\,(H_2O)_5\,Cl]\,Cl_2 \xrightarrow[AgNO_3]{\text{Excess}} [Cr\,(H_2O)_5\,Cl]^{2+} + 2\,NO_3^- + 2AgCl$$

2 mol Cl^- 2 mol Cl

∴ Milliequivalent of Cl^- in complex = milliequivalent of Cl^- in AgCl

But no. of mol of Cl^- ions in 200 mL of 0.05 M complex = 2 × 200 × 0.05/1000 = 0.02; mass of AgCl (mol. wt. = 108 + 35.5 = 143.5) = 0.02 × 143.5 = 0.287 g

9. See reaction of question no. 8 above. The number of ionisable Cl^- ions = 2. Thus, no. of millimoles = 2 × molarity × volume (in mL) = 2 × 0.01 × 40 = 0.8. But : millimoles = molarity × volume (in mL) ; 0.8 = 0.2 × volume ; volume = 0.8/0.2 = 4 mL

10. Maximum no. of tripetides = $(x)^3 = x^3$.

CHAPTER – 30

1. $K = C_{\text{solute – alcohol}}/C_{\text{solute – water}}$;
I . 0.048/0.174 = 0.276 ; II. 0.3/1.08
= 0.277 III. 0.5/1.8
= 0.277. Since value of K is constant, the data obeys distribution law.

2. $K = C_{\text{solute – water}}/C_{\text{solute – alcohol}}$;
I = 0.174/0.048 = 3.6;
II. 1.08/0.3 = 3.6 ;
III. 1.8/0.5 = 3.6. Value of K is constant = 3.6.

3. C_1 = Csuccinic acid-ether
= 0.15/60 g cm^{-3} = 0.0208 g cm^{-3};
$C_1/C_2 = 2.5 \times 10^{-3}/0.0208 = 0.1202 = K$.

4. C_1 = Csuccenic acid-water/Csuccinic acid-ether = 2.5/120 = 0.0208 g cm^{-3};
C_2 = Csuccinic acid-ether = 0.15/60
= 2.5×10^{-3} g cm^{-3} ;
$C_1/C_2 = 0.0208/2.5 \times 10^{-3} = 8.32$

5. Conc. of compound in 80 mL
H_2O = $1/5 \times 80/1000$
= 0.016. Let compound extracted
in 20 mL ether = a mol. So, conc. of compound in
20 mL ether = $a/20$. At equilibrium, conc. of compound in 80 mL water
= $0.016 - a/80$. Hence,
$K = (a/20)/0.016 - a/80$. Hence,
$a = 0.013$ **Ans.**

6. $K = 6/1 = 6$. Let degree of dissociation
= α; compound present in 30 mL
of S = $(0.4/18) \times 30 = 0.67$ g; Total
compound mixed = 9 g. Compound present in 40 mL
H_2O = 9 – 0.67 = 8.33 g
Conc. of compound in water = $8.33\,(1 - \alpha)/M \times 40$
= C_1 ; conc. of compound in
solvent, $S = 0.67/M \times 30 = C_2$; $C_1/C_2 = K = 6$.
$\therefore$ $6 = [8.33\,(1 - \alpha)/40\,M]/0.67/30M$.
So, α = 0.3565 or 0.3565 × 100 = 35.65%.

7. $C_1(H_2O)/C_2\,(C_6H_6) = K$. I. $5.02/(0.146)^{1/2}$
= 13.1; II. $7.98/(0.362)^{1/2} = 12.9$
III. $10.90/(0.705)^{1/2} = 13.0$. Value of K being constant, benzoic acid exists as a dimer.

Appendix (ii)

ATOMIC NUMBER AND ATOMIC MASS OF ELEMENTS

Element	*Symbol*	*Atomic number*	*Atomic mass*
Actinium	Ac	89	[†](227)
Aluminium	Al	13	25.9815
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	(210)
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.0122
Bismuth	Bi	83	208.980
Bohrium	Bh	107	(262)
Boron	B	5	10.820
Bromine	Br	35	79.904
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9332
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Darmstadtium	Ds	110	(270)
Dubnium	Db	105	(262.114)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(294)
Erbium	Er	68	167.26
Europium	Eu	63	152.00
Fermium	Fm	100	(253)
Fluorine	F	9	19.0
Francium	Fr	87	(223)

Element	*Symbol*	*Atomic number*	*Atomic mass*
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	196.67
Hafnium	Hf	72	178.49
Hassium	Hs	108	(265)
Helium	He	2	4.0026
Holmium	Ho	67	164.930
Hydrogen	H	1	1.00797
Indium	In	49	114.81
Iodine	I	53	126.9044
Iridium	Ir	77	192.2
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	183.91
Lawrencium	Lr	103	(257)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.312
manganese	Mn	25	54.9380
Meitnerium	Mt	109	(268)
Mendelevium	Md	101	(256)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.183
Neptunium	Np	93	(237)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.906
Nitrogen	N	7	14.0067
Nobelium	No	102	(254)
Osmium	Os	76	190.2

[†] Values in parentheses are mass numbers of the most stable or the best known isotopes.

Element	*Symbol*	*Atomic number*	*Atomic mass*
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.9738
Platinum	Pt	78	195.09
Plutonium	Pu	94	(242)
Polonium	Po	84	(210)
Potassium	K	19	39.102
Praseodymium	Pr	59	140.007
Promethium	Pm	61	(147)
Protactinium	Pa	91	(231)
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.905
Rontgenium	Rg	111	(272)
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261.11)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.956
Seaborgium	Sg	106	(263)

Element	*Symbol*	*Atomic number*	*Atomic mass*
Selenium	Se	34	78.96
Silicon	Si	14	28.086
Silver	Ag	47	107.868
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulphur	S	16	32.064
Tantalum	Ta	73	180.948
Technetium	Tc	43	(99)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.924
Thallium	Tl	81	204.37
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.942
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.905
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

Appendix (iii)

ELECTROCHEMICAL SERIES STANDARD ELECTRODE (REDUCTION) POTENTIALS AT 298 K

Electrode		*Half-Cell Reaction* *(Oxidised form + ne^- $\longrightarrow$ Reduced form)*				*E° (Volts)*
$F_2\|F^-$	STRONGEST OXIDIZING AGENT	$F_2(g) + 2e^-$	$\longrightarrow$	$2F^-(aq)$	WEAKST REDUCING AGENT	2.87
$Co^{3+}\|Co^{2+}$		Co^{3+} + e–	$\longrightarrow$	Co^{2+}		1.81
$H_2O_2\|H_2O$		$H_2O_2 + 2H^+ + 2e^-$	$\longrightarrow$	$2H_2O$		1.78
$MnO_2, H^+\|Mn^{2+}$		$MnO_2(s) + 4H^+ + 2e^-$	$\longrightarrow$	$Mn^{2+} + 2H_2O$		1.61
$Au^{3+}\|Au$	↑	$Au^{3+} + 3e^-$	$\longrightarrow$	$Au(s)$	↓	1.50
$MnO_4^-\|Mn^{2+}$		$MnO_4^- + 8H^+ + 5e^-$	$\longrightarrow$	$Mn^{2+} + 4H_2O$		1.49
$Cl_2\|Cl^-$		$Cl_2(g) + 2e^-$	$\longrightarrow$	$2Cl^-$		1.36
$Cr_2O_7^{2-}, H^+\|Cr^{3+}$		$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\longrightarrow$	$2Cr^{3+} + 7H_2O$		1.33
$O_2, H^+\|H_2O$		$O_2 + 4H^+ + 4e^-$	$\longrightarrow$	$2H_2O$		1.23
$Br_2\|Br^-$		$Br_2(l) + 2e^-$	$\longrightarrow$	$2Br^-$		1.09
$NO_3^-, H^+\|NO$		$NO_3^- + 4H^+ + 3e^-$	$\longrightarrow$	$NO(g) + 2H_2O$		0.97
$Hg^{2+}\|Hg_2^{2+}$		$2Hg^{2+} + 2e^-$	$\longrightarrow$	Hg_2^{2+}		0.92
$Hg^{2+}\|Hg$		$Hg^{2+} + 2e^-$	$\longrightarrow$	Hg		0.85
$Ag^+\|Ag$		$Ag^+ + e^-$	$\longrightarrow$	Ag		0.80
$Hg_2^{2+}\|Hg$		$Hg_2^{2+} + 2e^-$	$\longrightarrow$	$2Hg$	INCREASING STRENGTH OF REDUCING AGENT	0.79
$Fe^{3+}\|Fe^{2+}$		$Fe^{3+} + e^-$	$\longrightarrow$	Fe^{2+}		0.77
$MnO_4^-\|MnO_4^{2-}$		$MnO_4^- + e^-$	$\longrightarrow$	MnO_4^{2-}		0.56
$I_2\|I^-$		$I_2 + 2e^-$	$\longrightarrow$	$2I^-$		0.54
$Cu^+\|Cu$		$Cu^+ + e^-$	$\longrightarrow$	Cu		0.52
$Cu^{2+}\|Cu$	INCREASING STRENGTH OF OXIDIZING AGENT	$Cu^{2+} + 2e^-$	$\longrightarrow$	Cu		0.34
$AgCl\|Ag$		$AgCl + e^-$	$\longrightarrow$	$Ag + Cl^-$		0.22
$Cu^{2+}\|Cu$		$Cu^{2+} + e^-$	$\longrightarrow$	Cu^+		0.15
$AgBr\|Ag$		$AgBr + e^-$	$\longrightarrow$	$Ag + Br^-$		0.10
$H^+\|H_2$		$2H^+ + 2e^-$	$\longrightarrow$	$H_2(g)$		0.0
$Fe^{3+}\|Fe$		$Fe^{3+} + 3e^-$	$\longrightarrow$	Fe		–0.04
$Pb^{2+}\|Pb$		$Pb^{2+} + 2e^-$	$\longrightarrow$	Pb		–0.13
$Sn^{2+}\|Sn$		$Sn^{2+} + 2e^-$	$\longrightarrow$	Sn		–0.16
$Ni^{2+}\|Ni$		$Ni^{2+} + 2e^-$	$\longrightarrow$	Ni		–0.25
$Fe^{2+}\|Fe$		$Fe^{2+} + 2e^-$	$\longrightarrow$	Fe		–0.44
$Cr^{3+}\|Cr$		$Cr^{3+} + 3e^-$	$\longrightarrow$	Cr		–0.74
$Zn^{2+}\|Zn$		$Zn^{2+} + 2e^-$	$\longrightarrow$	Zn		–0.76
$Al^{3+}\|Al$		$Al^{3+} + 3e^-$	$\longrightarrow$	Al		–1.66
$Mg^{2+}\|Mg$		$Mg^{2+} + 2e^-$	$\longrightarrow$	Mg		–2.36
$Ce^{3+}\|Ce$		$Ce^{3+} + 3e^-$	$\longrightarrow$	Ce		–2.48
$Na^+\|Na$		$Na^+ + e^-$	$\longrightarrow$	Na		–2.71
$Ca^{2+}\|Ca$		$Ca^{2+} + 2e^-$	$\longrightarrow$	Ca		–2.87
$Ba^{2+}\|Ba$	WEAKEST OXIDIZING AGENT	$Ba^{2+} + 2e^-$	$\longrightarrow$	Ba	STRONGEST REDUCING AGENT	–2.91
$Cs^+\|Cs$		$Cs^+ + e^-$	$\longrightarrow$	Cs		–2.92
$K^+\|K$		$K^+ + e^-$	$\longrightarrow$	K		–2.93
$Li^+\|Li$		$Li^+ + e^-$	$\longrightarrow$	Li		–3.05

Appendix (iv)

DEGREES, MINUTES AND SECONDS TO RADIANS

Units in degrees, minutes or seconds	*Degrees to Radians*	*Minutes to Radians*	*Seconds to Radians*
10	0.174 5329	0.002 9089	0.000 0485
20	0.349 0659	0.005 8178	0.000 0970
30	0.523 5988	0.008 7266	0.000 1454
40	0.698 1317	0.011 6355	0.000 1939
50	0.872 6646	0.014 5444	0.000 2424
60	1.047 1976	0.017 4533	0.000 2909
70	1.221 7305	(0.020 3622)	(0.000 3394)
80	1.396 2634	(0.023 2711)	(0.000 3879)
90	1.570 7963	(0.026 1800)	(0.000 4364)
100	1.745 3293	……………………	……………………
200	3.490 6585	……………………	……………………
300	5.235 9878	……………………	……………………

Appendix (v)

RADIANS TO DEGREES, MINUTES AND SECONDS

Radians	**1.0**	**0.1**	**0.01**	**0.001**	**0.0001**
1	57° 17′ 44.8″	5° 43′ 46.5″	0° 34′ 22.6″	0° 03′ 26,3″	0° 00′ 20.6″
2	114° 35′ 29.6″	11° 27′ 33.0″	1° 08′ 45.3″	0° 06′ 52.5″	0° 00′ 41.3″
3	171° 53′ 14.4″	17° 11′ 19.4″	1° 43′ 07.9″	0° 10′ 18.8″	0° 01′ 01.9″
4	229° 10′ 59.2″	22° 55′ 05.9″	2° 17′ 30.6″	0° 13′ 45.1″	0° 01′ 22.5″
5	286° 28′ 44.0″	28° 38′ 52.4″	2° 51′ 53.2″	0° 17′ 11.3″	0° 01′ 43.1″
6	343° 46′ 28.8″	34° 22′ 38.9″	3° 26′ 15. 9″	0° 20′ 37.6″	0° 02′ 03.8″
7	401° 04′ 13.6″	40° 06′ 25.4″	4° 00′ 38.5″	0° 24′ 03.9″	0° 02′ 24.4″
8	458° 21′ 58.4″	45° 50′ 11.8″	4° 35′ 01.2″	0° 27′ 30.1″	0° 02′ 45.0″
9	515° 39′ 43.3″	51° 33′ 58.3″	5° 09′ 23.8″	0° 30′ 56.4″	0° 03′ 05.6″

Appendix (vi)

NATURAL TRIGONOMETRIC FUNCTIONS

For degrees shown in the left hand column use the column headings at the top. For degrees shown in the right hand column use the column headings at the bottom.

Deg.	Rad	Sin	Cos	Tan	Ctn	Sec	Csc		
0	0.0000	0.0000	1.0000	0.0000	....	1.0000	....	1.5708	90
1	0.0175	0.0175	0.9998	0.0175	57.290	1.0002	57.299	1.5533	89
2	0.0349	0.0349	0.9994	0.0349	28.636	1.0006	28.654	1.5359	88
3	0.0524	0.0523	0.9986	0.0524	19.081	1.0014	19.107	1.5184	87
4	0.0698	0.0698	0.9976	0.0699	14.301	1.0024	14.336	1.5010	86
5	0.0873	0.0872	0.9962	0.0875	11.430	1.0038	11.474	1.4835	85
6	0.1047	0.1045	0.9945	0.1051	9.5144	1.0055	9.5668	1.4661	84
7	0.1222	0.1219	0.9925	0.1228	8.1443	1.0075	8.2055	1.4486	83
8	0.1396	0.1392	0.9903	0.1405	7.1154	1.0098	7.1853	1.4312	82
9	0.1571	0.1564	0.9877	0.1584	6.3138	1.0125	6.3925	1.4137	81
10	0.1745	0.1736	0.9848	0.1763	5.6713	1.0154	5.7588	1.3963	80
11	0.1920	0.1908	0.9816	0.1944	5.1446	1.0187	5.2408	1.3788	79
12	0.2094	0.2079	0.9781	0.2126	4.7046	1.0223	4.8097	1.3614	78
13	0.2269	0.2250	0.9744	0.2309	4.3315	1.0263	4.4454	1.3439	77
14	0.2443	0.2419	0.9703	0.2493	4.0108	1.0306	4.1336	1.3265	76
15	0.2618	0.2588	0.9659	0.2679	3.7321	1.0353	3.8637	1.3090	75
16	0.2793	0.2756	0.9613	0.2867	3.4874	1.0403	3.6280	1.2915	74
17	0.2967	0.2924	0.9563	0.3057	3.2709	1.0457	3.4203	1.2741	73
18	0.3142	0.3090	0.9511	0.3249	3.0777	1.0515	3.2361	1.2566	72
19	0.3316	0.3256	0.9455	0.3443	2.9042	1.0576	3.0716	1.2392	71
20	0.3491	0.3420	0.9397	0.3640	2.7475	1.0642	2.9238	1.2217	70
21	0.3665	0.3584	0.9336	0.3839	2.6051	1.0711	2.7904	1.2043	69
22	0.3840	0.3746	0.9272	0.4040	2.4751	1.0785	2.6695	1.1868	68
23	0.4014	0.3907	0.9205	0.4245	2.3559	1.0864	2.5593	1.1694	67
24	0.4189	0.4067	0.9135	0.4452	2.2460	1.0946	2.4586	1.1519	66
25	0.4363	0.4226	0.9063	0.4663	2.1445	1.1034	2.3662	1.1345	65
26	0.4538	0.4384	0.8988	0.4877	2.0503	1.1126	2.2812	1.1170	64
27	0.4712	0.4540	0.8910	0.5095	1.9626	1.1223	2.2027	1.0996	63
28	0.4887	0.4695	0.8829	0.5317	1.8807	1.1326	2.1301	1. 0821	62
29	0.5061	0.4848	0.8746	0.5543	1.8040	1.1434	2.0627	1.0647	61
30	0.5236	0.5000	0.8660	0.5774	1.7321	1.1547	2.0000	1.0472	60
31	0.5411	0.5150	0.8572	0.6009	1.6643	1.1666	1.9416	1.0297	59
32	0.5585	0.5299	0.8480	0.6249	1.6003	1.1792	1.8871	1.0123	58
33	0.5760	0.5446	0.8387	0.6494	1.5399	1.1924	1.8361	0.9948	57
34	0.5934	0.5592	0.8290	0.6745	1.4826	1.2062	1.7883	0.9774	56
35	0.6109	0.5736	0.8192	0.7002	1.4281	1.2208	1.7434	0.9599	55
36	0.6283	0.5878	0.8090	0.7265	1.3764	1.2361	1.7013	0.9425	54
37	0.6458	0.6018	0.7986	0.7536	1.3270	1.2521	1.6616	0.9250	53
38	0.6632	0.6157	0.7880	0.7813	1.2799	1.2690	1.6243	0.9076	52
39	0.6807	0.6293	0.7771	0.8098	1.2349	1.2868	1.5890	0.8901	51
40	0.6981	0.6428	0.7660	0.8391	1.1918	1.3054	1.5557	0.8727	50
41	0.7156	0.6561	0.7547	0.8693	1.1504	1.3250	1.5243	0.8552	49
42	0.7330	0.6691	0.7431	0.9004	1.1106	1.3456	1.4945	0.8378	48
43	0.7505	0.6820	0.7314	0.9325	1.0724	1.3673	1.4663	0.8203	47
44	0.7679	0.6947	0.7193	0.9657	1.0355	1.3902	1.4396	0.8029	46
45	0.7854	0.7071	0.7071	1.0000	1.0000	1.4142	1.4142	0.7854	45
		Cos	**Sin**	**Ctn**	**Tan**	**Csc**	**Sec**	**Rad**	**Deg.**

Appendix (vii)

LOGARITHMS AND ANTILOGARITHMS TABLES

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

(Contd.)

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9217	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9360	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9916	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3

(Contd.)

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1798	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11

(Contd.)

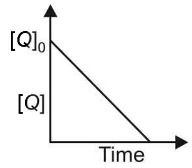
ANTILOGARITHMS

0	1	2	3	4	5	6	7	8	9		Mean Differences								
											1	2	3	4	5	6	7	8	9
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8616	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9793	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

Appendix (viii)

Solutions to Numericals set in JEE-Advanced, 2013

1. *In the reaction, $P + Q \rightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is :*



(a) 2 (b) 3 (c) 0 (d) 1

Sol. Let $t_{50\%} = x$ for P. So, $t_{75\%} = 2x$. Thus, the order with respect to $P = 1$. From the given graph, it is clear that the concentration Q decreases linearly with time. Hence, order with respect to Q is zero. The rate law expression will be :

$$r = k\,[P]^1\,[Q]^0$$

$\therefore$ Order of reaction = 1 + 0 = 1. So, the correct answer is (*d*)

2. *Consider the following complex ions, P, Q and R. P is $[FeF_6]^{-3}$, Q is $[V(H_2O)_6]^{2+}$ and $R = [Fe(H_2O)_6]^{2+}$. The correct order of the complex ions according to their spin-only magnetic moment values (in B.M) is:*

(a) $R < Q < P$ (b) $Q < R < P$ (c) $R < P < Q$ (d) $Q < P < R$

Sol. $P = [Fe\,F_6]^{3-}$. Here, oxidation state of Fe is + 3

$[\because$ Fe + 6 F$^-$ = – 3 ; Fe = – 3 + 6 = + 3$]$

$\therefore {}_{26}Fe^{3+} = (Ar)^{18}\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\ 3d^5$

($\because$ Fe^{3+} has e^-s = 26 – 3 = 23)

Here no. of unpaired electrons = 5

Magnetic moment, $\mu = [n(n + 2)]^{1/2}$ B.M.

$= [5(5 + 2)]^{1/2} = (35)^{1/2} = 5.92$ B.M.

$Q = [V(H_2O)_6]^{2+}$; Oxidation state of $V = +2$

$[\because V + 6H_2O = +2 ; V + 6(0) = +2$; So, $V = +2]$; ${}_{23}V^{2+}$ has e^-s= 23 – 2 = 21.

$\therefore {}_{23}V^{2+} = (Ar)^{18}\ \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\ }\boxed{\ }$ 3*d*

$\therefore$ No. of unpaired electrons = 3

Magnetic moment = $[3(3 + 2)]^{1/2} = [15]^{1/2} = 3.87$ B.M.

$R = [Fe(H_2O)_6]^{2+}$; Oxidation state of Fe = +2

$[\because$ Fe + 6H$_2$O = + 2 ; Fe + (6 × 0) = + 2 ; Fe = + 2$]$; ${}_{26}Fe^{2+}$ has e^-s = 26 – 2 = 24

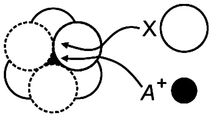
$\therefore {}_{26}Fe^{2+} = (Ar)^{18}\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\ 3d$

No. of unpaired electrons = 4

Magnetic moment = $[4(4 + 2)]^{1/2} = (24)^{1/2} = 4.90$ B.M.

$\therefore$ The correct order of values of spin-only magnetic moment is : $Q < R < P$. So, the correct answer is (*b*)

3. *The arrangement of X^- ions around A^+ ions in solid AX is given in the figure (not shown to scale). If the radius of X^- is 250 pm, the radius of A^+ is :*



(*a*) 104 pm (*b*) 125 pm (*c*) 183 pm (*d*) 57 pm

Sol. From the figure it is clear that the cation A^+ occupies octahedral void. Hence :

$$\frac{r_{A^+}}{r_{X^-}} = 0.414\ ;\ \frac{r_{A^+}}{250\text{ pm}} = 0.414\ \ (\because \text{given } r_{X^-} = 250\text{ pm})$$

$\therefore r_{A^+} = 0.414 \times 250\text{ pm} = 103.5 \simeq 104$ pm. So, the correct answer is (*a*).

4. *The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose (s) at 25°C are –400 kJ/mol, –300 kJ/mol and – 1300 kJ/mol, respectvely. The standard enthalpy of combustion per gram of glucose at 25°C is :*

(*A*) + 2900 KJ (*B*) –2900 KJ (*C*) –16.11 KJ (*D*) +16.11 KJ

Sol. Given reactions are :

(*i*) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -400$ kJ mol$^-$

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -300$ kJ mol$^-$

(*iii*) $6\,C(s) + 6\,H_2(g) + 3\,O_2(g) \rightarrow C_6H_{12}O_6(s)$; $\Delta H = -1300$ kJ mol$^-$

Required equation is :

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$; ΔH = ? ...(A)

(6 × 12) + (12 × 1) + (6 × 16)

= 180 *g* = 1 mol

In order to get equation (*A*), we have :

– Equation (*iii*) + 6 × equation (*i*) + 6 × equation (*ii*).

Thus :

$$\left.\begin{array}{l} -6\,C(s) - 6\,H_2(g) - 3\,O_2(g) \\ +6\,C(s) + 6\,O_2(g) + 6\,H_2(g) \\ +3\,O_2(g) \end{array}\right] \rightarrow \begin{array}{l} -C_6H_{12}O_6(s) + 6CO_2(g) \\ +\,6\,H_2O(l) \end{array}$$

ΔH in kJ is

– (–1300) = + 1300 kJ

+ 6(– 400) = – 2400 kJ

+ 6(–300) = – 1800 kJ

Total = – 2900 kJ

OR

$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O\,(l)$;

$\Delta H = -2900$ kJ

180 *g* of $C_6H_{12}O_6$ produce heat = 2900 kJ

$\therefore$ 1g of $C_6H_{12}O_6$ produce heat = $\frac{2900}{180}$ = 16 kJ

or $\Delta H = -16$ kJ

So, the correct answer is (*c*)

5. *The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M) at 25°C. The Ka of HA is :*

(a) 1×10^{-4} *(b)* 1×10^{-5} *(c)* 1×10^{-6} *(d)* 1×10^{-3}

Sol. (*i*) Rate with respect to weak acid :

$$r_1 = k\,[H^+] \text{ weak acid}$$

(*ii*) Rate with respect to strong acid :

$$r_2 = k\,[H^+] \text{ strong acid}$$

Hence : $\frac{r_1}{r_2} = \frac{k\,[H^+] \text{ weak acid}}{k\,[H^+] \text{ strong acid}} = \frac{1}{100} = 0.01$ M

$\therefore$ $[H^+]$ weak acid = 0.01 M

$$HA \rightleftharpoons H^+ + A^-$$

$$1 - 0.01 \simeq 1M \quad 0.01 \quad M \; 0.01 \; M$$

$$\therefore Ka = \frac{[H^+][A^-]}{[HA]} = \frac{0.01 \times 0.01}{1} = 1 \times 10^{-4}$$

So, the correct answers is (*a*).

6. *The atomic masses of He and Ne are 4 and 20 a.m.u respectively. The value of de Broglie wavelength of He gas at – 73°C is M times that of the de Broglie wavelength of Ne at 727°C. M is.......*

Sol. We know that de Broglie wavelength,

$$\lambda = \frac{h}{(2\,m \times K.E)^{1/2}} \; ; \frac{\lambda_{He}}{\lambda_{Ne}} = \left[\frac{m_{Ne} \times K.E._{Ne}}{m_{He} \times K.E_{Ne}}\right]^{1/2}$$

$$\text{or } \frac{\lambda_{He}}{\lambda_{Ne}} = \left[\frac{m_{Ne} \times T_{Ne}}{m_{He} \times T_{He}}\right]^{1/2} \quad [\because K.E. \propto T]$$

$$= \left[\frac{20 \times (727 + 273)\,K}{4 \times (-73 + 273)\,K}\right]^{1/2} = \left[\frac{20 \times 1000}{4 \times 200}\right]^{1/2} = 5$$

$\therefore$ $\lambda_{He} = 5 \times \lambda_{Ne}$ **Ans.**

7. *The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M Ag NO_3 solution is :*

(a) 1.1×10^{-11} *(b)* 1.1×10^{-10}

(c) 1.1×10^{-12} *(d)* 1.1×10^{-9}

Sol. $Ag_2CrO_4 \rightleftharpoons 2\;Ag^+ + CrO_4^{2-}$ (ionisation)

Solubility $\quad 2S \quad S$

$$Ag\,NO_3 \rightleftharpoons \underset{0.1\,M}{Ag^+} + \underset{0.1\,M}{NO_3^-} \text{ (ionisation)}$$

$\therefore$ $[Ag^+] = 2S + 0.1 \simeq 0.1$ M ; $[CrO_4^{2-}] = S$

$\therefore$ $K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$

or $[CrO_4^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1.1 \times 10^{-12}}{(0.1)^2} = 1.1 \times 10^{-10}$ mol L^-

$\therefore$ S = 1.1×10^{-10} mol L^-. So, the correct answer is (*b*).

8. *The **standard** reduction potential data at 25°C is given below.*

E°(Fe³⁺, Fe²⁺) *= + 0.77 V ; E° (Fe²⁺, Fe) = – 0.44 V*

E°(Cu²⁺, Cu) *= + 0.34 V ; E° (Cu⁺, Cu) = + 0.52 V*

E°[O₂(g) *+ 4H⁺ + 4e⁻ → 2 H₂O] = + 1.23 V*

E° (O₂(g) *+ 2H₂O + 4e⁻ → 4OH⁻ = + 0.40 V*

E°(Cr³⁺, Cr) *= – 0.74 V ; E° (Cr²⁺, Cr) = – 0.91 V*

Match *E° of the redox pair in list 1 with the values given **in list II** and select the correct answer using the code given below the lists.*

	List I		*List II*
P.	*E° (Fe^{3+}, Fe)*	*1.*	*–0.18 V*
Q.	*E° ($4H_2O \rightleftharpoons 4H^+ + 4OH^-$)*	*2.*	*–0.4 V*
R.	*E° ($Cu^{2+} + Cu \rightarrow 2\,Cu^+$)*	*3.*	*–0.04 V*
S.	*E° (Cr^{3+}, Cr)*	*4.*	*–0.83 V*

	P	*Q*	*R*	*S*
(a)	*4*	*1*	*2*	*3*
(b)	*2*	*3*	*4*	*1*
(c)	*1*	*2*	*3*	*4*
(d)	*3*	*4*	*1*	*2*

Sol. **P :**

$$\begin{array}{l} Fe^{3+} + 1e^- \rightarrow Fe^{2+} ; \Delta G_1^\circ = -\,1F \times 0.77 \\ Fe^{2+} + 2e^- \rightarrow Fe \; ; \Delta G_2^\circ = +\,2F \times 0.44 \\ \hline Fe^{3+} + 3e^- \rightarrow Fe \; ; \Delta G_3^\circ = -\,3F \times E^\circ_{Fe^{3+}/Fe} \end{array}$$

But $\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$

$\therefore$ $-3F \times E^\circ_{Fe^{3+}/Fe} = -\,0.77\,F + 0.88\,F$

or $-3\,E^\circ_{Fe^{3+}/Fe} = 0.11\,V$ (After dividing both sides by F)

$\therefore$ $E^\circ_{Fe^{3+}/Fe} = -\frac{0.11}{3}\,V = -\,0.036\,V \simeq 0.04\,V$

Q : $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; E° = – 1.23 V

$$\text{Add : } \begin{array}{l} 2H_2O + O_2 + 4e^- \rightarrow 4OH^- ; E^\circ = +\,0.4\,V \\ \hline 4H_2O \rightarrow 4H^+ + 4OH^- \; ; E^\circ = -\,0.83\,V \end{array}$$

R : $Cu^{2+} + 2e^- \rightarrow Cu$; E° = + 0.34 V

$$\text{Add : } \begin{array}{l} 2Cu \rightarrow Cu^+ + 2e^- \; ; E^\circ = -\,0.52\,V \\ \hline Cu^{2+} + Cu \rightarrow 2\,Cu^+ \; ; E^\circ = -\,0.18\,V \end{array}$$

S :

$$\begin{array}{l} Cr^{3+} + 3e^- \rightarrow Cr \; ; \Delta G_1^\circ = +\,3 \times F \times 0.74 \\ Cr \rightarrow Cr^{2+} + 2e^- \; ; \Delta G_2^\circ = +\,2 \times F \times 0.91 \\ \hline Cr^{3+} + 1e^- \rightarrow Cr^{2+} \; ; E^\circ = -\,0.4\,V \end{array}$$

So, the correct answer is (*d*).

Appendix (ix)

Solutions to Numericals set in NEET, 2013

1. *At 25°C, molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 ohm^{-} cm^{2} mol^{-1} and at infinite dilution, its molar conductance is 238 ohm^{-} cm^{2} mol^{-}. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is :*

   (*a*) 4.008 % (*b*) 40.800% (*c*) 2.080% (*d*) 20.800%

Sol. Molar conductivity at conc., c (λ^{c}_{m}) = 9.54 ohm^{-} cm^{2} mol^{-}. Molar conductivity at infinite dilution,

$$\lambda^{\infty}_{m} = 238 \text{ ohm}^{-}\text{cm}^{2}\text{ mol}^{-}$$

$\therefore$ Degree of dissociation,

$$\alpha = \frac{\lambda^{c}_{m}}{\lambda^{\infty}_{m}} = \frac{9.54 \text{ ohm}^{-}\text{ cm}^{2}\text{ mol}^{-}}{238 \text{ ohm}^{-}\text{ cm}^{2}\text{ mol}^{-}}$$

$$= 0.04008$$

$$= 0.04008 \times 100 = 4.008\%$$

So, the correct answer is (*a*).

2. *A metal has a fcc lattice. The edge length of the unit cell is 404 pm. The density of the metal is 2.72 g cm^{-3}. The molar mass of the metal is : (Avogadro's constant = 6.02 × 10^{23} mol^{-})*

   (a) 27 g mol^{-} (b) 20 g mol^{-} (c) 40 g mol^{-} (d) 30 g mol^{-}

Sol. For fcc structure, $Z = 4$; $N_A = 6.02 \times 10^{23}$ mol^{-} ; $a = 404$ pm = 404×10^{-10} cm ; Molar mass ; M = ?. We know that :

$$d = \frac{Z\,M}{N_A\,a^3} \text{ or } M = \frac{d\,N_A\,a^3}{Z}$$

$$\therefore \frac{2.72 \text{ g cm}^{-3} \times 6.02 \times 10^{23} \text{mol}^{-} \times (404 \times 10^{-10})^3 \text{ cm}^3}{4}$$

$= 26.99 \simeq 27$ *g* mol^{-}

$\therefore$ The correct answer is (*a*).

3. *What is the activation energy for a reaction, if its rate doubles when the temperature is raised from 20°C to 35°C (R = 8.314 JK^{-} mol^{-})*

   (a) 34.7 kJ mol^{-} *(b) 15.1 kJ mol^{-}*
   (c) 342 kJ mol^{-} *(d) 269 kJ mol^{-}*

Sol. Here $k_2 = 2k_1$; $T_1 = 20 + 273 = 293\ K$; $T_2 = 35 + 273 = 308\ K$; $R = 8.314$ JK^{-} mol^{-}. Substituting these values in :

$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right], \text{ we get :}$$

$$\log \frac{2k_1}{k_1} = \frac{Ea}{2.303 \times 8.314 \text{ JK}^{-}\text{ mol}^{-}}\left[\frac{1}{293\ K} - \frac{1}{308\ K}\right]$$

$$\log 2 = \frac{Ea}{2.303 \times 8.314 \text{ J mol}^{-}} \times \frac{15}{293 \times 308}$$

$$0.3010 = \frac{Ea}{2.303 \times 8.314 \text{ J mol}^{-}} \times \frac{15}{293 \times 308}$$

$$\therefore Ea = 0.3010 \times 2.303 \times 8.314 \text{ J mol}^{-} \times \frac{293 \times 308}{15}$$

= 34673 J mol^{-} $\simeq$ 34.7 kJ mol^{-}. So, the correct answer is (*a*)

4. *A magnetic moment of 1.73 BM will be shown by one among the following*

   (a) Ti Cl$_4$ *(b) [Co Cl$_6$]$^{4-}$*
   (c) [Cu (NH$_3$)$_4$]$^{2+}$ *(d) [Ni (CN)$_4$]$^{2-}$*

Sol. Magnetic moment, $\mu = (n\,(n + 2))^{1/2}$ where '*n*' is the number of unpaired electrons.

(*a*) In TiCl$_4$, oxidation state of Ti = + 4 [$\because$ Ti + 4 Cl^{-} = 0; Ti + 4 (–1) = 0. Hence, Ti = + 4]

$_{22}$Ti^{4+} = 22 – 4 = 18 *e*$^{-}$*s*. So, Ti^{4+} = (Ar)^{18}. It has no unpaired electron.

(*b*) [Co Cl$_6$]$^{4-}$. In this complex, oxidation state of cobalt is + 2 [$\because$ Co + 6 (–1) = – 4 ; Co = – 4 + 6 = + 2]

$_{27}$Co^{2+} = 27 – 2 = 25 *e*$^{-}$*s* ; electron configuration

$$= (\text{Ar})^{18}\ \overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$$

So, there are three unpaired electrons. Hence, $\mu = [3\,(3 + 2)]^{1/2} = (15)^{1/2} = 3.87$ BM.

(*c*) (Cu (NH$_3$)$_4$)$^{2+}$, In this complex, oxidation state of Cu = +2 [$\because$ Cu + 4(0 of NH$_3$) = + 2 ; So, Cu = +2]

$_{29}$Cu^{2+} = 29 – 2 = 27 *e*$^{-}$*s* ; electron configuration

$$= (\text{Ar})^{18}\ \overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}}$$

So, there is one unpaired electron or $n = 1$

$\therefore \mu = [n\,(n + 2)]^{1/2} = [1(1 + 2)]^{1/2} = (3)^{1/2} = 1.73$ BM.

(*d*) In [Ni (CN)$_4$]$^{2-}$, oxidation state of Ni = +2. So, $_{28}$Ni^{2+} = 28 – 2 = 26 *e*$^{-}$*s* ; electron configuration is (Ar)^{18} 3$d^{2+2+2+1+1}$ with two unpaired electrons So, $\mu = [2(2 + 2)]^{1/2} = (8)^{1/2} = 2.82$ BM.

So, the correct answer is (*c*)

5. *Number of carbon atoms per unit cell of diamond unit cell is :*

   (a) 6 *(b) 1* *(c) 4* *(d) 8*

Sol. Diamond has zinc blende (ZnS) like structure. Carbon forms ccp (fcc) and also occupies half of the tetrahedral voids.

∴ Total number of carbon atoms per unit cell =

$$\underset{\text{(corners)}}{(8 \times 1/8)} + \underset{\text{(Face centred)}}{\left(6 \times \frac{1}{2}\right)} + \underset{\text{(Tetrahedral voids)}}{4} = 8$$

So, the correct answer is (*d*).

6. *A button cell used in watches functions as follows :*

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightleftharpoons 2\,Ag_{(s)} + Zn^{2+}(aq) + 2OH^-(aq)$$

If half-cell potentials are

(i) $Zn^{2+}(aq) + 2e^- \rightarrow Zn_{(s)}$; $E° = -0.76$ V

(ii) $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2\,Ag(s) + 2\,OH^-(aq)$; $E° = 0.34$ V

The cell potential will be :

(a) 0.84 V (b) 1.34 V (c) 1.10 V (d) 0.42 V

Sol. Required reaction is :

$Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2\,Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$; $E° = ?$

In order to get above equation, we have :

Given equation (*ii*) – given equation (*i*). Thus :

$$\left.\begin{array}{l} Ag_2O(s) + H_2O(l) + 2e^- \\ -Zn^{2+}(ag) - 2e^- \end{array}\right] \begin{array}{l} \rightarrow 2Ag(s) + 2OH^-(ag) - Zn(s); \\ E^\circ = 0.34 - (-0.76) = 1.10\text{ V} \end{array}$$

or $Zn(s) + Ag_2O(s) + H_2O(\underline{l}) \rightarrow 2\,Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$

So, the correct answer is (*c*).

7. *6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of this solution is :*

(a) 0.001 M (b) 0.1 M (c) 0.02 M (d) 0.01 M

Sol. Mol of urea $= \dfrac{6.02 \times 10^{20}}{6.02 \times 10^{23}} = 0.001$

∴ Concentration of solution $= \dfrac{0.001}{100} \times 1000 = 0.01$ M

So, the correct answer is (*d*)

8. *How many grams of concentrated nitric acid Should be used to prepare 250 mL of 2.0 M HNO_3 ? The concentrated acid is 70% HNO_3.*

(a) 70.0 g conc. HNO_3 (b) 54.0 g conc. HNO_3

(c) 45.0 g conc. HNO_3 (d) 90.0 g conc. HNO_3

Sol. We know molarity,

$$M = \frac{\text{Mass of solute} \times 1000}{\text{Mol. Wt. of solute} \times \text{vol in mL}}$$

$$\therefore 2 = \frac{\text{Mass of solute} \times 1000}{63 \times 250} \quad \left[\begin{array}{l} \because \text{Mol.wt. of } HNO_3 = \\ 1+14+3(16) = 63\text{ g mol}^- \end{array}\right.$$

$$\therefore \text{Mass of solute} = \frac{63 \times 250 \times 2}{1000} = 31.5\text{ g}$$

$$\therefore \text{Mass of acid} \times \frac{70}{100} = 31.5$$

$$\text{Or Mass of acid} = \frac{31.5 \times 100}{70} = 45\text{ g}$$

So, the correct answer is (*c*)

9. *The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s^-. Which value is closest to the wave length in nanometer of a quantum of light with frequency of $6 \times 10^{15}\ s^-$?*

(a) 50 (b) 75 (c) 10 (d) 25

Sol. $\lambda = ?$; $C = 3 \times 10^{17}$ nm s^- ; $\nu = 6 \times 10^{15}\ s^-$. We know that :

$$\lambda = \frac{C}{\nu} \quad \therefore \lambda = \frac{3 \times 10^{17}\text{ nm } s^-}{6 \times 10^{15}\ s^-} = 50\text{ nm}.$$

So, the correct answer is (*a*)

10. *A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm. pressure. The oxidation potential of the electrode would be*

(a) 0.118 V (b) 1.18 V (c) 0.059 V (d) 0.59 V

Sol. $$\underset{1\text{ atm}}{H_2(g)} \rightarrow \underset{10^{-10}}{2H^+} + \underset{n=2}{2e^-} \quad \left[\begin{array}{l} \because pH = -\log(H^+) \\ \quad 10 = -\log(H^+) \\ \therefore [H^+] = 10^{-10} \end{array}\right.$$

Using Nernst equation, we have :

$$E_{H_2/H^+} = 0 - \frac{0.059}{2} \log \frac{(10^{-10})^2}{1}$$

$$\text{or } E_{H_2/H^+} = \frac{-0.059}{2} \times 2 \log 10^{-10} = (-)\ (-10) \times 0.059$$

log 10 = 10 × 0.059 × 1 = 0.59 V

So, the correct answer is (*d*).

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