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CHEMICAL ARITHMETIC**1.1 MOLE CONCEPT**

The 'mole' in Latin means heap or mass or pile. A mole is a collection of atoms or molecules or ions whose total weight in grams is equal to the atomic weight of an element or molecular weight of a compound or formula weight of an ion respectively.

Equal number of mole of different elements contains equal number of atoms. Therefore, it is convenient to express amounts of the elements in terms of moles. The concept of mole is based upon **Avogadro's hypothesis**.

Avogadro's hypothesis: Under similar conditions of temperature and pressure, equal volumes of all gases contain equal number of molecules and hence equal number of moles.

e.g., $v \propto n$ if P and T are constant

$$v = kn \text{ at STP} \quad k = \frac{V}{n} = 22.4 \text{ litres/mole}$$

Standard molar volume: Volume of 1 mole of gas at STP is called standard molar volume. Numerically, it is equal to 22.4 litres.

1.1.1 Application of Avogadro vs Hypothesis

- 1. Determination of Atomicity:** Atomicity means number of atoms present in one molecule of an elementary gas, e.g., H₂, N₂ and O₂ have atomicity of 2 while noble gases have atomicity of 1 etc. However, atomicity is not defined for a compound.
- 2. Relationship between molecular mass and vapour density:** The vapour density of any gas is the ratio of densities of the gas and hydrogen under similar conditions of temperature and pressure.

$$VD = \frac{\rho_{\text{gas}}}{\rho_{\text{H}_2}} = \frac{\text{Mol. mass}}{2}$$

Avogadro number: The number of atoms of carbon present in 12 g of C-12 has been found experimentally to be 6.02×10^{23} . This number is also known as Avogadro's number.

1.1.2 Different Ways of Expressing Mole

$$(i) \text{ Number of g mole or g molecule or mole of molecule} = \frac{\text{Weight in gram}}{\text{Molecular weight}}$$

$$= \frac{\text{Number of molecule}}{\text{Avogadro number (N}_A\text{)}}$$

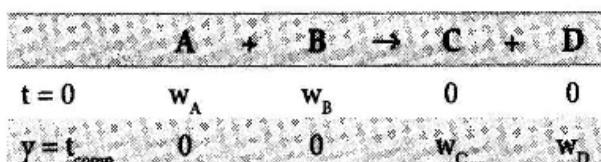
$$(ii) \text{ Number of g mole or g atom or mole of atoms} = \frac{\text{Weight in gram}}{\text{Atomic weight}} = \frac{\text{Number of atoms}}{\text{Avogadro number (N}_A\text{)}}$$

$$(iii) \text{ Number of moles of gases} = \frac{\text{Volume of gas at NTP}}{\text{Standard molar volume}} = \frac{\text{Number of molecules}}{\text{Avogadro number (N}_A\text{)}}$$

1.2 LAWS OF CHEMICAL COMBINATION

Formation of chemical substances occurs through certain rules. These rules are called law of chemical combination.

- (a) **Law of conservation of mass:** This law was given by Lavoisier in 1774. It is also known as law of indestructibility of matter.



from law of conservation of mass, $w_A + w_B = w_C + w_D$

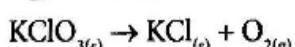
The more generalized form of law of conservation of mass is the principle of atomic conservation.

Principle of atomic conservation (POAC): According to this principle during a chemical change atoms remain conserved and if atoms remain conserve, then mole of atom will also be conserved.

i.e., number of atoms of an element in a reactant = number of atoms of that element in a product.

⇒ Mole of atoms of element in a reactant = mole of atoms of that element in a product.

e.g., if we consider the decomposition of KClO_3 ,



If we want to relate amount of KClO_3 with amount of O_2 , then we apply POAC for O atom

Mole of atom of O in KClO_3 = Mole of atom of O in O_2 .

⇒ $3 \times \text{mole of } \text{KClO}_3 = 2 \times \text{mole of } \text{O}_2$

$$\Rightarrow 3 \times \frac{W_{\text{KClO}_3}}{M_{\text{KClO}_3}} = 2 \times \frac{W_{\text{O}_2}}{M_{\text{O}_2}}$$

Advantages of POAC over other methods:

1. POAC can be applied even in an unbalanced reaction.
2. POAC can be applied in those cases where all reaction steps and their sequence are not given in the problem.

- (b) **Law of definite or constant proportion:** 'A chemical compound always contains the same elements combined together in fixed proportion by mass,' i.e., chemical compound has a fixed

composition and it does not depend on the method of its preparation or the source from which it has been obtained. It is observed that C and O are always combined in the ratio of 3:8, to form CO_2 .

Note:

This law is not followed for isomers.

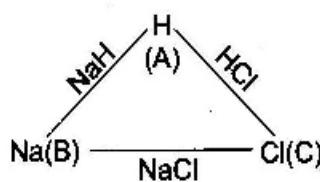
- (c) **Law of multiple proportions:** This law was given by Dalton in 1808. According to this law, 'if two elements combine to form more than one compound, then the different masses of one element which combine with a fixed masses of the other element bear a simple ratio to one another.' N and O combine to form five products as tabulated hereunder.

N	O	Simple ratio
N_2O	28 parts 16 parts	1
N_2O_2	28 parts 32 parts	2
N_2O_3	28 parts 48 parts	3
NO_2	28 parts 64 parts	4
N_2O_5	28 parts 80 parts	5

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

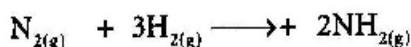
- (d) **Law of reciprocal proportions:** This law was given by Richter in 1794. According to this law, 'when definite mass of an element A combines with two other elements B and C to form a compound, their combining masses are in same proportion or bear a simple ratio to the masses of B and C which combine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

e.g., Na, H and Cl



when Na and Cl combine with 1 part of hydrogen, then the ratio of their weight will be some whole number multiple of ratio in which they combine themselves.

- (e) **Law of gaseous volumes:** 'Gases react with each other in the simple ratio of their volumes and if the product is also in gaseous state, the volume of the product also bears a simple ratio with the volume of gaseous reactants, when all volumes are measured under similar conditions of temperature and pressure.'



Example: 1 volume 3 volume 2 volume

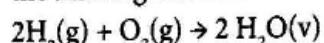
1 : 3 : 2

1.3 TERMS USED IN STOICHIOMETRY

(a) **Limiting reactant:** Reactant that is present in the smallest stoichiometric amount.

or

If two or more reactants are mixed and if the reaction were to proceed according to the chemical equation to completion whether it does or not, the reactant that would first disappear is termed as the limiting reactant.



Moles before reaction	10	7	0
Moles after reaction	0	2	10

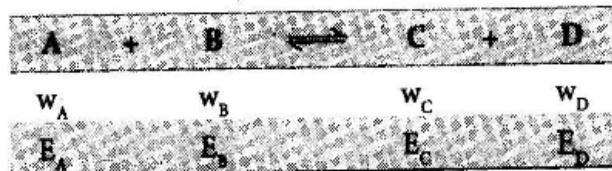
The reaction stops only after consumption of 5 moles of O_2 as no further amount of H_2 is left to react with untreated O_2 . Thus, H_2 is a limiting reagent in this reaction.

(b) **Per cent Yield:** The amount of product obtained by assuming that the reaction goes cleanly and completely is called theoretical yield. The actual yield of a product is the amount present after separating it from other products and reactants and purifying it. It is always less than the theoretical yield.

$$\text{per cent Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

1.4 LAW OF CHEMICAL EQUIVALENCE

During a chemical change, number of gram equivalent of reactants and products involved are always equal.



$$\Rightarrow \text{Number of gram equivalent of a substance} = \frac{\text{Amount of substance in gram}}{\text{Equivalent mass of the substance}}$$

$$\text{From law of chemical equivalence, } \frac{w_A}{E_A} = \frac{w_B}{E_B} = \frac{w_C}{E_C} = \frac{w_D}{E_D}$$

1.5 EQUIVALENT MASS

Equivalent mass or chemical equivalent: The number of parts by mass of the substance which combine or displace directly or indirectly 1.008 parts by mass of hydrogen or 8 parts by mass of oxygen or 35.5 parts by mass of chlorine or 108 parts by mass of silver.

Relation between atomic mass, equivalent mass and valency:

$$\text{Equivalent mass} = \frac{\text{Atomic mass}}{n}; \text{Atomic mass} = \text{equivalent mass} \times \text{valency}$$

$$\text{Equivalent weight of element} = \frac{\text{Atomic weight}}{\text{Valency}} ; \text{Compound} = \frac{\text{Molecular weight}}{\text{Valency factor}}$$

$$\text{Acid} = \frac{\text{Molecular weight}}{\text{Basicity}} ; \text{Base} = \frac{\text{Molecular weight}}{\text{Acidity}} ;$$

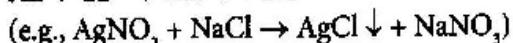
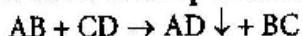
$$\text{Ion} = \frac{\text{Formula weight}}{\text{Charge}} ; \text{Acid salt} = \frac{\text{Molecular weight}}{\text{Replaceable H-atoms}}$$

1.6 METHOD OF DETERMINING EQUIVALENT WEIGHT

- (i) **Hydrogen displacement method:** This method is used for metals which react with an acid to evolve hydrogen gas. Equivalent weight of the metal is the weight of the metal which displaces 1.008 g of H_2 or 11200 c.c. of H_2 at STP.
- (ii) **Oxide formation or reduction of the oxide method:** In this method, a known weight of the metal is converted into its oxide directly or indirectly. Knowing the weight of the metal oxide formed, the weight of oxygen combined can be calculated. Alternatively, a known weight of the metal oxide may be reduced to metal whose weight is determined.
Equivalent of the metal is the weight of the metal which combines with 8 g of oxygen.
- (iii) **Chloride formation method:** A known weight of the element is converted into its chloride directly or indirectly whose weight is determined.
Equivalent weight of element is the weight of the elements which combines with 35.5 g of chlorine.
- (iv) **Metal displacement method:** This method is based upon the fact that a more electropositive metal displaces a less electropositive metal from its salt and one gram equivalent of the metal added displaces one gram equivalent of the metal. Hence,
- $$\frac{\text{Weight of metal added}}{\text{Weight of metal displaced}}$$

$$= \frac{\text{Equivalent weight of metal added}}{\text{Equivalent weight of metal displaced}}$$

- (v) **Double decomposition method:** For a reaction of the type



$$\frac{\text{Weight of AB taken}}{\text{Weight of AD formed}} = \frac{\text{Equivalent weight of AB}}{\text{Equivalent weight of AD}}$$

$$= \frac{\text{Equivalent weight of A} + \text{Equivalent weight of B}}{\text{Equivalent weight of A} + \text{Equivalent weight of D}}$$

Knowing the equivalent weights of any two radicals out of A, B and D, that of the third can be calculated.

1.7 METHODS OF DETERMINING ATOMIC WEIGHT

Dulong and petit's method: According to dulong and petit's law, for solid elements (except Be, B, C and Si),

Atomic weight \times Specific heat = 6.4 approx.

$$\therefore \text{Approx. atomic weight} = \frac{6.4}{\text{Sp. heat}}$$

Exact atomic weight = Equivalent weight \times Valency

$$\therefore \text{Valency} = \frac{\text{Approx. atomic weight}}{\text{Equivalent weight}}$$

Vapour density method: If we consider a chloride of formula XCl_n with vapour density D, then

$$\text{Valency (n)} = \frac{2 \times D}{E_x + 35.5}$$

$$\Rightarrow A_x - n \times E_x$$

1.8 EMPIRICAL AND MOLECULAR FORMULA

Empirical formula: It is the simplest formula of a compound which gives the simplest whole number ratio of the atoms of the various elements present in one molecule of the compound, e.g., empirical formula of glucose ($C_6H_{12}O_6$) is CH_2O .

(i) **Molecular formula:** It is the actual formula of a compound which gives the actual number of atoms of various elements present in one molecule of the compound, e.g., molecular formula of glucose is $C_6H_{12}O_6$.

(ii) **Relationship between empirical formula and molecular formula**

Molecular formula = $n \times$ empirical formula where n is any integer such as 1, 2, 3etc.

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

(iii) **Calculation of empirical formula mass:** It is obtained by adding the atomic masses of the various atoms present in the empirical formula.

(iv) **Calculation of molecular mass**

$$\text{Molecular mass} = 2 \times \text{Vapour density (VD)}$$

Calculation of empirical formula: First calculate percentage of oxygen = 100 – Sum of percentages of all other elements, then EF is calculated through the following steps:

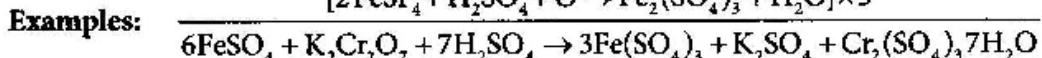
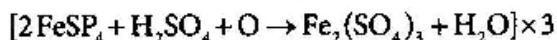
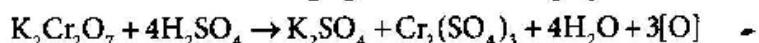
Element	Percentage	Relative number of atoms % age	Simplest atomic ratio	Simplest whole number ratio
		= $\frac{\text{Percentage}}{\text{Atomic mass}}$		

1.9 VOLUMETRIC ANALYSIS

It is a method which involves quantitative determination of the amount of any substance present in a solution through volume measurements. For the analysis, a standard solution is required. The purpose of any titration is to make a non-standard solution standard or for identification of an unknown compound. All volumetric calculations are based upon law of chemical equivalence.

Different types of titrations are possible which are summarized as follows:

- (i) **Redox titrations:** To determine the strength of oxidizing agents or reducing agents by titration with the help of standard solution of reducing agents or oxidizing agents.



Number of g equation of oxidizing agent used = Number of g equation of reducing agent used

- (ii) **Acid-base titrations:** To determine the strength of acid or base with the help of standard solution of base or acid.

Example: $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ and $\text{NaOH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$, etc.

Solution required to bring about the completion of the reaction with a measured volume of the unknown solution.

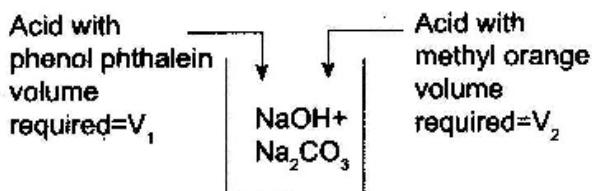
Simple titration $N_1 V_1 = N_2 V_2, \therefore N_1 = \frac{N_2 \times V_2}{V_1}$

Back titration: Back titration is used to find the percentage purity of the impure substance.

The g equation of substance under estimation = $(N_1 V_1 - N_2 V_2)$

Double titration: Mixture of NaOH and Na_2CO_3 in a solution:

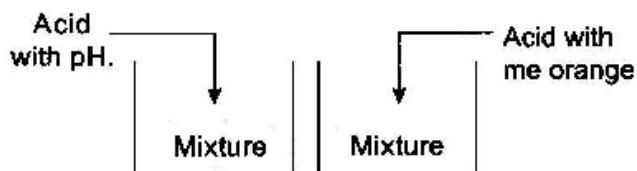
For Same beaker problem



$$NV_1 = \text{Meq of NaOH} + \text{meq of } 1/2$$

$$\text{Na}_2\text{CO}_3, \quad NV_2 = \text{Meq of } 1/2 \text{Na}_2\text{CO}_3,$$

For separate beaker problem



$$NV_2 = \text{Meq of (NaOH + Na}_2\text{CO}_3)$$

1.10 VOLUME STRENGTH OF H_2O_2

Hydrogen peroxide is highly reactive and unstable, and hence, it is packed and sold in the form of its aqueous solutions. The concentration of such solutions is expressed as 'volume strength'.

$$\therefore \text{Molarity of solution, (M)} = \frac{V}{11.2}$$

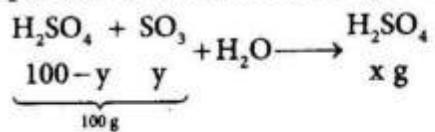
$$\Rightarrow \text{Normality of solution, (N)} = \frac{V}{5.6}$$

$$\Rightarrow \text{Strength of solution} = \frac{17V}{5.6}$$

1.11 PER CENT STRENGTH OF OLEUM

Mixture of H_2SO_4 and SO_3 is called oleum. It is also known as fuming H_2SO_4 . Concentration of oleum sample is expressed in terms of per cent strength of oleum.

X per cent of oleum means 100 g of oleum sample on dissolving in water that produces x g of H_2SO_4 .



$$\Rightarrow X - 100 = y \left(\frac{98}{80} - 1 \right) = y \times \frac{18}{80}$$

$$\Rightarrow y = \frac{(X - 100) \times 80}{18} = \frac{(X - 100) \times 40}{9}$$

$$\therefore \text{per cent of free } SO_3 \text{ in oleum} = \frac{(X - 100) \times 40}{9}$$

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ATOMIC STRUCTURE

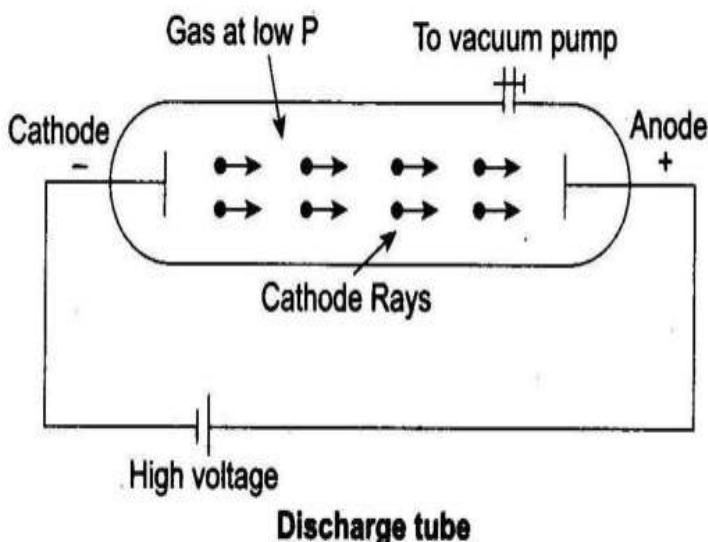
2.1 DALTON'S ATOMIC THEORY

This theory was proposed by John Dalton in 1803. The important features are listed below:

- (i) Atom is the basic unit of all the elements and molecules.
- (ii) Atom is indivisible.
- (iii) It can neither be created nor be destroyed.
- (iv) Atoms of different elements differ in terms of their atomic masses due to which their properties differ from each other.

2.2 DISCOVERY OF CATHODE AND ANODE RAYS

Cathode rays were discovered by William Crookes with the help of a discharge tube, which was invented by Julius Plucker.

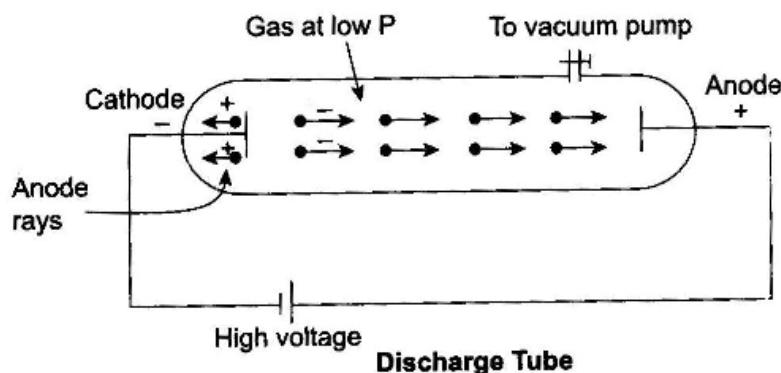


- Colour of light depends upon the nature of a gas in the discharge tube.
- The value of e/m for cathode rays = 1.76×10^8 coulombs/gm.
- The fluorescence was caused due to the bombardment of the walls of the tube by rays emanating from cathode. So, they are called as **cathode rays**.

Properties of cathode rays:

- (i) They travel in a straight line.
- (ii) They have heating effect.
- (iii) They consist of material particles because they can rotate light paddle wheel.
- (iv) They are deflected towards +ve plate when an electric field is applied. It shows that they are -vely charged.
- (v) When a magnetic field is applied perpendicular to the path of cathode rays, they get deflected in the direction expected for -ve particles.
- (vi) They can ionise the gas through which they pass.
- (vii) They can produce X-rays.
- (viii) They can penetrate through thin metal foils.
- (ix) The e/m ratio for the particles in the cathode is independent of the nature of the gas taken in the discharge or the nature of the cathode.

Anode or cathode rays: Anode rays were discovered by Goldstein in 1886. He used a perforated cathode in the discharge tube.



For anode rays, $e/m = 9.58 \times 10^4$ coulombs/g.

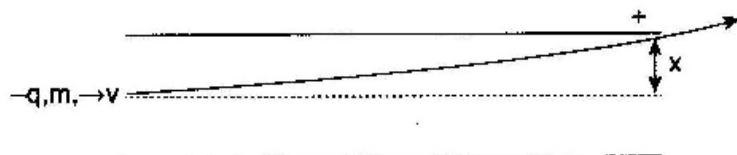
Properties of anode rays:

- (i) They travel in a straight line.
- (ii) They show heating effect.
- (iii) They consist of material particles.
- (iv) In an electric field, they are deflected towards -ve charged plate. Hence, they are positively charged.
- (v) In a magnetic field, they are deflected in the direction expected for +ve particles.
- (vi) They can ionize the gas through which they pass.
- (vii) They can produce X-rays.
- (viii) They can penetrate through thin metal foils.
- (ix) e/m ratio of anode rays is independent from the nature of anode but it depends upon the nature of gas taken in the discharge tube.

2.2.1 Determination of the Ratio of Charge to Mass (e/m) of Electron

When a charge particle of charge (q) and mass (m) moves through an electric field region of intensity (E), then specific charge of particle $\frac{q}{m} = \frac{2 \times v^2}{E \ell^2}$, where v is velocity of particles, x is vertical deflection between

electrical plate and l is length of electrical region with intensity (E) velocity of particle (V) = $\frac{E}{B}$. Where B is magnetic field intensity and specific charge $\left(\frac{q}{m}\right) = \frac{2 \times E}{B^2 l^2}$.

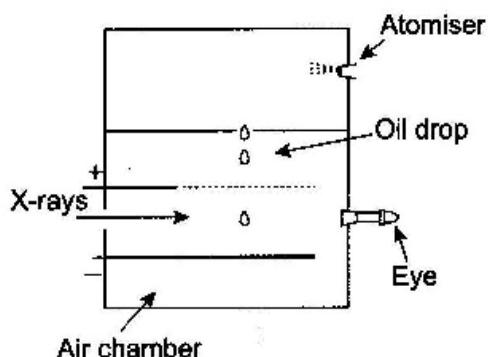


2.3 MILLIKAN'S OIL DROP EXPERIMENT

This experiment was performed by R. E. Millikan in 1909 for the determination of charge on a particle. If a spherical oil drop is moving with constant velocity (v) through air with coefficient of viscosity (η), then

radius of oil droplet $r = \sqrt{\frac{9\eta v}{2(\rho - \rho_0)}}$. However, when thin oil droplet is passed through an electric field,

$$\text{then charge on oil drop } q = \frac{18\pi}{E} \sqrt{\frac{\eta^3 v^3}{2(\rho - \rho_0)g}}$$



$$e = \frac{18\pi}{nE} \sqrt{\frac{\eta^3 v^3}{2(\rho - \rho_0)g}} \quad \because q = ne$$

S. No.	Fundamental Particles	Mass	Charge	Discoverer
1.	Electron (e^-)	$9.1 \times 10^{-31} \text{ kg}$	$-1.6 \times 10^{-19} \text{ C}$	J. J. Thomson
2.	Proton (P)	$1.672 \times 10^{-27} \text{ kg}$	$+1.6 \times 10^{-19} \text{ C}$	Goldstein
3.	Neutron (n)	$1.675 \times 10^{-27} \text{ kg}$	0	Chadwick

Note:

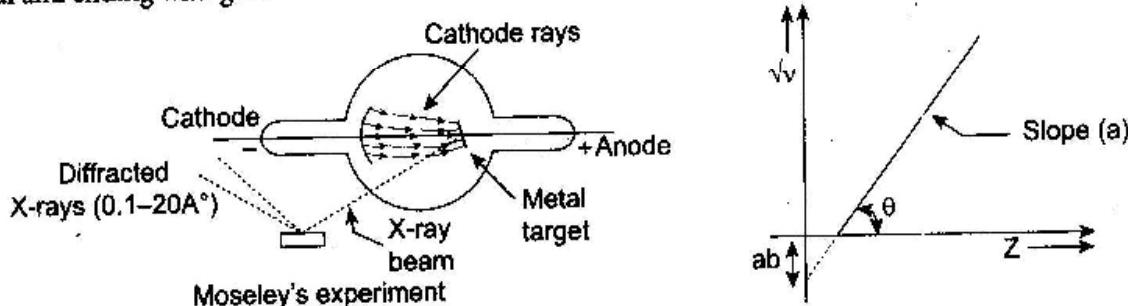
In this experiment X-rays are used to ionize the molecule of air so that electrons freed from air molecule may stick to oil droplets to make droplets electrically sensible.

2.4 DISCOVERY OF ATOMIC NUMBER

He observed that the frequency of a particular spectral line gradually increased with the increase of atomic mass of the element. But it was soon realized that the frequency of the particular spectral line was more precisely related with serial number of the element in the periodic table which he termed as **atomic number (z)**.

$\sqrt{v} = a(z - b)$; where v is frequency of spectral line, a is slope of line in plot between \sqrt{v} and z and ab is intercept made by line on \sqrt{v} axis.

The term **atomic number** was given by H. G. J. Moseley in 1912–1913. To perform this, he considered gas discharge tube in which he took variety of metal targets (anode) starting from aluminium metal and ending with gold.

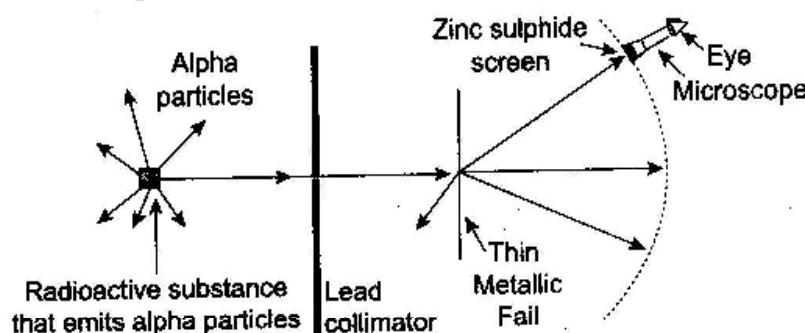


2.5 RUTHERFORD'S ATOMIC MODEL

2.5.1 Rutherford's Experiment (1908–1909)

Observation:

- Most of the α particles passed through the metal foil straight without any deflection.
- Some of them (1 per cent) got deflected at different angles.
- About 1 out of 8000 α particles got deflected at 180° .



2.5.2 Rutherford's Nuclear Atomic Model (1911)

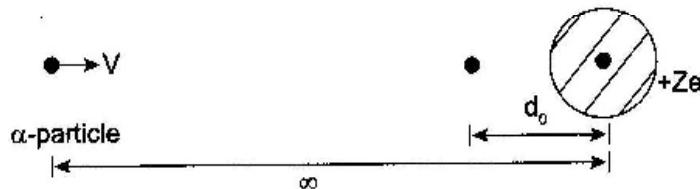
- Most of the inner part of an atom is empty.
- All protons are accumulated at the centre of the atom in a very small volume called **nucleus**. Nucleus is a highly charged body which contains almost entire mass of the atom.
- The electrons are present in the **extra-nuclear space** and are not stationary but move with high velocity under the influence of the centripetal force (CPF). Due to this motion, the centrifugal force (CF) is also developed which according to Rutherford counter balances the CPF. Therefore, electron follows a circular path called **orbit**.

2.5.3 Significances of Rutherford's Atomic Model

2.5.3.1 Calculation of distance of closest approach or effective nuclear radius

Effective nuclear radius or distance of closest approach is defined as that radius of the sphere or spherical region around the nucleus from where the α -particles gets deflected.

$$\therefore \text{Distance of closest approach, } d_0 = \frac{4ze^2}{4\pi\epsilon_0 mv^2} = \frac{ze^2}{\pi\epsilon_0 mv^2} = \frac{1}{4\pi\epsilon_0} \frac{2ze^2}{KE}$$



2.5.3.2 Calculation of radius of nucleus

In an atom, the radius of nucleus is proportional to the cube root of the number of nucleons within it.

$$R = R_0 A^{1/3} \text{ cm; where } R_0 = 1.33 \times 10^{-13} \text{ cm,}$$

A = number of nucleons or mass number, and

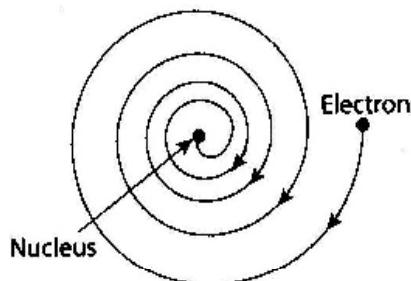
R = radius of the nucleus.

2.5.3.3 Number of α particles striking at an angle θ

$N(\theta) \propto \frac{z^2}{\sin^4(\theta/2)}$; $N(\theta)$ = Number of α -particles per unit area that reach the screen at a scattering angle of θ .

2.5.4 Demerits of Rutherford's Atomic Model

Clark Maxwell's Theory: According to Clark Maxwell, when a moving charged particle is subjected to acceleration, it always loses energy in the form of electromagnetic radiations.



1. In Rutherford's model, an electron moves in circular orbits. Being a charged particle, it should lose energy as it is continuously subjected to acceleration. If this happens, e^- should start moving in smaller orbits and should finally hit the nucleus. This will make an atom unstable. However, an atom is stable suggesting that the Clark Maxwell law is not valid.
2. The spectrum was found to be discontinuous.
3. What is the cause of origin of spectrum?

2.6 QUANTUM THEORY

Quantum theory was given by **Max Planck** in **1901**. He developed this theory to explain the mode of **absorption** and **emission** of energy by black bodies. Later on, Einstein said that this theory is of general applicability. The important points are summarized hereunder.

Note:

Einstein gave another name **photon** for quanta. One photon is equal to $h\nu$.

- (i) The absorption or emission of energy is a discontinuous process.
- (ii) The energy is absorbed or emitted in the form of massless bundles. The energy associated with each bundle is known as one quanta and is given by $E = h\nu$; where h = Planck's constant; ν = frequency of radiation absorbed or emitted.
- (iii) The energy can never be absorbed or emitted in fractions. It is absorbed or emitted either as $h\nu$ or its +ve integral multiples, $E = nh\nu$; (where $n = 1, 2, 3, \dots$).

2.7 BOHR'S ATOMIC MODEL

2.7.1 Bohr's Atomic Model

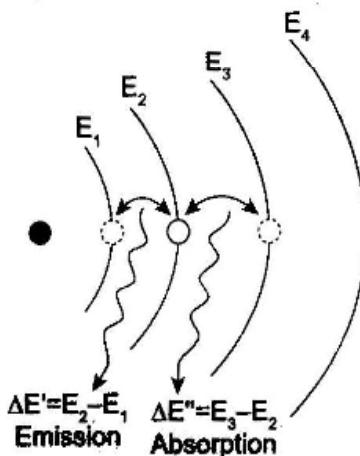
In 1913, Bohr applied quantum theory on atoms and gave the following postulates.

1. Electrons follow a circular path called **orbit**.
2. An atom may contain many circular orbits. Each orbit is associated with **quantized** (i.e., fixed) amount of energy. Some orbits are of special kind and are known as '**stationary states**'. An electron prefers to be in the stationary state because then its energy does not change.
3. The angular momentum of an electron moving in a circular orbit is quantized and is given by

$$mv r = n \frac{h}{2\pi}$$
; where h = Planck constant, n = Principal quantum number.

The angular momentum generates orbital energy of an electron. Since $mv r$ is quantized the orbital energy of an electron will also be quantized (i.e., fixed) and different for different orbits.

4. An electron may change its energy by changing its original circular orbit. This electron may achieve by **absorbing** or **emitting** a quantized amount of energy.



2.7.2 Significances or (Merits) of Bohr's Atomic Model

2.7.2.1 The radius of the orbits or the size of the atom

$$r = \left[\frac{(4\pi\epsilon_0)h^2}{4\pi^2 me^2} \right] \frac{n^2}{z} = \frac{n^2}{z} \cdot x a_0 ; \text{ where } n = 1, 2, 3, \dots$$

where a_0 is Bohr radius having the value 0.529 Å.

2.7.2.2 Velocity of the electron

$$V_n = \left[\frac{2\pi e^2}{4\pi\epsilon_0 h} \right] \frac{z}{n} = V_0 \frac{z}{n} ; \text{ where } V_0 \text{ is Bohr velocity having the value } 2.18 \times 10^6 \text{ m/second.}$$

2.7.2.3 Frequency of revolution

$$f = \left(\frac{me^4}{4\epsilon_0^2 h^3} \right) \frac{z^2}{n^3} = f_0 = \frac{z^2}{n^3} = 6.56 \times 10^{15} \frac{z^2}{n^3} \text{ revolution/second}$$

2.7.2.4 Energy of the electron

Let E_k and E_p be the kinetic energy and the potential energy respectively of the electron in the nth orbit. Then, the total energy is equal to the sum of E_k and E_p ,

$$\text{i.e., } E_n = E_k + E_p = \left[\frac{2\pi^2 me^4}{(4\pi\epsilon_0)^2 h^2} \right] \frac{z^2}{n^2} = -2.18 \times 10^{-18} \left(\frac{z^2}{n^2} \right) \frac{\text{J}}{\text{atom}} = -13.6 \left(\frac{z^2}{n^2} \right) \frac{\text{eV}}{\text{atom}}$$

$$3.827 \times 10^{-20} \text{ cal} = 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$1 \text{ cal} = 4.184 \text{ J} = 2.61 \times 10^{19} \text{ eV}$$

$$1 \text{ ev/atom} = 96.485 \text{ kJ/mol}$$

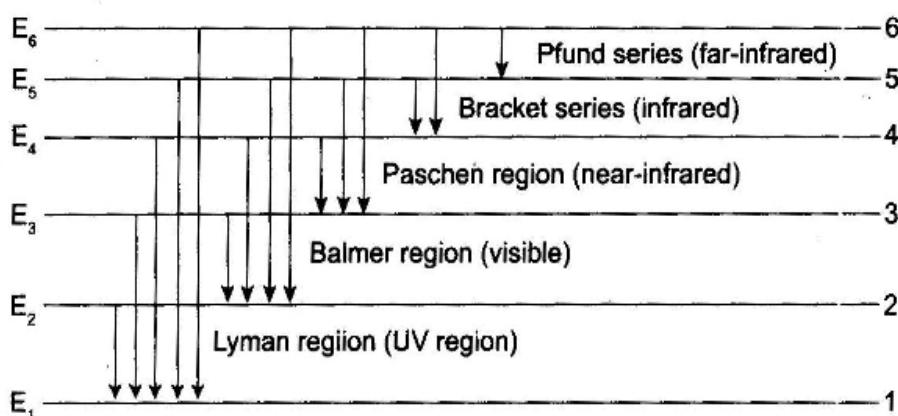
2.8 ELECTRONIC SPECTRUM

- (i) **Emission spectra:** When the light emitted from some source is directly passed on to a prism and then observed on a photographic film after dispersion, the resultant spectrum is called emission spectrum.
- (ii) **Types of emission spectra:** If the source of light emits white light, e.g., sun or bulb, the spectrum consists of seven bands of colours (VIBGYOR) lying continuously and the spectrum is called continuous spectrum. If some volatile salt is placed in a Bunsen flame or electric discharge is passed through a gas at low pressure and the light emitted is resolved through a prism, the spectrum consists of a number of bright lines against a dark background and is called line spectra or atomic spectra.
- (iii) **Absorption spectra:** When white light is passed through the solution or vapours of a chemical substance and then analysed by the spectroscope, some dark lines are observed in the otherwise continuous spectrum at the background. The spectrum thus observed is called absorption spectrum. These dark lines are observed at the same wavelengths where coloured lines were obtained in the emission spectrum of the same substance.

- (iv) Every element gives a characteristic line spectrum differing from line spectra of all other elements. Hence, it is like a finger print of the element.
- (v) In case of atoms, the energies are emitted or absorbed during electronic transition only thereby giving lines in the spectrum. Hence, their spectrum is called line spectrum or atomic spectrum. In case of molecules energies are absorbed for rotational, vibrational and electronic transition thereby producing groups of lines called bands and their spectrum is called band spectrum.

2.8.1 Line Spectrum of Hydrogen

- (i) The line spectrum of hydrogen consists of Lyman, Balmer, Parchen, Bracpet, Pfund and Humphrey series. The first series lies in the ultraviolet region, the second in the visible region, the next two in the infrared region and the last two in the far-infrared region.
- (ii) Rydberg's formula for calculation of wave number of lines in the hydrogen spectrum is R and is called Rydberg constant and its value is 109677 cm^{-1} .



Note:

1. Total number of spectral lines obtained from any energy level n to ground state = $n(n - 1)/2$.
2. Total number of spectral line between any two energy states n_1 and n_2 = $(n_2 - n_1) \frac{(n_2 - n_1 + 1)}{2}$.
3. In any series, first line = transition from $(n_i + 1) \rightarrow n_i$, also called α -line, second line = transition from $(n_i + 2) \rightarrow n_i$, also called β -line and so on. e.g., In Lyman series a-line = $2 \rightarrow 1$; b-line = $3 \rightarrow 1$; g-line = $4 \rightarrow 1$.

Determination of wavelength of transition:

When the electron in the initial stationary orbit of PQN (n_1) jumps to the another stationary orbit of PQN(n_2), then the difference in energy

$$\Delta E = E_{n_2} - E_{n_1} = -\frac{2\pi^2 me^4 z^2}{(4\pi\epsilon_0)^2 h^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\Delta E = \frac{2\pi^2 me^4 z^2}{(4\pi\epsilon_0)^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda} = hc\bar{\nu}; \text{ where } \bar{\nu}, \text{ is wave number.}$$

$$\Rightarrow \bar{\nu} = \frac{1}{\lambda} = R_H z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ is Rydberg's equation.}$$

where $\frac{me}{8 \cdot 2 \cdot h^3 c} = 1.097373 \times 10^7 \text{ m}^{-1}$, is known as **Rydberg's constant**.

Experimental value of $R = 1.096768 \times 10^7 \text{ m}^{-1}$, is known as **Ritz constant**.

Thus, there is very good agreement between the Rydberg and Ritz constants and this also support the postulates of Bohr.

2.8.2 Determination of Ionization Potential (IP) or Ionization Energy (IE)

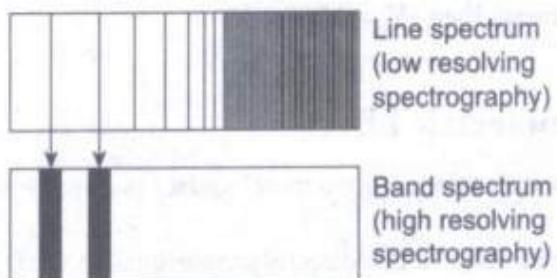
Ionization energy (IE) or **ionization potential** is defined as the amount of energy required to remove the most loosely bound **electron** from an **isolated gaseous atom** of an element. The lesser the ionization energy, the greater is the ease of the formation of a cation.

In an atom there are **infinite number of orbits**. To remove an electron from an atom means to send electron in infinite number of orbits i.e., $n_2 = \infty$.

$$\Rightarrow \text{IP or IE} = E = \frac{R_H h c z^2}{n_1^2} = \frac{2.18 \times 10^{-18} z^2}{n_1^2} \text{ J/atom} = \frac{13.6 z^2}{n_1^2} \text{ eV/atom}$$

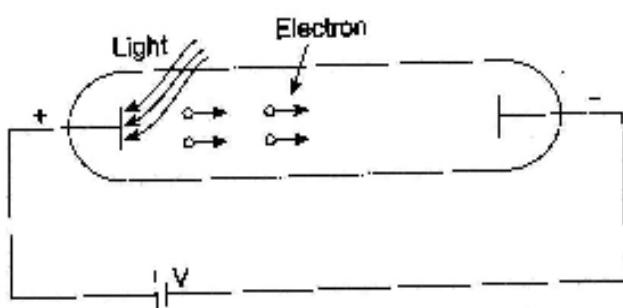
2.9 DEMERITS OF BOHR'S ATOMIC MODEL

- When the energy of electron present in a **multielectron system** was determined with the help of Bohr's postulate, it was found to be not in agreement with experimental values. It means that **Bohr theory is applicable only for the system containing only one electron**. e.g., H, He⁺, Li⁺⁺, etc.
- According to Bohr, an electron follows a fixed path, i.e., a circular orbit. If this is true, then position and velocity both can be determined simultaneously with high degree of accuracy. This is against the **Heisenberg's uncertainty principle**, according to which an electron never follows a fixed path.
- Bohr's theory failed to explain the **directional nature of a covalent bond** and hence the shape of the covalent molecules.
- Bohr's theory failed to explain the **band (or fine) spectrum** of hydrogen.
- Bohr's theory could not explain the splitting of lines of (**Zeeman effect**) and influence of an electric field (**Stark effect**).



2.10 PHOTOELECTRIC EFFECT

Emission of an electron from a metal surface when exposed to light radiations of appropriate wavelength is called **photoelectric effect**. The emitted electrons are called **photoelectrons**.



According to Einstein: Theory of photoelectric effect maximum KE of ejected electron = absorbed energy - work function.

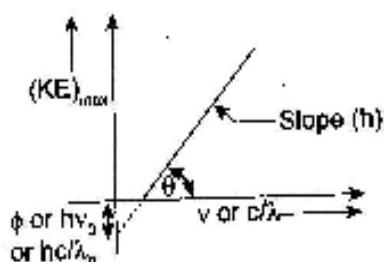
$$\Rightarrow (KE)_{max} = hv - \phi$$

$$KE_{max} = hv - hv_0 - hc \left[\frac{1}{\lambda} - \frac{1}{\lambda_0} \right];$$

where v_0 and λ_0 are threshold frequency and threshold wavelength respectively.

2.10.1 Work Function or Threshold Energy

It may be defined as the minimum amount of energy required to eject electrons from a metal surface. It is represented by ϕ . The energies of electrons liberated by light depend on the frequency of the light.



2.10.2 Stopping Potential

The minimum potential at which the plate photoelectric current becomes zero is called stopping potential. If V_0 is the stopping potential, then $eV_0 = h(v - v_0)$.

2.10.3 Laws of Photoelectric Effect

- Rate of emission of photoelectrons from a metal surface is directly proportional to the intensity of incident light.
- The maximum KE of photoelectrons is directly proportional to the frequency of incident radiation; moreover, it is independent of the intensity of light used.
- There is no time lag between incident of light and emission of photoelectrons.
- For emission of photoelectrons, the frequency of incident light must be equal to or greater than the threshold frequency.
- The greater the work function of a metal, the more the energy is needed for an electron to leave the surface and the higher the critical frequency for photoelectric emission to occur.

Note:

$$\lambda_{\min} = \frac{hc}{eV} = \frac{1.240 \times 10^{-6}}{V} m = \lambda_{\min} \propto \frac{1}{V}$$

The X-rays produced at a given accelerating potential V vary in wavelength but none has wavelength shorter than a certain minimum value λ_{\min} . Increasing V decreases λ_{\min} .

2.11 DUALITY OF MATTER

Photoelectric effect phenomenon can be explained on the basis of particle nature of electron but it is not possible to explain the interference and the diffraction phenomenon which are properties of wave.

In 1905, Einstein suggested that light has dual nature. By 1920, it has been suggested that the matter has dual nature.

In 1924, De Broglie postulated that the electron also has dual nature, i.e., particle as well as wave. He succeeded in deriving an expression which showed relationship between the wave and particle nature of a moving electron.

$$\text{De Broglie wavelength: } \lambda = \frac{h}{mv} = \frac{h}{p} = \frac{h}{\sqrt{2eVm}} = \frac{h}{\sqrt{2mKE}}$$

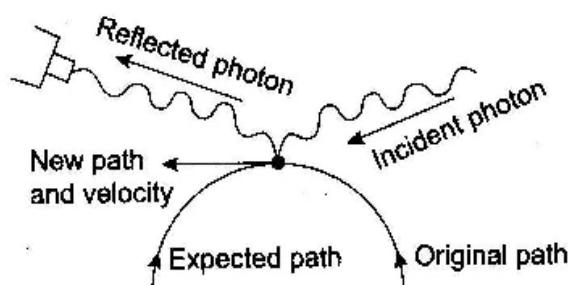
2.12 HEISENBERG'S UNCERTAINTY PRINCIPLE

The position and velocity of a big particle can be determined simultaneously with high degree of accuracy. However, this is not true for the tiny particles like electron, proton, neutron, etc. This principle states that:

If we try to determine the position of a tiny particle accurately then there will be some uncertainty associated with the determination of its velocity and if the velocity is known accurately then its position will have some uncertainty.

According to principle of optics, the accuracy with which the position of a particle can be measured depends upon the wavelength of light used. The uncertainty in position is $\pm \lambda$. The shorter the wavelength means higher the frequency and higher the energy. This high-energy photon on striking the electron changes its speed as well as direction.

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \text{ and } \Delta x \times \Delta v \geq \frac{h}{4\pi m}$$



Orbital: The small volume around the nucleus where the probability of finding an electron is maximum, i.e., 90 to 95 per cent is known as orbital.

2.13 WAVE MECHANICAL MODEL

The wave mechanical model is based on quantum mechanics which is developed independently by Schrödinger and Heisenberg. In quantum mechanics, duality of matter is taken into consideration.

Important features of wave mechanical model:

- (i) The exact position and velocity of e^- cannot be determined simultaneously with high degree of accuracy. However, electron is present in a 3-dimensional space around the nucleus where probability of finding the e^- is maximum. This space is called an orbital.
- (ii) Each orbital possess an unique orbital wave function value, these values; are outcome of solution of Schrödinger wave equation.
- (iii) Many orbital wave functions are possible for an e^- , therefore there exist many quantized energy orbitals.
- (iv) The wave function ψ is simply a function of coordinate of e^- and has no physical significance as such. However, ψ^2 gives us the probability of finding e^- at a point inside an atom.
- (v) By finding ψ^2 at different points around the nucleus in an atom we can predict the region of space around the nucleus called orbital.
- (vi) All the information about an electron is stored in its orbital wave function value and Schrödinger wave equation makes it possible to extract this information out of ψ .

Schrödinger wave equation: For an e^- moving in 3-dimensional space around the nucleus.

$H\psi = E\psi$; where H is a mathematical operator called Hamiltonian operator.

$H = T + V$; where T is kinetic energy operator and V is potential energy operator.

$$T = -\frac{\hbar^2}{2m} \nabla^2 \text{ where } \nabla^2 = \text{Laplacian operator}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0$$

2.14 SHAPE OF ORBITAL

The position and energy of an electron may be determined with the help of certain numbers called **quantum numbers**. An electron is said to be identified or described or characterized when its position and energy is known. For the complete description of an electron, we need help of the following four quantum numbers.

- (i) Principal quantum number (PQN) (**Bohr**).
- (ii) Azimuthal quantum number or subsidiary quantum number or secondary quantum number or angular momentum quantum number or orbital quantum number (**Sommerfield**).
- (iii) Magnetic quantum number (MQN) (**Lande**).
- (iv) Spin quantum number (**Uhlenbeck and Goudsmith**).

Principal quantum number represents the main shell, **azimuthal quantum number** represents the number of subshells present in the main shell, **magnetic quantum number** represents the number of orbitals present in the subshell and **spin quantum number** tells the direction of spin of the electron, i.e., clockwise or anticlockwise. Further, **principal quantum number** tells about the size, **azimuthal quantum number** about the shape and **magnetic quantum about the orientation of the orbital**. Also, principal quantum number tells about the energy of the electron, whereas azimuthal quantum number tells about the angular momentum of the electron.

The values of quantum number are related to each other as follows:

$$n = 1, 2, 3, 4, \dots$$

For a given value of n , $l = 0$ to $n - 1$

For a given value of l , $m = -l$ to $+l$ including '0'

For a given value of m , $s = +1/2, -1/2$

Designation of the subshells:

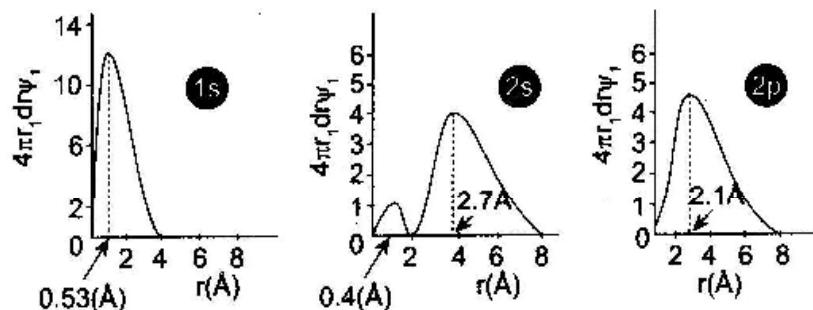
Value of l	Sub-shell
0	s
1	p
2	d
3	f

Thus, number of subshells in the n th shell = n

Number of orbitals in a subshell = $2l + 1$

Number of orbitals in n th shell = n^2

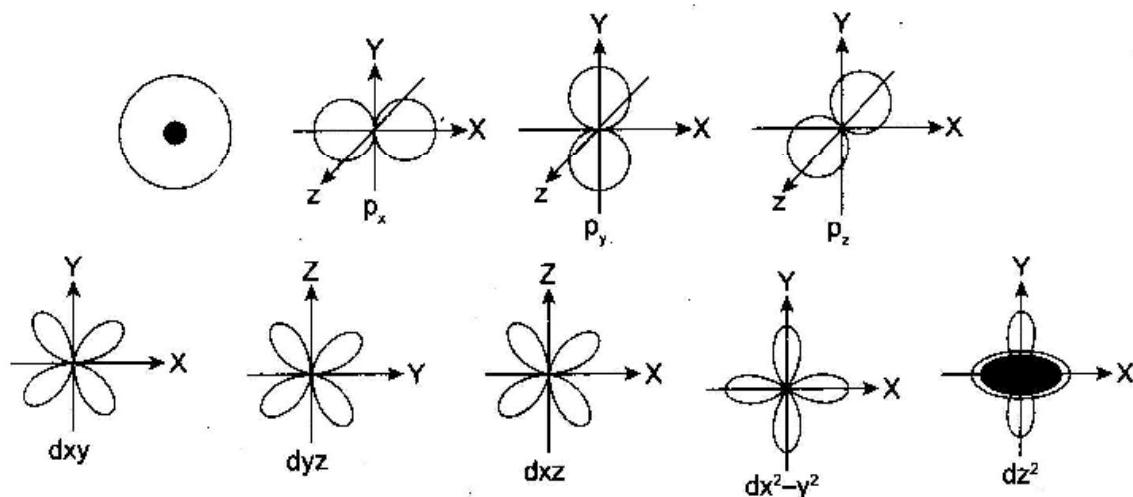
Radial probability distribution curves: Radial probability is $R = 4\pi r^2 dr\psi^2$. The plots of R versus distance from nucleus are as follows:



In the plots of radial probability versus distance from the nucleus, number of peaks i.e., region of maximum probability = $n - 1$.

For example, 2s has two peaks, 3s will have 3 peaks, 2p has one peak, 3p has two peaks and so on.

Shapes of s, p and d-orbitals



Spherical (radial) nodes and nodal planes

A spherical surface within an orbital on which the probability of finding the electron is zero is called a **spherical or radial node**. The number of spherical or radial nodes in an orbital = ($n - l - 1$).

For example, 1s orbital ($n = 1, l = 0$) has no spherical node

2s orbital ($n = 2, l = 0$) has one spherical node

2p orbital ($n = 2, l = 1$) has no spherical node

3p orbital ($n = 3, l = 1$) has one spherical node and so on.

A plane passing through the nucleus on which the probability of finding the electron is zero is called a **nodal plane**. The number of nodal planes in an orbital = l for example

s orbital ($l = 0$) no nodal plane

p orbital ($l = 1$) one nodal plane

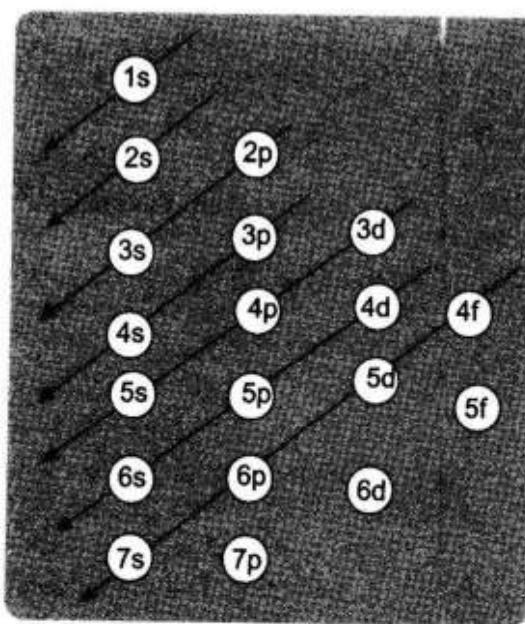
d orbital ($l = 2$) two nodal planes and so on.

Pauli's exclusion principle: Pauli exclusion principle states that 'No two electrons in an atom can have the same set of four quantum number' or 'an orbital can have maximum two electrons and they must have opposite spin.'

Aufbau principle

Aufbau principle states that 'in the ground state of the atom, the orbitals are filled in order of their increasing energies, starting with the orbital of lowest energy.' The word aufbau is a German word which means building up. The increasing order of energy and hence that of filling of orbitals is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5p, 6s, 4f, 5d, 6p...

This can be remembered from the adjoining diagram in which starting from the top, the direction of arrows give the order of filling.



Note:

In case of H-atom, the energies of atomic orbitals increase as follows:

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$ and so on.

i.e., subshells of the same main shell have equal energies.

The order of energies and hence that of filling of orbitals can be calculated by $(n + l)$ rule which states as follows:

- (i) Orbitals are filled in order of increasing $(n + l)$ values.
- (ii) If two orbitals have the same $(n + l)$ values, the orbital with lower value of n is filled first.

2.14.1 Hund's Rule

Hund's rule of maximum multiplicity states that 'pairing of electrons in the orbitals belonging to the same sub-shell (degenerate orbitals) does not take place till each orbital of that sub-shell has got one electron each, i.e., is singly occupied. Orbitals must have their electron with spin in the same direction (so that repulsion is minimum and stability is maximum).

Half-filled and fully-filled electronic configurations are more stable because of (i) greater symmetry and (ii) greater exchange energy.

2.15 ELECTRONIC CONFIGURATION OF ION

First write the electronic configuration of a neutral atom. For cation, remove the number of electrons equal to the units of +ve charge on the cation, starting from the outermost shell. For anion, add number of electrons equal to the units of -ve charge on the anion.

2.16 DIAMAGNETIC AND PARAMAGNETIC SUBSTANCES

2.16.1 Diamagnetic Substances $\downarrow\downarrow$ (Paired Spin)

Substances having all electrons paired are known as diamagnetic substances and their magnetism as diamagnetism.

The magnitude of diamagnetism is very small because of cancellation of magnetic moment due to spin motion and also due to quenching of orbital motion (nullified due to other atom's orbitals molecule).

2.16.2 Paramagnetic Substances \uparrow (Parallel Spin)

All substances having one or more unpaired electrons are called paramagnetic substances and their magnetism paramagnetism. The magnitude of paramagnetism is much higher than diamagnetism because of full contribution of spin motion of the electron.

The magnitude of paramagnetism increases with increase of number of unpaired electrons. In general, paramagnetic substances are more reactive than diamagnetic substances.

Magnetic moment of paramagnetic substances

$$\mu = \sqrt{N(N+2)} \text{ BM} \quad (1 \text{ BM} = 9.27 \times 10^{-24} \text{ J/T}) ; \text{ where } N \text{ is the number of unpaired electrons.}$$

- (i) All paramagnetic substances except hydrogen also have some diamagnetism but converse is not true.
- (ii) Ion with unpaired electron in d or f orbitals will be coloured. For example Cu^+ with electronic configuration $[\text{Ar}] 3d^{10}$ is colourless and Cu^{2+} with electronic configuration $[\text{Ar}] 3d^9$ (one unpaired electron in 3d) is coloured (blue).

GASEOUS STATE

3.1 STATES OF MATTER

Matter exists in three states, viz. solid, liquid and gas. All the three phases can exist together at a particular temperature and pressure, e.g., ice (s) \rightleftharpoons water (l) \rightleftharpoons water (g) vapour can exist together at 0.01°C and 4.58 mm pressure.

S. No.	Solids	Liquids	Gases
1.	Molecules are closely packed	Molecules are less closely packed	Molecules are sufficiently apart from one another
2.	Mutual forces of attraction are the strongest	Mutual forces of attraction are weaker than those in solids	Mutual forces of attraction are almost negligible
3.	The density of solids is high	The density of liquids is lower than that of solids but is much higher than gases	Gases generally have low densities
4.	The positions of molecules in the crystal lattice are fixed and hence solids do not have translatory or rotatory motion but only possess vibratory motion	Molecules of a liquid have greater freedom of movement. They have some translatory and rotatory motions in addition to the vibratory motion	Molecules of a gas have large rotatory, vibratory and translatory motions
5.	Molecules of a solid possess lowest energy	Molecules of a liquid have higher energies than that of solids	Gas molecules are most energetic
6.	Solids have both a definite shape and a definite volume	Liquids do not have definite shape but have definite volumes	Gases neither have definite shape nor definite volumes
7.	Solids possess least compressibility and thermal expansion	Liquids have slightly higher compressibility and thermal expansion than those of solids	Gases possess high compressibility and thermal expansion

3.2 CHARACTERISTIC PROPERTIES OF GASES

There are four parameters that can describe the characteristics of a gas completely.

- (i) Amount of gas
- (ii) Temperature (T)
- (iii) Pressure (P)
- (iv) Volume (V)

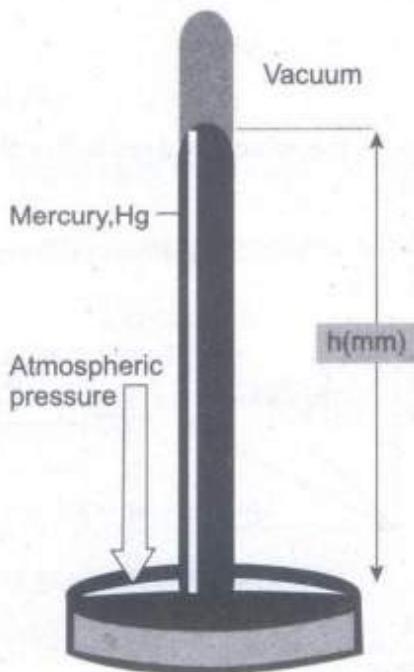
3.2.1 Unit of Volume

$$1 \text{ litre (L)} = 10^3 \text{ cm}^3 = 1 \text{ dm}^3 = 10^3 \text{ ml}$$

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 = 10^3 \text{ L}$$

3.2.2 Pressure

Atmospheric pressure is measured with a barometer from the height of the mercury column that stands in a tube filled with mercury and inverted into a trough containing mercury. $P = \rho gh$
 ρ = density g = gravitational constant h = height of mercury in column



Pressure of a gas is measured with a manometer and is equal to the difference in levels of Hg in the two limbs with a closed limb manometer and is equal to atm pressure minus difference in levels in case of an open limb manometer.

$$\begin{aligned} 1 \text{ atm} &= 76 \text{ cm of Hg} = 760 \text{ mm of Hg} = 760 \text{ torr} \\ &= 101,325 \text{ Pa or } \text{Nm}^{-2} \\ &= 101.325 \text{ kPa} \end{aligned}$$

Note:

Mercury is filled in barometer because it is the heaviest liquid and its thermal expansivity is minimum.

3.3 GAS LAWS

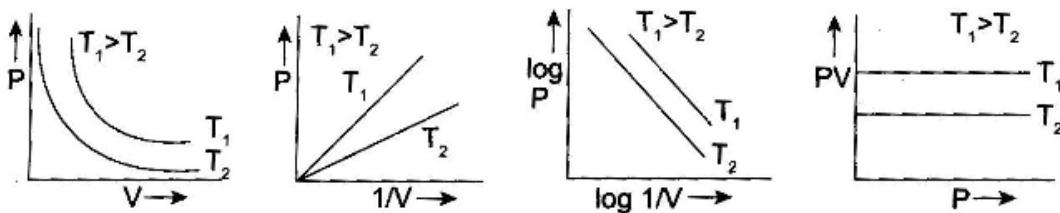
3.3.1 Boyle's Law

Robert Boyle in 1662 gave a relationship between volume and the pressure of gas which is known as Boyle's law. According to this law, 'At constant temperature, the pressure of a given mass of a gas is inversely proportional to the volume of a gas.' It means that if we increase the pressure, volume will decrease and vice versa. $P \propto 1/V$ (at constant temperature);

$$\therefore PV = \text{Constant} \quad \dots \dots \dots (i)$$

Equation (i) shows that PV is a constant. It means that if we increase pressure, the volume will decrease in the same proportion and ultimately their product will remain constant.

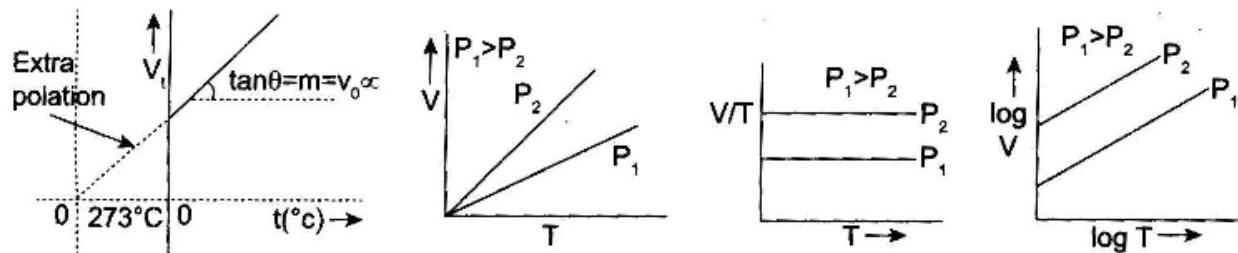
$$P_1 V_1 = P_2 V_2$$



3.3.2 Charle's Law

At constant pressure and number of mole, the volume of a gas is directly proportional to the absolute temperature, $V \propto T$ (n and P are constant)

$$\Rightarrow V/T = \text{constant i.e. } \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3} = \dots \text{ where } T \text{ is temperature in Kelvin.}$$



$$\Rightarrow V_t = V_0 (1 + \alpha t) \text{ where } \alpha = \frac{1}{273.15}$$

Changing origin to -273° C , we get a straight line passing through origin. Then at that scale temperature T in K will be $T = 273.15 + t$.

3.4 GAY LUSSAC'S LAW OR AMONTON'S LAW

Pressure of a given mass of a gas is directly proportional to its absolute temperature if its volume is kept constant.

$$\therefore \frac{P_1}{T_1} = \frac{P_2}{T_2} = \frac{P_3}{T_3} = \dots \quad (\text{At constant } v \text{ and } n)$$

3.4.1 Avogadro's Law

It states that under similar conditions of temperature and pressure equal volume of different gases contains equal number of molecules and hence equal number of moles.

$$\therefore V \propto n \text{ (at constant P and T)}$$

Where n is the number of moles of gases

$$\therefore V = k \times n \quad (k \text{ is constant})$$

$$V/n = k \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2} = \frac{V_3}{n_3} = \dots$$

Alternative form of Avogadro's law, $P/M = \text{constant}$ if P and T are constants.

3.4.2 Combined Law

It is the combined result of Boyle's law and Charles' law,

$$\frac{PV}{T} = \text{constant} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

3.5 IDEAL GAS EQUATION

Ideal gas equation is obtained by combining all the gas laws. Consider a gas having pressure P, temperature T and volume V.

For a gas having variable pressure, volume, temperature and number of mole;

$$\frac{PV}{T} \propto n \quad \Rightarrow \frac{PV}{T} = R \times n \quad \Rightarrow PV = nRT$$

where R = Universal gas constant and is same for all gases

$$\therefore PV = nRT$$

The above equation is called ideal gas equation

Relationship between density and pressure of an ideal gas

If m is the mass of the gas and M is its molecular mass, then $n = \frac{w}{M}$

Substituting this value of $PV = nRT$, we get

$$PV = \frac{w}{M} RT \text{ or } P = \frac{w RT}{V M} \text{ or } P = d \frac{RT}{M}; \text{ where } d = \frac{m}{V} \text{ density of the gas}$$

is directly proportional to its pressure at constant temperature.

Nature of the gas constant, r

Value of the gas constant R in terms of different units

R = Work done per degree per mol.

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1} = 82.1 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}
 &= 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 8.314 \text{ k Pa dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \\
 &= 8.314 \times 10^7 \text{ ergs degree}^{-1} \text{ mol}^{-1} \\
 &\approx 1.987 \approx 2 \text{ cal degree}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

3.6 DALTON'S LAW OF PARTIAL PRESSURE

'If two or more gases which do not react chemically are enclosed in a vessel, then the total pressure exerted by the gaseous mixture is equal to the sum of the partial pressures that each gas would exert when present alone in the same vessel at the same temperature'. Mathematically $P = P_1 + P_2 + P_3 + \dots$

- (i) **Aqueous tension:** The pressure exerted by the water vapour at a particular temperature is called aqueous tension at that temperature. It depends only on temperature. Its value becomes atmospheric pressure at boiling point of liquid.
- (ii) **Calculation of pressure of a dry gas from that of the moist gas:** When a gas is collected over water at $t^\circ\text{C}$, it is moist. According to Dalton's law of partial pressures.

$$P_{\text{moist gas}} = P_{\text{dry gas}} + \text{aq. tension (at } t^\circ\text{C}) \text{ or } P_{\text{dry gas}} = P_{\text{moist gas}} - \text{aqueous tension (at } t^\circ\text{C)}$$

$$\text{Relative humidity: } R.H. = \frac{\text{Partial pressure of water vapour in air}}{\text{Saturated vapour pressure i.e., aq tension}} \times 100$$

3.7 AMAGAT'S LAW OF PARTIAL VOLUME

Amagat's law of partial volumes: This law is similar to Dalton's law of partial pressures. According to this law, 'the total volume of a mixture of non-reacting gases is the sum of their partial volumes where partial volume of a gas is the volume occupied by that gas at the same temperature and at the pressure of the mixture'. Mathematically $V_T = v_1 + v_2 + v_3 + \dots$

Average molecular weight of a gaseous mixture:

$$M_{\text{avg}} = \frac{\sum n_i M_i}{\sum n_i}; \text{ where } n_i \text{ is the number of moles and } M_i \text{ is the molecular weight of component i.}$$

3.8 DIFFUSION AND EFFUSION

'Under similar conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square root of their densities'. Mathematically

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \quad (\because \text{Molar Mass} = 2 \times \text{Vapour Density})$$

$$\begin{aligned}
 \text{Rate of diffusion} &= \frac{\text{Volume of gas diffused}}{\text{Time taken}} = \frac{\text{Number of mole of gas diffused}}{\text{Time taken}} \\
 &= \frac{\text{Pressure of gas diffused}}{\text{Time taken}} = \frac{\text{Distance travelled by the gas}}{\text{Time taken}}
 \end{aligned}$$

For the volumes diffused in the same time ($t_1 = t_2$)

$$\frac{V_1}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

- For a gas effusing through a small hole of area A_0 , rate of effusion, $r = \frac{PA_0N_A}{\sqrt{2\pi MRT}}$ where P is applied pressure; N_A is avogadro number; M is molecular mass of gas and T is applied temperature.

Difference between diffusion and effusion: Diffusion refers to the spreading of a gas throughout the space or into a second gas or substance, whereas effusion refers to the escape of a gas through an orifice (a tiny hole).

3.9 KINETIC THEORY OF GASES

- Every gas is made up of a large number of extremely small particles called molecules. All the molecules of a particular gas are identical in mass and size and differ in these from gas to gas.
- The molecules of a gas are separated from each other by large distances so that the actual volume of the molecules is negligible as compared to the total volume of the gas.
- The distance of separation between the molecules is so large that the forces of attraction and repulsion between them are negligible.
- The force of gravitation on the molecules is also supposed to be negligible.
- The molecules are supposed to be moving continuously in different directions with different velocities. Hence, they keep on colliding with one another (called molecular collisions) as well as on the walls of the containing vessel.
- The pressure exerted on the walls of the containing vessel is due to the bombardment of the molecules on the walls of the containing vessel.
- The molecules are supposed to be perfectly elastic hard spheres so that no energy is wasted when the molecules collide with one another or with the walls of the vessel. The energy may however, be transferred from some molecules to the other by collision.
- Since the molecules are moving with different velocities they possess different kinetic energies. However, the average kinetic energy of the molecules of a gas is directly proportional to the absolute temperature of the gas.

3.9.1 Kinetic Gas Equation

$PV = \frac{1}{3} mn V_{rms}^2$; where P = pressure of the gas, V = volume of the gas, m = mass of each molecule, n = total number of molecules, V_{rms} = RMS velocity (RMS = root mean square velocity)

Relationship between average KE and Absolute temperature

$$PV = \frac{1}{3} mn V_{rms}^2 = \frac{1}{3} MV_{rms}^2 = \frac{2}{3} \cdot \frac{1}{2} MV_{rms}^2 = \frac{2}{3} KE$$

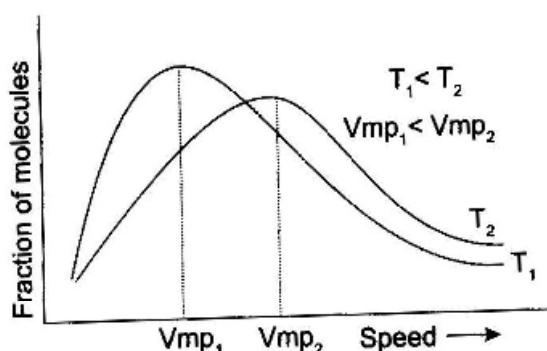
$$\therefore KE = \frac{3}{2} PV = \frac{3}{2} RT \text{ for 1 mol of an ideal gas}$$

$$\overline{KE} = \frac{3}{2} \frac{R}{N} T = \frac{3}{2} kT = \text{Average kinetic energy per molecule; where } N \text{ is Avogadro's number and}$$

$$k = R/N = \text{Boltzmann constant.}$$

3.10 VARIOUS SPEED TERMS USED FOR GASES

It is a plot of fraction of molecules versus the corresponding velocities at a particular temperature. This is shown below alongwith the effect of temperature.



Most probable velocity (V_{mp}): This is the velocity possessed by the maximum fraction of the molecules at a particular temperature. $V_{mp} = \sqrt{\frac{2RT}{M}}$

Root mean square (RMS) velocity (V_{rms}): It is the square root of the mean of the squares of the velocities of the molecules, i.e., $V_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{P}}$

Average velocity (V_{av}): It is the average of the different velocities of the molecules i.e.

$$\text{Average velocity } (v) = V_{av} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n} = V_{av} = \sqrt{\frac{8RT}{\pi M}}$$

Relationship between V_{mp} , V_{av} and V_{rms} :

$$V_{av} = 0.921 V_{rms}$$

$$V_{mp} = 0.816 V_{rms}$$

$$V_{mp} : V_{av} : V_{rms} = 1 : 1.128 : 1.224$$

$$\text{At a given temperature, } V_{mp} < V_{av} < V_{rms}$$

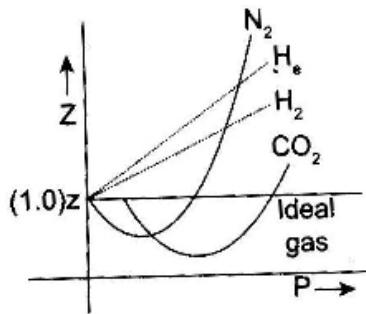
3.11 REAL GASES

A gas which obeys Boyle's law, etc. or ideal gas equation ($PV = nRT$) under all conditions of temperature and pressure is called an ideal gas. A gas which obeys these laws only when temperature is high or pressure is low is called a real gas.

3.12 COMPRESSIBILITY FACTOR

The extent of deviation of a real gas from an ideal behaviour is expressed in terms of compressibility factor, Z, defined as $Z = \frac{PV}{nRT}$

For ideal gas, $Z = 1$ at all temperatures and pressures. For real gases, greater is the departure in the value of Z from 1, greater is the deviation from ideal behaviour. When $Z < 1$, the gas is said to show negative deviation. This implies that gas is more compressible than expected from ideal behaviour and under such a condition, attractive forces are dominating over repulsive forces. When $Z > 1$, the gas is said to show positive deviation. This implies that gas is less compressible than expected from ideal behaviour. Under such a condition, repulsive force are dominating over attractive forces.



3.13 VAN DER WAAL GAS EQUATION

Van der Waal's equation: $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ for 1 mol of the gas and $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

for n moles of the gas, a and b are constant called Van der Waals constants

Significance and units of Van der-Waals constants: 'a' gives the idea of the magnitude of attractive forces among the gas molecules. As correction in pressure is $p = \frac{an^2}{V}$, therefore, $a = \frac{(p \times V^2)}{n^2} = \text{atm L}^2 \text{ mol}^{-2}$. As correction in volume $v = nb$, therefore, $b = v/n = L \text{ mol}^{-1}$.

3.14 CRITICAL TERMS USED FOR GASES

The temperature at which the gas behaves ideally to a certain range of pressure is known as **Boyle's temperature**. $T_B = \frac{a}{Rb}$

The temperature above which the gases cannot be liquified even by the application of high pressure is called critical temperature. $T_C = \frac{8a}{27 Rb}$

Note:

(i) Critical pressure, $P_c = \frac{a}{27b^2}$ and critical volume, $V_c = 3b$

(ii) Guldberg's rule $T_{BP} = \frac{2}{3} T_c$, where T_{BP} is boiling point and T_c is critical temperature of the substance.

Trouton's rule: $\frac{\Delta H_{vap}}{T_b} \approx 88 \text{ J/mol.k}$

(iii) Inversion temperature, $T_i = \frac{2a}{Rb}$

\therefore We can say that $T_i = 2T_B$

$$T_c = 8/27 T_B$$

For any substance, $T_{BP} < T_c < T_B < T_i$

THERMODYNAMICS

4.1 INTRODUCTION

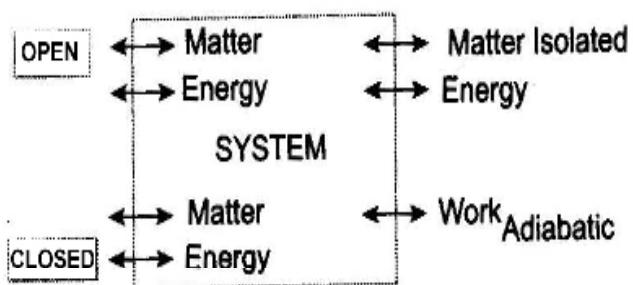
It is the study of energy changes associated with various physical and chemical processes. In thermodynamics, speed of change is not considered and it also does not consider the time element involved in transformation. Laws of thermodynamics are also not applicable at microscopic level.

- In a closed system, boundaries are impermeable.
- In an open system, boundaries are permeable.

4.1.1 Terms Used in Thermodynamics

System and surrounding: System is the specified portion of the universe in which we are observing physical or chemical change. It is surrounded by real or imaginary boundary. Rest of the universe outside the defined system is called surrounding.

4.1.2 Types of System



4.1.3 Thermodynamic Properties

- (a) **Intensive properties:** Properties which are independent of quantity of matter, e.g., pressure, specific heat, surface tension, viscosity, boiling point, specific volume, etc.
- (b) **Extensive properties:** Properties which depends upon quantity of matter, e.g., total mass, volume, number of moles, etc.

- All thermodynamic quantities whose name include prefix specific or molar are always intensive.
- Extensive properties are additives, whereas intensive properties are not additives.
- Ratio of two extensive variables are always intensive.
- An intensive property depends only on intensive variables, whereas extensive properties depend upon both intensive and extensive variables.

4.1.4 State Function or State Variable

A physical quantity is a state function if its value depends only upon the state of the system and not upon the path by which state is reached, e.g., temperature, pressure, volume, enthalpy, entropy, internal energy, etc.

4.1.5 Path Function and Path Variables

A quantity which depends not only on the state of the system but also on the path or route by which the state is reached, e.g., work done by heat supplied, etc.

4.1.6 Thermodynamic Process

- (a) Isothermal ($T = \text{constant}$, i.e., $\Delta T = 0$)
- (b) Isobaric ($P = \text{constant}$, i.e., $\Delta P = 0$)
- (c) Isochoric ($V = \text{constant}$, i.e., $\Delta V = 0$)
- (d) Adiabatic (in which no heat enters or leaves the system, i.e., $q = 0$)

Reversible or quasistatic or pseudostatic process: Thermodynamic process in which driving force is infinitesimally greater than that of restoring force and where direction of change can be reversed by increasing the restoring force by infinitesimal amount is called reversible or quasistatic process.

All slow processes are considered as reversible; however, perfectly reversible process is that which requires infinite number of steps for their completion.

4.1.7 Thermodynamic Equilibrium

Thermodynamic equilibrium in a system implies the existence of the following three equilibria simultaneously:

- (i) Thermal equilibrium, i.e., no flow of heat from one part to another, i.e., $T = \text{constant}$
- (ii) Mechanical equilibrium, i.e., no flow of matter from one part to another, i.e., $P = \text{constant}$
- (iii) Chemical equilibrium, i.e., no change in composition of any part of the system with time.

4.2 FIRST LAW OF THERMODYNAMICS

According to this law, energy can neither be created nor it can be destroyed but it can be transformed from one form to another. Let a system was having E_1 as its internal energy and q amount of heat was supplied to it. Now if w amount of work is done over it then, lets say final internal energy becomes E_2 .

$$E_2 = E_1 + q + w \quad E_2 - E_1 = q + w \quad \Delta E = q + w$$

Alternative statement of first law of thermodynamics is 'It is impossible to construct a perpetual motion machine, i.e., a machine which can produce energy without expenditure of energy'.

4.2.1 Internal Energy

The energy stored within a substance is called internal energy. Its absolute value cannot be determined, for it is the sum of various form of energies contained in the system.

$$\text{i.e., } E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \dots$$

In thermodynamics, we are concerned with energy change which occurs when a system moves from one state to another, i.e., $\Delta E = E_{\text{final (f)}} - E_{\text{initial (i)}}$.

Internal energy is a state function and is an extensive property, as $\Delta E = nC_v \Delta T$.

4.2.2 Work Done in Expansion or Compression

If a system changes its volume from V_1 to V_2 against external pressure, then $\Delta V = (V_2 - V_1)$

$$W = -P_{\text{ext}} \Delta V$$

In case of expansion work done is negative, and in case of compression, work done is positive.

Work done appears at the boundary of the system.

4.2.3 Heat supplied

The energy which crosses the system boundary on account of temperature difference between the system and its surrounding is called heat supplied. It is a path function quantity.

4.2.4 Enthalpy

Heat content of the system at constant pressure and constant temperature is called enthalpy. It is represented by H .

$$H = U + PV \Rightarrow \Delta H = \Delta U + \Delta(PV)$$

$$\Delta H = \Delta U + P\Delta V \text{ and at constant pressure } \Delta H = \Delta U + \Delta n_g RT$$

4.3 MOLAR HEAT CAPACITY

It is defined as the amount of heat required to raise the temperature of one mole of substance by 1°C . It can be at constant volume (C_v) or at constant pressure (C_p). If heat is supplied at constant volume, then it causes change in the internal energy:

If dT rise in temperature is caused by heat supplied dE

$\therefore 1^\circ$ rise in temperature is caused by heat supplied $= dE/dT$

$$\therefore C_v = dE/dT$$

$$\text{Similarly } C_p = dH/dT$$

$$\text{Meyer's equation, } C_p - C_v = R$$

4.3.1 Special Case of First Law of Thermodynamics: Isothermal Expansion of an Ideal Gas

In isothermal expansion heat is allowed to flow in or out of system so that the temperature remains constant and if temperature is constant then ΔT and ΔE are zero. As there will not be any change in internal energy.

\therefore From first law of thermodynamics, $\Delta E = q + w$

$$0 = q + w \Rightarrow q = -w$$

\therefore Work will be done at the expense of heat absorbed but their magnitude depends upon whether the process is carried out reversibly or irreversibly.

4.3.2 Work Done in Reversible Isothermal Expansion

Let an ideal gas is enclosed in a cylinder fitted with a weightless and frictionless piston. It is not insulated and initially $P_{ext} = P$.

If external pressure fall by dP , then the gas will expand by small volume dV , till its pressure also becomes equal to external pressure ($P - dP$) and infinitesimally cooling produced by this expansion is compensated by absorption of heat from outside. The small work done in this expansion will be

$$dw = -(P_{ext} - dP)dV = -P_{ext}dV + dPdV$$

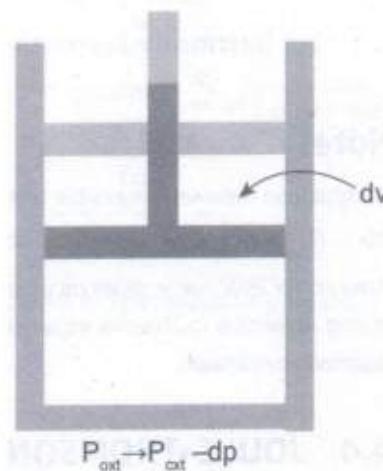
$dPdV$ can be neglected as it is very small.

Therefore, $dw = -PdV$

If the gas expands from V_1 to V_2 then the total work done can be

given by $w = - \int_{V_1}^{V_2} PdV$; We know that $PV = nRT$, i.e., $P = \frac{nRT}{V}$;

$$w = \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V}; w = -2.303 nRT \log \frac{V_2}{V_1} = -2.303 nRT \log \frac{P_1}{P_2}$$



4.3.3 Work Done in Irreversible Isothermal Expansion

Irreversible isothermal expansion can be free expansion (in vacuum) or intermediate expansion (when external pressure is less than the pressure of gas). In free expansion, the work done is zero as there is no net

pressure. In intermediate expansion, from volume V_1 to V_2 , the work done is $w = - \int_{V_1}^{V_2} P_{ext} dV = -P_{ext}(V_2 - V_1)$

Work done in irreversible isothermal expansion is less than reversible isothermal expansion as P_{ext} is less than gas.

4.3.4 Adiabatic Expansion

In adiabatic expansion, no heat is allowed to flow into or out of the system. Therefore, $q = 0$.

\therefore From $\Delta E = q + w$; We have $\Delta E = w$

∴ Work done accompanies the change in internal energy of the system, $dE = C_v dT$

$$\therefore w = \Delta E = C_v \Delta T$$

(a) **Reversible Adiabatic Expansion:** If P is external pressure then work done will be $C_v dT = -P dV$

$$\text{For 1 mole of gas } P = \frac{RT}{V}; C_v dT = -\frac{RT}{V} dV$$

$$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\Rightarrow TV^{\gamma-1} = \text{Constant}; P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\therefore PV^\gamma = \text{Constant}$$

$$\Rightarrow \left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma} \text{ We know that work done}$$

$$w = \frac{nR}{(\gamma-1)}(T_2 - T_1) = nC_v(T_2 - T_1)$$

(b) **Irreversible adiabatic expansion:** In free expansion, work done is zero.

$$\therefore \Delta E = 0 \text{ and thus } \Delta T = 0, w = 0 \text{ and } \Delta H = 0.$$

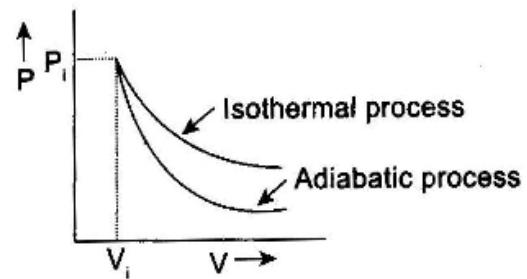
$$\text{For intermediate expansion, } w = -P_{\text{ext}}(V_2 - V_1); w = C_v(T_2 - T_1) = -P_{\text{ext}} \times R \left(\frac{P_1 T_2 - P_2 T_1}{P_1 P_2} \right)$$

Note:

Comparison between reversible isothermal and adiabatic expansion.

$$\Rightarrow P_{\text{ISO}} > P_{\text{ADIA}} \Rightarrow V_{\text{ISO}} > V_{\text{ADIA}}$$

Area under P-V curve gives us work done. Therefore, work done during reversible isothermal expansion is greater than that of during adiabatic expansion.



4.4 JOULE-THOMSON EFFECT

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect. The gas is compressed on the left-hand side. Thus, work is done on the gas. It is equal to $P_1 V_1$.

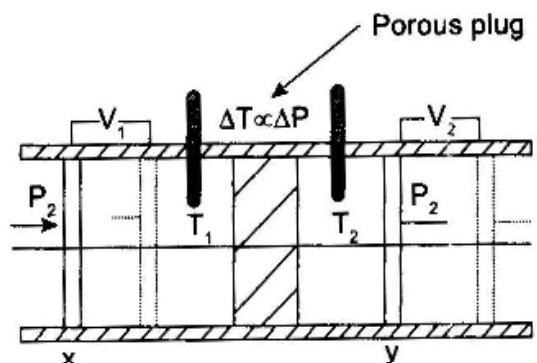
The work done on the right-hand side by the gas is equal to $P_2 V_2$. Total work done by the gas $= P_1 V_1 - P_2 V_2$.

As $q = 0$, the work done by the gas lowers its internal energy and consequently temperature falls.

$$\Delta E = P_1 V_1 - P_2 V_2$$

$$E_2 - E_1 = P_1 V_1 - P_2 V_2$$

$$(E_2 + P_2 V_2) - (E_1 + P_1 V_1) = 0 \text{ or } H_2 - H_1 = 0 \text{ or } \Delta H = 0.$$



Note:

Joule-Thomson effect occurs at constant enthalpy; therefore, it is also called isoenthalpic process. When an ideal gas undergoes expansion under adiabatic condition in vacuum, no change takes place in its internal energy.

Alternatively, the internal energy of a given quantity of an ideal gas at a constant temperature is independent of its volume, i.e., $(\partial U / \partial V)_T = 0$

4.4.1 Joule-Thomson Coefficient

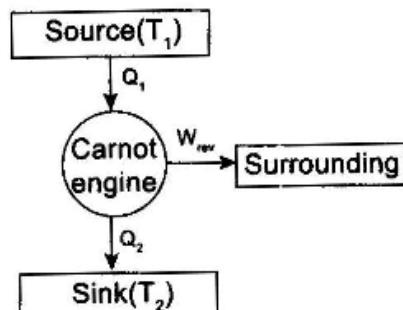
The number of degrees of temperature change produced per unit drop in atmospheric pressure under constant enthalpy condition when a gas is allowed to expand from a region of high pressure to a region of low pressure is known as Joule-Thomson coefficient. $\mu_n = \left(\frac{dT}{dP} \right)_H$

If μ is positive then gas cools on expansion and if μ is negative then gas warms on expansion. Every gas has a definite value of temperature where μ changes sign from negative to positive (as there is a temperature above which the forces of attraction among molecules become negligible) and that temperature is called inversion temperature. $T_i = \frac{2a}{Rb}$; where a and b are Van der Waal constants.

4.4.2 Carnot Engine

$$\text{Thermodynamic efficiency, } (\eta) = \frac{\text{Work done output}}{\text{Heat input}} = \frac{W_{rev}}{Q_{input}}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1} = \frac{Q}{T} = \text{Constant}$$



4.4.3 Spontaneous Process

A process which proceeds of its own accord without any external help is known as spontaneous process, e.g.,

1. Flow of heat from higher temperature to lower temperature
2. A ball rolling down the hill
3. Diffusion of various gases

It is considered that a process takes place because of its tendency to minimize energy but if it is so then exothermic reaction should only be spontaneous, but it is not so because endothermic reactions are also spontaneous. Therefore, decrease in energy is not the sole criteria for spontaneity. There is another criteria and it is increase in entropy (disorder) of system.

4.4.4 Second Law of Thermodynamics

Statement I: It is impossible to convert heat completely into equivalent amount of work done without compensation.

Statement II: Heat cannot transfer by itself from a cold body to a hot body.

Statement III: When-ever a spontaneous process takes place, then it is accompanied by total increase of entropy.

4.4.5 Entropy of the System

Entropy is the measurement of randomness or disorder of the system. It is a state function quantity and can be formulized as follows.

$$\Delta S = S_2 - S_1 = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}; \Delta S = \frac{Q_2 - Q_1}{T} \text{ if process is isothermal, } \Delta S = \frac{Q_{rev}}{T}.$$

(a) Physical significance of entropy:

- (i) In case of isothermal process, increase in entropy is directly proportional to amount of heat supplied.
- (ii) If heat supplied is kept constant, then increase in entropy is greater at lower temperature as compared to that at higher temperature.

(b) Change in entropy of reversible process:

Heat taken by system = Heat given by surrounding

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{system}} = \frac{Q_{\text{rev}}}{T}; \quad \Delta S_{\text{surrounding}} = -\frac{Q_{\text{rev}}}{T}$$

Entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero, i.e., $\Delta S = 0$; $\Delta S_{\text{universe}} = 0$ and for a reversible process, change in entropy of universe must be equal to zero.

(c) Change in entropy of irreversible process: In case of irreversible process, change in entropy of universe must be positive. $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$ (d) Determination of change in entropy: If $dS = \frac{Q_{\text{rev}}}{T}$ and $Q_{\text{rev}} = dU - W_{\text{rev}}$

$$dU = nC_V dT \text{ for ideal gas and } W_{\text{rev}} = -pdV$$

$$\Rightarrow dS = \frac{nC_V dT + pdV}{T}$$

$$\Rightarrow dS = \frac{nC_V dT}{T} + nR \frac{dV}{V} \text{ For ideal gas } P = \frac{nRT}{V}$$

$$\Rightarrow \Delta S = 2.303n \left[C_V \log_{10} \frac{T_2}{T_1} + R \log_{10} \frac{V_2}{V_1} \right] = 2.303n \left(C_p \log_{10} \frac{T_2}{T_1} + R \log_{10} \frac{P_1}{P_2} \right)$$

$$\text{Case I: For isothermal process: } \Delta S = 2.303nR \log_{10} \frac{V_2}{V_1} = 2.303 nR \log_{10} \frac{P_1}{P_2}$$

$$\text{Case II: For isochoric process: } \Delta S = 2.303nC_V \log_{10} \frac{T_2}{T_1}$$

$$\text{Case III: For isobaric process: } \Delta S = 2.303nC_p \log_{10} \frac{T_2}{T_1}$$

$$\text{Case IV: For adiabatic process: } \Delta S = 0 = \frac{Q_{\text{rev}}}{T} \because Q_{\text{rev}} = 0$$

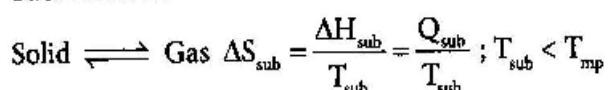
In case of adiabatic process, change in entropy = 0. It is also called isoentropic process.

4.4.6 Entropy of Physical Changes

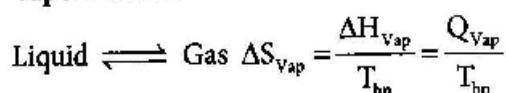
(a) In case of fusion :

$$\text{Solid} \Rightarrow \text{liquid}, T_{\text{mp}} = \text{melting point}, \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{mp}}} = \frac{Q_{\text{fusion}}}{T_{\text{mp}}}$$

(b) **Sublimation:**



(c) **Vaporization:**



(d) **Transition:** Conversion of one allotropic form of a substance into another form is called transition.



$$\Delta S_{\text{Trans}} = \frac{\Delta H_{\text{Trans}}}{T_{\text{Trans}}} = \frac{Q_{\text{Trans}}}{T_{\text{Trans}}}$$

4.4.7 Helmholtz Free Energy Change

Helmholtz free energy, $A = U - TS$

It is a state function quantity.

Decrease in Helmholtz free energy change = Maximum work done = Work function of process.

(a) **Gibb's free energy change:** Gibbs free energy, $G = H - TS$

It is a state function as $\Delta G = \Delta H - T\Delta S$.

ΔG = Useful work done.

(b) **Maxwell's equations:**

$$(i) \quad dU = TdS - PdV$$

$$(ii) \quad dH = TdS + VdP$$

$$(iii) \quad dA = -SdT - PdV$$

$$(iv) \quad dG = -SdT + VdP$$

If V is constant, then dV is zero. Then, equation (i) yields

$$\Rightarrow \left(\frac{\partial U}{\partial S} \right)_V = T. \text{ If } S \text{ is constant, then } \left(\frac{\partial U}{\partial V} \right)_S = -P.$$

4.5 THERMOCHEMISTRY

Thermochimistry is the branch of physical chemistry that deals with energy changes accompanying chemical reactions. In a chemical reaction, old bonds get broken with the absorption of energy and the formation of new bonds takes place with the release of energy. If there is net absorption of energy, then the reaction is called endothermic. Then, at constant pressure $H_p > H_R \Rightarrow \Delta H = H_p - H_R = +ve$;

If there is net release of energy, then the reaction is called exothermic.

Then, $H_p < H_R$; at constant pressure, $\Delta H = H_p - H_R = -ve$;

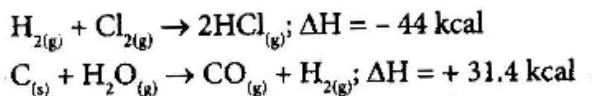
Note:

Most of the reactions are carried out in open vessels so that the pressure remains constant during that process.

So heat evolved or absorbed during the reaction will be equal to the enthalpy change in the reaction.

4.5.1 Heat of Reaction or Enthalpy of Reaction

It is defined as the amount of heat absorbed or evolved when the quantities of the substance indicated by balanced chemical equation have completely reacted, e.g.,



4.5.1.1 Factors which influence the heat of reaction

- (i) **Physical state of reactant and product:** Heat of reaction depends on the physical state of reactant and product.

e.g., Consider the following reaction $\text{H}_{2(g)} + 1/2\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)}; \Delta H = -57.8 \text{ kcal}$

$\text{H}_{2(g)} + 1/2\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(g)}; \Delta H = -68.32 \text{ kcal}$

More heat is released when water formed is in liquid state. It is because of the reason that heat is released during condensation of steam.

- (ii) **Allotropic forms of the element:** The heat of reaction depends upon the allotropic forms of the element

e.g., $\underbrace{\text{C}_{(s)}}_{\text{Diamond}} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}; \Delta H = -394 \text{ KJ/mol}$

$\underbrace{\text{C}_{(s)}}_{\text{Graphite}} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}; \Delta H = -393.5 \text{ KJ/mol}$

This difference in the heat of reaction in two allotropic forms is due to the difference in the arrangement of atoms in these allotropic forms.

- (iii) **Enthalpy of solvation:** The amount of enthalpy change when the substance reacts with each other in dry state will be different than when they react in solution

e.g., $\text{H}_2\text{S}_{(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI} + \text{S}; \Delta H = -17.2 \text{ kcal}$

$\text{H}_2\text{S}_{(g)} + \text{I}_{2(\text{solution})} \rightarrow 2\text{HI} + \text{S}; \Delta H = -21.93 \text{ kcal}$

This difference is because of the reason that in solution there is involvement of energy in the form of solvation.

- (iv) **Temperature:** The amount of enthalpy change depends upon temperature as the heat capacities of system varies with temperature. The standard temperature for the calculation of enthalpies of various reaction is 25° C or 298 K.

4.5.2 Enthalpy of Formation or Heat of Formation

It is defined as the amount of heat evolved or absorbed when 1 mole of a compound is formed from its constituent elements.

e.g., $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}; \Delta H = -97.5 \text{ kcal/mol}$

$\text{H}_{2(g)} + \text{Cl}_{2(g)} \rightarrow 2\text{HCl}_{(g)}; \Delta H = -44 \text{ kcal/mol}$

Since on formation of 2 moles of HCl, 44 kcal of heat is released. Therefore, in the formation of 1 mole of HCl, 22 kcal of heat will be released or we can say that the heat of formation of HCl is 22 kcal. Heat of a reaction can be calculated if the values of enthalpy of formation of reactants and products are known by using

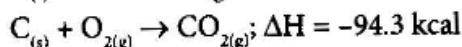
$$\Delta H^\circ(\text{reaction}) = \sum \Delta H^\circ_f(\text{product}) - \sum \Delta H^\circ_f(\text{reactants})$$

Note:

If the reaction is carried out at standard conditions (i.e., at 25°C and 1 atm. pressure), then the heat of formation is called standard heat of formation and it is denoted by ΔH° . For the determination of enthalpy of formation of compound, we take standard enthalpies of free elements as zero (arbitrarily).

4.5.3 Enthalpy of Combustion

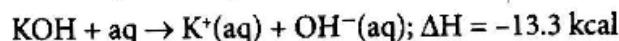
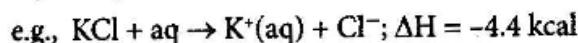
It is defined as the amount of heat evolved when 1 mole of a substance is completely oxidized.



The enthalpy of combustion of carbon is 94.3 kcal and not 26 kcal, as the complete oxidation of carbon produces carbon dioxide.

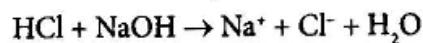
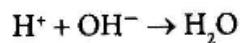
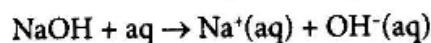
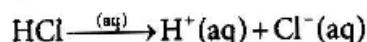
4.5.4 Enthalpy of Solution

It is defined as the amount of heat evolved or absorbed when 1 mole of a substance is dissolved in that much quantity of solvent that further dilution does not cause any heat change.

**4.5.5 Enthalpy of Neutralization**

It is defined as the heat evolved when 1 gram equivalent of an acid is neutralized by 1 gram equivalent of base in dilute solution.

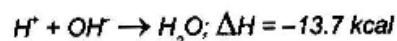
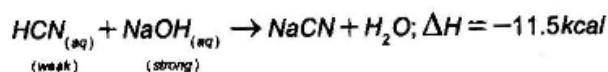
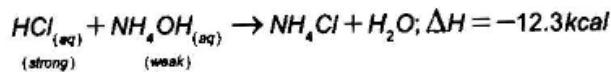
e.g., Consider the neutralization of HCl with NaOH



Therefore neutralization reaction is the reaction between H^+ ion and OH^- ion and the heat evolved by using a strong base and strong acid will always be the same as they will ionize completely in the solution.

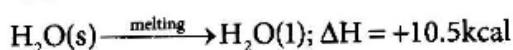
Note:

The heat evolved during the neutralization of weak acid by strong base or weak base by strong acid or weak acid by weak base will be less than 13.7 kcal as certain amount of heat is absorbed for the ionization of weak acid or weak base.



4.5.6 Enthalpy of Fusion

It is defined as the heat absorbed when 1 mole of a substance changes its state from solid to liquid at its melting point.



4.5.7 Enthalpy of Sublimation

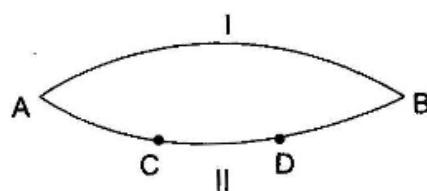
It is defined as heat absorbed when 1 mole of a substance changes into vapour state at a given temperature below its melting point, e.g., $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$; $\Delta H = +14.9 \text{ kcal}$.

It is equal to the sum of enthalpy of fusion and the enthalpy of vapourisation

$$\Delta H_{\text{Sublimation}} = \Delta H_{\text{Fusion}} + \Delta H_{\text{Vapourization}}$$

4.6 HESS'S LAW OF CONSTANT HEAT SUMMATION

It states that the enthalpy of a reaction is dependent only on the initial and final stages whether it takes place in one step or in number of steps. Let us consider that a substance A is changed into B by two ways.



By the Ist way A is converted into B in one step and in the IInd step it is first converted into C and then into D and finally D is converted into B. Let us say that in the I step the heat evolved is more than IInd way, then we can go from A to B through the Ist way and then return to A through the IInd step. In this way the amount of energy released will be more than the energy absorbed in the cyclic process and as a result of which there is net production of energy which is in contradiction with law of conservation of energy.

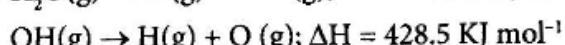
Application of Hess's Law: Hess's law gave the following three indirect methods for the calculation of heat of reaction: $\Delta H_{\text{reaction}} = \sum \text{Bond energy of reactants} - \sum \text{Bond energy of products}$.

$$\Delta H_{\text{reaction}} = \sum \text{Heat of combustion of reactants} - \sum \text{Heat of combustion of products.}$$

$$\Delta H_{\text{reaction}} = \sum \text{Heat of formation of products} - \sum \text{Heat of formation of reactants.}$$

4.7 BOND ENERGY AND BOND ENTHALPY

The average bond dissociation energy required to break each bond in a compound is called bond energy.



$$\text{Bond energy} = \frac{497.8 + 428.5}{2} = 463.15 \text{ KJ/mol}$$

The same amount of energy is released when the bond is formed between hydrogen and oxygen.

4.7.1 Applications of Bond Energy

- (a) **Determination of heat of reaction:** In a chemical reaction old bonds get broken and formation of new bonds takes place among the reactant molecules, and the energy is absorbed to break the bonds and among product molecules the energy is released on the formation of new bonds. The net amount of energy absorbed or evolved is known as heat of reaction.

Note:

Heat of reaction = \sum Bond energy of reactants - \sum Bond energy of products.

- (b) **Determination of resonance energy:** A compound which shows resonance has more stability and its heat of formation will be different than what we have calculated from bond energies. This difference is called resonance energy.

Note:

Resonance energy = Experimental or actual heat of formation or calculated heat of formation.

4.8 INFLUENCE OF TEMPERATURE ON THE HEAT OF REACTION

Heat of formation of reactants. We know that $\Delta H = H_p - H_r$

$$\text{Differentiating the above equation w.r.t. } T \text{ at constant } P = \left(\frac{d \Delta H}{dT} \right)_P = \left(\frac{d H_p}{dT} \right)_P - \left(\frac{d H_r}{dT} \right)_R$$

$$\frac{d \Delta H}{dT} = (C_p)_{\text{products}} - (C_p)_{\text{Reactants}} \quad \dots\dots (i)$$

$$d \Delta H = \Delta C_p dT$$

On integrating equation (i) we have

$$\int_{T_1}^{T_2} d \Delta H = \int_{T_1}^{T_2} \Delta C_p dT$$

$$\Rightarrow \frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_p ; \text{ Kirchoff's equation at constant pressure:}$$

Difference in the heat capacities of product and reactants is constant. If heat is supplied at

$$\text{constant volume, then } \frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_v$$

Above equation is known as Kirchoff's equation at constant volume.

CHEMICAL EQUILIBRIUM

5.1 CHARACTERISTICS OF EQUILIBRIUM STATE

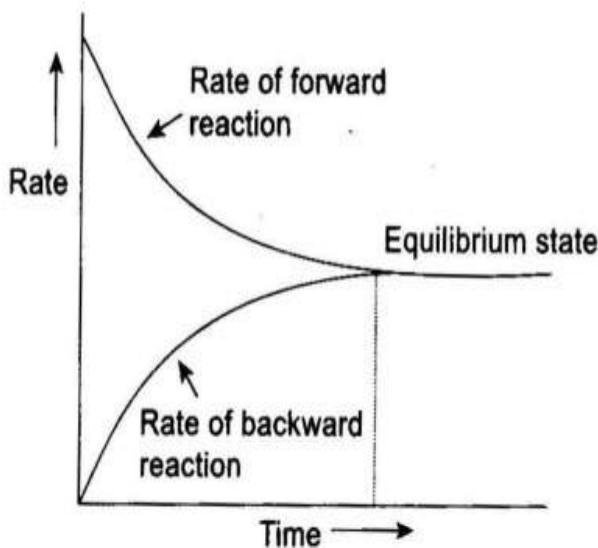
Chemical equilibrium: Chemical equilibrium is the most important characteristic property of a reversible reaction. At equilibrium state, concentration of all reactants and all products do not change with time chemical equilibrium is attained only when rate of forward reaction becomes equal to the rate of backward reactions. Chemical equilibrium is dynamic in nature. Therefore, it is also called pseudo steady state.

Considering a simple reversible reaction $A + B \rightleftharpoons C + D$

For forward reaction, i.e., $A + B \xrightarrow{k_f} C + D$

For backward reaction, i.e., $C + D \xrightarrow{k_b} A + B$

If we plot a curve between rate of reaction versus time, we get



5.1.1 Characteristics of Equilibrium State

- (i) Equilibrium state can be achieved if a reversible reaction is carried out in closed space. However, this condition holds only for gaseous phase reaction.
- (ii) Chemical equilibrium is attained from either side, i.e.,



- (iii) Chemical equilibrium is attained earlier by using a catalyst; however, the presence of the catalyst does not alter the equilibrium state.
- (iv) It is dynamic in nature, i.e., reaction does not stop but both forward and backward reactions take place at equal rate.
- (v) Change of pressure, concentration or temperature favours one of the reaction (forward or backward) resulting in shift of equilibrium point in one direction. If we plot a curve between concentration versus time, there are three possibilities.

5.2 LAW OF MASS ACTION

This law was proposed by Guldberg and Wage: According to this law, the rate of chemical reaction is directly proportional to the product of the active masses of the reacting substances.

For a general reversible reaction, $aA + bB \rightleftharpoons mM + nN$

According to law of mass action

Rate of the forward reaction, $r_f \propto [A]^a [B]^b$ or $r_f = K_f [A]^a [B]^b$

Rate of the reverse reaction, $r_b \propto [M]^m [N]^n$ or $r_b = K_b [M]^m [N]^n$

At equilibrium, rate of forward reaction = rate of backward reaction

i.e., $k_f [A]^a [B]^b = K_b [M]^m [N]^n$

$$\Rightarrow \frac{k_f}{k_b} = k_{eq} = k_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} = \text{equilibrium constant}$$

where k_c is equilibrium constant in terms of concentration.

5.3 RELATIONSHIP BETWEEN VARIOUS EQUILIBRIUM CONSTANTS

Relationship between K_p and K_c :

$K_p = k_c RT^{\Delta n}$, where $\Delta n = n_p - n_r$ = number of mole of gaseous product – number of mole of gaseous reactant

K_p = Equilibrium constant in terms of pressure

K_c = Equilibrium constant in terms of concentration

K_x = Equilibrium constant in terms of mole fraction

K_n = Equilibrium constant in terms of moles

Relationship between K_p and K_x :

$$k_p = k_x (P_t)^{\Delta n}$$

$$\text{Relationship between } K_p \text{ and } K_n: k_p = k_n \left(\frac{P_t}{\Sigma n} \right)^{\Delta n}$$

$a \propto [M]$ or $a = \gamma \times [M]$

$\therefore [M]$ = molar concentration

α = active mass

γ = activity coefficient

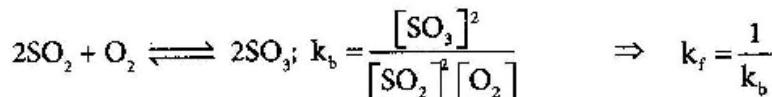
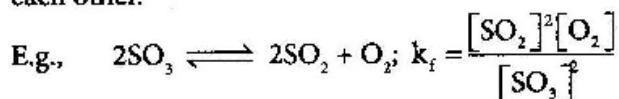
Activity coefficient for dilute solution $\gamma = 1$.

Thus if rate \propto active mass

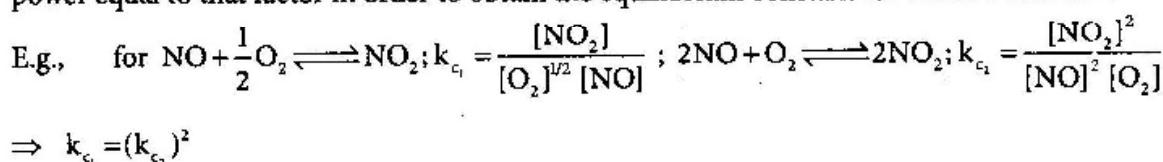
\Rightarrow Rate \propto molar concentration.

5.4 EFFECT OF ALGEBRAIC OPERATION ON EQUILIBRIUM CONSTANT

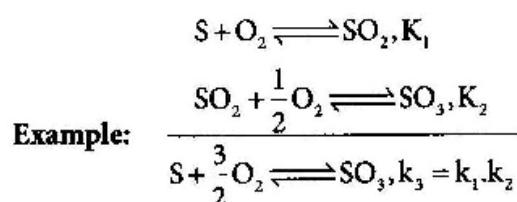
- (i) The equilibrium constant of a forward reaction and that of its backward reaction are reciprocal of each other.



- (ii) If a chemical reaction is multiplied by a certain factor, its equilibrium constant must be raised to a power equal to that factor in order to obtain the equilibrium constant for the new reaction.



- (iii) If two or more reversible reactions are added to give a net reversible reaction, then the equilibrium constant of net reaction is product of equilibrium constant of individual reversible step added.



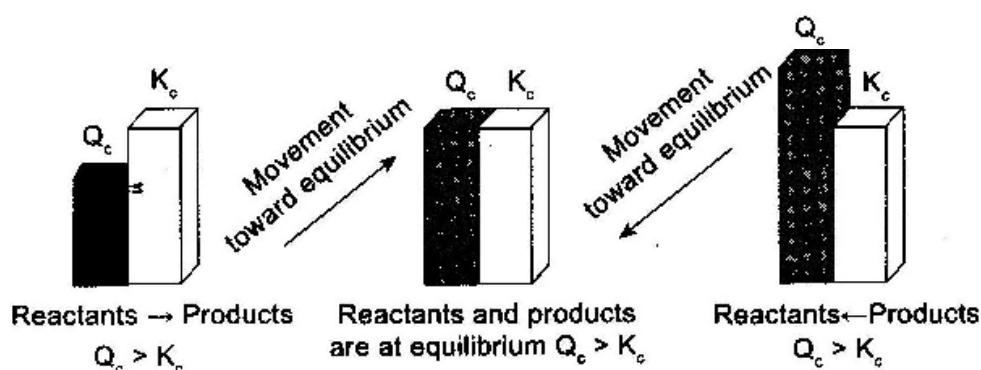
Note:

- (i) If number of moles of product is equal to number of moles of a reactant, i.e., $\Delta n = 0$
 $\Rightarrow k_p = K_c = k_f = k_h$

- (ii) For a mixture of real gases, $\gamma_i = \frac{f_i}{P_i} \Rightarrow f_i = \gamma_i P_i$, where f_i is fugacity of i^{th} component.

5.5 MASS ACTION RATIO, I.E., REACTION QUOTIENT

Reaction Quotient: At any point in a reversible reaction, ratio of the concentration terms in the same form as in the equilibrium constant expression can be formulated. This ratio is referred to as reaction quotient or mass action ratio (Q_c).



5.6 SPONTANEITY OF A REACTION

If the free energy change of a chemical reaction is negative, the reaction can take place spontaneously, i.e., it is feasible. If the free energy change is zero, the reaction is in a state of equilibrium and if the free energy change is positive, the reaction would not proceed. For a reaction to be spontaneous, ΔG must have a negative value.

$$\Delta G = \Delta H - T\Delta S \text{ for which } \Delta H \text{ should be negative and } T\Delta S \text{ should be positive.}$$

Role of temperature: Temperature being a multiplying parameter for entropy factor ($T\Delta S$) of a system, plays an important role in controlling the spontaneity of a reaction.

- (a) **At high temperature, the entropy factor predominates:** In the case of an endothermic reaction, ΔH is always positive. Thus, the energy factor does not favour the reaction. But if the reaction is accompanied by even a small increase of entropy, the high temperature will increase the entropy factor $T\Delta S$ by a large extent. Hence, ΔG may become negative at a sufficiently high temperature. This explains that endothermic reactions become feasible at increasing temperatures.
- (b) **At low temperature, energy factor predominates:** In the case of an exothermic reaction, ΔH is always negative. Thus, the energy factor always tends to favour the reaction. If such a reaction takes place at a low temperature, then even if it is accompanied by decrease of entropy, the opposing factor $T\Delta S$ may remain very small and therefore the value of ΔG may still have a large negative value. This points explain why exothermic reactions in many cases remain feasible at decreasing temperatures.

Standard free energy of formation of a compound: Standard free energy of formation of a compound is defined as free energy change involved in the formation of a compound in standard state (25°C and 1 atm) from its elements in their standard states. This is denoted by ΔG_F° .

$$\Delta G_F^\circ = \Delta H_F^\circ - T\Delta S_F^\circ$$

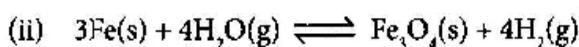
Standard free energy change of a reaction may be calculated with the help of standard free energy change of formation of compounds involved in the reaction, $\Delta G^\circ = [\Delta G_F^\circ]_{\text{Products}} - [\Delta G_F^\circ]_{\text{Reactants}}$.

5.7 HETEROGENEOUS EQUILIBRIA

When reactants and products present in an equilibrium have more than one phase in such a case pure solids and pure liquids have essentially constant concentrations. Thus, we ignore pure solids and pure liquids in writing equilibrium constant expression.



$$K_p = p_{\text{CO}_2} = n_{\text{CO}_2} \times \frac{P}{\sum n}$$



$$K_p = \frac{(p_{\text{H}_2})^4}{(p_{\text{H}_2\text{O}})^4} = \frac{(n_{\text{H}_2})^4}{(n_{\text{H}_2\text{O}})^4} \times \left(\frac{P}{\sum n} \right)^0$$

As a general rule, the concentrations of pure solids and pure liquids are not included when writing an equilibrium equation because their concentrations are constants that are incorporated into the value of the equilibrium constant. We include only the concentrations of gases and the concentrations of solutes in solutions because only those concentrations can be varied.

The equilibrium constant K_p is related to standard free energy change (ΔG°) by the relation $\Delta G^\circ = -2.303 RT \log_{10} K_p$ at standard state, $T = 25^\circ\text{C}$; $P = 1 \text{ atm}$.

When $\Delta G^\circ = -ve$, forward reaction is thermodynamically feasible ($K > 1$)

$\Delta G^\circ = +ve$ or $K < 1$, reverse reaction is feasible.

$\Delta G^\circ = 0$, then $k = 1$, i.e., equilibrium condition.

5.8 DEGREE OF DISSOCIATION

Degree of dissociation is defined as the fraction of one mole of a molecule dissociated. It is denoted by α . Its value is always less than 1. When the value becomes equal to 1, it is said that the substance is completely dissociated.

Experimental determination of degree of dissociation, is determined by measuring vapour density of a reaction mixture at equilibrium. Considering a general reversible reaction

Initial number of moles	A	\rightleftharpoons	nB
	1		0
Number of mole at equilibrium	$(1 - \alpha)$		$n\alpha$
Total number of moles at equilibrium	$(1 - \alpha) + n\alpha = 1 + (n - 1)\alpha$		

5.8.1 Determination of Degree of Dissociation by Measurement of Vapour Density

If d be the observed vapour density at a particular temperature when degree of dissociation is α and D be

$$\text{the vapour density when there is no dissociation, then } \alpha = \frac{D-d}{(n-1)d}$$

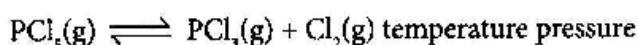
In terms of molecular mass, $\alpha = \frac{M-m}{(n-1)m}$, where M = initial molecular mass

m = molecular mass at equilibrium

e.g., (i) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$, here $n = 2$

$$\alpha = \frac{D-d}{(2-1)d} = \frac{D-d}{d}$$

Degree of dissociation by using pressure-temperature determination: Consider the following gaseous reaction.



$$t = 0 \quad a \quad 0 \quad 0 \quad T_1 \quad P_1$$

$$t_{eq} \quad a - a\alpha \quad a\alpha \quad a\alpha \quad T_2 \quad P_2$$

$$\Rightarrow \alpha = \frac{T_1 P_2 - T_2 P_1}{T_2 P_1}$$

5.9 LE CHATELIER'S PRINCIPLE AND ITS APPLICATION

Le Chatelier's Principle: According to this principle, if an equilibrium is subjected to a stress, the equilibrium adjusts in such a manner that the effect of the disturbance is minimized.

- (i) **Effect of change of pressure:** By increasing the pressure, equilibrium shifts in the direction in which there is decrease in volume or less number of molecules and vice versa.

E.g., (i) $N_2 + 3H_2 \rightleftharpoons 2NH_3$; By increasing the pressure, more NH_3 will be formed.



By increasing the pressure less PCl_5 will be dissociated.

- (ii) **Effect of change of temperature:** By increasing the temperature the equilibrium shifts in the direction in which heat is absorbed, i.e., in which direction reaction is endothermic.



By increasing the temperature, formation of NH_3 decreases.

Effect of adding inert gases:

(i) If P is a constant and $\Delta n = 0$, K_p is unaffected by the addition of the inert gas.

(ii) If P is constant and $\Delta n_g \neq 0$, and if we add an inert gas, equilibrium will shift in the direction where Δn_g is positive.

(iii) If V is a constant and an inert gas is added, no change in equilibrium takes place.

- (iii) **Effect of change of concentration:** In a chemical equilibrium increasing the concentration of the reactants results in shifting the equilibrium in favour of the products while increasing the concentration of the products results in shifting equilibrium in favour of the reactants.

Le Chatelier's principle in case of physical equilibrium:

- (i) **Effect of pressure on boiling point:**



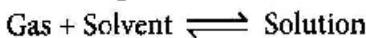
An increase in pressure will favour backward reaction, i.e., the reaction in which volume decreases ($V_{\text{vapour}} > V_{\text{water}}$). Thus, more water will exist at equilibrium, i.e., boiling point of water (solvent) increases with increase in pressure.

- (ii) Effect of pressure on the freezing point of a liquid (or melting point of a solid)

(a) **For ice \rightleftharpoons water equilibrium:** An increase in pressure will favour forward reaction because $V_{\text{ice}} < V_{\text{water}}$. Thus, more and more ice will melt or the melting point of ice is lowered with increase in pressure.

(b) **For a solid \rightleftharpoons liquid equilibrium:** An increase in pressure will favour backward reaction because $V_{\text{liquid}} > V_{\text{solid}}$ and thus more solid will exist at equilibrium, i.e., melting point of solid increases with increase in pressure.

- (iii) **Effect of pressure on solubility of gases:**



Since $V_p > V_b$, an increase in pressure will favour forward reaction and thus solubility of gas increases with increase in pressure.

Henry's law: It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

$W(g) \propto P(g)$ or $W(g) = KP(g)$; where $W(g)$ is amount of gas dissolved in solution and $P(g)$ is the partial pressure of the gas over the solution and K is Henry's constant which is different for each gas.

- (iv) **Effect of temperature on solubility of solids:**

- (a) **Solute + Solvent \rightleftharpoons Solution; $\Delta H = +ve$**

An increase in temperature always favours endothermic process and thus solutes having endothermic dissolution (e.g., urea, glucose) show an increase in their solubility with increase in temperature.

- (b) **Solute + Solvent \rightleftharpoons Solution; $\Delta H = -ve$**

Solutes having exothermic dissolution (e.g., lime, NaOH, acids, etc.) show a decrease in their solubility with increase in temperature. Le Chatelier principle is not valid for solid-solid heterogeneous equilibrium.

IONIC EQUILIBRIUM

6.1 INTRODUCTION

Arrhenius theory: According to this theory, 'Acids are the substances which give H⁺ on dissolution in water while bases are the substances which give OH⁻ on dissolution in water.'

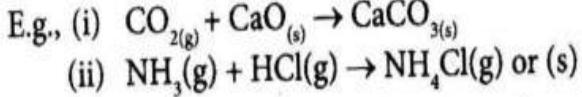
Examples:

- (i) HCl(g) + Water \rightleftharpoons H⁺(aq) + Cl⁻(aq)
- (ii) CH₃COOH + Water \rightleftharpoons H⁺_(aq) + CH₃COO⁻_(aq)
- (iii) Ca(OH)₂ + Water \rightleftharpoons Ca²⁺_(aq) + 2OH⁻_(aq)

The high dielectric constant of water lowers the force of attractions between the oppositely charged ions and thus causes the dissociations of the electrolyte. The greater the number of H⁺ or OH⁻ ions given by an acid or a base in water, the greater will be the strength of the acid or the base.

6.1.1 Limitation of Arrhenius Theory

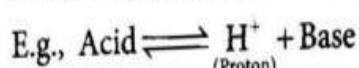
- (a) It fails to explain the behaviour of acids and bases in non-aqueous solvents.
- (b) It fails to explain the neutralization reactions giving rise to salt formation in absence of a solvent.



- (c) It fails to explain the acidic character of certain salts, e.g., AlCl₃, BF₃, etc. and basic character of NH₃, PH₃, etc.

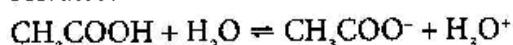
6.1.2 Proton Transfer Theory (Bronsted and Lowry Concept)

According to this theory, 'An acid is a substance which has a tendency to donate a proton to other substances, and a base is a substance which has a tendency to accept a proton from any other substances.'

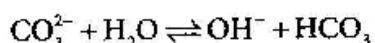
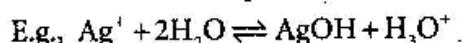


(a) Characteristic of Proton Transfer Theory:

(i) The proton donated by an acid is incapable of independent existence and is always solvated.

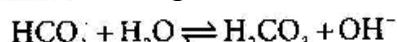


(ii) A cation may behave as an acid and an anion may behave as a base in water, however, some of them behave as amphoteric.



A substance which can act both as an acid as well as a base in different reactions is called amphoteric.

An acid-base pair which differs by a proton is called conjugate acid-base pair.



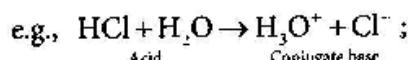
where HCO_3^- is amphoteric

6.1.3 Conjugate Acids and Bases

Pairs of the substances which can be formed from one another by the gain or loss of a proton are known as conjugate acid-base pair.

Acid	Conjugate Base	Base	Conjugate Base
HCl	Cl^-	NH_3	NH_4^+
H_2SO_4	HSO_4^-	CH_4	CH_3^+
NH_3	NH_2^-	H_2O	H_3O^+

The stronger an acid, the weaker must be its conjugate base and vice versa.



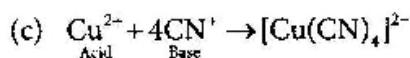
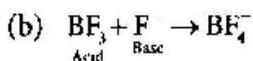
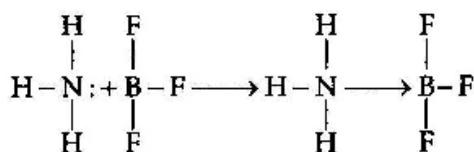
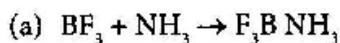
$\text{HCl} > \text{CH}_3\text{COOH}$ and order of basic strength of conjugate bases are $\text{CH}_3\text{COO}^- > \text{Cl}^-$.

All Arrhenius acids are Bronsted acids while all Arrhenius bases is not Bronsted bases, e.g., NaOH, is an Arrhenius base as it furnishes OH^- but is not a Bronsted base as it is not capable of accepting a proton as such.

Leveling Effect: In a solvent like H_2O , all strong acid are almost completely dissociated and therefore their acidic strength cannot be compared. This phenomenon is termed as leveling effect.

6.1.4 Lewis concept of Acids and Bases

According to this theory, 'An acid is a species that is capable of accepting a pair of electrons to form a dative covalent bond and a base is a species that is capable of donating a pair of electrons to form a dative covalent bond'.

Example:(a) **Classification of Lewis Acid:**

- (i) Molecules in which central atom has an incomplete octet, e.g., BF_3 , AlCl_3 , etc.
- (ii) Molecules which have a central atom with empty d-orbitals, e.g., SiX_4 , GeX_4 , PX_3 , TiCl_4 , etc.
- (iii) Molecules having multiple covalent bond between atoms of dissimilar electronegativity,
e.g., CO_2 , SO_2 , SO_3 , etc.

(b) **Characteristics of Lewis Bases:**

- (i) Neutral species having at least one lone pair of electrons.



- (ii) Negatively charged species, e.g., CN^- , OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , etc.

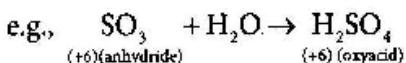
6.1.5 Classification of Acids

(a) **Hydroacids:** Some example of hydroacids are HCN , H_2S , H_2Se , H_2Te , HCl , HBr , HF , HI , N_3H , etc. For hydroacids as we move down in the group the acidic strength increases as well as when we move from left to right in a period acid strength increases.

e.g., (i) $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$; (in group)

(ii) $\text{NH}_3 < \text{H}_2\text{O} < \text{HF}$; (in period)

(b) **Acid anhydride and oxyacids:** Oxides of non-metals having same oxidation number of a non-metal in their respective oxyacids and themselves are known as acid anhydrides. The acid anhydrides on dissolution in water give their respective oxyacids.



e.g., $\text{H}_4\text{P}_2\text{O}_7$ is not an acid because there is no replacable hydrogen.

- For obtaining acid anhydride from any oxyacid, subtract H_2O in such a way that no hydrogen remains.
- If an acid anhydride can form more than one oxyacids (containing all the central atom in each case in same oxidation state) then we must consider ortho, meta and pyronotation.

6.1.5.1 Acidic strength of oxyacids

- (a) Higher the oxidation number of common central atom in oxy acids, more will be the acidic character if basicity is same.

e.g., $\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

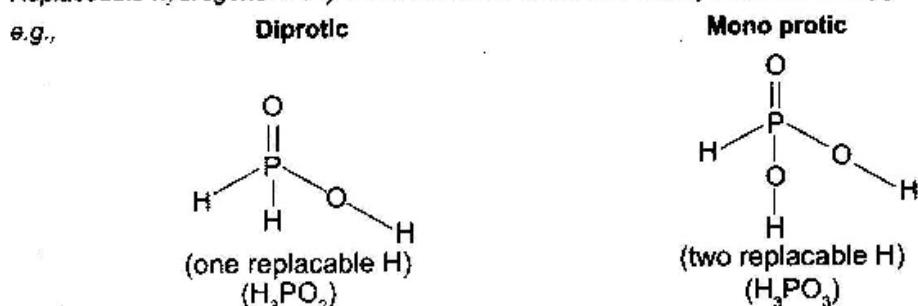
- (b) If central atom is different but basicity is same then as the electronegativity of central atom increases acidic strength of oxyacid also increases $\text{HClO}_4 > \text{HBrO}_4 > \text{HIO}_4$

Notes:

- Ions of acids containing-ic suffix are written as-ate, while those containing-ous suffix can be written as-ite.

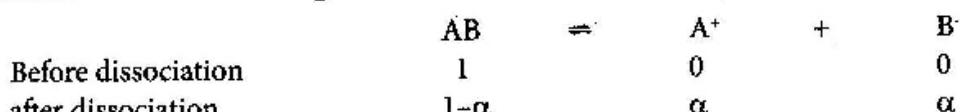


- Replaceable hydrogens in oxy acids are those which are directly attached to oxygen atoms.



6.2 ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

According to this theory, 'An electrolyte on dissolution in water furnishes two type of ions, positive (cation) and negative (anion). A chemical equilibrium exists between undissociated electrolyte and dissociated ions.' If α is the degree of dissociation of an electrolyte AB, then



where degree of dissociation (α) = $\frac{\text{Moles dissociated}}{\text{Total moles present initially}}$

The degree of dissociation of a strong electrolyte is assumed to be unity at infinite dilution, i.e., $\alpha = 1$.

6.2.1 Strong and Weak Electrolytes

- (a) **Strong Electrolytes:** Electrolytes which ionize almost completely when dissolved in water are called strong electrolytes, e.g., (all salts except CdBr_2 , HgCl_2), mineral acids like HCl , H_2SO_4 , HNO_3 , etc and bases like NaOH , KOH , etc.

(b) **Weak Electrolytes:** Substances which dissociate only to a small extent in aqueous solution are weak electrolytes, e.g., all organic acids (except suphonic acids), inorganic acids like HCN , H_3BO_3 , etc. and bases like NH_3 , amines, etc.

6.2.2 Factors Influencing Degree of Dissociation

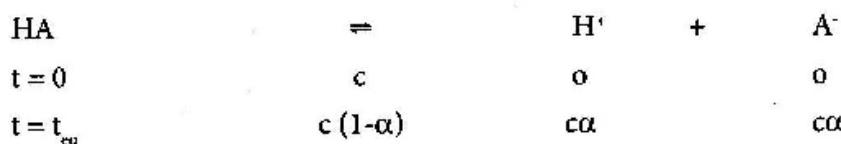
The variation of ' α ' of an electrolyte is governed by:

- Nature of solute:** All ionic compounds, i.e., strong electrolytes have $\alpha \approx 1$ at normal dilution. Most of the polar covalent compounds, i.e., weak electrolytes have $\alpha \ll 1$.
- Nature of solvent:** Solvents having high dielectric constants are themselves feebly ionized but an electrolyte in such a solvent show higher degree of dissociation than in a solvent of low dielectric constant (say methanol).
- Dilution:** The extent of dissociation of an electrolyte increases with dilution of solution.
- Temperature:** The extent of dissociation of an electrolyte increases with an increase in temperature.
- Common ion effect:** Addition of another solute having ion common to that of weak electrolyte shows a decrease in degree of dissociation of a weak electrolyte. This is known as common ion effect.

6.2.3 Ostwald Dilution Law

The application of law of mass action to weak electrolytes is known as Ostwald dilution law.

Considering a weak electrolyte HA in equilibrium



According to law of chemical equilibrium, $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$, where K_a is dissociation constant of an acid.

Since for a weak electrolyte, $\alpha \ll 1$

$$\Rightarrow K_a = c\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{c}} \quad K_b = \text{dissociation constant of a base}$$

$$K_b = \frac{c\alpha^2}{1-\alpha} \text{ and } K_b = c\alpha^2 \text{ and } \alpha = \sqrt{\frac{K_b}{c}}$$

Notes:

- Ostwald dilution law is not applicable for strong electrolytes.
- The smaller the value of K_a , the weaker the acid.

- Relative strength of weak acids and weak bases:** Relative strength of two weak acids is a measure of $[H_3O^+] = [H^+]$ when concentrations of two acids are same, i.e., $c_1 = c_2$,

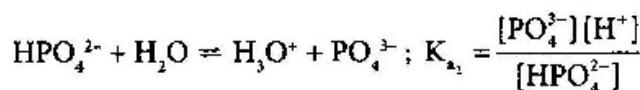
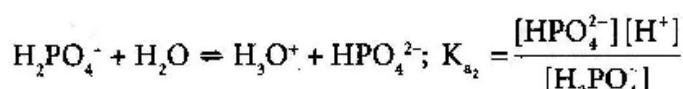
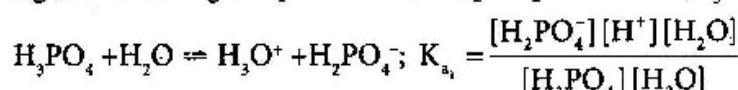
$$\Rightarrow \frac{\text{Relative strength of acid 1}}{\text{Relative strength of acid 2}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

Relative strength of two weak bases is a measure of $[OH^-]$

$$\Rightarrow \frac{\text{Relative strength of base 1}}{\text{Relative strength of base 2}} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

(b) **Dissociation of polyprotic acids:** Substance which are capable of furnishing more than one proton to water are known as polyprotic or polybasic acids.

e.g., Considering a triprotic acid, i.e., phosphoric acid (H_3PO_4)



The value of the three ionization constants follow a decreasing trend $K_{a_1} > K_{a_2} > K_{a_3}$.

The reason for the decrease in the dissociation constant of successive stages is that in the first stage of dissociation, the proton comes from a neutral molecule while in the second stage of dissociation, the proton is detached from a negatively charged ion and in the third dissociation, it is detached from a doubly charged negative ion.

(c) **Acidity and pK_a :** The dissociation constant of an acid (K_a) is usually expressed in terms of pK_a , i.e., negative logarithm of K_a .

$pK_a = -\log K_a$; similarly ($pK_b = -\log K_b$). For bases

The strength of a base is inversely related to pK_b values of the base, i.e., the larger is the value of pK_b the weaker is the base.

Notes:

■ Acidic strength $\propto K_a \propto \frac{1}{pK_a}$

■ Basic strength $\propto K_b \propto \frac{1}{pK_b}$

(d) **Ionic Product of Water:** Since water is amphiprotic it gives H_3O^+ and OH^- as a result of self ionization (auto protolysis).



Applying the law of mass action, law of dissociation constant

$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2} = \frac{[H^+][OH^-]}{[H_2O]}$$

Since dissociation takes place to a very small extent, hence the concentration of undissociated water molecules $[H_2O]$ may be regarded as constant.

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \text{ at } 25^\circ C$$

The numerical value of K_w increases with increase in temperature.

Since in pure water, the concentration of H^+ and OH^- ions must be equal to one another, hence,

$$\text{Hence } [H^+] = [OH^-] = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

(i) If $[H^+] > \sqrt{K_w}$ the solution is acidic.

If $[H^+] = \sqrt{K_w}$ the solution is neutral.

if $[H^+] < \sqrt{K_w}$ the solution is basic.

Molarity and degree of dissociation of water

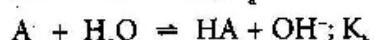
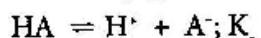
e.g., An aqueous solution in which $[H^+]$ is less than 1×10^{-7} mol/litre is said to be alkaline.

$\therefore [H^+] = c\alpha = 10^{-7}$ and concentration or molarity of water = 55.6

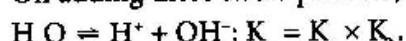
$$\therefore \alpha - \frac{10^{-7}}{55.6} = 1.8 \times 10^{-9} \text{ or \% dissociation} = 1.8 \times 10^{-7}.$$

(e) Relation between K_w , K_a and K_b :

For a conjugate acid, base pair HA and A⁻ in aqueous solution,



On adding these two equations, we get



This relationship shows that product of dissociation constant of an acid and the dissociation constant of its conjugate base is the ionic product of water.

i.e., $K_w = K_a \times K_b$

$$\Rightarrow pK_w = pK_a + pK_b = 14 \text{ at } 25^\circ C.$$

6.3 THE pH VALUE AND pH SCALE

The concept of pH was introduced by Soren Sorensen. According to him, 'the pH of a solution is the negative logarithm (to the base 10) of the concentration of H⁺ ions which it contains.'

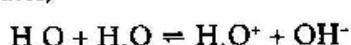
$$\text{Thus, } pH = -\log_{10}[H^+] = -\log_{10}[H_3O^+]$$

$$\Rightarrow [H^+] = [H_3O^+] = 10^{-pH}$$

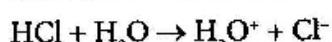
$$\Rightarrow pH + pOH = pK_w = 14 \text{ at } 25^\circ C.$$

6.3.1 pH of Strong Acids or Strong Bases

When a strong acid is added to water, as in an aqueous solution of HCl, in addition to the self-ionization of water,



ionization of acid also occurs.



The self-ionization of water occurs to a slight extent while ionization of HCl goes essentially to completion. As a result, we conclude that,

- (a) In calculating [H₃O⁺] in an aqueous solution of a strong acid, the strong acid is the only significant source of H₃O⁺, unless the solution is extremely dilute (e.g., less than 10⁻⁶ M).

$$\text{Total } [H_3O^+] = 10^{-7} + 10^{-8} M \Rightarrow pH < 7$$

- (b) In calculating [OH⁻] in an aqueous solution of a strong base, the strong base is the only significant source of OH⁻ unless the solution is extremely dilute. (e.g., less than 10⁻⁶ M).

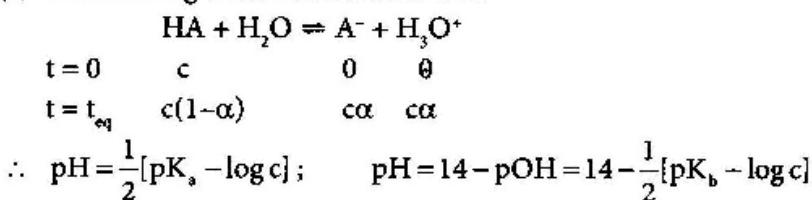
$$\text{Total } [OH^-] = 10^{-7} + 10^{-8} = 11 \times 10^{-8} M \Rightarrow pOH < 7$$

Notes:

- Total $[H_3O^+]$ or $[OH^-]$ in two strong acids / base $[H_3O^+] = \frac{\Sigma NV}{\Sigma V}; [OH^-] = \frac{\Sigma NV}{\Sigma V}$
- The resultant solution of a mixture of a strong acid (Normality N_1 , volume V_1) and a strong base (Normality N_2 , volume V_2)
 - (i) is neutral if $N_1 V_1 = N_2 V_2$
 - (ii) is basic if $N_2 V_2 > N_1 V_1$, and resultant $[OH^-] = \frac{N_2 V_2 - N_1 V_1}{V_1 + V_2}$
 - (iii) is acidic if $N_1 V_1 > N_2 V_2$, and resultant $[H_3O^+] = \frac{N_1 V_1 - N_2 V_2}{V_1 + V_2}$

6.3.2 pH of weak acids and weak bases

- (a) Considering a weak monobasic acid

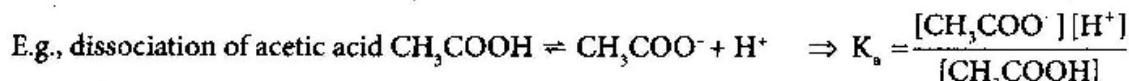


(b) Total $[H_3O^+]$ in a mixture of two weak acids can be given as $[H_3O^+] = \sqrt{K_{a_1}c_1 + K_{a_2}c_2}$

■ Total $[OH^-]$ in a mixture of weak bases can be written as $[OH^-]_T = \sqrt{K_{b_1}C_1 + K_{b_2}C_2}$

6.3.3 Common Ion Effect

If a salt of a weak acid is added to a solution of the acid itself, the dissociation of the acid is diminished. So, 'The suppression of the dissociation of a weak acid or a weak base on the addition of its own ions is called common ion effect.'

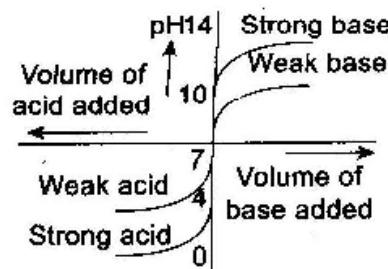


The equilibrium constant K_a has a definite value at a given temperature. If another electrolyte containing CH_3COO^- or H^+ ions can be added to the given solution, it will increase the $[\text{CH}_3\text{COO}^-]$ and $[\text{H}^+]$ ions, and in order to K_a remain a constant, the $[\text{CH}_3\text{COOH}]$ must increase, so that equilibrium will shift to the left side.

6.4 BUFFER SOLUTIONS

Buffers are the solution which resists the change in their pH on addition of a small amount of a strong acid or a strong base.

In order for a solution to act as a buffer it must have two compounds, one of which is able to neutralize acids, and the other bases. Common buffer solution are mixtures containing a

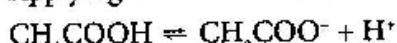


- (i) weak acid and its conjugate base (one of its salts), i.e., acidic buffer
- (ii) weak base and its conjugate acid (one of its salts), i.e., basic buffer
- (iii) salt buffer

6.4.1 Buffer of a Weak acid and its Salt with a Strong Base

It is possible to prepare a buffer solution by the addition of a weak acid and a salt of the acid. We shall explain the buffer action by the following example, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$

Applying law of mass action to the dissociation equilibrium of CH_3COOH



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\Rightarrow [\text{H}^+] = \frac{K_a[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} ; \text{ where } [\text{CH}_3\text{COO}^-] = [\text{Salt}] = \text{Initial concentration of the salt}$$

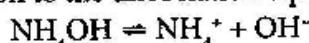
$[\text{CH}_3\text{COOH}] = [\text{acid}] = \text{Initial concentration of acid}$; taking log of both sides and multiplying by -ve sign we get.

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

This equation is known as Henderson's equation.

6.4.2 Buffer of a Weak base and its Salt with a Strong Acid

It consists of a weak base and its salt with strong acid, e.g., $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$, and applying law of mass action to the dissociation equilibrium of NH_4OH .



$$\Rightarrow K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

$$\text{Hence, } [\text{OH}^-] = \frac{K_b[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} ; \text{ where } [\text{NH}_4^+] = [\text{salt}] = \text{Initial concentration of the salt.}$$

$[\text{NH}_4\text{OH}] = [\text{base}] = \text{Initial concentration of base}$

$$\Rightarrow \text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

(a) **Buffer Capacity:** The capacity of a solution to resist alteration in its pH is known as its buffer capacity.

Buffer capacity of a solution is defined as the change in the concentration of a buffer acid (or base) required for changing its pH value by one unit keeping total concentration of acid + salt or base + salt constant.

Considering an acidic buffer solution with concentration of acid and the concentration of salts $\text{pH} = \text{p}K_a + \log_{10} S/a$. To this buffer solution, if small amount of a strong base Δb is added then the

new pH becomes $\text{pH}_2 = \text{p}K_a + \log \left(\frac{S + \Delta b}{a - \Delta b} \right)$, change in pH of the solution.

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1 = \log \frac{S + \Delta b}{a - \Delta b} - \log \frac{S}{a}$$

$$= \log_{10} \left(\frac{(S + \Delta b)a}{(a - \Delta b)S} \right) = \log_{10} \left(\frac{1 + \Delta b/S}{1 - \Delta b/a} \right) = \frac{1}{2.303} \ln \left(\frac{1 + \Delta b/S}{1 - \Delta b/a} \right)$$

$\therefore \frac{\Delta b}{S} \ll 1$ and $\frac{\Delta b}{a} \ll 1$

$$\Rightarrow \Delta \text{pH} = \frac{1}{2.303} \left(\frac{\Delta b}{S} + \frac{\Delta b}{a} \right) \Rightarrow \Delta \text{pH} = \frac{\Delta b}{2.303} \left(\frac{a + S}{a \times S} \right) \Rightarrow \frac{\Delta b}{\Delta \text{pH}} = 2.303 \times \left(\frac{a \times S}{a + S} \right)$$

(b) **Buffer Range:** The range of pH over which a buffer is most effective is termed as the buffer range.

- (i) An acidic buffer will be effective with the pH range ($\text{pK}_a - 1$) to ($\text{pK}_a + 1$), i.e., ($\text{pK}_a \pm 1$).
- (ii) A basic buffer will be effective over the pH range ($\text{pK}_w - \text{pK}_b \pm 1$).

Note:

To make a buffer solution of a given pH, first it is necessary to choose a weak acid or weak base whose pK_a or pK_b value is as close as possible to the required pH.

6.4.2.1 Salient features of buffer solutions

- (i) It has definite pH, i.e., it has reserve acidity or alkalinity.
- (ii) Its pH does not change on standing for long.
- (iii) Its pH does not change on dilution.
- (iv) Its pH is slightly changed by the addition of small amount of acid or base.
- (v) More efficient buffers are those which have pH between 3 and 11.
- (vi) No strong acid or base should remain till the end after their addition in a buffer solution.

6.4.2.2 Uses of buffer solution

- (a) Qualitative analysis of a mixture, e.g., removal of phosphate.
- (b) Industrial process such as manufacture of paper, dyes, inks, paints, drug, etc.
- (c) Digestion of food.
- (d) Preservation of foods and fruits.
- (e) Agriculture and dairy products preservations.

Blood as a Buffer Solution: The normal pH value of blood plasma is 7.4. Severe illness or death can result from sustained variations of a few tenths of a pH unit. Dissolved ratio of HCO_3^- to H_2CO_3 is helpful in controlling pH of blood.

6.5 VOLUMETRIC TITRATIONS

6.5.1 Indicators

An indicator is a substance which is used to determine the end point of a reaction or a substance which indicates the completion of a reaction.

The nature of an indicator depends upon the nature of a titrant used. There are many types of indicators known.

- (i) Acid-base indicators, e.g., phenolphthalein, methyl orange, etc.
- (ii) Redox indicators, e.g., KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc.
- (iii) Adsorption indicators, e.g., Starch paper with I_2 .

Acid-Base Indicators: An acid-base indicator is a substance which possesses one colour in acid solution and different colour in alkaline medium or the substances whose colour changes with change in pH.

6.5.2 Theory of Indicators

Ostwald Theory: According to this theory

- (i) Indicators are either weak acids or weak bases.
- (ii) Their unionized molecules possess different colour from those of the ions which they give in the solution.
- (iii) An acidic indicator yields a coloured anion while a basic indicator gives coloured cation in solution.
- (iv) Since they are weak electrolytes, they are not sufficiently ionized in solution. But in presence of strong acid or base, their degree of ionization is considerably high and they produce a large number of coloured ions.
- (v) An indicator changes colour when the concentration of $[\text{H}^+]$ in solution is equal to dissociation constant of the indicator, i.e., indicator is 50 per cent dissociated.

$$\text{pH} = \text{pK}_{\text{In}} + \log_{10} \frac{[\text{In}^-]}{[\text{HIn}]}$$

For a person to observe both colour of a solution, minimum change in pH must be equal to 2 units.

Range of Indicators: It is the range of pH in which indicator does not work.

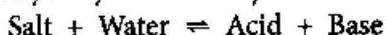
Lower and higher values of pH between which exact colour of indicator cannot be seen are known as range of indicator. Range of indicator is from $\text{pK}_{\text{In}} - 1$ to $\text{pK}_{\text{In}} + 1$.

6.6 SALT HYDROLYSIS

The phenomenon of the interaction of anions and cations of the salt with H^+ and OH^- ions furnished by water yielding acidic or alkaline (or sometimes even neutral) solutions is known as salt hydrolysis.

Salt are strong electrolytes, here when dissolved in water, they dissociate almost completely into cations and anions.

In salt hydrolysis, cation or anion or both of a salt react with water to produce acidity or alkalinity. The process of hydrolysis is actually the reverse of neutralization.

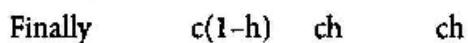
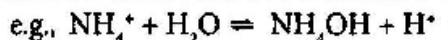


Note:

- Only that component of a salt can participate in hydrolysis which is derived from a weak electrolyte.
- The nature of a solution depends upon the component of a salt which is derived from a strong electrolyte.
- Depending on the nature of an acid or a base there can be four types of salts.

6.6.1 Salt of a Strong Acid and a Weak Base

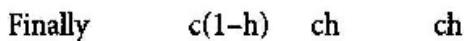
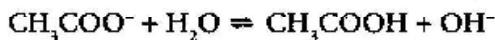
The cation of a salt which comes from a weak base take part in hydrolysis.



$$\Rightarrow \text{pH} = 7 - 1/2 \text{pK}_b - 1/2 \log c.$$

6.6.2 Salt of a Weak Acid and a Strong Base

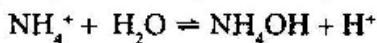
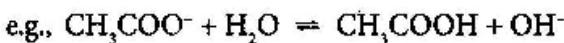
The anion of a salt which comes from a weak acid takes part in hydrolysis, e.g., CH_3COONa



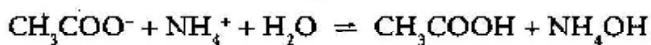
$$\Rightarrow \text{pH} = \text{pK}_a - \text{pOH} = 7 + 1/2 \text{pK}_a + 1/2 \log c$$

6.6.3 Salt of a Weak Acid and Weak Base

Both the anion and cation of a salt take part in hydrolysis



Combined these two, we get



$$\Rightarrow \text{pH} = 7 + 1/2 \text{pK}_a - 1/2 \text{pK}_b$$

6.6.4 Salt of a strong acid and a strong base

Salt of a strong acid and a strong base do not undergo hydrolysis because both the ions are not reactive.

Note:

Degree of hydrolysis always increases with increase in temperature because at elevated temperature, increase in K_w is greater as compared to K_a and K_b .

6.7 SOLUBILITY AND SOLUBILITY PRODUCT

6.7.1 Solubility Product

The solubility product of a sparingly soluble salt forming a saturated solution in water is given by the product of the concentrations of the ions raised to a power equal to the number of times of ions occur in the equation representing the dissociation of the electrolyte.

Considering a sparingly soluble salt, $A_m B_n \rightleftharpoons mA^{n+} + nB^{m-}$

$$K_{sp} = [A^{n+}]^m [B^{m-}]^n$$

If molar solubility of this salt is S moles/litre, then $K_{sp} = (ms)^m (ns)^n$

$$K_{sp} = (m^m n^n) s^{n+m}.$$

6.7.2 Applications of Solubility Product Principle

(a) Predicting Precipitation Reaction: A substance gets precipitated when the ionic product, i.e., the product of concentration of its ions present in a solution exceeds the solubility product of the substance. When

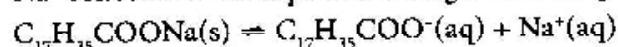
- (i) Ionic product (IP) $> K_{sp}$; Precipitation takes till IP equals K_{sp} .
- (ii) Ionic product (IP) $< K_{sp}$; A precipitate will not be formed and the solution will be unsaturated.
- (iii) Ionic product (IP) $= K_{sp}$; A precipitate will not form and the solution is saturated in that salt.

(b) Preferential Precipitation of an Insoluble Salt: It can be explained on the basis of their respective solubility product. As a rule, the compound with the lower solubility product get precipitated in preference.

Since K_{sp} of AgI $< K_{sp}$ of AgCl

\therefore AgI gets precipitated in preference to AgCl.

(c) Salting out of Soap: The saturated solution of soap ($RCOONa$), the sodium salt of higher fatty acids show precipitation of soap on addition of NaCl. This is because of the fact that an increase in Na^+ concentration helps in crossing over ionic product to their K_{sp} value.



$$K_{sp} = [C_{17}H_{35}COO^-][Na^+].$$

When NaCl is added, $[Na^+]$ increases due to which ionic product also increases which results in precipitation of soap:

(d) Cationic analysis: Cation analysis is based on the principle of K_{sp} and common ion effect.

The decrease in the ionization (solubility) of a weak electrolyte in the presence of a common ion from a strong electrolyte is called common ion effect, e.g., ionization of H_2S (weak acid) decreases in presence of HCl (H^+ is the common ion).

Group I: Cations (Ag^+ , Hg_2^{2+} , Pb^{2+}) are precipitated as chlorides since their K_{sp} values are low.

Group II: Cations (Pb^{2+} , Cu^{2+} , Cd^{2+} , Hg^{2+} , Bi^{3+} , Sb^{3+}) are precipitated as their sulphides since their IP values are decreased due to low $[S^{2-}]$ because of common ion effect.

Group III: Cations (Al^{3+} , Fe^{3+} , Cr^{3+}) are precipitated as their hydroxides, since their IP values are decreased by the addition of NH_4Cl to NH_4OH .

Group IV: Cations (Zn^{2+} , Mn^{2+} , Ni^{2+}) are precipitated as their sulphides, since their IP values are decreased due to increased $[S^{2-}]$ because of common ion effect.

(i) CH_3COONa , $NaCN$, Na_2CO_3 , Na_3PO_4 , etc.

(ii) NH_4Cl , $CuSO_4$, $Al(NO_3)_3$, NH_4NO_3 , etc.

(iii) CH_3COONH_4 , $Mg(CN)_2$, $CaCO_3$, $(NH_4)_3PO_4$, etc.

SOLUTION AND COLLIGATIVE PROPERTIES**7.1 DEFINITION**

A solution is defined as a homogeneous mixture of two or more components having uniform properties throughout and constitute a single phase.

7.1.1 Components of a Solution

Solutions have two components.

- (i) **Solute:** Component of a solution which is present in a small amount is known as a solute.
- (ii) **Solvent:** Component of a solution which is present in a large amount and is present in same physical state as a solution will be known as a solvent.

7.2 CONCENTRATION MEASUREMENT UNITS

Concentration measurements units are of two types.

- (i) Volume independent concentration measurement units
 - (a) Weight fraction and weight percentage:

$$\text{Weight fraction } (\omega) = (\omega) = \frac{W}{W}$$

$$\text{Weight percentage} = \omega \times 100$$

- (b) Mole fraction and mole percentage:

$$\text{Mole fraction of A } (x_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole percentage} = X_A \times 100$$

- (c) **Molality:** It is the number of moles of a solute dissolved in 1 kg of a solvent.

$$m = \frac{W_B}{M_B \times W_A} \times 1000 \text{ moles kg}^{-1} \text{ i.e., molal}$$

(ii) Volume dependent concentration measurement units

(a) Volume fraction and volume percentage:

$$(i) \text{ For a solid in liquid \% by volume} = \frac{\text{Wt. of solute}}{\text{Volume of solution}} \times 100$$

$$(ii) \text{ For a liquid in liquid and gas in gas, \% by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

(b) **Molarity:** It is the number of moles of a solute dissolved in one litre of a solution. It is represented by M.

$$M = \frac{w_B}{M_B \times V} \times 1000 ; V \text{ is volume of the solution in ml, } n \text{ is the number of moles of solute, } w_B \text{ is}$$

the weight of solute in grams and M_B is the molecular mass of the solute.

(c) **Normality:** It is defined as the number of gram equivalent of a solute present in one litre of a solution.

$$N = \frac{\text{gm equivalent of solute}}{\text{volume of solution in litre}} = \frac{w}{E V}$$

where w = Wt. of the solute; E = equivalent weight and V = Volume of the solution in litre.

(d) **Strength:** Amount of solute in grams present in 1 litre of a solution

$$\Rightarrow S = \frac{w}{V} ; \text{ where } w = \text{weight of solute in gm and } V = \text{volume of the solution in litre.}$$

(e) **Formality:** It is the number of formula units of an ionic species present in one litre of a solution and it is represented by (F).

$$F = \frac{\text{Number of formula mass of ion}}{\text{Volume of solution in litre}}$$

(f) **Parts per million (ppm):** Number of parts by mass of solute per 10^6 parts of the solution.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

$$\text{ppb} = \frac{\text{amount of solute in gram}}{\text{amount of solution in gram}} \times 10^9$$

$$\text{ppt} = \frac{\text{amount of solute in gram}}{\text{amount of solution in gram}} \times 10^{12}$$

7.2.1 Relationship between various concentration measurement units

$$\Leftrightarrow N = M \times n - \text{factor}$$

$$\Leftrightarrow \frac{X_A}{X_B} = \frac{m \cdot M_B}{1000}$$

$$\Leftrightarrow N = \frac{x \times d \times 10}{E_A}$$

$$\Leftrightarrow M = \frac{x \times d \times 10}{M_A}$$

$$\Leftrightarrow S = M \times M_A$$

$$\Leftrightarrow m = \frac{1000M}{1000d - MM_A}$$

where N is normality; M is molarity; m is molality; d is density in g/ml; x is % by mass of solute

M_A is molecular mass of solute; E_A is equivalent weight of solute and S is strength of solution in g/litre.

7.3 SOLUBILITY

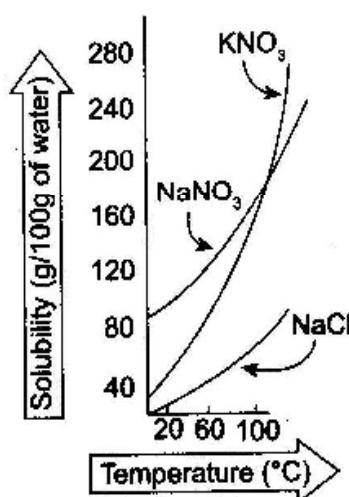
The solubility of a solid in a liquid depends upon 'lattice energy' and 'hydration energy'. Lattice energy is the amount of energy required to dissociate one mole of an ionic crystal into its ions. Hydration energy is the amount of energy released when one mole of ions undergo hydration. If hydration energy > lattice energy, the solid dissolves otherwise not.

$$\Leftrightarrow m = \frac{S \times 10}{M_A}, \text{ where } S \text{ is solubility.}$$

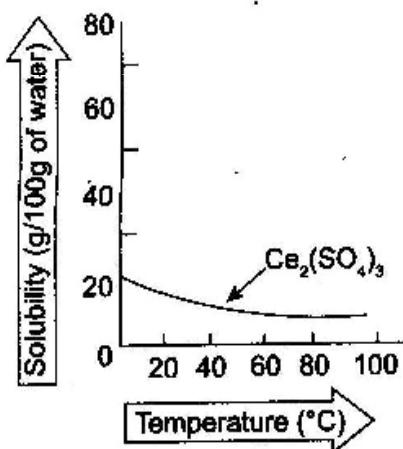
\Leftrightarrow Solubility is the maximum amount of solute dissolved in 100 g of the solvent.

7.4 FACTORS AFFECTING SOLUBILITY OF GASES IN LIQUID

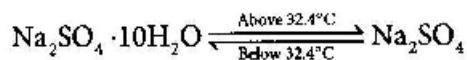
- (a) **Nature of the gas:** More liquefiable gases possess higher solubility.
- (b) **Nature of the solvent:**
- (c) **Effect of Temperature:** On the basis of the effect of temperature on solubility in water, the various ionic substances are divided into three categories.
 - (a) Those whose solubility increases continuously with increase of temperature.
For example, NaNO_3 , KNO_3 , NaCl , etc.



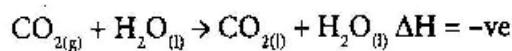
- (b) Those whose solubility decreases continuously with increase of temperature. For example, cerium sulphate, lithium carbonate, sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), etc.



(c) Those substances whose solubility does not increase or decrease continuously. There are some substances which on heating change at a particular temperature from one polymorphic form to another (like α to β -form as in the case of ammonium nitrate) or from one hydrated form to another (like $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{CaCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) or from hydrated to anhydrous form (e.g., $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4$) Such substances do not show a continuous increase or decrease of solubility. For example, in case of sodium sulphate, the solubility first increases up to 32.4°C and then begins to decrease. The temperature at which one form of the substance changes into another is called transition temperature. Thus, in case of sodium sulphate,



On increasing temperature, solubility of a gaseous solute in liquid decreases



Clausius–Clapeyron Equation: $\log_{10}\left(\frac{S_2}{S_1}\right) = \frac{\Delta H_{\text{soln}}}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

where S_1 and S_2 are solubilities of gas at temperature T_1 and T_2 .

(d) **Effect of Pressure:** The relationship between the solubility and pressure is given by Henry's law.

Henry's Law: The solubility of a gas at a given temperature is directly proportional to the pressure of the gas in equilibrium with the liquid at that temperature

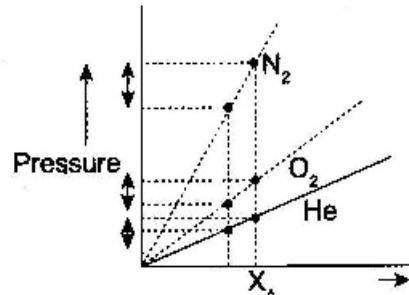
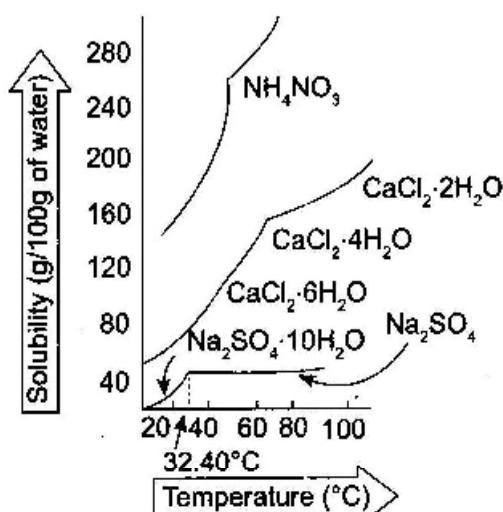
$$\Rightarrow S \propto P \Rightarrow S = kP$$

Alternatively, mole fraction of the gas dissolved in the solution is directly proportional to the partial pressure of the gas over the solution $P_{\text{gas}} \propto X_{\text{gas}}$

$$\Rightarrow P_A = K_H X_A$$

where K_H is known as Henry's constant. Its unit is the unit of pressure. The value of K_H depends only on temperature as its value increases with temperature.

As the liquification tendency of a gas increases, its solubility in liquid also increases.



7.4.1 Applications of Henry's Law

- (i) High pressured bottles of soft drinks and soda water.
 - (ii) Deep sea divers dilute O_2 with He instead of N_2 because of less solubility of He in blood over N_2 at high pressure.
 - (iii) Storage of acetylene in acetone.
- Vapour pressure is independent from volume and surface area of a container.

7.4.2 Limitations of Henry's Law

- (i) The pressure is not too high.
- (ii) The temperature is not too low.
- (iii) The gas is not highly soluble and does not participate into chemical combination with the solvent.
- (iv) The gaseous molecule do not dissociate or associate during the process.

7.5 VAPOUR PRESSURE

The vapour pressure or saturated vapour pressure is defined as the pressure exerted by the vapours of a solvent when they are in dynamic equilibrium with its liquid at a given temperature.

7.5.1 Factors Affecting Vapour Pressure

- (i) **Temperature:** The vapour pressure increases non-linearly with increasing temperature.
- (ii) **Nature of solvent:** A solvent with higher boiling point, i.e., one having higher attraction among their molecules (i.e., high Van der Waal's constant) possesses less tendency for evaporation and thus has low vapour pressure.
- (iii) **Addition of a non-volatile solute:** A non-volatile solute added to the liquid solution reduces the capacity of the solvent molecules to move from liquid phase to gas phase as it occupies a part of surface area available for evaporation. So, rate of evaporation decreases due to which vapour pressure decreases.

7.5.2 Ideal and non-ideal solution

An **ideal solution** of the components A and B is defined as the solution in which the intermolecular interactions between A and B are of the same magnitude as between the pure components or it is a solution in which there is no volume change and enthalpy change on mixing ($\Delta V_{\text{mixing}} = 0$, $\Delta H_{\text{mixing}} = 0$) or it is a solution in which each component obeys Raoult's law at all temperatures and concentrations.

7.5.3 Raoult's law

The partial pressure of any volatile component at a given temperature is directly proportional to the mole fraction of a component present in the solution. If p_A is the partial pressure of component A

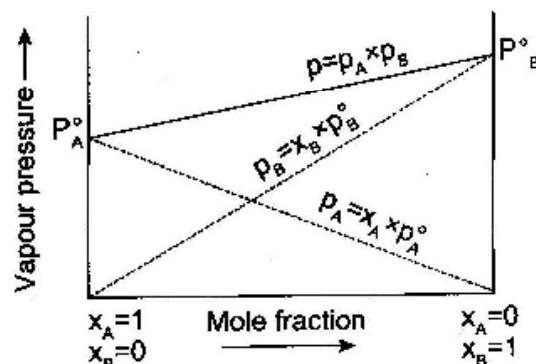
$$\Rightarrow p_A = X_A P_A^\circ \quad \text{and} \quad p_B = X_B P_B^\circ$$

Raoult's law in terms of mole fraction of a liquid: If the vapour of a liquid behaves like an ideal gas, then according to Dalton's law of partial pressures, the total vapour pressure P is given by $P = x_A p_A^\circ + x_B p_B^\circ \Rightarrow P = p_B^\circ + x_A (p_A^\circ - p_B^\circ)$.

If A is a more volatile component, then the composition of the liquid and vapour that are in mutual equilibrium is not necessarily the same.

Let the mole fractions of vapours A and B be y_A and y_B , respectively. Let p_A and p_B be the partial pressures of vapours A and B, respectively and total pressure P.

$$\Rightarrow \frac{1}{P} = \frac{y_A}{p_A^\circ} + \frac{y_B}{p_B^\circ}$$



Non-ideal solution: The solutions which deviates from ideal behaviour are called non-ideal solutions or real solutions.

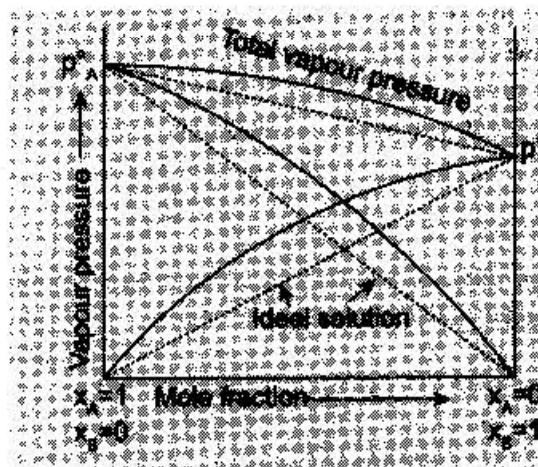
For non-ideal solutions

1. Raoult's law is not obeyed.
2. $\Delta H_{\text{mixing}} \neq 0$.
3. $\Delta V_{\text{mixing}} \neq 0$.

Positive Deviation from Raoult's law

- (i) $\Delta H_{\text{mix}} > 0$, i.e., heat is absorbed.
- (ii) $\Delta V_{\text{mix}} > 0$, i.e., volume is increased after dissolution.
- (iii) For a binary solution having component (A + B). $p_A > p^\circ_A X_A$ and $p_B > p^\circ_B X_B$

$$p > p^\circ_A X_A + p^\circ_B X_B$$
- (iv) Attractive force between A - B should be weaker than A - A and B - B.
- (v) Escaping tendency of both components A and B is high, so vapour pressure is higher than the expected.
- (vi) Plot between vapour pressure and mole fraction.

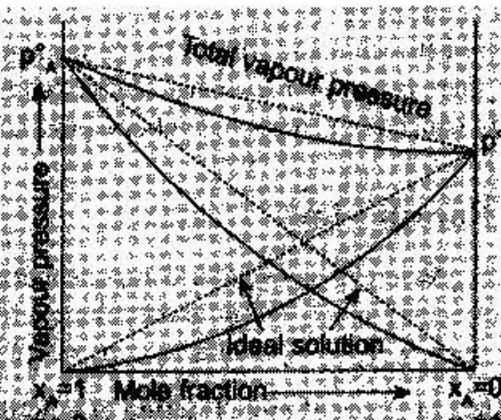


e.g., acetone + ethanol; acetone + CS_2 ; H_2O + methanol; H_2O + ethanol; CCl_4 + toluene; CCl_4 + CHCl_3 ; acetone + C_6H_6 ; CCl_4 + CH_3OH ; cyclohexane + ethanol.

Negative Deviation from Raoult's law

- (i) $\Delta H_{\text{mix}} < 0$, i.e., heat is evolved.
- (ii) $\Delta V_{\text{mix}} < 0$, i.e., volume is decreased during dissolution.
- (iii) For a binary solution having component (A + B). $p_A < p^\circ_A X_A$ and $p_B < p^\circ_B X_B$

$$\Rightarrow p < p^\circ_A X_A + p^\circ_B X_B$$
- (iv) Attractive force between A - B should be stronger than A - A and B - B.
- (v) Escaping tendency of both components A and B is low, so vapour pressure is lower than the expected.
- (vi) Plot between vapour pressure and mole fraction.



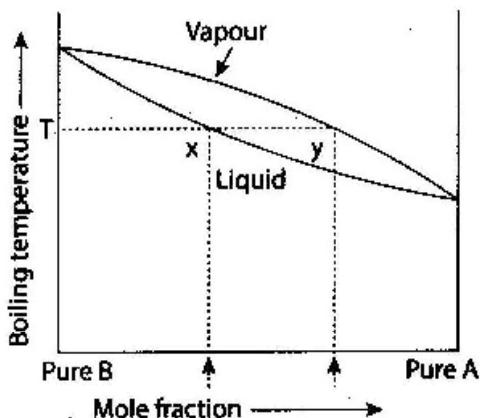
e.g., acetone + aniline; acetone + CHCl_3 ; CH_3OH + CH_3COOH ; H_2O + HNO_3 ; CHCl_3 + diethyl ether; water + HCl ; CH_3COOH + pyridine; Chloroform + benzene.

7.5.4 Fractional Distillation

The process of separation of one liquid from another liquid having different boiling point by distillation is termed fractional distillation. The separation is possible only when the vapour phase has a composition different from that of the boiling liquid mixture.

Note:

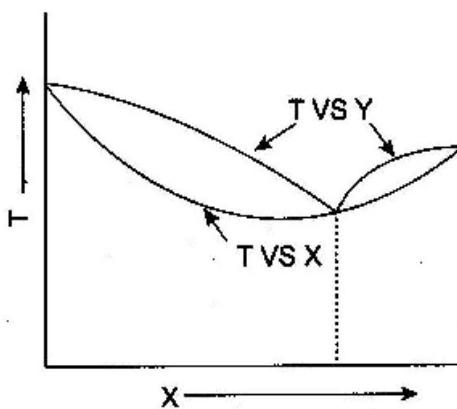
$T \times y$ is known as tie line at which, a liquid with composition x will be in equilibrium with a vapour of composition y at the temperature T .



Azeotropic mixture: For a non-ideal solution there does exist a composition at which equilibrium composition of vapour and liquid becomes same. This mixture is called azeotropic mixture. At this point, distillation becomes useless because no separation is possible. Azeotropic mixtures have a constant boiling point. Azeotropic mixtures are of two types.

- (i) Minimum boiling azeotropic mixture and
- (ii) Maximum boiling azeotropic mixture

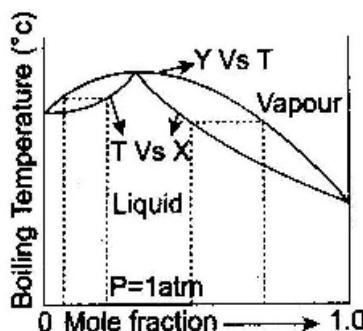
(i) **Minimum boiling azeotropic mixture:**



- e.g., (a) water-ethanol mixture (95.6 per cent ethanol) at 78.15°C
- (b) pyridine-water mixture (57 per cent pyridine) at 92.6°C
- (c) Ethanol-benzene mixture (32.4 per cent ethanol) at 67.8°C
- (d) Acetic acid-toluene mixture (28 per cent acetic acid) at 105.4°C.

(ii) **Maximum boiling azeotropic mixture.**

- e.g., (a) Nitric acid-water mixture (68 per cent nitric acid) at 125.5°C
- (b) Acetic acid-pyridine mixture (65 per cent pyridine) at 139.0°C
- (c) Chloroform-acetone mixture (80 per cent chloroform) at 65.0°C
- (d) Hydrochloric acid-water mixture (79.8 per cent water) at 108.6°C



7.6 COLLIGATIVE PROPERTIES

Colligative properties are those which depend entirely upon the number of particles of the solute contained in a known volume of a given solvent and not at all upon the nature (i.e., chemical composition) of the solute.

The various colligative properties are:

- (i) Relative lowering in vapour pressure.
- (ii) Osmotic pressure
- (iii) Elevation in boiling point.
- (iv) Depression in freezing point.

In colligative properties solute is invariably taken as non-volatile. Colligative properties are essentially the properties of the dilute solutions, i.e., ideal solutions.

Relative Lowering in Vapour Pressure

According to Raoult's law, 'The relative lowering in vapour pressure of a dilute solution is equal to mole fraction of the solute present in the solution.'

If n is the number of moles of a solute and N is the number of moles of the solvent,

$$\text{then, from Raoult's law, } \frac{P_0 - P_s}{P_0} = \frac{n}{n + N} = X_{\text{solute}}.$$

If m is the molality of the solution and M_2 is the molecular mass of the solvent, then for a dilute solution,

$$\frac{P_0 - P_s}{P_0} = X = \frac{mM_2}{1000}; \text{ where } X \text{ is the mole fraction of the solute.}$$

Experimental determination of relative lowering in vapour pressure

- (i) **Static method:** In this method, differential manometer is used.
- (ii) **Dynamic method:** This method is also known as Ostwald and Wacker method.

7.7 OSMOTIC PRESSURE

Osmosis is defined as the spontaneous flow of solvent molecules through a semi-permeable membrane from a pure solvent to a solution or from a dilute to a concentrated solution.

'The extra pressure developed on the solution side as a result of the solvent flow is called osmotic pressure'. It is represented by π .

(a) Determination of osmotic pressure

- (i) **Berkeley and Hartley's method:** The best known method for measurement of osmotic pressure was given by Berkeley and Hartley. In this method, a porcelain tube containing copper ferrocyanide membrane in its walls is enclosed in a metallic jacket. This technique permits quick determinations of osmotic pressure. Here instead of measuring developed as a result of the entry of the solvent into the solution gradually increasing pressure is applied on the solution itself and the pressure which is just enough to prevent the entry of the solvent into the solution is known as osmotic pressure.

- (ii) Townsend's porous disc method
 - (iii) Morse and frazer's method
- (b) 1. Comparison of solutions in terms of osmotic pressure:
- (i) Hypotonic solution: A solution of low osmotic pressure is termed a hypotonic solution.
 - (ii) Hypertonic solution: A solution of high osmotic pressure is termed a hypertonic solution.
 - (iii) Isotonic solution: Solutions having same osmotic pressures are termed isotonic solutions.
2. Biological importance of osmosis:
- (i) The pressure developed inside a cell due to the inflow of water is called turgor.
 - (ii) If the cell comes in contact with a solution of higher osmotic pressure, the cell would shrink due to flow of water from the cell through the cell membrane. This shrinking of the cell is called plasmolysis or crenation (Osmotic Pressure (π) = CRT, where C is the molar concentration).

7.7.1 Applications of Osmotic Pressure

Osmosis is the phenomenon in which there is a net flow of solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semi-permeable membrane.

Osmotic pressure is the equilibrium hydrostatic pressure of the column set up as a result of osmosis or it is the minimum pressure that must be applied on the solution to prevent the entry of the solvent into the solution through the semi-permeable membrane.

Molecular masses of polymers are best determined by osmotic pressure method firstly because other colligative properties give so low values that they cannot be measured accurately and secondly, osmotic pressure measurements can be made at room temperature and do not require heating which may change the nature of the polymer.

7.8 ELEVATION IN BOILING POINT

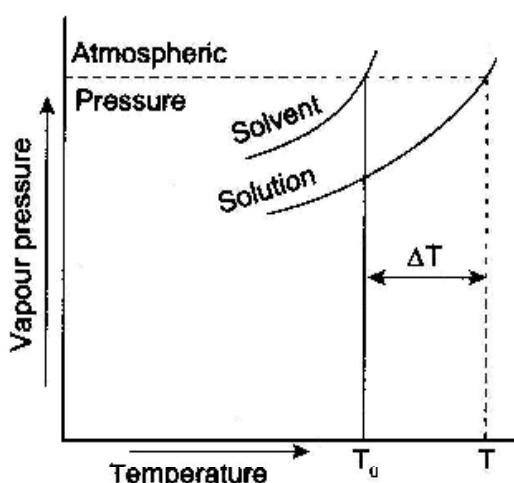
The boiling point (T_b) of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. When a non-volatile solute is added to a liquid, the vapour pressure of the liquid is decreased. Hence, it must be heated to a higher temperature in order that its vapour pressure becomes equal to that of the atmospheric pressure.

Elevation of boiling point (ΔT_b) = Boiling point of the solution(T_b) – Boiling point of pure solvent (T_b^o).

$\Delta T_b = K_b \times m$; K_b is also known as ebullioscopic constant.

Method for the determination of elevation of boiling point is known as ebullioscopy.

$$K_b = \frac{RT_b^{o2}}{1000L_v} \text{, where } L_v \text{ is the latent heat of vapourization per gram of the solvent.}$$



7.9 DEPRESSION IN FREEZING POINT

Freezing point of a substance is defined as the temperature at which the vapour pressure of the liquid is equal to the vapour pressure of the corresponding solid.

When a non-volatile solute is added to a liquid, the escaping tendency of solvent molecules from liquid to solid phase diminishes, whereas the reverse escaping tendency from solid to liquid phase remains unaffected.

Depression in freezing point (ΔT_f) = freezing point of the solvent-freezing point of the solution.

$$\Delta T_f = K_f m; K_f = \frac{RT_f^{2/3}}{1000L_f} \text{ where } k_f \text{ is also known as cryoscopic constant.}$$

7.10 ABNORMAL COLLIGATIVE PROPERTIES

When the molecular mass of a substance is determined by using colligative properties, does not come out to be same as expected theoretically, it is said to show abnormal molecular mass.

Abnormal molecular mass is obtained when the substance in the solution undergoes dissociation (e.g., NaCl in water) or association (e.g., organic acids in benzene). Dissociation results in the increase in the number of particles and hence increase in the value of colligative property and decrease in the molecular mass. Association results in the reverse.

7.10.1 Van't Hoff Factor

This is the ratio of the experimental value of the colligative property to the calculated value of the colligative property, i.e.,

$$\text{As molecular mass} \propto \frac{1}{\text{Colligative property}}$$

$$i = \frac{\text{Experimental value of the colligative property}}{\text{Calculated value of the colligative property}}; i = \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}} = \frac{M_c}{M_o}$$

Modified formulae for substances undergoing dissociation or association in the solution are

$$\Delta T_b = iK_b m; \Delta T_f = i K_f m \text{ and } \pi = i c RT$$

7.10.2 Degree of Dissociation

If one molecule of a substance A dissociates to form n molecules or ions and α is the degree of dissociation, then starting with one mole of A



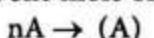
$$t = 0 \quad 1 \text{ mole} \quad 0$$

$$t = t_{eq} \quad 1 - \alpha \quad n\alpha$$

$$\text{Total number of moles at equilibrium} = 1 - \alpha + n\alpha$$

$$i = \frac{1 - \alpha + n\alpha}{1} \quad \text{or} \quad \alpha = \frac{i - 1}{n - 1}$$

In n molecules of a substance A associate to form A_n and α is the degree of association then starting with one mole of A



$$t = 0 \quad 1 \text{ mole} \quad 0$$

$$t = t_{eq} \quad 1 - \alpha \quad \alpha/n$$

$$\text{Total number of moles at equilibrium} = 1 - \alpha + \frac{\alpha}{n}$$

$$i = \frac{1 - \alpha + \frac{\alpha}{n}}{1} \quad \text{or} \quad \alpha = (1 - i) \frac{n}{n - 1}$$

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(National or Local Level)
In a question
of JEE-Advanced 2014
and finally
winning through
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SOLID STATE**8.1 DEFINITION**

The solid state represents the physical state of matter in which the constituent molecules, atoms or ions have no translatory motion although they vibrate about the fixed position that they occupy in a crystal lattice.

8.2 CLASSIFICATION OF SOLIDS

They are of two types: Crystalline and Amorphous solids

8.2.1 Comparative Study Between Crystalline and Amorphous Solids

S. No.	Property	Crystalline solids	Amorphous solids
1	Shape	They have definite and regular geometrical form	They do not have definite and regular geometrical form. They are considered as super cooled liquid.
2	Melting point	They have definite and sharp melting point	Gradually softer over a range of temperature
3	Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion
4	Compressibility	They are rigid and incompressible	They may be compressed to any appreciable extent.
5	Cutting with a tool	They can break into two pieces with plane and smooth surface	They can break into two pieces with irregular surface
6	Range order	They have a long-range order in terms of arrangement of constituents	They have a short-range order

S. No.	Property	Crystalline solids	Amorphous solids
7	Isotropy and anisotropy	They are anisotropic in nature	They are isotropic in nature
8	Examples	Quartz, diamond, NaCl, KCl, etc.	Glass, rubber, plastics, etc.

8.2.2 Classification of Crystalline Solid

S. No.	Types of solids	Constituent particles	Bonding/ attractive forces	Examples	Physical nature	Electrical conductivity	Melting point
1.	Molecular solid						
	(i) Non-polar Molecules		Dispersion forces	Ar, CCl ₄ , H ₂ , I ₂ , CO ₂	Soft	Insulator	Very low
	(ii) Polar		Dipole-dipole interactions	HCl, SO ₂	Soft	Insulator	Low
	(iii) Hydrogen bonding		Hydrogen bonding	H ₂ O (ice)	Hard	Insulator	Low
2.	Ionic solid	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
3.	Metallic solids	Positive ions in a sea of delocalized electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
4.	Covalent or network solids		Covalent bonding	SiO ₂ (quartz), SiC (diamond), AlN, C ₆₀ (graphene)	Hard and soft	Insulator and conductor (exception)	Very high

1. By heating and cooling, amorphous solid acquires some crystalline characteristic; due to this fact, old window glass panels look milky.
2. Amorphous solids show fluidity under the influence of gravity; due to this fact, old window glass panels become thick at the bottom.
3. Amorphous silicon is one of the best photovoltaic material used for converting sunlight into electricity. nm

8.3 ANALYSIS OF CRYSTALLINE SOLID

8.3.1 Crystal

A regular arrangement of the constituent particles of a crystal in the three-dimensional space is called crystal lattice or space lattice.

Unit cell: The smallest three-dimensional portion of the space lattice which when repeated over and over again in different directions produces the complete space lattice is called the unit cell.

8.3.2 Types of Unit Cells

- (i) **Simple.** Here, the particles are present only on the corners. It is represented by P.
- (ii) **Face-centred.** Here in addition to the particles on the corners, there is one particle present on the centre of every face. It is represented by F.
- (iii) **End centred.** Here in addition to the particles on the corners, there is one particle in the centre of two opposite faces. It is represented by C.
- (iv) **Body-centred.** Here in addition to the particles on the corners, there is one particle present with in the body of the unit cell. It is represented by I.

8.3.3 Types of Crystal system and Bravais Lattice

S. No.	System	Length Parameter	Angle Parameter	Bravais Lattice	Examples
1.	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	P,I,F	NaCl, KCl, ZnS, diamond, alums, CaF ₂ , Pb, Ag, Hg.
2.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P,I,F,C	KNO ₃ , BaSO ₄ , K ₂ SO ₄ , rhombic sulphur, PbCO ₃
3.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P,I	TiO ₂ , PbWO ₄ , SnO ₂ , NH ₄ Br, NiSO ₄
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	P,C	Monoclinic sulphur, KCIO ₃ , CaSO ₄ ·2H ₂ O, Na ₂ B ₄ O ₇ ·10H ₂ O, Na ₂ SO ₄ ·10H ₂ O
5.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	P	CuSO ₄ ·5H ₂ O, H ₃ BO ₃ , K ₂ Cr ₂ O ₇
6.	Hexagonal	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 120^\circ$	P	ZnO, CdS, HgS, SiC, AgI, PbI ₂ , Mg, graphite
7.	Rhombohedral or Trigonal	$a=b=c$	$\alpha = \beta = \gamma \neq 90^\circ$	P	NaNO ₃ , ICl, quartz, CaCO ₃

8.4 BRAGG'S EQUATION

$$2d \sin \theta = n \lambda$$

where d = distance between successive atomic planes

θ = angle of the incident X-rays with the crystal surface i.e., glancing angle

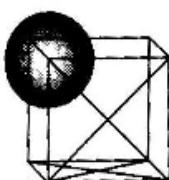
λ = wavelength of the X-rays used

$n = 1, 2, 3, \dots$ called the order of diffraction

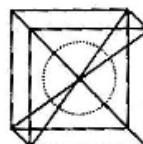
Note:

The diffracted beam makes an angle of 2θ with the direction of the incident beam.

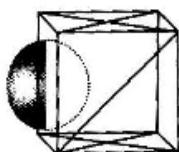
8.5 LATTICE POINT AND THEIR CONTRIBUTION PER UNIT CELL



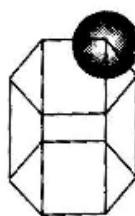
Corner; contribution = 1/8



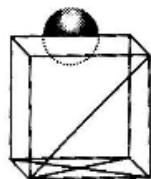
Body centre; contribution = 1



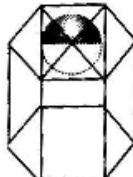
Face centre ; contribution = 1/2



Corner of HCP; contribution = 1/6



Edge centre ; contribution = 1/4



Face centre of HCP; contribution = 1/2

Note:

Number of atoms present per unit cell is called rank of unit cell.

8.6 ANALYSIS OF BRAVAIS LATTICES BELONGING TO CUBIC SYSTEM

In cubic arrangement, three kinds of Bravais lattices are there.

- (i) **Primitive or simple cubic lattice:** In a simple cubic lattice, constituents are present only at the corner of each unit cell. Let the length of edge of cube is a and radius of each atom is r .

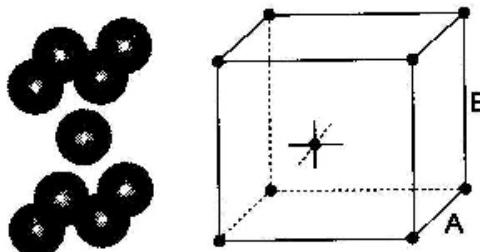
Therefore, radius of atom (r) = $a/2$

Rank of unit cell = $8 \times 1/8 = 1$

Percentage occupied space = 52.4 per cent

(ii) **Body centered cubic (BCC) lattice:**

In a body centered cubic lattice arrangement, constituents are present at the corners as well as at the centre of each cube.



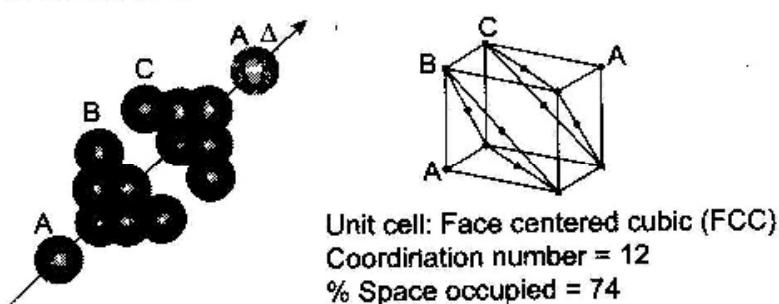
$$\text{Therefore, radius of atom } r = \frac{a\sqrt{3}}{4}$$

$$\text{Rank of unit cell} = 8 \times \frac{1}{8} + 1 \times 1 = 2$$

Percentage occupied space = 68 per cent

(iii) **Face centered cubic (FCC) lattice:**

In a face centered cubic arrangement, constituents are present at the corners as well as at the centre of each of the six faces of the cube.



$$\text{Therefore, radius of atom } (r) = a/2\sqrt{2}$$

$$\text{Rank of unit cell} = 8 \times 1/8 + 6 \times 1/2 = 4$$

Percentage occupied space = 74 per cent

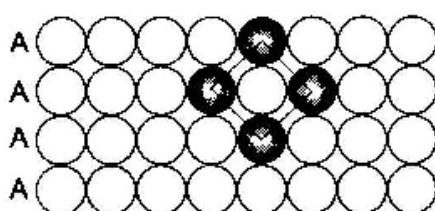
8.7 CLOSEST PACKING OF SPHERE

In crystals, the atoms, ions or molecules are arranged in a regular way in three-dimensional space. The arrangement has minimum energy and hence, maximum stability. For maximum stability a constituent in the aggregate must be surrounded by the maximum of neighbours. This is called the close packing.

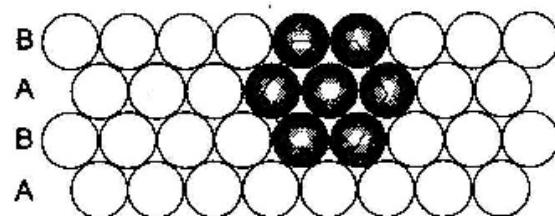
In a two-dimensional plane, each sphere is in contact with six other spheres (all are uniform in size) in close packing. Let us denote this layer of spheres by A. Around a sphere x, six vacant sites are leveled as 1, 2, 3, 4, 5 and 6. Let us denote the second layer of spheres by B. We can prepare the second layer by putting spheres either on vacant sites 1, 3, 5 or on vacant sites 2, 4 and 6.

Two dimensional bravais lattices passes five types of unit cell such as square, rectangular, parallelogram, hexagonal and rhombic.

8.7.1 Two-dimensional lattice

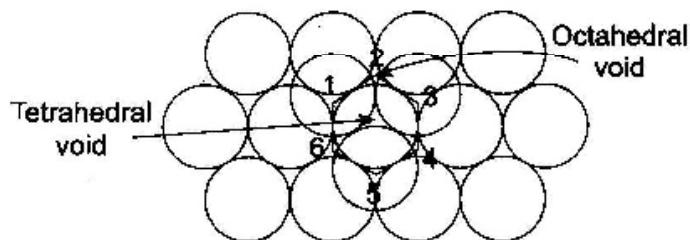


Square closed packing



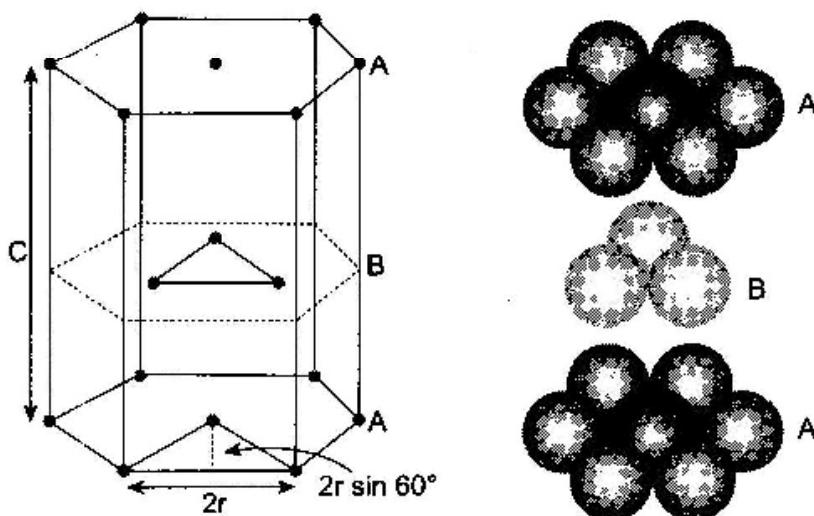
Hexagonal closed packing

8.7.2 Three-dimensional lattice



8.8 HEXAGONAL CLOSED-PACKED STRUCTURE

In this arrangement constituents are present at corner and at face centre and three constituents are present at midway of unit cell in the form of an equilateral triangle.



$$\text{Rank of unit cell} = 12 \times \frac{1}{6} + 2 \times \frac{1}{2} + 3 \times 1 = 6; \quad \text{Number of octahedral void/unit cell} = 6$$

$$\text{Number of tetrahedral void/unit cell} = 12; \quad \text{Volume of unit cell} = \text{Base area} \times \text{height of unit cell}$$

$$\text{Base area} = 6\sqrt{3}r^2;$$

$$\text{Height of unit cell} = 4 \times \sqrt{\frac{2}{3}} \times r$$

$$\text{Volume of unit cell} = 24\sqrt{2}r^3;$$

$$\text{Packing fraction} = 74 \text{ per cent}$$

Layered structure ABABAB.....type;

e.g., He, H₂, Cr, Be, Mg, Ca, Mo, V, Zn, Co, Cd, etc.

8.9 ANALYSIS OF VOIDS

8.9.1 Coordination Number

It is defined as the number of nearest neighbours that an atom has in a unit cell. In a crystal, there exists two types of coordination number.

1. Primary coordination number

2. Secondary coordination number

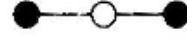
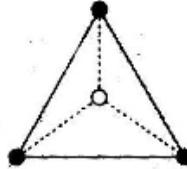
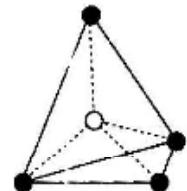
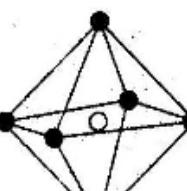
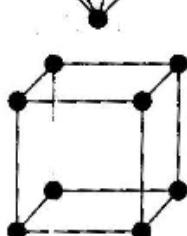
8.9.2 Primary Coordination Number.

Number of nearest oppositely charged constituents in surrounding of a given constituent is called primary coordination number. Primary coordination number depends upon the type of voids present inside the crystal which inturn is governed by the radius ratio value.

8.10 RADIUS RATIO

An ionic compound will have more stability if each cation is surrounded by maximum anions and vice versa because the magnitude of electrostatic force of attraction will be maximum. The number of oppositely charged ions surrounding each ion is known as coordination number and it depends upon the size of cation and anion or the ratio of their radii which is known as radius ratio.

$$\text{Radius ratio} = \frac{\text{Radius of cation} (r_+)}{\text{Radius of anion} (r_-)}$$

Primary Co-ordination Number	Radius Ratio r^+/r^-	Type of Void	Geometry
2	0-0.155	Linear	
3	0.155-0.225	Triangular	
4	0.225-0.414	Tetrahedral	
6	0.414-0.732	Octahedral	
8	0.732-1.0	Cubic	

8.10.1 Secondary Coordination Number

Number of nearest like constituents in surrounding of a given constituent is called secondary coordination number. Secondary coordination number depends upon the type of Bravais lattice present.

Unit Cell	Secondary Coordination Number
Simple cubic	6
Body centered cubic	8
Face centered cubic	12
Hexagonal closed packed	12

8.11 DENSITY OF SOLID

$$\rho = \frac{Z \times M}{a^3 \times N_A \times 10^{-30}} \text{ g/cm}^3$$

where Z = No. of atoms present per unit cell

M = Atomic mass of the element

a = Edge of the cubic crystal in pm.

N_A = Avogadro's number

8.12 ANALYSIS OF VARIOUS IONIC STRUCTURES

S. No.	Types of Crystal Structure	Brief Description	Examples	Co-ordination Number	Rank of Crystal	% Occupied Space
Type AB (i) type	Rock salt (Cl) has FCC arrangement in which sodium ions (Na^+) occupy all the octahedral sites	Chloride ions (Cl^-) has FCC arrangement in which sodium ions (Na^+) occupy all the octahedral sites	Halides of Li, Na, K, Rb, AgF , AgBr , NH_3 , NH_4Cl , NH_4Br , NH_4I oxides and sulphides of alkaline earth metal except BeO and BeS.	$\text{Na}^+ = 6$ $\text{Cl}^- = 6$	4	79.34%
(ii)	Caesium chloride type	Chloride ions (Cl^-) adopts a simple cubic lattice in which caesium ions (Cs^+) are present at body centres (cubic sites)	CsCl , CsBr , CsI , CsCN , TlCl , TlBr , TlI , TlCn , TlCl , TlBr , TlI	$\text{Cs}^+ = 8$ $\text{Cl}^- = 8$	1	72.93%

S. No.	Types of Crystal Structure	Brief Description	Examples	Co-ordination Number	Rank of Crystal	% Occupied Space
(iii)	Zinc blende type	Sulphide ions (S) adopts a FCC arrangement in which zinc ions (Zn) are present in alternative tetrahedral sites.	CuCl, CuBr, Cul, AgI, BeS, BeO	Zn ²⁺ = 8 S ²⁻ = 8	4	74.84%
Type AB ₂ type	Fluorite	Cation occupies FCC lattice whereas anion occupies all the tetrahedral voids.	BaF ₂ , BaCl ₂ , SrE, SrCl ₂ , CdF ₂ , PdF ₂ , etc.	Ca ²⁺ = 8 F ⁻ = 4	4	75.7%
Type A ₂ B type	Anti-fluorite	Oxide ions (O ²⁻) adopts FCC arrangement in which sodium ions (Na ⁺) are present in all the tetrahedral sites.	Na ₂ O, Li ₂ O, K ₂ O, Na ₂ S, Li ₂ S, K ₂ S, etc.	Na ⁺ = 8 O ²⁻ = 4	4	75.7%

1. Corundum structure

The closest packing of anions is hexagonal rather than cubic. Not all the octahedral holes are occupied, only 2/3 of them contain cations. There are 6 octahedral holes per unit cell in HCP anions. Number of anions = 12 (at corner) \times 1/6 + 2 (at face center) \times 1/2 + 3 (within unit cell) \times 1 = 6.

Number of cations = 6 (octahedral void) \times 2/3 \times 1 = 4.

General formulae = A₄X₆ or A₂X₃, e.g., Fe₂O₃, AlO₂O₃, Cr₂O₃ etc.

2. Spinel structure

Oxide ions are arrangement in CCP whereas 1/8 tetrahedral void are occupied by Zn²⁺ and 50 per cent of octahedral holes are occupied by Fe³⁺ ions.

Formulae of the compound number of O²⁻ ions = 8 (at corner) \times 1/8 + 6(at face centre) \times 1/2 = 4

Number of Zn²⁺ ions = 8 (at tetrahedral void) \times 1/8 \times 1 = 1

Number of Fe³⁺ ions = 4(at octahedral void) \times 1/2 \times 1 = 2

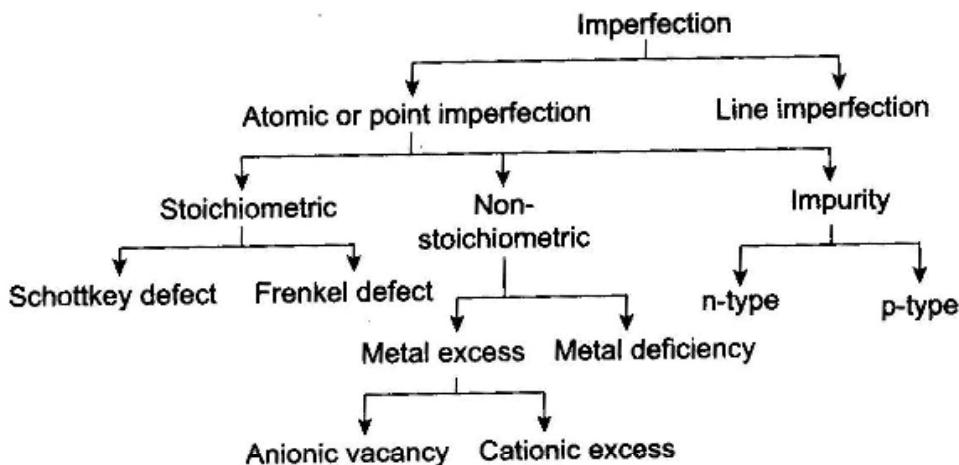
i.e., ZnFe₂O₄

3. Diamond structure

The unit cell of diamond is made of 8 atoms. Four carbon atoms occupy CCP lattice while remaining four atoms occupy half of the tetrahedral voids alternately.

8.13 IMPERFECTION OR DEFECTS IN SOLIDS

The term imperfection or defect is generally used to describe any deviation of the ideally perfect crystal from the periodic arrangement of its constituents.



Classification of imperfection:

1. Point defects or atomic defects:

If the deviation occurs at a particular point because of missing atoms, displaced atoms or extra atoms then imperfection is termed as point defect. They are of two types as discussed here under.

(a) **Stoichiometric defects:** In this type of defect the ratio of cation and anion remains same as represented by molecular formulae. These are of two types as discussed here under.

(i) **Schottkey defects:** When a cation and anion are missing from normal position in the crystal lattice, we get voids or vacancies in the crystal.

This sort of defect occurs mainly in strong ionic compounds, i.e., where the positive and negative ions are of comparable size and with high coordination number, e.g., KCl, KBr and NaCl, etc.

Due to Schottkey defect in a crystal

- | | |
|---------------------------------------|---|
| (i) density of crystal decreases. | (ii) electrical conductivity increases. |
| (iii) stability of crystal decreases. | (iv) LE of the crystal decreases. |

(ii) **Frenkel defects :** In this defect an ion is not completely missing but shifts to an interstitial position in the lattice leaving a vacancy in its own position. This type of defect is favoured by a large difference in size between the positive and negative ions and low coordination number. e.g. ZnS, AgCl, AgBr, AgI, etc. Due to frenkel defect in a crystal.

- | | |
|--|---|
| (i) Density of crystal does not change. | (ii) Electrical conduction increases. |
| (iii) Stability as well as L.E. decreases. | (iv) Leading to high dielectric constant. |

2. Non-stoichiometric defects :

This defect results in change in the ratio of cations to that of anions. It can be of two types.

- | | |
|------------------|-----------------------|
| (i) Metal excess | (ii) Metal deficiency |
|------------------|-----------------------|

Metal excess: Metal excess defects occur in two different ways.

(a) **Anionic deficiency or F centres:** When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl . This happens by loss of electron by sodium to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result, the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *f-centres* (from the German word *Farbenzenter* for colour centre).

Due to f centres solids are

- | |
|--|
| (i) colored (f means farbe means colour) |
| (ii) paramagnetic |

- (iii) capable of becoming photoconductors
 - (iv) such that capable of becoming n-type semiconductors
 - (v) their density of crystal decreases
- (b) Cationic excess:** In this type of metal excess defects, an extra +ve ion occupies an interstitial position in the lattice and electrical neutrality is maintained by the inclusion of an interstitial electron. This kind of metal excess defect is much more common than the first and is generally formed in crystals which would be expected to form Frenkel defects, e.g., ZnO , CdO , Fe_2O_3 and Cr_2O_3 .
- Due to this type of defect solids are:**
- (i) colored
 - (ii) paramagnetic
 - (iii) capable of becoming photoconductors
 - (iv) such that the density of crystal decreases
- e.g., ZnO is white when cold but yellow when hot.
- Soln. $\text{ZnO} \xrightarrow{\Delta} \text{Zn}^{2+} + 1/2\text{O}_2 + 2\text{e}^-$.

Metal deficiency: This type of defect is common among metals showing variable valency. In this defect a metal cation is missing from lattice site and some other cation of higher oxidation state acquire vacancy in order to maintain electrical neutrality. E.g., FeO , FeS , NiO .

Due to metal deficiency

- (i) density decreases
- (ii) lattice energy as well as stability decreases

Impurity defect: If molten NaCl containing a little amount of SrCl_2 is crystallized, some of the sites of Na^+ ions are occupied by Sr^{2+} and each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to that of Sr^{2+} ions. Another similar example is the solid solution of CdCl_2 and AgCl . Whenever we add elements of group 13 such as Ga or Al and the elements of group 15 such as P or As to the covalent solid of group 14 such as Si or Ge, then impurity defect is obtained.

Addition of group 13 element results in the electron deficiency in the crystal and creates holes. This type of semiconductor is called p type semiconductor.

On the other hand, the addition of elements of group 15 produces excess electrons, in the crystal, due to which n-type semiconductors are formed.

8.14 MAGNETIC PROPERTIES OF SOLIDS

- (i) **Diamagnetic substances:** These substances are weakly repelled by the magnetic field and do not have any unpaired electron. e.g., NaCl , N_2 , Zn , Cd , Cu^+ , TiO_2 , V_2O_5 , etc.
- (ii) **Paramagnetic substances:** The substances which are weakly attracted by external magnetic field, are called paramagnetic substances. This property is exhibited by solids due to the presence of unpaired electrons. The unpaired electrons show magnetic moment due to spin of electrons but their random orientation cancel each other's effect. However, in the presence of an external magnetic field, these unpaired electrons are aligned and show the temporary magnetism.
e.g., Cr , Mn , Ni , Co , VO_2 , CuO , Cu^{2+} , Ni^{2+} , Fe^{3+} etc.
- (iii) **Ferromagnetic substances:** Strong magnetic field generated by group of paramagnetic atom also called domain is known as ferromagnetism and such substances are termed as ferromagnetic substances. These substances are attracted by the magnetic field and show permanent magnetism even in the absence of a magnetic field. E.g., Fe , Co , Ni , CrO_2 , etc.

(iv) **Anti-ferromagnetic Substances:** ॥ ॥ ॥ ॥

The domains explained as above cancel each other due to an exactly antiparallel alignment and therefore the net magnetic moment is zero. E.g., MnO, MnO₂, Mn₂O₃, CrO₃, FeO, Fe₂O₃, CoO, Co₃O₄, NiO V₂O₅ etc.

(v) **Ferrimagnetic Substances:** ॥ ॥ ॥ ॥ ॥

The domains are not aligned in a specific pattern, some are antiparallel while others are parallel thus the net magnetic moment is not zero but a small value. E.g., Fe₃O₄, ferrites (MFe₂O₄) where M is any divalent cation such as Mg, Zn, Cu, etc.

8.15 DIELECTRIC PROPERTIES OF SOLIDS

A dielectric is a substance in which an electric field gives rise to no net flow of electric charge. This is due to the fact that electrons in a dielectric are tightly held by individual atoms. However, under the effect of an applied field displacement of charges takes place, resulting in the creation of dipoles.

The alignment of these dipoles in different ways, i.e., compensatory way (zero dipole or non-compensatory way (net dipole) impart certain characteristic properties to solids.

- Piezoelectricity:** A dielectric crystal which has a resultant dipole moment can produce or show electrical property when external pressure, i.e., mechanical stress is applied. Such a crystal is known as piezoelectric crystal and this property is called piezoelectricity or pressure electricity. Piezoelectric crystals are used in record players where electrical signals are produced on applying pressure. They are also used in microphones, ultrasonic generators and sonar detectors. E.g., BaTiO₃, PbTiO₃, lead zirconate (PbZrO₃), ammonium dihydrogen phosphate (NH₄H₂PO₄) quartz etc.
- Pyroelectricity:** Some polar crystals upon heating produce small electric current. This phenomenon is known as pyroelectricity. In this process, actually certain atoms or ions get displaced upon heating, e.g., Tourmaline.
- Ferroelectricity:** In certain piezoelectric crystals, the dipoles are permanently polarized even in the absence of applied electric field. However, the direction of polarization may change on applying current. This phenomenon is known as ferroelectricity and the effect involved is called ferroelectric effect. e.g., KH₂PO₄, Rochelle salt [NaOOC CH(OH)CH (OH) COOK] and BaTiO₃ (barium titanate).
- Anti-ferroelectricity.** When the dipoles in an alternate lattice point up and down, the two dipoles cancel one another so that there is no resultant dipole moment. Such crystals are known as anti-ferroelectric crystals and the phenomenon is called anti-ferroelectricity, e.g., PbZrO₃.

8.16 SILICATES

Silicates are the compounds having SiO₄ tetrahedra as the basic building units. They are linked by corners and never by edges.

8.16.1 Types of silicates

- Orthosilicates** which contain discrete SiO₄⁴⁻ tetrahedra, e.g., zircon(ZnSiO₄) and forestrite(Mg₂SiO₄).
- Pyrosilicates** in which two SiO₄⁴⁻ tetrahedra share one corner, e.g., thortveitite, Se₂(Si₂O₇), hemimorphite, Zn₃(Si₂O₇), Zn(OH)₂, H₂O, etc.
- Cyclic/Ring silicates** in which two corners are shared to form a closed ring, e.g., beryl, Be₃Al₂Si₆O₁₈.
- Chain silicates** in which two corners are shared to form a long chain, e.g., pyroxenes and asbestos.
- Sheet silicates** in which three corners are shared to form a two-dimensional sheet.
- Three-dimensional silicates** in which all the four corners are shared to form a three-dimensional lay network, e.g., quartz.

CHEMICAL KINETICS

9.1 INTRODUCTION

Chemical kinetics is the branch of science that deals with rate of reaction, the factors affecting the rate of reaction and mechanism of the reaction.

9.2 RATE OF REACTION

'The change in the molar concentration of any reactants or product per unit time is known as rate of reaction.'

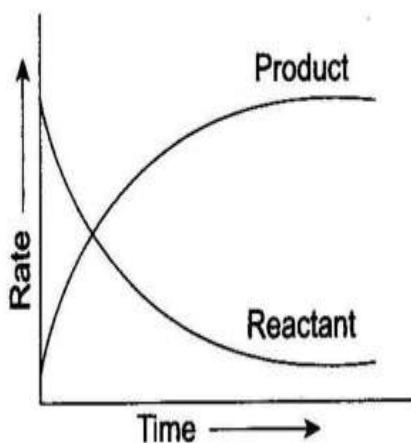
Rate of reaction of reactant A, i.e., rate of disappearance of A

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} \left[\frac{\text{mol}}{\text{litre sec.}} \right]$$

Rate of reaction of product P, i.e., rate of formation of p

$$r_p = \frac{1}{V} \frac{dN_p}{dt} \left[\frac{\text{mol}}{\text{litre sec.}} \right]$$

- -ve sign means disappearance while +ve sign indicates the formation rate. Units of the rate of reaction are $\text{mol L}^{-1} \text{ time}^{-1}$. Rate of reaction does not remain constant during the complete reaction because rate depends upon the concentration of reactants which decreases with time.



Rate of disappearance of A

$-r_A = -\frac{1}{V} \frac{dN_A}{dt} \left[\frac{\text{mol}}{\text{litre second}} \right]$; -ve sign means disappearance while +ve sign indicates the formation rate.

$$\text{Average rate of reaction: } r_{\text{average}} = \frac{\text{Change in conc of one of the reactant or products}}{\text{Time taken for the change}} = \frac{\Delta x}{\Delta t}$$

9.3 AVERAGE AND INSTANTANEOUS RATE OF REACTION

The rate measured as average over a long time interval is called **average rate** and the rate measured at a particular instant of time (or average rate for an infinitesimally small time interval) is called **instantaneous rate**.

9.3.1 Graphical method for determination of rate of reaction

The rate of reaction at any instant of time may be calculated by drawing a tangent to the curve at a point corresponding to that time and then calculating the slope of the tangent.

9.3.2 Dependency of Rate Equation on Stoichiometry

Considering a single phase reaction $aA + bB \rightarrow rR + sS$

The rate of reaction of all reactants and products are related by $\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$

9.4 FACTORS AFFECTING RATE OF REACTION

Reactions involving cleavage of strong bond in reactant molecules are slower when compared to reactions involving weak bond in reactants molecules



Reaction (ii) is faster than reaction (i).

9.4.1 Concentration of the Reactants

An increase in the concentration of the reactants increases the reaction rate because increase in concentration brings more frequent collisions between the reactant molecules, thereby increasing the number of effective collisions which results in a faster chemical change.

9.4.2 Surface area of the reactants

Larger the surface area of the reactants, greater will be the rate of reaction.

9.4.3 Catalyst

Presence of a catalyst increases as well as decreases the rate of a reaction depending upon the nature of the catalyst.

9.4.4 Temperature

Reaction rates are normally favoured by increasing temperature.

9.5 ELEMENTARY AND NON-ELEMENTARY REACTIONS

9.5.1 Elementary Reactions

Reactions in which the rate equation corresponds to a stoichiometric equation are called elementary or simple reactions. In elementary reactions, only one reaction step is involved.

e.g., for a reaction $A + B \rightarrow R$

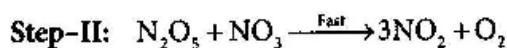
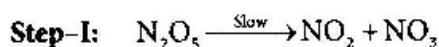
$$\text{if } -r_A = k c_A c_B$$

i.e., here rate expression is corresponding to stoichiometry and for elementary reactions order of reaction is equal to its molecularity.

9.5.2 Non-elementary Reaction

When there is no direct correspondence between stoichiometry and rate then we have non-elementary or complex reactions. Two or more elementary reactions when added give a complex or non-elementary reactions. The set of elementary reactions which on addition gives a complex reaction is said to be the mechanism of that reaction.

Example:



Step I: is known to be the rate determining step

$$\text{Rate} = K [N_2O_5]$$

If first step of the reaction is the slowest step then molecularity of the slowest step is the order of the overall reaction. All the reaction steps which appear, before the slowest step must be reversible.

Final rate law must be independent from the concentration of reaction intermediate.

9.6 ORDER OF REACTION

The order of a reaction is defined as the number of molecules whose concentrations determine the rate of the chemical reaction at a given temperature. Alternatively, we may define the order of the reaction as the sum of powers to which the concentration terms are raised in rate law equation in order to determine the rate of the reaction.

e.g., for a reaction $aA + bB \rightarrow \text{Products}$

$$\text{Rate} \propto [A]^m [B]^n$$

Then, order of reaction with respect to A = m

Then, order of reaction with respect to B = n

\therefore Overall order of reaction = m + n

9.7 MOLECULARITY OF REACTION

The molecularity of an elementary reaction is defined as the minimum number of molecules, atoms or ions of reactants required for the reaction to occur. Molecularity is a theoretical value and is derived from the mechanism of the reaction.

e.g., for a reaction $aA + bB \rightarrow \text{Products}$

$$\text{Molecularity} = a + b$$

So, if $a + b = m + n$, then the reaction is called elementary.

Difference between order and molecularity of reaction

Order of Reaction

- (i) Order is an experimental property and it is concerned with kinetics of the reaction.
- (ii) Order may be any number, integral or fraction including zero.
- (iii) It is defined for both elementary and non-elementary reactions.
- (iv) Reaction with order ≥ 3 are rare.

Molecularity of Reaction

- (i) Molecularity is a theoretical concept which concerned with mechanism of the reaction.
- (ii) Molecularity is always an integer except zero.
- (iii) Defined only for elementary reaction.
- (iv) Reaction with molecularity > 2 are rare.

9.8 RATE CONSTANT OF THE REACTION

The rate constant or velocity constant or specific reaction rate of a reaction, in general, is equal to the rate of reaction when the concentration of each of the reactants is unity.

e.g., For an elementary reaction



$$\text{Rate of reaction } r = k c_A^a c_B^b c_C^c$$

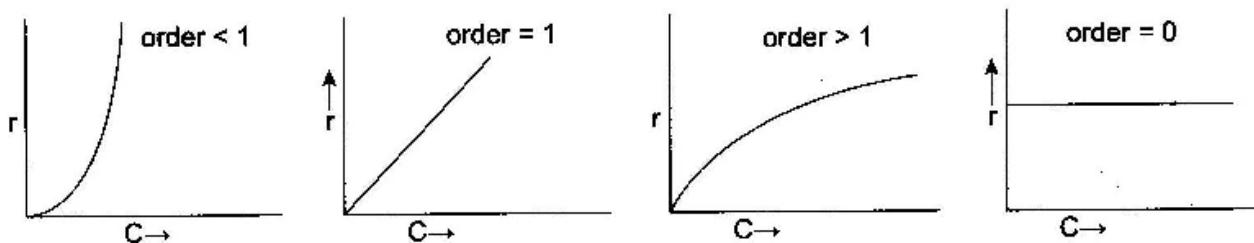
If $c_A = c_B = c_C = 1$, then $r = k$.

The value of k is independent from concentration; it depends only on the temperature and catalyst used.

$$\text{units of rate constant for } n^{\text{th}} \text{ order reaction, } k_n = \frac{\text{unit of rate}}{\text{unit of } (C^n)} = \text{conc}^{1-n} \text{ time}^{-1}$$

9.9 DIFFERENTIAL RATE LAW OF A REACTION

It is the differential equation which gives rate of reaction as a function of concentration. For rate of formation, formation step is +ve while disappearance step is -ve and vice versa for rate of disappearance.



9.10 INTEGRATED RATE LAW OF A REACTION

9.10.1 First-order Reactions

Consider the reaction, $A \rightarrow \text{Products}$

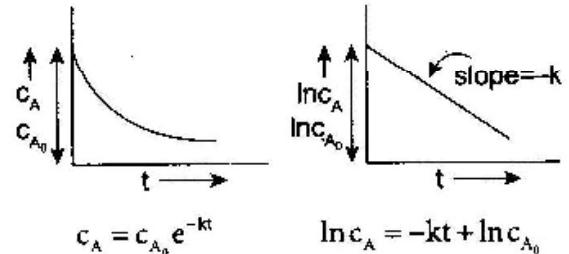
$$\text{Rate of reaction, } -r_A = -\frac{dc_A}{dt} = kc_A$$

$$\text{or } -r = -\frac{dc}{dt} = kc$$

Separating and integrating, we get

$$-\int_{c_{A_0}}^{c_A} \frac{dc_A}{c_A} = k \int_0^t dt - \ln \frac{c_A}{c_{A_0}} = kt \Rightarrow \ln c_A = -kt + \ln c_{A_0}$$

$$\Rightarrow t = \frac{2.303}{k} \log_{10} \frac{C_{A_0}}{C_A} \Rightarrow c_A = c_{A_0} e^{-kt}$$



9.10.2 Second-order Reactions

Consider an elementary reaction, $A \rightarrow \text{Products}$

$$t = 0 \quad c_{A_0}$$

$$\text{at } t \quad c_A$$

$$-r_A = -\frac{dc_A}{dt} = kc_A^2 \quad \text{or} \quad -r = -\frac{dc}{dt} = kc^2$$

$$\text{Rearranging and integrating we get } t = \frac{1}{k} \left[\frac{1}{c_A} - \frac{1}{c_{A_0}} \right]$$

9.10.3 n^{th} -order Reaction

Considering an elementary reaction, $A \rightarrow \text{Products}$, $-r_A = -\frac{dc_A}{dt} = kc_A^n$

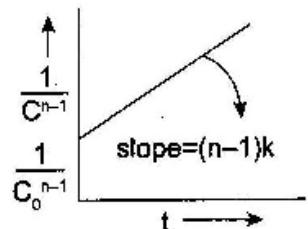
$$\text{or } -r = -\frac{dc_A}{dt} = kc^n$$

$$\text{Integrating, we get } t = \frac{1}{(n-1)k} \left[\frac{1}{c^{n-1}} - \frac{1}{c_0^{n-1}} \right] \quad n \neq 1$$

For completion of reaction $C_A = 0$ if $n > 1$, $t = \infty$.

Reaction with order $n > 1$ can never go to completion in finite time.

Reaction with order less than 1 requires finite time for its completion.

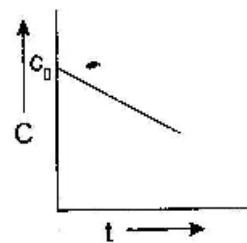


9.10.4 Zero-order Reaction

A reaction is said to be zero order when the rate of reaction is independent of the concentration of reactants.

Consider of reaction, $A \rightarrow \text{Products}$

$$\text{Rate of reaction, } -r = -\frac{dc}{dt} = k; \text{ Integrating on both sides, we get } t = \frac{c_0 - c}{k}.$$



9.11 HALF LIFE TIME OF A REACTION

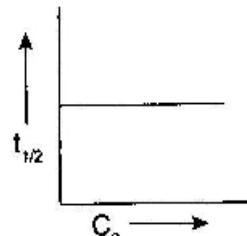
The half-life ($t_{1/2}$) of the reaction is the time needed for the concentration of reactants to drop to one-half of the original value.

A zero order reaction can never be elementary because molecularity of a reaction can never be zero. Time of completion of zero order reaction is double of its half life time

9.11.1 $t_{1/2}$ for a First-order Reaction

$$\text{When } t = t_{1/2}; c_A = \frac{c_{A_0}}{2} \quad t_{1/2} = -\frac{1}{k} \ln \frac{c_{A_0}}{2c_{A_0}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

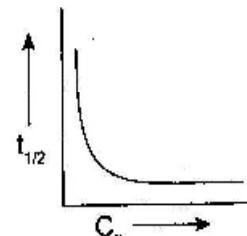
For a first-order reaction, half life time is independent from initial concentration



9.11.2 $t_{1/2}$ for a Second-order Reaction

$$\text{For a second-order reaction, } \frac{1}{c_A} - \frac{1}{c_{A_0}} = kt.$$

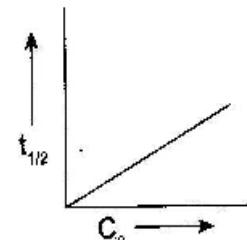
$$\text{When } t = t_{1/2}; c_A = \frac{c_{A_0}}{2}; t_{1/2} = \frac{1}{c_{A_0} k}.$$



9.11.3 $t_{1/2}$ of a Zero-order Reaction

$$\text{For a zero-order reaction, } c_{A_0} - c_A = kt$$

$$\text{When } t = t_{1/2}; c_A = \frac{c_{A_0}}{2}; t_{1/2} = \frac{c_{A_0}}{2k}.$$



9.11.4 $t_{1/2}$ of a nth-order Reaction

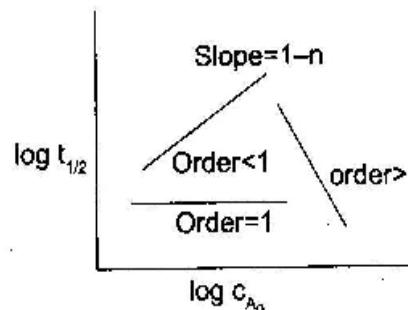
$$\text{For an } n^{\text{th}} \text{ order reaction, } c_A^{1-n} - c_{A_0}^{1-n} = k(n-1)t$$

$$\text{When } t = t_{1/2}; c_A = \frac{c_{A_0}}{2}; t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)c_{A_0}^{n-1}}$$

Taking log of both sides, we get

$$\log t_{1/2} = (1-n) \log c_{A_0} + \log \left[\frac{2^{n-1} - 1}{k(n-1)} \right]$$

If we plot a graph of $\log t_{1/2}$ vs. $\log c_{A_0}$



Some important relationship between time for different fraction of reaction of first order to complete

$$t_{75\%} = 2t_{1/2}; t_{87.5\%} = 3t_{1/2}; t_{93.75\%} = 4t_{1/2}; t_{96.87\%} = 5t_{1/2}; t_{99.9\%} = 10t_{1/2}$$

9.12 EXPERIMENTAL METHOD FOR DETERMINATION OF RATE LAW

9.12.1 Volumetric Method

In this method, a known volume of the reaction mixture is removed at various times and to a larger volume of ice cold water is rapidly added, which effectively stops the reaction or at least slows it down considerably. This is widely used in cases where reactants or products are acids or bases or species undergoing a redox reaction.

9.12.1.1 Decomposition of H_2O_2



$$t = 0 \quad c_{A_0} \quad v_0$$

$$\text{At time } t \quad c_A \quad v_\infty$$

Volume of $KMnO_4$ used is \propto concentration of H_2O_2 present

$$k = \frac{2.303}{t} \log \frac{c_{A_0}}{c_A} = \frac{2.303}{t} \log \frac{V_0}{V_t}.$$

Acid hydrolysis of ethyl acetate



$$t = 0 \quad c_{A_0} \quad 0 \quad 0 \quad v_0$$

$$\text{At time } t \quad c_A \quad c_{A_0} - c_A \quad c_{A_0} - c_A \quad v_1$$

$$\text{At } t = \infty \quad 0 \quad c_{A_0} \quad c_{A_0} \quad v_\infty$$

$$\text{Volume of alkali used is } \mu \text{ concentration of acid present, } k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}.$$

9.13 PRESSURE CHANGE METHOD

This is to be used in a gaseous phase reaction. As reaction proceeds, there may be a change in final pressure. By measuring initial and total pressure at the start and after time t , value of c_{A_0} and c_A can be determined in terms of total pressures for the reactions.



$$\text{At } t = 0 \quad P_0 \quad 0$$

$$\text{At time } t \quad P_0 - x \quad yx$$

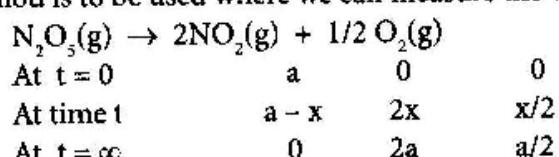
$$k = \frac{2.303}{t} \log \frac{P_0(y-1)}{yP_0 - P_t}$$

e.g., $CH_3COCH_3(g) \rightarrow CO(g) + CH_3 - CH_3(g)$ here $y = 2$

$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

9.14 VOLUME MEASUREMENT METHOD

This method is to be used where we can measure the volume of one of gaseous substances evolved.

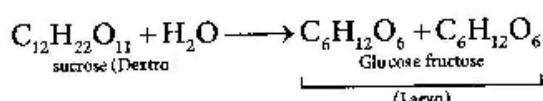


$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{(V_{\infty} - V_t)},$$

9.14.1 In Terms of Rotation of Optically Active Species

Angle of rotation is directly proportional to the concentration of optically active substance present.

Hydrolysis of sucrose:



Angle of rotation of plane polarized light at:

- (i) $t = 0$ θ_0
 - (ii) t θ_t
 - (iii) $t = \infty$ θ

Angle of rotation (θ) is \propto total concentration of optically active substance present

$$k = \frac{2.303}{t} \log \frac{\theta_x - \theta_0}{\theta_x - \theta_1}$$

9.15 TEMPERATURE-DEPENDENT TERM OF A RATE EQUATION

9.15.1 Effect of Temperature on Reaction Rates

It is a common experience that increase of temperature has marked effect on the rate of a chemical reaction.

The ratio of the rate constants of a reaction at two temperatures differing by 10°C is known as the **temperature coefficient** of the reaction. The temperatures usually selected for this purpose are 25°C and 35°C .

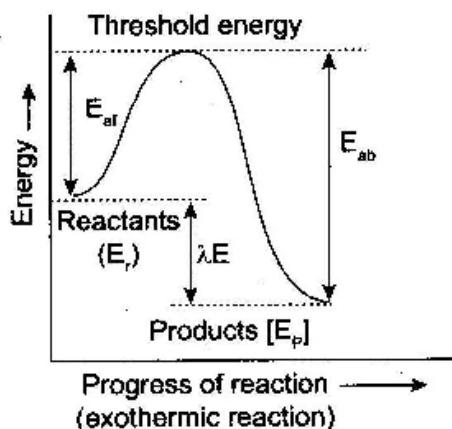
$$\mu = \frac{\text{Rate constant at } (T+10)^\circ\text{C}}{\text{Rate constant at } T^\circ\text{C}} = 2 \text{ to } 3 ; \quad \frac{K_{T_2}}{K_{T_1}} = \mu^{\frac{(T_2 - T_1)}{10}}$$

9.16 COLLISION THEORY

Increase in rate of a reaction with temperature can be explained by collision theory. This theory was proposed by Arrhenius and vant Hoff. Important features of this theory are listed hereunder:

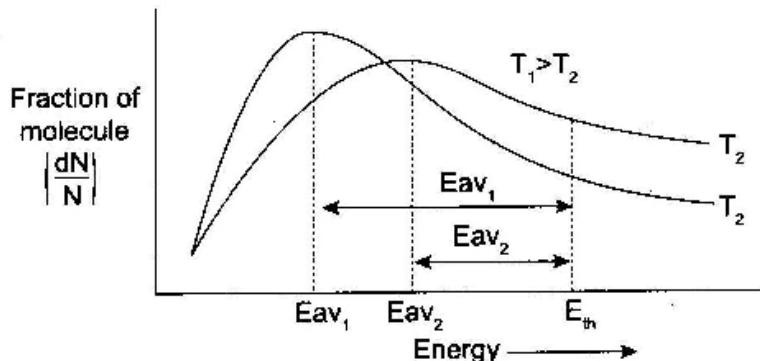
- (i) For chemical reactions to occur, there must be collisions between the reactant molecules. However, most of the collisions taking place between the reactant molecules are ineffective.

- (ii) Only those collisions result in chemical reactions in which the colliding molecules are associated with a certain minimum energy called the threshold energy.
- (iii) Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- (iv) At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the rate of reaction.
Passive molecule \rightleftharpoons Active molecules; $\Delta H = +ve$.



9.16.1 Activation energy

The extra energy that the reactant molecule required in order to cross the energy barrier is known as **activation energy** (E_a). $(E_a) = \text{Threshold energy} - \text{Average energy}$.



9.16.2 Energy Barrier

The minimum amount of energy that the reactant molecule has in order to convert into product is known as **threshold energy** and this state is termed as **energy barrier**.

- $\Delta H = E_{af} - E_{ab}$
- Whether given reaction is slow or fast at a given temperature depends upon the activation energy of the reaction. A reaction which has lower activation energy will proceed at a faster rate at a given temperature.

9.16.3 Effective Collision

According to the collision theory, effective collision is one which results into the product.

9.16.4 Collision Frequency

Number of collisions that taken place per second per unit volume of the reaction mixture is called collision frequency.

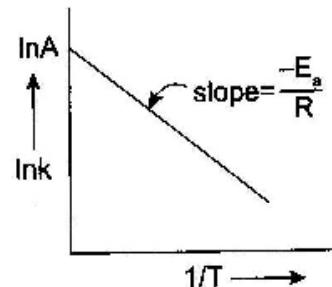
9.17 THE ARRHENIUS THEORY

Arrhenius proposed an empirical equation for calculating the energy of activation of a reaction having rate constant at temperature T.

$$\ln k = \frac{-E_a}{RT} + \ln A$$

$K = Ae^{-E_a/RT}$; where E_a is activation energy of the reaction.

Where a is Arrhenius constant or pre-exponential factor or frequency factor.



- Both E_a and A are independent from temperature.
- Arrhenius equation cannot be used for nuclear reactions.

- $\ln \frac{k_2}{k_1} = \frac{E_a}{T} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$. This equation is known as the integrated Arrhenius equation.

9.18 PHOTOCHEMICAL REACTIONS

Photochemical reactions are those reactions which take place only in the presence of light but not in the dark. Red light has lowest energy. Hence, photochemical reactions which can be initiated by red light can be initiated by all other radiations of visible light.

9.18.1 Characteristic of Photochemical Reactions

- Temperature has very little effect on the rate of a photochemical reaction. Instead, the intensity of light has a marked effect.
- Free energy change (ΔG) of a photochemical reaction may not be negative. This is because a part of the light energy absorbed by the reaction is converted into free energy of the products.
- A photosensitizer is a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change. e.g., chlorophyll in photosynthesis and Hg vapours in dissociation of H_2 .
- Quantum yield or quantum efficiency of a photochemical reaction is

$$\Phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

- Photosynthesis of HCl has high quantum yield, whereas photosynthesis of HBr has low quantum yield. This is because after the primary process ($Cl_2 \xrightarrow{h\nu} 2Cl$ or $Br_2 \xrightarrow{h\nu} 2Br$), the first step of the secondary process of photosynthesis of HCl ($Cl + H_2 \rightarrow HCl + H$) is exothermic, whereas that of HBr ($Br + H_2 \rightarrow HBr + H$) is endothermic.
- Vision is a fast photochemical reaction in which the compound, retinal, present in the eye undergoes geometrical isomerization by absorbing a photon of light.

ELECTROCHEMISTRY**10.1 INTRODUCTION**

Electrochemistry is a branch of science which deals with chemical changes caused in matter by passage of electric current and conversion of chemical energy into electrical energy and vice versa.

All electrochemical reactions involve transfer of electrons and are therefore redox reactions.

Substances which allow the passage of electric current through them are called electrical conductors while those which do not are called insulators.

10.2 ELECTRICAL CONDUCTION

The property which allows the flow of electricity through a body is called conduction, and the body which allows passage of electricity through it is called a conductor. Conductor is of two types as listed hereunder.

- (i) Metallic conductor and
- (ii) Electrolytic conductor.

Comparative study between metallic and electrolytic conductors:

Metallic conductor	Electrolytic Conductor
(i) Electric current flows by movement of electrons	(i) Electric current flows by movement of ion
(ii) No chemical change occurs	(ii) Ions are oxidized or reduced at the electrodes
(iii) It does not involve the transfer of any matter	(iii) It involves transfer of matter in the form of ions
(iv) Ohm's law is followed	(iv) Ohm's law is followed
(v) Resistance increases with increase of temperature	(v) Resistance decreases with increase of temperature
(vi) Faraday's law is not followed	(vi) Faraday's law is followed

- The average kinetic energy of the solute ions increases as the temperature is raised and therefore, the resistance of electrolytic conductors generally decreases.

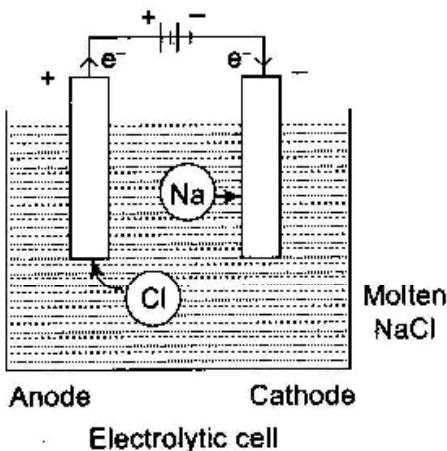
- In case of metallic conduction on increasing temperature the kernels in the metal start vibrating which hinders the mobility of electrons and thus resistance increases and conductance decreases.

Factors affecting electrolytic conductivity:

- The nature of the electrolyte added.
- Size of the ions produced and their solvation.
- The nature of the solvent and its viscosity.
- Concentration of the electrolyte.
- Temperature.

10.3 ELECTROLYTIC CELL AND ELECTROLYSIS

In an electrolytic cell, electrons are received from the negative end of the battery by the negative electrode of the cell, these are used up at the cathode in the form of a reduction reaction. The number of electrons received at the negative electrodes is given back to the positive end of the battery from the positive electrode of the cell where electrons are released as a result of oxidation.



10.3.1 Electrolysis

Faraday's first law of electrolysis: According to Faraday's first law of electrolysis, the weight of a substance deposited is directly proportional to the charge passed through an electrolytic solution.

$$W = Z \times Q;$$

where 'Z' is Electrochemical equivalent of a cell

$$W = Z \times I \times t \quad \therefore Q = I \times t$$

Faraday's second law of electrolysis: If same quantity of electricity is passed through two different electrolytes, then the amount of different substance discharged is proportional to their equivalent masses. That is, $w \propto E$ if Q is constant.

Charge of 1 mole e^- = charge of 1 gram equivalent e^- = 1 F

\therefore If 1 gram is passed, then 1 gram equivalent of a substance is discharged.

$$\Rightarrow \text{If } Q = 1 \text{ F}, \text{ then } w/E = 1 \Rightarrow w = E$$

$$\Rightarrow E = Z \times F \Rightarrow Z = E / F$$

$$\therefore w = \frac{EIt}{F} = \frac{MIt}{nF}$$

10.3.2 Prediction of product of Electrolysis

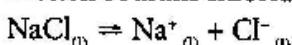
10.3.2.1 Preferential discharge theory

According to this theory if more than one type of ions are present inside the solution then discharged ion is the one which requires least amount of energy for their deposition. Amount of energy needed for deposition is expressed in terms of deposition potential.

- Deposition potential of a metal $\propto \frac{1}{E_{\text{red}}^{\theta} \text{ value}}$
- Deposition potential of a non-metal $\propto E_{\text{red}}^{\theta}$ value

(i) Electrolysis of molten sodium chloride

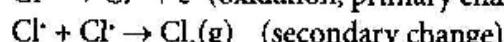
Molten sodium chloride contains Na^+ and Cl^- ions.



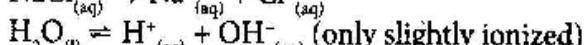
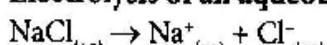
On passing electricity, Na^+ ions move towards cathode while Cl^- ions move towards anode.

At cathode: $\text{Na}^+ + e^- \rightarrow \text{Na}$ (reduction, primary change)

At anode: $\text{Cl}^- \rightarrow \text{Cl}^\cdot + e^-$ (oxidation, primary change)

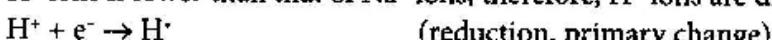


(ii) Electrolysis of an aqueous solution of NaCl: Sodium chloride and water ionize as under



On passing electricity, $\text{Na}^+_{(\text{aq})}$ and $\text{H}^+_{(\text{aq})}$ move towards the cathode while $\text{Cl}^-_{(\text{aq})}$ and $\text{OH}^-_{(\text{aq})}$ ions move towards the anode.

At cathode: Both $\text{Na}^+_{(\text{aq})}$ and $\text{H}^+_{(\text{aq})}$ are present near the cathode. Since the **discharge potential** of H^+ ions is lower than that of Na^+ ions, therefore, H^+ ions are discharged in preference to Na^+ ions.



Thus, H_2 gas is evolved at the cathode while Na^+ ions remain in the solution.

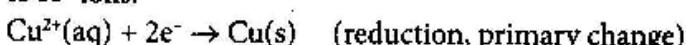
At anode: Both Cl^- and OH^- ions are present near the anode. Since the discharge potential of Cl^- ions is lower than that of OH^- ions, therefore, Cl^- ions are discharged in preference to OH^- ions.



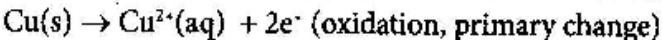
Thus, Cl_2 gas is evolved at the anode while OH^- ions remain in the solution.

(iii) Electrolysis of aqueous CuSO_4 using Cu electrode

On passing electricity, Cu^{2+} and H^+ move towards cathode while OH^- and SO_4^{2-} ions move towards anode. Both Cu^{2+} and H^+ ions are present near the cathode. But the **discharge potential** of Cu^{2+} ions is lower than that of H^+ ions, therefore, Cu^{2+} ions are discharged in preference to H^+ ions.



At anode: Unlike electrolysis of CuSO_4 using platinum electrodes, no ions are liberated here. Instead, anode itself undergoes oxidation (i.e., loses electrons) to form Cu^{2+} ions which go into the solution. This is due to the reason that Cu is more easily oxidised than both OH^- and SO_4^{2-} ions.



Thus the net result of electrolysis is that copper is deposited at the cathode from the solution and an equivalent amount of copper from the anode dissolves into the solution to form Cu^{2+} ions. This principle of electrolysis is widely used in electroplating and purification of less reactive metals such as Pb, Cu, Ag, etc.

10.4 CONDUCTANCE MEASUREMENT

Electrolytic Conductance: The reciprocal of the electrical resistance is called **conductance**. It is usually represented by C or G.

$$\text{Thus } C = \frac{1}{R}$$

Specific Conductance: "The reciprocal of resistivity is known as **specific conductivity** or simply **conductivity**. It is denoted by (kappa) or κ . Thus, if κ is the specific conductivity and C is the conductance of the solution, then

$R = \rho (\ell/A)$; (where ρ is a constant of proportionality, called **specific resistance** or **resistivity**. Its value depends upon the material of the conductor.)

$$R = 1/C \text{ and } \rho = 1/\kappa$$

$$\therefore \frac{1}{C} = \frac{1}{\kappa} \times \frac{\ell}{A}$$

$$\kappa = C \times \frac{\ell}{A}$$

Unit of κ is $\Omega^{-1} \text{ m}^{-1}$ or $\Omega^{-1} \text{ cm}^{-1}$ or S cm^{-1} or Sm^{-1} .

■ Conductance of an electrolyte inside a solution depends upon the following three factors.

- (i) Number of ions present inside the solution.
- (ii) Magnitude of charge present on each ion.
- (iii) Ionic mobility.

Equivalent Conductance: Equivalent conductivity of a solution at a dilution V is defined as the conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in V cm³ of the solution.

$$\Lambda_{eq} = \kappa \times \phi$$

where ϕ is volume of solution in cm³ containing 1 gram equivalent of electrolyte.

$$= \Lambda_{eq} = \kappa \times \frac{1000}{N} \text{ its unit is } \Omega^{-1} \text{ cm}^2 \text{ geq}^{-1} \text{ or } \text{S cm}^2 \text{ geq}^{-1}$$

$$\text{In terms of } \Omega^{-1} \text{ m}^2 \text{ geq}^{-1}; \Lambda_{eq} = \frac{\kappa}{1000 \times N}$$

Molar Conductance: The molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm³ of the solution. It is usually represented by Λ_m .

$$\Lambda_m = \kappa \times V$$

$$\text{or } \Lambda_m = \kappa \times \frac{1000}{c} = \kappa \times \frac{1000}{\text{Molarity}}; \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ or } \text{S cm}^2 \text{ mol}^{-1}$$

where κ is the specific conductivity and V is the volume of the solution containing one mole of the electrolyte and c is the molar concentration, i.e., mol L⁻¹ (or mol dm⁻³).

$$\text{In terms of } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}; \Lambda_m = \frac{\kappa}{1000 \times M}$$